

## Self-Assembly

## Exploring the Effect of Ligand Structural Isomerism in Langmuir– Blodgett Films of Chiral Luminescent Eu<sup>III</sup> Self-Assemblies

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Dedicated to Professors Andrey R. Kaul and Natalia P. Kuzmina on the occasion of their 70th and 65th birthdays, respectively

**Abstract:** Here we have investigated the influence of the antenna group position on both the formation of chiral amphiphilic  $Eu^{III}$ -based self-assemblies in CH<sub>3</sub>CN solution and, on the ability to form monolayers on the surface of quartz substrates using the Langmuir–Blodgett technique, by changing from the 1-naphthyl (2(*R*), 2(*S*)) to the 2-naphthyl (1(*R*), 1(*S*)) position. The evaluation of binding constants of the self-assemblies in CH<sub>3</sub>CN solution was achieved using conventional techniques such as UV/Visible and luminescence spectroscopies along with more specific circular dichroism (CD) spectroscopy. The binding constants obtained for **EuL**, **EuL**<sub>2</sub>

## and $EuL_3$ species in the case of 2-naphthyl derivatives were comparable to those obtained for 1-naphthyl derivatives. The analysis of the changes in the CD spectra of 1(R) and 1(S) upon addition of $Eu^{III}$ not only allowed us to evaluate the values of the binding constants but the resulting recalculated spectra may also be used as fingerprints for assignment of the chiral self-assembly species formed in solution. The obtained monolayers were predominantly formed from $EuL_3$ ( $\approx 85\%$ ) with the minor species present in $\approx 15\%$ $EuL_2$ .

## Introduction

Supramolecular chemists have synthesised a vast variety of self-assembled systems in which the formation of macromolecular constructions is based on the interactions between organic ligands with metal ions.<sup>[1,2]</sup> The interest in the use of f-metal

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ions (e.g., lanthanides, Ln) for such applications is fast growing as they possess many useful properties, such as luminescence, magnetism, high coordination requirements, and so on,<sup>[3]</sup> leading to the development of new functional materials.<sup>[3g]</sup> In the past we have developed several examples of luminescent Lnbased self-assembly systems<sup>[4]</sup> that have been based on the functionalization of 2,6-pyridinedicarboxylic acid  $(H_2 dpa)^{[4a-g]}$ and 2,6-bis(1,2,3-triazol-4-yl)pyridine (**btp**)<sup>[4h-k]</sup> motifs, which provide a terdentate coordination pocket and as such enable full saturation of the coordination environment of Ln ion through the formation of tris-complexes.<sup>[4,5]</sup> To this end, various self-assemblies (such as  $bundles^{[4a-k]}$  and  $helicates^{[4l-n]}$ ) have been formed from chiral H2dpa ligands. This includes the use of chiral naphthyl-ethylamines as well as chiral amino acids.<sup>[4]</sup> Similarly, others have taken advantage of the use of chirality in the formation of Ln<sup>III</sup>-based self-assemblies; recent examples including contributions from Bünzli et al., Piguet et al., Albrecht et al., Mazzanti et al., Muller et al. and Leigh et al.;<sup>[6]</sup> Leigh having used such ligands to form the first examples of ( $\Delta$  and  $\Lambda$ ) "molecular trefoil knots".<sup>[6i,j]</sup> Given the crucial importance of chirality in all living systems, there is a need for the development of Ln<sup>III</sup>-based self-assemblies for applications in catalysis, sensing, imaging, and so on.<sup>[7]</sup> Whereas many examples of Ln-molecules/complexes have been developed for such applications, the generation of new self-assembly materials, like mono-layers, gels, nanoparticles, using self-assembly formation with f-metals has been less exploited. In particular, the application of such architectures in medical devices would

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often require the possibility of their thin-film formation. The development of responsive Ln<sup>III</sup>-based films is starting to gain more attention amongst various research groups.<sup>[8]</sup> Recently, the development of deposition techniques to create smart surfaces and devices from luminescent coordination compounds has attracted great interest.<sup>[9]</sup> Such devices usually consist of the generation of several layers obtained using chemical deposition techniques or spin-coating. However, often the thickness of such films (on a molecular level) is tricky to control. In contrast, the use of Langmuir-Blodgett (LB)<sup>[10a]</sup> film formation advantageously allows one to form monolayers in a more controllable manner.<sup>[10b-d]</sup> This technique allows for the generation of mono- and multilayers of self-assembled materials that can possess a range of properties. For instance, by changing the monolayer(s), the refractive index of the glass can be modified, or the adhesive and/or wetting properties of the surface altered. Alternatively, magnetic, non-linear optical and sensing capabilities can be brought to the system.<sup>[11]</sup> Herein, we present the generation of amphiphilic chiral Ln tris self-assemblies using the red emitting Eu<sup>III</sup> f-metal ion and the chiral ligand derivatives of H<sub>2</sub>dpa 1(R) and 1(S), which possess a long hydrophobic hexadecyl chain and a (R)- or (S)-1-(2-naphthyl)-ethylamine antenna (Scheme 1). Focusing on the self-assembly studies of these systems in solution, we investigated their various photophysical properties, which included the evaluation of the self-assembly formation in real time using absorbance, fluorescence and Eu<sup>III</sup>-centred emission spectra; comparing these to self-assemblies based on related isomers, 2(R) and 2(S).<sup>[12]</sup> Furthermore, the changes in the circular dichroism (CD) spectra and the circularly polarised luminescence (CPL) were also investigated. CD allowed us to gain greater insight into both the self-assembly process as well as allowing us to quantify the generation of different chiral assemblies formed.<sup>[4]</sup> Moreover, morphological properties of monolayers of chiral luminescent  $Eu^{III}$  self-assemblies were evaluated using atomic force microscopy (AFM).

## **Results and Discussion**

# Synthesis of ligands 1(S) and 1(R) and their corresponding $Eu^{III}$ complexes

The synthesis of ligands 1(R) and 1(S) is detailed in full in Scheme 2 involving a four step procedure. Of these, the first three steps have been previously reported by us,<sup>[4c]</sup> which involved the initial monoprotection of 2,6-pyridinedicarboxylic acid (3) using benzyl bromide (4) and NaHCO<sub>3</sub> in DMF at 60  $^\circ$ C for 48 h. This gave 6-(benzyloxycarbonyl)picolinic acid (5) as a white solid in 31% yield; the successful formation of which was confirmed using <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>), <sup>13</sup>C NMR spectroscopy (100 MHz, CDCl<sub>3</sub>) and high resolution mass spectrometry (HRMS) (see the Supporting Information, Figures S1 and S2).<sup>[4c, 12]</sup> The introduction of the appropriate (*R* or *S*) chiral 2-(1aminoethyl)-naphthalene antenna (6(R or S)) was achieved using peptide coupling methodology using 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDCI·HCI), Hydroxybenzotriazole (HOBt) and triethylamine in THF under argon at  $0^{\circ}$ C. The reaction mixture was then allowed to reach RT and stirred for 48 h, affording 7(R) and 7(S) in 74% and 65% yields, respectively. Characteristic resonances verifying the successful synthesis of compounds 7(R) and 7(S) were found to occur at  $\delta$  = 1.73 ppm and 5.49 ppm in the <sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>) representing the aliphatic CH<sub>3</sub> and CH groups of the naphthalene chiral moiety (see the Supporting Information, Figures S3–S6). Catalytic hydrogenation using triethylsilane and Pd/C successfully removed the benzyl ester protecting groups<sup>[13]</sup> after a minimum of 30 min at RT, giving **8**(*R*) and 8(S) in 76% and 78% yields, respectively; the disappearance of



Scheme 1. Structural formulas of the chiral ligands 1(R), 1(S) and 2(R), 2(S) and their self-assemblies with Eu<sup>III</sup> forming Langmuir–Blodgett monolayers.

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Scheme 2. General synthetic route towards ligands 1(R) and 1(S).

the benzyl protons being clearly observed in the <sup>1</sup>H NMR spectrum (see the Supporting Information, Figures S7–S10).

In the final step, compounds 8(R) and 8(S) were coupled to hexydecyl amine using a peptide coupling method identical to that described above, giving both 1(R) and 1(S) in 84% yields. These were fully characterised by 1D, HSQC and HMBC NMR experiments (see the Supporting Information, Figures S11-S16). As shown in the <sup>1</sup>H NMR spectrum of **1(R)** (600 MHz, CDCl<sub>3</sub>, the Supporting Information, Figure S11), the resonances corresponding to the long alkyl chain occurred at  $\delta =$ 3.30 ppm, 3.34 ppm, 1.48 ppm, 1.28-1.19 ppm and 0.88 ppm (see the Supporting Information, Figure S13 for <sup>1</sup>H NMR spectrum of **1(S)**). Further characterisation involving <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>), HRMS and IR spectroscopy verified the formation of the desired ligands 1(R) and 1(S). Moreover, the structures of both compounds 1(R) and 1(S) were determined by X-ray crystallography, as shown in Figure 1, clearly demonstrating that these two compounds were obtained as pair of enantiomers. The use of CD spectroscopy further confirmed their enantiomeric purity (see further discussion below).

Preparation of the chiral mononuclear  $Eu^{III}$  complexes  $[Eu(1(R))_3(CF_3SO_3)_3]$  and  $[Eu(1(S))_3(CF_3SO_3)_3]$  was achieved by treating 1(R) or 1(S) with  $[Eu(CF_3SO_3)_3]$  in a 1:3 stoichiometric M/L ratio in  $CH_3CN$  under microwave irradiation for 30 min at 80 °C. Slow evaporation of the solvent afforded the desired complexes in 67% and 65% yields, respectively. Similarly,  $[Eu(CIO_4)_3]$  was used to give  $[Eu(1(R))_3(CIO_4)_3]$  and  $[Eu(1(S))_3(CIO_4)_3]$  as transparent oils, which solidified upon standing.  $[Eu(1(R))_3(CF_3SO_3)_3]$  and  $[Eu(1(S))_3(CF_3SO_3)_3]$  were characterised by <sup>1</sup>H NMR spectroscopy (see the Supporting Information, Figures S17 and S18), IR and high resolution MALDI-TOF mass spectrometry. Broadening and shifting of signals in



**Figure 1.** Ball-and-stick representation of **1(5)** (left) and **1(***R***)** (right) in two different orientations, showing one of the two molecules in the asymmetric unit. The other unit and one molecule of  $H_2O$  have been omitted for clarity.

the <sup>1</sup>H NMR spectrum (400 MHz, CD<sub>3</sub>CN) signified successful complexation of the paramagnetic Eu<sup>III</sup> ion. The IR showed a shift in the amide carbonyl group stretching frequency due to direct coordination to the Eu<sup>III</sup> centre (from 1651 cm<sup>-1</sup> to 1636 cm<sup>-1</sup> for Eu(1(*R*))<sub>3</sub> and from 1651 cm<sup>-1</sup> to 1637 cm<sup>-1</sup> for Eu(1(*S*))<sub>3</sub> (for both counterions)). Neither Eu(1(*R*))<sub>3</sub> nor Eu(1(*S*))<sub>3</sub> was detectable by MALDI-TOF mass spectra, however both their 1:1 counterparts were observed for all four complexes synthesised, whereas the 1:2 stoichiometry was only seen for

