Enhanced Deep-Red Luminescence of Tris(hexafluoroacetylacetonato)samarium(III) Complex with Phenanthroline in Solution by Control of Ligand Coordination

Yasuchika Hasegawa,*,[†] Shin-ichi Tsuruoka,[‡] Takahiko Yoshida,[‡] Hideki Kawai,[§] and Tsuyoshi Kawai[†]

Graduate School of Materials Science, Nara Institute of Science and Technology, 8916-5 Takayama, Ikoma, Nara 630-0192, Japan; USHIO Chemix, Co. Ltd., 2252-1 Goudo, Omaezaki, Shizuoka, 437-1613, Japan; and Research Institute of Electronics, Shizuoka University, 3-5-1 Johoku, Hamamatsu, Shizuoka 432-8011, Japan

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The effect of solvent molecule on the emission properties of Sm(hfa)$_3$(phen)$_2$ (hfa = hexafluoroacetylacetonato, phen = phenanthoroline) was investigated using acetone, acetonitrile, and pyridine. $^5G_{5/2} \rightarrow {}^5H_{9/2}$ transition intensities in pyridine were found to be larger than those in corresponding acetone and acetonitrile. The radiative rate constant in pyridine (4.8×10^2 s^{-1}) was 2 times larger than those in acetonitrile (2.6×10^2 s^{-1}) and acetone (2.3×10^2 s^{-1}), although the nonradiative transition via vibrational relaxation ($k_{nr} = 1.7 \times 10^4$ s^{-1}) in pyridine was the same as those in acetone and acetonitrile ($k_{nr} = 1.8 \times 10^4$ s^{-1}), resulting in the enhanced emission quantum yield of Sm(III) complex in pyridine (2.7%). The coordination structures of Sm(hfa)$_3$(phen)$_2$ in acetonitrile, acetone, and pyridine were estimated by X-ray single-crystal analyses. These results indicate that enhancement of the emission properties in pyridine is due to faster radiative rate related to formation of asymmetrical nine-coordinated structure, Sm(hfa)$_3$(phen)(py) (py = pyridine).

Introduction

Lanthanide(III) ions are the most popular luminescent materials for application in display devices because of their highly monochromatic clear emission with fwhm.[1] Especially, the monochromatic emission of Eu(III) ion plays an important role of construction of red element in the full-color display.[2] A large number of studies about red luminescent nanoparticles, complexes, and nanomaterials including Eu(III) ions have been reported.[3] The red emission of Eu(III) ion mainly comes from the f−f transitions with no Storks shift.[4] The emission bands of Eu(III) ion are observed at around 580 nm ($^5D_0 \rightarrow {}^7F_0$: zero−zero band), 595 nm ($^5D_0 \rightarrow {}^7F_1$: magnetic dipole transition), 615 nm ($^5D_0 \rightarrow {}^7F_2$: electric dipole transition), 650 nm ($^5D_0 \rightarrow {}^7F_3$: forbidden), and 700 nm ($^5D_0 \rightarrow {}^7F_4$: forbidden). The emission wavelength of Eu(III) is in principle independent of the crystal or ligand field because of characteristic feature of the f−f transition. The red emission wavelength (615 nm) of Eu(III) ion cannot be tuned to the deep-red color wavelength (around 650 nm). According to the chromaticity diagram, narrow deep-red emission at 650 nm leads to improvement of full-color display reproduced natural products (Figure 1a). Luminescent materials having narrow deep-red emission are strongly desired for high-quality display devices.[5]

