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Luminescent Lanthanide Ions Hosted in a Fluorescent Polylysin Dendrimer. Antenna-Like Sensitization of Visible and Near-Infrared Emission

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Abstract: We have investigated the complexation of the luminescent Nd^{3+}, Eu^{3+}, Gd^{3+}, Tb^{3+}, Er^{3+}, and Yb^{3+} ions by a polylysin dendrimer containing 21 amide groups in the interior and, in the periphery, 24 chromophoric dansyl units which show an intense fluorescence band in the visible region. Most of the experiments were performed in 5:1 acetonitrile/dichloromethane solution at 298 K. On addition of the lanthanide ions to dendrimer solutions, the fluorescence of the dansyl units is quenched; in Nd^{3+}, Er^{3+}, and Yb^{3+}, a sensitized near-infrared emission of the lanthanide ion is observed. At low metal ion concentrations, each dendrimer hosts only one metal ion and when the hosted metal ion is Nd^{3+} or Eu^{3+}, the fluorescence of all the 24 dansyl units of the dendrimer is quenched with unitary efficiency. Quantitative measurements were performed in a variety of experimental conditions, including protonation of the dansyl units and measurements in rigid matrix at 77 K where a sensitized Eu^{3+} emission could also be observed. The results obtained have been interpreted on the basis of the energy levels and redox potentials of dendrimer and metal ions.

Introduction

Cascade molecules,[1] commonly called dendrimers,[2] are well-defined, highly branched nanoscale molecules. They consist of a core upon which radially branched layers, termed generations, are attached. Because of their three-dimensional architectures, the high degree of order achievable, and the possibility of containing selected chemical units in predetermined sites of their structure, dendrimers are currently attracting wide attention in the fields of basic research and technology.[3] Dendrimers containing photoactive components (for some leading papers, see refs 4−14) are particularly interesting since (i) luminescence signals offer a handle to better understand the dendritic structures and superstructures, (ii) cooperation among the photoactive components can allow the dendrimer to perform useful functions such as light harvesting, (iii) changes in the photophysical properties can be exploited for sensing purposes with signal amplification, and (iv) photochemical reactions can change the structure and other properties of dendrimers.

Another important characteristic of dendrimers is the presence of internal latent (dynamic) cavities where ions or neutral molecules can be hosted.[8e,g,h,j,l,15−20] More specifically, when a

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dendrimer contains coordinating units, it can be used as a ligand for metal ions.[17−20]

Encapsulation of luminescent metal ions into a luminescent dendrimer can lead to systems capable of exhibiting novel and unusual properties. A particularly interesting class of luminescent metal ions is that of the lanthanide family because of their long-lived and linelike emission bands which cover a spectral range from the near-ultraviolet to the visible and the near-infrared region.[21,22] Direct excitation of lanthanide ions, however, is difficult because of the forbidden nature of their electronic transitions.[21,22] To overcome this difficulty, the luminescent lanthanide ions are usually coordinated to ligands containing organic chromophores whose excitation, followed by energy transfer, causes the sensitized luminescence of the metal ion (antenna effect).[23] Another drawback of lanthanide luminescence is the quenching of the emitting excited state by energy loss to high-frequency vibrational modes of the solvent,[21,22] which can be at least in part overcome by enclosing the metal ion in suitably designed ligands.[23,24] Most of the investigations in the field of luminescent lanthanide complexes have been devoted to Eu^{3+} and Tb^{3+} compounds,[23,25] which emit in the visible spectral region and are used as sensors[25] and as luminescent labels in fluoroimmunoassays and time-resolved microscopy.[26] Currently, however, much interest is also devoted to lanthanide ions emitting in the near-infrared (NIR) region[27−29] for both fundamental reasons and possible applications in long-range optical data transport.

Combining the notions illustrated above, we have designed a luminescent dendrimer which is able to play the role of a

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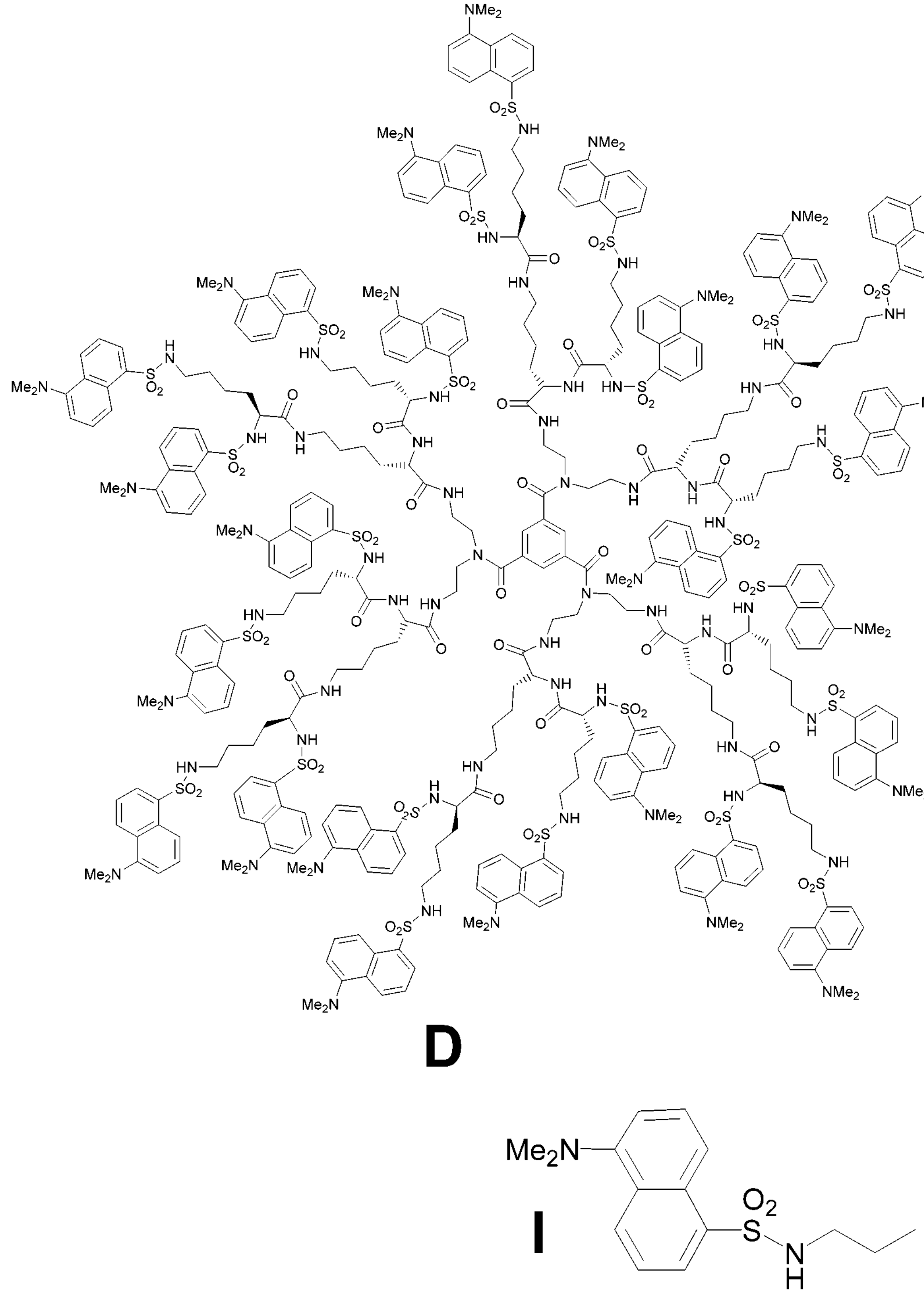

