Visible light sensitization of luminescent europium(III) complex with helicene ligands
(Hokkaido Univ.) OHNO, Ryohsuke; KITAGAWA, Yuichi; NAKANISHI, Takayuki; FUSHIMI, Koji; HASEGAWA, Yasuchika

[Introduction] Eu(III) complexes exhibit characteristic red luminescence such as high color purity and long emission lifetimes, which are attributed to the inner 4f electrons of a lanthanide ion. Ligands play an important role in light-harvesting abilities and luminescence properties of these complexes [1]. The extended $\pi$-conjugation results in large absorption coefficients in the visible region and supramolecular architectures through $\pi-\pi$ interactions [2], which are expected to create new photo-functional properties of the Eu(III) complexes. The triplet state level (T1) of the $\pi$-conjugated ligands should be higher than the emitting energy level of Eu(III) ($^5D_0 = 17200 \text{ cm}^{-1}$) for effective photosensitized luminescence (e.g., anthracene, T1 = 14900 cm$^{-1}$) [3]. In this study, we report synthesis and luminescence properties of lanthanide complexes coordinated by $\pi$-conjugated systems based on a novel molecular design.

[Experimental] A novel molecular design based on molecular orbitals was investigated. We found that a helical $\pi$-conjugation system maintains T1 state energy because of a small change in the HOMO–LUMO gap energy. Based on the photophysical finding, novel Eu(III) complex (Eu(hfa)$_3$(HPO)$_2$) with a [5]-helicene derivative (HPO) as a ligand had attempted to prepared. The ligand was synthesized from (S)-2,2'-dimethyl-1,1'–binaphthyl via a four-step reaction [4-5]. Subsequently, Eu(hfa)$_3$(HPO)$_2$ was synthesized by the chelation of HPO ligand with Eu(hfa)$_3$(H$_2$O)$_2$ in toluene. The HPO ligand and Eu(hfa)$_3$(HPO)$_2$ were identified by $^1$H-NMR, $^{31}$P-NMR, ESI-MASS, and IR spectroscopy. Photophysical properties of the compounds were estimated using the electronic absorption, emission spectra and emission lifetime measurements.

Fig. 1 Synthetic scheme of Eu(hfa)$_3$(HPO)$_2$.
[Results and Discussion] The electronic absorption and emission ($\lambda_{ex} = 310$ nm) spectra of the HPO ligand are shown in Fig. 2. Characteristic absorption (386 and 408 nm) and emission (417 and 438 nm) bands were observed in the visible region. The Stokes shift was relatively small (610 cm$^{-1}$).

The electronic absorption bands of Eu(hfa)$_3$(HPO)$_2$ are observed in almost the same visible region as that of HPO molecule. The absorption band originates from the $\pi-\pi^*$ transition band of HPO molecules. The luminescence spectrum of Eu(hfa)$_3$(HPO)$_2$ excited at 375 nm exhibits a broad emission band (445 nm) and narrow 4f-4f emission bands (578, 613, 651, and 699 nm) (Fig. 3) [4, 6]. The board emission band is assigned to phosphorescence of HPO ligand attached with Eu(III) complex. We successfully observed effective luminescence under blue-light irradiation (450 nm), which indicates that helicene in HPO ligand is a suitable ligand to photosensitize Eu(III) to visible light. This is the first successful demonstration of photosensitized Eu luminescence using a large $\pi$-conjugated system (22-$\pi$-electron system).

![Fig. 2 Absorption and fluorescence spectra of HPO in CHCl$_3$.](image1)

![Fig. 3 Fluorescence spectrum of Eu(hfa)$_3$(HPO)$_2$ in CHCl$_3$.](image2)