Generation of amplified spontaneous emission from rare-earth complexes dispersed in phenol + AOT self-assembled organogels

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Abstract

The rare-earth complex $\text{Eu(hfa)}_3(\text{phen})$ is dispersed in the self-assembled organogel of *p*-chlorophenol and surfactant AOT. The time profiles of the emission intensity observed from the complex–organogel system suggest the possible generation of amplified stimulated emission when excited with a strong excitation pulse. As the host material, the organogel can support eight times as much of the complex along with better emission quantum yield. A theoretical estimation of the laser

gain factor of the complex–organogel also suggested that this system might have application in laser systems.

Keywords

organogel, soft material, self-healing material, Eu complex, laser material

1. Introduction

Self-assembled organogels composed of small organic molecules have been used to hosting materials that contain rare-earth complexes [1,2], nanoparticles [3,4], nanofibers [5], nanorings [6], or lipophilic compounds [7]. Such doping processes rely on the organogel network structure, where interactions between the network and dopants are critical. The network structure fluctuates either in the temporal and spatial phase, which is characteristic of soft materials. An earlier paper of ours discussed the distribution of the time constant of the structural fluctuation of organogels in the nanosecond region [8].

An advantage of using organogels as host materials is that they easily reformat when assembled in a solid vessel. The self-healing of organogels is also attractive [6,9]. However, organogels may exhibit turbidity owing to their microscopic structure, which could hinder applications to optical devices.

In a previous study, we dispersed Eu^{3+} and Tb^{3+} complexes in an optically transparent phenol + AOT organogel [2]. The organogel structure, which was suggested by Simmons and coworkers [10], is shown in Chart 1a. These complex–organogel systems have been applied to additive emission color-tuning in the visible region [2]. Another advantage of the phenol + AOT organogel as host material is that we can disperse in it the $\text{Eu}(\text{hfa})_3(\text{phen})$ complex, which is 8 times denser than the liquid, along with higher emission quantum yield Φ_f . Table 1 lists Φ_f and the maximum concentration of $\text{Eu}(\text{hfa})_3(\text{phen})$ c_{max} . Note that hexafluoroacetylacetone (hfa) and 1,10-phenanthroline (phen) were chosen as the ligands for this complex, as shown in Chart 1b. We have also reported that the complexes emit independently even in the organogel environment, as the organogel network can separate the mutual interactions between the complexes. Furthermore, it has been shown that the interplay between the organogel architecture and the complexes hardly affects the excited state of the rare earths [2].

In this study, we have used the properties of the organogel in a laser material by dispersing $\text{Eu}(\text{hfa})_3(\text{phen})$ in the organogel. Previously, we dispersed $\text{Eu}(\text{hfa})_3(\text{TPPO})_2$ [11] and its derivatives

possessing various ligands [12] into thin polystyrene films, where the ligand TPPO represents triphenylphosphine oxide, and monitored the time profiles of the emission intensity $I(t)$. The $I(t)$ profiles clearly depend on the laser excitation-pulse energy E_{ex} , the results of which have been ascribed to the generation of amplified spontaneous emission (ASE), which is a kind of cavity-less laser action and the light amplification process of spontaneous emission (i.e. fluorescence) by stimulated emission through the inverted population generated by the photoexcitation [13]. According to the previous reports [11,12], Eu^{3+} complexes have thus been shown to be candidate laser materials when dispersed in thin films. In the present study, we will show that the organogel can also be used as an environment for laser materials, while maintaining the previously described attractive characteristics of soft materials. The estimated laser gain factor of the organogel system suggests potential applicability to laser materials. We hereafter denote a system where a Eu complex is dispersed in organogel, film, and liquid solvent as “**Eu@gel**,” “**Eu@film**,” and “**Eu@liq**,” respectively.

