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 $[\text{Eu}(\text{hfa})_3(\text{phen})]$ and $[\text{Eu}(\text{hfa})_3(\text{TPPO})_2]$ 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 $[\text{Eu}(\text{hfa})_3(\text{phen})]$ localizes around the fibrous structure of the organogel architecture, whereas $[\text{Eu}(\text{hfa})_3(\text{TPPO})_2]$ 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 $[\text{Eu}(\text{hfa})_3(\text{phen})]$ and $[\text{Eu}(\text{hfa})_3(\text{TPPO})_2]$ complexes, which can be regarded as “gelaphilic” and “solvophilic,” respectively.

Keywords

organogel, soft material, Eu complex, gelaphilic, solvophilic

1. Introduction

Eu^{3+} 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 Eu^{3+} complexes are due to the remarkably high quantum efficiency of emission (Φ_{em}). Moreover, the dominant 4f–4f emission from Eu^{3+} complexes, which is assigned to the $^5\text{D}_0$ – $^7\text{F}_2$ transition (appearing at around 610 nm), typically has a very narrow spectral bandwidth in solution ($\leq 80 \text{ cm}^{-1}$). These properties make Eu^{3+} 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 Eu^{3+} ion when compared to that of other rare earth (Ln^{3+}) ions, which inhibits the nonradiative transition of the excited ion [5]. On the other hand, the environment around the Eu^{3+} ligands or solvents alters both the maximum wavelength and spectral bandwidth of their emission spectra to a lesser degree. These properties are also characteristic of the 4f–4f transition.

In our previous report [6], the Eu^{3+} complex $[\text{Eu}(\text{hfa})_3(\text{phen})]$ 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 Eu^{3+} 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 μm and 0.5 μm , respectively. Moreover, precise analysis of steady-state emission spectra of the system [8] suggests that $[\text{Eu}(\text{hfa})_3(\text{phen})]$ is localized around the exterior of the fiber bundle when dispersed in the gel. Because of such a specific structure, $[\text{Eu}(\text{hfa})_3(\text{phen})]$ can be dispersed in the organogel up to a maximum concentration of $c_{\text{max}} = 1.0 \times 10^{-3} \text{ mol dm}^{-3}$. This c_{max} value is a magnitude higher than

that of the $[\text{Eu}(\text{hfa})_3(\text{phen})]$ complex dissolved in the *m*-xylene solvent, where $c_{\text{max}} = 1.0 \times 10^{-4}$ mol dm^{-3} . We have proposed that such a specific dispersing structure of $[\text{Eu}(\text{hfa})_3(\text{phen})]$ in the organogel would make ASE generation possible.

On the other hand, Eu^{3+} complexes possessing both hfa and a ligand with a P=O group have been known to have Φ_{em} as high as 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, [Eu(hfa)₃(TPPO)₂], or tris(1,1,1,5,5,5-hexafluoropentane-2,4-dionato){bis(triphenylphosphine oxide)}europium(III), was synthesized as follows. [Eu(hfa)₃(H₂O)₂] (1.43 g, 1.77×10^{-3} mol) and TPPO (0.93 g, 3.35×10^{-3} mol) were dissolved in 30 cm³ 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 C₅₁H₃₃EuF₁₈O₈P₂·H₂O: 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 Eu³⁺ complexes into the organogel, [Eu(hfa)₃(phen)] or [Eu(hfa)₃(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 ILF-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 a Nd:YAG laser ($\lambda_{\text{ex}} = 355$ nm), from B. M. Industries (10 Hz, 9 ns), was used as an excitation light source. The hfa moiety of [Eu(hfa)₃(phen)] or [Eu(hfa)₃(TPPO)₂] was excited at $\lambda_{\text{ex}} = 355$ nm and emission from the Eu³⁺ 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 Eu³⁺ ⁵D₀–⁷F₂ emission. This was recorded with a digital oscilloscope at 1 GHz.

