Effect of Coordination Environment on the Photophysical Properties of Luminescent Europium(III) Complexes

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A series of Eu(III) complexes with various neutral ligands (2,2':6',2''-terpyridine (T), diglyme (D), $1N$-(2-dimethylamino)ethyl)-$1N$, $2N$, $2N$-trimethylethane-1,2-diamine (PT), di-(2-picolyl)-amine derivative (HT), and multidentate terpyridine derivative (DT)) were synthesized to investigate the effect of coordination environment on the sensitized luminescence of Eu(III) complexes. The nine coordination sites of the Eu^{3+} ion are occupied by three bidentate carboxylate moieties and one neutral ligand. The highest emission intensity is obtained for Eu^{3+}-[NA]$_3$ (PT), due to the difference in energy transfer efficiency and symmetry of the first coordination sphere of Eu^{3+} ion. But, the lowest emission intensity is obtained for Eu^{3+}-[NA]$_3$(T). Terpyridine may not play an important role antenna for photosensitizing Eu^{3+} ion. It could be attributed to the weak spectral overlap integral J value between its phosphorescence band and Eu^{3+} ion absorption band. Therefore, different coordination environment of Ln^{3+} ion play an important role in providing sensitization of lanthanide ion emission.

Key Words: Neutral ligand. Lanthanide-cored complex. Sensitized luminescence. Coordination environment. Quantum efficiency

Introduction

The organic lanthanide (Ln) complexes have been of great interest due to their potential applications, such as electroluminescence[1-3] and optical amplifier.[4,5] The complex formation between Ln^{3+} ion and organic ligand has an important parameter to enhance the photoluminescence (PL) efficiency because sensitization process via energy transfer is much more effective than the direct excitation of Ln^{3+} ions.[6] Generally, excited state of the Ln^{3+} ions is effectively quenched by interactions with high energy vibrations like O-H ($\nu_{O-H} \approx 3400$ cm^{-1}) group in solvent or water as quenchers.[7] In our previous results, the coordination number of complexed ligands with lanthanide ions has an important parameter to increase the PL intensity of lanthanide(III) complex.[8] Therefore, the general strategies in the design of highly luminescent Eu(III) complexes are to synthesize a organic ligand that comprises preferably charged oxygen donor atoms such as carboxylate for preventing the non-radiative process and to maintain higher triplet level of the ligand than the emissive level ($^5D_0$) of the Eu^{3+} ion for the efficient energy transfer process. In addition, to yield more stable 9-coordinated Ln(III)-cored complexes, the terpyridine has been used as a Lewis base to be accounted for the contribution of photosensitizing the luminescence of Ln(III) ion in the present complexes, since terpyridine is well-known as a good antenna for photosensitizing the luminescence of Ln(III) ion.[9] However, instead of terpyridine, other neutral ligands have not been systematically studied to form 9-coordinated Ln(III)-cored complexes.

Here, to investigate the effect of coordination environment on the sensitized luminescence of Eu(III) complexes, we have synthesized a series of Eu(III) complexes with various neutral ligands. The nine coordination sites of the Eu^{3+} ion are occupied by three bidentate carboxylate moieties and one neutral ligand as depicted in Fig. 1. Various neutral ligands used in this paper may be expected to effectively block luminescent deactivating molecules like water or solvent, increasing sensitized emission.

Experimental

Synthesis and Characterization. Solvents and other chemicals were used after purification, according to standard literature methods.[10] Flash chromatography was carried out with Silica Gel 60 (230-400 mesh). ^{1}H-NMR spectra were recorded with the use of Varian Oxford 300 MHz spectrometers. Chemical shifts were reported in ppm units with tetramethylsilane (TMS) 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. The elemental analyses were carried out by means of EA1110 (CE Instrument). Steady-state absorption spectra were recorded by a Shimadzu UV-2401PC spectrophotometer and photoluminescence spectra were measured by steady-state fluorimeter (Edinburgh FS920) with 450 W Xe-lamp. The excitation light from 300 mm focal length monochromator was focused on the sample. The fluorescence from the sample was collected and refocused to the emission monochromator with 300 mm focal length. Visible emission spectra were taken with a PMT system (Hamamatsu R955). All spectra were taken at the room temperature. Time-resolved emission measurements on the millisecond time scale were performed with an excitation at 290 nm by using a Nd:YAG laser (EXSPLA NT342) and OPO system. The excitation beam had a 5 ns pulse width at 10 Hz repetition rate. The emission spectrum was analyzed with a monochromator (Acton Spectrapro 2300i) and detected

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with a photomultiplier followed by a boxcar averager (Stanford Research System) or a digital oscilloscope (Agilent infinium 54832B DSO).

