Switching 'on' the luminescence of one metal ion with another: selectivity characteristics with respect to the emitting and triggering metal

A. Prasanna de Silva, H. Q. Nimal Gunaratne, Terence E. Rice and Siobhan Stewart

School of Chemistry, Queen's University, Belfast, UK BT9 5AG

Complexes 1a·Eu^{III} and 1b·Eu^{III}, but not 1a·Tb^{III} and 1b·Tb^{III}, display strong 'off–on' switching of delayed luminescence with alkali cations; the switching efficiency of 1b·Eu^{III} is stronger with K$^+$ rather than Na$^+$.

Light emission of many organic molecules[1] and supermolecules[2] can be triggered by metal ions. This forms the basis of fluorescent sensors for metal ions.[3] Conversely, metal-centred emission can be induced by non-metal guests in a few carefully designed instances.[4] The third combination, that of organic molecular emission arising from the complexation of organic species, is also being developed in several laboratories.[5] The final combination of this quartet, that of metal ion-triggered metal-centred emission, is currently unavailable according to the best of our knowledge.[6] Metal-containing, but not metal-centred, emissive systems have been switched 'on' or 'off' by various species including metal ions.[7] We now fill this gap with examples of europium(III) complexes whose luminescence is switched 'on' with alkali metal ions.[8] We also note an interesting selectivity aspect in that the corresponding terbium(III) complexes are relatively immune to alkali cation-induced switching. Following this proof of principle, it will be possible to design delayed luminescent[9] sensors for metal ions of medical and environmental interest which operate in aqueous solution. Many suitable metal ion receptors[10] and lanthanide lumophores[11] are available[6] for incorporation into this design.

The following systems are designed as delayed luminescent versions of fluorescent PET (photoinduced electron transfer) sensors[2b,3a] for alkali cations.[12] Ligands **1a**,**b** were synthesized from the known compound 4,4″-bis(*p*-tolyl)-6,6″-bis-(methoxycarbonyl)-2,2′:6′,2″-terpyridine[13] **1c** by bromination with *N*-bromosuccinimide and amination with the appropriate monoazacrown ether.† The binding of **1a**,**b** with Tb^{III} or Eu^{III}, when monitored by UV absorption spectroscopy, fits a 1:1 binding isotherm.[14] The conformational locking of the terpyridyl diester by the lanthanide ion leads to the growth of long-wavelength bands upto 340 nm. Monitoring of the complexation process in **1c** by ^{1}H NMR spectroscopy shows Eu^{III}-induced upfield displacement of the methoxycarbonyl signal by 0.6 ppm as well as displacements of the other signals by upto 1.0 ppm. Much higher lanthanide ion concentrations than those employed here are needed before they bind to the azacrown moieties of **1a**,**b**.[10b] Binding of alkali cations to the azacrown units of **1a**·Eu^{III} and analogues leads to small but measurable hypsochromic shifts in their UV absorption spectra. These allow determination of the binding constants β_{Na} and β_K, which are in close agreement with literature values for the binding of alkali cations to unsubstituted monoazacrown ethers.[10b]

Most importantly, the delayed luminescence of **1a**·Eu^{III} and **b**·Eu^{III} is enhanced by over an order of magnitude when the azacrown units are bound by alkali cations (Fig. 1). Luminescence quantum yields reach values as high as 0.47 (for **1a**·Eu^{III}–K$^+$ in MeOH). Such switching 'on' of luminescence arises from the alkali cation-induced suppression of PET from the azacrown nitrogen to the lumophore.[12] Eu^{III} complexes are known to participate in PET processes.[15] It is notable that K$^+$ produces the larger luminescence enhancement (LE) with **1b**·Eu^{III} in spite of its lower charge density than Na$^+$. This is probably because the loosely fitting Na$^+$ moves away from the soft nitrogen towards the harder oxygens, thus lessening the PET suppression. Analysis of these luminescence intensity (I_{Lum}) – $(M)_{total}$ profiles (M = Na or K) gives β_{Na} and β_K values which are gratifyingly close to the values determined absorptiometrically. The average number of lanthanide-bound MeOH molecules[16] (q), determined by comparison of luminescence lifetimes (τ) in MeOH and MeOD, is two. This suggests that the usual minimum coordination number of nine[17] is made up by two counterions, which is reasonable given the substantial ion-pairing in the moderately dielectric medium and the tripositive nature of **1a**·Eu^{III} and analogues.

