

Sensitized Near IR Luminescence of Er(III) Ion in Lanthanide Complexes Based on Diketone Derivatives: Synthesis and Photophysical Behaviors

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Two β -diketone derivatives bearing triphenylene (1-naphthalene-2-yl-3-triphenylene-2-yl-propane-1,3-dione (NTPD)) and naphthalene (1,3-di-naphthalene-2-yl-propane-1,3-dione (DNPD)) and their Ln(III) complexes (Ln = Er or Gd) were synthesized and their photophysical properties were investigated. The sensitized emission of Er³⁺ ion in Er³⁺-[NTPD]₃(terpy) and Er³⁺-[DNPD]₃(terpy) was observed upon excitation at absorption maximum of ligands. Their photophysical studies indicate the sensitization of Er³⁺ luminescence by energy transfer through the excited triplet state of β -diketone ligand. The energy transfer rate through the excited triplet state of β -diketone ligand to Er³⁺ ion occurs faster than that of the oxygen quenching rate.

Key Words : Lanthanide(III)-cored complexes, Energy transfer pathway, Triplet state, Near infrared (NIR) emission

Introduction

The 4f electrons in lanthanide (Ln³⁺) 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 which properties are applied to various research fields. Especially near infrared emission of lanthanide ion has drawn much attention in a wide variety of photonic applications such as planar waveguide amplifiers, plastic lasers, light-emitting diodes and luminescent probes.¹⁻⁶ However, the 4fⁿ-4fⁿ absorption and emission cross section of lanthanide ion is too low. To overcome these shortcomings, luminescent organic ligands are introduced to complexes of these metals.^{7,8} The lanthanide ions in luminescent lanthanide complexes are sensitized by energy transfer from the organic ligand to lanthanide ion, resulting in high luminescent quantum yield of lanthanide ion.

Among the numerous organic ligands, β -diketone ligands were well-known as a sensitizer to be utilized for the development of luminescent lanthanide complexes with the visible Ln³⁺ emissions, such as Eu³⁺, Tb³⁺ and Sm³⁺ ions.⁹ Their sensitization process is that a central metal ion is excited through the excitation of the ligand and then the excited energy of the ligand is transferred to the central ions through the ligand's triplet energy level.¹⁰⁻¹² The energy transfer between the triphenylene functionalized antenna and metal ion takes place through the triplet state of triphenylene because of high intersystem crossing (ISC) efficiency of triphenylene. In this paper, we have synthesized Er(III)-cored complexes based on triphenylene- and naphthalene-functionalized β -diketone and investigated the photophysical processes.

Experimental

Synthesis and Analysis

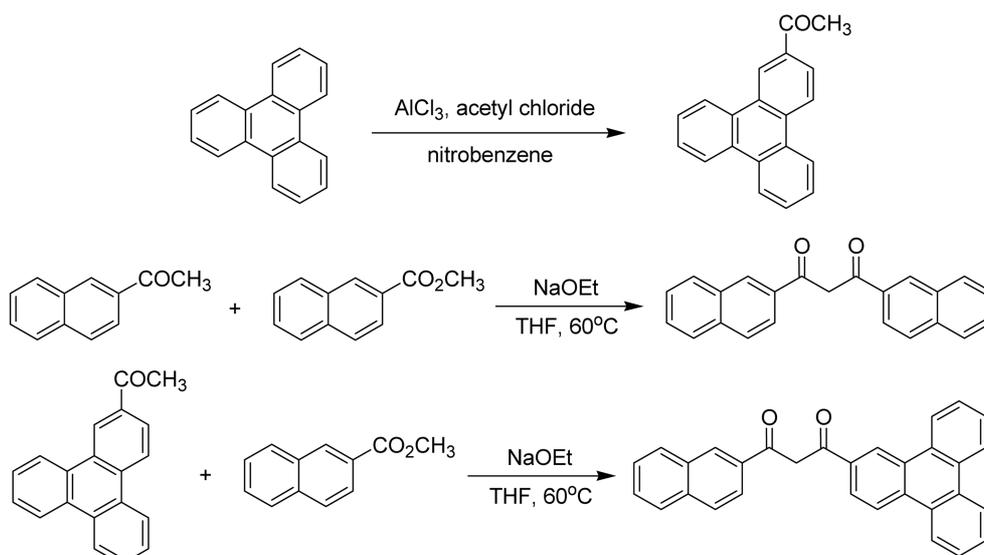
2-Acetyltriphenylene: To anhydrous solution of nitrobenzene (10 mL), triphenylene (1.0 g, 4.38 mmol) and AlCl₃ (1.17 g, 8.76 mmol) and acetyl chloride under N₂ were added. The mixture was stirred at 0 °C for 2 h and cooling bath was removed and the reaction mixture was stirred at room temperature overnight. The mixture was poured into ice water, extracted with CHCl₃, the organic layer was washed with water, and dried with anhydrous MgSO₄. The crude mixture was finally purified by column chromatography (SiO₂, CHCl₃). Yield: 99%.