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the perchlorate complexes (see the Supporting Information, Figures S19 and S20). Unfortunately, we were unable to obtain single crystals suitable for X-ray crystal structure analysis as we expect a mixture of at least two geometrical isomers (*mer-* and *fac-*) for the 1:3 complexes.<sup>[6k]</sup> However, we anticipated that three hydrophobic hexadecyl chains were all oriented in one direction as was found by Drozdov et al. using Ln<sup>III</sup>-based complexes formed from acylpyrazolonato ligands.<sup>[14]</sup>

#### Crystal structures of 1(R) and 1(S)

As discussed above, crystal structures of both ligands were obtained. The enantiomers crystallised in the P21 space group; the asymmetric unit containing two molecules of either 1(R) or 1(S) and a single water molecule. The aromatic groups display  $\pi$ - $\pi$  interactions either face to face (between the naphthalene of residue #1 and the pyridine group of residue #2) or edge to face (between the naphthalene of residue #2 and both the pyridine of a neighbour residue #2 and the naphthalene of residue #1). The hexadecyl chains demonstrate irregular "bentlike" structures with a sharp kink in the C(6) atom, as can be clearly seen from Figure 1. The structure is layered along the c axis alternating hydrophobic layers that contain the hexadecyl chains and hydrophilic layers in which hydrogen bonds between the amide groups and water molecules predominate. Amide groups of residue #1 are hydrogen bond donors to O(3), which belongs to the amide group next to the naphthyl group in residue #2. On the other hand, there is one water molecule O(5) near residue #2 that receives hydrogen bonds from both amides and donates to O(1) and O(2) of two different molecules. No interactions were found for O(4). The absolute structure for both crystals is known from synthesis, but it is also confirmed by the Flack parameter (see the Supporting Information, Table S1).

#### Photophysical properties of ligands and complexes

The UV/Visible absorption spectra of 1(R) and 1(S) consisted of an absorption band centred at  $\lambda_{max} = 223 \text{ nm}$  ( $\epsilon = (9.35 \pm$ 0.20 × 10<sup>4</sup> L mol<sup>-1</sup> cm<sup>-1</sup>) assigned to the n  $\rightarrow \pi^*$  transition of the pyridyl unit, and a second band occurring at  $\lambda_{max} = 275 \text{ nm}$ ( $\epsilon_{275nm}$  = (1.27 ± 0.01)×10<sup>4</sup> L mol<sup>-1</sup> cm<sup>-1</sup>) representing the  $\pi \rightarrow \pi^*$ transition of the naphthalene antenna moiety in CH<sub>3</sub>CN (the Supporting Information, Figure S21). Neither of these ligands gave rise to strong fluorescence emission in CH<sub>3</sub>CN. The UV/Visible absorption spectra of [Eu(1(R))<sub>3</sub>(CF<sub>3</sub>SO<sub>3</sub>)<sub>3</sub>] and  $[Eu(1(S))_3(CF_3SO_3)_3]$  showed that the  $\pi \rightarrow \pi^*$  transitions were redshifted compared with those of the free ligands, occurring at  $\lambda_{max} = 281$  nm. Upon excitation at  $\lambda_{max} = 281$  nm, characteristic Eu<sup>III</sup>-centred long-lived luminescence was observed, as shown in the Supporting Information, Figure S22, with typical line-like emission bands occurring at 595 nm, 615 nm, 650 nm and 695 nm, respectively, assigned to deactivation of the Eu<sup>III 5</sup>D<sub>0</sub> excited state to  ${}^{7}F_{J}$  (J=1-4), indicating effective sensitisation of the <sup>5</sup>D<sub>0</sub> state by energy transfer from the naphthalene antennae.

The excited state lifetimes for both complexes were recorded in CH<sub>3</sub>OH and CD<sub>3</sub>OD ( $c = 1 \times 10^{-4}$  M) solutions. The lifetime measurements were also carried out in H<sub>2</sub>O and D<sub>2</sub>O suspensions, although the complexes were not fully soluble in aqueous media. The excited state decays in both solutions and in suspensions were best fitted to mono-exponential decay, indicating the presence of only one major luminescent species in solution (the Supporting Information, Tables S2 and S3). From these findings, the hydration state, or the number of metal-bound water molecules (the *q* value), was determined as zero for [Eu(1(*R*))<sub>3</sub>(CF<sub>3</sub>SO<sub>3</sub>)<sub>3</sub>] and [Eu(1(*S*))<sub>3</sub>(CF<sub>3</sub>SO<sub>3</sub>)<sub>3</sub>], by using Parker's Equation,<sup>[15]</sup> demonstrating that indeed the complexes were formed in the desired 1:3 stoichiometry.

Further photophysical analysis of these complexes was carried out in CH<sub>3</sub>CN solution. Their Eu<sup>III</sup> luminescence quantum yields ( $\Phi_{L}^{Eu}$ ) were determined using a method developed by Bünzli et al.,<sup>[16]</sup> using Cs<sub>3</sub>[Eu(**dpa**)<sub>3</sub>]-9H<sub>2</sub>O as a standard. The results are shown in Table 1, demonstrating that both were

<b>Table 1.</b> Overall europium-centred luminescence quantum yields and sensitisation efficiencies for $[Eu(1(R))_3(CF_3SO_3)_3]$ and $[Eu(1(S))_3(CF_3SO_3)_3]$ re- corded in $CH_3CN$ .								
Complex	$\varPhi^{\rm Eu}_{ m L} [\%]$	$\tau_{\rm obs}~{\rm [ms]}$	$ au_{\rm rad}~[{\rm ms}]$	$arPsi_{ extsf{Eu}}^{ extsf{Eu}}$ [%]	η <sub>sens</sub> [%]			
$[Eu(1(R))_3(CF_3SO_3)_3]$	$3.1\pm0.1$	1.65±0.05	$7.7\pm0.1$	21.4±0.1	$14\pm1$			
[Eu(1(S)) <sub>3</sub> (CF <sub>3</sub> SO <sub>3</sub> ) <sub>3</sub> ]	$2.6\pm0.1$	$1.61\pm0.03$	$7.5\pm0.1$	$21.4\pm0.1$	$12\pm1$			
[Eu(2(S)),(CF,SO,),]	$7.0 \pm 0.1$	$1.63 \pm 0.01$	$8.2 \pm 0.1$	$20.0 \pm 0.1$	$35\pm1$			

weakly emissive, with  $\Phi_{\rm L}^{\rm Eu}\!pprox\!2.6\!-\!3.1\,\%$ ; this being 50% less emissive than that seen for [Eu(2(S))3(CF3SO3)3] possessing the 1-naphthyl group ( $\Phi_{\rm L}^{\rm Eu}$  = 7.0  $\pm$  0.1 %, Table 1). This comparison confirms the general trend observed for the whole class of symmetrical and asymmetrical chiral compounds investigated within our research group on the basis of these two antennae, all of which show that the 1-naphthyl groups are more emissive.<sup>[4a,c,d]</sup> Further understanding of the differences in the luminescence quantum yields was attempted by calculating sensitisation quantum efficiencies ( $\eta_{sens}$ ), in which  $\eta_{sens}$  of 13% was determined for [Eu(1)<sub>3</sub>(CF<sub>3</sub>SO<sub>3</sub>)<sub>3</sub>], whereas  $\eta_{sens}$  of 35% was observed for [Eu(2(S))<sub>3</sub>(CF<sub>3</sub>SO<sub>3</sub>)<sub>3</sub>]. Similarly, the intrinsic lanthanide-centred luminescence quantum yield ( $\Phi_{Fu}^{Eu}$ ) was almost the same for both systems, being 20% for  $[Eu(2(S))_3(CF_3SO_3)_3]$ and 21% for  $[Eu(1)_3(CF_3SO_3)_3]$ . This would indicate that the difference in overall luminescence quantum yield is due to the nature of the sensitisation process for these two types of antennae and not due to a different lanthanide-localised excited state quenching by external oscillators.

# Complexation studies between 1(R) and 1(S) with $Eu^{III}$ in $CH_3CN$ solution

A series of UV/Visible absorption and luminescence photophysical titrations were also conducted in  $CH_3CN$  to investigate the self-assembly of ligands **1**(*R*) and **1**(*S*) with Eu<sup>III</sup> in situ upon addition of known equiv aliquots of  $[Eu(CF_3SO_3)_3]$ . The overall changes in the absorption and luminescence spectra were the

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**Figure 2.** (A) The changes in the absorption spectrum of 1(R) upon gradual addition of  $Eu^{III}$  ( $0 \rightarrow 4$  equiv) in CH<sub>3</sub>CN at 25 °C; (B) Binding isotherms representing the changes in the main absorbance bands and their corresponding fit; (C) Speciation distribution diagram.

same for both enantiomers. The changes observed in the UV/ Visible absorption spectrum of 1(R) and 1(S) are shown in Figure 2A, and the Supporting Information, Figure S23, indicating significant changes being observed upon self-assembly formation. The fluorescence emission intensity of ligands 1(R)and 1(S) upon excitation at 281 nm was weak and did not change significantly throughout the self-assembly process. Therefore, only the emergence of Eu<sup>III</sup>-centred emission from each solution was monitored throughout the titration since these changes were substantial enough to allow for thorough analysis (Figures 3 A, 3 B, and the Supporting Information, Figures S24 and S25).

The gradual enhancement in the Eu<sup>III</sup>-centred emission was observed upon the addition of  $0 \rightarrow 0.35$  equiv of Eu<sup>III</sup> with characteristic transitions appearing at 595 nm, 615 nm, 650 nm and 695 nm, respectively, as shown in Figure 3B,C, and the Supporting Information, Figure S25. This demonstrates that for both ligands, the 1:3 stoichiometry Eu(1)<sub>3</sub> is the dominant species formed. Upon further additions of Eu<sup>III</sup>, a sharp decrease in the Eu<sup>III</sup> emission was, however, observed, most likely due to the formation of lesser emissive 1:2 and 1:1 species (e.g., Eu(1)<sub>2</sub> and Eu(1)) at higher metal ion concentrations.

To quantify the self-assembly process in solution the above global changes (in both the UV/Visible absorption and  $Ln^{III}$ -centred emission) were fitted using non-linear regression anal-

ysis. The stepwise equilibrium equations used as a model for the formation of the various  $Eu^{III}$  complexes in solution can be expressed as follows: 1) M+L $\rightleftharpoons$ ML; 2) M+2L $\rightleftharpoons$ ML<sub>2</sub>; 3) M+ 3L $\rightleftharpoons$ ML<sub>3</sub>.

