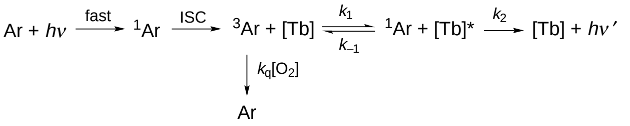
Taking advantage of the pH and pO_2 sensitivity of a luminescent macrocyclic terbium phenanthridyl complex

David Parker* and J. A. Gareth Williams

Department of Chemistry, University of Durham, South Road, Durham, UK DH1 3LE

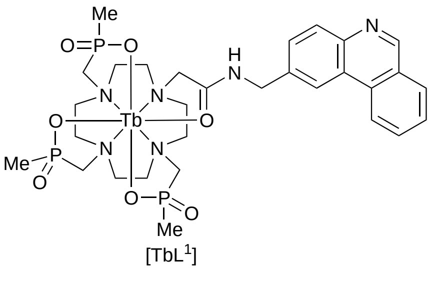
Strong metal-based emission with [TbL^1] in aqueous media occurs in the absence of protons and oxygen; dissolved molecular oxygen quenches the phenanthridyl triplet ($1/K_{SV}$ = 58 Torr O_2) but back-energy transfer to the organic triplet occurs efficiently only with the excited protonated complex ($pK_a'' = 5.7$).

Responsive luminescent probes that signal the presence of molecules or ions in aqueous solution are of current interest because of their application to the analysis of biological or environmental samples.[1] There have been some recent reports of pH responsive luminescent lanthanide complexes[2] in which the delayed luminescence from the metal allows time-gating in monitoring the emission, so that problems such as autofluorescence and Rayleigh-scattering are obviated. As a consequence of the low absorption coefficients associated with lanthanide f–f transitions, a sensitising chromophore needs to be built in to such complexes, preferably one that can efficiently absorb incident light at wavelengths greater than 340 nm.[3] Several different aromatic chromophores can be used under ambient conditions, provided that they possess a triplet energy *ca.* 1500 cm^{-1} greater than that of the emissive lanthanide state. If this condition is not fulfilled, then competitive thermally activated back-energy transfer will occur and the metal-based luminescence will become sensitive to the presence of dissolved O_2.[3,4] Such a situation is depicted in Scheme 1, wherein molecular oxygen may quench the aromatic triplet excited state and similarly affect the lanthanide luminescence, depending on the relative magnitude of k_1, k_{-1}, $k_q[O_2]$ and k_2. Of course, sensors for molecular oxygen that operate on the quenching of an aromatic triplet excited state are well known and include polyaza ruthenium and palladium porphyrin complexes,[5] where values of k_q are typically of the order of 1.5×10^9 $dm^3\ mol^{-1}\ s^{-1}$.[6]



Scheme 1

The complex [TbL^1]† was prepared by reaction of the triphosphinate-phenanthridine ligand H_3L^1 reported previously[2a] with $Tb(OAc)_3$ in water, followed by purification by alumina chromatography. The fluorescent emission from the phenanthridine group at 403 nm was monitored together with the delayed luminescence from the terbium centre (λ_{em} = 547 nm) as a function of pH (Fig. 1), following excitation at the isosbestic wavelength (304 nm). The ligand-based fluorescence increases in intensity by a factor of 3 as the phenanthridyl nitrogen is protonated, consistent with the suppression of photoinduced electron transfer associated with protonation. The apparent pK_a was 4.2(1), in reasonable agreement with the value of 4.4(1) obtained with the analogous europium complex.[2a] The metal-based luminescence showed a luminescence enhancement of 125 but in the opposite sense. The neutral complex was highly emissive (φ_{H_2} = 0.025, τ_{H_2O} = 0.98 ms) and the protonated complex was not ($\varphi_{H_2O} = 9 \times 10^{-4}$, $\tau_{H_2O} < 0.1$ ms).



