Reversible Luminescence Modulation in Photochromic Europium(III) Complex Having Triangle Terthiazole Ligands

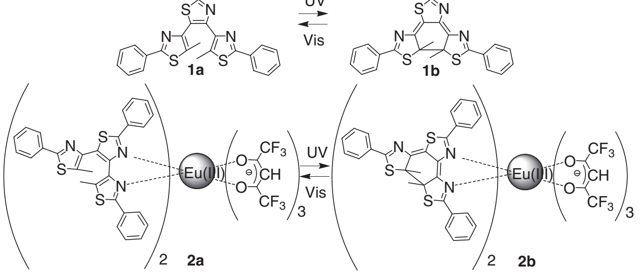
Tetsuya Nakagawa, Kazuhiko Atsumi, Takuya Nakashima, Yasuchika Hasegawa,* and Tsuyoshi Kawai*
Graduate School of Materials Science, Nara Institute of Science and Technology,
8916-5 Takayama, Ikoma 630-0192

(Received November 29, 2006; CL-061407; E-mail: hasegawa@ms.naist.jp; tkawai@ma.naist.jp)

Luminescent Eu^{III} complex having photochromic ligand is synthesized, and its reversible control of the luminescent properties based on photochromic reaction was demonstrated.

Development of luminescent molecule is an active area of photofunctional material chemistry.[1] Especially, the construction of photofunctionalized lanthanide(III) (Ln^{III}) complexes showing strong luminescence is currently of great interest because of their characteristic luminescence with narrow emission band and ideal four level transitions. These characteristic properties of the lanthanide(III) complexes allow them to be the practical candidate for various applications in organic laser, luminescent displays and plastic optical devices.[2] The reversible change of the luminescence properties of Ln^{III} complex may open some unique photonic applications such as a photoswitching laser and luminescent devices. In the present paper, we study on a luminescent Ln^{III} complex having photochromic molecule as a photoresponsive ligand for reversible change of Ln^{III} luminescence. Photochromic molecules have been widely studied as photoswitching units for controlling various properties of molecules and polymers.[3] The fluorescence of photochromic transition-metal complexes has also been modulated by changes of the MLCT energy levels of the complexes.[4] In order to realize reversible control of Ln^{III} luminescence, we designed novel photochromic terarylene derivative as the photoresponsive ligand with relatively high photochromic performance[5a] as a photo-switching unit. The colored closed-ring isomers of terarylene derivatives show characteristic absorption band at around 600 nm. Therefore, the luminescence of Ln^{III}, especially Eu^{III}, is expected to be efficiently quenched when the photochromic unit is converted from the colorless open-ring form to the closed-ring form upon UV light irradiation, resulting in change of the emission intensity.

In this letter, luminescent Ln^{III} complex having photochromic ligand is reported for the first time. An Eu^{III} complex with a photochromic unit, tris(hexafluoroacetylacetonato)-bis[4,5-bis(5-methyl-2-phenylthiazolyl)-2-phenylthiazole]europium(III), $[Eu(HFA)_3(THIA)_2]$ (**2a**) was synthesized with a photochromic ligand, 4,5-bis(5-methyl-2-phenyltiazolyl)-2-phenylthiazole (THIA, **1a**), which is an analogue of photochromic triangle-terthiophene.[5] The reversible luminescent control of the Eu^{III} complex based on the photochromic reaction is successfully demonstrated.



Scheme 1.

THIA, **1a** was prepared by cross-coupling reaction of 4,5-dibromo-2-phenylthiazole and 5-methyl-2-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolane-2-yl)thiazole. **1a** was purified by column chromatography (alumina, hexane:ethyl acetate = 10:1) and recrystallized from hexane. The molecular structure of **1a** was characterized by ^{1}H NMR, ESI-Mass, and X-ray structure analysis.[6] Detailed photochromic properties will be reported elsewhere.[5b] $[Eu(HFA)_3(THIA)_2]$ (**2**) was prepared by reaction of $[Eu(HFA)_3(H_2O)_2]$[7] with **1a** in methanol/chloroform mixed solution under reflux. Obtained powder was washed with chloroform and hot hexane for several times. **2a** was also characterized by ^{1}H NMR, ESI-Mass, IR, and elemental analysis.[8] The coordination of **1a** to Eu^{III} ion was confirmed by the chemical shifts and broadening of the ^{1}H NMR signals of **2a**. From elemental analysis and ESI-Mass spectroscopy, the Eu^{III} complex **2a** was determined to be $[Eu(HFA)_3(THIA)_2]$. The emission quantum yield of **2a** excited at 465 nm was determined by standard procedure with an integrating sphere.[7] The emission lifetime was determined by using a Nd:YAG laser and a dye laser (coumarin 460: $\lambda_{ex} = 465$ nm) as the pulsed excitation light source.

Colorless solution of open-ring isomer **1a** turned blue upon irradiation with UV light ($\lambda = 365$ nm). The blue color disappeared after irradiation with visible light ($\lambda > 440$ nm). **1a** showed no absorption band in visible range, and a new absorption band appeared at 591 nm upon irradiation with UV light, which corresponds to the formation of **1b** (closed-ring isomer). **1b** was isolated by HPLC and characterized by ^{1}H NMR measurements.[6]

Absorption spectral change of **2a** upon irradiation with UV light ($\lambda = 365$ nm) are shown in Figure 1. Photochromic behavior of **2a** is similar to that of ligand **1a**. A new absorption band and an isosbestic point were observed at 591 and 330 nm for the photochromic reactions of **2**, which coincided with those of **1a**. In the ^{1}H NMR measurement, signals of free photochromic ligand (both open-ring isomer **1a** and closed-ring isomer **1b**) were not observed after irradiation with UV light at 365 nm. Similar photochromic behavior was also observed in PMMA film. These results indicate the formation of **2b** without dissociation of the photochromic ligands, **1a** nor **1b**. Because of characteristic feature of lanthanide(III) complex, optical properties of organic ligands in the complex roughly coincide with those of the free ligands. One may evaluate maximum conversion of