The binding constants for the self-assembly processes being reported herein as  $\log \beta_{M/L}$  values in Table 2. It has to be noted that the effect of the solvation was not taken into account when evaluating the binding constants here, although the importance of this new formalism was recently introduced and discussed for  $Ln^{III}$ -based self-assemblies.<sup>[17]</sup>

As expected, the factor analysis of the UV/Visible absorption data for both enantiomers pointed to the presence of four ab-

Table 2. Summary of binding constants calculated from both UV/Vis absorption and luminescence data.							
1( <i>R</i> )	Absorbance	Fluorescence	Phosphorescence				
$\begin{array}{l} \text{log}\beta_{1:1} \\ \text{log}\beta_{1:2} \\ \text{log}\beta_{1:3} \end{array}$	$7.3 \pm 0.2 \\ 13.9 \pm 0.4 \\ 21.2 \pm 0.4$	$7.4 \\ 15.0 \pm 0.3 \\ 22.2 \pm 0.4$	7.8 15.3±0.2 22.8±0.2				
1( <i>S</i> )	Absorbance	Fluorescence	Phosphorescence				
$\begin{array}{c} \text{log}\beta_{1:1} \\ \text{log}\beta_{1:2} \\ \text{log}\beta_{1:3} \end{array}$	$7.4 \pm 0.2 \\ 14.4 \pm 0.4 \\ 21.5 \pm 0.5$	$7.8 \\ 15.1 \pm 0.3 \\ 22.4 \pm 0.3$	7.7 15.0±0.2 22.3±0.3				



**Figure 3.** (A) The changes in the fluorescence and (B) Eu<sup>III</sup>-centred emission spectra of **1**(*R*) upon addition of Eu<sup>III</sup> ( $0 \rightarrow 4$  equiv) in CH<sub>3</sub>CN at 25 °C ( $\lambda_{ex} = 281$  nm); (C) Binding isotherms representing the changes in  ${}^{5}D_{0} \rightarrow {}^{7}F_{J}$  (J = 1, 2, 4) transitions of Eu<sup>III</sup> versus number of equiv of metal ion added to the solution.

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sorbing species in solution, namely, the ligand itself, the 1:1 (Eu(1)), the 1:2 (Eu(1)<sub>2</sub>) and the 1:3 (Eu(1)<sub>3</sub>) species. The speciation distribution diagrams obtained following fitting the analysis of the absorption titration data are shown in Figure 2C, indicating that upon addition of  $0 \rightarrow 0.33$  equiv of Eu<sup>III</sup> the predominant species for both ligands was in fact the desired 1:3 (Eu $(1)_3$ ) stoichiometry, being formed in 87% and 83% yields for  $Eu(1(R))_3$  and  $Eu(1(S))_3$ , respectively. At higher equivalents of Eu<sup>III</sup> the equilibrium was shifted towards the formation of the 1:2  $(Eu(1(R))_2 \text{ and } Eu(1(S))_2)$  species, whereas further addition of Eu<sup>III</sup> gave rise to the formation of the 1:1 (Eu(1(R)) and Eu(1(S))) species; these being the major assemblies present after the addition of 3 equiv of Eu<sup>III</sup> (the Supporting Information, Figure S26). Analysis of the fluorescence titration data, shown in Figure 3A, yielded binding constant values comparable to those obtained by monitoring absorption spectra changes, (Table 2 and the Supporting Information, Figures S27 and S28) further confirming the binding processes occurring between the chelating ligand and europium ions in the solution as discussed above.

The most significant changes observed in the above titration were those seen in the Eu<sup>III</sup>-centred emission; as the emission was "switched on" upon the formation of the Eu<sup>III</sup> complexes (Figure 3 B). A good fit was obtained (Figure 3 C, and the Supporting Information, Figures S29 and S30) for analysis of all of the  ${}^{5}D_{0} \rightarrow {}^{7}F_{I}$  transitions, with binding constants that were complementary to those observed for both the changes in the absorption and the fluorescence emission (Table 2). Moreover, the binding constants corresponded well to the values found for symmetrical systems with (R)- or (S)-1-(2-naphthyl)ethylamine antennae,<sup>[4d]</sup> although they appeared to be higher compared to those of analogous Eu<sup>III</sup> assemblies with asymmetrical "halfhelicate" ligands.<sup>[4c]</sup> Moreover, the binding constants of Eu<sup>III</sup> with 2(R) and 2(S) ligands (Scheme 1)<sup>[12a]</sup> were comparable to those found here indicating only minor influence of ligand isomerism on the self-assembly processes in CH<sub>3</sub>CN solution.

# CD and CPL spectroscopy of the ligands and $\text{Eu}^{\text{\tiny III}}$ complexes in CH\_3CN solution

The spectra of **1**(*R*) and **1**(*S*) recorded in CH<sub>3</sub>CN at  $c=1\times 10^{-5}$  M were mirror images of one another as shown in Figure 4A, confirming the enantiomeric purity of the ligands in solution. The structural differences between ligands **1**(*R*), **1**(*S*) and **2**(*R*), **2**(*S*) reflected in the shape of their CD spectra.<sup>[12a]</sup>

For 1(R), both negative and positive Cotton effects were observed, with a positive band being centred at 230 nm, whereas negative ones were located at 220 and 275 nm; with opposite Cotton effects seen for 1(S). In both cases Davydov splitting of 44 and 9 nm were observed. The enantiomeric purity of the Eu<sup>™</sup> complex was also confirmed by recording the CD spectra of the isolated Eu<sup>III</sup> complexes, the CD showing bands of equal magnitude with opposite signs for  $[Eu(1(R))_3(CF_3SO_3)_3]$  and [Eu(1(S))<sub>3</sub>(CF<sub>3</sub>SO<sub>3</sub>)<sub>3</sub>] in CH<sub>3</sub>CN (Figure 4A). Furthermore, the overlaid spectra of the ligands and the complexes in Figure 4A clearly demonstrate that dramatic changes occur in the CD spectra upon complex formation between the ligands and the Eu<sup>III</sup> ions. In the case of  $[Eu(1(R))_3(CF_3SO_3)_3]$ , the magnitude of the various signals is clearly different (all measured at the same concentration) to that seen for the ligand, and cannot be considered to be due to additive effects of the three ligands coordinated to the Eu<sup>III</sup> centre alone. Several Cotton effects were also observed, with positive CD signals detected for the bands centred at 288, 226 and 218 nm, whereas a negative one was seen for the band centred at 247 nm (with Davydov splitting of 42 and 20 nm); opposite Cotton effects were seen for [Eu(1(S))<sub>3</sub>(CF<sub>3</sub>SO<sub>3</sub>)<sub>3</sub>]. The significant difference in the structure of the CD spectra of the complexes versus that seen for ligands prompted us to investigate further the self-assembly process by using CD, in which Eu<sup>III</sup> titrations of 1(*R*) and 1(*S*) in CH<sub>3</sub>CN were carried out in an analogous manner to that discussed above.<sup>[4a,c]</sup> This will be discussed below in greater detail.

The circularly polarised luminescence spectra (CPL) of  $[Eu(1(R))_3(CF_3SO_3)_3]$  and  $[Eu(1(S))_3(CF_3SO_3)_3]$  were also recorded in CH<sub>3</sub>CN (Figure 4B). Upon excitation of the ligand, chiral



Figure 4. (A) CD spectra of the ligands 1(R), 1(S) and Eu<sup>III</sup> complexes recorded at  $c = 1 \times 10^{-5}$  M in CH<sub>3</sub>CN; (B) Corresponding CPL spectra of Eu<sup>III</sup> complexes.

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Eu<sup>III</sup>-centred emission with positive and negative bands was observed. As above, the CPL spectra demonstrated that these complexes were enantiomers; evidencing that the Eu<sup>III</sup> ion was residing in a chiral environment of opposite handedness in each case.<sup>[4,12]</sup> The spectra are structurally similar to what was observed for other chiral Eu<sup>III</sup>-based self-assemblies formed from structurally related H<sub>2</sub>dpa ligands. Dissymmetry factor values  $(g_{lum})$  were determined from the spectra in Figure 4B, with  $g_{\text{lum}}$  values of -0.14 and 0.16 being calculated for  $\Delta J = 1$ , and  $g_{lum} = 0.08$  and -0.07, for the  $\Delta J = 2$  transition of  $[Eu(1(R))_3(CF_3SO_3)_3]$  and  $[Eu(1(S))_3(CF_3SO_3)_3]$ , respectively. These values are similar to what was seen for 1-naphthyl antennabased systems.<sup>[4c, 12]</sup> A comparison of the CPL spectra in Figure 4B with CPL spectra of other Eu<sup>III</sup> dpa-based complexes allowed us to determine their absolute configuration<sup>[4c,d, 12]</sup> as  $\Lambda$ and  $\Delta$  for  $[Eu(1(R))_3(CF_3SO_3)_3]$  and  $[Eu(1(S))_3(CF_3SO_3)_3]$ , respectively.

As is evident from Figure 4A, large differences were observed for the CD of the ligands versus that of the resulting 1:3 complexes. Hence, we carried out Eu<sup>III</sup> titrations in which we probed the changes in the CD of the ligands. The overall changes in the CD spectra of 1(R) upon increasing concentrations of  $[Eu(CF_3SO_3)_3]$  (0 $\rightarrow$ 4 equiv) are shown in Figure 5. Titrations were also performed using 1(S) (see the Supporting Information, Figure S31); the overall spectral changes being mirror images of that observed for 1(R) in Figure 5A. The titrations demonstrate a gradual shift from the ligand CD spectrum to that of the complexes, with the emergence of three isoelliptic points at 205, 232 and 257 nm upon the addition of 0  $\rightarrow$ 0.50 equiv of Eu<sup>III</sup>, which disappear upon further addition of metal ion as can be seen in the Supporting Information, Figures S32 and S33. Closer analysis indicates that the overall changes are complex and that several equilibria are at play. Upon gradual addition of Eu<sup>III</sup> (0 $\rightarrow$ 0.50 equiv) to **1**(*R*) the negative band centred at 276 nm now becomes positive, reaching the plateau at 0.50 equiv of Eu<sup>III</sup>. At the same time the positive band centred at 230 nm merges with a negative band centred at 221 nm, forming a new positive band, which is now centred at 224 nm. Again, this band forms a plateau upon addition of 0.50 equiv of Eu<sup>III</sup> to the solution (Figure 5 C). These results correspond well to previously obtained CD titration data for asymmetrical chiral ligands with Eu<sup>III</sup> and therefore suggest similar structural changes upon self-assembly formation in solution.<sup>[4c]</sup> Fitting these changes, using non-linear regression analysis<sup>[18]</sup> allowed us to determine the presence of four CD-responsive species, these being assigned to L, EuL, EuL<sub>2</sub> and EuL<sub>3</sub>, as was done previously for the UV/Vis and the luminescence titrations above (see the Supporting Information, Table S4 for the values of binding constants). In addition to this, we used the nonlinear regression analysis data to obtain recalculated spectra of the three different self-assemblies EuL, EuL<sub>2</sub> and EuL<sub>3</sub>. The results of these calculations are shown in Figure 5B. Of these, the recalculated spectra of EuL<sub>3</sub> (e.g., [Eu(1(R))<sub>3</sub>(CF<sub>3</sub>SO<sub>3</sub>)<sub>3</sub>]) structurally matches that seen in Figure 4A. These calculations also show that the remaining two assemblies have very different spectra to that seen for EuL<sub>3</sub>. Hence, these CD spectra can be used as unique fingerprints for identification of the three self-assemblies in solution. This analysis adds significant value to our understanding and guantifying the self-assembly formation. It also has the potential to be used to identify structural features and geometries of such transient species in solution in real-time analysis.<sup>[4a]</sup>

