Nondestructive luminescence intensity readout of a photochromic lanthanide(III) complex

Tetsuya Nakagawa, Yasuchika Hasegawa* and Tsuyoshi Kawai*

Graduate School of Materials Science, Nara Institute of Science and Technology, Takayama, Ikoma, Nara 630-0192, Japan.

E-mail: hasegawa@ms.naist.jp, tkawai@ms.naist.jp

Electronic Supplementary Information

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

Synthesis of Tris(hexafluoroacetylacetonato)[1,2-bis(2-methyl-1-benzothiophene-1,1-dioxide-3-yl) perfluorocyclopentene]europium(III), Eu-BTFO4 $Eu(hfa)_3(H_2O)_2$[1] (60 mg, 0.11 mmol) and 1,2-bis(2-methyl-1-benzothiophene-1,1-dioxide-3-yl) perfluorocyclopentene : BTFO4[2] (90 mg, 0.11 mmol) were dissolved in methanol (10 ml) / chloroform (5 ml) solution. The solution was then refluxed and stirred. After 1 day of stirring, the reaction mixture was evaporated. The reaction mixture was washed with chloroform and hot hexane several times to afford Eu-BTFO4 (80 mg, yield: 56 %). ^{1}H NMR (300 MHz, $CDCl_3$) δ = 2.13 (s, 3H), 2.30 (s, 3H), 7.22 (d, 2H), 7.48 (m, 2H), 7.62 (m, 2H), 7.80 (m, 2H). IR (ATR)= 3300 w, 2929 m, 2852 m, 1648 s, 1535 s, 1461 s, 1251 s, 1203 s, 1139 s cm-1. ESI-Mass (m/z) $[M]^+$ Calcd. for $C_{33}H_{16}EuF_{18}O_8S_2$ 1098.92; Found, 1098.92.

Optical Measurements. Absorption spectra of Eu-BTFO4 in ethyl acetate (1.6 x 10^{-5} M) were measured on a JASCO V-550. Emission spectra of Eu-BTFO4 in ethyl acetate (1.6 x 10^{-5} M) were measured on a JASCO FP-6500 spectrophotometer. Photoirradiation was carried out using an exciting light source. UV light (313 nm) was obtained by passing the light through a monochromater (Shimazu, SPG120-S). Visible light ($\lambda \geq$ 420 nm) was obtained by passing the light through a colored glass filter (SIGMA KOKI, SCF-50S-42L). The solution of Eu-BTFO4-C in ethyl acetate was obtained by reacting $Eu(hfa)_3(H_2O)_2$ with one equivalent of BTFO4-C which was separated from the colored solution by HPLC. The intrinsic emission quantum efficiencies of Eu-BTFO4-O and Eu-BTFO4-C in ethyl acetate were evaluated by utilizing $Eu(hfa)_3$(BIHEPO) as the standard of $\Phi_{Ln} = 0.60$.[3] The emission lifetimes of Eu-BTFO4-O and Eu-BTFO4-C in ethyl acetate were determined using a Q-switched Nd: YAG laser (Spectra Physics, fwhm = 5 ns, λ = 1064 nm) and a photomultiplier (Hamamatsu Photonics R7400U-03). Samples were excited by the third harmonic (355 nm) of the fundamental nanosecond pulse. Emission decays of Eu(III) ion were monitored with a digital oscilloscope (Tektronix, TDS3052) synchronized to single-pulse excitation. The emission bands of Eu(III) ion are assigned to the electronic transitions, $^5D_0 - {}^7F_J$ (J = 0, 1, 2, 3 and 4). These transition processes are based on the single emitting level, $^5D_0$. There is no wavelength dependence on the emission life time, because these transitions are occurred from single $^5D_0$ state.

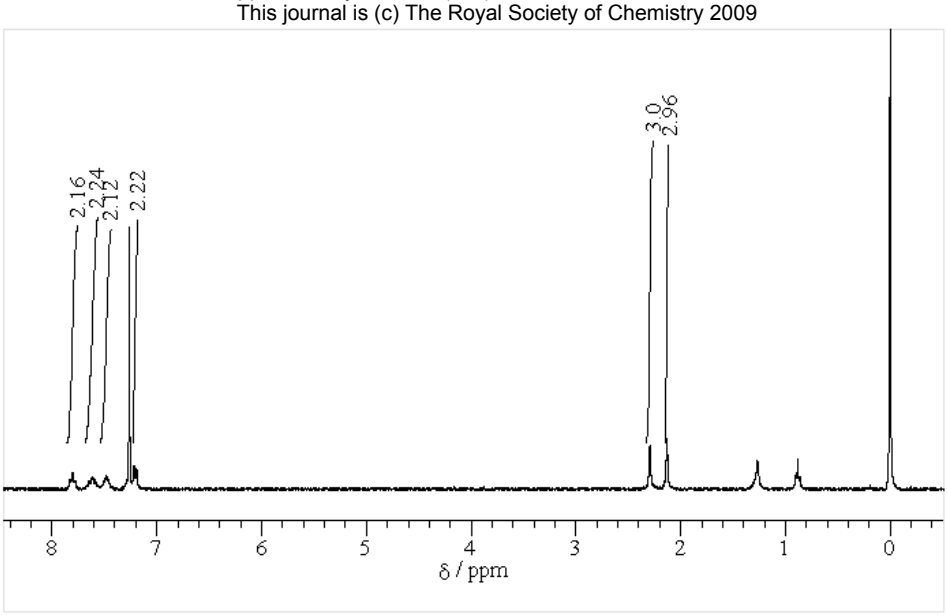

Fig. S1. ^{1}H NMR spectrum of **Eu-BTFO4-O**.

