PERKIN 2

Sensitised luminescence from phenanthridine appended lanthanide complexes: analysis of triplet mediated energy transfer processes in terbium, europium and neodymium complexes†

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Time resolved luminescence spectroscopy and laser flash photolysis have been used to probe the energy transfer processes in the europium, neodymium and terbium complexes of ligand, **1**. The ligand, chosen because of the high kinetic stability of lanthanide complexes derived from amide-functionalised azamacrocycles, bears a phenanthridine chromophore that absorbs light at 355 nm, and which can be protonated at low pH. We show that triplet mediated energy transfer to the metal centre occurs in the protonated complexes.

Introduction

Lanthanide luminescence in solution has become increasingly important in recent years due to the considerable interest shown in the use of lanthanide complexes for time-delayed bioassay and time resolved imaging, as well as in the study of the solution state structure of lanthanide complexes in solution.[1–4] Since lanthanides themselves have low extinction coefficients, interest has tended to centre on the use of indirect excitation methods.[5] These permit population of the emissive state of the lanthanide from the excited state of an aromatic antenna group possessing a comparatively large extinction coefficient for absorption of light. The indirect excitation approach has been shown to work for intermolecular energy transfer to lanthanide ions in solution,[6] but is much more efficient when both the antenna and the chromophore are held in proximity in co-ordination complexes that are stable on the timescale of the luminescence experiment.[5]

Solution state studies on luminescent lanthanides have concentrated on the lanthanide ions that luminesce in the visible region of the spectrum, namely europium, terbium, samarium and dysprosium.[7–11] The main body of work in this area has dealt with europium and terbium complexes, which have long (millisecond order) luminescence lifetimes that are simple to detect and measure.[12–14] More recently, a number of groups have begun to exploit developments in detection of near-IR luminescence to study the luminescence from neodymium and ytterbium complexes, to the point where these too may be applied in assays.[15–19]

The mechanism of energy transfer from the sensitising chromophore to the metal has been widely discussed,[20,21] and both Förster and Dexter energy transfer mechanisms have been suggested. The most widely accepted involves Förster energy transfer from the excited state of the antenna to the metal ion.[22] This model has been used by Horrocks *et al.*[19] to study donor–metal ion distances in protein systems. For any triplet mediated process to be feasible, the triplet state energy must be greater than or equal to, the energy gap (ΔE) between the excited state and ground state of the metal for phonon assisted and resonant energy transfer respectively. In cases where the triplet state and the excited state of the metal are similar in energy, the energy transfer process becomes reversible due to thermal re-population of the triplet state, providing further evidence for the intermediacy of the triplet.[23]

The alternative theory of energy transfer suggests that a stepwise electron transfer and back-electron transfer process mediates energy transfer, sometimes referred to as an internal redox mechanism. This is distinct from the classical Dexter transfer mechanism which may be thought of as an electron exchange process in which the electrons are transferred in a concerted fashion. The charge transfer excited state of the antenna formally acts as a donor in a photoelectron transfer process, while the metal centre acts as an acceptor. Back electron transfer then regenerates the antenna group, leaving the metal(III) ion in its emissive state. This process has been proposed to occur in certain ytterbium complexes such as modified proteins and is less widely accepted.[19]

van Veggel and co-workers have studied the emission from lanthanide complexes of polydentate ligands and demonstrated the intermediacy of the triplet state in such complexes.[24] Their complexes are conformationally flexible, and possess triplet states with double exponential decays as a direct result, making analysis more complicated. We now show that the triplet-mediated mechanism can also be demonstrated for a relatively rigid series of complexes, which are conformationally inert on the timescale of the luminescence experiments described. The growth and decay of the luminescence have been examined for a family of complexes [Ln·**1**], which are kinetically and thermodynamically stable over the pH range 1–10.[25] We hereby show how time-resolved spectroscopy has been used to demonstrate how the growth and decay of the lanthanide centred luminescence can be related to the lifetime of the triplet state.