Preparation of Hexyl-bis-pyridin-2-yl-methylamine (HT). The mixture of di-(2-picolyl)amine (1.11 g, 5.57 mmol), 1-bromohexane (0.94 mL, 6.69 mmol), and K_2CO_3 (2.31 g, 16.71 mmol) in acetonitrile was heated at reflux and stirred for 24 hrs. The mixture was allowed to cool and evaporated to dryness under reduced pressure. The crude product was purified flash column chromatography (CH_2Cl_2): Yield 82%. ^{1}H-NMR (CDCl$_3$, 300 MHz) δ 8.53 (d, $J = 4.5$ Hz, 2H), 7.65 (t, $J = 7.2$ Hz, 2H), 7.57 (d, $J = 7.8$ Hz, 2H), 7.15 (t, $J = 7.2$ Hz, 2H), 3.81 (s, 4H), 2.54 (t, 2H), 1.54 (m, 2H), 1.29-1.22 (m, 6H), 0.85 (t, 6H); FAB-Mass: m/z calcd for $C_{18}H_{25}N_3$ 283.20, found (M$^-$) 283.

Preparation of 1,4-Bis-dodecyloxy-benzene (1). To a 100 mL round-bottomed flask fitted with a nitrogen inlet tube was added hydroquinone (2.0 g, 18.16 mmol), KOH (3.1 g, 54.49 mmol), 1-bromododecane (9.16 mL, 38.14 mmol), and 50 mL of EtOH. The reaction mixture was stirred for 12 hrs under reflux and then was poured into a 5 N hydrochloric acid. The crude mixture was recrystallized from MeOH: Yield 87%. ^{1}H-NMR (CDCl$_3$, 300 MHz) δ 6.82 (s, 2H), 3.89 (t, 4H), 1.75 (m, 4H), 1.52-1.26 (m, 36H), 0.88 (t, 6H).

Preparation of 1,4-Bis-bromomethyl-2,5-bis-dodecyloxy-benzene (2). The reaction mixture of 1,4-bis-dodecyloxy-benzene (2.0 g, 4.48 mmol), $(CH_2O)_n$ (4.0 g, 13.43 mmol), and NaBr (1.38 g, 13.43 mmol) in acetic acid was stirred for 1 h under reflux and then was added H_2SO_4:AcOH (1:1) until disappear starting material. The crude mixture was extracted with dichloromethane and recrystallized from CH_2Cl_2/Hexane: Yield 82%. ^{1}H-NMR (CDCl$_3$, 300 MHz) δ 6.85 (s, 2H), 4.52 (s, 4H), 3.98 (t, 4H), 1.81 (m, 4H), 1.52-1.27 (m, 36H), 0.88 (t, 6H).

Preparation of 1,4-[(Bis-pyridin-2-ylmethyl-amino)-methyl]-2,5-bis-dodecyloxy-benzene (DT). A mixture of 2 (1.25 g, 1.98 mmol), di-(2-picolyl)amine (0.87 g, 4.35 mmol), and K_2CO_3 (1.37 g, 9.88 mmol) in acetonitrile was heated at reflux and stirred for 24 hrs. The mixture was allowed to cool and evaporated to dryness under reduced pressure. The crude product was purified flash column chromatography (CH_2Cl_2/ Hexane, 2:1): Yield 88%. ^{1}H-NMR (CDCl$_3$, 300 MHz) δ 8.51 (d, $J = 4.5$ Hz, 4H), 7.62 (m, 8H), 7.13-7.10 (m, 6H), 3.85 (m, 12H), 3.72 (s, 4H), 1.71 (t, 4H), 1.39-1.27 (m, 36H), 0.88 (t, 6H); FAB-Mass: m/z calcd for $C_{56}H_{80}N_6O_2$ 868.63, found (M$^-$) 869.

Preparation of Eu(III) Complexes. The Eu(III) complexes having various neutral ligands were synthesized through the ligand-exchange reaction using EuCl$_3$ developed in our laboratory. A mixture of 1-naphtoic acid (3.0 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 EuCl$_3$ (1.0 equiv.) and appropriated neutral ligand (NL) (1.1 equiv.) 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, hexane and diethyl ether, yielding a yellowish solid. The complexes all gave similar IR spectra.