#### Langmuir–Blodgett monolayers of Eu<sup>III</sup> self-assemblies

Having studied the self-assembly formation above, we next embarked on forming self-assembly monolayers of both  $[Eu(1(R))_3(CF_3SO_3)_3]$  and  $[Eu(1(S))_3(CF_3SO_3)_3]$  at the water/air interface. The results above clearly demonstrate the dynamic nature that exists in solution between self-assembles formed from lanthanides and dpa-based ligands. Consequently, it was necessary to carefully choose the appropriate solvent system for the deposition of these complexes onto the water subphase to obtain stable LB monolayers, as partial or complete dissociation of  $Eu(1(R))_3$  and  $Eu(1(S))_3$  self-assemblies has to be prevented. In our previous work, we used a 9:1 mixture of CHCl<sub>3</sub>/CH<sub>3</sub>OH for the deposition process.<sup>[12]</sup> Consequently, the same solvent system was initially employed here by preparing a  $2.5 \times 10^{-4}$  m solution of  $[Eu(1(R))_3(CF_3SO_3)_3]$  and  $[Eu(1(-1)_3)_3(CF_3SO_3)_3]$ S))<sub>3</sub>(CF<sub>3</sub>SO<sub>3</sub>)<sub>3</sub>]. However, significant dissociation occurred in this mixture over a period of 30 min. This dissociation was observed by monitoring the excited state decay of the Eu<sup>III</sup>centred emission; on all occasions the decay was best fit to a biexponential function. Consequently, CH<sub>3</sub>OH was replaced



**Figure 5.** (A) The changes in CD spectrum of  $\mathbf{1}(\mathbf{R})$  ( $c = 1 \times 10^{-5}$  M) in CH<sub>3</sub>CN upon addition of Eu<sup>III</sup> ( $0 \rightarrow 4$  equiv); (B) Recalculated spectra obtained by fitting the data using non-linear regression analysis; (C) Binding isotherms and their corresponding fits.

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with CH<sub>3</sub>CN. Here no dissociation was detected and lifetime studies in a 9:1 CHCl<sub>3</sub>/CH<sub>3</sub>CN solution were best fit to a monoexponential decay, in which the presence of an emissive species ( $\tau \approx 1.44 \pm 0.01$  ms) was assigned to the desired 1:3 stoichiometry ( $[Eu(1(R))_3(CF_3SO_3)_3]$  or  $[Eu(1(S))_3(CF_3SO_3)_3]$ ; in the concentration range from  $2.5 \times 10^{-4}$  to  $5 \times 10^{-5}$  M). Hence, LB monolayer formation was undertaken by spreading 20 µL of a CHCl<sub>3</sub>/CH<sub>3</sub>CN solution of the complexes onto the surface of a water sub-phase. The solvent was allowed to evaporate for about 20 min before the barriers of the LB trough were closed (6 mm min<sup>-1</sup>) and the surface pressure was monitored. Surface pressure/area isotherm graphs were obtained for both complexes and are shown in Figure 6A. The exact nature of the Langmuir monolayer and the slight differences observed between the two complexes are unknown, however, film collapse occurs at 29–33 mNm<sup>-1</sup> corresponding to an area occupancy of  $(120 \pm 15)$  Å<sup>2</sup> per molecule. This cross-sectional area is larger than expected for three alkyl chains and may reflect the specific orientation of the alkyl chains imparted by the dpa scaffold when coordinated to Eu<sup>III</sup>.<sup>[12,19]</sup> The high stability of the films suggest that the polar Eu<sup>III</sup> coordination spheres are closely packed and orientated towards the water sub-phase with the hexadecyl chains pointing out, perpendicular to the plane of the sub-phase.<sup>[12,14]</sup> To assess the stability of the Langmuir monolayers, the surface pressure was monitored over time (>60 min), as shown in Figure 6B, confirming film stability as the decrease in surface pressure was small and reaching a plateau. These results indicate that the monolayers of  $[Eu(1(R))_3(CF_3SO_3)_3]$  and  $[Eu(1(S))_3(CF_3SO_3)_3]$  display acceptable stability properties.

The monolayers were transferred onto the surface of quartz solid substrates for further evaluation of their spectroscopic properties. It was anticipated that this deposition occurs through hydrophilic interactions between the polar head groups of the amphiphilic complexes and the surface of the hydrophilic quartz slide (10 mm  $\times$  2 mm  $\times$  50 mm). When the

surface pressure was kept constant at  $16 \text{ mN m}^{-1}$  during the quartz slide upstroke, the barrier position change and the surface area of the quartz slide were in excellent agreement, indicating a transfer ratio very close to 1. The deposition process was repeated a number of times to ensure reproducibility. The morphology of the films was evaluated using AFM (the Supporting Information, Figures S34 and S35) and although we were unable to resolve the image of Eu<sup>III</sup> self-assemblies on a molecular level, the roughness of the LB surface was evaluated a homogenously formed layer. We also attempted the deposition of more than one layer on the solid substrate, but unfortunately, after several attempts only the delamination of the monolayer upon dipping of the quartz slide into the aqueous medium was observed.

#### Photophysical properties of Eu<sup>III</sup> self-assembly monolayers

photophysical properties of the immobilised The  $[Eu(1(R))_3(CF_3SO_3)_3]$  and  $[Eu(1(S))_3(CF_3SO_3)_3]$  monolayers were next evaluated. The UV/Visible absorption spectra of both LB films, shown in Figure 7A, displayed identical profiles to that observed for these systems in solution with two  $\lambda_{max}$  bands located at 225 nm and 275 nm. Upon excitation at  $\lambda_{ex} = 275$  nm, Eu<sup>III</sup>-centred luminescence was also exhibited by both immobilised films, with bands centred at  $\lambda = 580 \text{ nm} ({}^{5}\text{D}_{0} \rightarrow {}^{7}\text{F}_{0})$ , 590 nm ( ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ ), 614 nm ( ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ ), 649 nm ( ${}^{5}D_{0} \rightarrow {}^{7}F_{3}$ ) and 695 nm ( ${}^{5}D_{0} \rightarrow {}^{7}F_{4}$ ). The excitation spectra of the films confirm successful sensitisation of the Eu<sup>III</sup> centre through antennae effect in the solid (the Supporting Information, Figure S36A).

The excited-state decay of Eu<sup>III</sup>-centred emission was also determined for immobilised monolayers of  $[Eu(1(\textbf{R}))_3(CF_3SO_3)_3]$  and  $[Eu(1(\textbf{S}))_3(CF_3SO_3)_3]$  self-assemblies and in both cases were best fit to bi-exponential decay functions indicating the presence of possibly two luminescent species within each film. Lifetime values of  $\tau_1 = (1.1 \pm 0.1)$  ms  $(85 \pm 4\%)$  and  $\tau_2 = (0.24 \pm 1.5\%)$ 



**Figure 6.** (A) Pressure/area isotherms of the complexes  $[Eu(1(R))_3(CF_3SO_3)_3]$  and  $[Eu(1(S))_3(CF_3SO_3)_3]$  showing successful formation of Langmuir monolayers; (B) Surface pressure/time stability graphs.

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Figure 7. (A) Absorbance, Eu<sup>III</sup>-centred emission ( $\lambda_{ex} = 275$  nm) and (B) CPL spectra of [Eu(1(*R*))<sub>3</sub>(CF<sub>3</sub>SO<sub>3</sub>)<sub>3</sub>] and [Eu(1(*S*))<sub>3</sub>(CF<sub>3</sub>SO<sub>3</sub>)<sub>3</sub>] LB monolayers.

0.03) ms (15 ± 4%) for  $[Eu(1(\textbf{R}))_3(CF_3SO_3)_3]$  and  $\tau_1 = (1.29 \pm$ 0.07) ms (93  $\pm$  1 %) and  $\tau_2{=}(0.19\pm0.04)$  ms (7  $\pm$  1 %) for [Eu(1(-**S**))<sub>3</sub>(CF<sub>3</sub>SO<sub>3</sub>)<sub>3</sub>] were determined (the Supporting Information, Figure S36B and C). The longer excited state lifetime values  $(\tau_1)$  were comparable to those obtained in solution for **EuL**<sub>3</sub> assemblies. These were shown to be slightly shorter ( $\tau_1 \approx 1.5$  ms in CH<sub>3</sub>CN solution) to that seen in solution, which would suggest some degree of quenching of the luminescent excited state due to the surface or self-quenching due to the "high concentration" of the complexes within the monolayer. This confirms the presence of the fully saturated complex species within the LB monolayers. The second, shorter-lived species may be assigned to the presence of EuL<sub>2</sub>; occurring due to a partial dissociation of the complex during the LB process. As can be seen from Figure 7A, a slight difference was observed in the Eu<sup>III</sup> emission of the  ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$  and  ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$  bands of  $[Eu(1(R))_3(CF_3SO_3)_3]$  and  $[Eu(1(S))_3(CF_3SO_3)_3]$  monolayers, which might be caused by the variations between the ratios of EuL<sub>3</sub> and EuL<sub>2</sub> species within the LB films. These results differ from our previous work<sup>[12]</sup> in which Eu<sup>III</sup> complexes with the ligands containing 1-naphthyl antenna were used and EuL<sub>3</sub> monolayers were deposited on quartz surface (Scheme 1). In that case no dissociation of the complexes was observed, which can be due to the possibility of  $\pi$ - $\pi$  stacking interaction between naphthyl groups for [Eu(2(R))<sub>3</sub>(CF<sub>3</sub>SO<sub>3</sub>)<sub>3</sub>] and [Eu(2(S))<sub>3</sub>(CF<sub>3</sub>SO<sub>3</sub>)<sub>3</sub>] stabilising the structure of EuL<sub>3</sub> complex in the solid state unlike here for [Eu(1(R))<sub>3</sub>(CF<sub>3</sub>SO<sub>3</sub>)<sub>3</sub>] and [Eu(1(S))<sub>3</sub>(CF<sub>3</sub>SO<sub>3</sub>)<sub>3</sub>], which has been observed in our previous work for symmetrical Eu<sup>III</sup> complexes.<sup>[4d]</sup>

The enantiomeric purity of the monolayers was also investigated using a CD and CPL spectroscopy. Unfortunately a CD signal was not detectable from either of the LB films. However, CPL spectra from both of the monolayers displayed chiral Eu<sup>III</sup>centred luminescence with the signals corresponding to the  $\Delta J$ =1 and 2 transitions of similar amplitude but opposite sign (Figure 7B). These results strongly indicate that the complex retains the same chiral geometry within the monolayer. Unfortunately, because of the extremely low intensity of luminescence it was not possible to calculate the dissymmetry factor values from these spectra. The quantum yield of complexes used in our previous work<sup>[12]</sup> is almost 2.7 times higher than what was observed for  $[Eu(1)_3(CF_3SO_3)_3]$  here (Table 1).