[TbL^1]

The phenanthridine triplet energies were estimated from the phosphorescence spectra of [GdL^1] at 77 K in an MeOH–EtOH glass and were found to be 22 000 cm^{-1} for the unprotonated form and 21 300 cm^{-1} for the protonated complex. These values are 1500 and 800 cm^{-1} higher than the energy of the Tb^{3+} emissive state ($^5D_4$, 20 500 cm^{-1}), respectively. Deactivation of the terbium complex by back-energy transfer to the organic triplet is thus much more significant for the protonated form. The excited-state pK_a of 5.75(10) for [TbL^1] is close to the pK_a reported for the triplet state of phenanthridine itself (5.7),[7] and is consistent with the establishment of an equilibrium between the triplet phenanthridyl excited state and the terbium $^5D_4$ excited state (Scheme 1). Further support for this hypothesis came from the effect of varying the partial pressure of O_2 in the sample. Removal of dissolved oxygen led to an increase in the overall quantum yield $\{\varphi = 0.12,\ pO_2 = 0,\ (H_2O)\}$ and a concomitant increase in the terbium luminescent lifetime [τ_{H_2O} = 1.82 ms (pO_2 = 0)].† The triplet phenanthridyl excited state is quenched by O_2, and the extent of quenching is a function of dissolved [O_2] and is reported by changes in the terbium lifetime and emission intensity.‡ The N-methylated complex [TbL^2]$^+$ (prepared by alkylation in MeI–MeCN at 20 °C) also behaved as an oxygen sensor, with pO_2 ($S = \frac{1}{2}$) of 58 Torr, and an associated linear Stern–Volmer plot (Fig. 2).

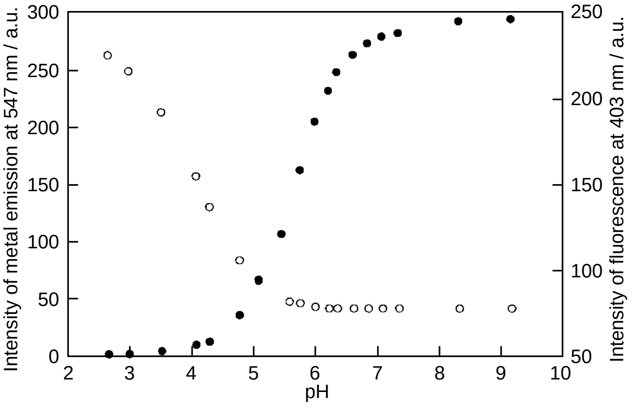


Fig. 1 Delayed luminescence emission intensity (●) and ligand-based fluroescence intensity (○) as a function of pH for [TbL^1], following pulsed excitation at 304 nm (isosbestic wavelength) and using a delay time of 0.1 ms [293 K, I = 0.1 (NMe_4ClO_4)]

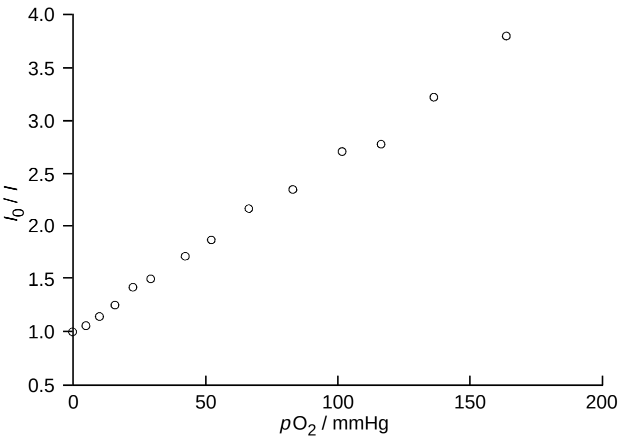


Fig. 2 Stern–Volmer plot of I_o/I *vs.* pO_2 for $[TbL^2]^+$ [293 K, I = 0.1 NMe_4ClO_4)]. Similar behaviour was exhibited by $[Tb(HL^1)]^+$.

The luminescence of this N-alkylated complex was independent of pH in the range 2–9.

The complex $[TbL^1]$ possesses several attractive sensory features. It exhibits a pH dependence in aqueous solution that embraces the range 3–7, because of the ability to examine either the ligand based fluorescence ($pK_a' = 4.2$) or the metal-based phosphorescence ($pK_a'' = 5.75$). Moreover, the luminescent enhancement factors for the former are at least 500, when an excitation wavelength of 375 nm is used, because the unprotonated complex does not absorb at this wavelength {*cf.* $\varepsilon_{375} = 3 \times 10^3$ dm^3 mol^{-1} cm^{-1} for $[Tb(HL^1)]^+$}, as was found for the analogous complex $[EuL^1]$.[2a]

The change in the lifetime of the terbium excited state upon protonation ($\Delta\tau_{H_2O}$ = 1 ms), means that lifetime measurements, rather than luminescence intensity measurements, may be used to characterise the pH dependence over the range 5–7, which may be usefully applied to biological systems. In addition, in the pH range 2–9 the sensitivity of the N-methylated salt to dissolved oxygen may be harnessed to determine pO_2 in aqueous solutions, measuring the lifetime or emission intensity from the Tb excited state. Finally, given that strong terbium luminescence (Table 1), occurs only when both acid and O_2 are not present, the complex $[TbL^1]$ could be construed as behaving as a molecular NAND logic gate[8] with H^+ and O_2 as the 'inputs' and delayed terbium luminescence as the signal 'output'.

