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# Sensitized Emission of Luminescent Lanthanide Complexes Based on 4-Naphthalen-1-yl-Benzoic Acid Derivatives by a Charge-Transfer Process

Yong Hee Kim, Nam Seob Baek, and Hwan Kyu Kim<sup>\*,[a]</sup>

*The photophysical properties of 4-naphthalen-1-yl-benzoic acid ligands and their Eu<sup>III</sup>-cored complexes were systematically investigated to elucidate the effective energy-transfer pathway in luminescent lanthanide complexes. A series of 4-naphthalen-1-yl-benzoic acid ligands, such as 4-naphthalen-1-yl-benzoic acid (NA-1), 4-[4-(4-methoxyphenyl)-naphthalen-1-yl]-benzoic acid (NA-2), and 4-[4-[4-(4-methoxyphenyl)-naphthalen-1-yl]-benzyloxy]-benzoic acid (NA-3), were synthesized and utilized for the synthesis of their Eu<sup>III</sup>-cored complexes, corresponding to NAC-1, NAC-2, and NAC-3. The fluorescence spectra of NA-1 and NA-2 show large Stokes shifts with increasing solvent polarity. These large Stokes shifts might be dominantly due to the formation of an intramolecular charge transfer (ICT) complex in the excited state. Also, the intensive luminescence of the Eu<sup>III</sup> ions by the photoexcitation of the ligand in NAC-1 and NAC-2 in polar solvents supports that*

*the energy transfer from the ligand to the Eu<sup>III</sup> ion takes place efficiently. In the case of NA-3, which has a –CH<sub>2</sub>OPh– group that acts as a blocking group, there is no dependence of the fluorescence spectrum on the solvent nature and no luminescence of the Eu<sup>III</sup> ions by the photoexcitation of the ligand, indicating no formation of the ICT state. This can be due to the fact that the formation of the ICT state in NA-3 was prevented because the –OCH<sub>2</sub>– group acts as a blocking group by interrupting the  $\pi$ -conjugation between the benzoic acid and the naphthalene unit. From these photophysical studies, we suggest that the ICT state plays a very important role in the energy-transfer pathway from the ligand to the Eu<sup>III</sup> ion. To our best knowledge, this is the first demonstration of sensitized emission of luminescent lanthanide complexes based on 4-naphthalen-1-yl-benzoic acid derivatives by the charge-transfer process.*

## 1. Introduction

The luminescent lanthanide complexes have drawn much attention because of their versatile applications, such as planar waveguide amplifiers, plastic lasers, and light-emitting diodes.<sup>[1–5]</sup> In most cases, the luminescent lanthanide complexes consist of a lanthanide ion and its chelating organic ligand as a photosensitizer. The organic ligand contains a light-absorbing moiety as an antenna chromophore and a tightly chelating organic moiety. The antenna chromophore moiety efficiently absorbs and transfers light to the central lanthanide ions by the energy-transfer process. In this way, the central lanthanide ions accumulate light from the organic chromophores, resulting in an intensive lanthanide emission. This sensitization process is much more effective than the direct excitation of Ln<sup>3+</sup> ions, since the absorption coefficients of organic chromophores are many orders of magnitude larger (typically 3–5) than the intrinsically low molar absorption coefficients (typically 1–10 M<sup>–1</sup> cm<sup>–1</sup>) of Ln<sup>3+</sup> ions.

Two possible energy-transfer pathways for the sensitized emission in luminescent lanthanide complexes have been proposed. It is well known that, in general, only the triplet state of the luminescent ligand is involved in photosensitization. The sensitization process of luminescent lanthanide complex is strongly affected by the subsequent intersystem crossing efficiency and the energy-transfer efficiency to the lanthanide ion in the excited triplet state.<sup>[6,7]</sup> The probability of an energy transfer from the singlet state of the luminescent ligand 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). However, several reports mentioned the energy transfer from the excited singlet state to the lanthanide ion.<sup>[8–10]</sup> Hebbink and co-workers<sup>[8]</sup> reported that the energy transfer in dansyl- and lissamine-functionalized Nd<sup>III</sup> complexes occurred from the singlet state of the sensitizers to the Nd<sup>3+</sup> centers, but no sensitized Yb<sup>III</sup> or Er<sup>III</sup> emission was observed. Vicinelli and co-workers<sup>[9]</sup> also observed the energy transfer between the singlet state of a polylysine dendrimer and the Nd<sup>3+</sup> ions. Recently, Yang and co-workers<sup>[10]</sup> reported that the energy transfer in a dipyrzoly-triazine-functionalized Eu<sup>III</sup> complex occurred from the singlet state of the sensitizers to the Eu<sup>III</sup> centers.

To get a highly efficient lanthanide emission by the energy transfer between the luminescent ligand and the lanthanide ion, we have recently developed naphthalene-based luminescent ligands, such as 4-naphthalen-1-yl-benzoic acid (NA-1), 4-

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[4-(4-methoxyphenyl)-naphthalen-1-yl]-benzoic acid (NA-2), and 4-{4-[4-(4-methoxyphenyl)-naphthalen-1-yl]-benzyloxy}-benzoic acid (NA-3), as chelating ligands and luminescent sensitizers (see Scheme 1), which provides enough coordinated sites for the formation of inert, stable nine-coordinated lanthanide complexes.<sup>[11–12]</sup> The formation of inert, stable nine-coordinated lanthanide complexes is a key parameter to obtain a strong emission intensity of lanthanide(III)-cored complexes. Previously, we reported that highly coordinated lanthanide-cored complexes (with a coordination number of at least eight to nine) have a higher photoluminescence (PL) efficiency than unsaturated six-coordinated complexes.<sup>[11b]</sup> Also, NA-1 and NA-2 have a naphthalene group directly linked to a phenyl group in the benzoic acid with a  $\pi$ -conjugation interaction between the naphthalene unit and the benzoic acid unit. However, NA-3 has a naphthalene group indirectly linked to a phenyl group in the benzoic acid—with no  $\pi$ -conjugation interaction between them—in which the  $-\text{OCH}_2-$  group acts as a blocking group by interrupting the  $\pi$ -conjugation interaction between them. Thus, the  $\text{Eu}^{\text{III}}$ -cored complex based on this indirect ligand does not have an external heavy-atom effect, which is induced by the heavy and paramagnetic lanthanide ion. As a result, one can distinguish between two different types of luminescent ligands: the direct ligands, such as NA-1 and NA-2, and the indirect ligand, such as NA-3, which have rather different photophysical behaviors. These will be discussed below.