¹H-NMR (CDCl₃, 300 MHz) [ppm]: δ 9.19 (d, 1H), 8.70-8.58 (m, 5H), 8.16 (dd, 1H), 7.70-7.64 (m, 4H), 2.77 (s, 3H); ¹³C-NMR (CDCl₃, ppm): δ 197.74, 134.98, 133.13, 130.54, 129.76, 129.33, 128.72, 128.24, 127.66, 127.42, 127.31, 126.06, 123.88, 123.47, 123.27, 123.22, 26.91.

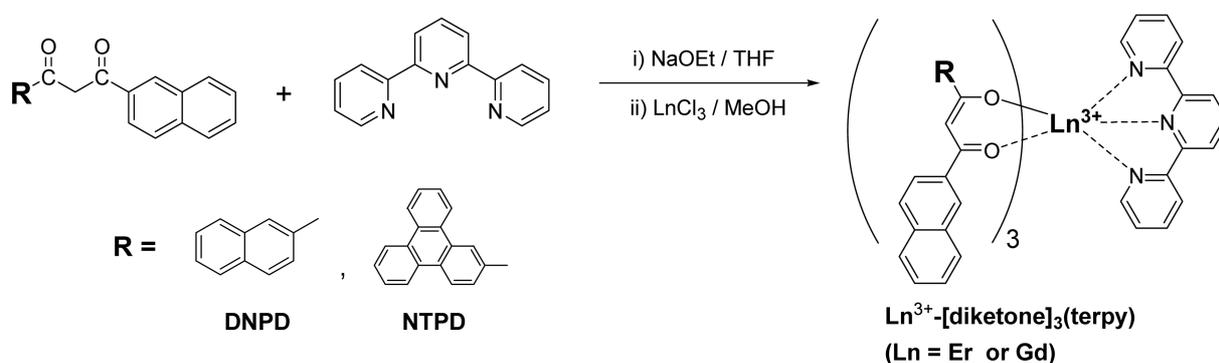
1,3-Di-naphthalen-2-yl-propane-1,3-dione (DNPD): A solution of 2-acetonaphthalene (2.0 g, 11.75 mmol) and methyl 2-naphthalenoate (2.63 g, 14.10 mmol) in dry THF (70 mL) was purged with N₂ for 10 min. The sodium ethoxide (0.96 g, 14.10 mmol) was added and the mixture was stirred for 24 hrs at 60 °C. After cooling down, hydrochloric acid was added and the organic layer exhaustively extracted with chloroform. The combined organic layers were washed with a saturated solution of NaHCO₃, then with water, dried (Na₂SO₄) and concentrated under reduced pressure. The crude mixture was finally purified by column chromatography (SiO₂, CHCl₃). Yield: 66%.

¹H-NMR (CDCl₃, 300 MHz) [ppm]: δ 8.59 (d, 2H), 8.08-7.89 (m, 8H), 7.62-7.43 (m, 4H), 7.15 (s, 1H); EI-MS: *m/z* calcd for C₂₃H₁₆O₂ 324.37, found [M⁺] 324.

1-Naphthalen-2-yl-3-triphenylene-2-yl-propane-1,3-dione



Scheme 1



Scheme 2

(NTPD): Synthesis of NTPD was carried out in a similar manner to that of DNPD. Yield: 65%.

$^1\text{H-NMR}$ (CDCl_3 , 300 MHz) [ppm]: δ 9.34 (d, 1H), 8.82 (m, 1H), 8.75 (d, 1H), 8.70-8.63 (m, 4H), 8.26 (dd, 1H), 8.12-7.92 (m, 4H), 7.75-7.70 (m, 4H), 7.63-7.59 (m, 2H), 7.31 (s, 1H); EI-MS: m/z calcd for $\text{C}_{31}\text{H}_{20}\text{O}_2$ 424.15, found $[\text{M}^+]$ 424.

