Er(III)-chelated Prototype Complexes Based on Benzoate and Pentafluorobenzoate Ligands : Synthesis and Key Parameters for Near IR Emission Enhancement

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New synthetic methodology of the saturated and unsaturated Er(III)-chelated prototype complexes based on benzoate and pentafluorobenzoate ligands was developed through ligand-exchange reaction. The saturated 8-coordinated Er(III) complexes exhibit stronger near-IR emission than those of the unsaturated 6-coordinated Er(III) complexes, obtained from the direct photoexcitation of Er ions with 488 nm. Three H_2O molecules coordinated in the unsaturated 6-coordinated complexes seriously quenched the near IR emission by the harmonic vibration relaxation decay of O-H bonds. Also, the stronger emission of the Er(III) complexes was obtained by the indirect photoexcitation of ligands than by the direct photoexcitation of the Er(III) ions, due to the energy transfer between the excited ligand and the erbium ion. Furthermore, the saturated Er(III)-chelated complex with C-F bonds shows much stronger near IR emission than that of the saturated Er(III)-chelated complex with C-H bonds. It is attributed to the influence of C-F bonds on near IR emission.

Key Words : Erbium-chelated prototype complexes, Ligand-exchange reaction, Emission enhancement, Planar waveguide amplifiers

Introduction

Very recently, the lanthanide(III) materials play an important role in the development of integrated planar waveguide optical amplifiers in the superhigh speed communication systems.[1] In particular, wavelength division multiplexing (WDM)-integrated planar waveguide amplifiers are recognized to be essential for successfully realizing photonic devices in WDM technology. However, the problem still remains to be unsolved in the materials for the planar waveguide amplifiers. At present, erbium-doped silica amplifiers are widely used. The optical amplification (OA) gain of erbium-doped waveguide amplifiers (EDWA) utilizing this material is currently not enough for amplifying the optical signals in small-sized photonic devices, although the OA gain of current erbium-doped fiber amplifiers (EDFA) based on Er(III)-doped silica materials is not a problem for intercontinental telecommunication networks with long pathway. Therefore, in order to enhance the amplified luminescence intensity, the development of luminescent lanthanide complexes based on the energy transfer mechanisms by using the supramolecular ligands has been extensively studied.[2-7] Luminescent lanthanide complexes consist of a lanthanide ion as a photonic active component and its chelating luminescent ligands as sensitizers, which can transfer excitation energy from the ligands to the lanthanide ion. However, luminescent lanthanide complexes were not developed in specific reference to advanced 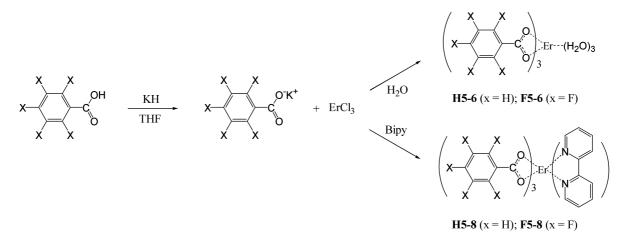photonic materials by now. They are simply supramolecular complexes containing well-known antenna chromophores to photoexcite the lanthanide ions *via* the energy transfer process. They were not satisfied with the quantum yield of energy transfer and the luminescence efficiency yet. Such efforts are just in the early stage. Not only the useful synthetic methodology as well as the basic concept has not been established, but also the structure-property relationship is not clearly understood yet.[1]

Recently, we studied the synthesis and photophysical properties of the luminescent lanthanide complexes based on coumarin,[8] porphyrin[9] and naphthalene[10] derivatives for advanced photonic application, such as planar waveguide amplifiers and light-emitting diodes, in order to get the highly efficient lanthanide emission *via* the energy transfer between luminescent ligand and lanthanide ion.

Very recently, we also attempted to synthesize Er(III)-chelated benzoate and pentafluorobenzoate complexes as prototype complexes in order to investigate important key parameters for near infrared (IR) emission enhancement (see Scheme 1). Er(III)-chelated prototype complexes were carried out by using the Er(III) acetate, according to the previously reported synthetic method for the 6-coordinated erbium complexes.[11] But, the successful synthesis of 6- or 8-coordinated erbium complexes was not always achieved.[12,13] Thus, we have attempted to develop a new synthetic method for 6- and 8-coordinated Er(III)-cored prototype complexes through the ligand-exchange reaction using $ErCl_3$. In this paper, therefore, we report the synthesis of novel Er(III)-chelated complexes through the ligand-exchange reaction and the investigation of important key parameters for near infrared (IR) emission enhancement.

