

Singlet Energy Transfer as the Main Pathway in the Sensitization of Near-Infrared Nd³⁺ Luminescence by Dansyl and Lissamine Dyes

Gerald A. Hebbink,^[a] Stephen I. Klink,^[a] Lennart Grave,^[a] Patrick G. B. Oude Alink,^[a] and Frank C. J. M. van Veggel^{*[a,+]}

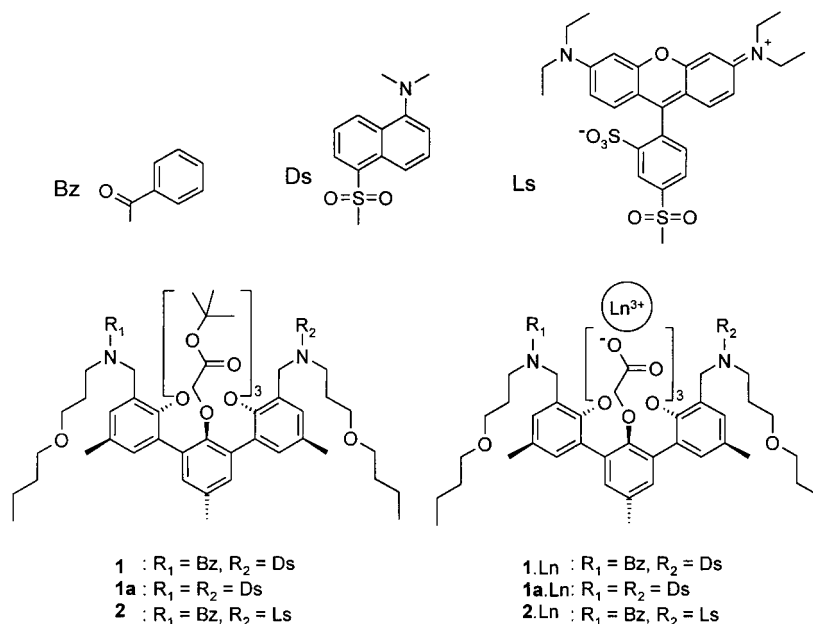
In general, sensitization of lanthanide(III) ions by organic sensitizers is regarded to take place via the triplet state of the sensitizers. Herein, we show that in dansyl- and lissamine-functionalized Nd³⁺ complexes energy transfer occurs from the singlet state of the sensitizers to the Nd³⁺ center. No sensitized emission was observed in the corresponding complexes with Er³⁺, Yb³⁺, and Gd³⁺ ions. Furthermore, the fluorescence of the sensitizers was quenched only in the Nd³⁺ complex and not in the complexes with the other ions.

Only Nd³⁺ centers can accept energy from the singlet state of the dyes, because the excited states of Nd³⁺ have a high spectral overlap with the fluorescence of the dansyl and lissamine sensitizers, and because the selection rules allow a fast energy transfer, which apparently is competitive with the fluorescence.

KEYWORDS:

lanthanides · luminescence · neodymium · sensitizers · singlet state

The sensitization of the lanthanide(III) ion luminescence by energy transfer from organic chromophores usually takes place via the triplet state of the sensitizer.^[1–3] Therefore, most research towards lanthanide(III) ion sensitizers has been focused on chromophores with a triplet state matching the receiving lanthanide ion energy level such that efficient energy transfer is obtained.^[4–6] Although seldom observed, energy transfer from the singlet state cannot be ruled out, and several reports mention this sensitization pathway as being possible.^[7–12] Thorne et al. concluded that energy transfer from the singlet state of an acetyl pyrazolone based ligand to a Tb³⁺ center is an important pathway.^[12] This conclusion is based on the comparison between the excited-state kinetics of both the Tb³⁺ and the Gd³⁺ complexes of that ligand. Recently, we have reported a number of fluorescent dyes as being efficient sensitizers for near-infrared (NIR) Nd³⁺ luminescence, including fluorescein,^[13] dansyl^[14] (**1** and **1·Ln**, where Ln = lanthanide ion), and lissamine^[14–16] (**2** and **2·Ln**; Scheme 1). In the case of fluorescein, it has been established experimentally that the energy transfer takes place from the triplet state of the dye.^[8, 13b] Although fluorescein has an extremely low intrinsic intersystem-crossing quantum yield ϕ_{ISC} , this value is close to unity for the Ln³⁺ complex due to an external heavy-atom effect induced by the heavy and paramagnetic lanthanide ion (Figure 1).^[17, 18] This increase of ϕ_{ISC} for the Ln³⁺ complex is accompanied by a concomitant decrease of the antenna fluorescence intensity. We