Eu^{3+}-[NA]$_3$(T): Yield 74%. Anal. Calcd. for $C_{48}H_{32}N_3O_6$
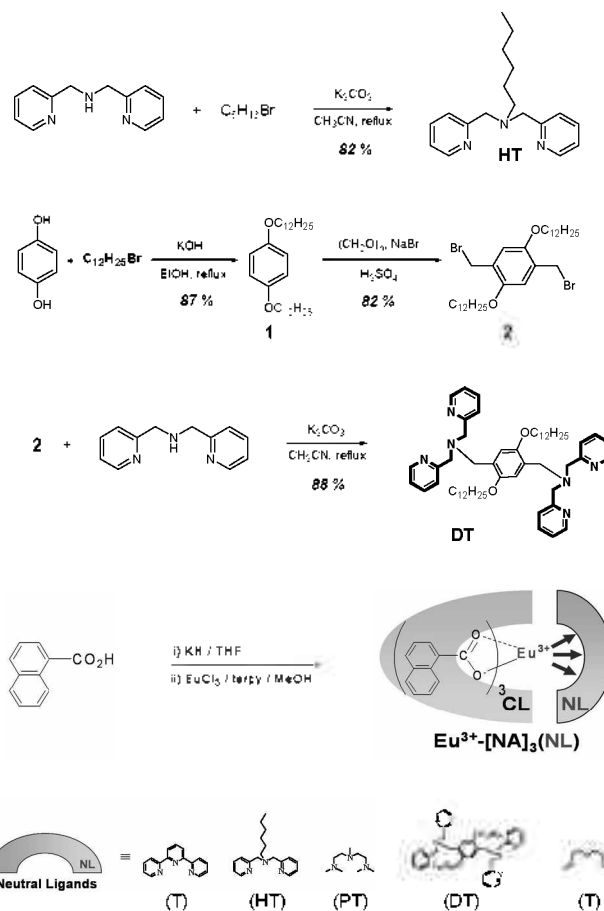

Figure 1. Synthesis of neutral ligands and their Eu(III) complexes based on 1-naphthoic acid.

Eu: C, 64.15; H, 3.59; N, 4.68; Eu, 16.91, found C, 63.58; H, 3.72; N, 4.45.

Eu^{3+}-[NA]$_3$(HT): Yield 66%. Anal. Calcd. for $C_{51}H_{46}N_3O_6$ Eu: C, 64.55; H, 4.89; N, 4.43; Eu, 16.01, found C, 64.55; H, 4.89; N, 4.43.

Eu^{3+}-[NA]$_3$(DT): Yield 72%. Anal. Calcd. for $C_{122}H_{122}N_6$ $O_{14}Eu_2$: C, 66.60; H, 5.59; N, 3.82; Eu, 13.81, found C, 65.45; H, 4.94; N, 3.68.

Eu^{3+}-[NA]$_3$(PT): Yield 97%. Anal. Calcd. for $C_{42}H_{44}N_3O_6$ Eu: C, 60.14; H, 5.29; N, 5.01; Eu, 18.12, found C, 60.75; H, 5.59; N, 5.24.

Eu^{3+}-[NA]$_3$(D): Yield 76%. Anal. Calcd. for $C_{36}H_{35}O_6Eu$: C, 58.58; H, 4.41; Eu, 19.00, found C, 57.98; H, 4.56.

Gd^{3+}-[NA]$_3$(T): Yield 68%. Anal. Calcd. for $C_{48}H_{32}N_3O_6Gd$: C, 63.77; H, 3.57; N, 4.65; Gd, 17.39, found C, 62.98; H, 3.69; N, 4.53.