Results and discussion

Europium and terbium complexes of ligand **1** have been shown to display a marked dependence of the luminescence intensity on the protonation state of the phenanthridinium chromophore. Protonation of this chromophore causes a shift to lower energy for both the ground state and the excited singlet and

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† Electronic supplementary information (ESI) is available: absorption and total emission spectra of $[\mathrm{Eu{\cdot}H1}]^{4+}$ in aerated aqueous solution. See http://www.rsc.org/suppdata/p2/b0/b009624p/

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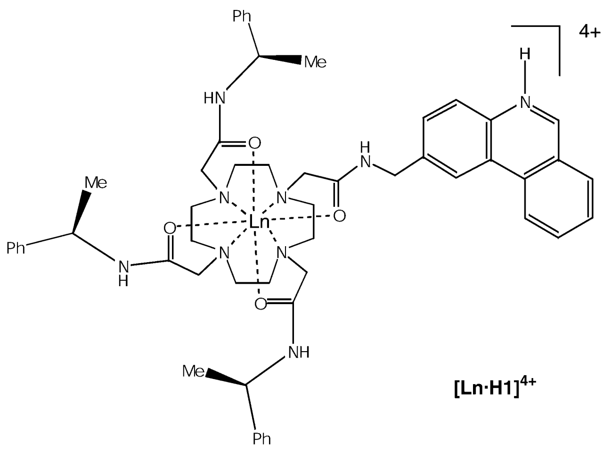


[Ln·H1]$^{4+}$

triplet states as determined by absorption, fluorescence and phosphorescence spectroscopy.[25,26] The singlet state shifts by 1500 cm^{-1} to lower energy on protonation, while the triplet level reduces by 800 cm^{-1}. The triplet state has been implicated in energy transfer to proximate lanthanides for related aryl chromophores, notably phenanthrene. However, little is known about the precise nature of the energy transfer process. As will be seen from the results described herein, the concept of simple energy transfer from the triplet to the metal represents an over-simplification in all but exceptional cases. For energy transfer to occur efficiently, there should be spectral overlap between the donor and acceptor states. In addition, the triplet state of the chromophore must be of higher energy than the acceptor state of the lanthanide, but the energy gap must be at least $10k_BT$, (= 2000 cm^{-1}) to effectively preclude back energy transfer at room temperature.

Ligand **1** was used to investigate energy transfer from the phenanthridinium chromophore to a variety of bound lanthanide ions—specifically, Eu^{3+}, Tb^{3+}, and Nd^{3+}—while the gadolinium complex was used to investigate the triplet–triplet absorption spectrum, by flash photolysis, and E_T, by phosphorescence emission spectroscopy in an optical glass and determination of the 0,0 transition. Solutions were made up so as to maintain the pH around 2.5 (± 0.2) (by addition of 150 µl aliquots of trifluoroacetic acid to solutions of the complex in 5 ml of water) to ensure that the protonated chromophore (pK_a $S_1 = 3.4$)[27] predominated in solution. At this pH, the pK_a implies that around 11% of the chromophores in solution are still unprotonated. While this figure is relatively large, excitation at 355 nm circumvents the problem, since the extinction coefficient for the protonated complex is much higher than that of the unprotonated species [*e.g.* for the europium complex, $\varepsilon_{355}(\text{Eu·1H})^{4+}/\varepsilon_{355}(\text{Eu·1})^{3+} > 20$]. Thus any contribution from the unprotonated species is less than 0.5% of the total signal, well within the range of experimental error.

As well as measuring the luminescent lifetimes of the lanthanides, the grow-in of the luminescent emission was also measured. For europium, terbium and samarium, measurement of the grow-in was achieved by examination of the early part of the decay, and by fitting the decay to a double exponential function. This was assisted by recording the temporal profile of the decay over a range of time-bases (0.1 µs to 10 ms for Tb). Where appropriate, these studies were carried out at a variety of wavelengths to take account of the possible transitions from different metal-centred excited states. Additionally, measurements were undertaken in aerated and deoxygenated solutions to determine the effectiveness of quenching of the triplet state by dissolved oxygen. Neodymium complexes have relatively short lifetimes (<< 1 µs for the aqua ions)[15] and the observed decay is convoluted with the detector response. Kinetic information can be extracted from the observed decays by iterative re-convolution and non-linear least squares analysis. In these cases, measurements in emission were undertaken using interference filters to select the metal centred emission bands.

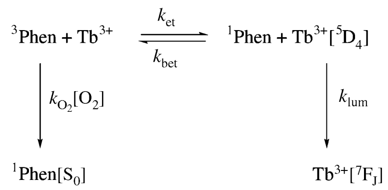
The transient triplet–triplet absorption spectrum was also studied to allow correlation between the depopulation of the triplet state and the grow-in of the metal centred luminescence for aerated and degassed solutions of the lanthanide complexes. The complex [HGd·**1**]$^{4+}$ was used as a control, since the emissive levels of the metal (around 32000 cm^{-1}) are much higher in energy than the triplet state of the phenanthridinium chromophore.[28] This allows determination of the triplet state lifetime in the absence of energy transfer mechanisms.

