The recognition of anions using delayed lanthanide luminescence: The use of Tb(III) based urea functionalised cyclen complexes†

Cidália Maria Gomes dos Santos and Thorfinnur Gunnlaugsson*

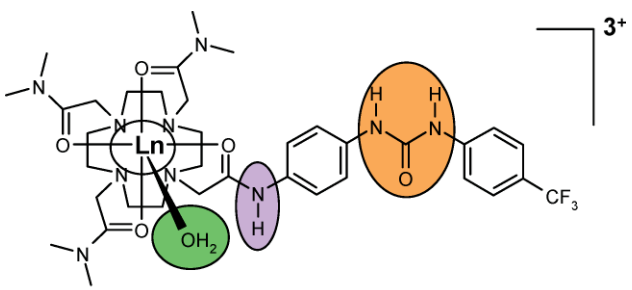
Received 12th February 2009, Accepted 9th April 2009
First published as an Advance Article on the web 7th May 2009
DOI: 10.1039/b902955a

A cyclen based lanthanide luminescent sensor, **Tb.1**, has been developed by taking advantage of a combination of hydrogen bonding and *f*-metal ion coordination binding sites for anionic species. Analysis of the ground state, the emission from the singlet and the Tb(III) excited states clearly show the ability of the Tb(III) complex to signal the presence of anions in CH_3CN, through multiple binding interactions consisting of hydrogen bonding and metal coordination. The delayed lanthanide luminescence from the Tb(III) diaryl–urea complex was found to be significantly enhanced only upon recognition of $H_2PO_4^-$, at the same time as displaying good selectivity over other competitive anions, such as CH_3COO^-.

Introduction

The development of luminescent and colorimetric sensors for anion recognition is currently a highly topical area of research.[1–14] Anions are essential to life in many biological processes, in industry and in agriculture, which also puts them in the class of environmental pollutants. Because of this, much effort is currently being directed towards the development of synthetic anion receptors. In general, anion recognition has been achieved by the use of: ammonium[15,16] or guanidinium moieties;[17,18] coordination complexes using transition metal ions or lanthanides;[19–24] and charge neutral hydrogen bonding receptors, such as thioureas and ureas,[25–35] amides,[36,37] amidoureas/thioureas.[38–46] For sensing, these systems often employ fluorescence as the mode of detection, which can be affected by auto-fluorescence from surrounding biological environments or light scattering. To overcome this, luminescent sensors that possess long-lived excited states have been designed. These include the use of delayed lanthanide luminescence for sensing purposes which have been widely employed, as Ln(III) ions possess large Stokes shift, narrow emission bands, and long excited state lifetimes.[47–55] Further, their Lewis acid character, and strong electrostatic bonding nature, as well as the sensitivity of the hyperfine transitions of Eu(III) and Tb(III) to changes in their local coordination environment, makes the Ln(III) ideal candidates for anion sensing. However, for the luminescent sensing of anions, the use of hydrogen bonding motives and lanthanide metal coordination within a single structure, has, to the best of our knowledge, not been much explored to date.[56,57]

We and others, have employed cyclen (1,4,7,10-tetraazacyclododecane) derivatives as such sensors for both, inorganic, aliphatic and aromatic anions in competitive aqueous media using Ln(III) ions.[19,23,24,51,57–61] With the aim of developing novel luminescent anion sensors that possess maximum binding affinity, arising from the use of combinations of different anion binding sites, including hydrogen binding (*e.g* from urea and amide moieties) as well as direct interaction with the metal centre, we designed the lanthanide complexes **Tb.1** and **Eu.1**.[62] In these systems, the di-aryl amidourea moiety, works as a combined sensitising antenna and a hydrogen bonding anion receptor.[63] In addition, direct interaction with the metal centre, by displacement of the solvent molecule, offers a third binding site for the anions. Consequently, we foresaw that these binding interactions would perturb the photophysical properties of both the receptor as well as the lanthanide centre. Herein we present the results obtained from the studies carried out in **Tb.1** upon titration with various anions in CH_3CN, and we demonstrate that our design gives rise to high anion binding affinity, which occurs through multiple binding interactions, which results in significant changes in the Tb(III) emission.



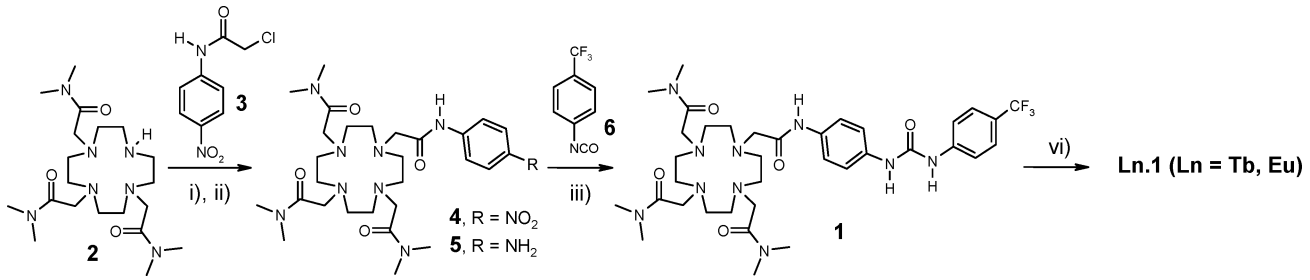
Ln.1 (Ln = Tb, Eu)

Results and discussion

Synthesis of 1 and corresponding Ln(III) complexes

The synthesis of ligand **1**, is shown in Scheme 1, and involves the coupling of the tri-arm acetamide cyclen derivative **2** and chloro-*N*-(nitrophenyl) acetamide **3**, in CH_3CN under reflux conditions, in the presence of Cs_2CO_3 and KI. This gave compound **4** in 74% yield after purification by column chromatography on neutral alumina, using a gradient elution (CH_2Cl_2 to 20% CH_3OH). This was followed by the reduction of the nitro group to the corresponding amine, **5**, using $N_2H_4{\cdot}H_2O$ in the presence of 10% Pd/C in EtOH under reflux. Finally, **5** was reacted with trifluoro-*p*-tolyl isocyanate, **6**, in dry $CHCl_3$ at

School of Chemistry, Centre of Synthesis and Chemical Biology, University of Dublin, Trinity College Dublin, Dublin 2, Ireland. E-mail: gunnlaut@tcd.ie
† Electronic supplementary information (ESI) available: Spectra and speciation data for **Tb.1** and **Eu.1** See DOI: 10.1039/b902955a



Scheme 1 Synthesis of **1** and corresponding **Ln.1** complexes: (i) CH_3CN, Cs_2CO_3 and KI; (ii) EtOH, $N_2H_4.H_2O$, 10% Pd/C; (iii) $CHCl_3$; (iv) CH_3CN, $Ln(CF_3SO_3)_3$.

room temperature, yielding **1** in 67% after column chromatography on neutral alumina, using a gradient elution (CH_2Cl_2 to 20% CH_3OH).

The ^{1}H-NMR spectra (400 MHz, $CDCl_3$) of **1** showed the presence of the expected three N–H resonances, occurring at 10.07, 9.94 and 9.43 ppm, respectively (see ESI† Fig. S1). The synthesis of the lanthanide complexes **Tb.1** and **Eu.1** was then achieved by refluxing **1** with equivalent amounts of $Ln(CF_3SO_3)_3$ in CH_3CN. The ^{1}H-NMR spectra (400 MHz, CD_3OD) of both complexes showed the presence of the paramagnetic Ln(III) ions, as was evident from the broad resonances appearing over a large range (ESI†Fig. S2a). The ESMS for both **Tb.1** and **Eu.1** showed the expected isotopic distribution patterns (ESI† Fig. S2b). The complex formation was also evident from the IR spectrum, as upon Ln(III) complexation the IR stretching frequency of the carbonyl bands decreased from 1646 cm^{-1}, in **1**, to 1619 cm^{-1} and 1618 cm^{-1} for **Tb.1** and **Eu.1**, respectively.

The hydration number, q, of the complexes was determined by measuring the excited state lifetimes (τ) of **Tb.1** and **Eu.1** in H_2O (τ_{H_2O}) and D_2O (τ_{D_2O}), taking into account the quenching contributions of proximate NH and OH oscillators, by direct excitation of the lanthanide ions at 366 and 395 nm for Tb(III) and Eu(III), respectively.[47] A mono-exponential decay was observed for both Eu(III) and Tb(III) complexes. Lifetimes for **Tb.1** in H_2O and D_2O were measured to be 1.36 ms and 2.04 ms, respectively. From these values, a q value of 0.93 was determined, indicating the presence of a single metal bound water molecule. In contrast, **Eu.1** gave rise to shorter decays in both solvents, from which lifetimes of 0.25 ms and 0.40 ms were determined for H_2O and D_2O respectively, from which a q value of 1.17 was found, indicating that **Eu.1** also possess a single metal bound water molecule.

