DOI: 10.1002/asia.200900515

Europium Directed Synthesis of Enantiomerically Pure Dimetallic Luminescent “Squeezed” Triple-Stranded Helicates; Solution Studies

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Dedication to Gunnlaugur Þorfinnsson on the occasion of his 82nd birthday

The incorporation of lanthanide (*f*-) ions in supramolecular systems has become a valuable strategy in the field of time resolved luminescent imaging and sensing for in vivo application, as well as in the development of targeting MRI contrast agents.[1,2] The use of various *f*-metal ions to direct the synthesis of more complexed self-assembly supramolecular systems using organic ligands has also become an active area of research.[3,4] In particular, through the pioneering work of Bünzli, Piguet, and several others, the formation of self-assembly structures possessing a single or more *f*-metal ions or the combination of both *f*- and *d*-metal ions, has been elegantly demonstrated.[5–8] In the analysis of the formation or the properties of such systems, the unique photophysical properties of the visibly emitting $\mathrm{Eu^{III}}$ and $\mathrm{Tb^{III}}$ ions, which possess line-like emission bands and relatively long lived excited states (sub μs–ms time frame), have been intensively employed.[9,10] We have recently focused our research on the development of lanthanide luminescent self-assemblies, both in solution[11,12] and on solid supports, such as on flat gold and gold nanoparticles.[13,14] We have also developed novel chiral supramolecular systems by employing *f*-metal ion directed synthesis, where we have formed mono- (*sliotar*) and di-metallic (helical) architectures.[15,16] An example of ligands employed for such *f*-directed synthesis are the enantiomeric pair **1** (*R,R*) and **2** (*S,S*) (Figure 1), which give rise to the formation of dimetallic triple stranded helicates ($\mathbf{1}_3\cdot\mathbf{Eu}_2$ and $\mathbf{2}_3\cdot\mathbf{Eu}_2$) in the presence of $\mathrm{Eu^{III}}$.[16] Our investigation showed that the 4,4′-methylenediphenyl spacer between the two coordinating pyridyl units in **1** and **2**, greatly influences the formation as well as the shape of the resulting helicates, which possessed a sizable central cavity lined by three aryl spacers. Herein, we present ligands **3** (*R,R*) and **4** (*S,S*), which are structural isomers of **1** and **2**, and the formation of enantiomerically pure dimetallic triple stranded helicates $\mathbf{3}_3\cdot\mathbf{Eu}_2$ and $\mathbf{4}_3\cdot\mathbf{Eu}_2$, the formation of which was monitored in solution using various spectroscopic techniques. We demonstrate herein that this simple structural modification results in the formation of $\mathbf{3}_3\cdot\mathbf{Eu}_2$ and $\mathbf{4}_3\cdot\mathbf{Eu}_2$, in high yield and with greater stability than seen for $\mathbf{1}_3\cdot\mathbf{Eu}_2$ and $\mathbf{2}_3\cdot\mathbf{Eu}_2$. This we believe arises from the fact that the central cavity of $\mathbf{3}_3\cdot\mathbf{Eu}_2$ and $\mathbf{4}_3\cdot\mathbf{Eu}_2$ is more *“squeezed”* (confirmed using MM2 molecular modelling), enabling tighter binding of the two $\mathrm{Eu^{III}}$ ions.

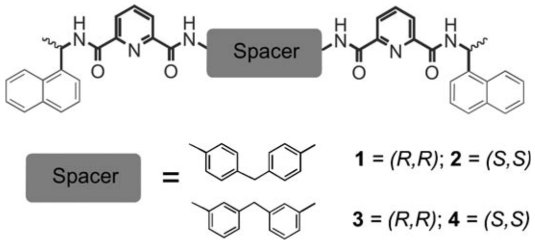

Figure 1. Schematic representation of ligand **1** and **2**, and the structural isomers **3** and **4** used in the current solution study.

