The effect on the lanthanide luminescence of structurally simple Eu(III) cyclen complexes upon deprotonation of metal bound water molecules and amide based pendant arms

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A series of substituted 1,4,7,10-tetraazacylcododecane ligands **1–4**, possessing sensitizing nitrobenzene or naphthalene antennae, as one of the amide pendant arms, and their complexes with europium(III) were synthesised. The protonation constants and the metal ion stability constants of two of these ligands were determined by potentiometric titration. The pK_a of the water molecules coordinated to the complexed metal ion were determined by both luminescent and potentiometric measurements. The luminescence pH dependence of a further three Eu(III) complexes, **5–7**, which lack any antennae, were also studied with the aim of gaining a better understanding of the role of the metal bound water molecules in the luminescence properties of such complexes upon direct excitation of the lanthanide ion. The results from these luminescent measurements demonstrate that the Eu(III) emission was significantly modulated as a function of pH for all the complexes, which we assigned to changes occurring in the coordination environment of the ion within the cyclen system, caused by deprotonation of metal bound water molecules and/or deprotonation of pendent amide arms.

Introduction

Due to the unique magnetic, luminescent and coordination properties of the lanthanides, they have become extensively employed in the synthesis and study of novel coordination networks[1] and metal directed synthesis,[2] in functional supramolecular structures[3] and self-assemblies.[4] Their use in luminescent sensing[5] and imaging technology,[6–8] and as contract agents for MRI is also very well established.[9] They have also been used for mimicking the function of biological species, such as metallo based enzymes.[10,11] While the properties of the lanthanide ion itself is central to all of these functions, the direct, or synergetic, actions of metal bound water molecules (usually mono- or di-aqua species) in such structures is also important to the overall function of such complexes.[12] One of the most commonly used ligands for forming such functional lanthanide complexes/devices is cyclen (1,4,7,10-tetraazacyclododecane).[13] The cyclen structure can be relatively easily synthetically modified, to incorporate a variety of pendant arm functionalities, which, upon complexation to lanthanides, give structures with one or two metal bound water molecules.[14–16] We have employed such structures extensively in our research endeavours as catalysts for phosphodiester hydrolysis and as luminescent probes, and we have demonstrated that their function/activity is usually highly pH dependent.[17] For instance, we, and others, have shown that the emission of cyclen based Eu(III) and Tb(III) complexes can be tuned as a function of pH in systems possessing sensitizing antenna conjugated to the cyclen macrocycle *via* a carboxylamide linkage.[18–20] However, to the best of our knowledge, a dedicated study into the effect of pH on the luminescent properties of such simple lanthanide cyclen complexes, that do not have proton acceptors, *e.g.* heterocycles or amino functionalities, has not been carried out in any detail to date.

With this in mind, we set out to investigate these effects by synthesizing a series of novel cyclen derivatives **1–4** as well as investigating three known cyclen based structures, **5–7**, which lack any sensitizing antennae, Fig. 1. Our aim was to attempt to correlate results from potentiometric pH titrations with that of lanthanide luminescent pH titrations for these complexes, and gain understanding of the effect that metal bound water molecules,

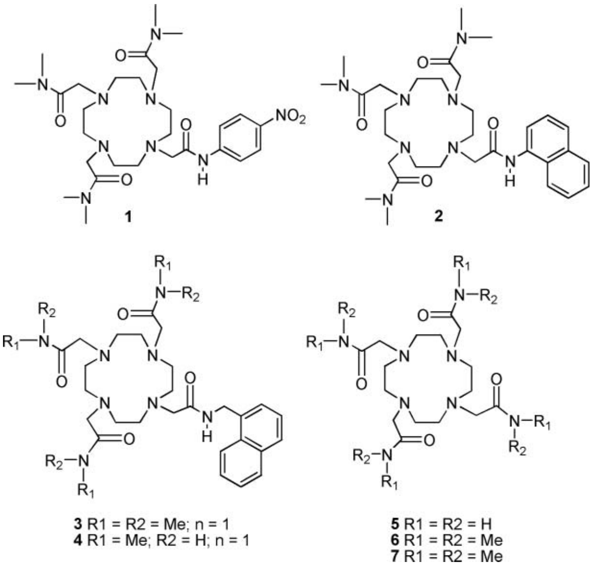
1
2
3 R1 = R2 = Me; n = 1
4 R1 = Me; R2 = H; n = 1
5 R1 = R2 = H
6 R1 = R2 = Me
7 R1 = R2 = Me

Fig. 1 Compounds **1–7** employed in the current study.

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as well as pendant arms, possessing protonating/deprotonating amide functional groups, have on the photophysical properties of these structurally simple complexes. The results obtained should allow for the accurate assignment of the various species in solutions, and correlate these to the changes in luminescence properties.

Results and discussion

Synthesis and characterization of 1–7

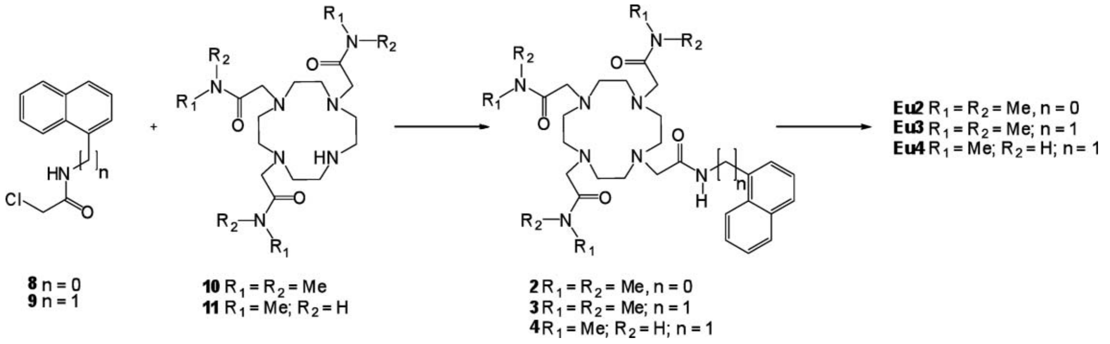
We have previously employed the naphthalene chromophore as a sensitizing antenna in lanthanide luminescent complexes for use as luminescent sensors for anions as well as in the development of lanthanide mediated self-assemblies.[15] Herein, examples **2–4** were developed by incorporating the naphthalene antenna through a pendant amide linkage, either *via* a methylene spacer or as part of the amide functionality. All the complexes were designed so that they would give rise to an eight coordinate environment around the lanthanide ion, which should ensure that each metal would possess a single metal bound water molecule, giving an overall nine coordinate complex. These structures should provide us with two possible scenarios, where in the case of **2**, the aryl amide possesses an acidic amide proton which can be deprotonated leading to concomitant modulation in the lanthanide luminescence, and in the cases of **3** and **4**, the antenna would not be expected to be as sensitive to changes in pH. Hence, for **3** and **4**, any significant luminescent changes observed as a function of pH should only be as a direct consequence of deprotonation of metal bound water molecules.