Evaluating the photophysical properties of Tb.1 and Eu.1

The design of **Tb.1** and **Eu.1** envisaged indirect excitation of the Ln(III) metal centre through the covalently attached di-aryl amidourea antenna in **1**, *via* the triplet excited state, to the Tb(III) $^5D_4$ and Eu(III) $^5D_0$ accepting levels.

The spectra of **Tb.1** and **Eu.1** are shown in Fig. 1, when recorded in CH_3CN by exciting at 280 nm (antenna λ_{max}). It clearly shows the characteristic emission bands for the Tb(III) and Eu(III) ions due to the radiative deactivation of the $^5D_4$ and $^5D_0$ to the ground states, ^7F_J, demonstrating the successful sensitisation from the antenna. By plotting these as relative intensities in Fig. 1, it is clear that

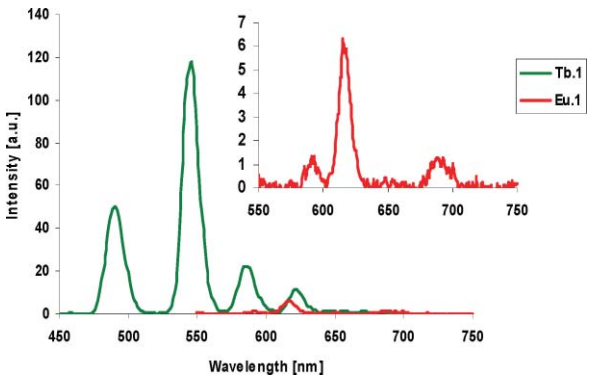


Fig. 1 Lanthanide luminescence spectra of **Tb.1** and **Eu.1**. Inset shows the weaker sensitisation of the Eu(III) ion.

Eu.1 showed much weaker sensitizer than **Tb.1**.‡ Therefore, the following discussion will only focus on the studies carried out on **Tb.1** in the presence of anions.

The binding between anions (**G**) and **Tb.1** (**H**) (4 μM) was investigated by observing the changes in both the ground and the singlet excited states, as well as the changes in the Ln(III) luminescence. As the anion recognition at the antenna moiety occurs *via* hydrogen binding interactions, which are generally difficult to achieve in aqueous environments,[32] all anion titrations discussed herein, were carried out in non aqueous CH_3CN solution. The anions studied were CH_3COO^-, $H_2PO_4^-$, $H_2P_2O_7^{2-}$, F^-, and Cl^- (used as their tetrabutylammonium salts (TBA^+) solutions) all of which are expected to bind to either the antenna *via* hydrogen bonding or at the metal centre.

The absorption spectrum of **Tb.1** exhibits a broad band centred at 280 nm (Fig. 2, blue spectrum), which we assign to the π–π* transitions of the antenna. Excitation at this wavelength gave rise to a very weak fluorescence emission (Fig. 2, red spectrum), while the spectrum for the lanthanide emission (Fig. 2, green spectrum) shows four well defined bands at 490, 546, 586, and 622 nm, corresponding to the deactivation of $^5D_4$ to the ground states, ^7F_J ($J = 6$, $J = 5$, $J = 4$ and $J = 3$, respectively).

‡ Such inefficiency could be predicted from the lifetime experiments discussed above. The accepting energy levels of Eu(III) are much lower than those of Tb(III). Consequently, the low emission arising from Eu(III) is most likely due to non-radiative deactivation pathways. Because of this, no further studies were performed on the Eu(III) complex, **Eu.1**. No significant changes were observed in the Eu(III) emission upon binding to anions.

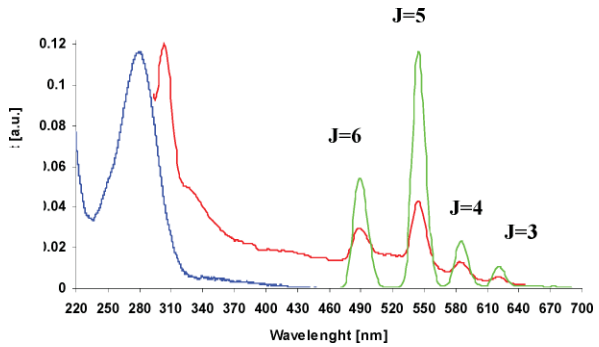


Fig. 2 Absorption (blue), Fluorescence (red), Phosphorescence (green) spectra of **Tb.1** in CH_3CN, upon excitation at 280 nm.

Changes in the absorption spectra of Tb.1 upon titration with anions

The changes observed in the **Tb.1** spectra upon titration with CH_3COO^-, shown in Fig. 3, clearly demonstrate that the binding interaction between this anion and the **Tb.1** complex has significant effect on the ground state. Here, the band at *ca.* 278 nm was red shifted to *ca.* 288 nm with the formation of a "pseudo" isosbestic point at *ca.* 281 nm. The changes observed at 270 nm and 300 nm, *vs* the number of equivalents of CH_3COO^-, are also shown as inset in Fig. 3. These changes clearly illustrate the presence of different binding stoichiometries in solution, and complex host–guest interactions, where at least two distinct processes occur. The first of these, takes place up to one equivalent CH_3COO^-, corresponding to an increase in absorbance at 278 nm, while the second binding interaction, which gives rise to the decrease in absorbance at 270 nm, occurs between 1 → 4 equivalents of CH_3COO^-.

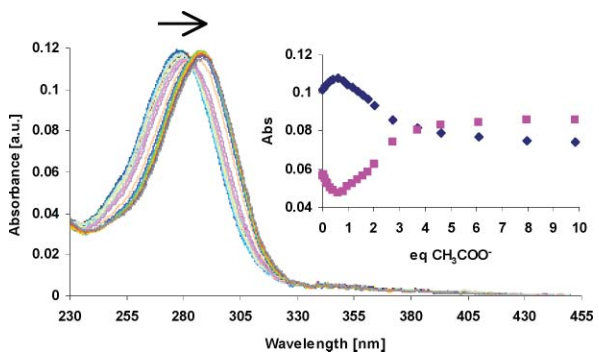


Fig. 3 Changes in the absorption spectra of **Tb.1** (4 μM) upon gradual additions of CH_3COO^- (0 → 74.9 μM) in CH_3CN. Inset shows the titration profile at 270 nm (blue) and 300 nm (pink), *vs* the number of equivalents of CH_3COO^-.

By fitting these changes to 1:1 (**G**:**H**) and 2:1 (**G_2**:**H**) binding stoichiometries, using the non-linear least squares regression analysis program SPECFIT, an excellent fit was observed as shown in Fig. 4. From this analysis, binding constants for both the 1:1 and the 2:1 stoichiometries were determined, as log $K_{1:1} = 6.27 \pm 0.12$ and log $K_{2:1} = 5.84 \pm 0.09$. From these binding constants, speciation distribution diagram was obtained (inset in Fig. 4), which clearly shows that **G_2**:**H** complex formation dominates the binding process upon an excess addition of CH_3COO^-.

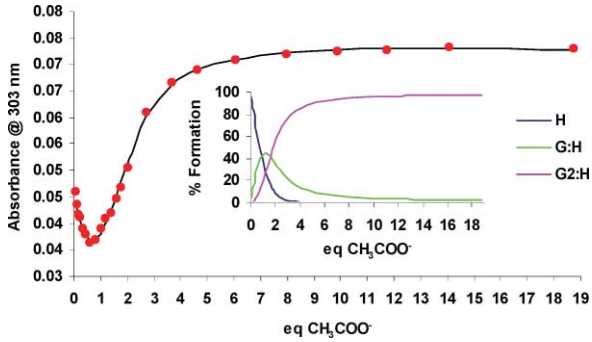
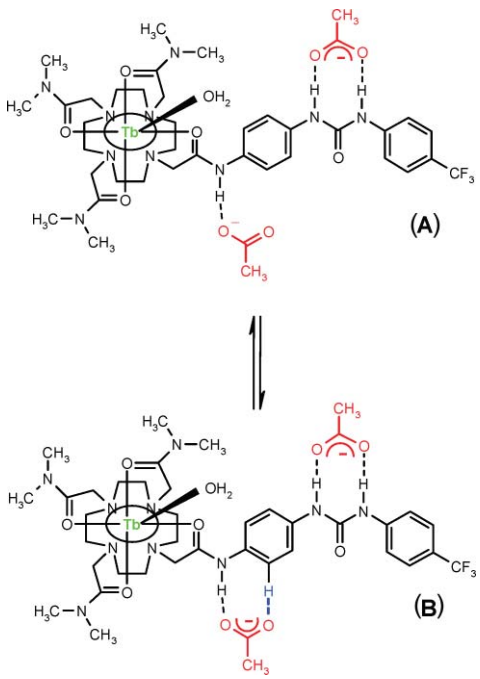


Fig. 4 Experimental binding isotherm for the UV-Visible titration of **Tb.1** (4 μM) with CH_3COO^- in CH_3CN (●) and corresponding fit using SPECFIT (—). Inset shows the speciation distribution diagram obtained from the fit.