Surprisingly, we observed that the energy-transfer pathway in 4-naphthalen-1-yl-benzoic acid ligands may occur by the charge-transfer process in the excited singlet state, but not by the intersystem crossing process to form the excited triplet state. To date, even though many organic ligands, which easily form the charge-transfer state in the excited state, have the highly forbidden character of the  $S_1 \rightarrow T_1$  transition, no system-

atic studies have been carried out to explore the energy-transfer pathway of the luminescent lanthanide complexes based on such kind of ligands. Herein, we have investigated the photophysical properties of 4-naphthalen-1-yl-benzoic acid ligands and the energy-transfer process on their corresponding  $\text{Eu}^{\text{III}}$  complexes. We will also discuss the spectroscopic results in relation to the charge-transfer state of the present ligands in the excited state as a main energy-transfer pathway in luminescent lanthanide complexes.

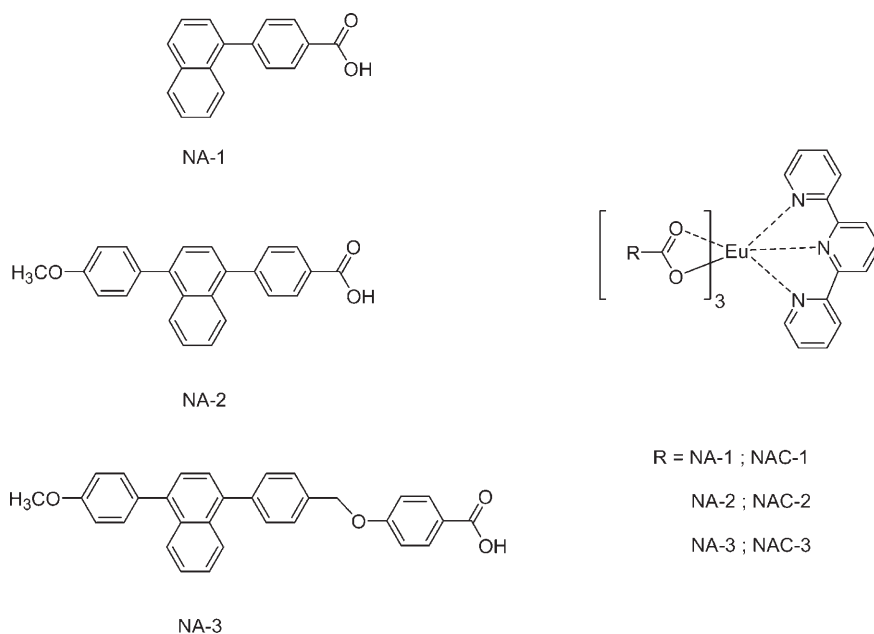
## 2. Results and Discussion

### 2.1. Photophysical Studies of Luminescent Ligands Based on 4-Naphthalen-1-yl-Benzoic Acid Derivatives

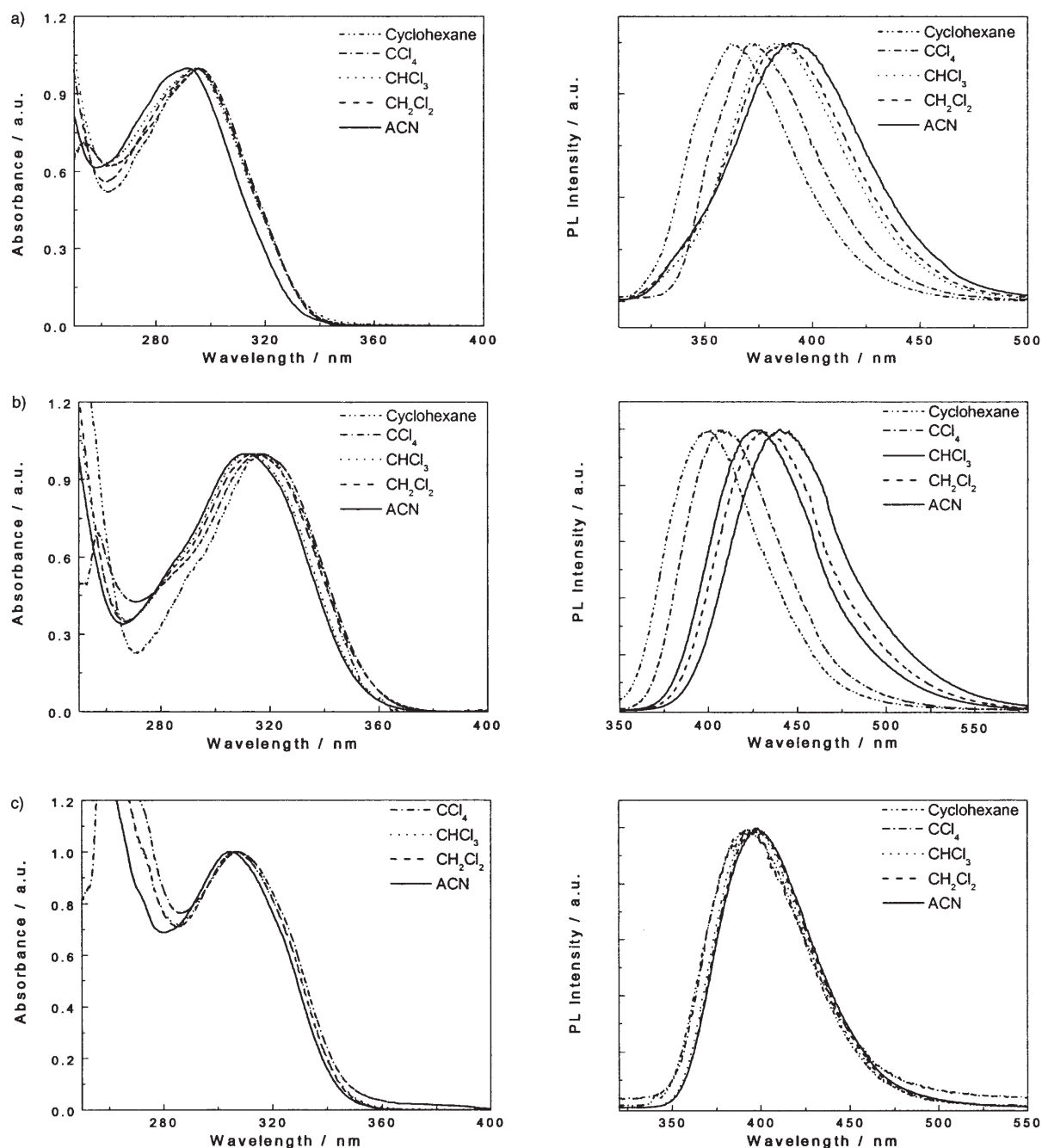
Figure 1 shows the absorption and fluorescence spectra of free 4-naphthalen-1-yl-benzoic acid ligands of NA-1, NA-2, and NA-3 in various solvents, such as the aprotic nonpolar solvents: cyclohexane and  $\text{CCl}_4$  and the aprotic polar solvents: dichloromethane, chloroform, and acetonitrile, at room temperature. The absorption spectra of NA-1, NA-2, and NA-3 exhibit maximum absorption bands around 290, 310, and 304 nm, respectively. Their extinction coefficients are about  $10^4 \text{ M}^{-1} \text{ cm}^{-1}$ . The fluorescence spectra of NA-3 display a small change—upon excitation at the maximum absorption wavelength—as the solvent polarity increases. This indicates that the characteristic nature of the electronic state does not change in the excited state.

