# Account

## Recent Progress in Luminescent Lanthanide Complexes for Advanced Photonics Applications

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We have designed and developed novel luminescent lanthanide complexes for advanced photonics applications. Lanthanide(III) ions ($Ln^{3+}$) were encapsulated by the luminescent ligands such as metalloporphyrins and naphthalenes. The energy levels of the luminescent ligands were tailored to maintain the effective energy transfer process from luminescent ligands to $Ln^{3+}$ ions for getting a higher optical amplification gain. Also, key parameters for emission enhancement and efficient energy transfer pathways for the sensitization of $Ln^{3+}$ ions by luminescent ligands were investigated. Furthermore, to enhance the optophysical properties of novel luminescent $Ln^{3+}$ complexes, aryl ether-functionalized dendrons as photon antennas have been incorporated into luminescent $Ln^{3+}$ complexes, yielding novel Ln(III)-cored dendrimer complex. The novel Ln(III)-cored dendrimer complex has much higher PL intensity than the corresponding simple complex, due to the efficient site-isolation effect. In this article, we will deal with recent progress in the synthesis and photophysical studies of inert and stable luminescent $Ln^{3+}$ complexes for advanced photonics applications. Also, our review will include the exploratory investigation of the key parameters for emission enhancement and the effective energy transfer pathways from luminescent ligands to $Ln^{3+}$ ions with Ln(III)-chelated prototype complexes.

**Key Words :** Luminescent lanthanide complexes, Lanthanide-cored dendrimer complexes, Near infrared emission, Energy transfer pathways, Advanced photonics applications

### Introduction

Very recently, the development of integrated planar waveguide optical amplifiers is extremely essential for the realization of superhigh speed communication systems of large capacity optical communication, information storage, and processing.[1] At present, erbium-doped silica amplifiers are widely used. But, the poor solubility of lanthanide cations ($Ln^{3+}$) in conventional inorganic/organic media leads to low amplification property. When the higher doping

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concentration of $Ln^{3+}$ was introduced, clustered $Ln^{3+}$ species can be formed, which in turn have limited amplification property. It is ascribed to the cooperative energy-transfer processes (*i.e.*, self-quenching process) between the clustered $Ln^{3+}$ species. Their processes reduced the intensity of luminescence. Because of this reason, it is impossible to obtain high efficiency of optical amplification by doping $Er^{3+}$ ions in silica optical fiber. Also it is difficult to expect optical amplification of 30 dB in planar waveguide form, since the amplified luminescence intensity in $Ln^{3+}$ ions by direct excitation is very low due to their low absorption and emission cross sections.

In order to enhance the amplified luminescence intensity, luminescent ligands are being used to excite the $Ln^{3+}$ ions via an energy transfer from the luminescent ligands to the $Ln^{3+}$ ions. The development of luminescent $Ln^{3+}$ complexes based on the energy transfer mechanisms by using the supramolecular complexes as organic ligands has been extensively studied and attracted considerable attention because of their academic interest and potential utility in a wide variety of applications, such as planar waveguide amplifiers, plastic lasers, and light-emitting diodes.[2-19] In most cases, luminescent $Ln^{3+}$ complexes consist of a $Ln^{3+}$ ion and a chelating luminescent ligand which acts as a sensitizer that transfers excitation energy to the encapsulated $Ln^{3+}$ ion; the presence of this kind of ligand overcomes the lanthanide ion's intrinsically low luminescence intensity by direct excitation of the $Ln^{3+}$ ion having low absorption and emission cross-sections. Luminescent ligands efficiently absorb and transfer energy to the central $Ln^{3+}$ ions. The

central $Ln^{3+}$ ions accumulate energy from the antenna chromophores, producing a strong and narrow bandwidth emission.

For examples, Reinhoudt *et al.* synthesized polydentate hemispherand complexes containing triphenylene[5,6] or lissamine group,[7,8] where triphenylene and lissamine act as antenna chromophores. The $Ln^{3+}$ complexes showed the near infrared (IR) emissions by the indirect excitation of antenna chromophores. The $Ln^{3+}$ complexes show a relatively high intersystem crossing (ISC) quantum efficiency such that $Ln^{3+}$ ions are easily excited by the triplet state of chromophores. They found that the near IR emission takes place through the energy transfer process between the triplet state of chromophores and a $Ln^{3+}$ ion.
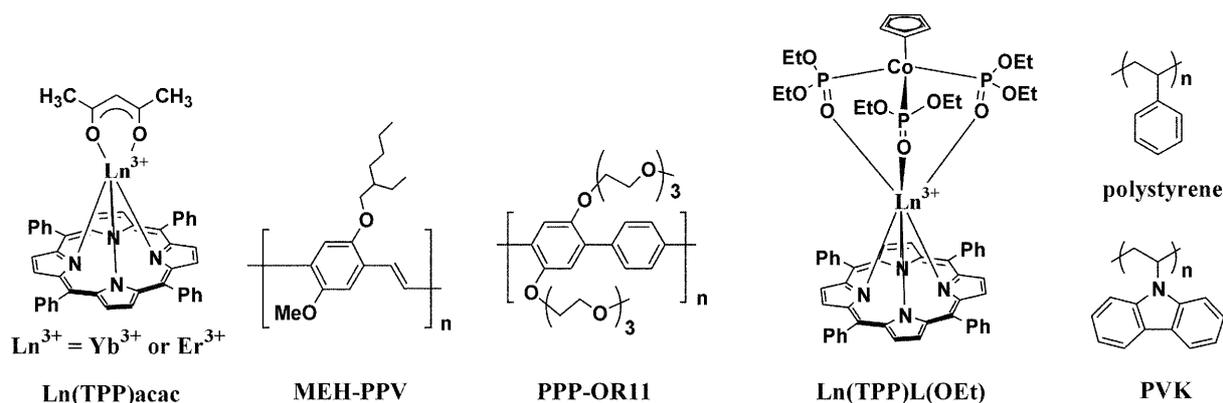
Werts *et al.*[9] synthesized luminescent $Er^{3+}$ complexes such as AMFLU-DTPA and AMEO-DTPA based on fluorescein and tetra-bromoeosin and they observed near IR luminescence. They reported that the effective ISC efficiency was required for getting the stronger emission bands.

Gillan and Curry[10-12] synthesized a series of Er(III)-cored complexes based on tris(8-hydroxyquinoline) for the use of the applications such as optical amplification (OA) materials and light-emitting devices (LED). They observed near IR luminescence and electroluminescence at 1.54 $\mu$m in the multilayered light-emitting devices (LED). Also, Yanagita *et al.*[13-15] synthesized $Ln^{3+}$ complexes using tris(dibenzoyl-methanato) ligand and observed near IR electroluminescence from organic LEDs by utilizing them.



**ErQ₃**                    **Ln(DBM)₃bath**

$Ln^{3+} = Yb^{3+}, Nd^{3+}$ or $Er^{3+}$
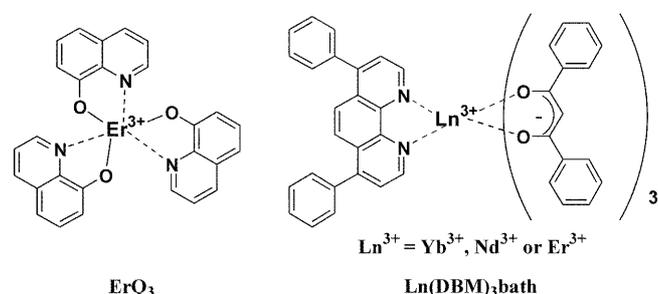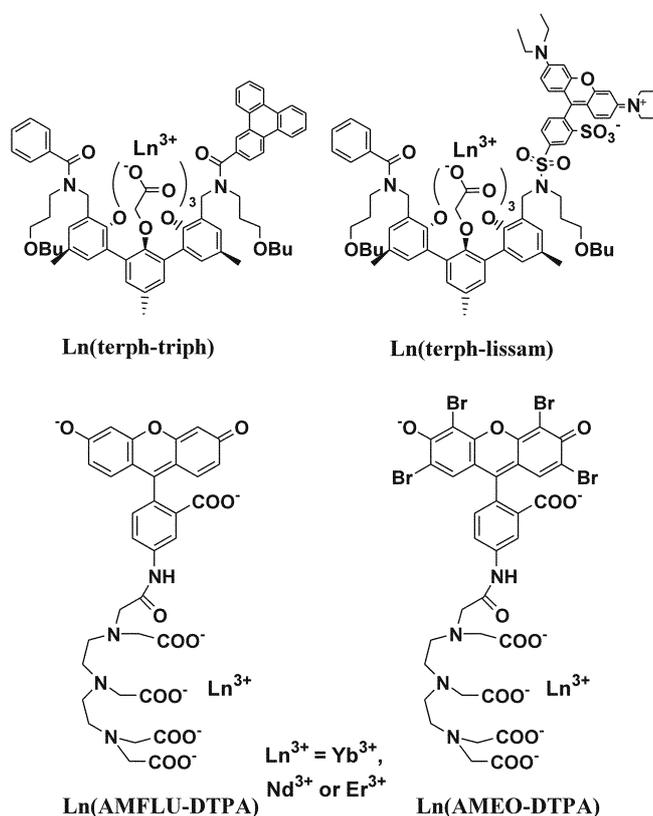
Harrison *et al.*[16] synthesized an Er(TPP)acac complex by using porphyrin as a ligand, and demonstrated the possibility of light-emitting material by doping in PPV series polymer materials. Recently, Schanze *et al.* studied the fabrication of near IR polymer LED using blending a series of lanthanide tetraphenylporphyrin (LnTPP) complexes in non-conjugated host polymers.[17] Recently, Destri *et al.*[18] synthesized Er(III)-cored complexes based on oligothiophene derivatives and observed near IR luminescence via energy transfer process, taking place between $Er^{3+}$ ion and oligothiophene derivative.

