Molecular Design and Photophysical Criteria for Lanthanide Emission Enhancement in Erbium(III)-Cored Complexes Based on Dendritic Ligands for Information Technology

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Introduction

Recently, luminescent lanthanide complexes have considerable interest because of their academic interests and potential utility in a wide variety of photonic applications, such as planar waveguide amplifiers, plastic lasers, light-emitting diodes, and luminescent probes.[1-5] The $4f$ electrons in lanthanide (Ln^{3+}) ions are slightly perturbed by the effects of lattice phonons and static strain fields in the coordination environment of ions, since the f-electrons are shielded by the outer $5s$ and $5p$ electrons. It leads to the sharp spectral line-like emission bands. Also, the forbidden $4f^n$-$4f^n$ electronic transitions renders the low absorption and emission cross-section of lanthanide ions, while luminescent lifetime is relatively long. To overcome these shortcomings, recently, luminescent ligands are being used to excite Ln^{3+} ions via an energy transfer from the luminescent ligands to the Ln^{3+} ions. In most cases,[2-17] the luminescent Ln^{3+} ions are usually coordinated to the organic luminescent ligands, acting as sensitizers or antenna chromophores, which efficiently absorb and transfer light to excite Ln^{3+} ions via energy transfer process.[6,7] This sensitization process is much more effective than the direct excitation of Ln^{3+} ions, since the absorption coefficients of organic chromophores are many orders of magnitude larger than the intrinsically low molar absorption coefficients (typically 1-10 M^{-1} cm^{-1}) of Ln^{3+} ions.

Recently, several research groups have focused on developing the efficient artificial light-harvesting (LH) lanthanide complexes, in which the use of dendrimers for light harvesting systems has been widely demonstrated.[8-16] The encapsulation of luminescent Ln^{3+} ions into a luminescent dendrimer can lead to a system capable of shielding central Ln^{3+} ion from nonradiative environment and efficiently transferring excited energy from the peripheral chromophores to the focal point of the dendrimer. For example, Fréchet et al. have reported the site isolation and antenna effects on luminescent properties of spherical lanthanide(III)-cored dendrimer complexes.[8,11,16] Although its spectral overlap integral (J) between the emission band of peripheral antenna and the absorption band of Ln^{3+} ions was not satisfactorily large to obtain the effective energy transfer, the Fréchet aryl-ether typed dendrons were widely used as light-harvesting antenna.[8,11]

Moreover, very recently, to enhance the near-infrared (NIR) emission intensity and maintain the effective energy transfer process, our research efforts have been focused on developing stable and inert Er(III)-encapsulated complexes with artificial light-harvesting systems using dendritic luminescent ligands based on metalloporphyrins,[17] naphthalenes,[18] and anthracenes[19] bearing the Fréchet aryl-ether dendrons, namely, (Er^{3+}-[Gn-Pt-Por]$_3$(terpy), Er^{3+}-[Gn-Naph]$_3$(terpy) and Er^{3+}-[Gn-An]$_3$(terpy)). We observed that the NIR emission intensity of the lanthanide complexes was dramatically enhanced with increasing the generation number (n) of the Fréchet aryl-ether dendrons, due to the site-isolation and light-harvesting effects.

Two possible energy transfer (ET) pathways for the sensitized emission in luminescent Ln(III) complexes have been suggested, as schematically illustrated in Scheme 1. It is well-believed that in general only energy transfer from the
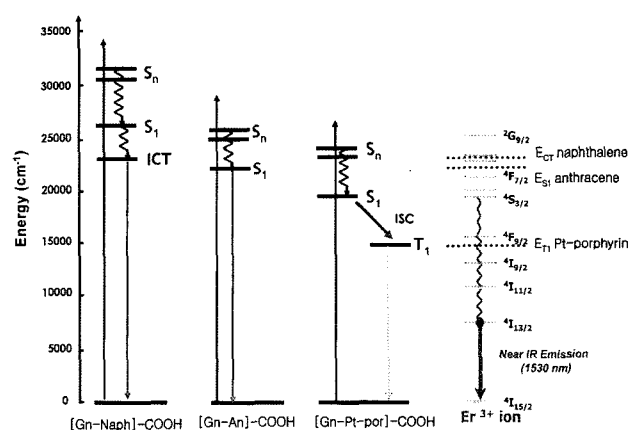
Scheme I. Schematic diagram of the photophysical processes leading to sensitized luminescence of Er^{3+}-[G2-An]$_3$(terpy), Er^{3+}-[G2-Naph]$_3$(terpy), and Er^{3+}-[G2-Pt-Por]$_3$(terpy).