Analysis of results

The observed rate constants for the decay of the ligand triplet states and the rise-times and decay of the lanthanide luminescence are shown in Table 1. As expected, the various lanthanide complexes differ markedly in their photophysical properties.

The terbium complex is the most easily understood system in this group: the inaccessibility of Tb(II) rules out the existence of an electron-transfer/back-transfer mechanism as the first step of such a process would not be thermodynamically feasible. In the case of this complex, the difference between measurements at high and low pH has already been discussed.[26,27] At high pH the triplet energy of phenanthridine is sufficiently greater than that of the $^5D_4$ state of terbium to preclude back energy transfer, while at low pH, the energy gap is reduced on protonation to the point at which back energy transfer becomes possible ($\Delta E = 800$ cm^{-1}). This leads to changes in luminescence lifetime with changing oxygenation of the sample.

As part of our continuing studies on the terbium complex, we carried out investigations into the growth and decay of the metal centred luminescence with reference to the decay of the chromophore centred triplet state. The intermediacy of the triplet state is clearly shown by the results in Table 1. Transient absorption spectroscopy of the degassed solution of the complex revealed a decay which could be fitted to a dual exponential function. One of these correlates with the growth of the metal centred luminescence and the second with its decay. Similar observations have been made for other lanthanide complexes and are indicative of a system in which the triplet energy of the chromophore is only slightly higher than the emissive metal ion.[24] This process is analogous to E-type delayed fluorescence: the higher energy level, which in this compound is the triplet state of the phenanthridinium antenna, is repopulated by thermal activation of the lower level species, in this case the excited metal ion. Such a process can occur when the energy gap between the two is small, $\Delta E < 10k_BT$. This is illustrated in Scheme 1. Under these circumstances the lifetimes of the triplet state and the emissive state of the metal ion are observed to be similar, and, in degassed media, metal centred luminescence is the principal quenching pathway of the antenna's triplet state.



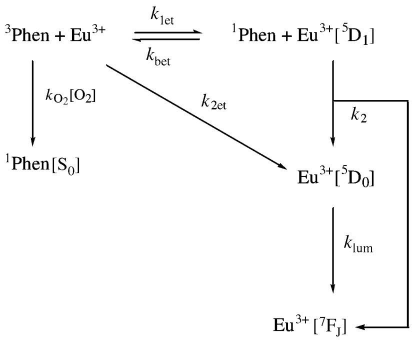
Scheme 1 Suggested pathways for energy transfer in the terbium complex, showing the possibility of back energy transfer and the quenching of the triplet state of the donor by oxygen.

However, in aerated solutions, the luminescence is of much shorter duration, implying that quenching by oxygen becomes a significant factor. Indeed, [HTb·**1**]$^{4+}$ has been demonstrated to act as a singlet oxygen sensitiser, $\Phi_\Delta = 0.2$.[29] Unlike the triplet

Table 1 Observed rate constants for growth and decay of luminescence [a] from $[HLn{\cdot}\mathbf{1}]^{4+}$ (Ln = Gd, Eu, Nd, Tb) and their correlation to the lifetime of the excited phenanthridinium triplet state [b]

