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Exploring the luminescent sensing of anions by the use of an urea functionalised 1,10-phenanthroline (*phen*)-based (3:1) Eu(III) complex

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The design, synthesis and photophysical evaluation of the Eu(III) complex **1_3Eu**, formed from the aryl-urea-based 1,10-phenanthroline (*phen*) heteroditopic receptor **1**, is described. The complex, which was formed in 3:1 [ligand:Eu(III)] stoichiometry, was used to sense anions such as acetate, phosphate and halides, in CH_3CN. Here, the mechanism for the sensing of these anions by **1_3Eu** was through hydrogen bonding at the urea moiety, and in the case of F^-, also by the displacement of metal-bound water molecules. Both these binding modes gave rise to significant modulation in spectroscopic output of the Eu(III) complex.

Keywords: anions; sensing; lanthanide; europium; self-assembly; displacement assays

Introduction

Over the years, much effort has been devoted to the development of selective sensors for detecting anions (*1–4*). In particular, the use of hydrogen bonding receptors such as those based on the use of urea/thioureas (*5*), pyrroles (*6*) and indoles (*7*) has been extensively researched. At the same time, the use of transition metal ion complexes for binding ions, with subsequent changes in the photophysical properties of the metal ion complex, has also been a fruitful area of research (*8*). More recently, the use of lanthanide ion complexes in anion sensing has also become a fast growing area of research, where the anion sensing occurs via a direct coordination at the metal ion itself (*9–12*). In contrast to these developments, then the use of a combination of two modes of binding, e.g. hydrogen bonding donors and metal ion complexes, for anion recognition and sensing has been much less explored, and mostly through the use of transition metal ions (*13*). With the aim of developing such sensors for anions using lanthanide ions, we have recently synthesised Tb(III)-based cyclen complexes that possess a diaryl-based urea pendant arm (*14*). Here, the hydrogen-donating urea moiety acted as an anion receptor, as well as a sensitiser, or an antenna, for the population of the Tb(III) excited state. In this work, we showed that the Tb(III) could be sensitised by an excitation of the antenna, and that the sensitisation process could be modulated upon recognition of several anions such as acetates and phosphates at the urea moiety in non-aqueous solution. We also demonstrated that for this same system, at high concentration, additional anion binding occurred at the lanthanide ion centre directly through the mechanism of displacement of metal-bound water molecules (*15*).

In this communication, we set out to further explore the use of a combination of hydrogen bonding receptors and the lanthanides for anion sensing, by using acyclic ligands. Here, we describe the synthesis and the photophysical evaluation of **1_3Eu**, formed from the *phen*-based urea heteroditopic receptors **1** and Eu(III), and we demonstrate that the photophysical properties of **1_3Eu** are significantly modulated upon recognition of anions in organic solvent. While similar ideas have been developed by several other researchers such as Goodman et al. (*16*), Amendola et al. (*17*), Norsten et al. (*18*) and Turner et al. (*19*), these examples have all been based on the use of transition metal ions, and not lanthanide ions. Hence, the formation of lanthanide complexes has not, to the best of our knowledge, been achieved to date.

Results and discussion

Synthesis

The synthesis of **1** was achieved in two steps from the commercially available 5-nitro-1,10-phenanthroline by firstly converting it to the corresponding amine **2** in 92% yield, by using hydrazine monohydrate in the presence of 10% Pd/C catalyst in ethanol at 95°C, followed by reaction with trifluoro-*p*-tolyl isocyanate, in chloroform at room temperature, which gave **1** as an off-white precipitate, in 88% yield after recrystallisation from a mixture of $CHCl_3$:MeOH (*20*) (Scheme 1). The synthesis of the Eu(III) complex of **1** was accomplished by reacting **1** with