The immeasurably weak delayed luminescence of complexes **1a**·Tb^{III} and **b**·Tb^{III} is not noticeably enhanced by Na$^+$ or K$^+$ ions. However protons, the strongest PET suppressants of all,

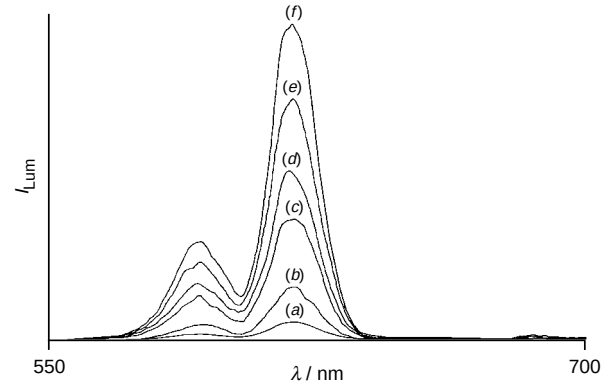
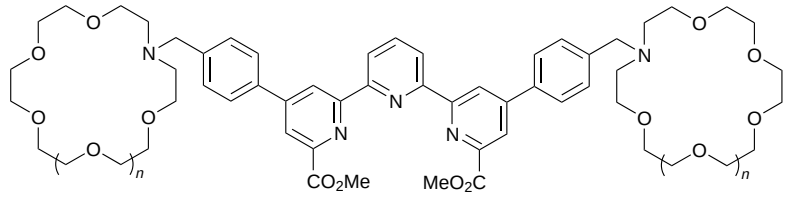


Fig. 1 Delayed luminescence emission spectra of **1b**·Eu^{III} upon addition of K$^+$. The spectra are uncorrected for the wavelength response of the detector which degrades rapidly at wavelengths longer than 650 nm. pK_{total} = (*a*) ∞, (*b*) 5.0, (*c*) 4.4, (*d*) 4.2, (*e*) 4.0 and (*f*) 3.4.



1a n = 0
b n = 1

Table 1 Optical and ion-binding parameters[a]

Parameter	**1a**·Eu^{III}	**1b**·Eu^{III}	**1a**·Tb^{III}	**1b**·Tb^{III}
λ_{Abs}/nm (log ε)[b]	294 (4.88)	294 (5.02)	294 (4.94)	294 (5.03)
	333 (4.59)	333 (4.80)	333 (4.66)	333 (4.76)
	345 (4.58)	345 (4.77)	345 (4.76)	345 (4.73)
log β[c]	4.9	4.8	4.7	4.9
ϕ_{Lum}[d]	0.027	0.026	< 0.001	< 0.001
log β_{Na}[c]	2.5,[e] 2.3[f]	2.9,[e] 2.6[f]	—,[e,g] 2.4[f]	—,[e,g] 2.4[f]
log β_{K}[c]	2.2,[e] 2.3[f]	4.3,[e] 4.6[f]	—,[e,g] 2.5[f]	—,[e,g] 4.3[f]
$\phi_{Lum\cdot Na}$ (LE_{Na})[h]	0.32 (12)	0.23 (9)	< 0.001 (—)[g]	< 0.001 (—)[g]
$\phi_{Lum\cdot K}$ (LE_{K})[h]	0.20 (7)	0.47 (18)	< 0.001 (—)[g]	< 0.001 (—)[g]
$\phi_{Lum\cdot H}$ (LE_{H})[h]	0.47 (17)	0.46 (18)	0.016 (> 16)	0.014 (> 14)
τ/ms[i]	0.67	0.66	0.32	0.33
q[j]	2.0	1.9	2.3	2.0