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triplet state of luminescent ligands, which is converted from the excited singlet state via the intersystem crossing process caused by the heavy lanthanide ion effect, to Ln^{3+} ion, is the most dominant mechanism (ETt).[20] Therefore, most researches towards lanthanide ion sensitizers have been focused on developing the luminescent ligands containing chromophores with a triplet state matching the receiving lanthanide ion energy level to maintain efficient energy transfer from the triplet state to Ln^{3+} ion. Interestingly, however, several reports mentioned the energy transfer from the excited singlet state to Ln^{3+} ion (ETs).[21] Very recently, we reported all possible ET pathways using Pt(II)-porphyrin[17b] as well as β-diketone (ETt),[22] anthracene ligands (ETs),[19] and demonstrated the unusual ET pathway through the intramolecular charge transfer state (ICT) of the naphthalene ligand to Ln^{3+} ion (ETc) for the first time (see Scheme I).[23] Even though efficient energy transfer pathways are very important in advanced photonics technology, particularly for the development of new and useful luminescent Ln(III) complexes with efficient Ln^{3+} emission, efficient ET pathways have not yet been understood clearly. Therefore, the ET efficiency comparison for all three ET pathways should necessarily be investigated towards the exploration of the mostly dominant ET pathway among them for the highly efficient Ln^{3+} emission.

In this article, we deal with recent progress in Er(III)-cored complexes based on dendritic ligands for information technology. Moreover, we focus on discussing the photophysical properties of Er(III)-cored complexes based on anthracene, naphthalene and metalloporphyrin bearing the second generation Fréchet aryl-ether dendron (Er^{3+}-[G2-An]$_3$(terpy), Er^{3+}-[G2-Naph]$_3$(terpy) and Er^{3+}-[G2-Pt-Por]$_3$(terpy)) in order to establish the design and photophysical criteria of lanthanide emission enhancement in the Er(III)-cored dendrimer complexes for efficient energy transfer pathways.

Experimental

General Measurements. ¹H-NMR spectra were recorded with the use of Varian Oxford 300 MHz spectrometers. Chemical shifts were reported in ppm units with tetramethylsilane as an internal standard. Infrared spectra were measured on KBr pellets using a Perkin-Elmer Spectrometer. The mass spectra were taken by a JEOL JMS-AX505WA mass spectrometer. MALDI-TOF-MS spectrometry was performed on a Voyager-DETM STR Biospectrometry. The elemental analyses were carried by means of EA1110 (CE Instrument). UV-visible absorption spectra were recorded by a Shimadzu UV-2401PC spectrophotometer and photoluminescence spectra were measured by steady-state fluorimeter (Edinbugh Instruments FS920) with 450 W Xe lamp. The excitation light from 300 mm focal length monochromator was focused on the sample. The luminescence signal from the sample was collected and refocused to the

emission monochromator with 300 mm focal length. The luminescence spectra in visible region were taken with a PMT system (Hamamatsu R955) and the luminescence spectra in near infrared region were taken with Ge-detector (Edinburgh Instruments EI-L) cooled by liquid nitrogen. All spectra were taken at the room temperature. To collect the PL decay signal from the samples, a hand-made luminescence system was used. The pump wavelength was selected to 355 nm from the ns-Nd : YAG laser system with a third-harmonic generation. The laser output has ~5 ns pulse width with a repetition rate of 10 Hz. For Er^{3+}-(Gn-Pt-Por)$_3$(terpy), the pump laser pulse wavelength was modulated by the hydrogen gas filled Raman shifter. The final pump laser pulse wavelength was selected to 416 nm. The luminescence signals were focused on the monochromater with 300 mm focal length and were taken with a PMT system (Hamamatsu R928). The electric output signals were collected with a digital oscilloscope system (Agilent Infinium 54832B).

Thin Film Preparation. A transparent film of dendritic ligands and their Er(III) complexes were prepared by spin-coating method. The solution contains about 3% compounds by weight in 1,2-dichloroethane. Uniform and pin-hole free films with the thickness of about 350 nm were easily obtained.

Synthesis of Ln³⁺-[G2-ligand-COO]₃(terpy). *General Procedure*: A mixture of G2-ligand-CO$_2$H (3 equiv), and KH (3.3 equiv.) was stirred in freshly distilled THF at room temperature for overnight until there was no more H$_2$ gas to generate. After the completion of salts, the methanol solution of anhydrous ErCl$_3$ (1 equiv.) and 2,2' : 6',2''-terpyridine (1.1 equiv.) was added to the reaction solution, and then stirred for 2 days. The resulting solution was filtered and the solvents were removed. The resultant solid was washed sequentially with methanol, and diethyl ether. The complexes all gave similar IR spectra. Experimental evidences for the proposed structures were provide by FT-IR and elemental analysis of the Er^{3+}-[G2-ligand-COO]$_3$(terpy).

Er^{3+}-[G2-Pt-por]$_3$(terpy) was prepared in the same manner as a orange solid in the yield of 72%. FT-IR (KBr) [cm⁻¹]: 1595, 1505, 1455, 1375, 1240, 1155, 1055, 835, 735; Anal. Calcd for C$_{591}$H$_{470}$N$_{15}$O$_{69}$Er: C, 73.64; H, 4.91; N, 2.18; Er, 1.74, found: C, 73.93; H, 5.05; N, 2.15; Er, 1.78. UV-vis (THF): λ_{max} (log ε) 279 (5.0538), 406 (5.8575), 512 (4.8615), 539 (4.0334).

Er^{3+}-[G2-An]$_3$(terpy) was prepared in the same manner as a yellowish solid in the yield of 73%. FT-IR (KBr) [cm⁻¹]: 1595, 1510, 1419, 1238, 1154, 1053, 829, 735; Anal. Calcd for C$_{243}$H$_{188}$N$_3$O$_{27}$Er: C, 77.84; H, 5.05; N, 1.12; Er, 4.46. found: C, 77.93; H, 5.25; N, 1.15; Er, 4.53.