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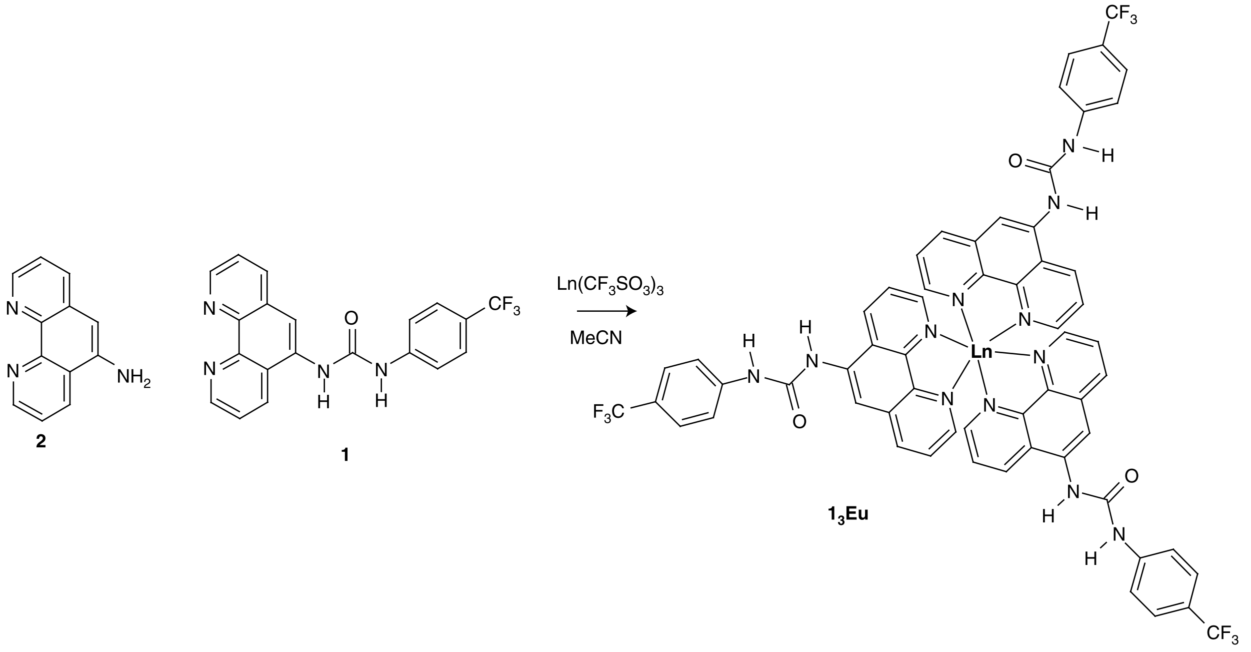

Scheme 1. Synthesis of **1** and the Eu(III) complex of **1**, **1_3Eu** (several structural isomers were expected to be formed).

0.5 equiv. of $Eu(CF_3SO_3)_3$ in CH_3CN at room temperature overnight. The observed off-white precipitate was isolated by filtration, and dried under vacuum to produce a bright yellow solid in a modest 28% yield. The successful synthesis of **1_3Eu** was supported by NMR spectroscopy and HRMS. Although the ^{1}H NMR was not greatly shifted (due to the presence of the paramagnetic Eu(III) ion), the formation of **1_3Eu** complex was clear in the ^{1}H NMR, which showed significant broadening for the *phen* protons, indicating the presence of a single species in solution possessing high symmetry. The ^{19}F spectrum also revealed the presence of the CF_3 group at -60.56 ppm as well as a resonance at -78.29 ppm, which we assigned to the triflate counter ions. The ES-MS also showed the expected europium isotopic distribution pattern for **1_3Eu**, for instance for the *m*/*z* centred at 647 assigned to the [M/2] peak.

Photophysical studies

The formation and the stability of the complex between Eu(III) and **1** was investigated by observing the changes in the ground and the singlet excited state of **1** (10 μM), and the Eu(III) emission upon titration with $Eu(CF_3SO_3)_3$ in CH_3CN under ambient conditions. The changes observed in the absorption spectra of **1**, which had a λ_{max} of 265 nm and a shoulder at 320 nm, are shown in Figure 1.

Upon binding to Eu(III), small shifts were observed in the absorption spectra, where the 265 nm band was blue shifted to 260 nm and the 320 nm shoulder was concomitantly red shifted by *ca.* 5 nm. Three distinct isosbestic points were also observed at 280, 300 and 323 nm, respectively. The titration profile for the changes at 253 nm is also shown as an insert in Figure 1, which demonstrated the formation of a complex with 1:3 stoichiometry (e.g. **1_3Eu**) as no significant changes occurred after *ca.* 0.33 equiv. of Eu(III) added. The homogeneous changes in the absorption spectra also demonstrate that the complex does not aggregate in solution.