Results and Discussion

Treatment di-(2-picolyl)amine with alkyl bromide or benzyl bromide (2) in the presence of K_2CO_3 in acetonitrile afforded neutral ligands. The chemical structure of monomers was characterized by FT-IR, ^{1}H-NMR, FAB-mass, absorption and emission spectroscopies. In particular, the observed δ value for benzyl protons in 2 is 4.52 ppm. After reaction, the benzyl
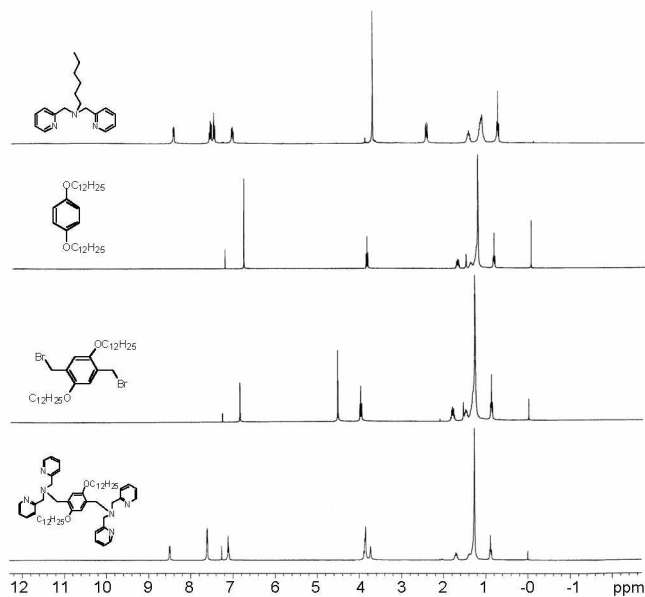
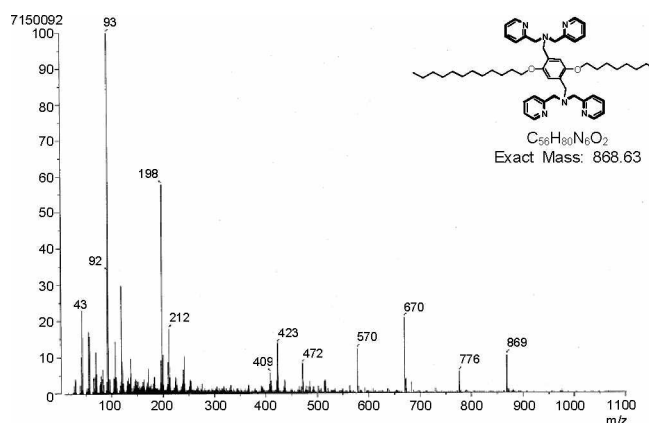**Figure 2.** ^{1}H NMR spectrum of neutral ligand in CDCl$_3$.

C$_{56}$H$_{80}$N$_6$O$_2$
Exact Mass: 868.63

Figure 3. FAB-mass spectrum of neutral lignad (DT).

Figure 4. FT-IR spectra of ligand and their Eu(III) complexes.

Figure 5. UV-Vis absorption (---), excitation (-·-·-, λ_{em} = 367 nm), and emission (--, λ_{ex} = 295 nm) spectra of 1-naphthoic acid (NA) in CH$_3$CN at 298K.

proton in DT unit was shifted at 3.72 ppm (Fig. 2). The synthesized HT and DT ligand were also analyzed by FAB mass spectroscopies. The FAB mass spectra exhibited peaks at 283 (m/z) for HT and 869 (m/z) for DT, respectively (Fig. 3). Experimental evidences for the proposed structures of Eu(III) complex were provided by IR spectra and elemental analysis.

Although MALDI-TOF spectroscopy did not obtained a signal corresponding to the Eu(III) complex, the signal of the typical isotope pattern was detected. From the FT-IR spectra (Fig. 4), the C=O streching band from the free ligand (NA) was observed at 1720 cm^{-1}. In comparison with free ligand, stretching vibration modes of the carboxylate group was observed at ~1600 cm^{-1}, which indicates that the carboxylic acid group was converted into carboxylate anion as a result of the formation of the stable Eu(III) complexes.[11,12]

