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Photophysical Properties of Near-Infrared-Emitting Ln(III) Complexes with 1-(9-Anthryl)-4,4,4-trifluoro-1,3-butandione (Ln = Nd and Er)

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We report the synthesis and photophysical properties of Nd(III) and Er(III) complexes with 1-(9-anthryl)-4,4,4-trifluoro-1,3-butandione (9-ATFB). The complexes of $[Nd(9\text{-}ATFB)_4]^-$ and $[Er(9\text{-}ATFB)_4]^-$ produced sensitized near-infrared (NIR) luminescence via the excitation of anthracene. This suggests that the intramolecular energy transfer occurred from the singlet excited state of anthracene to the resonance levels of the metal ions, since the phosphorescence of anthracene is forbidden under normal conditions. The observed quantum yield of the visible luminescence showed that the energy transfer is more efficient for $[Nd(9\text{-}ATFB)_4]^-$ than for $[Er(9\text{-}ATFB)_4]^-$. The lifetimes of the NIR luminescence of the complexes were in the microsecond range. The quantum yields of the sensitized NIR of the complexes were estimated using the lifetime and the energy-transfer quantum yield.

Introduction

Lanthanide complexes, especially Eu(III) and Tb(III) complexes, have attracted much attention due to their unique luminescence properties in the visible region for application in organic light-emitting diodes.[1] In general, however, the f → f absorption coefficients of lanthanide ions are very small. In an effort to obtain high-efficient luminescence, a strong absorbing organic ligand is introduced as an antenna to complexes of these metals. In this system, intramolecular energy transfer takes place from the triplet excited state of the antenna to the localized intra-4f shell of the lanthanide ion, resulting in luminescence with a high quantum yield. Typical ligands used as an antenna are β-diketonate, 1,10-phenanthroline, and their combination. Re-

cently, near-infrared (NIR)-emitting lanthanide ions, such as Nd(III) and Er(III), have received increasing attention for their potential applications in the telecommunication devices, plastic lasers, and light-emitting diodes.[2] Taking advantage of the lanthanide ions, Bünzli et al. performed the critical review on the photophysical properties with the synthetic strategies.[3]

Anthracene-fuctionalized antennas have been investigated as energy donors or acceptors.[4] In most of cases, the energy transfer takes place between the anthracene-fuctionalized antenna and other coordinated chromophore in the transition metal complex. The singlet and triplet excited states of anthracene act as energy donating and receiving levels, respectively. In this study, we prepared Nd(III) and Er(III) complexes with anthracene-fuctionalized β-diketone (see Chart 1) and characterized their photophysical properties in various solvents. We observed the energy transfer from the singlet excited state of the anthracene moiety to the Ln(III) ions.

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CHART 1: Molecular Structure of [Ln(9-ATFB)$_4$]$^-$ Complex
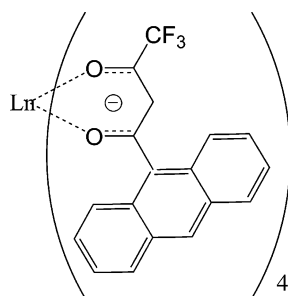
Experimental Section

Synthesis and Composition Analysis. All reagents were purchased from Aldrich and used without further purification. The lanthanide and sodium ion contents were analyzed using an atomic absorption spectrometer (Perkin-Elmer 2380) and ICP (Thermo Elemental IRIS DUO). The carbon and hydrogen contents were determined using a CE EA-1110 elemental analyzer.

9-ATFB. Ethyl trifluoroacetate (1.2 equiv, 1.43 mL, 12 mmol) was added dropwise to sodium hydride (3 equiv, 0.72 g, 30 mmol) in benzene (30 mL) solution, with stirring. After 5 min, 1 equiv (10 mmol) of 9-acetyl anthracene was added and stirred overnight at room temperature under N$_2$(g). The resulting solution was quenched with 3 M hydrochloric acid (50 mL), and the solution was extracted twice with ethyl acetate (70 mL). The organic layer was dried over MgSO$_4$, filtered, and evaporated to dryness. The product was obtained as yellow solid (3.0 g, 95% yield). Mp: ~87−88 °C [lit. ~82−83 °C].[5] ^{1}H NMR (400 MHz, CDCl$_3$): δ 14.9 (s, 1H,O*H*), δ 8.51 (s, 1H, anthracene), δ 7.98 (m, 4H, anthracene), δ 7.46 (m, 4H, anthracene) δ 6.32 (s, 1H, C*H*).