Recently, Kawa and Fréchet have also reported the site isolation and antenna effects on luminescent properties of spherical Ln(III)-cored dendrimer complexes.[19] The poor solubility of $Ln^{3+}$ cations in inorganic media leads to clustered $Ln^{3+}$ species, limiting the amplification achievable. To achieve the site isolation of $Ln^{3+}$ cations such as $Eu^{3+}$, $Tb^{3+}$ or $Er^{3+}$ ions, lanthanide ions were surrounded by the dendritic shell such as aryl-ether type dendrons. They found



**Ln(terph-triph)**                    **Ln(terph-lissam)**



**Ln(AMFLU-DTPA)**          $Ln^{3+} = Yb^{3+}, Nd^{3+}$ or $Er^{3+}$          **Ln(AMEO-DTPA)**

Ln(TPP)acac          MEH-PPV          PPP-OR11          Ln(TPP)L(OEt)          PVK

that the enhanced luminescent intensities depend significantly on the morphology of the dendrimer and efficient energy transfer from the photonic antennas to rare earth ion at the focal point. However, Er(III)-cored dendrimer complexes did not exhibit near IR emission. Although the aryl-ether type dendrons were widely used to photonic antennas, its spectral overlap between the emission band of photonic antenna and the absorption band of $Ln^{3+}$ cation was not satisfied to obtain the effective energy transfer between the photonic antenna and the $Ln^{3+}$ cation.

Up to date, luminescent $Ln^{3+}$ complexes containing supramolecular ligands as antenna chromophores were not developed for the real use in various photonics applications, such as erbium-doped fiber amplifiers (EDFA), erbium-doped waveguide amplifiers (EDWA) and light-emitting diodes. They are simply supramolecular complexes containing well-known antenna chromophores to photoexcite the $Ln^{3+}$ ions via the energy transfer process. The quantum yield of energy transfer and the luminescence efficiency were not satisfied yet. Also, 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, the dependence of $Ln^{3+}$ ion and ligand structure on amplification principles (such as the optical amplification lifetime, excited state dynamics, etc.) need to be systematically established. Based on the relationship established, the design and synthesis of luminescent $Ln^{3+}$ complexes using molecular engineering approach need to be investigated.

Therefore, recently, we have systematically designed and developed Ln(III)-cored complexes based on metalloporphyrins and naphthalenes, in a novel synthetic method developed in our laboratory, for advanced photonics applications.[20-22] $Ln^{3+}$ ions were encapsulated by the luminescent ligands such as metalloporphyrins and naphthalenes. Also, key parameters for emission enhancement and efficient energy transfer pathways for the sensitization of $Ln^{3+}$ ions by luminescent ligands were investigated.[22] We found that the saturated 8- or 9-coordinated complexes have the much stronger PL intensity than the unsaturated 6-coordinated complex. Very recently, we have incorporated a G2-aryl-ether functionalized dendron into the Er(III)-cored complex, yielding novel Er(III)-cored dendrimer complex bearing the Pt(II)-porphyrin. The Er(III)-cored dendrimer complex shows the stronger near IR emission intensity than the corresponding complex based on Pt(II)-porphyrin by 7 times in solid state.

In this article, we will deal with recent progress in the synthesis and photophysical studies of inert and stable luminescent $Ln^{3+}$ complexes for advanced photonics applications. Also, our review will include the exploratory investigation of the key parameters for emission enhancement and the effective energy transfer pathways from luminescent ligands to $Ln^{3+}$ ions with Ln(III)-chelated prototype complexes.

## Lanthanide Ions and Basic Optical Amplification Principle of Lanthanide Ions

The electronic configurations of $Ln^{3+}$ ions, referred to as the lanthanide ions or rare earth ions, have $4f^n$ ($n$ = 1-14) structures, which fill the $4f$ orbital according to the atomic numbers starting from $Ce^{3+}$ to $Lu^{3+}$ ions. These ions all have an incompletely filled $f$ subshell in which the $f$-electrons are shielded by the outer $5s$ and $5p$ electrons, which are lower in energy, but spatially located outside the $4f$ orbitals. These electrons are slightly perturbed by the effects of lattice phonons and static strain fields in the coordination environment of ions, lead to the sharp spectral lines. Since the spin-orbit interaction is larger than the effect of the crystal field, the luminescence spectra consist of groups of lines which arise from crystal field splittings of $J$ multiplets of the free ion in general.[23,24]

Judd[25] and Ofelt[26] independently derived expressions for the oscillator strength of induced dipole transitions within the $4f^n$–$4f^n$ configuration. Since their results are similar and were published simultaneously, their results are known as the Judd-Ofelt theory. They summed over the intensities of the individual crystal field components of a given state. The fundamental mechanism of the Judd-Ofelt theory is the perturbation caused by mixing of the crystal field potentials between the orbitals with different parities and $4f^n$ orbitals. The $4f^n$–$4f^n$ transitions are forbidden because $4f^n$ of rare earth ions and energy levels of electron shells have equal parity. However, absorption spectra between $4f^n$–$4f^n$ transition are experimentally observed. This is explained by assuming that a higher-lying opposite parity configuration is

mixed into the $4f^n$ states via the potential due to the ligand field.[27] On the contrary, $4f^n - 4f^{n-1}5d^1$ transitions or charge transfer transitions ($4f^n - 4f^{n-1}5L^1$, L = ligand) are partly allowed by mixing with the odd-parity wave functions via the potential due to the crystal field. The absorption and emission cross-sections are very small in solid phase and the corresponding fluorescence decay times are sufficiently long (as of the order of $m$s), compared with the rate at which it is populated in the excitation process. Also there is a Stark splitting between the degenerated $4f$ energy levels by the effect of electric field near $Ln^{3+}$ ions removing the degeneracy of the $4f$ level.

In analyzing the mechanisms of excited state relaxation of lanthanides in crystal hosts, two modes of relaxation are recognized: radiative and radiationless (or non-radiative) processes. Axe[28] represented the radiative processes in quantitative terms using the Judd-Ofelt theory. Radiationless relaxation was formulated in terms of multiphonon relaxation processes.[29,30] Such processes become less probable as the energy gap between an excited state and the next lower energy state increases. Since excited state relaxation is generally achieved prior to transitions to several lower-lying states, a total radiative relaxation rate can be defined as a summation over all states lower in energy than the fluorescing state. Scheme 1 shows the principal fluorescence states of the $Ln^{3+}$ ions in crystal hosts.[31] Fluorescence from many of these levels is observed only at low temperatures

since rapid relaxation of an excited state by radiationless processes compete strongly with the radiative mode unless the energy gap to the next lower level is large. As the gap increases, the process rapidly decreases in probability such that radiative decay can efficiently compete with a relaxation mechanism. Usually both radiative and radiationless processes operate to relax an excited state. The total fluorescence lifetime of the state is a sum of the radiative rate and the rates of the various radiationless processes.

Several lanthanide ions, such as $Pr^{3+}$, $Nd^{3+}$, $Dy^{3+}$, $Er^{3+}$, and $Yb^{3+}$ ions, show luminescence in the near infrared region. The luminescence of wavelengths 1.54 $\mu$m from $Er^{3+}$ ion and 1.34 $\mu$m from $Nd^{3+}$ ion is used as standard wavelengths in optical communications, in which light is used to transport information between different users. Some of lanthanide ions, such as $Sm^{3+}$, $Tb^{3+}$ and $Eu^{2+}$ ions, exhibit the emission band in the visible region. Their luminescent complexes have been considered the potential candidates for light-emitting diodes.

