



## Emission properties of Sm(III) complexes having remarkably deep-red emission band

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### ABSTRACT

Novel Sm(III) complexes were synthesized by the reaction of hexafluoroacetylacetonato (hfa) and triphenylphosphine oxide (TPPO), 2,2'-bipyridine (bpy), 1,10-phenanthroline (phen). Emission bands were observed at “deep-red” region and were attributed to f–f transitions. The branching ratio (electric-dipole transitions 644 nm vs. magnetic dipole transition 598 nm) of the Sm(hfa)<sub>3</sub>(TPPO)<sub>2</sub> was much larger than that of Sm(hfa)<sub>3</sub>(bpy)<sub>2</sub>, Sm(hfa)<sub>3</sub>(phen)<sub>2</sub>. Those emission properties are due to coordination number and asymmetrical structures of novel Sm(III) complexes.

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### 1. Introduction

White light-emitting diodes (LEDs) attract considerable attention for new illumination, because of high luminance and low power consumption. However those LED devices are unnatural tone, since red light intensity is very weak. The strong red fluorescence is required to achieve a natural tone LED devices. Lanthanide(III) ions have been extensively studied as the attractive luminescent center for display devices [1–4]. The monochromatic emission of lanthanide(III) ion mainly comes from the f–f transition with no Stokes shift [2]. The emission wavelength of lanthanide(III) is in principle independent of the crystal or ligand field because of characteristic feature of the f–f transition. It is difficult to tune to the “deep-red” emission wavelength (around 650 nm) using Eu(III) ions having the red emission (615 nm). Luminescent materials having narrow deep-red emission are strongly desired for high-quality devices [5–8].

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 ten coordination structures [9,10]. 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 Sm(III) complexes having remarkably deep-red emission for developing luminescent materials. Sm(III) complexes were synthesized by the reaction of hexafluoroacetylacetonato (hfa) and triphenylphosphine oxide (TPPO), 2,2'-bipyridine (bpy), 1,10-phenanthroline (phen) (Fig. 1). The relationship between ligands structures and emission properties is demonstrated in organic solutions.

### 2. Experimental

#### 2.1. Materials

Samarium(III) acetate tetrahydrate (99.9%), triphenylphosphine oxide and polystyrene beads were purchased from Wako Pure Chemical Industries Ltd. Hexafluoroacetylacetonato, 2,2'-bipyridine, 1,10-phenanthroline, were obtained from Tokyo Kasei Organic Chemicals. All other chemicals were reagent grade and were used as received.

#### 2.2. Preparation of samarium(III) complexes

Tris(hexafluoroacetylacetonato) samarium(III) bis(triphenylphosphine oxide): Sm(hfa)<sub>3</sub>(TPPO)<sub>2</sub> was prepared by the reaction of between Sm(hfa)<sub>3</sub>(H<sub>2</sub>O)<sub>2</sub> and the triphenylphosphine 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 45%.

Tris(hexafluoroacetylacetonato) samarium(III) bis(2,2'-bipyridine): Sm(hfa)<sub>3</sub>(bpy)<sub>2</sub> and tris(hexafluoroacetylacetonato) samarium(III) bis(1,10-phenanthroline): Sm(hfa)<sub>3</sub>(phen)<sub>2</sub> were also prepared by the reaction of Sm(hfa)<sub>3</sub>(H<sub>2</sub>O)<sub>2</sub> and 2,2'-bipyridine, 1,10-phenanthroline. Sm(hfa)<sub>3</sub>(H<sub>2</sub>O)<sub>2</sub> was dissolved of acetonitrile

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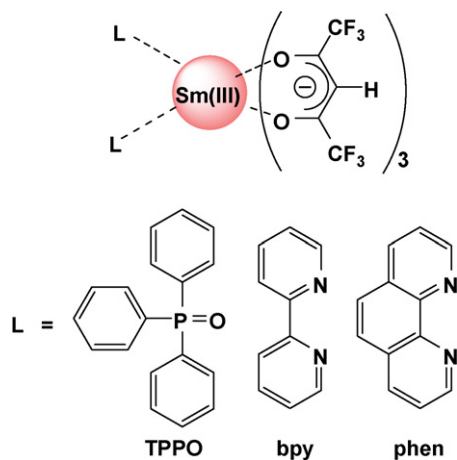


