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Exploring energy transfer between pyrene complexes and europium ions- potential routes to oxygen sensors

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Pyrene chromophores are shown to exhibit reversible energy transfer to europium ions, resulting in oxygen dependent lanthanide luminescence. Two different pathways can give rise to oxygen dependence: rapid reversible energy transfer between the T_1 state and the emissive state, or slow T_1-$^5D_0$ energy transfer on the timescale of triplet state quenching.

Lanthanide luminescence has been widely deployed in imaging and assay,[1, 2] since the long-luminescence lifetimes associated with such luminescence can readily be separated from background signals using time-gating techniques.[3] Generally, complexes used for such applications also incorporate a sensitizing chromophore to circumvent the problem of low absorption coefficients for f-f transitions. These systems require the effective absorption properties of organic molecules or d-block metal complexes to be combined with the emissive properties of the lanthanide.[2, 4, 5]

In most such complexes, energy transfer occurs via the triplet state of the sensitizing chromophore,[4, 6] though LMCT states have been shown to mediate energy transfer in ytterbium complexes.[7] Normally, energy transfer from the triplet to the lanthanide is rapid and irreversible, meaning that the luminescence intensity and lifetime is essentially independent of oxygen concentrations. However, in cases where thermal repopulation of the triplet state from the lanthanide emissive state is facile (as shown in Scheme 1), the intensity of the lanthanide emission becomes dependent on the concentration of dissolved oxygen.[8] This effect has been exploited in oxygen responsive molecular probes. While most such probes exploit terbium-centred luminescence,[9] the effect can be observed for any lanthanide ion.[10]

We recently realised that the triplet energy of the pyrene monomer (16890 cm^{-1})[11] would be compatible with engineering oxygen-responsive behaviour in europium containing systems, and now report a study of the pyrene-sensitised luminescence from a range of europium complexes. Here, we show how the oxygen-responsive properties of such complexes can be tuned by varying the chromophore-lanthanide separation. We have previously reported a range of lanthanide complexes with pyrene antenna chromophores: these exhibited near-IR luminescence from neodymium and ytterbium ions.[12, 13]

We initially employed a strategy of ternary complex formation in order to validate the viability of pyrene as a sensitising chromophore for oxygen sensitive lanthanide emission. In previous studies with Yb and Nd complexes, an excess of pyrene had been employed for sensitisation. However, we found that adding an equimolar amount of pyrene acetic acid to a 10^{-5} M solution of **Eu.L^1** in methanol was sufficient to achieve metal centred emission. As anticipated, the pyrene chromophore was able to sensitise the Eu complex in an oxygen dependent manner (Figure 2(a)) showing a 3.8-fold decrease in emission intensity (λ_{Em} = 616 nm) when moving from degassed to aerated conditions. These results are consistent with rapid and reversible energy transfer from pyrene to the europium excited state. Furthermore, since energy transfer through space falls off with the sixth power of the donor-acceptor separation, we can be confident that any lanthanide emission will arise as a consequence of assembly.

The next step in the study required us to assess the oxygen response of covalently bound pyrene chromophores. We resolved to study the luminescence behaviour of **L^3** and **L^4**.

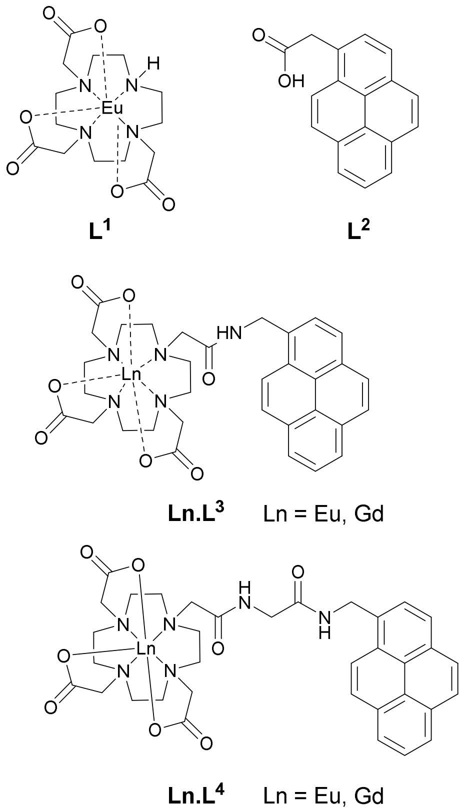


Figure 1 Structures of the Eu- and Gd-pyrene complexes investigated in this study.

