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# Fabrication and luminescence properties of Eu-complex/polyimide composite nanoparticles

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**Abstract** Nanoparticles composed of Eu-complex and polyimide were successfully fabricated through an improved reprecipitation method, followed by a chemical imidization. In this process, the excess addition of triethylamine, which inhibits acid decomposition of Eu-complex, provided intense luminescent nanoparticles. These nanoparticles showed intense red luminescence assigned to $Eu^{3+}$, which showed broader peaks compared with an Eu-complex powder and peak shifts. These results imply that Eu-complex molecules were dispersed in the PI matrix homogeneously and strongly affected by the matrix. Moreover, composition with polyimide improved UV resistance of Eu-complex.

## Introduction

Rare earth complexes, particularly those consisting of ligands such as $\beta$-diketonates and aromatic carboxylic acid, have excellent photoluminescence properties, high luminescence efficiency, and high colorimetric purity due to the sharp luminescence peaks, which derive from f–f transitions. Therefore, these complexes have attracted significant interest for potential use in photo- and electro-luminescence devices, and numerous studies on rare earth complexes have been reported [1–6]. Recently, fabrications of rare earth complex/polymer composites have been studied, because these possess an improved processing ability, chemical stability, and mechanical strength. It has been reported that the composition with polymers gives unique luminescence properties [7–12]. Most of the studies on these composites were focused on fabrication of films and bulk materials, though nanostructured materials composed of rare earth complex and polymer are also promising materials for biological assays [13, 14]. Polymers have good properties for optical materials, such as transparency, easy processability, low density, and low costs. However, ordinary polymers have lower stability against heat and light as compared to inorganic materials. Polyimide (PI) is one of the most promising high-performance polymers possessing chemical and high thermal stabilities and good mechanical properties [15]. We have already reported on fabrication of spherical PI nanoparticles [16], porous PI nanoparticles [17], and $Eu^{3+}$-doped PI nanoparticles [18] through the reprecipitation method [19], and shown useful properties. It is considered that a preparation of nanoparticles composing of rare earth complex and polyimide gives high-performance organic phosphors. In this study, we fabricated rare earth complex/PI composite nanoparticles through the reprecipitation method and investigated their luminescence properties.

## Experimental

The poly(amic acid) (PAA) used as the precursor polymer of PI was produced by the polyaddition reaction of 4,4′-(hexafluoroisopropylidene)diphthalic anhydride (6FDA)

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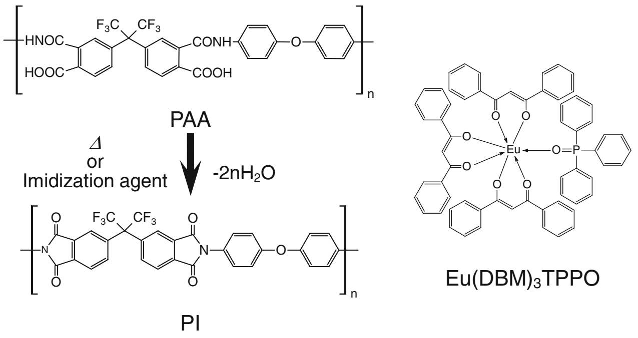

**Fig. 1** Chemical structures of PAA, PI (6FDA-ODA), and Eu-complex (Eu(DBM)$_3$TPPO) used

and 4,4′-oxydianiline (ODA) in *N*-methyl-2-pyrrolidinone (NMP), and its average molecular weight was approximately 120,000. Eu(DBM)$_3$TPPO were supplied from Mitsubishi Chemical Corporation. Chemical structures are shown in Fig. 1. A mixed solution of Eu(DBM)$_3$TPPO and PAA was prepared as follows. Triethylamine (5× excess amount to carboxylic acid group contained in PAA solution) was added to a diluted NMP solution of PAA and then Eu(DBM)$_3$TPPO was dissolved to this solution. The weight ratio of PAA to NMP was 0.007 and that of Eu(DBM)$_3$TPPO to PAA was 0.3. When a mixed solution is provided without triethylamine, luminescence of rare earth complex is drastically quenched due to acid decomposition. Eu(DBM)$_3$TPPO/polyimide composite nanoparticles were prepared thorough the reprecipitation method. Above mixed solution (100 μL) was rapidly injected using a microsyringe into the vigorously stirred cyclohexane (10 mL) as the poor solvent, and the dispersion liquid of Eu(DBM)$_3$TPPO/PAA composite nanoparticles were obtained instantly. Note that cyclohexane contained a small amount of the dispersing agent, Acrydic A-1381 (Dainippon Ink and Chemicals). And then, composite PAA nanoparticles were chemically imidized in the following manner and composite PI nanoparticles were obtained. Triethylamine (TEA, 125 μL to 6.25 mL) was added to above dispersion, followed by acetic anhydride (50 μL) as the cyclodehydration reagent. PAA was quantitatively converted to PI by stirring for 3 h at room temperature. Eu(DBM)$_3$TPPO/PI composite nanoparticles in the resultant liquid were centrifuged at 12,000 rpm, washed with cyclohexane, and redispersed into cyclohexane. Finally, dispersion liquid was cast on a glass slide. Scanning electron microscopy (SEM) images were recorded using a JEOL JSM-6700F instrument operated at acceleration voltage of 15 kV and an emission current of 10 μA. UV exposure was performed using a battery-operated UV lamp (Spectroline EF-160C/J, 254 nm, 6 W). Luminescence and excitation spectra were recorded on a Hitachi F-2500 fluorescence spectrometer.