3. Results and discussion

3.1 Steady-state emission spectra of Eu³⁺ complexes

Figure 1 illustrates steady-state emission spectra of the Eu³⁺ complexes studied in this work. As expected, the three dominant bands from the Eu³⁺ emission were in the region of 580, 593, and 610–620 nm due to the ⁵D₀–⁷F₀, ⁵D₀–⁷F₁, and ⁵D₀–⁷F₂ transitions, respectively [9]. Notably, these transitions are classified as forbidden, magnetic-dipole, and electric-dipole transition bands, respectively [9]. In the present complexes, the ⁵D₀–⁷F₂ band is 10 times more intense than the ⁵D₀–⁷F₁ band, owing to an asymmetric environment around the Eu³⁺ center [13, 14]. Hasegawa and coworkers have reported that the ligand coordination geometry should be a square antiprism for [Eu(hfa)₃(TPPO)₂], which has an asymmetric structure around the Eu³⁺ ion [12]. We therefore suggest that [Eu(hfa)₃(phen)] can also have an asymmetric coordination, which enhances the intensities of the ⁵D₀–⁷F₂ band, detected at 612 nm or 614 nm either in the solvent or gel.

Because of the $^5D_0-^7F_2$ transition of $[Eu(hfa)_3(phen)]$, the band in the gel shifts by ≈ 2 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 $[Eu(hfa)_3(phen)]$ complex. On the one hand, the $^5D_0-^7F_2$ transition of **TPPO@liq** has three bands at 612, 614, and 617 nm, with the transition at 614 nm having the maximum intensity. On the other hand, the **TPPO@gel** spectrum is rather broad and appears like a single band. However, upon closer observation, some shoulders are discernible at 612 nm in both **TPPO@gel**, and **TPPO@liq**. Notably, the spectral peaks for both **TPPO@gel** and **TPPO@liq** can be observed at 617 nm. This suggests that when $[Eu(hfa)_3(TPPO)_2]$ is dispersed in the gel environment, some part of the complex may still remain in the solvent domain.

The emission spectra shown in Figure 1 suggest that Φ_{em} of the complexes depends on both the type of ligand used (TPPO vs. phen) and the nature of their environment (gel vs. solvent), (Table 1). Thus, Φ_{em} of **TPPO@liq** and **TPPO@gel** are ca 1.5–2 times larger than those of the phen derivatives in the corresponding environment. This increase can be ascribed to the P=O bond inhibiting the nonradiative transition. On comparing the gel and solvent environments, Φ_{em} of **TPPO@gel** was found to be smaller than that of **TPPO@liq**. This is entirely opposite to that of $[Eu(hfa)_3(phen)]$, where Φ_{em} of **phen@gel** is greater than that of **phen@liq**.

Figure 2a depicts the c_{disp} dependence of the $[Eu(hfa)_3(TPPO)_2]$ emission spectra, where c_{disp} was varied between 50 and $800 \times 10^{-6} \text{ mol dm}^{-3}$. If c_{disp} is as low as $50-100 \times 10^{-6} \text{ mol dm}^{-3}$, then the spectra are rather broad, as discussed in Figure 1. When c_{disp} exceeds $200 \times 10^{-6} \text{ mol dm}^{-3}$, the spectra shift toward the blue side and shoulders appear at 612 nm and 614 nm. The spectra detected with $c_{disp} = 400 \times 10^{-6} \text{ mol dm}^{-3}$ or more are somewhat similar to that in the solvent, drawn as **TPPO@liq**.

We then tried to reproduce a spectral function observed at a certain concentration, $I(c_{disp})$, with the assumption that:

$$I(c_{\text{disp}}) = f_{\text{dil}}I_{\text{dil}}(c_{\text{disp}}) + f_{\text{liq}}I_{\text{liq}}(c_{\text{disp}}) \quad (1)$$

