Emission properties of Sm complexes substituted with asymmetric β -diketonato ligands in solution

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Abstract

Trivalent samarium (Sm) complexes show four emission bands due to the 4f–4f transition in the visible 550–750 nm region, where the 645 nm transition has the dominant intensity. In this paper we have synthesized the three Sm complexes with varying pybox and β -diketonato ligands, to investigate the relative intensity among the emission bands. We have shown that the β -diketonato ligands with asymmetric molecular structures enhance the relative intensity of the 645 nm transition by approximately 20% compared to that with symmetric ligands. By virtue of such a property, Sm complexes can be used as possible candidates for deep red emitting materials. As a strategy on the molecular design, it has also been confirmed that the introduction of heavy atoms such as fluorine to the β -diketonato moiety should be of essential to obtain a high emission quantum yield.

Keywords

Sm complex, rare-earth material, β -diketonato, pybox, additive color tuning, molecular symmetry

1. Introduction

Trivalent rare-earth complexes have been intensively studied because of their potential applications to bioimaging [1-3], laser materials [4,5], solid-state luminescent materials [6,7]. With respect to photochemical properties of rare-earth complexes, organic ligands serve as light-harvesting antennas. After the excitation energy transfer from the ligands to the rare earth, the complexes emit at the wavelength according to the metal property [8]. An advantage of using luminescent rare-earth complexes is that we can obtain sharp emission spectra due to their 4f–4f transitions.

In our previous paper [9] the luminescent properties of europium (Eu) and terbium (Tb) complexes dispersed in the phenol + AOT organogel have been investigated. Hexafluoroacetylacetone (hfa) and 1,10-phenanthroline (phen) have been used as the ligands in that paper, owing to a high emission quantum yield according to the literature [10]. In the organogel environment, $\text{Eu}(\text{hfa})_3(\text{phen})$ and $\text{Tb}(\text{hfa})_3(\text{H}_2\text{O})_2$ have been shown to provide specific emissions around 615 nm and 545 nm, respectively, which correspond to orange and green emissions. In our report [9] an additive color-tuning of the Eu and Tb complexes has been performed, which shows yellow emission. We have also proven that these complexes emit independently in their excited states, which may be applicable to color manipulation processes. To achieve a color-tuning procedure which covers the global visible region, however, another type of a complex emitting in the deep red region is required.

Samarium (Sm) complexes, which are known to have the dominant emission around 645 nm, are candidates among such materials [11,12]. In addition to the emission being dominant in the intensity at 645 nm, Sm complexes have secondary transitions at 565, 600, and 705 nm, ranging in the green, orange, to deep red region [11,12]. We have found that the relative intensity among these emission bands is dramatically altered by the choice of the ligands [12]. An effective choice of the ligands that enhances the dominant emission band at 645 nm has been proposed in the earlier literatures [10-12]. For rare-earth complexes, it has been suggested that asymmetrizing the coordination structure around

the rare-earth ion may allow the $4f-4f$ transitions, which would magnify the transition being sensitive to the environment [13,14]. Under such a strategy, the 645 nm transition of Sm complexes can thus be enhanced.

In this paper we have synthesized three Sm complexes with β -diketonato, and bis(oxazolinyl)pyridine (pybox) ligands and studied their emitting properties. Figure 1 illustrates the chemical structures of the Sm complexes; Sm·hfa, Sm·bta, and Sm·tta. Regarding β -diketonato derivatives, hfa complexes with mono- or bidentate neutral ligands are known to produce a low symmetry coordination structure that allows emitting processes [10,12]. Moreover, fluorized hfa ligands may prohibit molecular vibrations that give rise to the radiationless deactivation [15]. Among the complexes we study presently, Sm·bta and Sm·tta have the asymmetric β -diketonato ligands, whereas Sm·hfa has a symmetric ligand structure. On the other hand pybox ligands can be easily modified with various substituent groups, which have potential applications for functional extensions [16,17]. Another advantage of using pybox is that this ligand is tridentate, which would make the coordination structure stable for a complex with a high coordination number, such as Sm complexes [11,18]. As a result, we discuss how the ligand asymmetry enhances the relative intensity of the dominant emission band at 645 nm, on the basis of steady-state spectroscopy, and the emission lifetime and emission quantum yield measurements.

