

pH Dependence of the energy transfer mechanism in a phenanthridine-appended ytterbium complex †

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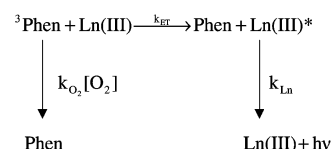
Intramolecular energy transfer from a non-protonated phenanthridine chromophore to ytterbium occurs rapidly despite negligible overlap of the triplet state of phenanthridine with the absorption band of the metal centre. This can be explained by a sequential electron transfer and back electron transfer, or redox, mechanism. When the phenanthridine is protonated, this energy transfer pathway ceases to be thermodynamically feasible. Under these circumstances, energy transfer to the metal becomes rate determining and is mediated by the phenanthridinium triplet state, despite its near-zero spectral overlap with the metal-centred absorption band.

Luminescent lanthanide complexes are of considerable interest² owing to their potential for application in bioassay³ and time-resolved imaging.⁴ In addition, the luminescent lanthanides are very useful in the determination of solution state structure, *e.g.* hydration state,⁵ and in the calculation of chromophore/binding site separations.⁶ Traditionally, research into luminescent lanthanide complexes has concentrated on europium and terbium: these metal ions are very emissive in the visible region and have long excited state lifetimes. However, the large energy gaps between the emissive and acceptor states in these ions restrict the choice of chromophore to the point where relatively long wavelength excitation of sensitising chromophores may be regarded as noteworthy.⁷

More recently, a number of groups, including our own, have begun to exploit developments in detection of near-IR luminescence to study the luminescence from neodymium⁸ and ytterbium-containing complexes. Since their emissive states are much lower in energy, these ions allow a much wider range of sensitising chromophores to be used.^{8–10}

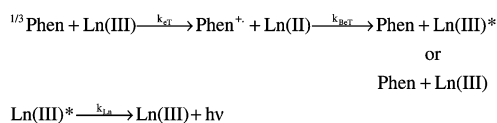
The mechanism of energy transfer from the ligand to the lanthanide has been widely discussed for a range of complexes. In general, the triplet state of the ligand chromophore is believed to be involved in the energy transfer process.¹¹ This appears to be the case for most of the lanthanides, including neodymium,¹² which has a large number of excited states that may in themselves be emissive (though this has not been detected in solution), or that may undergo relaxation down the manifold to the main emissive state. These states offset the large energy gap between the majority of triplet states and the neodymium-centred emissive state.

For ytterbium, there is only one excited state (²F_{5/2}, *E* = 10300 cm⁻¹) and the mechanism of energy transfer to this state from a chromophore has been the subject of mild controversy. Two hypotheses have been put forward. The first suggests that energy transfer occurs in a fashion similar to that observed for many of the other lanthanide ions. Energy is transferred from the relatively long lived triplet state of the antenna to the metal by a Förster or Dexter-type mechanism¹³ (Scheme 1), despite the large difference in energy between the donor triplet state and the metal-centred excited state. The alternative view suggests that a rapid, but sequential, electron exchange mechanism,



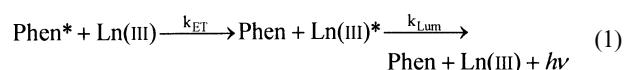
Scheme 1 Triplet-mediated energy transfer in lanthanide complexes, showing the effect of oxygen on the triplet state.

ism, also referred to as a redox mechanism, between the excited state of the chromophore and the readily reduced ytterbium(III) ion is responsible for energy transfer to the lanthanide (Scheme 2).¹⁴ It should be noted that this differs from the electron



Scheme 2 Electron exchange or redox energy transfer mechanism.

exchange mechanism often encountered in energy transfer between chromophores, which occurs by a concerted process. This second route is clearly only a viable alternative where both electron transfer steps are thermodynamically feasible, *i.e.* $\Delta G < 0$. Horrocks and co-workers have shown that both Eu(III) and Yb(III) will undergo this reaction with cod parvalbumin, and that, in the case of Eu(III), the back electron transfer step, k_{BE} , only gives rise to non-emissive states of the metal ion. For Yb(III), however, this step was found to be sufficiently exoergic to give rise to the emissive ²F_{5/2} state of the ion. Working with the assumption that the rate of the back electron transfer reaction is fast, we can reduce the two mechanisms to a common, sequential reaction in which we have two rate constants; the rate of energy transfer, k_{ET} , and the rate of luminescence, k_{Lum} :