Fig. 1. Chemical structures of Sm(III) complexes.

solutions by stirring at 0 °C. 2,2'-Bipyridine and 1,10-phenanthroline 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 30% ( $\text{Sm}(\text{hfa})_3(\text{bpy})_2$ ) and 56% ( $\text{Sm}(\text{hfa})_3(\text{phen})_2$ ).

### 2.3. Characterization

Infrared spectra used to identify synthesized materials were obtained with a JASCO FT/IR-410 spectrometer.  $^1\text{H}$  NMR data were obtained with a Varian Mercury plus 400 MHz spectrometer 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). The emission quantum yields were determined by absolute PL quantum yields measurement system (Hamamatsu, C9930-02).

## 3. Results and discussion

### 3.1. Emission spectra

The emission spectra of the Sm(III) complexes in acetone were measured for the excitation at 355 nm ( $\pi-\pi^*$  transition of the hexafluoroacetylacetonate ligands). The emission spectra were shown in Fig. 2. The emission bands of  $\text{Sm}(\text{hfa})_3(\text{TPPO})_2$  were observed at 562, 598, 644 and 706 nm and are attributed to f-f transition  $^4\text{G}_{5/2} \rightarrow ^6\text{H}_{5/2}$  (forbidden transition),  $^4\text{G}_{5/2} \rightarrow ^6\text{H}_{7/2}$  (magnetic dipole transition),  $^4\text{G}_{5/2} \rightarrow ^6\text{H}_{9/2}$  (electric-dipole transition),  $^4\text{G}_{5/2} \rightarrow ^6\text{H}_{11/2}$  (forbidden transition), respectively. The emission spectra in Fig. 2 were normalized with respect to the

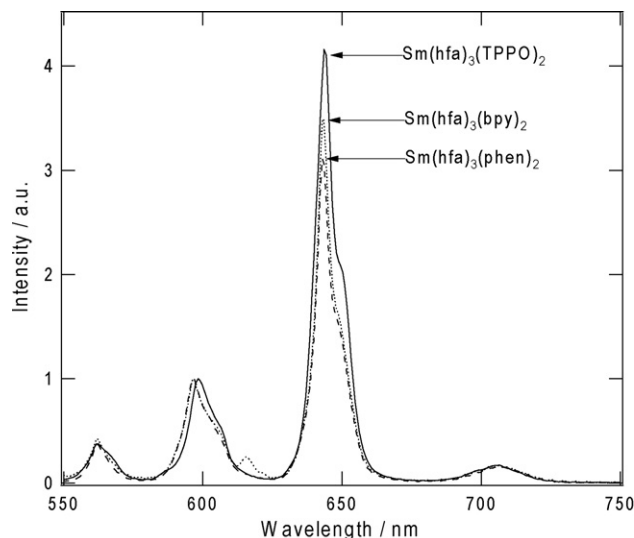


Fig. 2. Normalized emission spectra of Sm(III) complexes in acetone solutions (0.01 M) excited at 355 nm.

magnetic dipole transition (598 nm). The emission intensities of electric-dipole transition (644 nm) were extremely enhanced as compared with those of corresponding Sm(III) ions in inorganic glass matrixes.

The full width at half maximum (FWHM) of emission peak (644 nm) and the relative intensities of the electric-dipole transition (644 nm) to the magnetic dipole transition (598 nm) are summarized in Table 1. The FWHM and the relative emission intensity of the  $^4\text{G}_{5/2} \rightarrow ^6\text{H}_{9/2}$  transition (644 nm) of  $\text{Sm}(\text{hfa})_3(\text{TPPO})_2$  was larger than those of  $\text{Sm}(\text{hfa})_3(\text{bpy})_2$  and  $\text{Sm}(\text{hfa})_3(\text{phen})_2$ . The electric-dipole transition is directly linked to the coordination structures related to odd parity. The geometrical structure of  $\text{Sm}(\text{hfa})_3(\text{phen})_2$  complex shows ten-coordination square antiprism without inverted center in the crystal field [10]. On the other hand, the  $\text{Sm}(\text{hfa})_3(\text{TPPO})_2$  have the eight-coordination structure due to the three hexafluoroacetylacetonate (hfa) ligands and two TPPO ligands. The degree of enhanced emission intensities and widths of the Sm(III) complexes should be caused by the coordination structures.

