



Emission properties of [Eu(hfa)₃(phen)] and [Eu(hfa)₃(TPPO)₂] dispersed in a fibrous network comprising *p*-chlorophenol + AOT organogels

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ABSTRACT

The rare-earth complexes [Eu(hfa)₃(phen)] and [Eu(hfa)₃(TPPO)₂] were dispersed in the fibrous network structure of an organogel of phenol and surfactant AOT. Steady-state and time-resolved emission properties arising from the complex–organogel interactions of these two complexes were investigated. The results suggest that [Eu(hfa)₃(phen)] localizes around the fibrous structure of the organogel architecture, whereas [Eu(hfa)₃(TPPO)₂] favors the solvent domain even when dispersed in the gel environment. These properties characterize the steady state and time-resolved behavior in the emission processes of the [Eu(hfa)₃(phen)] and [Eu(hfa)₃(TPPO)₂] complexes, which can be regarded as “gelaphilic” and “solvophilic,” respectively.

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1. Introduction

Eu³⁺ complexes have been extensively employed as emitting devices, which can be applied to circularly polarized emitters [1,2], bioassay [3], and phosphors for temperature sensing [4]. Such versatile applications of Eu³⁺ complexes are due to the remarkably high quantum efficiency of emission (Φ_{em}). Moreover, the dominant 4f–4f emission from Eu³⁺ complexes, which is assigned to the ⁵D₀–⁷F₂ transition (appearing at around 610 nm), typically has a very narrow spectral bandwidth in solution (≤ 80 cm^{−1}). These properties make Eu³⁺ complexes suitable as bright, luminescent, and monochromatic light sources. Specifically, the high efficiency of Φ_{em} can be explained by the larger energy difference between the ground and excited states of the Eu³⁺ ion when compared to that of other rare earth (Ln³⁺) ions, which inhibits the nonradiative transition of the excited ion [5]. On the other hand, the environment around the Eu³⁺ ligands or solvents alters both the maximum wavelength and spectral bandwidth of their emission spectra to a lesser degree. These properties are also a characteristic of the 4f–4f transition.

In our previous report [6], the Eu³⁺ complex [Eu(hfa)₃(phen)] was dispersed in an organogel composed of *p*-chlorophenol and surfactant AOT in *m*-xylene solvent. Hexafluoroacetylacetone (hfa) and 1,10-phenanthroline (phen) were used as the ligands for the Eu³⁺ complex (Chart 1). Nanosecond laser spectroscopy was used to detect the emission time profile, $I(t)$, of the system. Based on the detailed analysis of $I(t)$, we have concluded that the system generates amplified spontaneous emission (ASE) upon laser excitation [6]. In our previous paper, ASE generation has been ascribed to the specific structure of the complex dispersed in the gel. Atomic force microscopy [7] and optical microscopy in this study show that the organogel formed from *p*-chlorophenol and AOT has a “fiber bundle” structure with a length and diameter of 15 μ m and 0.5 nm, respectively. Moreover, precise analysis of steady-state emission spectra of the system [8] suggests that [Eu(hfa)₃(phen)] is localized around the exterior of the fiber bundle when dispersed in the gel. Because of such a specific structure, [Eu(hfa)₃(phen)] can be dispersed in the organogel up to a maximum concentration of $c_{max} = 1.0 \times 10^{-3}$ mol dm^{−3}. This c_{max} value is a magnitude higher than that of the [Eu(hfa)₃(phen)] complex dissolved in the *m*-xylene solvent, where $c_{max} = 1.0 \times 10^{-4}$ mol dm^{−3}. We have proposed that such a specific dispersing structure of [Eu(hfa)₃(phen)] in the organogel would make ASE generation possible.

On the other hand, Eu³⁺ complexes possessing both hfa and a ligand with a P=O group have been known to have Φ_{em} as high as

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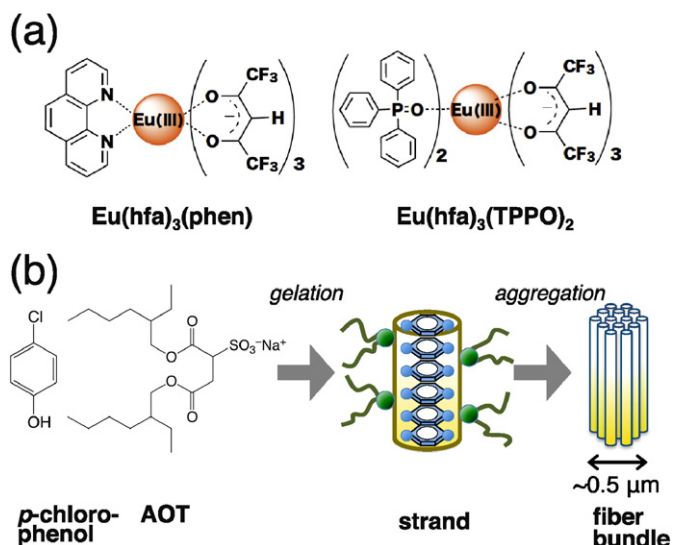