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Scheme 1. New synthetic route to Er-chelated complexes based on benzoate and pentafluorobenzoate ligands and their chemical structures.

Experimental Section

General Procedures. All manipulations were carried out under N_2 atmosphere with standard Schlenk technique. All reagents were used as received without further purification. THF were dried and deoxygenated over sodium/benzophenone kethyl and freshly distilled prior to use. FT-IR spectra were recorded on Perkin-Elmer 1000 FT-IR spectrometer with a conventional KBr pellet method. UV-visible spectra were measured with Shimazu UV-2401PC spectrophotometer. TGA analysis was carried out with Dupont 9900 Model 951 thermogravimetric analyzer with the heat rate of 10 $^{\circ}$C/min under N_2 atmosphere.

Synthesis of [Er(benzoate)$_3$(H$_2$O)$_3$] (5H-6). To the dried Schlenk flask, a mixture of benzoic acid (0.500 g, 4.094 mmol) and KH (0.164 g, 4.094 mmol) in THF (100 mL) was added and stirred at room temperature for overnight. The salt was precipitated with gas evolution during reaction and then the methanol solution of anhydrous ErCl$_3$ (0.373 g, 1.364 mmol) in methanol (10 mL) was added dropwise to the reaction solution. After 2 days of stirring at room temperature, the resulting solution was filtered and removed solvents to give the residue. This residue was redissolved with THF and the insoluble solid was filtered off. The solvent was removed in vacuo to give a solid. The solid was washed with n-hexane and diethyl ether, and then dried to afford **5H-6** as a white solid (0.502 g, 0.859 mmol, 63%). Anal. (%) Calc. for $C_{21}H_{21}ErO_9$: C 43.14, H 3.62, Er 28.61; Found: C, 43.01, H 3.76, Er, 28.55. UV-vis. (λ nm ($\varepsilon \times 10^{-3}$, M^{-1}cm^{-1}) in DMSO) 259 (1.44), 301 nm (0.29). FT-IR (KBr pellet, cm^{-1}) 3371, 1604, 1526, 1418, 718, 685, 669.

Synthesis of [Er(pentafluorobenzoate)$_3$(H$_2$O)$_3$] (F5-6). According to the similar procedure above, Er(pentafluorobenzoate)$_3$(H$_2$O)$_3$ as white solid (0.422 g, 0.494 mmol, 63%) was prepared from the reaction of ErCl$_3$ (0.215 g, 0.785 mmol) in methanol (10 mL) with pentafluorobenzoic acid (0.500 g, 2.357 mmol) and KH (0.094 g, 2.357 mmol) in THF (100 mL). Anal. (%) Calc. for $C_{21}H_6ErF_{15}O_9$: C 29.52, H 0.71, Er 19.57; Found: C, 29.41, H 0.72, Er 19.50. UV-vis. (λ nm ($\varepsilon \times 10^{-3}$, M^{-1}cm^{-1}) in DMSO) 271 (4.23), 277 (3.51)

nm. FT-IR (KBr pellet, cm^{-1}) 3404, 2991, 2937, 1651, 1617, 1528, 1488, 1409, 1114, 1028, 996, 773, 749.

Synthesis of [Er(benzoate)$_3$(bipyridine)] (H5-8). To a mixture of benzoic acid (0.200 g, 1.637 mmol), bipyridine (0.255 g, 1.637 mmol) and KH (0.066 g, 1.654 mmol), 100 mL of THF was transferred through cannula and the suspension was stirred at room temperature for overnight. A suspension was formed during reaction with gas evolution. After the complete formation of salts, the methanol solution of anhydrous ErCl$_3$ (0.149 g, 0.545 mmol) in methanol (10 mL) was added dropwise to the reaction solution. After 2 days of stirring at room temperature, the resulting solution was filtered and removed solvents to give a white solid. The solid was sequentially washed with methanol, n-hexane and diethylether, and then dried to afford Er(benzoate)$_3$-(bipyridine) as a white soild (0.228 g, 0.332 mmol, 61%). Anal. (%) Calc. for $C_{31}H_{23}ErN_2O_6$: C 54.21, H 3.38, N 4.08, Er 24.35; Found: C, 54.25, H 3.42, N 4.01, Er 24.33. UV-vis. (λ nm ($\varepsilon \times 10^{-3}$, M^{-1}cm^{-1}) in DMSO) 279 (18.45) nm. FT-IR (KBr pellet, cm^{-1}) 3060, 1640, 1600, 1540, 1410, 1310, 1181, 1160, 1070, 1010, 860, 770, 720, 690, 670, 570, 430.