The changes in the fluorescence emission were also monitored upon excitation at 265 and 320 nm. On both occasions, a broadband centred at 422 nm was observed. Upon addition of Eu(III), the emission intensity arising from this transition was quenched by 33%, without any changes in λ_{max}. By plotting the changes in the emission intensity at 422 nm versus equivalents of Eu(III), in a manner similar to that described above, again demonstrates the formation of the desired 1:3 stoichiometry in solution.

The formation of this complex was also clearly evident from the changes in the Eu(III) emission (Figure 2), which shows the formation of new bands centred at 594, 616, 652 and 700 nm, corresponding to the deactivation of the Eu(III) $^5D_0$ excited state to the ^7F_J ground states ($^5D_0 \rightarrow {}^7F_J$, $J = 1$–4), respectively. These results confirm that the *phen* ligand is capable of successfully sensitise the Eu(III) excited state. Furthermore, as can be seen in Figure 2, the $J = 2$ band, occurring at 616 nm, gave rise to large changes in the Eu(III) emission upon formation of **1_3Eu**. This transition is highly sensitive to its coordination environment, so these results are indicative of direct

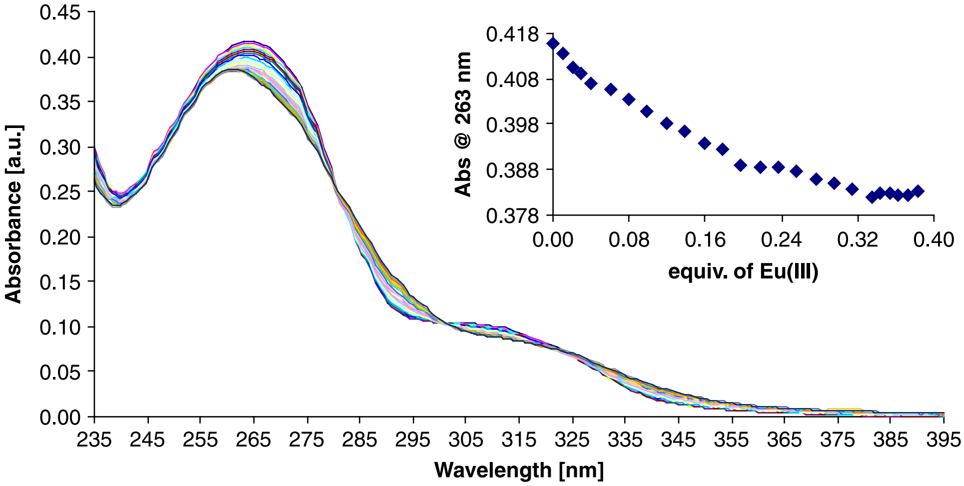

Figure 1. Changes in the absorption spectra of **1** (10 μM) upon addition of Eu(CF_3SO_3)$_3$. Inset: The changes in absorbance at 263 nm as a function of equivalents of Eu(III).

coordination between the *phen* ligand and the Eu(III) ion. Analysis of the changes in the $J = 2$, shown as inset in Figure 2, demonstrates the formation of the desired 1:3 complex, and its formation was further confirmed by using Job's plot analysis ($m/n = f_{\max}/(1 - f_{\max})$), given $f_{\max} = 0.25$ and $m/n = 1/3$, for the changes in the 616 mm band.

The luminescence changes observed in Figure 2 were also analysed by fitting the data using the nonlinear least-squares fitting programme SPECFIT. The results of this fitting are shown in Table 1 and demonstrate the stepwise formation of **1Eu**, **1$_2$Eu** and **1$_3$Eu** complexes in solution, and that the **1$_3$Eu** complex is formed with log $K_{1:3}$ of ~6. Similar analysis was carried out on the changes observed in both the ground and the singlet excited state spectrum. On all occasions, the stepwise formation of **1$_3$Eu** was also observed (Table 1; expressed as log β), where a good correlation was observed between all three spectroscopic techniques.