Figure 1. Structure formula of the polylysin dendrimer **D** and of the monodansyl reference compound **I**.

ligand for luminescent lanthanide ions.[30] The polylysin dendrimer used (**D**, Figure 1) consists of a benzene core, branched in the 1, 3, and 5 positions. Each branch starts with a (dialkyl)-carboxamide-type moiety and carries six aliphatic amide groups and eight fluorescent 5-(dimethylamino)-1-naphthalenesulfonyl (dansyl) units. All together, the dendrimer contains 21 amide groups in the interior and 24 dansyl units in the periphery. The amide functions are known[23,25a] to strongly coordinate lanthanide ions, and the dansyl chromophoric units, which display intense absorption bands in the near-UV spectral region and an intense fluorescence band in the visible region, are extensively used for sensing or labeling purposes.[32] In this paper, dendrimer **D**

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(30) Extending the current nomenclature[31] (see, e.g., cryptand, spherand, torand, carcerand) a dendrimer that plays the role of a ligand can be called *dendrimerand* and the resulting metal complexes can be called *dendrimerate* (see, e.g., cryptate, sepulchrate).

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has been used as a ligand for Nd^{3+}, Eu^{3+}, Gd^{3+}, Tb^{3+}, Er^{3+}, and Yb^{3+} ions, which exhibit widely different energy level patterns[21,22] as well as redox properties.[22a] A preliminary communication on the results obtained with Nd^{3+} has been published.[8m] A few papers about dendrimers containing lanthanide metal ions have already appeared.[33]

Experimental Section

The scientific name of dendrimer **D** (Figure 1) is <24-Cascade: benzene−(1,3,5)tricarbonamide[6-*N*, *N*, *N*′,*N*′, *N*″, *N*″]:(3,4-diaza-2-oxo-hexylidene)[2−1,1]:(2-oxo-3-azapropylidene:2-oxo-3-azaheptylidene):N−(5′-dimethylaminonaphth-1-ylthiodioxo)amine:N−(5′-dimethylaminonaphth-1-ylthiodioxo)butylamine>. Synthesis and characterization of dendrimer **D** has been described elsewhere.[8i] $Ln(NO_3)_3 \cdot 6H_2O$ (Ln^{3+} = Nd^{3+}, Eu^{3+}, Gd^{3+}, Tb^{3+}, Er^{3+}, and Yb^{3+}) were commercial, high-purity reagents.

Most of the experiments were carried out in acetonitrile/dichloromethane 5:1 v/v solution at 298 K. When necessary, the behavior in rigid acetonitrile/dichloromethane 5:1 matrix at 77 K was also investigated. The equipment used for measuring the absorption spectra and the photophysical properties (fluorescence spectra, quantum yields, and excited-state lifetimes) has been described elsewhere.[8g] Luminescence spectra in the near-infrared (NIR) region were recorded by a homemade apparatus based on an Edinburgh CD900 spectrofluorimeter, which uses a Xenon lamp as the excitation source and a liquid nitrogen cooled hyperpure germanium crystal as a detector.

Nanosecond flash spectroscopy measurements have been performed using as an excitation source a Continuum, Surelite I-10, neodymium laser (λ_{exc} = 355 nm, pulse width 7 ns), as an analyzing light source a 150 W xenon lamp in an Applied Photophysic housing equipped with a 03−102 arc lamp pulser unit, and as a detection system a Hamamatsu R928 phototube and a fast photomultiplier housing coupled with a Tektronix Model TDS 380 oscilloscope.

The estimated experimental error is ±2 nm and ±10 nm on the position of the band maximum in the UV−vis and NIR region, respectively, ±10% on the luminescence intensity, and ±5% on excited-state lifetimes.

For the experiment in deaerated conditions, the solutions were degassed by repeated freeze−pump−thaw cycles.

Results and Discussion

Properties of the Dendrimer. The properties of dendrimer **D** (Figure 1) have been previously described.[8i]

The absorption and emission spectrum of the dendrimer in acetonitrile/dichloromethane 5:1 v/v solution is shown in Figure 2. The 21 amide groups contained in the interior of the dendrimer do not show any appreciable absorption or emission band in the near-UV−vis spectral region, whereas the 24 dansyl units show intense absorption bands in the near-UV region and an intense fluorescence band in the visible region.