2. Materials and methods

2.1 Materials.

The synthesis of the phenol + AOT organogel and $\text{Eu}(\text{hfa})_3(\text{phen})$ were previously reported [2,8]. We followed Simmons et al. for the organogel synthesis [10]. Briefly, 0.14 mol dm^{-3} *p*-chlorophenol and 0.10 mol dm^{-3} AOT (bis(2-ethylhexyl)sulfosuccinate) dissolved in *m*-xylene solvent were combined to form the gel at room temperature (298 K). To prepare **Eu@gel**, $\text{Eu}(\text{hfa})_3(\text{phen})$ was added to the organogel and then both were heated up to 353 K in a water bath to obtain an isotropic solution. Subsequently, they were cooled to obtain a gel phase, and the heating and cooling cycles were repeated several times. A $\text{Eu}(\text{hfa})_3(\text{phen})$ solution in *m*-xylene was used as **Eu@liq**. Regarding the dispersing concentration of $\text{Eu}(\text{hfa})_3(\text{phen})$, c_{max} was chosen either for **Eu@gel** and **Eu@film**, as given in Table 1.

2.2 Measurements of the photochemical and optical properties.

The steady-state absorption and emission, or excitation, spectra were recorded with a Hitachi U2800 spectrometer and a Jasco FP-6500 spectrofluorometer, respectively. A Jasco ILF-533 integrating sphere was employed for the Φ_f measurements. A DR-A1 (Atago) Abbe refractometer was used to measure the refractive index. The time-dependent measurements were performed with the equipment we had previously used [11,12]. The third harmonics of a Nd:YAG laser from B. M. Industries [10 Hz, full-width-at-half-maximum (fwhm) $\approx$ 9 ns] was used as the excitation light source, with wavelength $\lambda_{\text{ex}} = 355$ nm. As a result, the $\lambda_{\text{ex}} = 355$ nm for the $I(t)$ measurements gives rise to the photoexcitation of the hfa ligand, followed by energy transfer to Eu^{3+} that causes emission [2]. Using a cylindrical lens, the laser beam was focused onto the front side of a foursquare quartz cuvette at normal incidence. The beam travelled 2 mm inside the sample. The emission was monitored from the side direction with a photomultiplier (Hamamatsu R928), which formed a perpendicular configuration between the excitation pulse and the emission to be monitored. A monochromator was used to collect the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ emission of Eu^{3+} at the maximum of around 614 nm. The $I(t)$ profiles were recorded with a digital oscilloscope and a sampling duration of 1 GHz.

3. Results and discussion

3.1 The steady-state emission spectra of **Eu@liq** and **Eu@gel**.

Figure 1 compares the emission spectra of **Eu@liq** using *m*-xylene and **Eu@gel** for $\lambda_{\text{ex}} = 355$ nm. The emission spectra of **Eu@liq** and **Eu@gel** were independent of λ_{ex} . The spectral maximum of **Eu@gel** appears at 614 nm, which is 2 nm (53 cm^{-1}) red-shifted compared with that of **Eu@liq** (612 nm). We have also found that the fwhm of the **Eu@gel** spectrum corresponds to 127 cm^{-1} , which is about 50% broader than that of **Eu@liq** (80 cm^{-1}). For precision, the $^7\text{F}_2$ level of Eu^{3+} was five-fold degenerate the ligands resolved the degeneracy [12,14]. We can therefore ascribe the spectral red

shift observed in **Eu@gel** to environmental differences around $\text{Eu(hfa)}_3(\text{phen})$, compared with the organogel and liquid. The organogel environment may produce more inhomogeneity, which causes broader fwhm in the emission spectrum.

3.2 The emission time profiles and the excitation pulse energy.

In this subsection, we discuss the $I(t)$ profiles detected with varying E_{ex} , similarly to previous studies [11,12]. Figure 2 displays the $I(t)$ profiles for **Eu@liq** and **Eu@gel**, which can be fitted with a bi-exponential function

$$I(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2) \quad (1),$$

where τ_i ($i = 1$ or 2) stands for the lifetime and A_i denotes the pre-exponential factor with $A_1 + A_2 = 1$. Table 2 summarizes the quantities determined with Eq. (1) by using the least square method. The $I(t)$ profile of **Eu@liq** at $E_{\text{ex}} = 0.02$ mJ was not detected because of insufficient pulse energy.