From Table 1, it is clear that the 1:3 stoichiometry dominates in solution, and hence the Eu(III) ion would be expected to be hexa-coordinated. The overall coordination number of **1$_3$Eu** was further confirmed, by measuring the hydration state (q), or the number of metal-bound water molecules associated with the **1$_3$Eu** structure, by measuring the excited state lifetimes for the Eu(III) emission in H_2O and D_2O, respectively, by direct excitation of the Eu(III) centre at 395 nm. This gave values of 0.333 and 1.83 ms for τ_{H_2O} and τ_{D_2O}, respectively, which translates, using the Horrocks (*21*) modified equation developed by Beeby et al. (*22*),

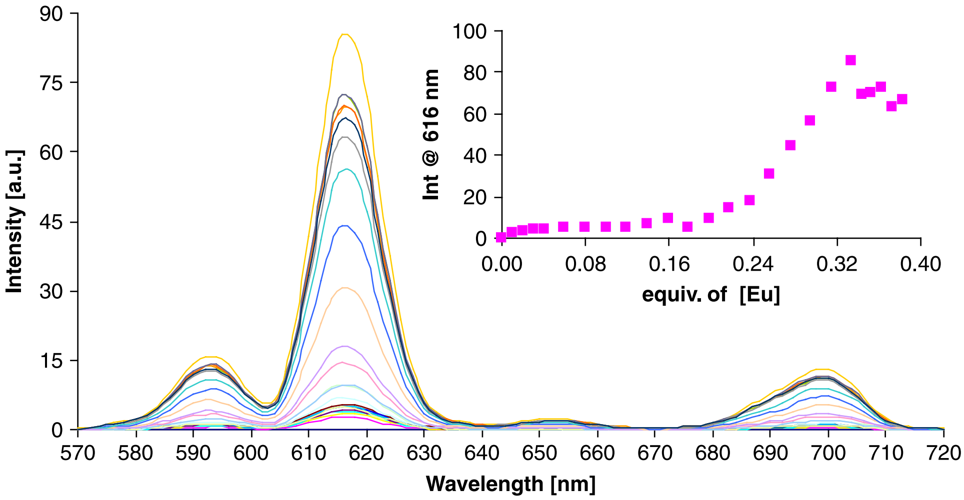

Figure 2. Changes in the Eu(III) emission of **1** (10 μM), which is enhanced upon addition of Eu(CF_3SO_3)$_3$. Inset: The changes in lanthanide emission at 616 nm as a function of equivalents of Eu(III) added, upon excitation at 265 nm.

Table 1. Binding constants and binding modes between Eu(III) and **1**, obtained upon fitting the changes in the absorption, the fluorescence and the Eu(III) emission.

Technique	Species (Eu$_n$:1$_m$)	Log β	Std. deviation
Absorbance	**Eu1**	3.86	0.012
	Eu1$_2$	7.54	0.016
	Eu1$_3$	13.46	0.031
Fluorescence	**Eu1**	3.88	0.008
	Eu1$_2$	7.48	0.016
	Eu1$_3$	13.38	0.024
Phosphorescence	**Eu1**	3.61	0.011
	Eu1$_2$	7.28	0.016
	Eu1$_3$	13.30	0.017

into a *q* value of 2.6, confirming the overall coordination number of **1$_3$Eu** as nine in aqueous solution.

Anion sensing

Having successfully synthesised and, analysed the formation of **1$_3$Eu** in solution, we next investigated its ability to bind/recognise anions. As **1$_3$Eu** has three urea-based ligands, all of which are capable of participating in the recognition of anions through hydrogen bonding, we expected to see significant changes in the photophysical properties of the complex upon such binding. Moreover, and as demonstrated above, the complex has three metal-bound solvent molecules, all of which could be displaced by other competitive coordinating ligands, such as anions, with concomitant changes in the coordination environment of the lanthanide ion and hence, in its photophysical properties. Hence, the anion-sensing ability of **1$_3$Eu** could occur through either of these modes, or through the combination of both.