Fig. 5 shows absorption, excitation and photoluminescence spectra of 1-naphthoic acid (NA). The free ligand displayed absorbance maximum at 295 nm in acetonitrile solution, which is attributed to the π-π* transition of the π-conjugated segment.
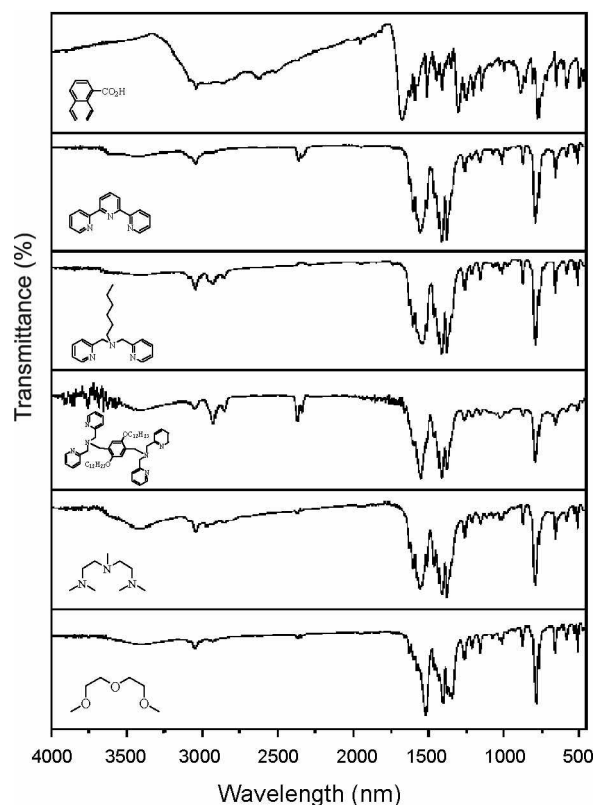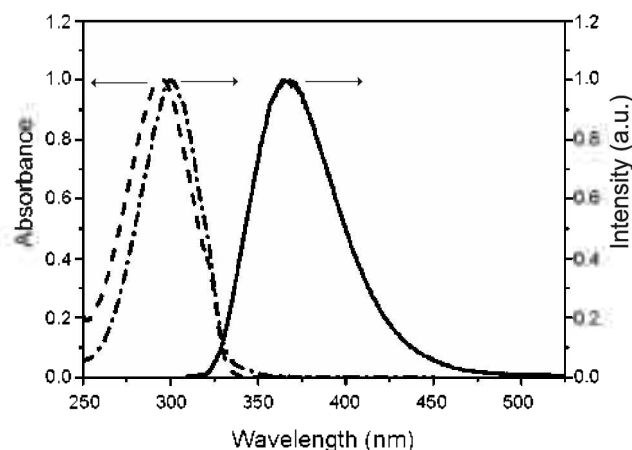
With an excitation wavelength of 295 nm, the NA ligand shows a strong luminescent band around 367 nm and the excitation spectrum of this ligand luminescence nearly matches the absorption of the ligand. The effect of solvent was described in a previous literature.[13] Complexation of the Eu^{3-} ion with NA did not cause any change in the absorption spectra and there are no absorption bands in various neutral ligands except 2.2':6'.2"-terpyridine (T) and absorption band of terpyridine unit overlaps with the NA absorption (Fig. 6).

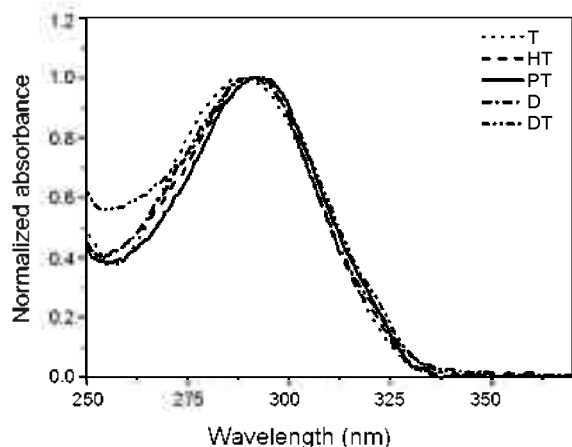To compare the PL intensity of the Eu(III) complexes under

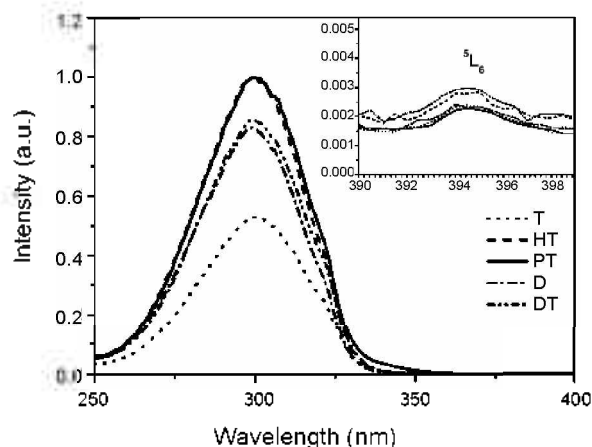**Figure 6.** UV-Vis absorption spectra of a series of Eu³⁺-[NA]₃(NL) in CH₃CN at 298 K.

