Photoresponsive Europium(III) Complex Based on Photochromic Reaction

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Luminescence properties and their photoinduced control of the electric dipole transitions of a Eu(III) complex that has photochromic triangle terarylenes ligands, tris(hexafluoroacetylacetonato)bis[4,5- bis(5-methyl-2-phenylthiazol-4-yl)-2-phenylthiazole]europium(III) ($Eu(hfa)_3(THIA)_2$), were studied. Fairly high photochromic reactivity of the ligand between the open-ring and closed-ring forms were found to be maintained even in the complex, and reversible color change could be observed many times. The photocyclization and the cycloreversion quantum yields of the $Eu(hfa)_3(THIA)_2$ were found to be 37% and 3.4%, respectively. The thermal stability of the closed-ring form of THIA ligand is significantly improved in the Eu(III) complex. The $^5D_0$-$^7F_2$ transition intensity of the Eu(III) complex with open-ring form ligands ($Eu(hfa)_3(THIA)_2-O$) is larger than that of the Eu(III) complex with closed-ring form ligands ($Eu(hfa)_3(THIA)_2-C$). The radiative rate constants of $Eu(hfa)_3(THIA)_2-O$ and $Eu(hfa)_3(THIA)_2-C$ are estimated to be 1.7×10^2 and 1.5×10^2 s^{-1}, respectively. The reversible control of the emission properties of the Eu(III) complex by the photochromic reactions is demonstrated for the first time.

Introduction

Recently, photoresponsive molecules and polymers have been extensively studied for their light irradiation abilities that modulate certain physical and chemical properties of molecular electronic and photonic devices for future use.[1] Considerable interest has been focused on photochromic molecules,[2] such as azobenzene,[3] spiropyrane[4] and diarylethene,[5] which undergo reversible photoisomerization reactions between two isomers upon irradiation of appropriate wavelengths. In particular, photochromic diarylrthenes, which undergo a photocyclization reaction from the hexatriene-type structure to the cyclohexadiene-type structure and backward cycloreversion reaction upon light irradiation, have potential for use as molecular photomemory and photoactive switching materials because they show high thermal stability in both colored and bleached states, excellent fatigue resistance and relatively high photochromic reactivity even in a solid state.[6] The photoswitching phenomena of diarylethenes and related molecules have been extensively studied to control various chemical and physical properties such as fluorescence intensity and wavelength,[7] refractive index,[8] electronic conductions,[9] electrochemical response,[10] magnetic interactions[11] and self-assembling behavior[12] of molecules and polymers. Among these, photoswitching and photomodulation manipulation of various properties of molecular and polymer materials, photoresponsive modulation of fluorescence emission has been most extensively studied because of the potential capability of application for 3D-high density memory[13] and single molecular memory,[14] and even photoresponsive laser emission materials.[15] In the early stage, study on the fluorescence switching phenomenon of diarylethene looked at the simple diarylethene molecule itself and its doping effects on the emission properties of conjugated polymers.[7a] Lehn et.al. were the first to proposed nondestructive readout memory on the basis of fluorescence modulation with a diarylethene derivative.[7b] A number of fluorescent molecules that have diarylethene units and organic and inorganic fluorescence units have also been proposed until now.

The photoswitching phenomena of diarylethenes have been mainly controlled by the functional groups of the organic framework. To improve the photochromic properties and their photoswitching functionality, photochromic metal complexes that have diarylethene units as the photoresponsive ligand are desirable for advanced photonic applications.[16] Characteristic photoswitching properties by using a photochromic metal complex have been reported, and various applications for future molecular switching devices are expected.[17]

We focus here on photoswitching modulation of the emission properties of lanthanide(III) ion, which is the most popular luminescent element for practical applications, such as luminescent display, laser, and optical devices, on the basis of their characteristic 4f−4f transition processes.[18] As practical emission materials, the lanthanide(III) complex has unique characteristics, such as narrow emission band, which enable them to show clear emission of color with high color purity, and wide variation of emission color from the visible to near-IR range depending on the central metal ion. Because the emission of the lanthanide(III) ions mainly comes from the electric dipole (ED) transitions in 4f orbitals, the wavelength of the emission lines of their complexes is insensitive to the nature of the ligand and coordination structure. The charge-transfer interaction between the lanthanide(III) ion and organic ligands is not major, which mainly control the MLCT emission in the case of d-group metal complexes such as Ru and Os.[16l] No marked change in the emission properties of the lanthanide(III) complex with the photochromic ligands would be indicated by the change in the MLCT interaction. However, the emission intensity of the lanthanide(III) complexes has been significantly sensitive to the fine structure of the coordination chemistry.[19] The ED transition of the 4f orbitals is intrinsically La Porté-forbidden and is markedly sensitive to the asymmetric structure of the coordination field. It is thus expected to achieve photochromic control