All of the three spectroscopic techniques discussed above were used to monitor the recognition of anions by **1$_3$Eu** such as acetate, dihydrogenphosphate, fluoride and chloride as their tetrabutylammonium salts (TBA$^+$), in CH_3CN. Upon titrating AcO^-, the absorption spectrum was significantly affected as demonstrated in Figure 3. These changes were accompanied by the formation of four isosbestic points at 256, 280, 303 and 322 nm, which were attributed to the interaction of the anion with the three urea moieties. Analysis of the changes in the absorption spectrum is shown as an inset in Figure 3, and demonstrated that these changes occurred up to *ca.* 3 equiv. of AcO^-, signifying the formation of hydrogen bonding complexes between these anion and the urea moieties. Fitting this data using SPECFIT, however, only gave accurate binding constants for two of these binding events, namely the 1:1 and the 2:1 (ion:complex) between **1$_3$Eu** and AcO^-, with binding constants $\log K_{1:1}$ and $\log K_{2:1}$ of 6.23 ($\pm$0.257) and 6.17 ($\pm$0.169), respectively, for these interactions. Similar changes were also observed in the absorption spectrum of **1$_3$Eu** for the titration of $H_2PO_4^-$ and F^-. As in the case of AcO^-, then for F^-, we were only able to fit the spectral changes of two binding events. However, for $H_2PO_4^-$, the best fits were observed only when the data were fitted to binding events, which involved the 1:1 and 1:2 complex formation as well as the 2:1 and 2:2 complex between **1$_3$Eu** and $H_2PO_4^-$. In contrast to these results, the titration of Cl^-, Br^- and I^- only gave rise to the formation of 1:1 complexes. In the case of Cl^- and Br^-, the changes in the absorption spectra of **1$_3$Eu** were of similar nature, at the same time as being overall smaller to that observed above. However, in the case of I^-, only absorption enhancements were observed without the formation of clear isosbestic points.

The fluorescence emission of **1$_3$Eu** was also affected upon carrying out anion titrations. After excitation at either 260 or 330 nm, fluorescence enhancements of 62, 58, 34, 10 and 16% were observed for AcO^-, F^-, Cl^-, Br^-

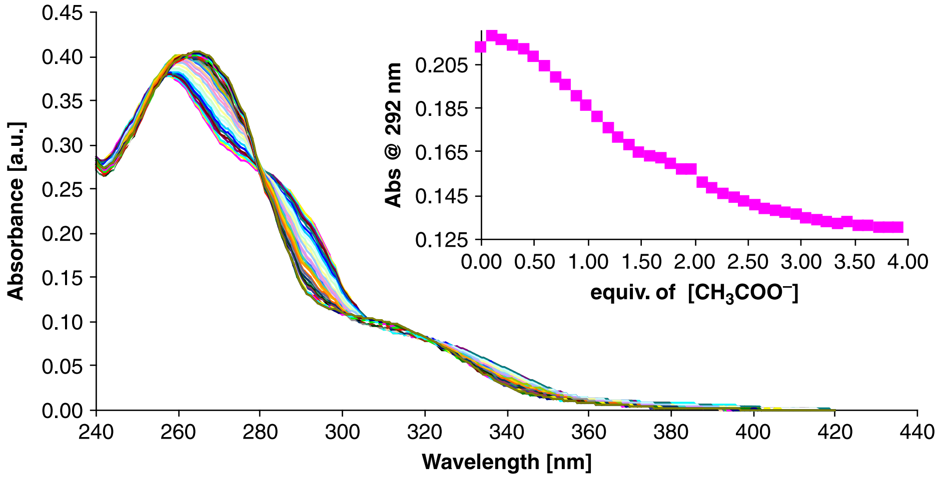

Figure 3. Changes in the absorbance of **1$_3$Eu** (4 µM) upon addition of AcO^-. Inset: Shows changes in absorbance at 292 nm as a function of equivalents of acetate added.