Scheme 1. Molecular structures of the compounds **1·Ln**, **1a·Ln**, **1a·2·Ln**, and **2**. Bz = benzoyl.

[a] Prof. Dr. Ir. F. C. J. M. van Veggel, Dr. Ir. G. A. Hebbink, Dr. S. I. Klink, Ing. L. Grave, Ing. P. G. B. Oude Alink
 Laboratories of Supramolecular Chemistry and Technology and MESA⁺ Research Institute
 University of Twente
 P.O. Box 217, 7500 AE Enschede (The Netherlands)
 Fax (+31) 53-4894645

[+] Current address:
 University of Victoria
 Department of Chemistry
 PO Box 3065, Victoria, BC
 Canada V8W 3V6
 E-mail: fvv@uvic.ca

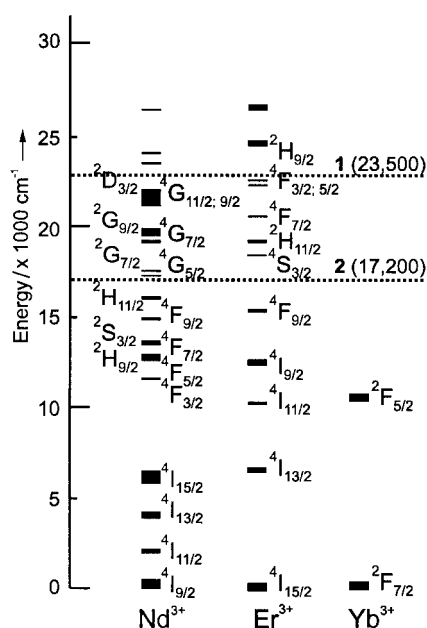


Figure 1. Energy-level diagram containing the 4f energy levels of Nd³⁺, Er³⁺, and Yb³⁺, and the excited-singlet-state energy levels of 1·Ln and 2·Ln. The lanthanide ion energy levels are obtained from ref. [25]. The singlet-state energy level of the dansyl moiety is the average of the absorption and fluorescence maxima in energy units, the singlet level of the lissamine moiety is the crossing point of the absorption and fluorescence spectra.^[26]

have also incorporated dansyl and lissamine into our terphenyl-based Nd³⁺ complexes. Despite the low ϕ_{ISC} of dansyl and lissamine, sensitization of the Nd³⁺ center was observed in both complexes. A decrease of the antenna fluorescence intensity of the complexes led us to believe that the efficient sensitization of the Nd³⁺ center is the result of an enhanced antenna ϕ_{ISC} and of a subsequent energy transfer from the triplet state.^[19] However, studying the dansyl- and lissamine-functionalized Nd³⁺ complexes in greater detail, we conclude now that this in fact is not the case. Herein, we show that the dansyl- and lissamine-dye-sensitized Nd³⁺ luminescence is the direct result of an energy transfer from the singlet excited state of the dye to the lanthanide ion.