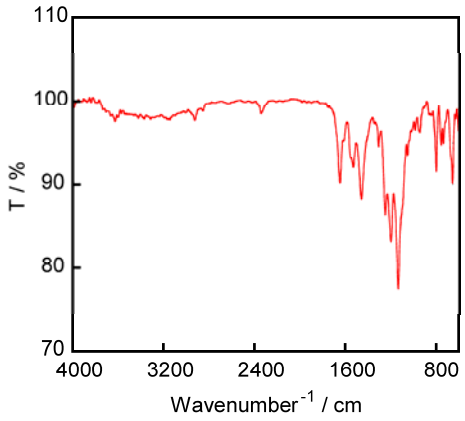

Fig. S2. IR spectra of **Eu-BTFO4-O**.

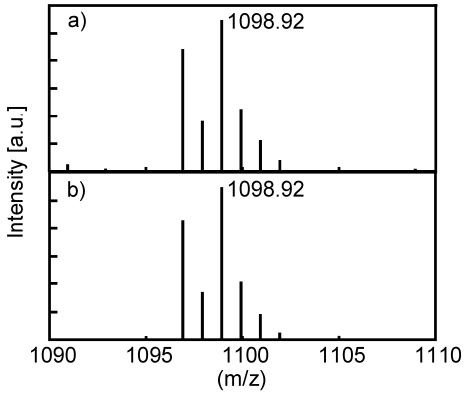

Fig. S3. ESI-Mass spectra of **Eu-BTFO4-O**. (a) measured. (b) calcd.

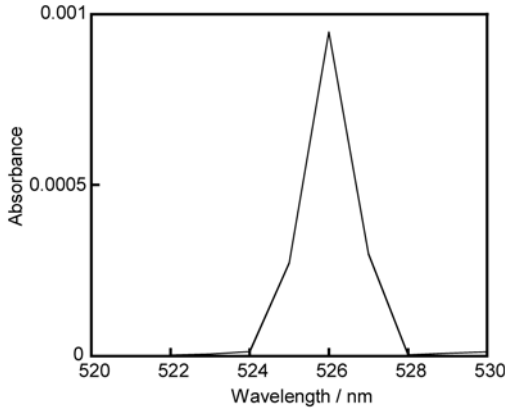

Fig. S4. Absorption spectrum of **Eu-BTFO4-O** in ethyl acetate.

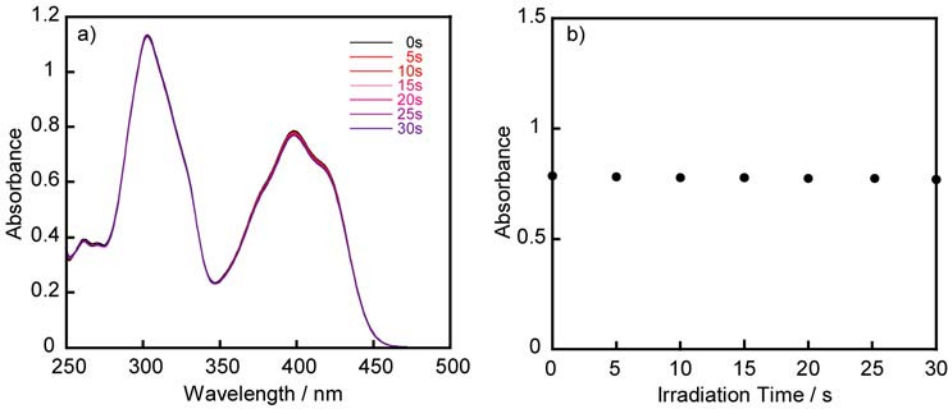

Fig. S5. (a) Absorption spectra of **Eu-BTFO4-C** in ethyl acetate upon visible light irradiation (λ = 526 nm). Each trace was measured for 0 s, 5 s, 10 s, 15 s, 20 s, 25 s and 30 s. (b) Absorbance at 398 nm of **Eu-BTFO4-C** plotted versus irradiation time.

References

1 Y. Hasegawa, M. Yamamuro, Y. Wada, N. Kanehisa, Y. Kai and S. Yanagida, *J. Phys. Chem. A*, 2003, **107**, 1697.

2 Y. C. Jeong, J. P. Han, Y. Kim, E. Kim, S. L. Yang and K. H. Ahn, *Tetrahedron*, 2007, **63**, 3173-3182.

3 K. Nakamura , Y. Hasegawa , H. Kawai , N. Yasuda , Y. Tsukahara and Y. Wada, *Thin. Solid. Films*, 2008, **516**, 2376-2381.