The ligands **3** and **4** were isolated in high yields in a three step synthesis from the mono-protected pyridine-2,6-dicarboxylic acid **5**, Scheme 1. The intermediates **6** and **7** were obtained in ca. 80% yields using a standard peptide coupling methodology, using the *R* or *S* isomers of 1-(1-naphthyl)-ethylamine, followed by deprotection.[16] The final peptide coupling reaction, using EDCI·HCl and 3,3′-diaminodiphenylmethane gave **3** and **4** in ca. 80% yields. The ^{1}H NMR (400 MHz, CD$_3$OD) analysis of **3** (Figure S1 in the

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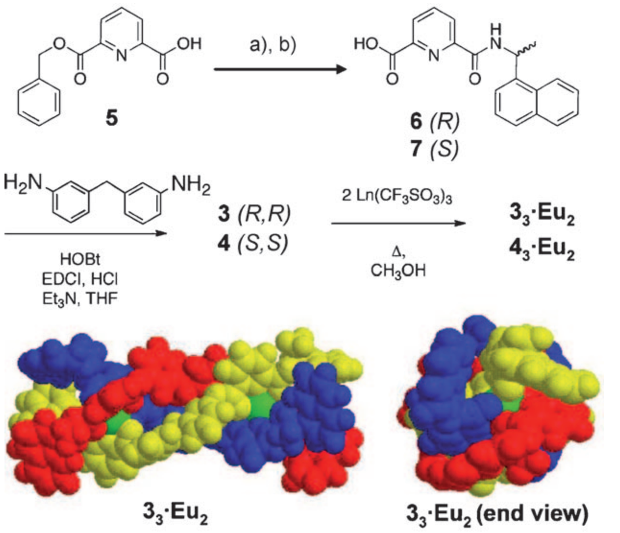
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/asia.200900515.



Scheme 1. a) (*R*)- or (*S*)-1-(1-Naphthyl)-ethylamine, HOBt, EDCI, Et_3N, and DMAP in THF 0 °C→RT, 24 h. b) H_2/Pd, CH_3OH, 12 h. Also shown is the structure obtained by molecular modelling of $\mathbf{3_3{\cdot}Eu_2}$ (site and top view) in the MM2 force field, showing how the three ligands (**3**) wrap around the two Eu^{III} ions in a helical fashion and the occurrence of the 'squeezed' cavity.

Supporting Information) demonstrated the presence of C_2 symmetry; while the CD spectra of **3** and **4**, Figure 1 a, confirmed that each of the ligands retained the chirality of the amine employed. The complexes $\mathbf{3_3{\cdot}Eu_2}$ and $\mathbf{4_3{\cdot}Eu_2}$ were synthesized by refluxing a 3:2 ratio of **3** or **4** with $Eu(CF_3SO_3)_3$ in MeOH, followed by precipitation from diethyl ether, giving $\mathbf{3_3{\cdot}Eu_2}$ and $\mathbf{4_3{\cdot}Eu_2}$ in 63 % and 75 % yields, respectively. The characteristic broadening and shifts in the ^1H NMR of **3** and **4**, caused by the binding to the paramagnetic Eu^{III} ion was observed in the ^1H NMR spectrum demonstrating the formation of the desired helicates. As an example, the resonance characteristic of the methylene linker protons (see $\mathbf{4_3{\cdot}Eu_2}$ in MeOD in Figure S1a in the Supporting Information) appeared as a singlet at 4.13 ppm, signifying the formation of a single helical (*rac*) isomer.[16,17] Using **3**, we carried out a ^1H NMR titration using Lu^{III} (Figure S2 in the Supporting Information), which showed that significant changes occurred in the ^1H NMR spectra upon formation of the helicate, that is, from 0→0.6 equiv of Lu^{III}. Furthermore, changes also occurred between the addition of 0.6→1.0 equiv of Lu^{III}, which would suggest the formation of a second species at higher Lu^{III} concentrations, occurred. By comparing the CD spectra of $\mathbf{3_3{\cdot}Eu_2}$ and $\mathbf{4_3{\cdot}Eu_2}$, which were of equable and of opposite signs, to that of **3** and **4**, it was clear that while the short wavelength transitions were similar in appearance for all four compounds, then the long wavelength transitions of $\mathbf{3_3{\cdot}Eu_2}$ and $\mathbf{4_3{\cdot}Eu_2}$, assigned to the naphthalene antenna, were greatly reduced in intensity to that seen for **3** and **4**, signifying substantial conformational changes in these ligands upon formation of $\mathbf{3_3{\cdot}Eu_2}$ and $\mathbf{4_3{\cdot}Eu_2}$. Such dramatic changes were not observed previously for $\mathbf{1_3{\cdot}Eu_2}$ nor $\mathbf{2_3{\cdot}Eu_2}$; clearly demonstrating the influence the diaryl spacer has on the resulting supramolecular structures.

