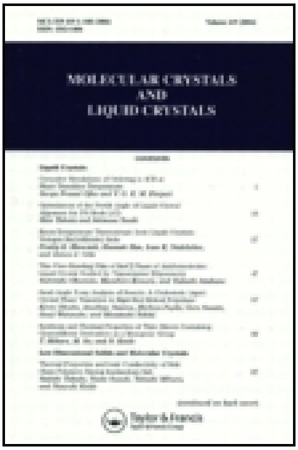

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Synthesis and Photophysical Properties of Luminescent Erbium(III) Complexes Based on Coumarin Derivatives for Advanced Photonics Applications

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SYNTHESIS AND PHOTOPHYSICAL PROPERTIES OF LUMINESCENT ERBIUM(III) COMPLEXES BASED ON COUMARIN DERIVATIVES FOR ADVANCED PHOTONICS APPLICATIONS

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The luminescent Er(III)-chelated complexes based on coumarin derivatives such as coumarin-3-carboxylic acid and coumarin 343 were prepared by ligand-exchange reaction in the presence of $ErCl_3$ and potassium coumarin derivative salts. The chemical structures of the present complexes were confirmed by elementary analysis, thermal gravimetric analysis. FT-IR, absorption and emission spectroscopies. The coumarin-based Er(III) complexes exhibited the near IR emission, corresponding to the characteristic $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition of trivalent erbium ions, taking place in the region of 1512 or 1530 nm. Their PL intensity also depends on the degree of the spectral overlap between the emission band of coumarin derivative and the absorption band of Er ion.

Keywords: advanced photonics applications; coumarin derivatives; luminescent Er(III) complexes; photophysical properties

INTRODUCTION

More recently, luminescent lanthanide complexes play an important role in photonic applications such as planar waveguide amplifiers, plastic lasers and light-emitting diodes [1–10]. In general, luminescent lanthanide complexes consist of a lanthanide ion as a photonic active component and a

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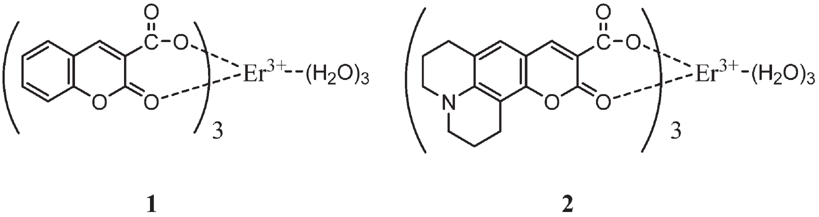
luminescent ligand as a sensitizer, which can transfer excitation energy from the ligand to the encapsulated lanthanide ion, despite the parity forbidden for optical transition within the 4f subshells of the lanthanide ion due to lanthanide ion's intrinsically low absorption and emission cross sections. The luminescent ligand contains a light-absorbing group as sensitizer of an organic (or antenna) chromophore and a tightly chelating organic molecule. They efficiently absorb and transfer lights to the central lanthanide ions, in analogy to the light-harvesting center in photosynthetic reaction center, through the energy transfer. Therefore, the opto-physical properties of luminescent lanthanide complexes can be optimized and maximized during artificial light gathering and transferring by way of using principles of naturally existing photo-synthetic antenna. Up to date, however, luminescent lanthanide complexes based on supramolecular ligands as antenna chromophores were not developed in specific References [1]. They are simply supramolecular complexes containing well-known antenna chromophores to photoexcite the lanthanide ions via the energy transfer process. The quantum yield of the energy transfer and the luminescence efficiency were not satisfied yet. Such efforts are just in the early stage. Not only the useful synthetic methods as well as the basic concept have not been established, but also the structure-property relationship has not been clearly understood yet.

The luminescent lanthanide complexes based on coumarin acid derivatives, except for Eu(coumarin-3-carboxylate)$_n$(X)$_{3-n}$, solvents (X $=$ Cl$^-$, ClO$_4^-$, NO$_3^-$: n $=$ 1, 2; solvents $=$ H$_2$O, n-BuOH) [11], were not known, to the best of our knowledge. These materials reported previously were not satisfied with photonic materials, since they exhibited several emission bands [11]. In this paper, we have investigated the synthesis and photophysical properties of luminescent Er(III) complexes based on coumarin derivatives such as coumarin-3-carboxylic acid and coumarin 343 for advanced photonic applications such as planar waveguide amplifiers and near IR light-emitting diodes.

