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Comparative study of the luminescent properties of europium and terbium coordinated with thenoyltrifluoroacetone or pyridine-2,6-dicarboxylic acid in aqueous solutions

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The chelates formed with europium(III) and terbium(III) coordinated with either thenoyltrifluoroacetone or pyridine-2,6-dicarboxylic acid were studied. The formation and the composition of the chelates were compared with respect to the number of donor groups of the ligand and the coordination number of the lanthanide ion. The luminescent properties of the chelates were investigated and compared in terms of the relative luminescence intensity, the linear dynamic range and the detection limit. The results are discussed with respect to the stoichiometry of the chelate, the lifetime of the emitting level and the energy gap between the donor level of the ligand and the emitting level of the ion.

Keywords: *Europium; terbium; organic ligand; sensitized luminescence; relative sensitivity*

Some trivalent lanthanide and actinide ions are luminescent in solutions at room temperature, when present as aqua ions.[1] However, the luminescence is very weak because these ions exhibit weak fluorescence quantum yields and weak absorption coefficients. The first limitation originates from the vibronic coupling of the excited ions with the OH oscillators of coordinated water molecules, providing a path for radiationless deactivation. Luminescence decay studies have shown that the OH oscillators act independently and that the rate of deactivation is proportional to the number of OH oscillators in the first coordination sphere.[2,3] The second limitation, *i.e.*, the low absorbing capacity, can be overcome by using laser excitation to produce greater amounts of excited species. In addition, temporal resolution of the luminescence signal can be used to improve the selectivity.[4] An elegant way of overcoming both these limitations is to form fluorescent chelates with highly absorbing organic ligands often associated with synergic agents. The broad intense absorption band of the ligand is used to supplement the weak narrow absorption band of the ion. The absorbed energy is then transferred intramolecularly to the chelated ion which releases part of this energy as a narrow-band, line-type fluorescence. Moreover, on chelation with oxygen or nitrogen donor ligands, some of the OH oscillators are replaced by the ligand which is less effective in causing radiationless deactivation.

Trivalent lanthanide ions form stable coordination complexes with a variety of organic ligands. These chelates have been used in a number of areas including the fluorimetric determination of the ions, or conversely, of organic analytes used as ligands,[5,6] and the development of fluorescent labels in clinical chemistry and molecular biology.[7,8] Most of the studies previously reported on sensitized lanthanide ion luminescence are based on complexes with β-diketone ligands, such as thenoyltrifluoroacetone (TTA).[4] However, these ligands provide six or eight oxygen atoms available for coordination to the rare-earth ion, while terbium and europium have nine coordination sites.[1,9] Completing the coordination sphere can be achieved by using synergic agents such as trioctylphosphine oxide (TOPO) which has a good lone oxygen for coordination to the ion.[10] Many other organic ligands giving higher coordination number complexes have therefore been studied in order to protect the chelates against the solvent molecules. Among these compounds, pyridine-2,6-dicarboxylic acid (DPA) has been shown to be an efficient ligand for sensitizing the luminescence of several lanthanide ions in the solid[11,12] or liquid phase.[9,13,14] DPA is a tridentate ligand which is able to coordinate by an oxygen of each carboxylate group and by the nitrogen of the pyridine ring. The ligand is expected to form tris structures corresponding to nine coordination sites.[15,16] Some applications of Ln–DPA chelates have already been reported for studies in chemical and biological systems[17,18] and the photoluminescence of the Tb–DPA chelate has been used to detect bacterial endospores.[19]

The luminescence of Ln^{3+} chelates is also related to the efficiency of the intramolecular energy transfer between the donor energy level of the ligand and the emitting level of the ion, which depends on the energy gap between the two levels.[20] When the energy difference is large, the fluorescence yield is expected to decrease because the overlap between the donor and acceptor spectra is reduced. Moreover, energy transfer from the lowest triplet state of the ligand is generally favoured owing to the longer lifetime of this state and the spin invariance of the transfer process.[21] Efficient energy transfer can be achieved by choosing ligands whose triplet energy level is just higher than the emitting energy level of the ion.