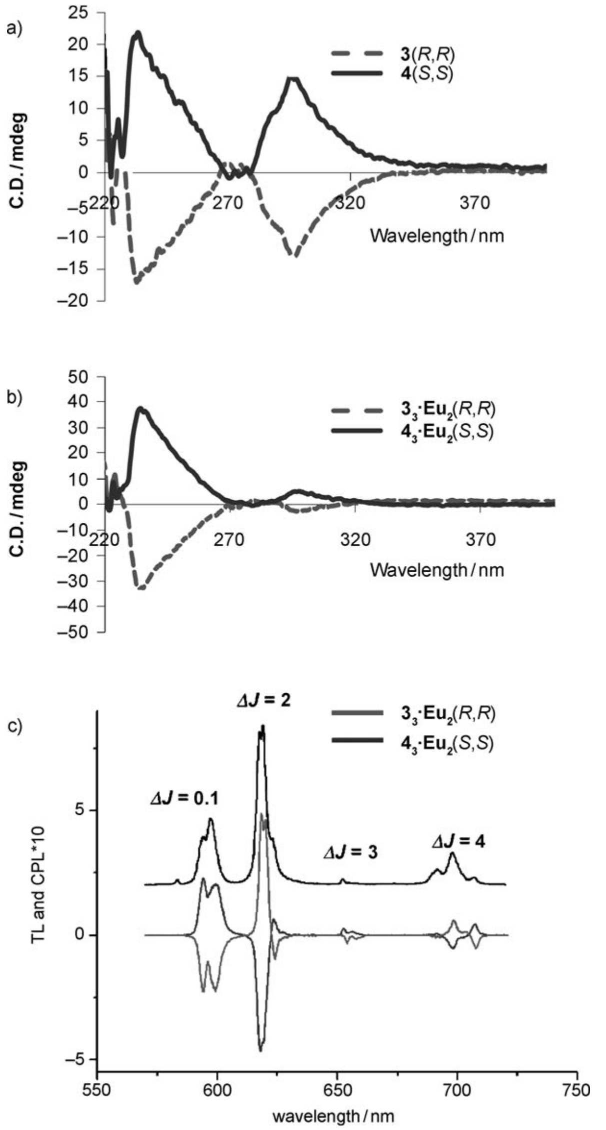


Figure 2. a) The CD spectra of **3** and **4** in MeOH. b) The corresponding CD spectra of $\mathbf{3_3{\cdot}Eu_2}$ and $\mathbf{4_3{\cdot}Eu_2}$ in MeOH. c) The total Eu^{III} emission, shown in black, arising from the deactivation of the Eu^{III} $^5D_0$ excited state to the ^7F_J ($J=0, 1, 2, 3, 4$) ground state of $\mathbf{3_3{\cdot}Eu_2}$. The corresponding circularly polarised emission (CPL) is shown "up" and "down" for $\mathbf{3_3{\cdot}Eu_2}$ and $\mathbf{4_3{\cdot}Eu_2}$, respectively.

The photophysical properties of $\mathbf{3_3{\cdot}Eu_2}$ and $\mathbf{4_3{\cdot}Eu_2}$ were performed in CH_3CN, H_2O, and D_2O under ambient conditions. Upon excitation of the naphthalene antennae, characteristic Eu^{III} metal centered emission, Figure 2 c, occurring at 580, 595, 616, 655, and 701 nm was observed; demonstrating the successful sensitization of the Eu^{III} $^5D_0$ excited state. This was further confirmed by recording the excitation spectra of these helicates, which closely matched their UV/Vis absorption spectrum (Figure S3 in the Supporting Information). Moreover, the presence of the of $\Delta J=0$ band in Figure 2 c also suggests that the symmetry at each of the Eu^{III}

