Luminescence from ytterbium(III) and its complexes in solution†

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Time-resolved studies of luminescence from ytterbium in solution are reported offering opportunities for luminescent imaging in the near IR, and allowing the use of a wide range of aromatic antennae to sensitise the metal centre; the luminescence of the solvated ion and of a wide variety of complexes is examined, both by direct excitation and by inter- and intra-molecular energy transfer.

Time-resolved luminescence of lanthanide complexes has been of interest for some years.[1–3] However, interest has centred almost exclusively on the sensitised luminescence of complexes of Eu^{III} and Tb^{III}. Such complexes have the advantage of possessing long luminescent lifetimes, but they are excited by long-wavelength UV radiation over the same range ($\lambda < 360$ nm) as biological molecules. This seriously limits the utility of such complexes for direct *in vivo* applications. An additional problem arises from the relatively large energy gap between the emissive and ground states, which requires the use of aromatic antennae with relatively high triplet state energies to sensitise the metal efficiently.[4]

Lanthanides which emit at longer wavelengths have relatively small energy gaps between the excited and the ground state. This allows the use of antennae with much lower triplet state energies, avoiding the competitive excitation of biological chromophores. Time-resolved luminescence from neodymium has been studied recently by deconvolution of the detector response from a nitrogen-cooled germanium diode, allowing the resolution of lifetimes as short as 30 ns. Emission spectra over the range 800–1800 nm were obtained.[5] Ytterbium is another lanthanide which offers the possibility of long-wavelength luminescence. There is only one excited state and it is luminescent ($^2F_{5/2}$) emitting at 980 nm $^2F_{5/2}$–$^2F_{7/2}$). The Yb^{III} ion is not readily reduced ($E_{1/2} = -1.35$ V, *cf.* -0.35 V for $Eu^{III/II}$), so that competitive photoinduced electron transfer to the Yb from an excited singlet state of an antenna is not likely to occur. Ytterbium luminescence in the solution state has been largely neglected, and reports have concentrated on measurement of the emission spectra of simple systems with no time resolution.[6,7] We have examined the time-resolved luminescence from the ytterbium ion in a variety of solvents by direct excitation or energy transfer from co-dissolved chromophores, and describe examples of intramolecular energy transfer from energy-matched aryl groups in stable complexes with aza-macrocycle based ligands.

Initially, the possibility of intermolecular energy transfer from co-dissolved 4-carboxypropylpyrene ($\lambda_{exc} = 355$ nm, $\tau = 0.34$ μs in 50:50 MeOH–H_2O) and 9-hydroxymethylanthracene ($\lambda_{exc} = 266$ nm, $\tau = 0.81$ μs in MeOH) was investigated. Deconvolution and fitting of the decay curves was used to establish the lifetime of emission from the ytterbium centre. Deconvolution from the detector response was made possible by measuring the detector response using a short-lived pump (in our case the laser dye **DCM**). The lifetime was determined by minimising residuals and reduced χ^2 over a range of lifetimes.‡[5] The lifetimes shown in Table 1 are much longer than those of neodymium in aqueous and methanolic solutions {*cf.* $\tau_{H_2O}[Nd(NO_3)_3] = 30$ ns, $\tau_{MeOH}[Nd(NO_3)_3] = 70$ ns}.[5] These differences relate to the more facile quenching of Nd^{3+} by energy-matched O–H and C–H oscillators.[5]

Demonstration of direct excitation with ytterbium is more difficult. The absorption and emission spectra of ytterbium are very similar owing to the fact that there is only one readily populated excited state of ytterbium. The ytterbium ion was selectively excited using the output from a YAG driven optical parametric oscillator (OPO) producing photons at 970 nm. Emission was observed in the low energy tail of the emission band by using a 1055 nm interference filter with a 40 nm bandpass.§ As can be seen from the data in Table 1, the lifetimes are solvent dependent. The lifetime is longer in strongly coordinating solvents, such as Me_2SO, in which the ligating group stretching harmonics do not correspond well to the energy of the Yb $^2F_{5/2}$ state.

Meshkova and coworkers have reported the use of (2-pyridazo)-2-naphthol in the luminescent determination of ytterbium, but reported no time-resolved studies.[7,8] The 1:1 complex of the azo dye with ytterbium was prepared and the lifetime of the luminescence measured. Deconvolution techniques were employed to obtain the lifetime of the known 3:1 complex[9] with dibenzoylmethane ($\lambda_{exc} = 532$ nm, H_2O). The luminescent lifetime of the pyridazo complex increased from 557 to 1250 ns on solvent deuteriation. This effect occurs

Table 1 Lifetimes of ytterbium complexes and salts in protiated and deuteriated solvents (293 K; errors on lifetimes are ± 15%)

Complex[c]	Solvent	Lifetime[a,b]/μs	λ_{exc}/nm
$Yb(CF_3SO_3)_3$	D_2O	3.95	970
	Me_2SO	5.26	970
	$(CD_3)_2SO$	9.45	970
$Yb(O_2CMe)_3$	D_2O	3.84	970
$Yb(dbm)_3$	CH_3OH	0.50	355
	CD_3OD	7.55	355
	CD_3OD	7.33	970
$[YbL^1]^-$	H_2O	4.53	266
	D_2O	8.90	266
	D_2O^d	9.03	970
$[YbL^2]$	H_2O	1.87	266
	D_2O^d	6.70	266
$[YbL^3]^{3+}$	H_2O	0.70	266
	D_2O	6.18	266
$[YbL^4]^{3+}$	H_2O	0.77	266
	D_2O	7.48	266
$[YbL^5]^{3+}$	H_2O	0.83	266
	D_2O	5.00	266
$[Yb(nta)_2]^{3-}$	D_2O	8.10	970
$[Yb(edta)_2]^{5-}$	D_2O^d	10.9	970
	H_2O	2.18	970
$[Yb(dtpa)]^{2-}$	D_2O^d	8.23	970
	H_2O	0.73	970