with

$$f_{\text{dil}} + f_{\text{liq}} = 1$$

where the subscripts “dil” and “liq” mean the gel with the most diluted concentration ($c_{\text{disp}} = 50 \times 10^{-6} \text{ mol dm}^{-3}$ in the case of $[\text{Eu}(\text{hfa})_3(\text{TPPO})_2]$), and the *m*-xylene solvent, respectively; f_x denotes the weighting factor for the spectral function. Figure 2b is an example of the reproduction of the spectrum with $c_{\text{disp}} = 200 \times 10^{-6} \text{ mol dm}^{-3}$, where the observed spectrum is well reconstructed from Eq. (1). Notably, such a reproduction was generally applicable to the spectra in the region of $c_{\text{disp}} = 100\text{--}800 \times 10^{-6} \text{ mol dm}^{-3}$ for $[\text{Eu}(\text{hfa})_3(\text{TPPO})_2]$. It is commented that an obvious isoemissive point is not recognized in Figure 2a, because the ordinate of Figure 2a is normalized to unity. Even in this procedure, we emphasize that the spectral reproduction according to Eq. (1) was proven to be appropriate in the global c_{disp} region. On the other hand, we have already shown that a similar reproduction is also possible for $[\text{Eu}(\text{hfa})_3(\text{phen})]$ both in the gel and solvent [8].

Figure 2c compares the trends of f_{dil} and f_{liq} for both complexes. When c_{disp} is increased, f_{liq} increases while f_{dil} decreases monotonically. We underline that f_{dil} and f_{liq} were determined from the spectral functions I_{dil} and I_{liq} which are normalized to unity in their intensities. A quantitative analysis for f_{dil} and f_{liq} with taking raw intensities of I_{dil} and I_{liq} into concern may be rather difficult, due to experimental requirements on the emission measurements. However, we can discuss the c_{disp} -dependent behaviors f_{dil} and f_{liq} , at least in a qualitative level. Keeping the appropriate spectral reproduction in mind, the trends of f_{dil} and f_{liq} imply a “two-state model” for the complex dispersion structure in the organogel, where a part of the complex is close to the organogel structure, and the other is in the solvent domain, free from the gel architecture. We have already proposed such a model for $[\text{Eu}(\text{hfa})_3(\text{phen})]$ in the previous report [8]. In the current study, the two-state model is

also proven to be applicable to $[\text{Eu}(\text{hfa})_3(\text{TPPO})_2]$. In the case of **phen@gel**, on the other hand, we have proposed that a number of $[\text{Eu}(\text{hfa})_3(\text{phen})]$ groups localize around the exterior of the fiber bundle [8], which in turn brings about ASE generation [6].

With a detailed view of Figure 2c, f_{liq} of $[\text{Eu}(\text{hfa})_3(\text{TPPO})_2]$ increases with c_{disp} more steeply than that of $[\text{Eu}(\text{hfa})_3(\text{phen})]$. For instance, f_{liq} of $[\text{Eu}(\text{hfa})_3(\text{TPPO})_2]$ reaches 0.5 at $c_{\text{disp}} = 200 \times 10^{-6} \text{ mol dm}^{-3}$, whereas f_{liq} of $[\text{Eu}(\text{hfa})_3(\text{phen})]$ attains this value at $c_{\text{disp}} = 400 \times 10^{-6} \text{ mol dm}^{-3}$. Based on such different behavior, we can tentatively propose that $[\text{Eu}(\text{hfa})_3(\text{TPPO})_2]$ favors the solvent domain to the organogel domain. To test such a hypothesis, we performed optical microscopy, discussed in the ensuing subsection.

3.2. Organogel surface structures by optical microscopy

Figure 3 shows the images of the organogel surface structures of **phen@gel** and **TPPO@gel** obtained by optical microscopy, where c_{disp} was varied between 200 and $800 \times 10^{-6} \text{ mol dm}^{-3}$ and between 200 and $3,200 \times 10^{-6} \text{ mol dm}^{-3}$, respectively. The images captured by the microscopy correspond to the fiber bundle presented in Chart 1. According to the analysis of the microscopy images, when $c_{\text{disp}} = 200 \times 10^{-6} \text{ mol dm}^{-3}$ for **phen@gel**, the average length l and diameter d of the fiber bundle are $l = 15 \text{ }\mu\text{m}$ and $d = 0.5 \text{ }\mu\text{m}$, respectively. When c_{disp} is increased to $800 \times 10^{-6} \text{ mol dm}^{-3}$, which is close to c_{max} of **phen@gel**, l shrinks to $10 \text{ }\mu\text{m}$ and d decreases to $\approx 0.4 \text{ }\mu\text{m}$. These findings agree with the trends shown by the dispersion structure in the gel environment in our previous studies [6, 8]. Assuming that $[\text{Eu}(\text{hfa})_3(\text{phen})]$ is mainly located in the exterior of the fiber bundle, it can be surmised that the increase in c_{disp} could interfere with the further growth of the fiber bundle. We have estimated that because of such a localized structure, an effective concentration of $[\text{Eu}(\text{hfa})_3(\text{phen})]$ cannot be less than 1 mol dm^{-3} [6]. Alternatively, we can assume that the decrease in the size of the fiber bundle may be ascribed to the increased complex–complex interactions.