A detailed study of the luminescent properties of europium when chelated with TTA and TOPO in aqueous solutions of Triton X-100 has been reported in a previous paper.[22] The purpose of this work was to compare the luminescent properties of europium and terbium chelated with TTA or DPA in aqueous solutions. The formation and the fluorescent properties of the chelates formed separately with each ion and each ligand were examined. The results are discussed in terms of the relative sensitivity of each system with respect to the composition of the chelates and the energy levels of both the ligand triplet and of the emitting state of the lanthanide ion.

Experimental

Apparatus

Absorption spectra were recorded on a Beckman M25 UV/VIS spectrophotometer. Steady-state luminescence measurements were carried out using a Jobin–Yvon JY3 spectrofluorimeter equipped with an R928 (Hamamatsu) photomultiplier tube. The sample cell was a 1 cm or a 1.5 mm quartz cell. Fluorescence experiments were performed by exciting into the absorption band of the chelate. With TTA, the absorption spectrum of the chelate was different from that of the free ligand and the

excitation wavelength was set at about 355 nm; with DPA, both spectra were not resolved and the excitation wavelength was set at 280 nm. The fluorescence was measured using the peak height at 615 nm for europium and at 490 nm for terbium. For Tb^{3+}, the $^5D_4 \rightarrow {}^7F_6$ transition was selected instead of the more intense $^5D_4 \rightarrow {}^7F_5$ transition because of the presence of a scattering signal near 545 nm. pH measurements were performed with a digital readout pH-meter and a TC 200 glass and reference unitubular electrode.

Reagents

TTA, TOPO, DPA, Triton X-100, hexadecyltrimethylammonium bromide (CTABr), europium chloride and terbium chloride were of analytical-reagent grade and were used without further purification. The buffer solutions used were prepared from either acetic acid and sodium hydroxide or tris(hydroxymethyl)-methylamine (Tris) and hydrochloric acid. Standard solutions of Eu^{3+} and Tb^{3+} were prepared by dissolving the required amount of the chloride salt in distilled water. Separate stock solutions of TTA and TOPO were prepared in absolute ethanol. The solubility of DPA in water is about 2.8×10^{-2} mol l^{-1}. The ligand exists as neutral (H_2DPA), monoanionic ($HDPA^-$) or dianionic (DPA^{2-}) species. The first dissociation constant ($pK_1 = 2.2$) is well known,[23,24] while there was a lack of agreement about the value of the second dissociation constant. pK_2 was determined by titrating an aqueous solution of 10^{-2} mol l^{-1} H_2DPA with sodium hydroxide. A value of 4.9 was found, which is close to the value reported by Tichane and Bennett.[23]

Methods

Working solutions were prepared with distilled water and 10^{-2} mol l^{-1} of the specified buffer adjusted to the required pH. Appropriate concentrations of TTA, TOPO and DPA in the test solution were freshly prepared by dilution of the stock standard solutions. When specified, the required amount of surfactant (% m/m) was added to the solution. The composition of the chelate and optimization of the fluorescence were investigated by varying the concentration of one of the components (TTA, TOPO, DPA, ion, surfactant) while the rest remained constant. All solutions were prepared in polystyrene containers to avoid memory effects of europium and terbium adsorbed on glass vessels. The analytical procedure used to construct the calibration graphs was the same as that previously described.[22]

Results and discussion

Absorption spectra and stoichiometry of the chelates

The absorption spectra of DPA and TTA and of the ligands chelated with terbium or europium are compared in Fig. 1. For the Ln–DPA systems, the absorption spectra of the free ligand and of the chelate are positioned in the same wavelength range; the chelate spectrum differs from that of the free ligand only by the presence of two peaks centered at 278 and 270 nm on the absorption band. The absorption spectrum of the free ligand depended slightly on the pH with a transition around pH 5, indicating a difference between the monoanionic and dianionic forms. In contrast, the intensity and the shape of the absorption spectrum of the chelate exhibited very little pH dependence between pH 3 and 11. For the Ln–TTA systems, the absorption spectrum of the chelate is different from that of the free ligand, when the pH is below 6 (Fig. 1). Above this pH value, the absorption band of the free ligand is red shifted and, as in ethanol,[25] the absorption spectrum of the chelate is not distinct from that of the free ligand. As shown in a previous paper,[22] the formation of the chelate is evidenced only in the presence of TOPO.

