Metal directed synthesis of enatiomerially pure dimetallic lanthanide luminescent triple-stranded helicates

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1. General Experimental Section

All NMR spectra were recorded at 400 MHz for ^{1}H-NMR and 100 MHz for ^{13}C-NMR. Electrospray mass spectra were recorded on a Mass Lynx NT V 3.4 on a Waters 600 controller connected to a 996 photodiode array detector with HPLC-grade methanol, or acetonitrile as carrier solvents. Accurate molecular weights were determined by a peak-matching method, using leucine enkephaline (H-Tyr-Gly-Gly-Phe-Leu-OH) as the standard internal reference (*m/z* = 556.2771); all accurate mass were calculated to ≤ 5 ppm.

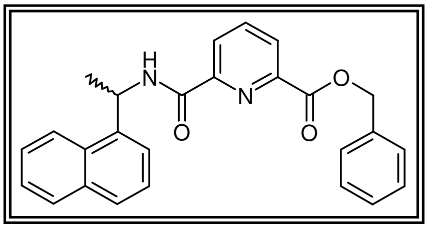
2. UV/Vis and Fluorescence Measurements

UV-visible absorption spectra and optical density were recorded by means of a Varian CARY 50 spectrophotometer. Solutions were measured in 3 cm (10 mm x 10 mm) cuvettes. Baseline correction measurements were used for all spectra. All solutions were prepared freshly prior to measurement.

Fluorescence and luminescence measurements were made with a Varian Carey Eclipse Fluorimeter equipped with a 1.0 cm path length quartz cell. The solvents used were of HPLC grade.

3. Synthesis

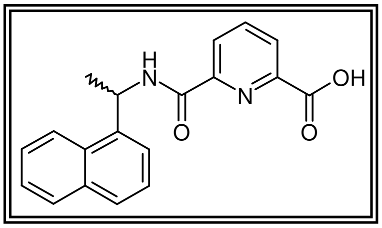
6-(1-Naphthalen-1-yl-ethylcarbamoyl)-pyridine-2-carboxylic acid benzyl ester, (4 (*R*), 5 (*S*))



To a stirred solution of the appropriate 1-(1-naphthyl)-ethylamine (*R* or *S* isomer, 0.630 mL, 3.9 mmol) in 30 mL anhydrous THF, HOBt (0.527 g, 3.9 mmol) and monobenzyl ester **3** (1 g, 3.9 mmol) were added. This solution was then stirred for further 30 min at 0 °C under an inert atmosphere of argon. To this solution, EDCI·HCl (0.785 g, 4.1 mmol) and triethylamine (0.571 mL, 4.1 mmol) were then added and the reaction mixture left stirring at 0 °C for 30 min. The mixture was then left stirring at room temperature for 18 h. The insoluble residue was filtered off and the solvent removed under reduced pressure. DCM was added to the crude oil and washed twice with 1 M HCl, a saturated solution of

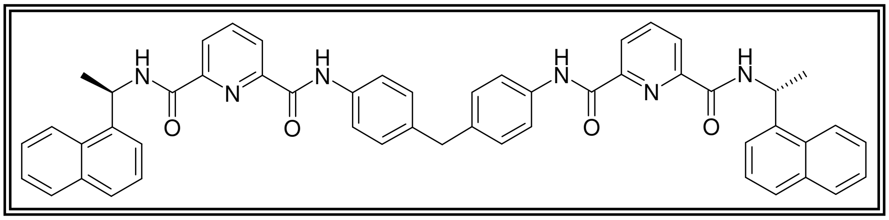
$NaHCO_3$ and finally with water. The organic layer was dried over $MgSO_4$, filtered and evaporated to dryness. If necessary, purification of the crude product by flash column chromatography using neutral silica was carried out. In each case pale yellow oil was obtained. **4** (***R***): 1.30 g, 81% yield. Calculated for $C_{26}H_{22}N_2O_3Na$: $(M+Na)^+$ *m/z* = 433.1528; Found: 433.1532; δ_H (400 MHz, $CDCl_3$, 298.2 K) 8.54 (1H, d, *J* = 8.5 Hz, NH), 8.44 (1H, d, *J* = 8.0 Hz, pyridine-H), 8.24 (1H, d, *J* = 8.5 Hz, nap-H), 8.20 (1H, t, *J* = 8.0 Hz, pyridine-H), 7.99 (1H, t, *J* = 8.0 Hz, pyridine-H), 7.89 (1H, d, *J* = 7.5 Hz, nap-H), 7.83 (1H, d, *J* = 7.5 Hz, nap-H), 7.64 (1H, d, *J* = 7.0 Hz, nap-H), 7.58-7.38 (8H, m, 3 napH, 5 Ar-H), 6.20 (1H, m, CH), 5.42 (2H, s, (CH_2), 1.82 (3H, d, 7.0 Hz, CH_3); δ_c (100 MHz, ($CDCl_3$, 298.2 K) 163.7, 161.9, 149.7, 146.1, 138.1, 137.9, 134.9, 133.5, 130.6, 128.4, 128.2, 128.0, 127.8, 126.8, 126.0, 125.3, 125.1, 124.9, 122.9, 122.2, 67.0, 44.5, 20.9; IR (NaCl) υ_{max} (cm^{-1}) 3381, 1724, 1667, 1587, 1508, 1305, 1291, 1236, 1131, 1078, 1029, 997, 963, 909, 843, 800, 777, 750, 696, 647. **5** (***S***): 1.26 g, 79% yield. Calculated for $C_{26}H_{22}N_2O_3Na$: $(M+Na)^+$ *m/z* = 433.1528; Found: 433.1549; δ_H (400 MHz, $CDCl_3$, 298.2 K) 8.51 (1H, d, *J* = 8.5 Hz, NH), 8.44 (1H, d, *J* = 7.5 Hz, pyridine-H), 8.23 (2H, d, nap-H, pyridine-H), 8.00 (1H, t, *J* = 7.5 Hz, pyridine-H), 7.89 (1H, d, *J* = 8.5 Hz, nap-H), 7.83 (1H, d, *J* = 8.5 Hz, nap-H), 7.64 (1H, d, *J* = 7.0 Hz, nap-H), 7.57-7.38 (8H, m, 3 nap-H, 5 Ar-H), 6.19 (1H, m, CH), 5.42 (2H, s, (CH_2), 1.82 (3H, d, 7.0 Hz, CH_3); δ_c (100 MHz, ($CDCl_3$, 298.2 K) 163.7, 161.9, 149.7, 146.0, 138.0, 137.9, 134.9, 133.5, 130.6, 128.4, 128.2, 128.0, 127.8, 127.7, 126.8, 126.0, 125.3, 125.1, 124.9, 122.9, 122.2, 67.0, 44.5, 20.9; IR (NaCl) υ_{max} (cm^{-1}) 3381, 1718, 1651, 1588, 1305, 1155, 1077, 966, 722.

6-(1-Naphthalen-1-yl-ethylcarbamoyl)-pyridine-2-carboxylic acid, (72 (*R*), 73 (*S*))