Among them, erbium-based materials have attracted much attention because they have the authentic optical amplification (OA) property with the strong stimulated emission band. This specific property renders erbium-based materials to use in several photonics applications, such as erbium-doped fiber amplifiers (EDFA), erbium-doped waveguide amplifiers (EDWA) and light-emitting diodes.[1,21] The basic optical amplification principle of $Er^{3+}$ ion is described in
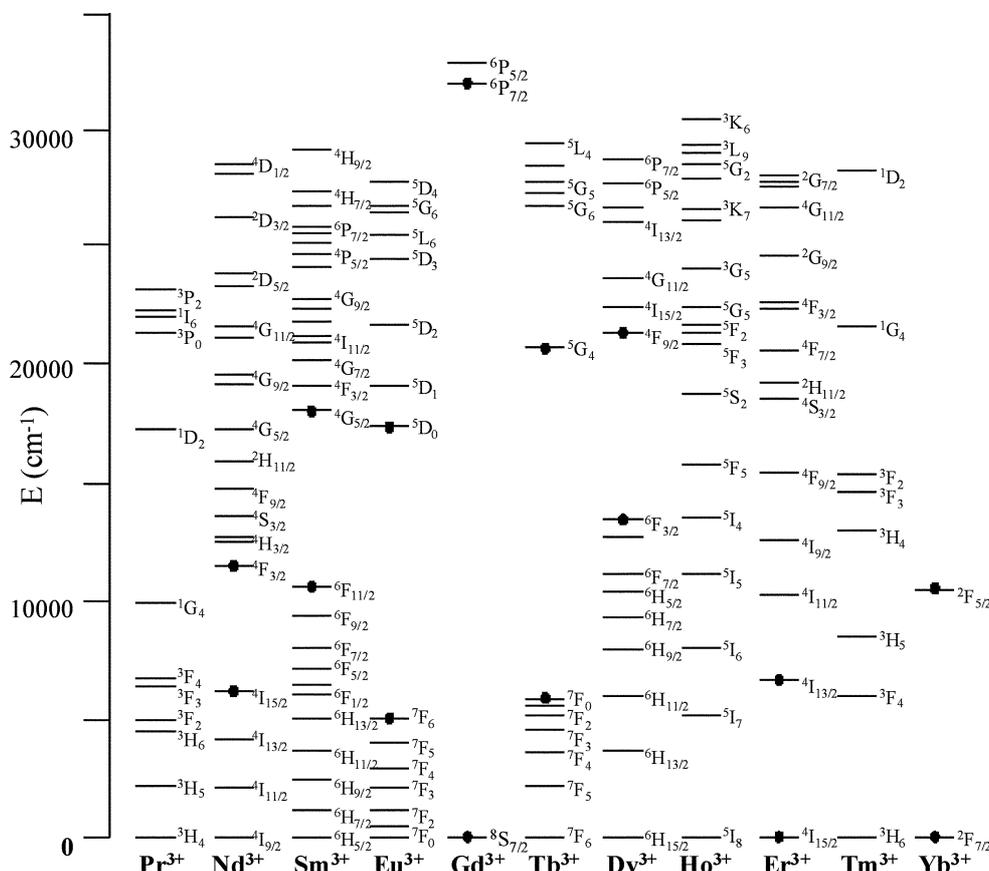


**Scheme 1.** Energy levels of $Ln^{3+}$ ions.
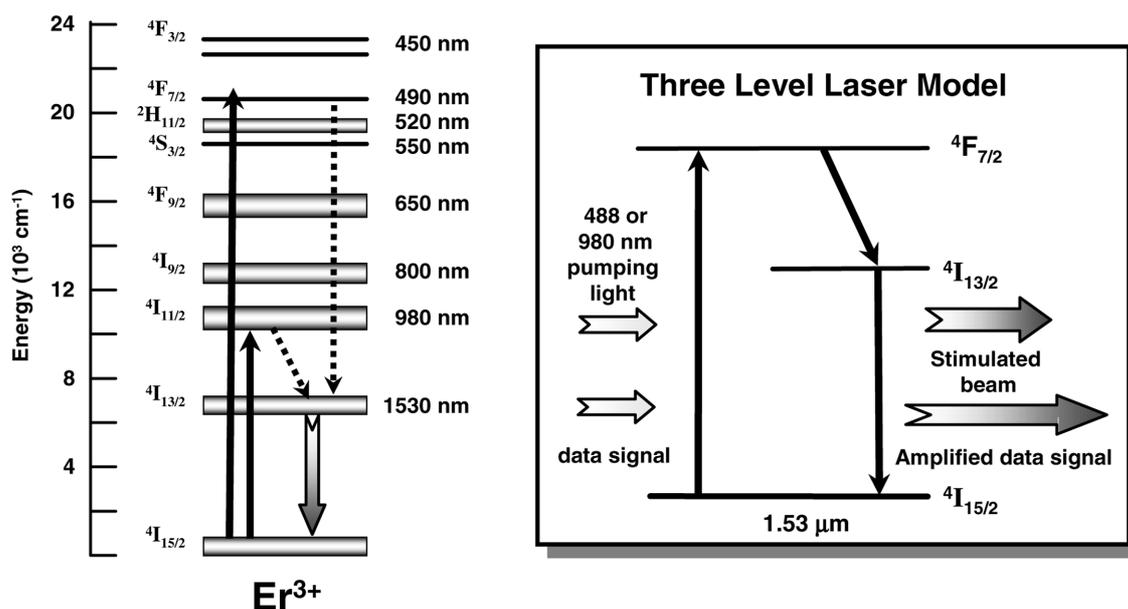
**Scheme 2**. Basic optical amplification principle of $Er^{3+}$ ions for advanced photonics applications.

Scheme 2. The $Er^{3+}$ ion is excited to the upper energy level than the lower excited energy level ($Er^{3+}$, $^4I_{13/2}$) of the lanthanide ions, by absorbing photons of pumping laser such as 488 or 980 nm, etc. And then, the excited state of the upper energy level is transited to the lower excited energy level ($Er^{3+}$, $^4I_{13/2}$) of the $Ln^{3+}$ ions through the lattice relaxation process (or the vibrational relaxation process). The population inversion inherently takes place at the energy level of the lanthanide ions ($Er^{3+}$, $^4I_{13/2}$). Finally, it loses the photon energy in a radiative decay to fall back to the ground state ($Er^{3+}$, $^4I_{15/2}$) of the $Ln^{3+}$ ions, emitting the stimulated light at 1.54 $\mu$m. When the same input signal with the metastable excited state is introduced at the same time, the input signal and the stimulated emission beam are summed to generate the amplified output signal, due to the power interchange between the input signal and the stimulated emission beam. The stimulated emission lifetime of the $^4I_{13/2}$ → $^4I_{15/2}$ radiative transition at 1.54 $\mu$m of $Er^{3+}$ ion in a solid,

which depends on the presence of impurities and defects in the host, is of the order of 10 *m*s. In luminescent $Ln^{3+}$ complexes, instead of direct excitation of $Er^{3+}$ ion in a solid, the luminescent ligands, as photon sensitizers, efficiently absorb and transfer the light to excite the $Ln^{3+}$ ions via an energy transfer between the luminescent ligand and the $Ln^{3+}$ ion. It is very important to note that the accumulating photon energy from the excited state of the luminescent ligands can excite the $Ln^{3+}$ ions as much as possible, thus enhancing the optical amplification gain.

## Er(III)-chelated Prototype Complexes: Exploratory Synthesis and Key Parameters for Near IR Emission Enhancement

For the first of all, we attempted to synthesize Er(III)-chelated complexes using Er(III) acetate, according to the previous Fréchet's method.[19] But, the reaction did not take
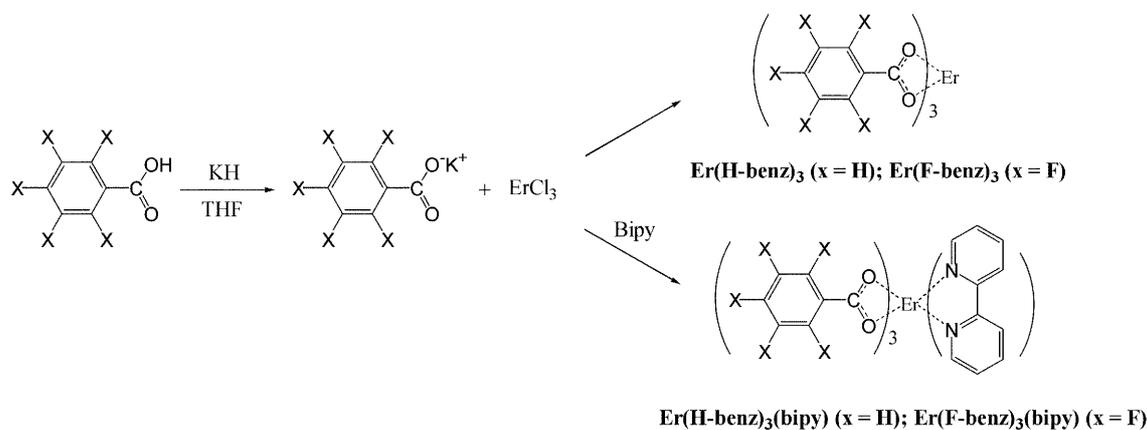


**Scheme 3**. New synthetic route to Er(III)-chelated complexes based on benzoate and pentafluorobenzoate ligands and their chemical structures.
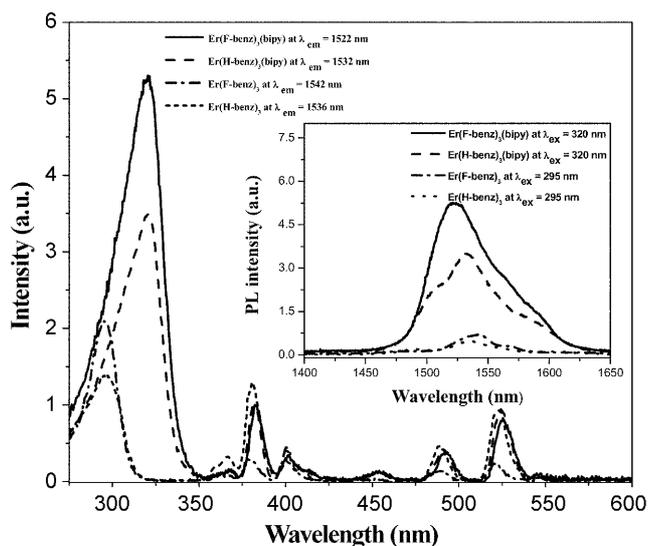
**Figure 1**. Excitation spectra of the 6- or 8-coordinated model complexes for Er(F-benz)$_3$(bipy) at $\lambda_{em}$ = 1522 nm, Er(H-benz)$_3$(bipy) at $\lambda_{em}$ = 1532 nm, Er(F-benz)$_3$ at $\lambda_{em}$ = 1542 nm, and Er(H-benz)$_3$ at $\lambda_{em}$ = 1536 nm in a solid state. Here, the $\lambda_{em}$ means the emission wavelength. The inset shows near IR spectra of Er(F-benz)$_3$(bipy) at $\lambda_{ex}$ = 320 nm, Er(H-benz)$_3$(bipy) at $\lambda_{ex}$ = 320 nm, Er(F-benz)$_3$ at $\lambda_{ex}$ = 295 nm, and Er(H-benz)$_3$ at $\lambda_{ex}$ = 295 nm in solid state. Here, the $\lambda_{ex}$ means the excitation wavelength.