## Results and discussion

Figure 2 shows excitation spectra of the dispersion liquid containing Eu(DBM)$_3$TPPO/PI composite nanoparticles prepared by adding various amount of TEA. Excitation bands ascribed to the ligand was observed from 320 to 420 nm. Under standard condition of chemical imidization (1×, 125 μL addition of TEA), luminescence intensity markedly decreased, though strong red luminescence was observed before chemical imidization. However, luminescence intensity of composite PI nanoparticles increased with increase in addition of TEA, and the nanoparticles, fabricated by adding 50× amount of TEA, showed intense luminescence. It is considered that addition of TEA disturbed the acid decomposition of rare earth complex by acetic acid, which was produced from acetic anhydride in the chemical imidization process.

SEM image of composite PI nanoparticles fabricated was shown in Fig. 3. In previous research, we had obtained spherical PI nanoparticles (not composite nanoparticles) [16]. In the present study, however, we obtained the nanoparticles with different morphologies. This result suggests that these nanoparticles consist of PI and rare earth complex. Actually, when we fabricated nanoparticles from a mixed solution of PAA and other polymers (e.g., poly(acrylic acid)), their morphologies were not spherical, but rather golf-ball-like shapes [17]. Addition of other compound to the PAA solution induces a change in physical properties of the solution, giving nonspherical shape. We have considered the formation mechanism of PAA nanoparticles as follows. First, distortional droplets of a solution are formed by shear force just after injecting the solution to cyclohexane, stirred vigorously. The droplets are simultaneously induced to spherical shape by interfacial energy between the solvents.

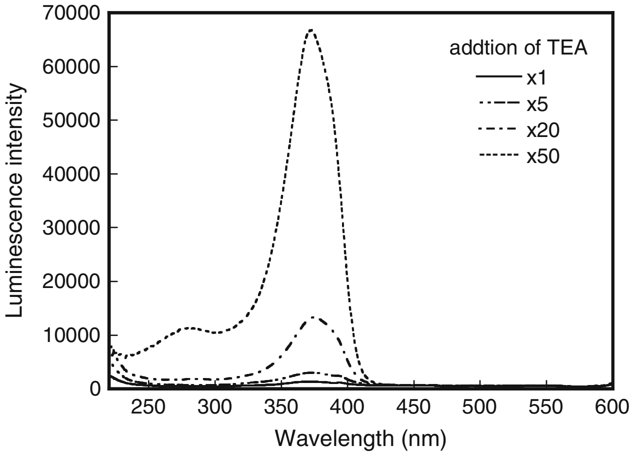

**Fig. 2** Excitation spectra of dispersion liquids of Eu(DBM)$_3$TPPO/PI composite nanoparticles fabricated by chemical imidization after adding various amount of TEA. 1× means standard condition (125 μL addition of TEA). Monitored wavelength was 618 nm

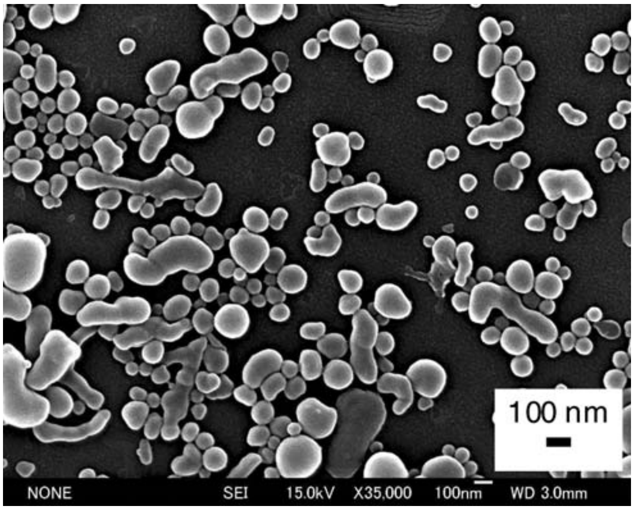

**Fig. 3** SEM image of Eu(DBM)$_3$TPPO/PI composite nanoparticles fabricated by chemical imidization after adding 6.25 mL TEA, 50× as much as the standard condition

