Enhanced Luminescence of Lanthanide(III) Complexes in Polymer Matrices

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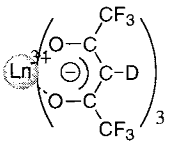
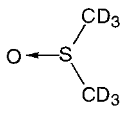
Effectively luminescent organic polymers were successfully fabricated by incorporating deuterated hexafluoroacetylacetonato Nd(III) or Eu(III) complex and DMSO-d_6 in polyalkylmethacrylate matrices with low percentage of H atoms.

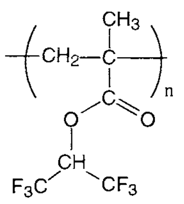
Amplified spontaneous emission of lanthanide(III) ions using their ideal 4 level f-f transition leads to development of high-power laser materials. Especially, the optical-fiber laser system incorporating a lanthanide(III) ion is one of the most excellent candidates in view of laser emission conversion efficiency. Zellmer reported about Nd(III)-doped fiber laser for the first time in 1995.[1] Liu and Ueda suggested the importance of the optical-fiber laser structures.[2] Furthermore, Weber et al reported that optical fibers doped with lanthanide element can serve as in-line lasers and amplifiers for fiber-optic telecommunication systems.[3] However, these systems were achieved using only inorganic glass matrices. On the other hands, Kobayashi *et al* introduced the possibility of organic fiber laser systems using Eu(III)-incorporated organic optical fibers of polymethylmethacrylate (PMMA) in 1997.[4] In our earlier studies on luminescence of Nd(III) in liquid media, we found the importance of suppression of vibrational excitation and energy migration from excited Nd(III),[5a-c] and effect of anti-symmetric ligands and photosensitization for efficient excitation of Nd(III).[5d-f] Furthermore, we recently found that deuterated DMSO molecules (DMSO-d_6) play an important role in enhancement of the luminescence of the Nd(III) complex with deuterated hexafluoroacetylacetone (HFA-D) through specific coordination.[5b, 6] With these photophysical findings, we have succeeded in fabrication of effectively luminescent organic polymers by incorporating luminescent Nd(III) or Eu(III) complexes in polyhexafluoroisopropylmethacrylate (P-FiPMA) matrices.



Ln = Nd(III), Eu(III)



DMSO-d_6



P-FiPMA

Table 1. Luminescence of lanthanide (III) ions in polymer matrices

Ln(III) complex	matrix	transmittance / % [b]	quantum yield / % [c]
Nd(HFA-H)$_3$	PMMA	79	< 0.01
Nd(HFA-D)$_3$	PMMA	79	0.1 ± 0.1
Nd(HFA-D)$_3$	PMMA / DMSO-d_6 [a]	83	0.5 ± 0.1
Nd(HFA-D)$_3$	P-FiPMA / DMSO-d_6 [a]	90	0.7 ± 0.1
Nd(HFA-D)$_3$	DMSO-d_6	90	1.1 ± 0.2
Eu(HFA-H)$_3$	PMMA	79	8 ± 1
Eu(HFA-H)$_3$	PMMA / DMSO-d_6 [a]	74	11 ± 1
Eu(HFA-D)$_3$	PMMA	79	20 ± 2
Eu(HFA-D)$_3$	PMMA / DMSO-d_6 [a]	83	44 ± 5
Eu(HFA-D)$_3$	P-FiPMA / DMSO-d_6 [a]	90	72 ± 7
Eu(HFA-D)$_3$	DMSO-d_6	90	60 ± 10

[a] Composition of polymerization; Nd(III) or Eu(III), 0.7w%; AIBN, 0.05w%; DMSO-d_6, 6.6w%. [b] Transmittances of Nd(III) and Eu(III) complexes were measured at 1060 nm and 615 nm, respectively. Optical lengthes are 4 mm. [c] Nd(III) complex was excited at 585 nm ($^4I_{9/2} \rightarrow {}^4G_{3/2}$), and Eu(III) complex weas excited at 465 nm ($^4F_0 \rightarrow {}^4D_1$).

