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COMMUNICATION

Lanthanide directed self-assembly formations of Tb(III) and Eu(III) luminescent complexes from tryptophan based pyridyl amide ligands†‡

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The formation of self-assembly complexes between the ligands 1 (*SS*) and 2 (*RR*) and terbium or europium was undertaken and shown (using various spectroscopic titrations) to give rise to the exclusive formation of 2 : 1 (L : Ln) stoichiometry and not the anticipated 3 : 1 stoichiometry.

The formation of luminescent self-assemblies and complexes using lanthanide ions has attracted significant attention in recent times in supramolecular chemistry.[1–3] Due to the high coordination requirements of the lanthanides,[4] which themselves have interesting magnetic and luminescent properties,[5,6] many examples of lanthanide based coordination networks, MOFS or single structured architectures such as helicates, have been achieved.[7–9] We have recently developed examples of such systems, where we have used the lanthanides to direct the synthesis of simple molecular self-assemblies,[10] molecular-squares,[11] chiral bimetallic triple stranded helicates[12] and molecular bundles.[13] The latter two examples are formed by utilising ligands based on 2,6-dipicoline amides, which are known to have high affinity for lanthanides.[14–16] Herein we present **1** and **2**, Fig. 1, formed from 2,6-dipicoline by using the naturally occurring amino acid tryptophan. Here, the tryptophan chromophores can be employed as antennae to populate the lanthanide excited states of ions such as Eu(III) and Tb(III); but could also provide an opportunity to form higher order peptide-based self-assemblies through modification of the carboxyl terminal of **1** and **2**. Both ligands, through the central nitrogen moiety of the pyridyl ring and the two amide oxygens, provide three coordination sites for lanthanides, and by first approximation, would be expected to form complexes with the ions in a 1 : 3 (Ln : L) ratio (*e.g.* form $\mathbf{1_3Tb}$ and $\mathbf{2_3Tb}$ with Tb(III)).[13,17] However, such picolinate based ligands have also been shown to form a 2 : 1 complexes with lanthanides; even though examples of such structures are less common. However, we foresaw that because of the presence of the tryptophan esters in **1** and **2**, this could favour the formation of the 1 : 2 stoichiometries (*e.g.* $\mathbf{1_2Ln}$ and $\mathbf{2_2Ln}$) in preference of the 1 : 3 stoichiometries, as two additional donor-atoms could be provided by each ligand by these functionalities.

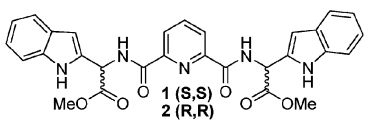

Fig. 1 The structure of **1** and **2** developed for the current study, formed using the protected α-amino acid (*S* or *R*) tryptophan.

The synthesis of **1** and **2** was achieved in two different ways in moderate to good yields. The initial formation involved a two step synthesis from the dipicolinic acid, *via* the formation of the di-acid chloride, which upon reacting with the *S* and the *R* forms of tryptophan in dry organic solvents (THF or $CHCl_3$) gave **1** and **2**, respectively. Alternatively, the picolinic acid was reacted with tryptophan using peptide-coupling reactions, in the presence of triethylamine, HOBt and EDCI. In our hands, the second synthesis gave rise to cleaner products after aqueous based workup. Both **1** and **2** were characterised using conventional methods (see ESI‡), the ^{1}H NMR of both were identical, demonstrating that the two were formed as enantiomers which was confirmed by recoding their CD-spectra (see ESI‡). Slow evaporation of **1** and **2** from a methanol and CH_2Cl_2 mixture gave crystals suitable for single crystal X-ray diffraction analysis, Fig. 2, again confirming their enantiomeric nature, and the expected C_{2v} symmetry.[18] As tryptophan has been shown to be a good sensitising antenna for Tb(III),[19] both **1** and **2** were initially reacted with $Tb((CF_3)SO_3)_3$ in a 3 : 1 (ligand : Tb) ratio, in refluxing CH_3CN for 12 hours. After precipitation from diethyl ether, the resulting solids were re-crystallised from MeOH, and isolated by filtration. The ^{1}H NMR (see ESI‡) of these two

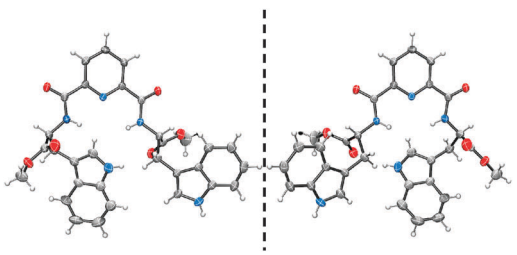

Fig. 2 The X-ray crystal structures of the enantiomers **1** and **2**.