The two isomers **6** (***R***) and **7** (***S***) were obtained by hydrogenation of **4** (***R***) (1.24 g) and **51** (***S***) (1.22 g), respectively, in CH_3OH, with a 10 % Pd/C catalyst (0.1 equiv.) under 3 atm of hydrogen gas, using a Parr hydrogen shaker apparatus. The resulting solution containing the two products were passed through a celite filter and the solvent evaporated to dryness under reduced pressure. The reaction furnished the two carboxylic acid derivatives as yellow solids. No further purification was needed. **6 (*R*)**: 0.94 g, 98%, m.p. 116-120 °C. Calculated for $C_{19}H_{16}N_2O_3 \cdot ½ H_2O$: C, 69.29; H, 5.20; N, 8.51%; Found: C, 69.43; H, 5.06; N, 8.31 %; Calculated for $C_{19}H_{16}N_2O_3Na$ $(M+Na)^+$ *m/z* = 343.1059; Found: 343.1062; δ_H (400 MHz, $CDCl_3$, 298.2 K) 8.51 (1H, d, *J* = 8.5 Hz, N<u>H</u>), 8.38 (1H, d, *J* = 7.5 Hz, pyridine-<u>H</u>), 8.21 (1H, d, *J* = 7.5 Hz, pyridine-<u>H</u>), 8.08 (1H, d, *J* = 8.5 Hz, nap-<u>H</u>), 7.97 (1H, t, *J* = 7.5 Hz, pyridine-<u>H</u>), 7.78 (1H, d, *J* = 8.0 Hz, nap-<u>H</u>), 7.69 (1H, d, *J* = 8.0 Hz, nap-<u>H</u>), 7.50 (2H, m, 2 nap-<u>H</u>), 7.45 (1H, t, *J* = 8.0 Hz, nap-<u>H</u>,), 7.33 (1H, t, *J* = 7.5 Hz, nap-<u>H</u>,), 6.03 (1H, m, C<u>H</u>), 1.67 (3H, d, 7.0 Hz, C<u>H</u>$_3$); δ_c (100 MHz, ($CDCl_3$, 298.2 K) 164.8, 162.7, 148.5, 145.0, 138.5, 137.6, 133.0, 130.3, 128.2, 127.5, 126.2, 125.9, 125.7, 125.2, 124.7, 122.7, 122.2, 44.7, 20.3; IR (neat sample) υ_{max} (cm^{-1}) 3271, 3050, 2977, 2936, 1752, 1651, 1524, 1452, 1345, 1255, 1172, 1118, 1076, 1000, 921, 846, 799, 776, 745, 681. **7 (*S*)**: 0.85 g, 90%, m.p. 116-120 °C. Calculated for $C_{19}H_{16}N_2O_3 \cdot ½ H_2O$: C, 69.29; H, 5.20; N, 8.51%; Found: C, 69.23; H, 5.13; N, 8.34 %; Calculated for $C_{19}H_{16}N_2O_3Na$ $(M+Na)^+$ *m/z* = 343.1059; Found: 343.1061; δ_H (400 MHz, $CDCl_3$, 298.2 K) 8.49 (1H, d, *J* = 8.5 Hz, N<u>H</u>), 8.44 (1H, d, *J* = 7.5 Hz, pyridine-<u>H</u>), 8.23 (1H, d, *J* = 8.5 Hz, nap-<u>H</u>), 8.19 (1H, d, *J* = 7.5 Hz, pyridine-<u>H</u>), 7.99 (1H, t, *J* = 7.5 Hz, pyridine-<u>H</u>), 7.88 (1H, d, *J* = 8.0 Hz, nap-<u>H</u>), 7.82 (1H, d, *J* = 8.0 Hz, nap-<u>H</u>), 7.65 (1H, d, *J* = 7.0 Hz, nap-<u>H</u>), 7.56 (1H, t, *J* = 7.0 Hz, nap-<u>H</u>,), 7.49 (2H, m, 2 nap-<u>H</u>,), 6.20 (1H, m, C<u>H</u>), 1.83 (3H, d, 7.0 Hz, C<u>H</u>$_3$); δ_c (100 MHz, ($CDCl_3$, 298.2 K) 163.3, 161.5, 148.8, 144.5, 139.1, 137.2, 133.4, 130.6, 128.4, 128.1, 126.4, 126.2, 126.2, 125.4, 124.8, 122.7, 122.4, 44.6, 20.3; IR (neat sample) υ_{max} (cm^{-1}) 3282, 3049, 2977, 2936, 1751, 1651, 1524, 1452, 1345, 1255, 1172, 1118, 1076, 1000, 921, 846, 799, 776, 745, 681.

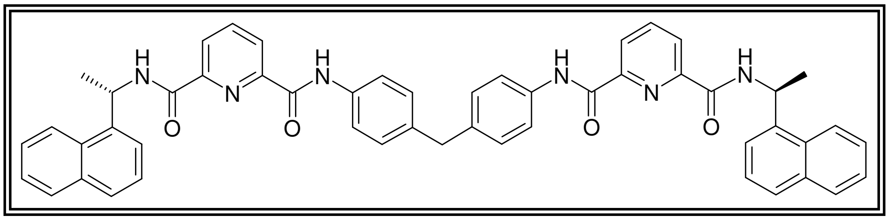
N,N'-[Methylenebis(phen-1,4-ylene)]bis(6-(*R*)-1-Naphthalen-1-yl-ethylcarbamoyl)-pyridine-2-carboxamide) (1 (*R*,*R*))



To a mixture of 4,4'-diamino-diphenylmethane (0.195 g, 0.985 mmol), **6** (0.630 g, 1.97 mmol), HOBt (0.280 g, 2.07 mmol) in THF (*ca.* 25 mL), EDCI·HCl (0.397 g, 2.07 mmol), triethylamine (0.288 mL, 2.07 mmol) and DMAP

(0.144 g, 1.18 mmol) were added, after cooling the reaction mixture at 0 °C. The work-up carried out was the same as that described for **4** and resulted in orange oil (94.5% yield). The crude oil was dissolved in DCM and then dropped slowly onto dry diethyl ether (60-70 mL).The final product was collected as an off-white solid by filtration through a hirsch funnel in 60% yield. m.p. decomposes above 148 °C. Calculated for $C_{51}H_{42}N_6O_4 \cdot$ ½ $H_2O \cdot$ ½ DCM: C, 72.40; H, 5.19; N, 9.84%; Found: C, 72.56; H, 5.43; N, 9.75 %; δ_H (400 MHz, $CDCl_3$, 298.2 K) 9.30 (2H, s, 2 N<u>H</u>), 8.44 (2H, d, *J* = 7.5 Hz, pyridine-<u>H</u>), 8.41 (2H, d, *J* = 7.5 Hz, pyridine-<u>H</u>), 8.22 (2H, d, *J* = 8.0 Hz, nap-<u>H</u>), 8.09 (2H, t, *J* = 7.5 Hz, pyridine-<u>H</u>), 8.06 (2H, d, *J* = 8.0 Hz, 2 N<u>H</u>), 7.91 (2H, d, *J* = 7.5 Hz, nap-<u>H</u>), 7.85 (2H, d, *J* = 8.0 Hz, nap-<u>H</u>), 7.65 (2H, d, *J* = 7.0 Hz, nap-<u>H</u>,), 7.60-7.47 (6H, m, 6 nap-<u>H</u>,), 7.43 (4H, d, *J* = 8.0 Hz, Ar-<u>H</u>), 7.14 (4H, d, *J* = 8.0 Hz, Ar-<u>H</u>), 6.12 (2H, m, 2 C<u>H</u>), 3.95 (2H, s, C<u>H</u>$_2$), 1.85 (6H, d, 7.0 Hz, 2 C<u>H</u>$_3$); δ_c (100 MHz, ($CDCl_3$, 298.2 K) 162.0, 160.6, 148.4, 148.2, 138.8, 137.5, 137.2, 134.6, 133.6, 130.5, 129.0, 128.5, 128.2, 126.3, 125.5, 125.0, 124.8, 124.7, 122.8, 122.5, 119.9, 45.3, 40.3, 20.5; IR (neat sample) υ_{max} (cm^{-1}) 3298, 3049, 2979, 2934, 2079, 1661, 1588, 1517, 1444, 1411, 1320, 1234, 1179, 1118, 1075, 999, 944, 916, 842, 800, 776, 749, 677.

_N,N_'-[Methylenebis(phen-1,4-ylene)]bis(6-(_S_)-1-Naphthalen-1-yl-ethylcarbamoyl)-pyridine-2-carboxamide) (2 (_S,S_))



To a mixture of 4,4'-diamino-diphenylmethane (0.165 g, 0.83 mmol), **7 (*R*)** (0.545 g, 1.70 mmol), HOBt (0.235 g, 1.74 mmol) in THF (*ca.* 20 mL), EDCI·HCl (0.334 g, 1.74 mmol), triethylamine (0.245 mL, 1.74 mmol) and DMAP (0.122 g, 1.00 mmol) were added, after cooling the reaction mixture at 0 °C. DMAP is a strong base and was added to insure the completion of the reaction. The work-up carried out was the same as that described in **4** and resulted in an off-white fluffy solid (52% yield). The crude product was purified by column chromatography on silica using 100% CH_2Cl_2, with a gradient elution to 95:5, DCM:MeOH mobile phase. The final product was collected as an off-white solid in 44% yield. m.p. decomposes above 149 °C.

Calculated for $C_{51}H_{42}N_6O_4 \cdot H_2O \cdot ½$ DCM: C, 71.64; H, 5.25; N, 9.73%; Found: C, 71.65; H, 5.03; N, 9.59 %; δ_H (400 MHz, $CDCl_3$, 298.2 K) 9.36 (2H, s, 2 N$\underline{H}$), 8.42 (2H, d, *J* = 7.5 Hz, pyridine-$\underline{H}$), 8.37 (2H, d, *J* = 7.5 Hz, pyridine-$\underline{H}$), 8.18 (4H, 2 d (overlapping), 2 N$\underline{H}$ and 2 nap-$\underline{H}$), 8.06 (2H, t, *J* = 7.5 Hz, pyridine-$\underline{H}$), 7.88 (2H, d, *J* = 8.0 Hz, nap-$\underline{H}$), 7.81 (2H, d, *J* = 8.5 Hz, nap-$\underline{H}$), 7.61 (2H, d, *J* = 7.0 Hz, nap-$\underline{H}$), 7.57-7.42 (6H, m, 6 nap-$\underline{H}$,), 7.41 (4H, d, *J* = 8.5 Hz, Ar-$\underline{H}$), 7.08 (4H, d, *J* = 8.5 Hz, Ar-$\underline{H}$), 6.08 (2H, m, 2 C$\underline{H}$), 3.91 (2H, s, C$\underline{H}_2$), 1.81 (6H, d, 7.0 Hz, 2 C$\underline{H}_3$); δ_c (100 MHz, ($CDCl_3$, 298.2 K) 162.5, 161.3, 148.3, 147.9, 137.9, 137.8, 137.0, 134.3, 133.1, 130.4, 128.3, 128.2, 127.5, 125.9, 125.3, 124.9, 124.4, 124.2, 122.8, 122.3, 121.1, 44.8, 40.1, 20.5; IR (neat sample) υ_{max} (cm^{-1}) 3298, 3049, 2977, 2934, 2084, 1655, 1588, 1521, 1444, 1411, 1320, 1233, 1179, 1118, 1075, 999, 944, 916, 842, 800, 776, 749, 678.