We here focus on Sm(III) ion as a deep-red luminescent center. The emission bands of Sm(III) ion are assigned to $^4G_{5/2} \rightarrow {}^6H_{5/2}$ (zero−zero band), $^4G_{5/2} \rightarrow {}^6H_{7/2}$ (magnetic dipole transition), $^4G_{5/2} \rightarrow {}^6H_{9/2}$ (electric dipole transition), and $^4G_{5/2} \rightarrow {}^6H_{11/2}$ (forbidden).[1] Generally, the emission quantum yields of Sm(III) compound are much smaller than those of Eu(III) compound because of smaller energy gap of Sm(III) ions (Sm(III): 7500 cm^{-1}; Eu(III): 12500 cm^{-1}).[1,2] The excited state of Sm(III) ion having smaller energy gap are easily quenched by high-vibrational O−H bonds of coordinating water.[6] In order to enhance the emission quantum yield of Sm(III), protection by using some organic ligands for prevention of coordinating water should be needed. Several luminescent Sm(III) compounds having organic ligands have been reported.[7] While most of the emission spectra of Sm(III) complexes reports in the literature, Petoud has reported that the emission quantum yield of Sm(III) complex with 2-hydroxyisophthalamide chelating unit excited at 347 nm was 1%.[7l] To our the best knowledge, this is the best emission quantum yield of Sm(III) complexes. In order to improve the luminescent Sm(III) complex, molecular-designed Sm(III) complex needed not only higher emission quantum yield excited at f−f transition but also evaluation of the radiative rate, the nonradiative rate, the photosensitized energy transfer efficiency, and guide principle for enhancement of luminescent properties. For example, Sm(III) compound with characteristic asymmetric structures is expected to have increased radiation probability and emission quantum yield, since the $^4G_{5/2} \rightarrow {}^6H_{9/2}$ electric dipole transition would be partly allowed with the odd parity of the transition process.[8] As reported in a preliminary paper, we succeeded in observing the deep-red emission of a 10-coordinated Sm(III) complex, bis(phenanthroline)tris(hexafluoroacetylacetonato)samarium(III), in acetone (Sm(hfa)$_3$(phen)$_2$, Figure 1b).[9] The Sm(III) complex has (1) low-vibrational hfa ligands for suppression of radiationless transition via vibrational relaxations[6] and (2) phenanthroline ligands for addition of asymmetrical ligand field in the coordination space[8] and forms remarkable 10-coordination structure in acetone. The total quantum yields excited at absorption bands of the ligands (380 nm: $\pi-\pi^*$ transition) and Sm(III) ion (480 nm: f−f transition) in acetone were 0.36 and 1.4%, respectively. Enhanced emission quantum yield of

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* Corresponding author: Tel 81-743-72-6180; Fax 81-743-72-6180; e-mail hasegawa@ms.naist.jp.

[†] Nara Institute of Science and Technology.

[‡] USHIO Chemix, Co Ltd.

[§] Shizuoka University.

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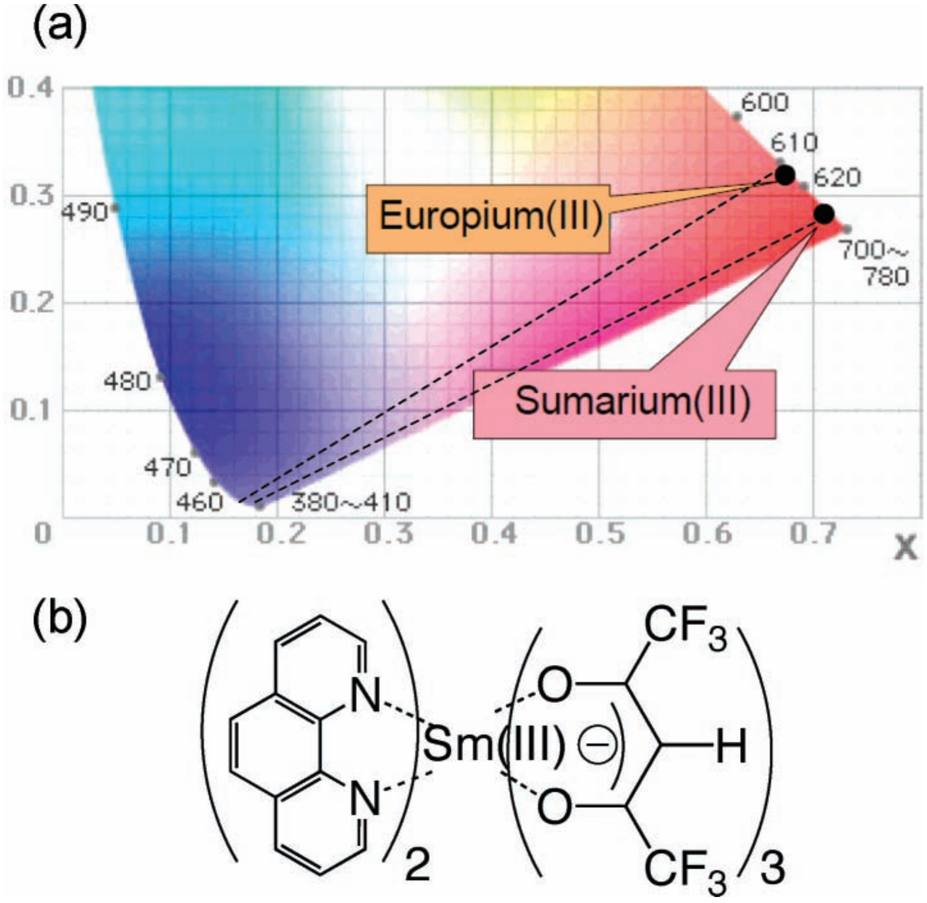