In contrast to NA-3, which exhibits no significant spectral dependence on the solvent polarity, the fluorescence spectra of NA-1 and NA-2 show a strong red shift of 30 and 40 nm, respectively, of the emission maximum as the solvent polarity increases from cyclohexane to acetonitrile. This may indicate a change of the nature of the excited electronic state. It is well

known that the excited charge-transfer state is controlled solely by the polarity of the medium solvent and the molecular geometry.<sup>[13,14]</sup> Accordingly, the nature of the excited electronic state should be the excited charge-transfer state. Cho et al.<sup>[15]</sup> reported that the fluorescence spectrum of 4-biphenyl carboxylic acid (4-BPCA) shows a vibrational structure in nonpolar solvents and a largely Stokes-shifted emission maximum without the vibrational structure in polar solvents. The observed largely Stokes-shifted emission maximum is due to an increase of the dipole moments or to a change of the polarity in the excited state. The authors proposed that the large Stokes shift of 4-BPCA in a polar solvent is due to an intramolecular-charge-



**Scheme 1.** The chemical structures of the ligands NA-1, NA-2, and NA-3 and their  $\text{Eu}^{\text{III}}$ -cored complexes NAC-1, NAC-2, and NAC-3.



**Figure 1.** Normalized absorption and emission spectra of the ligands in various solvents (concentration =  $2.0 \times 10^{-5}$  M): a) NA-1; b) NA-2; c) NA-3.

transfer (ICT) interaction between the phenyl group that acts as an electron donor and the benzoic acid that acts as an acceptor. They also explained that the molecular geometry of 4-BPCA in the excited state could change toward a coplanar conformation by internal rotation around the central C–C bond. The excited-state geometry change is hindered in polar solvents; however, the biphenyl moiety of the excited 4-BPCA in polar solvents would remain as twisted as in the ground state.

Here, NA-1 has a naphthalene group directly linked to a phenyl group in the benzoic acid. The vibrational structure in the fluorescence spectra of NA-1, associated with the lack of the molecular geometry changes toward coplanarity of the

naphthalene moiety in the excited state, was not clear compared to other charge-transfer molecules.<sup>[14]</sup> This may be due to the large steric hindrance between the naphthalene and the phenyl ring in the benzoic acid. Actually, the dihedral angle between the naphthalene and the phenyl ring in NA-1 was calculated to be  $68.8^\circ$  by using a semi-empirical method. Such a dihedral angle may be wide enough to prevent it from having another coplanar conformation. Therefore, the excited-state geometry of NA-1 in a polar solvent may remain as twisted as in the ground state. Also, it is well known that a pretwisted molecule undergoes a facile conversion to the ICT state because the twist angle is required to be small for the formation

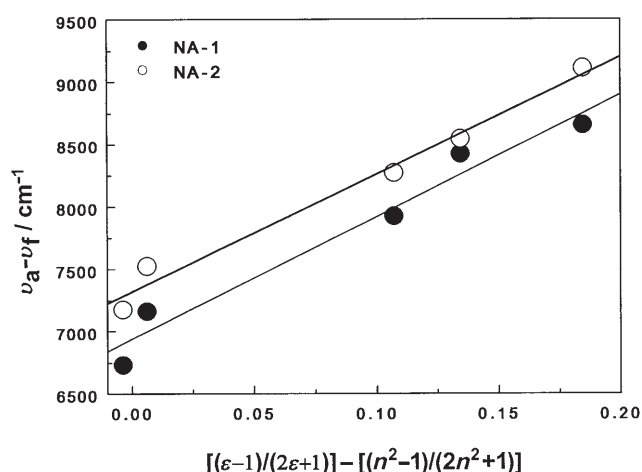
of the ICT structure from the pretwisted molecule. Therefore, NA-1 may easily tend to undergo a facile conversion to the ICT state.

In the chemical structure of NA-2, the methoxy phenyl group is connected in the *para* position to naphthalene, and both the *p*-methoxy phenyl group and the phenyl ring in the benzoic acid are placed out-of-plane with respect to the naphthalene group because of the large steric hindrance in the *p*-methoxy phenyl group, the naphthalene and the benzoic acid. All the dihedral angles in the *p*-methoxy phenyl group, the naphthalene, and the benzoic acid were calculated to be 71.3°. It is noteworthy that the photoinduced charge separation is maximized and the ICT state is more stabilized when the molecules contain both donor and acceptor groups in a small molecule, such as the NA-2 molecule, in which the *p*-methoxy phenyl group and the benzoic acid behave as an electron donating group and an electron withdrawing group, respectively. Therefore, NA-2 may tend to undergo a more facile conversion to the ICT state than NA-1. The fluorescence spectra of NA-2 show a strong red shift (of 40 nm) of the emission maximum. This large Stokes shift of the emission maximum in polar solvents may be due to an increment of the dipole moment or the polarity in the excited state, implying the formation of the ICT state in the excited state.