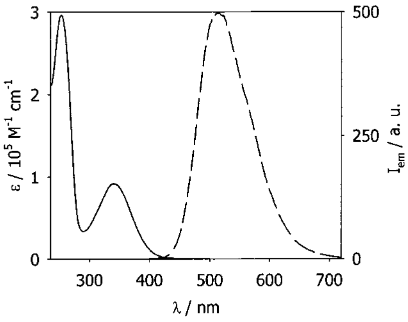

Figure 2. Absorption (full line) and emission (dashed line) spectra of dendrimer **D** in 5:1 acetonitrile/dichloromethane solution at 298 K.

The intense absorption bands of the dendrimer in the near-UV spectral region (λ_{max} = 253 and 341 nm) are practically at the same wavelengths as in a monodansyl model compound **I** (λ_{max} = 252 and 338 nm). The molar absorption coefficients (ϵ_{max} = 296000 and 91800 $M^{-1}\ cm^{-1}$, respectively) are less than 2% smaller than expected for 24 independent dansyl units. The strong fluorescence (Figure 2) exhibited by **D** in the visible region has band maximum (514 nm), quantum yield (0.28), and lifetime (15 ns) comparable to the monodansyl model compound **I** (λ_{max} = 509 nm, $\Phi = 0.30$, τ = 12 ns).[8i] These results show that in the dendrimer the interaction among the 24 dansyl groups is, at most, very small. Neither the monodansyl model compound nor the dendrimer exhibit any phosphorescence band in rigid matrix at 77 K.

The energy of the fluorescent excited state of the dansyl unit, as estimated from the onset of the corresponding fluorescence band (Figure 2), is about 22200 cm^{-1}. The energy of the lowest triplet excited state is supposed to be around 18000 cm^{-1}.[27f] Electrochemical experiments in acetonitrile solution on the monodansyl model compound **I** showed[8g] that the dansyl group undergoes a chemically irreversible one-electron oxidation process ($E_{1/2}$ about +0.9 V vs SCE), assigned to the amine subunit, and a one-electron reduction process, reversible only at low temperature (223 K), with $E_{1/2} = -2.02$ V (vs SCE), assigned to the aromatic subunit. It follows[34] that the fluorescent excited state of the dansyl unit is a weak oxidant, E(*DANS/DANS$^-$) ca. +0.7 V, and a strong reductant, E(DANS$^+$/*DANS) ca. −1.9 V.

It is well known that the absorption and emission properties of the dansyl group are very sensitive to the addition of acid because the dansylamine subunit undergoes protonation.[8i] In the fully protonated dendrimer, $\mathbf{D}\cdot 24H^+$, the absorption bands of the dansyl units with λ_{max} = 253 and 341 nm are no longer observable and a new absorption band is present with λ_{max} = 288 nm (ϵ_{max} = 172600 $M^{-1}\ cm^{-1}$), accompanied by a smaller feature with λ_{max} = 320 nm (Figure 3). Besides the changes in absorbance, protonation causes the disappearance of the strong dansyl fluorescence band with λ_{max} = 514 nm and the appearance of a weaker ($\Phi = 0.002$), shorter-lived ($\tau < 1$ ns) fluorescence band with λ_{max} = 336 nm (onset energy ca. 31000 cm^{-1}), typical of naphthalene-type chromophoric units (Figure 3, inset).

In contrast with the dansyl units, the protonated ones show an intense phosphorescence band in rigid matrix at 77 K with λ_{max} = 540 nm and lifetime 1.1 s, again typical of naphthalene-type compounds (Figure 3, inset). The protonated dansyl group does not show the oxidation process at +0.9 V exhibited by the deprotonated species, since the electron pair of the amine

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[32] (a) De Santis, G.; Fabbrizzi, L.; Licchelli, M.; Sardone, N.; Velders, A. H. *Chem. Eur. J.* **1996**, *2*, 1243. (b) Ikeda, H.; Nakamura, M.; Ise, N.; Oguma, N.; Nakamura, A.; Ikeda, T.; Toda, F.; Ueno, A. *J. Am. Chem. Soc.* **1996**, *118*, 980. (c) Schuster, M.; Sandor, M. *Fresenius' J. Anal. Chem.* **1996**, *356*, 326. (d) Nelissen, H. F. M.; Venema, F.; Uittenbogaard, R. M.; Feiters, M. C.; Nolte, R. J. M. *J. Chem. Soc., Perkin Trans. 2* **1997**, 2045. (e) Ikunaga, T.; Ikeda, H.; Ueno, A. *Chem. Eur. J.* **1999**, *5*, 2698. (f) Prodi, L.; Bolletta, F.; Montalti, M.; Zaccheroni, N. *Chem. Eur. J.* **1999**, *5*, 445.

[33] (a) Kawa, M.; Fréchet, J. M. J. *Chem. Mater.* **1998**, *10*, 286. (b) Caravan, P.; Ellison, J. J.; McCurry, T. J.; Lauffer, R. B. *Chem. Rev.* **1999**, *99*, 2293. (c) Tominaga, M.; Hosogi, J.; Konishi, K.; Aida, T. *Chem. Commun.* **2000**, 719. (d) Takahashi, M.; Hara, Y.; Aoshima, K.; Kurihara, H.; Oshikawa, T.; Yamashita, M. *Tetrahedron Lett.* **2000**, *41*, 8485.

[34] (a) Gilbert, A.; Baggot, J. *Essentials in Molecular Photochemistry*; Blackwell: London, 1991, Chapter 5. (b) Murov, S. L.; Carmichael, I.; Hug, G. L. *Handbook of Photochemistry*; Dekker: New York, 1993.