Synthesis of Ln^{3+} -[diketone] $_3$ (terpy): General Procedure.^{5c} A mixture of appropriate diketone ligand (3 equiv.) and NaOEt (3.3 equiv.) was stirred in freshly distilled THF at room temperature for 1 h. After the formation of salts was completed, the methanol solution of anhydrous LnCl_3 (1 equiv.) ($\text{Ln}=\text{Er}$, or Gd) and 2,2':6'2''-terpyridine (1.1 equiv.) was added to the reaction solution, and then stirred for 48 hrs. The resulting solution was filtered and the solvents were removed. The resultant solid was washed sequentially with methanol, hexane and diethyl ether, yielding a yellowish solid.

Er^{3+} -[DNPD] $_3$ (terpy): Yield: 51%. Anal. Calcd for $\text{C}_{84}\text{H}_{56}\text{N}_3\text{O}_6\text{Er}$: C, 73.61; H, 4.12; N, 3.07; Er, 12.20; found: C, 72.23; H, 4.57; N, 2.78; Er, 12.69.

Gd^{3+} -[DNPD] $_3$ (terpy): Yield: 66%. Anal. Calcd for $\text{C}_{84}\text{H}_{56}\text{N}_3\text{O}_6\text{Gd}$: C, 74.15; H, 4.15; N, 3.09; found: C, 73.35;

H, 4.73; N, 2.82.

Er^{3+} -[NTPD] $_3$ (terpy): Yield: 72%. Anal. Calcd for $\text{C}_{108}\text{H}_{68}\text{N}_3\text{O}_6\text{Er}$: C, 77.63; H, 4.10; N, 2.51; Er, 10.01; found: C, 76.86; H, 4.37; N, 2.36; Er, 10.32.

Gd^{3+} -[NTPD] $_3$ (terpy): Yield: 46%. Anal. Calcd for $\text{C}_{108}\text{H}_{68}\text{N}_3\text{O}_6\text{Gd}$: C, 78.10; H, 4.13; N, 2.53; found: C, 76.98; H, 4.63; N, 2.42.

Spectroscopic measurements. All solvents for the optical measurements were the spectroscopic grade and used without further purification. Steady-state UV-vis absorption spectra were recorded with a Shimadzu UV-2401PC spectrophotometer at room temperature. The fluorescence emission and excitation spectra were measured using an Edinburgh FS920 fluorometer with 450W Xe-lamp. Visible emission spectra were taken with a PMT system (Hamamatsu R955) and near-infrared emission spectra were taken with Ge-detector (Edinburgh EI-L) cooled by the liquid nitrogen. To measure low-temperature luminescence, the samples were degassed by argon bubbling for 30 min. and measured by using optical dewar. Fluorescence quantum yields (ϕ_f) of ligand and complexes were estimated using a 9,10-diphenylanthracene as a standard with a known value of $\phi_f = 0.9$.¹³

The microsecond time-resolved emission measurements were carried out by using a Nd:YAG laser. The third harmonic generation (355 nm, 5 ns pulse width at 10 Hz repetition rate) of Nd:YAG laser (EXSPLA NT342) system was used to excite the ligand moiety. The emission spectrum was analyzed with a monochromator (Acton spectrapro 2300i) and detected with a photomultiplier followed by a digital oscilloscope (Agilent infinium 54832B DSO).

Results and Discussion

We have developed lanthanide(III) (Ln(III) or Ln^{3+})-cored complexes based on 1,3-di-naphthalene-2-yl-propane-1,3-dione (DNPD) and 1-naphthalene-2-yl-3-triphenyl-2-yl-propane-1,3-dione (NTPD) for near IR emission to investigate the energy transfer pathway from the antenna ligand to the Ln^{3+} ion. Ln(III) complexes were prepared by ligand-exchange reaction using anhydrous LnCl_3 , as illustrated in

Scheme 2. The highly-coordinated complexation of the Ln^{3+} ion with NTPD or DNPD as well as one terpyridine (terpy) was formed. Ln^{3+} ions were effectively encapsulated by a β -diketone derivatives and terpyridine. The chemical structures of all materials were identified by FT-IR, ^1H - and EI-mass, EA, UV-vis absorption and emission spectroscopic methods.