3{*N,N*'-[Methylenebis(phen-1,4-ylene)]bis(6-(*R*)-1-Naphthalen-1-yl-ethylcarbamoyl)-pyridine-2-carboxamide)}. 2Eu. 6(CF_3SO_3) (1 (*R,R*))

Ligand **1 (*R,R*)** (0.03 g, 0.037 mmol) and $Eu(CF_3SO_3)_3$ (0.0148 g, 0.025 mmol) were added to a 5 mL single neck RBF that contained 3 mL of $CH_3CN/CHCl_3$ (50 : 50, v/v). The solution was then refluxed for 24 hrs. The resulting solution was cooled to room temperature and then dropped slowly onto dry diethyl ether. A pale brown solid precipitated out of solution and was collected by Hirsch filtration in 48.5% yield. m.p. decomposes above 280 °C. Calculated for $C_{159}H_{126}N_{18}O_{30}Eu_2F_{18}S_6 \cdot 2\ CHCl_3$: C, 50.28; H, 3.35; N, 6.56%; Found: C, 49.77; H, 3.55; N, 6.48 %; δ_H (600 MHz, CD_3CN, 298.2 K) 8.99 (3 × 2H, br. s, nap-$\underline{H}$), 8.21 (3 × 4H, br. s, Ar-$\underline{H}$), 8.06 (3 × 2H, br. s, C$\underline{H}$), 7.98 (3 × 2H, br. s, nap-$\underline{H}$), 7.81 (3 × 4H, br. s, Ar-$\underline{H}$), 7.62 (3 × 4H, br. s, nap-$\underline{H}$), 7.16 (3 × 2H, br. s, nap-$\underline{H}$), 6.78 (3 × 2H, br. s, 2 N$\underline{H}$), 6.58 (3 × 2H, br. s, nap-$\underline{H}$), 6.41 (3 × 2H, br. s, pyridine-$\underline{H}$), 6.24 (3 × 2H, br. s, nap-$\underline{H}$), 5.73 (3 × 2H, br. s, pyridine-$\underline{H}$), 5.26 (3 × 2H, br. s, pyridine-$\underline{H}$), 4.38 (3 × 2H, br. s, C$\underline{H}_2$), 4.08 (3 × 2H, br. s, 2 N$\underline{H}$), C$\underline{H}_3$ obscured by solvent peak at 1.99 ppm; δ_c (CD_3CN, 298.2 K obtained by inverse detection through HSQC experiment, quaternary excluded) 153.3, 129.7, 128.8, 127.0, 126.7, 125.9, 124.4, 124.4, 122.1, 120.0, 91.0, 90.6, 40.4, 21.6; IR (neat sample) υ_{max} (cm^{-1}) 3267, 3087, 2096, 1629, 1585, 1553, 1511, 1457, 1416, 1380, 1348, 1275, 1243, 1225, 1162, 1028, 956, 918, 839, 801, 778, 754, 699, 677, 662.

3{*N,N*'-[Methylenebis(phen-1,4-ylene)]bis(6-(*S*)-1-Naphthalen-1-yl-ethylcarbamoyl)-pyridine-2-carboxamide)}. 2Eu. 6(CF_3SO_3) (2 (*S,S*))

Ligand **2** (***S,S***) (0.0835 g, 0. 1 mmol) and $Eu(CF_3SO_3)_3$ (0.0415 g, 0.07 mmol) were added to a 50 mL single neck RBF that contained 15 mL of MeOH. The solution was then refluxed for 24 hrs under an argon atmosphere. The resulting solution was cooled to room temperature and then dropped slowly onto dry diethyl ether. A pale yellow solid precipitated out of solution and was collected by Hirsch filtration in 92% yield. m.p. decomposes above 280 °C. Calculated for $C_{159}H_{126}N_{18}O_{30}Eu_2F_{18}S_6 \cdot 2\,H_2O \cdot 2MeOH$: C, 52.16; H, 3.75; N, 6.80%; Found: C, 51.95; H, 3.61; N, 6.90 %; δ_H (400 MHz, CD_3CN, 298.2 K) 9.04 (3 × 2H, br. s, nap-$\underline{H}$), 8.28 (3 × 4H, br. s, Ar-$\underline{H}$), 8.18 (3 × 2H, br. s, C$\underline{H}$), 7.98 (3 × 2H, br. s, nap-$\underline{H}$), 7.84 (3 × 4H, br. s, Ar-$\underline{H}$), 7.58 (3 × 4H, br. s, nap-$\underline{H}$), 7.10 (3 × 2H, br. s, nap-$\underline{H}$), 6.69 (3 × 2H, br. s, 2 N$\underline{H}$), 6.49 (3 × 2H, br. s, nap-$\underline{H}$), 6.29 (3 × 2H, br. s, pyridine-$\underline{H}$), 6.12 (3 × 2H, br. s, nap-$\underline{H}$), 5.59 (3 × 2H, br. s, pyridine-$\underline{H}$), 5.12 (3 × 2H, br. s, pyridine-$\underline{H}$), 4.37 (3 × 2H, br. s, C$\underline{H}_2$), 3.96 (3 × 2H, br. s, 2 N$\underline{H}$), C$\underline{H}_3$ obscured by solvent peak at 1.97 ppm; IR (neat sample) υ_{max} (cm^{-1}) 3266, 3088, 1629, 1585, 1552, 1511, 1457, 1416, 1379, 1348, 1274, 1242, 1225, 1161, 1028, 956, 917, 838, 801, 778, 754, 728, 699, 678, 662.

3. Figures

Figure S1. ^{1}H-NMR (400 MHz, $CDCl_3$) of ligand 1*(R,R)*.

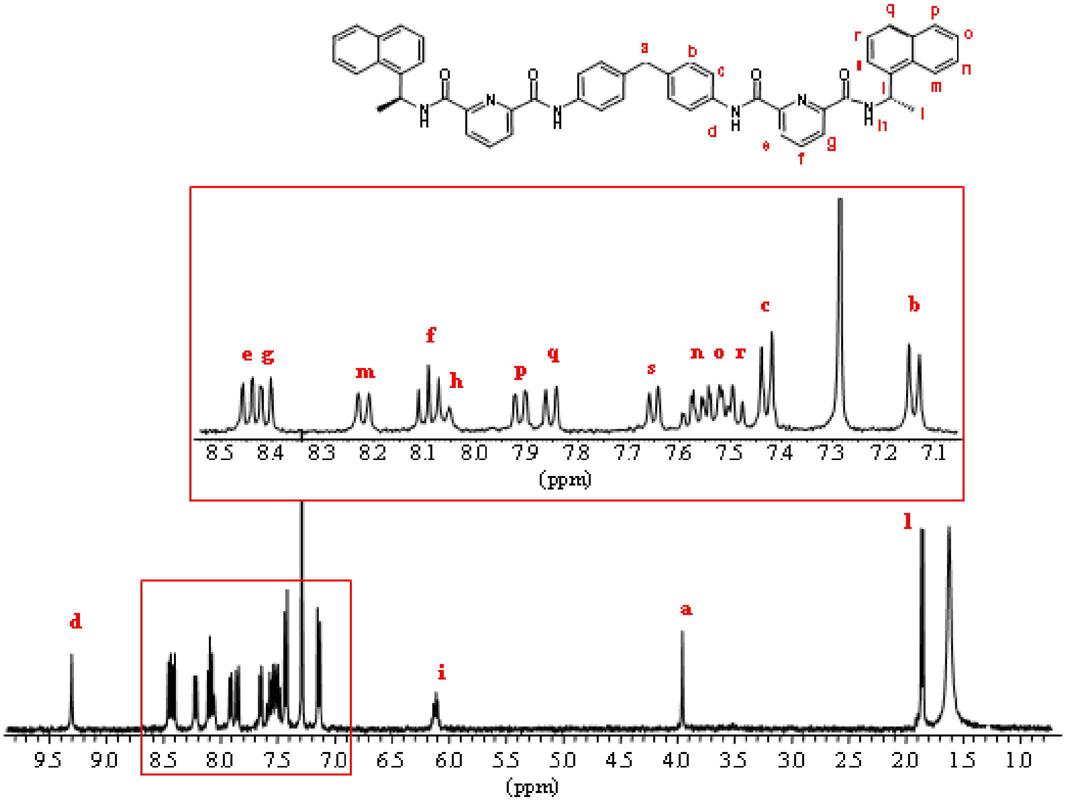


Figure S2. CD spectra of ligands 1 *(R,R)* shown in blue (Abs at 281 nm = 2.088) and 2 *(S,S)* shown in red (Abs at 281 nm = 1.624) in MeOH.