Er^{3+}-[G2-Naph]$_3$(terpy) was prepared in the same manner as a yellowish solid in the yield of 52%. FT-IR (KBr) [cm⁻¹]: 1598, 1416, 1238, 1156, 1052, 829, 788, 740; Anal. Calcd

for $C_{231}H_{182}N_3O_{27}Er$: C, 77.09; H, 5.10; N, 1.17; Er, 4.65; found: C, 76.65; H, 5.64; N, 0.96; Er, 4.82.

Results and Discussion

In our previous reports, some of the key parameters, governing the enhancement of the near IR emission in luminescent lanthanide complexes, are the type of luminescent lanthanide complexes such as a direct complex or an indirect complex as well as the coordination number of lanthanide ions with the complexed ligands[1,23,24] : (1) The direct luminescent Ln(III) complexes have much higher PL efficiency than the indirect luminescent Ln(III) complexes, due to much higher intersystem crossing (ISC) efficiency in the direct complex.[23] Our direct complexes possess a naphthalene group directly linked to phenyl group in benzoic acid with the π-conjugation interaction between a naphthalene unit and a benzoic acid unit. But, the indirect complex has a naphthalene group indirectly linked to phenyl group in benzoic acid with no π-conjugation interaction between them, in which the -OCH$_2$- group plays a role as a blocking group to interrupt the π-conjugation interaction between them. As a result, the indirect complex does not have an external heavy atom effect which is induced by the heavy and paramagnetic lanthanide ion. (2) Highly coordinated lanthanide-cored complexes (at least 8 to 9 coordination number) have much higher PL efficiency than unsaturated 6-coordinated complex.[1,25] Therefore, 2,2' : 6',2"-terpyridine unit used in this paper may be expected to effectively block luminescent deactivating molecules, leading to the formation of 9-coordinated, direct Ln(III)-cored complexes.

Here, we demonstrate that the stable and inert Er(III)-encapsulated complexes based on anthracene, naphthalene and metalloporphyrin ligands bearing a second generation Fréchet aryl-ether dendron exhibit strong near-IR emission bands, by taking the efficient light-harvesting effect, in which a highly efficient energy transfer process takes place from the fluorescent excited states of the peripheral antenna through luminescent anthracene or metalloporphyrin ligands to Er^{3+} ions. The chemical structures of dendritic anthracene, naphthalene and Pt(II)-porphyrin ligands and their stable, inert and direct lanthanide(III)-encapsulated complexes are shown in Scheme II.

In FT-IR spectra, the characteristic bands of the carboxylic acid group for all dendritic ligands exhibit around 1690 cm^{-1}. In comparison with these ligands, all spectra for Er(III)-cored dendritic complexes are very similar with two characteristic bands in the region of 1600-1400 cm^{-1}, asymmetric (~1600 cm^{-1}) and symmetric (~1400 cm^{-1}) stretching vibration mode of the carboxylate group. It indicates that the carboxylic acid group was converted into carboxylate anion as a result of the formation of the stable Er(III)-cored complexes.[26] But, the paramagnetic properties of the lanthanide
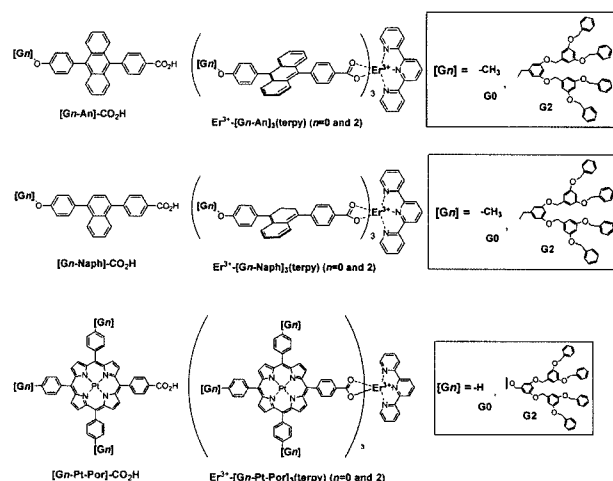
Scheme II. The chemical structures of Er(III)-cored complexes based on dendritic anthracene, naphthalene, and Pt-porphyrin ligands.

ion do not permit NMR studies of the luminescent lanthanide complexes. UV-vis absorption and photoluminescence spectra of a series of [Gn-An]-CO$_2$H, [Gn-Naph]-CO$_2$H, and [Gn-Pt-Por]-CO$_2$H (n = 0 and 2) in solutions are shown in Figure 1. The molar extinction coefficient or absorbance of the Fréchet aryl-ether typed dendron, appearing at 290 nm, increased with the generation number n of dendrons. This phenomenon is in an excellent agreement with the previous results in the literature due to the cooperative effect in the dendrons.[10]