Figure 8. Excitation spectra of a series of Eu³⁺-[NA]₃(NL) in CH₃CN at 298 K (λ_{em} = 615 nm).

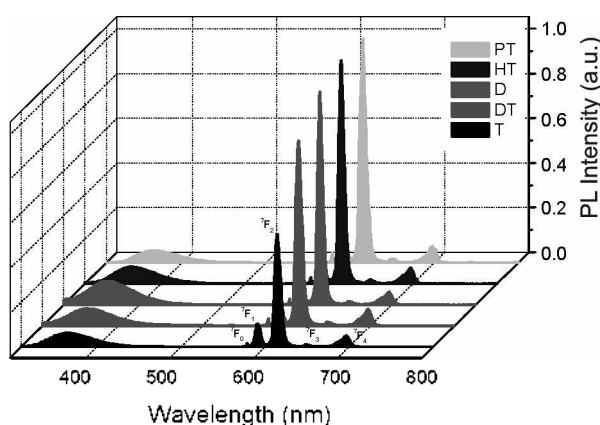**Figure 7.** Emission spectra of various Eu³⁺-[NA]₃(NL) in CH₃CN (λ_{ex} = 295 nm).
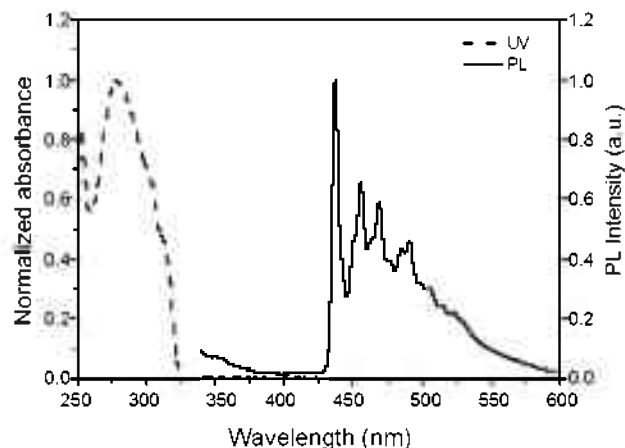

Figure 9. Absorption and phosphorescence spectra of terpyridine in m-THF at 77 K.

same measurement condition, the excitation wavelength was fixed to 295 nm and integration region of emission spectra was chosen between 500 nm to 800 nm and emission intensities have been corrected for the absorbance of Eu(III) complexes. A series of Eu³⁺-[NA]₃(NL) exhibited the typical line-like Eu³⁺ ion emission corresponding to the $^5D_0 \rightarrow$ ^7F_J transitions upon photoexcitation of the NA as shown in Fig. 7.

The typical emission bands of Eu³⁺ ion consist of a relatively intense band at 610 nm (corresponding to the $^5D_0 \rightarrow$ $^7F_2$) and weaker several bands, indicating low symmetric binding site around Eu³⁺ ion. As depicted in Fig. 8, the excitation spectra of its complex are dominated by strong absorption band at 300 nm (π-π transition of naphtoate ligand) with weak shoulder at 395 nm. The latter weak broad band at 395 nm can be assigned to the normal *f-f* transition of Eu³⁺ ion. Its excitation spectrum closely resembled the absorption spectrum of the NA ligand (Fig. 6). The excitation spectra around 300 nm proves the occurrence of sensitized emission through the NA unit and furthermore, a dramatic quenching of the PL intensity of the NA ligand was observed and quenching by energy transfer is expected to cause sensitization of Eu³⁻ luminescence. From the above results, these phenomena indicate that energy trans-

fer from the NA ligand to the Eu³⁻ ion takes place as expected and indirect excitation is much more efficient way to achieve the population of the Eu excited state than by direct excitation at 395 nm. Direct excitation of Eu³⁻ ion at 395 was not showed.