Figure 1 shows the UV-vis absorption spectra of NTPD, DNPD and their Ln(III) complexes. NTPD and DNPD exhibit the absorption bands in the spectral regions of 250-300 nm, which are attributable to triphenylene and naphthalene, in addition to the broad and structureless absorption band centered at around 360-400 nm are assigned to spin-allowed π - π^* transitions. Such absorptions spectra of NTPD and DNPD have been previously identified in the other β -diketone derivatives.¹⁴ Absorption spectra of ligands and complexes show very similar spectral features, indicating that the lanthanide ion does not significantly influence

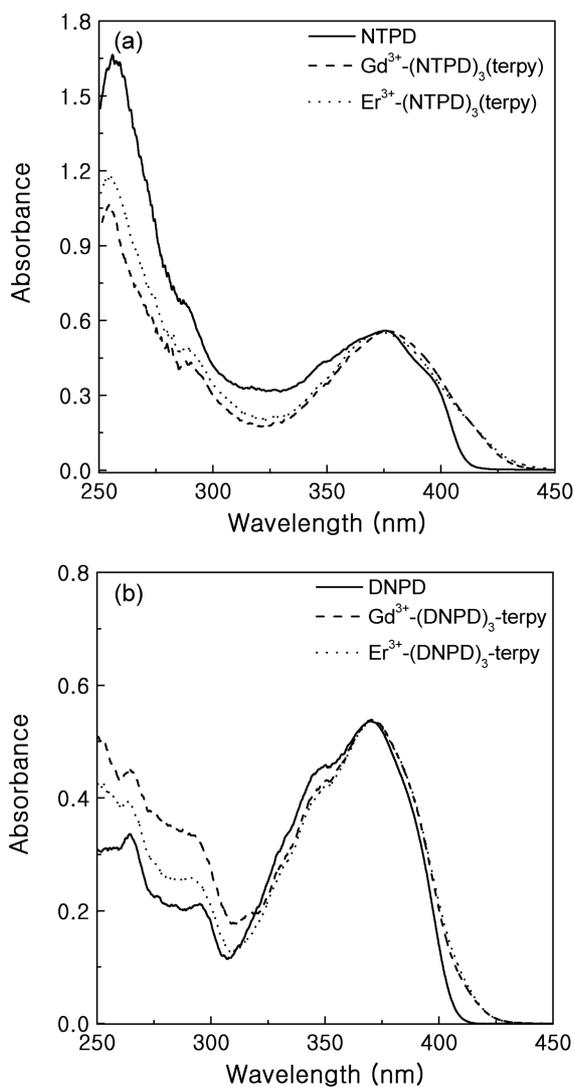


Figure 1. UV-vis absorption spectra of (a) NTPD and Ln^{3+} -[NTPD]₃(terpy) (b) DNPD and Ln^{3+} -[DNPD]₃(terpy) at 298 K in THF ($\lambda_{\text{ex}} = 375$ nm, Conc. = 2.0×10^{-5} M).