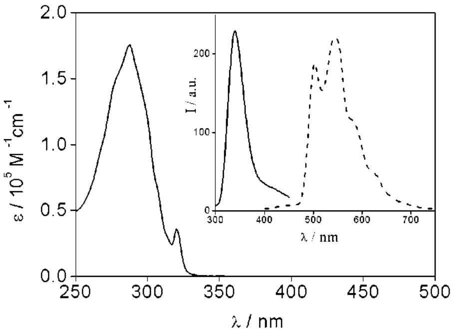

Figure 3. Absorption and emission (inset) spectra (full lines) in 5:1 acetonitrile/dichloromethane solution at 298 K of the fully protonated dendrimer $\mathbf{D}\cdot 24H^+$, obtained by protonation with trifluoromethane sulfonic acid of the 24 dansyl units of dendrimer **D**. The strong phosphorescence observed at 77 K is also shown (dashed line in the inset).

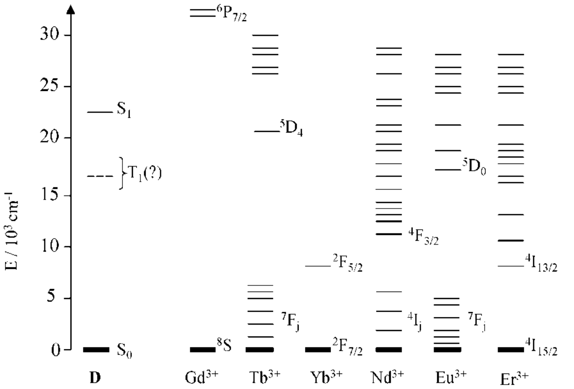

Figure 4. Energy level diagrams for the dansyl units of dendrimer **D** and the investigated lanthanide ions. The position of the triplet excited state of **D** is uncertain because no phosphorescence can be observed.

subunit is engaged with the proton. Therefore, the excited states of the protonated dansyl units are not expected to exhibit reducing properties.

Properties of the Lanthanide Ions. Dendrimer **D** was expected to play the role of a ligand for lanthanide ions because it contains many aliphatic amide groups, which are known to exhibit a strong affinity for lanthanide ions.[23,25a] To investigate the formation of dendrimer/lanthanide complexes, we have chosen six luminescent lanthanide ions spanning a wide range of excited-state energies (from the UV to the near-IR spectral region), namely, Nd^{3+}, Eu^{3+}, Gd^{3+}, Tb^{3+}, Er^{3+}, and Yb^{3+} (Figure 4). Among these ions, Eu^{3+} and Yb^{3+} are rather easy to reduce ($E° = -0.35$ and -1.1 V, respectively, for the aqua ions, vs standard hydrogen electrode[22a]), whereas none of them can be easily oxidized.[35] The relative facility of Eu^{3+} and Yb^{3+} to be reduced is also shown by the appearance of ligand-to-metal charge-transfer bands in the absorption spectra of their complexes with reducing ligands.[22a]

Quenching of the Dendrimer Fluorescence. Addition of the lanthanide ions (as $Ln(NO_3)_3\cdot 6H_2O$ salts) to a 5.0×10^{-6} M solution of **D** did not cause any change in the absorption spectrum. However, a quenching of the fluorescence intensity of the dendrimer dansyl units was observed. Figure 5 shows the plots obtained upon titration of 5.0×10^{-6} M **D** in 5:1 acetonitrile/dichloromethane solution with the examined metal ions. A dynamic quenching mechanism cannot account for the observed results since the lifetime of the fluorescent excited state of the dansyl unit is too short (15 ns) and the metal ion concentration (from 5.0×10^{-7} to 2.5×10^{-5} M) is too low to cause sizable effects, even in the quite unlikely case of a diffusion controlled process.[36] The lack of dynamic quenching is also consistent with the absence of quenching in the monodansyl reference compound **I**. Therefore, the observed quenching must originate from association between dendrimer and metal ion.

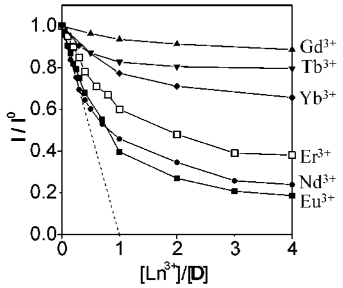

Figure 5. Changes in the dansyl fluorescence intensity at 515 nm upon titration of a 5.0×10^{-6} M solution of **D** in 5:1 acetonitrile/dichloromethane solution with the metal ions. $\lambda_{exc} = 338$ nm.

The peripheral dansyl groups are unlikely to be involved in metal coordination, since their absorption bands are unaffected. The fact that the dansyl groups are not involved in metal coordination is also consistent with the small fluorescence quenching observed when a fourth generation poly(propylene amine) POPAM dendrimer[8h] containing 32 peripheral dansyl groups in the periphery was titrated with Eu^{3+} ions. Therefore, we can conclude that, as expected, the observed quenching is caused by metal ions coordinated by the aliphatic amide groups contained in the interior of the dendrimer.

The fluorescence quenching is very large for Nd^{3+} and Eu^{3+}, moderate for Er^{3+} and Yb^{3+}, small for Tb^{3+}, and very small for Gd^{3+} (Figure 5). For the best quenchers, at low metal ion concentration (i.e., when each dendrimer cannot contain more than one metal ion), the $I/I°$ value decreases linearly with increasing metal ion concentration. Under such conditions, each metal ion quenches 24 (± 2) dansyl units, as is also indicated by the extrapolation of the initial straight-line of the titration plot to a $[Ln^{3+}]/[\mathbf{D}]$ value very close to unity. This means that upon coordination of a Nd^{3+} or Eu^{3+} ion by a dendrimer, all the dansyl units of that dendrimer are quenched when they are excited. The species containing a metal ion are hereafter indicated by $[Ln^{3+}\subset\mathbf{D}]$. Most likely, one or more anions accompany the lanthanide ion into the dendrimer.