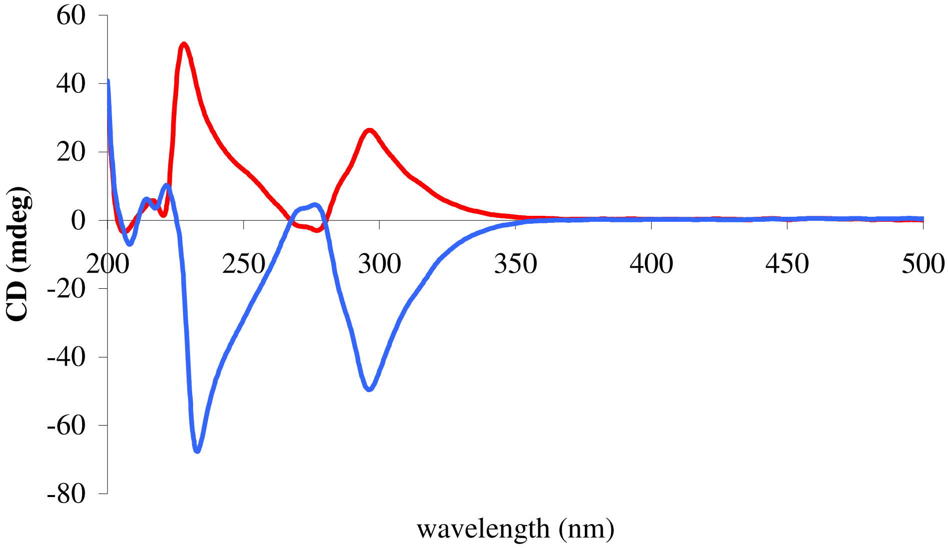


Figure S3. ^{1}H-NMR (400 MHz, CD_3OD) of **Tb_2:1_3**.

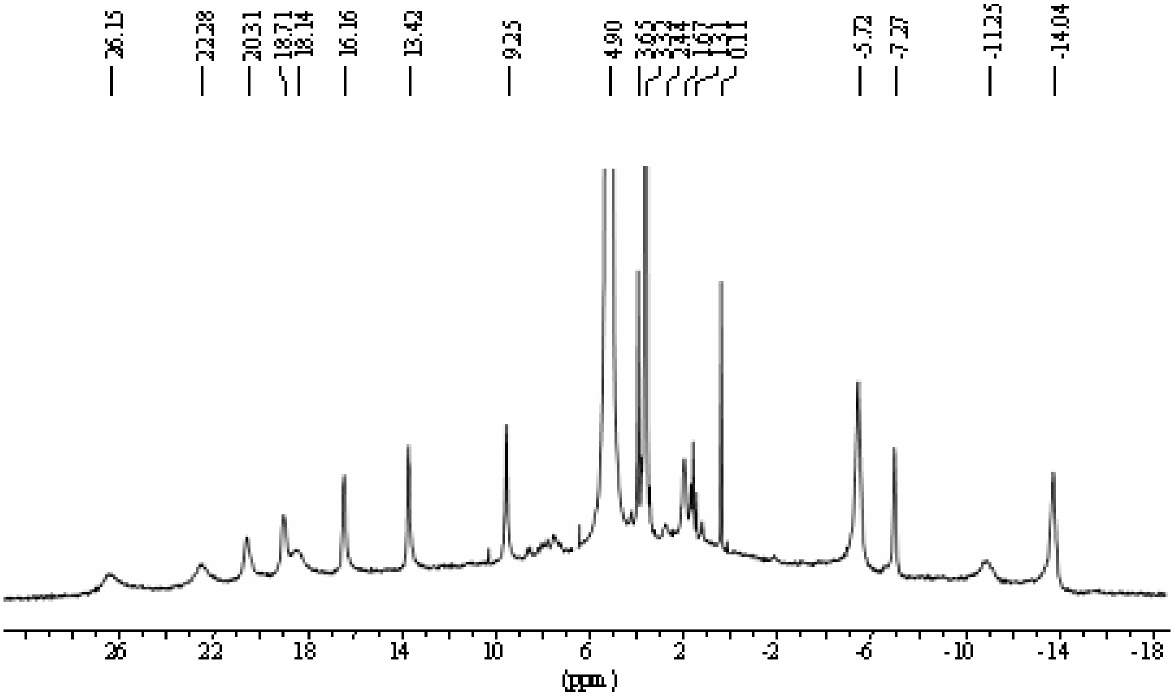


Figure S4. The CD spectra of the Eu^{III} complexes **Eu_2:1_3** (Abs at 281 nm 1.374) (orange) and **Eu_2:2_3** (Abs at 281 nm = 1.104) (green) in MeOH.

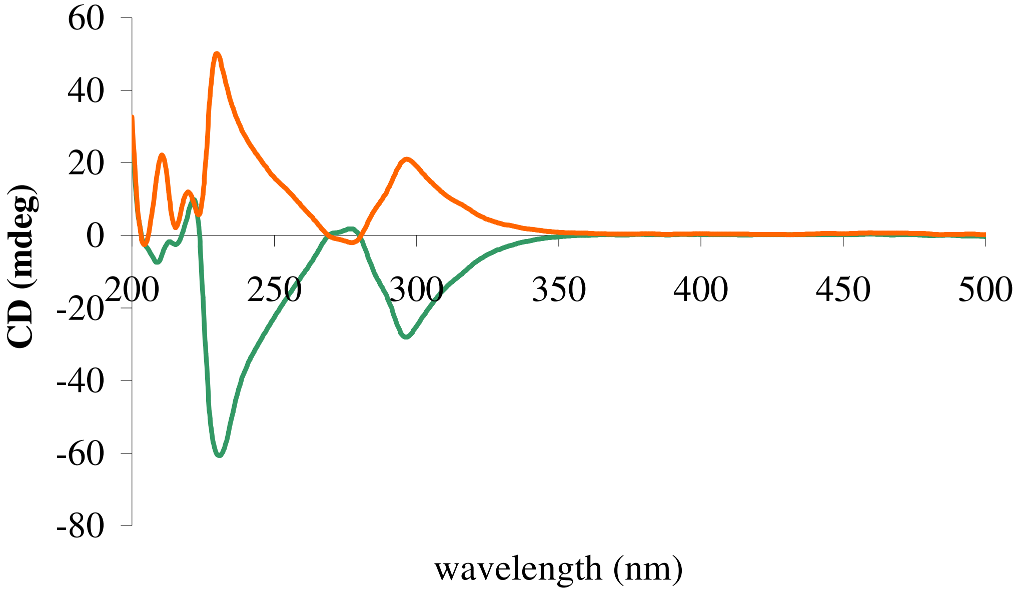


Figure S5. HSQC (^{1}H – ^{13}C) spectrum (600 MHz, CD$_3$CN) of $\mathbf{Eu_2{:}1_3}$ (*R*,*R*). The coloured rectangles and corresponding asterisks indicate the spin systems in the molecule.