Results and Discussion

The shape of the NIR emission spectra of the 1·Nd and 2·Nd complexes are similar (Figure 2) and show the characteristic Nd³⁺ emission lines at 890 (⁴F_{3/2} → ⁴I_{13/2}), 1066 (⁴F_{3/2} → ⁴I_{11/2}), and 1330 nm (⁴F_{3/2} → ⁴I_{9/2}). The correspondence of the excitation and absorption spectra (Figure 3) proves that the Nd³⁺ emission is the result of the excitation of the dansyl and the lissamine moieties in 1·Nd and 2·Nd, respectively. The luminescence lifetimes of Nd³⁺ in both complexes are similar. In DMSO, the luminescence lifetime is 1.1 μs, whereas it increases to 2.1 μs in [D₆]DMSO (Table 1). To enable a direct comparison between the sensitizing efficiencies of the two dyes, the emission intensities in Figure 2 have been corrected for the absorbances of the samples and for differences in the excitation intensity as a function of the wavelength. The sensitized emission intensity of

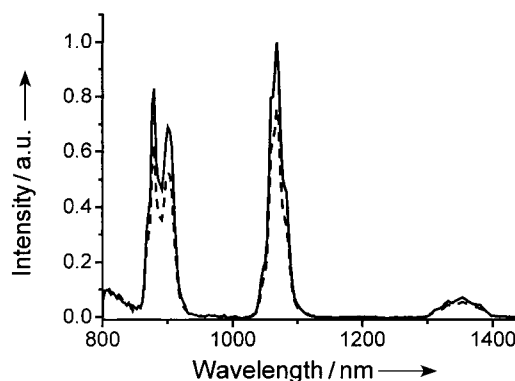


Figure 2. Sensitized NIR emission of 1·Nd (λ_{exc} 350 nm; —) and 2·Nd (λ_{exc} 567 nm; ----) in [D₆]DMSO solution.

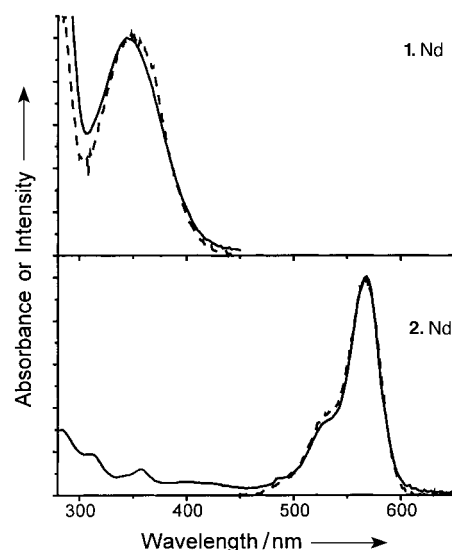


Figure 3. Absorption (—) and excitation (---) spectra (λ_{em} = 1066 nm) of 1·Nd and 2·Nd in [D₆]DMSO solution.

Table 1. NIR luminescence of 1·Nd and 2·Nd.			
Complex	τ_D [μs] ^[a]	τ_H [μs] ^[b]	I/I_{1-Nd} ^[b]
1·Nd	2.09	1.10	1.00
2·Nd	2.19	1.16	0.70

[a] Lifetime of Nd³⁺ at 1066 nm, λ_{exc} = 337 nm (N₂ laser) in [D₆]DMSO (τ_D) and in DMSO (τ_H); error ± 10%. [b] Nd³⁺ emission intensity in DMSO, corrected for absorption and for the lamp (photon) intensity at the excitation wavelength (1·Nd, λ_{exc} = 350 nm; 2·Nd, λ_{exc} = 567 nm).

2·Nd is approximately 70% of that of 1·Nd, which indicates that dansyl is a more efficient sensitizer than lissamine. Deoxygenation of the samples did not increase the sensitized emission intensities of 1·Nd or 2·Nd. Molecular oxygen is a triplet-state quencher, and this result could imply that the triplet state is either depopulated relatively fast or is not involved at all, that is, energy transfer occurs from the singlet state.

When other NIR-emitting lanthanide ions such as Yb³⁺ and Er³⁺ were complexed with 1 and 2, no sensitized Yb³⁺ or Er³⁺ emission was observed (data not shown). Apparently, the dansyl

and lissamine dyes are only able to sensitize Nd³⁺ luminescence but not Yb³⁺ or Er³⁺ luminescence. There is no reason to assume that in these latter complexes the excited states of Yb³⁺ and Er³⁺ are completely quenched once the energy has been transferred. It must therefore be concluded that energy transfer does not take place in these complexes. This observation is in striking contrast with that made with other sensitizers that we have investigated in the past, that is, fluorescein,^[13] triphenylene,^[20] ruthenium complexes,^[21] and β -diketonates,^[22] and cannot simply be explained in terms of the position of the triplet-state energies of lissamine and dansyl groups with respect to the luminescent energy levels of the Yb³⁺ or Er³⁺ ions.