Figure 2a shows that the $I(t)$ profiles for **Eu@liq** at 0.05–0.2 mJ mostly overlap with each other and the lifetime is around $\tau_2 = 1.5$ ms. This τ_2 value is assigned to the lifetime of $\text{Eu(hfa)}_3(\text{phen})$ in *m*-xylene solvent. When we increase E_{ex} to 0.5 mJ or higher, the $I(t)$ profiles were fitted well with a biexponential function. In Table 2, the A_2 value for **Eu@liq** drops drastically between $E_{\text{ex}} = 0.2 - 0.5$ mJ. This phenomenon is due to the appearance of the fast component, with its amplitude of A_1 . We have assigned the slower component τ_2 also to the intrinsic lifetime of $\text{Eu(hfa)}_3(\text{phen})$ for each E_{ex} because τ_2 varies only by ~10% compared to the lifetime for E_{ex} of 2.0 mJ or less. Two possibilities can explain the appearance of the fast component τ_1 : ASE and the annihilation process, where one excited molecule interact with another excited molecule because of high concentration of the excited species. Further study is needed to clarify the origin of τ_1 of **Eu@liq**; however, that appears at much higher E_{ex} compared to **Eu@gel** regardless of the origin.

On the other hand, the $I(t)$ profiles for **Eu@gel** in Figure 2b are much more complicated. A fast component was observed even with an excitation energy as low as $E_{\text{ex}} = 0.02$ mJ. Looking closely, both τ_1 and τ_2 become dramatically faster when we increase E_{ex} , whereas A_1 becomes dominant.

As an indication of the total photon number emitting from the sample upon excitation, we introduce the parameter $J(E_{\text{ex}})$

$$J(E_{\text{ex}}) = \int_{t=0}^{\infty} I(t) dt \quad (2).$$

To estimate $J(E_{\text{ex}})$ using Eq. (2), the absolute intensity of the $I(t)$ profiles was scaled in accordance with the sensitivity of the photomultiplier used in the measurements. Figure 3 shows the estimated $J(E_{\text{ex}})$, which is normalized as $J(E_{\text{ex}} = 2.0 \text{ mJ}) = 1.0$ for **Eu@gel**. We have found that $J(E_{\text{ex}})$ for **Eu@gel** drastically increases when E_{ex} becomes large. On the contrary, $J(E_{\text{ex}})$ for **Eu@liq** shows only a weak increase against E_{ex} . The trends of $J(E_{\text{ex}})$ indicate that strong E_{ex} increases the emitting photons for **Eu@gel**, whereas such an obvious increment is not applicable to **Eu@liq**.

We next focus our attention on how E_{ex} influences the pre-exponential factor A_1 in Eq. (1). Figure 4 plots A_1 for **Eu@gel** as a function of E_{ex} . Also shown in Figure 4 is the corresponding data set for **Eu@film**, which is taken from ref [11]. When E_{ex} is increased, both plots increase as a general trend. It is commented that the large error bars for **Eu@gel** data in the small E_{ex} region is as a consequence of small signal intensity when detected. In Figure 4, we find a systematic offset ΔA_1 between the data sets of **Eu@gel** and **Eu@film**, with $\Delta A_1 = 0.2$ – 0.3 . Apart from ΔA_1 , the upward tendency with increasing E_{ex} for both data sets is similar. With regard to the **Eu@film**, it has been proven that when E_{ex} is 0.02 mJ, the $I(t)$ profile is expressed by single exponential decay that causes $A_1 = 0$. Even with employing various ligands for **Eu@film**, a similar trend regarding the increase in A_1 according to E_{ex} has been previously reported [12].

In earlier reports [11,12], we confirmed that **Eu@film** provides ASE when excited with E_{ex} of adequate magnitude. In ref [11, 12], the assignment of ASE is due to the systematic rise of A_1 and the

appearance of the fast component τ_1 , both of which are associated with the increase in E_{ex} . In this context, the observed emission behavior of **Eu@gel** can also be attributed to ASE. The upward tendency for A_1 in Figure 4 for **Eu@gel** is similar to that of **Eu@film**. Furthermore, the emitting photon number measured using $J(E_{\text{ex}})$ dramatically increases with E_{ex} . Such features are characteristic to **Eu@gel** and not applicable to **Eu@liq**.