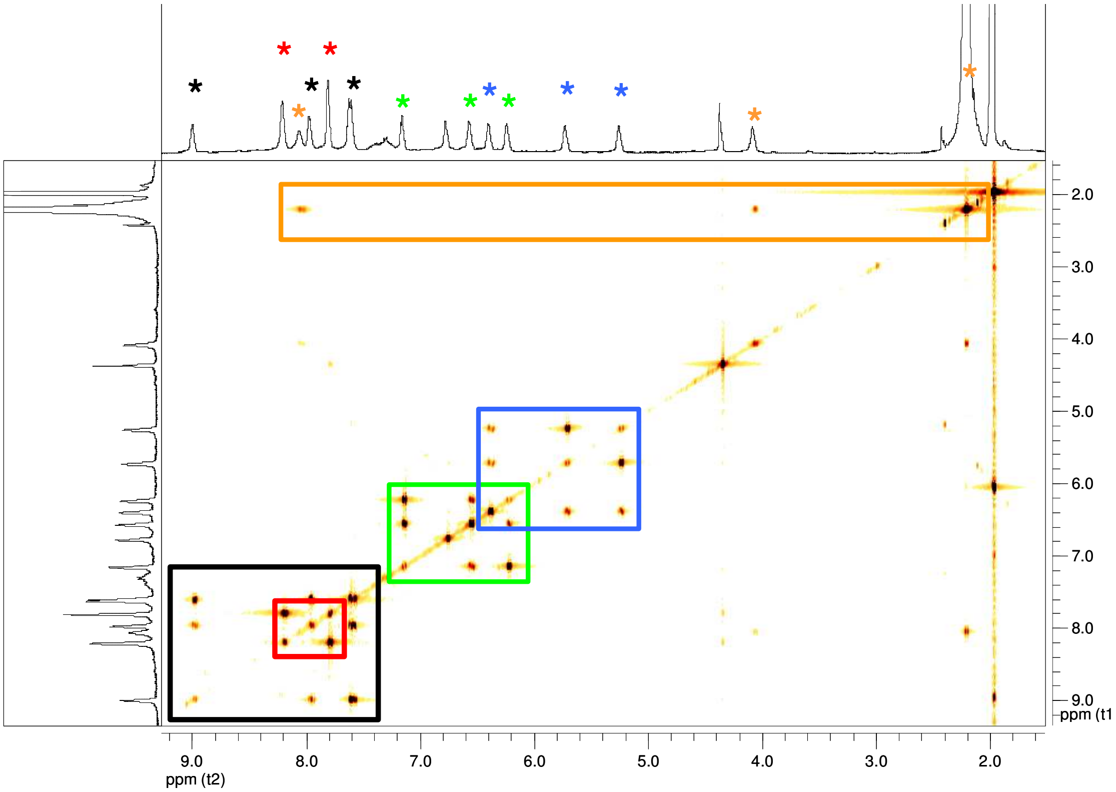


Figure S6. HSQC (^{1}H – ^{15}N) spectrum (600 MHz, CD$_3$CN) of 74 (*R*,*R*). (δ ^{15}N = 79.5 and 79.2 ppm).

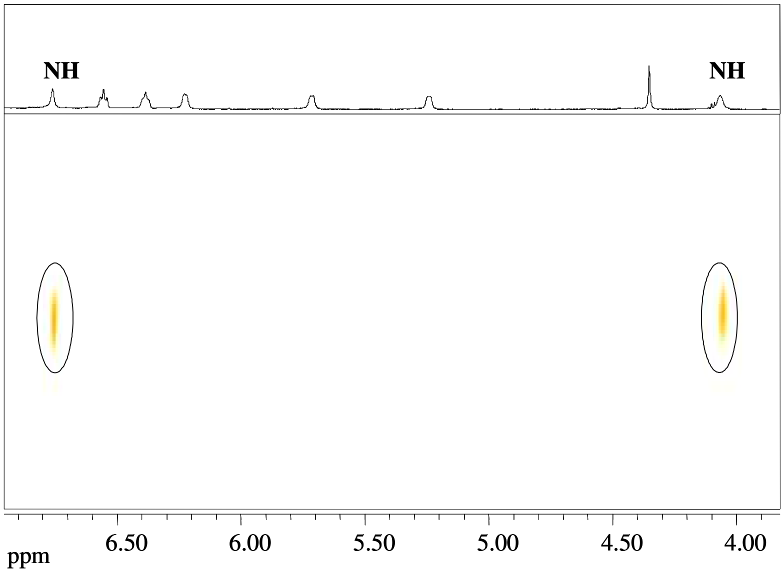


Figure S7. 1 ^{1}H-NMR spectra (400 MHz, $CD_3CN/CDCl_3$, 50:50, v/v) of ligand **1** *(R,R)* upon titration of $Eu(CF_3SO_3)_3$, [**1** (*R,R*)] = 1.24 x 10^{-3} M, [Eu^{III}] = 2 x 10^{-2} M, (0-1 eq); the red box highlights the formation of the H_8 resonance and simultaneous disappearance of the NH signal. The appearance of the resonance at 9.69 ppm is also highlighted. Top: structure of ligand **1** *(R,R)* indicating the two protons: NH and H_8.

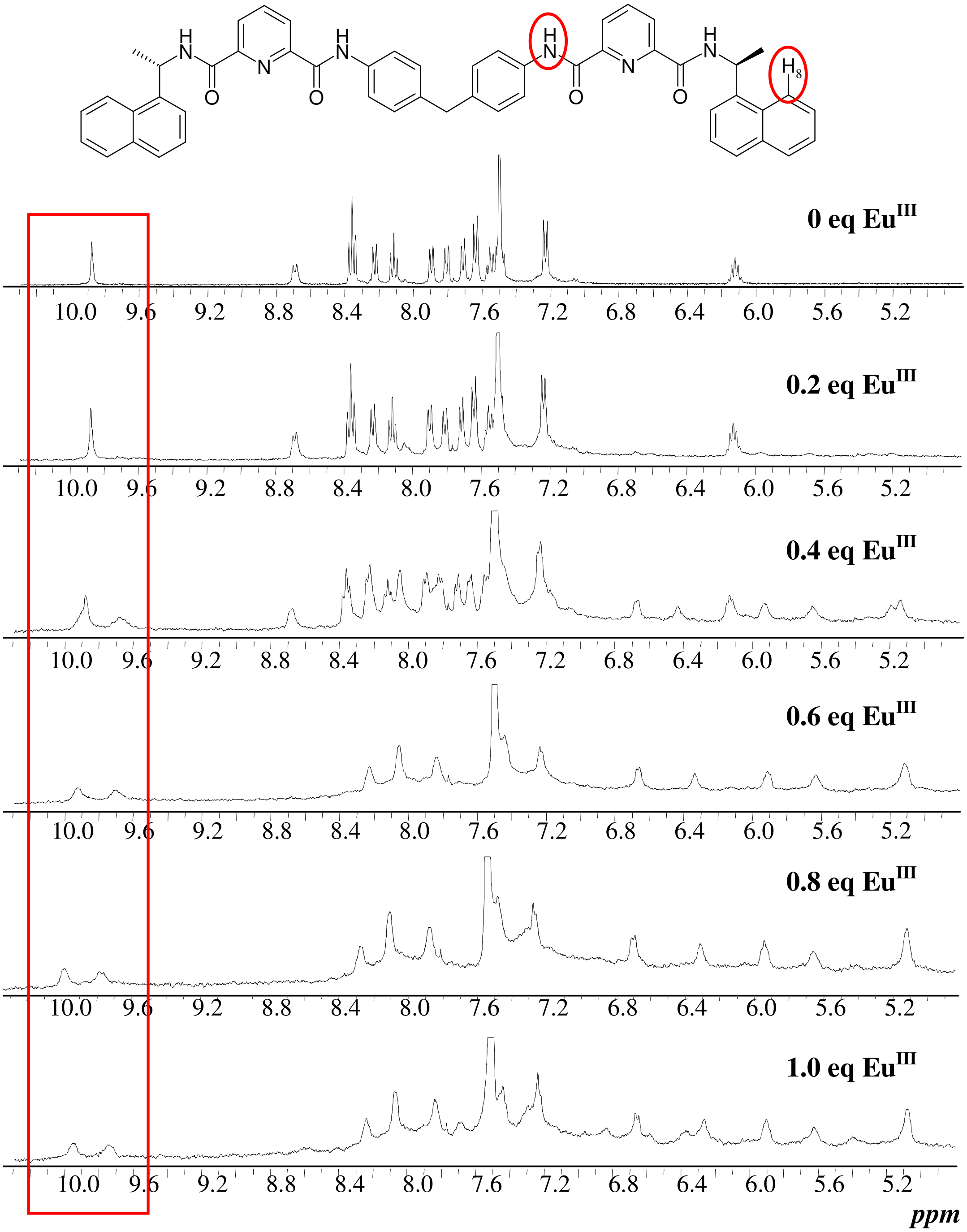


Figure S8. Integration of the appearing signal at 9.88 ppm (in Figure S7) as a function of the equivalent of Eu^{III} added in the ^{1}H-NMR (400 MHz, $CD_3CN/CDCl_3$, 50:50, v/v) titration of ligand **1** *(R,R)*.

