

Lanthanide luminescent anion sensing: evidence of multiple anion recognition through hydrogen bonding and metal ion coordination†

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The delayed lanthanide luminescence of the terbium [Tb(III)] diaryl-urea complex **1**·Tb is significantly enhanced upon sensing of dihydrogenphosphate (H_2PO_4^-) in CH_3CN , which occurs through multiple anion binding through hydrogen bonding interactions and potential metal ion coordination to Tb(III).

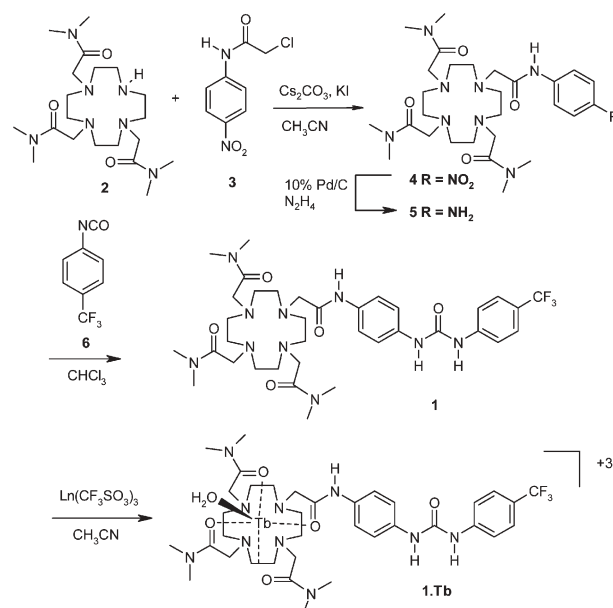
The luminescent and colorimetric sensing of anions is both a challenging and highly topical area of research.^{1–3} The most common methods for achieving such anion recognition has been *via* the use of: (i) transition metal ion coordination complexes;⁴ (ii) ammonium or guanidinium moieties,⁵ and (iii) charge neutral hydrogen bonding moieties, such as amides, ureas, thiourea, *etc.*⁶ Using heptadentate tri-arm cyclen (1,4,7,10-tetraazacyclododecane) Tb(III) and Eu(III) complexes, we and others have recently demonstrated the sensing of both aliphatic and aromatic carboxylates, *via* the formation of ternary complexes in buffered solution, where the emission was either enhanced or reduced upon coordination of these anions to the f-metal ions.^{7,8} Similarly, using chromophores, based on charge neutral receptors, we have developed numerous examples of both fluorescent and colorimetric anion sensors, which can function in both organic and aqueous solutions.^{2,9,10} Nevertheless, the combination of these two anion binding interactions in a single molecule, with the aim of achieving maximum luminescent ‘output’ coupled with high anion affinity, has not been demonstrated to date using members of the f-metal ion family. However, such sensing has recently been shown to work well using d-metal ions.¹¹ With the objective of demonstrating such dual sensing interactions using f-metal ions, we synthesised the Tb(III) complex **1**·Tb from **1**. Herein, we demonstrate the results from this investigation and prove that this design gives rise to: (a) high anion binding affinity, (b) multiple binding interactions and (c) large Tb-luminescence enhancements.

The Tb(III) $^5\text{D}_4$ transition is Laporte-forbidden and direct excitation of Tb(III) is often difficult.¹² Nevertheless, excitation *via* the use of ligand or antennae, gives rise to sensitised emission.^{12–14} In **1**, the aryl-urea has a dual role, it can function as both the sensitizing antenna¹² and the hydrogen bonding anion receptor.² Therefore, we anticipated that anion binding at the urea moiety would modulate the sensitization process to the lanthanide excited state, and hence, the Tb(III) emission.

The synthesis of **1** (Scheme 1), involved the coupling of the tri-arm acetamide cyclen **2**¹⁵ and chloro-*N*-(nitro-phenyl) acetamide,

