

Synthesis and Photophysical Properties of Luminescent Lanthanide Complexes Based on Coumarin-3-carboxylic Acid for Advanced Photonic Applications

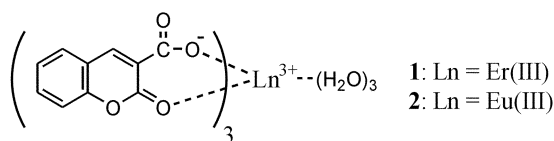
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Recently, luminescent lanthanide complexes have attracted much attention because of their academic interests as well as potential utility of this technology in a wide variety of photonic applications such as planar waveguide amplifiers, plastic lasers, and light-emitting diodes.¹⁻⁸ In most cases, luminescent lanthanide complexes consist of a lanthanide ion and its chelating luminescent ligands as a sensitizer, which can transfer excitation energy to the encapsulated lanthanide ion. The luminescent ligand is generally referred to as the antenna chromophore, in analogy to the light-harvesting center in photosynthetic reaction center. They efficiently absorb and transfer lights to the central lanthanide ions through the energy transfer. The central lanthanide ions accumulate lights from the antenna chromophores. To date, however, luminescent lanthanide complexes were not developed in specific references to luminescent lanthanide complexes.¹ Such efforts are just in the early stage and not only the basic concept not established, but also the structure-property relationship is not yet clearly understood.

Therefore, very recently, in order to get the highly efficient lanthanide emission *via* the energy transfer between luminescent ligands and lanthanide ions, we have investigated the synthesis and photophysical properties of luminescent lanthanide complexes based on a coumarin derivative for advanced photonic applications such as planar waveguide amplifiers and light-emitting diodes. The luminescent lanthanide complexes based on coumarin-3-carboxylic acid, except for $\text{Eu(III)(coumarin-3-carboxylate)}_n(\text{X})_{3-n} \cdot \text{solvent}$ ($n = 1-2$; X: Cl^- , ClO_4^- , or NO_3^- ; solvent: H_2O or ROH),⁹ were not known, to the best of our knowledge. These known complexes were not really synthesized for advanced photonic applications, since they exhibited two fluorescence bands emitting from lanthanide ions and the ligand.⁹



We successfully synthesized luminescent lanthanide complexes based on coumarin-3-carboxylic acid through the

ligand-exchange reaction using LnCl_3 ,^{10,11} in which the Er(III)- and Eu(III)-chelated complexes were prepared by reacting the coumarin-3-carboxylate salt with ErCl_3 or $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$.¹¹ The chemical structures of the complexes **1** and **2** were confirmed by elementary analysis, thermal gravimetric analysis (TGA), FT-IR, absorption and emission spectroscopies. Details of the experimental procedures were described in Ref. [12].

The FT-IR spectrum of the Ln(III)-chelated complex exhibited the vibration modes of the carbonyl moieties of the unidentate-like carboxylate and aryl ester around 1724 and 1671 cm^{-1} , respectively. Also, two bidentate-like carboxylate bands appeared in the region of 1561 and 1412 cm^{-1} , indicating the formation of bidentate complex. These results suggest that the carbonyl moieties for the carboxylate and aryl ester are explicitly coordinated to the lanthanide(III) ion.^{9,11} But, the paramagnetic properties of the lanthanide ion do not permit NMR characterization of the coumarin-based complexes. The coumarin ligand in Ln(III)-chelated complexes has the same UV absorption feature, comparing to that of the coumarin derivative itself. It indicates that the chelated ligand and the lanthanide ion do not perturb each other. In other words, the ligand in the Ln(III) complexes behaves independently like the inherent coumarin derivative and the ground state of the lanthanide ion even in the Ln(III) complex was not influenced by the ligand.

In TGA traces, at least three H_2O molecules coordinated in the unsaturated 6-coordinated complexes were confirmed by determining the releasing water amount of 7% up to 180 °C in atmospheric condition. The presence of the H_2O molecules in the complex reduces the near IR (NIR) emission intensity because of the harmonic vibration relaxation decay of O-H bonds in these H_2O molecules. However, the complex **1** exhibits the strong NIR emission bands, corresponding to the characteristic $^4\text{I}_{13/2} \rightarrow ^4\text{I}_{15/2}$ transition of trivalent erbium ions taking place at 1530 nm (see Fig. 1). Also, the stronger NIR emission intensity was obtained than the direct photoexcitation of erbium ions with 488 nm, when Er(III)-chelated complex was photoexcited by using the absorption wavelength of the coumarin ligand at 325 nm (see Fig. 1). It means that the energy transfer process between organic ligands and Er(III) ions occurs. This could be ascribed to the fact that the spectral overlap between the photoluminescence (PL) band of organic ligands and the absorption band of