The absorption spectra of all dendritic ligands exhibited no significant red-shift of the ligand absorption bands with increasing the generation number of 0 to 2, indicating that there is no π-electron interaction between the aryl-ether dendron and the ligand unit. Also, in Figure 1, the fluorescence of the G2-aryl ether dendron in the dendritic ligands was totally quenched when they were excited at 290 nm of the dendron absorption band. However, a significant decrease in G2-aryl ether fluorescence is accompanied by a strong increase in the fluorescence intensity of anthracene or Pt(II)-porphyrin units according to a growing number of generation in [G2-An]-CO$_2$H or [G2-Pt-Por]-CO$_2$H, except for [G2-Naph]-CO$_2$H. These results indicate that a highly efficient energy transfer from the aryl ether dendron to anthracene or Pt-poryrin moiety takes place. We also observed that the excitation spectra of the aryl-ether dendritic ligands, monitored around the maximum wavelength of anthracene, naphthalene or Pt(II)-porphyrin moiety, are very similar to their absorption spectra. It suggests that the ground state and the excited state of the aryl-ether dendritic ligands based on anthracene, naphthalene or Pt(II)-porphyrin ligands of [G2-An]-CO$_2$H, [G2-Naph]-CO$_2$H, or [G2-Pt-Por]-CO$_2$H, have a same chemical structure. The Er(III)-
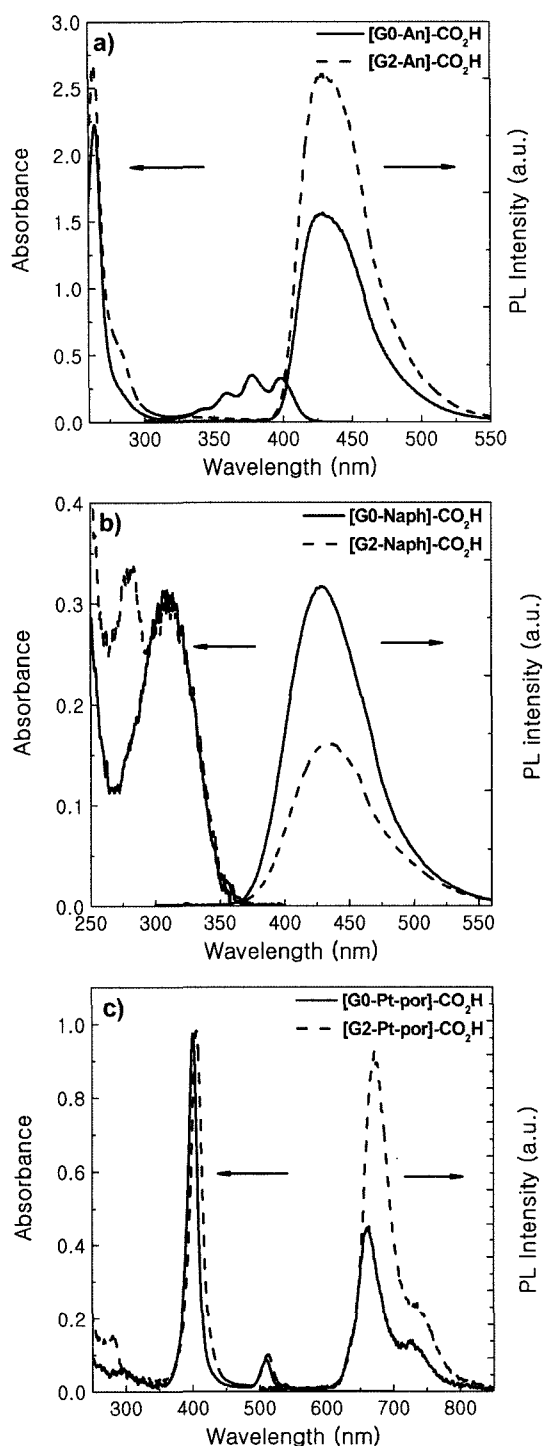
Figure 1. UV-vis absorption and photoluminescence spectra (upon photoexcitation at wavelength of 290 nm) of [Gn-An]-CO$_2$H (n = 0 and 2) in DMSO (2.0 × 10^{-5} M) (a), [Gn-Naph]-CO$_2$H (n = 0 and 2) in acetonitrile (2.0 × 10^{-5} M) (b), and [Gn-Pt-Por]-CO$_2$H (n = 0 and 2) in THF (1.0 × 10^{-6} M) (c).

cored dendritic complexes of Er^{3+}-[G2-An]$_3$(terpy), Er^{3+}-[G2-Naph]$_3$(terpy), and Er^{3+}-[G2-Pt-Por]$_3$(terpy), have simi-

lar UV-vis absorption phenomena to the corresponding dendritic ligand, in which the absorbance of the Fréchet aryl-ether typed dendrons increased with the generation number n of dendrons at 290 nm and the absorbance of the ligand moiety was exhibited to remain constant, as shown in Figure 1.