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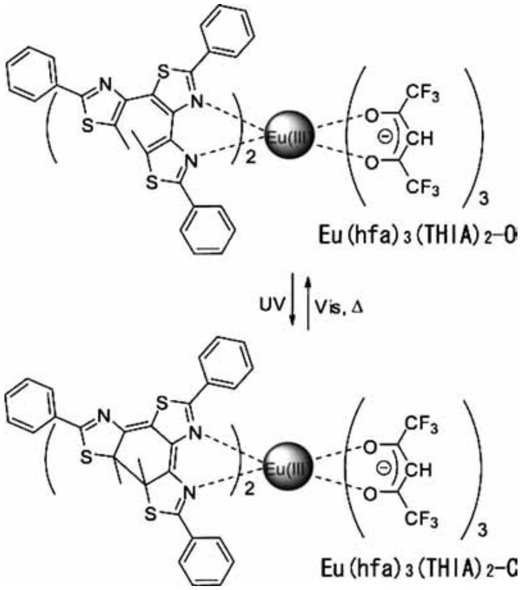
SCHEME 1: Photochemical and Thermal Reactions of $Eu(hfa)_3(THIA)_2-O$ and $Eu(hfa)_3(THIA)_2-C$



of the emission property of the lanthanide(III) complex if the photochromic unit is introduced as the ligand and if the symmetry of the ligand field, so-called “odd parity”,[20] is modulated by the photochromic reactions of the ligands. In such a case, change in the optical absorption band related to the photochromic reaction might also result in a phototunable, resonance-energy-transfer quenching[21] and modulation of emission intensity in response to the photochromic reactions of the ligands. In an our preliminary letter, reversible photomodulation in the luminescent intensity of a Eu(III) complex with photochromic terarylene units, tris(hexafluoroacetylacetonato)bis[4,5-bis(5-methyl-2-phenylthiazol-4-yl)-2-phenylthiazole]europium(III) $[Eu(hfa)_3-(THIA)_2]$, has been demonstrated (Scheme 1).[22] We also have reported that a photochromic terarylene with three thiazole groups shows excellent photochromic properties[23] and it gives significant photomodulation in the visible absorption band. In addition, the photochromic reaction also changes their geometry and odd parity of the ligand field. That is, the reversible photomodulation in the emission properties of $Eu(hfa)_3(THIA)_2$ would be attributed not only to the photoresponsive change in the resonance energy transfer from the Eu(III) ion to the photochromic unit, which decrease emission efficiency in the colored state, but also to the change in the symmetry of the coordination structure around the Eu(III) center which affects on the emission rate constant. The ED transition of the Eu(III) complex at 614 nm is known to be affected by the geometrical structure related to the odd parity[24] of the electric ligand field, whereas the magnetic dipole (MD) transition of the 4f orbitals of the Eu(III) ion at 592 nm is insensitive. Therefore, fine comparison of the emission profile of the open-ring colorless form of the Eu(III) complex, $[Eu(hfa)_3(THIA)_2-O]$, with that of the closed-ring colored form of the Eu(III) complex, $[Eu(hfa)_3(THIA)_2-C]$, is directly linked to evaluation of the photochemical characterization of the photochromic lanthanide(III) complex. For the detailed study of the photomodulation effects in the $[Eu(hfa)_3(THIA)_2]$, it is desired to obtain conversion samples in the colored and bleached states, and to avoid the effects of the photochromic reactions during the emission property measurements.

In the present paper, we report on the photochromic properties of $[Eu(hfa)_3(THIA)_2]$ and the emission properties of open- and closed-ring forms of the Eu(III) complex. The photochromic quantum yields and thermal stabilities of the Eu(III) complex are estimated on the basis of spectral change of the absorption bands related to the photochromic ligand. The ED emission intensity of $Eu(hfa)_3(THIA)_2$ is normalized with respect to the MD transition ($^5D_0-^7F_1$: 592 nm) intensity for estimating the probability of ED transition. The emission quantum yields, the emission lifetimes, and radiative rate constants of open- and closed-ring forms of the Eu(III) complex are studied at 80 K, to prevent photochromic bleaching reaction. Furthermore, molecular structures and charge distributions of the photochromic units are estimated by X-ray single crystal analysis and density functional theory (DFT) calculations. On the basis of the experimental study, photoinduced control of the ED transition of the photochromic lanthanide(III) complex will be discussed.

Experimental Section

Apparatus. ^1H NMR spectra were recorded on a JEOL AL-300 spectrometer (300 MHz). ^1H NMR chemical shifts were determined using tetramethylsilane (TMS) as an internal standard. IR spectra were recorded on a JASCO FT/IR-420 spectrometer. Mass spectra (ESI-Mass) were measured with mass spectrometers (JEOL JMS-700 MStation).

Synthesis of Tris(Hexafluoroacetylacetonato)europium(III) Dehydrates $Eu(hfa)_3(H_2O)_2$. $Eu(HFA)_2(H_2O)_2$ was obtained by the same method as previously reported.[24] Europium acetate monohydrate (5.0 g, 12.5 mmol) was dissolved in 20 mL of distilled water by stirring at 0 °C. A solution of 1,1,1,5,5,5-hexafluoro-2,4-pentanedione (7 g, 33.6 mmol) in methanol (5 mL) was added dropwise to the solution. The mixture produced a precipitation of white yellow powder after stirring for 3 h. The reaction mixture was filtered and the resulting white yellow needle crystals were recrystallized from methanol/water. Yield: 95%. IR (KBr): 1650 (st), 1258−1145 (st) cm^{-1}. ^{19}F NMR (CD_3COCD_3): $\delta = -72.80$ (s, CF_3) ppm. Anal. Calcd for $C_{15}H_7O_8F_{18}Eu$: C, 22.48; H, 0.88. Found: C, 22.12; H, 1.01.