The formation and the stoichiometry of the chelates were then compared using the mole-ratio method. For the Ln–TTA–TOPO systems, the absorbance was measured at 355 nm where residual absorbance of the free ligand was small. Measurements were achieved by adding increasing amounts of europium or terbium ions to the TTA–TOPO–surfactant solution, giving two straight lines intersecting at the stoichiometric ratio. As shown in Figs. 2 and 3, the amount of chelate formed, at constant TTA concentration, depends on the concentration of TOPO and the equivalence Ln : TTA mole ratio varies accordingly. When the amount of TOPO is large enough, the formation of the chelate is limited by the concentration of TTA. For the Tb–TTA–TOPO system, this limit corresponds to a Tb : TTA mole ratio close to 0.33, which corresponds to the expected 1 : 3 stoichiometry. In contrast, for the Eu–TTA–TOPO system, the stoichiometry is less defined with a mole ratio increasing up to about 0.5 when the TOPO concentration is greater than the TTA concentration. The plots of absorbance *versus* the Ln : TOPO mole ratio exhibited similar features. When the amount of TTA was large enough, the formation of the chelate was limited by the concentration of TOPO. The Tb : TOPO mole ratio maximized at 0.5, while the Eu : TOPO mole ratio increased up to about 0.75 when the concentration of TTA was greater than that of

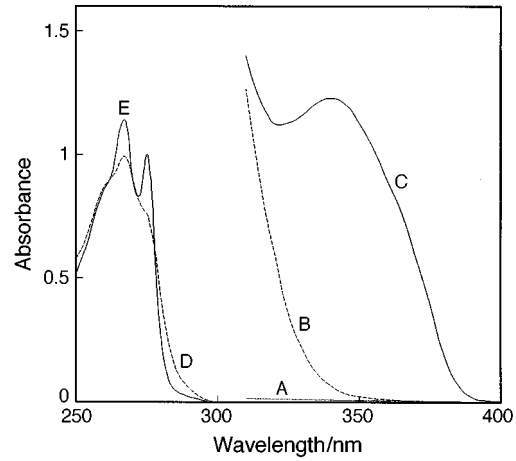

Fig. 1 Absorption spectra of (A), 10^{-4} mol l^{-1} TOPO + 10^{-4} mol l^{-1} Ln^{3+}, (B), 3×10^{-4} mol l^{-1} TTA only or with 10^{-4} mol l^{-1} Ln^{3+}, (C), 3×10^{-4} mol l^{-1} TTA + 10^{-4} mol l^{-1} TOPO + 10^{-4} mol l^{-1} Ln^{3+}, (D), 2×10^{-4} mol l^{-1} DPA and (E), 2×10^{-4} mol l^{-1} DPA + 5×10^{-5} mol l^{-1} Ln^{3+}. (A–C) are in water + acetate buffer of pH 4.7 + 0.1% Triton X-100 and (D,E) are in water + Tris buffer of pH 7.5.

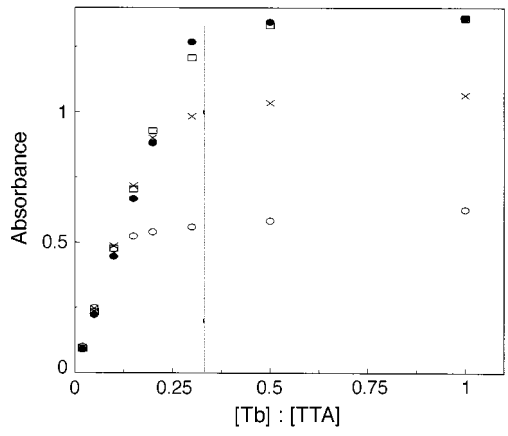

Fig. 2 Absorbance of the Tb–TTA–TOPO chelate at 355 nm as a function of the [Tb] : [TTA] mole ratio in water + acetate buffer + 0.1% Triton X-100 + 10^{-4} mol l^{-1} TTA with (○) 2.5×10^{-5}, (×) 5×10^{-5}, (□) 10^{-4} and (●) 2×10^{-4} mol l^{-1} TOPO. The vertical line indicates the 1 : 3 composition.