Synthesis of [Er(pentafluorobenzoate)$_3$(bipyridine)] (F5-8). Through the similar procedure for synthesis of **H5-8**, Er(pentafluorobenzoate)$_3$(bipyridine) as a white solid (0.185 g, 0.193 mmol, 61%) was prepared from the reaction of ErCl$_3$ (0.086 g, 0.314 mmol) in methanol (10 mL) with pentafluorobenzoic acid (0.200 g, 0.943 mmol), KH (0.037 g, 0.943 mmol) and bipyridine (0.147 g, 0.943 mmol) in THF (100 mL). Anal. (%) Calc. for $C_{31}H_8ErF_{15}N_2O_6$: C 38.92, H 0.84, N 2.93, Er 17.48; Found: C, 39.12, H 0.97, N 2.75, Er 17.35. UV-vis. (λ nm ($\varepsilon \times 10^{-3}$, M^{-1}cm^{-1}) in DMSO) 283 (19.94) nm. FT-IR (KBr pellet, cm^{-1}) 3100, 2930, 1650, 1610, 1600, 1490, 1400, 1320, 1300, 1110, 1070, 1000, 940, 770, 700, 650, 510.

Photophysical Property Measurement. Photoluminescence spectra were measured by steady-state fluorimeter (Edinburgh FS920) with 450 W Xe-lamp (295 or 320 nm), He-Cd laser (325 nm), and Ar-ion laser (488 nm). The excitation light selected by 300 mm focal length monochromator was focused on the sample. The fluorescence

from the sample was collected and refocused to the emission monochromator with 300 mm focal length. Visible emission spectra were taken with a PMT system (Hamamatsu R955) and near infrared emission spectra were taken with liquid nitrogen cooled Ge-detector (Edinburgh EI-L). The excitation laser powers were adjusted to the same value at the sample with neutral density (ND) filters. All spectra were taken at room temperature.

Results and Discussion

Er(III)-chelated prototype complexes were carried out through the ligand-exchange reaction using ErCl₃. At first, the salts of benzoate or pentaflurobenzoate were prepared from the reaction of the organic ligands with KH in dry THF and then the corresponding salts of the ligands reacted with ErCl₃. The successful synthesis of Er(III)-chelated prototype complexes was proved by elementary analysis, thermal gravimetric analysis (TGA), FT-IR, absorption and emission spectroscopies. But, the paramagnetic properties of Er complexes do not permit NMR characterization of the model complex. FT-IR spectra of Er(III) carboxylate complexes showed two characteristic bands in the region of 1650-1604 and 1418-1395 cm⁻¹ (see Figure 1).[14]

As seen from Figure 2, at least three H_2O molecules coordinated in the unsaturated 6-coordinated complexes **H5-**
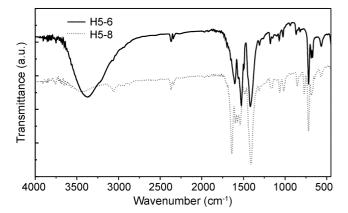

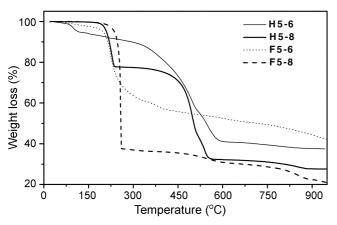
Figure 1. FT-IR spectra of **H5-6** and **H5-8**.

Figure 2. TGA traces of **H5-6**, **H5-8**, **F5-6** and **F5-8**.

6 and **F5-6**, which was confirmed by determining the releasing water amount of 6% up to 190 °C in atmospheric condition in a TGA trace. However, the 8-coordinated Er(III)-chelated complex **H5-8** shows two obvious weight loss processes in TGA curve. The first one with the weight loss of 23% is assigned to the releasing of bipyridine from 170 °C to 237 °C, and the second one is assigned to the loss of benzoate ligands up to *ca.* 550 °C. The 8-coordinated Er(III)-chelated complex **F5-8** also shows one weight loss process in TGA curve, all pentafluorobenzoate and bipyridine liagnds are simultaneously released from 170 °C to 260 °C. Therefore, 8-coordinated model complexes **H5-8** and **F5-8** showed no releasing water up to 170 °C, indicating that 8-coordinated model complexes contain no coordinated H_2O molecules. Here, for the first time to our knowledge, the first inert, saturated 8-coordinated Er(III)-chelated complexes of Er(benzoate)₃(bipyridine) **H5-8** and Er(pentafluorobenzoate)₃(bipyridine) **F5-8** were investigated. It is also very important for the formation of inert, saturated erbium complexes to get a higher near IR emission (see below).