Synthesis of 4,5-Bis(5-methyl-2-phenylthiazol-4-yl)-2-phenylthiazole (THIA). THIA was synthesized as reported previously.[23] To a solution of 4,5-dibromothiazole (730 mg, 2.3 mmol) in 1,4-dioxane (60 mL) and K_3PO_4 aq (2M, 9 mL) were added under a N_2 atmosphere 5-methyl-2-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)thiazole (1.71 g, 5.7 mmol), $Pd(Pph_3)_4$ (158 mg, 0.14 mmol) and triphenylphosphine (60 mg, 0.228 mmol). The solution was stirred at 90 °C for 3 days, and then distilled water was added. The reaction mixture was neutralized with HCl aq and extracted with ethyl acetate. The organic layer was dried over $MgSO_4$, filtered and evaporated. Residue was purified by column chromatography (alumina, ethyl acetate/hexane, 1:10) to afford 4,5-bis(5-methyl-2-phenylthiazol-4-yl)-2-phenylthiazole (780 mg, yield: 67%). ^1H NMR (300 MHz, $CDCl_3$): $\delta = 2.11$ (s, 3H), 2.52 (s, 3H), 7.33 (m, 3H), 7.43 (m, 6H), 7.80 (m, 2H), 7.93 (m, 2H), 8.07 (m, 2H) ppm. ESI-Mass (*m*/*z*) = 508.1 ($M^+ + H$).

Synthesis of Tris(hexafluoroacetylacetonato)bis[4,5-bis(5-methyl-2-phenylthiazol-4-yl)-2-phenylthiazole]europium(III), $Eu(hfa)_3(THIA)_2$. $Eu(hfa)_3(H_2O)_2$ (607 mg, 0.75 mmol) and 4,5-bis(5-methyl-2- phenylthiazol-4-yl)-2-phenylthiazole, (380 mg, 0.75 mmol) were dissolved in methanol (15 mL)/chloroform (38 mL). The solution was refluxed and stirred for 36 h. The solution was evaporated. Residue was washed with chloroform and hot hexane several times to afford tris(hexafluoroacetylacetonato)bis[4,5-bis(5-methyl-2-phenylthiazol-4-yl)-2-phenylthiazole]europium(III) (380 mg, yield: 28%). Found: C, 48.32; H, 2.70; N, 4.76. Anal. Calcd for $C_{73}H_{45}N_6O_6S_6F_{18}Eu \cdot H_2O$: C, 48.54; H, 2.62; N, 4.65. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.11$ (s, 3H), 2.53 (s, 3H), 7.42 (m, 9H), 7.80−8.10 (m, 6H) ppm. ESI-Mass (m/z) = 1581.07 (M^+). IR (ATR) = 3330 (w), 3060 (m), 2923 (m), 1652 (s), 1554 (m), 1529 (m), 1467 (s), 1251 (s), 1203 (s), 1141 (s) cm^{-1}.

Optical Measurements. Absorption spectra of Eu(hfa)$_3$(THIA)$_2$ in toluene (8.0×10^{-6} M) were measured with either a JASCO V-550 or V-660 spectrophotometer with a temperature control unit (JASCO, ETC-505T). Emission spectra of Eu(hfa)$_3$(THIA)$_2$ in toluene (1.3×10^{-4} M) at room temperature were measured with a JASCO FP-6500 spectrophotometer. Emission spectra of Eu(hfa)$_3$(THIA)$_2$ (ethanol:methanol = 4:1; 1.0×10^{-4} M) at 80 K were measured with a spectrograph system (ACTON spectrapro 2300i) equipped with a cryostat (Oxford, optistat). Emission lifetimes of Eu(hfa)$_3$(THIA)$_2$ (ethanol:methanol = 4:1; 1.2×10^{-4} M) at 80 K were measured with a nanosecond pulse N_2 laser (USHO, KEC-160, $\lambda = 337$ nm, pulse width ≤ 0.5 ns) and a streak scope (Hamamatsu, C4780). The emission quantum yield of Eu(hfa)$_3$(THIA)$_2$ in 1,4-dioxane (1.3×10^{-3} M) at room temperature was determined by the standard procedures with an integral sphere (diameter 60 mm) mounted on a spectrofluorometer (ACTON spectrapro 2300i). The emission quantum yield, Φ, was calculated by

$$\Phi = \frac{N_{\text{emission}}}{N_{\text{absorption}}} = \frac{\int \frac{\lambda}{hc} I_{\text{em}}(\lambda)\, d\lambda}{\int \frac{\lambda}{hc}\{I_{\text{ex}}(\lambda_{\text{ref}}) - I_{\text{ex}}(\lambda_{\text{sam}})\}\, d\lambda} \tag{1}$$

where $I_{\text{ex}}(\lambda_{\text{ref}})$ and $I_{\text{ex}}(\lambda_{\text{sam}})$ denote the light intensity of 1,4-dioxane without and with 1.3×10^{-3} M of the Eu(III) complex. The corrected intensity functions of the light absorption (from eq 1) were determined by the excitation spectra in the wavelength range between 460 and 470 nm, whereas the corrected intensity function of the emission, $I_{\text{em}}(\lambda)$, was determined by the emission spectra ($580 \leq \lambda \leq 720$ nm). The quantum yield of Rodamine 6G evaluated by this procedure agreed well with the reported value (0.94 ± 0.05 in ethanol).[25] The emission quantum yields of Eu(hfa)$_3$(THIA)$_2$−O and Eu(hfa)$_3$(THIA)$_2$−C at 80 K were evaluated by utilizing Eu(hfa)$_3$(THIA)$_2$ as the standard of $\Phi_{\text{emi}} = 0.036$ at room temperature.[22]

Crystallography. A blue colored single crystal of the closed-ring form of THIA obtained from chloroform solution was mounted on a glass fiber using epoxy resin glue. X-ray diffraction profile was collected and analyzed with an X-ray diffractometer (Rigaku R-AXIS RAPID/s) with the Mo Kα radiation. Of the 22950 reflections that were collected, 5568 were unique ($R_{\text{int}} = 0.042$); equivalent reflections were merged. The linear absorption coefficient, μ, for Mo Kα radiation is 3.263 cm^{-1}. An empirical absorption correction was applied, which resulted in transmission factors ranging from 0.597 to 0.943. The data were corrected for Lorentz and polarization effects. The structure was evaluated by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. All calculations were performed using the Crystal Structure crystallographic software package.

