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Formation of luminescent terbium(III) self-assemblies from pyridyl bis-amidothioureas based ligands in MeOH and in water–DMSO solutions and their use in anion sensing application†‡

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The self-assembly between the amidothiourea ligands **1** and **2** and Tb(III) gave rise to the formation of 1 : 1 and 3 : 1 (ligand–Tb) supramolecular architectures that were shown to be luminescent in both MeOH and in water–DMSO solutions; preliminary investigations in the latter system also showed that their emission was modulated upon interacting with anions such as acetate and phosphate due to host–guest formation.

The formation of luminescent self-assemblies, formed through the use of lanthanide directed synthesis, has become an active area of research within the field of coordination–supramolecular chemistry.[1] In addition to their interesting structural features,[2,3] resulting from the high coordination requirements of the lanthanide ions, such complexes have also been developed for purposes such as for use in material chemistry,[4a,b] as well as in luminescent sensing and for use in imaging of biological matter.[1c,e,4c,d] Many examples of lanthanide luminescent sensors have been developed to date, where the lanthanide ions are usually contained within well-defined ligand structures (or cavities).[5] Here the sensing can occur *via* direct coordination to the lanthanide centre itself[6] (as in the case of sensing of anions),[7–10] or through the use of appended synthetic receptor moieties. The latter are often formed as part of antennae, since the population of the excited states of the lanthanides is Laport-forbidden, and best achieved by using sensitisation *via* a chormophoric anteanna.[7–11] To date, only a few examples of lanthanide sensors have been developed for anions, where hydrogen bond donors are employed.[12,13] Due to the importance of anions in industrial and environmental applications, as well as their physiological roles, the sensing of anions has become an extremely active area of research.[14,15] Amidothiourea/urea based receptors have been shown to detect the presence of anions in highly competitive media.[16] Recently we have reported the colorimetric sensing of anions in aqueous solution using a charge neutral, cleft like, pyridyl based amidothiourea receptor **1**.[17] As 2,6-dicarboxyamidopyridine based ligands are known to

form strong complexes with lanthanide ions,[18,19] we set out to explore the use of such thiourea based ligands, *i.e.* **1** and **2**, Fig. 1, in the formation of lanthanide self-assembly complexes, and if such complexes could then be subsequently used for anion sensing. We foresaw that the binding of the anions would most likely occur at the thiourea moieties, and not at the metal ion centre, and this would give rise to concomitant changes in the lanthanide emission due to modulation in the sensitisation process form the antennae (which the thiourea moieties are part of) to the Tb(III) $^5D_4$ excited state.[20]

The synthesis of **1** and **2** has recently been reported by us.[17,21] Both were formed in a similar manner where the commercially available 2,6-pyridinedicarboxylic acid was first converted to its corresponding di-ethyl ester which was then reacted with hydrazine monohydrate, under reflux in ethanol, giving the dihydrazide, which was finally reacted with the respective
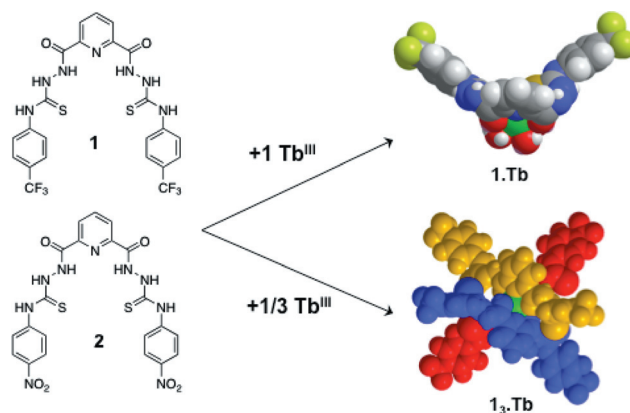
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Fig. 1 The ligands **1** and **2** used in this current study. Schematic representation of the formation of the expected 3 : 1 and 1 : 1 self-assemblies complexes between **1** and Tb(III) (here represented as MM2 simulation) in 1 : 1 and 3 : 1 stoichiometries.