To get an insight into the formation of the ICT state in the excited state, the spectral dependency of NA-1 and NA-2 on solvent polarity was studied on the basis of the Lippert–Mataga model.<sup>[16]</sup> Since the molecule–solvent interaction has primarily dipole–dipole characteristics, the Stokes shift ( $\bar{\nu}_a - \bar{\nu}_f$ ) depends on the solvent polarity parameters, as expressed in Equation (1):

$$\bar{\nu}_a - \bar{\nu}_f = \frac{2}{hc} \times \left( \frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{n^2 - 1}{2n^2 + 1} \right) \times \frac{(\mu_e - \mu_g)^2}{a^3} + \text{const.} \quad (1)$$

where,  $\mu_e$  and  $\mu_g$  are the dipole moments of the molecules in the lowest excited singlet state and the ground state, respectively,  $h$  is the Planck constant,  $c$  is the speed of light in vacuum, and  $a$  is the Onsager radius cavity. Figure 2 shows the plot of the Stokes-shifted fluorescence of NA-1 (closed circles) and NA-2 (open circles) as a function of the solvent polarity parameter, according to Equation (1). From the slope of the straight line, the value of  $\mu_e - \mu_g$  can be evaluated with the  $a$  parameter. The Onsager radii,  $a$ , of NA-1 and NA-2 were calculated, by using a semi-empirical method, to be 5.5 and 8 Å, respectively. The evaluated values of  $\mu_e - \mu_g$  are 0.6 and 13.4 D for NA-1 and NA-2, respectively. The values of the dipole moment in the ground state were calculated, by the AM1 method, to be 2.44 and 3.42 for NA-1 and NA-2, respectively. Therefore, the  $\mu_e$  values of the dipole moment in the excited state were determined to be 10.0 and 16.8 D for NA-1 and NA-2, respectively. As a result, these high values of the excited-state dipole moment indicate a high probability of the excited ICT state in NA-1 and NA-2.

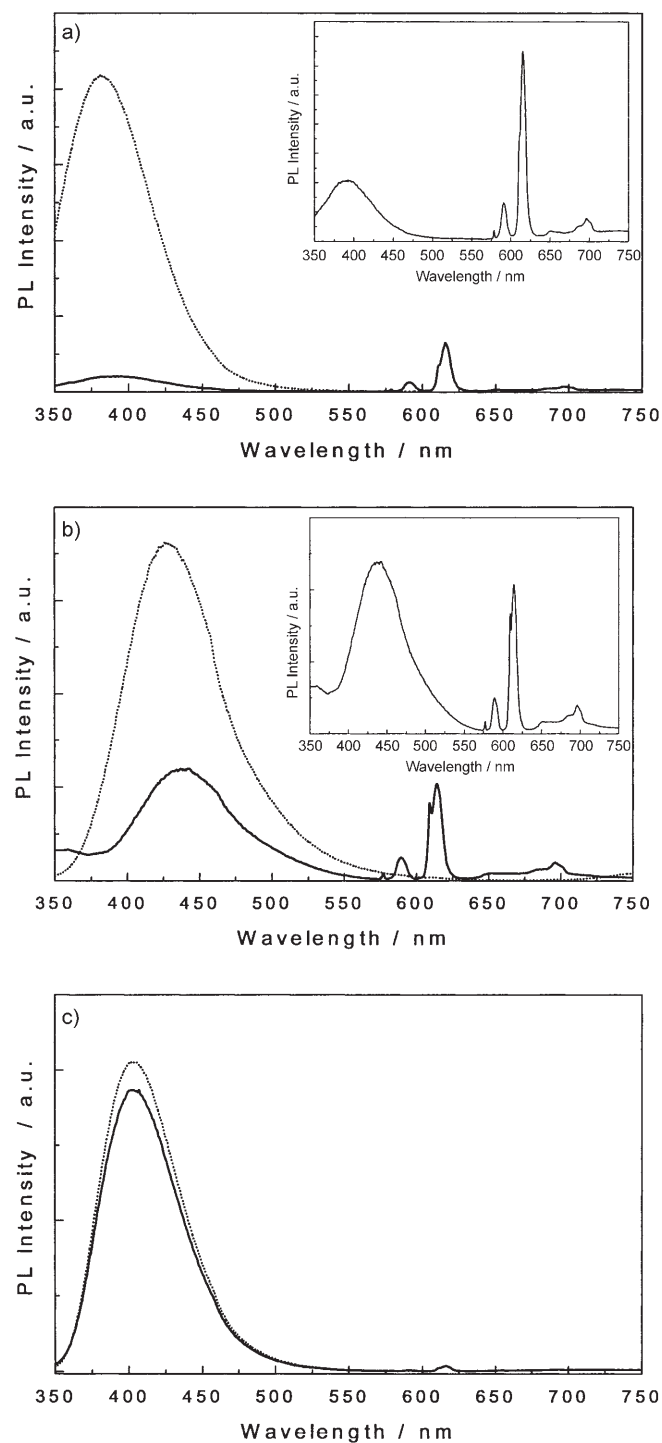


**Figure 2.** The Stokes-shifted fluorescence of NA-1 (●) and NA-2 (○) as a function of the solvent polarity parameters.

## 2.2. Sensitized Emission of Eu<sup>III</sup> Ions in Eu<sup>III</sup>-Cored Complexes Based on NA-1, NA-2, and NA-3

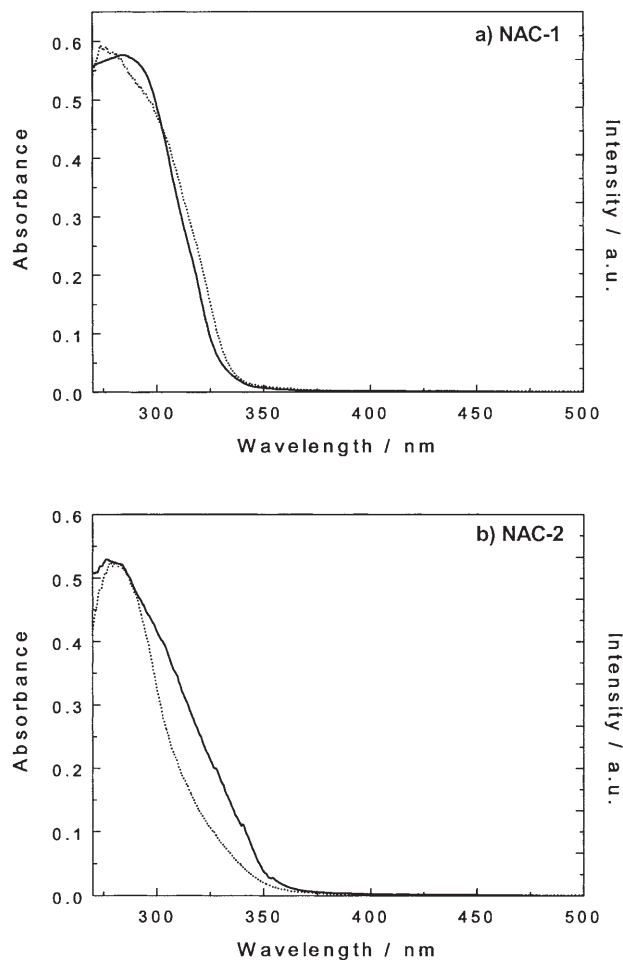
Figure 3 shows the emission spectra of free ligands (NA-1, NA-2, and NA-3) and their Eu<sup>III</sup>-cored complexes (NAC-1, NAC-2, and NAC-3) in acetonitrile. Upon photoexcitation at the wavelength of the absorption maximum of the corresponding ligands, the typical narrow emission bands of the Eu<sup>III</sup> ions in NAC-1 and NAC-2 are exhibited in the region: 550–750 nm, while the emission intensities of the ligands in NAC-1 and NAC-2 are significantly diminished, compared to those of the free corresponding ligands. A strong decrease of the ligand fluorescence intensity in the Eu<sup>III</sup> complexes is accompanied by a strong increase of the visible emission of the Eu<sup>III</sup> ion. However, in the case of NAC-3, the emission intensity of the NA-3 ligand in the complex is almost identical to that of the free NA-3 ligand, and a very weak emission of the central lanthanide ion was observed. Thus, one can distinguish between two different types of luminescent lanthanide complexes: The direct complexes, such as NAC-1 and NAC-2, and the indirect complexes, such as NAC-3, which have rather different photophysical behaviors. The direct complexes, NAC-1 and NAC-2, exhibited a strong emission of Eu<sup>III</sup> ions in acetonitrile, while the indirect complex, NAC-3, did not.