A first clue into the anomalous behavior of the lissamine and dansyl groups can be found by comparison of the antenna fluorescence lifetimes and quantum yields of the 1·Ln and 2·Ln complexes (Table 2). In DMSO, the lissamine moiety gives rise to

Table 2. Fluorescence lifetimes of dansyl (1·Ln) and lissamine (2·Ln) complexes in DMSO solution. The fluorescence quantum yields are denoted in brackets.^[a]

Ln ³⁺	1 [ns]	2 [ns]
–	16.2 (0.66)	2.92 (0.75)
Nd ³⁺	2.75 (0.12)	1.67 (0.27)
Gd ³⁺	16.2 (0.61)	2.85 (0.78)
Er ³⁺	16.4 ^[b] (0.58)	2.77 (0.71)
Yb ³⁺	16.7 ^[b] (0.59)	2.87 (0.72)

[a] Quantum yields were determined with sulforhodamine 101 in ethanol ($\phi = 1.00$), 5-carboxytetramethylrhodamine in methanol ($\phi = 0.68$), and quinine sulfate in 1.0 N H₂SO₄ ($\phi = 0.56$) as standards; error $\pm 10\%$. [b] Both 1a·Er and 1a·Yb complexes contain two dansyl chromophores, which makes the conditions slightly different. However, the absence of quenching is clear. The corresponding Nd³⁺ complex is quenched.^[14]

an intense fluorescence band around 580 nm, and the dansyl group to a fluorescence band around 540 nm. The Gd³⁺ ion has no energy levels below 32 000 cm⁻¹, and therefore cannot accept any energy from the triplet and singlet states of the lissamine and dansyl groups. The 1·Gd and 2·Gd complexes could thus be used as models to study the antenna fluorescence in the presence of a lanthanide ion (possible external heavy-atom effect), but in the absence of energy transfer. The fluorescence quantum yield and lifetime of the dyes in 1·Gd and 2·Gd are the same as in the free ligands 1 and 2 (Table 2). Apparently, in the present geometry of the complexes, the lanthanide ions cannot provide an external heavy-atom effect on the lissamine and dansyl units. Therefore, the decreased fluorescence quantum yields and lifetimes of the dyes in 1·Nd and 2·Nd can only be attributed to a direct energy transfer from the singlet state to the Nd³⁺ ion. Furthermore, no phosphorescence of 1·Gd and 2·Gd was detected at 77 K in an ethanol/methanol glass, thus the formation of triplet states in the complexes is not significant. Only the 1·Nd and 2·Nd complexes exhibit a decreased fluorescence lifetime and fluorescence quantum yield compared to those of the free ligands 1 and 2 (Table 2). Moreover, the fluorescence lifetime of the lissamine unit in 2·Nd is 1.7 ns, whereas its lifetime is around 2.8 ns in the other lissamine-functionalized complexes 2·Yb and 2·Er, and in the free

ligand 2. Additionally, only the fluorescence lifetime of the dansyl antenna in 1·Nd is reduced from approximately 16 ns (free ligand) to 2.8 ns. The fluorescence quantum yield is reduced from 66% (for 1) to 12% (1·Nd) and from 75% (for 2) to 27% (2·Nd). The quantum yield of the other complexes is virtually the same as that of the free ligands. The fact that antenna fluorescence quantum yield and lifetime decreases only for those complexes in which energy transfer takes place (i.e. 1·Nd and 2·Nd) indicates that the fluorescence reduction is *not* the result of an external heavy-atom effect induced by the complexed lanthanide ion but that of a depopulation of the antenna singlet-excited-state by energy transfer in 1·Nd and 2·Nd.