Finally, we compare the microscopic environments of the organogel and liquid that support $\text{Eu(hfa)}_3(\text{phen})$. The c_{max} in Table 1 is the *bulk* concentration of $\text{Eu(hfa)}_3(\text{phen})$ in the gel or liquid environment. When liquid solvent is used, an isotropic solution is obtained. In contrast, we have reported that the majority of $\text{Eu(hfa)}_3(\text{phen})$ is localized in the exterior of the “fiber-bundle” structure of the organogel, as illustrated in Chart 1a [2]. Under such conditions, we roughly estimate the effective concentration $c_{\text{eff}}(\text{Eu@gel})$ of $\text{Eu(hfa)}_3(\text{phen})$ in the organogel. It is assumed that the complex is located within a space of 0.1 nm from the fiber bundle and solvent interface, estimated by the dimension of the complex. We used atomic force microscopy [15] to obtain the diameter of the fiber bundle and the density of the fiber bundle sustained in the solvent in the gel matrix. As a result, we obtain $c_{\text{eff}}(\text{Eu@gel}) \approx 1 \text{ mol dm}^{-3}$ that is 10^4 times higher than the c_{max} of **Eu@liq**. Such a dense dispersion environment for $\text{Eu(hfa)}_3(\text{phen})$ in the organogel should lead to stronger interactions between the complexes, when photoexcited. This is plausible explanation for the biexponential lifetime of **Eu@gel** even for small E_{ex} gives rise to the offset ΔA_1 between **Eu@gel** and **Eu@liq**, as shown in Figure 4. We suggest that such an environment specific to the organogel is likely responsible for the generation of ASE.

3.3 Estimation of the laser gain factor for **Eu@gel**.

We estimate the laser gain factor for **Eu@gel** applied to a laser material. The gain factor γ at the lasing frequency ν is calculated with [13]

$$\gamma(\nu) = (N_1 - N_2) \frac{c^2}{8\pi n^2 \nu^2 t_{\text{spont}}} g(\nu) \quad (3),$$

where N_i ($i = 1$ or 2) expresses the atom number in state i . In this notation, states 1 and 2 respectively correspond to the ground and excited states of the emitting atom. c , n , and t_{spont} denote the speed of light, the refractive index of the medium, and the spontaneous lifetime of the emitting atom, respectively. The last undefined term in Eq. (3) is $g(\nu)$, which is the spectral shape function of the transitions between states 1 and 2. The parameters in Eq. (3) were estimated according to the following steps. $\nu = 4.88 \times 10^{14}$ from the emission maximum of **Eu@gel** at 614 nm, and $N_1 - N_2 = 4.82 \times 10^{17} \text{ cm}^{-3}$ based on the comparison of the Eu^{3+} number for **Eu@gel** in the optical cuvette and the photon density of the laser excitation pulse irradiated in the cuvette. $t_{\text{spont}} = 1.5 \times 10^{-3} \text{ s}$, which corresponds to τ_2 of **Eu@liq** associated with the average data for $E_{\text{ex}} = 0.05\text{--}0.2 \text{ mJ}$. In that region of E_{ex} , the $I(t)$ profiles decay with a single component. Moreover, $g(\nu)$ is approximately $4.54 \times 10^{-13} \text{ s}$, taken from the inverse of the emission spectral bandwidth with maximum at 614 nm [13]. Relying on the result for **Eu@gel**, $n = 1.4963$, we obtained $\gamma(\nu) \approx 0.001 \text{ cm}^{-1}$. This $\gamma(\nu)$ value corresponds to 1% amplification when light travels 1 cm inside the medium. Note that a conventional helium–neon laser has a gain of $\gamma_{\text{HeNe}}(\nu) \approx 0.005 \text{ cm}^{-1}$ [13].

We have shown above that the emission from **Eu@gel** can be attributed to ASE, based on the $I(t)$ properties of **Eu@film** [11,12]. Along with the estimated $\gamma(\nu)$ above, we suggest that **Eu@gel** might be useful as a laser medium.

