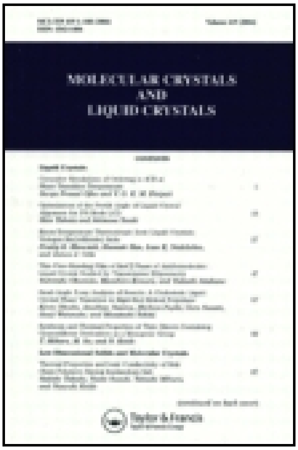

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Synthesis and Photophysical Properties of Luminescent Lanthanide Complexes Based on Dansyl-N-Methyl-Aminobenzoic Acid for Advanced Photonics Applications

Soo-Gyun Roh [a] , Yong Hee Kim [a] , Nam Seob Beak [a] , Kyong-Soo Hong [a] & Hwan Kyu Kim [a]

[a] Center for Smart Light-Harvesting Materials and Department of Polymer Science & Engineering, Hannam University, Daejeon, Korea

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Soo-Gyun Roh
Yong Hee Kim
Nam Seob Beak
Kyong-Soo Hong
Hwan Kyu Kim
Center for Smart Light-Harvesting Materials and Department of Polymer Science & Engineering, Hannam University, Daejeon, Korea

Novel luminescent Ln(III)-chelated complexes based on dansyl-N-methyl-aminobenzoic acid exhibited the strong near IR emission bands of the characteristic $^4I_{13/2} \rightarrow {}^4I_{15/2}$ *transition of Er(III) ion around 1530 nm and the characteristic* $^4F_{3/2} \rightarrow {}^4F_{9/2}$, $^4F_{3/2} \rightarrow {}^4F_{11/2}$ *and* $^4F_{3/2} \rightarrow {}^4F_{13/2}$ *transitions of Nd(III) ion around 880, 1060 and 1330 nm. Their photoluminescence intensity depends on the degree of the spectral overlap between the emission band of the ligand and the absorption band of lanthanide(III) ion. The radiative life times of Er(III) and Nd(III) ions in the lanthanide(III) complex films were estimated to be 1.6 and 1.2 μs, respectively.*

Keywords: advanced photonics applications; dansyl-*N*-methyl-aminobenzoic acid; luminescent Er(III) and Nd(III) complexes; photophysical properties

INTRODUCTION

At present, the development of integrated planar waveguide optical amplifiers in superhigh speed communication system is essential to overcome the problem for the low efficiency of the optical amplification

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Address correspondence to Hwan Kyu Kim, Center for Smart Light-Harvesting Materials and Department of Polymer Science & Engineering, Hannam University, Daejeon 306-791, Korea. E-mail: hwankkim@mail.hannam.ac.kr

due to lanthanide ion's intrinsically low absorption and emission cross sections, the poor solubility in organic/inorganic matrix, and aggregation at high concentration (EDWA) [1,2]. In order to enhance the amplified luminescence intensity, more recently, luminescent lanthanide materials have extensively been studied and attracted considerable attention because of several potential applications such as integrated planar waveguide optical amplifiers, plastic lasers and light-emitting diodes [1,2]. In most cases, luminescent lanthanide complexes consist of a luminescent lanthanide ion as a photonic acceptor and a strong chelating ligand as a photonic donor, which can transfer luminescent energy from the ligand to the central Ln(III) ion, despite the parity forbidden for optical transition within the 4f subshells of the lanthanide ion. The luminescent ligand contains a light-absorbing group as sensitizer of an organic (or antenna) chromophore and a tightly chelating organic molecule. They efficiently absorb and transfer lights to the central lanthanide ions. Up to date, however, the quantum yield of the energy transfer and the luminescence efficiency in luminescent lanthanide complexes were not satisfactorily fulfilled yet. Such efforts are just in the early stage. Not only their useful synthetic methods and basic concepts have not been established, but also their structure-property relationships have not been clearly understood.

Recently, dendrimer [3], crown and azacrown ethers [4], β-cyclodextrins [5] and cyclen [6] (cyclen = 1,4,7,10-tetraazacyclododecane) compounds based on fluorescent dansyl groups as antenna have been studied in the wide range of potential applications such as magnetic resonance imaging [7], radiotherapeutic [8], fluorescent chemosensors [9] or catalysis [10]. However, dansyl-based Ln(III)-chelated complexes were not nearly studied except Ln(III)-chelated complexes based on polylysin dendrimer [3b], poly(propylene amine) dendrimers [3c] and cyclen [6] bearing dansyl units. Also, Er(III)- and YNd(III)-chelated complexes based on dansyl-based ligands are rare [3b].