Taking into account the discussion above, we suggest that the strongest binding, corresponding to the formation of the 1:1 (**G**:**H**) complex, occurs through hydrogen bonding between the anion (CH_3COO^-) and the urea moiety of **Tb.1**, Scheme 2 Form A. We propose that the second binding interactions takes place between the amide moiety in **Tb.1** and CH_3COO^-, which can also interact with an aromatic CH as depicted in Scheme 2 Form B. The presence of such aryl H-bonding to anions has been shown to enhance considerably the anion binding affinity by Hay *et al.*[67] This proposed binding was further supported by carrying out both UV-Visible and ^{1}H-NMR titrations on di-aryl model compounds possessing both the acetamide and the urea moieties.[38] This model receptor, which is structurally similar to the recognition/antenna component of **Tb.1**, gave rise to analogous binding interactions. However, and as expected due to the absence of the lanthanide ion, the binding constants were found to be lower than those observed for **Tb.1**.



Scheme 2 Proposed binding interaction for the formation of the 2:1 (**G_2**:**H**) complex between **Tb.1** and CH_3COO^-.

Similarly, the interaction between **Tb.1** and $H_2PO_4^-$ also gave rise to a red shift in the absorption spectrum (to *ca.* 288 nm), although two "pseudo" isosbestic points were observed at *ca.* 250 and *ca.* 294 nm, Fig. 5. Again, the lack of well defined isosbestic points is an indication of possible multiple binding interactions.[64] This was further supported by fitting the changes in Fig. 5, using SPECFIT, which resulted in the determination of several binding constants, which are summarised in Table 1. Similarly, titrations were carried out using the structurally related pyrophosphate ($H_2P_2O_7^{2-}$). Although similar changes were observed to that seen in Fig. 5 (see ESI† Fig. S3 for $H_2P_2O_7^{2-}$) only the titrations using $H_2PO_4^-$ gave rise to the formation of a 3:1 (**G_3:H**) species in solution with a strong binding constant of $\log K_{3:1} > 7$ (7.95 ± 0.21). As shown in Fig. 6, this species was found to be the predominant one in solution after the addition of *ca.* 1.5 equivalents of $H_2PO_4^-$. This is a rather unusual binding stoichiometry as it would suggest that the anion binds to the urea moiety, and to the metal centre, where the latter binding mode seem to affect the changes in the absorption spectra as well. A good fit to the experimental data was obtained for the titrations of **Tb.1** with $H_2P_2O_7^{2-}$ and $H_2PO_4^-$ using SPECFIT (see ESI† Fig. S4 and S5, respectively). Both

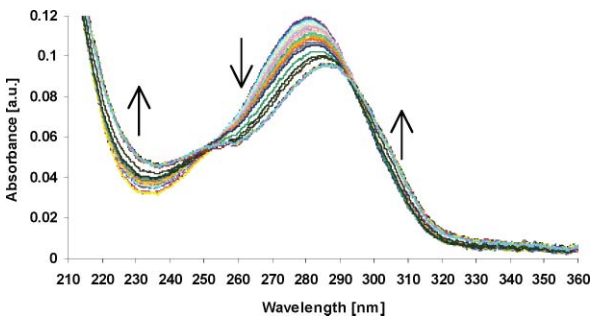


Fig. 5 Changes in the absorption spectra of **Tb.1** (4 μM) upon gradual additions of $H_2PO_4^-$ (0 → 57.3 μM) in CH_3CN.

Table 1 Binding constants determined from the absorption titration data for the interaction of **Tb.1** with the various anions in CH_3CN[a]

Anion	Species	log*K*	Std. deviation (±)
CH_3COO^-	**G:H**	6.27	0.12
	G_2:H	5.84	0.09
	G:H	>7 (7.06)[b]	0.24
	G:H_2	4.87	0.47[c]
$H_2PO_4^-$	**G_2:H**	5.66	0.95[c]
	G_2:H_2	6.79	0.37
	G_3:H	>7 (7.95)	0.21
	G:H	>7 (7.47)[b]	0.19
	G:H_2	5.50	0.33
$H_2P_2O_7^{2-}$	**G_2:H**	6.02	0.30
	G_2:H_2	5.70	0.94[c]
	G:H	5.97	0.18
	G:H_2	4.73	0.31[c]
	G_2:H	5.16	0.16
F^-	**G_2:H_2**	5.52	0.45[c]
	G_3:H	4.49	0.19
	G_4:H	4.82	0.31
	G_5:H	3.51	0.70[c]
Cl^-	**G:H**	5.49	0.07

[a] Obtained by fitting the spectroscopic data using SPECFIT. [b] Binding constant too large to be accurately determined using SPECFIT. [c] Species present in less than 10%.

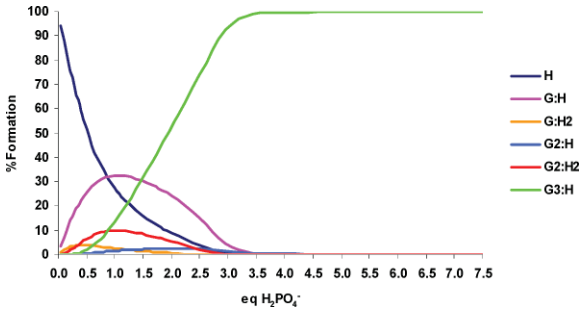


Fig. 6 Speciation distribution diagram for the UV-Visible titration of **Tb.1** (H) with $H_2PO_4^-$ (G) in CH_3CN.

ions gave rise to strong 1:1 (**G**:**H**) interactions with log $K > 7$ (Table 1). Furthermore, the presence of a 1:2 (**G_2**:**H**) stoichiometry, which would suggest the formation of a self-assembly structure in solution was also observed, but as can be seen from Fig. 6, only as a minor species. Such binding was not observed for CH_3COO^-, and can be ascribed to the ability of both $H_2PO_4^-$ and $H_2P_2O_7^{2-}$ to bind in a bidentate manner. Such anion mediated self-assembly formation using $H_2P_2O_7^{2-}$ has previously been seen in our laboratory.[44]

We next carried out titration using F^- (see ESI†Fig. S6). The changes observed for the interaction with F^- deviated significantly from that seen above. Upon analysis of the binding stoichiometries, at least two different processes were observed. The first of these, occurred within the range of 0 → 7 equivalents of F^-, where a bathchromic shift of *ca.* 3 nm (280 nm to 283 nm, with two isosbestic points at *ca.* 249 nm and *ca.* 285 nm) was observed. The second change, occurred between the additions of 8 → 17 equivalents of F^-, and resulted in a hypsochromic shift with the loss of the isosbestic points. Such changes can be assigned to multiple binding interactions between F^- and **Tb.1**, as well as possible deprotonation of both the urea and amide moieties to form HF_2^-, which are often seen in non-aqueous solution.[11,32,33,65,66] The complexity of these interactions, was difficult to quantify accurately (see ESI† Fig. S7). However, from the fit of the experimental data, we were able to determine several possible binding interactions, which are summarised in Table 1. These constants were found to be significantly lower than those observed for CH_3COO^- and $H_2PO_4^-$.

In contrast to the results discussed above, interaction with Cl^- gave rise to less prominent changes in the absorption spectra. The band centred at 280 nm experienced a small decrease, which was accompanied by a minor bathochromic shift (see ESI† Fig. S8). By fitting these changes the 1:1 (**G:H**) complex was the only species formed upon titration of **Tb.1** with Cl^-, from which a log $K_{1:1} = 5.49 \pm 0.07$ was determined.

Changes in the singlet excited state of Tb.1 upon titration with anions

With the aim of further investigate the binding interactions of **Tb.1** with these anions; the fluorescence emission arising from the antenna was also monitored. Excitation at 280 nm gave rise to a weak emission intensity exhibiting a broad band centred at 330 nm. Moreover, the main four transitions of Tb(III) were also observed at longer wavelengths, Fig. 7.

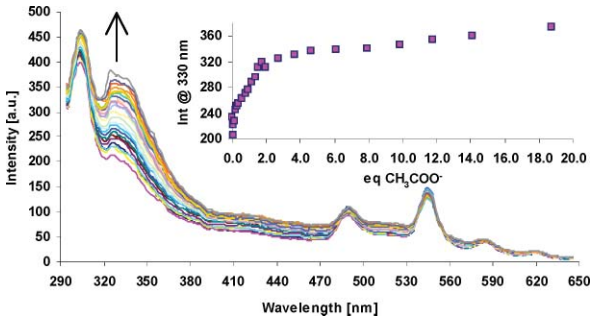


Fig. 7 Changes in the fluorescence emission intensity of **Tb.1** (4 μM) upon addition of CH_3COO^- (0 → 74.9 μM) in CH_3CN. Inset shows the titration profile at 330 nm *vs* the equivalents of CH_3COO^-.