The values provided by **TPPO@gel**, namely $l = 10\ \mu\text{m}$ and $d = 0.6\ \mu\text{m}$, are hardly altered by an increase in c_{disp} . The assumption that $[\text{Eu}(\text{hfa})_3(\text{TPPO})_2]$ would stay in the solvent domain irrespective of the increase of c_{disp} could also be plausible.

With these observations, we can draw a schematic diagram of how the complexes are dispersed in the organogel architecture depending on c_{disp} . As illustrated in Figure 4, $[\text{Eu}(\text{hfa})_3(\text{phen})]$ favors the exterior of the fiber bundle, which we may call “gelaphilic” in character, while $[\text{Eu}(\text{hfa})_3(\text{TPPO})_2]$ favors the solvent domain even though it is dispersed densely in the gel, and this can be labeled as “solvophilic” in nature. These observations can explain the c_{disp} dependences of the emission spectra and optical microscopy. Moreover, we confirmed that c_{max} for $[\text{Eu}(\text{hfa})_3(\text{TPPO})_2]$ both in the gel and *m*-xylene solvent is $3,200 \times 10^{-6}\ \text{mol dm}^{-3}$. To be rephrased, $[\text{Eu}(\text{hfa})_3(\text{TPPO})_2]$ in the gel environment less “senses” the fibrous gel architecture. Such a feature also corresponds to a diagram shown in Figure 4.

3.3. Emission time profiles depending on the excitation pulse energy

The characteristic properties of $[\text{Eu}(\text{hfa})_3(\text{phen})]$ and $[\text{Eu}(\text{hfa})_3(\text{TPPO})_2]$ that we have classified as gelaphilic and solvophilic, respectively, may emerge in different aspects, as has been discussed in the previous subsections. Figure 5 compares the $I(t)$ profiles of **TPPO@liq** and **TPPO@gel** depending on E_{ex} , along with the typical data-sets of $[\text{Eu}(\text{hfa})_3(\text{phen})]$. For **TPPO@liq**, all the profiles mostly overlap, as seen in Figure 5a. These profiles exhibit a single exponential decay with lifetime $\tau = 0.70 \pm 0.02\ \text{ms}$, which is scarcely dependent on E_{ex} . In the solvent, the $I(t)$ profiles of **phen@liq** decay with a single lifetime; for instance, $\tau = 1.56 \pm 0.01\ \text{ms}$ when $E_{\text{ex}} = 0.1\ \text{mJ}$. The fast decay which was recognized with $E_{\text{ex}} = 0.5\ \text{mJ}$ or more has been attributed to the annihilation, due to the interaction between excited-state species under the high concentration of the complex [6].

For the organogel, all the $I(t)$ profiles of **phen@gel** were fitted with the fast and slow components, and the latter of which corresponds to the **phen@liq** lifetime. Based on detailed and careful analysis, we have concluded that the $I(t)$ behavior of **phen@gel** is due to ASE generation

[6]. On the contrary, the **TPPO@gel** profiles decay with a single lifetime ($\tau = 0.73 \pm 0.01$ ms), even in the gel. This value is very similar to that of **TPPO@liq**.