3,¹⁶ in dry CH_3CN in the presence of Cs_2CO_3 and KI at 85 °C for 72 h. This gave **4**, which was purified by column chromatography on alumina. This was followed by the reduction of the nitro group, using N_2H_4 in ethanol at 90 °C, in the presence of 10% Pd/C catalyst, to yield **5**, which was reacted with trifluoro-*p*-tolyl isocyanide, **6**, in dry CHCl_3 at room temperature, giving **1** in 80% yield. The ^1H -NMR (CDCl_3) spectrum of **1**† showed the presence of three characteristic N–H resonances at 9.61, 9.38 and 9.01 ppm. The complex, **1**·Tb, was finally formed in 51% yield by refluxing **1** with one equivalent of $\text{Tb}(\text{CF}_3\text{SO}_3)_3$ in CH_3CN under argon, followed by precipitation from diethyl ether. The ESMS of **1**·Tb showed the expected isotopic distribution pattern and the ^1H NMR (CD_3OD) spectrum showed the shifted resonance for the equatorial and the axial protons of the cyclen and the $\alpha\text{-CH}_2$ due to the presence of the paramagnetic metal ion. Analysis of the excited state lifetimes of the Tb(III) emission in D_2O and H_2O , respectively, gave the hydration state^{12,13} ~ 1 , indicating a single metal bound water molecule.

The absorption spectra of **1**·Tb showed a broad band centred around 280 nm in CH_3CN , assigned to the urea antenna moiety. The changes in the spectra were monitored as a function of added anions such as AcO^- , H_2PO_4^- , F^- and Cl^- (as their TBA salt solutions). The addition of ions such as AcO^- and H_2PO_4^- caused the absorption maximum to shift towards the red, with concomitant $\sim 20\%$ reduction in the absorption, showing the



Scheme 1 Synthesis of **1** and the Tb(III) sensors **1**·Tb.

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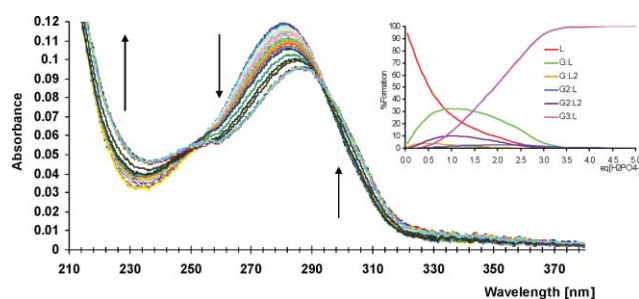


Fig. 1 The changes observed in the absorption spectra of **1**·Tb (4 μ M) upon addition of H_2PO_4^- (0–57.3 μ M) in MeCN. Arrows indicate the changes upon increasing concentration of H_2PO_4^- . Insert: The speciation distribution diagram for the binding of H_2PO_4^- .

binding of the anions to the receptor, as demonstrated for H_2PO_4^- in Fig. 1. The titration profile obtained from plotting the absorption changes in Fig. 1, suggested that the anion binding was more complex than a simple 1 : 1 stoichiometry (see ESI†). Fitting these changes, using the nonlinear least squares regression program SPECFIT (see ESI†), gave several binding constants, reflecting that the anions were bound through the proposed ‘multiple’ binding interactions. These results are summarised in Table 1, for H_2PO_4^- and AcO^- . Here, the stoichiometry (shown as the guest : **1**·Tb ratio $G_n : L_n$) and binding values ($\log K$) clearly shows that **1**·Tb initially binds both of these anions with large 1 : 1 binding affinity, where H_2PO_4^- is bound marginally stronger than AcO^- . We assign such a strong anion binding affinity to the neighbouring lanthanide ion, which, being a strong Lewis acid makes the urea protons stronger hydrogen bonding donors.

From these changes, the speciation distribution diagram was also determined (shown as insert for H_2PO_4^- in Fig. 1), which demonstrated that initially the 1 : 1 binding event (shown as a green line) dominates, but is then replaced at higher anion concentrations with higher order stoichiometries such as $G_3 : L_1$. Similarly, for AcO^- , both the $G_1 : L_1$ and $G_2 : L_1$ binding stoichiometries were observed. The binding of Cl^- was also observed in the absorption spectra. However, in comparison to the results in Table 1, it was weak and spectral changes only occurred at high anion concentrations. The titration of F^- gave rise to significant changes in the absorption spectra assigned to multiple F^- binding interactions as well as the deprotonation of the urea moiety by F^- , to give HF_2^- .¹⁷ However, the binding constants for F^- were significantly lower than those observed for H_2PO_4^- and AcO^- in Table 1 (see ESI†).