Upon addition of CH_3COO^-, only a minor increase was observed in the fluorescence intensity, centred at *ca.* 330 nm, Fig. 7. Analysing these changes in a manner described above, binding constants of $\log K_{1:1} = 5.78 \pm 0.30$ and $\log K_{2:1} = 5.11 \pm 0.51$ were determined, which are in good agreement with the results obtained for the absorption studies.

In contrast to the titration of CH_3COO^-, the changes seen upon titration with $H_2PO_4^-$, $H_2P_2O_7^{2-}$ (Fig. 8) and F^- gave rise to more dramatic changes, in the fluorescence emission. As can be seen from Fig. 8, the fluorescence emission increased substantially with the formation of a new band centred at *ca.* 422 nm, with enhancements of *ca.* 10, 15, and 5 fold for $H_2PO_4^-$, $H_2P_2O_7^{2-}$ and F^-, respectively (see ESI† Fig. S9 and S10 for titrations with $H_2PO_4^-$ and F^-, respectively). The binding constants determined from these changes are summarised in Table 2, and were found to be in very good agreement with the results obtained for the ground state. As for the absorptions studies, $H_2P_2O_7^{2-}$ was observed to form strong 1:1 binding with $\log K_{1:1} > 7$ (7.68 ± 0.13), while $H_2PO_4^-$ gave rise to the formation of the 3:1 (**G**$_3$:**H**) complex with a very high binding constant of $\log K_{3:1} > 7$ (7.95 ± 0.20), which was the predominant species in solution after the addition of *ca.* 1.5 equivalents of $H_2PO_4^-$, Fig. 9. All the binding constants obtained from these titrations are listed in Table 2.

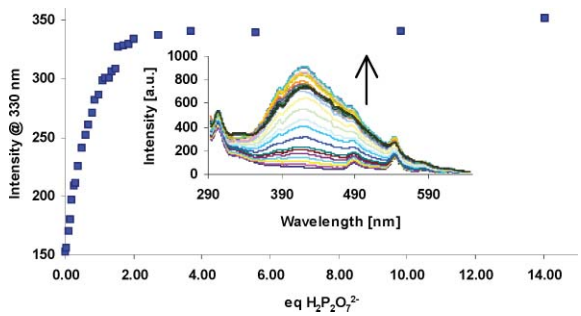


Fig. 8 Experimental binding isotherm of the fluorescence emission intensity at 330 nm *vs* the equivalents of $H_2P_2O_7^{-2-}$. Inset shows the changes in the spectra of **Tb.1** (4 μM) upon addition of $H_2P_2O_7^{-2-}$ (0 → 56.3 μM) in CH_3CN.

As previously observed, F^- showed a different behaviour to the anions discussed above. In this case, upon addition of 0 → 5 equivalents, the emission intensity experienced an enhancement in the 330 nm band. Nonetheless, only upon excess addition of F^- (5 → 17 equivalents) was the new band centred at *ca.* 422 nm formed (see ESI†Fig. S10). This latter phenomenon can be compared with the second process in the absorption spectra (which gave rise to the hypsochromic shift) as both the absorption and fluorescence spectra change around the same equivalents of F^-. Complex interactions were once again observed to take place between F^- and **Tb.1**, giving rise to several binding interactions that were difficult to quantify accurately. Nevertheless, we were able to determine binding values from these changes, see Table 2, which were in good agreement with that previously seen above, and demonstrate the ability of F^- to function as a base under these experimental conditions.

Once again, and as observed for the absorption spectra, interaction with Cl^- gave only rise to minimal changes in the singlet excited state emission (see ESI† Figure S11). By fitting these changes, a binding constant of $\log K_{1:1} = 5.39 \pm 0.06$ was determined for the 1:1 (**G**:**H**) binding interaction which was found to be in very good agreement with that obtained for the absorption studies.

Table 2 Binding constants determined from the fluorescence titration data for the interaction of **Tb.1** with the various anions in CH_3CN[a]

Anion	Species	log *K*	Std. deviation (±)
CH_3COO^-	**G:H**	5.78	0.30
	G$_2$**:H**	5.11	0.51
	G:H	6.86	0.21
	G:H$_2$	5.15	0.25[c]
$H_2PO_4^-$	**G**$_2$**:H**	5.34	0.94[c]
	G$_2$**:H**$_2$	6.84	0.53[c]
	G$_3$**:H**	> 7 (7.95)[b]	0.20
	G:H	> 7 (7.68)[b]	0.13
$H_2P_2O_7^{2-}$	**G:H**$_2$	6.19	0.28
	G$_2$**:H**	6.48	0.25
	G$_2$**:H**$_2$	5.83	0.71[c]
	G:H	6.29	0.11
	G:H$_2$	3.92	0.87[c]
	G$_2$**:H**	5.58	0.25
F^-	**G**$_2$**:H**$_2$	5.11	0.53[c]
	G$_3$**:H**	5.44	0.09
	G$_4$**:H**	5.07	0.23
	G$_5$**:H**	5.69	0.15
Cl^-	**G:H**	5.39	0.06

[a] Obtained by fitting the spectroscopic data using SPECFIT. [b] Binding constant too large to be accurately determined using SPECFIT. [c] Species present in less than 10%.

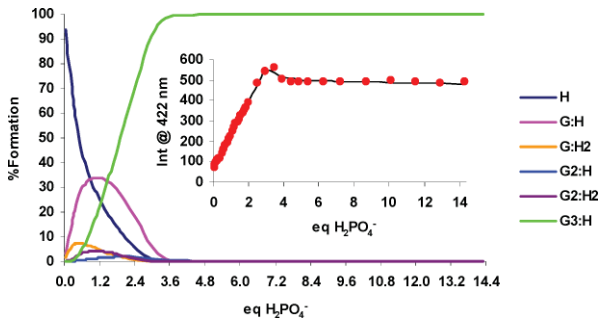


Fig. 9 Speciation distribution diagram for the fluorescence titration of **Tb.1** (4 μM) with $H_2PO_4^-$ (0 → 57.3 μM). Inset shows the experimental binding isotherm (●) and corresponding fit (—) obtained using SPECFIT.

Changes in the Tb(III) luminescence of Tb.1 upon titration with anions

Having investigated the changes in both the ground and the singlet excited states of **Tb.1** upon titration with the various anions, the changes in the Tb(III) emission (when exciting into the antenna at 280 nm) were investigated.

Upon titration with CH_3COO^- the emission intensity was quenched by *ca.* 56% (see ESI† Fig. S12). These results, clearly demonstrate that the energy transfer process from the antenna excited state of the anion-bound complex to the Tb(III) excited state ($^5D_4$) are effected upon anion binding at the antenna. By fitting the changes using SPECFIT, a good fit to the experimental data was observed (see ESI† Fig. S13), from which binding constants of log $K_{1:1} = 6.87$ and log $K_{2:1} = 5.12$ were determined. Once again, these were found to be in a excellent agreement with the results obtained from previous investigations.

Upon titrating **Tb.1** with $H_2PO_4^-$, $H_2P_2O_7^{2-}$, and F^- the overall Tb(III) emission was also significantly modulated. As seen in the singlet excited state results, these changes can be divided into two distinct processes. As in the case of CH_3COO^-, the Tb(III) emission was initially quenched, by *ca.* 70%, 28%, and 72% for $H_2PO_4^-$, $H_2P_2O_7^{2-}$, and F^- respectively. This was however, followed by significant enhancements in the emission intensity at higher anion concentration, indicative of the multiple binding phenomenon observed in both the ground and the singlet excited state studies. In the case of $H_2PO_4^-$, an enhancement, in the order of *ca.* 14 fold, was observed, Fig. 10, which clearly demonstrate the sensitivity of the Tb(III) emission to changes in the local environment of **Tb.1**. The profile of the emission intensity changes at 546 nm *vs* the equivalents of $H_2PO_4^-$, are shown as inset in Fig. 10, and clearly demonstrate this affect. From these changes, it can be seen that upon addition of one equivalent of $H_2PO_4^-$ the emission intensity was reduced, which was immediately followed by a increase up to two equivalents of anion. However, the major luminescence changes occur between 2 and 3 equivalents of $H_2PO_4^-$, giving rise to "switching on" of the Tb(III) emission. The excellent fit to the changes seen in Fig. 10, is shown as an inset in Fig. 11. From this fit several binding constants were once again determined (and are summarised in Table 3), which were found to be in very good agreement with those obtained for the changes in both the ground and the singlet excited states (*cf.* Table 1 and 2 respectively). Once again, the predominant species were found to be the 1:1 (**G**:**H**) and the 3:1 (**G$_3$**:**H**), as shown in the speciation distribution diagram,

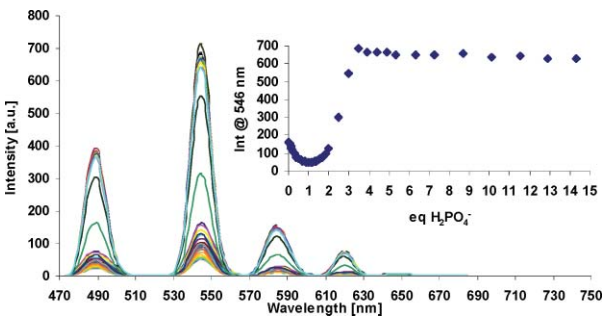


Fig. 10 Changes in the Tb(III) emission intensity of **Tb.1** (4 μM) upon addition of $H_2PO_4^-$ (0 → 57.3 μM) in CH_3CN. Inset shows the titration profile at 546 nm *vs* the equivalents of $H_2PO_4^-$.

