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Synthesis and luminescence properties of a kinetically stable dinuclear ytterbium complex with differentiated binding sites†

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The complex Yb_2L contains two DO3A units separated by a phenol bridging group and gives time-resolved luminescence spectra in solution consistent with the presence of two types of binding site.

Luminescence from lanthanide complexes is of considerable interest from the viewpoint of synthesising complexes for bioassay and time-gated imaging applications as well as being relevant to the preparation of new luminescent materials.[1] In such applications, the problems associated with the inherently low extinction coefficients of lanthanide ions can be circumvented by using sensitising chromophores or 'antenna groups'.

In recent years, considerable interest has centred on lanthanide ions which are emissive in the near-IR, particularly neodymium[2] and ytterbium[3] complexes. These absorb and emit outside the range associated with biological molecules, making them ideal for high sensitivity bioassays.[3] We and others have devoted considerable effort to understanding the mechanisms associated with sensitised luminescence from these ions,[4] and observed that ytterbium ions can be sensitised through the LMCT state as well as *via* the ligand centred triplet state, meaning that a wide range of chromophores can be used as antennae.

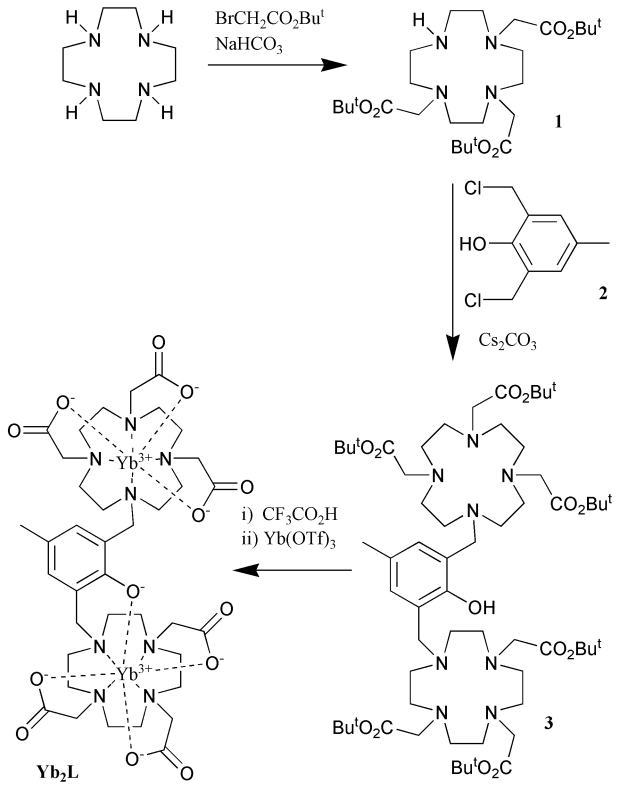
Multinuclear complexes containing more than one lanthanide ion are comparatively rare in macrocyclic chemistry.[5,6] Nearly all the systems reported are based on kinetically unstable complexes derived from acyclic ligands, and only a handful of studies have been carried out on complexes that are emissive in the near IR.[7]

We now report the synthesis of a well-defined, kinetically stable, binuclear ytterbium complex, **Yb_2L**, whose luminescence properties demonstrate that there are two distinct lanthanide environments on the luminescence timescale.

The complex was prepared as shown in Scheme 1.‡ Trialkylation of cyclen with *tert*-butyl bromoacetate by established procedures yielded the triester **1**, which was reacted further with the dichloride, **2**, to yield the bis macrocycle **3**. Hydrolysis using trifluoroacetic acid yielded **L**. Complexation was carried out in methanol using ytterbium triflate, to yield **Yb_2L**.

Luminescence spectroscopy was used to probe the local environment around the lanthanide ion in aqueous solution.§ Excitation at 337 nm gave rise to a typical ytterbium centred time resolved emission spectrum (Fig. 1). This indicates that energy transfer must occur from the ligand chromophore to the metal, as ytterbium has no absorption bands at this wavelength, while the ligand chromophore absorbs strongly.