The luminescence intensity does not go to zero at high metal ion concentration. Such an effect is analogous to that previously observed in the titration of poly(propylene amine) dendrimers by Co^{2+} ions.[8g] It can be explained by the fact that, since the metal ions are added as $Ln(NO_3)_3\cdot 6H_2O$ salts, at high metal ion concentration the solution also contains very high concentrations of nitrate anions (which are good ligands for lanthanide ions)[21,22] and water molecules which compete with dendrimers in the complexation of lanthanide ions.

Whereas the fluorescence decay of the "free" dendrimer **D** is strictly monoexponential, a more complex decay pattern is observed after addition of metal ions. Quantitative experiments were performed only in the case of the two best quenchers, Nd^{3+}

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(35) The less positive $Ln^{4+/3+}$ reduction potential estimated for the aqua ions is that for Ln = Tb (+3.3 V vs standard hydrogen electrode).[22a]

(36) Bimolecular quenching processes involving lanthanide ions are usually much slower than the diffusion controlled limit because of a small electronic interaction of the reaction partner with the inner f orbitals of the lanthanide compound. See, e.g., Sabbatini, N.; Indelli, M. T.; Gandolfi, M. T.; Balzani, V. *J. Phys. Chem.* **1982**, *86*, 3585.

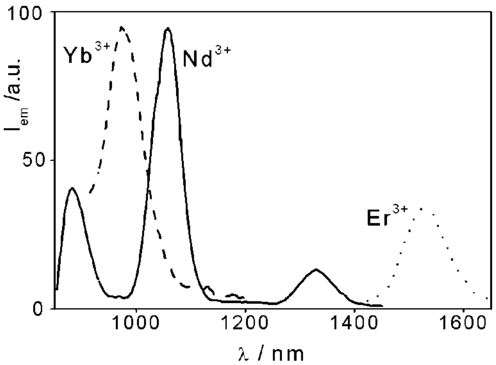

Figure 6. Sensitized NIR emission of Nd^{3+}(full line), Er^{3+}(dotted line), and Yb^{3+} (dashed line) ions in a 5:1 acetonitrile/dichloromethane solution containing 8.0×10^{-6} M **D** and 2.4×10^{-5} M metal ions. $\lambda_{exc} = 343$ nm.

and Eu^{3+}, with similar results. For example, in a solution containing 4.2×10^{-6} M **D** and 1.1×10^{-6} M Nd^{3+}, ca. 25% of the dansyl fluorescence intensity was quenched, as expected for the presence of 25% dendrimers containing Nd^{3+} ions and 75% "free" dendrimers (vide supra). Under such conditions, a biexponential decay was observed with lifetimes 15 ns (relative weight 86%), assigned to the empty dendrimers, and 6 ns (relative weight 14%). If these were the only fluorescent decay processes in the system, the quenching of the intensity should have been 8%, which is clearly inconsistent with the ca. 25% quenching observed from steady-state measurements. Such an inconsistency shows that, when the dendrimer contains a Nd^{3+} ion, most of the dansyl units decay with rate constants too fast to be measured with our equipment (i.e., with $\tau < 0.2$ ns). According to this picture, there are two different sites (or, more likely, two families of different sites) for coordination of the metal ion by the dendrimer: (i) a more populated site, presumably closer to the dendrimer core, from which the metal ion can completely quench all the dansyl units of the dendrimer and (ii) a less populated site, presumably closer to the periphery, from which the metal ion can quench completely the closer dansyl units and partially the most distant ones. This last process would account for the shorter (6 ns) lifetime observed in our experiments. The presence of different sites for hosting guest molecules has been demonstrated for other dendrimers,[8j,8l,15b] and the complexity of fluorescence quenching processes in dendrimers containing many fluorescent units has been emphasized.[11e]

Sensitization of the Metal Ion Luminescence. All the investigated metal ions are known to be luminescent.[21,22] In the titration experiments of the dendrimer with the metal ions, light excitation at 252 or 338 nm, corresponding to the absorption maxima of the dansyl units ($\epsilon = 296000$ and 91800 M^{-1} cm^{-1}, respectively, Figure 2) cannot cause direct excitation of the lanthanide ions, whose narrow absorption bands have molar absorption coefficients around, or even much lower than, 1 M^{-1} cm^{-1}.[21,22] Therefore, if the luminescence of a metal ion is observed in the titration experiments, the metal-centered excited state has to be formed by sensitization from the excited dansyl units. Such a sensitized luminescence has clearly been observed in fluid solution at 298 K in Nd^{3+}, Er^{3+}, and Yb^{3+}, as shown in Figure 6. In rigid matrix at 77 K, a sensitized emission is observed also in Eu^{3+} (vide infra).

Quenching Mechanisms. As mentioned above, the quenching of the dansyl fluorescence is very large for Nd^{3+} and Eu^{3+}, moderate for Er^{3+} and Yb^{3+}, small for Tb^{3+}, and very small for Gd^{3+} (Figure 5). It is well known that the most efficient quenching mechanisms are those involving energy or electron transfer.[34,37] According to some literature reports,[27f,29a] the quenching of the fluorescence of dyes by lanthanide ions takes place via paramagnetic and heavy-atom induced singlet−triplet intersystem crossing followed, in some cases, by energy transfer from the T_1 excited state of the dye to the metal ion.

A necessary condition for quenching by electron transfer is that the process must be thermodynamically allowed. The above-reported redox properties of the excited dansyl unit and of the lanthanide ions show that this can only be the case for Eu^{3+} (ΔG ca. −1.55 eV) and Yb^{3+} (ΔG ca. −0.75 eV).

