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Structure Control of Eu(III) Complexes for Amplified Spontaneous Emission in Polymer Thin Films

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Novel Eu(III) complex derivatives for laser medium were synthesized and investigated. The photophysical properties (emission spectra and lifetimes) were depend on ligand structures. The emission from the edge of the polymer thin films containing those complexes decayed following single- exponential kinetics at the lowest excitation power. While the emission decays at high excitation energy consisted of normal component and a faster component. The ratio of the faster component increased with increasing excitation energy. These observations indicate that the faster component is due to amplified spontaneous emission from the complexes in the microcavity.

Keywords Amplified spontaneous emission; coordination structures; emission decay; Eu(III) complexes; polymer thin films

Introduction

Lanthanoid metals have been regard as attractive light emitting devices. Especially, the lanthanide(III) ions are ideal molecules as a lasing medium, because they have 4-level electric transitions for effective formation of population inversion [1–4].

We have observed effective lasing phenomena by using strong luminescent lanthanide(III) complexes [5–7]. An important purpose of the study described here is to control lasing properties from f-f electric transitions of lanthanide(III) ions by the addition of chemical species. We treated the chemical species for control of the electric transitions in f-orbitals, which are parity forbidden. It is well-known that reducing the symmetry of the lanthanide complex enhances its photophysical properties [8–13]. The electric transition in f-orbitals related to the emission and lasing properties can be enhanced by control of the coordination symmetry of lanthanide(III) complexes. The chemical species can act as a key species which control the symmetry of the coordination sphere around lanthanide(III) ions.

According to these photophysical properties, we focused on Sm(III) ions as a luminescent center and reported the emission properties of Sm(III) complexes having nine and

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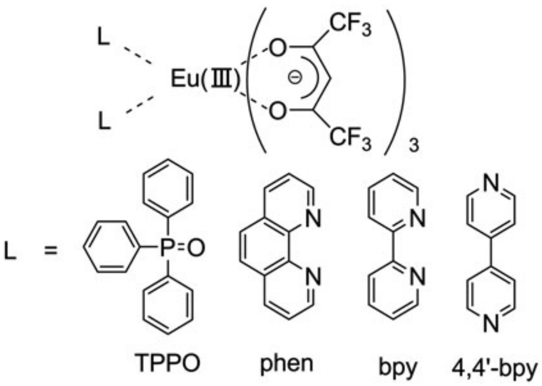

Figure 1. Chemical structures of Eu(III) complexes.

ten coordination structures [14–16]. The Sm(III) complexes with characteristic asymmetric structures are expected to have increased radiation probability and emission quantum yields.

In the present study, we report the Eu(III) complexes having a low threshold level for the amplified spontaneous emission (ASE). Eu(III) complexes were synthesized by the reaction of hexafluoroacetylacetonato (hfa) and triphenylphosphine oxide (TPPO), 1,10-phenanthroline (phen), 2,2′-bipyridine (2,2′-bpy), and 4,4′-bipyridine (4,4′-bpy) (Fig. 1). The relationship between ligands structures and emission properties is demonstrated in organic solutions and polymer thin films.

Experimental

Europium(III) acetate tetrahydrate (99.9%), triphenylphosphine oxide and polystyrene beads (M.W. ca 100,000) were purchased from Wako Pure Chemical Industries Ltd. Hexafluoroacetylacetone, 1,10-phenanthroline, 2,2′-bipyridine and 4,4′-bipyridine were obtained from Tokyo Kasei Organic Chemicals. All other chemicals were reagent grade and were used as received.

Tris(hexafluoroacetylacetonato) europium(III) bis(triphenylphospine oxide): $Eu(hfa)_3(TPPO)_2$ was prepared by the reaction of between $Eu(hfa)_3(H_2O)_2$ and the triphenylphospine oxide (TPPO) in methanol under reflux for 6 h. The reaction mixture was concentrated using a rotary evaporator. Reprecipitation by addition of excess hexane solution produced crude crystals, which were washed in toluene several times. Recrystallization from hot methanol gave white crystals in 37%.