### 3.2. Emission lifetimes and quantum yields

The emission lifetimes of the Sm(III) complexes in acetone 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 in acetone. The emission lifetimes were determined from the slope of logarithmic plot of the decay profiles. The emission lifetimes of the  $\text{Sm}(\text{hfa})_3(\text{bpy})_2$  and  $\text{Sm}(\text{hfa})_3(\text{phen})_2$  complexes were found to be 31 and 37  $\mu\text{s}$ , respectively. However, those of  $\text{Sm}(\text{hfa})_3(\text{TPPO})_2$  complex are about three

Table 1

Photophysical properties of Sm(III) complexes in acetone solutions.

	FWHM <sup>a</sup> (nm)	$I_{644}/I_{598}$ <sup>b</sup>	$\Phi$ <sup>c</sup>	$\tau^d$ ( $\mu\text{s}$ )	$k_r^e$ ( $\times 10^{-2} \text{ s}^{-1}$ )	$k_n^e$ ( $\times 10^{-2} \text{ s}^{-1}$ )
$\text{Sm}(\text{hfa})_3(\text{TPPO})_2$	10.0	4.2	0.041	97	4.2	99
$\text{Sm}(\text{hfa})_3(\text{bpy})_2$	7.0	3.6	0.016	31	5.2	320
$\text{Sm}(\text{hfa})_3(\text{phen})_2$	8.1	3.2	0.019	37	5.1	270

<sup>a</sup> Full width at half maximum of emission peak (644 nm).

<sup>b</sup> Relative intensities of the  $^4\text{G}_{5/2} \rightarrow ^6\text{H}_{9/2}$  (electric-dipole transition: 644 nm) to the  $^4\text{G}_{5/2} \rightarrow ^6\text{H}_{9/2}$  (magnetic dipole transition: 598 nm).

<sup>c</sup> Emission quantum yields were measured by the excitation at 480 nm (f-f transition).

<sup>d</sup> Emission lifetime.

<sup>e</sup> Radiative rates ( $k_r$ ) and non-radiative rates ( $k_n$ ) were determined using emission lifetimes and emission quantum yields ( $\Phi = k_r/(k_r + k_n)$ ,  $\tau = 1/(k_r + k_n)$ ).

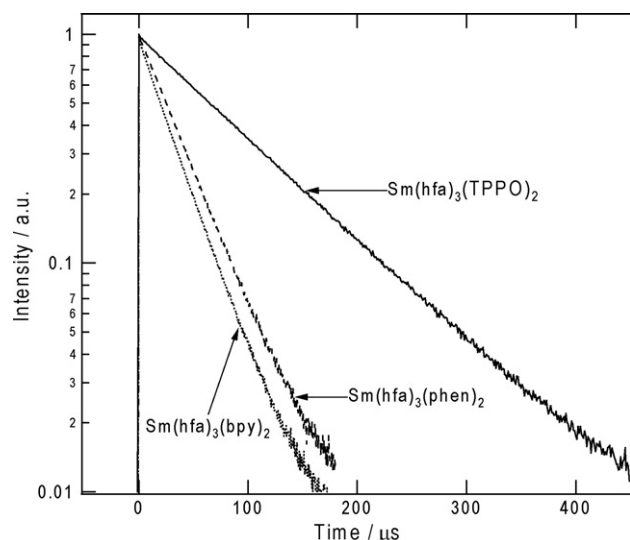


Fig. 3. Emission decays of Sm(III) complexes in acetone solutions (0.01 M) excited at 355 nm.