Efficient quenching by energy transfer requires a good overlap between the donor emission and the acceptor absorption bands.[34a] Figures 2 and 4 show that for the fluorescent excited state (S_1) of dansyl, such a condition is (i) very well satisfied in Nd^{3+}, Eu^{3+}, and Er^{3+}, (ii) much less for Tb^{3+}, and (iii) not at all for Gd^{3+} and Yb^{3+}. Quenching by energy transfer is of course expected to cause sensitization of the metal ion luminescence. The results obtained for the [$Ln^{3+}\subset$**D**] inclusion complexes will now be discussed on the basis of the above considerations.

[$Gd^{3+}\subset$D]. Neither energy- (Figure 4) nor electron-transfer quenching are allowed. The very small quenching effect (Figure 5) can be assigned either to induced intersystem crossing or to a charge perturbation on the fluorescent dansyl excited state. In the first case, the triplet excited state of the dansyl unit (T_1) should be formed[27f] and, in rigid matrix at 77 K, the phosphorescence of T_1 should be observed. The emission spectrum recorded under such conditions, however, shows no evidence of phosphorescence. We are therefore inclined to attribute the very small quenching effect to a perturbation on the radiative rate constant of the S_1 excited state, which has a noticeable charge-transfer character. In any case, the results obtained for Gd^{3+} show that the much larger quenching effects observed for other lanthanide ions cannot be due to induced intersystem crossing of the S_1 excited state of dansyl.

[$Nd^{3+}\subset$D]. In this case, quenching by electron transfer of the dansyl fluorescence is thermodynamically forbidden. The strong quenching effect observed (Figure 5) is accompanied by the sensitized NIR emission (Figure 6) of the $^4F_{3/2}$ excited state of the metal ion (Figure 4). This result shows that quenching takes place by energy transfer. In principle, the high efficiency of the energy-transfer process can be accounted for by (a) direct energy transfer from the S_1 excited state of dansyl units to a manifold of isoenergetic excited states of Nd^{3+} or (b) a metal ion induced $S_1 \rightarrow T_1$ intersystem crossing, followed by energy transfer from the T_1 excited state to the metal ion. The former interpretation is supported by the extensive overlap between the dansyl emission band (Figure 2) and the energy levels of Nd^{3+} (Figure 4), whereas the latter one is quite unlikely in view of the results obtained for [$Gd^{3+}\subset$**D**].

[$Eu^{3+}\subset$D]. In this case, both energy- and electron-transfer quenching are thermodynamically allowed. The strong quenching on the dansyl fluorescence (Figure 5) is not accompanied by the sensitized emission of the metal ion. Redox products have not been detected upon quenching of the dansyl fluorescence by nanosecond laser flash spectroscopy experiments (λ_{exc}

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(37) Balzani, V.; Moggi, L.; Manfrin, M. F.; Bolletta, F.; Laurence, G. S. *Coord. Chem. Rev.* **1975**, *15*, 321.

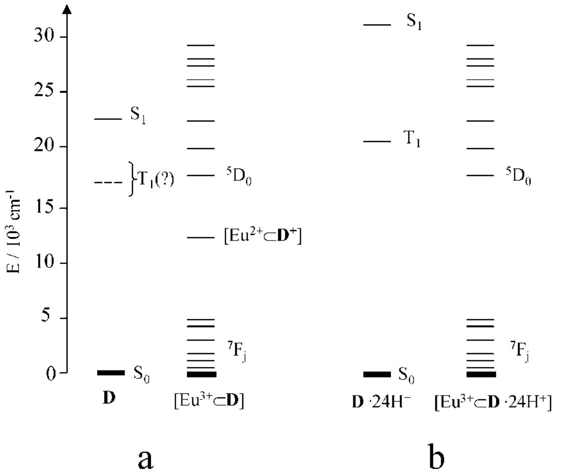

Figure 7. Energy level diagrams for **D** and [Eu^{3+}⊂**D**] (a); **D**·24H$^+$ and [Eu^{3+}⊂**D**·24H$^+$] (b). Notice the presence of a low-energy [Eu^{2+}⊂**D**$^+$] electron-transfer level in [Eu^{3+}⊂**D**].

= 355 nm); this result does not exclude the formation of a nonemissive CT [Eu^{2+}/**D**$^+$] state, this could only mean that redox products cannot be observed in our time window because of the presence of fast back-electron-transfer processes leading to the ground state. Therefore, considering that the lowest excited state is an electron-transfer level (Figure 7a), we believe that either an electron-transfer quenching process leads directly to the nonemissive [Eu^{2+}⊂**D**$^+$] level or an energy transfer to the luminescent ^{5}D$_0$ metal-centered level is followed by an electron-transfer process, faster than the ^{5}D$_0$ emission, to the [Eu^{2+}⊂**D**$^+$] level. Interestingly, in rigid matrix at 77 K, that is, under conditions in which electron-transfer processes are disfavored,[38] the quenching of the dansyl fluorescence is accompanied by the sensitized emission of the Eu^{3+} ion in the visible region, as expected for an energy-transfer quenching mechanism.

Lowe and Parker[25b] have recently reported that Eu^{3+} complexes carrying a dansyl unit on a ligand exhibit a sensitized Eu^{3+} emission when the dansyl unit is protonated. In agreement with this result, we have found that upon complete protonation of the dansyl units of a 6.6×10^{-6} M **D** solution containing 3.3×10^{-6} M Eu^{3+}, Eu^{3+} emission can indeed be observed. We have verified that protonation of the dansyl units does not cause escaping of Eu^{3+} from the dendrimer interior but causes the formation of an inclusion complex that can be formulated as [Eu^{3+}⊂**D**·24H$^+$]. This conclusion is drawn by the fact that addition of 10-fold excess of Gd^{3+} ions to the above solution quenches the sensitized Eu^{3+} emission, as expected for replacement of Eu^{3+} by Gd^{3+} ions inside the protonated dendrimers. In the [Eu^{3+}⊂**D**·24H$^+$] species, the sensitized emission is not accompanied by the quenching of the fluorescence of the excited state of the protonated dansyl units. This result suggests that energy transfer takes place from the T$_1$ excited state of the protonated dansyl units (Figure 7b). For a [Eu^{3+}]/[**D**·24H$^+$] 0.5/1 stoichiometric ratio, in rigid matrix at 77 K one can indeed observe, besides the phosphorescence of the protonated dansyl units of the empty dendrimers ($\tau = 1.1$ s), the Eu^{3+} emission with a rise time of 0.2 ms corresponding to the energy transfer from T$_1$ excited state, followed by a decay with $\tau = 1.6$ ms (Figure 8). These results confirm that the quenching is static in nature, which means that the metal ion is enclosed into the protonated dendrimer.[39]