Chart 1. Chemical structures employed in this work. (a) Eu^{3+} complexes and (b) the organogel.

those with a phen ligand when applied to emitting materials [9,10]. Triphenylphosphine oxide (TPPO) is a representative ligand comprising the P=O group. Hasegawa, Nakamura and coworkers have suggested that the vibration frequency of the P=O group can also inhibit nonradiative transitions of Eu^{3+} or Ln^{3+} 4f–4f emission, which eventually enhances the radiative path [9,10]. It is also reported that the C–F group in the hfa ligand plays a similar role in the emission process [9]. Given the ligand-driven properties of Eu^{3+} complexes that behave as emitting materials, a question arises on the emission behavior of the TPPO ligands when dispersed inside the fibrous network of the organogel.

In this report, steady-state emission spectra and $I(t)$ measurements suggest that $[\text{Eu}(\text{hfa})_3(\text{TPPO})_2]$ and $[\text{Eu}(\text{hfa})_3(\text{phen})]$ show completely opposite behavior when dispersed in the organogel: whereas $[\text{Eu}(\text{hfa})_3(\text{TPPO})_2]$ favors the solvent domain, $[\text{Eu}(\text{hfa})_3(\text{phen})]$ localizes in the vicinity of the organogel fibrous network. We, therefore, propose that $[\text{Eu}(\text{hfa})_3(\text{phen})]$ and $[\text{Eu}(\text{hfa})_3(\text{TPPO})_2]$ may be called “gelaphilic” and “solvophilic,” respectively. This study shows the differences in emission properties due to the contrasting natures of these complexes. Henceforth, we denote the systems where $[\text{Eu}(\text{hfa})_3(\text{phen})]$ and $[\text{Eu}(\text{hfa})_3(\text{TPPO})_2]$ are dispersed in the organogel as “phen@gel” and “TPPO@gel,” respectively. In an analogous way, we refer to the samples with these complexes dissolved in the *m*-xylene solvent as “phen@liq” and “TPPO@liq,” respectively.

2. Materials and methods

2.1. Materials

The preparation of $[\text{Eu}(\text{hfa})_3(\text{phen})]$, or tris(1,1,1,5,5,5-hexafluoropentane-2,4-dionato)(1,10-phenanthroline)europium(III), has been described in our previous report [8]. In this work, $[\text{Eu}(\text{hfa})_3(\text{TPPO})_2]$, or tris(1,1,1,5,5,5-hexafluoropentane-2,4-dionato) {bis(triphenylphosphine oxide)europium(III)}, was synthesized as follows. $[\text{Eu}(\text{hfa})_3(\text{H}_2\text{O})_2]$ (1.43 g , $1.77 \times 10^{-3} \text{ mol}$) and TPPO (0.93 g , $3.35 \times 10^{-3} \text{ mol}$) were dissolved in 30 cm^3 methanol, and the solution was stirred for 24 h under reflux. After the reaction, the solvent was removed with a rotary evaporator to yield brown viscous oil. After filtration, excess toluene was added to obtain a solution phase. The solvent remaining in the filtrated solution-phase was removed by the evaporator. The resulting solid was recrystallized from hot methanol. The grain crystal thus obtained was collected by filtration and dried in vacuo. Yield: 22%. ^1H NMR (acetone- d_6 , 400 MHz, 293 K) δ : 8.5–8.1 (broad), 7.8–7.5 (m, aromatic), 5.4–5.1 (broad) ppm. FTIR (ATR): 1740, 1651

(C=O), 1500, 1250 (C–F), 1192, 1142 (P=O), 795, 721, 687, 660 cm^{-1} . Anal. Found: C, 45.29; H, 2.57; N, 0.13%. Calcd. for $\text{C}_{51}\text{H}_{33}\text{EuF}_{18}\text{O}_8\text{P}_2 \cdot \text{H}_2\text{O}$: C, 45.45; H, 2.62; N, 0.00%.