centers (the local symmetry) is C_3, while the symmetry of the dimetallic helicates as the overall symmetry for the self-assembly would be expected to be D_3. The Eu^{III} emission was also found to be long-lived, being 3.0 and 3.4 ms for $\mathbf{3_3{\cdot}Eu_2}$ and $\mathbf{4_3{\cdot}Eu_2}$, respectively, when recorded in D_2O (see Table S1 and Figure S4 in the Supporting Information), where the excited state decays were best fitted to a mono-exponential decay. The excited state decays in H_2O (bi-exponential) and D_2O were also used to determine the hydration states (q) of $\mathbf{1_3{\cdot}Eu_2}$ and $\mathbf{2_3{\cdot}Eu_2}$; which was determined as $q \approx 0$ (See Table S1 in the Supporting Information) for both, demonstrating that each of the Eu^{III} ions were coordinatively saturated within the helical structure through coordination to the pyridyl nitrogens and the two amides of each ligand, giving a total of nine coordination environments for each ion center. The quantum yield for the Eu^{III} emission was also recorded in water, being 0.006 and 0.007 for $\mathbf{3_3{\cdot}Eu_2}$ and $\mathbf{4_3{\cdot}Eu_2}$, respectively, which is somewhat smaller than we have observed for analogous chiral mono-nuclear Eu^{III} *sliotar* complexes,[15] and that of chiral lanthanide complexes developed by Parker co-workers, using the same chiral antenna.[18] Also shown in Figure 2c are the circular polarized luminescence (CPL)[19] spectra of $\mathbf{3_3{\cdot}Eu_2}$ and $\mathbf{4_3{\cdot}Eu_2}$. The CPL demonstrates that the Eu^{III} emission is chiral for both complexes; indicating that the Eu^{III} ions are sitting within a chiral environment, which is induced by the chirality of ligand **3** and **4**, respectively. These results, in addition to the CD and the ^{1}H NMR results discussed above, suggest the formation of $\mathbf{3_3{\cdot}Eu_2}$ and $\mathbf{4_3{\cdot}Eu_2}$ as a pair of enantiomers. Comparison with the CPL of the very similar mono nuclear *sliotar* complexes,[15] whose absolute configuration has been determined by X-ray crystallography, enables us to predict the absolute configurations of $\mathbf{3_3{\cdot}Eu_2}$ and $\mathbf{4_3{\cdot}Eu_2}$ to be Λ,Λ and Δ,Δ, respectively. From the CPL spectra in Figure 1c, the dissymmetry factor for $\mathbf{3_3{\cdot}Eu_2}$ ($g = 2\Delta I/I$) was determined as -0.207 and 0.165 for the $\Delta J = 1$ (at 600 nm) and 2 (at 619 nm) transitions, respectively. This relatively large dissymmetry factor[19] demonstrates that $\mathbf{3_3{\cdot}Eu_2}$ is formed enantomerically pure and is homochiral in solution.

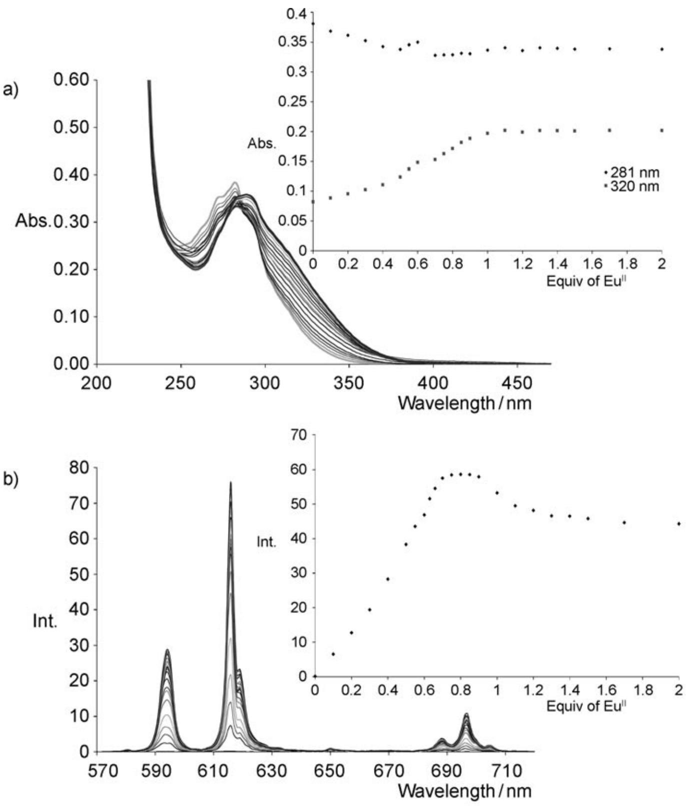


Figure 3. a) The changes in the absorption spectra of **4** upon formation of $\mathbf{4_3{\cdot}Eu_2}$.Inset The changes at 281 and 320 nm versus equiv of Eu^{III}. b) The overall changes in the Eu^{III} emission upon formation of $\mathbf{4_3{\cdot}Eu_2}$. Inset: The changes in the $\Delta J = 2$ transition versus equiv of Eu^{III}.

