Photochemical Modulation of Europium Ion Fluorescence Using a Tetraazamacrocyclic Derivative Bearing a Spirobenzopyran and Three Carboxymethyl Moieties

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The fluorescence properties of a Eu^{3+} complex with a tetraazamacrocyclic derivative bearing a spirobenzopyran and three carboxymethyl moieties were investigated. The enhanced fluorescence of Eu^{3+}, which proved that the spirobenzopyran moiety worked as an antenna for the sensitization, was controlled photochemically.

Lanthanoid ions, such as Eu^{3+} and Tb^{3+}, are known to show specific emissions with long lifetimes and narrow half bandwidths in the visible region. Those properties are caused by the parity-forbidden transition resulting from 4f orbitals. Therefore, the characteristic line-like emission has been applied to the development of fluorescent materials,[1–3] chemosensors,[4–6] and fluorescent labels.[7] However, it is difficult to obtain strong fluorescence from lanthanoid ions in aqueous solution by exciting them directly, because their molar extinction coefficients are very small. On the other hand, the drawback has been solved by using organic chromophores with large molar extinction coefficients as sensitizers. Recently, on/off switching systems of lanthanoid fluorescence using organic chromophores which respond to external stimuli (pH, thermal, etc.) have been studied,[8] and applications to bio-imaging are now in progress.

Spirobenzopyran is known as a typical photochromic compound which is isomerized from its electrically neutral colorless spiropyran (SP) form to the corresponding zwitterionic merocyanine (MC) form by UV-light irradiation and vice versa by visible-light irradiation.[9–13] It is expected that spirobenzopyran can be used as a photo-controllable sensitizer. In our group, a tetraazacrown ether derivative **1** bearing a spirobenzopyran and three carboxyl moieties was synthesized to give high affinities for multivalent metal ions such as lanthanoid ions in a recent research (Figure 1).[14] Here, we report the fluorescence properties of the Eu^{3+}–**1** complex under dark and visible-light irradiation conditions.

The absorption, fluorescence, and excitation spectra of **1** and the Eu^{3+}–**1** complex in a methanol/water (9/1) solution are shown in Figures 2 and 3. In absorption spectra, the peak based on the MC form in the visible region was clearly observed under dark conditions, and the peak exhibited a hypsochromic shift of more than 30 nm by complexation with Eu^{3+}. This result shows that the spirobenzopyran moiety mostly exists as its MC form under dark conditions, and that the MC moiety strongly interacted with Eu^{3+}. In fluorescence spectra, a broad peak around 500–700 nm was observed by excitation at 350 nm under dark conditions, and the fluorescence intensity was remarkably decreased by visible-light irradiation. This demonstrates that almost all of the fluorescent MC form was isomerized to the non-fluorescent SP form by visible-light irradiation. In excitation spectra, a larger fluorescence intensity was observed in the visible region under dark conditions compared with that under visible-light irradiation conditions because the MC form can be efficiently excited by the visible light. Under dark conditions, in addition to the broad fluorescence resulting from the MC form, the Eu^{3+} florescence with emission bands at 579, 592, 614, and 652 nm resulting from $^5D_0 \rightarrow {}^7F_J$ transitions with $J = 0$, 1, 2, and 3, respectively, was simultaneously observed upon excitation of the ligand at 350 nm (not upon direct excitation of Eu^{3+}) (Figure 3b). On the other hand, under visible-light irradiation conditions, only the Eu^{3+} fluorescence was observed (Figure 3a). In addition, the excitation spectrum monitored at 617 nm of the Eu^{3+}–**1** complex under dark conditions was similar to that under visible-light irradiation conditions, and the fluorescence intensity based on the MC form of the Eu^{3+}–**1** complex was much lower than that of **1** under dark conditions. These results suggest that the Eu^{3+} fluorescence originated from energy transfer from the spirobenzopyran moiety of **1** as an antenna to Eu^{3+}.