Surprisingly, very recently, our photophysical results suggested that the site-isolation effect was dominant over the light-harvesting effect in the series of Er^{3+}-[Gn-An]$_3$(terpy) as well as Er^{3+}-[Gn-Pt-Por]$_3$(terpy) (see Scheme III), even though the present Er(III)-cored dendrimer systems consist of lanthanide(III)-cored supramolecular complexes and light-harvesting dendritic photon antenna with a cascade-typed energy gradient from the light-harvesting dendrons through luminescent ligands to Er^{3+} ions.[17,19] As a result, the aryl ether-typed dendrons are not effective to sensitize Er^{3+} luminescence through Pt(II)-porphyrin units by LH effect, but are able to shield Er^{3+} ion, so-called, the site-isolation effect. It is considered to be due to the intrinsically low quantum yield of aryl-ether dendron (Φ_f = 0.02) for exciting Pt(II)-porphyrin or anthracene units. In other words, aryl ether-typed dendrons in the dendritic ligands do not effectively sensitize the Er^{3+} luminescence through ligand units by LH effect, but, they provide the efficient site-isolation effect enough to shield central Ln^{3+} ion from nonradiative environment as well as prevent the intermolecular interaction between Er^{3+} ions, which limits near IR intensity. Thus, this site-isolation effect can allow the present systems to significantly enhance the near IR emission intensity as a function of the generation number of aryl ether-typed dendrons in thin films.

Upon the excitation wavelength of 357 nm for anthracene ligand, 310 nm for naphthalene ligand or 410 nm for Pt-porphyrin ligand, at which only anthracene, naphthalene or Pt(II)-porphyrin moiety absorbs, the fluorescence of anthracene, naphthalene or Pt(II)-porphyrin moiety is strongly quenched in the lanthanide complexes (see Figure 2).

As a result, a strong decrease of the fluorescence quantum yield of at least 77% in anthracene ligand, 90% in naphthalene ligand, and 77% in Pt(II)-porphyrin ligand, respectively, as quantitatively compared the emission intensity in the visible region of each dendritic ligand with the corresponding Er(III)-cored dendritic complex, is accompanied by a strong increase in the near-IR emission of the Er^{3+} ion. It could be attributed to the efficient energy transfer process between dendritic ligand and Er^{3+} ion, since the spectral overlap integral between the emission band of each luminescent moiety and the absorption bands of Er^{3+} ion is sufficiently large (see Figure 3).