Figure 1. (a) Positions of Eu(III) and Sm(III) in the chromaticity diagram. (b) Chemical structure of Sm(hfa)$_3$(phen)$_2$.

Sm(hfa)$_3$(phen)$_2$ would be based on the characteristic 10-coordination structure having no coordinated water.

It is known that the emission properties of the lanthanide(III) complexes are affected by coordination ability of the solvent molecules.[6b] Introduction of solvent molecules with strong coordination capability such as pyridine would induce transformation of the coronation structure and the enhancement of the emission properties. In the present paper, the effect of solvent molecule on the emission properties of Sm(hfa)$_3$(phen)$_2$ is studied using acetone, acetonitrile, and pyridine. The emission quantum yield, the emission lifetimes, radiative rates, nonradiative rates, and energy transfer efficiencies of Sm(hfa)$_3$(phen)$_2$ were determined in acetone, acetonitrile, and pyridine. The geometrical structures of the complex in each solution are estimated by using X-ray single-crystal analyses. The relationship between the emission characteristics and geometrical structures is discussed in terms of symmetricity of Sm(hfa)$_3$(phen)$_2$ in respective solvents.

Experimental Section

Apparatus. Infrared spectra used to identify synthesized materials were obtained with a Shimadzu FTIR-8300 spectrometer. Elemental analyses were performed with a J-Science Lab JM10. ^{1}H NMR data were obtained with a Varian Mercury plus 400 MHz spectrometer and were determined using tetramethylsilane (TMS) as an internal standard.

Materials. Sammarium(III) chloride (99.5%), 1,1,1,5,5,5-hexafluoro-2,4-pentanedione (hfa-H$_2$), and 1,10-phenanthroline (phen) were purchased from Wako Pure Chemical Industries Ltd. Acetone-d_6 (CD$_3$COCD$_3$, 99.8%) was obtained from Aldrich Chemical Co. Inc. All other chemicals were reagent grade and were used as received.

Preparation of Bis(1,10-phenanthroline)tris(hexafluoroacetylacetonato)sammarium(III) (Sm(hfa-H)$_3$(phen)$_2$). Ethanol (30 mL) containing 1,1,1,5,5,5-hexafluoro-2,4-pentanedione (2.39 g, 11.5 mmol), 1,10-phenanthroline (phen) (2.07 g, 11.5 mmol), and potassium hydroxide (0.46 g, 11.5 mmol) was stirred. A solution of sammarium chloride (1.4 g, 3.84 mmol) in water (5 mL) was added dropwise to the above solution and reacted at 60 °C for 2 h. The reaction mixture was concentrated, and the obtained mixture was washed with toluene/water several times. The organic layer was separated, dried by anhydrous magnesium sulfate, and concentrated. Recrystallization from water/methanol gave crystals of Sm(hfa-H)$_3$(phen)$_2$. Yield: 50−60%. IR (KBr): 1658 (st, C═O), 1529 (st, C═C), 1211, and 1197 cm^{-1} (st, C−F). ^{1}H NMR (CD$_3$COCD$_3$) δ: 8.5 (4H, Ar), 8.0 (4H, Ar), 7.6 (4H, Ar), 7.5 (4H, Ar), and 6.7 ppm (s, 3H, C−H). Anal. Calcd for SmC$_{39}$H$_{19}$O$_6$F$_{18}$N$_4$: C, 41.38; H, 1.69; N: 4.95%. Found: C, 41.09; H, 1.68; N, 4.94%. Decomposition point: 288 °C.

