

Efficient Energy Transfer Pathways for the Sensitization of Lanthanide Ions by Luminescent Ligands in Luminescent Lanthanide Complexes

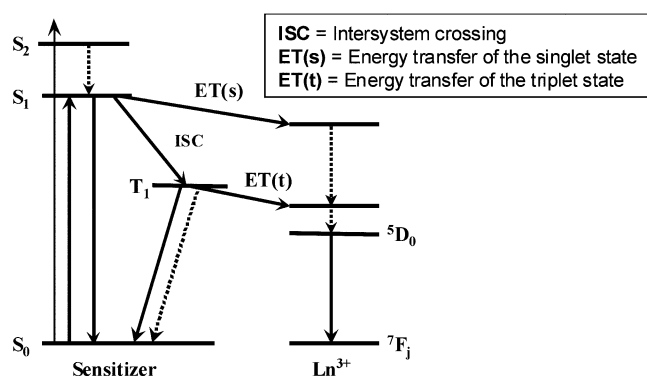
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Luminescent lanthanide complexes have attracted much recent attention because of both their academic interest and their potential utility in a wide variety of applications, such as planar waveguide amplifiers, plastic lasers, and light-emitting diodes.¹⁻³ In most cases, luminescent lanthanide complexes consist of a lanthanide ion and a chelating luminescent ligand which acts as a sensitizer that transfers excitation energy to the encapsulated lanthanide ion. The presence of the luminescent ligand overcomes the lanthanide ion's intrinsically low luminescence intensity by direct excitation of the lanthanide ion with low absorption and emission cross-sections. Despite extensive research, the energy transfer pathways for the sensitization of the lanthanide ions by the luminescent ligands in these complexes are still not fully understood. Efficient energy transfer pathways are very important in advanced photonics technology, particularly in the development of new and useful luminescent lanthanide complexes with efficient lanthanide emission.¹

Two possible energy transfer pathways are schematically illustrated in Scheme 1. Although theoretical analysis of energy transfer from the luminescent ligand to the lanthanide ion does not rule out the possibility of energy transfer from the singlet state of the luminescent ligand (ET(s)), previous experiments have indicated that in general only the triplet state of the luminescent ligand is involved in photosensitization (ET(t)). No energy transfer pathway from the singlet

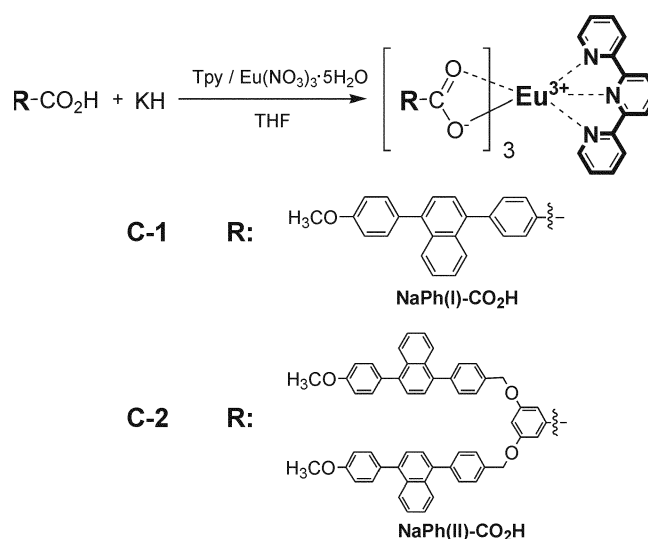


Scheme 1. Two possible energy transfer pathways.

state has previously been observed in luminescent lanthanide complexes, which is thought to be because this process is usually too slow to compete with other processes such as luminescent ligand fluorescence and intersystem crossing (ISC).⁴

In order to investigate the pathways for energy transfer from luminescent ligands to lanthanide ions, we have systematically designed and developed naphthalene-based luminescent ligands as sensitizers, which provide enough coordinated sites for the formation of inert, stable 9-coordinated lanthanide complexes, as shown in Scheme 2.⁵⁻⁷ These naphthalene-based derivatives were synthesized using the well-known Suzuki cross coupling reaction with moderate yield.⁵ We used $\text{Eu}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ to successfully synthesize saturated 9-coordinated europium (Eu)(III)-cored complexes with these naphthalene-based derivatives, which enable the formation of more stable complexes and shield the Eu(III)-chelated complexes more efficiently.^{6,7}

The UV-visible spectra of Naph(I)-CO₂H and Naph(II)-CO₂H have broad and intense band edges with a maximum absorption wavelength of 312 nm and with a maximum absorption wavelength of 306 nm, respectively. The photo-excitation of Naph(I)-CO₂H and Naph(II)-CO₂H with light of wavelength 325 nm results in PL spectra with strong



Scheme 2. Synthetic strategy for the synthesis of the Eu(III)-cored complexes based on naphthalene derivatives.