Compound **1** was also investigated for comparison, as the presence of the 4-nitro moiety in the aryl antenna would make the amide proton even more acidic and hence deprotonation at lower pH would be expected. The synthesis of ligands **1**, **5–7** and **Eu5–7** are established and reported elsewhere.[4,21,22] The synthesis of ligands **2–4** was achieved as shown in Scheme 1. The α-chloroamide compounds **8** and **9** were prepared from the reaction of the primary amine derivatives with triethylamine and either chloroacetyl chloride or chloroacetic anhydride, respectively, in DCM at 0 °C. Compound **8** was then reacted with the tri-substituted cyclen derivative **10** in the presence of Cs_2CO_3 in DMF to yield ligand **2**. Under similar conditions compound **9** was reacted with either the tri-substituted cyclen derivates **10** or **11** to yield ligands **3** or **4**, respectively. The Eu(III) complexes of **1** and **2** were made by reacting one equivalent of $Eu(ClO_4)_3$ with the ligand in MeOH at room temperature, giving complexes, **Eu1** and **Eu2**, respectively. In compounds **2–4**, the naphthyl-based antenna, has T_1 energy states lower than 20 000 cm^{-1}, as this prevents the effective population of Tb(III) excited states (due to quenching by O_2) and hence, only the Eu(III) complexes were made. The Eu(III) complexes of **3** and **4** were made by refluxing one equivalent of $Eu(CF_3SO_3)_3$ with the ligand in CH_3CN, giving complexes, **Eu3** and **Eu4**, respectively. All the Eu(III) complexes gave rise to significant chemical shifts in the ^{1}H NMR spectra due to the presence of the paramagnetic Eu(III) ion. The characterization of these ligands and their corresponding Eu(III) complexes is given in the experimental section.

The hydration state, or the number of metal bound water molecules was also determined, by measuring the lifetimes of the deactivation of the Eu(III) excited state in H_2O and D_2O respectively.[22] For **Eu2**, **Eu3** and **Eu4**, these were determined as 1.25, 1.11 and 1.55 (± 0.3), respectively, indicating that all of these complexes possessed a single metal bound water molecule. For **Eu4**, a *q* value of 1.55 is quite high, which might indicate that a second water molecule might be partially coordinating. Similarly, complexes **Eu1** and **Eu5–7** were also shown to have single metal water bound molecule. Having successfully synthesized the above compounds we next undertook the potentiometric analysis of ligands **1** and **2** and their corresponding Eu(III) complexes, with the aim of determining the pK_a of these metal bound water molecules.

Potentiometric determination of pK_a

The pK_a's of the protonated ligands **1**, Fig. 2, and **2** were determined in 50 : 50 water–methanol (v/v) solution to ensure complete solubilization. The ligands were acidified with $HClO_4$ and titrated against NEt_4OH under argon at 25 °C with $I = 0.1$ M (NEt_4ClO_4). The logarithm of the stepwise protonation constants for ligands **1** and **2**, obtained from the mathematical treatment of their respective potentiometric titration data are represented in Table 1; the conditions for each titration are listed below the table. Four pK_a's were determined for the protonated ligands **1** and **2** and these were assigned to the protonated macrocyclic amines. The incorporation of a naphthyl pendant arm in comparison to a nitro phenyl pendant arm had only a very small effect on the protonation constants of the ligands. The nitro phenyl pendant arm causes a slight increase in the overall acidity of the ligand in comparison to the naphthyl pendant arm. This can be attributed to differences in steric bulk of the two ligands, which alters the hydrophobicity of the system.



Scheme 1 Synthesis of compounds **2–4** and their corresponding Eu(III) complexes.

Table 1 Results from the potentiometric titration of **1** and **2**

pK_a	**1**	**2**
$[L][H^+]/[H(L)^+]$	8.52 ± 0.04	9.63 ± 0.03
$[LH][H^+]/[H_2(L)^{2+}]$	7.32 ± 0.04	8.17 ± 0.05
$[LH_2][H^+]/[H_3(L)^{3+}]$	6.85 ± 0.06	6.99 ± 0.06
$[LH_3][H^+]/[H_4(L)^{4+}]$	2.80 ± 0.09	2.63 ± 0.06

[**1**] = 5.60×10^{-4} mol dm^{-3}, $[H^+] = 4.40 \times 10^{-4}$ mol dm^{-3}, $[NEt_4OH] =$ 0.105 mol dm^{-3}; [**2**] = 4.33×10^{-4} mol dm^{-3}, $[H^+] = 9.01 \times 10^{-4}$ mol dm^{-3}, $[NEt_4OH] = 0.098$ mol dm^{-3}. All at 25 °C.

Table 2 Results form the potentiometric titration of **1** and **2** with Eu(III)

Equilibrium Quotient	**1**	**2**
$[Eu(L)^{3+}]/[Eu^{3+}][L]$	20.59 ± 0.02	20.89 ± 0.09
$[[Eu(LH_{-1})^{2+}]][H^+]/[Eu(L)^{3+}]$	6.55 ± 0.05	6.53 ± 0.09
$[Eu(LH_{-2})^+]\,[H^+]/[Eu(LH_{-1})^{2+}]$	7.97 ± 0.03	8.54 ± 0.09

[**1**] = 5.60×10^{-4} mol dm^{-3}, $[Eu^{3+}] = 1.00 \times 10^{-3}$ mol dm^{-3}, $[H^+] = 4.40 \times 10^{-3}$ mol dm^{-3}, $[NEt_4OH] = 0.105$ mol dm^{-3}. [**2**] = 6.72×10^{-4} mol dm^{-3}, $[Eu^{3+}] = 1.00 \times 10^{-3}$ mol dm^{-3}, $[H^+] = 9.01 \times 10^{-3}$ mol dm^{-3}, $[NEt_4OH] =$ 0.0986 mol dm^{-3}. All at 25 °C.

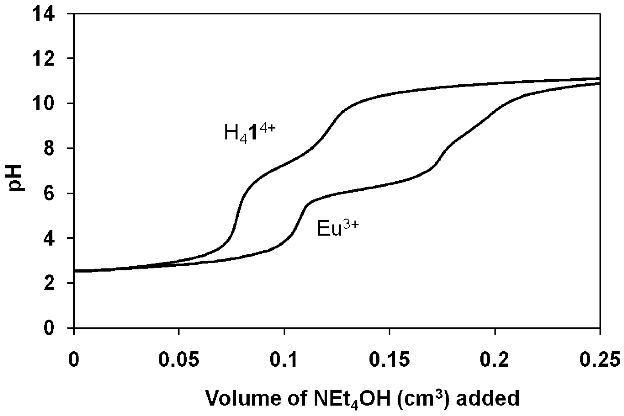


Fig. 2 Titration curve for protonated ligand **1** formed in solution where [**1**] = 5.60×10^{-4} mol dm^{-3} and $[H^+] = 4.40 \times 10^{-3}$ mol dm^{-3}, 25 °C with $I =$ 0.1 M (NEt_4ClO_4), 50 : 50 (v/v) MeOH–H_2O. The titration curve is also shown for the same solution, except that $[Eu^{3+}] = 1.00 \times 10^{-3}$ mol dm^{-3} is also present. Titrant $[NEt_4OH] = 0.105$ mol dm^{-3}.