With the aim of further investigating these multiple binding interactions, both the fluorescence and the Tb(III) emission were monitored upon anion titration. For the former, the emission from the antenna ($\lambda_{\text{ex}} = 280$ nm) gave rise to a broad band centred at 340 nm (see ESI†), that was both weak and significantly polluted by the contribution from the Tb(III) emission, which occurs at longer wavelength. However, upon titration with either H_2PO_4^- or AcO^- the emission was significantly modulated. Even though, the spectra were of poor quality (see ESI†), we were able to obtain binding constants from these changes. These are in reasonable agreement with those obtained for the changes in the ground state, Table 1, further supporting the determined anion binding stoichiometries. However, in contrast to these results, the most significant findings from these investigations were observed in the lanthanide emission, which showed striking changes for the

Table 1 Results from the binding constant evaluation of H_2PO_4^- and AcO^- , upon binding to **1**·Tb in CH_3CN ^a

Anion	Technique	Stoichiometry	LogK	Std deviation
H_2PO_4^-	UV-Vis	G : L	7.07 ^b	0.23
		G : L ₂	4.87	0.47 ^c
		G ₂ : L	5.64	0.95 ^c
		G ₂ : L ₂	6.79	0.37
		G ₃ : L	7.94 ^b	0.21
H_2PO_4^-	Fluorescence	G : L	6.86	0.21
		G : L ₂	5.15	0.25 ^c
		G ₂ : L	5.34	0.94 ^c
		G ₂ : L ₂	6.84	0.53 ^c
		G ₃ : L	7.95 ^b	0.20
H_2PO_4^-	Tb(III) emission	G : L	7.04 ^b	0.14
		G : L ₂	4.59	0.24 ^c
		G ₂ : L	4.90	0.82 ^c
		G ₂ : L ₂	7.20	0.18 ^c
		G ₃ : L	8.04 ^b	0.12
AcO^-	UV-Vis	G : L	6.27	0.116
		G ₂ : L	5.84	0.087
AcO^-	Fluorescence	G : L	5.78	0.302
		G ₂ : L	5.11	0.511
AcO^-	Tb(III) emission	G : L	6.87	0.475
		G ₂ : L	5.12	0.497

^a Obtained by fitting the spectroscopic data using SPECFIT.

^b Binding constant is large and consequently SPECFIT has difficulties giving accurate determination for $\log \beta$. ^c Species present in less than 10%.

deactivation of the Tb(III) excited state [$^5\text{D}_4 \rightarrow ^7\text{F}_J$ ($J = 6-3$)] upon titration with H_2PO_4^- and excitation at 280 nm.[‡]

The overall Tb(III) luminescence changes for titrations of H_2PO_4^- are shown in Fig. 2. These results were fully reproducible and clearly demonstrate that the Tb-emission is significantly more sensitive to the anion recognition than seen in either the ground or the singlet excited states. Furthermore, the Tb(III) emission, and hence, the Tb(III) excited state lifetimes (ESI†), are modulated in a two ‘step’ process, where the initial addition of H_2PO_4^- leads to ca. 70% quenching in the Tb(III) emission (insert Fig. 2). This is subsequently followed by over ca. 90% luminescent enhancement between ca. 1 \rightarrow 3 eq. of H_2PO_4^- . This is, to the best of our knowledge, the first time that a lanthanide luminescence is modulated in this manner by an anion.

Moreover, by further analysing the changes in the 546 nm transition vs. the number of eq. of H_2PO_4^- , it was found that the

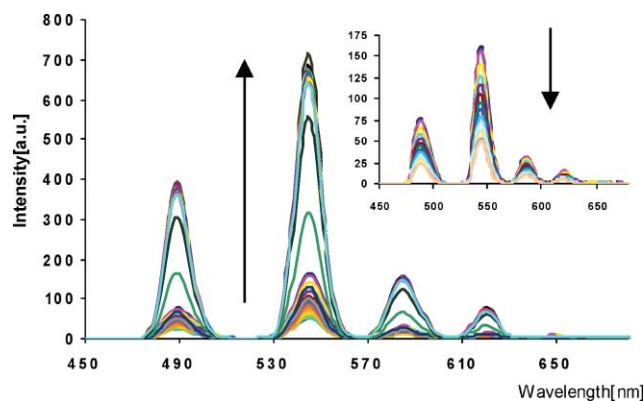


Fig. 2 The Tb(III) emission spectra showing the changes in the intensity of **1**· (4 μ M) upon titration with H_2PO_4^- (0 \rightarrow 57.3 μ M) in MeCN. Insert: The changes observed upon addition of 0 \rightarrow 1 eq. of H_2PO_4^- , which caused quenching in the Tb(III) emission.