A theoretical treatment by Malta et al. shows that the singlet state can indeed be a donating state in the sensitization of, for example, Eu³⁺ and Sm³⁺ ions.^[10] However, these calculations have shown that rates in these complexes are orders of magnitude lower for singlet energy transfer than for triplet energy transfer. Balzani and co-workers have recently reported a dendrimer that was functionalized with 24 dansyl units at the periphery.^[23] Addition of Nd³⁺ ions to the solution led to a quenching of the dansyl group fluorescence and to NIR Nd³⁺ luminescence.^[9] The authors suggested that the Nd³⁺ sensitization is due to energy transfer from the singlet state of the dansyl chromophore, because phosphorescence is hardly observed for the dansyl fluorophore.^[24]

In the case of fluorescein, which has a comparably low intrinsic ϕ_{ISC} , the presence of the lanthanide facilitates the sensitization pathway via the triplet state due to a heavy-atom effect. Since the lissamine and dansyl groups have extremely low intrinsic ϕ_{ISC} and since there is no external heavy-atom effect, the gate to a sensitization pathway via the triplet state remains closed. The question remains why in the present cases singlet energy transfer takes place and why it takes place only in the Nd³⁺ complexes and not in the Er³⁺ and Yb³⁺ complexes.

For a fast energy transfer, the antenna singlet excited state and the accepting lanthanide energy level should match (see Figure 1), that is, there should be spectral overlap between the donating and accepting energy levels. Based on the huge energy gap between the singlet excited state of both the dansyl ($E_S \approx 23\,500\text{ cm}^{-1}$) and lissamine units ($E_S \approx 17\,200\text{ cm}^{-1}$) and the Yb³⁺ excited state ($^2F_{5/2}$ level at 10 200 cm⁻¹), it is unlikely that the energy transfer will be fast, and therefore it cannot compete with the antenna fluorescence rate. At first sight, both the Nd³⁺ and also the Er³⁺ center have a number of energy levels that are possible candidates for singlet energy transfer from the dansyl and lissamine units. However, the accepting lanthanide energy level should also obey the selection rules for energy transfer. For energy transfer from an excited singlet state to the (^{2S+1})Γ_J levels of lanthanide ions, these rules are $|\Delta J| = 0, 1$ ($J = J' = 0$ excluded) for an exchange mechanism (Dexter type) or $|\Delta J| = 2, 4, 6$ for a multipolar mechanism (Förster type).^[10, 17]

In general, Dexter-type mechanisms have the highest probability, whereas the probability of multipolar energy transfer decreases with increasing order of polarity. Applying these considerations to the dansyl and lissamine Nd³⁺ and Er³⁺ complexes, we found that Nd³⁺ possesses energy levels that

allow Dexter energy transfer from the lissamine and dansyl units, but Er³⁺ does not. The levels of Nd³⁺ that can accept energy from the dansyl unit are the ⁴G_{11/2}, ²G_{9/2}, and ⁴G_{7/2} levels (see Figure 1) and from the lissamine unit the ²H_{11/2} and ⁴F_{9/2} levels. No excited energy levels of Er³⁺ obey these selection rules besides the ⁴I_{15/2} → ⁴I_{13/2} transition at 6400 cm⁻¹, for which the same accounts as for the sensitization of Yb³⁺, that is, the energy gap is too large for fast energy transfer.

Singlet energy transfer has seldom been observed in the sensitization of lanthanide ions because this transfer cannot compete with the fast intersystem crossing process and subsequent triplet energy transfer. In most antenna-functionalized lanthanide complexes, intersystem crossing is fast due to the external heavy-atom effect induced by the lanthanide ion, which is exemplified in the aforementioned fluorescein-functionalized complexes. In the lissamine- and dansyl-functionalized complexes, there is no detectable external heavy-atom effect, and the singlet energy transfer process can take place. At this point, it remains a question why the structurally related dyes lissamine and fluorescein incorporated in structurally similar complexes behave so differently. A striking similarity of the dansyl and lissamine dyes is the presence of a tertiary amine, which has a quadrupole moment. This could be the reason for the highly forbidden character of the S₁ → T₁ transition. An amine moiety is also found in other complexes, which were reported or suspected to exhibit energy transfer from the singlet excited state.^[7–12]

In conclusion, the sensitization of Nd³⁺ luminescence by dansyl and lissamine derivatives takes place exclusively via the antenna singlet state. This is due to the appropriate energy levels of the Nd³⁺ ion, which obey the energy transfer selection rules for a fast transfer of excitation energy from the singlet excited states of the dyes.