The fluorescence properties of the Eu^{3+}–**1** complex under dark and visible-light irradiation conditions are listed in Table 1. Although the total quantum yield ($\phi_{\text{total,vis}} = 8.3 \times 10^{-5}$) under visible-light irradiation conditions was smaller than that ($\phi_{\text{total,dark}} = 1.4 \times 10^{-4}$) under dark conditions, the quantum yield ($\phi_{\text{Eu,vis}} = 8.3 \times 10^{-5}$) based on the Eu^{3+} fluorescence under visible-light irradiation conditions was doubled as compared with that ($\phi_{\text{Eu,dark}} = 4.4 \times 10^{-5}$) under dark conditions. This result demonstrates that the energy transfer to Eu^{3+} from the SP form rather than the MC form was more efficient. Possibly, since the deactivation process of the excitation energy by the fluorescence of spirobenzopyran itself does not exist in the case of the SP form, the quantum yield of Eu^{3+} fluorescence increased under visible-light irradiation conditions.

This study shows the possibility of a complete on/off control of lanthanoid emissions using an appropriate photochromic ligand. The application of this system to photo-controllable lanthanoid fluorescence materials is highly anticipated.

Experimental

General Procedures. The synthesis of **1** was performed according to a previous paper.[14] The concentrations of ligand and $Eu(NO_3)_3$ were kept at 1.0×10^{-4} M (=mol dm^{-3}). After the

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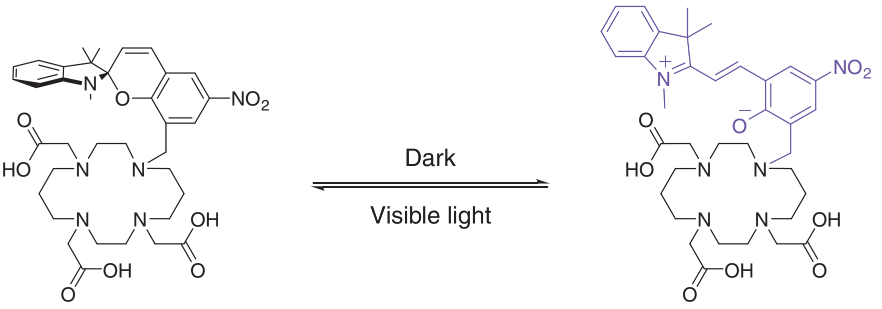

1 (Spiropyran form) 1 (Merocyanine form)

Figure 1. Photochromic ligand used in this study.

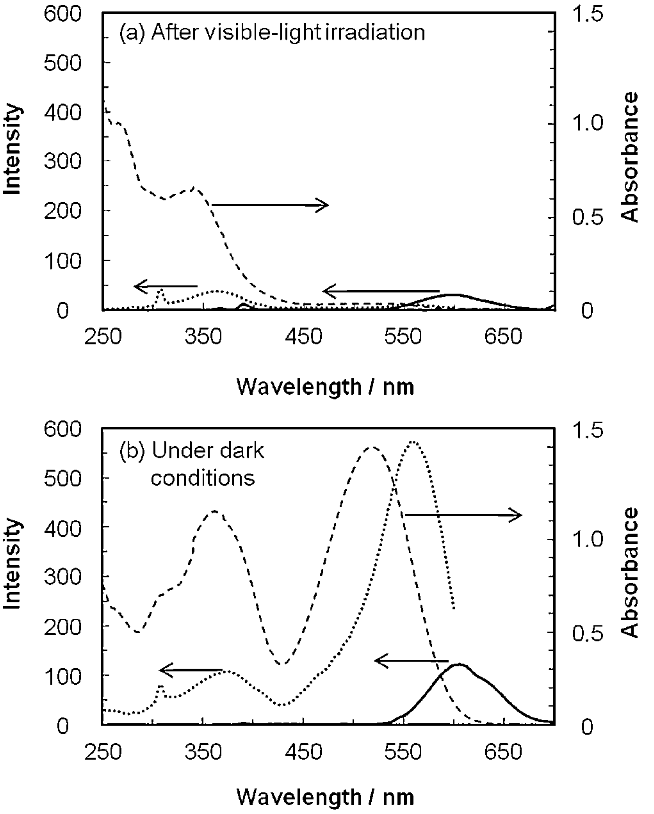

Figure 2. Absorption (dash line), fluorescence ($\lambda_{ex} = 350$ nm, full line), and excitation ($\lambda_{em} = 615$ nm, dotted line) spectra of **1**. (a) After visible-light irradiation and (b) under dark conditions.