We also determined the pK_a's of ligands **5–7** at 25 °C with $I =$ 0.1 mol dm^{-3} (NEt_4ClO_4) in 100% H_2O. However, we were only able to determine three pK_a's accurately for each of the ligands. For **5**, which possesses primary amides these were 10.71 ± 0.02, 8.93 ± 0.02 and 6.35 ± 0.03. Whereas, for **6**, possessing secondary amides, the three pK_a's were determined as: 9.13 ± 0.04, 5.60 ± 0.01 and 2.24 ± 0.01, and for **7**, with tertiary amides, these were determined as 9.50 ± 0.07, 6.34 ± 0.03 and 2.93 ± 0.03, respectively. The exact assignment of these pK_a's is difficult based only on this experimental data. However, based on analysis of similar systems[23] it is anticipated that for **6** and **7** the three pK_a's determined may be attributed to the protonation of the cyclen based amines. With the fourth cyclen based amine occurring at a very acidic pH. Whereas for **5**, only two of the pK_a's would be attributed to the cyclen based amines (third and fourth being too acidic for measurement); the other pK_a is most likely to be from one of the primary amide pendant arms.

Evaluating the formation of Eu1 and Eu2 by potentiometric titrations

The complexation constants and stoichiometry of the Eu(III) complexes of **1** and **2**, were determined using the above method, in the presence of Eu(III), Table 2. The metal ion competes with protons in the acidic media for ligand coordination sites; this alters the pH of the solution and results in a different titration curve as can be seen for **1** in Fig. 2. The basicity of the donor atoms is known to directly influence the stability of the complex, and as already mentioned, this is affected by the presence and type of pendant arm. The ligands presented here have been designed to coordinate lanthanide ions in an octadentate coordination "cage", leaving the lanthanide ion coordinatively unsaturated. Hence, the remaining site is then occupied by a water molecule. Two pK_a values for the metal ion complexes of ligands **1** and **2** with Eu^{3+} were determined. From the potentiometric titrations alone the exact assignment of these pK_a values is not possible. However, it can be anticipated that one of these pK_a values could be assigned to the deprotonation of the metal bound water molecule.

It has been previously reported by us and others that the incorporation of an electron withdrawing group in a position adjacent to the amide bearing the donor oxygen lowers the pK_a of the nitrogen in the amide.[15,16] Therefore, it can be assumed that the other pK_a corresponds with the deprotonation of the nitrogen in the bonding amide. The speciation distribution diagram for the titration of **1** with Eu(III) as a function of pH is shown in Fig. 3, and demonstrates three possible pH windows that could modulate the luminescence of the complex. The slight variation in the pK_a values for the two complexes, **Eu1** and **Eu2**, may be attributed to the differences in steric bulk. The determination of the stability constants for **5–7** was also attempted, however, on all occasions precipitation occurred under potentiometric titration conditions. The formation of insoluble metal hydroxide species at the high concentrations required for potentiometry is commonly observed for such cyclen based lanthanide complexes.[11]

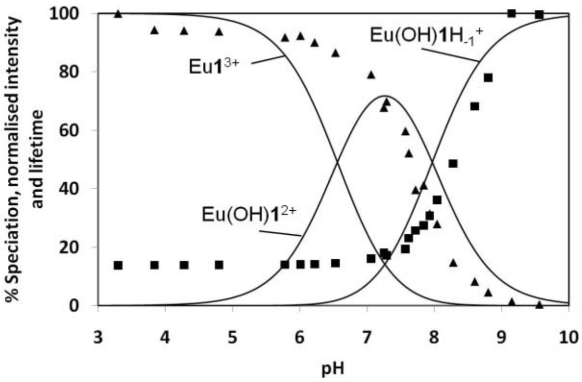


Fig. 3 Speciation variation of **Eu1** showing the species present in 50 : 50 (v/v) MeOH–H_2O at various pH in which [**1**] = 5.60×10^{-4} mol dm^{-3}, $[Eu^{3+}] = 1.00 \times 10^{-3}$ mol dm^{-3}, 25 °C with $I = 0.1$ M (NEt_4ClO_4). Speciation is shown relative to the total concentration of **1**. The normalized change in lifetime (■) and the Eu^{3+} emission intensity at 616 nm (▲) of the complex **Eu1** with pH is also shown.

Photophysical investigations as a function of pH of ligands 1 and 2 and their Eu(III) complexes

The lanthanide ions are considered to be photophysically inert with low molar absorptivity due to Laporte forbidden f–f transitions. While the lanthanide excited state can be formed by direct excitation, then these are often generated indirectly by using a sensitizing chromophore, or an antenna; these being the nitrobenzene and the naphthalene in ligands **1–4**.

The Eu^{3+} complexes **Eu1** and **Eu2**, were excited at their absorption maxima 298 nm and 280 nm, respectively. On both occasions, sensitized luminescence was observed from the metal ion centre in these complexes in 50 : 50 (v/v) MeOH–H_2O. The Eu^{3+} emission spectra recorded for **Eu1** in acidic media, following excitation of the nitrophenyl moiety at 298 nm, displayed five bands arising from the deactivation of ^5D_o level to ^7F_J ($J = 1$, 2, 3 and 4). In contrast to these results, when the same solution was excited in alkaline media at 298 nm, the Eu^{3+} emission is essentially fully quenched, Fig. 4. This is quite a striking result, as unlike many antennae previously reported in the literature it is only the amide moiety in the pendant arm that can be deprotonated under these conditions[13] as the antenna themselves do not possess groups capable of donating a proton. Consequently, we carried out a detailed luminescence pH titration of **Eu1**, the overall results of which are shown in Fig. 3.

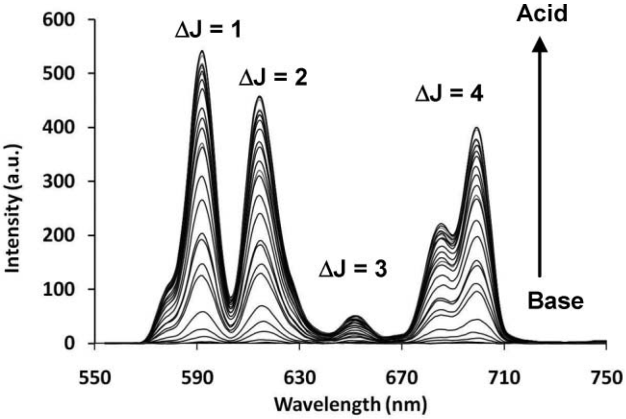


Fig. 4 Switching ON of the Eu^{3+} emission of **Eu1** (5×10^{-6} mol^{-1} dm^{-3}) as a function of pH (base → acid) for λ_{max} 278 nm, 25 °C with $I = 0.1$ mol^{-1} dm^{-3} (NEt_4ClO_4) in 50 : 50 (v/v) MeOH–H_2O.