**Figure 2**. Near IR emission spectra of the 6- or 8-coordinated model complexes for (a) Er(F-benz)$_3$, (b) Er(H-benz)$_3$(bipy), and (c) Er(F-benz)$_3$(bipy) in a solid state.

place because of the side reactions.[20] Very recently, we have developed a new synthetic method for 6- and 8-coordinated Er(III)-cored model complexes through the ligand-exchange reaction using ErCl$_3$ (see Scheme 3):[22] 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 ErCl$_3$. 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$^{3+}$ complexes do not permit NMR characterization of the model complex. From TGA analysis, at least three H$_2$O molecules coordinated in the unsaturated 6-coordinated complexes were confirmed by determining the releasing water amount of 6% up to 190 °C in atmospheric condition. However, 8-coordinated model complexes Er(H-benz)$_3$(bipy) and Er(F-benz)$_3$(bipy) showed no releasing water up to 170 °C, indicating that 8-coordinated model complexes contain no coordinated H$_2$O molecules.

The absorption spectra of 8-coordinated prototype complexes of Er(H-benz)$_3$(bipy) and Er(F-benz)$_3$(bipy) show a very intense absorption band at 310 nm, which is attributed to $\pi$-$\pi$* electronic transition. The emission spectra of all compexes at the selected photoexcitation wavelength exhibit the emission bands in the near IR region of 1.47-1.63 $\mu$m, which are assigned to the characteristic $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition of Er$^{3+}$ ions. Figure 1 shows the the emissoin spectra of the 6- and 8-coordinated complexes at the photoexcitation wavelength of 295 or 320 nm (see the inset). The saturated 8-coordinated complexes show much stronger
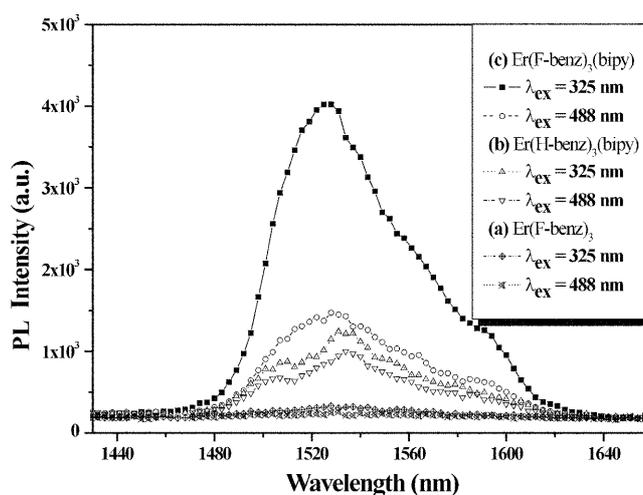
PL intensity than that of the unsaturated 6-coordinated complex. The similar result has been shown in a previous report.[21] The excitation spectra of the 8-coordinated proto-type complexes of Er(H-benz)$_3$(bipy) and Er(F-benz)$_3$(bipy), monitored at the maximum emission band, show a strong maximum band at 335 nm in the utraviolet region, whereas the excitation spectra of the 6-coordinated complexes of Er(H-benz)$_3$ and Er(F-benz)$_3$ exhibit the bands at 295 nm. Also, the several additional excitation bands appeared in the region of 350-550 nm. These excited bands spectrally overlap well with the absorption bands of the inherent Er$^{3+}$ ion.[1,21] Thus, the energy transfer between the excited organic ligand and the ground Er$^{3+}$ ion takes place.

Figure 2 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 Er$^{3+}$ ions taking place at 1.53 $\mu$m, upon a photoexcitation wavelength of 325 or 488 nm. Here, upon the photo-excitation wavelength of 325 nm, the energy transfer process between the excited ligand and Er$^{3+}$ ion takes place possibly to generate the emission of the central Ln$^{3+}$ ion (Er$^{3+}$ ion), while, upon the photoexcitation wavelength of 488 nm, the emission of the inherent Ln$^{3+}$ ion (Er$^{3+}$ ion) was obtained through the direct excitation of Er$^{3+}$ ion without the energy transfer process between the excited ligand and Er$^{3+}$ ion. The saturated 8-coordinated complexes show much stronger PL intensity than that of the unsaturated 6-coordinated complex as shown in Figure 1 & 2, in which the highly coordinated Ln(III)-chelated complexes (at least 8 to 9 coordination) have the higher PL efficiency than the unsaturated Ln(III)-chelated complexes (6 coordination).[21] In the latter complex, at least three H$_2$O 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$_2$O 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 $Er^{3+}$ ions with 488 nm by 80 times

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 (Er(F-benz)$_3$(bipy)) with that of a 8-coordinated model complex with C-H bonds (Er(H-benz)$_3$(bipy)). 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. Figure 2 shows that Er(F-benz)$_3$(bipy) has much stronger PL intensity than that of Er(H-benz)$_3$(bipy) by four times, due to the multi-phonon relaxation process arising from the harmonic vibration motion of C-H bonds. In this section, our main material efforts have been focused on developing the new synthetic methodolgy of the inert, saturated $Er^{3+}$ complexes and investigating important key parameters for near IR emission enhancement. The new synthetic methodolgy developed in our laboratory opens the development of a series of novel inert and stable Ln(III)-cored nanophotonics systems with highly efficient light-harvesting effect and the investigation of efficient energy transfer pathways for the sensitization of $Ln^{3+}$ ions by luminescent ligands in luminescent $Ln^{3+}$ complexes.[1,32]

## Efficient Energy Transfer Pathways for the Sensitization of Ln³⁺ Ions by Luminescent Ligands in Luminescent Ln³⁺ Complexes

Despite extensive research efforts, the energy transfer pathways in these complexes for the sensitization of the $Ln^{3+}$ ions by the luminescent ligands are still not fully understood. Efficient energy transfer pathways are very important in advanced photonics technology, particularly in the development of new and useful luminescent $Ln^{3+}$ complexes with efficient lanthanide emission. For example, the development of integrated planar waveguide optical amplifiers is essential to the realization of superhigh speed communication systems.[1,2] An optical amplification of 30 dB in a planar waveguide form is required.

Two possible energy transfer pathways for the sensitized emission in luminescent $Ln^{3+}$ complexes were proposed, as shown in Scheme 4. It is well known that in general only the triplet state of the luminescent ligand is involved in photosensitization (ET(t)). The sensitization process of $Ln^{3+}$
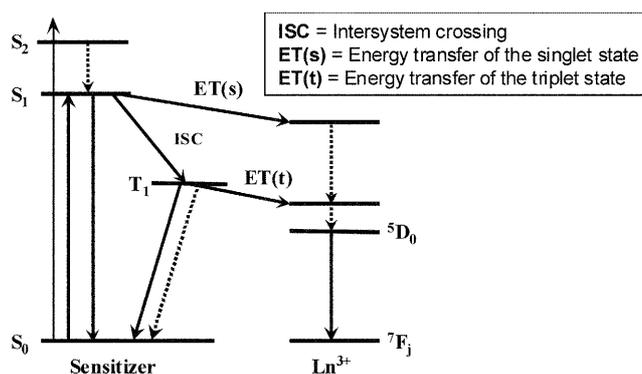