TOPO. These results mean that, for the Tb–TTA–TOPO system, the stable composition is 1 : 3 : 2; this composition corresponds to eight oxygen atoms coordinated to the ion, leaving one coordination site available for solvent coordination. For the Eu–TTA–TOPO system, the composition can differ from the above stoichiometry depending on the relative concentrations of the ligand and the synergic agent.[22]

For the Ln–DPA systems, the formation of the chelate was followed by measuring the height of the characteristic peak centered at 278 nm. In this case, the formation of the chelate was followed by adding increasing amounts of the ligand to the rare earth ion solution buffered at pH 7.5. As shown in Fig. 4, the stoichiometric mole ratio is close to 2 and 3 DPA molecules per Eu^{3+} and Tb^{3+} ion, respectively. In the most favourable 1 : 3 composition, three ligands correspond to three nitrogen atoms and six oxygen atoms and the nine-membered coordination sphere of the lanthanide ion is saturated.

Optimization of ion luminescence

Luminescence of europium and terbium is assigned to transitions originating from the $^5D_0$ and $^5D_4$ multiplets, respectively. The energy levels of these multiplets are compared with the energy levels of the ligand triplets, representing the energy available for transfer to the lanthanide ion (Table 1). The effect of the ligand concentration on the fluorescence of europium and terbium was investigated. In the presence of an appropriate amount of the synergic agent TOPO, ion luminescence maximizes when the concentration of TTA is at least 3 and 10 times that of terbium and europium, respectively (Fig. 5). For the Ln–DPA system, increasing amounts of the lanthanide ion were added to the DPA solution in order not to change the absorbance too much during the experiment. In this case, the luminescence intensity maximizes for a Ln : DPA mole ratio close to 0.3 and 0.4 with terbium and europium, respectively (Fig. 6). With terbium, the results mean that the number of TTA or DPA ligands per ion that are necessary to achieve maximum

Table 1 Energy levels involved in the intramolecular energy transfer process between the ligands and the lanthanide ions

Ligand triplet level/cm^{-1}		Ion resonance level/cm^{-1}	
TTA	DPA	Tb^{3+}	Eu^{3+}
20 660[26]	26 600[27]	20 500 ($^5D_4$)[5]	17 260 ($^5D_0$)[28]
20 300[26]			19 020 ($^5D_1$)[28]
			≈ 21 500 ($^5D_2$)[29]
			≈ 24 500 ($^5D_3$)[29]

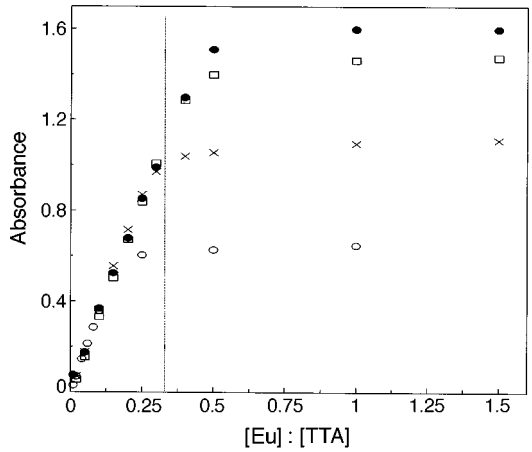

Fig. 3 Absorbance of the Eu–TTA–TOPO chelate at 355 nm as a function of the [Eu] : [TTA] mole ratio in water + acetate buffer + Triton X-100 + 10^{-4} mol l^{-1} TTA with (○) 2.5×10^{-5}, (×) 5×10^{-5}, (□) 10^{-4} and (●) 2×10^{-4} mol l^{-1} TOPO. The vertical line indicates the 1 : 3 composition.

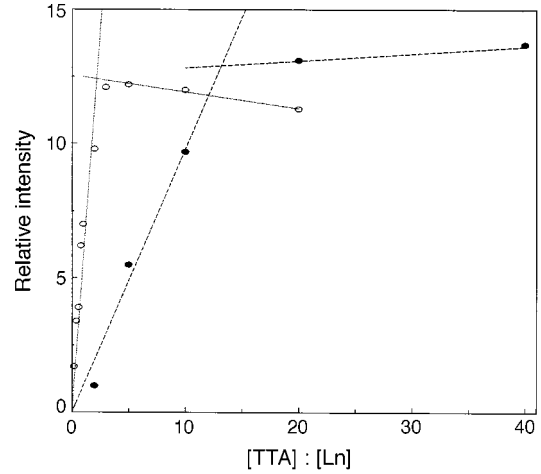

Fig. 5 Fluorescence intensity as a function of the [TTA] : [Ln] mole ratio in water + acetate buffer + Triton X-100 + 10^{-4} mol l^{-1} TOPO with (●) 10^{-6} mol l^{-1} Eu^{3+} and (○) 10^{-5} mol l^{-1} Tb^{3+}. The two curves have different *y*-axis scales.