Optical Measurements. Solution (0.01 M) of the Sm(III) complex was prepared in 1 mL of acetone and was degassed with nitrogen for optical measurements. Emission spectra were measured at room temperature using an ACTON Research Corp. SpectraPro 2300i system with a CCD detector (Roper PIXIS 100). The spectra were corrected for detector sensitivity and lamp intensity variations. Emission lifetimes were measured with the third harmonics (355 nm) of a Q-switched Nd:YAG laser (Spectra Physics, INDI-50, fwhm = 5 ns, λ = 1064 nm) and a photomultiplier (Hamamatsu photonics, R5108, response time $\leq$1.1 ns). Nanosecond light pulses used to produce excitations in the samples (λ = 481 nm, power = 0.1 mJ) were generated by a dye laser (USHO optical systems DL-50, dye = coumarin 120). Emissions from the samples were filtered using a low-

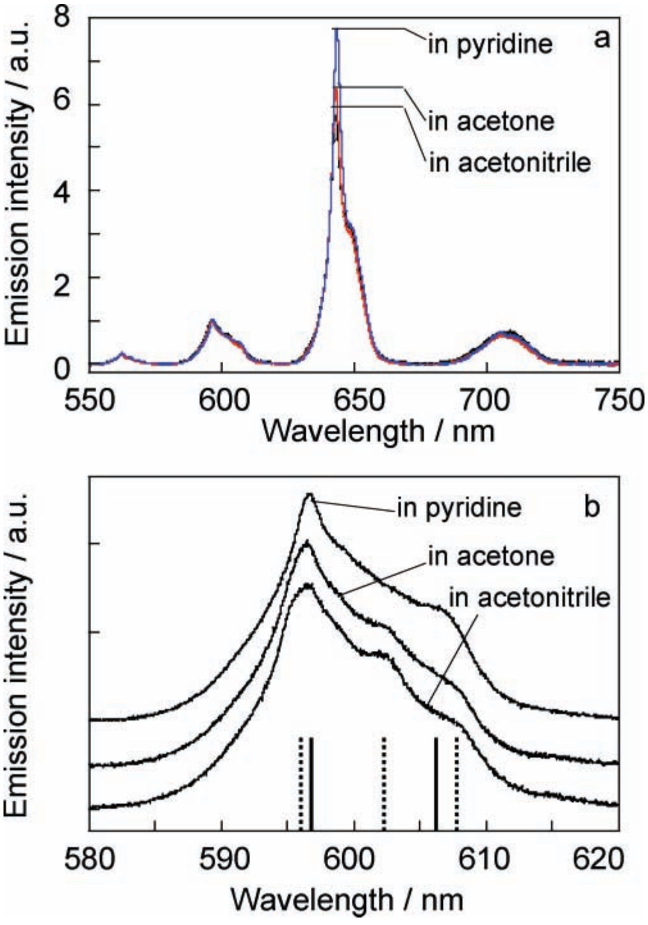

Figure 2. (a) Emission spectra of $Sm(hfa)_3(phen)_2$ in various solvents excited at 481 nm. (b) Emission spectra of $^5G_{5/2} \rightarrow {}^5H_{9/2}$ transition of $Sm(hfa)_3(phen)_2$ in various solvents at 481 nm. Bold (in pyridine) and dashed (in acetone and acetonitrile) lines on the wavelength axis are positions of energy levels in Stark splittings.

cut filter (Sigma SCF-50S-52Y) placed in front of the detector. The Nd:YAG response was monitored with a digital oscilloscope (Sony Tektronix, TDS3052, 500 MHz) synchronized to the single-pulse excitation. Quantum yields were determined using a standard integrating sphere (diameter 6 cm).[6] Optical path length of the cell was 5 mm. Quantum yields of rhodamine 6G in ethanol (1.0×10^{-7} M, excitation wavelength = 510 nm, emission quantum yield = 95%) determined by the present procedure agreed well with reported value.[10]

Crystallography. Colorless single crystals of the Sm(III) complex obtained from acetonitrile and pyridine solutions were mounted on a glass fiber using epoxy resin glue. X-ray diffraction intensities were collected with a Rigaku RAXIS-RAPID imaging plate diffractometer using graphite-monochromated Mo Kα radiation in $\omega - 2\theta$ scan mode. Corrections for decay and Lorentz-polarization effects were made, with empirical absorption corrections solved by direct methods and expanded using Fourier techniques. Non-hydrogen atoms were refined anisotropically. The final cycle of full-matrix least-squares refinement was based on observed reflections and variable parameters. All calculations were performed using the Crystal Structure crystallographic software package.