		Degassed				Aerated		
Complex	Solvent	$k_{\mathrm{triplet}}/\mathrm{s}^{-1}$	$k_{\mathrm{grow\text{-}in}}/\mathrm{s}^{-1}$	$k_{\mathrm{decay}}/\mathrm{s}^{-1}$	Φ_f^{e}	$k_{\mathrm{triplet}}/\mathrm{s}^{-1}$	$k_{\mathrm{grow\text{-}in}}/\mathrm{s}^{-1}$	$k_{\mathrm{decay}}/\mathrm{s}^{-1}$
$[HGd{\cdot}\mathbf{1}]^{4+}$	H_2O	0.91×10^4	—	—	1	1.5×10^5	—	—
$[HGd{\cdot}\mathbf{1}]^{4+}$	D_2O	1.01×10^4	—	—	—	1.4×10^5	—	—
$[HNd{\cdot}\mathbf{1}]^{4+c}$	H_2O	1.0×10^7	1.8×10^7 (1050)	5.5×10^6 (1050)	0.71	[c]	2.2×10^7 (1050)	5.3×10^6 (1050)
$[HNd{\cdot}\mathbf{1}]^{4+c}$	D_2O	0.83×10^7	0.84×10^7 (1050)	2.9×10^6 (1050)	—	[c]	9.6×10^6 (1050)	2.8×10^6 (1050)
$[HEu{\cdot}\mathbf{1}]^{4+}$	H_2O	2.8×10^5	2.8×10^5 (595) 2.9×10^5 (690)	1.71×10^3 (595) 1.73×10^3 (690) 2.5×10^5 (535)	0.65	3.8×10^5	3.4×10^5 (595)	1.75×10^3 (595) 1.72×10^3 (690) 3.5×10^5 (535)
$[HEu{\cdot}\mathbf{1}]^{4+}$	D_2O	2.6×10^5	2.8×10^5 (595) 2.9×10^5 (690)	0.46×10^3 (595) 0.48×10^3 (690) 2.8×10^5 (535)		3.0×10^5	2.8×10^5 (595) 2.9×10^5 (690)	0.43×10^3 (595) 0.45×10^3 (690) 3.5×10^5 (535)
$[HTb{\cdot}\mathbf{1}]^{4+d}$	H_2O	1×10^3 1.1×10^5	1.8×10^5 (545)	1.14×10^3 (545)	0.91	2.5×10^5	3.3×10^5 (545)	9.8×10^3 (545)
$[HTb{\cdot}\mathbf{1}]^{4+d}$	D_2O	1.16×10^3 1.1×10^5	1.9×10^5 (545)	0.94×10^3		2.8×10^5	2.9×10^5 (545)	8.3×10^3 (545)

[a] Wavelengths (nm) at which emission was monitored are shown in brackets. Errors in measurement of luminescence rate constants are ±10%, while for the transient, triplet, errors are ±20%; in the case of degassed Nd complexes, poor signal to noise ratio gives rise to a ±40% error. [b] Values for k_{triplet} were obtained by observing the time-dependence of the depletion of the $T_n \rightarrow T_1$ transition at 600 nm, by flash photolysis. [c] Due to rapid quenching of the T_1 state, good T–T absorption spectra were not obtained. [d] In degassed solution, a double exponential decay was observed due to repopulation of the triplet state by back energy transfer from the metal centre. [e] Quantum yields of fluorescence are reported relative to the quantum yield for the protonated gadolinium complex.



Scheme 2 Suggested pathways for energy transfer in the europium complex illustrating how energy transfer from the chromophore can occur to both the $^5D_1$ and $^5D_0$ states.

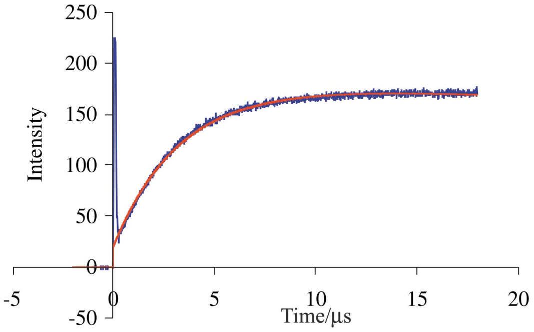


Fig. 1 Time resolved profile of the early part of the lanthanide centred emission for the europium complex in aerated D_2O (blue line). From the fitted curve (red line), it can be seen that there are two components in the rise of the luminescence. One of these is instantaneous, while the second occurs more slowly, following an exponential function. The spike at $t = 0$ arises due to scatter and residual fluorescence from the phenanthridinium chromophore not rejected by the monochromator. $\lambda_{ex} = 355$ nm, $\lambda_{em} = 595$ nm.

states of organic chromophores, these lanthanide ions are not readily quenched by molecular oxygen. For the lanthanide ion lifetime to be reduced by the presence of oxygen there must be a back-energy transfer step to regenerate the organic antenna's excited state, which in turn is quenched by oxygen.

Study of the other lanthanides reveals a far more complex picture. For the europium complex, there are many variables: not only is the Eu^{2+} state accessible in the deprotonated complex, but also there are two emissive states: $^5D_1$ and $^5D_0$. The upper $^5D_1$ state gives rise to short-lived luminescence on a microsecond timescale and decays non-radiatively to the $^5D_0$ state. The lower lying $^5D_0$ state gives rise to the characteristic emission spectrum of the Eu^{3+} ion and the millisecond lifetimes commonly observed for Eu^{3+} complexes. Unlike ytterbium complexes, for which ligand to metal charge transfer (LMCT) can result in metal centred emission,[19,30] the charge transfer pathway for europium complexes represents an inefficient means of sensitising the metal centre.