**Scheme 4**. Two possible energy transfer pathways.
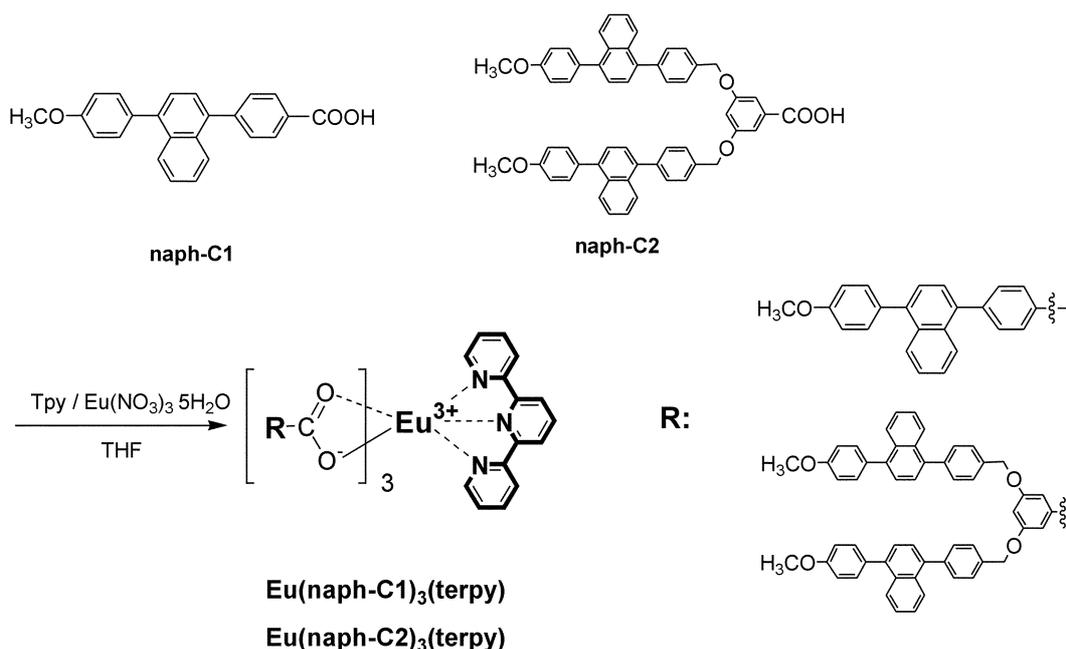


**Scheme 5**. Synthetic strategy for the Eu(III)-cored complexes.
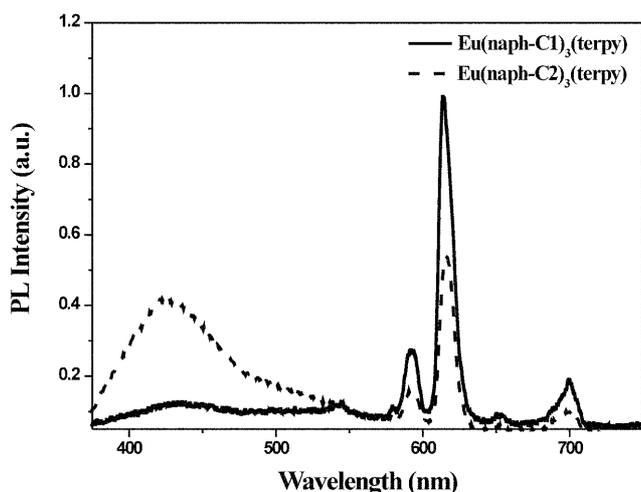
**Figure 3**. Emission spectra of the saturated complexes of Eu(naph-C1)$_3$(terpy) ($\lambda_{ex}$= 353 nm) and Eu(naph-C2)$_3$(terpy) ($\lambda_{ex}$= 394 nm).

complex is strongly affected by the subsequent intersystem crossing efficiency, and the energy transfer efficiency to Ln$^{3+}$ ion in the excited triplet state.[6,33] The possibility of energy transfer from the singlet state of the luminescent ligand (ET(s)) 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). Interestingly, however, several reports mentioned the energy transfer from the excited singlet state to Ln$^{3+}$ ion.[34-36] van Veggel *et al.*[34] reported that the energy transfer in dansyl- and lissamine-functionalized Nd$^{3+}$ complexes occured from the singlet state of the sensitizers to Nd$^{3+}$ centers, but no sensitized Yb$^{3+}$ or Er$^{3+}$ emission was observed. Balzani *et al.*[36] also observed the energy transfer between the singlet state of polylysin dendrimer and Nd$^{3+}$ ions. Very recently, Wang *et al.*[37] reported that the energy transfer in a dipyrazolyltriazine-functionalized Eu$^{3+}$ complex occured from the singlet state of the sensitizers to Eu$^{3+}$ centers.

In order to investigate the pathways for energy transfer from luminescent ligands to Ln$^{3+}$ ions, we have systematically designed and developed naphthalene-based luminescent ligands as sensitizers, as shown in Scheme 5. These naphthalene-based luminescent derivatives were synthesized using the well-known Suzuki cross coupling reaction with moderate yield.[21b] The UV-visible spectra of naph-C1 and naph-C2 have broad and intense band edges, which are due to $\pi$-$\pi^*$ electronic transitions, tailing up to 374 nm with a maximum absorption wavelength of 312 nm, and tailing up to 360 nm with a maximum absorption wavelength of 306 nm, respectively. The photoexcitation of naph-C1 and naph-C2 with the light wavelengths of 344 and 350 nm results in PL spectra with strong emission bands at 429 and 400 nm, respectively.

The Eu(III)-chelated complexes were obtained with a quantitative yield by a promising new synthetic method developed in our laboratory. The complexing of the naphthalene-based luminescent derivatives in Eu(III)-cored

luminescent complexes does not alter their UV absorption features. This indicates that the chelated ligands and Ln$^{3+}$ do not perturb each other. In other words, the ground states of the Ln$^{3+}$ ions are not influenced by the organic ligands, even in Eu$^{3+}$ complexes. The emission spectra of the Eu$^{3+}$ complexes Eu(naph-C1)$_3$(terpy) and Eu(naph-C2)$_3$(terpy), obtained using different excitation wavelengths corresponding to the absorption maximum positions of the ligands, contain an intra 4f electronic transition from the first excited state ($^5D_0$) to the ground state ($^7F_2$) at 612 nm (see Figure 3). Eu(naph-C1)$_3$(terpy) has a much stronger PL intensity than Eu(naph-C2)$_3$(terpy). This observation can be explained in terms of the more effective energy transfer between the ligands and the Ln$^{3+}$ ions that occurs in Eu(naph-C1)$_3$(terpy) (ET(t)). Eu(naph-C1)$_3$(terpy) has a higher ISC efficiency for the conversion of the singlet state into the triplet state than Eu(naph-C2)$_3$(terpy); this higher ISC efficiency is due to the heavy metal effect that arises in Eu(naph-C1)$_3$(terpy), because naph-C1 is directly connected to the Ln$^{3+}$ ions without a molecular spacer.

Eu(naph-C1)$_3$(terpy) and Eu(naph-C2)$_3$(terpy) also have qualitatively different PL spectra. Eu(naph-C1)$_3$(terpy) produces one strong photoluminescence band with maximum wavelength around 612 nm, while Eu(naph-C2)$_3$(terpy) produces two PL bands: a strong emission band around 612 nm and an emission band of moderate intensity around 400 nm. The latter band is assigned to fluorescence from the singlet state of the naphthalene-based luminescent ligand, because its absorption and emission spectra are mirror images of each other. This assignment is confirmed by the time-resolved transient decay. Further, the intensity of the emission band at 400 nm was reduced, but the emission band at 612 nm was simultaneously increased. The presence of an emission band near 400 nm indicates that no effective energy transfer occurs between the naph-C2 ligand in Eu(naph-C2)$_3$(terpy) and the Ln$^{3+}$ ion. This might be because this indirect luminescent Ln$^{3+}$ complex contains a molecular spacer as a building block. In other words, the naphthalene-based luminescent derivatives are connected through building blocks to the Ln$^{3+}$ ions. Thus, the effective formation of triplet states does not occur in complex Eu(naph-C2)$_3$(terpy), because there is no heavy metal effect. However, Eu(naph-C2)$_3$(terpy) exhibits much lower fluorescence intensity around 400 nm than the naph-C2 ligand, presumably due to the singlet energy transfer from the luminescent ligand to the Ln$^{3+}$ ion (ET(s)).

In summary, we have designed and developed novel luminescent Ln$^{3+}$ complexes based on naphthalene derivatives for exploratory investigation of efficient energy transfer pathway from luminescent ligands to Ln$^{3+}$ ions. Ln$^{3+}$ ions were encapsulated with two types of the naphthalene-based luminescent ligands. One of them can lead to the direct formation of luminescent Ln$^{3+}$ complexes without a molecular spacer and the other can render the indirect formation of luminescent Ln$^{3+}$ complexes through a molecular spacer as a building block. With them, the involvement of the energy transfer of the singlet state of the luminescent ligand in

Eu(III)-chelated complexes was investigated and demonstrated for the first time to the best our knowledge. This conclusion opens up the possibility of the development of a series of novel Ln(III)-cored nanophotonics systems based on porphyrins, as well as of new antenna chromophores with highly efficient light harvesting dendritic arrays.[1,32,39]

## Erbium(III)-Cored Complexes Based on Metalloporphyrins Bearing Aryl-ether Dendron for Optical Amplification: Synthesis and Emission Enhancement

Porphyrin derivatives were chosen for supramolecular ligands, since they are well-known as photon antenna for natural photosynthetic system.[38] Also, porphyrin ligands should have the following properties: First, they have enough donor atoms and specific isolation space for guest metal ions. It is possible to obtain the encapsulation of lanthanide ions and the isolation from light quenchable solvents such as water. Second, they have specific functional groups, in which they will be used to couple with antenna systems or light-harvesting systems. Third, the energy level of the triplet state of metalloporphyrins has the spectral overlap well with the $^4F_{9/2}$ sublevel of $Er^{3+}$ ions, which is another key parameter to maintain the effective energy transfer process from metalloporphyrin ligands to $Er^{3+}$ ions (see Figure 4).[30,37,39]