Experimental

The complexes were synthesized according to the procedure described elsewhere.^[14] They were characterized by MS-FAB with magic bullet (MB, which is a 1:5 w/w mixture of dithioerythritol and dithiothreitol) as the matrix. The MS-FAB results are reported in Table 3. Absorption spectra were recorded on an HP8452A diode array spectrometer. Emission spectra in the visible and in the NIR and

Table 3. MS-FAB characterization of the complexes.

	Molecular formula	Experimental m/z	Calcd m/z	fragment
1 a ^[a]	C ₇₄ H ₉₉ N ₃ O ₁₄ S	1415.9	1415.7	[M+H] ⁺
1 · Nd	C ₆₂ H ₇₂ N ₃ O ₁₄ SNd	1259.4	1259.6	[M+H] ⁺
1 · Gd	C ₆₂ H ₇₂ N ₃ O ₁₄ SGd	1273.3	1273.6	[M+H] ⁺
1 a · Er ^[a]	C ₆₇ H ₈₀ N ₄ O ₁₅ S ₂ Er	1412.6	1412.8	[M+H] ⁺
1 a · Yb ^[a]	C ₆₇ H ₈₀ N ₄ O ₁₅ S ₂ Yb	1418.5	1418.6	[M+H] ⁺
2	C ₇₇ H ₉₂ N ₄ O ₁₈ S ₂ Na	1447.7	1447.6	[M+Na] ⁺
2 · Nd	C ₇₇ H ₈₉ N ₄ O ₁₈ S ₂ Nd	1566.6	1566.5	[M+H] ⁺
2 · Gd	C ₇₇ H ₈₉ N ₄ O ₁₈ S ₂ Gd	1580.6	1580.5	[M+H] ⁺
2 · Er	C ₇₇ H ₈₉ N ₄ O ₁₈ S ₂ Er	1589.5	1589.5	[M+H] ⁺
2 · Yb	C ₇₇ H ₈₉ N ₄ O ₁₈ S ₂ Yb	1596.7	1596.5	[M+H] ⁺

[a] The complex with two dansyl moieties.

decay traces in the visible were measured on an Edinburgh Analytical Instruments FLS900 fluorimeter, equipped with a 450 W Xe lamp as steady-state source and an H₂-filled flashlamp for time-resolved experiments in the nanosecond region. The excitation light was passed through a monochromator (single grating, 1800 lines mm⁻¹) and focused on a quartz cuvette (1.00 × 1.00 cm²) filled with the sample. The emitted visible light was passed through a second monochromator (1800 lines mm⁻¹ grating) and collected with a Hamamatsu R955 photomultiplier tube. Near-infrared light was passed through a monochromator (600 lines mm⁻¹ grating) and, after optical chopping (89 Hz), collected by an Edinburgh Analytical Instruments liquid-nitrogen-cooled Ge detector (EI-P), using standard lock-in techniques. All excitation and emission spectra were corrected for the instrumental spectral response.

Nanosecond lifetimes were fitted by deconvolution of the decay trace with the instrument response measured on a highly scattering sample (Ludox). Lifetimes in the NIR were measured on an Edinburgh Analytical Instruments LP900 system with a pulsed N₂ laser as the excitation source (operating at 337.1 nm and 10 Hz). The emitted signal was collected with a North Coast liquid-nitrogen-cooled Ge detector. The signal traces were averaged by an oscilloscope and digitized. Fitting of the lifetimes in the microsecond region was performed with Edinburgh Analytical Instruments LP900 software, and deconvolution of the traces was performed using the instrument response measured with IR140 (Aldrich) in methanol (τ < 1 ns, which is much faster than the instrument response of about 200 ns). Measurements were performed on solutions in 1.00 × 1.00 cm² cuvettes with an absorption below 0.3.

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