Computational Details. DFT geometry optimizations, TD-DFT excitation energy calculation and electrostatic potential calculation of THIA were carried out with the Gaussian 03 package[26] employing the three-parameter hybrid functional of Becke based on the correlation functional of Lee, Yang, and Parr (B3LYP).[27] The 6-31G(d) basis sets were used for all atoms.

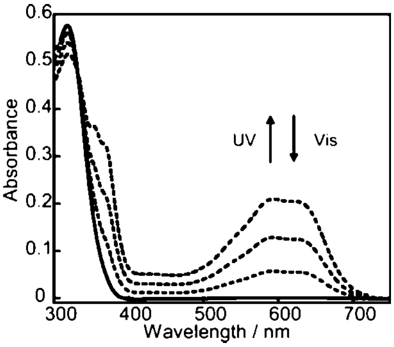


Figure 1. Absorption spectral change of Eu(hfa)$_3$(THIA)$_2$−O in toluene by photoirradiation. The concentration of Eu(hfa)$_3$(THIA)$_2$−O were 8.0×10^{-6} M.

TABLE 1: Absorption Maxima and Coefficients of the Open- and Closed-Ring Form of Eu(hfa)$_3$(THIA)$_2$ Together with the Quantum Yields in Toluene

	$\lambda_{\max}$/nm	$10^{-4}\epsilon$/M^{-1} cm^{-1}	$\phi_{\text{o-c}}$/%	$\phi_{\text{c-o}}$/%
Eu(hfa)$_3$(THIA)$_2$−O	316	7.3	37	
Eu(hfa)$_3$(THIA)$_2$−C	594	3.2[a]		3.4

[a] Assumed to be twice of that of the free THIA−C ligand.

Results and Discussion

Photochromic Reactions of the Eu(III) Complex with Terarylene Ligand. Colorless solutions of the Eu(hfa)$_3$(THIA)$_2$−O were observed to turn blue upon irradiation with UV light ($\lambda = 365$ nm). The colored solution was bleached by visible light irradiation ($\lambda > 440$ nm). The absorption spectral change of Eu(hfa)$_3$(THIA)$_2$ are shown in Figure 1. An isosbestic point appeared at 330 nm supported the reversible quasi two components photochromic reactions as illustrated in Scheme 1. As shown in Figure 1, Eu(hfa)$_3$(THIA)$_2$−O shows no absorption band in the visible range and a new absorption band appeared at 594 nm upon irradiarion with UV light. The coloration and bleaching cycles were repeated for more than 20 cycles using alternating irradiation, with UV and visible light, without marked degradation. The conversion ratio from Eu(hfa)$_3$(THIA)$_2$−O to Eu(hfa)$_3$(THIA)$_2$−C at the photostationaly state, which was achieved by irradiation with UV light ($\lambda = 365$ nm), was evaluated, by assuming no difference between the absorption coeffients of the free and bound ligands, to be about 80%. This assuption is fairly reasonable in the case of the lanthanide(III) complex and can be confirmed with the fact that the absorption coeffient of the Eu(hfa)$_3$(THIA)$_2$−O in the wavelength range between 300 and 400 nm is well reproduced by the sum of three hfa ligands and two THIA−Os with a deviation less than 5% in all wavelengths. The conversion ratio estimated on the basis of the absorption spectrum was also confirmed by analysis with HPLC (silica-gel/methanol), after decomposition of the colored complex with HNO_3 solution under the dark condition. The conversion ratio larger than 50% indicates that the two adjacent photochromic ligands in a complex should turn to the closed-ring form.[9c] The photochromic quantim yields of the bound THIA ligand were evaluated by the standard procedure with THIA as a reference.[23] The valus of $\lambda_{\max}$, ϵ and photochromic quantum yields of Eu(hfa)$_3$(THIA)$_2$−O and Eu(hfa)$_3$(THIA)$_2$−C are summalized in Table 1. The photochemical quantum yields of the ring cyclization

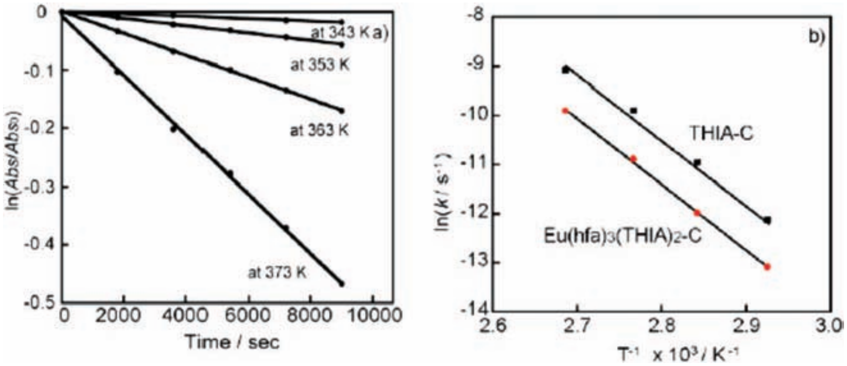


Figure 2. (a) Decay of peak absorbance upon thermal cycloreversion reactions of Eu(hfa)$_3$(THIA)$_2$−C at various temperatures. (b) Temperature dependence of the thermal fading rate constants of free ligand (THIA−C: black square) and Eu(III) complex (Eu(hfa)$_3$(THIA)$_2$−C: red square).