And then, PAA nanoparticles are generated, resulting from the mutual diffusion between NMP and cyclohexane. Therefore, the resultant PAA nanoparticles, fabricated by using NMP solution containing only PAA, are spherical in shape. In the present case, we guessed that the spherical transformation of droplets had occurred very slowly because of their high viscosity, which was due to the strong interaction between rare earth ion in complex and carboxyl group of PAA. Hence, deformative nanoparticles were obtained.

Figure 4 exhibits luminescence spectra of Eu(DBM)$_3$TPPO powder, Eu(DBM)$_3$TPPO/PAA solution, and Eu(DBM)$_3$TPPO/PI composite nanoparticles. Typical luminescence peaks, ascribed to $^5D_0 \rightarrow {}^7F_0$ (ca. 580 nm), $^5D_0 \rightarrow {}^7F_1$ (ca. 590 nm), and $^5D_0 \rightarrow {}^7F_2$ (ca. 620 nm) transitions, were observed in all the samples. Composite nanoparticles gave broad luminescent peaks compared to Eu-complex powder. Moreover, peak positions of composite nanoparticles were different with that of the Eu-complex powder. These results mean that PI matrix affects the environment around Eu-complex molecules. Generally, absorption and luminescence of rare earth ions, mainly derived from f–f transition, give sharp peaks, and these peak positions are not almost influenced by ligand fields. It is known that the f–f transitions of rare earth compound crystals particularly provide sharp peaks. However, f–f transition peaks of rare earth ion, isolated in amorphous materials such as a glass, broaden [20]. Therefore, it is considered that Eu-complex molecules were dispersed in PI nanoparticles homogeneously. Eu$^{3+}$ has been used to study the local environment of rare earth ions [21]. The $^5D_0 \rightarrow {}^7F_2$ luminescence (ca. 620 nm) is hypersensitive and the intensity can vary by orders of magnitude, depending on the local environment. When Eu$^{3+}$ occupies a spherically symmetric site, the intensity is zero but increases with increasing asymmetry of the site. The $^5D_0 \rightarrow {}^7F_1$ transition (ca. 590 nm) is a magnetic transition that can be used as a reference because its intensity is not sensitive to the environment. Hence, the $^5D_0 \rightarrow {}^7F_2/{}^5D_0 \rightarrow {}^7F_1$ luminescence ratio can be utilized as a measure of the site symmetry of Eu$^{3+}$. In the case of Eu-complex powder, larger intensity ratios were observed, indicating that Eu$^{3+}$ ions are located on more asymmetric site in Eu(DBM)$_3$TPPO crystal. On the other hand, intensity ratio of composite nanoparticles almost agreed with that of the solution. These facts declare that Eu-complex molecules exist as a solution-like state in composite nanoparticles, i.e., Eu-complex disperses in the PI nanoparticle matrix homogeneously.

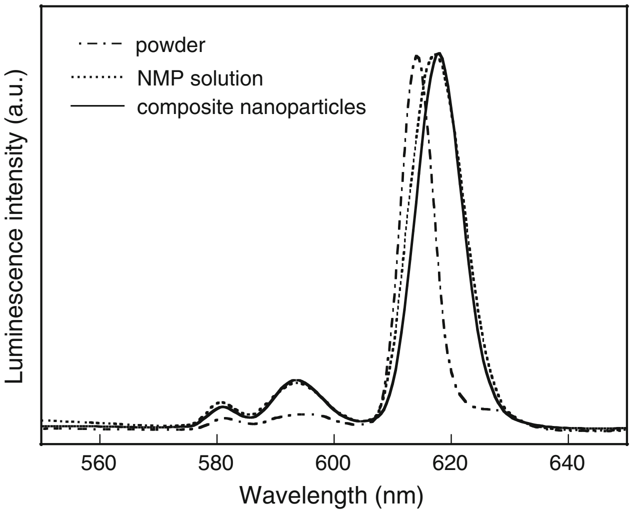

**Fig. 4** Luminescence spectra of Eu(DBM)$_3$TPPO, mixed NMP solution of Eu(DBM)$_3$TPPO and PAA, and Eu(DBM)$_3$TPPO/PI composite nanoparticles. Excitation wavelength were 411, 405 and 371 nm, respectively