In addition, a photoexcitation study at the wavelength of the absorption maximum of the terpyridine ligand was carried out to investigate the possibility of sensitized emission of the central lanthanide ion by energy transfer between terpyridine and the central lanthanide ion, since terpyridine is also well known as a good antenna for photosensitizing the luminescence of the Eu<sup>III</sup> ion. However, we observed that the quantum yield of terpyridine is much lower than that of benzoic acid derivatives. We could not observe any significant Eu<sup>III</sup> emission band by photoexciting the terpyridine ligand either in NAC-1 and NAC-2 under nonpolar conditions nor in NAC-3. If terpyridine plays, in our system, a role as a good antenna for photosensitizing, we should observe a significant Eu<sup>III</sup> emission band in NAC-3. Thus, terpyridine is not playing a role as an antenna for photosensitizing in our systems.



**Figure 3.** Emission spectra of the ligands and the sensitized  $\text{Eu}^{\text{III}}$  ion in acetonitrile (concentration =  $1 \times 10^{-5}$  M): Dotted (.....) and solid (—) lines represent the emission of the free ligands and the corresponding complexes, respectively. The inset shows a magnification of the emission of the  $\text{Eu}^{\text{III}}$  complexes: a) NAC-1, b) NAC-2, c) NAC-3.

The excitation spectra of  $\text{Eu}^{\text{III}}$ -cored complexes, monitored at an emission wavelength of 616 nm, arising from the electronic transition  $^5\text{D}_0 \rightarrow ^7\text{F}_2$  of the  $\text{Eu}^{\text{III}}$  ion closely matched the absorption spectra of the corresponding ligand in acetonitrile, as illustrated in Figure 4. Upon photoexcitation of the NAC-1 and NAC-2



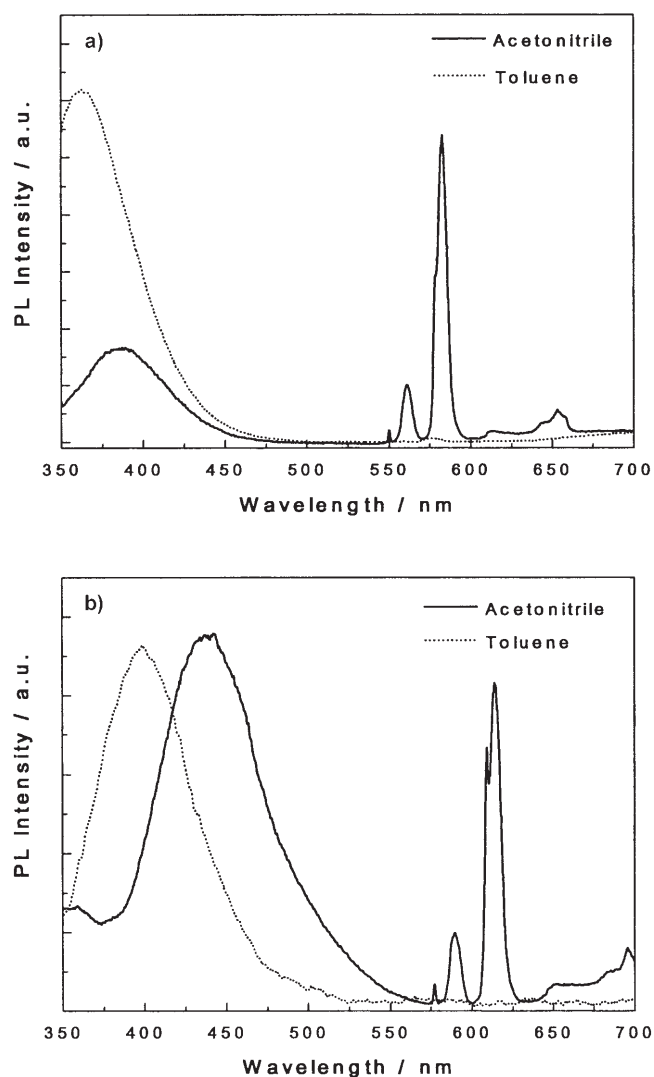
**Figure 4.** Absorption (—) and fluorescence excitation spectra (.....) of  $\text{Eu}^{\text{III}}$  complexes in acetonitrile ( $\lambda_{\text{em}} = 616$  nm and concentration =  $10^{-5}$  M): a) NAC-1 and b) NAC-2.

ligands with the wavelength of the absorption maximum in the  $\text{Eu}^{\text{III}}$  complexes, the effective sensitization of the  $\text{Eu}^{\text{III}}$  ion takes place.

Figure 5 shows the fluorescence spectra of the NAC-1 and NAC-2 complexes in polar and nonpolar solvents. The fluorescence maxima of the corresponding ligands in NAC-1 and NAC-2 are red-shifted to longer wavelengths in polar solvents, compared to those in nonpolar solvents. Furthermore, it is noteworthy that no luminescence of the central metal ion was observed in nonpolar solvents, while a strong luminescence of  $\text{Eu}^{\text{III}}$  ion was obtained in polar solvents. This suggests that the energy transfer in these complexes could be influenced by the solvent polarity.