The lanthanide complexes, Ln (Nd(III) or Eu(III))·(HFA-D)$_3$·(D$_2$O)$_2$, were prepared by exchange reaction via keto-enol tautomerism in CD$_3$OD for 6 h under vacuum as described in our previous paper.[4a] After evaporation of the solution under vacuum (~10^{-3} Torr) to dryness, the resulting Ln(HFA-D)$_3$· (D$_2$O)$_2$ (0.05 M) was dissolved in a 1-mL mixture of purified anhydrous hexafluoroisopropylmethacrylate (FiPMA), or methylmethacrylate (MMA), AIBN and DMSO-d_6 in a Pyrex tube. In fabrication of PFiPMA systems, MMA (10 w%) was added in FiPMA in order to solve AIBN and Ln complexes in FiPMA. The Pyrex tube was closed under 10^{-3} Torr, and thermostated at 60 °C for polymerization of FiPMA or MMA. For comparison, PMMA polymers incorporating DMSO-d_6 and Ln(HFA-D)$_3$·(D$_2$O)$_2$ or Ln(HFA)$_3$·(H$_2$O)$_2$ were similarly prepared. The resulting polymer films gave the transmittance of more than 70% at 4 mm thickness. Interestingly, the P-FiPMA matrices were found to give more transparent films with transmittance of 90% (Table 1). Emission spectra were measured by a photomultiplier and Ge detector. The quantum yields were determined by standard procedures using an integral sphere (diameter 9 cm).[4b] Optical path length of the cell was 1 mm. Quantum yield, Φ, was calculated by,

$$\Phi = \frac{N_{emission}}{N_{absorption}} = \frac{\int \frac{\lambda}{hc} Iem(\lambda) d\lambda}{\int \frac{\lambda}{hc} (Iex(\lambda 0) - Iex(\lambda S)) d\lambda}$$

The corrected intensity functions of the light absorption (from Eq above) ($I_{ex}(\lambda_o)$: without sample, $I_{ex}(\lambda_s)$: with sample) were determined by the excitation spectra of the system, and the corrected intensity function of the emission, $I_{em}(\lambda)$, was determined by the emission spectra of the sample. The quantum yield of LHG-8 (Nd(III) doped phosphate glass) determined by the procedure agreed well with the reported value (95±0.05 %). The emission quantum yields of lanthanide(III) ions thus obtained in various matrices are shown in Table 1. The typical emission spectra of the polymer systems containing Nd(III) or Eu(III) were obtained by excitation at 585 nm ($^4I_{9/2} \rightarrow {}^2G_{7/2}$) for Nd(III) and at 465 nm ($^4F_0 \rightarrow {}^2D_1$) for Eu(III) (Figure 1a and c).

In particular, the coordination of Nd(III) complexes with

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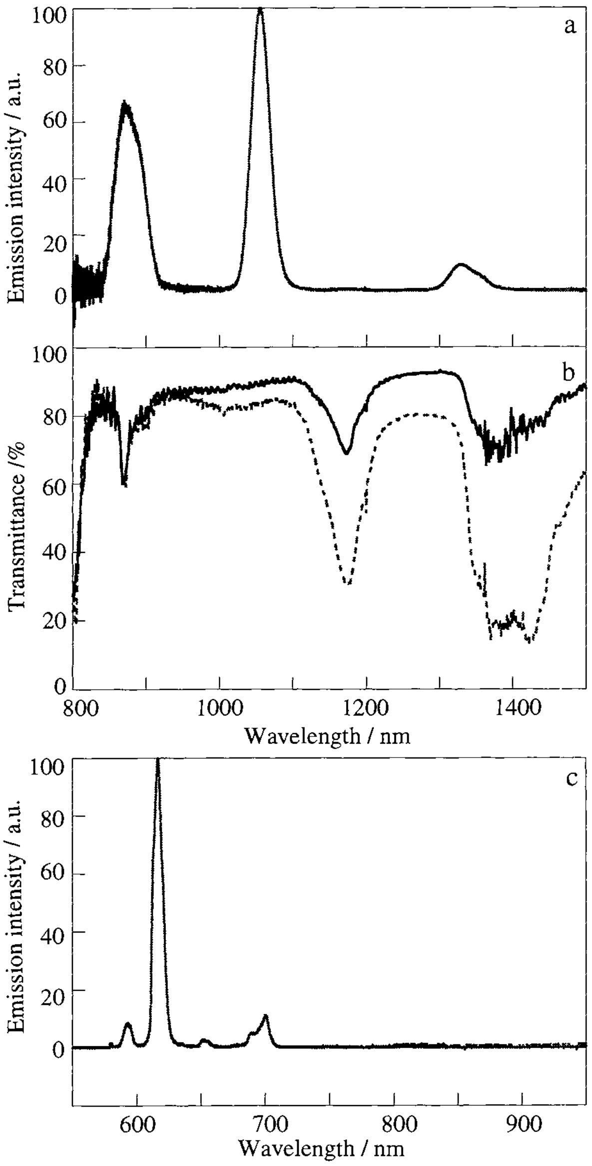

