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Synthesis and luminescence properties of dinuclear lanthanide complexes derived from covalently linked macrocyclic ligands

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A series of homo-binuclear lanthanide complexes have been prepared from DO3A derived systems containing seven-coordinate binding domains linked *via* an aromatic. The luminescence properties of xylyl bridged complexes show that the lanthanide ions behave as isolated centres, while the combination of the lanthanide contraction and the lipophilicity of the linker group limits inner-sphere hydration around the metal centres for later lanthanides such as ytterbium.

Introduction

Lanthanide complexes are widely used in a variety of applications, particularly as contrast agents in magnetic resonance imaging (MRI).[1] In recent years, the solution state luminescence properties of a variety of lanthanide ions have also begun to find uses, especially in the related areas of bioassay,[2] imaging,[3] and sensor development.[4] In these applications, the long-lived luminescence of lanthanide ions can readily be separated from background using time-gating techniques, eliminating fluorescent background noise. The ligands used also differ subtly from those used in MRI, not least in that they should exclude solvent from the binding site to as great an extent as possible, since lanthanide excited states are quenched by proximate O–H oscillators.[3,5] Furthermore, lanthanide ions have low extinction coefficients, necessitating the incorporation of sensitising chromophores into the complex to optimize the sensitivity of the system. These sensitising chromophores must have a donor state significantly higher in energy than the emissive state of the lanthanide.

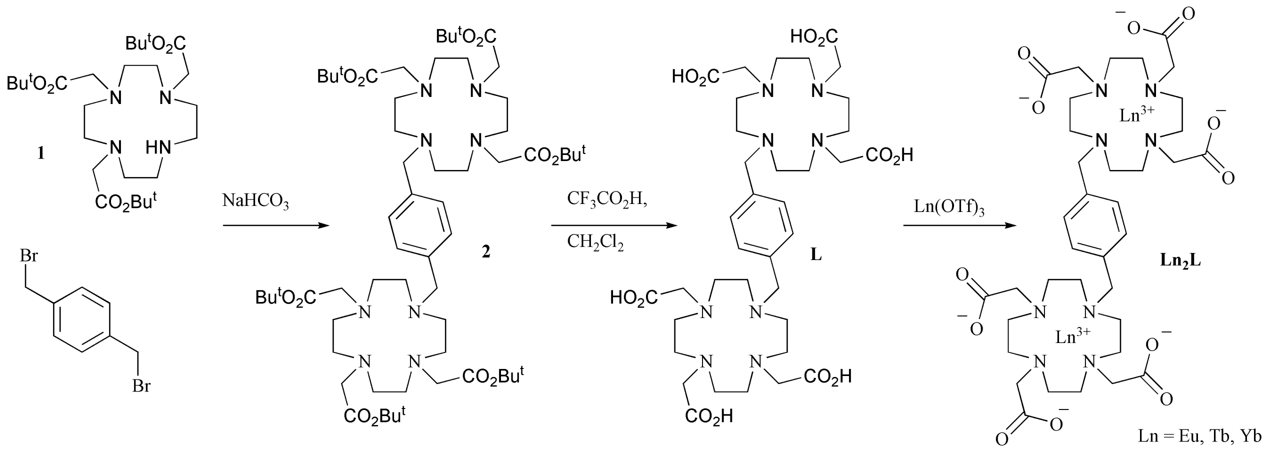
Historically, interest has centred on the use of lanthanides such as europium and terbium, which have very long luminescence lifetimes; typically of millisecond order. However, sensitised luminescence from both ions is mediated by ligand chromophore triplet states.[6] This restricts the use of long-wavelength sensitisers, which offer possibilities for greater tissue penetration and increased sensitivity, since energy transfer has been shown to proceed *via* the chromophore triplet state for both ions.[6] Recently, solution-state studies have established that neodymium,[7] erbium[8] and ytterbium[9] are luminescent in the near-IR. These ions can be sensitised by a much wider range of chromophores. In the case of ytterbium, the mechanism by which emission is sensitized can also vary, with either the metal triplet or a ligand–metal-charge transfer (LMCT) state acting as the intermediate, depending on the nature of the chromophore.[7b,10]

Multinuclear lanthanide complexes, particularly helicates, are widely known, and many of these have been shown to be luminescent, some of them in the near-IR.[11] However, multinuclear complexes based on macrocyclic ligand systems are much rarer,[12,13] and the area has been dominated by dendrimer chemistry.[14] We now report a study on complexes containing a single chromophore and two lanthanide ions.