[a] For excitation at 970 nm, decay curves were observed using a 1050 nm interference filter with a 40 nm bandpass with the aid of a polariser to block scattered light from the laser source. [b] Lifetimes were independent of the concentration of dissolved oxygen. [c] dbm = dibenzoylmethane anion, nta = nitrilotriacetate and dtpa = diethylenetriamine pentaacetate. [d] The rate constant for luminescent quenching in these cases was shown to be directly proportional to the mole fraction of H_2O present in H_2O–D_2O mixtures.

because the complex formed in solution does not completely encapsulate the metal centre. This allows close diffusion of solvent molecules which quench the luminescence due to coupling between the O–H oscillators and the metal centre. Relaxation *via* O–D oscillators is much less efficient, since only higher harmonics overlap with the metal excited state and the Frank–Condon overlap factor is less favourable. The lifetime of the dibenzoylmethane complex was similarly affected by the nature of the solvent.

In developing probes for long-wavelength luminescence one aim is to provide new methods for the imaging of biological systems. It is necessary that the complexes formed should be kinetically stable and that vibrational quenching by energy-matched oscillators should be minimised. With this in mind, we have investigated the behaviour of complexes of a variety of [12]aneN$_4$ based ligands (L^1–L^5) and selected acyclic chelating agents . The lifetimes of these complexes have been determined

L^1 R = Bn L^2

L^3 Ar = Ph
L^4 Ar = *p*-BrC$_6$H$_4$
L^5 Ar = 1-Naphthyl
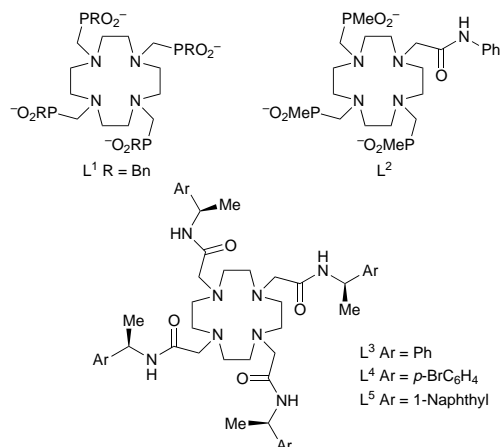
and are reported in Table 1. The longest lifetimes were observed for the complex of the tetrabenzyl phosphinate, [YbL^1]$^-$, (τ_{H_2O} = 4.5 µs; τ_{D_2O} = 9.0 µs independent of [O$_2$]) and may be related to the complete encapsulation of the metal centre by the ligand. Recent crystallographic studies on complexes of L^1 with Y, Eu, Gd and Yb have shown that there are no coordinated water molecules.[10] Thus quenching of the metal centre is greatly reduced, and a relatively long lifetime is observed, with a small difference between the lifetimes in protiated and deuteriated solvents.[13] The residual quenching effect ($\Delta k_{H_2O/D_2O}$ = 1.11 × 10^5 s^{-1}) can be assigned to a contribution from closely diffusing, unbound water molecules. This complex is particularly hydrophobic and probably sets a lower limit on this 'outer-sphere' quenching effect.[2,3] Complexes of the related mono-amide triphosphinate L^2 with Eu and Tb allow a hydrogen-bonded water molecule to approach the metal centre more closely.[11] This leads to an increased difference between the lifetimes in protiated and deuteriated solvents, and results in slightly shorter lifetimes in water than are observed with the tetraphosphinate. The ytterbium complexes of the tetramide ligands L^3–L^5 (ref. 12) and dtpa show considerably shorter lifetimes. The presence of one Yb-bound water molecule in these cases is in accord with published crystallographic information on related structures.[14]

The quenching effect of O–H oscillators on the rate constants for ytterbium luminescence may be fitted to eqn. (1),

$$q = A(k_{H_2O} - k_{D_2O}) - B \qquad (1)$$

where q is the number of water molecules coordinated to the metal, k_{H_2O} the quenching rate constant in H$_2$O, k_{D_2O} that in D$_2$O, A is a constant reflecting quenching sensitivity and B is a term representing the quenching effect of outer-sphere water molecules (0.1 < B < 0.3). The results in Table 1 allow A to be estimated to be 1.0 µs. Similar empirical relationships have been devised for analogous complexes of europium and terbium,[13] and were modified recently in light of the definition of an outer-sphere quenching effect.[2,3]

In summary, stable complexes of ytterbium have been shown to undergo emission in the near-IR on a microsecond timescale. Such behaviour renders ytterbium complexes attractive candidates for luminescent imaging *in vivo*, particularly since time-gating is possible using existing technologies and sensitised excitation is possible in the range 450–600 nm. In addition, the luminescence method allows the assessment of the hydration state of ytterbium complexes in solution. The results of selected *in vivo* imaging experiments using such systems are under investigation.

Footnotes

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