[a] **1a** or **1b** 10^{-6} M in MeOH with $TbCl_3^{III}$ or $EuCl_3^{III}$ (3×10^{-5} M) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (10^{-4} M) as proton scavenger, except when $\phi_{Lum\cdot H}$ (LE_H) values are being determined. Na^+ and K^+ added as acetates. H^+ added as trifluoroacetate. The λ_{Abs} (log ε) values for **1a** and **1b** are 240 (5.05), 276sh (4.86) and 324sh (4.07), and 240 (5.14), 276sh (5.03) and 324sh (4.32) nm, respectively. Lanthanide luminescence emission spectra were obtained by excitation at the isosbestic wavelength of 340 nm, with a delay time of 0.1 ms and a gate time of 1.5 ms for all four lanthanide complexes. [b] Extinction coefficient ε in units of $M^{-1}\,cm^{-1}$. [c] The binding constant for the **1**–lanthanide (Ln) interaction was obtained by analysing absorbance (A) − (Ln) profiles according to: $\log[(A - A_{min})/(A_{max} - A)] = \log[(Ln)_{total} - (\mathbf{1})_{total}(A - A_{min})/(A_{min})/(A_{max} - A)] + \log\beta$ (ref. 14). Log $\beta_{Na\ or\ K}$ values for the **1**·Ln–Na or **1**·Ln–K interaction were similarly determined by analysing absorbance − $(M)_{total}$ profiles according to: $\log[(A - A_{min})/(A_{max} - A)] = \log[(M)_{total} - (\mathbf{1}\cdot Ln)_{total}(A - A_{min})/(A_{max} - A)] + \log\beta_{Na\ or\ K}$. M = Na^+ or K^+. Luminescence intensity can be used instead of absorbance as the dependent variable for determining log $\beta_{Na\ or\ K}$. [d] Luminescence quantum yields obtained by comparison with the Eu^{III} complex of the carboxylate form of **1c** (ref. 13) and the Tb^{III} complex with EDTA and sulfosalicyclic acid (ref. 19). [e] Luminescence measurements. [f] Absorbance measurements. [g] Spectroscopic change is too small to permit measurement. [h] Ion (Na^+, K^+ or H^+) induced luminescence enhancement factor, *e.g.* $LE_{Na} = \phi_{Lum\cdot Na}/\phi_{Lum}$. [i] Determined by the first-order decay expression for luminescence intensity. τ values are given as an average (±0.01 ms) in the presence of Na^+, K^+ or H^+ for Eu^{III} complexes. Only the value in the presence of H^+ is accessible for Tb^{III} complexes. [j] q values are given as an average (±0.1) in the presence of Na^+, K^+ or H^+ for Eu^{III} complexes. Only the value in the presence of H^+ is accessible for Tb^{III} complexes.

produce measurable, but still small, luminescent quantum yields of 0.016 and 0.014, respectively. The weakness of this emission is probably due to an additional deactivation channel of the Tb^{III} $^5D_4$ emissive state. The triplet level of the complexed ligand, as measured from the 77 K phosphorescence maximum of **1c**·Gd^{III}, lies only 4.1 kcal mol^{-1} (1 kcal = 1 kJ) above the Tb^{III} $^5D_4$ state, which means that rapid back energy transfer occurs under ambient conditions.[18] This leads to the complexed ligand triplet and subsequent de-excitation *via* the ligand state manifold. Such back energy transfer is absent in **1a**·Eu^{III} and **1b**·Eu^{III} owing to the much larger triplet Eu^{III} $^5D_0$ state energy gap of 13.2 kcal mol^{-1}.

In conclusion, metal-triggered metal-centred emission has been demonstrated. The selectivity determinants are (i) the ability of the triggering metal to block PET from an azacrown nitrogen and (ii) the energy separation of the ligand triplet and the metal emitting state.

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Footnotes and References

* E-mail: a.desilva@qub.ac.uk

† *Selected data* for **1a**; *m/z* 963;4625 ($C_{53}H_{65}N_5O_{12}$ requires 963.4630); δ_H 2.84 (t, 8 H, NCH_2CH_2O), 3.57–3.69 (m, 32 H, CH_2O), 3.76 (s, 4 H, $ArCH_2$), 4.10 (s, 6 H, CO_2CH_3), 7.51–8.98 (m, 15 H, Ar*H*). For **1b**: *m/z* 1051.51492 ($C_{57}H_{73}N_5O_{14}$ requires 1051.51540); δ_H 2.82 (t, 8 H, NCH_2CH_2O), 3.60–3.72 (m, 40 H, CH_2O), 3.75 (s, 4 H, $ArCH_2$), 4.10 (s, 6 H, CO_2CH_3), 7.53–8.99 (m, 15 H, Ar*H*).

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