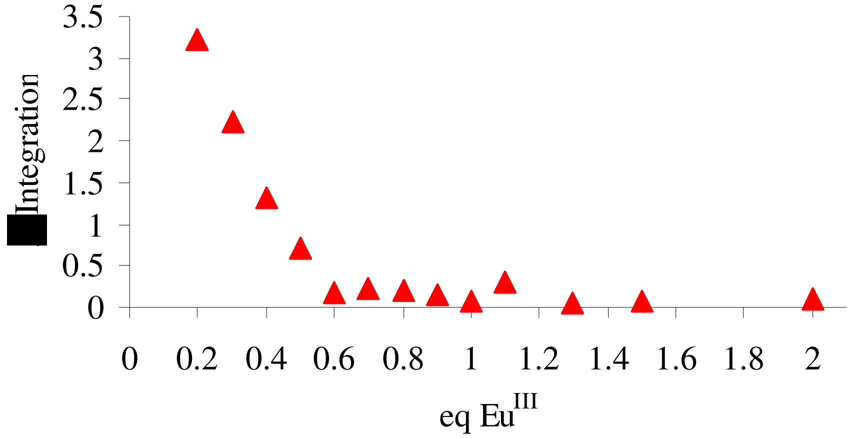


Figure S9. Eu(III) excited stated decay observed for **Eu_2:1_3** in H_2O and D_2O (**a** and **b**, respectively) and the observed fitting of the decay.

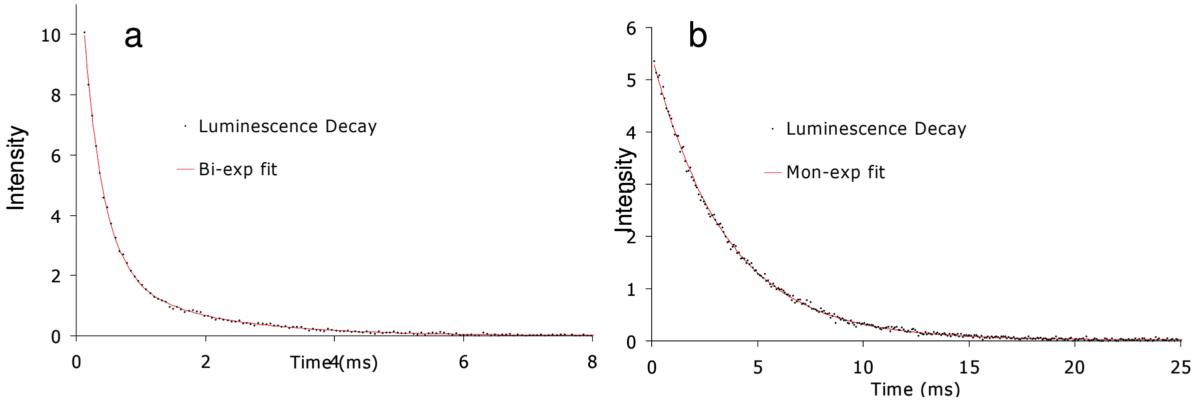


Figure S10. Eu(III) excited stated decay observed for **Eu_2:2_3** in H_2O and D_2O (**a** and **b**, respectively) and the observed fitting of the decay.

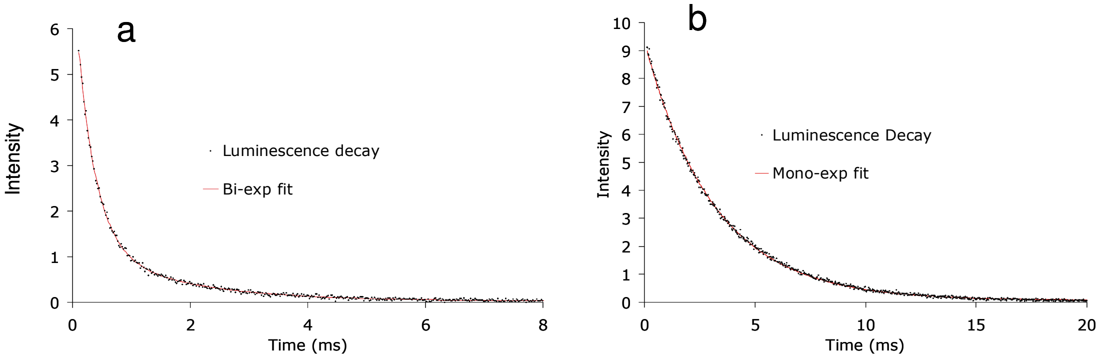


Figure S11. The UV-Vis absorption spectra of **Eu$_2$:1$_3$** in: MeOH and H_2O (*NB* recorded at two different concentrations).

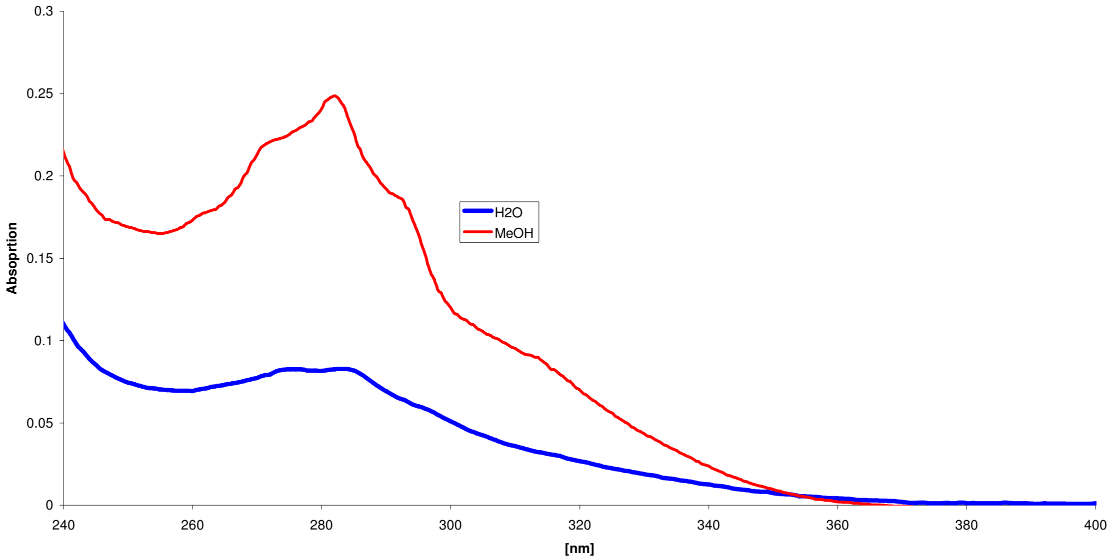


Figure S12. The UV-Vis absorption spectra of **Eu$_2$:2$_3$** in: MeOH and H_2O (*NB* recorded at two different concentrations).

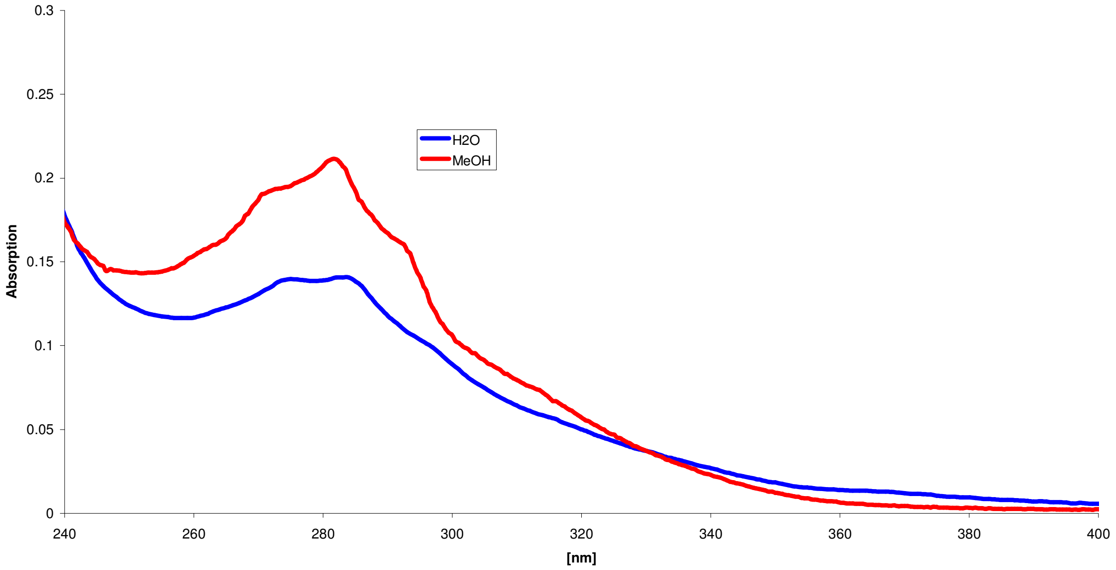


Figure S13. The fluorescence emission spectra of **Eu$_2$:1$_3$** in MeOH.