Examination of the change in emission intensity as a function of pH showed that the emission intensity was unchanged until around pH 6.5, where upon a dramatic reduction in intensity follows as the pH is increased. Full quenching of the Eu^{3+} emission occurs above pH 10. The pH range over which the Eu^{3+} emission intensity changes suggests that the complex, **Eu1**, undergoes two deprotonation steps. The pK_a's determined for the deprotonation of the **Eu1** complex from the potentiometric titrations correlate very well with the pH range over which the Eu^{3+} emission intensity changes. The lifetimes of the **Eu1** complex as a function of pH were also recorded and were only observed to change above pH 7, as demonstrated in Fig. 3.

By plotting the changes in Eu^{3+} emission intensity and the lifetime of the complex with the changes in species of the **Eu1** complex determined potentiometrically as a function of pH the species can be assigned based on the resultant photophysical changes, Fig. 3. The change in the lifetime of the complex above pH 7 suggests that the pK_a at 7.97 corresponds with the deprotonation of the metal bound water. The lifetime of the complex would be expected to be significantly altered upon deprotonation of metal bound water. Therefore, deprotonation of the nitrogen in the bonding amide can be assigned to the pK_a occurring at 6.55. This pK_a is significantly lower than may be expected, but can be accounted for by the inclusion of the lanthanide ion and an electron withdrawing group. This is supported by the change in the fluorescence emission as a function of pH, Fig. 5. The largest change in fluorescence emission for **Eu1** occurs between pH 4–7; over 70% of the total change in fluorescence intensity occurs over this range. The fluorescence intensity is observed to plateau above pH 7. Deprotonation of the amide nitrogen adjacent to the nitrophenyl group would be expected to result in the largest change in fluorescence intensity. It is also important to note that the photophysical measurements along with the potentiometric titrations were carried out in the same solvent system, 50 : 50 (v/v) MeOH–H_2O, to allow for comparison.

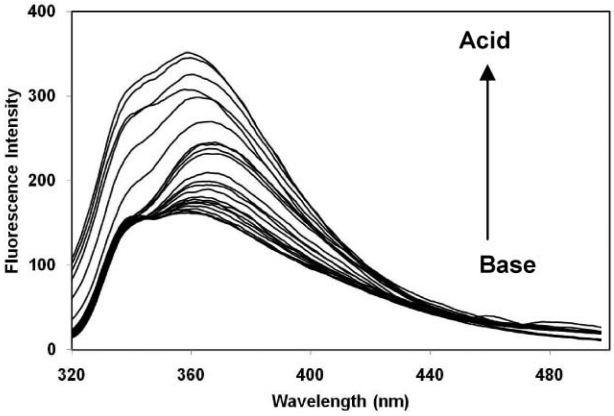


Fig. 5 Total changes in the fluorescence emission spectra with pH for **Eu1** (5×10^{-6} mol^{-1} dm^{-3}) (λ_{max} 278 nm, 25 °C with $I = 0.1$ mol^{-1} dm^{-3} (NEt_4ClO_4), 50 : 50 (v/v) MeOH–H_2O).

In a similar manner, excitation of **Eu2** at 280 nm gave rise to fluorescence from the naphthalene group and sensitized emission from the Eu^{3+} centre. The luminescence emission from the Eu^{3+} was sensitive to pH. Excitation at low pH gave rise to strong emission from the Eu^{3+} centre, increasing the pH resulted in a significant decrease in intensity of the metal-based emission; a number of protonation steps were visible. The steps were identified by monitoring all six *J* bands as a function of pH. From the resultant data protonation steps occurring between 6.5–7.0 and 8.0–8.5 can be observed. These values correspond extremely well with the values reported from the potentiometric titration. Examination of the change in intensity and lifetimes of the complex as a function of pH plotted against the speciation diagram for **Eu2**, Fig. 6 allows for assignment of the protonation steps. It is worth pointing out that the profile within the neutral and acidic media is quite different from that observed for **Eu2**, which is most likely due to the difference in the nature of the antenna itself. This is also supported by the change in fluorescence intensity as a function of pH (not shown). The fluorescence emission was only observed to undergo significant modulation between the pH ranges of

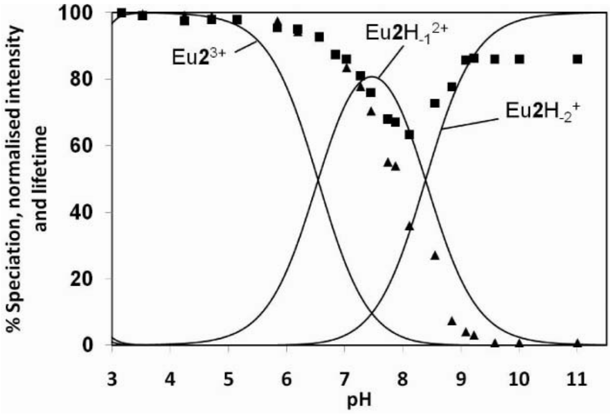


Fig. 6 Speciation variation of **Eu2** showing the species present in 50 : 50 (v/v) MeOH–H_2O at various pH in which [**2**] = 7.5 × 10^{-4} mol dm^{-3}, [H^+] = 1.1 × 10^{-2} mol em^{-3}, [Eu(III)] = 1 × 10^{-3} mol dm^{-3}, [NEt_4OH] = 0.11 mol dm^{-3}, *I* (NEt_4ClO_4) = 0.1 mol dm^{-3}. Speciation is shown relative to the total concentration of 1. The normalized change in lifetime (■) and the Eu^{3+} emission intensity at 616 nm (▲) of the complex **Eu2** with pH is also shown.

5–7. This indicates that the deprotonation of the nitrogen amide adjacent to the naphthalene residue occurs over this pH range.

The combination of the four types of data (potentiometric, fluorescence, luminescence and lifetimes) has allowed for accurate assignment of the species in solution and their physical properties for both **Eu1** and **Eu2**. This would not have been possible had the data not be examined in conjunction with each other. The accurate assignment of the species in solution, especially the deprotonation of the metal bound water *vs.* the amide is especially important for the synthesis and activity of enzyme mimics.

Photophysical investigations of Eu3 and Eu4 a function of pH

With the view of exploring the effect that introducing a spacer between the antenna and the coordinating amide has on photophysical properties **Eu3** was synthesized. In addition **Eu4** was also synthesized to examine if changing the pendant arms, which do not contain the antenna moiety, from a tertiary to a secondary amide has an effect on Eu(III) emission as a function of pH. Both **Eu3** and **Eu4** had absorption maxima centred around 280 nm, assigned to the π–π* transition of the naphthalene group. This is similar to **Eu2** as expected. Slight hyperchromic shifts were observed for the band centered at 280 nm for both complexes at elevated pH; the largest changes been seen between pH 10–13. The effect was reversible in each case.

Similar pH dependent changes were seen in fluorescence emission spectrum over the same pH range, where the emission was *ca.* 50% quenched in alkaline pH. For both **Eu3** and **Eu4**, upon excitation at 278 nm, the formation of an emission band centered at ~340 nm was observed, which was similar to that seen for **Eu2** above.