The formation of $\mathbf{3_3{\cdot}Eu_2}$ and $\mathbf{4_3{\cdot}Eu_2}$ was also investigated in situ in CH_3CN solution by monitoring the changes in the absorption and the fluorescence emission spectra of **3** and **4** (1×10^{-5} M) upon titration with Eu^{III} (as triflate salt) and by observing the concomitant evolution of the Eu^{III} emission. The overall results in the absorption spectra for the formation of $\mathbf{4_3{\cdot}Eu_2}$ is shown in Figure 3a, and demonstrates that a significant change occurred in the absorption spectra of **4** upon coordination to the Eu^{III} ions. These changes occur up to ca. ~0.7 equivalents of Eu^{III}, where the transition centered at 281 nm had both hypochromically and hypsochromically shifts, while only a hyperchromic effect was observed for the 320 nm band. This demonstrated the formation of a supramolecular species with a stoichiometry of 3:2 (**4**/Eu^{III}). However, some further changes were also observed upon further addition of Eu^{III}, up to ca. 1 equivalent, which is indicative of the displacement of the above 3:2 equilibrium towards the formation of the species consisting of a 2:2 stoichiometry, for example, $\mathbf{3_2{\cdot}Eu_2}$. The changes in the fluorescence emission spectra were less pronounced (Figure S5 in the Supporting Information), but coincided with that observed in the absorption spectra. Here, only minor changes were observed in the high energy transitions, centered around 350 nm, whereas a broad emission, centered at ca. 450 nm, was slightly quenched. Analysis of these changes, again showed that they occurred dominantly within the addition of ~0.7 equivalents of Eu^{III}, and that thereafter, between one and two equivalents, the fluorescence emission was quenched. The appearance of the Eu^{III} emission at long wavelength was also observed in the fluorescence emission spectra (Figure S5 in the Supporting Information), and analysis of these changes again showed that Eu^{III} emission was ‘switched on’ in parallel with the quenching observed in the fluorescence emission. We thus next analyzed the changes in the Eu^{III} emission (using time-delay mode). The overall changes observed in the Eu^{III} emission are shown in Figure 3b, and clearly demonstrate that the emission arising from all the ΔJ transitions were ‘switched on’ upon addition of Eu^{III}. Analysis of these transitions (e.g., $\Delta J = 1$ and 2) showed that the largest changes are seen up to the addition of ~0.7 equivalents of Eu^{II}, which then plateau up to 1 equivalent of Eu^{III}, after which the addition of Eu^{III} results in minor luminescence quenching (see inset in Figure 3b and Figure S6 in the Supporting Information for **3**). Again, these results indicate that initially the desired 3:2 helicate was formed, followed by the formation of another system consisting of the 2:2 stoichiometry. This was also confirmed by carrying out Job's plot analysis (method of continuous variations) in CH_3CN (see Figure S7 in the Supporting Information for $\mathbf{4_3{\cdot}Eu_2}$). However, to gain a better understanding of the formation of these supramolecular species in solution, the changes in the absorption and the Eu$^{\mathrm{III}}$ emission were analyzed using the non-linear regression analysis program SPECFIT. The fit and the speciation distribution diagram obtained for the changes in the absorption spectrum of **4** upon titration with Eu$^{\mathrm{III}}$, is shown in Figure 4 (See Figure S8 in the Supporting Information for the analysis of the Eu$^{\mathrm{III}}$ emission), and demonstrates a good fit to the experimental data. From this analysis, the predominant formation of $\mathbf{4_3{\cdot}Eu_2}$ helicate was confirmed after the addition of ~0.7 equivalents of Eu$^{\mathrm{III}}$, being formed in ca. 70 % yield, with a high binding constant of $\log \beta_{3:2} = 26.7 \pm 0.6$. However, upon further addition of Eu$^{\mathrm{III}}$, the displacement of this equilibrium towards a new species, consisting of the 2:2 stoichiometry, takes place with $\log \beta_{2:2} = 20.0 \pm 0.5$, becoming the dominant species after the addition of one equivalent of the metal ion. Hence, it is possible that in the ^{1}H NMR studies shown above, this structural isomer is also present to some extent. Similar results were also observed for **3** which formed the $\mathbf{3_3{\cdot}Eu_2}$ helicate at low concentration of Eu$^{\mathrm{III}}$ and the $\mathbf{3_2{\cdot}Eu_2}$ structure at higher Eu$^{\mathrm{III}}$ concentrations. The high binding constants determined for either $\mathbf{3_3{\cdot}Eu_2}$ or $\mathbf{4_3{\cdot}Eu_2}$, clearly demonstrate the significant role that the diaryl-spacer plays in the self-assembly process. While we have been unable to obtain suitable crystals for crystallographic analysis of either $\mathbf{3_3{\cdot}Eu_2}$ or $\mathbf{4_3{\cdot}Eu_2}$, we have been able to elucidate their possible helical structure by using MM2 force field based molecular modelling experiments. The calculated energy minimized structure of $\mathbf{3_3{\cdot}Eu_2}$ is shown in Scheme 1, and demonstrates that a 'tight fit' is obtained for the 'helical' wrapping of the three ligands around the two Eu$^{\mathrm{III}}$ ions (shown in green), giving the cylindrical D_3 geometry of the overall topology. Moreover, the central diaryl spacers are shown to be oriented towards the exterior of the helix. The consequence of this, is the formation of a more 'squeezed' central area, where the cavity, previously seen in our analysis of $\mathbf{1_3{\cdot}Eu_2}$ and $\mathbf{2_3{\cdot}Eu_2}$, is removed.[16] This structure also presents more favourable π–π bonding interactions between the antennae and the pyridyl units exists for both $\mathbf{3_3{\cdot}Eu_2}$ and $\mathbf{4_3{\cdot}Eu_2}$, which is similar to that observed for their mono-metallic analogues.[15] In summary, we have developed the novel chiral ligands **3** and **4**, and by using *f*-directed synthesis, formed two enantiomerically pure dimetallic triple stranded helicates $\mathbf{3_3{\cdot}Eu_2}$ and $\mathbf{4_3{\cdot}Eu_2}$. The Eu$^{\mathrm{III}}$ emission of these new self-assemblies was found to be both chiral (using CPL) and long-lived within the visible region, where high binding constants were determined for both $\mathbf{3_3{\cdot}Eu_2}$ and $\mathbf{4_3{\cdot}Eu_2}$ in CH_3CN. We are currently exploring the use of *f*-metal ion directed synthesis of other supramolecular architectures.