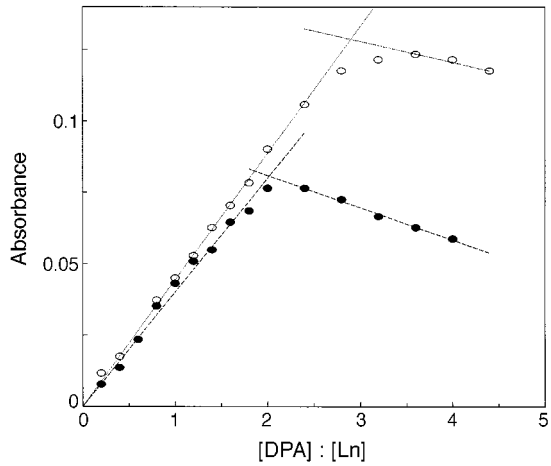

Fig. 4 Height (in absorbance) of the 278 nm chelate peak as a function of the [DPA] : [Ln] mole ratio for (●) europium and (○) terbium in water + Tris buffer of pH 7.5 + 5×10^{-5} mol l^{-1} Ln^{3+}.

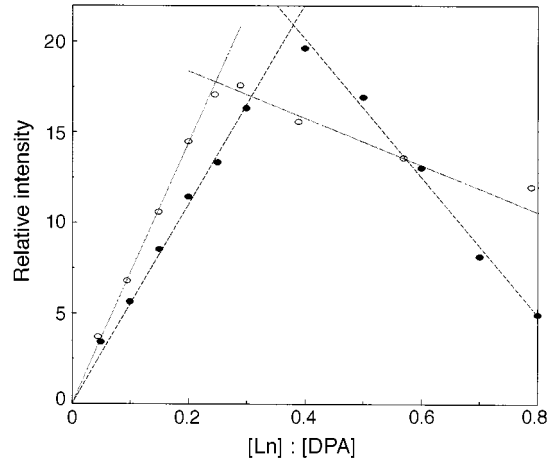

Fig. 6 Fluorescence intensity as a function of the [Ln] : [DPA] mole ratio in water + Tris buffer of pH 7.5 + 10^{-4} mol l^{-1} DPA with (●) europium and (○) terbium.

fluorescence correspond approximately to the stoichiometry of the chelate. When europium is chelated with TTA, the number of ligands necessary is much greater. In the DPA system, the fluorescence still increases once the 1 : 3 mole ratio has been reached, indicating that other species such as $Eu(DPA)_2$ or even EuDPA may be present. Moreover, once the maximum has been reached the luminescence decreases faster with europium than with terbium.

These results are in agreement with those obtained from absorbance measurements and corroborate that europium and terbium chelates do not have exactly the same composition. If the 1 : 3 : 2 and 1 : 3 compositions are the most likely for terbium chelated with TTA in combination with TOPO and with DPA, respectively, other compositions are possible with europium.

The effects of the buffering system, of the pH and of surfactants on the fluorescence of europium in the TTA/TOPO system have been extensively studied in a previous paper.[22] Acetate buffer of pH 4.7 with 0.1% Triton X-100 was found to be the most appropriate solution. The same conclusions were valid for terbium.