2. Experimental

2.1. Synthesis of rare-earth complexes.

Precursors. As the precursor complexes of Sm·hfa, Sm·bta, and Sm·tta, $\text{Sm}(\text{hfa})_3(\text{H}_2\text{O})_2$, or diaquatrakis(1,1,1,5,5,5-hexafluoropentane-2,4-dionato)samarium(III), $\text{Sm}(\text{bta})_3(\text{H}_2\text{O})_2$, or diaquatrakis(4,4,4-trifluoro-1-phenyl-1,3-butane-2,4-dionato)samarium(III), and $\text{Sm}(\text{tta})_3(\text{H}_2\text{O})_2$, or diaquatrakis[4,4,4-trifluoro-1-(2-thienyl)-1,3-butane-2,4-dionato]samarium(III)], respectively, were prepared according to the procedure reported elsewhere [17].

Apparatus. ^1H NMR was obtained with a JEOL AL-400 spectrometer. Electrospray ionization mass spectrometry (ESI-MS) and FTIR measurements were carried out with a Bruker micrOTOF-Q II mass spectrometer and a Jasco FTIR-420 spectrometer, respectively. Elemental analyses were performed with a Sumigraph NCH-900.

Materials. hfa, or 1,1,1,5,5,5-hexafluoropentane-2,4-dione, bta, or 4,4,4-trifluoro-1-phenyl-1,3-butane-2,4-dione, tta, or 4,4,4-trifluoro-1-(2-thienyl)-1,3-butane-2,4-dione, europium triacetate *n*-hydrate, terbium triacetate tetrahydrate (Wako) and *R*-ipr-pybox, or 2,6-bis(4*R*-isopropyl-2-oxazolin-2-yl)pyridine (TCI) were used as received.

Preparation of Sm·hfa. $\text{Sm}(\text{hfa})_3(\text{H}_2\text{O})_2$ (0.50 g, 6.2×10^{-2} mol) and *R*-ipr-pybox (0.19 g, 6.2×10^{-2} mol) were dissolved in 25 cm³ tetrahydrofuran (THF) and refluxed overnight. The solution was evaporated and white powder was obtained. The white solid was dissolved in hot acetonitrile and the solution was left at rest. After slow evaporation of solvent, white precipitated solid was collected by filtration. The solid was washed with *n*-hexane and dried in vacuo. Yield: 12%. ESI-MS (positive): 862.021 ($[\text{M}-(\text{hfa})]^+$) *m/z*. ^1H NMR (deuterated dimethyl sulfoxide ($\text{DMSO}-d_6$), 400 MHz, 298 K) δ : 8.5–8.0 (m, Ar), 5.4 (s, br, $\text{C}=\text{OCHC}=\text{O}$), 4.7 (t), 4.5 (t), 4.2–4.1 (m), 1.0–0.9 (d, iPr), 0.9–0.8 (d, iPr) ppm. FTIR (ATR): 2972, 1651 (sh, $\text{C}=\text{O}$), 1589, 1556, 1525, 1487, 1379, 1250, 1190, 1134 (st, $\text{C}-\text{F}$), 1095 cm⁻¹. Anal. Found: C, 34.90; H, 4.15; N, 2.48%. Calcd. for $\text{C}_{32}\text{H}_{26}\text{F}_{18}\text{N}_3\text{O}_8\text{Sm} \cdot 1.1\text{H}_2\text{O}$: C, 35.17; H, 3.85; N, 2.60%.