Replacement of the neutral ligands results in quite different emission, instead of terpyridine. The highest emission intensity is obtained for Eu³⁺-[NA]₃(PT), due to the difference in energy transfer efficiency and symmetry of the first coordination sphere of Eu³⁺ ion. But, the lowest emission intensity is obtained for Eu³⁻-[NA]₃(T). It could be explained as follows: Terpyridine usually shows a strong π-π* transition and a very weak n-π* transition around 250-325 nm and 355 nm, respectively, and it exhibits the phosphorescence spectrum around 425-600 nm (Fig. 8). Therefore, terpyridine may not play an important role antenna for photosensitizing Eu³⁻ ion, due to the weak spectral overlap integral *J* value between its phosphorescence band and Eu³⁻ ion absorption band. In other words, terpyridine absorbs at 295 nm, but it does not effectively transfer its excited energy to Eu³⁺ ion. It should be noted that Eu(III) complexes with a highly asymmetric coordination sphere have I_{7F2}/I_{7F1} intensity ratios ranging from 8 to 12, whereas an intensity ratio of 1.8 has been previously described

Table 1. Calculated values of τ_R, k_r, k_{nr}, and Φ_{Eu} using experimental data

	$\phi_{rel}{}^a$	τ_R (ms)^b	τ_{obs} (ms)^c	k_r(ms^{-1})	k_{nr} (ms^{-1})	$\Phi_{Eu}{}^d$
NA	1	-	-	-	-	-
Eu^{3+}-[NA]$_3$(T)	0.04	4.25	0.70	0.24	1.19	0.16
Eu^{3+}-[NA]$_3$(DT)	0.06	3.75	0.73	0.27	1.10	0.19
Eu^{3+}-[NA]$_3$(D)	0.08	3.27	0.69	0.31	1.14	0.21
Eu^{3+}-[NA]$_3$(HT)	0.05	3.48	0.75	0.29	1.05	0.22
Eu^{3+}-[NA]$_3$(PT)	0.04	3.23	0.77	0.31	0.99	0.24

^{a}Relative quantum yield of naphthalene unit at 365 nm. ^{b}Calculated from equation ($1/\tau_R = A_{MD,0}n^3(I_{tot}/I_{MD})$). ^{c}Monitored at 615 nm in CH$_3$CN. ^{d}Calculated from $\Phi_{Ln} = \tau_{obs}/\tau_R$

Table 2. Radiative lifetimes and I_{tot}/I_{MD} ratio for Eu(III) complexes.

	Eu^{3+}-[NA]$_3$(PT)	Eu^{3+}-[NA]$_3$(D)	Eu^{3+}-[NA]$_3$(HT)	Eu^{3+}-[NA]$_3$(DT)	Eu^{3+}-[NA]$_3$(T)
$n^3\tau_R$/ms	7.84	7.94	8.45	9.11	10.32
I_{tot}/I_{MD}	8.70	8.60	8.08	7.49	6.62
τ_R(ms)	3.23	3.27	3.48	3.75	4.25

for the centro-symmetric 6-coordinated Eu(III) complex.[8] In the present case the I_{7F2}/I_{7F1} intensity ratios for Eu^{3+}-[NA]$_3$(NL) are ranged from 4.9 to 7.9. The single peak at 580 nm indicates that there is only one type of Eu^{3+} species in solution. The relative area of the magnetic dipole $^5D_0 \rightarrow {}^7F_1$ transition band is similar for all complexes, but the hypersensitivity $^5D_0 \rightarrow {}^7F_2$ transition band is rather different.

The radiative lifetime is a very important parameter in the photophysical properties of near IR emission because the overall rate of non-radiative deactivation is determined by both τ_{obs} and τ_R and non-radiative process (k_{nr}) influences the observed luminescence lifetime. For all Eu^{3+} complexes, the results of calculated values of τ_R, k_r, k_{nr}, and Φ_{Eu} using experimental data are given in Table 1. The overall quantum yield is the product of the efficiency of sensitization (η_{sens}) and intrinsic quantum yield (Φ_{Ln}). The intrinsic quantum yields ($\Phi_{Ln} = \tau_{obs}/\tau_R$) were calculated from the observed lifetimes ($\tau_{obs} = (k_r + k_{nr})^{-1}$) and the pure radiative lifetimes ($\tau_R = k_r^{-1}$) of the Eu^{3+} ion were calculated from the eq. ($1/\tau_R = A_{MD,0}n^3(I_{tot}/I_{MD})$)^{14}, where $A_{MD,0}$ is spontaneous emission probability for the $^5D_0 \rightarrow {}^7F_1$ transition, theoretically calculated value of 14.65 s^{-1}. n is refractive index of the medium, and [I_{tot}/I_{MD}] is the ratios of total integrated area of Eu^{3+} emission to the area of the $^5D_0 \rightarrow {}^7F_1$ emission band (Table 2). The typical lifetime of τ_R has a value of 3 ms for Eu^{3+} ion.[14] In all cases the lifetime showed the monoexponential decay curves and the determined lifetimes are presented in Table 1.