Results and discussion

The ligand (**L**) and its complexes were prepared as shown in Scheme 1. Reaction of the well-known tris *tert*-butyl ester of DO3A (1)[15] with α,α′-dibromoxylene in the presence of sodium hydrogencarbonate, yielded the hexaester **2** in 64% yield. This was converted to the hexaacid (**L**) using trifluoroacetic acid in dichloromethane. Complexation reactions were carried out by addition of two molar equivalents of the lanthanide trifluoromethanesulfonate in methanol, yielding Ln_2**L**.

All complexes gave ESMS or MALDI mass spectra consistent with the formulation of the dinuclear lanthanide complex. An example is shown in Fig. 1 where the broad cluster of peaks, associated with the incorporation of two ytterbium ions, is



Scheme 1 Synthesis of **L** and its complexes.

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Table 1 Luminescence lifetimes of the complexes

Compound	τ_{H_2O}/ns	τ_{D_2O}/ns	q
Eu_2L	360	1060	1.9
Tb_2L	1340	2490	1.4
Yb_2L	1.45	6.07	0.4

[a] Errors are ± 10%.

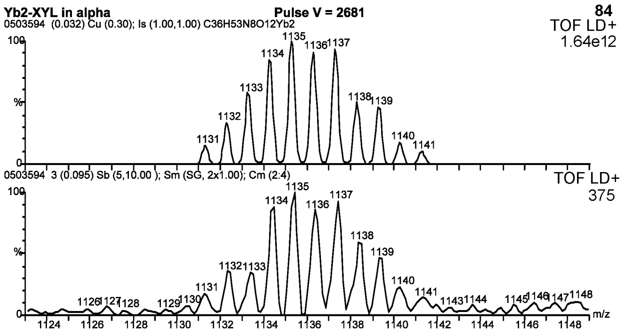

Fig. 1 MALDI mass spectrum (alpha) of $\{M + H\}^+$ (where M = Yb_2**L**). Top: theoretical isotopic distribution. Bottom: actual.

clearly in agreement with the calculated theoretical isotopic distribution. IR spectroscopy of the free ligand was most informative with regard to the carboxylic acid functional groups, the ν(C=O) of which was observed as a broad intense band at 1670 cm^{-1}. Typically, this stretching frequency decreased on coordination of **L** to the lanthanide ions by approximately 70–90 cm^{-1}. For complexes Ln_2**L** there was an increase in ν(C=O) across the lanthanide series (Eu ≈ Tb < Yb) indicating a weakening of the interaction between ion and ligand (since within the CO_2^- moiety increased donor ability will reduce C=O strength). The proton NMR spectra of the lanthanide complexes with **L** were broadened and shifted considerably by the presence of paramagnetic metal centres. In the case of the europium complex at 500 MHz the broadening is small relative to the paramagnetic shift so dispersion is relatively high, and the NMR spectroscopy of related complexes is well assigned. In this case, the relative simplicity of the spectrum, as judged by the number of axial ring protons, implies that both lanthanide binding domains are averaged on the NMR timescale, and that the lanthanide sites are likely to be dynamically equivalent. In the case of the terbium complex at 65 MHz the observed linewidths were large even in comparison to the considerable chemical shift range, possibly indicating dynamic processes on the NMR timescale at ambient temperature.