Preparation of Sm·bta. $\text{Sm}(\text{bta})_3(\text{H}_2\text{O})_2$ (0.40 g, 4.8×10^{-2} mol) and *R*-ipr-pybox (0.15 g, 4.8×10^{-2} mol) were dissolved in 25 cm³ THF and refluxed overnight. The reaction solution was evaporated and white powder was obtained. The solid was dissolved in hot acetonitrile and the solution was left at rest. After slow evaporation of solvent, yellow crystals were collected by filtration. The solid was washed with *n*-hexane and dried in vacuo. Yield: 28%. ESI-MS (positive): 878.124 ($[\text{M}-(\text{bta})]^+$) *m/z*. ^1H NMR ($\text{DMSO}-d_6$, 400 MHz, 298 K) δ : 8.1–8.0, 7.6–7.3 (br, Ar), 4.5 (t), 4.2–4.0 (m), 1.0 (d, iPr), 0.9 (d, iPr) ppm. FTIR (ATR): 2964, 2873, 1616 ($\text{C}=\text{O}$), 1576, 1533, 1483, 1439, 1371, 1313, 1286,

1242, 1173, 1144, 1128 (st, C–F), 1076, 1026 cm^{-1} . Anal. Found: C, 51.44; H, 4.22; N, 3.97%. Calcd. for $\text{C}_{47}\text{H}_{41}\text{F}_9\text{N}_3\text{O}_8\text{Sm}\cdot 0.1\text{CH}_3\text{CN}$: C, 51.48; H, 3.94; N, 3.78%.

Preparation of Sm·tta. $\text{Sm}(\text{tta})_3(\text{H}_2\text{O})_2$ (0.50 g, 5.9×10^{-2} mol) and *R*-ipr-pybox (0.18 g, 5.9×10^{-2} mol) were dissolved in 25 cm^3 THF and refluxed overnight. The reaction solution was evaporated and white powder was obtained. The solid was dissolved in THF and the solution was left at rest. After slow evaporation of solvent, yellow precipitated solid was collected by filtration. The solid was washed with *n*-hexane and dried in vacuo. Yield: 35%. ESI-MS (positive): 890.036 ($[\text{M}(\text{tta})]^+$) m/z . ^1H NMR ($\text{DMSO-}d_6$, 400 MHz, 298 K) δ : 8.2–7.9, 7.3–7.2 (br, Ar), 4.5 (t), 4.2–4.1 (m), 1.0 (d, iPr), 0.9 (d, iPr) ppm. FTIR (ATR): 2968, 2875, 1603 (C=O), 1535, 1504, 1469, 1414, 1371, 1354, 1298, 1244, 1225, 1173, 1130 (st, C–F), 1084, 1057 cm^{-1} . Anal. Found: C, 44.30; H, 4.03; N, 3.21%. Calcd. for $\text{C}_{41}\text{H}_{35}\text{F}_9\text{N}_3\text{O}_8\text{S}_3\text{Sm}$: C, 44.15; H, 3.77; N, 3.16%.

2.2. Steady-state spectroscopy and emission lifetime measurements.

The absorption spectra, and the emission and excitation spectra were respectively measured with a Hitachi U-2800 spectrometer and a Jasco FP-6500 spectrofluorometer. The emission lifetimes in the μs domain were measured using a N_2 laser (Usho KEN-910, the excitation wavelength $\lambda_{\text{ex}} = 337$ nm) as an excitation source, and the signal from the global emitting region (550–750 nm) that was collected with a pin photodiode was analyzed with a digital oscilloscope (Techtronix TDS 1012B).

2.3. Measurements of emission quantum yields of Sm complexes with respect to the 4f–4f transition (Φ_{em}).

The Φ_{em} values were determined with a relative comparison method between the absorption and emission integration intensities, following the protocol in the earlier report [12]. Briefly, $\text{DMSO-}d_6$ solutions of the Sm complexes (1.0×10^{-2} mol dm^{-3}) were used for the measurements. The 0.10 mol dm^{-3} $\text{Sm}(\text{hfa})_3(\text{H}_2\text{O})_2$ in $\text{DMSO-}d_6$ solution was employed as the reference material, where it has been determined that $\Phi_{\text{em}} = 0.031$ [12]. To obtain Φ_{em} for the present complexes, we compared the

integration intensity of the absorption band around 480 nm corresponding to the direct absorption of the Sm ion, and that of the emission bands ranging from 550 nm to 750 nm under $\lambda_{\text{ex}} = 480$ nm.