The luminescence lifetimes of these complexes are similar. In CH$_3$CN, the luminescence lifetimes are in the range of 0.69 ~ 0.77 ms. The lifetime of Eu^{3+}-complexes are relatively longer than the lifetime of EuCl$_3$ in solution, which may be contributed to the shielding effects of the encapsulating ligand from the high-energy vibrational O-H or C-H band.
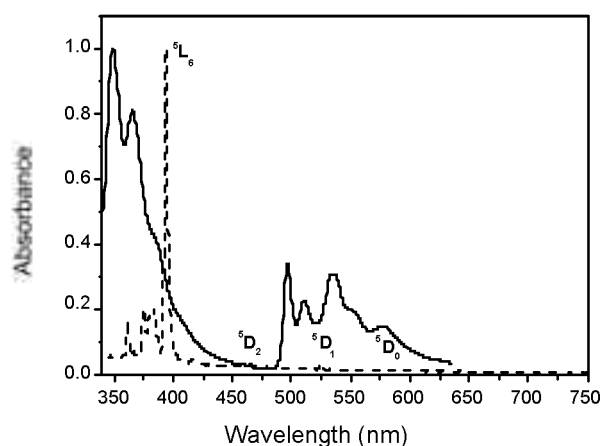
Figure 10. Phosphorescence spectrum of Gd^{3+}-[NA]$_3$(T) in m-THF at 77 K (solid line) overlayed with the absorption spectrum of EuCl$_6$ · H$_2$O in H$_2$O (dashed line).

From equation and the experimental results, it was found that the radiative lifetime is almost in agreement with theoretical curve.[15] The coordination of terpyridine causes a much smaller increase of the hypersensitive transition, with I_{7F2}/I_{7F1} ratio of approximately 5. Calculated intrinsic quantum yields of Eu^{3+} ion emission were 0.16 for Eu^{3+}-[NA]$_3$(T) and 0.24 for Eu^{3+}-[NA]$_3$(PT) and the emission intensity of Eu^{3+}-[NA]$_3$(T) is approximately 50% of that of Eu^{3+}-[NA]$_3$(PT), which indicates that terpyridine unit is a less efficient than other neutral ligands because quantum yield of terpyridine unit is quite low relative to the 1-naphthoic acid. It is consistent with the previous result depicted in Fig. 8. Therefore, inefficient sensitization of Eu^{3+}-[NA]$_3$(T) is the result of a non-radiative process of terpyridine unit.

The luminescence spectrum of Gd^{3+}-[NA]$_3$(T) showed an intense phosphorescence band with some vibrational structure (Fig. 9). From the position of the highest energy band in the spectrum, the lowest triplet state energy of 20161 cm^{-1} of the acid-functionalized naphthalene moiety, which is generated by intersystem crossing from the singlet state of ligand was determined from 0-0 transition in m-THF.[16] This value is approximately 1000 cm^{-1} lower in energy than the triplet state of unfunctionalized naphthalene[17] due to the electron-withdrawing carbonyl group at the 1-position and is placed for potential sensitization of $^5D_1$ state (19020 cm^{-1}) and $^5D_0$ state (17250 cm^{-1}).[18] The energy difference between the ligand triplet state and receiving $^5D_1$ state should be approximately higher 1500 cm^{-1} for efficient energy transfer. In our system, this energy difference is small and becomes possible back energy transfer between two states, leading to energy loss. However, upon excitation at 295 nm, efficient energy transfer from the triplet state of ligand to the $^5D_1$ state of Eu^{3+} ion is possible and various coordination environment of Eu^{3+} ion play an important role in providing sensitization of lanthanide ion emission. Consequently, the enhanced luminescence intensity and quantum yield of Eu(III) complex can be caused by introducing high binding sites around Eu^{3+} ion and low symmetry of Eu(III) complex compared to the unsaturated environment condition.

Conclusions

We have systematically synthesized novel luminescent Eu (III) complexes based on the 1-naphthoic acid and various neutral ligands (2.2':6'.2"-terpyridine, diglyme, di-(2-picolyl) amine derivative, and multidentate terpyridine derivative). The Eu(III) complex containing di-(2-picolyl)amine derivative has much stronger emission intensity than the terpyridine based europium complex, indicating that different coordination environment of Ln^{3+} ion play an important role in providing sensitization of lanthanide ion emission.

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