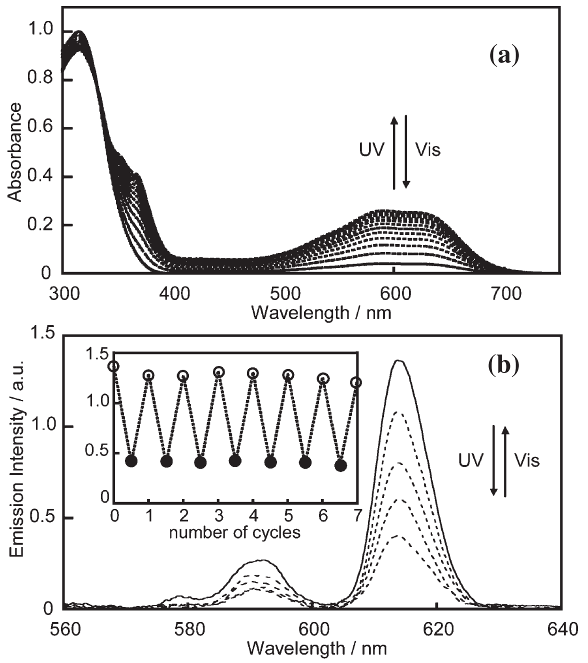


Figure 1. (a) Absorption (concn: 1.4×10^{-4} M, optical path length: 1 mm, intervals of the measurements: 30 s) and (b) emission spectral changes of [Eu(HFA)$_3$(THIA)$_2$] under irradiation with 365 nm light in dioxane. (concn: 1.2×10^{-3} M, optical path length: 1 mm, intervals of the measurements: 2 s) $^7F_0$–$^5D_2$ (465 nm) was excited for the luminescence measurements. Inset: reversible change of the emission intensity at 614 nm with the alternative irradiation cycles of UV (●) and visible (○) light.

the coordinating ligand under UV (365 nm) light irradiation to be about 70% under assumption of same extinction coefficient of the coordinating **1b** in the colored Eu^{III} complex at the photostationary state as that of free **1b**. We, thus, expect **2b**, [Eu (HFA)$_3$(**1b**)$_2$] as well as [Eu(HFA)$_3$(**1b**)(**1a**)] as the colored photoproducts.

In order to characterize the luminescence modulation in Eu^{III} complexes, the emission spectra shown in Figure 1b were measured under excitation at 465 nm ($^7F_0$–$^5D_2$: excited at Eu^{III} ion), at this wavelength absorbance is less than 0.1 even in the colored state.[9] The emission bands were observed at 579, 592, and 614 and are attributed to the f–f transitions $^5D_0$–$^7F_0$, $^5D_0$–$^7F_1$, $^5D_0$–$^7F_2$, respectively. The emission quantum yield and the emission lifetime of **2a** excited at 465 nm were found to be 3.6% and 0.4 ms, respectively.

The emission of the Eu^{III} complex was suppressed after UV light irradiation as also shown in Figure 1b. The emission intensity at the photostationary state (614 nm) was about 30% of the original intensity. The reversible changes in emission intensity at 614 nm with the alternative irradiation cycles of UV ($\lambda = 365$ nm) and visible light ($\lambda > 440$ nm) are shown in Figure 1 (inset). The emission intensity change with the photochromic reactions can be repeated for many times reversibly. The quenching effect in the colored state seems to be attributed to the resonance energy transfer from the $^5D_0$ excited state to the ligand in the colored closed-ring form.[10] It should also be noted that the decrease in the emission intensity at 614 nm of the colored state (modulation efficiency = 70%) is much more significant in comparison with that at 592 nm (modulation efficiency = 64%). Since both emission lines originate from the same excited state $^5D_0$, the change in the emission profile would be attributed to not only the energy-transfer quenching, but to change in the symmetry of the coordination structure around the Eu^{III} center, which will be discussed in detail elsewhere.

A large change in emission intensity at the photostationary state was not observed with continuous irradiation of 465 nm, where both bleached and colored ligands scarcely absorb the irradiation light. The low photochromic sensitivity against the excitation light leads to quasi-nondestructive read-out capability[11] as the optical recording materials. The photochromic lanthanide complex is expected to be a novel photofunctional molecule with unique photoswitching properties.

References and Notes

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6 **1a**: ^{1}H NMR (300 MHz, CDCl$_3$) δ 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). ESI-Mass (m/z) 508.1 ($M^+ + H$). **1b**: ^{1}H NMR (300 MHz, CDCl$_3$) δ 2.10 (s, 3H), 2.12 (s, 3H), 7.50 (m, 9H), 7.92 (m, 2H), 8.05 (m, 4H).

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8 **2a**: Anal. Found: C, 48.32; H, 2.70; N, 4.76%. 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$_3$) δ 2.11 (s, 3H), 2.53 (s, 3H), 7.42 (m, 9H), 7.80–8.10 (m, 6H). ESI-Mass (m/z) 1581.07 (M^+). IR (KBr) 3421 w, 3062 m, 3024 m, 1654 s, 1558 m, 1531 m, 1475 s, 1255 s, 1205 s, 1146 s. $\varepsilon_{315\text{nm}} = 7.4 \times 10^4$ M^{-1} cm^{-1}.

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