Excitation of the antenna at 278 nm in **Eu3** and **Eu4** also gave rise to Eu(III) centred emission. At neutral pH, the hydration states were found to be 1.1 and 1.5 for **Eu3** and **Eu4**, respectively. The intensity of the Eu(III) emission when excited at 281 nm was also recorded as a function of pH. The Eu(III) emission for both **Eu3** and **Eu4** was enhanced by *ca.* 10 fold at high pH (above pH 10), This indicates that both **Eu3** and **Eu4** have a pK_a in the range of 11.5–12, *e.g.* Fig. 7, for **Eu3**. On comparison of the pH range over which both the Eu^{3+} emission intensity and the fluorescence intensity changes for **Eu2** and **Eu3** we can see that the acidity of the system decreased as the distance between the amide and the aromatic group increased. This supports the argument that the presence of an electron withdrawing group adjacent to the amide significantly alters the acidity of this group, with concomitant changes in the pH response of the Eu(III) emission.

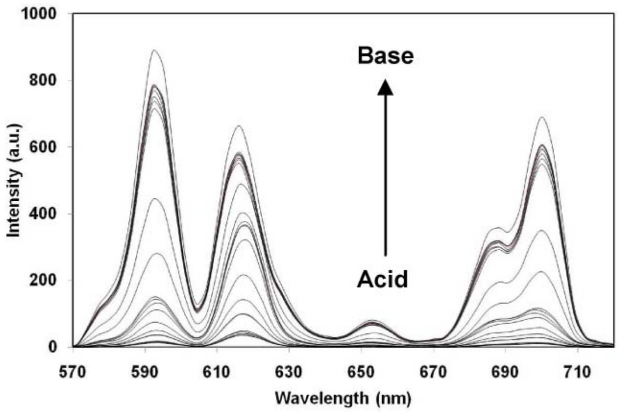


Fig. 7 Variation of the Eu^{3+} emission intensity with pH for **Eu3** (2.0 × 10^{-5} mol^{-1} dm^{-3}) (λ_{max} 278 nm, 25 °C with *I* = 0.1 mol^{-1} dm^{-3} (NEt_4ClO_4), 50 : 50 (v/v) MeOH–H_2O).

Photophysical investigations of Eu5–7 as a function of pH

With the view of attempting to quantify the effect of pH on the Eu(III) emission further, we next investigated a series of complexes that lack any antennae. It was anticipated that the results from these investigation would help quantify the effect of pH on lanthanide bound water molecules as well as give some insight into the effect pH has on structural changes within such simple cyclen based systems; where only the amide moieties are modified, being NH_2, NHMe and NMe_2 for **5**, **6** and **7**, respectively.

In the case of **Eu5–Eu7**, which are well known structures, the lack of antennae means excitation of the Eu(III) ion can only be achieved through direct excitation at the metal centre at 395 nm. The changes in the Eu(III) emission as a function of pH were monitored in a similar manner to that seen for **Eu1** and **Eu2**. The overall changes in the Eu(III) emission of **Eu5** as a function of pH is shown in Fig. 8A, which demonstrates significant emission changes as a function of pH. By plotting the intensity changes against pH as shown in Fig. 8B, it can be seen that within acidic and neutral pH regions, the emission can be considered as being pH independent. While at more alkaline pH the emission from the hypersensitive $\Delta J = 2$ transition is initially "enhanced" up to *ca.* pH 11, but thereafter, the emission is quenched. In contrast, the emission arising from the $\Delta J = 1$ and 4 transitions, is quenched within the same alkaline region.

With the view of further analyzing this pH dependence, the excited state lifetimes of the Eu(III) emission were recorded as a function of pH, which showed that in acidic and neutral pH regions (*ca.* pH 2 → 8) the lifetimes in water remained constant. However, above pH 8 a slight shift occurred and above pH 11 the lifetimes became significantly longer. Plotting the changes as

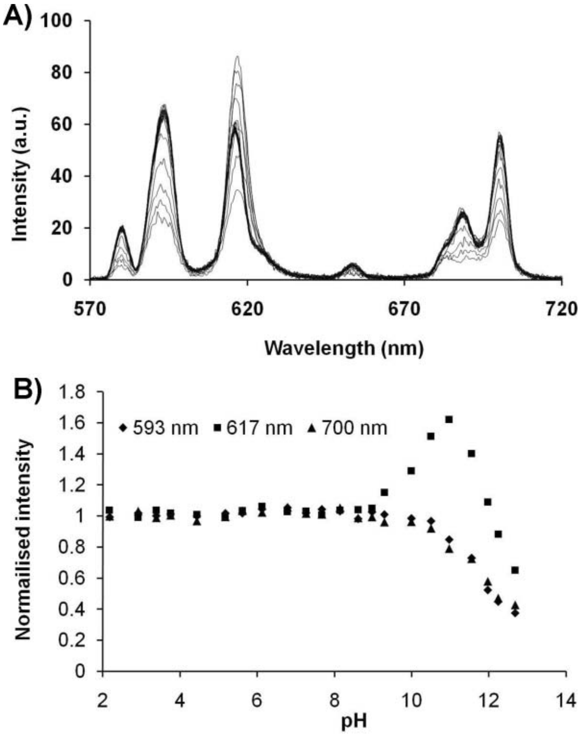


Fig. 8 A) The overall changes in the Eu(III) emission of **Eu5** (5×10^{-4} mol dm^{-3}) upon excitation into the Eu(III) ion directly in NEt_4OH at 298.2 (± 0.2) K, $I = 0.01$ M (NEt_4ClO_4) in 100% H_2O solution. B) The normalized emission changes observed at 593, 617 and 700 nm, respectively, for the Eu(III) emission as a function of pH.

a function of pH, gave a profile that resembled that seen for the changes in the $\Delta J = 2$ transition.

We next repeated the pH titrations using **Eu6** and **Eu7**. Similar changes were seen in the Eu(III) emission spectra of these complexes as was seen for **Eu5**, with the exception that the $\Delta J = 2$ transition was not quenched at high pH.

The analysis of the three transitions $\Delta J = 1$, 2 and 4 is shown in Fig. 9A and Fig. 9B, for **Eu6** and **Eu7**, respectively. This demonstrates again, that the emission from the hypersensitive $\Delta J = 2$ transition is enhanced in alkaline pH, while the $\Delta J = 1$ and 4 transitions are quenched. While we were unable to fit this data to give accurate protonation constants, it is clear from these profiles that the nature of the amide substituent has a significant affect on the emission. The change in Eu(III) emission can only be assigned to either, the deprotonation of metal bound water molecules, or the deprotonation of the amides. The former, would be expected to have pK_a around pK_a ~8–9. Hence, as the emission is most significantly affected for the primary amide **5**, we propose that the observed modulation in the Eu(III) emission is more to do with deprotonation of the amide moieties, or that in highly basic media, the complexes undergo some structural changes that effects $\Delta J = 2$, which is highly sensitive to the coordination environment of the complexes.

Unfortunately, we were, as discussed above, unable to determine the pK_a's of these complexes using potentiometric measurements due to early precipitation for these systems. The pH at which precipitation of these complexes occurred supports the formation of the metal bound hydroxyl species. However, at the low concentrations required for spectroscopy, this process in these systems does not give rise to significant changes in the Eu(III) emission, clearly demonstrating that the interruption of any such changes in the metal centred emission can be difficult to elucidate.