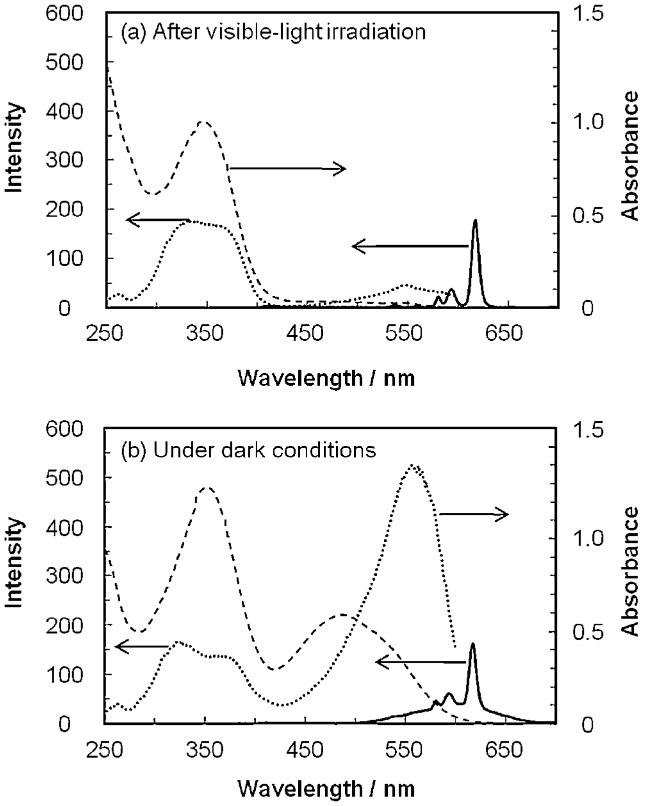

Figure 3. Absorption (dash line), fluorescence ($\lambda_{ex} = 350$ nm, full line), and excitation ($\lambda_{em} = 615$ nm, dotted line) spectra of the Eu^{3+}–**1** complex. (a) After visible-light irradiation and (b) under dark conditions.

Table 1. Fluorescence Properties of the Eu^{3+}–**1** Complex

	ε/cm^{-1} M^{-1} at 366 nm	$\lambda_{em,max}$ /nm	ϕ_{total}	ϕ_{Eu}
Dark	1.2×10^4	617	1.4×10^{-4}	4.4×10^{-5}
Visible	8.2×10^3	617	8.3×10^{-5}	8.3×10^{-5}

sample solutions prepared were allowed to stand for 24 h under dark conditions, all the experiments were carried out in methanol/water (9/1) in the presence of Eu^{3+} under dark or visible-light irradiation conditions.

Spectroscopic Measurements. The UV–vis spectroscopic measurements were performed with a V-550 UV/VIS Spectrophotometer (Jasco) at 25 °C and with cells of 1 cm optical path length. Temperature control was carried out using an EHC-477T Temp. Controller (Jasco). The fluorescence and excitation spectra of the Eu^{3+}–**1** complex were recorded at room temperature (298 K) with a RF-5300PC Spectrofluorophotometer (SHIMADZU). The fluorescence quantum yields upon excitation at 366 nm were calculated using quinine sulfate dihydrate ($\phi = 0.546$ in 0.5 M sulfuric acid), as a standard. The total quantum yield (ϕ_{total}) was calculated by all of the fluorescence intensity. The quantum yield (ϕ_{Eu}) based on the Eu^{3+} fluorescence was calculated by subtracting the fluorescence intensity originating from spirobenzopyran as the background from the total fluorescence intensity. The visible light was irradiated to a quartz cell containing a sample solution through a light filter (VY-49) with a Xe lamp for 3 min.

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