The intensity of luminescence at any instant is proportional to the concentration of the excited state, [Ln(III)*], and is given by the equation

† Near-IR luminescence and energy transfer in lanthanide complexes. Part 2.¹

Table 1 Observed rate constants for growth and decay of luminescence^a from the protonated and unprotonated ytterbium complex and their correlation to the lifetime of the excited phenanthridinium triplet state^b

Complex	Degassed			Aerated				
	Solvent	$k_{\text{triplet}}/\text{s}^{-1}$	$k_{\text{grow-in}}/\text{s}^{-1}$	$k_{\text{decay}}/\text{s}^{-1}$	ϕ_{f}^c	$k_{\text{triplet}}/\text{s}^{-1}$	$k_{\text{grow-in}}/\text{s}^{-1}$	$k_{\text{decay}}/\text{s}^{-1}$
[HYb·L] ⁴⁺	H ₂ O	4.1×10^4	1.9×10^6 (1000)	4.1×10^4 (1000)	0.92	2.0×10^5	1.9×10^6 (1000)	2.0×10^5 (1000)
[HYb·L] ⁴⁺	D ₂ O	3.8×10^4	1.9×10^5 (1000)	3.8×10^4 (1000)	0.94	1.8×10^5	1.9×10^5 (1000)	1.7×10^5 (1000)
[Yb·L] ³⁺ ^d	H ₂ O	—	$>3 \times 10^7$ (1000)	1.1×10^6 (1000)	0.64	—	$>3 \times 10^7$ (1000)	1.1×10^6 (1000)
[Yb·L] ³⁺ ^d	D ₂ O	—	$>3 \times 10^7$ (1000)	1.3×10^5 (1000)	0.64	—	$>3 \times 10^7$ (1000)	1.3×10^5 (1000)

^a Wavelengths (nm) at which emission was monitored are shown in brackets. Errors in measurement of luminescence rate constants are $\pm 10\%$, while for the transient triplet, errors are $\pm 20\%$. ^b Values for k_{triplet} were obtained by observing the time dependence of the depletion of the $T_n \leftarrow T_1$ transition at 600 nm by flash photolysis. ^c Quantum yields of fluorescence are reported relative to the quantum yield for the protonated gadolinium complex, in which the metal-centred excited state is too high in energy to act as an acceptor and the reduction potential is similarly inaccessible. The high fluorescence quantum yield is indicative of the relative inefficiency of energy transfer to the ytterbium centre. ^d Due to rapid quenching of the T_1 state, the T-T absorption decay and, hence, triplet lifetime could not be obtained for the deprotonated complex.

$$[\text{Ln(III)}^*] \propto \frac{k_{\text{ET}}}{k_{\text{lum}} - k_{\text{ET}}} \cdot (e^{-k_{\text{ET}}t} - e^{-k_{\text{lum}}t}) \quad (2)$$

In this paper, we have used a range of spectroscopic techniques to show that both energy transfer mechanisms can be observed for an ytterbium complex bearing an antenna group whose protonation state and, hence, oxidation potential, varies with pH and demonstrate that for the protonated species $k_{\text{ET}} \ll k_{\text{Lum}}$, and for the unprotonated species $k_{\text{ET}} \gg k_{\text{Lum}}$.

Results and discussion

The complex [Yb·L]¹⁵ contains a phenanthridine chromophore held in close proximity to a tightly bound metal ion. Analogues of this complex have been shown to exhibit sensitised luminescence from a variety of lanthanide ions, including europium, terbium and neodymium.¹⁶ In all these cases, energy transfer is mediated by the triplet state and examination of the phosphorescence spectra of the aryl chromophores reveals good overlap with absorption bands associated with the metal ions. However, in the case of the ytterbium complex studied here, the phenanthridine triplet state ($E_T = 22\,000\text{ cm}^{-1}$) and the phenanthridinium triplet state ($E_T = 21\,300\text{ cm}^{-1}$) both have negligible overlap with the excited state of the metal. This led us to believe that the energy transfer process in this system might be unusual. We have studied the time-resolved luminescence from the metal ion and the fluorescence and triplet-triplet absorption band of the phenanthridine antenna in both acidic and neutral H₂O and D₂O. The effects of oxygenation, an efficient triplet quencher, have also been investigated. From these data we can establish the kinetics of the energy transfer and emission steps and, hence, elucidate the mechanisms of the energy transfer under the different conditions.