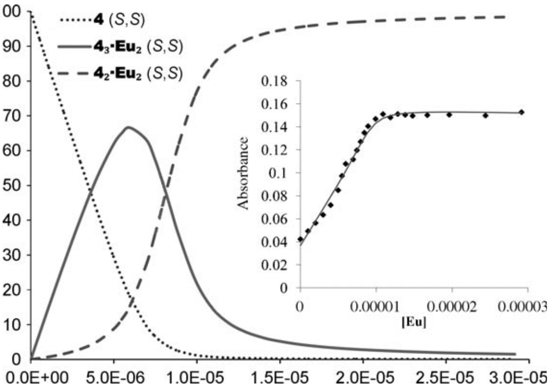


Figure 4. The speciation distribution diagram as a total ligand distribution, obtained after the fitting, using SPECFIT, of the changes in the absorption spectra of **4** (shown as **L** in the inset), demonstrating the formation of the desired helicate $\mathbf{4_3{\cdot}Eu_2}$ and the formation of the 2:2 species ($\mathbf{4_2{\cdot}Eu_2}$) at higher concentraion of Eu$^{\mathrm{III}}$.

Experimental Section

***N,N′*-[Methylenebis(phen-1,3-ylene)]bis(6-(*S*)-1-naphtalen-1-yl-ethylcarbamoyl)-pyridine-2-carboxyamide) (3)**. To a solution of 3,3′-methylene-(diphenylamine) (100 mg, 0.31 mmol) in THF (12 mL) was added HOBt (44.3 mg, 0.33 mmol). The solution was cooled down to 0 °C and stirred for 15 min under inert atmosphere. EDCI (62.8 mg, 0.33 mmol), DMAP (22.1 mg, 0.16 mmol), and triethylamine (33.2 mg, 0.33 mmol) were added portionwise. After 30 min, the resulting suspension was allowed to warm up slowly to room temprature and was reacted overnight under argon. The solid residue was filtered off and solvent removed under reduced pressure. The resulting crude oil was dissolved in CH_2Cl_2 and washed with HCl (1 M), a saturated solution of $NaHCO_3$, and finally with water. The organic layer was dried over $MgSO_4$ and solvent removed. Compound **3** was collected as an off-white solid in 63.2 % yield (79.2 mg, 0.098 mmol). M.p.: Decomposed > 152 °C.; IR (neat): $\tilde{\nu}_{max} = 3292$, 3040, 2977, 2934, 1654, 1589, 1521, 1488, 1445, 1316, 1229, 1167, 1119, 1074, 908, 866, 799, 739, 677 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta_H = 9.63$ (2 H, s, 2NH), 8.74 (2 H, d, $J = 8.52$ Hz, 2NH), 8.35 (2 H, d, $J = 7.5$ Hz, Pyr-H), 8.18 (2 H, d, $J = 7.52$z, Pyr-H), 8.03 (2 H, d, $J = 8.5$ Hz, Pyr-H), 7.92 (2 H, t, $J = 7.5$ Hz, Naph-H), 7.72 (2 H, d, $J = 7.7$ Hz, Naph-H), 7.58 (2 H, d, $J = 8.5$ Hz, Naph-H), 7.46–7.38 (4 H, m, Naph-H), 7.35 (2 H, d, $J = 7.5$ Hz, Naph-H), 7.13 (2 H, t, $J = 7.5$ Hz, Phen-H), 7.08 (2 H, s, Phen-H), 6.99–6.91 (4 