Very recently, in order to get the highly efficient lanthanide emission via the energy transfer between luminescent ligand and Ln(III) ion, we also studied the synthesis and photophysical properties of the luminescent lanthanide complexes based on benzoic acid and pentafluorobenzoic acid [11], coumarin [12], metalloporphyrin [13] and naphthalene [14] derivatives for advanced photonic applications, such as planar waveguide amplifiers and light-emitting diodes. In this paper, we have investigated the synthesis and photophysical properties of novel luminescent Er(III)- and Nd(III)-chelated complexes based on dansyl-*N*-methyl-aminobenzoic acid (DABAH) for advanced photonic applications such as planar waveguide amplifiers and near IR light-emitting diodes.

EXPERIMENTAL SECTIONS

Synthesis

Synthesis of dansyl-N-methyl-aminobenzoic Acid (DABAH)

N-methyl-aminobenzoic acid methyl ester (1.345 g, 8.142 mmol) and dansyl chloride (2.415 g, 8.956 mmol) were dissolved in dry CH_2Cl_2 (150 mL) and slowly added pyridine (0.98 mL, 24.426 mmol). The suspension was stirred for 3 days at room temperature under an inert atmosphere. After reaction, the solvent was removed by evaporation and the salt of the residue was at first separated with CH_2Cl_2 by short silica column chromatography. The dansyl-*N*-methyl-aminobenzoic acid methylester was purified with ethyl acetate/*n*-hexane (=3/2) by silica column chromatograpy. The final product was obtained with the treatment of dansyl-*N*-methyl-aminobenzoic acid methylester (2.709 g, 6.798 mmol) and NaOH (1.631 g, 40.790 mmol) in a mixture of THF (100 mL) and H_2O (50 mL) at room temperature for 3 days. When a salts was produced, the salt solution was reached at pH = 7 with the addition of 2 M HCl aqueous solution. And then, after extraction with CH_2Cl_2, the solvent was removed to give a pale yellow solid, DABAH (2.567 g, 6.677 mmol, 98%).

^1H NMR ($CDCl_3$, ppm) 8.52 (d, J = 8.4 Hz, 1H, dansyl), 8.10 (d, J = 6.9 Hz, 1H, dansyl), 7.94 (m, 3H, dansyl and phenyl), 7.46 (t, J = 7.8, 7.5 Hz, 1H, dansyl), 7.26 (m, 3H, dansyl), 7.00 (d, J = 7.2 Hz, 1H, dansyl), 3.24 (s, 3H, NCH_3), 2.853 (s, 6H, dansyl-$N(CH_3)_2$). IR (KBr, Pellet, cm^{-1}): 2972, 2926, 2893, 2863, 2834, 2788, 2862, 2557, 1689, 1606, 1573, 1510, m1456, 1430, 1334, 1316, 1278, 1197, 1147, 1048, 917, 872, 851, 795, 771, 702, 643, 553.

UV-vis. (CH_2Cl_2) λ_{max} (ε, $M^{-1}cm^{-1}$); 227 (22629), 258 (21193), 348 (3936). EI-MS: m/z 384.

Synthesis of $Er(DABA)_3$(terpyridine) 1

To a mixture of DABAH (0.301 g, 0.780 mmol) and KH (0.034 g, 0.857 mmol) was transferred 150 mL of THF through cannula and this orange solution was stirred at room temperature for overnight. The reaction was proceeded with gas evolution and the methanol solution of anhydrous $ErCl_3$ (0.096 g, 0.351 mmol) in 10 mL was added to the reaction solution. After 2 days of stirring at room temperature, the resulting solution was removed solvents to give an orange solid. This solid was washed with methanol and diethylether to afford $Er(DABA)_3$(terpyridine) as an orange solid (0.272 g, 0.330 mmol, 98%). IR(KBr, Pellet, cm^{-1}): 3070, 2977, 2940, 2866, 2831, 2785, 1602, 1561, 1451, 1415, 1340, 1263, 1170, 1140, 1061, 1021, 944, 878, 789, 708, 627, 568. UV-vis. (CH_2Cl_2) λ_{max} nm (ε, $M^{-1}cm^{-1}$): 227 (90250), 254 (85014), 287 (sh, 46639), 316 (21801), 336 (10937), 353 (sh, 10268). Anal. Calcd for $C_{75}H_{68}ErN_9O_{12}S_3$: C, 58.08; H, 4.42; Er, 10.78; N, 8.13; S, 6.20. Found: C, 57.86; H, 4.81; Er, 10.55; N, 8.19; S, 5.97.