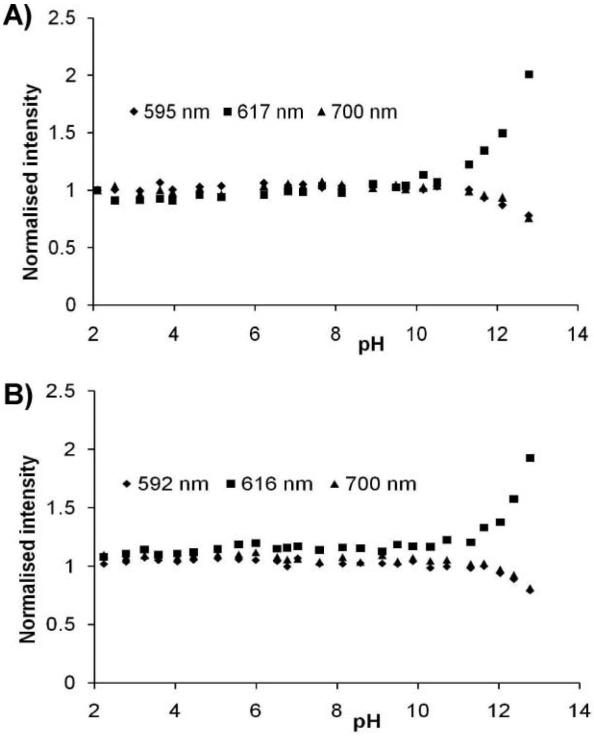


Fig. 9 A) The normalized Eu(III) emission changes for **Eu6** observed at 592, 617 and 700 nm as a function of pH. B) The same observed for **Eu7**.

Conclusions

In conclusion, we have shown how a range of physical measurements can be exploited in the effort to understand the formation of species in solution. By comparing changes in physical properties through a range of techniques the assignment of complex protonation steps was made feasible. We have also demonstrated that the emission arising from the lanthanide ion can be highly sensitive to the nature of the pendant arms, as the Lewis acid nature of lanthanide and the nature of the amide substituent's can enable various competitive deprotonation processes to be activated which result in the modulation of the lanthanide emission.

Experimental

2-Chloro-*N*-naphthalen-1-yl-acetamide 8

1-Amino naphthalene (1 g, 6.9 mmol) was dissolved in a solution of DCM (40 cm^3) and triethylamine (1.78 cm^3, 13 mmol), the mixture was cooled to 0 °C. A solution of chloroacetyl chloride (0.828 cm^3, 10.4 mmol) in DCM (30 cm^3) was then added dropwise to the reaction mixture at 0 °C. The reaction was left to warm to room temperature overnight and then quenched with a dropwise addition of water (15 cm^3). The organic layer was then washed with 0.1 mol dm^{-3} hydrochloric acid and a saturated solution of sodium hydrogen carbonate. The organic layer was then dried and the solvent removed under reduced pressure to give a brown solid. Purification by means of a silica squat column [100% DCM, R_f 0.8] yielded an off white solid (1.11 g, 74%), δ_H (400 MHz; $CDCl_3$) 4.38 (2H, s, CH_2Cl), 7.51–7.60 (3H, m, Ar-H), 7.77 (1H, d, Ar-H), 7.91 (2H, t, Ar-H), 8.00 (1H, d, Ar-H); δ_C (100 MHz; $CDCl_3$) 42.9 (CH_2Cl), 119.7, 120.1, 125.5, 125.8, 126.0, 126.2, 126.4, 128.4, 130.6, 133.6 (Ar-H), 163.9 (C=O); m/z (ESMS) (M − Na^+) Found: 242.0341. $C_{12}H_{10}NONaCl$ requires 242.0349, $C_{12}H_{10}NClO$: C, 65.61; H, 4.59; N, 6.38; Found: C, 65.35; H 4.51; N, 6.08; Calculated for $C_{12}H_{10}NClO$, IR ν_{max}/cm^{-1} 3255, 3051, 3028, 2922, 2852, 1665, 1557, 1397, 1348, 1268, 1248, 1207, 967, 960, 813, 790, 769, 742, 718.

2-Chloro-*N*-naphthalen-1-yl-methyl-acetamide 9

The naphthalene methylamine (0.46 cm^3, 3.18 mmol) was added to a stirred solution of chloroacetic anhydride (547 mg, 3.19 mmol), and triethylamine (0.1 cm^3, 0.73 mmol) in DCM (25 cm^3). The solution was left stirring overnight at room temperature. The solution was washed with acid (1 mol dm^{-3} HCl, 30 cm^3) and distilled water (30 cm^3) and then dried over magnesium sulfate. The solution was filtered and the solvent removed under reduced pressure. The resulting solid was dried under vacuum for several hours to yield a white solid (0.417 g, 56%). Calculated for $C_{13}H_{12}NClO$: C, 66.81; H 5.18; N, 5.99, Found: C, 66.63; H, 4.96; N, 5.99; Calculated for $C_{13}H_{12}NClO$: [M + Na peak] m/z = 256.69, Found, 256.05: δ_H (400 MHz, $CDCl_3$) 7.98 (1H, d, J = 7.52 Hz, Ar-CH), 7.91 (1H, d, J = 7.52, Ar-CH), 7.85 (1H, m, Ar-CH), 7.56 (2H, m, Ar-CH), 7.52 (2H, m, Ar-CH), 6.85 (1H, s, N–H), 4.95 (2H, d, J = 5.52 Hz, CH_2), 4.11 (2H, s, CH_2); δ_C (100 MHz, $CDCl_{3)}$ 165.56 (C=O), 133.82 (qC), 132.47 (qC), 131.25 (qC), 128.9 (Ar-CH), 128.84 (Ar-CH), 126.78 (Ar-CH), 126.69 (Ar-CH), 126.08 (Ar-CH), 125.34 (Ar-CH), 123.13 (Ar-CH), 42.53 ($CH_{2)}$ 41.93 (CH_2); Mass Spec (MeCN, ES+) m/z Expected: 233.7, found 234.1 (M + H), 256.0 (M + Na); IR ν_{max}/cm^{-1} 3281, 3059, 3043, 3010, 2956, 2887, 1644, 1546, 1511, 1471, 1422, 1397, 1226, 799, 784, 730, 703, 675, 563, 554, 449.

1,4,7-Tris(dimethylcarbamoylmethyl)-1,4,7,10-tetraazacyclododecane 10

Cyclen (1 g, 5.8 mmol) and sodium hydrogen carbonate (1.42 g, 17.4 mmol) were dissolved in CH_3CN and the solution cooled to 0 °C, a solution of the α-chloroamide of dimethylamine (2.11 g, 17.4 mmol) in CH_3CN was then added quickly. The reaction was then heated at reflux for 4 days. The reaction was then filtered through Celite and the solvent removed under reduced pressure. The residue was then re-dissolved in DCM (20 cm^3) and the solution filtered. Purification by column chromatography [gradient elution 100% DCM–MeOH 80 : 20 (v/v), R_f 0.3] yielded ligand **10** as an off white solid (1.5 g, 60%); δ_H (400 MHz; $CDCl_3$) 2.84 (8H, s, cyclen CH_2), 2.89 (9H, s, CH_3), 2.97 (6H, s, CH_3), 3.04 (3H, s, CH_3), 3.09 (8H, s, cyclen CH_2), 3.58 (4H, s, CH_2N), 3.59 (2H, s, CH_2N); δ_C (100 MHz; $CDCl_3$) 34.9, 36.0, 36.4, 45.7, 49.3, 50.5, 51.2, 53.3, 55.2 (CH_2N and CH_3N), 169.9, 169.8 (C=O); m/z (ESMS) 450.4 (M − Na^+).