Time resolved luminescence spectroscopy gives more information about the local environment around the lanthanide ions. Luminescence lifetimes in H_2O and D_2O solution were obtained from the time resolved emission spectra by iterative reconvolution with the detector response, which is comparable with the luminescence lifetimes. Unusually for ytterbium containing systems, reconvolution with a single exponential did not yield a satisfactory fit, as judged by residual squared and reduced chi squared. By contrast, fitting to two exponential decay components yielded very good fits in all cases. A typical fitted decay is shown in Fig. 2, while the lifetimes obtained are shown in Table 1. It is worth noting that the relative weighting of the short and long components is the same in protiated and deuteriated solvents. This implies that there are two distinct lanthanide containing environments. In all cases, energy transfer occurs within the envelope of uncertainty (*i.e.* < 25 ns), which is consistent with an energy transfer process mediated by



Scheme 1 Synthesis of **Yb_2L**.

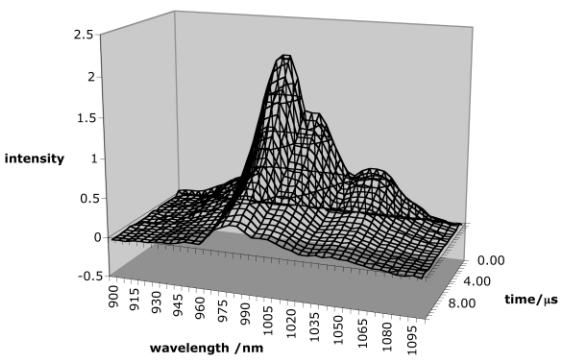


Fig. 1 Time resolved emission spectrum of **Yb_2L** in solution in D_2O.

† Electronic supplementary information (ESI) available: ^1H NMR spectrum of **Yb_2L**. See http://www.rsc.org/suppdata/cc/b3/b303012a/

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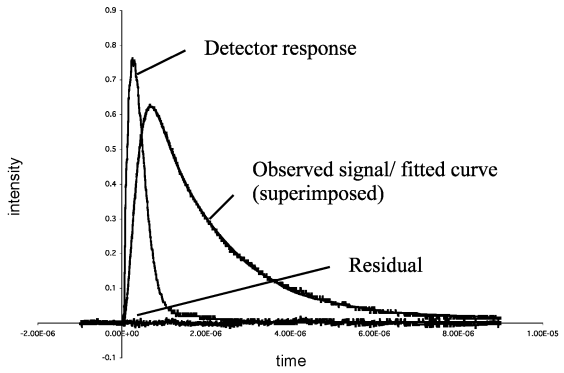

Fig. 2 Time resolved profile of the luminescence from a solution of **Yb_2L** in H_2O. The graph shows changes in intensity of the luminescence at 980 nm with time and is fitted by reconvolution of the detector response with two exponential components corresponding to τ = 0.51 and 1.67 μs.

Table 1 Luminescence lifetimes and inner sphere hydration numbers (q) for **Yb_2L**

τ_{H_2O}/μs	1.67 (67%),	0.51 (33%)
τ_{D_2O}/μs	4.95 (67%),	1.17 (33%)
q	0.3,	1.0

Luminescence lifetimes have errors of ±10%, relative weightings are quoted in brackets.

the LMCT state, as might be expected with an electron donating phenolate antenna group. Systems containing very similar chromophores do not act as sensitisers for europium,[6] where the LMCT state is lower in energy than the excited state. In the case of ytterbium this situation is reversed, making LMCT a suitable pathway to sensitising the emissive state of the metal.[4]

For a lanthanide complex, the inner sphere hydration number, q, can be established using the equation

$$q = A_{Ln}(1/\tau_{H_2O} - 1/\tau_{D_2O} - B)$$

where A_{Ln} is a proportionality constant unique to a given lanthanide (A_{Yb} = 1.0 μs), τ_{H_2O} and τ_{D_2O} are the luminescence lifetimes in water and D_2O measured in microseconds and B is a correction term which accounts for the presence of outer sphere water molecules (B = 0.1 μs for ytterbium).[8] In this case we can obtain two q values. It is reasonable to pair the components with similar weightings with one another, particularly in the case of ytterbium, where significant quenching by O–D is possible. Such a treatment gives inner sphere hydration numbers of 0.3 and 1.0 (Table 1).