RESULTS AND DISCUSSION

We have synthesized the novel luminescent Er(III)-chelated complexes based on coumarin derivatives through the ligand-exchange reaction using ErCl$_3$ and potassium coumarin derivative salts. It was achieved by a new synthetic strategy, developed in our laboratory, for a series of new and practically useful lanthanide-cored supramolecular complexes with a quantitative yield [12,13]. The chemical structures of Er-chelated complexes are shown in Scheme 1.

The successful synthesis of **1** and **2** was confirmed by elementary analysis, thermal gravimetric analysis (TGA), FT-IR, absorption and emission



SCHEME 1 Luminescent Er(III)-chelated complexes based on coumarin derivatives.

spectroscopies. The FT-IR spectrum of the Er-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 [11]. The stretching vibration modes for the carbonyl moieties of the carboxylate and aryl ester in the coumarin-based Er(III) complexes were simultaneously shifted within 18 and 9 cm^{-1}, by comparison with the coumarin-3-carboxylic acid, respectively [11]. Two bidentate-like carboxylate bands also appeared in the region of 1561 and 1412 cm^{-1}, indicating the formation of bidendate complex [14]. These results suggest that the carbonyl moieties for the carboxylate and aryl ester are explicitly coordinated to the Er(III) ion (see Fig. 1).

Unfortunately, the crystal growth of two complexes was attempted, but it was not achieved successfully. Thus, X-ray pattern could not be obtained for the molecular structure determination yet. But, the paramagnetic properties of the lanthanide ion do not permit NMR studies of the

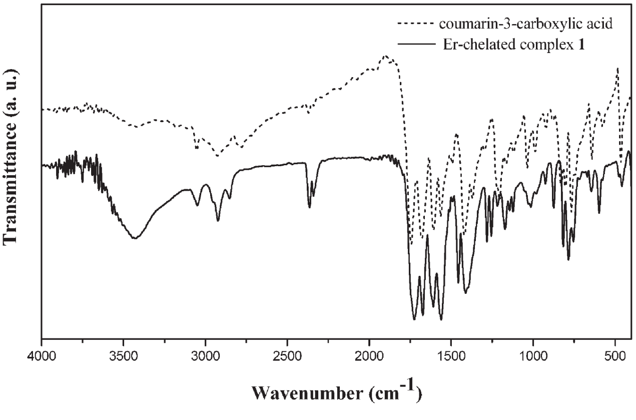


FIGURE 1 FT-IR spectra of coumarin-3-carboxylic acid and its Er(III)-chelated complex **1** in KBr pellets.

coumarin-based complexes. Er(III)-chelated complexes have the similar UV absorption feature to the ligand, comparing to that of the coumarin derivative itself, since the ligand in the Er(III) complexes behaves independently like the inherent coumarin derivative. It suggests that the chelated ligand and the lanthanide ion do not perturb each other. In other words, the ground state of the lanthanide ion even in the Er complex was not influenced by the organic ligand.

In a TGA trace, the unsaturated 6-coordinated Er(III) complexes were coordinated at least three H_2O molecules to the Er(III) ion by determining the releasing water amount of the respective Er(III)-chelated complexes in atmospheric condition (see Fig. 2). In particular, it reduces the near IR emission intensity, due to the harmonic vibration relaxation decay of O−H bonds. However, the Er(III) chelated complexes **1** and **2** exhibit the strong near IR emission bands, which correspond to the characteristic $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition of trivalent erbium ions taking place at 1512 or 1530 nm (see Fig. 3). It could be attributed to the effective energy transfer process between organic ligands and Er ions, since the spectral overlap between the PL band of organic ligands and the absorption band of Er ions occurs. Also, the stronger near-IR emission intensity was obtained from the photoexcitation of organic ligands by using the absorption wavelength of 325 nm for the complex **1** and 482.5 nm for the complex **2** rather than by the direct photoexcitation of the Er(III) ions with 488 nm. It could be explained by the effective energy transfer between the triplet state of ligand and lanthanide ions through the formation of triplet state in the complex, due to the heavy metal effect, whereas coumarin ligands are directly connected to lanthanide ions without a molecular spacer [15].