All Er(III)-cored dendrimer complexes showed strong near-IR emission bands at 1530 nm, originated from 4f-4f electronic transition of the first excited state (^{4}I$_{13/2}$) to the ground state (^{4}I$_{15/2}$) of the partially filled 4f shell. The emis-
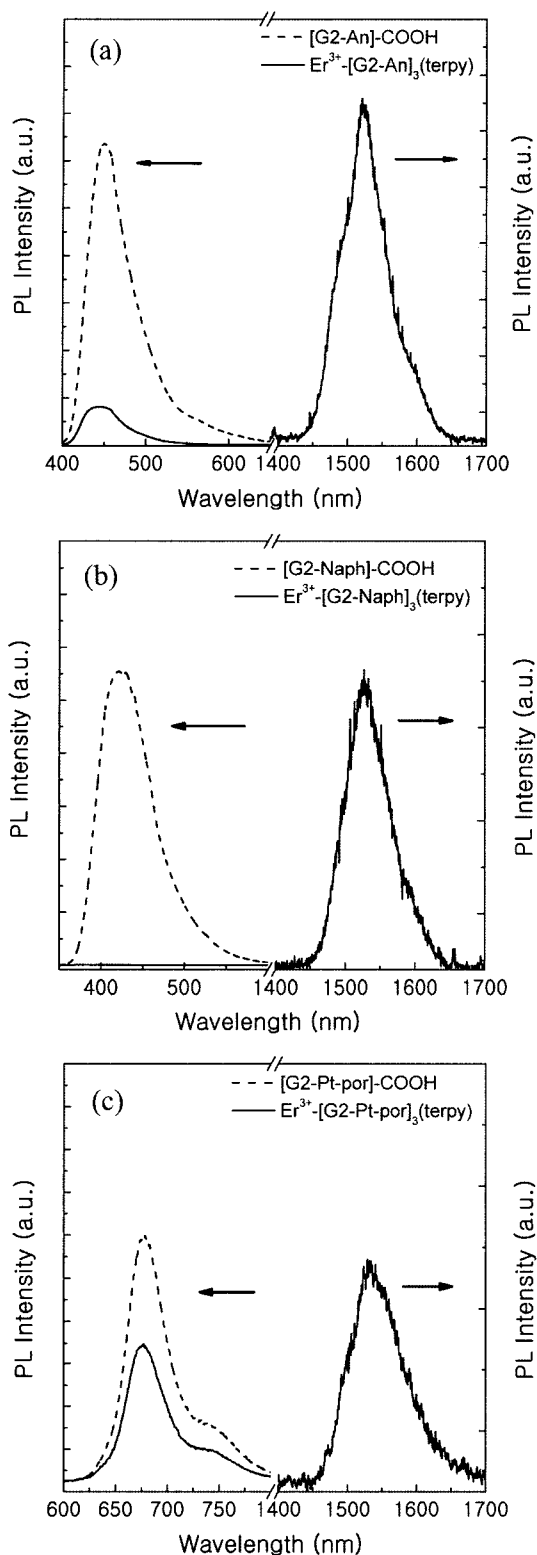
Figure 2. Photoluminescence spectra of [G2-An]-CO$_2$H and Er^{3+}-[G2-An]$_3$(terpy) (a), [G2-Naph]-CO$_2$H and Er^{3+}-[G2-Naph]$_3$(terpy) (b), and [G2-Pt-Por]-CO$_2$H and Er^{3+}-[G2-Pt-Por]$_3$(terpy) (c) in thin film, upon photoexcitation of the ligand at the absorption maximum wavelength.
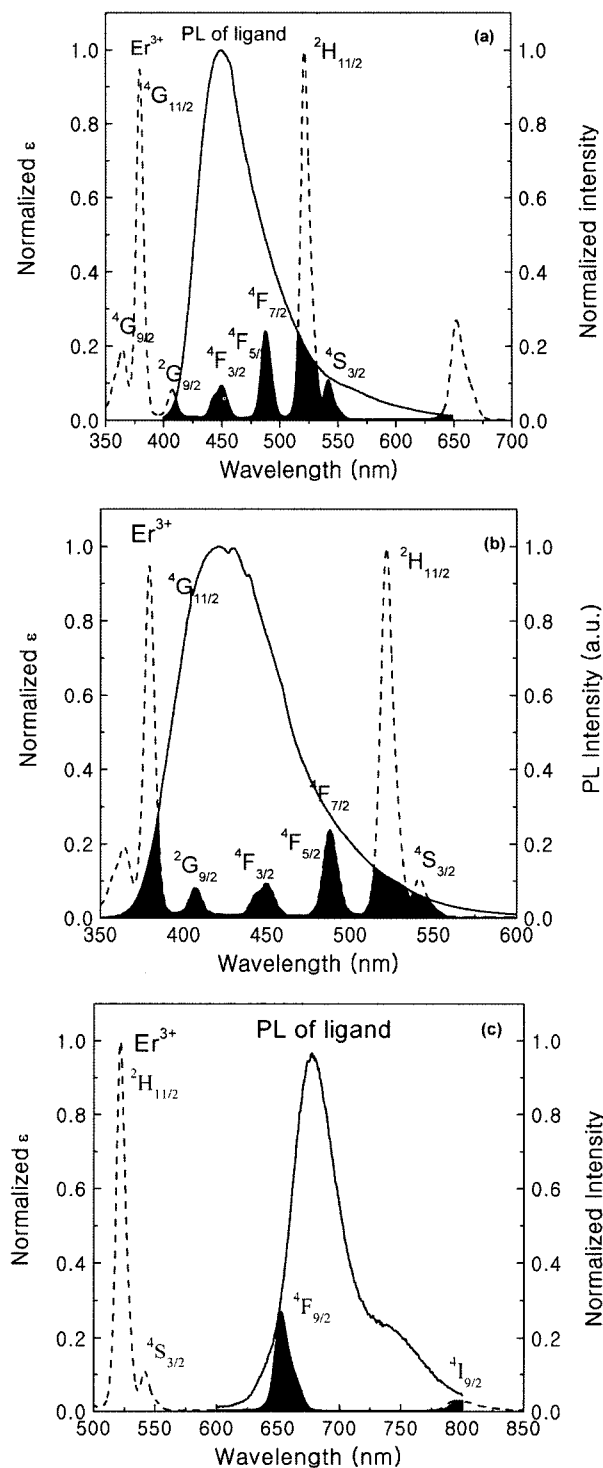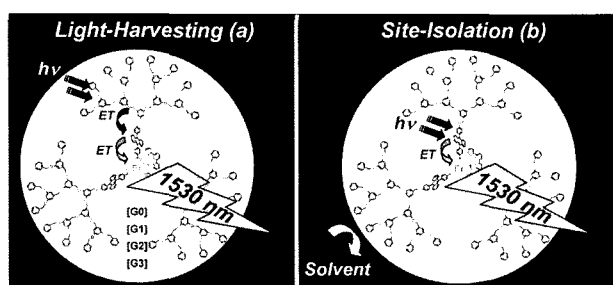
Figure 3. UV-vis absorption and photoluminescence spectra of anthracene (a) in DMSO solution, naphthalene (b) in acetonitrile solution, Pt-porphyrin dendritic units (c) in THF solution (solid), and UV-vis absorption spectrum of ErCl$_3$ (dashed line).

sion intensity of the lanthanide complexes was dramatically enhanced with increasing the generation number n of the

Scheme III. Distinction between light-harvesting effect (a) and site-isolation effect (b) in a series of lanthanide(III)-cored complexes containing light-harvesting dendritic antenna with a cascade-typed energy gradient.

dendrons, due to the site-isolation effect. For example, the emission intensity of Er^{3+}-[G2-An]$_3$(terpy) was 25 times stronger than that of Er^{3+}-[G0-An]$_3$(terpy) (see Figure 4). As a result, aryl-ether typed dendritic ligand renders the efficient site-isolation effect enough to prevent intermolecular interaction between Er^{3+} ions, which limits near-IR intensity.