Synthesis of Nd(DABA)$_3$(terpyridine) 2

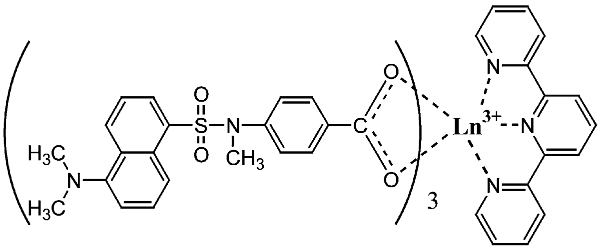
In a similar procedure to the preparation of Er(DABA)$_3$(terpyridine) as described above, Nd(DABA)$_3$(terpyridine) (0.206 g, 0.152 mmol, 83%) as an orange solid was synthesized from $NdCl_3$ (0.085 g, 0.233 mmol), DABAH (0.206 g, 0.701 mmol), and KH (0.031 g, 0.771 mmol). FT-IR (KBr, Pellet, cm^{-1}): 3074, 2974, 2940, 2867, 2834, 2786, 1603, 1567, 1541, 1417, 1341, 1269, 1236, 1172, 1144, 1102, 1064, 1017, 879, 790, 712, 630, 568, 502, 466. UV-vis. (CH_2Cl_2) λ_{max} nm (ε, $M^{-1}cm^{-1}$): 254 (95519), 287 (43816), 317 (24753), 334 (20857), 360 (13158). Anal. Calcd for $C_{75}H_{68}NdN_9O_{12}S_3$: C, 58.96; H, 4.49; N, 8.25; Nd, 9.44; S, 6.30. Found: C, 58.78; H, 4.71; N, 8.29; Nd, 9.42; S, 6.33.

Photophysical Property Measurement

Thin films of the present ligand and complexes were obtained by spin-coated from a sample blended with polystyrene in dichloroethane on glass plate. The corrected emission spectra were measured on an Edinburgh FS920 fluorometer with the excitation source from a 450 W Xe-lamp and Hamamatsu R955 PMT. Fluoroscence spectra of near IR region were detected with a liquid-nitrogen-cooled Ge detector. Time-resolved emission measurements on the microsecond time scale were performed with an excitation at 355 nm by using a Nd:YAG laser (EXSPLA NT342). 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 with an IR PMT (H917 0-75) followed by a boxcar averager (Stanford Research System) or a digital oscilloscope (Agilent infiniium 5482B DSO).

RESULTS AND DISCUSSION

We have synthesized the novel luminescent Er(III)- and Nd(III)-chelated complexes based on dansyl-*N*-methyl-aminobenzoic acid (DABAH) through the ligand-exchange reaction using $ErCl_3$ and potassium DABA salts. It was achieved by a new synthetic strategy, developed in our laboratory, for a series of new and practically useful lanthanide-cored supramolecular complexes with a quantitative yield [15]. The chemical structures of Ln(III)-chelated complexes are shown in Scheme 1. In the present Ln(III)-chelated complexes,



Er(DABA)$_3$(terpy) 1; Nd(DABA)$_3$(terpy) 2

SCHEME 1 The saturated Ln(III)-chelated complexes (Ln = Er, Nd) based on DABA and terpyridine, where DABA is dansyl-*N*-methyl-aminobenzoate.

dansyl-*N*-methyl-aminobenzoate (DABA) is directly connected to lanthanide ions without a molecular spacer, yielding a direct complex type. The formation of the direct complex with the direct coordination of the organic ligands to lanthanide ions is a key parameter to obtain a strong near-IR emission intensity of lanthanide(III)-cored complexes [14].