The results of this series of measurements are shown in Table 1; typical fitted decays for the triplet absorption spectra and metal-centred luminescence are shown in Fig. 1. Fig. 2 shows the early part of the time-resolved profile of a typical luminescence signal for a protonated complex.

In our complex, there is such a large difference between the triplet state energy and the metal excited state that back energy transfer is extremely unlikely. Changes in rate constant brought about by aeration may be therefore assigned to triplet-dependent steps, since it is well established that lanthanide excited states are not quenched directly by oxygen. It is normally the case in sensitised lanthanide complexes that the triplet state of the antenna mediates the energy transfer process and that this step is rapid, $k_{\text{ET}} \gg k_{\text{Lum}}$. Under these conditions, the growth of the metal-centred luminescence mirrors the decay of the triplet state, and the metal-centred luminescence decay is determined by k_{Lum} . However, in cases where the energy transfer step is rate determining, *i.e.* $k_{\text{ET}} \ll k_{\text{Lum}}$, it can be seen from eqn. 2 that the observed decay constant would mirror the decay

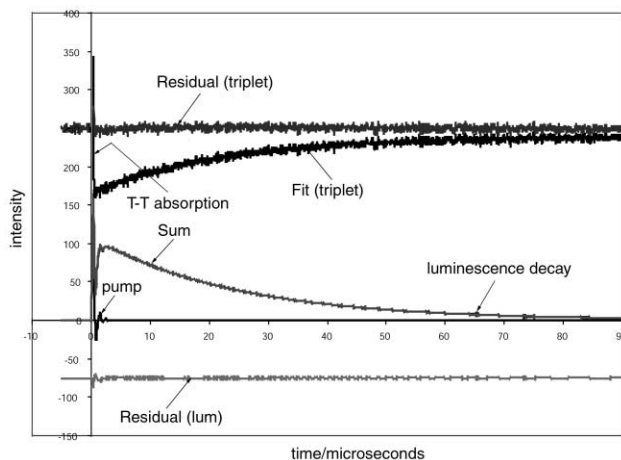


Fig. 1 Time-resolved luminescence profile and transient triplet-triplet absorption spectrum for the protonated complex in degassed H₂O ($k_{\text{triplet}} = 4.1 \times 10^4\text{ s}^{-1}$, $k_{\text{grow-in}} = 1.9 \times 10^6\text{ s}^{-1}$). The fitted curves for the luminescence and triplet absorption superimpose almost exactly onto the respective data. The triplet absorption spectrum and the residuals for both triplet and luminescence fitting are all shown offset for clarity.

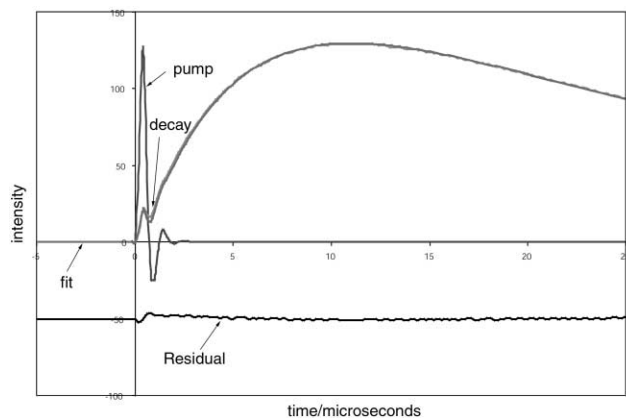
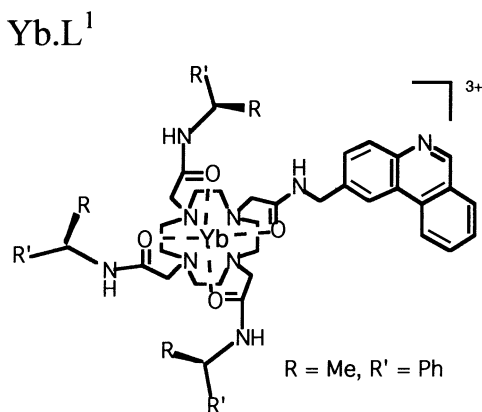