On the other hand, we explore the photophysical criteria for lanthanide emission enhancement for three present Er(III)-cored dendritic complexes, as summarized in Table I. The Er(III)-cored dendritic complex of Er^{3+}-[G2-An]$_3$(terpy) exhibits the stronger PL intensity than the Er(III)-cored dendritic complex of Er^{3+}-[G2-Naph]$_3$(terpy) or the Er(III)-cored dendritic complex of Er^{3+}-[G2-Pt-Por]$_3$(terpy) by 1.6 or 8.3 times, respectively, upon photoexcitation of the ligand at the absorption maximum wavelength (see Figure 4 and Figure 5). It may be due to the fact that the anthracene ligand in Er^{3+}-[G2-An]$_3$(terpy) has a higher spectral overlap integral (J) value and a higher luminescence quantum efficiency than naphthalene moiety or Pt(II)-porphyrin ligand in Er(III)-encapsulated dendrimer complexes. Accordingly to our previous photophysical studies, we reported that the sensitization of Ln^{3+} luminescence by energy transfer through the excited singlet state of anthracene ligand, by energy transfer through the excited intramolecular charge transfer state of naphthalene ligand, and by energy transfer through the excited triplet state of Pt(II)-porphyrin ligand occurs, respectively (see Scheme I).[17-19]

Also, our photophysical results indicate that the energy transfer pathway between the luminescent ligand and Ln^{3+} ion is not a crucial parameter in determining the overall quantum yield in the energy transfer system, since the sensitization of Ln^{3+} luminescence by energy transfer through the excited singlet state of anthracene ligands[19] takes place more effectively than by energy transfer through the excited triplet state of Pt(II)-porphyrin ligand[17b] or by energy transfer through the excited intramolecular charge transfer state of naphthalene ligand.[18]

To date, however, most recent researches towards Ln^{3+} ion sensitizers have been focused on developing the luminescent ligands containing chromophores with a triplet state matching the receiving Ln^{3+} ion energy level as follows: It is well-known that only the triplet state of the luminescent ligand is involved in photosensitization. The sensitization process of luminescent lanthanide complex is strongly affected by the subsequent intersystem crossing efficiency, and the energy transfer efficiency to lanthanide ion in the excited triplet state.[6,7]

The possibility of the energy transfer from the singlet state of the luminescent ligand was thought to be very low, because this process is usually too slow to compete with other processes such as luminescent ligand fluorescence and intersystem crossing (ISC). More interestingly, as depicted in Table I, the intrinsic quantum efficiency of the luminescent ligand, no matter what the energy transfer pathway between the luminescent ligand and Ln^{3+} ion is through the excited singlet or triplet states, is the more important parameter in determining the overall quantum yield in the energy transfer system, since the Er^{3+} ions can be excited via the anthracene moiety more effectively than via Pt(II)-porphyrin ligand or via the naphthalene moiety.

Conclusions

We present that the stable and inert Er(III)-encapsulated complexes based on anthracene, naphthalene, and Pt(II)-porphyrin ligands bearing a second generation Fréchet aryl-ether dendron (G2) exhibit much stronger near-IR emission bands at 1530 nm, originated from the 4f-4f electronic transition of the first excited state ($^4I_{13/2}$) to the ground state ($^4I_{15/2}$) of the partially filled 4f shell. A strong decrease of fluores-

Table I. Summary on Photophysical Results for Lanthanide Emission Enhancement in Luminescent Lanthanide Complexes

Material — Factor	ET Pathway	Rel. J^a	ET Efficiency	$\Phi_{lig.}$	Relative Intensity of Er(III)	τ_{obs}	$\Phi_{Ln.}$
Er^{3+}-(G2-An)$_3$(terpy)	Singlet	3.4	77%	0.77^b	8.33	1.8 μs	2.3×10^{-4}
Er^{3+}-(G2-Naph)$_3$(terpy)	CT	4.66	>90%	0.57^b	1.6	1.3 μs	1.6×10^{-4}
Er^{3+}-(G2-Pt-Por)$_3$(terpy)	Triplet	1	77%	0.45^c	1	1.65 μs	2.1×10^{-4}