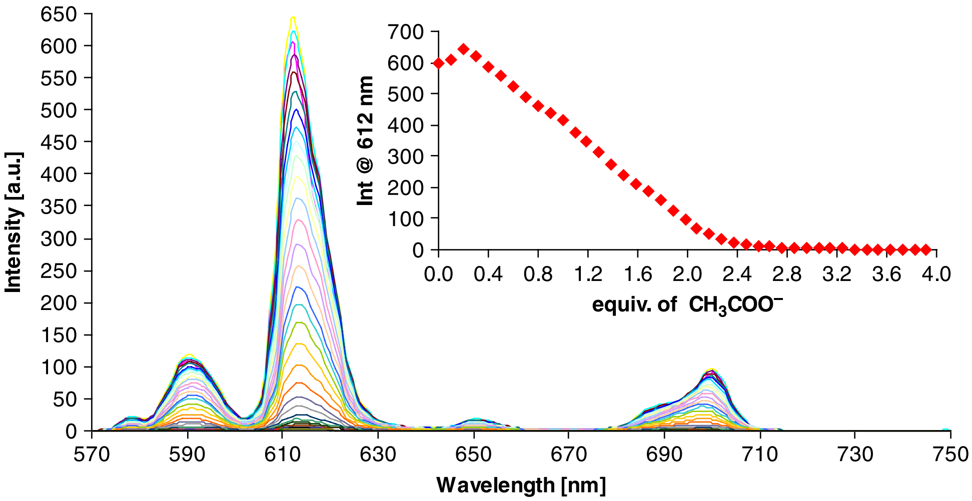

Figure 4. Changes in the lanthanide emission intensity of **1_3Eu** (4 μM), which was quenched upon titration with AcO^-. Inset: Shows changes in intensity at 612 nm as a function of added equivalents of AcO^-.

and I^-, respectively, with no apparent shifts in the 420 nm band. These changes were analysed in the same manner as described above for the ground state changes. As an example, then in the case of AcO^-, plotting the changes as a function of added equivalents clearly showed that the changes occur up to the binding of 3 equiv. of AcO^-, indicative of the 3:1 binding stoichiometry. However, in the case of $H_2PO_4^-$, initial quenching was also observed of *ca*. 15%. Nevertheless, after the addition of 0.5 equiv. of $H_2PO_4^-$, the emission was enhanced in a similar manner to that observed above.

However, from these spectroscopic anion titrations, the most significant changes were observed in the Eu(III) emission of **1_3Eu**, which was quenched up to *ca*. 2 equiv. of AcO^- (after initial slight enhancement ~3%) (Figure 4). The inset in Figure 4 also shows the profile of the changes in luminescence intensity at 612 nm ($J = 2$ band) as a function of the number of equivalents of AcO^- added, and in a similar manner to that observed for the UV–visible and fluorescence titrations above demonstrates that 2 equiv. of AcO^- were needed to fully quench the lanthanide emission. We propose that this quenching can be attributed to an energy mismatch between the lowest triplet state (T_1) of the antenna and the excited state of europium, hence making the transfer of energy unfavourable from the triplet state of the antenna, T_1, to the excited state of the Eu(III), $^5D_0$, upon anion recognition. Alternatively, it is also possible that some contribution from dissociation, or displacement of **1** from the Eu(III) centre in **1_3Eu**, could occur upon formation of hydrogen bonding complex between the urea and the anions; however, to date we have been unable to fully quantify whether such displacement is occurring. With the aim of evaluating these binding modes of the anion, analysis of the changes seen in Figure 4 was undertaken using SPECFIT. As had been observed for the changes in the ground state, the fitting of the changes observed in the AcO^- showed that the 1:1 and the 2:1 stoichiometries were the most dominating, with $\log K_{1:1}$ and $\log K_{2:1}$, of 6.56 (±0.118) and 7.0 (±0.061), respectively, which are in agreement with those values observed from the ground and the singlet state changes. In a similar manner, $H_2PO_4^-$ also gave rise to luminescent quenching. However, these changes were best fitted using a variety of binding equilibriums such as 1:1, 1:2, 2:1 and 2:2, which would indicate that the anion is bound to **1_3Eu** in a more complicated manner than AcO^-. However, for both of these anions, the main binding seems to be through hydrogen bonding at the urea moieties, with lesser contribution from direct binding to the lanthanide centre, via the displacement of metal-bound solvent molecules.

However, such binding combination was observed for the titration of **1_3Eu** using F^- (Figure 5), where the Eu(III) emission was initially significantly enhanced up to *ca*. 1 equiv. of the ion, which we propose is due to the displacement of a metal-bound solvent molecule by F^-. However, these changes were subsequently followed by almost complete quenching in the Eu(III) emission, as demonstrated in the inset in Figure 5 for the changes in the 612 nm transition, in a manner similar to that observed for AcO^- above. This second binding, we assign to the recognition of the anion at the urea site. From these luminescence changes, analysis, using SPECFIT, gave good fitting of the experimental data, from which we were able to obtain two binding constants, $\log K$ of 10.35 and 8.2 for the 1:1 and 1:2 bindings, respectively. These are significantly higher binding values than observed for AcO^- or $H_2PO_4^-$, respectively, which might further support the different mode of binding experienced by F^-. In contrast to these results, the titration with Cl^-, Br^-