### Conclusion

In this work we have completed the study of this series of chiral ligand derivatives of  $H_2$ dpa, with (*R*)- or (*S*)-1-(2-naph-thyl)-ethylamine antenna, and have investigated the effect the position of the naphthyl group has not only on the formation of amphiphilic Eu<sup>III</sup> self-assemblies in solution, but also on the deposition of their monolayers using the LB technique.

Compounds 1(R) and 1(S) were synthesised and fully characterised including determination of their crystal structures by Xray crystallography elucidating their solid state packing interactions. Complexation of ligands 1(R) and 1(S) with 0.33 equiv of Eu<sup>™</sup> resulted in isolation of luminescent solid state complexes with hydration state values of  $q \approx 0$ , confirming that the lanthanide ion was indeed located in fully saturated coordination environment, surrounded by three terdentate ligands within 1:3 complexes. The luminescence quantum yield of Eu<sup>III</sup> was in the range of 2.6-3.1% indicating less efficient energy transfer from the ligand to the metal centres in comparison to that seen for the 1-naphthyl analogues. Using both CD and CPL analysis it was confirmed that the chirality of ligands 1(R) and 1(S) was retained and transferred to the Eu<sup>III</sup> centre upon complexation and that  $[Eu(1(R))_3(CF_3SO_3)_3]$  and  $[Eu(1(S))_3(CF_3SO_3)_3]$ exist as a pair of enantiomers, displaying chiral Eu<sup>III</sup>-centred long-lived emission. Detailed CD titrations gave further insight into the structural changes of the various species generated in the self-assembly process. The most significant changes are observed upon the formation of the desired 1:3 species, in which the lanthanide ion is coordinatively saturated. The recalculated spectra obtained as a result of fitting the changes in the CD spectra allowed us to use them as fingerprints for the identification of the species as they are formed during the course of the titration, giving an insight into the various selfassembly pathways that are at play. The self-assembly formation between either 1(R) or 1(S) with  $[Eu(CF_3SO_3)_3]$  was moni-

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tored in CH<sub>3</sub>CN solution using spectroscopic techniques and illustrated that three stoichiometric species were present in solution (1:1, 1:2 and 1:3), with the 1:3 species predominantly formed upon the addition of approximately 0.33 equiv of Eu<sup>III</sup> LB monolayers of  $[Eu(1(R))_3(CF_3SO_3)_3]$  and  $[Eu(1(S))_3(CF_3SO_3)_3]$ complexes were then immobilised onto a guartz solid substrate and the photophysical properties of the luminescent films investigated. Transfer of the complexes onto a quartz solid substrate was achieved with a transfer ratio of  $\approx 1$  in both cases. The roughness of the LB surface was evaluated by AFM analysis and the films were found to be homogeneously formed. These LB films display Eu<sup>III</sup>-centred long-lived luminescence whereas CPL measurements were employed to verify that the luminescence emitted from the films was chiral, retaining the chirality measured in solution, and although luminescence dissymmetry factors were not measurable the sign of the most intense transitions was retained. We are currently developing other lanthanide luminescent LB films, based on the  $\mathbf{H_2dpa}$  and cyclen ligands^{[20]} for use in sensing of biological ions and molecules and for applications in catalysis.

## **Experimental Section**

All chemicals were purchased from commercial sources and used without further purification. Hydrochloric acid, sodium bicarbonate, sodium sulphate, magnesium sulphate, 2,6-pyridinedicarboxylic acid (H<sub>2</sub>dpa), benzyl bromide, 1-hydroxybenzotriazole hydrate (HOBt), triethylamine, triethylsilane, palladium on carbon (10 wt.%),  $[Eu(CF_3SO_3)_3] \cdot 6H_2O$  and  $[Eu(CIO_3)_3]$  (50 wt.% solution) were purchased from Sigma-Aldrich, whereas N,N-dimethylformamide, (R)-2-(1-aminoethyl)naphthalene, (S)-2-(1-aminoethyl)naphthalene, 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide (EDCI) were purchased from TCI Europe. Deuterated solvents for NMR analysis (CDCl<sub>3</sub>, [D<sub>6</sub>]DMSO) were purchased from Apollo Scientific. The <sup>1</sup>H NMR spectra were recorded at 400 MHz and the <sup>13</sup>C NMR spectra were recorded at 100 MHz using a Bruker DPX 400 instrument. NMR spectra were also recorded using a Bruker AV-600 instrument operating at 600.1 MHz for <sup>1</sup>H NMR spectroscopy and 150.9 MHz for <sup>13</sup>C NMR spectroscopy. Chemical shifts were reported in ppm using the deuterated solvent as the internal reference, J in Hz; data were processed with Bruker Topspin 2.1°. All the NMR spectra were carried out at 293 K. Mass spectrometry was carried out using HPLC grade solvents. Electrospray mass spectra were determined on a Micromass LCT spectrometer and high resolution mass spectra were determined relative to a standard of leucine enkephaline. Maldi-Q-TOF mass spectra were carried out on a MALDI-Q-TOF-Premier (Waters Corporation, Micromass MS Technologies, Manchester, UK) and high resolution mass spectrometry was performed using Glu-Fib with an internal reference peak of m/z 1570.6774. Infrared spectra were recorded on a PerkinElmer Spectrum One FT-IR spectrometer equipped with universal ATR sampling accessory. Melting points were determined using an Electrothermal IA9000 digital melting point apparatus. Complexation reactions were carried out in 2-5 mL Biotage microwave vials in a Biotage Initiator Eight EXP microwave reactor. Reactions were performed at 80 °C for 30 min in HPLC grade acetonitrile. Tapping mode images of all samples were performed using an Asylum MFP-3D AFM. RMS roughness values were obtained by analysing the topographic images.

#### Crystallographic data

Single crystals of ligand 1(R) and 1(S) were grown by slow evaporation from the mixture of isopropanol/water at ambient conditions and their solid state structures were determined at 100 K. Reflections were collected on a Bruker APEX 2 DUO CCD diffractometer using Incoatec IµS Cu<sub>Ka</sub> ( $\lambda$  = 1.54178 Å) radiation. Crystals were mounted on a MiTeGen micromount and collected at 100(2) K using an Oxford Cryosystems Cobra low temperature device. Data was collected using omega and phi scans and corrected for Lorentz and polarisation effects.<sup>[21a]</sup> The structures were solved by direct methods and refined by full-matrix least-squares procedures on F<sup>2</sup> using SHELXL-2013 software.<sup>[21b]</sup> All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were added geometrically in calculated positions and refined using a riding model. Geometric restraints had to be applied to disordered parts of the structure. Details of the data collection and refinement are given in Table S1 (the Supporting Information). CCDC 1429937 (1(S)) and 1429938 (1(R)) contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

#### **Photophysical measurements**

Unless otherwise stated, all measurements in solution were performed at 298 K in acetonitrile (spectroscopical grade, Aldrich). UV/ Visible absorption spectra were measured in 1 cm quartz cuvettes on a Varian Cary 50 spectrophotometer. Baseline correction was applied for all spectra. Emission (fluorescence, phosphorescence and excitation) spectra and lifetimes were recorded on a Varian Cary Eclipse Fluorimeter. Fluorescence measurements on solid samples were collected on Horiba Jobin Yvon Fluorolog 4 modular fluorimeter in steady state mode using front-face configuration for collecting the emitted light, phosphorescence on a Horiba Jobin Yvon Fluoromax 4 fluorimeter equipped with pulsed lamp, using a right-angle (45 $^{\circ}$ ) configuration. Absorption spectra on solid samples were recorded with a PerkinElmer Lambda 1050 UV/Vis-NIR spectrophotometer. Quartz cells with a 1 cm path length from Hellma were used for solution measurements.

#### **Phosphorescence lifetimes**

Phosphorescence lifetimes of the Eu<sup>III</sup> (<sup>5</sup>D<sub>0</sub>) excited state were measured in methanol/deuterated methanol solutions or water/deuterated water suspensions in time-resolved mode. For each lanthanide complex the lifetime values are averages of three independent measurements, which were made by monitoring the emission decay at 616 nm, which corresponds to the maximum of the Eu<sup>IIII</sup> <sup>5</sup>D<sub>0</sub> $\rightarrow$ <sup>7</sup>F<sub>2</sub> transition, enforcing a 0.1 ms delay, and were analysed using Origin Pro 8.5<sup>®</sup>. The number of water molecules directly bound to Eu<sup>III</sup> centres (*q* value) was determined according to Equation (1) developed by Parker et al.<sup>[15b]</sup>

$$(q \pm 0.5): q = A \left[ \frac{1}{\tau_{OH}} - \frac{1}{\tau_{OD}} - B \right]$$
 (1)

in which *A* is a proportionality constant specific to the given lanthanide ion: for Eu<sup>III</sup> it is 1.2 ms in water. In methanol solution, the constant is multiplied by two, given the fact that only one O–H oscillator is present in each solvent molecule.  $\tau_{OH}$  is the lifetime measured in water or methanol,  $\tau_{OD}$  in deuterated solvents; *B* is a corrective factor and corresponds to 0.25 ms<sup>-1</sup> for Eu<sup>III</sup>.

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#### Luminescence quantum yield

The luminescence quantum yield ( $\Phi_{rel}^{Eu,L}$ ) was measured by the relative method developed by Bünzli et al.<sup>[16]</sup> using Cs<sub>3</sub>[Eu(**dpa**)<sub>3</sub>]·9H<sub>2</sub>O ( $7.5 \times 10^{-5}$  M) and Cs<sub>3</sub>[Tb(**dpa**)<sub>3</sub>]·9H<sub>2</sub>O ( $6.5 \times 10^{-5}$  M) complexes in 0.1 m Tris-buffer (pH 7.45) ( $\Phi_{rel}^{Eu} = 24.0 \pm 2.5$ %,  $\Phi_{ref}^{Tb} = 22.0 \pm 2.5$ %) as standards with known quantum yields, to which the absorbance and the emission intensity of the samples are compared according to the following Equation (2):

$$\Phi_{x} = \Phi_{r} \frac{E_{x}}{E_{r}} \times \frac{A_{r}(\lambda_{r})}{A_{x}(\lambda_{x})} \times \frac{I_{r}(\lambda_{r})}{I_{x}(\lambda_{x})} \times \frac{n_{x}^{2}}{n_{r}^{2}}$$
(2)

In which *r* is the reference and *x* is the sample; *E* is the integrated luminescence intensity; *A* is the absorbance at the excitation wavelength; *I* is the intensity of the excitation light at the same wavelength; and *n* is the refracting index of the solution. The estimated error for quantum yields is  $\pm 10\%$ .

