Anthracene as a sensitiser for near-infrared luminescence in complexes of Nd(III), Er(III) and Yb(III): an unexpected sensitisation mechanism based on electron transfer

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Introduction

Near-infrared (NIR) luminescence from lanthanide(III) complexes such as Pr(III), Nd(III), Er(III) and Yb(III) has attracted much interest because of its significant technological applications in areas ranging from medical imaging to optical communications. [1] The very low extinction coefficients for the Laporte-forbidden f-f transitions means that generation of the relevant emissive excited state is usually achieved indirectly, via energy-transfer from a suitable strongly-absorbing chromophore. [2] This works shows how an anthracene antenna pendant from a [Ln(hfac)$_3$(diimine)] core, using the ligand L^1 (Fig. 1), can act as a sensitiser for NIR luminescence from a range of Ln(III) centres. Anthracene (An) differs from many aromatic antennas used because of its redox activity at modest potentials: in addition to being able to participate in photoinduced energy-transfer processes in its excited state it can also act as either an electron acceptor or an electron donor. Accordingly the mechanism by which the anthracene chromophore sensitises the lanthanide-based excited state is not straightforward. We show evidence for anthracene→diimine photoinduced electron-transfer being the first step in the eventual energy-transfer process.
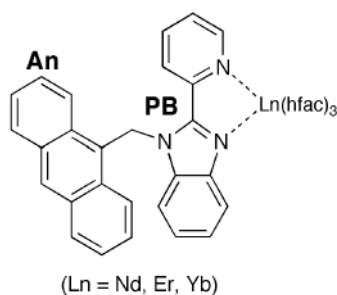

Figure 1. Structure of [Ln(hfac)$_3$(L^1)] complexes.

Results and discussion

Luminescence studies

Ligand L^1 shows the usual highly-structured fluorescence from the anthracene unit with a sequence of peaks between 395 and 500 nm. Addition of any Ln(hfac)$_3$(H$_2$O)$_2$ (Ln = Gd, Yb, Er, or Nd) resulted in essentially complete quenching of the fluorescence as the 1:1 adduct [Ln(hfac)$_3$(L^1)] formed.

Some degree of quenching of the An fluorescence is to be expected upon complexation to those lanthanides (Ln = Yb, Er, Nd) which have low-energy f-f excited states that can be sensitised by energy-transfer from the anthracene, assuming the usual sensitisation mechanism that energy-transfer occurs from the triplet state of the An chromophore following singlet→triplet inter-system crossing. In this case we would expect the triplet excited state of anthracene (^{3}An*), with an energy content of *ca.* 14500 cm^{-1}, [3] to be able to transfer its energy to the lower-lying f-f states of Yb(III), Er(III) or Nd(III), resulting in sensitised luminescence from the Ln(III).

However, the complete quenching of anthracene-based fluorescence following addition of Gd(hfac)$_3$(H$_2$O)$_2$ to L^1 in CH$_2$Cl$_2$ is unexpected: Gd(III) has no low-energy f-f states which could act as energy-acceptors; its lowest excited state (^{6}P$_{7/2}$) lies at *ca.* 32,000 cm^{-1}, in the UV region.

We must therefore consider photoinduced electron-transfer (PET): ^{1}An*→(diimine) PET occurring in the complexes.

The Rehm-Weller equation (eq. 1) was used to estimate the driving force for PET, ΔG_{ET}:

$$\Delta G_{ET} = e_o(E_{ox} - E_{red}) - E_s - w \qquad (1)$$

- where e_o is the elementary electronic charge, E_{ox} is the oxidation potential of the electron donor, E_{red} is the reduction potential of the electron acceptor, E_s is the energy of the singlet excited state of the chromophore (energy-donor) group, and w represents the stabilisation due to a Coulombic interaction between the components of the ion pair. From an irreversible oxidation of anthracene in L^1 (+0.92 V vs. (Fc/Fc$^+$)) in CH$_2$Cl$_2$, w as 0.15 eV, an estimate of reduction of free L^1, assumed to be PB-centred, at –2.24 V, and taking into account that the reduction potential of diimines ligands becomes at least 0.3 V less negative upon coordination to the metal centre, equation 1 gives ΔG_{ET} as approximately -0.3 V, indicating that ^{1}An*→(diimine) PET is thermodynamically possible.