In summary, we have developed novel luminescent Er(III)-chelated complexes based on coumarin derivatives using a new synthetic strategy

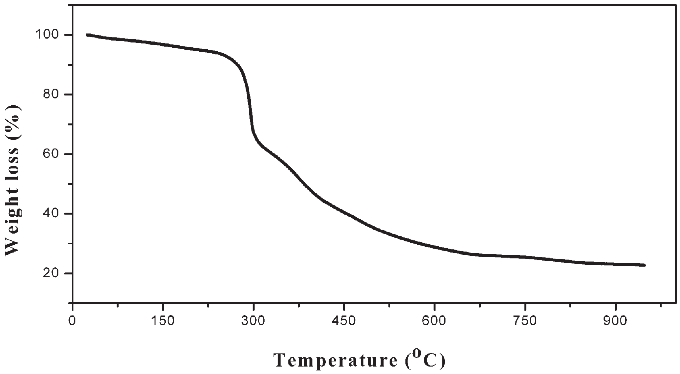
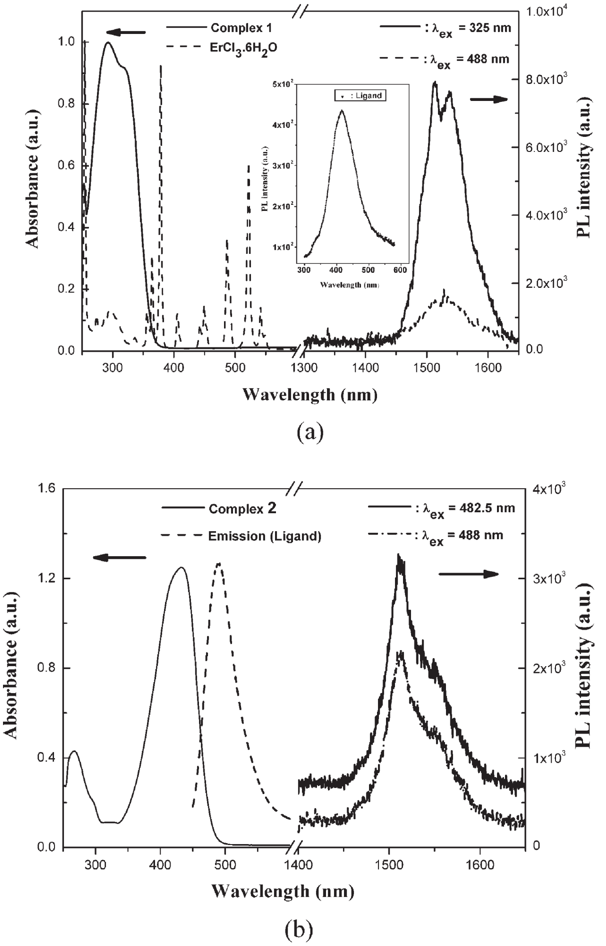


FIGURE 2 TGA trace of the Er(III)-chelated complex **1** in atmospheric condition.



(a)

(b)

FIGURE 3 UV-visible absorption and emission spectra of the Er(III)-chelated complexes (a) **1** (with Ar$^+$ and He-Cd lasers) and (b) **2** (with Xe lamp). The inset shows the emission spectrum of the coumarin-3-carboxylic acid as ligand itself.

developed in our laboratory. Er(III)-chelated complexes exhibited a strong emission band from the first excited state ($^4\mathbf{I}_{13/2}$) to the ground state ($^4\mathbf{I}_{15/2}$), taking place in the near-IR region of 1512 or 1530 nm. The stronger emission band of Er(III)-chelated complexes was obtained by the indirect photoexcitation of coumarin-based ligands via the effective energy transfer rather than by the direct photoexcitation of the Er(III) ions. It could be explained by the effective energy transfer between the triplet state of coumarin ligands and lanthanide ions through the formation of triplet state in the complexes, due to the heavy metal effect. These new luminescent Er(III)-chelated complexes based on coumarin derivatives can be used in photonic applications such as planar waveguide amplifiers and near IR light-emitting diodes.

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