The successful synthesis of **1** and **2** was confirmed by elementary analysis, thermal gravimetric analysis (TGA), FT-IR, absorption and emission spectroscopies. The FT-IR spectra of the Ln(III)-chelated complexes exhibited the characteristic bands of bidentate-like carboxylate around 1600 and 1400 cm^{-1}, respectively [16] (see Fig. 1).

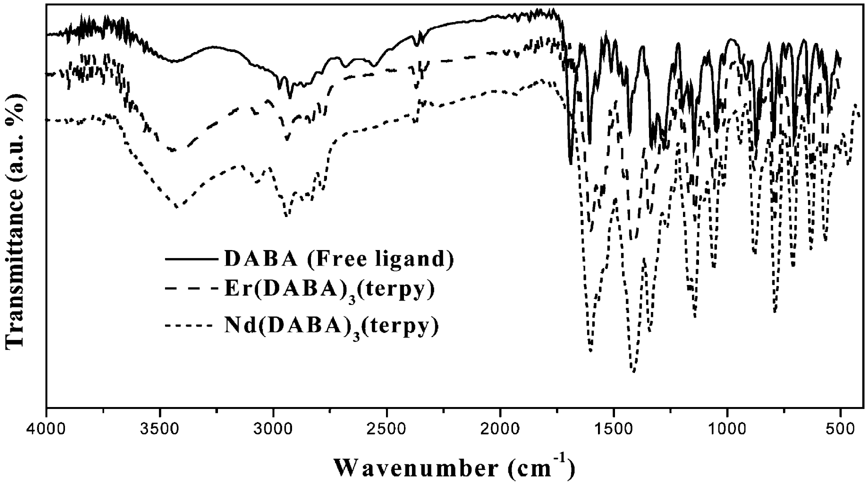


FIGURE 1 FT-IR spectra of DABAH and its Er(III)- and Nd(III)-chelated complexes in KBr pellets.

But, the paramagnetic properties of the lanthanide ion do not permit NMR studies of the dansyl-based complexes. Ln(III)-chelated complexes have the similar UV absorption feature to the free ligand, since the ligand in the Ln(III) complexes behaves independently like the inherent dansyl-based ligand except terpyridine. It suggests that the chelated ligand and the lanthanide ion do not perturb each other. In other words, the ground state of the lanthanide ion even in the Er complex was not influenced by the organic ligand.

In a TGA trace, the saturated 9-coordinated Ln(III) complexes showed no releasing water up to 200°C, indicating that complexes contain no coordinated H_2O molecules in atmospheric condition [1b]. The Er(III)-chelated complex **1** exhibits the strongest near IR emission bands at the excitation wavelength of 425 nm, among the excitation wavelength of 325, 425, and 488 nm, at which two excitation wavelengths of 325 and 488 nm excite the lanthanide ion directly. The near IR emission bands, corresponding to the characteristic $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition of Er(III) ion around 1530 nm, were exhibited (see Fig. 2). Also, the Er(III) ions by the indirect photoexcitation of organic ligands