4. Summary and future perspective

For this study, we dispersed the $\text{Eu}(\text{hfa})_3(\text{phen})$ complex in an organogel of *p*-chlorophenol and AOT that spontaneously gelled in the nonpolar *m*-xylene solvent. The sample, **Eu@gel**, was excited by the third harmonics of a Nd:YAG laser (355 nm) and the time profile of the emission intensity $I(t)$

was monitored. The $I(t)$ profiles of **Eu@gel** were fitted with a biexponential function. With increasing pulse excitation energy (E_{ex}), the pre-exponential factor of the fast component (A_1) increases and the lifetime (τ_1) markedly decreases (0.06 ms) compared with the usual lifetime of Eu complexes (1.5 ms). In earlier papers we had dispersed $\text{Eu(hfa)}_3(\text{TPPO})_2$ [11] and its derivatives [12] in a polystyrene thin film, which we call **Eu@film**. The E_{ex} -dependent feature of A_1 in **Eu@gel** is rather similar with that reported for the **Eu@film**, which has been assigned to the generation of amplified spontaneous emission (ASE). The total photon number emitting from **Eu@gel** increases as E_{ex} increases, which also implies the presence of ASE. In contrast, such a feature was not detected in the $\text{Eu(hfa)}_3(\text{phen})$ liquid solution.

On the other hand, we have estimated that the laser-gain factor γ for **Eu@gel** resulted in $\gamma \approx 0.001 \text{ cm}^{-1}$. This corresponds to 1% amplification when light travels 1 cm in the medium. In connection with our prior results on **Eu@film**, we suggest that **Eu@gel** can be also used as a laser material. If rare-earth complexes are realized as laser materials, one can obtain lasing wavelengths that are not available from conventional LD lasers, without relying on the wavelength-conversion technique. Furthermore, organogel materials can be easily reformatted when used in optical equipment. This is an advantage of using organogel materials as dispersing media.

We can disperse $\text{Eu(hfa)}_3(\text{phen})$ as much as $8.0 \times 10^{-4} \text{ mol dm}^{-3}$ in this type of organogel. This is 8 times more than the saturation level of $\text{Eu(hfa)}_3(\text{phen})$ dissolved in *m*-xylene. Furthermore, in the present organogel environment, $\text{Eu(hfa)}_3(\text{phen})$ is localized in the exterior of the fiber-bundle structure [2]. We estimated the effective concentration $c_{\text{eff}}(\text{Eu@gel})$ of $\text{Eu(hfa)}_3(\text{phen})$ localized in the organogel architecture, $c_{\text{eff}}(\text{Eu@gel}) = 1 \text{ mol dm}^{-3}$, which is 10^4 times as much as that in organic solvents. Such a characteristic dense dispersion environment of $\text{Eu(hfa)}_3(\text{phen})$ in the organogel offers specific interactions between the complexes followed by photoexcitation. The $I(t)$ profile depending on E_{ex} is an example caused by such interactions, as shown in this study. Another merit of the specific organogel environment is that the emission quantum yield of **Eu@gel** ($\Phi_f = 0.22$) is enhanced, compared with that of **Eu@liq** ($\Phi_f = 0.16$). On the other hand, the interaction between the

rare-earth complex and organogel structure may also be critical in such characteristic photochemical behavior. Further studies to clarify the dispersion structure of the complexes and the interaction mechanisms are needed.

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Table 1. $c_{\max}$ and Φ_f of $\text{Eu(hfa)}_3(\text{phen})$ dispersed in the organogel and organic solvent.

sample	$c_{\max}$ $10^{-4} \text{ mol dm}^{-3}$	Φ_f
Eu@gel	8.0 ^{a)}	0.22
Eu@liq ^{b)}	1.0 ^{a)}	0.16

^{a)} Data are from ref [2].

^{b)} Dispersed in *m*-xylene solvent.