In the case of the ytterbium complex, proton NMR spectra were recorded at both 65 and 500 MHz. The 500 MHz spectrum shows considerably better dispersion than the 65 MHz spectrum, and suggests two distinct peaks for each type of DO3A ring proton, with some evidence of dynamics for one of the sets of peaks. It is also worth noting that the shifts recorded are significantly dependent on the magnetic field-strength, particularly for those peaks shifted to lowest frequency in each spectrum (Fig. 2), suggesting that the contact term may be non-negligible for these protons. Only the data recorded at 500 MHz are reported in the experimental section.

Luminescence studies

Having prepared the complexes, their luminescence properties were established. All complexes gave characteristic emission spectra, indicating incorporation of the lanthanide ions within metal binding sites. Luminescence lifetimes of the complexes are given in Table 1.

Ln_2L complexes. The incorporation of chromophores with high molar extinction coefficients into ligands bound to lanthanide ions is an established method for circumventing the inherently poor absorption properties of the metal ions. It is well known that Eu^{3+}, Tb^{3+} and Yb^{3+} can be sensitised *via* a chromophore-centred triplet-state.[6] In aqueous solution the free *p*-xylene-bridged ligand showed absorptions at 261 (400 mol^{-1} dm^3 cm^{-1}), 217 (sh) (7400 mol^{-1} dm^3 cm^{-1}) and 199 (14900 mol^{-1} dm^3 cm^{-1}) nm ascribed to π–π* transitions of the xylyl chromophore. Complexation of the ligand with 2 equivalents of Ln^{3+} (where Ln = Eu, Tb) resulted in a near-identical absorption spectrum in comparison with the free ligand. The complex Yb_2**L** showed an additional extremely weak feature at *ca.* 970 nm, characteristic of an Yb^{3+} $^2F_{7/2} \longrightarrow {}^2F_{5/2}$ absorption.

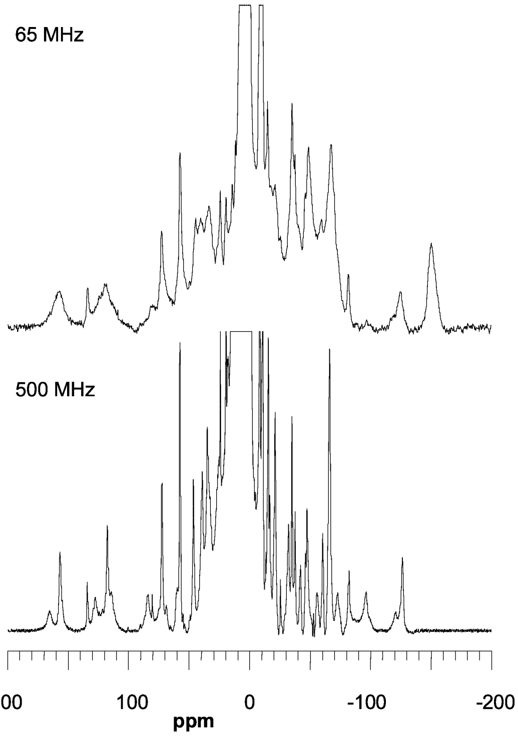

Fig. 2 NMR spectra of the ytterbium complex at 65 MHz (top) and 500 MHz (bottom).

Luminescence lifetime measurements of the complexes, obtained in water and deuterium oxide, allow an understanding of the degree of inner-sphere solvation (q) at the coordinated metal ion. In general, q is calculated from the relation $q = A[(k_H - k_D) - B]$ (where for Eu^{3+} $A = 1.2$, $B = 0.25$, for Tb^{3+} $A = 5$, $B = 0.06$ ms and for Yb^{3+} $A = 1$, $B = 0.1$ µs).[16] The values of q for these Ln^{3+} dimers are typical of DO3A derived ligands with seven donor atoms in the coordination sphere. The excitation spectra for these complexes shows that irradiation in the UV region results in intense lanthanide based emission (Fig. 3).