Tris(hexafluoro- acetylacetonato) europium(III) bis(1,10- phenanthroline): $Eu(hfa)_3(phen)_2$, tris(hexafluoroacetylacetonato) europium(III) bis(2,2′-bipyridine): $Eu(hfa)_3(2,2'\text{-}bpy)_2$ and tris(hexafluoroacetylacetonato) europium(III) bis(4,4′-bipyridine): $Eu(hfa)_3(4,4'\text{-}bpy)_2$ were also prepared by the reaction of $Eu(hfa)_3(H_2O)_2$ and 1,10-phenanthroline, 2,2′-bipyridine and 4,4′-bipyridine. $Eu(hfa)_3(H_2O)_2$ was dissolved of acetonitrile solutions by stirring at 0°C. 1,10-phenanthroline, 2,2′-bipyridine and 4,4′-bipyridine in acetonitrile solutions were added dropwise to the above solutions and reacted at 0°C for 2 h, respectively. The reaction mixtures were concentrated using a rotary evaporator. Reprecipitation by addition of excess hexane solution produced crude crystals, which were washed in toluene several times. Recrystallization from hot methanol/distilled water gave white crystals in 23% ($Eu(hfa)_3(phen)_2$), 40% ($Eu(hfa)_3(2,2'\text{-bpy})_2$) and 17% ($Eu(hfa)_3(4,4'\text{-bpy})_2$).

Polystyrene beads were dissolved in 5 mL of anisole. The Eu(III) complexes were then added to the solution. Eu(III) thin films(10 wt%) were prepared on a quartz substrate from the anisole solution via the spin-coating method (3000 rpm, 60 s).

Infrared spectra used to identify synthesized materials were obtained with a JASCO FT/IR-550 spectrometer. ^{1}H-NMR data were obtained with a JEOL JNM-AL300 (300 MHz) and determined using tetramethylsilane (TMS) as an internal standard. Samples were excited by the third harmonic (355 nm) of a Q-switched Nd:YAG laser (B.M. industries 502DNS, 10 Hz, FWHM 9 ns). The emission spectra were measured using a photo multichannel analyzer system with a CCD detector (Hamamatsu, PMA-11) at room temperature. The emission lifetimes were measured by a nanosecond Nd:YAG laser and a photomultiplier (Hamamatsu, R928). Emission from the sample was guided to the photomultiplier through a monochromator (Jobin-Yvon, H20-VIS). Emission decays were monitored with a digital oscilloscope (Sony Tektronix, TDS540).

Results and Discussion

The emission spectra of the Eu(III) complexes in cyclohexanone solutions were measured for the excitation at 355 nm (π–π^* transition of the hexafluoro- acetylacto ligands). The emission spectra were shown in Fig. 2. The emission bands of $Em(hfa)_3(TPPO)_2$ were observed at 580, 593 and 614 nm and are attributed to f–f transition $^5D_0 \rightarrow {}^7F_0$ (forbidden transition), $^5D_0 \rightarrow {}^7F_1$ (magnetic dipole transition), $^5D_0 \rightarrow {}^7F_2$ (electric-dipole transition), respectively. $Eu(hfa)_3(phen)_2$, $Eu(hfa)_3(2,2'\text{-bpy})_2$ and $Eu(hfa)_3(4,4'\text{-bpy})_2$ exhibited slightly red-shift in the electric-dipole transition. The relative emission intensity of $Eu(hfa)_3(phen)_2$, $Eu(hfa)_3(2,2'\text{-bpy})_2$ and $Eu(hfa)_3(4,4'\text{-bpy})_2$ were lagere than those of $Eu(hfa)_3(TPPO)_2$. The electric-dipole transition is directly linked to the coordination structures related to odd parity. The geometrical structure of $Eu(hfa)_3(TPPO)_2$ complex shows eight -coordination square antiprism without inverted center in the crystal field [5]. On the

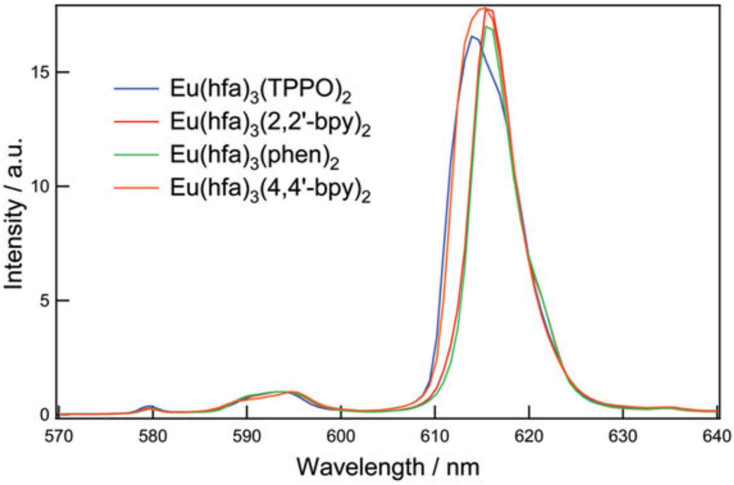

Figure 2. Normalized emission spectra of Eu(III) complexes in cyclohexanone solutions (0.01 M) excited at 355 nm.