The lifetimes of the $^5D_1$ state were established by monitoring the emission at 535 nm ($^5D_1 \rightarrow {}^7F_1$). The rate of decay of the $^5D_1$ state was observed to be essentially independent of the degree of sample aeration, and of solvent deuteriation (Table 1). The risetime of the ($^5D_1 \rightarrow {}^7F_n$) luminescence is so short as to be essentially instantaneous using the available instrumentation, ($t_{\mathrm{grow\text{-}in}} < 25$ ns). The relatively slow decay of the $^5D_1$ state has been reported by several other workers who have noted that, unlike the lower $^5D_0$ level, it is not affected by solvent deuteriation: the closeness between the $^5D_0$ and $^5D_1$ states means that the energy transfer processes occur too quickly for intermolecular processes to compete effectively.[12,25,31] The close correlation between the decay of the $^5D_1$ state and triplet state suggests that either energy transfer to the $^5D_1$ state is rate determining (*i.e.* $k_{1et} < k_2$ in Scheme 2), or that there is back energy transfer from the $^5D_1$ state of the metal ion to regenerate the triplet state of the antenna.

The profile of the luminescence from the $^5D_0$ state is far less simple than that of the terbium complex. Analysis of the luminescence at 595 nm ($^5D_0 \rightarrow {}^7F_0$) and 690 nm ($^5D_0 \rightarrow {}^7F_4$) suggests that there are at least two components to the grow-in of the luminescence. One of these has a lifetime that correlates well with the decay of the $^5D_1$ state and antenna triplet state. Fitting the early part of the curve (Fig. 1) appears to show that there is an instant (<50 ns) grow-in, but the presence of a substantial spike (arising from scatter and incomplete stray light rejection by the monochromator) makes it impossible to ascertain this beyond reasonable doubt. Such a rapid grow-in would, if real, be consistent with the intermediacy of the $^5D_1$ state that has been suggested elsewhere.[12] From the data presented in Table 1 it is clear that energy transfer from the triplet state accounts for the grow-in, and the relaxation of the excited state of the metal ion for the decay portion of the curve. It is

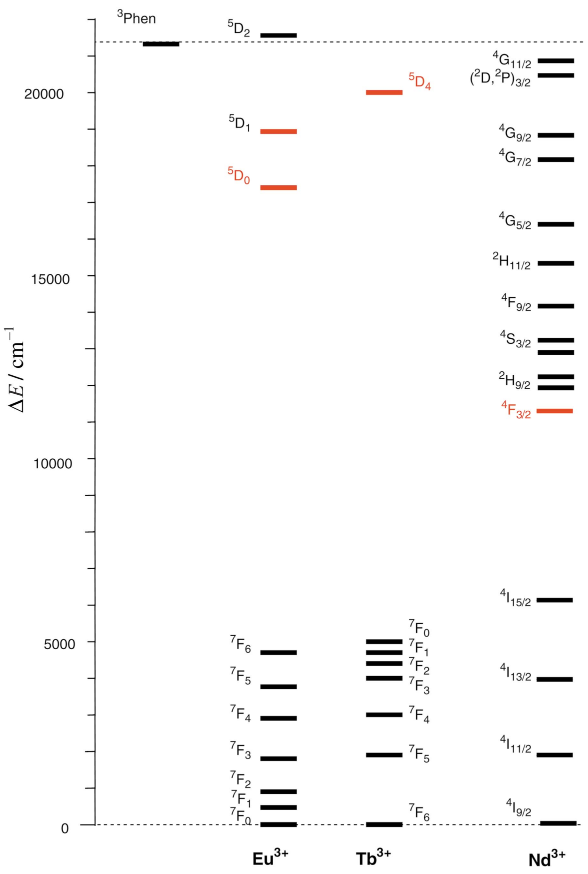


Fig. 2 Energy level diagram, showing the triplet state of the phenanthridinium chromophore and the accessible lanthanide-centred states. It can be seen that the ^{5}D$_4$ state of the terbium ion lies close in energy to the donor triplet, giving rise to facile back energy transfer. For europium, the ^{5}D$_1$ and ^{5}D$_0$ states are both accessible; both are emissive, and the energy transfer processes are more complex than for terbium. For neodymium, there is a manifold of acceptor states, giving rise to highly complex energy transfer. Emission has been observed from the states shown in red.

not possible to make a simple assignment of the relative importance of direct transfer from the triplet state and transfer mediated by the ^{5}D$_1$ state (effectively since $k_{1\mathrm{et}}$ determines the population of ^{5}D$_1$ while $k_{2\mathrm{et}} = k_{1\mathrm{et}}$). These energy transfer pathways are illustrated in Scheme 2.