The absorption spectra of 8-coordinated prototype complexes **H5-8** and **F5-8** show a very intense absorption band at 310 nm, which is attributed to π-π^* electronic transition, respectively. The emission spectra of all compexes at the selected photoexcitation wavelength exhibit the emission bands in the near IR region of 1.470-1.630 μm, which are assigned to the characteristic $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition of trivalent erbium ions. Figure 3 shows the the emissoin spectra of the 6- and 8-coordinated complexes at the photoexcitation wavelength of 295 or 320 nm. The saturated 8-coordinated complexes show much stronger PL intensity than that of the unsaturated 6-coordinated complex as shown in Figure 3. The similar result was obtained in a previous report.[9] The excitation spectra of the 8-coordinated prototype complexes (**H5-8** and **F5-8**), monitored at the maximum emission band, show a strong maximum band at 335 nm in the utraviolet region, whereas the excitation
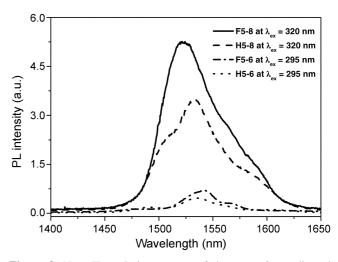

Figure 3. Near IR emission spectra of the 6- or 8-coordinated model complexes for **F5-8** at λ_{em} = 320 nm, **H5-8** at λ_{em} = 320 nm, **F5-6** at λ_{em} = 295 nm, and **H5-6** at λ_{em} = 295 nm in a solid state. Here, the λ_{ex} means the excitation wavelength.
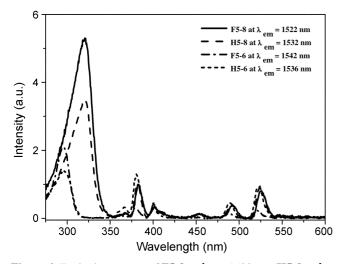
Figure 4. Excitation spectra of **F5-8** at λ_{em} = 1522 nm, **H5-8** at λ_{em} = 1532 nm, **F5-6** at λ_{em} = 1542 nm, and **F5-6** at λ_{em} = 1536 nm in solid state. Here, the λ_{em} means the emission wavelength.

spectra of the 6-coordinated complexes of **H5-6** and **F5-6** exhibit the bands at 295 nm (see Figure 4). Also, the several additional excitation bands were exhibited in the region of 350-550 nm. These excited bands are consistent with the absorption bands of erbium ions.[1,8] Thus, these excited bands correspond to the absorption bands of the inherent Er(III) ion. With these results, it should be noted to spectrally visualize that the energy transfer between the excited organic ligand and the ground erbium ion takes place (Figure 3 & 4).

Figure 5 shows the near IR emission bands of the 6-coordinated and 8-coordinated prototype complexes, corresponding to the characteristic $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition of trivalent erbium ions taking place at 1.53 μm, upon a photoexcitation wavelength of 325 or 488 nm. Here, upon the photoexcitation wavelength of 325 nm, the energy transfer process between the excited ligand and Er ion takes
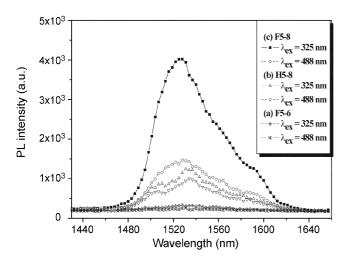

Figure 5. Near IR emission spectra of the 6- or 8-coordinated model complexes for (a) **F5-6**, (b) **H5-8**, and (c) **F5-8** in a solid state.