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isothiocyanate in CH_3CN. Both ligands, should, through coordination involving the nitrogen atom of the central pyridyl moiety and the two amide carbonyl oxygens, give rise to the formation of complexes with Tb(III) in a 3 : 1 stoichiometry (*e.g.* $1_3 \cdot Tb$ for **1**) where the Tb(III) ion would be overall nine coordinated. This is shown schematically in Fig. 1, using MM2 calculations.[22] However, it also possible that the thioura moieties may also be directly involved in the lanthanide coordination through the $C=S$ bonds. This would result in the formation of either 1 : 1 or 2 : 1 stoichiometries involving possibly five donor atoms from **1** or **2** coordinating to Tb(III) through the central pyridyl nitrogen, the two carboxylic amides and through the sulfur atoms of the two thiourea moieties. Of these the 1 : 1 stoichiometry, which would also require the use of three solvent molecules to fulfil the high coordination requirement of Tb(III), is shown in Fig. 1, in a side view. As these ligands can also be used as sensitize antennae to populate the excited state of Tb(III), we set out to investigate their formation by monitoring their various spectroscopic properties.

Results and discussion

Tb(III) directed formation of self-assemblies of 1 and 2 in solution to give $1_3 \cdot Tb$ and $2_3 \cdot Tb$

The formation of the Tb(III) complexes of **1** and **2** was initially studied in MeOH by carrying our spectroscopic titrations using $Tb(ClO_4)_3$ (to minimise the binding of the counterion at the amidothiourea moieties). The changes in the absorption spectra of **1** and **2** in MeOH exhibited bands centred at *ca.* 376 nm and 381 nm, respectively, which were assigned to the phenylthiourea moieties. The changes in the absorption spectra in MeOH upon addition Tb(III) to **1** is shown in Fig. 2, while the changes for **2** are shown in the ESI.‡§

For both systems, significant changes were observed in the ground state upon binding to Tb(III). In the case of **1**, Fig. 2, the 376 nm band enhanced in absorption and the band centred at 275 nm was slightly hypochromically shifted with the formation of an isosbestic point at 293 nm. Plotting the changes in the 376 nm band as a function of added equivalents showed that a plateau was reached after the addition of *ca.* 0.8–0.9 equivalents of Tb(III). Similar changes were also observed for **2** (see ESI§) with an isobestic point being forming at 297 nm. The plateau at *ca.* unity would suggest that the major species in solution would be the 1 : 1 stoichiometry. This was indeed also shown to be the case by carrying out Job's plot analysis on **1**, which exhibited a maximum for $\chi_{Tb} = 0.5$, again suggesting the 1 : 1 stoichiometry was the dominate one in solution. We also evaluated the changes in the absorption spectra using $TbCl_3$ $Tb(OAc)_3$. On both occasions, similar changes were seen in the UV-Vis absorption spectra to that seen above. For both systems, the formation of a complex between either **1** or **2** and Tb(III) also resulted in the appearance of metal centred emission, as a result of the sensitisation of the $^5D_4$ excited state of the Tb(III) ion, with emission occurring at 490, 546, 586 and 622 nm due to deactivation to the