TABLE 2: Arrhenius Parameters of Thermal Cycloreversion and Half-Lifetimes from the Closed-Ring Form to the Open-Ring Form

compound	E_a/kJ mol^{-1}	A/s^{-1}	$\tau_{1/2}$ (20 °C)/year
THIA−C	112	7.1×10^{11}	3.3
Eu(hfa)$_3$(THIA)$_2$−C	112	3.1×10^{11}	9.7

and of cycloreversion reaction were evaluated to be 37% and 3.4%, respectively. The ring-cyclization quantum yeild of the bound THIA ligand was similar to that of the free THIA ligand, 0.4 (ca. 40%).[23]

The thermal cycloreversion kinetics of Eu(hfa)$_3$(THIA)$_2$−C were also studied at various temperatures in toluene. The absorption spectra of the colored state were measured at elevated temperature, and the fading of visible absorption band was studied over several hours. Normalized absorbance change, Abs/Abs$_0$, was plotted as the function of time in logarithmic scale in Figure 2a, which shows the first order decay lines of the absorbance of the closed-ring form of Eu(hfa)$_3$(THIA)$_2$−C at several temperatures.

The first-order rate constants of the thermal cycloreversion reaction at various temperatures were evaluated from Figure 2a and their temperature dependence is shown in Figure 2b. The cycloreversion kinetics can be expressed with the Arrhenius's equation as usual photochromic diarylethenes[5b] and terarylenes[23] and the calculated activation energy (E_a) and frequency factor (A) with those of the bound and the free THIA ligand (THIA−C) are summarized in Table 2. The E_a of the bound THIA−C was the same as that of free THIA−C. Because the activation energy in the cycloreversion process of diarylethenes[5b] and terarylenes[23] is known to be dominantly determined by the difference of aromaticity in the closed- and the open-ring forms, there seems to be no marked effect of the Eu(III) ion on the electronic structure, aromaticity of the ligand and E_a value. The agreements in both ϵ and quantum yields of the free and bound THIA may also support the minor or neglectable effect of the Eu(III) ion on the properties of the ligand and its photochromic reactivity. It should, however, be noted that contribution of the triplet excited state in the ring-cyclization reaction of the diarylethenes in some metal complex has recently been suggested.[16i,k,o] The rough agreements in the ring-cyclization quantum yield in the present study might be thus a result of complicated effects of the triplet excited state and of interaction between THIA ligands in the excited state. On the other hand, A of Eu(hfa)$_3$(THIA)$_2$−C was considerably smaller than that of THIA−C. Extrapolation of the temperature dependence indicates that the half-lifetimes of the Eu(hfa)$_3$(THIA)$_2$−C and THIA−C at 20 °C are 9.7 and 3.3 year, respectively. We also observed the difference in the vibronic progression in the visible absorption band of Eu(hfa)$_3$(THIA)$_2$−C from that of the free THIA−C (see Supporting Information). These results indicate that the THIA−C ligand is kinetically stabilized by the coordination of Eu(III) ion.

Evaluation of the Electric Dipole Transition Probability of the Photochromic Eu(III) complex. The emission spectra of Eu(hfa)$_3$(THIA)$_2$−O and colored form irradiated by UV light ($\lambda = 365$ nm, colored form) were measured under the excitation at 465 nm ($^7F_0$−$^5D_2$: excited at Eu(III) ion) at room temperature. The emission bands were observed at 579, 592, 614, 651, and 698 nm and are attributed to the f−f transitions $^5D_0$−$^7F_0$ (zero-zero band: forbidden transition), $^5D_0$−$^7F_1$ (magnetic dipole transition: MD), $^5D_0$−$^7F_2$ (electric dipole transitions: ED), $^5D_0$−$^7F_3$ (forbidden transition), $^5D_0$−$^7F_4$, (electric dipole transitions: ED), respectively. The intensity of the $^5D_0$−$^7F_1$ (MD) transition is known to be independent of the surrounding environment of the Eu(III) ion.[28] On the other hand, the $^5D_0$−$^7F_2$ (ED) transition is extremely sensitive to the odd parity of the crystal field.[24] The ED transition probability of a Eu(III) complex is, therefore, estimated with the relative intensity ratio of the $^5D_0$−$^7F_2$ (ED) transition against the $^5D_0$−$^7F_1$ (MD) transition in the emission spectrum. The measured emission spectra were, thus, normalized with respect to the $^5D_0$−$^7F_1$ (MD) transition, as shown in Figure 3a. The normalized emission intensity at $^5D_0$−$^7F_2$ transition intensity of the colored form was significantly smaller than that of Eu(hfa)$_3$(THIA)$_2$−O. The decrease of the normalized emission intensity of the ED band in the colored form is explained by the decrease of the ED transition probability of the $^5D_0$−$^7F_2$. The odd parity of Eu(hfa)$_3$(THIA)$_2$−C seems, thus, to be less than that of Eu(hfa)$_3$(THIA)$_2$−O. The reversible changes of relative emission intensity at 614 nm are also observed by the alternative irradiation cycles of UV ($\lambda = 365$ nm) and visible light ($\lambda > 440$ nm) (Figure 3a (inset)). As has been reported in our previous letter, the total emission intensity of the Eu(hfa)$_3$(THIA)$_2$ was also modulated, which should be attributed to change in the emission quantum yield.