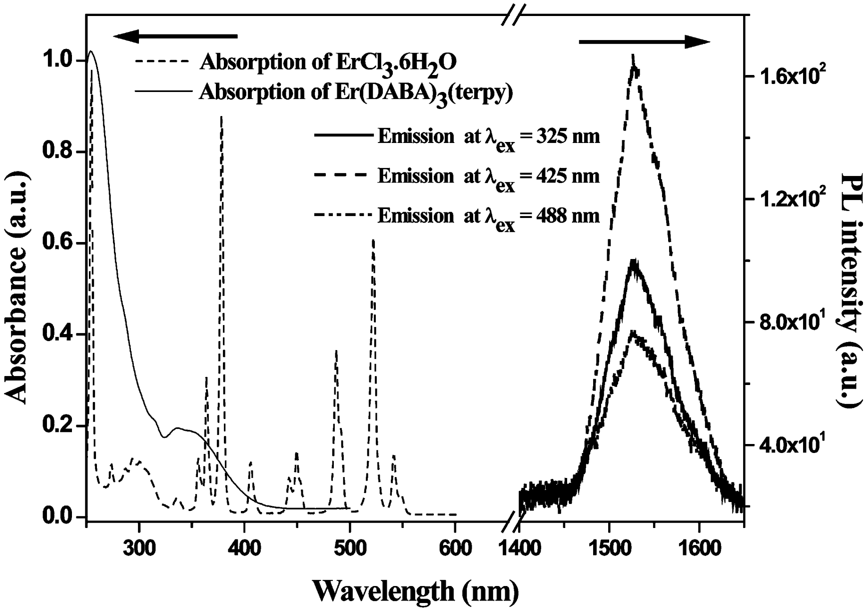


FIGURE 2 UV-visible absorption and near IR emission spectra of **1** at $\lambda_{ex} = 325$ and 425, 488 nm in solid state. Here, the λ_{ex} means the excitation wavelength.

with 425 nm emit the stronger near-IR emission intensity than by the direct photoexcitation of the Er(III) ions with 325 nm or 488 nm. Similarly, the stronger near-IR emission intensity of **2**, which corresponds to the characteristic $^4F_{3/2} \rightarrow {}^4F_{9/2}$, $^4F_{3/2} \rightarrow {}^4F_{11/2}$, and $^4F_{3/2} \rightarrow {}^4F_{13/2}$ transitions of Nd(III) ion in the region of 880, 1060, and 1330 nm, was obtained from the indirect photoexcitation of organic ligands with 425 nm rather than by the direct photoexcitation of the Nd(III) ions with 325 nm (see Fig. 3). These results indicate that the effective energy transfer process between organic ligands and lanthanide ion takes place, since the spectral overlap between the PL band of organic ligands and the absorption band of Er ions is sufficiently large.

The strong near IR emission intensity of **1** and **2** in thin film state was exhibited with the significant reduction of the visible emission intensity of DABA ligands in Ln(III) complexes by comparison with that of the inherent DABA (see Fig. 4). Also, these results showed that **1** and **2** have the effective energy transfer efficiency between the excited state of ligand and lanthanide ions. Furthermore, from the PL decay profiles (see Fig. 5), the radiative life times of Er(III) ion and Nd(III) ion in the thin film state of its lanthanide(III) complexes

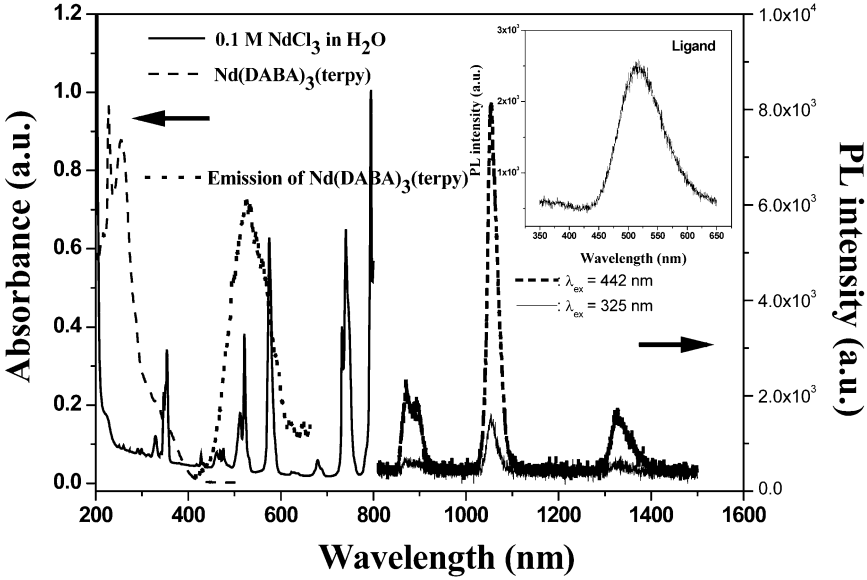


FIGURE 3 UV-visible absorption and near IR emission spectra of **2** at $\lambda_{ex} = 325$ and 442 nm in solid state. Here, the λ_{ex} means the excitation wavelength. The inset shows PL spectrum of free ligand (DABAH).