Na[Ln(9-ATFB)$_4$] (Ln = Nd, Gd, and Er). The 9-ATFB (1.33 mmol) was dissolved in 15 mL ethanol. Then, 0.333 mmol of LnCl$_3$·6H$_2$O dissolved in 5 mL of water was added dropwise to the solution. A yellow precipitate formed rapidly. The pH of the mixed solution was adjusted to neutral with dilute NaOH, and the resultant solution was stirred overnight. After being filtered and washed several times with water and ethanol, alternately, the yellow precipitation was dried in an electric oven for 1 day. For Nd, elemental analysis: Nd 9.0, C 54.9, H 2.8, Na 3.7%. Calcd for Na[Nd(C$_{18}$H$_{11}$O$_2$F$_3$)$_4$]: Nd 10.1, C 60.4, H 3.1, Na 1.6%. For Gd, elemental analysis: Gd 10.6, C 57.9, H 3.1, Na 0.7%. Calcd for Na[Gd(C$_{18}$H$_{11}$O$_2$F$_3$)$_4$]: Gd 10.9, C 59.8, H 3.1, Na 1.6%. For Er, elemental analysis: Er 11.5, C 58.8, H 2.8, Na 1.4%. Calcd for Na[Er(C$_{18}$H$_{11}$O$_2$F$_3$)$_4$]: Er 11.5, C 59.4, H 3.0, Na 1.6%.

Spectroscopic Measurements. For the measurements of optical properties, the prepared Na[Ln(9-ATFB)$_4$] (Ln = Nd, Er, and Gd) complexes were dissolved at a concentration of a few 10^{-5} M in various organic solvents. The solvents used in this study are *N,N*-dimethylformamide (DMF, Aldrich), chloroform (J. T. Baker), and 2-methyltetrahydrofurane (MTHF, TCI).

UV−vis absorption spectra were recorded by a Shimadzu UV-2401PC spectrophotometer. Luminescence and excitation spectra were measured by an Edinburgh FS920 fluorescence photometer. The excitation light from a 300-mm monochromator was focused on the sample. Visible and NIR luminescence spectra were recorded with a PMT system (Hamamatsu R955) and a Ge-detector (Edinburgh Instruments EI-L) cooled with liquid nitrogen, respectively. All spectra were taken at the room
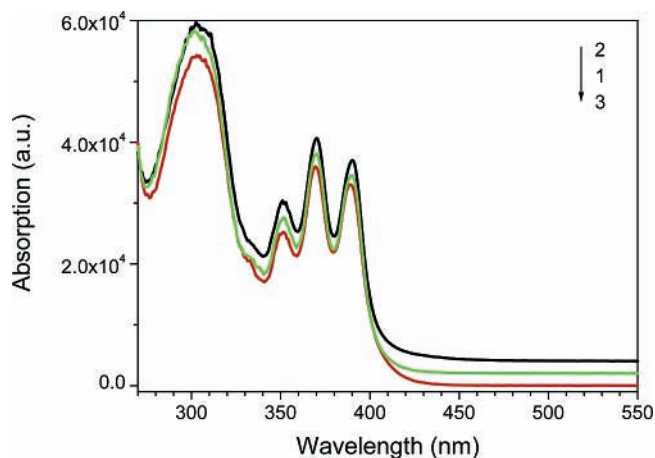

Figure 1. UV−vis absorption spectra of [Ln(9-ATFB)$_4$]$^-$ complexes in DMF (1, Nd; 2, Er; and 3, Gd).

temperature. For low-temperature luminescence measurements, the sample dissolved in MTHF was transferred into a quartz tube and then degassed using liquid nitrogen. The sealed quartz tube was placed on the coldfinger of a closed-cycle helium refrigerator (CTI-cryogenics). The luminescence spectrum in the visible region was measured at a 90° angle with an ARC 0.5 m Czerny−Turner monochromator equipped with a cooled Hamamatsu R-933-14 PM tube. The sample was irradiated with the light from an Oriel 1000 W Xe lamp (working power, 400 W) passing through an Oriel MS257 monochromator.

The quantum yield of the visible luminescence for each sample (Φ_s) was determined by the relative comparison procedure, using a reference of a known quantum yield (quinine sulfate in diluted H$_2$SO$_4$ solution, Φ_r = 0.546). The general equation used in the determination of relative quantum yield[6] is given as follows:

$$\Phi_s = \Phi_r \left(\frac{A_r(\lambda_r)}{A_s(\lambda_s)} \right) \left(\frac{I(\lambda_r)}{I(\lambda_s)} \right) \left(\frac{n_s^2}{n_r^2} \right) \left(\frac{D_s}{D_r} \right) \quad (1)$$

In the equation, $A(\lambda)$ is the absorbance, $I(\lambda)$ is the relative intensity of the exciting light at wavelength λ, n is the average refractive index of the solvent, and D is the integrated area under the corrected emission spectrum.