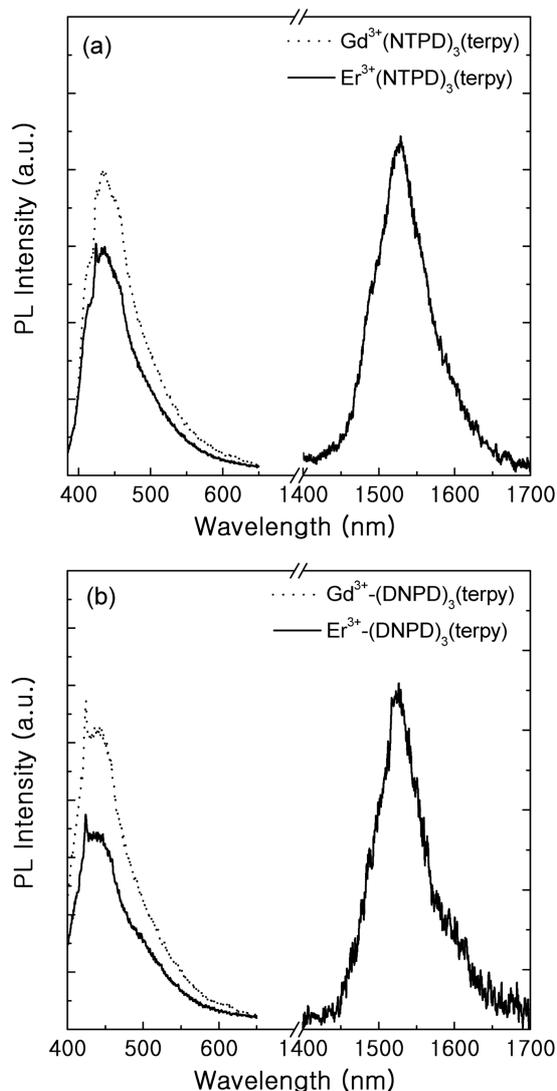


Figure 2. PL spectra of (a) Ln^{3+} -[NTPD]₃(terpy) (b) Ln^{3+} -[DNPD]₃(terpy) at 298 K in THF ($\lambda_{\text{ex}} = 375$ nm, Conc. = 2.0×10^{-5} M).

the energy state of the NTPD or DNPd.

The PL spectra of NTPD, DNPd and their Ln(III) complexes with an excitation at 375 nm under same experimental conditions were obtained (Figure 2). The fluorescence spectra of the free ligands, NTPD and DNPd in m-THF showed very weak emission band. The fluorescence quantum yield of free ligands in Ln(III)-cored complexes is slightly decreased, compared with those of the free NTPD and DNPd ligand, although the intensity decrement is very small. This fact that the fluorescence quantum yield of the NTPD and DNPd ligands is very low may be due to the higher ISC efficiency of ligands, resulting in enhancing the formation of the excited triplet state of the ligands. The decreased fluorescence quantum yield in the Ln(III) complexes is attributed to the fact that the intersystem crossing quantum yield is increased by heavy atom effect. In addition, sensitized emission spectra of Er^{3+} ion in the complexes

were observed at 1530 nm, originated from $4f-4f$ electronic transition of the first excited state (${}^4\text{I}_{13/2}$) to the ground state (${}^4\text{I}_{15/2}$) of the partially filled $4f$ shell.

The excitation spectrum of the Er^{3+} -cored complex, monitored at the emission wavelength of 1530 nm which arises from the electronic transition of ${}^4\text{I}_{13/2} \rightarrow {}^4\text{I}_{15/2}$ of Er^{3+} ion, closely matched the absorption spectrum of the corresponding ligand in the complex. It indicates that, upon the photoexcitation of the ligands, the excitation energy was mainly absorbed by the NTPD and DNPd ligands, and then transferred to the Er^{3+} ion. Generally, it is accepted that the emission spectra and decay time measurements for the Gd(III)-cored complexes allow the identification of the lowest triplet state of a ligand, which is generated by ISC process from the excited singlet state, because Gd^{3+} ion has a heavy atom effect and no energy level below $32,000\text{ cm}^{-1}$. As shown in Figure 3, in the case of Gd^{3+} -[NTPD] $_3$ (terpy) and Gd^{3+} -[DNPd] $_3$ (terpy), the luminescence spectra of Gd^{3+} -complexes in m-THF at 77 K exhibit a strong phosphorescence band with the fluorescence band of the corresponding ligands.

The lowest triplet state of NTPD and DNPd was determined from the 0-0 transition in phosphorescence spectra, which values are about 19300 cm^{-1} in both of them. On the other hand, no phosphorescence was observed in both Er^{3+} -[NTPD] $_3$ (terpy) and Er^{3+} -[DNPd] $_3$ (terpy) upon photoexcitation at 375 nm, implying that efficient energy transfer between the ligands and Er^{3+} ion takes place. As a result, the strong quenching of phosphorescence led us to postulate that excitation energy of the triplet excited state was transferred to the resonance levels of Er^{3+} ion.