In polar solvents, it was observed that the fluorescence quantum yields of the ligands in NAC-1 and NAC-2 decreased compared with those of the corresponding free ligands. The strong decrease of the ligand fluorescence intensity in the  $\text{Eu}^{\text{III}}$  complexes of NAC-1 and NAC-2 is accompanied by a strong increase in the visible emission of the  $\text{Eu}^{\text{III}}$  ions, which might be ascribed to the energy transfer of a certain excited state of the ligands to the  $\text{Eu}^{\text{III}}$  ion. Generally, the quenching of the ligand fluorescence in the complexes may be due to either the





**Figure 5.** Emission spectra of  $\text{Eu}^{\text{III}}$  complexes in polar and nonpolar solvents: a) NAC-1 and b) NAC-2 in toluene (.....) and acetonitrile (—) ( $\lambda_{\text{ex}} = 290 \text{ nm}$ ).

energy transfer to the lanthanide ion or the ISC process, since the fluorescence of the ligands in lanthanide(III) complexes competes with the ISC process caused by the heavy-atom effect. The ISC process, arising from the heavy-atom effect of the  $\text{Eu}^{\text{III}}$  ions, could lead to a conversion of the fluorescence into phosphorescence of the ligands in lanthanide(III) complex via a triplet state from a singlet excited state.

To detect the phosphorescence of the ligands in lanthanide(III) complexes,  $\text{Gd}^{\text{III}}$ -cored complexes based on NA-1 and NA-2 were synthesized according to our new synthetic method<sup>[1,11]</sup> for the following reasons: The  $\text{Gd}^{\text{III}}$  ion has no energy levels below  $32000 \text{ cm}^{-1}$ , and the fluorescence emissions of NA-1 and NA-2 are in the region of  $22000\text{--}29000 \text{ cm}^{-1}$ . Thus, the  $\text{Gd}^{\text{III}}$  ion cannot accept any energy from either the triplet nor the singlet state of NA-1 and NA-2. Therefore, the  $\text{Gd}^{\text{III}}$  ion can provide a triplet state formed by the heavy-atom effect in the  $\text{Gd}^{\text{III}}$  complexes.<sup>[17]</sup> We have attempted to investigate the phosphorescence of the NA1-Gd and NA2-Gd complexes in the de-

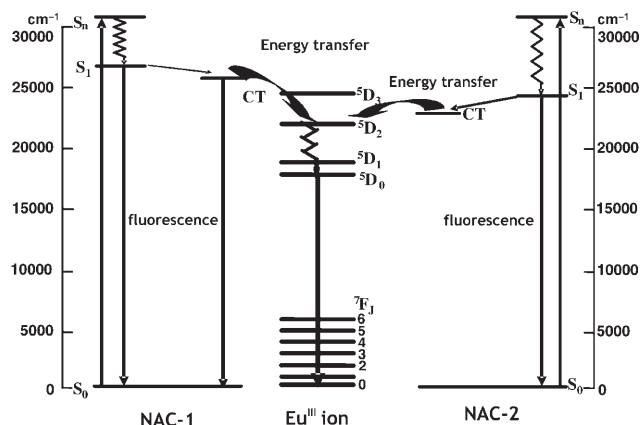
gassed, mixed solvent methanol : ethanol (4:1). However, we could not detect any significant phosphorescence spectra for the NA1-Gd and NA2-Gd complexes even at 77 K. This indicates that the lanthanide(III) ion in these lanthanide complexes cannot retain an external heavy-atom effect for NA-1 and NA-2. Thus, the triplet state in these complex systems is not concerned with the main energy-transfer pathway for the decreased fluorescence intensity of the ligands in NAC-1 and NAC-2.

Alternatively, to explore the phosphorescence of the ligands in the lanthanide(III) complexes of NAC-1 and NAC-2, we have studied the spectral dependency of the phosphorescence on the oxygen concentration as follows: Oxygen may affect the energy transfer efficiency between the excited triplet state of the ligand and the lanthanide ion, because the excited triplet state is quenched by oxygen<sup>[7]</sup> if the energy-transfer pathway takes place through the triplet state. In the deoxygenated condition, the emission intensity of the  $\text{Eu}^{\text{III}}$  ion should be enhanced in comparison with the aerated condition. However, the deoxygenation of NAC-1 and NAC-2 did not increase the sensitization emission of the  $\text{Eu}^{\text{III}}$  ion. Therefore, we could rule out the possibility that the ISC process is involved in the sensitization emission of the  $\text{Eu}^{\text{III}}$  ion to form a triplet state, leading to the decrement of the ligand emission intensity in the  $\text{Eu}^{\text{III}}$ -cored complexes.

Another possible energy-transfer pathway, which might explain the strong decrease of the ligand fluorescence intensity in the  $\text{Eu}^{\text{III}}$ -cored complexes of NAC-1 and NAC-2, accompanied by the strong emission bands of the  $\text{Eu}^{\text{III}}$  ions, is through the singlet state of the luminescent ligand to the  $\text{Eu}^{\text{III}}$  ions. To obtain an effective energy transfer between the singlet luminescent ligand and the lanthanide ion, the emission energy level of the ligands should overlap well with the absorption energy level of the  $\text{Eu}^{\text{III}}$  ion.<sup>[18]</sup> The energy level of the  $\text{Eu}^{\text{III}}$  ion for the highest oscillation strength of its absorption bands is estimated to be  $25300 \text{ cm}^{-1}$  and overlaps well with the singlet excited state of NA-2 ( $25000 \text{ cm}^{-1}$ ). If the energy-transfer process could take place via the singlet excited state, the sensitized emission of the  $\text{Eu}^{\text{III}}$  complex based on NA-2 should not exhibit a solvent polarity dependence. However, we cannot observe the sensitized emission of the  $\text{Eu}^{\text{III}}$  complex based on NA-2 in nonpolar solvents. In other words, the emission of the sensitized  $\text{Eu}^{\text{III}}$  ions occurs only in polar solvents, but not in nonpolar solvents. These results suggest that the involvement of the singlet excited state of the two ligands based on NA-1 and NA-2 in the photosensitization of the  $\text{Eu}^{\text{III}}$  ions in the  $\text{Eu}^{\text{III}}$ -cored complexes could be negligible.