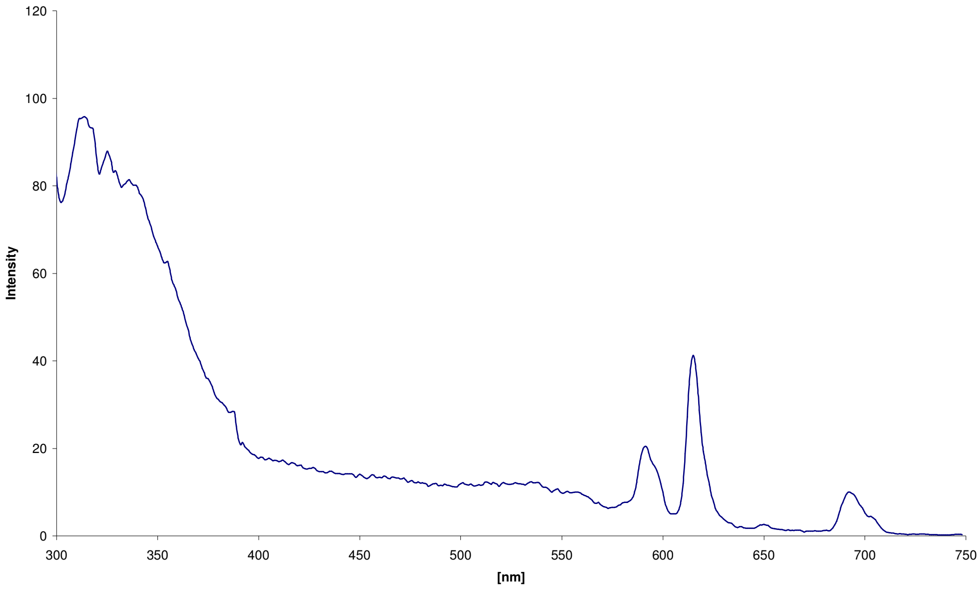


Figure S14. The fluorescence emission spectra of **Eu$_2$:1$_3$** in 1:1 $CH_3CN:CHCl_3$.

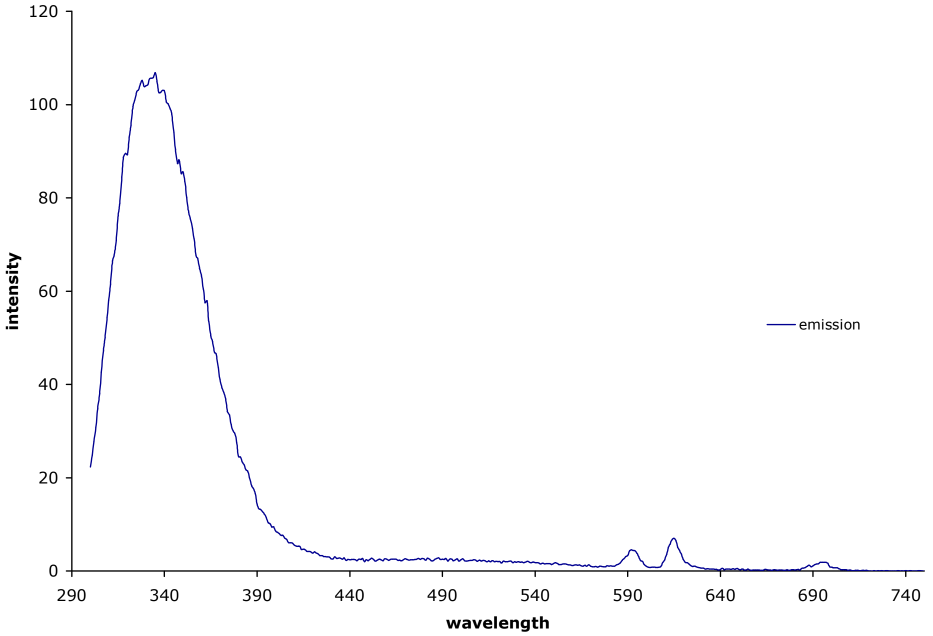


Figure S15. The Eu(III) emission spectra of **Eu_2:1_3** in MeOD (red) and MeOH (blue), excitation 281 nm. Settings in MeOD: Emission Slit = 1.5 nm; Excitation Slit= 20 nm; PMT: 650; Delay: 0.1 ms; Average time: 0.49 Data interval: 0.5 nm. Settings in MeOH: Settings are the same except Emission slit = 2.5 nm

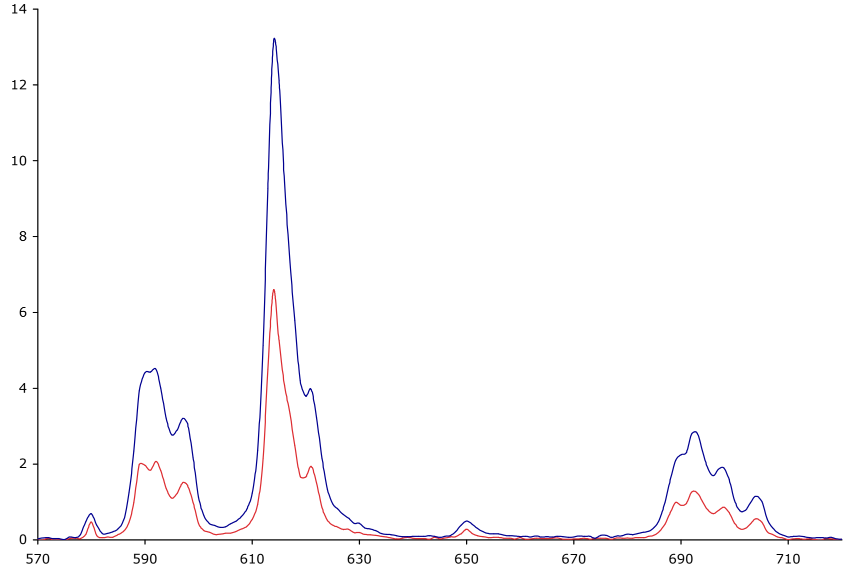


Figure S16. The Eu(III) emission spectra of **Eu_2:2_3** in MeOD (red) and MeOH (blue), excitation 281 nm. Settings in MeOD: Emission Slit = 1.5 nm; Excitation Slit= 20 nm; PMT: 650; Delay: 0.1 ms; Average time: 0.49 Data interval: 0.5 nm. Settings in MeOH: Settings are the same except: Emission slit = 2.5 nm.

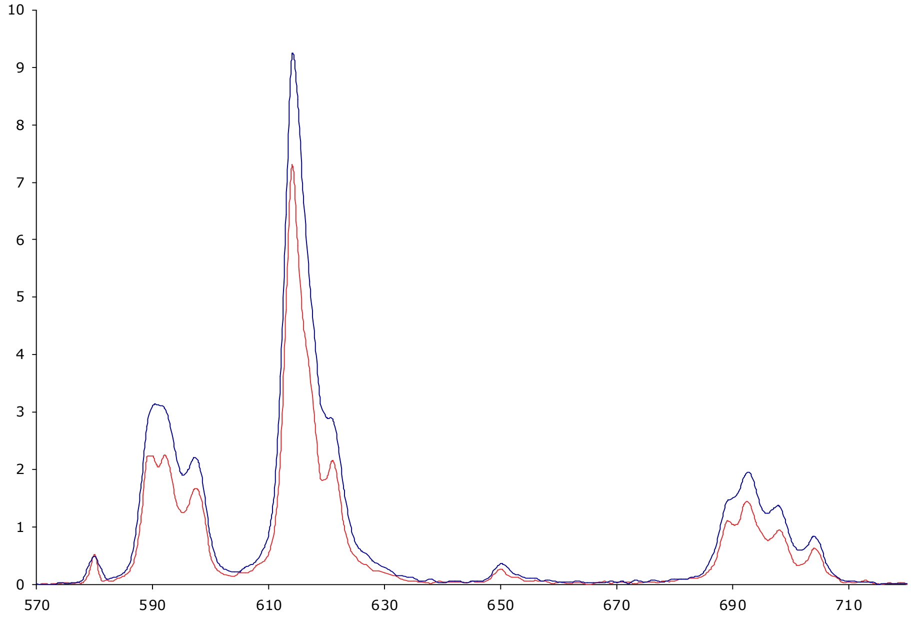


Figure S17. The Eu(III) emission spectra of **Eu_2:1_3** in a 1:1 mixture of CH_3CN:$CHCl_3$ (excitation 281 nm) and the corresponding excitation spectra (emission 615 nm).