For Eu<sup>III</sup> complexes it was possible to calculate the sensitisation quantum efficiency following the procedure described by Verhoeven et al.<sup>[22]</sup> The overall luminescence quantum yield of the complex upon excitation of the antenna chromophore is determined by the sensitisation efficiency ( $\eta_{sens}$ ) and the quantum yield of the lanthanide luminescence step ( $\Phi_{ln}^{Ln}$ ):

$$\Phi_{\rm rel}^{\rm Ln,L} = \eta_{\rm sens} \Phi_{\rm Ln}^{\rm Ln} \tag{3}$$

If the radiative lifetime  $\tau_R$  is known,  $\varPhi_{Ln}^{Ln}$  can be calculated using the observed luminescence lifetime  $\tau_{obs}$ .

$$\Phi_{\rm Ln}^{\rm Ln} = \frac{\tau_{\rm obs}}{\tau_{\rm R}} \tag{4}$$

For  $Eu^{III}$  compounds, the radiative lifetime is readily determined from the emission spectrum by:

$$\frac{1}{\tau_R} = A_{MD,0} n^3 \frac{I_{tot}}{I_{MD}}$$
(5)

where  $A_{MD,0}$  is the spontaneous emission probability (constant, equal to 14.65 s<sup>-1</sup>) for the  ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$  transition, *n* is the refractive index of the solvent,  $I_{tot}$  is the integrated emission spectrum and  $I_{MD}$  is the area of  ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$  transition for the Eu<sup>III</sup> ion. It is possible to assume that both the energy and the dipole strength of the latter are constant, since the transition is only magnetic dipole allowed, hence not influenced by the chemical surroundings of the ion. Following on from these assumptions, it is possible to use the  ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$  transition as a reference for the dipole strength; unlike all the other lanthanide ions, since none of them has an only magnetic dipole-allowed transition.

#### **Circular dichroism**

Circular dichroism (CD) spectra were recorded in acetonitrile solution on a Jasco J-810–150S spectropolarimeter.

#### **Circularly polarized luminescence**

Circularly polarized luminescence (CPL) measurements were carried out on a home built instrument constructed round a Fluoromax 2. The emitted light was analysed by passing it through a photoelastic modulator and plane polarizer. The signal from the photomultiplier, after a/d conversion, was processed by a lock-in amplifier that extracts the AC (CPL) and DC (TL) signals.

These are not the final page numbers! 77

#### Spectrophotometric titrations and binding constants

The formation of the luminescent 1:1, 1:2 and 1:3 (**M**/**L**, in which  $\mathbf{M} = \mathbf{Eu}^{|||}$  and  $\mathbf{L} = \mathbf{1}(\mathbf{R})$ ,  $\mathbf{1}(\mathbf{S})$ ) species was ascertained by UV/Visible, luminescence and circular dichroism titrations of a solution of  $\mathbf{L}$  ( $1 \times 10^{-5}$  M) with [Eu(CF<sub>3</sub>SO<sub>3</sub>)<sub>3</sub>]·6H<sub>2</sub>O (0 $\rightarrow$ 4 equiv). The data were fitted using the non-linear regression analysis program, SPEC-FIT<sup>\*</sup>.<sup>[18]</sup>

#### Langmuir–Blodgett film formation and monolayers deposition

Pressure/area isotherms and time stability curves were measured at 25 °C on a KSV MiniMicro Langmuir-Blodgett trough (KSV, Finland) with a surface area between 1700 and 8700 mm<sup>2</sup>. Water was purified with Milli-Q<sup>®</sup> integral system (Millipore), and its resistivity was measured to be higher than 18 M $\Omega$  cm<sup>-1</sup>. A 9:1 mixture of  $CHCl_3/CH_3CN$  was used as spreading solvent for the complexes (c = $2.5 \times 10^{-4}$  M). Typically drops (20 µL) of the surfactant solutions were carefully deposited on the water sub-phase using a Hamilton microsyringe. After leaving the solvent to evaporate for 20 min, the barriers were compressed at 6 mm min<sup>-1</sup> and the surface pressure was monitored using a platinum Wilhelmy plate. Monolayers of the complexes were deposited on quartz slides previously washed with piranha solution and rinsed with Millipore water. The quartz slide (25×10×2 mm) was lowered and submerged into the water phase before the amphiphilic complex was spread onto the surface. The amphiphile was then organised into the LC phase (by compressing the barriers until a surface pressure of 16-18 mNm<sup>-1</sup> was obtained) and allowed to stabilise (>20 min) before emersion of the slide by means of an upward stroke (at a speed of 4 mm min<sup>-1</sup>), which resulted in monolayer transfer with transfer ratios of  $\approx$  1.

#### Syntheses

Synthesis of 6-((benzyloxy)carbonyl)pyridine-2-carboxylic acid (5): 2,6-Pyridinedicarboxylic acid (3, 1.13 g, 6.8 mmol) and NaHCO<sub>3</sub> (previously put in the oven to dry overnight, 0.601 g, 7.1 mmol) were added to N,N-dimethylformamide (70 mL) and stirred at 60 °C under argon for 30 min. Benzyl bromide (4, 0.81 mL, 6.8 mmol) in 5 mL of N,N-dimethylformamide was added dropwise to the white suspension. The reaction was left under stirring at 60°C under a CaCl<sub>2</sub> valve for 48 h. Resulting opaque yellow suspension was diluted with 150 mL of water and neutralised with 50 mL of a saturated solution of NaHCO<sub>3</sub>, then extracted with diethyl ether  $(3 \times$ 100 mL) to remove the diester side product. The aqueous layer was then acidified with conc. HCl until  $pH \approx 3$  and extracted with ethyl acetate (4×50 mL). After that, the organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> and the solvent was removed in vacuo, the resulting solid was dissolved in dichlorometane (50 mL), washed with brine (3×100 mL) and water (100 mL). The organic layer was finally dried over Na<sub>2</sub>SO<sub>4</sub> and evaporated, yielding a white powder (0.54 g, 2.1 mmol, 31% yield). M.p. 133 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta_{\rm H} =$ 8.39 (dd, J = 8 Hz, 2 H,  $CH_{py}$ ), 8.11 (t, J = 8 Hz, 1 H,  $CH_{py}$ ), 7.48 (m, J =8 Hz, 2 H, CH<sub>ph</sub>), 7.39 (m, 3 H, CH<sub>ph</sub>), 5.46 ppm (s, 2 H, CH<sub>2</sub>); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta_{c} = 163.41$ , 146.73, 146.40, 139.60, 134.95, 128.85, 128.72, 128.54, 126.77, 68.01 ppm; IR:  $\tilde{\nu}_{max} = 3065$ , 3038, 2880, 2560, 1736, 1694, 1610, 1576, 1500, 1467, 1452, 1418, 1376, 1329, 1303, 1289, 1243, 1167, 1152, 1084, 1033, 1006, 995, 957, 941, 915, 901, 856, 840, 797, 785, 754, 729, 711, 691 cm<sup>-1</sup>; HRMS (ESI<sup>-</sup>): *m*/*z* calcd for C<sub>14</sub>H<sub>10</sub>NO<sub>4</sub>: 256.0615 [*M*-H]<sup>-</sup>; found: 256.0607. Synthesis of 7(R) and 7(S): General procedure: 1-Hydroxybenzotriazole hydrate (HOBt, 1 equiv) and 6-((benzyloxy)carbonyl)pyri-

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dine-2-carboxylic acid (**5**, 1 equiv) were added to a stirred solution of (*S* or *R*)-2-(1-aminoethyl)naphthalene (**6**, 1 equiv) in 60 mL anhydrous THF. The solution was stirred for 30 min with CaCl<sub>2</sub> filled drying tube before adding the solution of 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide (EDCl, 1 equiv) and triethylamine (1 equiv) in 30 mL of anhydrous THF with a dropping funnel. The reaction mixture was stirred for 30 min at 0 °C, then allowed to reach room temperature and left stirring for 48 h. The THF was removed in vacuo, then the oily residue was redissolved in 35 mL of dichloromethane. The resulting solution was washed with 1 m HCl (3× 25 mL), a saturated solution of NaHCO<sub>3</sub> (2×30 mL), and water (2× 30 mL), dried on MgSO<sub>4</sub>, filtered, finally removing the solvent under reduced pressure.

Synthesis of benzyl (R)-6-((1-(naphthalen-2-yl)ethyl)carbamoyl)picolinate (7(R)): 6-((Benzyloxy)carbonyl)pyridine-2-carboxylic acid (5, 1.0 g,  $4.0 \times 10^{-3}$  mol) and HOBt (0.56 g,  $4.1 \times 10^{-3}$ ) were added to a stirred solution of (R)-2-(1-aminoethyl)naphthalene 6(R)  $(0.70 \text{ g}, 4.1 \times 10^{-3} \text{ mol})$  in 60 mL of anhydrous THF, and left stirring for 30 min at 0  $^{\circ}$ C with a CaCl<sub>2</sub> drying tube. Then EDCI (0.7 mL, 4×  $10^{-3}$  mol) and triethylamine (0.7 mL,  $5 \times 10^{-3}$  mol) solution in 30 mL of anhydrous THF was added dropwise and the resulting product was purified according to the general procedure, yielding 1.20 g of **7(R)** with 74% yield. M.p. 127 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta_{\rm H} =$ 8.49 (d, J=8 Hz, 1 H, NH), 8.39 (d, J=8 Hz, 1 H, PyH), 8.23 (d, J=8 Hz, 1 H, PyH), 7.99 (t, J=8 Hz, 1 H, PyH), 7.84-7.81 (m, 4 H, NaphH), 7.53 (d, J=12 Hz, 1H, PhH), 7.47-7.45 (m, 4H, PhH), 7.35-7.34 (m, 3H, NaphH), 5.52 (q, J=5Hz, 1H, CH), 5.44 (s, 2H, CH<sub>2</sub>), 1.73 ppm (d, J=8 Hz, 3 H, CH\_3);  $^{13}\text{C}$  NMR (100 MHz, CDCl\_3):  $\delta_{\text{C}}{=}$ 164.16, 162.59, 150.15, 146.50, 140.41, 138.46, 135.37, 133.33, 132.72, 128.61, 128.50, 128.43, 128.15, 127.92, 127.55, 127.25, 126.11, 125.80, 125.43, 124.62, 124.60, 67.47, 49.11, 21.95 ppm; IR:  $\tilde{\nu}_{max} =$  3397, 3062, 2927, 1733, 1681, 1603, 1589, 1504, 1453, 1440, 1424, 1382, 1310, 1283, 1271, 1263, 1230, 1183, 1166, 1152, 1122, 1084, 1034, 1022, 1002, 992, 960, 953, 929, 899, 873, 863, 842, 816, 791, 771, 749, 731, 715, 690, 663 cm<sup>-1</sup>; HRMS (ES<sup>+</sup>) *m/z* calcd for C<sub>26</sub>H<sub>22</sub>N<sub>2</sub>NaO<sub>3</sub>: 433.1523 [*M*+Na]<sup>+</sup>; found: 433.1524.