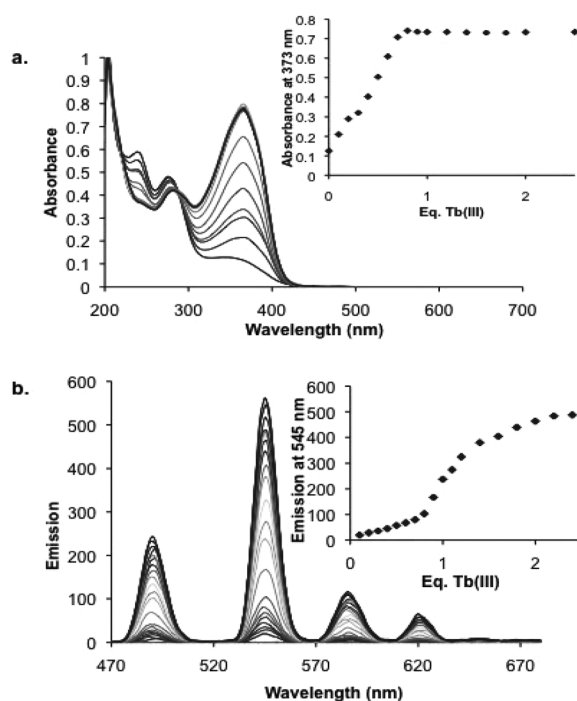§ We also observed a small contribution from residual emission of the $Tb(ClO_4)_3$ in aqueous solvents.

Fig. 2 (a) Changes observed in the UV-vis absorption of **1** ($C = 2 \times 10^{-5}$ M) upon the addition of $Tb(ClO_4)_3$ in MeOH. *Inset*: The changes observed at 373 nm as a function of added Tb(III) equivalents. (b) Changes observed in the terbium emission ($\lambda_{ex} = 297$ nm) of **1** upon the addition of $Tb(ClO_4)_3$ in MeOH. *Inset*: The changes observed at Changes at 545 nm as a function of added Tb(III) equivalents.

^7F_J ($J = 6, 5, 4, 3$) ground states of the forming self-assembly. In the case of **2**, somewhat different behaviour was observed, as here the changes in the Tb(III) were initially small up to the addition of *ca.* 0.8 equivalent of Tb(III), after which the luminescence intensity was greatly enhanced to *ca.* 1.5 equivalents, before finally levelling at *ca.* 2 equivalents of Tb(III). In contrast the changes in the fluorescence emission were small and difficult to analyse for both ligands. On both occasions some residual emission was observed beyond the addition of one equivalent of $Tb(ClO_4)_3$.

The changes obtained in the UV-Vis absorption spectra of **1** and **2** and in the Tb(III) emission were analysed by fitting the global changes using non-linear regression analyses programme SPECFIT. For the changes in the absorption spectra, good fits were observed (see ESI§). The fitting of these changes also suggested that the formation of 1 : 1 species dominated in solution, but only at higher Tb(III) concentrations, and in fact, at low Tb(III) concentrations, the 3 : 1 (ligand–Tb) stochiometries $1_3 \cdot Tb$ and $2_3 \cdot Tb$ were formed as major species in solution (see ESI§ for the titration of **2** with Tb(III)) upon the addition of 0.3 equivalents of Tb(III). From these analyses, the binding constant log $\beta_{3:1}$ of 18.4 and 17.6 were determined for $1_3 \cdot Tb$ and $2_3 \cdot Tb$, respectively. However, at higher Tb(III) concentrations the equilibrium was, as discussed above, displaced towards the strong formation of the 1 : 1 complexes, which were formed with log $\beta_{1:1}$ of 7.8 and 7.7 for $1 \cdot Tb$ and $2 \cdot Tb$, respectively. In these analysis, the 2 : 1 species was also detected but its formation remained minor throughout the titrations, being less than 20% with log

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$\beta_{2:1}$ of 11.6 and 11.9, respectively at one equivalent of Tb(III).¶ For all of these titrations, the fitting of the changes in the Tb(III) emission gave poorer fits and hence, binding constant determination was not obtained with high accuracy.

As had been done above, we also observed the changes in the Tb(III) centred emission upon titration of **1** with TbCl$_3$ Tb(OAc)$_3$. On both occasions, the Tb(III) emission was enhanced as seen above. However, in the case of TbCl$_3$, the relative 'slow' enhancement observed between the additions of $0 \rightarrow 1$ equivalent was much less pronounced, whereas for Tb(OAc)$_3$ it was more pronounced (see ESI§). This clearly indicates that the anion does have an effect on the formation of the self-assembly between **1** and Tb(III), possibly due to some direct interactions with the amidothioure moieties.