This hypothesis was confirmed by complete quenching of fluorescence from L^1 in solution following addition of (i) Zn^{2+} ions, or (ii) acid, rationalised in terms of PET from ^{1}An* to the protonated (or metallated) pyridyl-benzimidazole unit of L^1. It is significant that electron transfer must occur from ^{1}An* and not from the triplet state ^{3}An* because the much lower energy of ^{3}An* (≈1.8 eV)

would mean that the $^3An^* \rightarrow PB$ electron-transfer would be highly endergonic. Thus, in $[Gd(hfac)_3(L^1)]$, $^1An^* \rightarrow PB$ PET must occur faster than $^1An^* \rightarrow ^3An^*$ inter-system crossing.

Near-infrared luminescence measurements on CH_2Cl_2 solutions of the complexes $[Ln(hfac)_3(L^1)]$ (Ln = Yb, Er, Nd) showed in every case that selective excitation of the An unit at 380 nm resulted in sensitised luminescence from the Ln(III) centre at the wavelengths characteristic of these metals [Yb(III), $^2F_{5/2} \rightarrow ^2F_{7/2}$ at 980 nm; Nd(III), $^4F_{3/2} \rightarrow ^4I_{11/2}$ and $^4F_{3/2} \rightarrow ^4I_{11/2}$ at 1060 and 1340 nm respectively; Er(III), $^4I_{13/2} \rightarrow ^4I_{15/2}$ at 1530 nm]. In each case there are two exponential components to the Ln(III) luminescence profile: a grow-in (rise-time) with a lifetime of ≈ 130 ns, and then a characteristic decay.

The slow rise time of the NIR emission is consistent with a conventional Förster or Dexter energy-transfer mechanism. It suggests that the charge-separated $[An^{\bullet+}-(PB^{\bullet-})Ln(hfac)_3]$ state collapses fast to the $[^3An^*-(PB)Ln(hfac)_3]$ state, containing the $^3An^*$. The $^3An^*$ is then the ultimate energy-donor to the Ln(III) units in the typical way.

The overall mechanism is presented in Fig. 2. We used transient absorption measurements to test the proposed sensitisation mechanism.
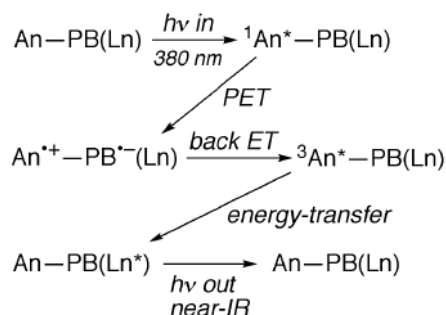

Figure 2. Proposed sensitization mechanism.

Nanosecond Transient Absorption
Transient absorption measurements were performed for the free ligand and $[Gd(hfac)_3(L^1)]$ and $[Nd(hfac)_3(L^1)]$ complexes in deoxygenated toluene solutions at room temperature under a selective excitation into the lowest-energy absorption feature of the An unit (390 nm), to test the charge-transfer sensitization mechanism suggested above. The spectra were recorded in the spectral range 420 – 800 nm. The possible presence of the charge separated state $[An^{\bullet+}-(PB^{\bullet-})Ln(hfac)_3]$ on the nanosecond time scale, and the presence of the $^3A^*$ state, were evaluated.

The presence of the charge-separated state would have been signalled unambiguously by an appearance of the characteristic $An^{\bullet+}$ band in the 700 nm region,[4] as well as other bands in the visible region characteristic of the reduced diimine radical anion.[5] No such bands were observed in any of the experiments on the time scale longer than 20 ns which is the limit of our experimental set-up. However, the transient absorption spectra obtained for free L^1 and $[Ln(hfac)_3(L^1)]$ (Ln = Nd, Gd) are identical, and all show an absorption band at *ca.* 430 nm, which is characteristic of $^3An^*$ absorbance (Fig. 3). No rise time for this absorbance was detected, which means

