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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 helicates12 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 13Tb and 23Tb 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. 13Ln and 23Ln) in preference of the 1 : 3 stoichiometries, as two additional donor-atoms could be provided by each ligand by these functionalities.

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 CHCl3) 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 1H 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 CH2Cl2 mixture gave crystals suitable for single crystal X-ray diffraction analysis, Fig. 2, again confirming their enantiomeric nature, and the expected C2v 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(CF3SO3)3 in a 3 : 1 (ligand : Tb) ratio, in refluxing CH3CN for 12 hours. After precipitation from diethyl ether, the resulting solids were re-crystallised from MeOH, and isolated by filtration. The 1H NMR (see ESI†) of these two

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

Fig. 2 The X-ray crystal structures of the enantiomers 1 and 2.
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 L₂Tb and not the expected L₃Tb stoichiometry, with a m/z = 1591 (for L₂Tb + 2 × CF₃SO₃⁻). On both occasions, the isotopic distribution patterns also matched the calculated ones, as shown in Fig. 3 for L₂Tb (see 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 λmax 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) 5D₄ excited state, with emission bands occurring at 487, 543, 581 and 614 nm due to the deactivation of 5D₄ to 5F_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 Δλ = 5.

We next analysed the formation of L₂Tb and 2Tb in situ, by observing the changes in the ground state of 1 and 2, and in the Tb(III) emission in CH₃CN, 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 λmax = 220 nm (ε = 62170 M⁻¹ cm⁻¹) and at λmax = 281 nm (ε = 13614 M⁻¹ cm⁻¹), assigned to the π → π* transitions of the pyridine and the tryptophan moieties. Upon excitation at λmax = 281 nm, each ligand gave rise to the typical tryptophan fluorescence emission, with λmax = 423 nm. The overall changes observed in the absorption spectra of 1 are shown in Fig. 4a, upon titration with Tb(III) (as Tb(CF₃SO₃)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).

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 CD₂OD 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. 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. 3](image-url) The MALDI MS of L₂Tb, showing the observed and the calculated spectra for L₂Tb + 2 × CF₃SO₃⁻.

![Fig. 5](image-url) The speciation distribution diagram of the titration of 1 with Tb(III). Inset: the fitting of the changes in the absorption spectra.
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 $\text{I}_2\text{Ta}$ is formed, with an average binding constant of $\log \beta_{1,2} = 11.1 \pm 0.11$, and $\log \beta_{2,1} = 4.6 \pm 0.3$ for the 1:1 binding.

In a similar manner, the fitting of the data obtained for the titration of 2 with Eu(III) in CH$_3$CN (inset) demonstrated that the binding of Eu(III) induced similar changes in the absorption spectra of Eu(III), directed the formation of the 3 : 1 stoichiometry and on 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 high yield. Moreover, the formation of the $\text{I}_2\text{Ta}$ and $\text{I}_2\text{Ta}$ 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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Notes and references