H, m, 2 × Naph-H+2 Phen-H), 6.72 (2 H, d, $J = 7.0$ Hz, Phen-H), 5.97 (2 H, m, CH), 3.39 (2 H, t, $J = 7.0$, CH_2), 1.57 ppm (6 H, d, $J = 7.0$ Hz, Me); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta_c = 162.2$, 161.5, 148.6, 148.1, 140.79, 138.2, 137.6, 136.3, 133.2, 130.5, 128.3, 128.1, 127.5, 126.0, 125.3, 125.1, 124.5, 124.4, 122.8, 122.4, 119.2, 44.7, 27.3, 20.1 ppm; MS (EI): *m*/*z* calcd for $C_{51}H_{42}N_6O_4$+Na: 825.3165; found: 825.3137; elemental analysis: calcd (%) for $C_{51}H_{42}N_6O_4{\cdot}1.33\,CH_3OH$: C 74.33, H 5.64, N 9.94; found: C 74.45, H 5.38, N 9.89.

***N,N′*-[Methylenebis(phen-1,3-ylene)]bis(6-(*R*)-1-naphtalen-1-yl-ethylcarbamoyl)-pyridine-2-carboxyamide) (4):** Ligand **4** was isolated, following the procedure exposed for its enantiomer **3**, as an off-white solid in 59.7 % yield (74.7 mg, 0.093 mmol). M.p.: Decomposed > 149 °C; IR (neat): $\tilde{\nu}_{max} = 3289$; 3066; 2992; 2955; 1630; 1588; 1557; 1489; 1447; 1376; 1238; 1164; 1082; 1044; 800; 777; 753; 730; 679 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta_H = 9.52$ (2 H, s, 2NH), 8.54 (2 H, d, $J = 8.5$ Hz, 2NH), 8.38 (2 H, d, $J = 7.5$ Hz, Pyr-H), 8.25 (2 H, d, $J = 7.5$ Hz, Pyr-H), 8.09 (2 H, d, $J = 8.5$ Hz, Pyr-H), 7.97 (2 H, t, $J = 7.5$ Hz, Naph-H), 7.77 (2 H, d, $J = 7.71$ Hz, Naph-H), 7.65 (2 H, d, $J = 8.5$ Hz, Naph-H), 7.54–7.43 (6 H, m, 4 × Naph-H+2Phen-H), 7.22 (2 H, d, $J = 7.5$ Hz, Naph-H), 7.08 (2 H, s, Phen-H), 7.05–7.00 (4H, m, 2×Naph-H+2×Phen-H), 6.80 (2H, d, $J=7.0$ Hz, Phen-H), 6.00 (2H, m, CH), 3.56 (2H, t, $J=7.04$, CH_2), 1.87 ppm (6H, d, $J=7.04$ Hz, Me); ^{13}C NMR ($CDCl_3$; 100 MHz): $\delta_c=162.3$, 161.5, 148.5, 148.1, 140.8, 138.3, 137.7, 136.3, 133.3, 130.6, 128.3, 128.1, 127.6, 126.0, 125.3, 125.1, 124.6, 124.6, 122.8, 122.4, 119.1, 44.8, 29.3, 20.1 ppm; MS (EI): m/z calcd for $C_{51}H_{42}N_6O_4$+Na: 825.3165; found: 825.3128; elemental analysis: calcd (%) for $C_{51}H_{42}N_6O_4\cdot 1.5\,CH_3OH$: C 74.10, H 5.69, N 9.88; found: C 74.04, H 5.24, N 9.83.