Luminescence measurements were obtained for the three complexes, the Eu^{3+} and Tb^{3+} dimers analysed for emission bands in the visible region and the Yb^{3+} complex in the near-IR. In each case the decay profiles were analysed as single exponential decays (no improvement of the residual squared and reduced χ^2 was noted on fitting to a dual exponential decay) indicative of both Ln^{3+} ions within the dinuclear species possessing the same coordination environment.

The dinuclear europium Eu_2**L** complex showed a typical emission spectrum (λ_{em} = 592 and 616 nm, Fig. 3) when excited at 260 nm; the emission from the europium ions is clearly sensitised by the xylene chromophore. The lifetimes in H_2O and D_2O are typical of europium complexes with DO3A derived ligands and $q \approx 2$ confirming their preference for nine-coordinate donor sets.[1a] It should be noted that the luminescence from the europium complex is relatively weak, consistent with non-radiative quenching by the LMCT state.

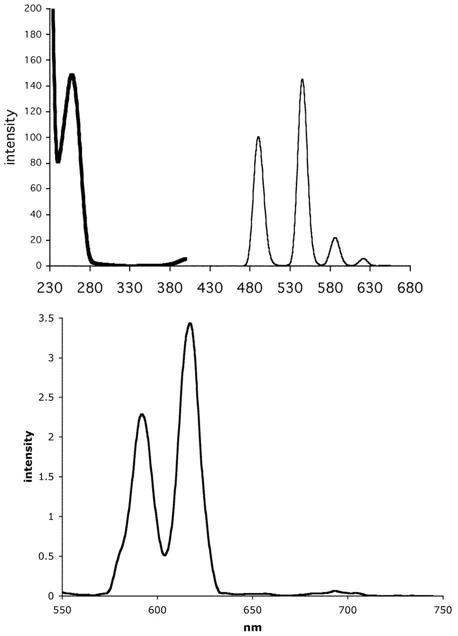

Fig. 3 Top: excitation (thick line) and emission spectra of Tb_2**L** in aqueous solution. Bottom: emission spectrum of Eu_2**L**. All spectra were recorded in aqueous solution and are shown uncorrected. Emission spectra obtained using $\lambda_{exc} = 260$ nm.

Similarly, for the dinuclear terbium analogue, Tb_2**L**, excitation of the chromophore at 260 nm led to a characteristic four-band emission in the visible region (Fig. 3). The lifetimes of the terbium-based luminescence (Fig. 4 shows a typical fit) are characteristically about 1 ms longer than in the europium analogue, and $q = 1.4$, reflecting the lipophilicity of the xylyl linkage. Unlike the other complexes, the luminescence lifetimes for Tb_2**L** are slightly longer in degassed solution, suggesting that there may be some degree of back energy transfer to the chromophore. The principal emission band (545 nm) was found to be significantly more intense than when the complex is excited directly *via* the terbium ions (λ_{exc} = 366 nm), clearly demonstrating the efficiency of energy transfer (antenna effect) in these systems.[17]

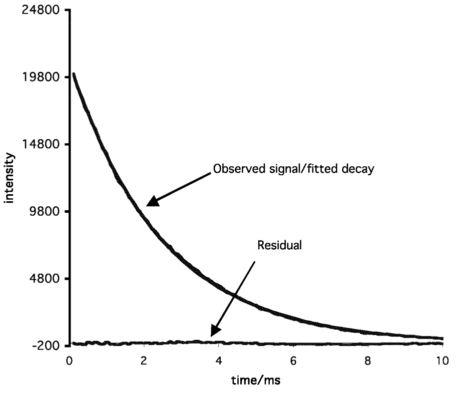

Fig. 4 Fitted decay for the emission from Tb_2**L** in D_2O (λ_{exc} = 260 nm, λ_{em} = 545nm).