L^3 (Figure 1) was synthesised as previously reported.[12] The europium and gadolinium complexes were prepared by reaction of **L^3** with europium or gadolinium trifluoromethanesulfonate respectively. **L^4** serves as an analogue with greater chromophore lanthanide separation. 2-chloro-N-(2-oxo-2-((pyren-1-ylmethyl)amino)-ethyl)acetamide was synthesised by coupling of chloroacetyl glycine to pyrenemethylamine using BOP and DIPEA in DMF, followed by alkylation of DO3A tris tert-butyl ester. TFA deprotection and complexation afforded **Eu.L^4** and **Gd.L^4**. (see Supporting Information). The NMR spectra of the europium complexes (see Supporting Information) differ in that the peaks observed for protons in **Eu.L^3** are much broader than those in **Eu.L^4,** suggesting that exchange between diastereoisomers is more facile in the former, presumably as a consequence of the bulky pyrenyl group being close to the lanthanide binding site.

The steady state luminescence spectra of **Eu.L^3** and **Eu.L^4** in normoxic and anoxic solution are shown in figure 2(a) and(b).

From these, it is clear that there is a dramatic change in behaviour between the two complexes, as well as between aerated and degassed solution. This is borne out by the luminescence lifetimes observed in aerated and degassed solution (Table 1).

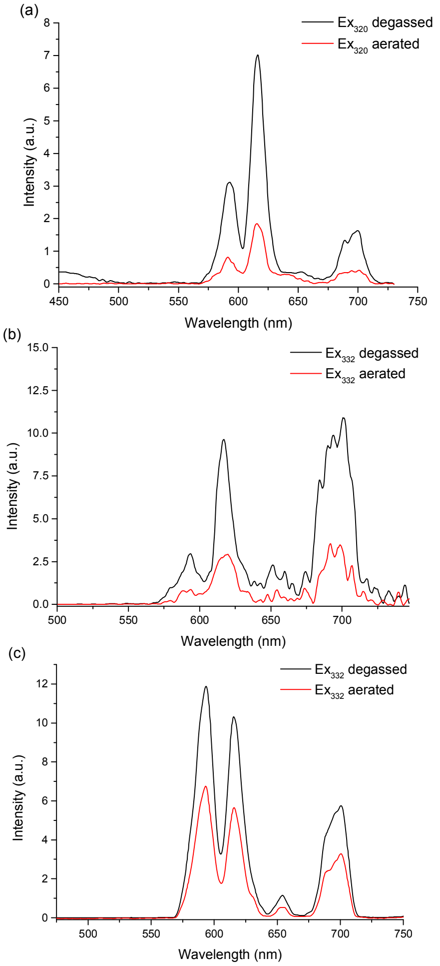


Figure 2 Emission spectra of (a) the ternary **Eu.L^1.L^2** complex (λ_{ex} = 320 nm) (b) **Eu.L^3** (λ_{ex} = 332) and (c) **Eu.L^4** (λ_{ex} = 332) in MeOH under degassed (black) and aerated (red) conditions.

In the case of **Eu.L^3**, there is a strong response to changes in oxygen concentration, coupled with a dramatic change in luminescence lifetime. However, the luminescence is weak- even in degassed solution.¶

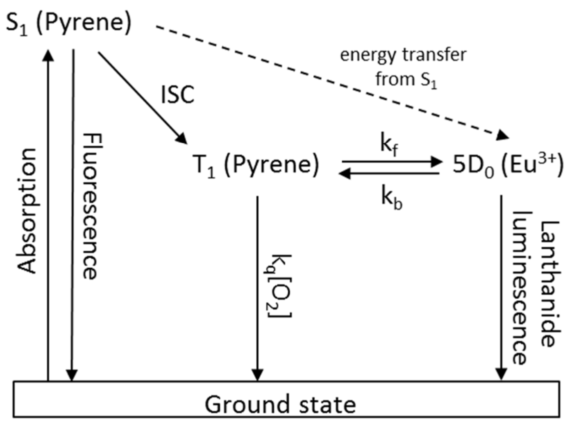
By contrast, and perhaps surprisingly, **Eu.L^4** displays a reduced response to changes in oxygen concentration, while the luminescence lifetimes obtained in aerated and degassed media are within error of one another.
If we are to attempt to explain these observations, we must consider the available pathways for energy transfer in the lanthanide complex. Scheme 1 shows the energy transfer cascade involved in sensitised emission. In such a system, the excited singlet and triplet states of the pyrene chromophore (S_1 and T_1) are potentially both involved in energy transfer to the $^5D_0$ state of europium, though transfer via the triplet state generally predominates. Where repopulation of the triplet state from $^5D_0$ is thermally achievable, both forward energy transfer (with rate constant k_f) and back energy transfer (with rate constant k_b) must be considered.