Tb(III) emission enhancements also occurred in a two step process; where the major contribution to these changes took place within the $2 \rightarrow 3$ eq. range of H_2PO_4^- . The changes in the 546 nm transition were fitted using the SPECFIT programme. This gave an excellent fit as shown in the ESI† from which several binding constants were determined. Again, the results from the fitting of the binding isotherm clearly indicated that $1\cdot\text{Tb}$ senses these anions through multi-step binding interactions and that the binding constants correlate well with that observed from the changes in both the absorption and the fluorescence spectra, Table 1. The speciation distribution diagram obtained from the changes in the Tb(III) emission upon titration with H_2PO_4^- is shown in the ESI† and clearly demonstrates that initially the 1 : 1 stoichiometry is formed with a high binding constant of $\log K = 7.0$. However, after the addition of *ca.* one eq. of anion the $G_3 : L_1$ binding begins to dominate. Interestingly, the 2 : 1 complex only formed in small quantities. In contrast to these results, the titration of $1\cdot\text{Tb}$ with AcO^- only gave rise to luminescent quenching. Furthermore, only two stoichiometries were determined; namely the $G_1:L_1$ and $G_2:L_1$, Table 1 (see ESI†). These results also showed that $1\cdot\text{Tb}$ selectively sensed H_2PO_4^- over AcO^- . This we confirmed by titrating H_2PO_4^- to a quenched solution of $1\cdot\text{Tb}$ bound AcO^- . On both occasions, the Tb-emission was 'switched on' in the same manner as seen above for the titration of H_2PO_4^- in Fig. 2 (See ESI†).

So what binding interactions constitute to this complex multiple anion recognition? We propose that the initial anion recognition is due to binding of the anion at the urea moiety of the antenna. This is then followed by a second binding event between these anions and the amide bridge, through anion $\cdots\text{H}-\text{N}$ hydrogen bonding interactions. We have confirmed this by carrying out UV-vis titrations of an acetamide analogue of the receptor/antenna part of $1\cdot\text{Tb}$, which also gave rise to both $G_1:L_1$ and $G_2:L_1$ binding for these anions (*cf.* 7 in ESI†). However, the binding constants are lower than observed for $1\cdot\text{Tb}$. In the case of binding of H_2PO_4^- to $1\cdot\text{Tb}$, the third binding interaction, $G_3:L_1$ is more difficult to determine without the aid of X-ray crystallography. However, this binding, clearly giving rise to the largest changes in the Tb(III) emission, is most likely taking place through a more direct interaction with the metal ion (and possibly *via* contribution from one of the aryl protons.¹⁸ Contribution from simple electrostatic interactions between the complex and the anion cannot be ruled out either). This may be occurring through the displacement of the aforementioned axial metal bound water molecule. Water is an effective quencher of the $^5\text{D}_4$ excited state and displacement of the water generally gives rise to luminescence enhancements.^{7,8} These changes are also observed in the ground state, which suggests that the Tb(III) ion also affects the electronic properties of the antenna.

In summary, we have developed a novel lanthanide luminescent sensor for anions by incorporating a hydrogen bonding receptor into a sensitizing antenna. Analysis of the ground state, and the emission from the singlet and the Tb(III) excited states, clearly demonstrated the formation of multiple species and hence multiple binding interactions in solution. It also showed that the Tb(III) is extremely sensitive to the changes in the local coordination environment. Furthermore, the selective detection of H_2PO_4^- over AcO^- by $1\cdot\text{Tb}$ was also observed, with the H_2PO_4^- forming both 1 : 1 and 3 : 1 complexes with $1\cdot\text{Tb}$, in CH_3CN . These results represent, to the best of our knowledge, the first examples of the

use of a combination of hydrogen bonding anion receptors and f-metal ion coordination for luminescent anion sensing.

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Notes and references

† The Eu(III) complex of **1**, $1\cdot\text{Eu}$, was also formed. However, the emission was very weak in comparison to that of $1\cdot\text{Tb}$, as the Eu(III) excited state is quenched by photoinduced electron transfer (*cf.* ESI†).

§ As these measurements are carried out in less competitive CH_3CN solvent the emission enhancement might even be more striking.

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