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1 Generation of amplified spontaneous emission from rare-earth 2 complexes dispersed in phenol + AOT self-assembled organogels

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A B S T R A C T

The rare-earth complex $\text{Eu}(\text{hfa})_3(\text{phen})$ 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.

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27 1. Introduction

28 Self-assembled organogels composed of small organic molecules
29 have been used to hosting materials that contain rare-earth complexes
30 [1,2], nanoparticles [3,4], nanofibers [5], nanorings [6], or lipophilic
31 compounds [7]. Such doping processes rely on the organogel network
32 structure, where interactions between the network and dopants are
33 critical. The network structure fluctuates either in the temporal or spa-
34 tial phase, which is characteristic of soft materials. An earlier paper of
35 ours discussed the distribution of the time constant of the structural
36 fluctuation of organogels in the nanosecond region [8].

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

42 In a previous study, we dispersed Eu^{3+} and Tb^{3+} complexes in an
43 optically transparent phenol + AOT organogel [2]. The organogel struc-
44 ture, which was suggested by Simmons and coworkers [10], is shown in
45 Chart 1a. These complex–organogel systems have been applied to addi-
46 tive emission color-tuning in the visible region [2]. Another advantage
47 of the phenol + AOT organogel as host material is that we can disperse
48 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 mu-
tual 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 repre-
sents 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 poten-
tial 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.

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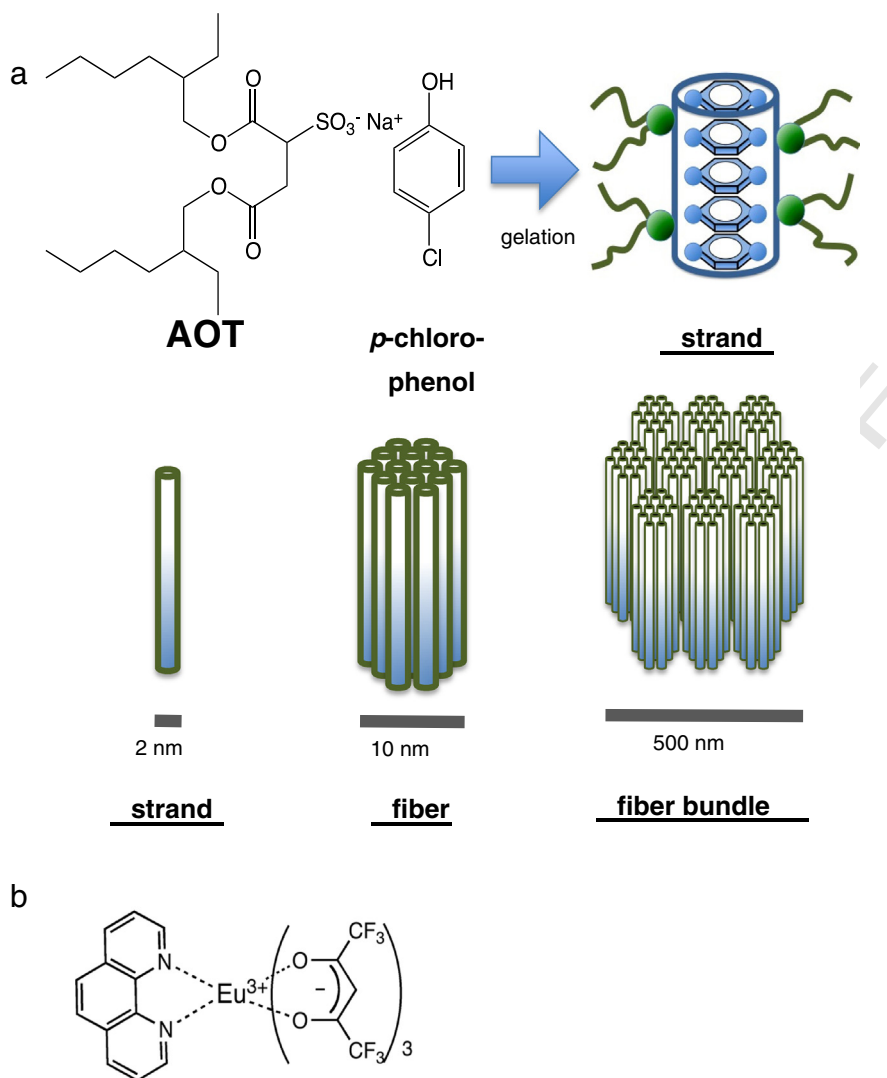


Chart 1. (a) Chemical components of the phenol + AOT organogel used in this study. The “strand” structure consists of stacked benzene rings, and the higher-order architectures “fiber” and “fiber bundle” are based on ref [10] for aromatic and alkane solvents. (b) The chemical structure of $\text{Eu}(\text{hfa})_3(\text{phen})$.

2. Materials and methods

2.1. Materials

The synthesis of the phenol + AOT organogel and $\text{Eu}(\text{hfa})_3(\text{phen})$ was 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 or Eu@liq, 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) $\approx 9 \text{ ns}$] was used as the excitation light source, with wavelength $\lambda_{\text{ex}} = 355 \text{ nm}$. As a result, the $\lambda_{\text{ex}} = 355 \text{ nm}$ 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 traveled 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

Table 1
 c_{max} and Φ_f of $\text{Eu}(\text{hfa})_3(\text{phen})$ 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.

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