For Yb_2**L** excitation at 337 nm, using a pulsed nitrogen laser, gave rise to an ytterbium based emission in the near-IR region at 980 nm (Fig. 5). Given that ytterbium possesses no absorption bands in the region of excitation, it is assumed that energy transfer must occur from the xylene chromophore (which absorbs at 337 nm, albeit weakly, thus necessitating the use of *ca.* 1×10^{-2} M solutions) to both ytterbium ions *via* the xylyl-centred triplet state. The luminescence lifetimes were measured in H_2O and D_2O at an emission wavelength of 980 nm and lifetime values were obtained by iterative reconvolution of the detector response with a single exponential decay component (Fig. 5).[7a] This would appear to suggest that the two environments implied by the high-field NMR spectrum are very similar to one another with respect to the local environment at the lanthanide ion. By contrast, in previous work, we have shown that incorporating a bridging chromophore with potential for coordination can lead to much larger differences between bound ytterbium ions.[12] For such a molecule the lifetime analyses can only be fitted to dual-exponential decays and hence two distinct *q* values are obtained. Here, for Yb_2**L** the inner-sphere hydration appears to be small ($q = 0.4$), probably reflecting both the size of the smaller Yb^{3+} ion and the hydrophobicity of the xylene moiety. The gradual decrease (from Eu_2**L** to Tb_2**L** to Yb_2**L**) in inner-sphere hydration number mirrors the lanthanide contraction, though it should be borne in mind that the hydration number represents the contribution of solvent molecules at an average metal–solvent separation, and that the quenching contribution of more distant inner-sphere solvent ions will be smaller than the 'average'.

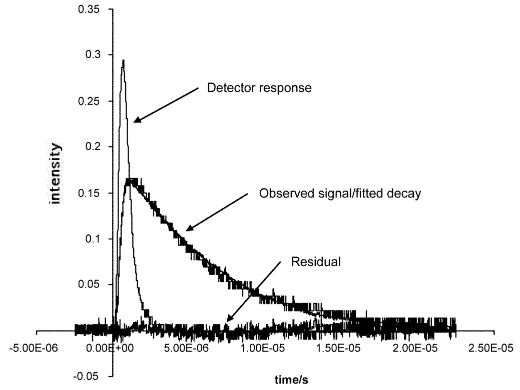

Fig. 5 Fitted decay for the complex Yb_2**L** in D_2O (λ_{exc} = 337 nm, λ_{em} = 980 nm). The fit was obtained by iterative reconvolution with the detector response by minimisation of residuals squared. The fitted curve and the observed decay are almost exactly superimposed.

Conclusions

This study demonstrates that triesters of DO3A can be used as building blocks for polynuclear lanthanide complexes containing a range of lanthanide ions. Luminescence measurements have revealed that in these xylyl bridged systems the lanthanide ions behave as independent metal centres, but with the same coordination environment. Further studies are in progress on these complexes to assess their potential as contrast agents and as hosts for molecular recognition. Routes towards higher nuclearity systems are also being probed.

Experimental

Synthesis of ligands and complexes

1,4,7-Tris(*tert*-butoxycarbonylmethyl)-1,4,7,10-tetraazacyclododecane 1. This was prepared as described in the literature.[15]