Table 3 Binding constants determined from the lanthanide luminescence titration data for the interaction of **Tb.1** with the various anions in CH_3CN[a]

Anion	Species	log *K*	Std. Deviation (±)
CH_3COO^-	**G:H**	6.87	0.46
	G$_2$:H	5.12	0.49
	G:H	> 7 (7.04)	0.14
	G:H$_2$	4.59	0.24[c]
$H_2PO_4^-$	**G$_2$:H**	4.90	0.82[c]
	G$_2$:H$_2$	> 7 (7.20)	0.18[c]
	G$_3$:H	> 7 (8.04)[b]	0.12
	G:H	> 7 (7.40)[b]	0.12
$H_2P_2O_7^{2-}$	**G:H$_2$**	5.94	0.26
	G$_2$:H	5.34	0.15
	G$_2$:H$_2$	5.89	0.43[c]
	G:H	6.07	0.02
	G:H$_2$	4.13	0.04[c]
	G$_2$:H	5.36	0.01
F^-	**G$_2$:H$_2$**	4.47	0.16[c]
	G$_3$:H	3.42	0.62[c]
	G$_4$:H	6.90	0.01
	G$_5$:H	2.85	0.77[c]
Cl^-	**G:H**	6.06	0.03

[a] Obtained by fitting the spectroscopic data using SPECFIT. [b] Binding constant too large to be accurately determined using SPECFIT. [c] Species present in less than 10%.

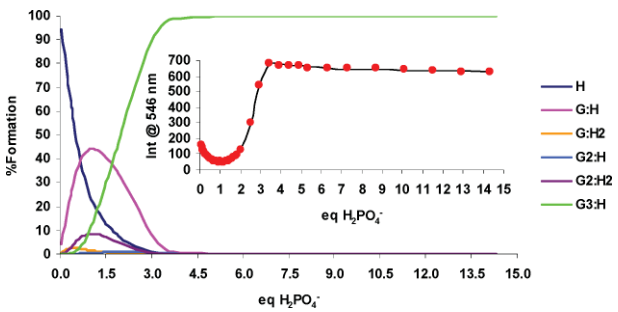
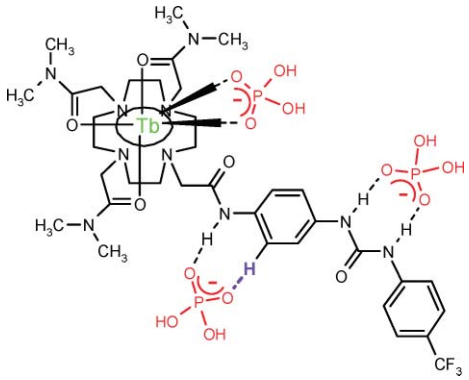


Fig. 11 Speciation distribution diagram for the lanthanide luminescence titration of **Tb.1** (4 μM) with $H_2PO_4^-$ (0 → 57.3 μM). Inset shows the experimental binding isotherm (●) and corresponding fit (—) obtained using SPECFIT.

Fig. 11, with high binding constants of log $K > 7$ (log $K_{1:1} = 7.04 \pm 0.14$ and log $K_{3:1} = 8.04 \pm 0.12$). These results also demonstrate that the emission is only "switched on" upon formation of the **G$_3$**:**H** complex between $H_2PO_4^-$ and **Tb.1**. This can be attributed to changes in the direct coordination environment of Tb(III), caused by the binding of $H_2PO_4^-$ to the Tb(III) centre directly. Such binding, would be caused by displacement of the bound solvent molecules, as shown in Scheme 3. Such enhancement of the emission intensity, was allied with the changes observed in the Tb(III) excited state lifetimes upon addition of $H_2PO_4^-$, (see ESI† Fig. S14).

The Tb(III) emission was also affected in a similar manner upon titration with both $H_2P_2O_7^{2-}$ and F^-. However, in contrast to that observed in Fig. 10, these changes were less prominent, and occurred at different concentration ranges. For instance, in the case of $H_2P_2O_7^{2-}$, the addition of the first 0.5 equivalents did result in quenching, which was followed by a sharp increase in the Tb(III) emission between *ca.* 0.5 → 1.4 equivalents of anion. However, upon further addition of $H_2P_2O_7^{2-}$ the emission intensity was once more observed to decrease (see Figure S15



Scheme 3 Proposed binding interaction for the formation of the 3:1 (**G**$_3$:**H**) complex between **Tb.1** and $H_2PO_4^-$.

in the ESI). By fitting these changes several binding constants were determined (see Table 3 and ESI† Fig. S16 for the fit and speciation distribution diagram), which were in good agreement with that observed from the ground and the single excited state results.

Titration with F^- however, gave rise to emission intensity enhancements only after the addition of four equivalents F^-. These results correlate well with the changes observed for the absorption/titration. Furthermore, the enhancement in the Tb(III) emission was also accompanied by a hypsochromic shift of *ca.* 2 nm on all the Tb(III) transitions (see ESI† Fig. S17). Such blue shift has previously been associated with the direct binding to the metal centre,[69] which we propose is the case for F^-. Fitting these changes using SPECFIT, once again showed the formation of complex binding interactions between F^- and **Tb.1**, from which several binding constants were determined, Table 3.

Similarly to what was observed for CH_3COO^-, titrations with Cl^- gave only rise to a decrease in the Tb(III) emission (see ESI† Fig. S18). Once again, and in agreement with the results obtained from both the ground and singlet excited states, the 1:1 (**G**:**H**) complex was found to be the only species present in solution (see ESI† Fig. S19) with a binding constant log $K_{1:1} = 6.06 \pm 0.03$.

From these studies it is very clear that the binding of these anions, and in particular $H_2PO_4^-$, has a significant affect on the coordination environment of **Tb.1**, and particularly have significant effect upon direct binding to the Tb(III) centre. Furthermore, the results clearly demonstrate that the Tb(III) emission is significantly more sensitive to the anion recognition process than either the ground or the singlet excited states.

Selectivity of Tb.1 to $H_2PO_4^-$ over CH_3COO^-

The above results from the lanthanide luminescence show that **Tb.1** is a promising sensor for anions. Amongst all the anions studied, $H_2PO_4^-$ gave rise to the largest changes in the Tb(III) emission. With the aim of demonstrating this selectivity towards $H_2PO_4^-$ (*Phos* in Fig. 12), the Tb(III) emission was recorded in the presence of CH_3COO^- (*Ac* in Fig. 12), which, as demonstrated above, only gave rise to quenching in the lanthanide emission. As can be seen from Fig. 12, the addition of $H_2PO_4^-$, gave rise to significant enhancements in the Tb(III) emission, in a similar

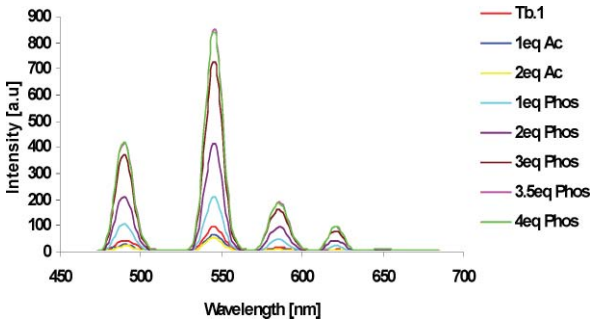


Fig. 12 Changes in the **Tb.1** (4 μM) emission spectra showing selectivity to $H_2PO_4^-$ (*Phos*) over CH_3OO^- (*Ac*).

manner observed in Fig. 10. Here, gradual emission enhancements were recorded up to the addition of *ca.* 3.5 equivalents of $H_2PO_4^-$, which resulted in *ca.* 14 fold overall enhancement. These changes, Fig. 12, clearly indicate that even in the presence of competitive anions, such as CH_3COO^-, **Tb.1** binds preferentially to $H_2PO_4^-$, which demonstrates the ability of **Tb.1** to function as a selective luminescent sensor for $H_2PO_4^-$.