2-(4,7-Bis-methylcarbamoylmethyl-1,4,7,10-tetraaza-cyclododec-1-yl)-*N*-methyl-acetamide 11

Cyclen (0.2645 g, 1.535 mmol), sodium hydrogen carbonate (0.379 g, 4.52 mmol) and 2-chloro-*N*-methyl acetamide (0.5 g, 4.67 mmol) were dissolved in CH_3CN (20 cm^3) and heated at reflux for 72 h. After removal of the solvent under reduced pressure the resultant yellow oil was redissolved in the minimum amount of ethanol and added dropwise to a stirred solution of diethyl ether. The solution was left to stir for 30 min during which a white precipitate became visible. The ether was removed and the solid dried under high vacuum to yield ligand **11** as an white solid (0.31 g, 52%). Calculated for $C_{17}H_{35}N_7O_3$: [M + H peak] m/z = 386.5, Found = 386.28: δ_H (400 MHz, $CDCl_3$) 8.12 (1H, N–H), 8.01 (1H, N–H), 7.95 (1H, N–H), 3.31 (4H, s, CH_2), 3.25 (2H, s, CH_2), 2.97 (8H, m, CH_2), 2.81 (5H, d, J = 4.52, CH_2), 2.77 (6H, d, J = 4.52, CH_2), 2.66 (3H, m, CH_3); δ_C (100 MHz, $CDCl_3$) 172.31 (C=O), 171.83 (C=O), 60.97 (CH_2), 56.09 CH_2), 55.93 (CH_2), 53.77 (CH_2), 52.33 (CH_2), 47.17 (CH_2), 26.03 (CH_3); Mass Spec (MeCN, ES+) m/z Expected: 385.5, Found: 386.2 (M + H), 408.2 (M + Na); IR ν_{max}/cm^{-1} 3534, 3266, 2943, 2830, 1667, 1651, 1634, 1563, 1557, 1456, 1411, 1310, 1244, 1163, 1109, 730.

1-(4-Aminonapthylcarbamoyl) tris(dimethyl-carbamoylmethyl)-1,4,7,10-tetraazacyclododecane 2

Compound **10** (400 mg, 0.93 mmol), compound **8** (204 mg, 0.93 mmol) and diissopropylethylamine (0.486 cm^3, 2.8 mmol) were dissolved in DMF and the reaction left to stir at room temperature for 7 days. The solvent was removed under reduced pressure and the residue was then redissolved in DCM and washed with water to yield a white solid (513 mg, 90%); δ_H (400 MHz; $CDCl_3$) 2.56 (16H, m, cyclen CH_2), 2.83 (6H, s, CH_3), 2.90 (6H, s, CH_3), 2.95 (6H, s, CH_3), 3.39 (2H, s, CH_2N), 3.44 (6H, s, CH_2N), 7.35–7.48 (4H, m, Ar-H), 7.76–7.87 (3H, d, Ar-H); δ_C (100 MHz; $CDCl_3$) 35.0, 35.67, 53.04, 54.26, 54.47, 54.53, 56.94 (CH_2N and CH_3N), 121.39, 123.74, 124.64, 124.74, 124.86, 125.12, 125.17, 125.37, 127.16, 128.09 (Ar-H), 170.26, 170.44, 170.55, (C=O); m/z (ESMS) 633 (M − Na^+); HRMS: m/z (ESMS) Found: 633.3866 $C_{32}H_{50}N_8O_4Na$ requires 633.3853.

N-Naphthalen-1-ylmethyl-2-(4,7,10- tris-dimethyl-carbamoyl methyl-1,4,7,10 tetraaza cyclododec-1-yl)- acetamide 3

Compound **10**. (197.6 mg, 0.461 mmol), compound **8** (110.4 mg, 0.472 mmol) and caesium carbonate (155.9 mg, 0.478 mmol) were dissolved in dry CH_3CN (15 cm^3) and heated at reflux under argon for 48 h. After refluxing the solution was left to cool to room temperature and was then filtered using Celite. The solvent was removed under reduced pressure and the resulting solid was dissolved in the minimum amount of DCM. This resin was then passed down an alumina column using DCM with increasing amounts of ethanol as a solvent to yield ligand **3** as a light yellow solid (0.195 g, 67.5%). Calculated for $C_{33}H_{52}N_8O_4$: [M + H peak] m/z = 624.83, Found = 625.42: δ_H (400 MHz, $CDCl_3$) 7.99 (1H, d, J = 8.04 Hz Ar-CH), 7.75 (1H, d, J = 7.53 Hz, Ar-CH), 7.60 (1H, d, J = 8.04 Hz, Ar-CH), 7.52 (1H, d, J = 6.53 Hz, Ar-CH), 7.39 (2H, m, Ar-CH), 7.27 (1H, m, Ar-CH), 4.75 (1H, s, N–H), 3.33 (2H, m, CH_2), 3.11 (2H, m, CH_2), 2.97 (5H, m, CH_2), 2.93 (10H, m, CH_2), 2.81 (1H, m, CH_2), 2.79 (15H, m, CH_2/CH_3), 2.31 (5H, m, CH_3); δ_C (100 MHz, $CDCl_{3)}$ 171.4 (C=O), 170.51 (C=O), 170.34 (C=O), 134.73 (qC), 133.23 (qC), 130.96 (qC), 128.12 (Ar-CH), 126.92 (AR-CH), 125.7 (Ar-CH), 125.25 (Ar-CH), 124.54 (AR-CH), 123.23 (Ar-CH), 57.03 (CH_2), 54.67 (CH_2), 54.46 (CH_2), 53.33 (CH_2), 51.04 (CH_2), 50.38 (CH_2), 40.11 (CH_2), 35.52 (CH_3), 35.17 (CH_3), 35.14 (CH_3); Mass Spec (MeCN, ES+) *m*/*z* Expected: 624.79, Found: 625.41 [M + H], 647.39 [M + Na].