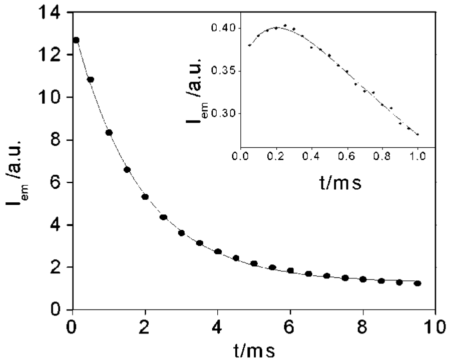

Figure 8. Rise and decay of the sensitized emission of Eu^{3+} in the [Eu^{3+}⊂**D**·24H$^+$] at 77K. $\lambda_{exc} = 287$ nm; $\lambda_{em} = 618$ nm.

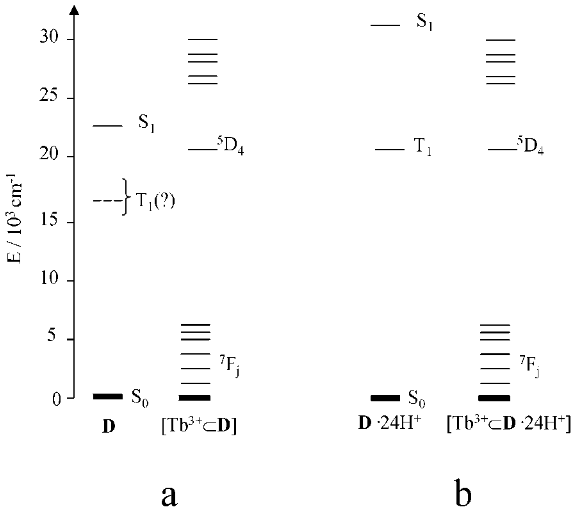

Figure 9. Energy level diagrams for **D** and [Tb^{3+}⊂**D**] (a); **D**·24H$^+$ and [Tb^{3+}⊂**D**·24H$^+$] (b).

[Tb^{3+}⊂D]. The quenching effect of Tb^{3+} (Figure 5) is small but larger than that of Gd^{3+}. Since there is no reason Tb^{3+} should exhibit an induced intersystem crossing or a charge-perturbation effect stronger than Gd^{3+}, another quenching mechanism must be effective. Electron transfer cannot occur because of thermodynamic reasons. We are therefore forced to conclude that a very low efficient energy-transfer process does take place with formation of the luminescent ^{5}D$_4$ excited state of Tb^{3+} (Figure 9a), whose weak emission, however, cannot be observed in our experimental conditions.

A sensitized Tb^{3+} emission can be observed upon protonation of the dansyl units. As in Eu^{3+}, we have observed that addition of an excess of Gd^{3+} quenches the sensitized emission by displacing Tb^{3+} from the protonated inclusion complex [Tb^{3+}⊂**D**·24H$^+$]. Again, the sensitized emission is not accompanied by the quenching of the fluorescent excited state of the protonated dansyl units, suggesting that energy transfer takes place from the T$_1$ excited state (Figure 9b). There is indeed a strong overlap between the phosphorescence band of the protonated dansyl units and the energy levels of Tb^{3+} (Figure 10). For a [Tb^{3+}]/

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(38) In rigid matrix the lack of solvent repolarization prevents stabilization of the electron-transfer products. For a discussion on this topics, see (a) Chen, P.; Meyer, T. J. *Chem. Rev.* **1998**, *98*, 1439. (b) Gaines, G. L., III; O'Neill, M. P.; Svec, W. A.; Niemczyc, M. P.; Wasielewski, M. R. *J. Am. Chem. Soc.* **1991**, *113*, 719.

(39) Under the diluted conditions used ([Eu^{3+}] = 3.3 10^{-6} M) energy transfer at 77 K cannot involve Eu^{3+} ions escaped from the dendrimer since the average distance between dendrimer and metal ion would be higher than 30 nm.

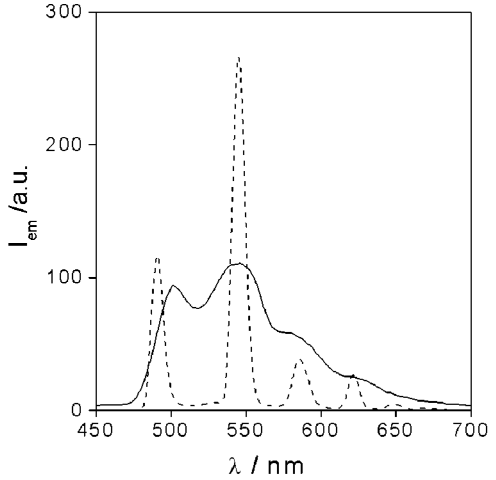

Figure 10. Phosphorescence band of **D**·24H$^+$ at 77 K (full line) and sensitized emission of Tb^{3+} in [Tb^{3+}⊂**D**·24H$^+$] (dashed line) at 77K. λ_{exc} = 287 nm.