Results and Discussion

Emission Spectra. The emission spectra of the Sm(III) complex $Sm(hfa)_3(phen)_2$ in acetone, acetonitrile, and pyridine are shown in Figure 2a. Emission bands were observed at around 562, 597, 643, and 705 nm and are attributed to f−f transitions $^5G_{5/2} \rightarrow {}^5H_{5/2}$ ($\Delta J = 0$, zero−zero band: forbidden transition), $^5G_{5/2} \rightarrow {}^5H_{7/2}$ ($\Delta J = 1$, magnetic dipole transition), $^5G_{5/2} \rightarrow {}^5H_{9/2}$ ($\Delta J = 2$, electronic dipole transitions), and $^5G_{5/2} \rightarrow {}^5H_{11/2}$ ($\Delta J = 2$, forbidden transition), respectively. Spectra shown in Figure 2a were normalized with respect to the $^5G_{5/2} \rightarrow {}^5H_{7/2}$ (magnetic dipole) transition. The $^5G_{5/2} \rightarrow {}^5H_{9/2}$ transition intensity in pyridine was found to be larger than those in corresponding acetone and acetonitrile. We also observed that the Stark splitting of $^5G_{5/2} \rightarrow {}^5H_{7/2}$ transition (bold lines on the wavelength axis, 596.7 nm: ~16 800 cm^{-1} and 607.1 nm: ~16 500 cm^{-1}) in pyridine was different from those in other solvents (dotted lines on the wavelength axis, 596.3 nm: ~16 800 cm^{-1}, 602.3 nm: ~16 600 cm^{-1} and 608.0 nm: ~16 400 cm^{-1}) (Figure 2b). The emission strength of the $^5G_{5/2} \rightarrow {}^5H_{9/2}$ transition and Stark splitting of $^5G_{5/2} \rightarrow {}^5H_{7/2}$ are directly linked to the coordination structure related to odd parity in liquid media.[3] Enhanced emission spectra of $Sm(hfa)_3(phen)_2$ in pyridine should be caused by the transformation of the coordination structure of Sm(III) complex.

TABLE 1: Characteritics of the Emission of $Sm(hfa)_3(phen)_2$ in Various Solvents[a]

solvent	I_{rel}	Φ(f−f)/%	τ/μs	k_r/s^{-1}	k_{nr}/s^{-1}
acetonitrile	5.9	1.3	56	2.6×10^2	1.8×10^4
acetone	6.1	1.4	54	2.3×10^2	1.8×10^4
pyridine	7.8	2.7	56	4.8×10^2	1.7×10^4

[a] The emission quantum yields (Φ(f−f)) and lifetimes (τ) of the Sm(III) complex in each solvent were the excitation at 481 nm ($^5H_{5/2} \rightarrow {}^5G_{5/2}{}^4I_{13/2\ \mathrm{and}\ 9/2}$). Radiative rate $k_r = (\Phi(f-f))/\tau$. Nonradiative rate $k_{nr} = (1/\tau) - k_r$.