As discussed previously, the spectral dependence studies of the NA-1 and NA-2 ligands on the solvent polarity strongly support the presence of their ICT state in polar solvents, according to the dipole moment values in the excited state. Also, the emission of the sensitized  $\text{Eu}^{\text{III}}$  ions in NAC-1 and NAC-2 was observed only in polar solvents. Thus, we can suggest that the charge-transfer state, formed only in polar solvents, might be involved in the energy-transfer pathway, but both the singlet and triplet excited states are not concerned with the energy transfer in the  $\text{Eu}^{\text{III}}$ -chelated complexes based on NA-1

and NA-2. Generally, the charge-transfer process in the organic molecules, which easily leads to the formation of the charge-transfer state, still competes with the ISC process. It is well known that the rate of the charge-transfer process is faster than that of the ISC process. Thus, the charge-transfer process is more dominant than the ISC process; for example, in the case of dansyl fluorophore, which is known as a representative chromophore in the formation of the charge-transfer state, the phosphorescence was hardly observed.<sup>[19,20]</sup> As a consequence, the decreased fluorescence intensities of the ligands in NAC-1 and NAC-2 may be due to energy transfer to the lanthanide(III) ion through the ICT state. From the above spectroscopic results, we can propose that the ICT states of NA-1 and NA-2 play a very important role in the energy-transfer pathway of the Eu<sup>III</sup> complexes described here. In other words, the energy transfer occurs through the ICT state of the ligands to the Eu<sup>III</sup> ion in the Eu<sup>III</sup> complexes based on NA-1 and NA-2 (see Scheme 2).



**Scheme 2.** Schematic diagram of the photophysical processes leading to sensitized luminescence of NAC-1 and NAC-2 in polar solvents.

In the case of NAC-3, the fluorescence intensity of the ligand in the Eu<sup>III</sup> complex is almost the same as that of the free ligand (NA-3), and no sensitized emission of the Eu<sup>III</sup> ion was observed in any organic solvent. These results indicate that no energy transfer takes place from the ligand to Eu<sup>III</sup> in NAC-3. This can be attributed to the fact that the formation of the charge-transfer state in NA-3 was prevented because the  $-\text{OCH}_2-$  group acts as a blocking group by interrupting the  $\pi$  conjugation between a naphthalene unit and a benzoic acid unit.<sup>[11]</sup> However, in the solid state, moderate emission bands of the Eu<sup>III</sup> ions in the Eu<sup>III</sup> complex of NAC-3 were observed, which could be due to the energy-transfer pathway, via the singlet excited state, to the Eu<sup>III</sup> ions, since a similar phenomenon was observed in previous studies.<sup>[9,10]</sup>

### 2.3. Energy Transfer Efficiency of NAC-1 and NAC-2

The fluorescence lifetimes of the Eu<sup>III</sup>-chelated complexes based on NA-1 and NA-2 were measured by using time-resolved emission spectroscopy with an excitation wavelength of 290 nm in acetonitrile. The fluorescence decays of the Eu<sup>III</sup>-che-

lated complexes were monitored at 616 nm, corresponding to the Eu<sup>III</sup> ion emission of the  $^5\text{D}_0 \rightarrow ^7\text{F}_1$  transition. The lifetimes of the Eu<sup>III</sup> ions in NAC-1 and NAC-2 were monoexponential with lifetimes in the millisecond region (ca. 1 ms), and the fluorescence lifetime of NAC-1 was slightly longer than that of NAC-2 (see Table 1). The quantum efficiency of the Eu<sup>III</sup> ion can be cal-

**Table 1.** Photophysical parameters for the Eu<sup>III</sup>-cored complexes of NAC-1 and NAC-2 in acetonitrile with  $\lambda_{\text{ex}} = 290$  nm.

	$\phi_{\text{lum}}$	$\tau_{\text{obs.}}^{[\text{a}]}$ Eu <sup>III</sup>	$I_{\text{tot.}}/I_{^5\text{D}_0 \rightarrow ^7\text{F}_1}$	$\tau_{\text{R}}$ [ms]	$\tau_{\text{obs.}}$ [ms]	$\phi_{\text{Eu}^{\text{III}}}$
NAC-1	0.09	1.09	7.87	2.7	1.09	0.40
NAC-2	0.06	1.07	7.25	2.9	1.07	0.37

[a] Monitored at 616 nm.

culated from the decay time ( $\tau_{\text{obs.}}$ ) of the Eu<sup>III</sup> ion and the radiative lifetime ( $\tau_{\text{R}}$ ) of the Eu<sup>III</sup> ion by Equation (2).<sup>[21]</sup> The radiative lifetime ( $\tau_{\text{R}}$ ) can be estimated by Equation (3), assuming that the energy of the  $^5\text{D}_0 \rightarrow ^7\text{F}_1$  transition (MD) and its oscillator strength are constant:

$$\Phi_{\text{Ln}} = \tau_{\text{obs.}}/\tau_{\text{R}} \quad (2)$$

$$1/\tau_{\text{R}} = A_{\text{MD}} \cdot n^3 \cdot (I_{\text{tot.}}/I_{^5\text{D}_0 \rightarrow ^7\text{F}_1}) \quad (3)$$

where  $A_{\text{MD}}$  is the spontaneous emission probability of the  $^5\text{D}_0 \rightarrow ^7\text{F}_1$  transition, which equals  $14.65 \text{ s}^{-1}$ , and  $n$  is the refractive index of the solvent.

The total luminescence quantum yields of the emission from the Eu<sup>III</sup> ion upon excitation of the ligands at 290 nm are 0.09 and 0.06 for NAC-1 and NAC-2, respectively (see Table 1). For NAC-1 and NAC-2, the calculated  $\tau_{\text{R}}$  and  $\Phi_{\text{Eu}^{\text{III}}}$  values with the experimentally determined values of  $\tau_{\text{obs.}}$  and  $\phi_{\text{lum}}$  are summarized in Table 1. The emission quantum efficiency of the Eu<sup>III</sup> ions in NAC-1 (40%) is higher than that of the Eu<sup>III</sup> ions in NAC-2 (37%). These values are quite good, compared to other Eu<sup>III</sup> complexes.<sup>[10,22]</sup>

To ensure that the energy-transfer process in the Eu<sup>III</sup> complexes takes place effectively, the emitting energy level of the luminescent ligands based on NA-1 and NA-2 should match well the absorption energy level of the Eu<sup>III</sup> ion in the complexes. Furthermore, the difference between the emitting energy level of the ligand and the absorption energy level of the Eu<sup>III</sup> ion should be moderate in the complexes. As stated above, the energy levels of the ICT states, which may take part in the energy-transfer pathway, were estimated to be 25380 and 22727  $\text{cm}^{-1}$  for NA-1 and NA-2, respectively. The spectral overlap integral ( $J$ ) between the ICT state of the ligands and the absorption of the Eu<sup>III</sup> ion is larger in NAC-1 than in NAC-2. This may lower the quantum efficiency in NAC-2 (see Table 1). Based on the energy levels of the ligands and the Eu<sup>III</sup> ion in the complexes, it seems that the excitation energy of NAC-1 and NAC-2 is transferred to the  $^5\text{D}_2$  states of the Eu<sup>III</sup> ion because the  $^5\text{D}_3$  state is a forbidden state.<sup>[23]</sup> The ICT state of NA-