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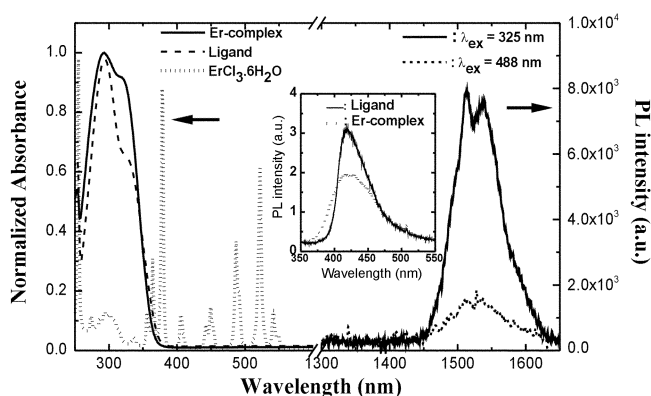


Figure 1. UV-visible absorption spectra of Er(III)-complex **1** (DMSO, 10^{-5} M), ligand (DMSO, 10^{-5} M), and Er(III) salt (H_2O , 0.1 M); and emission spectra of Er(III)-chelated complex **1** at $\lambda_{\text{ex}} = 325$ and 488 nm. The inset shows the emission spectra of ligand and Er-chelated complex **1** at $\lambda_{\text{ex}} = 318$ nm in a powder state. Here, the λ_{ex} means the excitation wavelength.

Er(III) ions takes place.^{1,10,11} But, an additional fluorescence band in the range of 375 to 550 nm, emitting from the excited ligands, was observed. The presence of the fluorescence band from the excited ligand indicates that the energy transfer process between organic ligands and Er(III) ions is not very effective. Very recently, we reported that the instability of the unsaturated 6-coordinated complex induces the lower intensity of the near IR emission band, due to its more chance of nonradiative relaxation decay than the saturated 9- or 10-coordinated complex.¹¹ It might also reduce the energy transfer efficiency.

The emission spectra of $\text{Eu(III)(coumarin-3-carboxylate)}_n(\text{X})_{3-n}$ in Ref. [9] show two fluorescence bands, emitting from both the ligand and the lanthanide ion. However, our Eu(III)-chelated complex **2** exclusively exhibits typical narrow sharp emission bands corresponding to the characteristic $^5\text{D}_0 \rightarrow ^7\text{F}_j$ transition of trivalent europium ions with the strongest emission band of the characteristic $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition of trivalent europium ions at 614 nm.

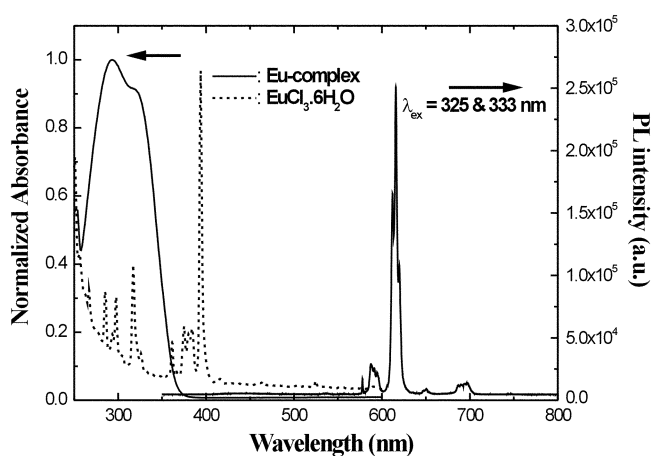


Figure 2. UV-visible absorption spectra of Eu(III)-complex **2** (DMSO, 10^{-5} M) and Eu(III) salt (H_2O , 0.1 M); and emission spectra of Eu(III)-chelated complex **2** at $\lambda_{\text{ex}} = 325$ and 333 nm in a powder state.

In addition, when the complex **2** was excited with the absorption wavelength of the ligand at 333 nm as well as the absorption wavelength of the Eu ion and the ligand at 325 nm, the emission spectra show almost the same emission intensity (see Fig. 2). The excitation wavelengths of 325 and 333 nm were chosen, because the ligand has a strong absorption at both wavelengths and Eu ion has a very weak absorption at 325 nm. From these results, the emission band of direct excitation of the Eu ion at 325 nm could be negligible. It might be due to the very low absorption and emission cross sections of the Eu ion. Also, in Fig. 2, no emission band from the excited ligand was observed. The absence of its emission band indicates that the energy transfer process between the coumarin ligand and the lanthanide ion occurs effectively.

In summary, we have designed and developed novel luminescent lanthanide complexes based on a coumarin derivative, using a new promising synthetic method developed in our laboratory. The unsaturated 6-coordinated complexes coordinated with three H_2O molecules were formed. The present Er(III)- and Eu(III)-chelated complexes showed an intra 4f shell electronic transition from its first excited state to the ground state taking place at 1530 and 614 nm, respectively. The stronger emission intensity was obtained by the photoexcitation of the coumarin-based ligand with the wavelength of 325 nm rather than by the direct photoexcitation of the lanthanide ions. It could be explained by the fact that the effective energy transfer between the coumarin ligand and the lanthanide ions takes place.

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- Supporting information materials for details of the experimental procedures are available from the corresponding author on request.