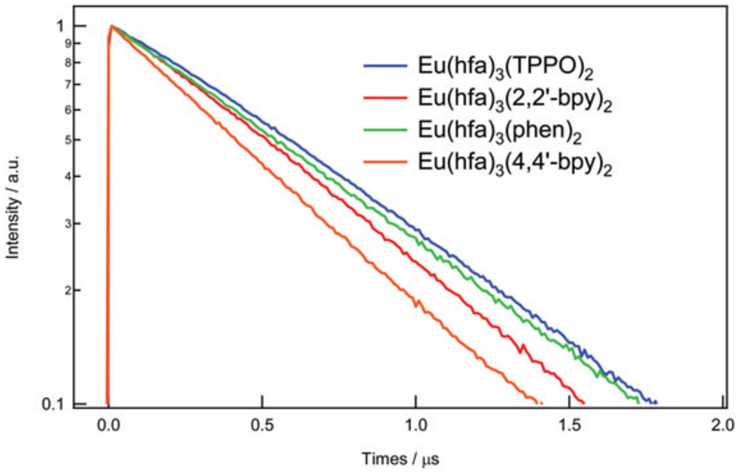

Figure 3. Emission decays of Eu(III) complexes in cyclohexanone solutions (0.01 M) excited at 355 nm.

other hand, the $Eu(hfa)_3(phen)_2$ and $Eu(hfa)_3(2,2'\text{-bpy})_2$ have the ten-coordination structure due to the three hexafluoroacetylacto (hfa) ligands and two phen or 2,2′-bpy ligands. The degree of enhanced emission intensities of the Eu(III) complexes should be caused by the coordination structures.

The emission lifetimes of the Eu(III) complexes in cyclohexanone solutions were measured for the excitation at 355 nm. The emission decays were shown in Fig. 3. Single exponential decays indicated the presence of a single luminescent element. The emission lifetimes were determined from the slope of logarithmic plot of the decay profiles. Normalized emission decays of the polystyrene film containing $Eu(hfa)_3(bpy)_2$ under different excitation energy are shown in Fig. 4. The emission decayed following single-exponential kinetics at the lowest excitation power (0.04 mJ). While the emission decays observed

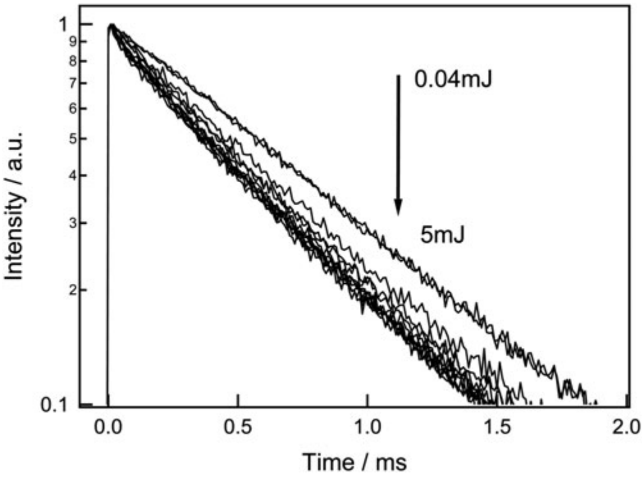

Figure 4. Normalized emission decays of the polystyrene film containing $Eu(hfa)_3(2,2'\text{-bpy})_2$ under different excitation energy.

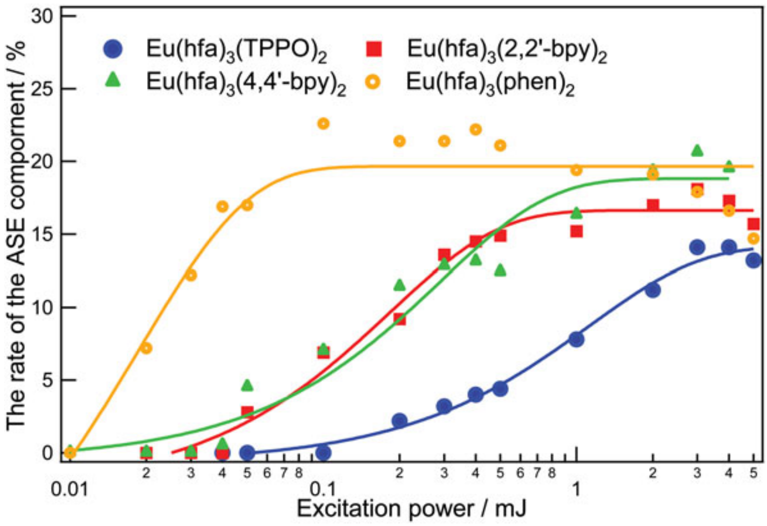

Figure 5. The rate of ASE component of polystyrene films containing Eu(III) complexes.

for the stronger excitation energy (>1 mJ) consisted of normal component (the spontaneous emission) and the faster component. The optical microcavity was constructed by the polystyrene films having a high refractive index on the quartz substrate. The emission are reflected numerous times on the interfacial surface of the polystyrene films and are amplified extremely. Because the amplified emission by the microcavity have a different lifetime from a normal emission, the faster decay component is attributed to the amplified spontaneous emission (ASE).