Fig. 2 Fitted time-resolved luminescence profile for the protonated complex in degassed D₂O ($k_{\text{grow-in}} = 1.9 \times 10^5\text{ s}^{-1}$, $k_{\text{triplet}} = 3.8 \times 10^4\text{ s}^{-1}$), showing the rise of the luminescence signal, which is of long duration compared to the detector response. The small spike at the beginning of the profile results from scattered light or insufficient stray light rejection. Residuals are offset for clarity.

of the triplet state of the chromophore and, therefore, be dependent on the degree of sample aeration. In such a case, the growth of the metal-centred luminescence signal is determined by k_{Lum} , and would be independent of aeration, but dependent on the nature of the solvent, since it relates to the metal-centred part of the process.

The protonated complex [HYb·L]⁴⁺ exhibits unusual kinetic behaviour. The temporal emission profile shows a growth in

intensity followed by decay. It may be seen that the lifetime of the emission is significantly longer in degassed solution compared to aerated solution and that the observed luminescence decay constants match, within experimental error, the decay constants of the antenna triplet state under the same conditions. The grow-in of the luminescence is independent of the degree of sample aeration. The energy transfer processes can be adequately described by Scheme 1, whereby the energy transfer step is slower than the rate of deactivation of the metal excited state, $k_{\text{ET}} \ll k_{\text{Lum}}$. As determined by eqn. 2, above the rate of emission from the metal, k_{Lum} is characterised by the rise time of the luminescence.



The slow energy transfer process may be accounted for by the large energy gap between the triplet state of the aryl chromophore and the metal excited state. Since ytterbium has no readily accessible higher excited states, the energy transfer has to take place directly to the low lying $^2F_{5/2}$ state, a process that occurs very slowly. This is borne out by the fact that the fluorescence quantum yield for the ytterbium complex is very low. The question of energy transfer to ytterbium has recently been considered by Horrocks and co-workers, who showed that the energy transfer from a tryptophan residue in cod parvalbumin to a bound Yb^{3+} ion occurs *via* an electron transfer pathway.¹⁴ They argued that energy transfer *via* a Förster-type mechanism was unlikely because of the poor overlap of the tryptophan energy levels and the ytterbium absorption spectrum, and instead proposed a two-step electron transfer mechanism. Given the redox potentials of tryptophan and the ytterbium ion, and the energy levels of the tryptophan excited states, they demonstrated that this pathway is thermodynamically feasible. Abusaleh and Meares have described such a mechanism for energy transfer to europium in complexes prepared from EDTA derivatives containing electron-donating motifs.¹⁷

In the case of $[\text{HYb} \cdot \text{L}^1]^{4+}$ however, this mechanism cannot occur. Cyclic voltammetry of phenanthridinium hydrochloride in acetonitrile (0.1 M, NBu_4ClO_4) shows no oxidation wave below 2.1 V, while luminescence measurements reveal $E_{\text{S}} = 3.30$ eV and $E_{\text{T}} = 2.64$ eV. Coupled with the reduction potential for Yb^{3+} in this and related tetraamide complexes [$E_{\text{red}} = -1.5$ V (298 K, $I = 0.1$ M) NMe_4ClO_4 , MeCN], these values reveal that the electron transfer mechanism is not thermodynamically feasible for our protonated system and is also less likely for simple aromatic chromophores which are difficult to oxidise.