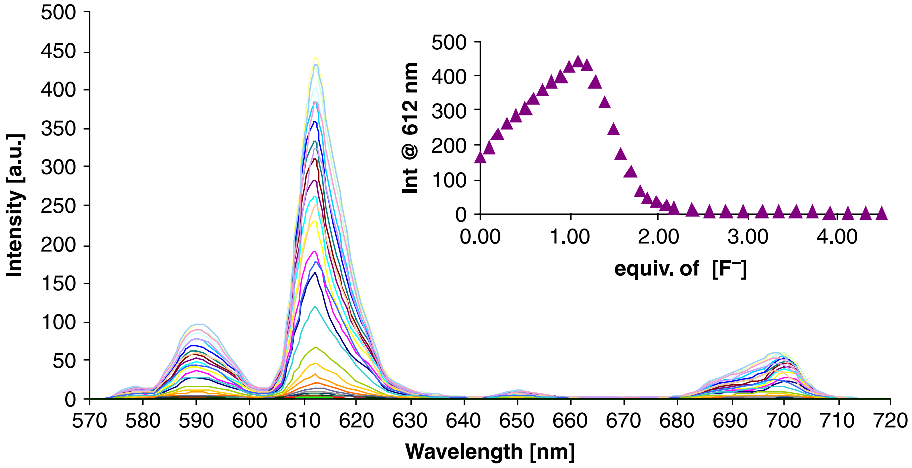

Figure 5. The overall changes in the Eu(III) emission of **Eu:1$_3$** (4 μM) upon addition of F^-. Inset: The changes in the intensity at 612 nm as a function of added equivalents of F^-.

and I^- only gave rise to 1:1 binding, with binding constant, $\log K_{1:1}$ of 6.34, 6.18 and 6.26, being determined for these anions, respectively. From these results, we have established that only for F^- is the emission enhanced, which demonstrates that the initial anion binding is caused by the binding of the anion at the meal ion centre and that the second equivalent of the anion binds to the complex via hydrogen bonding interactions at the urea site, which gives rise to quenching in the Eu(III) emission, as the efficiency of the sensitisation process is altered upon anion binding. Such binding interactions were also observed for the other anions investigated herein. We are currently in the process of evaluating these binding modes in greater detail as well as developing analogue systems that possess higher Eu(III) binding affinities and consequently could give rise to the sensing of anions by using such heteroditopic receptors and lanthanide luminescence in a more competitive aqueous environment.

Conclusion

In this communication, we have described the synthesis and the characterisation of a new lanthanide complex between a urea-based heteroditopic *phen* receptor and Eu(III). We demonstrate, using ground, single excited and phosphorescence spectroscopy, that the resulting complex is formed in 3:1 (ligand-to-metal ion) stoichiometry, and that this complex can interact with anions in CH_3CN. In particular, in the case of AcO^-, $H_2PO_4^-$, Cl^-, Br^- and I^-, the titration of these ions leads to significant changes in the Eu(III) emission, which was fully quenched, in the case of AcO^-, $H_2PO_4^-$, within the addition of 3 equiv. of these anions. This we propose as being the result of binding of these anions at the urea moieties in **1$_3$Eu**. In contrast, the titration of F^- gave rise to initial enhancement in the Eu(III) emission up to one equivalence, followed by luminescence quenching. This we assign to dual binding modes involving initial binding of the anion at the metal ion centre itself, with concomitant removal of one solvent molecule, and enhancement in the Eu(III) emission, followed by quenching in the Eu(III) emission upon binding of the anion at one or more of the urea moieties in **1$_3$Eu**.

Experimental

General

Reagents (obtained from Aldrich, St Louis, MO, USA) and solvents were purified using standard techniques. Melting points were determined using a GallenKamp melting point apparatus. Infrared spectra were recorded on a Mattson Genesis II FTIR spectrophotometer equipped with a Gateway 2000 4DX2-66 workstation. ^{1}H NMR spectra were recorded at 400 MHz using a Bruker Spectrospin DPX-400 instrument. ^{13}C NMR spectra were recorded at 100 MHz using a Bruker Spectrospin DPX-400 instrument.