times the value of other complexes. The emission quantum yields, the emission lifetimes and calculated emission rate constants are summarized Table 1. There is no significant difference in the radiative rate constant ( $k_r$ ) of the Sm(III) complexes. In contrast, the non-radiative rate constant ( $k_{nr}$ ) of the  $\text{Sm}(\text{hfa})_3(\text{TPPO})_2$  complex is much smaller than those of  $\text{Sm}(\text{hfa})_3(\text{bpy})_2$  and  $\text{Sm}(\text{hfa})_3(\text{phen})_2$  complexes. These results suggested that the vibrational relaxation process was inhibited by the coordination structure. Consequently, the emission quantum yield ( $\Phi$ ) of the  $\text{Sm}(\text{hfa})_3(\text{TPPO})_2$  (0.041) is two times larger than those of the  $\text{Sm}(\text{hfa})_3(\text{bpy})_2$  (0.016) and  $\text{Sm}(\text{hfa})_3(\text{phen})_2$  (0.019). The luminescence quantum yield of Pr(III)  $\beta$ -diketonate chelate which excited at ligand absorption band was observed to 0.006% at 605–645 nm [11]. We have already reported that energy transfer efficiency from hfa ligand to Sm(III) ion was found to be 26% in acetone solution [9]. The emission quantum yields of ligand excitation for  $\text{Sm}(\text{hfa})_3(\text{TPPO})_2$  complex was estimated to about 1%. The effective emission quantum yield of the Sm(III) complexes would be due to characteristic coordination

structures which lead to radiationless transition via vibrational relaxation.

#### 4. Conclusion

We have successfully designed novel Sm(III) complexes having remarkably deep-red emission, high branching ratio, high emission quantum yields by controlling the symmetry of the complexes with various ligands. Those emission properties are due to coordination number and asymmetrical structures of the Sm(III) complexes. Furthermore, we successfully fabricated the polymer thin films containing the Sm(III) complexes. Luminescent Sm(III) complexes appear to be the suitable candidate for enhancing color rendition of LED devices.

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#### References

- [1] G. Blasse, B.C. Grabmaier, *Luminescent Materials*, Springer-Verlag, New York, 1994.
- [2] F. Gan, *Laser Materials*, World Scientific, Singapore, 1995, p. 70.
- [3] M.P.O. Wolbers, F.C.J.M. van Veggel, B.H.M. Snellink-Ruel, J.W. Hofdtraat, F.A.J. Geurts, D.N. Reinhoudt, *J. Chem. Soc., Perkin Trans. 2* (1998) 2141.
- [4] J. Fang, C. Choy, D. Ma, E. Ou, *Thin Solid Films* 515 (4) (2006) 2419.
- [5] B. Chu, W.L. Li, Z.R. Hong, F.X. Zang, H.Z. Wei, D.Y. Wang, M.T. Li, C.S. Lee, S.T. Lee, *J. Phys. D: Appl. Phys.* 7 (2006) 4549.
- [6] R. Reyes, M. Cremona, E.E.S. Teotonio, H.F. Brito, O.L. Malta, *Thin Solid Films* 469 (2004) 59.
- [7] R. Reyes, M. Cremona, E.E.S. Teotonio, H.F. Brito, O.L. Malta, *Chem. Phys. Lett.* 396 (2004) 54.
- [8] Y.X. Zheng, L.S. Fu, Y.H. Zhou, J.B. Yu, Y.N. Yu, S.B. Wang, H.J. Zhang, *J. Mater. Chem.* 12 (2002) 919.
- [9] Y. Hasegawa, S. Tsuruoka, T. Yoshida, H. Kawai, T. Kawai, *J. Phys. Chem. A* 112 (2008) 803.
- [10] Y. Hasegawa, S. Tsuruoka, T. Yoshida, H. Kawai, T. Kawai, *Thin Solid Films* 516 (2008) 2704.
- [11] A.I. Voloshin, N.M. Shavaleev, V.P. Kazakov, *J. Lumin.* 93 (2001) 199.