Transition Process. Generally, asymmetrical coordination structure leads to enhancement of the emission property, in other words, the radiative rate from the emitting level ($^5G_{5/2}$).[8] In order to calculate the radiative rates from the emitting level in various solvents, the emission decays and the emission quantum yields of Sm(III) complex in each solvent were measured. Single-exponential decay emissions indicated the presence of a single luminescent element in each solvent. The emission lifetimes were determined from the slopes of logarithmic plots of decay profiles. The emission rate constant k_r was evaluated from the ratio of the emission quantum yield and emission lifetime, k_r = emission quantum yield/emission lifetime). Emission lifetimes, quantum yields, and calculated emission rate constants are summarized in Table 1. We found that the radiative rate constant in pyridine ($4.8 \times 10^2\ s^{-1}$) is 2 times larger than those in acetonitrile ($2.6 \times 10^2\ s^{-1}$) and acetone ($2.3 \times 10^2\ s^{-1}$), resulting in the enhanced emission quantum yield (2.7%). In contrast, the nonradiative transition via vibrational relaxation ($k_{nr} = 1.7 \times 10^4\ s^{-1}$) in pyridine was the same as those in acetone and acetonitrile ($k_{nr} = 1.8 \times 10^4\ s^{-1}$), resulting in the same relaxation process.

In order to estimate the photosensitized energy transfer efficiency from ligands to Sm(III) ion, we carried out the measurements of the emission spectra and the emission quantum yields of Sm(III) complex excited at 380 nm. The emission spectra for ligand excitation were the same shapes as those in Figure 2. We propose that the emission processes from the emitting level ($^5G_{5/2}$) for ligand excitations (380 nm) is the same as those for Sm(III) ion excitation (481 nm). The emission intensity of the Sm(III) complex excited at 380 nm was about 5 times larger than that at corresponding 481 nm. Those results indicate that $Sm(hfa)_3(phen)_2$ shows effective photosensitized luminescence. The photosentized energy transfer was calculated by using the emission quantum yield excited at 480 nm

TABLE 2: Photosensitized Energy Transfer Efficiencies of $Sm(hfa)_3(phen)_2$ in Various Solvents[a]

solvent	$\Phi(\pi-\pi^*)$/%	energy transfer efficiencies/%
acetonitrile	0.34	26
acetone	0.36	26
pyridine	0.66	25

[a] $\Phi(\pi-\pi^*)$ of the Sm(III) complex in each solvent were the excitation at 380 nm.

TABLE 3: Crystal Data, Data Collection, and Structure Refinement for Complexes 1 and 2

	crystal obtained from acetonitrile solution	crystal obtained from pyridine solution
chemical formula	$C_{39}H_{19}N_4O_6F_{18}$-$Sm(CH_3CN)$	$C_{32}H_{16}N_3O_6F_{18}$-Sm
formula weight	1173.03	1030.87
crystal system	monoclinic	triclinic
space group	$P2_1/n$ (#14)	P-1 (#2)
a/Å	11.6(9)	11.5(9)
b/Å	19.6(6)	17.5(4)
c/Å	20.6(3)	18.8(2)
α/deg		78.4(0)
β/deg	93.4(1)	84.1(2)
γ/deg		88.0(2)
V/Å^3	4731.7(2)	3739.0(7)
Z	4	4
T/°C	−100	−50
μ(Mo Kα)/cm^{-1}	13.64	17.11
no. of measured reflections	45 842	29 444
no. of unique reflections	10 817	13 084
R_{int}	0.124	0.028
R (R_w)	0.063 (0.074)	0.059 (0.0942)

(excitation at Sm(III) ion) and 380 nm (excitation at hfa ligands). The emission quantum yields excited at 380 nm and the energy transfer efficiencies are shown in Table 2. The emission quantum yield of Sm(III) complex in pyridine (0.66%) was 2 times larger than those in acetonitrile (0.34%) and acetone (0.36%). The emission quantum yields of $Sm(hfa)_3(phen)_2$ are smaller than that of Sm(III) complex with 2-hydroxyisophthalamide chelating unit. We propose that the energy transfer efficiencies of $Sm(hfa)_3(phen)_2$ might be smaller than previous reported Sm(III) complex.[7l] On the other hand, the energy transfer efficiency of $Sm(hfa)_3(phen)_2$ in pyridine (25%) was the same order as those in acetonitrile (26%) and acetone (26%). These results suggest that the energy transfer efficiency of that $Sm(hfa)_3(phen)_2$ is independent of the solvent effect, and Sm(III) ion is strongly coordinated by ligands without decomposition of the complex.

From the results of the emission quantum yields, the emission lifetimes, the radiative rate constants, and energy transfer efficiency, we conclude that the comparison of rate constants indicate that enhancement of the emission properties in pyridine is due to faster radiative rate related to odd parity.