Conclusions

Herein, we have discussed the synthesis and the characterisation of the urea based ligand **1** and the corresponding Tb(III) and Eu(III) complexes, **Tb.1** and **Eu.1**, which were determined to possess a single metal bound water molecule as part of their coordination sphere.

Analysis of the ground and the singlet excited states in CH_3CN, as well as the Tb(III) excited state, demonstrated that binding of anions to **Tb.1** gave rise to significant spectral changes, which were fitted using a non-linear regression analysis programme. From these analyses, evidence of multiple binding interactions for anions such as CH_3COO^-, $H_2PO_4^-$, $H_2P_2O_7^{2-}$, and F^- were observed. In general, binding constants determined (as log *K*) were found to be high, reflecting the strong affinity of **Tb.1** toward these anions in CH_3CN, which occurred through the combination of hydrogen bonding to the urea and amide sites, and *via* the direct coordination of some of these anions to the Tb(III). In contrast, the larger spherical Cl^- ion was observed to form only a 1:1 complex with the sensor. Amongst the anions investigated, $H_2PO_4^-$ was the one found to give rise to the largest enhancements in the Tb(III) emission, which was attributed to the direct binding of $H_2PO_4^-$ to the metal centre. Furthermore, as CH_3COO^- only gave rise to quenching in the Tb(III) emission, we were able to demonstrate the selective binding of $H_2PO_4^-$ to **Tb.1**, as the Tb(III) emission was significantly enhanced upon addition of the anion.

In summary, we have demonstrated the use of the lanthanide complex **Tb.1** to bind anions *via* multiple binding interactions, consisting of both hydrogen bonding and metal coordination, where the former gave rise to quenching in the Tb(III) emission for ions such as CH_3COO^- and Cl^-, while for $H_2PO_4^-$, $H_2P_2O_7^{2-}$, and F^- the emission was either quenched or enhanced depending on the anion concentration. We are currently investigating the use of other hydrogen bonding lanthanide complexes as anion sensors in non-aqueous solutions.[70]

Experimental

General methods and materials

All chemicals were purchased from commercial sources and unless specified used without further purification. Melting points were determined using an Electrothermal IA9000 digital melting point apparatus. Elemental analysis was carried out at the Microanalytical Laboratory, School of Chemistry and Chemical Biology, University College Dublin. Infrared spectra were recorded either on a Mattson Genesis II FTIR spectrometer equipped with a Gateway 2000 4DX2–66 workstation or a Perkin Elmer Spectrum One FT-IR Spectrometer fitted with a universal ATR sampling accessory. NMR spectra were recorded using a Brüker DPX-400 Avance spectrometer, operating at 400.13 MHz for ^{1}H-NMR, 100.6 MHz for ^{13}C-NMR, and 376.46 MHz for ^{19}F-NMR, or a Brüker AV-600 spectrometer, operating at 600.1 MHz for ^{1}H-NMR and 150.2 MHz for ^{13}C-NMR. NMR data were processed using Brüker Win-NMR 5.0 software. All spectra were recorded using commercially-available deuteriated solvents, and were referenced to solvent residual proton signals. Electrospray mass spectra were recorded on a Micromass LCT spectrometer, running Mass Lynx NT V 3.4 on a Waters 600 controller connected to a 996 photodiode array detector with HPLC-grade methanol or acetonitrile as carrier solvents. Detection was in positive (ES+) mode only. Accurate molecular masses were determined by a peak-matching method, using leucine enkephaline (H–Tyr–Gly–Gly–Phe–Leu–OH) as the standard internal reference (m/z = 556.2771); and reported within 5 ppm of the expected mass.

UV-Visible spectra were measured on a Varian Cary-50 spectrophotometer. Emission spectra and lifetimes were measured on a Varian Cary Eclipse luminescence spectrometer. All the stock solutions (10^{-3} M) were prepared in CH_3CN. Solutions with the molar concentrations used in the measurements (4 μM) were prepared by dilution of the corresponding 10^{-3} M stock solutions. The concentration of the ligands and complexes investigated were the same for both the UV-visible and luminescence measurements.

Synthetic methods

Previously described methods were used for the synthesis of the tri-arm acetamide cyclen derivative **2**.[68]

2-{4,7-bis-dimethylcarbamoylmethyl-10-[(4-nitrophenylcarbamoyl)-methyl]-1,4,7,10-tetraaza-cyclododec-1-yl}-*N*,*N*-dimethyl-acetamide (4). To a solution of **2** (0.282 g, 0.659 mmol) and **3** (0.156 g, 0.725 mmol) in MeCN (20 mL) was added KI (0.121 g, 0.725 mmol) and Cs_2CO_3 (0.236 g, 0.725 mmol). The reaction mixture was then refluxed under an argon atmosphere for 72 h. The brown solution was filtered through celite and the solvent was removed under reduced pressure. The compound was purified by alumina column chromatography under gradient elution conditions (DCM to 20% MeOH) to give the desired product, **4**, as a brown solid (0.297 g, 74% yield). m.p. 79–80°C; IR (KBr) υ_{max} (cm^{-1}) 3434, 2966, 2821, 1648, 1554, 1504, 1174, 1104; ^{1}H-NMR (400 MHz, $CDCl_3$) 11.26 (br s, 1H, NH), 8.17 (d, 2H, ArCH, J = 9.36 Hz), 8. 05 (d, 2H, ArCH, J = 9.36 Hz), 3.71 (s, 2H, CH_2), 3.5–2.0 (m, m, CH_2CONCH_3 + CH_2 cyclen); ^{13}C-NMR (100 MHz, $CDCl_3$) 171.81, 170.41, 170.21, 145.21, 142.11, 123.87, 119.04, 57.15, 54.64, 54.50, 53.04, 49.72, 35.75, 35.63, 35.22, 35.13; MS (ES$^+$) m/z 606.37 (M + H), 628.35 (M + Na); Calculated for $C_{28}H_{48}N_9O_6$ [M + H peak] m/z = 606.3734. Found m/z = 606.3728.

2-{4[(4-aminophenylcarbamoyl)-methyl]-7,10-bis-dimethylcarbamoylmethyl-1,4,7,10-tetraaza-cyclododec-1-yl)}-*N*,*N*-dimethyl-acetamide (5). To a stirring solution of **4** (0.078 g, 0.129 mmol) and 10% Pd/C catalyst in EtOH (3 mL), a solution of $N_2H_4.H_2O$ (0.052 g, 1.032 mmol) in EtOH (5 mL) was added dropwise. The reaction mixture was then heated under reflux overnight, under an argon atmosphere. The brown solution was filtered through celite and the solvent was removed under reduced pressure to yield the product **5**, as a brown resin (0.065 g, 88% yield); ^{1}H-NMR (400 MHz, $CDCl_3$) 10.07 (br s, 1H, NH), 7.57 (d, 2H, ArCH, J = 8 Hz), 6.54 (d, 2H, ArCH, J = 8.56 Hz), 3.4–2.4 (m, CH_2CONCH_3 + CH_2 cyclen); ^{13}C-NMR (100 MHz, $CDCl_3$) 170.97, 170.72, 169.80, 142.55, 130.74, 121.15, 114.93, 57.99, 54.95, 53.46, 52.42, 50.90, 36.25, 36.09, 35.65, 35.53; MS (ES$^+$) m/z 508.38 (M + Na); Calculated for $C_{28}H_{49}N_9O_4Na$ [M + Na$^+$] m/z = 598.3805. Found m/z = 598.3830.

2-(4,7-Bis-dimethylcarbamoylmethyl-10-{[4-(3-p-tolyl-ureido)-phenylcarbamoyl]-methyl}-1,4,7,10-tetraaza-cyclododec-1-yl)-*N*,*N*-dimethyl-acetamide (1). To a solution of **5** (0.150 g, 0.261 mmol) in $CHCl_3$ (7 mL) was added trifluoro-*p*-tolyl isocyanate (0.049 g, 0.264 mmol). The reaction mixture was left stirring under an argon atmosphere at room temperature overnight. The solvent was removed under reduced pressure to yield a pale brown solid. The compound was purified by alumina column chromatography under gradient elution conditions (DCM to 20% MeOH) to give the desired product **1**, as a yellow solid (0.133 g, 67% yield). m.p. 187–189°C; Anal. Calc. required for $C_{36}H_{54}N_{10}O_5F_3.CH_2Cl_2.2H_2O$: C, 50.28; H, 6.73; N, 15.85%; Found: C, 49.96; H, 6.32; N, 15.62%; IR υ_{max} (cm^{-1}) 3243, 2967, 2819, 1646, 1512, 1406, 1309, 1231, 1201, 1181, 1159, 1102, 1066, 1005, 951, 901, 842, 732; ^{1}H-NMR (400 MHz, $CDCl_3$) 10.07 (br s, 1H, NH), 9.94 (br s, 1H, NH), 9.48 (br s, 1H, NH), 7.76 (d, 2H, ArCH, J = 8.52 Hz), 7.59 (d, 2H, ArCH, J = 8.52 Hz), 7.42 (m, 4H, ArCH), 7.35 (d, 2H ArCH, J = 8.2 Hz), 3–2 (m, 42H, CH_2CONCH_3, CH_2CONH, and CH_2 cyclen); ^{13}C-NMR (100 MHz, $CDCl_3$) 170.47, 170.16, 169.48, 153.08, 143.30, 135.16, 133.13, 125.54, 125.27, 119.67, 118.40, 117.42, 57.50, 54.51, 54.31, 51.52, 50.36, 49.61, 36.04, 35.63, 35.49, 35.19, 35.02; ^{19}F-NMR (376 MHz, $CDCl_3$) -61.88 (CF_3). MS (ES$^+$) m/z 763.42 (M + H); Calcd. for $C_{36}H_{54}N_{10}O_5F_3$ [M + H] m/z = 763.4231. Found m/z = 763.4248.