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products were shown to be identical, indicating that the two complexes were formed as a pair of enantiomers; with broad resonances between −15 to 30 ppm. Also, the CD-spectra of both products confirmed their enantiomeric formation (see ESI‡). The FTIR of these products also showed that all the carbonyl stretches were shifted by *ca.* 40–50 cm^{-1} upon complexation to Tb(III), which might suggest that they all participated in the binding of Tb(III). Unfortunately, we have not been unable to date to grow crystals of high enough quality of these self-assemblies for solid state single crystal structure analysis. However, using MALDI MS (DCTB matrix) it was clear that the reaction of both **1** and **2** with Tb(III) showed on both occasions, only the formation of $\mathbf{L_2Tb}$ and not the expected $\mathbf{L_3Tb}$ stoichiometry, with a m/z = 1591 (for $\mathbf{L_2Tb}$ + 2 × $CF_3SO_3^-$). On both occasions, the isotopic distribution patterns also matched the calculated ones, as shown in Fig. 3 for $\mathbf{1_2Tb}$ (see $\mathbf{2_2Tb}$ in ESI‡).

The absorption, fluorescence and the Tb(III) emission spectra of the two were recorded in aerated MeOH solution at room temperature. The UV-Vis absorption spectrum of both systems was identical, giving rise to a broad absorption band centred at 286 nm, assigned to the tryptophan antenna. Excitation at λ_{max} gave rise to fluorescence emission, typical of that of tryptophan. The time-resolved Tb(III) emission was also observed for both complexes upon excitation at 286 nm, demonstrating the successful population of the Tb(III) $^5D_4$ excited state, with emission bands occurring at 487, 543, 581 and 614 nm due to the deactivation of $^5D_4$ to ^7F_J (J = 6–3). The Tb(III) emission was also not enhanced in de-gassed solution. The sensitisation processes were also confirmed by recording the fluorescence excitation spectra, which matched that of the absorption spectra, by setting the emission at ΔJ = 5.

We next analysed the formation of $\mathbf{1_2Tb}$ and $\mathbf{2_2Tb}$ *in situ*, by observing the changes in the ground state of **1** and **2**, and in the Tb(III) emission in CH_3CN, which was used to ensure full solubility, at room temperature. After each addition of Tb(III), the resulting solutions were allowed to equilibrate for *ca.* 5 minutes prior to recording the absorption spectra. In the absence of Tb(III), **1** had two major absorption bands at λ_{max} = 220 nm (ε = 62 170 M^{-1} cm^{-1}) and at λ_{max} = 281 nm (ε = 13 614 M^{-1} cm^{-1}), assigned to the $\pi \rightarrow \pi^*$ transitions of the pyridine and the tryptophan moieties. Upon excitation at λ_{max} = 281 nm, each ligand gave rise to the typical tryptophan fluorescence emission, with λ_{max} = 423 nm. The overall changes observed in the absorption spectra of **1** are shown in Fig. 4a, upon titration with Tb(III) (as $Tb(CF_3SO_3)_3$), where both absorption bands experienced a hyperchromic effect within the addition of 0.5 equivalents of Tb(III) (see inset in Fig. 4a, for the changes in the absorption spectra at 275 nm), which is indicative of the formation of a self-assembly in a 2 : 1 stoichiometry; confirming what had previously been seen in the MS (Fig. 3).

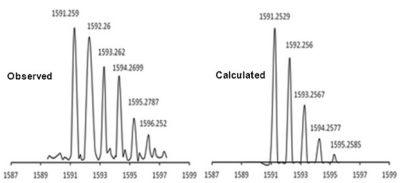

Fig. 3 The MALDI MS of $\mathbf{1_2Tb}$, showing the observed and the calculated spectra for $\mathbf{L_2Tb}$ + 2 × $CF_3SO_3^-$.

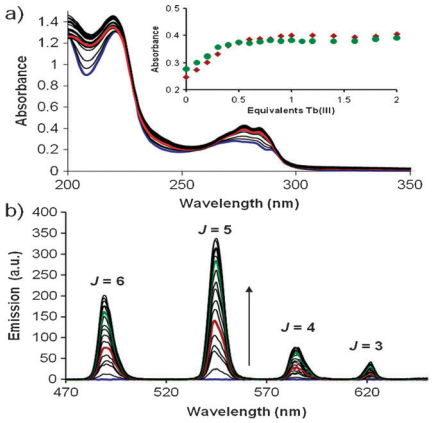

Fig. 4 (a) The changes in the UV-Vis absorption spectrum of **1** (upon titration with $Tb(CF_3SO_3)_3$) in CH_3CN. Inset: the changes at 275 nm for $\mathbf{1_2Tb}$ and $\mathbf{2_2Tb}$. (b) The corresponding changes in the Tb(III) emission.