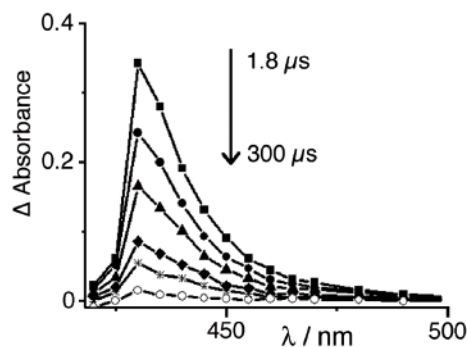**Figure 3. Transient absorption spectrum of $[Gd(hfac)_3(L^1)]$ in degassed toluene at RT, at different time delays following 390 nm excitation pulse: 1.8, 16.2, 37, 88, 138, 300 μs.**

that any rise time must be < 20 ns. We note that excitation at 355 nm (in which case ca. 15% of the light is absorbed by the PB unit) have also resulted in the purely $^3An^*$ spectrum. In this case the bleach of the ground state absorbencies was observed in the 360 – 390 nm region, the rate of recovery of which was identical to the decay rate of the $^3An^*$ transient absorption (Fig. 4). These observations are consistent with the suggestion given above, that the charge transfer state decays rapidly with formation of
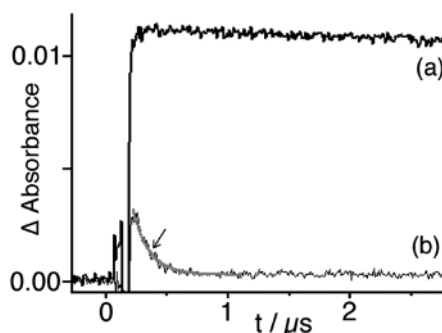

Figure 4. Decay kinetics of $^3An^*$ recorded at 430 nm in degassed toluene at RT under 390 nm excitation, for (a) $[Gd(hfac)_3(L^1)]$ and (b) $[Nd(hfac)_3(L^1)]$. The grey line on (b) (indicated with an arrow) represents a monoexponential fit to the decay of the transient absorption, with the lifetime 130 (± 20) ns. Instrument response ca. 20 ns.

$^3An^*$ on a time scale shorter than the instrument response. The $^3An^*$ state is strongly quenched in $[Nd(hfac)_3(L^1)]$ compared to $[Gd(hfac)_3(L^1)]$, confirming that it is the energy transfer from $^3An^*$ to the Ln(III) centre that is responsible for the sensitized NIR emission. This is further confirmed by the fact that the lifetime of the $^3An^*$ state in $[Nd(hfac)_3(L^1)]$ [130 (±20) ns] measured by transient absorption is the same, within error, as the rise-time of the sensitised Nd(III) emission. In contrast, in $[Gd(hfac)_3(L^1)]$ where there is no energy-transfer quenching, the $^3An^*$ absorption band is much more intense and long lived with $\tau \approx 70$ μs.

Conclusions
In the series of complexes $[Ln(hfac)_3(L^1)]$ (Ln = Nd, Er, Yb), that sensitisation of the Ln(III) centres by an anthracene antenna unit proceeds by an unusual mechanism involving electron-transfer steps, i.e. $[^1An^*-PB\{Ln(hfac)_3\}] \rightarrow [An^{\bullet+}-PB^{\bullet-}\{Ln(hfac)_3\}] \rightarrow$

$[^3\text{An*–PB\{Ln(hfac)}_3\}] \rightarrow [\text{An–PB\{Ln*(hfac)}_3\}]$. This mechanism is an alternative to the much more common sensitisation mechanism in which the singlet excited state of a chromophore converts to the triplet by inter-system crossing before donating the excitation energy to a Ln(III) centre, with no electron-transfer processes involved.

Experimental

Photophysical measurements.

NIR luminescence measurements were performed on a home-built set-up, comprising a Nd:YAG-pumped Sirah dye laser as an excitation source, and a liquid-N_2 cooled Ge diode (Edinburgh Instruments) as a detector.

Nanosecond transient absorption studies were performed using a home-built set-up comprising a Nd:YAG laser (9 ns pulse width) pumping a Sirah dye laser. The typical laser energy used was 1 – 3 mJ. A steady-state Xe lamp (Hamamatsu L 2273) was used as a probe source. The detection system includes a Hamamatsu R928 PMT, and a Tektronix 3032B oscilloscope, interfaced with a standard PC. The pump and probe lights were arranged in a collinear geometry.

Acknowledgements

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