place possibly to generate the emission of the central lanthanide ion (Er ion), while, upon the photoexcitation wavelength of 488 nm, the emission of the inherent lanthanide ion (Er ion) was obtained through the direct excitation of Er ion without the energy transfer process between the excited ligand and Er ion. The saturated 8-coordinated complexes show much stronger PL intensity than that of the unsaturated 6-coordinated complex as shown in Figure 5, in which the highly coordinated lanthanide-chelated complexes (at least 8 to 9 coordination) have the higher PL efficiency than the unsaturated lanthanide-chelated complexes (6 coordination).[9] In the latter complex, at least three H_2O molecules coordinated in the unsaturated 6-coordinated complexes seriously quenched the near IR emission by the harmonic vibration relaxation decay of O-H bonds in these H_2O molecules. It reduces greatly the intensity of the near IR emission. Also, the saturated 8-coordinated complexes, obtained with a photoexcitation wavelength at 325 nm, exhibit much higher PL intensity than that obtained from the direct photoexcitation of Er ions with 488 nm by 80 times.

$$W_{MPR} = W_o \exp\left[-\frac{\Delta E}{h\omega}\left(\ln\frac{\Delta E}{h\omega}\ \frac{1}{g(n+1)} - 1\right)\right] \qquad (1)$$

Furthermore, we have investigated the influence of C-F bonds on near IR emission by comparing the PL intensity of a 8-coordinated model complex with C-F bonds (**F5-8**) with that of a 8-coordinated model complex with C-H bonds (**H5-8**). The PL intensity at the near IR emission is proportional to the density of excited ions in the upper energy level ($^4I_{13/2}$). The higher the excited ion density increases, the stronger the PL intensity at the near IR emission obtains. Therefore, it is necessary to enhance the excited ion density in upper energy level for getting the stronger near IR emission intensity. The excited ion density in the upper energy level ($^4I_{13/2}$) strongly depends on the multi-phonon relaxation process. The multi-phonon relaxation process is one of the nonradiative transitions, where the photon energy is absorbed by the harmonic vibration motion to convert to the thermal energy, instead of light emission. The probability for the multi-phonon relaxation (W_{MPR}) is related to the energy difference (ΔE) between the upper level and the lower level, as given in eq. (1), where g and n are the bond constant of electron-lattice and Bose-Einstein distribution function, respectively.[15] If the energy difference (ΔE) decreases, W_{MPR} exponentially increases. When the harmonic vibration energy ($h\omega$) of the material matrix decreases, W_{MPR} also decreases exponentially.

In the case of the Er^{3+} ions, the energy difference (ΔE) between the upper level ($^4I_{13/2}$) and the nearest lower level ($^4I_{15/2}$) corresponds to the wavenumber of 7,000 cm^{-1} (or the wavelength of 1.53 μm). Er(III)-cored model complex with C-F bond has a very low W_{MPR}, because the harmonic vibration energy ($h\omega$) of the C-F bonds is much lower than this energy difference. However, in Er(III)-cored benzoate complex, the harmonic vibration energy of C-H overtone bands is similar to the energy difference (ΔE) of 7,000 cm^{-1}.

Therefore, it causes the increase of W_{MPR}, thus decreases the near IR emission intensity. In line with this reason, Figure 5 shows that F5-8 has much stronger PL intensity than that of H5-8 by four times. In this paper, our main material efforts have been focused on developing the new synthetic methodolgy of the inert, saturated Er complexes and investigating important key parameters for near IR emission enhancement. The new synthetic methodolgy opens the development of a series of novel lanthanide-cored nanophotonics systems based on porphyrins, and naphthalenes with highly efficient light-harvesting effect.[1,10]

Conclusion

We have synthesized the Er(III)-chelated prototype complexes based on benzoate derivatives through a new synthetic strategy developed in our laboratory and investigated the important key parameters for near IR emission enhancement. The saturated 8-coordinated Er(III) complexes exhibit stronger near-IR emission bands than those of the unsaturated 6-coordinated Er(III) complexes, obtained from the direct photoexcitation of Er ions with 488 nm. At least three H_2O molecules coordinated in the unsaturated 6-coordinated complexes seriously quenched the near IR emission by the harmonic vibration relaxation decay of O-H bonds in these H_2O molecules. It reduces greatly the intensity of the near IR emission, which takes place from the first excited state ($^4I_{13/2}$) to the ground state ($^4I_{15/2}$) at 1.53 μm. Also, the stronger emission band of the Er(III) complex was obtained by the indirect photoexcitation of ligands rather than by the direct photoexcitation of the Er(III) ions. It could be explained by the energy transfer between PL emission band of ligands and absorption band of erbium ion. The saturated Er(III)-chelated complex with C-F bonds shows much stronger near IR emission than the saturated Er(III)-chelated complex with C-H bonds. It is attributed to the influence of C-F bonds on near IR emission intensity.

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