Anion binding to 1$_3$·Tb and 2$_3$·Tb in solution

Having investigated the formation of these self-assemblies in methanol, we next investigated their formation in a mixture of organic and aqueous solution. Having previously reported the interaction of **1** and **2** with anions in 4 : 1 DMSO–H$_2$O solution (as it was necessary to use mixture of these solvents due to solubility issues in water), where the bind to the anions to the anion receptors was found to occur *via* hydrogen bonding interactions at the amidothiourea moieties,[17,20] we investigated the interaction of these ligands with Tb(III) self-assemblies of **1** and **2** in the same solvent system. Consequently, we first investigate the self-assembly formation in this solvent system. However, to our surprise, then in comparison to the results obtained in MeOH, no major changes were seen in the absorbance spectra of **1–2** upon binding to Tb(III). However, the Tb(III) centred emission was *switched on* for both, and in the greatest changes occurred within the addition of $0 \rightarrow 0.3$ equivalents of Tb(III), Fig. 3, in a similar manner to that seen above in MeOH. Thereafter, the Tb(III) emission gradually increased with added Tb(III) (see insert in Fig. 3). This can be explained by the initial formation of the 1$_3$·Tb and 2$_3$·Tb complexes followed by the formation of the 2 : 1 and the 1 : 1 species.¶ As before the spectral changes in the lanthanide emission of **1** were fitted using non-linear regression analysis (see ESI§). The speciation distribution diagram from these fitting showed indeed the initial formation of the desired 1$_3$·Tb self-assemblies in *ca.* 58% yield after the addition of 0.3 equivalent of Tb(III), with log $\beta_{3:1} = 13.5$. As expected, from the titration, the formation of the 1 : 2 (log $\beta_{2:1} = 8.3$) and 1 : 1 (log $\beta_{1:1} = 3.9$) complexes were also observed at higher concentration of
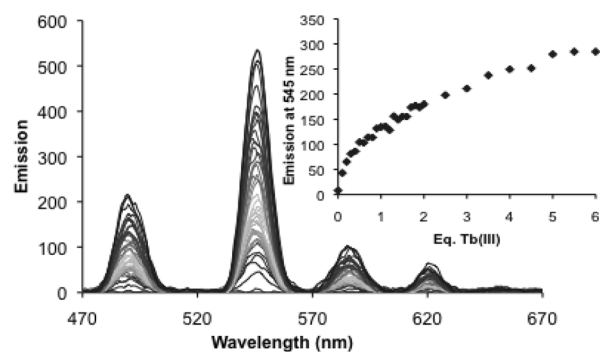

Fig. 3 Changes observed in the terbium emission of **1** ($C = 2 \times 10^{-5}$ M; $\lambda_{ex} = 281$ nm) in 4 : 1 DMSO–H$_2$O upon the addition of Tb(ClO$_4$)$_3$. *Inset*: the changes observed at 545 nm as a function of Tb(III) equivalents.

Tb(III). However, the calculation of the stepwise binding constants for the formation of each of these complexes have shown that 1$_3$·Tb was the most stable species in solution with log $K_3 = 5.3$, whereas 1$_2$·Tb gave log $K_2 = 4.4$. It can be concluded from these results that upon the addition of 0.3 equivalents of Tb(III) the quasi-selective formation of 1$_3$·Tb occurs. Similar changes were seen for the titration of **2** in this solvent system (see ESI§), however, these changes could not be fitted accurately with acceptable convergence factor. Nevertheless, these results show that the formation of self-assemblies between **1** or **2** and Tb(III) can take place either in MeOH or 4 : 1 DMSO–H$_2$O solutions at room temperature and in real-time.