To analyze the emission quantum yield and the absolute ED transition probability of the Eu(hfa)$_3$(THIA)$_2$−C, the fully colored state was prepared by UV (365 nm) light irradiation at 80 K, at which temperature the photocycloreversion reaction does not take place upon irradiation of visible light. It is known that the photochemical cycloreversion efficiency of diarylethenes shows thermal activation behavior and decreases markedly at low temperature. To achieve the high conversion ratio in the present study, the sample solution was irradiated at 80 K for about 10 min and then the sample temperature was elevated under dark conditions to about 250 K and the partly colored

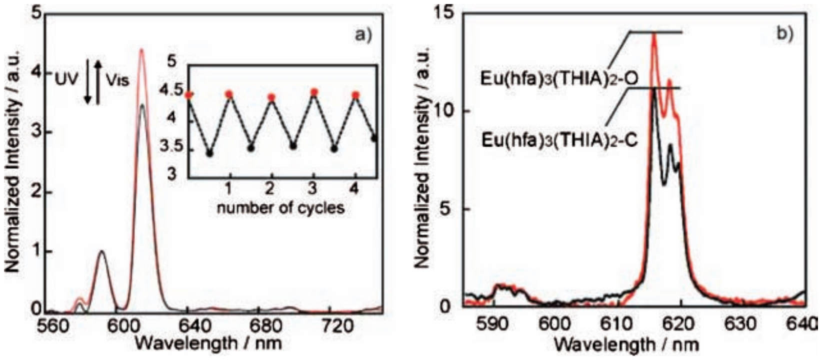


Figure 3. Normalized emission spectra of Eu(hfa)$_3$(THIA)$_2$−O (red line) and colored photostationary state (black line) under 365 nm. (a) In toluene solution at room temperature (excitation at 465 nm). (Inset: reversible change of relative emission intensity at 614 nm with the alternative irradiation cycles of UV and visible light.) (b) In EtOH/MeOH glass matrics at 80 K: Eu(hfa)$_3$(THIA)$_2$−O (red line) and Eu(hfa)$_3$(THIA)$_2$−C (black line). Emission spectra were normalized at 592 nm ($^5D_0$−$^7F_1$).

TABLE 3: Emission Quantum Yield, Emission Lifetime, and Radiative Rate Constant of Eu(III) Complex[a]

compound	T/K	$\Phi_{\text{emi-total}}$	$\Phi_{\text{emi-}^7F_2}$/%	τ/ms	$k_r{}^7F_2$/× 10^2 s^{-1}
Eu(hfa)$_3$(THIA)$_2$−O[b]	r.t.	3.6[d]	2.8[e]	0.40	
Eu(hfa)$_3$(THIA)$_2$−O[c]	80		10[f]	0.60	1.7
Eu(hfa)$_3$(THIA)$_2$−C[c]	80		7.6[f]	0.50	1.5

[a] The emission quantum yield of Eu(III) complexes were measured by excitation at 465 nm ($^7F_0$−$^5D_2$). The emission lifetimes of Eu(III) complexes were measured by excitation at 337 nm. Radiative rate constant = emission quantum yield/emission lifetime. [b] In 1,4-dioxane at room temperature. [c] In EtOH/MeOH glass matrix at 80 K. [d] Estimated from emission peak area between 580−720 nm. [e] Estimated from emission peak area between 600−630 nm. [f] estimated from data at r.t. and relative intensity of 615 nm at 80 K.

TABLE 4: N−N Length, N−N Dihedral Angles and Mulliken Charges of THIA Ligand

	$R_{\text{N1−N2}}$/Å	$\theta_{\text{N1−C1−C2−N2}}$/deg	charge density
THIA−O	3.00	−55.6	N1(−0.47), N2(−0.47)
THIA−C	2.98 [3.00][a]	2.93 [2.30][a]	N1(−0.51), N2(−0.48)

[a] Experimental data based on the X-ray crystallography.

liquid solution was stirred gently. The sample was then cooled again to 80 K and was irradiated with UV light. This low temperature irradiation and stirring at liquid phase cycle was repeated more than 7 times to achieve a photostationary state at 80 K. The conversion ratio from the open-ring form to the closed-ring form was evaluated by absorption spectrum to be more than 98%. In this estimation, the same absorption coefficients of the free and the bound ligands in the open- and closed-ring forms were assumed.

Emission spectra of Eu(hfa)$_3$(THIA)$_2$−O and Eu(hfa)$_3$(THIA)$_2$−C were measured at 80 K. The crystal fields splitting of the emission bands were clearly observed at 592 and 615 nm. Three-hold splitting observed in the emission band of $^5D_0$–$^7F_2$ transition at 615 nm is attributed to the crystal fields splitting of the $^7F_2$ level. Such a fine structure of the emission lines with the crystal filed splitting is known to be sensitive against the coordination number of the Eu(III) ion.[29] The emission wavelength of these lines and their relative intensity of Eu(hfa)$_3$(THIA)$_2$−C were found to be similar to those of Eu(hfa)$_3$(THIA)$_2$−O, indicating retention of coordination number upon the photochromic reactions. However, the relative ED transition intensity of Eu(hfa)$_3$(THIA)$_2$−C against the MD transition band at 592 nm was considerably smaller than that of Eu(hfa)$_3$(THIA)$_2$−O.