3. Results and Discussion

Figure 2 indicates the absorption spectra of the Sm complexes in THF synthesized in this work. The absorption bands are owing to the summation of the pybox and β -diketonato moieties, where the pybox ligand has absorption in the region shorter than 300 nm [19]. The maxima located at 300–350 nm are assigned to their β -diketonato ligands. The red-shifted maxima observed for Sm·bta and Sm·tta compared to Sm·hfa can be due to the extension of π -conjugation, where the trifluoromethyl group of the hfa ligand is substituted by the phenyl and 2-thienyl groups for Sm·bta and Sm·tta, respectively [17].

The emission spectra of the complexes are shown in Figure 3. They are detected with $\lambda_{\text{ex}} = 300$, 330, and 345 nm for Sm·hfa, Sm·bta, and Sm·tta, respectively, which has been chosen to correspond to their absorption maximum. In the spectra, the obvious maxima are detected at 563, 598, 645, and 704 nm, which are assigned to the $^4G_{5/2} \rightarrow ^6H_J$ transition with $J = 5/2, 7/2, 9/2$, and $11/2$, respectively [8,11]. The spectral intensities are scaled so as to adjust the magnitude of the $^4G_{5/2} \rightarrow ^6H_{7/2}$ transition (598 nm) to unity. It is known that the magnetic dipole transition is allowed for the $^4G_{5/2} \rightarrow ^6H_{7/2}$ band, which leads to a transition being insensitive to the environment in terms of the transition intensity [12]. Figure 4 illustrates the emission spectra of $\text{Sm}(\text{hfa})_3(\text{H}_2\text{O})_2$, $\text{Sm}(\text{bta})_3(\text{H}_2\text{O})_2$, and $\text{Sm}(\text{tta})_3(\text{H}_2\text{O})_2$. Notably, these compounds correspond to Sm·hfa, Sm·bta, and Sm·tta *without* the pybox ligands. In Figure 4, the spectral intensities are rescaled so as to make the $^4G_{5/2} \rightarrow ^6H_{7/2}$ transition appearing at 599 nm to unity. This rescaling procedure is the same as we did in Figure 3. We can thus compare the relative intensities of the $^4G_{5/2} \rightarrow ^6H_{9/2}$ transitions at around 645 nm, as given in Figures 3a and 4. It is obviously seen from these Figures that the $^4G_{5/2} \rightarrow ^6H_{9/2}$ intensities are 4 – 7 in Figure 4, whereas 2.5 – 3.5 in Figure 3a. Based on this comparison, it is concluded that introduction

of the pybox ligands even decrease the intensities of the $^4G_{5/2} - ^6H_{9/2}$ transitions. This result therefore implies that the pybox ligand coordinates to Sm, and it is *not* in the free state. It is also commented that we need the pybox ligand to obtain large Φ_{em} . This is because the pybox ligand has been shown to prevent coordination of water or organic solvents to the metal, and such coordination may enhance radiationless transitions [20].

In Figure 3, the Sm·bta and Sm·tta spectra are rather similar to each other. In contrast, the Sm·hfa spectrum is very different from the others, concerned with the relative intensity of the 645 nm transition and each emission bandshape. We suggest that the asymmetric bta and tta ligands respectively introduced to Sm·bta and Sm·tta may give rise to a different sort of the Stark splitting which is caused in the case of Sm·hfa introduced with the symmetric ligand [10]. On the other hand, Figure 3a shows that allowance of the electronic transition for Sm·bta and Sm·tta is enhanced compared to Sm·hfa, on the basis of the intensity comparison at 645 nm.