Such contrasting behavior of **phen@gel** and **TPPO@gel** in terms of $I(t)$ may be associated with the gelaphilic and solvophilic natures of the complexes, respectively. In a previous report, we proposed that ASE generation, due to the effective concentration of $[\text{Eu}(\text{hfa})_3(\text{phen})]$ dispersed in the gel, can be estimated to be as much as 1 mol dm^{-3} . This is about 10^4 times higher than that in the solvent [6]. Under such conditions, the gelaphilic species $[\text{Eu}(\text{hfa})_3(\text{phen})]$ is densely dispersed around the gel architecture and this could give rise to specific interactions between the excited complexes. **TPPO@gel**, a solvophilic complex, behaves as if the species were in the neat solvent throughout the photochemical processes. Thus, the gel architecture hardly affects the complex in either the ground or the excited state. Such a feature could bring about a single lifetime, indicating that the species emits almost independently even when excited with a sufficiently large E_{ex} . This is a plausible explanation for the general behavior of the two Eu^{3+} complexes studied in the organogel and solvent environments.

4. Summary and future perspective

In this report, we have dispersed the $[\text{Eu}(\text{hfa})_3(\text{phen})]$ and $[\text{Eu}(\text{hfa})_3(\text{TPPO})_2]$ complexes in an organogel composed of *p*-chlorophenol and AOT, which gelled by self-assembly in the nonpolar *m*-xylene solvent. UV excitation studies have shown the emitting properties of these systems, which we denoted as **phen@gel** and **TPPO@gel**, respectively. The steady-state emission spectra of **phen@gel** and **TPPO@gel** with a dispersion concentration, c_{disp} , were well reproduced as a summation of their spectra in the solvent (**phen@liq** and **TPPO@liq**, respectively), together with those in the gel with diluted c_{disp} conditions. We have therefore proposed a two-state model of how the complex is dispersed in the organogel architecture; a part of the complex is in the exterior of the fiber bundle, or the fibrous network of the gel, and the other in the solvent domain. Such a model

has already been proposed for **phen@gel** in our previous publication [8]. The present work has proven that such a two-state model is also appropriate for **TPPO@gel**. Optical microscopy in the submicrometer domain was also carried out to detect gel-surface structures, whose images again indicate the applicability of the two-state model. On the other hand, detailed investigations of the c_{disp} -dependent emission spectra and microscopy provided us with information regarding mutual interactions between the organogel architecture and the complexes; $[\text{Eu}(\text{hfa})_3(\text{phen})]$ favors the gel domain, while $[\text{Eu}(\text{hfa})_3(\text{TPPO})_2]$ favors the solvent domain. We call such characters of the complexes “gelaphilic” and “solvophilic,” respectively.

From another standpoint, the adsorption capacity of these Eu^{3+} complexes to the exterior of the gel structure can play an essential role for the gelaphilic and solvophilic features. We suggest that such differences in adsorption may also affect the organogel morphology. Further detailed investigation by means of small-angle X-ray scattering (SAXS), atomic-force microscopy (AFM), and FTIR should be indeed useful to determine the gel morphology with complexes dispersed. In the forthcoming paper [15], we will use these methods to elucidate higher-order structures and morphologies of organogels.

As regards **phen@gel**, where a high concentration of $[\text{Eu}(\text{hfa})_3(\text{phen})]$ localizes around the organogel architecture because of the gelaphilic feature, the emission time-profile $I(t)$ considerably depended on the excitation-pulse energy E_{ex} . $I(t)$ has shown double exponential decay in the global E_{ex} region, owing to the generation of amplified spontaneous emission (ASE), when $E_{\text{ex}} \geq 0.1$ mJ [6]. The solvophilic complex $[\text{Eu}(\text{hfa})_3(\text{TPPO})_2]$, on the other hand, remains in the solvent domain even when dispersed with a high c_{disp} . The complex exhibits $I(t)$ with a single lifetime of ≈ 0.7 ms, regardless of E_{ex} , and the environment (gel or solvent). An advantage of the **TPPO@gel** system is that the complex emits almost independently in various environments. Even when dispersed in the organogel, a solvophilic species behaves as though it were dissolved in a solvent upon photo-excitation. Such a property will be indeed beneficial when applied to monochromatic emitting devices. Another advantage of $[\text{Eu}(\text{hfa})_3(\text{TPPO})_2]$ over $[\text{Eu}(\text{hfa})_3(\text{phen})]$ as an emitting

source is the high emission quantum yield, namely, 0.46 and 0.38 in the solvent and gel, respectively. These values are about 1.5–2 times greater than those of [Eu(hfa)₃(phen)]. This increase is ascribed to the P=O group of [Eu(hfa)₃(TPPO)₂], which inhibits the nonradiative transition of the Eu³⁺ complex in the excited state. Further investigation on molecular designs for Eu³⁺ and Ln³⁺ complexes will be useful in advancing the development of emitting devices. In this context, the gelaphilic and solvophilic concepts proposed in this study should play a crucial role in determining a suitable environment in which Ln³⁺ complexes can be dispersed.