The ratio of ASE component of the polystyrene film containing the Eu(III) complexes in the whole emission are shown in Fig. 5. The emission lifetimes were analyzed by a least-squares fitting of the double-exponential function. The fractions of the faster components were determined by the branching ratio functions. The faster component increased with increasing excitation energy. The threshold energy of Eu(hfa)$_3$(TPPO)$_2$ was found to be 0.1 mJ. In contrast, the threshold energies of Eu(hfa)$_3$(phen)$_2$, Eu(hfa)$_3$(2,2′-bpy)$_2$ and Eu(hfa)$_3$(4,4′-bpy)$_2$ were much smaller than those of Eu(hfa)$_3$(TPPO)$_2$. Although the ligand structure of Eu(hfa)$_3$(phen)$_2$ is similar to that of Eu(hfa)$_3$(2,2′-bpy)$_2$, the threshold levels vary greatly. The phenyl ring of phenanthroline inhibit distortion of the ligand. The anti-symmetrical structure of Eu(hfa)$_3$(phen)$_2$ complexes have led to low threshold energy for the ASE oscillation. This amplification of the ASE should be ascribed by the coordination structures.

Conclusions

We have successfully designed novel Eu(III) complexes having a low threshold level for ASE by controlling the symmetry of the complexes with various ligands. Those emission properties are due to coordination number and asymmetrical structures of the Eu(III) complexes. The molecular design of luminescent lanthanide complexes is expected to open up new fields in molecular photonics.

References

[1] Sargent, M. III, Scully, M. O., Willis, E., & Lamb, J. (1974). *Laser physics*; Addison-Wesley, Advanced Book Program: Reading, MA.

[2] Gan, F. (1995). *Laser Materials*; World Scientific, Singapore, 70.

[3] Digonnet, M. J. F. (2001). *Rare-earth-doped fiber lasers and amplifiers*; Marcel Dekker: New York.

[4] Yersin, H. (2004). *Transition Metal and Rare Earth Compounds*; Springer: Berlin, Germany.

[5] Hasegawa, Y., Wada, Y., Yanagida, S., Kawai, H., Yasuda, N., & Nagamura, T. (2003). *Appl. Phys. Lett.*, *83*, 3599.

[6] Nakamura, K., Hasegawa, Y., Kawai, H., Yasuda, N., Kanehisa, N., Kai, Y., Nagamura, T., Yanagida, S., & Wada, Y. (2007). *J. Phys. Chem., A*, *111*, 3029.

[7] Nakamura, K., Hasegawa, Y., Kawai, H., Yasuda, N., Tsukahara, Y., & Wada, Y. (2008). *Thin Solid Films*, *516*, 2376.

[8] Wolbers, M. P. O., van Veggel, F. C. J. M., Snellink-Ruel, B. H. M., Hofdtraat, J. W., Geurts, F. A. J., Reinhoudt, D. N. (1998). *J. Chem. Soc., Perkin Trans. 2*, 2141.

[9] Fang, J., Choy, C., Ma, D., & Ou, E. (2006). *Thin Solid Films 515*, 2419.

[10] Chu, B., Li, W. L., Hong, Z. R., Zang, F. X., Wei, H. Z., Wang, D. Y., Li, M. T., Lee, C. S., & Lee, S. T. (2006). *J. Phys. D: Appl. Phys. 7*, 4549.

[11] Reyes, R., Cremona, M., Teotonio, E. E. S., Brito, H. F., & Malta, O. L. (2004). *Thin Solid Films 469* 59.

[12] Reyes, R., Cremona, M., Teotonio, E. E. S., Brito, H. F., & Malta, O. L. (2004). *Chem. Phys. Lett. 396*, 54.

[13] Zheng, Y. X., Fu, L. S., Zhou, Y. H., Yu, J. B., Yu, Y. N., Wang, S. B., & Zhang, H. J. (2002). *J. Mater. Chem. 12*, 919.

[14] Kawai, H., Zhao, C., Tsuruoka, S., Yoshida, T., Hasegawa, Y., & Kawai, T. (2008). *J. Alloys Compd. 488*, 612.

[15] Hasegawa, Y., Turuoka, S., Yoshida, T., Kawai, H., & Kawai, T. (2008). *J. Phys. Chem. A 112*, 803.

[16] Hasegawa, Y., Tsuruoka, S., Yoshida, T., Kawai, H., & Kawai, T. (2008). *Thin Solid Films 516*, 2704.