Weller and co-workers have described such electron transfer processes for exciplex formation.¹⁸ They have shown that the change in free energy on electron transfer, ΔG_{ET} in eV is given by

$$\Delta G_{\text{ET}} = (E_{\text{ox}} - E_{\text{red}}) - E_{\text{S}} - \frac{e_0^2}{\epsilon_{\text{a}}} \quad (3)$$

where E_{ox} is the oxidation potential of the donor (in this case the antenna group), E_{red} is the reduction potential of the

acceptor (Yb^{3+}), E_{S} is the singlet state energy of the donor group, $e_0^2/\epsilon_{\text{a}}$ is the attraction between the resulting radical ion pair. For an exciplex, $e_0^2/\epsilon_{\text{a}} \approx 0.15$ eV. In our case, where the separation between the donor and the acceptor is greater, this value will be smaller, but 0.15 eV serves as a good “worst case” limiting condition.

Thus, for the phenanthridinium complex,

$$\begin{aligned} \Delta G_{\text{ET}} &\geq (2.2 + 1.5) - 3.3 - 0.15 \text{ eV} \\ \Delta G_{\text{ET}} &\geq +0.25 \text{ eV} \end{aligned} \quad (4)$$

In reality, the oxidation potential is likely to be much greater than 2.2 eV, so an electron transfer process is ruled out as a potential energy transfer mechanism for the protonated system.

Instead, energy transfer between the antenna group and the metal centre may arise as a consequence of the small overlap between the $^2F_{5/2}$ state of the ytterbium ion and the aryl triplet state, with the excess energy dissipated to the O–H vibrational modes of the solvent. Such a mechanism of energy transfer was originally suggested by Crosby and Kasha to explain the energy transfer from a dibenzoylmethane ligand to Yb^{3+} ,¹⁹ but this hypothesis appears to have been neglected in more recent years. The observation of lower rates of energy transfer in D_2O (*ca.* a factor of ten) lends support to this hypothesis and is consistent with the more efficient dissipation of energy through the higher energy O–H vibrational manifold compared to the O–D system.

Another facet of the rate determining nature of the energy transfer step is that it would suggest that, in the case of ytterbium complexes, the twin goals of efficient energy transfer and long luminescent lifetime are not necessarily mutually compatible. While the use of different antenna groups, with lower triplet state energies, may increase the efficiency of energy transfer, the observed lifetime is also expected to decrease. As a result of the poor energy mismatch between the triplet state and the ytterbium excited state, the lifetimes of $[\text{HYb} \cdot \text{L}^1]^{4+}$ in degassed solutions are the longest reported to date for ytterbium complexes. Unfortunately, since the observed lifetime is dependent on the rate of the energy transfer process, this merely means that the process is extremely inefficient and that the luminescence quantum yield in aqueous solution is very low, due to competitive quenching of the triplet state by molecular oxygen. In cases where direct excitation of ytterbium complexes has been employed, the observed lifetime is of the order of 1–10 μs .¹⁴

At $\text{pH} \approx 6$, the phenanthridinium chromophore is completely deprotonated and the profile of the time-resolved luminescence is radically different. The rise time of the luminescence is very short ($\tau \ll 30$ ns) and cannot be resolved using our instrumentation, while the luminescent decay is independent of sample aeration, consistent with a metal-centred process ($\tau = 900$ ns). This change in profile indicates that $k_{\text{ET}} \gg k_{\text{Lum}}$, and we can conclude that there is a different energy transfer mechanism in the deprotonated complex. The double electron transfer pathway observed with cod parvalbumin¹⁴ can now be invoked to explain these observations. The neutral phenanthridine group is quite readily oxidised ($E_{\text{ox}} = +1.1$ V), and energy transfer mediated by a double electron transfer process becomes thermodynamically feasible. Using the equation above, we deduce that $\Delta G_{\text{et}} = -0.85$ eV for the electron transfer reaction from the excited singlet state of the phenanthridine chromophore, and $\Delta G_{\text{ET}} = -0.25$ eV for the reaction from the triplet state, indicating that the redox mechanism involving either excited state is thermodynamically feasible. The fluorescence yield of the complex at neutral pH is only slightly reduced compared to that observed from the protonated form, indicating that the singlet state is not significantly quenched. We conclude, therefore, that the electron transfer step is likely to occur from the triplet state of the phenanthridine chromophore to the metal. This process,

illustrated in Scheme 2, is favoured over a conventional triplet-mediated energy transfer process since the latter occurs much more slowly, owing to the need to dissipate excess energy through the solvent vibrational manifold.