The emission quantum yield (Φ_{emi}) and the emission lifetime (τ) of Eu(III) complexes at 80 K are summarized in Table 3. The emission profile measured using an integration sphere at room temperature was integrated, and the emission intensity was divided by the integrated absorption band at about 465 nm after correction of the wavelength dependence of the detection efficiency. The total emission efficiency $\Phi_{\text{emi-total}}$ and the $^5D_0$−$^7F_2$ emission efficiency $\Phi_{\text{emi-}^7F_2}$ were evaluated by integrating the emission profile in the ranges 580−720 and 600−630 nm, respectively. The obtained emission quantum yields of Eu(hfa)$_3$(THIA)$_2$−O at room temperature are also summarized in Table 3. The emission quantum yield of the $^5D_0$−$^7F_2$ transition at 80 K was roughly estimated on the basis of the relative emission peak intensity at 615 nm against that at room temperature and was significantly larger than that at room temperature. The larger emission quantum yield of

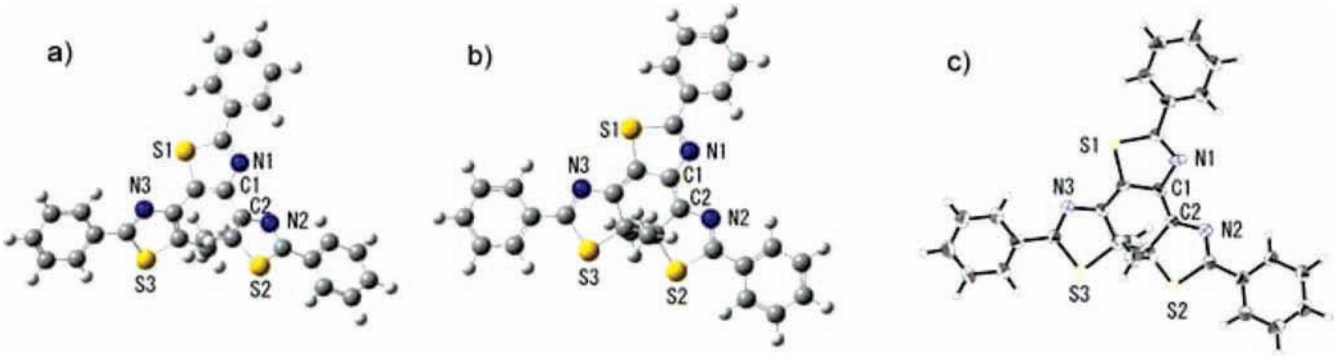


Figure 4. Optimized molecular structures of the open-ring isomer (THIA−O: a) and closed-ring isomer (THIA−C: b) based on DFT calculation in 6-31G(d) level. Key: C, gray; H,white; S, yellow; N, blue. (c) ORTEP diagram of THIA−C.

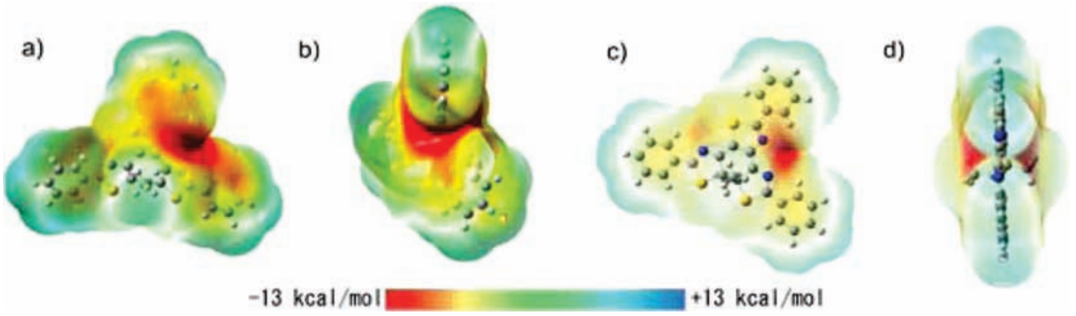


Figure 5. Electrostatic potential surface of THIA−O [a, front view; b, side view] and THIA−C [c, front view; d, side view].

Eu(hfa)$_3$(THIA)$_2$−O at low temperature might be due to the prevention of the nonradiative transition via vibrational coupling process. The emission lifetime of Eu(hfa)$_3$(THIA)$_2$−C was determined from single exponential decay of emission intensity under pulsed excitation and was considerably smaller than that of Eu(hfa)$_3$(THIA)$_2$−O. The radiative rate constants of the $^5D_0-^7F_2$ transition of Eu(hfa)$_3$(THIA)$_2$−C and Eu(hfa)$_3$(THIA)$_2$−O were estimated to be 1.5×10^2 and 1.7×10^2 s^{-1}, respectively. The decrease of about 10% is worth noticing from the viewpoint of emission properties of Eu(III) complexes with different ligands.[24]

The geometrical structure of the coordination field in Eu(hfa)$_3$(THIA)$_2$−C seems to be similar to that in the corresponding Eu(hfa)$_3$(THIA)$_2$−O because they both have the same crystal field splittings. We observed not only the decrease of the ED transition intensity but also a significant decrease of the radiative rate constant in Eu(hfa)$_3$(THIA)$_2$−C.

DFT Calculation of the THIA. The ED transition probabilities of a lanthanide(III) complex have been reported by Mason and Richardson to be dominated by (1) statically and (2) dynamically coupled ligand−lanthanide electrostatic interaction.[30] In the static coupling model, the ligand environment is represented in terms of a crystal field which is controlled by a static point charge of the coordinating atoms. In the dynamic coupling models, the ligand environment is represented in terms of anisotropic polarizability of the coordination field, which might be affected by charge distribution, existence and position of heavy atoms, and π conjugation expansion in the ligands.