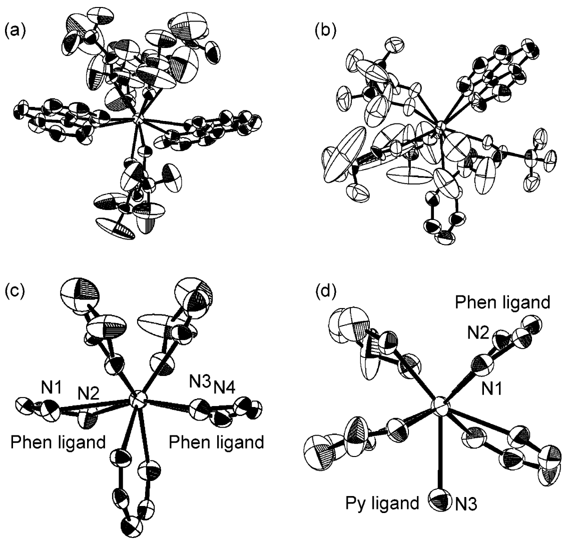

Figure 3. ORTEP view of $Sm(hfa)_3(phen)_2$ single crystals from acetonitrile (a: overview; c: coordination site) and pyridine (b: overview; d: coordination site) solutions.

Coordination Structure. In pyridine, we observed the enhanced electric dipole transition, different spectral shape, and faster radiative rate of $Sm(hfa)_3(phen)_2$. From the results of the emission properties, the coordination structure of $Sm(hfa)_3(phen)_2$ in pyridine is expected to be different from those of corresponding in acetone and acetonitrile. Here, we carried out the X-ray single crystal analyses of $Sm(hfa)_3(phen)_2$ using some crystals from pyridine and acetonitrile solutions. The ORTEP views by X-ray single crystal analyses are shown in Figure 3. The geometrical structure of the single crystal from acetonitrile solution was determined to a symmetrical 10-coordination structure (Figure 3a). The N1 and the N2 atoms in the structure are located in the nearly symmetrical positions by the Sm(III) center (the symmetry operation: *i*, Figure 3b). We propose that the coordination structure of $Sm(hfa)_3(phen)_2$ in acetone is similar to that in acetonitrile because of their similar emission properties (the spectral shapes, the emission quantum yields, radiative and nonradiative rates). The difference between the emission intensities in acetone and acetonitrile might be due to small structural change in liquid media.

In contrast, the geometrical structure of the single crystal from pyridine solution was a monocapped square-anti prism (MSAP: Figure 3b,d). We found that the 10-coordination structure of $Sm(hfa)_3(phen)_2$ was transformed to 9-coordination structure by addition of large amount of pyridine molecules. The 9-coordination structure shows no inverted center in the crystal field, resulting in an increase of the electron transition in the 4f orbitals due to the odd parity. The increase of the electron transition would leads to enhancement of the emission properties of the Sm(III) complex. The enhanced emission intensity in pyridine compared with those in acetone and acetonitrile (Figure 2) is linked with the asymmetrical 9-coordination structure obtained by the X-ray single-crystal analysis. These results have led us to the conclusion that the luminescent Sm(III) complex having 9-coordination structure are promising for applications such as a high-quality display device.

Conclusion

We found that the emission properties of $Sm(hfa)_3(phen)_2$ depended on the solvent. The use of pyridine donates the transformation of the coordination structure of $Sm(hfa)_3(phen)_2$. The 9- and 10-coordination structures of Sm(III) complex in pyridine and acetonitrile were estimated by the X-ray single-crystal analyses. The remarkable 9-coordination structure of $Sm(hfa)_3(phen)(py)$ leads to the enhancement of the emission properties in Sm(III) ion. We also found that the emission quantum yields of $Sm(hfa)_3(phen)(py)$ was found to be 2.7%. Luminescent Sm(III) complex having 9-coordination structure are expected to be useful in display applications such as organic EL devices.[5]

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Supporting Information Available: Structures of Sm(hfa)$_3$(phen)(py) and Sm(hfa)$_3$(phen)$_2$ (cif files). This material is available free of charge via the Internet at http://pubs.acs.org.

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