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Table 1. Φ_{em} of $[\text{Eu}(\text{hfa})_3(\text{phen})]$ and $[\text{Eu}(\text{hfa})_3(\text{TPPO})_2]$ dispersed in the organogel and organic solvents.

sample	complex	media	Φ_{em}
phen@liq	$[\text{Eu}(\text{hfa})_3(\text{phen})]$	<i>m</i> -xylene (liq.)	0.22 ^{a, b)}
phen@gel	$[\text{Eu}(\text{hfa})_3(\text{phen})]$	organogel	0.29 ^{a, c)}
TPPO@liq	$[\text{Eu}(\text{hfa})_3(\text{TPPO})_2]$	<i>m</i> -xylene (liq.)	0.46 ^{b)}
TPPO@gel	$[\text{Eu}(\text{hfa})_3(\text{TPPO})_2]$	organogel	0.38 ^{c)}

^{a)} Taken from our previous paper [6].

^{b)} Measured with $c_{\text{disp}} = 1.0 \times 10^{-4} \text{ mol dm}^{-3}$.

^{c)} Measured with $c_{\text{disp}} = 8.0 \times 10^{-4} \text{ mol dm}^{-3}$.

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

Figure 1. Steady-state emission spectra of [Eu(hfa)₃(phen)] and [Eu(hfa)₃(TPPO)₂] dispersed in the organogel and in the *m*-xylene solvent. $\lambda_{\text{ex}} = 355$ nm was used for measurements. The sample abbreviations are detailed in Table 1, and legends of the spectra are given in the inset. Assignments for dominant transitions around 580, 593, and 610–620 nm are provided inside the figure. The spectral data-sets of **phen@liq** and **phen@gel** are taken from our previous publication [6]. $c_{\text{disp}} = 1.0 \times 10^{-4}$ mol dm⁻³ was used for all the spectra.

Figure 2. (a) Concentration c_{disp} dependence of emission spectra of [Eu(hfa)₃(TPPO)₂]. Also shown is the **TPPO@liq** data as has been plotted in Figure 1. (b) The spectrum detected under $c_{\text{disp}} = 200 \times 10^{-6} \text{ mol dm}^{-3}$ (green solid line) and the reproduction according to Eq. (1) (dotted line). The spectral functions I_{dil} and I_{liq} , which are used for the reproduction, are also drawn; they are rescaled with their weighting factors f_{dil} and f_{liq} , respectively, with $f_{\text{dil}} = f_{\text{liq}} = 0.50$. (c) Concentration dependence of f_{dil} and f_{liq} provided in Eq. (1). The data-sets for [Eu(hfa)₃(phen)] are taken from our previous publication [8].

Figure 3. Microscopy of (a) **phen@gel** and (b) **TPPO@gel** depending on the dispersion concentration c_{disp} . Note that c_{disp} is given in $\times 10^{-6} \text{ mol dm}^{-3}$.

Figure 4. A schematic diagram of Eu^{3+} complexes dispersed in the solvent and in the organogel fibrous architecture, representing the “gelaphilic” and “solvophilic” concepts.

Figure 5. Time profiles of emission intensity $I(t)$ for (a) **TPPO@liq** and (b) **TPPO@gel**, respectively, excited with $\lambda_{\text{ex}} = 355$ nm. The excitation pulse energy E_{ex} is given in the boxes in each panel, although all the profiles in both panels mostly overlap. Also drawn in each panel in the thin gray lines are typical profiles of **phen@liq** and **phen@gel** taken from our previous report [6], where E_{ex} is given beside each profile.

Graphical Abstract