For the first of all, the porphyrin derivatives were synthesized according to previous procedures (see Scheme 6).[40,41] Using them, we achieved successfully the synthesis of Er(III)-cored supramolecular complexes based on porphyrins
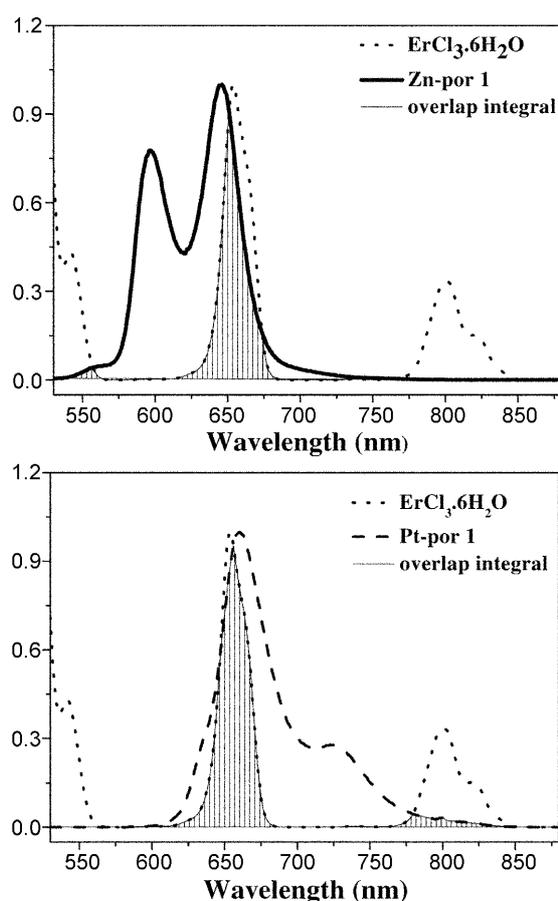


**Figure 4.** The spectral overlap integral between the emission band of porphyrin ligands and the absorption band of the erbium ion for the effective energy transfer process from porphyrin ligands to the of erbium ions.
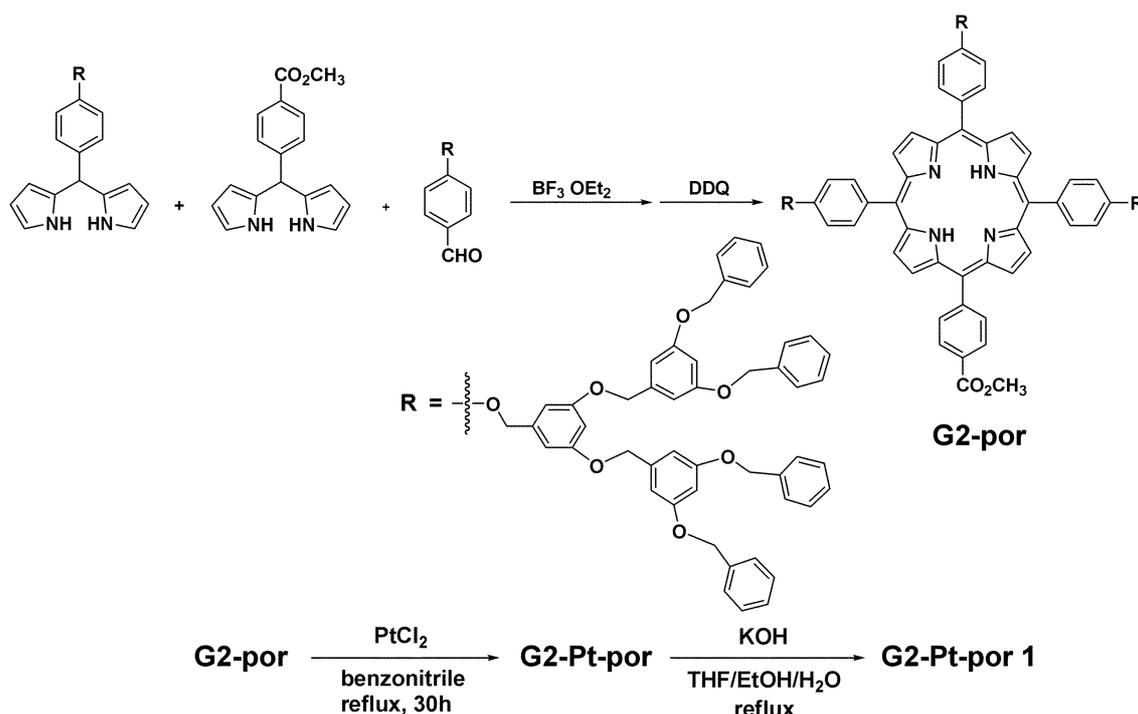


**Scheme 6.** Synthetic routes to G2-Por, G2-Pt-Por and G2-Pt-Por 1.
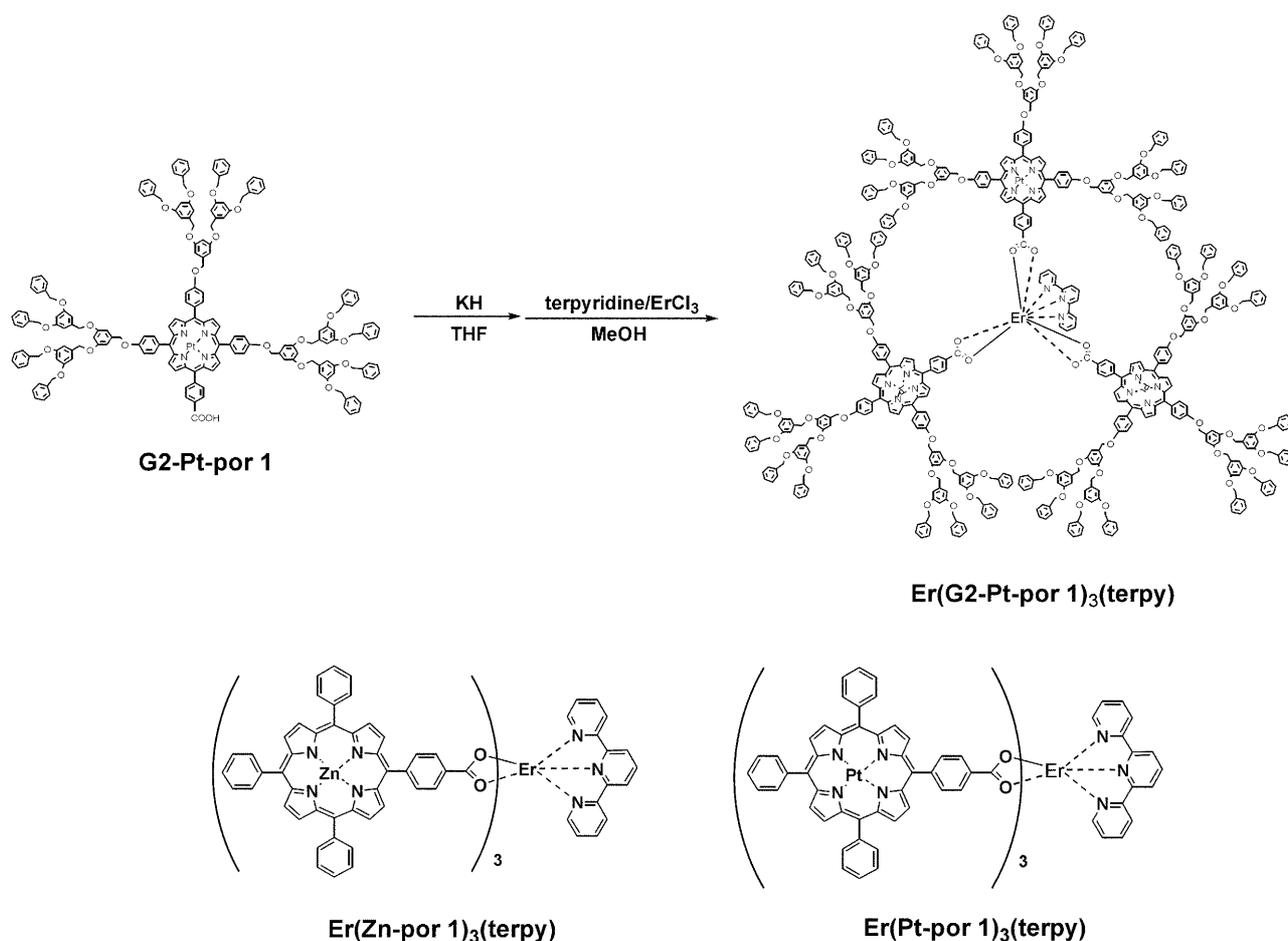
**Scheme 7**. Synthetic routes to G2-Pt-Por 1 and Er(G2-Pt-por 1)₃(terpy) as well as the chemical structures of Er(Zn-por 1)₃(terpy) and Er-(Pt-por 1)₃(terpy).

using ErCl₃ in a novel synthetic method developed in our laboratory, yielding more stable 9-coordinated Er(III)-cored complexes (see Scheme 7).[21,22,42,43] The chemical structures of Er(III)-cored complexes were identified by FT-IR, NMR, Mass, absorption and emission spectroscopies. The FT-IR spectra of the Er(III)-cored complex exhibited the two characteristic bands of bidentate-like carboxylate around 1600 and 1410 cm⁻¹, indicating the formation of bidentate complex.[21,44]

Figure 5 shows the absorption and emission spectra of FB-por 1, Zn-por 1, Pt-por 1 and G2-Pt-por 1. According to our previous report, the absorption of Pt(II)-por 1 exhibits a blue shift by 20-40 nm to Zn-por 1 and FB-por 1, due to a wide band gap of π-π* electronic transition arising from strong d-p orbital interaction between unoccupied d-orbital in Pt²⁺ ions and p-orbital in porphyrins.[45,46] G2-Pt(II)-porphyrin shows a very intense Soret band at 406 nm and the relatively weak Q bands at 511 and 540 nm as well as a moderate absorption band of G2 dendron at 276 nm. All absorption bands of G2-Pt(II)-porphyrin are shifted to longer wavelength, compared with Pt(II)-porphyrin.