Finally, the neodymium containing material presents an energy transfer pathway that is much more complex yet that can be modelled more simply. From the data obtained (Table 1), we suggest that the triplet is the most likely mediator of these processes and that energy transfer occurs rapidly to the emissive state of the metal ion. There is no effect of aeration on the emission profile and hence the energy transfer can be explained using Scheme 2, with the important omission of the back-energy transfer step and the additional fact that the decay processes for the levels higher in energy than the emissive ^{4}F$_{3/2}$ occur very rapidly.

The Nd^{2+} oxidation state is not readily accessible (for the complex $E_{1/2} > -2.5$ V) effectively ruling out the possibility of a sequential electron exchange energy transfer, or redox mechanism. Using the energy level diagram in Fig. 2 it can be seen that there are a number of metal-centred excited states lying between the triplet state and the metal-centred emissive state. All of these states can, in theory at least, act as acceptors from the triplet, and as intermediaries in the generation of lower lying states, including the emissive state. This means that the available pathways are too numerous to describe accurately using the methodology outlined in this paper. Kinetic studies on the intermediate states, though possible in solid samples containing Nd^{3+}, are currently precluded in aqueous solution by the available instrumentation. In any case, the large number of states which can be involved in the process will make it largely intractable to conventional methods of data analysis since the large number of contributing processes will make it difficult to distinguish differences in the quality of fit for luminescence growth and decay. For the neodymium complex, the energy transfer processes must be regarded as following a series of pathways analogous to, but more complicated than, those shown in Scheme 2 for the europium complex.

Conclusion

This work confirms the existing hypothesis that triplet mediated energy transfer is the most likely energy transfer pathway in cases where the triplet state is well matched with the acceptor state of the metal ion. It also occurs in cases where alternative energy transfer mechanisms are not thermodynamically feasible.

Experimental

Ligand synthesis

Ligand **1** was synthesised according to established procedures.[26,27] Lanthanide complexes were prepared by reaction of **1** 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.[26,27]

Photophysical measurements

Samples were excited at 355 nm by the frequency tripled output of a Q-switched Nd:YAG laser (Spectra Physics GCR-150-10) operating at 10 Hz. The radiation was delivered to the sample *via* a liquid light guide and typical pulse energies at the sample were in the range 0.1–2 mJ and had a duration of *ca.* 6 ns. Interference from stray 532 and 1064 nm radiation in the excitation beam was avoided by the use of optical filters.

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 onto 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 $T_n \leftarrow T_1$ transition. Deoxygenation of samples was achieved by subjecting the sample to at least three freeze–pump–thaw cycles.

Lanthanide luminescence in the visible region (for europium and terbium complexes) was studied using a similar set-up. Luminescence perpendicular to the laser excitation was collected, collimated and focused onto the entrance slits of the monochromator described above, with the bandpass set to 5 nm. Radiation corresponding to the lanthanide bands under study was selected using the monochromator and detected using a photomultiplier tube (Hamamatsu R928). The signal was captured over 1000 datapoints using a digital oscilloscope (Tektronix TDS320) from which data were transferred to a PC for analysis.

For near-IR luminescence (from neodymium complexes) a slightly different technique was used. The luminescence was

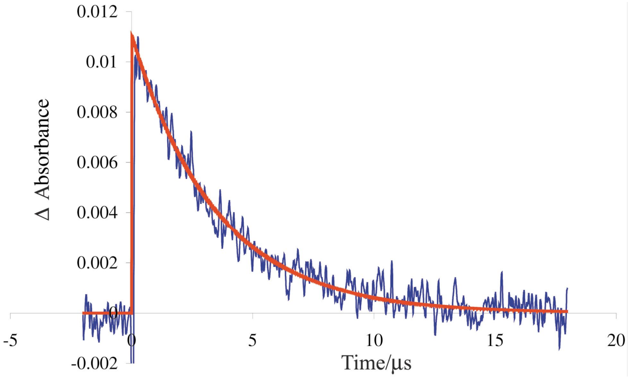


Fig. 3 Fitted decay of the transient triplet–triplet absorption spectrum of the terbium complex in aerated aqueous (H_2O) solution at 298 K. The fit corresponds to a triplet lifetime of 4 μs. $\lambda_{ex} = 355$ nm, $\lambda_{probe} = 420$ nm.