Taken together, the evidence implies the formation, either of a binuclear complex with two distinct binding sites, or of the co-existence of two forms of the complexes in solution. Both of these are consistent with the luminescence data, and with the complexity of the axial resonances in the proton spectrum of **Yb_2L**. One binding site is eight coordinate, while the other is seven coordinate since the bulk of the DO3A unit prevents both lanthanides from sharing the phenolate oxygen donor. The inner sphere hydration numbers are lower than might be expected, probably as a result of the lipophilicity of the linking phenolate unit preventing the close approach of additional water molecules. We are currently engaged in carrying out a systematic study of related **Ln_2L** complexes, the results of which will be reported in due course.

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Notes and references

‡ Analytical data for all compounds was consistent with the proposed structures. Sample data: **L** UV(H_2O) λ_{max} (ε) 205 (17500), 221 (6400), 288 (2000 dm^3 mol^{-1} cm^{-1}) nm; IR (solid) ν_{max} 3410 (br), 2981, 2856, 1666 (br), 1460, 1398, 1354, 1179, 1124, 1087 cm^{-1}. ES$^-$ MS (MeCN/H_2O): m/z 823 {M − H}$^-$; ES$^+$ MS (MeCN/H_2O): m/z 869 {M − H + 2Na}$^+$, 847 {M + Na}$^+$, 825 {M + H}$^+$. ^{1}H NMR (400 MHz, D_2O, 300 K) δ_H 2.2 (3H, s, $ArCH_3$), 2.7–3.9 (48H, m, NCH_2), 7.2 (2H, br, s, ArH). ^{13}C{^{1}H} NMR (100 MHz, D_2O, 300 K) δ_C 42.8, 48.2, 48.6, 49.3, 49.5, 50.6, 51.1, 52.2, 53.6, 56.2, 63.2 (br NCH_2), 116.8 (q, CF_3CO_2H), 133.6, 142.0 (br Ar), 163.6 (q, CF_3CO_2H), 169.9, 174.9 (CO). Found C, 41.82; H, 5.09; N, 8.95; calc. for $C_{37}H_{60}N_8O_{13}\cdot 4CF_3CO_2H$: C, 42.19; H, 5.0; N, 8.75 %.

Yb_2L IR (solid) ν_{max} 2860, 1591 (br), 1431, 1415, 1241, 1165, 1083, 1027 cm^{-1}; UV(H_2O) λ_{max} (ε) 202 (14500), 245 (2600), 307 (1300), 977 (20 dm^3 mol^{-1} cm^{-1}) nm; ES$^-$ MS (MeCN): m/z 1162 {M − H}$^-$. ^{1}H NMR (500 MHz, CD_3OD, 300 K) Peaks consistent with the proposed structure were observed (the spectrum is available as ESI. A relatively sharp peak was observed for each proton environment, together with a broader peak of roughly equal intensity somewhat shifted and in some cases partially overlapping, suggesting either inequivalent binding of the two ytterbiums, or the existence of two distinct forms of the complex in a 1 : 1 ratio, each having equivalent binding of the two ytterbiums. Selected peak positions for the sharp peaks are reported for the characteristic dipolar shifted regions. δ_H 156.9, 134.4, 118.0, 72.5, 57.8, 39.4, 35.2, −15.4, −21.0, −35.0, −47.5, −60.4, −65.9, −81.8, −126.5.

§ The sample was irradiated at 337 nm using the output from a pulsed nitrogen laser (PTI GL3300). Luminescence from the sample was collected at right angles to the incident beam and focused onto the slits of a monochromator (PTI-120). The growth and decay of the luminescence at selected wavelengths was detected using a germanium photodiode (Edinburgh Instruments, EI-P) and recorded using a digital oscilloscope (Tektronix TDS220).

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