The anion recognition ability of 1$_3$·Tb and 2$_3$·Tb were next investigated in 4 : 1 DMSO–H$_2$O solution. In both case, the complexes 1$_3$·Tb and 2$_3$·Tb were prepared *in situ*, by stirring each ligand with 0.33 equivalents of Tb(ClO$_4$)$_3$ for one hour in 4 : 1 DMSO–H$_2$O solution. Upon the addition of acetate to this 1$_3$·Tb solution the absorption centred at 333 nm experienced a 33% hyperchromic effect; where a plateau was reached after the addition of 10 equivalents of acetate, Fig. 4a. Concomitantly, the luminescence intensity of 1$_3$·Tb was significantly affected as demonstrated in Fig. 4b, particularly at higher anion equivalents. Here, the Tb(III) emission remained relatively unchanged upon the addition of the first five equivalents of acetate, but between the addition of $5 \rightarrow 12$ equivalents of acetates, the emission was increased by *ca.* 133% before reaching a final plateau. These results would indicate that the binding of the anions to the amidothiourea moieties does not give rise to significant changes except at high concentrations, which might suggest some direct binding to the Tb(III) ion itself. We also investigated the effect of other anions on the lanthanide emission; of these only phosphate gave rise to any changes in either the absorption or the Tb(III) emission (see ESI§). For the former, the absorption centred at 333 nm was slightly red shifted, but to a lesser extend to that seen for acetate. The changes in the Tb(III) emission were, however, significantly different to that seen for acetate; as within the initial addition of anions the emission stayed constant, but this was then followed by complete quenching with the addition of ten equivalents of phosphate. In a similar manner the anion binding to 2$_3$·Tb was also investigated. As **2** possess a nitro substituent, we anticipated to see larger changes in the absorption spectra to that seen for 1$_3$·Tb, due to the strong electron

¶We attempted to analyse this self-assembly formation further by carrying out ESMS analysis of the above solutions of either 1$_3$·Tb or 2$_3$·Tb formed above. Unfortunately, we were unable to demonstrate the 1 : 1 or the 3 : 1 (ligand to metal) stoichiometry from the ESMS (positive mode) results. This was also found to be the case for samples prepared by direct formation of the 3 : 1 complex 1$_3$·Tb by heading **1** with Tb(III) salts, followed by precipitation and analysis by ESMS. For both methods we concluded that either the complex did not survive the experiment or that the complex did not 'fly' and hence its appearance was not observed. Furthermore, while ^{1}H NMR analysis (400 MHz, DMSO-d$_6$) of a solution of 1$_3$·Tb showed shifted and broad resonances we were unable to assign the structure of the complex. Consequently, we could only rely on the data observed in the UV-Vis absorption and in the emission spectroscopies discussed above for the formation of these self-assemblies in solutions.
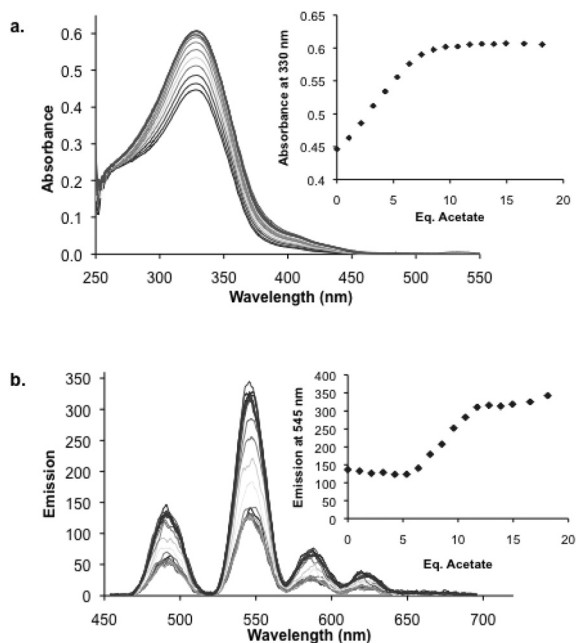
Fig. 4 (a) Changes observed in the UV-Vis absorption of $1_3 \cdot Tb$ ($C = 2 \times 10^{-5}$ M) upon the addition of TBAOAc *inset*: The changes at 330 nm as a function of anion equivalents. (b) Changes observed in the Tb(III) emission ($\lambda_{ex} = 333$ nm) of $1_3 \cdot Tb$ upon the addition of TBAOAc *inset*: Changes at 545 nm.