For the luminescence decay signal collection, a pump wavelength of 355 nm was selected using a ns-Nd:YAG laser system with third-harmonic generation (EKSPLA NT342-UV). The laser output has a ~5 ns pulse width with a repetition rate of 10 Hz. The electric output signals were collected with a digital oscilloscope system (Agilent Infiniium 54832B).

Results and Discussion

Absorption, Luminescence, and Excitation Spectra. Figure 1 shows the UV−vis absorption spectra of Na[Ln(9-ATFB)$_4$] dissolved in DMF. The three complexes produced a strong band peaking at 300 nm and three well-defined bands with moderate intensity in the 330−420 nm region in the absorption spectrum. These bands matched those of anthracene well.[7] As shown in Figure 2a, on the 366-nm excitation, the three complexes produced three well-structured luminescence at three wavelengths, 395, 417, and 445 nm, with a low-energy shoulder. These bands corresponded to fluorescence of anthracene. In addition, the characteristic emission bands were also observed in the NIR region for the Nd(III) and Er(III) complexes. For [Nd(9-ATFB)$_4$]$^-$, the observed 880-, 1060-, and 1330-nm bands
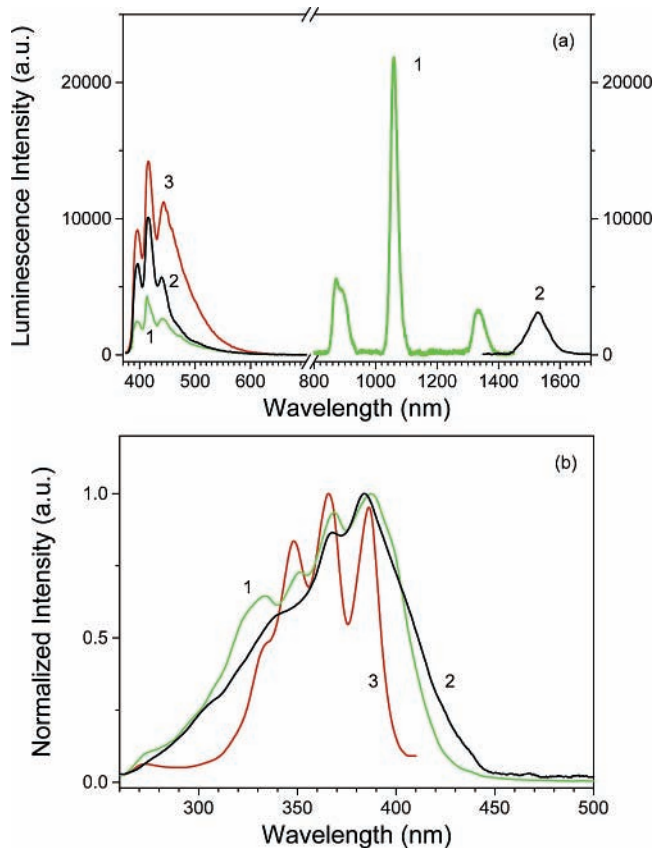
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Figure 2. Luminescence (a) and excitation (b) spectra of [Ln(9-ATFB)$_4$]$^-$ complexes in DMF (1, Nd; 2, Er; and 3, Gd): (a) λ_{exc} = 366 nm and (b) λ_{ems} = 1060 nm for Nd, 1530 nm for Er, and 417 nm for Gd.
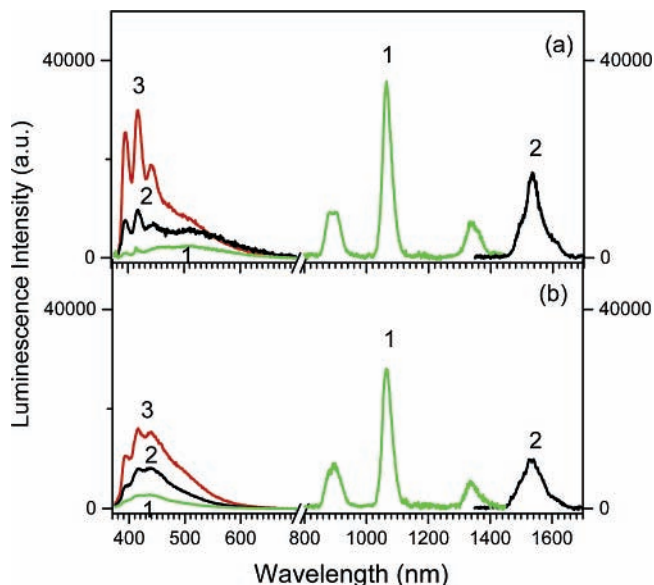