Table 2. Lifetimes and pre-exponential factors. ^{a)}

sample	$E_{\text{ex}} / \text{mJ}$	$\tau_1 / \text{ms} (A_1)$	$\tau_2 / \text{ms} (A_2)$
Eu@liq	0.05 ^{b)}	—	$1.54 \pm 0.01 (1.00)$
	0.1 ^{b)}	—	$1.56 \pm 0.01 (1.00)$
	0.2 ^{b)}	—	$1.48 \pm 0.01 (1.00)$
	0.5	$0.32 \pm 0.01 (0.30 \pm 0.02)$	$1.44 \pm 0.02 (0.70 \pm 0.02)$
	1.0	$0.22 \pm 0.01 (0.31 \pm 0.01)$	$1.40 \pm 0.01 (0.69 \pm 0.01)$
	2.0	$0.20 \pm 0.01 (0.34 \pm 0.00)$	$1.39 \pm 0.01 (0.66 \pm 0.00)$
Eu@gel	0.02	$0.60 \pm 0.09 (0.33 \pm 0.07)$	$1.50 \pm 1.10 (0.67 \pm 0.07)$
	0.05	$0.37 \pm 0.04 (0.28 \pm 0.04)$	$1.35 \pm 0.04 (0.72 \pm 0.04)$
	0.1	$0.28 \pm 0.01 (0.36 \pm 0.01)$	$1.30 \pm 0.02 (0.64 \pm 0.02)$
	0.2	$0.26 \pm 0.01 (0.38 \pm 0.01)$	$1.29 \pm 0.02 (0.62 \pm 0.01)$
	0.5	$0.18 \pm 0.01 (0.38 \pm 0.01)$	$1.21 \pm 0.01 (0.62 \pm 0.01)$
	1.0	$0.15 \pm 0.00 (0.41 \pm 0.01)$	$1.13 \pm 0.01 (0.59 \pm 0.01)$
	2.0	$0.08 \pm 0.00 (0.52 \pm 0.00)$	$0.83 \pm 0.01 (0.48 \pm 0.00)$

^{a)} The standard deviation is indicated to the second decimal.

^{b)} Only the component τ_2 was observed.

Figure and chart captions

Chart 1. (a) Chemical components of the phenol + AOT organogel used in this study. The “strand” structure consists of stacked benzene rings, and the higher-order architectures “fiber” and “fiber bundle” are based on ref [10] for aromatic and alkane solvents. (b) The chemical structure of $\text{Eu(hfa)}_3(\text{phen})$.

Figure 1. The emission spectra of **Eu@liq** with *m*-xylene (dashed line) and **Eu@gel** (solid) detected with $\lambda_{\text{ex}} = 355$ nm.

Figure 2. The time profiles of the emission intensity $I(t)$ for (a) **Eu@liq** and (b) **Eu@gel**, respectively, excited with $\lambda_{\text{ex}} = 355$ nm. The details of the excitation pulse energy E_{ex} are shown in the boxes in each panel, where representative values are provided besides the decay profiles for visual aid. The $I(t)$ profiles in panel (a) at $E_{\text{ex}} = 0.05\text{--}0.2$ mJ mostly overlap. The profile in panel (b) becomes monotonically faster with increasing E_{ex} .

Figure 3. The parameter $J(E_{\text{ex}})$ estimated with Eq. (2) as indicative of the photon number emitting from **Eu@liq** (triangles) and **Eu@gel** (circles) upon excitation. $J(E_{\text{ex}})$ is scaled to $J(E_{\text{ex}} = 2.0 \text{ [mJ]}) = 1.0$ for **Eu@gel**.

Figure 4. The excitation pulse energy (E_{ex}) dependence of the fast component of the pre-exponential factor (A_1) fitted to the emission time profile, $I(t)$, based on Eq. (1). The circles indicate the obtained A_1 for **Eu@gel**, along with the error bars which are from Table 2. The squares stand for **Eu@film**, the data set of which is taken from ref [11].

Figure

K. Nishiyama and coworkers, Chart. 1

K. Nishiyama and coworkers, Fig. 1.

K. Nishiyama and coworkers, Fig. 2.

K. Nishiyama and coworkers, Fig. 3.

K. Nishiyama and coworkers, Fig. 4.