1′,4′-Bis(1,4,7-tris(*tert*-butoxycarbonylmethyl)-1,4,7,10-tetraazacyclododecane-10-methyl)benzene (2). To a solution of the triester **1** (1.0 g, 1.94×10^{-3} mol) in acetonitrile (20 cm^3) under dinitrogen, was added an excess of $NaHCO_3$ (1.0g, 0.012 mol). α,α′-Dibromoxylene (0.256 g, 9.71×10^{-4} mol) was dissolved in acetonitrile (5 cm^3), added to the stirring solution and the reaction mixture heated to reflux for 48 h. The mixture was then cooled to room temperature, filtered and the solvent removed *in vacuo*, giving a glassy yellow solid. The residue was chromatographed on a neutral alumina column. Initially the column was eluted with dichloromethane (500 cm^3) and then dichloromethane–methanol (95 : 5). The product was collected as a thick yellow oil which ultimately solidifies when dry (yield 1.41, 64%). APCI$^+$ MS (MeCN): *m/z* 1154 $\{M + Na\}^+$, 1131 $\{M + H\}^+$, 1075 $\{M + H - C(CH_3)_3\}^+$. ^{1}H NMR (400 MHz, $CDCl_3$, 300 K): δ_H 1.3–1.5 (54H, m, *tert*-Bu), 2.2–3.4 (48H, br, m, NCH_2), 7.2–7.4 (4H, m, ArH). ^{13}C NMR (100 MHz, $CDCl_3$, 300 K): δ_C 26.5, 27.6, 27.7, 27.8 (C*C*H$_3$), 45.5, 47.3, 48.5, 49.0, 49.6, 50.2, 50.9, 51.1, 52.0, 55.5, 55.6, 55.7, 55.8, 55.9, 57.9, 58.0, 58.7, 59.0, 59.1, 59.2 (NCH_2), 81.3, 81.4, 81.8, 82.2, 82.3, 82.5, 82.7, 82.8 (*C*CH$_3$), 127.1, 127.8, 128.7, 129.6, 129.9, 130.3 (Ar), 169.5, 170.4, 172.2, 172.3, 172.4, 172.7, 173.2, 173.3 (CO). Found: C, 53.5; H, 8.32; N, 7.72; calc. for $C_{60}H_{106}N_8O_{12}\cdot 2NaBr$: C, 53.89; H, 7.93; N, 8.38%.

1′,4′-Bis(1,4,7-tris(carboxymethyl)-1,4,7,10-tetraazacyclododecane-10-methyl)benzene L. The hexaester **2** (0.5 g, 4.42 × 10^{-4} mol) was dissolved in dichloromethane (5 cm^3) and trifluoroacetic acid (5 cm^3) added dropwise to the stirred solution. The reaction mixture was allowed to stir at room temperature for 24 h. The solvents were then removed *in vacuo* and the residue washed and evaporated repeatedly with dichloromethane (4 × 5 cm^3) and methanol (4 × 5 cm^3) to remove residual trifluoracetic acid. The brown oil was then dissolved in methanol (3 cm^3) and a yellow solid precipitated with the addition of diethyl ether. The product was filtered, washed and isolated as the trifluoracetic acid adduct being an off-white, mildly hygroscopic solid (0.44g, 80%). IR (solid) ν_{max} /cm^{-1}: 3401 (br), 3094, 2971, 2850, 1670 (br), 1549, 1386, 1355, 1174, 1121 cm^{-1}. ES$^-$ MS (MeCN): *m/z* 837 $\{M - 3H + 2Na\}^-$, 815 $\{M - 2H + Na\}^-$, 793 $\{M - H\}^-$. UV-vis (H_2O) λ_{max} (ε/mol^{-1} dm^3 cm^{-1}): 261 (400), 217 (sh) (7400), 199 (14900) nm. ^{1}H NMR (400 MHz, D_2O, 300 K): δ_H 2.5–3.9 (48H, br, m, NCH_2), 7.3–7.7 (4H, br, ArH); ^{13}C NMR (100 MHz, D_2O, 300 K): δ_C 51.0 (br), 56.8 (br), 59.4, 65.4 (NCH_2), 118.5 (q, CF_3CO_2H), 130.3, 133.1 (br, Ar), 165.0 (q, CF$_3$*C*O$_2$H), 174.0 (br, CO). Found: C, 41.57; H, 5.4; N, 8.84; calc. for $C_{36}H_{58}N_8O_{12}\cdot 4CF_3CO_2H$: C, 42.24; H, 5.44; N, 8.96%.