Synthesis of benzyl (S)-6-((1-(naphthalen-2-yl)ethyl)carbamoyl)picolinate (7(S)): 6-((Benzyloxy)carbonyl)pyridine-2-carboxylic acid (5, 0.79 g,  $3.1 \times 10^{-3}$  mol) and HOBt (0.46 g,  $3.4 \times 10^{-3}$ ) were added to a stirred solution of (S)-2-(1-aminoethyl)naphthalene 6(S) (0.59 g,  $3.4\!\times\!10^{-3}\,\text{mol})$  in 50 mL of anhydrous THF, and the solution was left stirring for 30 min at 0°C with a CaCl<sub>2</sub> drying tube. Then a solution of EDCI (0.5 mL,  $3 \times 10^{-3}$  mol) and triethylamine (0.5 mL,  $4 \times 10^{-3}$  mol) in 25 mL of anhydrous THF was added dropwise and the resulting product was purified according to the general procedure, yielding 0.82 g of 7(S) with 65% yield. M.p. 125°C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta_{\rm H} = 8.49$  (d, J = 8 Hz, 1 H, NH), 8.39 (d, J = 8 Hz, 1H, PyH), 8.21 (d, J=8Hz, 1H, PyH), 7.99 (t, J=8Hz, 1H, PyH), 7.84-7.80 (m, 4H, NaphH), 7.53 (d, J=8 Hz, 1H, PhH), 7.47-7.46 (m, 4H, PhH), 7.35–7.34 (m, 3H, NaphH), 5.50 (q, J=7 Hz, 1H, CH), 5.44 (s, 2H, CH<sub>2</sub>), 1.73 ppm (d, J=8 Hz, 3H, CH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta_{C} = 164.16$ , 162.58, 150.14, 146.50, 140.40, 138.46, 135.37, 133.33, 132.72, 128.60, 128.50, 128.43, 128.15, 127.92, 127.55, 127.25, 126.11, 125.79, 125.43, 124.60, 124.60, 67.47, 49.11, 21.95 ppm; IR:  $\tilde{\nu}_{max} =$  3397, 3062, 2928, 1967, 1732, 1681, 1603, 1589, 1505, 1453, 1440, 1424, 1382, 1310, 1283, 1271, 1230, 1183, 1166, 1152, 1122, 1084, 1034, 1022, 1002, 992, 960, 953, 929, 899, 873, 863, 842, 816, 791, 771, 749, 731, 715, 690, 663 cm<sup>-1</sup>; HRMS (ES<sup>+</sup>): *m/z* calcd for C<sub>26</sub>H<sub>22</sub>N<sub>2</sub>NaO<sub>3</sub>: 433.1523 [*M*+Na]<sup>+</sup>; found: *m*/ z=433.1525.

**Preparation of 8(R) and 8(S).**<sup>[13]</sup> **General procedure**: A solution of triethylsilane (10 equiv) in 15 mL of methanol using a pressure equalised dropping funnel, keeping the mixture under an inert at-

mosphere of argon was added to a stirred solution of **7**(*R*) or **7**(*S*) (1 equiv) and 10 wt% Pd/C in 35 mL of methanol. The progress of the reaction was monitored using neutral silica TLC plates (95% dichloromethane/5% methanol). After 30 min the reaction was complete, so the mixture was filtered on Celite 645 and the resulting clear solution was evaporated under reduced pressure. The oily residue was taken into a saturated solution of NaHCO<sub>3</sub>, the aqueous layer was then washed with diethyl ether to remove residues of starting material and triethylsilane. The aqueous phase was acidified with 2 m HCl until pH  $\approx$  2, which resulted in the formation of white precipitate. This product was extracted from the aqueous layer with ethyl acetate, then the solvent was dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and evaporated under reduced pressure, yielding the product as a white solid.

Synthesis of (R)-6-((1-(naphthalen-2-yl)ethyl)carbamoyl)picolinic acid (8(R)): Triethylsilane (4.5 mL,  $2.8 \times 10^{-2}$  mol, 9.6 equiv) solution in 13 mL of methanol was added dropwise to the solution of 7(R)  $(1.20 \text{ g}, 2.92 \times 10^{-3} \text{ mol}, 1 \text{ equiv})$  and 10 wt % Pd/C (0.34 g) in 35 mL of methanol. After the workup described in the general procedure, a white crystalline powder was obtained (0.71 g, 76% yield), which was then kept under vacuum for two days to remove any traces of diethyl acetate. M.p. 115 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta_{\rm H}$ : 8.37 (dd,  ${}^{3}J_{\rm H-H}$  = 6.0 Hz,  ${}^{4}J_{\rm H-H}$  = 7.5 Hz, 2 H, CH<sub>Py</sub>), 8.23 (d, J = 7.7 Hz, 1 H, NH), 7.97 (t, J=7.8 Hz, 1 H, CH<sub>Py</sub>), 7.75 (m, 4 H, CH<sub>Naph</sub>), 7.44 (m, 3 H,  $CH_{Naph}$ ), 5.46 (q, J = 6.9 Hz, 1 H, CH), 1.63 ppm (d, J =6.9 Hz, 3 H, CH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta_{c} = 164.34$ , 162.58, 149.42, 145.22, 140.00, 139.59, 133.32, 132.84, 128.70, 127.98, 127.73, 126.85, 126.81, 126.46, 126.17, 124.94, 124.87, 49.30, 21.35 ppm; IR:  $\tilde{\nu}_{max}$  = 3284, 3059, 2978, 1752, 1731, 1642, 1526, 1453, 1335, 1252, 1184, 953, 893, 847, 819, 743, 679 cm<sup>-1</sup>; HRMS (ES<sup>-</sup>): *m/z* calcd for C<sub>19</sub>H<sub>15</sub>N<sub>2</sub>O<sub>3</sub>: 319.1088 [*M*-H]<sup>-</sup>; found: 319.1090.

Synthesis of (S)-6-((1-(naphthalen-2-yl)ethyl)carbamoyl)picolinic acid (8(S)): Triethylsilane (3.5 mL,  $2.2 \times 10^{-2}$  mol, 11 equiv) solution in 10 mL of methanol was added dropwise to the solution of 7(S)  $(0.825 \text{ g}, 2.00 \times 10^{-3} \text{ mol}, 1 \text{ equiv})$  and 10 wt % Pd/C (0.16 g) in 30 mL of methanol. After the workup described in the general procedure a white crystalline powder was obtained (0.50 g, 78% yield). The product was then kept under vacuum for two days to remove any traces of diethyl acetate. M.p. 116°C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta_{\rm H} = 8.44$  (d, J = 7.64 Hz, 1 H, CH<sub>Py</sub>), 8.30 (d, J =7.36 Hz, 1 H,  $CH_{Py}$ ), 8.14 (d, J = 7.96 Hz, 1 H, NH), 8.04 (t, J = 7.80 Hz, 1 H,  $CH_{Py}$ ), 7.79 (m, 4 H,  $CH_{Naph}$ ), 7.47 (m, 3 H,  $CH_{Naph}$ ), 5.50 (q, J =7.30 Hz, 1 H, CH), 1.70 ppm (d, J=6.88 Hz, 3 H, CH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta_{c} = 164.31$ , 162.61, 149.90, 145.56, 140.31, 140.09, 133.72, 133.24, 129.13, 128.35, 128.09, 127.31, 127.23, 126.82, 126.53, 125.20, 49.69, 21.82 ppm; IR:  $\tilde{v}_{max} = 3283$ , 3059, 2978, 1752, 1642, 1526, 1453, 1335, 1253, 1183, 953, 893, 847, 819, 743, 679 cm<sup>-1</sup>; HRMS (ES<sup>-</sup>): *m/z* calcd for C<sub>19</sub>H<sub>15</sub>N<sub>2</sub>O<sub>3</sub>: 319.1088 [*M*-H]<sup>-</sup>; found: 319.1089.

**Preparation of 1**(*R*) and 1(*S*): General procedure: A stirred solution of 8(*R* or *S*) (1 equiv) and hydroxybenzotriazole hydrate (HOBt, 1 equiv) in anhydrous THF was cooled down to 0 °C before adding hexadecylamine (9, 1 equiv). The solution was stirred for a further 30 min in a dry environment with a CaCl<sub>2</sub> filled drying tube. Then a solution of 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide (EDCl, 1 equiv) and triethylamine (1 equiv) in anhydrous THF was added dropwise; the resulting white suspension was stirred for a further 30 min at 0 °C, which was then allowed to reach room temperature and left stirring for 48 h. The THF was removed under reduced pressure, after which the oily residue was dissolved in dichloromethane. The resulting solution was washed with 1  $\bowtie$  HCl (adding brine to separate the white foam formed), then with a saturated solution of NaHCO<sub>3</sub>, water and brine. The organic layer was dried

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over MgSO<sub>4</sub>, filtered, and solvent was then removed under reduced pressure. A crude pale yellow oil was obtained which was purified using normal phase silica column chromatography (eluting with 95% chloroform and 5% methanol ( $R_{\rm f}$ =0.9)).

Synthesis of benzyl (R)-N<sup>2</sup>-hexadecyl-N<sup>6</sup>-(1-(naphthalen-2-yl)ethyl) pyridine-2,6-dicarboxamide (1(R)): Compound 1(R) was synthesized by stirring a solution of 8(R) (0.690 g,  $2.16 \times 10^{-3}$  mol), HOBt (0.31 g,  $2.29 \times 10^{-3}$  mol) and hexadecylamine (9, 0.53 g,  $2.19 \times$  $10^{-3}$  mol) in 50 mL of anhydrous THF for 30 min at 0 °C with a CaCl<sub>2</sub> drying tube before adding EDCI (0.4 mL,  $2.3 \times 10^{-3}$  mol) and triethylamine (0.45 mL,  $3.23 \times 10^{-3}$  mol) dropwise in 25 mL of dry THF according to the general procedure. After a further 30 min of stirring at 0°C the solution was allowed to reach room temperature and left stirring for 48 h. After the work-up described in the general procedure, the reaction yielded 0.985 g of a light-yellow crude oil in 84% yield. The crude oil was then purified using normal phase silica column chromatography using a 95% chloroform/5% methanol solvent mixture. <sup>1</sup>H NMR (600 MHz, CDCl<sub>2</sub>):  $\delta_{\mu}$  = 8.32 (d, J=8.3 Hz, 1 H, NH), 8.30 (d, J=7.7 Hz, 1 H, PyH), 8.26 (d, J= 7.7 Hz, 1 H, PyH), 7.96 (d, J=4.6 Hz, 1 H, NH), 7.90 (t, J=7.8 Hz, 1 H, PyH), 7.75 (m, 3H, NaphH), 7.71 (m, 1H, NaphH), 7.48 (d, J=8.6 Hz, 1H, NaphH), 7.42 (m, 2H, NaphH), 5.52 (q, J=7.4 Hz, 1H, NHCH), 3.32 (m, 2H, NHCH<sub>2</sub>), 1.66 (d, J=6.9 Hz, 3H, CHCH<sub>3</sub>), 1.50 (m, 2H,  $CH_3CH_2$ ), 1.25 (m, 26 H,  $(CH_2)_{13}$ ), 0.88 ppm (t, J=7.0 Hz, 3 H,  $CH_2CH_3$ ); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>):  $\delta_C = 163.35$ , 162.85, 148.87, 148.66, 140.14, 138.75, 133.17, 132.62, 128.45, 127.69, 127.53, 126.23, 125.94, 124.95, 124.90, 124.72, 124.48, 48.68, 39.54, 31.85, 29.63, 29.61, 29.59, 29.58, 29.56, 29.54, 29.48, 29.29, 29.24, 26.96, 22.62, 21.22, 14.05 ppm; IR  $\tilde{\nu}_{\rm max}$ : 3304, 2923, 2853, 1651, 1522, 1466, 1444, 1377, 1338, 1310, 1272, 1237, 1181, 1130, 1105, 1074, 1000, 953, 891, 855, 845, 817, 746, 675 cm<sup>-1</sup>; elemental analysis calcd (%) for  $C_{35}H_{49}N_{3}O_{2}{\cdot}0.3\,H_{2}O{:}$  C 76.54, H 9.10, N 7.65; found: C 76.85, H 9.05, N 7.43; HRMS (MALDI-MS<sup>+</sup>): *m/z* calcd for C<sub>35</sub>H<sub>49</sub>N<sub>3</sub>O<sub>2</sub>Na: 566.3722 [*M*+Na]<sup>+</sup>; found: 566.3701.