It should also be noted that the same electron transfer reaction is possible for the europium complex at high pH. However, the observed effect is more complex, since the triplet-mediated energy transfer in the europium complex is more favourable than in the case of the ytterbium complex, for the reasons discussed above.

One potential application of these materials is their use as luminescent probes in biological systems. The data above indicate that there would be no difficulty in performing time-gated experiments, avoiding detection of autofluorescence and scattered light. Readily available and low cost instrumentation permits time-gating on a timescale of < 5 ns, making the question of lifetime largely irrelevant to the issue of designing probes for use in time-resolved imaging applications. The design and application of antenna-bearing complexes, in which the efficiency of the energy transfer step is optimised, is probably more significant. This is being addressed in the light of these results.

Conclusion

The protonated ytterbium complex thus demonstrates 'classical' behaviour, as described in Scheme 1, though initial perusal of the data presented in Table 1 would suggest otherwise. In fact, the scheme applies more closely to the ytterbium complex than to the analogous samarium and neodymium complexes; there are no other readily accessible states of ytterbium to which competitive energy transfer might occur, and from which the excited metal might be competitively quenched.

The apparent dichotomy between the energy transfer pathways in acidic and basic solution is clearly intriguing and could potentially be exploited in the design of novel systems. Further investigation of the crossover between mechanisms and the potential applications of this phenomenon are in progress.

Experimental

Ligand synthesis

Ligand L¹ was synthesised according to established procedures.¹⁵ Lanthanide complexes were prepared by reaction of L¹ with a single equivalent of the anhydrous lanthanide trifluoromethanesulfonate in acetonitrile solution. The resultant precipitate was recrystallised from acetonitrile, to yield the analytically pure complex. Details of complex characterisation have been reported elsewhere.¹⁵

Luminescence measurements

The triplet state of the phenanthridinium group produced by laser excitation was observed by its transient absorption at 600 nm by absorption spectroscopy at 90° to the excitation pulse. Light from a 100 W tungsten filament lamp was focused through the sample, and the attenuated emergent light was focused onto the entrance slits of a 300 mm focal length monochromator (Bentham TM300V) equipped with a 1200 groove mm⁻¹ ruled grating, which was used to select 600 nm radiation. The intensity of the radiation was measured using a photomultiplier tube (Hamamatsu R928) and the output fed into a digital oscilloscope (Tektronix TDS320), from which data was transferred to a PC for analysis. The transient decay was recorded as an average over 32 pulses to improve the signal to noise ratio. At the wavelength used, the ground state of the phenanthridinium ion does not absorb, and the decays are assigned to the T_n ← T₁ transition. Deoxygenation of samples was achieved by subjecting them to at least three freeze-pump-thaw cycles.

The near-IR luminescence from ytterbium complexes was collected at 90° to the excitation pulse using narrow bandpass interference filters to select radiation of the desired wavelength. A 1000 nm interference filter with a FWHM of 25 nm (Comar) was used to detect luminescence from the red edge of the (²F_{5/2} → ²F_{7/2}) emission band. The selected radiation was detected by a liquid nitrogen-cooled germanium photodiode/amplifier (North Coast EO-817P) operating in high sensitivity mode. Under these conditions, the detector has a rise time of ca. 200 ns and a FWHM response of 400 ns. The signal was captured and averaged by a digital storage oscilloscope (Tektronix TDS320) and transferred to a PC for analysis. Instrument response functions were obtained using the fluorescence from a solution of a red laser dye (DCM), τ_F = 2.2 ns. The lifetime of this dye is very short compared to the response time of the detector and, therefore, can be considered to provide an instrument response profile for the detection system and is used as an alternative to a scatterer.

Data analysis

The decay of the phenanthridinium triplet state was analysed using a spreadsheet package (EXCEL) and the data fitted to a single exponential decay using a non-linear least squares procedure. Quality of fit was determined from the randomness of the residuals and reduced chi-squared. Fitting to a double exponential function did not yield an improvement in fit.

The luminescence lifetimes from ytterbium complexes are comparable with the detector response time and, hence, the data for the complexes were analysed by iterative deconvolution of the instrument response function with a single or double exponential decay, the best fit being judged by non-linear least squares analysis. The details of this approach have been discussed elsewhere.^{1,8,16}

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