1-[1,10]Phenanthrolin-5-yl-3-(4-trifluoromethyl-phenyl)-urea (1)

To a suspension of the amine (**2**) (1.0 g, 5.12 mmol) in $CHCl_3$ (40 ml), trifluoro-*p*-tolyl isocyanate (0.79 ml, 5.63 mmol) was added. After 5 min, all the amine was dissolved and a dark yellow solution was observed. The reaction mixture was stirred overnight at room temperature, under an argon atmosphere. An off-white precipitate was observed on the reaction vessel. This precipitate was filtered and washed with cold $CHCl_3$. The obtained solid was recrystallised from MeOH to yield a pale solid (1.38 g, 88% yield). The melting point decomposes above 290°C; calculated for $C_{20}H_{14}N_4OF_3$ $m/z = 383.1120$ $[M + H]$.

Found $m/z = 383.1107$. ^{1}H NMR (400 MHz, d_6-(CD$_3$)$_2$SO, δ_H): 9.55 (br s, 1H, NH), 9.16 (d, 1H, *phen*-CH, $J = 4.0$ Hz), 9.12 (br s, 1H, NH), 9.00 (d, 1H, *phen*-CH, $J = 4.0$ Hz), 8.65 (d, 1H, *phen*-CH, $J = 8.5$ Hz), 8.43 (d, 1H, *phen*-CH, $J = 8.0$ Hz), 8.39 (s, 1H, *phen*-CH), 7.89 (dd, 1H, *phen*-CH, $J = 4.0$ Hz), 7.72 (m, 5H, *phen*-CH + Ar-CH); ^{13}C NMR (100 MHz, d_6-(CD$_3$)$_2$SO, δ_C): 152.87, 149.87, 148.74, 145.89, 143.34, 143.13, 135.61, 132.08, 130.44, 128.50, 126.25, 126.22, 123.77, 123.68, 122.95, 122.21, 118.01, 116.07; ^{19}F NMR (376 MHz, d_6-(CD$_3$)$_2$SO, δ_F): -60.58 (CF$_3$); MS (ES$^+$) $m/z = 383.11$ (M + H). IR υ_{max} (cm^{-1}) 3394, 3284, 3211, 3089, 1711, 1613, 1563, 1505, 1472, 1411, 1377, 1329, 1310, 1270, 1202, 1162, 1153, 1108, 1097, 1066, 1017, 988, 945, 878, 848, 826, 803, 737, 711, 691.

Europium complex of 1, 1_3Eu

To a suspension of the urea (**1**) (0.10 g, 0.26 mmol) in CH$_3$CN (20 ml) was added Eu(CF$_3$SO$_3$)$_3$ (0.06 g, 0.11 mmol). Within few minutes, a clear yellow solution was observed. The reaction mixture was stirred overnight, at room temperature under an argon atmosphere. The precipitate was isolated by filtration, and dried under vacuum to produce a bright yellow solid (0.13 g, 28% yield). ^{1}H NMR (600 MHz, d_6-(CD$_3$)$_2$SO, δ_H): 9.52 (s, 1H, NH), 9.15 (br s, 1H, *phen*-CH), 9.10 (s, 1H, NH), 8.98 (br s, 1H, *phen*-CH), 8.64 (d, 1H, *phen*-CH, $J = 8.6$ Hz), 8.43 (d, 1H, *phen*-CH, $J = 7.6$ Hz), 8.35 (s, 1H, *phen*-CH), 7.88 (br s, 1H, *phen*-CH), 7.74 (d, 2H, Ar-CH, $J = 8.6$ Hz), 7.70 (br s, 1H, *phen*-CH), 7.69 (d, 2H, Ar-CH, $J = 8.6$ Hz); ^{19}F NMR (376 MHz, d_6-(CD$_3$)$_2$SO, δ_F): -60.56 (CF$_3$), -78.29 (CF$_3$SO$_3$); MS (ES$^+$) $m/z = 558.00$ [(M-2 *phen* ligands) + Na] 648.95 [M/2], 684.91 [(M/2) + 2H$_2$O]; IR υ_{max} (cm^{-1}) 3334, 1656, 1605, 1542, 1412, 1314, 1223, 1160, 1107, 1066, 1026, 844, 808, 733, 719, 695.

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