We examined UV-light resistance of Eu-complex powder and composite PI nanoparticles. Figure 5 displayed excitation spectra of Eu-complex powder (*upper*) and composite PI nanoparticles (*lower*) before and after UV exposure for 36 h. Eu-complex powder showed serious luminescence quenching due to photolysis of ligands. On the contrary, luminescence intensity of composite PI nanoparticles dramatically increased despite UV exposure for long time. We have already reported on luminescence enhancement of Eu$^{3+}$-doped PI by UV irradiation [18, 22]. In these literatures, though no luminescence peak was measured before UV-irradiation treatment, the red luminescence was observed by naked-eye after the treatment. In addition, broad excitation peaks appear at ca. 250 and 280 nm. We concluded that a structural change of the PI matrix upon UV irradiation led to the luminescence enhancement of the matrix, resulting in increase in the luminescence of the Eu$^{3+}$ due to the energy transfer from the matrix to Eu$^{3+}$. In

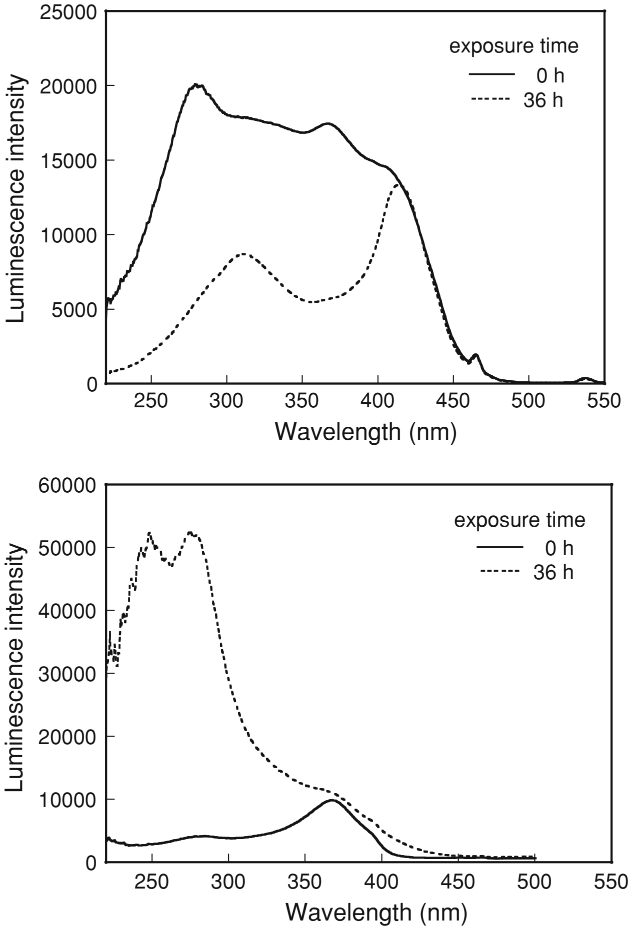

**Fig. 5** Excitation spectra of Eu(DBM)$_3$TPPO powder (*upper*) and Eu(DBM)$_3$TPPO/PI composite nanoparticles (*lower*) before and after UV exposure for 36 h. Monitored wavelength were 614 and 618 nm, respectively

addition, the enhancement of the luminescence intensity of Eu$^{3+}$ through the energy transfer results from the formation of phthalic acid–Eu$^{3+}$ complexes, produced by photolysis of PI [23, 24]. Actually, we have observed overall decrease in absorption intensities in the UV and IR region with increase in UV-exposure time, and increase in the intensity of absorption band assigned to OH stretching vibration. In the present system, although strong luminescence showed just after the fabrication of nanoparticles, it is apparent that same phenomena occurred because same excitation peaks appeared. Moreover, it is considered that implantation of Eu-complex into PI matrix resulted in improvement of decrease in luminescence intensity by UV exposure.

## Conclusions

We successfully fabricated luminescent Eu(DBM)$_3$TPPO/PI composite nanoparticles through the reprecipitation method improved by adding excess triethylamine, which inhibits the acid decomposition of Eu-complex caused by acetic acid produced from acetic anhydride in the imidization process. In the case of composite nanoparticles, broadening of luminescence peaks and peak shifts were observed, suggesting that Eu(DBM)$_3$TPPO molecules were dispersed in PI matrix homogeneously. Moreover, composition with PI improved the UV resistance of Eu(DBM)$_3$TPPO. Eu-complex/PI composite nanoparticles are promising phosphors for illuminations using near-UV or blue LEDs as an excitation source, EL display devices, and biological assays.

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