To obtain further information on the energy transfer process, we measured the phosphorescence decay profiles of Ln^{3+} -[NTPD] $_3$ (terpy) and Ln^{3+} -[DNPd] $_3$ (terpy) with an excitation at 355 nm. The decay profiles were monitored at 520 nm which corresponds to the emission of triplet state. The phosphorescence lifetimes of Gd^{3+} -[NTPD] $_3$ (terpy) and Gd^{3+} -[DNPd] $_3$ (terpy) were determined to be 7 and 2 ms, respectively. However, the decay times of Er^{3+} -[NTPD] $_3$ (terpy) and Er^{3+} -[DNPd] $_3$ (terpy) are too short to be analyzed. It is probably due to the fact that the excitation energy of triplet state in Er^{3+} -[NTPD] $_3$ (terpy) and Er^{3+} -[DNPd] $_3$ (terpy) is transferred to Er^{3+} ion very quickly. Considering the spectral tendency of phosphorescence and decay time of triplet state in Ln(III)-cored complexes with NTPD and DNPd, we can suggest that the energy transfer in Er^{3+} -[NTPD] $_3$ (terpy) and Er^{3+} -[DNPd] $_3$ (terpy) takes place through the triplet state. It is in a good agreement with the interpretation, from the spectral dependency of the phosphorescence on oxygen concentration, that the strong sensitized Er^{3+} emissions in Er^{3+} -[NTPD] $_3$ (terpy) and Er^{3+} -[DNPd] $_3$ (terpy) are observed in both aerated and deoxygenated THF solution, upon the photoexcitation of the ligand at 375 nm. On the basis of the results mentioned above, the energy transfer in Er^{3+} -[NTPD] $_3$ (terpy) and Er^{3+} -[DNPd] $_3$ (terpy) takes place through the triplet state and the energy transfer rate between the ligands and Er^{3+} has the

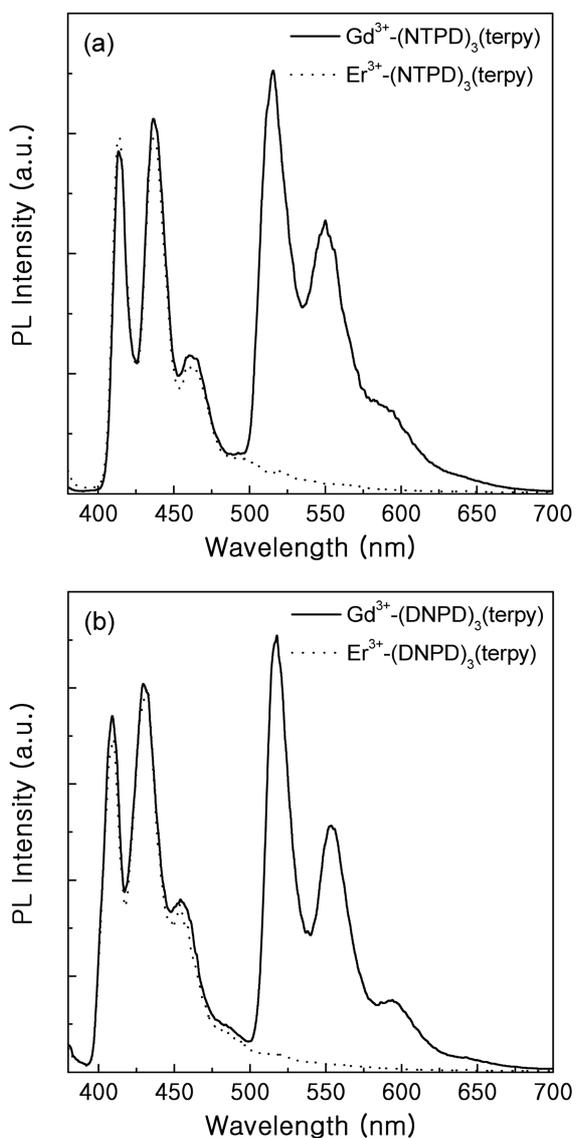


Figure 3. PL spectra of (a) Ln^{3+} -[NTPD] $_3$ (terpy) (b) Ln^{3+} -[DNPd] $_3$ (terpy) at 77 K in m-THF ($\lambda_{\text{ex}} = 375\text{ nm}$, Conc. = $2.0 \times 10^{-5}\text{ M}$).

larger order of magnitude than the oxygen quenching rate ($k_{\text{et}} > 10^7 \text{ s}^{-1}$).

Conclusions

We have developed the Er(III)-cored complexes based on NTPD and DNPD for near IR emission and investigated their energy transfer pathway using the steady state and time resolved spectroscopic measurement. Our experimental observations suggest that the Ln(III)-cored complexes based on NTPD and DNPD are effectively formed to be the triplet state by intersystem crossing process. The sensitization of Er³⁺ luminescence takes place by the effective energy transfer between the β -diketone ligand and Ln³⁺ ion through the excited triplet state of β -diketone ligand.

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