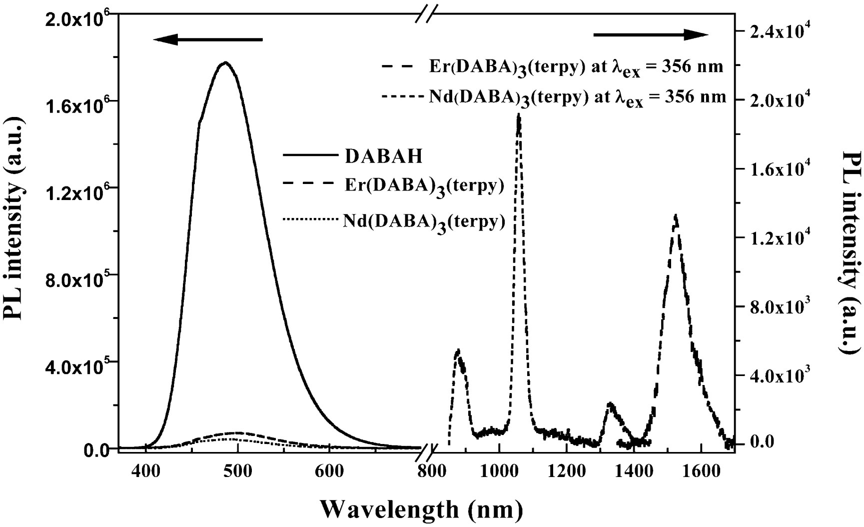


FIGURE 4 PL spectra of the Ln(III)-chelated complexes (a) **1** and (b) **2** at $\lambda_{ex} = 356$ nm in thin film state. Here, the λ_{ex} means the excitation wavelength.

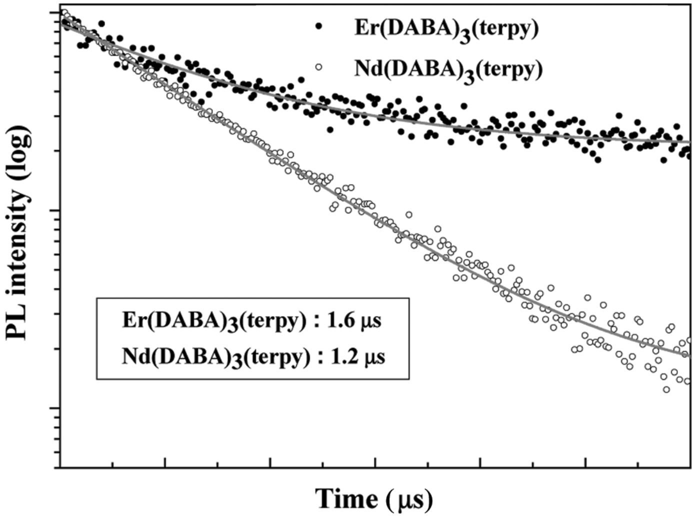


FIGURE 5 Photoluminescence decay traces of **1** and **2** in thin film state, $\lambda_{ex} = 355$ nm. Here, the λ_{ex} means the excitation wavelength.

at the excitation wavelength of 355 nm were calculated to be 1.6 and 1.2 μs, respectively.

In summary, we have prepared novel luminescent Ln(III)-chelated complexes (Ln = Er, Nd) based on dansyl-*N*-methyl-aminobenzoic acid (DABAH) using a new synthetic strategy developed in our laboratory. The dansyl-based Ln(III) complexes exhibited the strong near IR emission, corresponding to the characteristic $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition of Er(III) ion in the region of 1530 nm and the characteristic $^4F_{3/2} \rightarrow {}^4F_{9/2}$, $^4F_{3/2} \rightarrow {}^4F_{11/2}$, and $^4F_{3/2} \rightarrow {}^4F_{13/2}$ transitions of Nd(III) ion in the region of 880, 1060, and 1330 nm. The stronger emission bands of Ln(III)-chelated complexes were obtained through the photoexcitation of dansyl-based ligands via the effective energy transfer rather than by the direct photoexcitation of the Ln(III) ions, in which the emission intensity of dansyl-*N*-methyl-aminobenzoate in Ln(III)-chelated complexes was significantly reduced by comparing with that of free ligand in the visible region. It could be explained by the effective energy transfer between the excitation state of dansyl-based ligands and lanthanide ions, due to the heavy metal effect. These new luminescent Ln(III)-chelated complexes based on dansyl derivatives can be used in photonic applications such as planar waveguide amplifiers and near IR light-emitting diodes.

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