To discuss the origin of the photochromic modulation of the emission properties in the present Eu(III) complex, the geometrical structure and the electrostatic potential surface of the THIA ligand were calculated by the quantum chemical calculation based on the density functional theory (DFT) method in 6-31G(d) level. The optimized structures of the open- and closed-ring form of the THIA ligands are shown in Figure 4. The molecular structure of the THIA−C ligand calculated by the DFT method agreed well with that determined by X-ray single crystal analysis of THIA−C ligand (Figure 4c).[31] The length between N atoms, the torsion angle of N1−C1−C2−N2, and the charge density on the coordinating N atoms are summarized in Table 4. The estimated values of N1−N2 length (2.98 Å) and N−Mulliken charge density in THIA−C were similar to those of THIA−O. The N1−N2 lengths of THIA−O were supported by the X-ray single crystal analysis (3.00 Å). These data suggest that the nature of the static point charge of coordinating N atoms in THIA−O is almost the same as that in THIA−C. It should be noted that the significant change in the coplanarity of the ligand is expected to occur upon the photochromic reactions and the torsion angle of N1−C1−C2−N2 should decrease from −55.6° to +2.93° after the photochromic cyclization. Such a geometrical change might not affect the nature of the coordinating N atoms as the points of charge but may affect the nature of polarizability of the ligand. The charge distributions of THIA−O and THIA−C (the electrostatic potential surface) were also evaluated by the DFT calculation, as shown in Figure 5. The negative charges are clearly localized around the N atoms in both forms, and the charge distribution of THIA−O (Figure 5a,b), seems to be less symmetrical in comparison with that of THIA−C (Figure 5c,d), which has coplanar geometry. This change would be responsible for the larger radiative rate constant of [Eu(hfa)$_3$(THIA)$_2$−O]. The polarizability anisotropy of THIA−C might be smaller than that of THIA−O, which could be the origin because the polarizability anisotropy of the ligand affects the ED transition probability.[32] As a related matter, Richardson et al. have reported that the anisotropic polarizability influences the ED transition probability in trivalent Eu(ODA)$_3^-$ and Eu(DBM)$_3$H$_2$O complexes.[33] The calculated values of polarizability for THIA−O and THIA−C at 465 nm were 512 and 759 Bohr^3, respectively, and THIA−C seems to have a larger polarizability and thus lager polarizability anisotropy than those of THIA−O. Although there is an apparent discrepancy between the results obtained in our study of polarizability for the photochromic ligand and Richardson's models, it might be from the fact that our DFT calculations are based on the free photochromic units. Therefore, the effect on the anisotropic polarizability on the change of the ED transition probability might not be ruled out for Eu(hfa)$_3$(THIA)$_2$. On the other hand, the torsion angle N1−C1−C2−N2 is expected to change about 60 ° from the DFT calculation. The significant change of the direction of the robes of coordinating lone pairs on the N atoms against the Eu(III) ion suggests that the change in the ED transition probability might come from the change of the effect of the orbital overlap between the Eu(III) ion and the coordinating N atoms of the THIA. In the Eu(III) complex with the planer-shaped THIA−C (torsion angle of N1−C1−C2−N2: 2.93°), the sp^2 robes of coordinating lone pairs on the N atoms are directly coordinated to Eu(III) ions such as a phenanthroline ligand. On the other hand, those in the twisted THIA−O (torsion angle of N1−C1−C2−N2: −55.6°) might be combined with the nature of sp^3 by hybridization with the p$_z$ components (π orbitals) in the thiazole groups for coordination of Eu(III). The hybridization of the sp^2 robes and the p$_z$ components on the N atoms should lead to a change of the charges on the N atoms. We speculate at the present stage that the change of torsion angle N1−C1−C2−N2 upon the photochromic reactions would be linked to a change of the charges on the N atoms and the symmetry of the crystal field in Eu(hfa)$_3$(THIA)$_2$.

Conclusion

We successfully studied the photochromic and emission properties of a photochromic lanthanide(III) complex, Eu(hfa)$_3$-

$(THIA)_2$, and demonstrated for the first time the possibility of photon-mode control of the ED transition probability of the photochromic lanthanide(III) complex based on the change of ligand−lanthanide interaction. Relatively high photochromic reactivity of $Eu(hfa)_3(THIA)_2$ was also observed. In our additional experiments, the photochromic reactions of $Eu(hfa)_3(THIA)_2$ and improved stability of the closed-ring form were observed even in conventional polymer thin films such as zeonex or PMMA. Eu(III) complexes with photochromic ligand are expected to be a novel candidate for active materials of optical switching and memory devices. One may also expect that the nondestructive read-out of the luminescence emission at near-IR range would be achieved if NIR-emissive lanthanide(III) ion such as Yb(III) and Nd(III) were to be used, which will be descried elsewhere.

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Supporting Information Available: Detailed spectroscopic data including ^{1}H NMR, ESI-Mass, IR of the $Eu(hfa)_3(THIA)_2{-}O$, and the low temperature absorption spectra of THIA and $Eu(hfa)_3(THIA)_2$ upon UV light irradiation. CIF file of crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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(31) Crystallographic data for THIA−C: $C_{29}H_{21}N_3S_3$, $a = 13.4193(7)$ Å, $b = 10.3767(5)$ Å, $c = 17.7646(8)$ Å, $\beta = 97.4801(14)°$, $V = 2452.6(2)$ Å^3, space group $P2_1/c$, $Z = 4$, $R_{\text{int}} = 0.042$.

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