Figure 3. Luminescence spectra of [Ln(9-ATFB)$_4$]$^-$ complexes (1, Nd; 2, Er; and 3, Gd) in chloroform (a) and in MTHF (b).

were attributable to the transitions from the emitting $^4F_{3/2}$ level to the $^4I_{9/2}$, $^4I_{11/2}$, and $^4I_{13/2}$ levels of Nd(III), and for [Er(9-ATFB)$_4$]$^-$, the 1530-nm band was attributable to the transition from the emitting $^4I_{13/2}$ level to the ground $^4I_{15/2}$ level of Er-(III). The luminescence features of the three complexes dissolved in chloroform and MTHF are very similar to the cases in the DMF solution (see Figure 3). The excitation spectrum, measured while monitoring the NIR emission wavelength of each complex, had a spectral shape very similar to that of the 417-nm emission
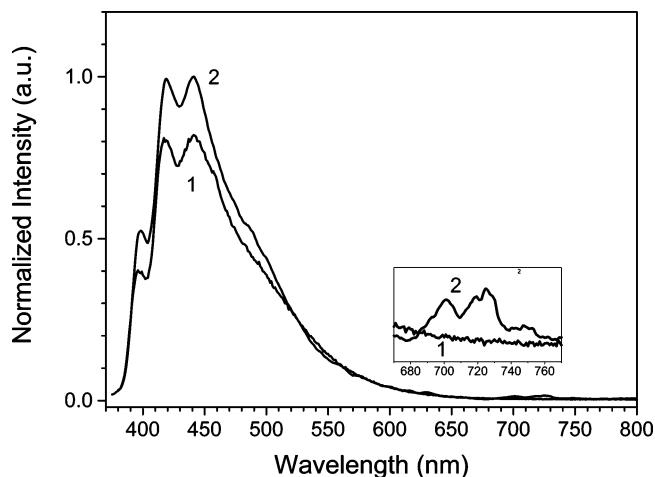

Figure 4. Luminescence spectra of [Gd(9-ATFB)$_4$]$^-$ complexes in MTHF measured at 298 K (1) and 10 K (2) (λ_{exc} = 366 nm).

TABLE 1: Quantum Yields and Luminescence Lifetime of [Ln(9-ATFB)]$^-$ Complexes in Various Solvents

| | [Ln(9-ATFB)$_4$]$^-$ | quantum yield | | | |
solvent		Φ_{fluo}	Φ_{ET}	Φ_{sens}	τ_{obs} (μs)
N,N-dimethyl-formamide	Gd	3.62×10^{-2}			
N,N-dimethyl-formamide	Nd	0.89×10^{-2}	0.754	3.44×10^{-3}	0.93
N,N-dimethyl-formamide	Er	1.70×10^{-2}	0.530	0.19×10^{-3}	1.53
chloroform	Gd	3.93×10^{-2}			
chloroform	Nd	0.87×10^{-2}	0.779	2.33×10^{-3}	0.63
chloroform	Er	1.60×10^{-2}	0.593	0.20×10^{-3}	1.57
2-methyltetra-hydrofurane	Gd	3.64×10^{-2}			
2-methyltetra-hydrofurane	Nd	0.98×10^{-2}	0.731	3.22×10^{-3}	0.87
2-methyltetra-hydrofurane	Er	1.80×10^{-2}	0.505	0.23×10^{-3}	1.87

from the anthracene moiety of [Gd(9-ATFB)$_4$]$^-$, as shown in Figure 2b. This indicates that the energy transfer from the 9-ATFB moiety to the central Nd(III) and Er(III) ions took place effectively. Note that the emitting level of Gd(III) is $^6P_{7/2}$ and its energy of 32200 cm^{-1} is much higher than the singlet excited state of anthracene. The paramagnetic Gd(III) ion increased the intersystem crossing of the chelating ligand, resulting in a reduction in the fluorescence and a subsequent increase in the phosphorescence. The emission spectrum of [Gd(9-ATFB)$_4$]$^-$ dissolved in MTHF was measured at room temperature and 10 K. As shown in Figure 4, the phosphorescence appeared as a trace in the 680−780 nm region at 10 K. However, it is very difficult to obtain the phosphorescence of anthracene at room temperature, as reported previously.[6a,7] This led us to postulate that energy was transferred from the singlet excited state of anthracene to the resonance levels of the lanthanide ion.