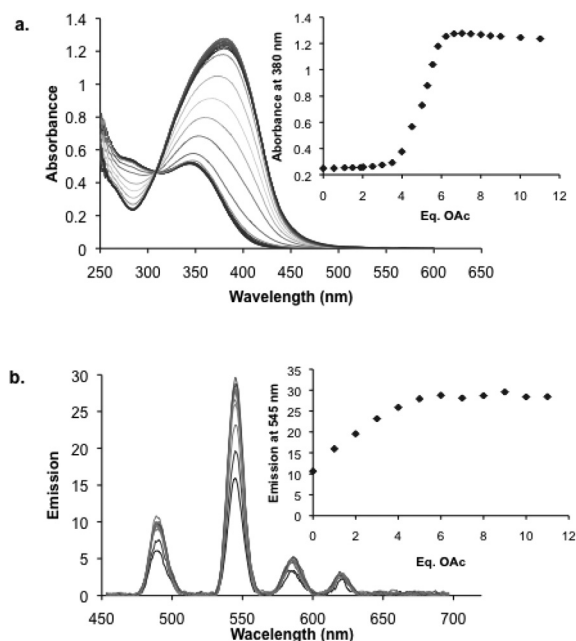**Fig. 5** (a) Changes observed in the UV-vis absorption of $2_3 \cdot Tb$ ($C = 2 \times 10^{-5}$ M) upon the addition of TBAOAc *inset*: Changes at 380 nm. (b) Changes observed in the terbium emission ($\lambda_{ex} = 286$ nm) of $2_3 \cdot Tb$ upon the addition of TBAOAc *inset*: Changes at 545 nm.

withdrawing nature of the nitro group. Indeed this was found to be the case as shown in Fig. 5a; however, unlike that seen for $1_3 \cdot Tb$ then only minor changes occurred within the addition of 4 equivalents of acetate. However, large changes were observed

between the additions of *ca.* 4 to 6 equivalents of acetate, where the absorption centred at 286 nm of $2_3 \cdot Tb$ was greatly red-shifted, with a λ_{max} at 385 nm, with the formation of an isosbestic point at 310 nm. This kind of shift is similar to that seen for the ligand alone in the presence of acetated.[17] In contrast, the Tb(III) centred emission of $2_3 \cdot Tb$ increased uniformly within the addition of $0 \rightarrow 6$ equivalents of acetate, as demonstrated in Fig. 5b, after which it remained constant. These results suggest, that for both $1_3 \cdot Tb$ and $2_3 \cdot Tb$ the anion recognition at the amidothiourea sites of these self-assembles does give rise to modulation in the Tb(III) emission, which could be a direct consequence of changes in the nature of the antennae. For both systems, all the lanthanide transitions were affected in a similar manner, which would suggest that the binding occur only at the amidothiourea sites. However, it cannot be excluded at present that the anions also, particularly at higher concentrations, do bind to the Tb(III) directly. The possibility of anion-initiated dissociation of the self-assembly, *i.e.* a displacement, seem also unlikely, particularly in the case of $1_3 \cdot Tb$, but cannot be discarded in the case of $2_3 \cdot Tb$ in the presence of phosphate as the Tb(III) emission is quenched. We are currently in the process of investigating these and related systems in greater detail with the view of exploring the use of lanthanide directed self-assembly formations in luminescent sensing and imaging applications.

Conclusions

In summary we demonstrated the formation of self-assemblies between the ligands **1** and **2** with Tb(III) in MeOH and 4 : 1 DMSO–H$_2$O mixture. We have also shown that the absorbance and the Tb(III) emission of the resulting complexes $1_3 \cdot Tb$ and $2_3 \cdot Tb$ is be modulated by the presence of acetate where for both self-assemblies the emission was enhanced.

Acknowledgements

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