Synthesis of benzyl (S)-N<sup>2</sup>-hexadecyl-N<sup>6</sup>-(1-(naphthalen-2-yl)ethyl) pyridine-2,6-dicarboxamide (1(S)): Compound 1(S) was synthesised by stirring a solution of 8(S) (0.484 g,  $1.51 \times 10^{-3}$  mol), HOBt (0.20 g,  $1.5 \times 10^{-3}$  mol) and hexadecylamine (9, 0.36 g,  $1.5 \times$  $10^{-3}\,mol)$  in 45 mL of anhydrous THF for 30 min at 0  $^\circ C$  with a CaCl<sub>2</sub> drying tube before adding EDCI (0.30 mL,  $1.7 \times 10^{-3}$  mol) and triethylamine (0.30 mL,  $2.1 \times 10^{-3} \text{ mol})$  dropwise in 20 mL of dry THF, according to the general procedure. After a further 30 min of stirring at 0 °C the solution was allowed to reach room temperature and then it was left stirring for 48 h. After the work-up described in general procedure, the reaction yielded 0.692 g of a light-yellow crude oil in 84% yield. The crude oil was then purified using normal phase silica column chromatography using 95% chloroform/5% methanol solvent mixture. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):  $\delta_{\rm H}$  = 8.36 (br m, 1 H, N*H*), 8.30 (d, *J* = 7.7 Hz, 1 H, Py*H*), 8.26 (d, J=7.7 Hz, 1 H, PyH), 8.00 (brm, 1 H, NH), 7.89 (t, J=7.7 Hz, 1 H, PyH), 7.74 (m, 3H, NaphH), 7.70 (m, 1H, NaphH), 7.47 (d, J=8.6 Hz, 1H, NaphH), 7.42 (m, 2H, NaphH), 5.52 (q, J=7.4 Hz, 1H, NHCH), 3.30 (m, 2H, NHCH<sub>2</sub>), 1.65 (d, J=6.9 Hz, 3H, CHCH<sub>3</sub>), 1.48 (m, 2H,  $CH_3CH_2$ ), 1.25 (m, 26 H,  $(CH_2)_{13}$ ), 0.88 ppm (t, J=7.0 Hz, 3 H, CH<sub>2</sub>CH<sub>3</sub>); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>):  $\delta_{C} = 163.36$ , 162.86, 148.85,  $148.65,\ 140.13,\ 138.72,\ 133.14,\ 132.59,\ 128.41,\ 127.67,\ 127.51,$ 126.21, 125.92, 124.93, 124.87, 124.72, 124.46, 48.64, 39.53, 31.84, 29.62, 29.60, 29.58, 29.57, 29.56, 29.53, 29.47, 29.28, 29.23, 26.94, 22.60, 21.21, 14.04 ppm; IR  $\tilde{v}_{max}$  = 3308, 2923, 2853, 1651, 1522, 1466, 1444, 1376, 1338, 1309, 1272, 1237, 1181, 1130, 1105, 1074, 1000, 953, 891, 854, 845, 817, 746, 670 cm<sup>-1</sup>; HRMS (MALDI-MS<sup>+</sup>): m/z calcd for C<sub>35</sub>H<sub>49</sub>N<sub>3</sub>O<sub>2</sub>Na: 566.3722 [*M*+Na]<sup>+</sup>; found: 566.3707; elemental analysis calcd (%) for  $C_{35}H_{49}N_3O_2\cdot 0.3\,H_2O\colon$  C 76.54, H 9.10, N 7.65; found: C 76.01, H 9.17, N 7.44.

**General synthesis of europium complexes:** Eu<sup>III</sup> complexes were prepared by heating at reflux ligands **1**(*R*) and **1**(**S**) with [Eu(-CF<sub>3</sub>SO<sub>3</sub>)<sub>3</sub>]·6 H<sub>2</sub>O or [Eu(ClO<sub>4</sub>)<sub>4</sub>] (50 wt.% in H<sub>2</sub>O; 0.33 equiv) in acetonitrile for 30 min at 80 °C under microwave irradiation. The solution was subsequently cooled to room temperature and complexes were precipitated out of the solution as colourless oils. *Caution: Perchlorate salts in presence of organic ligands are potentially explosive and therefore should be handled in small quantities following adequate precautions.* 

**Synthesis of [Eu(1(***R***))<sub>3</sub>(<b>CF**<sub>3</sub>**SO**<sub>3</sub>)<sub>3</sub>]: The complex was synthesised according to the general procedure using ligand 1(*R*) (0.0544 g,  $1.00 \times 10^{-4}$  mol) and [Eu(CF<sub>3</sub>SO<sub>3</sub>)<sub>3</sub>]·6H<sub>2</sub>O (0.0200 g,  $3.33 \times 10^{-5}$  mol). A sticky oil was obtained after solvent evaporation (0.0500 g, 67.3% yield). <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN):  $\delta_{H}$ =8.88, 8.75, 8.63, 8.27, 7.59, 7.21, 7.18, 7.08, 7.03, 6.98, 6.91, 6.69, 6.53, 6.50, 6.26, 6.20, 6.13, 6.04, 5.86, 5.72, 5.14, 5.08, 4.84, 4.75, 4.68, 4.56, 4.45, 4.23, 4.07, 3.97, 3.92, 3.79, 3.46, 3.13, 3.03, 2.74, 2.43, 2.29, 1.94, 1.73, 1.54, 1.46, 1.28, 0.88 ppm; IR  $\tilde{\nu}_{max}$ =3476, 3278, 3099, 2924, 1636, 1596, 1561, 1511, 1460, 1351, 1284, 1243, 1226, 1197, 1104, 1031, 1018, 921, 858, 841, 822, 753, 712, 660 cm<sup>-1</sup>; HRMS (MALDI-MS<sup>+</sup>): *m/z* calcd for C<sub>37</sub>H<sub>49</sub>N<sub>3</sub>O<sub>8</sub>F<sub>6</sub>S<sub>2</sub>Eu: 994.2078 [Eu(1(*R*))(CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub>]<sup>+</sup>; found: 994.2067 (only **1:1** M/L complex found); elemental analysis calcd (%) for C<sub>108</sub>H<sub>147</sub>EuF<sub>9</sub>N<sub>9</sub>O<sub>15</sub>S<sub>3</sub>: C 58.15, H 6.64, N 5.65; found: C 58.12, H 6.68, N 5.41.

Using the same procedure,  $[Eu(1(R))_3(ClO_4)_3]$  was synthesised with the  $ClO_4^-$  counterion using 1(R) (0.0302 g,  $5.52 \times 10^{-5}$  mol) and  $[Eu(ClO_4)_3]$  (0.0083 g,  $1.84 \times 10^{-5}$  mol). The oil obtained (0.0300 g, 78.4% yield) was analysed by HRMS. HRMS (MALDI-MS<sup>+</sup>) m/z calcd for  $C_{70}H_{98}N_6O_{12}Cl_2Eu$ : 1437.5832  $[Eu(1(R))_2(ClO_4)_2]^+$ ; found: 1437.5796 (only **1:2** M/L complex found).

**Synthesis of [Eu(1(5))<sub>3</sub>(CF<sub>3</sub>SO<sub>3</sub>)<sub>3</sub>]:** The complex was synthesized according to the general procedure using ligand **1(5)** (0.0520 g,  $9.56 \times 10^{-5}$  mol) and [Eu(CF<sub>3</sub>SO<sub>3</sub>)<sub>3</sub>]·6H<sub>2</sub>O (0.0191 g,  $3.19 \times 10^{-5}$  mol). A sticky oil was obtained after solvent evaporation (0.0465 g, 65.4% yield). <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN):  $\delta_{H}$ =8.88, 8.75, 8.63, 8.26, 7.96, 7.60, 7.29, 7.21, 7.18, 7.08, 7.03, 6.92, 6.68, 6.53, 6.50, 6.26, 6.19, 6.12, 6.03, 5.86, 5.72, 5.31, 5.12, 4.84, 4.75, 4.68, 4.55, 4.45, 4.23, 4.06, 3.97, 3.93, 3.79, 3.46, 3.14, 3.03, 2.74, 2.44, 2.24, 1.94, 1.28, 0.88, 0.67 ppm; IR  $\bar{\nu}_{max}$ =3283, 3102, 2926, 2855, 1637, 1596, 1564, 1511, 1460, 1350, 1283, 1243, 1226, 1197, 1170, 1106, 1031, 1018, 859, 842, 821, 750, 661 cm<sup>-1</sup>; elemental analysis calcd (%) for C<sub>108</sub>H<sub>147</sub>EuF<sub>9</sub>N<sub>9</sub>O<sub>15</sub>S<sub>3</sub>: C 58.15, H 6.64, N 5.65; found: C 58.42, H 6.74, N 5.74; HRMS (MALDI-MS<sup>+</sup>): *m/z* calcd for C<sub>37</sub>H<sub>49</sub>N<sub>3</sub>O<sub>8</sub>F<sub>6</sub>S<sub>2</sub>Eu: 994.2078 [Eu(**1(s**))(CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub>]<sup>+</sup>; found: 994.2093 (only **1:1** M/L complex found).

Using the same procedure,  $[Eu(1(S))_3(CIO_4)_3]$  was synthesized with the  $CIO_4^-$  counterion, using **1(S)** (0.0300 g,  $5.52 \times 10^{-5}$  mol) and  $[Eu(CIO_4)_3]$  (0.0083 g,  $1.84 \times 10^{-5}$  mol). The oil obtained (0.0288 g, 75.2% yield) was analysed by HRMS (MALDI-MS<sup>+</sup>): *m/z* calcd for  $C_{70}H_{98}N_6O_{12}CI_2Eu:1437.5832$   $[Eu(1(S))_2(CIO_4)_2]^+$ ; found: 1437.5809 (only **1:2** M/L complex found).

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## **FULL PAPER**

## Self-Assembly

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Exploring the Effect of Ligand Structural Isomerism in Langmuir– Blodgett Films of Chiral Luminescent Eu<sup>III</sup> Self-Assemblies



**Chiral monolayers**: The study of a series of chiral ligand derivatives of 2,6-pyridinedicarboxylic acid, with (*R*)or (*S*)-1-(2-naphthyl)-ethylamine antenna, investigated the influence the antenna group position has on both the formation of chiral amphiphilic Eu<sup>III</sup>based self-assemblies in CH<sub>3</sub>CN solution and, on the ability to form monolayers on the surface of quartz substrates using the Langmuir–Blodgett technique (see figure).

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