Preparation methods of the phenol + AOT organogel are detailed in our previous reports [6,8,11], and the gel architecture of this organogel has been discussed in detail by Simmons and coworkers [7]. In brief, 0.14 mol dm^{-3} *p*-chlorophenol and 0.10 mol dm^{-3} AOT (bis(2-ethylhexyl)sulfosuccinate) in the *m*-xylene solution were mixed to spontaneously produce a gel at room temperature (298 K). On dispersing the Eu^{3+} complexes into the organogel, $[\text{Eu}(\text{hfa})_3(\text{phen})]$ or $[\text{Eu}(\text{hfa})_3(\text{TPPO})_2]$ was added to the gel with a dispersing concentration c_{disp} , which is specified in the latter sections, and the system was heated up to 353 K to form an isotropic solution. The system was then cooled down to room temperature to reobtain the gel phase. Surface structures of the gel samples were observed with a Nikon Eclipse LV 100ND microscope, equipped with an objective lens (magnification $\times 150$). The microscopy images were recorded through a DS-Fi2 digital imaging camera. For optical microscopy, the gel sample was melted under 353 K, drop-cast onto a glass slide, and left to cool to room temperature for observation.

2.2. Measurements of the photochemical properties

Experimental setups of both steady-state and time-resolved spectroscopy are described in our previous paper [6]. In brief, a Jasco IIF-533 integrating sphere combined with a Jasco FP-6500 spectrofluorometer was used for the Φ_{em} measurements. For $I(t)$ measurements, we used the laser equipment reported elsewhere [6,10,12]. Third harmonics of an Nd:YAG laser ($\lambda_{\text{ex}} = 355 \text{ nm}$), from B. M. Industries (10 Hz, 9 ns), was used as an excitation light source. The hfa moiety of $[\text{Eu}(\text{hfa})_3(\text{phen})]$ or $[\text{Eu}(\text{hfa})_3(\text{TPPO})_2]$ was excited at $\lambda_{\text{ex}} = 355 \text{ nm}$ and emission from the Eu^{3+} ion was obtained as a result of the energy transfer from the hfa ligand to the rare earth ion. The gel or liquid sample was contained in a quartz cell, where the excitation beam traveled 2 mm with normal incidence. The emission from the system was monitored from a perpendicular side of the cell, which was monochromated at 614 nm to detect the Eu^{3+} $^5\text{D}_0$ – $^7\text{F}_2$ emission. This was recorded with a digital oscilloscope at 1 GHz.

3. Results and discussion

3.1. Steady-state emission spectra of Eu^{3+} complexes

Fig. 1 illustrates steady-state emission spectra of the Eu^{3+} complexes studied in this work. As expected, the three dominant bands from the Eu^{3+} emission were in the region of 580, 593, and 610–620 nm due to the $^5\text{D}_0$ – $^7\text{F}_0$, $^5\text{D}_0$ – $^7\text{F}_1$, and $^5\text{D}_0$ – $^7\text{F}_2$ transitions, respectively [9]. Notably, these transitions are classified as forbidden, magnetic-dipole, and electric-dipole transition bands, respectively [9]. In the present complexes, the $^5\text{D}_0$ – $^7\text{F}_2$ band is 10 times more intense than the $^5\text{D}_0$ – $^7\text{F}_1$ band, owing to an asymmetric environment around the Eu^{3+} center [13,14]. Hasegawa and coworkers have reported that the ligand coordination geometry should be a square antiprism for $[\text{Eu}(\text{hfa})_3(\text{TPPO})_2]$, which has an asymmetric structure around the Eu^{3+} ion [12]. We therefore suggest that $[\text{Eu}(\text{hfa})_3(\text{phen})]$ can also have an asymmetric coordination, which enhances the intensities of the $^5\text{D}_0$ – $^7\text{F}_2$ band, detected at 612 nm or 614 nm either in the solvent or gel.

Because of the $^5\text{D}_0$ – $^7\text{F}_2$ transition of $[\text{Eu}(\text{hfa})_3(\text{phen})]$, the band in the gel shifts by $\approx 2 \text{ nm}$ toward the red side of the spectrum when compared to that in the solvent. Moreover, the spectrum from phen@gel is broader than that of phen@liq. Such changes are attributed to the environment around the $[\text{Eu}(\text{hfa})_3(\text{phen})]$ complex. On the one hand, the $^5\text{D}_0$ – $^7\text{F}_2$ transition of TPPO@liq has three bands at 612, 614, and 617 nm, with the transition at 614 nm having the maximum intensity. In contrast, the TPPO@gel spectrum is rather broad and

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