Eu$_2$L. To a solution of **L** (0.1 g, 8 × 10^{-5} mol) in methanol (15 cm^3) was added two equivalents of Eu(OTf)$_3$ (0.096 g, 1.6 × 10^{-4} mol). The reaction mixture was then heated to 60 °C for 24 h. The solvent was concentrated to a few cm^3 and the product precipitated with diethyl ether. The solid was filtered off and washed with diethyl ether. Further precipitation was achieved using acetonitrile and diethyl ether. The desired complex was isolated as a pale yellow solid (0.076 g, 87%). IR (solid) ν_{max}/cm^{-1}: 1585 (br), 1221, 1172, 1025 cm^{-1}. ES$^-$ MS (MeCN): *m/z* 1134 broad cluster $\{M + MeCN\}^-$. UV-vis (H_2O) λ_{max} (ε/mol^{-1} dm^3 cm^{-1}): 261 (400), 218 (sh) (5200), 196 (16100) nm. ^{1}H NMR (500 MHz, CD_3OD, 300 K): δ_H −17, −16, −11, −9, −8, −6, −3, −2, −1, 9, 12, 33.

Tb$_2$L. To a solution of **L** (0.1 g, 8 × 10^{-5} mol) in methanol (15 cm^3) was added two equivalents of Tb(OTf)$_3$ (0.097 g, 1.6 × 10^{-4} mol). Reaction and work-up as above. The desired complex was isolated as a white solid (0.069 g, 78%). IR (solid) ν_{max}/cm^{-1}: 1584 (br), 1223, 1163, 1025 cm^{-1}. ES$^+$ MS (MeCN): *m/z* 1107 $\{M + H\}^+$, 554 $\{M + 2H\}^{2+}$. UV-vis (H_2O) λ_{max} (ε/mol^{-1} dm^3 cm^{-1}): 259 (350), 2178 (sh) (6300), 196 (17800) nm. ^{1}H NMR (65.5 MHz, D_2O, 300 K): δ_H −402, −350, −173, −93, 88, 228, 262, 408 (only resolved peaks outside the range +20 to −20 ppm reported).

Yb$_2$L. To a solution of **L** (0.1 g, 8 × 10^{-5} mol) in methanol (15 cm^3) was added two equivalents of Yb(OTf)$_3$ (0.099 g, 1.6 × 10^{-4} mol). Reaction and work-up as above. The desired complex was isolated as a white solid (0.083 g, 91%). IR (solid) ν_{max}/cm^{-1}: 1602 (br), 1242, 1167, 1027 cm^{-1}. MALDI$^+$ MS (alpha–MeOH–H_2O): *m/z* = 1135 broad cluster $\{M + H\}^+$. UV-vis (H_2O) λ_{max} (ε/mol^{-1} dm^3 cm^{-1}): 971 (20), 260 (300), 217 sh (6000), 197 (16500) nm. ^{1}H NMR (500 MHz, CD_3OD, 300 K): δ_H −127, −121, −82, −73, −66, −60, −56, −48, −42, −38, −35, −32, −21, −17, −15, 18, 19, 24, 26, 47, 58, 73, 84, 115, 118, 128, 134, 157, 166 (only resolved peaks outside the range +15 to −10 ppm reported).

Luminescence properties of the complexes

Luminescence properties of the terbium and europium complexes were determined using a Perkin-Elmer LS55 fluorimeter.

In the case of the ytterbium complex, the sample was excited using a pulsed nitrogen laser (PTI-3301, 337 nm) or a nitrogen pumped dye laser (PTI-330, 520 nm), operating at 10 Hz. Light emitted at right angles to the excitation beam was focused onto the slits of a monochromator (PTI120), which was used to select the appropriate wavelength. 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) before being transferred to a PC for analysis. Luminescence lifetimes were obtained by iterative reconvolution of the detector response (obtained by using a scatterer) with exponential components for growth and decay of the metal centred luminescence, using a spreadsheet running in Microsoft Excel. The details of this approach have been discussed elsewhere.[7a] Fitting to a double exponential decay yielded no improvement in fit as judged by minimisation of residual squared and reduced χ^2.

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