Since DPA can exist as different forms depending on the pH, the nature of its association with Eu^{3+} and Tb^{3+} and the fluorescence efficiency are expected to vary with pH. As shown in Fig. 7, the fluorescence maximizes at pH values above the second p*K* of the acid, indicating that the anionic chelate is the most emissive species. However, europium and terbium behave differently at pH values below the second p*K*. As suggested by Trout *et al.*,[30] the p*K* values of the free ligand are affected by coordination to the ion, and it is likely that this effect is more important with terbium, which would be more strongly coordinated than europium. The addition of surfactants, such as non-ionic Triton X-100 and Brij 35 or anionic sodium dodecyl sulfate (SDS), did not produce any change in the fluorescence intensity of both ions, indicating no further protecting effect of the micelles against non-radiative processes. In contrast, the effect of the cationic CTABr, especially on the luminescence of europium, is interesting. When the pH is greater than the pK_2 of DPA, the influence of CTABr on the fluorescence intensity, similarly to that observed with the other surfactants studied, is not significant. However, when the pH is below pK_2, *i.e.*, when neutral $Eu(DPA)_3$ or cationic $Eu(DPA)_2^+$ species are present, the plot of the fluorescence intensity *versus* the CTABr concentration exhibits a sharp increase at the critical micellization concentration of the surfactant (Fig. 8). Adding a surfactant results in the formation of micelles that create non-polar regions in the aqueous solution. Depending on the surfactant and the solute, electrostatic and/or hydrophobic interactions can induce specific changes in the properties of the solubilized species. In addition to their protecting effect, not observed for the Ln(DPA) chelates, micelles can make complex formation easier either by improving solubilization of the chelate or by changing the properties of the ligand. Since $Ln(DPA)_3^{3-}$ is readily soluble in water, the results obtained with CTABr can be interpreted as a change in the second dissociation step of the DPA ligand. In the presence of the cationic surfactant, the formation of the anionic chelate would be favoured at lower pH owing to a decrease in the pK_2 of the acid or an increase in the pH at the micellar interface. Indeed, p*K* shifts up to 2 or 3 units have been observed owing to electrostatic interactions in the Stern layer and ion exchange between ionic micelles and the bulk.[31,32] As a result, in the presence of CTABr, the fluorescence of europium and terbium is constant in the pH range 3.5–10.

Comparison of analytical performances

The calibration graphs and the analytical performances for europium and terbium chelated with either TTA–TOPO or DPA are compared in Fig. 9 and Table 2. With the TTA–TOPO system, the sensitivity is about 3–4 orders of magnitude greater for europium than for terbium. This is probably because the

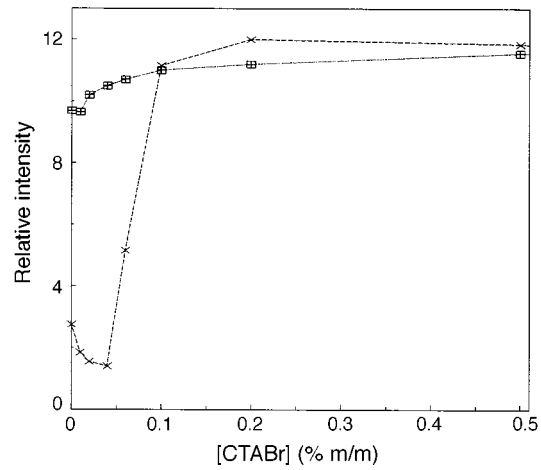

Fig. 8 Influence of the CTABr concentration on europium fluorescence in water + 10^{-4} mol l^{-1} DPA + 10^{-6} mol l^{-1} Eu^{3+} at (×) pH 3.5 (acetate buffer) and (⊞) at pH 7.5 (Tris buffer).

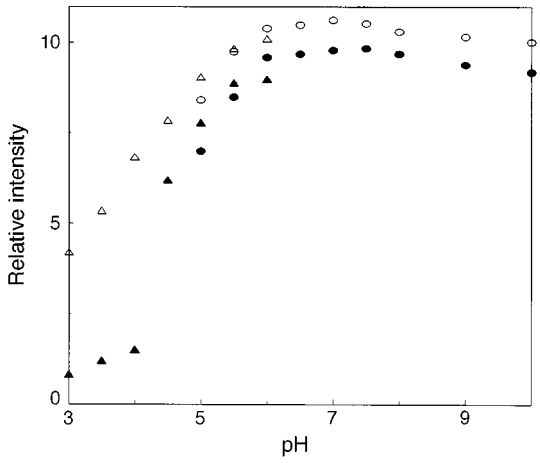

Fig. 7 Influence of pH on the fluorescence of (closed symbols) europium and (open symbols) terbium in water + 10^{-4} mol l^{-1} DPA + 10^{-6} mol l^{-1} Ln^{3+} with (triangles) acetate buffer and (circles) Tris buffer.