collected at 90° using narrow bandpass interference filters to select radiation of the desired wavelength. For the neodymium complex a 1050 nm interference filter with a FWHM of 25 nm (Comar) was used to monitor the ($^4F_{3/2}\rightarrow{}^4I_n$) transitions, while for ytterbium a 1000 nm interference filter with a FWHM of 25 nm (Comar) was used to detect luminescence from the red edge of the ($^2F_{5/2}\rightarrow{}^2F_{7/2}$) 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 risetime 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), $\tau_F = 2.2$ 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. Quality of fit was determined from the randomness of the residuals and reduced chi-squared (a sample fitted curve is shown in Fig. 3). Unless otherwise stated, fitting to a double exponential function did not yield an improvement in fit.

The growth and decay of the luminescence from europium and terbium complexes were analysed by fitting to a double exponential decay using a spreadsheet package (Excel). In many of the time-resolved emission traces a short-lived spike is observed as the laser fires. This is due to the broadband fluorescence of the phenanthridinium moiety and this part of the data is not included in the curve fitting. To ensure uniformity of fit over different parts of the decay, the fitting process was optimised using several decays recorded over a range of different time-bases. Quality of fit was again determined from the randomness of residuals and chi-squared. A typical fitted curve is shown in Fig. 4.

The luminescence lifetimes from neodymium complexes are comparable with the detector response time, and hence the data for the complexes were analysed by iterative reconvolution of the instrument response function with a single or double exponential decay, the best fit being judged by non-linear least squares analysis. The quality of fit was determined by the randomness of the residuals and chi-squared. A typical fitted response curve is shown in Fig. 5. The details of this approach have been discussed elsewhere.[15]

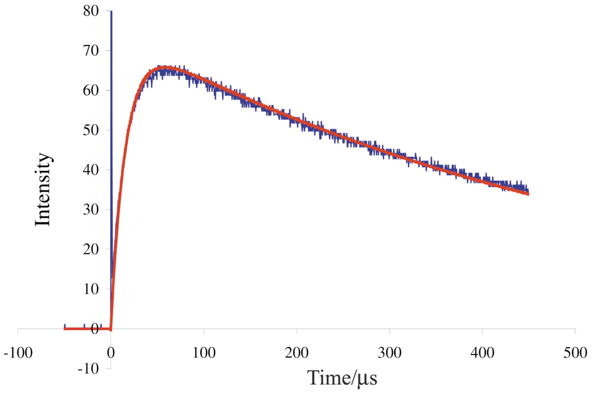


Fig. 4 Fitted temporal profile of the metal-centred luminescence for the terbium complex in aerated D_2O. The risetime of the luminescence is 3.4 μs, while the lifetime of the decay is 0.12 ms. The fitted curve is shown in red and the data in blue. $\lambda_{ex} = 355$ nm, $\lambda_{em} = 545$ nm.

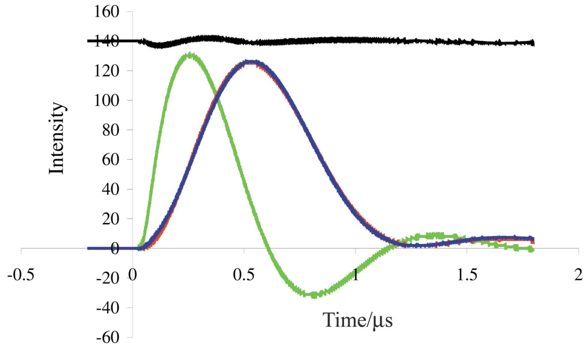


Fig. 5 Temporal profile of the observed signal from the neodymium complex in degassed H_2O solution, fitted by iterative reconvolution with the detector response to give a risetime of 120 ns and a decay lifetime of 340 ns. The data (blue), the fitted curve (red) and residuals (black) are shown. The residuals are offset for clarity. $\lambda_{ex} = 355$ nm, $\lambda_{em} = 1055$ nm.

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