Table 1 Lifetimes and quantum yields for lanthanide complexes (H_2O, 293 K, λ_{exc} 304 nm)[a]

Parameter	$[TbL^1]$	$[TbHL^1)]^+$	$[EuL^1]^{b,c}$	$(Eu(HL^1)]^+$
φ_{aer}	2.5×10^{-2}	9.1×10^{-4}	0.011	0.03
$\varphi_{degassed}$	0.12	4.6×10^{-2}	0.011	0.03
$\tau_{H_2O_{aer}}$/ms	0.98	*ca.* 0.1	0.71	0.71
$\tau_{H_2O_{degassed}}$/ms	1.82	0.83	0.71	0.71

[a] Lifetimes were obtained using a Perkin-Elmer LS50B (gate time 0.1 ms); [b] Data from ref. 2(*a*); [c] In D_2O, τ = 1.92 ms for the free and 1.95 ms for the protonated complex.

We thank EPSRC for grant support.

Footnotes and References

* E-mail: david.parker@dur.ac.uk

† *Selected data* for $[TbL^1]$: *m/z* (ESMS, H_2O): 839.4 (M^+ + 1); δ_P(pD 5.9) 648, 621, 484. Found: C, 38.4; H, 5.99; N, 7.31. $C_{30}H_{44}N_5O_7P_3Tb\cdot5H_2O$ requires: C, 38.8; H, 5.82; N, 7.54%.

‡ A laser flash photolysis study of several lanthanide complexes of a related enantiopure tetraamide ligand, incorporating the same pendant phenanthridine chromophore, has confirmed that in deoxygenated solution, the rate of decay of the phenanthridyl triplet matched the rate of growth of the Tb emission, *i.e.* in Scheme 1, $k_1 = 2 \times 10^5$ s^{-1}, k_2 = 1060 s^{-1} and $k_q = 0.7 \times 10^9$ dm^3 mol^{-1} s^{-1}. Full details will be reported elsewhere.

1 A. P. de Silva, H. Q. N. Gunaratne, T. Gunnlaugsson, A. J. M. Huxley, C. P. McCoy, J. T. Rademacher and T. R. Rice, *Chem. Rev.*, 1997, **97**, 1515.
2 (*a*) D. Parker, K. P. Senanayake and J. A. G. Williams, *Chem. Commun.*, 1997, 1777; (*b*) A. P. de Silva, H. Q. N. Gunaratne and T. E. Rice, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 2116.
3 N. Sabbatini, M. Guardigli and J.-M. Lehn, *Coord. Chem. Rev.*, 1993, **123**, 201.
4 D. Parker and J. A. G. Williams, *J. Chem. Soc., Dalton Trans.*, 1996, 3613; A. Beeby, D. Parker and J. A. G. Williams, *J. Chem. Soc., Perkin Trans. 2*, 1996, 1565.
5 A. Mills, *Platinum Met. Rev.*, 1997, **41**, 115; A. Mills and A. Thomas, *Analyst*, 1997, **122**, 63; I. Klimant and O. S. Wolfbeis, *Anal. Chem.*, 1995, **67**, 3160; P. Hartmann and W. Trettnak, *Anal. Chem.*, 1996, **68**, 2615.
6 At amospheric pressure $[O_2] = 0.29 \times 10^{-3}$ mol dm^{-3} in water: S. L. Murov, I. Carmichael and G. L. Hug, *Handbook of Photochemistry*, Marcel Dekker, New York, 2nd edn., 1993.
7 E. Van der Donckt, R. Dramaix, J. Nasielski and C. Vogels, *Trans. Faraday Soc.*, 1969, **65**, 3258.
8 For examples of other fluorescent 'logic' gates see *inter alia*: A. P. de Silva, H. Q. N. Gunaratne and C. P. McCoy, *J. Am. Chem. Soc.*, 1997, **119**, 7891; A. Gedi, V. Balzani, S. J. Langford and J. F. Stoddart, *J. Am. Chem. Soc.*, 1997, **119**, 2679.

Received in Cambridge, UK, 28th October 1997; 7/07754H