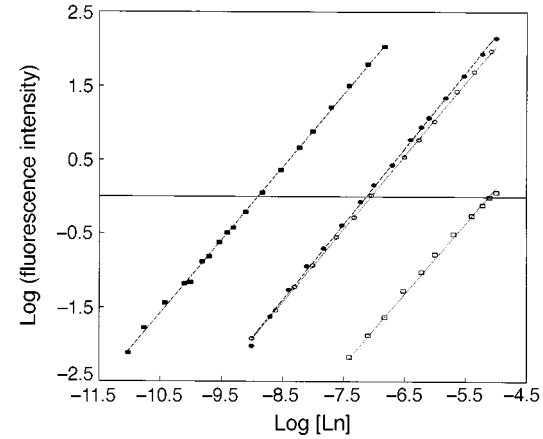

Fig. 9 Calibration graphs for (●) Eu–DPA and (○) Tb–DPA in water + Tris buffer of pH 7.5 + 10^{-4} mol l^{-1} DPA and for (■) Eu–TTA and (□) Tb–TTA in water + acetate buffer of pH 4.7 + 0.1% Triton X-100 + 10^{-4} mol l^{-1} TTA + 5×10^{-5} mol l^{-1} TOPO. The straight lines are linear regression results with $r \geqslant 0.998$.

Table 2 Analytical figures of merit for sensitized luminescence of Tb^{3+} and Eu^{3+} by TTA–TOPO and DPA, respectively

	TTA–TOPO		DPA	
	Tb^{3+}	Eu^{3+}	Tb^{3+}	Eu^{3+}
Relative intensity	≈0.016	71	1	1.3
Linearity range/mol l^{-1}	3×10^{-8}–10^{-5}	10^{-11}–10^{-5}*	10^{-9}–10^{-5}	2×10^{-9}–10^{-5}
Detection limit/mol l^{-1}	2×10^{-8}	6×10^{-12}	5×10^{-10}	10^{-9}

* Ref. 22.

multiplet of terbium is located at almost the same energy level as the ligand triplet, while for europium, the energy gap between the ligand triplet level and the resonance level of the ion is just appropriate to favour the energy transfer process. In contrast, with DPA, both europium and terbium are detected with the same sensitivity. While the detection of terbium is improved by almost two orders of magnitude with respect to that obtained with the TTA–TOPO system, that of europium is reduced by the same order. This is probably because the energy gap between the donor and acceptor levels is too large, thus reducing the efficiency of the energy transfer.

However, the relative sensitivity obtained for europium and terbium with DPA differs from the results obtained by Jenkins and Murray.[9] In their work, the lanthanide ion was excited by direct absorption of light and the sensitivity was about one order of magnitude greater for terbium than for europium. This result is consistent with the lifetimes reported for the emitting levels of terbium and europium.[16] In $Eu(DPA)_3^{3-}$, the lifetime of the $^5D_0$ level is 1.61 ms in water, against 3.19 ms in D_2O, while in $Tb(DPA)_3^{3-}$, the lifetime of the $^5D_4$ level is 2.13 ms in water against 2.21 ms in D_2O. These data seem to confirm that terbium is more strongly coordinated to DPA than europium, as indicated by our results on both the stoichiometric composition of the DPA chelates (Figs. 4 and 6) and the pH dependence of the fluorescence intensity (Fig. 7). In the well defined $Tb(DPA)_3^{3-}$chelate, all the coordination sites are satisfied by the ligand, thus preventing water coordination and non-radiative transitions.

The results in the present work differ in that excitation of the lanthanide ion does not occur by direct absorption of light, but *via* intramolecular energy transfer from the excited ligand. With indirect excitation, the sensitivity is generally greater provided that the energy absorbed by the ligand is efficiently transferred to the ion. According to the results obtained with DPA, one can assume that the energy transfer process is less efficient with terbium than with europium although, in both cases, the energy gap between the donor and acceptor species is of the same order. In terbium, only the $^5D_4$ level lies below the triplet level of DPA and the energy gap is large. In the europium chelate, the ligand triplet can transfer its energy, not only to the ^5D_o emitting level, but also to the upper $^5D_1$, $^5D_2$ or even $^5D_3$ levels which could then populate the emitting level by non-radiative deactivation.

In conclusion, sensitizing the luminescence of lanthanide ions by coordination with organic ligands depends on several factors including the number of atoms available from the ligand for coordination, the composition of the chelate and the excitation path used to promote the emitting level of the ion. When the ion is excited indirectly by intramolecular energy transfer from the ligand, the energy gap between the donor and acceptor levels is a critical parameter.

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