N-Naphthalen-1-ylmethyl-2-(4,7,10-tris-methylcarbamoyl-methyl-1,4,7,10tetraaza-cyclododec-1-yl)-acetamide 4

Compound **11** (0.0987 g, 2.56 mmol), compound **9** (0.0541 g, 2.314 mmol) and caesium carbonate (0.097 g, 0.298 mmol) were dissolved in dry CH_3CN (15 cm^3) and heated at reflux under argon for 48 h. After refluxing the solution was left to cool to room temperature and was then filtered using Celite. The solvent was removed under reduced pressure and the resulting solid was dissolved in the minimum amount of DCM. This resin was then passed down an alumina column using DCM and increasing amounts of ethanol as a solvent to yield ligand **4** as a light yellow solid (0.1014 g, 75.2%). Calculated for $C_{30}H_{46}N_8O_4$: [M + H peak] *m*/*z* = 583.75, Found = 583.37: δ_H (400 MHz, MeOH) 8.12 (1H, d, *J* = 8.0 Hz, Ar-CH), 7.92 (1H, m, Ar-CH), 7.83 (1H, d, *J* = 8.04 Hz, Ar-CH), 7.54 (3H, m, Ar-CH), 7.45 (1H, m, Ar-CH), 3.32 (6H, m, CH_2), 3.08 (8H, m, CH_2), 2.76 (20H, m, CH_2/CH_3), 2.36 (5H, m, CH_3); δ_C (100 MHz, $CDCl_3$) 173.21 (C=O), 172.80 (C=O), 172.18 (C=O), 134.37 (qC), 134.25 (qC), 134.18 (qC), 128.89 (Ar-CH), 128.73 (Ar-CH), 126.35 (Ar-CH), 125.95 (Ar-CH), 125.83 (Ar-CH), 125.54 (Ar-CH), 125.44 (Ar-CH), 123.32 (Ar-CH), 63.59 (CH_2), 61.65 (CH_2), 58.51 (CH_2), 57.11 (CH_2), 52.86 (CH_2), 51.13 (CH_2), 50.43 (CH_2), 25.35 (CH_3), 25.32 (CH_3); Mass Spec (MeCN, ES+) *m*/*z* Expected: 582.75, Found: 583.91 [M + H], 605.92 [M + Na]); IR ν_{max}/cm^{-1} 3419, 3266, 3073, 2945, 2824, 1664, 1554, 1451, 1411, 1355, 1310, 1240, 1160, 1107, 992, 971, 915, 890, 805, 780, 729, 600.

Eu(III) complex of ligand 1, Eu1

$Eu(ClO_4)_3$ (0.031 cm^3, 0.051 mmol) was added to a stirred solution of ligand **1** (31 mg, 0.051 mmol) in MeOH (2 cm^3) a precipitate formed, which was redissolved in CH_3CN (5 cm^3). The solvent was then left to evaporate and the resultant solid dried under reduced pressure to yield a yellow solid (27 mg, 70%); δ_H (400 MHz; $CDCl_3$) −8.47, −6.51, −0.99, 0.29, 1.13, 1.28, 1.33, 1.72, 1.97, 2.13, 2.92, 3.18, 3.43, 4.04, 8.26, 9.49, 10.13, *m*/*z* (ESMS) 378 (M^+/2); HRMS: *m*/*z* (ESMS) Found: 758.19 $C_{28}H_{47}N_9O_6Eu$ requires 757.69. Found C 31.67, H 4.77, N 10.11. Expected C 31.85, H 4.49, N 11.94 $C_{28}H_{47}N_9O_6Eu^+.(ClO_4^-)_3$.

Eu(III) complex of ligand 2, Eu2

$Eu(ClO_4)_3$ (0.080 cm^3, 0.132 mmol) was added to a stirred solution of ligand **2** (81 mg, 0.132 mmol) in MeOH (2 cm^3). A precipitate formed, which was redissolved in CH_3CN (5 cm^3). The solvent was then left to evaporate and the resultant solid dried under reduced pressure to yield a yellow solid. The solid was resuspended in CH_3CN and CH_2Cl_2, ether was then added and the resulting solid collected and dried under vacuum to yield **Eu2** (81.9 mg 81.5%); δ_H (400 MHz; $CDCl_3$) −7.92, −5.41, −0.36, 0.90, 1.29, 1.96, 2.83, 3.57, 3.85, 4.10, 7.59, 8.00, 8.12, 8.59, 15.1; *m*/*z* (ESMS) 861 ($C_{32}H_{51}N_8O_4EuClO_4^{2+}$) 381 ($M^+$/2); HRMS: *m*/*z* (ESMS) Found: 762.3196 $C_{32}H_{51}N_8O_4Eu$ requires 762.3232. Found C 31.67, H 4.77, N 10.11. Expected C 32.10, H 4.23, N 9.63 $C_{32}H_{51}N_8O_4Eu^{3+}.Na^+(ClO_4^-)_4.CH_2Cl_2.CH_3CN$.

Eu(III) complex of ligand 3, Eu3

A solution containing $Eu(CF_3SO_2)_3$ (0.173 mg, 0.246 mmol) and ligand **3** (0.153 mg, 0.246 mmol) in CH_3CN (15 cm^3) was freeze–thawed twice and then heated at reflux overnight. After, the solution was left to cool to room temperature. The solution was then added dropwise to a swirling solution of ether and was then left for a further 30 min. A precipitate formed. Ether was then removed and the resulting solid was dried under vacuum to yield **Eu3** as a light yellow solid (0.1757 g, 91.7%). Calculated for $C_{42}H_{54}N_8O_{14}S_3F_9Eu$: C, 38.35; H, 4.14; N, 8.52; Found: C, 30.44; H, 3.61; N, 7.70; δ_H (400 MHz, MeOH) 31.92, 10.87, 8.69, 7.74, 5.04, 3.39, 1.3, 0.17, −5.64, −7.56, −13.39, −15.65; δ_F (376 MHz, MeOH) 78.18; Mass Spec (MeCN, ES+) *m*/*z* Expected: 1224.12 Found: 1075.32 [M – triflate], 463.14 [M – 2triflate/2], 388.16 [M – 3triflate/2]; IR ν_{max}/cm^{-1} 3470, 1623, 1510, 1460, 1437, 1411, 1256, 1226, 1166, 1081, 1031, 958, 910, 824, 802, 781, 760, 639, 575, 517, 352.

Eu(III) complex of ligand 4, Eu4

Ligand **4** and $Eu(CF_3SO_3^-)_3$ were added in a 1 : 1 ratio to MeCN (15 cm^3). The solution was freeze–thawed twice and was then heated at reflux overnight while being stirred. After refluxing the solution was left to cool to room temperature. The solution was then added dropwise to a stirred solution of ether and was then left for a further 30 min. A precipitate formed. The ether was decanted off and the resulting solid was dried under vacuum to yield **Eu4** as a light yellow solid (0.1757 g, 91.7%). δ_H (400 MHz, MeOH) 28.12, 8.29, 7.39, 6.93, 6.54, 4.90, 3.49, 3.32, 2.77, 2.29, 2.04, 1.18, 0.97, 0.27, −1.99, −5.83, −7.76, −12.35, −13.39, −13.69; δ_F (376 MHz, MeOH) −80.54; Mass Spec (MeCN, ES+) *m*/*z* Expected: 1181.83, Found: 441.12 [M – 2triflate/2], 367.14 [M – 3triflate/3]; IR ν_{max}/cm^{-1} 3318, 3138, 2953, 2884, 1639, 1587, 1513, 1464, 1417, 1363, 1255, 1226, 1166, 1086, 1030, 994, 972, 936, 893, 831, 806, 794, 781, 761, 723, 639, 575, 517.

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