^{a}Spectral overlap integral J value between ligand and erbium ion. ^{b}Fluorescence quantum efficiency in solution. ^{c}Phosphorescence quantum efficiency in solution at 77 K.
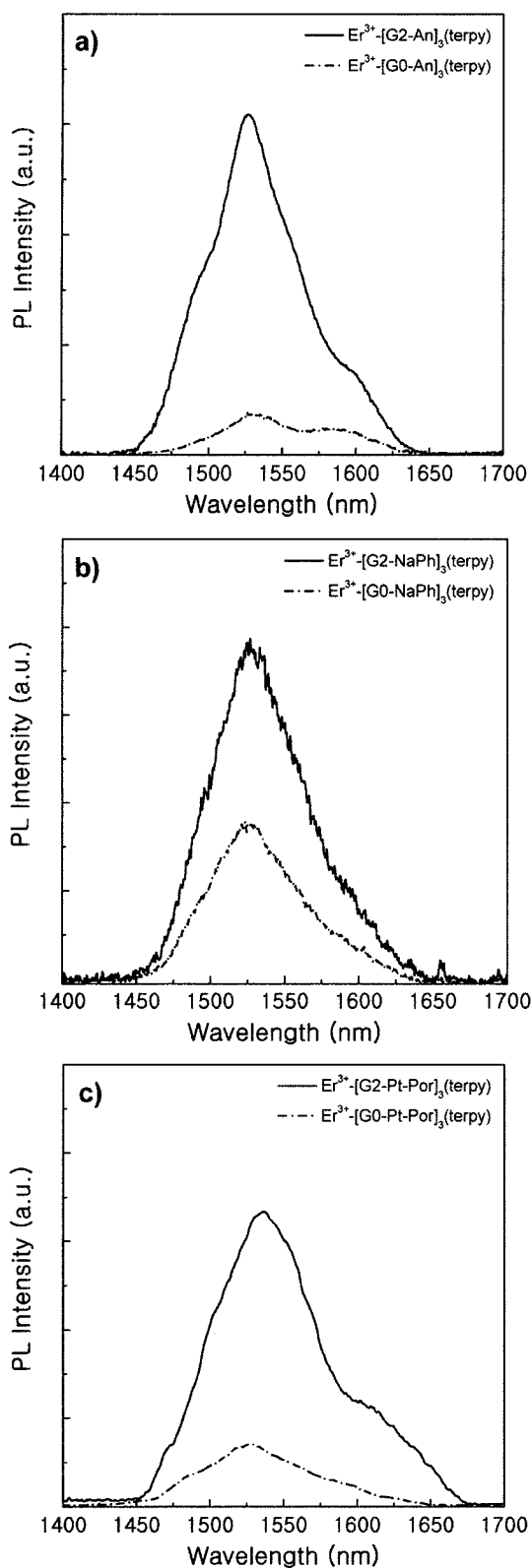
Figure 5. Near-IR emission spectra of Er^{3+}-[G2-An]$_3$(terpy), Er^{3+}-[G2-Naph]$_3$(terpy), and Er^{3+}-[G2-Pt-Por]$_3$(terpy) in thin film, upon photoexcitation of the ligand at the absorption maximum wavelength.

Figure 4. Near-IR emission spectra of Er^{3+}-[Gn-An]$_3$(terpy), Er^{3+}-[Gn-Naph]$_3$(terpy), and Er^{3+}-[Gn-Pt-Por]$_3$(terpy) (n = 0 and 2) in thin film, upon photoexcitation of the ligand at the absorption maximum wavelength.
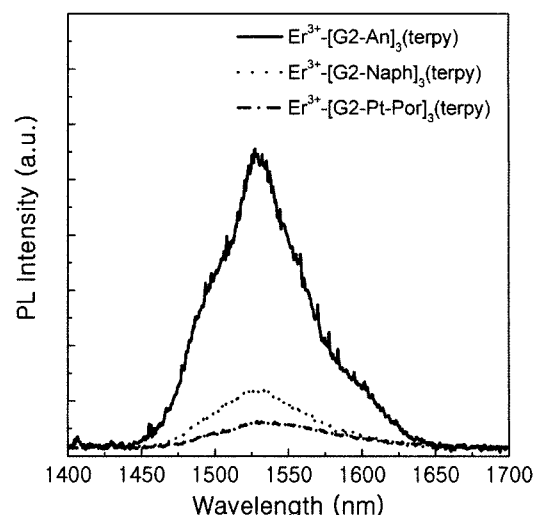
cence intensity of luminescent ligands, such as anthracene, naphthalene, and Pt(II)-porphyrin units, is accompanied by strongly increasing the near-IR emission of the Er^{3+} ions in Er(III)-encapsulated dendrimer complexes, upon photoexcitation of luminescent ligands at the corresponding absorption maximum wavelength. It could be attributed to the efficient energy transfer process occurring between dendritic luminescent ligand and Er^{3+} ion. The emission intensity of the lanthanide complexes, upon photoexcitation of luminescent ligand at the corresponding absorption maximum wavelength, was dramatically enhanced by introducing a second generation Fréchet aryl-ether dendron (G2), as compared with those of their corresponding Er(III)-encapsulated complexes, mainly due to the site-isolation effect. Surprisingly, our photophysical studies suggest that energy transfer pathway does not influence the lanthanide emission enhancement: Although ET process via the triplet state to Ln^{3+} ion is considered as main efficient ET pathway in Ln(III) complex, this sensitization process is not strongly dominated on Ln^{3+} emission, compared with other ET pathways via singlet or charge transfer state. In other words, the ISC process caused by the heavy Ln^{3+} ion effect in Ln(III) complexes is not dominant process over the ICT or the radiative relaxation process. Therefore, to enhance of the near-IR emission in luminescent lanthanide complexes, no matter which ET pathway takes place, the key parameters are the type of luminescent lanthanide complexes such as a direct complex or an indirect complex, the coordination number of lanthanide ions with the complexed ligands, the luminescence quantum efficiency of the ligand and the spectral overlap integral (J) value between the emission

band of the ligand and the absorption band of lanthanide ion: (1) The direct luminescent Ln(III) complexes have much higher PL efficiency than the indirect luminescent Ln(III) complexes. (2) Highly coordinated lanthanide-cored complexes (at least 8 to 9 coordination number) have much higher PL efficiency than unsaturated 6-coordinated complex. (3) The key factor for strong lanthanide emission is the ET efficiency between the organic ligand and Ln^{3+} ion, associated with the quantum yield of a ligand and a proper J value. This study can provide the criteria for designing the ligand to achieve efficient Ln^{3+} emission.

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