Further addition of the metal (0.5 → 1 equivalents) gave rise to only small enhancements in both absorption bands; reaching a plateau upon addition of 1 equivalent. Similarly, the fluorescence emission spectra of **1** were also affected upon binding to Tb(III), where *ca.* 40% quenching was observed for this titration (see ESI‡). The changes in the Tb(III) emission were monitored concomitantly, Fig. 4b, and clearly demonstrate the formation of a self-assembly between **1** and Tb(III), where the emission was "switched on" from 0 → 1 equivalents; but minor enhancements were also observed between 1 → 2 equivalents of Tb(III). The Tb(III) excited state lifetimes were also recorded using the **1** : Tb(III) stoichiometry of 1 : 1, 2 : 1, 4 : 1, 1 : 2 and 2 : 3, and these were best fitted to a mono-exponential decay; indicative of the formation of a unique luminescent species in solution. Furthermore, on all occasions, the Tb(III) excited state lifetimes were found to remain constant, with an average τ = 0.926 ms upon excitation of the antennae in MeOH, while in CD_3OD these lifetimes were found to be significantly longer. Unfortunately, we were unable to determine the hydration state of these complexes accurately.

The changes observed in the absorption spectrum above were further analysed by fitting the global changes using non-liner regression analysis programme SPECFIT.[20] The fitting of the changes seen in Fig. 4a absorption titration data is shown as an inset in Fig. 5. The speciation distribution diagram formed from the fitting of the data is also shown in Fig. 5, and the results showed that the best fit was observed by fitting the data to the formation of both 1 : 1 and 2 : 1 (**1** : Tb) stoichiometry. Here, the most stable species was the product with 2 : 1 stoichiometry,

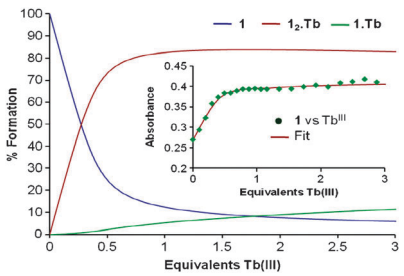

Fig. 5 The speciation distribution diagram of the titration of **1** with Tb(III). Inset: the fitting of the changes in the absorption spectra.

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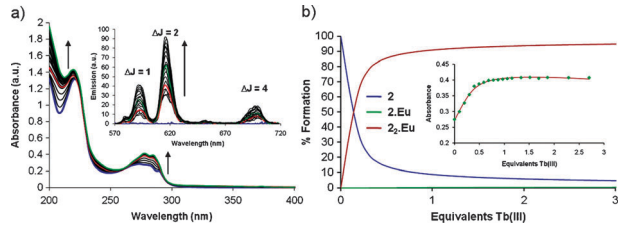

Fig. 6 (a) The changes in the absorption spectra upon formation of a self-assembly between **2** and Eu(III) in CH_3CN. Inset: the corresponding changes in the Eu(III) emission. (b) The speciation distribution diagram for the absorption titration of **2** with Eu(III) in CH_3CN. Inset: the fitting of the corresponding experimental data.

reaching a maximum formation of *ca.* 90% after the addition of 0.5 equivalents of Tb(III). This suggests that under these experimental conditions, the **1_2Tb** is formed, with an average binding constant of log $\beta_{2:1}$ = 11.1 (±0.11), and log $\beta_{1:1}$ = 4.6 (±0.3) for the 1:1 binding. In a similar manner, the fitting of the data obtained for the titration of **2** with Tb(III) showed that the **2_2Tb** stoichiometry was observed in *ca.* 73% yield, after the addition of 0.5 equivalents of Tb(III), with a binding constant log $\beta_{2:1}$ = 11.3 (±0.11) (see ESI‡). However, unlike that seen for **1**, then the 1 : 1 species was not detected and the 2 : 1 stoichiometry dominated after the addition of one equivalent of Tb(III) in solution.

Having successfully formed the 2 : 1 stoichiometry between **1** (and **2**) and Tb(III), we also investigated if Eu(III) could direct the synthesis of such systems using $Eu(CF_3SO_3)_3$) in CH_3CN. The changes in the absorption spectra of **2** are shown in Fig. 6a, demonstrating that the binding of Eu(III) induced similar changes to that seen in Fig. 4a for **1** and Tb(III). Plotting these changes as a function of added Eu(III), showed that after the addition of 0.5 equivalents of Eu(III) no major changes occurred in the absorption spectra (see ESI‡); again indicating the formation of the **2_2Eu** self-assembly and not the expected 3 : 1 stoichiometry. Fitting these changes using non-linear regression analysis gave an average binding constant of log $\beta_{1:1}$ = 4.1 (±0.6) and log $\beta_{2:1}$ = 10.9 (±0.3), which at 0.5 equivalents of Eu(III) corresponded to the formation of **2_2Eu** species in 86% yield, while the **2_1Eu** complex was only formed in less than 1% yield. The lifetimes of the lanthanide excited state were best fitted to mono-exponential decay, and did not change with different ligand–Eu(III) ratio.

As can be seen from the above results, neither Tb(III) nor Eu(III), directed the formation of the 3 : 1 stoichiometry and on all occasions the 2 : 1 self-assembly is formed in solution in high yield. Moreover, the formation of the **1_2Tb** and **2_2Tb** was also the sole product under thermodynamic conditions. This suggests that **1** and **2**, either through steric hindrance or by participation of the α-amino ester, prevents the formation of the expected 3 : 1 stoichiometry. These results clearly demonstrate that the structural nature of the antenna can greatly influence the overall stoichiometry of the self-assembly formation.

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