The PL spectrum of Zn-por 1 shows a moderate band at 596 nm and a strong band at 646 nm, while the PL spectrum of Pt-por 1 shows a strong band at 660 nm and a moderate
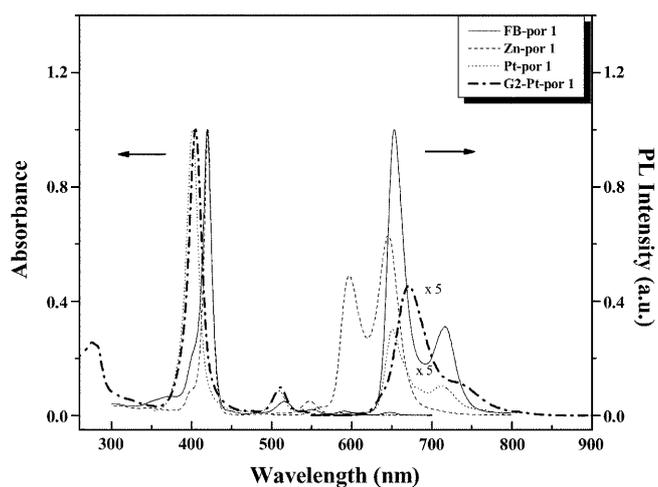


**Figure 5**. The UV-Vis. absorption and emission spectra of FB-por 1, Zn-por 1, Pt-por 1 and G2-Pt-por 1 in THF ($1 \times 10^{-5}$ M).

band at 725 nm. However, the PL intensity of Pt-por 1 is much lower than that of the Zn-por 1. It was previously explained by the fact that Pt(II)-porphyrin derivative has the higher ISC efficiency for the conversion of a singlet state into a triplet state than that of Zn(II)-porphyrin derivative,
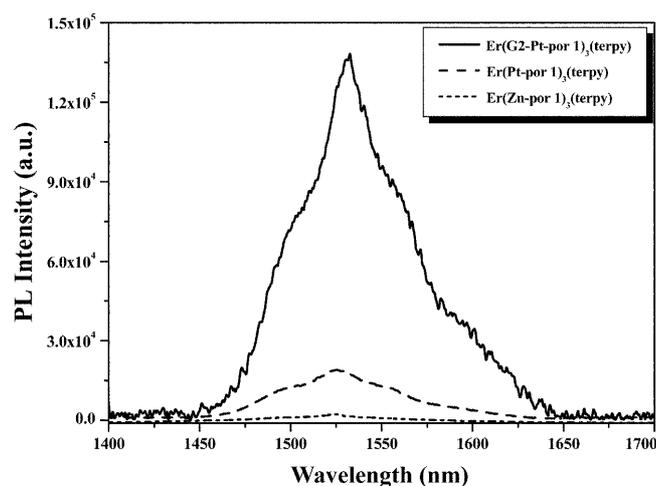
**Figure 6**. Near IR emission spectra of Er(Zn-por 1)$_3$(terpy), Er(Pt-por 1)$_3$(terpy), and Er(G2-Pt-por 1)$_3$(terpy) ($\lambda_{ex}$ = 514 nm from Ar$^+$ laser, solid state).



**Figure 7**. The photoluminescence spectra of Pt-porphyrin-COOH (Pt-por 1) and Er(Pt-por 1)$_3$(terpy) at room temperature in deoxygenated THF solutions (1 × 10$^{-5}$ M) upon a photoexcitation wavelength of 405 nm.

due to the heavy atom Pt(II) effect arising from the spin-orbital coupling interaction.[32,46] Upon a photoexcitation wavelength at the absorption maximum wavelength, the PL spectrum of G2-Pt(II)-porphyrin shows a moderate band at 676 nm and a relatively weak band at 730 nm, while the PL spectrum of Pt-por 1 showed a strong band at 653 nm and a moderate band at 713 nm. The similar result was observed with red shift for free G(n)-aryl ether typed porphyrin derivatives.[47]

The emission spectra of the saturated 9-coordinated Er(III)-cored complexes based on Zn(II)- and Pt(II)-porphyrin in a solid state were obtained from the excitation wavelengths of the absorption maximum positions of metalloporphyrins. They showed an intra 4f shell electronic transition from its first excited state ($^4I_{13/2}$) to the ground state ($^4I_{15/2}$), taking place at 1.53 μm (see Figure 6). Surprisingly, the Zn(II)-porphyrinate complex shows two strong PL bands at 596 and 646 nm, but, no near IR emission band. It indicates that Zn(II)-porphyrin could not act as a sensitizer in the Zn(II)-porphyrinate complex to maintain the energy transfer between the Zn(II)-porphyrin ligand and Ln$^{3+}$ ion, even though the spectral overlap integral of the Zn(II)-porphyrin ligand is similar to that of the Pt(II)-porphyrin ligand (see Figure 4). However, the Pt(II)-porphyrinate complex exhibits only the near IR emission band without the visible PL band of Pt-por 1. It is noteworthy that Pt(II)-porphyrin derivative has the higher ISC efficiency for the conversion of a singlet state into a triplet state than that of Zn(II)-porphyrin derivative, due to the heavy atom Pt(II) effect arising from the spin-orbital coupling interaction. It suggests that the emission bands of the Er(III)-cored complex based on Pt(II)-porphyrin in the visible region may be originated from the triplet state. It is apparently different from the origin of Zn(II)-porphyrin emission bands. Therefore, we can guess that the effective energy transfer from the ligand to Ln$^{3+}$ ion takes place through the triplet state.
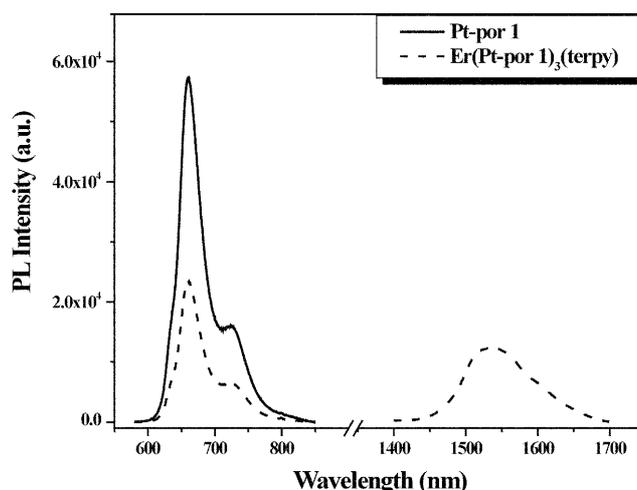
The direct evidence of the formation of the triplet state as an energy transfer state was confirmed by measuring the phosphorescence spectra of the Pt(II)-porphyrin ligand and its Er(III)-cored complex (see Figure 7) and the decay time for the Er(III)-cored complex in deoxygenated THF solutions at room temperature. The ligand exhibits a strong phosphorescence maximum band around 660 nm and a moderate phosphorescence maximum band around 725 nm. However, the complex shows the near IR emission band at 1.53 μm, but, the intensity of the phosphorescence bands was strongly reduced. The decay time of the phosphorescence band was found to be 30 μs for the Er(III)-cored complex. In addition, since the triplet state was seriously quenched by oxygen, we have investigated the oxygen effect for the sensitized near IR luminescence intensity in the Er(III)-cored Pt(II)-porphyrinate complex (see Figure 8).
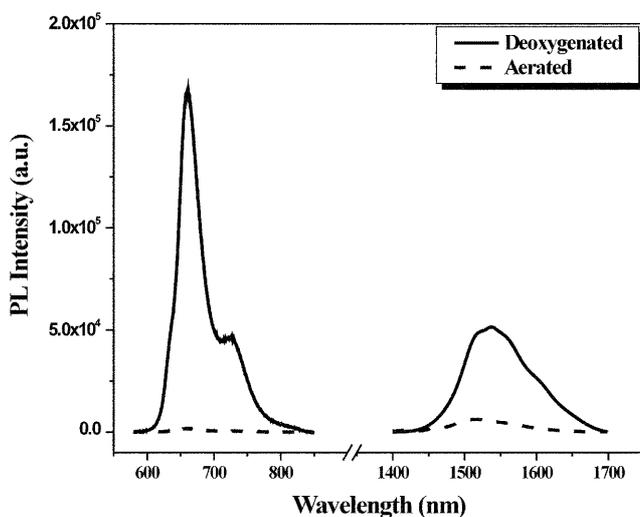


**Figure 8**. The photoluminescence spectra of (Pt-por 1)$_3$(terpy) at room temperature in a deoxygenated and an aerated THF solutions (1 × 10$^{-5}$ M) upon a photoexcitation wavelength of 405 nm.

The emission intensity in the aerated THF solution is seriously quenched not only in the visible region but also in the near IR region. It indicates that the energy transfer takes place through the triplet state of the Pt(II)-porphyrin ligands. Also, the effect of oxygen on the sensitized luminescence intensity gives an estimation of the energy transfer rate with the order of $10^7$–$10^8$ sec$^{-1}$.[6]

Furthermore, in order to enhance the photophysical properties of novel supramolecular systems, we have incorporated a G2-aryl ether-functionalized dendron into the Er(III)-cored Pt(II)-porphyrinate complex (see Scheme 7).[48,49] It is well-known that the excited state of the Ln$^{3+}$ ions is seriously quenched by interactions with close Ln$^{3+}$ ions.[50] It limits Er(III)-doped concentration on silica optic fiber up to 100-1000 ppm. With this reason, it is impossible to obtain the optical amplification gain of higher than 30 dB with Er$^{3+}$-doped silica optical fibers for developing integrated planar waveguide amplifiers (IPWAs).[23] Here, the Er(III)-cored dendrimer complex based on Pt(II)-porphyrin was designed to protect the interaction between the Ln$^{3+}$ ions and to isolate the Ln$^{3+}$ ion from the quenching molecules (solvents and H$_2$O).