Tb(III) complex (Tb.1)

A solution of **1** (0.05 g, 0.066 mmol) and $Tb(CF_3SO_3)_3$ (0.04 g, 0.066 mmol) in MeCN (5 mL) was heated under reflux, under an argon atmosphere for 48 h. The complex was isolated by precipitation from dry ethyl ether (200 mL) as a pale beige solid (0.067 g, 74% yield); Anal. Calcd. required for $C_{36}H_{54}N_{10}O_5F_3.Tb.(CF_3SO_3)_3.H_2O.3CH_2Cl_2$: C, 30.73; H, 3.74; N, 8.53%; Found: C, 30.17; H, 3.55; N, 8.91%; IR υ_{max} (cm^{-1}) 3488, 3354, 2940, 1619, 1538, 1514, 1411, 1316, 1242, 1224, 1158, 1114, 1081, 1068, 1027, 957, 910, 842, 824, 758; ^{1}H-NMR (400 MHz, CD_3OD) 75.92, 51.76, 47.91, 46.87, 40.93, 26.92, 24.70, 21.16, 11.17, 9.03, 7.29, 5.72; ^{19}F-NMR (376 MHz, CD_3OD) -64.20

(CF_3), -79.85 (CF_3SO_3); MS (ES^+) m/z 460.16 ([(M + H)/2); Calcd. for $C_{36}H_{52}N_{10}O_5F_3Tb$: m/z = 920.3228. Found m/z = 920.3286.

Eu(III) complex (Eu.1)

A solution of **1** (0.02 g, 0.02 mmol) and $Eu(CF_3SO_3)_3$ (0.01 g, 0.02 mmol) in MeCN (5 mL) was heated under reflux, under an argon atmosphere for 48 h. The complex was isolated by precipitation from dry ethyl ether (100 mL) as a hygroscopic pale beige solid (0.02 g, 68% yield). IR υ_{max} (cm^{-1}) 3293, 2928, 1617, 1538, 1513, 1410, 1317, 1242, 1224, 1157, 1112, 1081,1067, 1027, 956, 909, 838, 822, 757; ^{1}H-NMR (400 MHz, CD_3OD) 31.32, 10.86, 7.73, 7.66, 6.93, 4.90, 3.32, 3.03, 1.40, 1.30, 0.93, -8.11;^{19}F-NMR (376 MHz, CD_3OD) -63.81 (CF_3), -80.60 (CF_3SO_3); MS (ES^+) m/z: 457.03 [(M + H^+)/2], 531.99 [(M + trif)/2].

Acknowledgements

We would like to particularly thank Dr. Pablo Barrio Fernández and Dr. Joseph P. Leonard for their earlier contribution to this research area. We also would like to thank Enterprise Ireland, IRCSET (Basic Research Grant) and TCD for financial support; Dr. John E. O'Brien for assisting with the NMR and Dr. Martin Feeney and Dr. Dilip Rai for assistance with ESM analysis.