Complex $\mathbf{3_3{\cdot}Eu_2}$: Ligand **3** (15 mg; 1.8×10^{-6} mol) and $Eu(CF_3SO_3)_3$ (7.4 mg; 1.2×10^{-5} mol) were refluxed in MeOH (5 mL) for 24 h. Solvents were reduced under reduced pressure. The resulting concentrated solution is poured in diethylether and the complexe $\mathbf{3_3{\cdot}Eu_2}$ was collected in 75% yield (14.6 mg; 4.0×10^{-6} mol) after decantation. M.p.: Decomposed > 280 °C; IR (neat): $\tilde{\nu}_{max}=3280$, 2994, 2923, 2882, 1654, 1589, 1522, 1487, 1444, 1366, 1259, 1074, 1021, 799, 776 cm^{-1}; ^{1}H NMR (MeOD; 600 MHz): $\delta_H=8.81$ (3×2H, brs, naph-H), 8.65 (3×4H, brs, Ar-H), 8.25 (3×2H, brs, CH), 7.84 (3×2H, brs, Naph-H), 7.50 (3×4H, brs, Ar-H), 7.37 (3×2H, brs, Naph-H), 7.00 (3×2H, brs, Naph-H), 6.76 (3×2H, brs, NH), 6.55 (3×2H, brs, Naph-H), 6.32 (3×2H, brs, Pyr-H), 6.19 (3×2H, brs, Naph-H), 5.52 (3×2H, brs, Pyr-H), 4.05 (3×2H, brs, Pyr-H), 3.94 (3×2H, brs, CH_2), 1.81 ppm (3×2H, brs, CH_3).

Complex $\mathbf{4_3{\cdot}Eu_2}$: Complex $\mathbf{4_3{\cdot}Eu_2}$ was formed and collected in 49% (19.6 mg; 5.4×10^{-3} mmol) yields following the same procedure as described for $\mathbf{3_3{\cdot}Eu_2}$ (with 20 mg; 2.5×10^{-5} mol of **4** and 9.9 mg; 1.66×10^{-5} mol of $Eu(CF_3SO_3)_3$). M.p.: Decomposed > 278 °C; IR (neat): $\tilde{\nu}_{max}=3290$, 2974, 2931, 2882, 1631, 1589, 1559, 1485, 1450, 1350, 1259, 1166, 1029, 800, 779 cm^{-1}; ^{1}H NMR (MeOD; 600 MHz): $\delta_H=8.85$ (3×2H, brs, naph-H), 8.63 (3×4H, brs, Ar-H), 8.27 (3×2H, brs, CH), 7.83 (3×2H, brs, Naph-H), 7.49 (3×4H, brs, Ar-H), 7.40 (3×2H, brs, Naph-H), 6.98 (3×2H, brs, Naph-H), 6.80 (3×2H, brs, NH), 6.54 (3×2H, brs, Naph-H), 6.30 (3×2H, brs, Pyr-H), 6.23 (3×2H, brs, Naph-H), 5.48 (3×2H, brs, Pyr-H), 4.03 (3×2H, brs, Pyr-H), 3.89 (3×2H, brs, CH_2), 1.82 ppm (3×2H, brs, CH_3).

Acknowledgements

We would like to thank Dr. Floriana Stomeo for helping with the initial synthesis of ligand **4** and Dr. Colin P. McCoy (Queen's University of Belfast, School of Pharmacy) for his collaboration. We thank Trinity College Dublin for Postgraduate Award to CL, Science Foundation Ireland (SFI) for RFP funding (Research Frontier Programme 2006, 2008 and 2009), CSCB, and Jennifer Molloy for helping out with CD measurements. Professor Gunnlaugsson would like to thank University of Canterbury, Christchurch, New Zealand for the awarding of an Erskine Fellowship.

Keywords: chirality · helical structures · lanthanides · luminescence · self-assembly

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Received: October 1, 2009
Revised: December 21, 2009