[**D**] 0.5/1 stoichiometric ratio, in rigid matrix at 77 K one can observe the quenching of the phosphorescence of the T$_1$ excited state of the protonated dansyl units and, in the same spectral region, a strong sensitized emission of Tb^{3+}. The decrease of the emission intensity (at 545 nm) with time can be fitted by a three exponential decay with lifetimes of 4.4 ms (assigned to the Tb^{3+} luminescence), 30 ms (assigned to the partially quenched T$_1$ excited state of the protonated dansyl units of the dendrimers with Tb^{3+} inside), and 1.1 s (assigned to the T$_1$ excited state of empty dendrimers). These results again confirm that the metal ion is enclosed into the protonated dendrimer.

[Er^{3+}⊂D]. In this case, electron-transfer quenching is not allowed. The moderate quenching effect (Figure 5) is accompanied by the sensitized emission of the $^4I_{13/2}$ excited state of the metal ion (1525 nm, Figure 6). Therefore, the most important quenching mechanism is energy transfer from the S$_1$ excited sate of the dansyl units to a low-density isoenergetic manifold of metal ion excited states (Figure 4).

[Yb^{3+}⊂D]. In Yb^{3+}, a moderate quenching effect (Figure 5) is accompanied by the NIR sensitized emission of the $^2F_{5/2}$ Yb^{3+} level (Figures 4 and 6). The interpretation of this result is not straightforward. In fact, whereas the moderate quenching ability on the dansyl fluorescence could be assigned to an electron-transfer quenching mechanism, which is thermodynamically allowed (vide supra), the sensitization of the $^2F_{5/2}$ emission is an unexpected result since energy transfer from the S$_1$ excited state of the dansyl unit appears to be unlikely because of the lack of spectral overlap (Figure 11a).

However, for [Yb^{3+}⊂**D**], contrary to what happens in [Eu^{3+}⊂**D**], the [Yb^{2+}⊂**D**$^+$] electron-transfer level lies *above* the luminescent metal-centered level (Figure 11a). Therefore, quenching by electron transfer can be followed by a back electron transfer leading to the formation of the lower-lying, luminescent $^2F_{5/2}$ level rather than the $^2F_{7/2}$ ground state. Interestingly, in rigid matrix at 77 K, that is, under conditions in which the [Yb^{2+}⊂**D**$^+$] electron-transfer level moves to much higher energy,[38] the sensitized emission of the $^2F_{5/2}$ Yb^{3+} level can no longer be observed, confirming that the low-energy $^2F_{5/2}$ level cannot be populated by direct energy transfer from the S$_1$ excited state of the dansyl unit.

On protonation of the dansyl units, the electron-transfer quenching of the T$_1$ excited state is prevented for thermodynamic reasons. Conversely, there is no overlap between the phosphorescence band of protonated dansyl and the only available $^2F_{5/2}$ excited state of Yb^{3+} (Figures 3, 6, and 11b). Therefore, energy transfer cannot occur. Accordingly, at 77 K the phosphorescence band of protonated dansyl is not quenched and the NIR emission of Yb^{3+} is not sensitized.

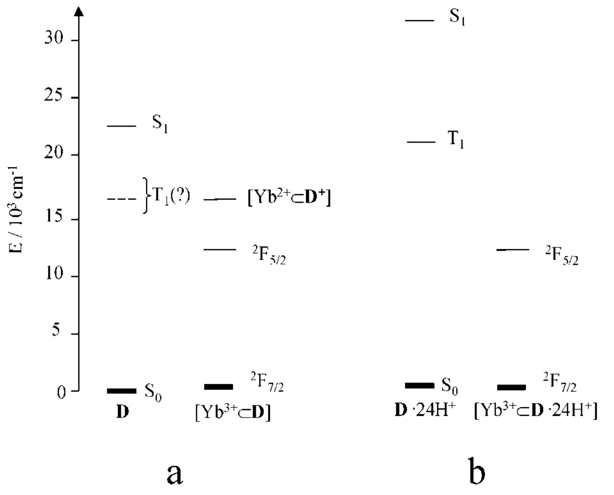

Figure 11. Energy level diagrams for **D** and [Yb^{3+}⊂**D**] (a); **D**·24H$^+$ and [Yb^{3+}⊂**D**·24H$^+$] (b). Notice the presence of a low-energy [Yb^{2+}⊂**D**$^+$] electron-transfer level for [Yb^{3+}⊂**D**].

Conclusions

We have investigated the complexation of dendrimer **D**, which contains 21 amide groups in the interior and 24 dansyl units in the periphery by six lanthanide ions (Nd^{3+}, Eu^{3+}, Gd^{3+}, Tb^{3+}, Er^{3+}, and Yb^{3+}) characterized by very different energy-level patterns and redox properties and capable of exhibiting their own luminescence. Formation of the metal complexes is accompanied by a quenching of the fluorescent excited state of the dansyl units. The quenching effect is very large for Nd^{3+} and Eu^{3+}, moderate for Er^{3+} and Yb^{3+}, small for Tb^{3+}, and very small for Gd^{3+}. In Nd^{3+}, Er^{3+}, and Yb^{3+}, the quenching of the dansyl fluorescence in fluid solution at 298 K is accompanied by the sensitized near-infrared emission of the lanthanide ion. Sensitized emission of Eu^{3+} and Tb^{3+} in the visible spectral region has been observed at 77 K when the dansyl groups of the dendrimer are protonated. Systematic investigations have allowed us to establish, in each case, the nature of the quenching mechanism. In the Yb^{3+} complex, the sensitized NIR emission takes place via the intermediate formation of an electron-transfer excited state.

The sensitized emission of lanthanide ions is currently exploited for a variety of applications from sensors to fluoroimmunoassay and from microscopy to display devices and information processing. The careful and systematic examination reported in this paper on the properties that control the so-called antenna effect (light absorption by ligands that exhibit very intense absorption bands, followed by light emission from long-lived excited states of the metal ion) will be very useful for the design of novel, more efficient systems.

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