Figure 1. Emission and transmittance spectra of Ln(III) complexes in P-FiPMA. a) The normalized emission spectra of Nd(HFA-D)$_3$(DMSO-d_6)$_n$ in P-FiPMA (870 nm: $^4F_{3/2}\rightarrow{}^4I_{9/2}$, 1060 nm: $^4F_{3/2}\rightarrow{}^4I_{11/2}$, 1350 nm: $^4F_{3/2}\rightarrow{}^4I_{13/2}$). b) The transmittance spectra of Nd(HFA-D)$_3$(DMSO-d_6)$_n$ in P-FiPMA (bold) and PMMA (dot). c) The normalized emission spectrum of Eu(HFA-D)$_3$(DMSO-d_6)$_n$ in P-FiPMA (590 nm: $^4F_0\rightarrow{}^4D_1$, 615 nm: $^4F_0\rightarrow{}^4D_2$, 650 nm: $^4F_0\rightarrow{}^4E_3$, 700 nm: $^4F_0\rightarrow{}^4D_4$, 820 nm: $^4F_0\rightarrow{}^4D_6$).

low vibrational HFA-D led to the observation of weak emission in PMMA matrix. The addition of DMSO-d_6 enhances the emission to some extent. However, the quantum yield of the system of Nd(HFA-D)$_3$ / DMSO-d_6 / PMMA was much smaller than that in liquid DMSO-d_6 medium. This is explained as due to radiationless transition via vibrational excitation of C-H bonds in the PMMA matrix. Weight percentage of H atoms in the resulting polymer system is 8.0%. In order to minimize the vibrational excitation of C-H bond in the polymer matrix, we attempted to polymerize FiPMA, i.e., C-F bond containing methacrylate, in the presence of Nd(HFA-D)$_3$ and DMSO-d_6. A transparent PFiPMA polymer matrix was obtained by polymerization of FiPMA with 10% MMA. The system of Nd(HFA-D)$_3$ / DMSO-d_6 / PFiPMA (the weight percentage of H atoms is 2.5%) was improved to give an effectively luminescent organic polymer of Nd(III). Near IR spectrum of Nd(HFA-D)$_3$(DMSO)$_n$ in P-FiPMA was compared with that in PMMA (Figure 1b). Absorption bands at 800 and 870 nm and those at 1170 and 1350-1500 nm were assigned to f-f transition of Nd(III) and vibrational harmonics of C-H bonds, respectively. The vibrational harmonic bands of Nd(HFA-D)$_3$(DMSO-d_6)$_n$ in P-FiPMA was smaller than that in corresponding PMMA because of a smaller amount of H atoms. This result suggests that P-FiPMA matrix can suppress the radiationless transition via vibrational excitation.

In contrast, we observed extraordinarily efficient luminescence of Eu(HFA-D)$_3$ in DMSO-d_6. This fact indicates that suppression of non-radiative dissipation of photoexcited Eu(III) systems should be achieved by use of HFA-D as ligands and DMSO-d_6 as solvent. Interestingly, the same suppression was found true in the PMMA matrix. When compared with the emission of the Eu(HFA)$_3$ / PMMA system, either the use of HFA-D or the addition of DMSO-d_6 enhanced quantum yield of Eu(III) in PMMA. The PMMA system which incorporated both Eu(HFA-D)$_3$ and DMSO-d_6 gave brighter luminescence. Surprisingly, the system of Eu(HFA-D)$_3$ / DMSO-d_6 / P-FiPMA gave a quantum yield (Φ) of 72%, which was much larger than those in PMMA ($\Phi \approx 44\%$) and in DMSO-d_6 ($\Phi \approx 60\%$). This may be explained as due to small weight percentage of H atoms in P-FiPMA (2.5 w%), i.e., probability of radiationless vibrational excitation was decreased by the presence of higher percentage of C-F bonds. Furthermore, the P-FiPMA solid matrix would prevent energy migration via diffusional collision of the Eu(III) complex. However, vibrational excitation of these systems was not suppressed perfectly, because the system still contains high vibrational C-H bonds. We are now trying to fabricate some more brightly luminescent organic polymers which have lower percentage of H atoms than in the case of the P-FiPMA system.

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