Notes and references

1 C. M. G. dos Santos, A. J. Harte, S. J. Quinn and T. Gunnlaugsson, *Coord. Chem. Rev.*, 2008, **252**, 2512–2527.
2 C. Caltagirone and P. A. Gale, *Chem. Soc. Rev.*, 2009, **38**, 520–563; P. A. Gale, S. E. García-Garrido and J. Garric, *Chem. Soc. Rev.*, 2008, **37**, 151–190.
3 P. Prados and R. Quesada, *Supramol. Chem.*, 2008, **20**, 201–216.
4 J. L. Sessler, P. A. Gale, and W.-S. Cho, '*Anion receptor chemistry*', Royal Society of Chemistry, 2006.
5 T. Gunnlaugsson, M. Glynn, G. M. Tocci, (nee Hussey), P. E. Kruger and F. M. Pfeffer, *Coord. Chem. Rev.*, 2006, **250**, 3094–3117.
6 P. A. Gale and R. Quesada, *Coord. Chem. Rev.*, 2006, **250**, 3219–3244.
7 J. W. Steed, *Chem. Commun.*, 2006, 2637–2649.
8 V. Amendola, M. Bonizzoni, D. Esteban-Gomez, L. Fabbrizzi, M. Licchelli, F. Sancenon and A. Taglietti, *Coord. Chem. Rev.*, 2006, **250**, 1451–1470.
9 M. H. Filby and J. W. Steed, *Coord. Chem. Rev.*, 2006, **250**, 3200–3218.
10 B. T. Nguyen and E. V. Anslyn, *Coord. Chem. Rev.*, 2006, **250**, 3118–3127.
11 T. Gunnlaugsson, H. D. P. Ali, M. Glynn, P. E. Kruger, G. M. Hussey, F. M. Pfeffer, C. M. G. dos Santos and J. Tierney, *J. Fluoresc.*, 2005, **15**, 287–299.
12 R. Martinez-Manez and F. Sancenon, *J. Fluoresc.*, 2005, **15**, 267–285.
13 R. Martinez-Manez and F. Sancenon, *Chem. Rev.*, 2003, **103**, 4419–4476.
14 A. Bianchi, K. Bowman-James, and E. Garcia-Espana, '*Supramolecular Chemistry of Anions*', Wiley-VCH, New York, 1997.
15 E. García-España, P. Díaz, J. M. Llinares and A. Bianchi, *Coord. Chem. Rev.*, 2006, **250**, 2952–2986.
16 J. M. Llinares, D. H. Powell and K. Bowman-James, *Coord. Chem. Rev.*, 2003, **240**, 57–75.
17 P. Blondeau, M. Segura, R. Pérez-Fernández and J. de Mendoza, *Chem. Soc. Rev.*, 2007, **36**, 198–210.
18 M. D. Best, S. L. Tobey and E. V. Anslyn, *Coord. Chem. Rev.*, 2003, **240**, 3–15.
19 T. Gunnlaugsson and F. Stomeo, *Org. Biomol. Chem.*, 2007, **5**, 1999–2009.
20 E. J. O'Neil and B. D. Smith, *Coord. Chem. Rev.*, 2006, **250**, 3068–3080.
21 C. R. Rice, *Coord. Chem. Rev.*, 2006, **250**, 3190–3199.
22 D. Parker and R. Pal, *Org. Biomol. Chem.*, 2008, **6**, 1020; D. Parker and R. Pal, *Chem. Commun.*, 2007, 474; S. Pandya, J. Yu and D. Parker, *Dalton Trans.*, 2006, 2757; J. H. Yu and D. Parker, *Eur. J. Org. Chem.*, 2005, 4249; J. J. Yu, D. R. A. Poole, G. Bobba, M. J. Cann, J.-C. Frias, D. Parker and R. D. Peackopck, *Org. Biomol. Chem.*, 2005, **3**, 1013; D. Parker, R. Pal, R. A. Poole and M. J. Cann, M., *J. Am. Chem. Soc.*, 2006, **128**, 2294; Bretonnière, M. J. Cann, D. Parker and R. Slater, *Org. Biomol. Chem.*, 2004, **2**, 1624.
23 J. P. Leonard, C. B. Nolan, F. Stomeo and T. Gunnlaugsson, *Top. Curr. Chem.*, 2007, **281**, 1–43.
24 J. P. Leonard and T. Gunnlaugsson, *J. Fluoresc.*, 2005, **15**, 585–595; D. Parker, R. S. Dickins, H. Puschmann, C. Cossland and J. A. K. Howard, *Chem. Rev.*, 2002, **102**, 1977; D H. Tsukube and S. Shinoda, *Chem. Rev.*, 2002, **102**, 2389.
25 L. Pescatori, A. Arduini, A. Pochini, F. Ugozzoli and A. Secchi, *Eur. J. Org. Chem.*, 2008, 109–120.
26 E. B. Veale and T. Gunnlaugsson, *J. Org. Chem.*, 2008, **73**, 8073–8076.
27 C. M. G. dos Santos, M. Glynn, T. McCabe, J. S. Seixas de Melo, H. D. Burrows and T. Gunnlaugsson, *Supramol. Chem.*, 2008, **20**, 407–418.
28 C. M. G. dos Santos, T. McCabe and T. Gunnlaugsson, *Tetrahedron Lett.*, 2007, **48**, 3135–3139.
29 M. Kumar, J. N. Babu, V. Bhalla and N. S. Athwal, *Supramol. Chem.*, 2007, **19**, 511–516.
30 S. J. Brooks, P. R. Edwards, P. A. Gale and M. E. Light, *New J. Chem.*, 2006, **30**, 65–70.
31 S. J. Brooks, P. A. Gale and M. E. Light, *Chem. Commun.*, 2005, 4696–4698.
32 R. M. Duke, J. E. O'Brien, T. McCabe and T. Gunnlaugsson, *Org. Biomol. Chem.*, 2008, **6**, 4089–4092; T. Gunnlaugsson, P. E. Kruger, P. Jensen, J. Tierney, H. D. P. Ali and G. M. Hussey, *J. Org. Chem.*, 2005, **70**, 10875–10878.
33 M. Boiocchi, L. Del Boca, D. E. Gomez, L. Fabbrizzi, M. Licchelli and E. Monzani, *J. Am. Chem. Soc.*, 2004, **126**, 16507–16514.
34 T. Gunnlaugsson, A. P. Davis, J. E. O'Brien and M. Glynn, *Org. Lett.*, 2002, **4**, 2449–2452.
35 T. Gunnlaugsson, A. P. Davis and M. Glynn, *Chem. Commun.*, 2001, 2556–2557.
36 S. O. Kang, M. A. Hossain and K. Bowman-James, *Coord. Chem. Rev.*, 2006, **250**, 3038–3052.
37 C. R. Bondy and S. J. Loeb, *Coord. Chem. Rev.*, 2003, **240**, 77–97.
38 C. M. G. dos Santos, T. McCabe, G. W. Watson, P. E. Kruger and T. Gunnlaugsson, *J. Org. Chem.*, 2008, **73**, 9235–9244.
39 R. Yang, W.-X. Liu, H. Shen, H.-H. Huang and Y.-B. Jiang, *J. Phys. Chem. B*, 2008, **112**, 5105–5110.
40 H. D. P. Ali, P. E. Kruger and T. Gunnlaugsson, *New J. Chem.*, 2008, **32**, 1153–1161.
41 W.-X. Liu and Y.-B. Jiang, *Org. Biomol. Chem.*, 2007, **5**, 1771–1775.
42 S. J. Brooks, P. A. Gale and M. E. Light, *Chem. Commun.*, 2006, 4344–4346.
43 L. S. Evans, P. A. Gale, M. E. Light and R. Quesada, *New J. Chem.*, 2006, **30**, 1019–1025.
44 F. M. Pfeffer, P. E. Kruger and T. Gunnlaugsson, *Org. Biomol. Chem.*, 2007, **5**, 1894; E. Quinlan, S. E. Matthews and T. Gunnlaugsson, *Tetrahedron Lett.*, 2006, **47**, 9333–9338; F. M. Pfeffer, T. Gunnlaugsson, P. Jensen and P. E. Kruger, *Org. Lett.*, 2005, **7**, 5357.
45 F.-Y. Wu, L. G. Zhao Li, X. Wang, M.-H. Lin, Y.-F. Zhao and Y.-B. Jiang, *Org. Biomol. Chem.*, 2006, **4**, 624–630.
46 L. Nie, Z. Li, J. Han, X. Zhang, R. Yang, W.-X. Liu, F.-Y. Wu, J.-W. Xie, Y.-F. Zhao and Y.-B. Jiang, *J. Org. Chem.*, 2004, **69**, 6449–6454.
47 A. Beeby, I. M. Clarkson, R. S. Dickins, S. Kaulkner, D. Parker, L. Royle, A. S. d. Sousa, J. A. G. Williams and M. Woods, *J. Chem. Soc., Perkin Trans.*, 1999, 493; W. W. Horrocks and D. R. Sudnik, *J. Am. Chem. Soc.*, 1979, **101**, 334.
48 S. J. A. Pope, *Polyhedron*, 2007, **26**, 4818–4824; S. J. A. Pope and R. H. Laye, *Dalton Trans.*, 2006, 3108–3113.
49 D. Parker and J. A. G. Williams, *J. Chem. Soc., Dalton Trans.*, 1996, 3613–3628.
50 J.-C. G. Bunzli, *Acc. Chem. Res.*, 2006, **39**, 53–61.
51 T. Gunnlaugsson and J. P. Leonard, *Chem. Commun.*, 2005, 3114–3131.
52 S. Faulkner and S. J. A. Pope, *J. Am. Chem. Soc.*, 2003, **125**, 10526; S. Faulkner, S. J. A. Pope and B. P. Burton-Pye, *Appl. Spectrosc. Rev.*, 2005, **40**, 1–31.
53 J.-C. G. Bunzli and C. Piguet, *Chem. Soc. Rev.*, 2005, **34**, 1048–1077.
54 Y. Kataoka, D. Paul, H. Miyake, T. Yaita, E. Miyoshi, H. Mori, H S. Tsukamoto, H. Tatewaki, S. Shinoda and H. Tsukube, *Chem.–Eur. J.*, 2008, **14**, 5258–5266; H. Tsukube, Y. Suzuki, D. Paul, Y. Kataoka and S. Shinoda, *Chem. Commun.*, 2008, 2533–2535; Y. Kataoka, D. Paul,

H. Miyake, S. Shinoda and H. Tsukube, *Dalton Trans.*, 2008, 2784–2791; S. Shinoda, H. Miyake, H. Tsukube, in 'Molecular recognition and sensing *via* rare earth complexes', 2005.
55 Frontiers in Lanthanide Chemistry, *Chem. Rev.*, 2002, 102, pp. 1807–2476.
56 C. G. Gulgas and T. M. Reineke, *Inorg. Chem.*, 2008, **47**, 1548–1559.
57 C. M. G. dos Santos, P. B. Fernandez, S. E. Plush, J. P. Leonard and T. Gunnlaugsson, *Chem. Commun.*, 2007, 3389–3391. Part of this work was previously communicated.
58 J. P. Leonard, C. M. G. dos Santos, S. E. Plush, T. McCabe and T. Gunnlaugsson, *Chem. Commun.*, 2007, 129–131.
59 A. J. Harte, P. Jensen, S. E. Plush, P. E. Kruger and T. Gunnlaugsson, *Inorg. Chem.*, 2006, **45**, 9465–9474.
60 S. J. A. Pope, B. P. Burton-Pye, R. Berridge, T. Khan, P. J. Skabara and S. Faulkner, *Dalton Trans.*, 2006, 2907–2912; S. Faulkner and B. P. Burton-Pye, *Chem. Commun.*, 2005, 259–260.
61 T. Gunnlaugsson, A. J. Harte, J. P. Leonard and M. Nieuwenhuyzen, *Supramol. Chem.*, 2003, **15**, 505–519.
62 S. E. Plush and T. Gunnlaugsson, *Dalton Trans.*, 2008, 3801–3804; S. E. Plush and T. Gunnlaugsson, *Org. Lett.*, 2007, **9**, 1919–1922.
63 P. Plitt, D. E. Gross, V. M. Lynch and J. L. Sessler, *Chem.–Eur. J.*, 2007, **13**, 1374–1381.
64 K. A. Connors, '*Binding constants : the measurement of molecular complex stability*', Jonh Wiley & Sons, 1987.
65 T. Gunnlaugsson, P. E. Kruger, T. C. Lee, R. Parkesh, F. M. Pfeffer and G. M. Hussey, *Tetrahedron Lett.*, 2003, **44**, 6575–6578.
66 I. G. Shenderovich, P. M. Tolstoy, N. S. Golubev, S. N. Smirnov, G. S. Denisov and H.-H. Limbach, *J. Am. Chem. Soc.*, 2003, **125**, 11710–11720.
67 V. S. Bryantsev and B. P. Hay, *J. Am. Chem. Soc.*, 2005, **127**, 8282–8283.
68 T. Gunnlaugsson, J. P. Leonard, S. Mulready and M. Nieuwenhuyzen, *Tetrahedron*, 2004, **60**, 105–113.
69 M. Montalti, L. Prodi, N. Zaccheroni, L. Charbonniere, L. Douce and R. Ziessel, *J. Am. Chem. Soc.*, 2001, **123**, 12694–12695.
70 C. M. G. dos Santos and T. Gunnlaugsson, *Supramol. Chem.*, 2009, **21**, DOI: 10.1080/10610270802588285.