With an excitation at the absorption maximum wavelength of the Pt(II)-porphyrin in a solid state, the Er(III)-cored dendrimer complex with Pt(II)-porphyrin bearing a G2-aryl ether dendron has the higher PL intensity than the saturated 9-coordinated Er(III)-cored Pt(II)-porphyrinate complex by 7 times (see Figure 6). It might be due to the fact that aryl ether-typed dendritic porphyrin renders the efficient site-isolation effect enough to prevent the intermolecular interaction between Er$^{3+}$ ions, which limits the near IR intensity. Also, we have measured the luminescence and the decay time of Er(III)-cored dendrimer complex with Pt(II)-porphyrin bearing a G2-aryl ether dendron in deoxygenated THF solution. The similar results were obtained to the Er(III)-cored Pt(II)-porphyrinate complex (see Figure 8), since the emission intensity in both the visible and near IR regions, in deoxygenated condition, is highly increased.[32(b)]

It indicates that the G2-aryl ether dendron in the Er(III)-cored dendrimer complex prevents the Er(III)-cored dendrimer complex from penetrating the oxygen into the cored Er$^{3+}$ ions. Thus, it reduces the effect of oxygen on the sensitized luminescence intensity.[6] Also, the decay time of the phosphorescence band in the Pt(II)-porphyrin was measured to be 40 $\mu$s for the Er(III)-cored dendrimer complex, indicating that the energy transfer takes place through the triplet state of the Pt(II)-porphyrin ligands like the Er(III)-cored complex based on Pt(II)-porphyrin. Therefore, Pt(II)-porphyrin derivatives bearing aryl ether-typed dendrons are good candidates for encapsulating supramolecules as well as the photon antennas to Er(III)-cored supramolecular complexes.

In progress, additionally, to efficiently introduce the light-harvesting effect into our Er(III)-cored supramolecular systems for optimizing and maximizing their optophysical properties, we have designed and synthesized a series of Er(III)-cored dendrimer complexes bearing new aryl ether-typed dendrons with energy gradient.[1,39,50,51] The synthetic strategy and the energy transfer pathway of novel lanthanide-cored supramolecular systems with highly efficient light-harvesting dendritic arrays are described in Scheme 8. Our supramolecular systems have both lanthanide-cored supramolecular complexes and light-harvesting dendritic photon antenna with such proper energy gradient. In our supramolecular systems, many exterior chromophores efficiently absorb and transfer the light through the interior chromophores to the supramolecular ligands via energy transfer process, so-called the light-harvesting effect, leading to the formation of the singlet state of the supramolecular ligands. And then, the singlet state of the supramolecular ligands is converted into their triplet state by ISC process. The triplet state of the supramolecular ligands must be tailored to maintain the upper energy level than the lower excited energy level (Er$^{3+}$, $^4I_{13/2}$) of the lanthanide ions, and then transited to the lower excited energy level (Er$^{3+}$, $^4I_{13/2}$) of the lanthanide ions through the vibrational relaxation
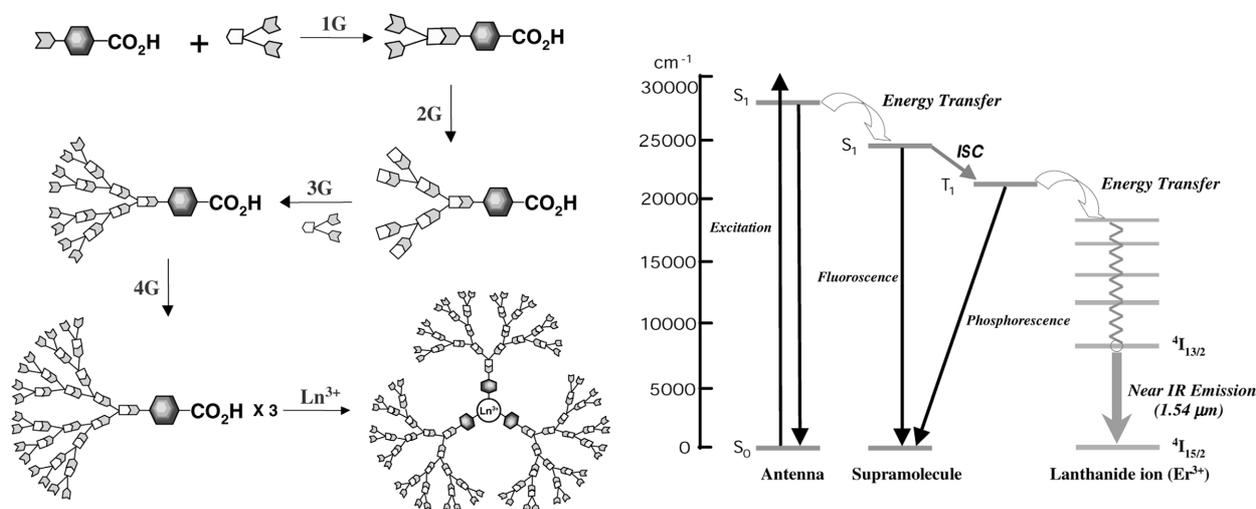


**Scheme 8.** Synthetic strategy and energy transfer pathway of novel lanthanide-cored supramolecular systems with highly efficient light-harvesting dendritic arrays.

process. Eventually, it falls back to the ground state ($Er^{3+}$, $^4I_{15/2}$) of the lanthanide ions, emitting the stimulated emission. It is very important to note that the accumulating photon energy from the triplet state of the supramolecular ligands can excite the lanthanide ions as much as possible, thus maximizing the optical amplification gain. Also, the optophysical properties of the lanthanide-encapsulated supramolecular systems are optimized and maximized during artificially light gathering and transferring by way of using the light-harvesting principle of naturally existing photo-synthetic antenna.

## Summary and Outlook

New synthetic methodology of the saturated and unsaturated Er(III)-chelated prototype complexes based on benzoate and pentafluorobenzoate ligands was successfully developed through the ligand-exchange reaction. The saturated 8-coordinated $Er^{3+}$ complexes exhibit stronger near-IR emission than those of the unsaturated 6-coordinated $Er^{3+}$ complexes. Also, 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. We also have designed and developed novel luminescent $Eu^{3+}$ complexes based on naphthalene derivatives in order to investigate and understand efficient energy transfer pathways from luminescent ligands to $Ln^{3+}$ ions in luminescent $Ln^{3+}$ complexes. The direct luminescent $Ln^{3+}$ complex has much higher PL efficiency than the indirect luminescent $Ln^{3+}$ complex, due to a higher ISC efficiency in a direct complex. In the indirect luminescent $Ln^{3+}$ complex, the involvement of the energy transfer of the singlet state of the luminescent ligand was investigated and demonstrated for the first time to the best our knowledge. Furthermore, we have developed novel inert and stable, direct Er(III)-cored supramolecular complexes based on metalloporphyrins. $Er^{3+}$ ions were encapsulated by the metalloporphyrins ligands, such as Zn(II)- and Pt(II)-porphyrins. The Er(III)-cored supramolecular complex based on Pt(II)-porphyrin has the much higher PL efficiency than Er(III)-cored supramolecular complex based on Zn(II)-porphyrin, due to the higher ISC efficiency for the conversion of a singlet state into a triplet state than that of Zn(II)-porphyrin derivative. The triplet state of Pt(II)-porphyrin in Er(III) complex based on Pt(II)-porphyrin was also detected with its lifetime of 30 ms. Also, the Er(III)-cored dendrimer complex with a G2-aryl ether dendron has the higher PL intensity than the saturated 9-coordinated complex by 7 times, due to the efficient site-isolation effect. This investigation opens the development of a series of novel Ln(III)-cored supramolecular systems based on metalloporphyrins and new antenna chromophores with highly efficient light-harvesting effect.

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, the dependences of $Ln^{3+}$ ion and ligand structure on ampli-

fication principles (such as the optical amplification lifetime, excited state dynamics, etc.) need to be systematically established. Based on the relationship established, the design and synthesis of the highly efficient light-harvesting integrated supramolecular systems based on Ln(III)-cored dendritic or supramolecular complexes using molecular engineering approach need to be investigated to optimize opto-physical properties during artificially light gathering and transferring by way of using principles of natural photo-synthetic antenna. In addition, the establishment of basic principles of amplification, including the dependence of $Ln^{3+}$ complexes and ligand structure on excited state dynamics and lifetimes, as well as the elucidation of basic energy transformation and transfer mechanisms, will be investigated with regard to understand the structure-property relationships.

Based on the structure-property relationships to be determined, ultrahighly efficient light-harvesting supramolecular structures will be optimized and their application as the future optical amplification devices will be examined. Utilizing our developed materials, we will have the leverage to lead the world in tomorrow's communication technology and the technological impact will be similar to the integrated circuit development in semiconductor industries. This will not only be considered to be the material revolution in the heart of exploratory materials in optical information and communication, but also will open up many new areas of applications of polymeric materials for use in ultrahigh speed communication and information systems for the future generation.

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