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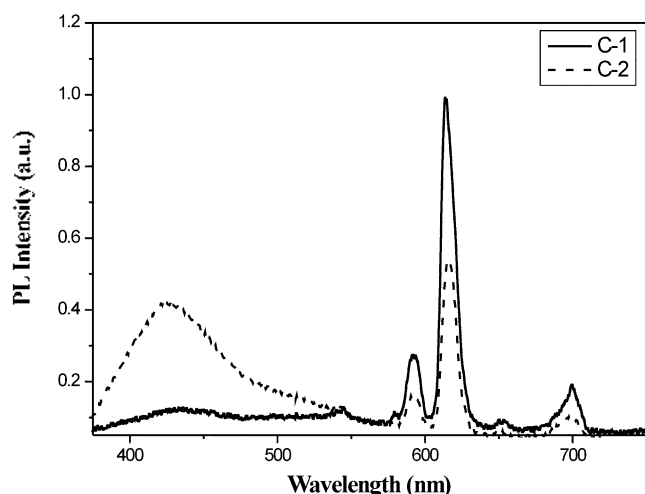


Figure 1. Emission spectra of the Eu(III) complexes of C-1 and C-2 ($\lambda_{\text{exc}} = 325$ nm, solid state).

emission bands at 429 nm and 400 nm, respectively.⁸ The complexing of the naphthalene-based luminescent derivatives in Eu(III)-cored luminescent complexes does not alter their UV absorption features. This indicates that the ground state of the lanthanide ions is not influenced by the organic ligands, even in Eu complexes. The emission spectra of the Eu(III)-chelated complexes (C-1 and C-2), obtained using excitation wavelengths at 325 nm of the He-Cd laser, contain an intra 4f electronic transition from the first excited state (5D_0) to the ground state (7F_2) at 612 nm (see Fig. 1). C-1 has a much stronger PL intensity than C-2. This observation can be explained in terms of the more effective energy transfer between the ligands and the lanthanide ions that occurs in C-1 (ET(t)). C-1 has a higher ISC efficiency for the conversion of the singlet state into the triplet state than C-2; this higher ISC efficiency is due to the heavy metal effect that arises in C-1, because Naph(I)-CO₂H is directly connected to the lanthanide ions.^{1,5,9}

C-1 and C-2 also have qualitatively different PL spectra. C-1 produces one strong photoluminescence band with maximum wavelength around 612 nm. C-2 produces two PL bands: a strong emission band around 612 nm and an emission band of moderate intensity around 400 nm. The latter band is assigned to fluorescence from the singlet state of the naphthalene-based luminescent ligand, because its absorption and emission spectra are mirror images of each other. This assignment is confirmed by the time-resolved transient decay, which shows that the lifetime of this excited state is less than 1 nanosecond (approx. 80 picoseconds). Further, the intensity of the emission band at 400 nm was reduced, but the emission band at 612 nm was simultaneously increased. The presence of an emission band near 400 nm indicates that no effective energy transfer occurs between the organic ligand in C-2 and the lanthanide ion.

This might be because the organic ligands are indirectly connected through building blocks to the lanthanide ions. Thus, the effective formation of triplet states does not occur in C-2, because there is no heavy metal effect. In addition, C-2 exhibits much lower fluorescence intensity around 400 nm than the Naph(II)-CO₂H ligand, presumably due to the singlet energy transfer from the luminescent ligand to the lanthanide ion (ET(s)). To the best of our knowledge, this is the first demonstration that energy transfer from the singlet state of the luminescent ligand is also involved in photosensitization.

In summary, we have designed and developed novel luminescent lanthanide complexes based on naphthalene derivatives using a promising new synthetic method developed in our laboratory. The emission spectra of the saturated 9-coordinated Eu(III) complexes contain an intra 4f electronic transition from the first excited state (5D_0) to the ground state (7F_2) at 612 nm. The direct lanthanide complex (C-1) has much higher PL efficiency than the indirect lanthanide complex (C-2), due to the higher ISC efficiency of its ligands for the conversion of the singlet state into the triplet state. In the indirect lanthanide complex, it was also found that energy transfer occurs from the singlet state of the luminescent ligand.

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- $\text{Eu}^3+[\text{NaPh(I)CO}_2^-]_3$ (terpyridine) (C-1): Yield 78%. FT-IR (KBr) [cm^{-1}]: 1596, 1402. Anal. Calcd. for $\text{C}_{87}\text{H}_{63}\text{EuN}_3\text{O}_9$: C, 72.29; H, 4.32; Eu, 10.51; N, 2.91. Found: C, 71.02; H, 3.92; Eu, 10.41; N, 2.74. $\text{Eu}^3+[\text{NaPh(II)CO}_2^-]_3$ (terpyridine) (C-2): Yield 82%. FT-IR (KBr) [cm^{-1}]: 1596, 1410. Anal. Calcd. for $\text{C}_{180}\text{H}_{134}\text{EuN}_3\text{O}_{18}$: C, 77.80; H, 4.86; Eu, 5.47; N, 1.51; found C, 76.56; H, 4.92; Eu, 5.62; N, 1.21.
- Supporting information materials for details are available from the corresponding author on request.
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