With a close look at the $^4G_{5/2} - ^6H_{7/2}$ transition centered around 598 nm for the present three Sm complexes in Figure 3b, a three-fold splitting located at 598, 604, and 609 nm can be recognized for Sm·bta and Sm·tta. In contrast, the Sm·hfa emission slightly shifts toward blue, by ≈ 1 nm compared to the others. Moreover, another weak shoulder at 590 nm appears in the emission spectrum. We commented that a similar spectral blue shift for Sm·hfa compared with Sm·bta and Sm·tta is also detected for the $^4G_{5/2} - ^6H_{9/2}$ transition around 645 nm.

It is reported that an entire structure change of Sm complexes causes an obvious change of the Stark splitting and emission intensity [12]. In our present work, the structures of the three Sm complexes are different to each other, because of the β -diketonato structure employed as the ligands. We here consider the coordination structures of the Sm complexes. It is assumed that the three Sm complexes with pybox and β -diketonato synthesized presently have similar nonacoordinated structures to each other. This assumption is based on earlier publications on the single crystal X-ray analysis of Eu complexes with pybox and hfa [17,21]. It is also reported that Yb complexes with P =

O bidentate ligands which have bta or hfa moieties show similar coordination structures [22]. With these previous findings, we suggest that the Sm complexes in this work can be almost similar, even though the different ligands are introduced. The emission spectral change of the Sm complexes as shown in Figure 3a is therefore ascribed to reasons other than the coordination structure change [23,24]. A possible explanation is that the charge distribution or dipole moment change of the ligands can lead to the emission change [25,26]. In the present complexes, the electron-withdrawing trifluoromethyl group introduced to hfa has been substituted by the electron-donating phenyl and 2-thienyl groups for bta and tta, respectively. We assume that such substitutions may cause a coordination environment which enhances the electric dipole transition centered at 645 nm.

On the other hand, the relative intensity of the 645 nm transition band I_{645} can be estimated as:

$$I_{645} = \int f_{em}(\nu) d\nu \quad (1)$$

where f_{em} denotes the emission spectral function with the transition frequency ν . The integration is taken for the corresponding transition band. In the present estimation the absolute value of I_{645} is scaled with the Sm·hfa band as unity, normalized with the intensity of the 598 nm band as stated previously. The electric dipole transition is allowed for the $^4G_{5/2} \rightarrow ^6H_{9/2}$ band at 645 nm, and it is reported that I_{645} can be magnified when an asymmetric coordination structure is achieved around the Sm ion [12]. Table 1 indicates that I_{645} for Sm·bta and Sm·tta are 20% larger than Sm·hfa. As a result, the symmetry breaking of the β -diketonato ligands to Sm complexes has enhanced the intensity of the $^4G_{5/2} \rightarrow ^6H_{9/2}$ transition.

Table 1 also summarizes the emission quantum yield as regards the 4f–4f transition (Φ_{em}), lifetime (τ_{em}), and radiative (k_r) and radiationless (k_{nr}) rate constants, respectively, of the Sm complexes. Based on Φ_{em} and τ_{em} as the experimental observables, we can calculate k_r and k_{nr} as follows:

$$\begin{aligned}\tau_{\text{em}} &= \frac{1}{k_r + k_{\text{nr}}}, \\ \Phi_{\text{em}} &= \frac{k_r}{k_r + k_{\text{nr}}}\end{aligned}\tag{2}$$

where we rely on the assumption that the entire process of the excited state is solely explained by k_r and k_{nr} [12]. The quantities presented in Table 1 were detected in DMSO- d_6 solvent in order to enhance the solubility of the Sm complexes. It has been reported that the more intense emission observed in deuterated solvents gives rise to more accurate estimation of Φ_{em} and relevant values [12]. In Table 1 Sm·hfa exhibits the largest Φ_{em} , and τ_{em} twice as long as the others. k_r for Sm·bta and Sm·tta are similar or larger compared to that of Sm·hfa, however, k_{nr} for them are twice or more as large as that of Sm·hfa. This is a plausible explanation of smaller Φ_{em} for Sm·bta and Sm·tta. We can therefore draw a conclusion that the asymmetrization process, which has removed the three fluorine atoms from the β -diketonato moiety, may give rise to the increase of k_{nr} . On the other hand the asymmetric β -diketonato ligands to Sm certainly magnifies the $^4\text{G}_{5/2} \rightarrow ^6\text{H}_{9/2}$ transition at 645 nm, which is the obvious band in the deep red region.