Quantum Yield and Lifetime. The quantum yields of the visible luminescence of the complexes were measured in the DMF solution state. The results were listed in Table 1. The quantum yield of the fluorescence of 9-ATFB moiety is 3.62% for [Gd(9-ATFB)$_4$]$^-$, 0.89% for [Nd(9-ATFB)$_4$]$^-$, and 1.70% for [Er(9-ATFB)$_4$]$^-$. Assuming that the paramagnetic effects of Nd(III) and Er(III) are almost equal to that of Gd(III), the estimated quantum yield of the energy transfer (Φ_{ET}) was 0.754 for [Nd(9-ATFB)$_4$]$^-$ and 0.530 for [Er(9-ATFB)$_4$]$^-$. The energy was transferred from the antenna to the Nd(III) ion more effectively than that to the Er(III) ion.

The decay curve of the NIR luminescence determined from time-resolved luminescence experiments fits a single-exponential

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component well. The obtained lifetimes of the sensitized luminescence of the Nd(III) and the Er(III) complexes (τ_{sen}) are also listed in Table 1. The quantum yield of the sensitized NIR luminescence of Ln(III) in the complex can be estimated using the following relationship between the experimentally determined lifetime of Ln(III) (τ_{obs}) and its natural lifetime (τ_0).[9]

$$\Phi_{sens} = \frac{\tau_{obs}}{\tau_0} \qquad (2)$$

Using the reported value of τ_0 of 0.27 ms for Nd(III) and 8.00 ms for Er(III),[10] we obtained the quantum yield of the sensitized luminescence: $\Phi_{sens} = 0.344\%$ for [Nd(9-ATFB)$_4$]$^-$ and $\Phi_{sens} = 0.019\%$ for [Er(9-ATFB)$_4$]$^-$. The quantum yield of the Er(III) complex is very close to the typical values of $0.01-0.04\%$ for usual Er(III) organic complexes.[11,12]

The sensitized luminescence consists of the excitation of the anthracene into its singlet excited state, the energy transfer from the singlet to the resonance level of Ln(III), and the subsequent relaxation to the emitting level. When we consider this pathway, the overall quantum yield of the sensitized luminescence can be expressed as

$$\frac{\tau}{\tau_0} = \Phi_{antenna}\Phi_{ET}\Phi_{rel} \qquad (3)$$

where the quantum yield of the Gd(III) complex is taken as $\Phi_{antenna}$ and Φ_{rel} is the relaxation efficiency strongly associated with radiationless transition. Substituting the experimentally determined values of $\Phi_{antenna}$ and Φ_{ET} into eq 3, we obtained $\Phi_{rel} = 12.6\%$ for [Nd(9-ATFB)$_4$]$^-$ and $\Phi_{rel} = 1.00\%$ for [Er-(9-ATFB)$_4$]$^-$. The energy loss during the relaxation for [Er(9-ATFB)$_4$]$^-$ was much greater than that for [Nd(9-ATFB)$_4$]$^-$. This may have been due to the larger energy gap (ΔE) between the singlet excited state of anthracene and the emitting level of the Er(III) ion: $\Delta E \cong 14650$ cm^{-1} for Nd(III) and 19500 cm^{-1} for Er(III).

The results of the chloroform and MTHF solution states are not very different from the cases of the DMF state, as listed in Table 1. The quantum yields of the sensitized luminescence of [Nd(9-ATFB)$_4$]$^-$ in chloroform and MTHF are 0.233% and 0.322%, respectively, and those of [Er(9-ATFB)$_4$]$^-$ in chloroform and MTHF 0.020% and 0.023%, respectively. Similarly, we also obtained the relaxation efficiency of the two complexes in the chloroform and MTHF solution states: for the Nd(III) complex, $\Phi_{rel} = 11.3\%$ and 12.9%, respectively, and for the Er(III) complex, $\Phi_{rel} = 0.84$ and 1.27%, respectively. These results indicate that the 9-ATFB ligand may form tetra

complexes with lanthanide ions in even a coordinating solvent, such as DMF.

Conclusion

The study showed that Nd(III) and Er(III) complexes with 9-ATFB produce sensitized NIR luminescence via the energy transfer from the singlet excited state of anthracene to the lanthanide ion. The efficient intramolecular energy transfer for the Nd(III) and Er(III) complexes was confirmed using fluorescence measurements of the Gd(III) complex. The estimated quantum yield of the sensitized NIR luminescence suggests that for the Er(III) complex energy loss during relaxation from the resonance level to the emitting level was much greater than for the Nd(III) complex. This could be due to the larger energy gap (ΔE) between the singlet excited state of anthracene and the emitting level of the Er(III) ion.

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