1 is higher than the  $^5D_2$  state of the  $\text{Eu}^{III}$  ion by  $3880\text{ cm}^{-1}$ , and the ICT state of NA-2 lies in a higher energy level than the  $^5D_2$  state of the  $\text{Eu}^{III}$  ion by  $1227\text{ cm}^{-1}$ , which is located between the  $^5D_3$  and  $^5D_2$  states in the  $\text{Eu}^{III}$  ion (Scheme 2). Generally, a small difference between the energy level of the ligand and that of the  $\text{Eu}^{III}$  ion in the complexes is required to render the efficient energy transfer between them, when the donor emission energy level of the ligand is higher than the acceptor absorption energy level of the  $\text{Eu}^{III}$  ion. Even though the donor emission energy level is higher, to some extent, than the acceptor absorption energy level, the small energy gap of less than  $1600\text{ cm}^{-1}$  between them could allow the back energy transfer to be significantly possible.<sup>[24]</sup> Thus, it is possible that the back energy transfer takes place in NAC-2 with an energy difference of  $1227\text{ cm}^{-1}$  between the donor emission energy level and the acceptor absorption energy level. Still, an efficient energy transfer may occur due to the relatively small energy difference. Similarly, it was previously observed that, in the case of  $\text{Eu-tris}(\beta\text{-diketonate})$ , the luminescent quantum yield was the highest one when the energy difference was  $\approx 1900\text{ cm}^{-1}$ . Also,  $[(\text{Eu}1)\text{bfa}]$  has a higher quantum efficiency than that of  $[(\text{Eu}1)\text{hfa}]$ , in which the energy difference is  $3000$  and  $2400\text{ cm}^{-1}$  for  $[(\text{Eu}1)\text{hfa}]$  and  $[(\text{Eu}1)\text{bfa}]$ , respectively.<sup>[18]</sup> In summary, we suggest that the slightly lowered quantum efficiency in NAC-2 may be due to back energy transfer and a smaller spectral overlap integral ( $J$ ).

### 3. Conclusions

One can distinguish between two different types of luminescent ligands: direct ligands, such as NA-1 and NA-2, and indirect ligands, such as NA-3, and between two different types of luminescent lanthanide complexes: direct complexes, such as NAC-1 and NAC-2, and indirect complexes, such as NAC-3, which have rather different photophysical behaviors. The fluorescence spectra of the NA-1 and NA-2 ligands show a large Stokes shift with increasing solvent polarity. We demonstrated, based on the Lippert–Mataga model, that these large Stokes shifts might be dominantly due to the formation of the ICT complexes in the excited state. Similarly, the  $\text{Eu}^{III}$ -cored complexes of NAC-1 and NAC-2 exhibit a significant fluorescence dependency on the solvent polarity: They show an intensive luminescence of the central  $\text{Eu}^{III}$  ions in polar solvents by photoexcitation of the ligand, but non in nonpolar solvents. Also, the strong decrease of the ligand fluorescence intensity in the  $\text{Eu}^{III}$  complexes of NAC-1 and NAC-2 is accompanied by strong emission bands of the  $\text{Eu}^{III}$  ion. In addition, we could not observe the phosphorescence spectra even in the  $\text{Gd}^{III}$ -cored complexes based on NA-1 and NA-2. Furthermore, we observed no spectral dependency of the ligand phosphorescence on the oxygen concentration in the  $\text{Eu}^{III}$  complexes of NAC-1 and NAC-2. These results also indicate no presence of their triplet excited state in the  $\text{Eu}^{III}$  complexes. However, in the case of NA-3, there is no dependence of the fluorescence spectrum on the solvent nature as well as no luminescence of the  $\text{Eu}^{III}$  ions by photoexcitation of the ligand. This can be due to the fact that the formation of the charge transfer state in NA-3

was prevented because the  $-\text{OCH}_2-$  group acts as a blocking group, interrupting the  $\pi$  conjugation between them. From our photophysical studies, we suggest that the ICT complexes also play a very important role in the effective energy-transfer pathway from the ligand to  $\text{Eu}^{III}$  in the complexes. In other words, the energy-transfer pathway occurs through the ICT state of the ligands, not through the excited triplet state, to the  $\text{Eu}^{III}$  ion in the  $\text{Eu}^{III}$ -chelated complexes based on NA-1 and NA-2. To our best knowledge, this is the first demonstration of sensitized emission of luminescent lanthanide complexes based on 4-naphthalen-1-yl-benzoic acid derivatives by a charge-transfer process. More interestingly, with the effective energy-transfer pathway through the ICT state of the ligands from the ligand to  $\text{Eu}^{III}$ , the intrinsic luminescence quantum yield of the  $\text{Eu}^{III}$  ions in the complexes is in the range: 37–40%, and these values are very good, compared to other  $\text{Eu}^{III}$  complexes.

### Experimental Section

4-Naphthalene-1-yl-benzoic acid-based ligands (NA-1, NA-2, and NA-3) and their  $\text{Eu}^{III}$ -cored complexes (NAC-1, NAC-2, and NAC-3) were synthesized according to a procedure described elsewhere.<sup>[11]</sup> All the organic solvents used were spectrograde, and the concentration of the ligands and complexes remained constant ( $2 \times 10^{-5}\text{ M}$ ).

The absorption spectra were recorded on a Shimadzu UV-2401PC spectrophotometer. The corrected fluorescence emission and excitation spectra were measured on an Edinburgh FS920 fluorometer with a 450 W Xe-lamp and a Hamamatsu R955 PMT. The optical density at the excitation wavelength was held constant when the fluorescence spectra of different solutions were measured. The quantum yields of all complexes were determined by comparison with a reference of a known quantum yield (Rhodamin 6G in ethanol,  $\Phi_f = 0.65$ ) using a method described elsewhere.<sup>[25]</sup> Time-resolved emission measurements on the millisecond timescale were performed with an excitation at 290 nm by using an Nd:YAG laser (EXSPLA NT342) and an 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 with a photomultiplier followed by a boxcar averager (Stanford Research System) or a digital oscilloscope (Agilent infinity 54832B DSO). The optimized molecular structures of the ligands were calculated by a semi-empirical method (PM3).

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