4. Summary

In the present work we have synthesized three Sm complexes possessing β -diketonato and bis(oxazolinyl)pyridine (pybox) ligands, Sm·hfa, Sm·bta, and Sm·tta, and investigated their emitting properties. Sm·bta and Sm·tta have the asymmetric β -diketonato ligands, whereas Sm·hfa has a symmetric β -diketonato moiety. It has been shown that an asymmetric ligand structure enhances the relative intensity of the Sm emission band at 645 nm by 20% compared to the symmetric structure, which exhibits the strongest intensity in the visible region. Meanwhile Sm·hfa gives rise to the highest emission quantum yield (Φ_{em}) compared to Sm·bta and Sm·tta. In this work a CF_3 group of the hfa ligand has been substituted by an aromatic ring, so as to asymmetrize the β -diketonato moiety. We suggest that a β -diketonato substituent possessing a longer perfluoroalkyl group than we used

presently, such as $-C_nF_{2n+1}$ ($n \geq 2$) would enhance the relative spectral intensity at 645 nm, and keeping Φ_{em} sufficiently large. We have already commenced further studies in line with such a strategy.

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Table 1. Summary of the relative intensity of the 645 nm transition, the emission quantum yield, lifetime, radiative and radiationless rate constants of the Sm complexes determined in DMSO-*d*₆ solvent.

	$I_{645}^{a)}$	$\Phi_{\text{em}} / \%$	$\tau_{\text{em}} / 10^{-6} \text{ s}$	$k_r / 10^2 \text{ s}^{-1}$	$k_{\text{nr}} / 10^3 \text{ s}^{-1}$
Sm·hfa	1.00	8.3	390	2.1	2.4
Sm·bta	1.21	3.8	170	2.2	5.7
Sm·tta	1.19	5.1	160	3.2	5.9

^{a)}Normalized with Sm·hfa as unity.

Figure captions

Figure 1. The chemical structures of Sm·hfa, Sm·bta, and Sm·tta.

Figure 2. The absorption spectra of Sm·hfa (drawn in the solid line), Sm·bta (dotted), and Sm·tta (dashed) detected in THF, detected with $c = 1.0 \times 10^{-5} \text{ mol dm}^{-3}$.

Figure 3. (a) The emission spectra of Sm·hfa (drawn in the solid line), Sm·bta (dotted), and Sm·tta (dashed) detected in THF, detected with $c = 1.0 \times 10^{-4} \text{ mol dm}^{-3}$ and $\lambda_{\text{ex}} = 300, 330, \text{ and } 345 \text{ nm}$ for Sm·hfa, Sm·bta, and Sm·tta, respectively. A longpass filter (L39) being applicable for the visible region was used for detection. (b) The enlarged view of Panel (a) on the emission bands at around 598 nm.

Figure 4. The emission spectra of Sm(hfa)₃(H₂O)₂ (drawn in the solid line), Sm(bta)₃(H₂O)₂ (dotted), and Sm(tta)₃(H₂O)₂ (dashed) detected in THF with $c = 1.0 \times 10^{-4} \text{ mol dm}^{-3}$ and $\lambda_{\text{ex}} = 300, 330, \text{ and } 345 \text{ nm}$ for Sm(hfa)₃(H₂O)₂, Sm(bta)₃(H₂O)₂, and Sm(tta)₃(H₂O)₂, respectively. A longpass filter being applicable for the visible wavelength (L39) was used for detection.

Figure

Figure 1

Figure 2

Figure 3

Figure 4

Graphical abstract