Table 1 Luminescence lifetimes for the complexes in aerated and degassed methanolic solution (λ_{ex} = 332 nm, λ_{em} = 616 nm)

Complex	τ/ms aerated	τ/ms degassed
Eu.L$_1$.L$_2$	0.40	0.43
Eu.L$_3$	0.55	0.79
Eu.L$_4$	0.31	0.30

Furthermore, all the intermediate states in the cascade can be quenched by other processes. In the case of pyrene, the S_1 state can be quenched by fluorescence (including via excimer formation), while the T_1 state is quenched by collisional quenching by oxygen.

We probed the involvement of the singlet state in energy transfer to the lanthanide by carrying out measurements of the singlet state lifetime using time correlated single photon counting methods. Since gadolinium (III) has no low lying excited states that can be populated from either pyrene excited state, any difference between the lifetime of the S_1 states of the gadolinium and europium complexes can be assigned to the existence of an energy transfer pathway directly from the singlet state. In the case of **Ln.L^3** (Ln = Gd and Eu), the lifetimes of both singlet excited states were within error of one another (10 ± 1 ns). However, for **Ln.L^4**, significant differences were observed: **Gd.L^4** exhibited a luminescence lifetime of 9 ns, while that of **Eu.L^4** was 7 ns. This implies some degree of energy transfer from the singlet state in **Eu.L^4**: the quantum efficiency of energy transfer from the singlet state can be calculated as 0.22, though the actual value may vary widely given a 10% error on the lifetime determination. Thus in both complexes, it is clear that energy transfer via the triplet state is the dominant pathway for energy transfer to the lanthanide.



Scheme 1 Energy transfer cascade for sensitised emission of **Eu.L^3** and **Eu.L^4**.

When considering the effect of oxygen, it is also necessary to consider the differences in the effect upon the lifetime of the lanthanide luminescence. In the case of **Eu.L^3**, there is a significant difference between the lifetimes in aearated and degassed solution, implying that pre-equilibrium is achieved between the T$_1$ state and the ^{5}D$_0$ state, and that quenching of both proceeds via two alternative pathways. For the relaxation of these two states to the ground state (if we assume that energy transfer to the system from the singlet state is rapid and irreversible and that pre-equilibrium is established), *k*, the observed rate constant for the luminescence, will be given by

$$k = \frac{k_f}{k_f + k_b} . k_{Eu} + \frac{k_b}{k_f + k_b} . k_q[O_2] \qquad (1)$$

Where the k$_{\mathrm{Eu}}$ is rate constant for lanthanide emission to the ground state, k$_f$ and k$_b$ are the rates of forward and back energy transfer between T$_1$ and ^{5}D$_0$ and and k$_q$[O$_2$] is the product of the rate constant for collisional quenching and the oxygen concentration. In the case of **Eu.L^3**, these assumptions are likely to be valid, and the second term will vanish in degassed solution; giving rise to a longer observed lifetime.

However, the case is altered for **Eu.L^4**. In this system, the absence of a change in lifetime, coupled with a significant change in signal intensity between degassed and aerated solution, imply that the assumption of pre-equilibrium cannot be valid. In this case the longer spacer will ensure that the rates of forward and backward energy transfer between the donor and the acceptor will be much slower in **Eu.L^4** than in **Eu.L^3** given the r^{-6} dependency of the Förster energy transfer mechanism.

Under such circumstances, energy transfer from T$_1$ to the lanthanide will be slow (though it is clearly not rate determining). Furthermore, in aerated solution, the triplet is being quenched before significant T$_1$-^{5}D$_0$ energy transfer can occur. Since the rate of back energy will also be slow, population of the ^{5}D$_0$ state directly from the S$_1$ state (as inferred above) will give rise to lanthanide luminescence *even if no energy transfer occurs from the triplet*.

In conclusion, these results show that there is more than one way of achieving oxygen dependent luminescence from a lanthanide complex. Furthermore, small changes in structure and chromophore-lanthanide separation can result in very different energy transfer processes being observed. In many ways, the use of systems in which relatively slow energy transfer allows quenching of the triplet before energy transfer can occur offers an appealing alternative to the traditional approach of exploiting close energy matches. This alternative strategy means that it may no longer be necessary to rely upon energy matches between chromophores and lanthanides to achieve oxygen dependent effects. We are currently exploring this prospect further.

Notes and references

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¶ Quantum yields for lanthanide emission were not determined, as a consequence of overlap between emission from the lanthanide and from pyrenyl in the total emission spectra.

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Oxygen dependent luminescence in a pyrene appended europium complexes is shown to arise in two different ways. The nature of the pathway can be controlled by varying the lanthanide-pyrene separation.