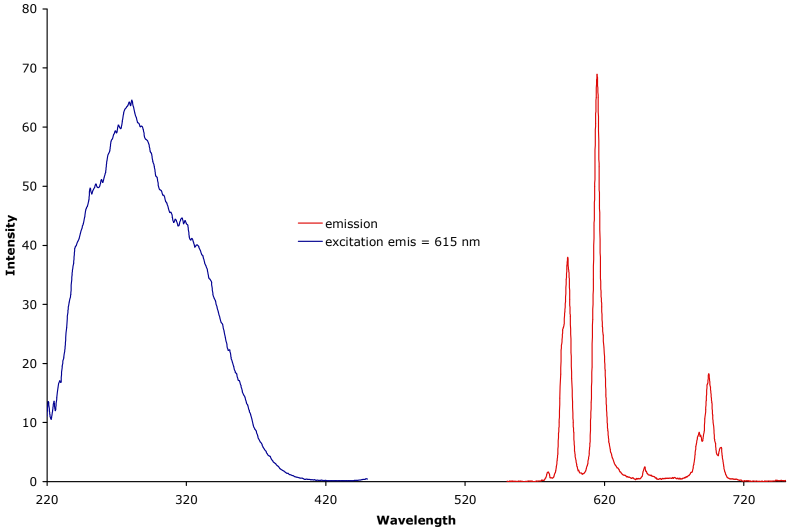


Figure S18. The Eu(III) emission spectra of **Eu_2:2_3** in MeOH (excitation 281 nm) and the corresponding excitation spectra (emission 615 nm).

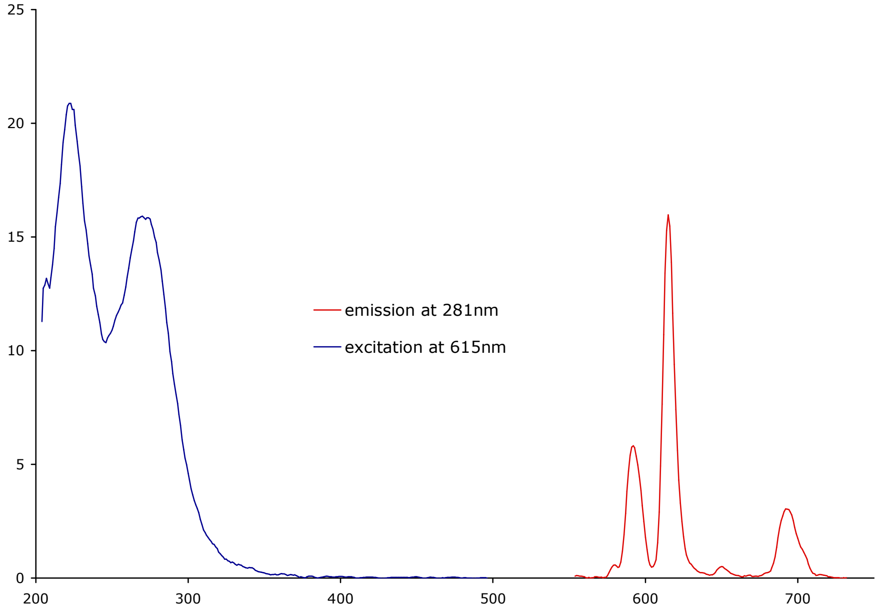


Figure S19. Changes in the UV-Vis absorption spectra upon titrating **1** [1× 10^{-5} M] with $Eu(CF_3SO_3)_3$ in $CH_3CN/CHCl_3$ (50:50, v/v).

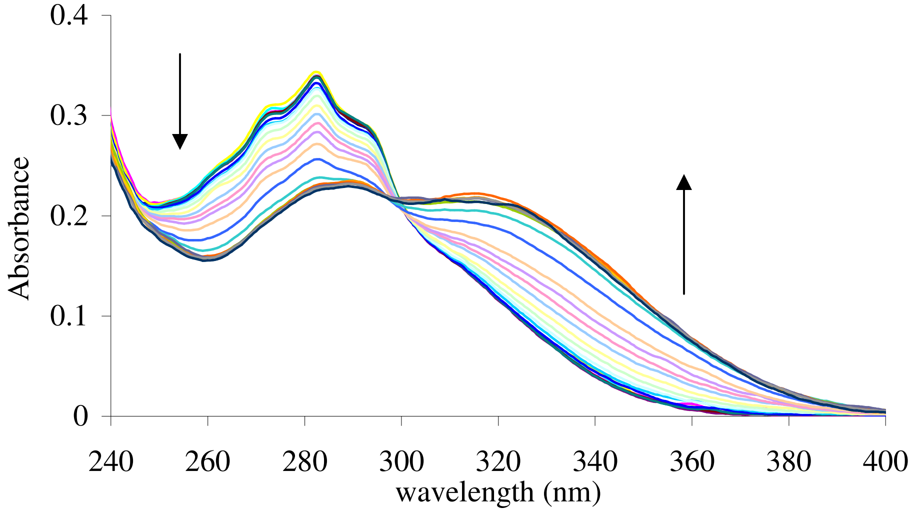


Figure S20. Changes in the UV-Vis absorption spectra upon titrating **1** [1× 10^{-5} M] with $Eu(CF_3SO_3)_3$ in CH_3CN.

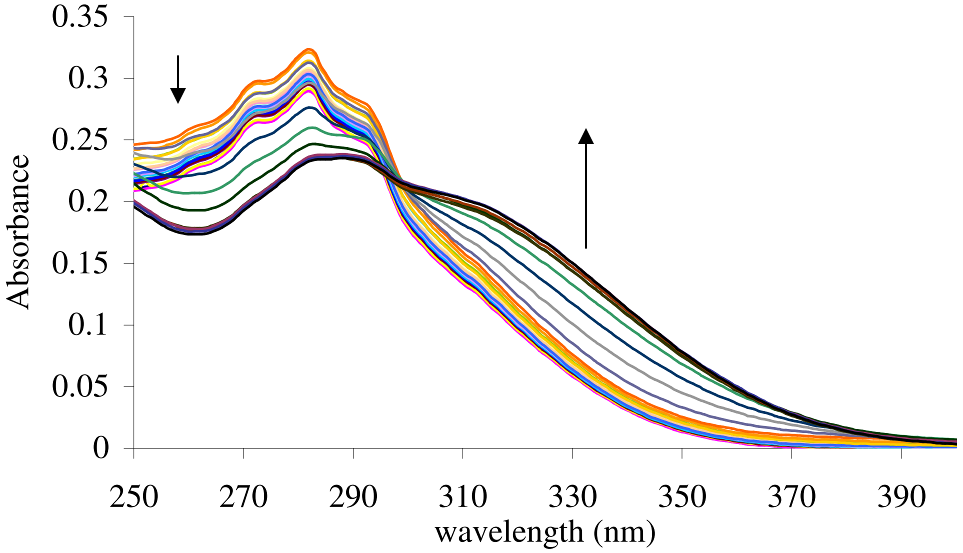


Figure S21. Changes in the Eu(III) emission spectra upon titrating **1** [1× 10^{-5} M] with $Eu(CF_3SO_3)_3$ in CH_3CN.

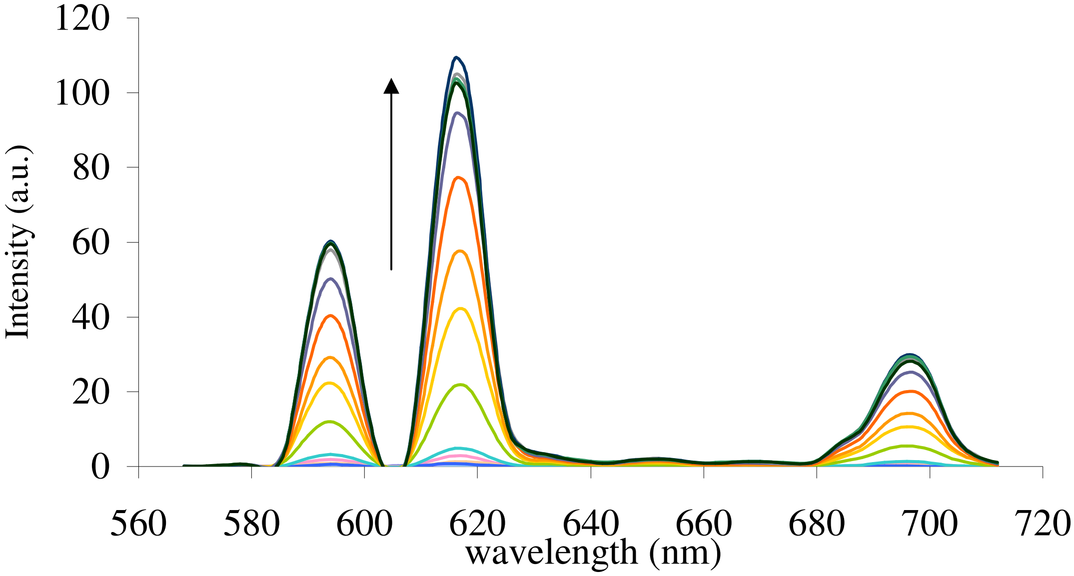


Figure S22. Changes in the Eu(III) emission spectra upon titrating **1** [1× 10^{-5} M] with $Eu(CF_3SO_3)_3$ in $CH_3CN/CHCl_3$ (50:50, v/v).

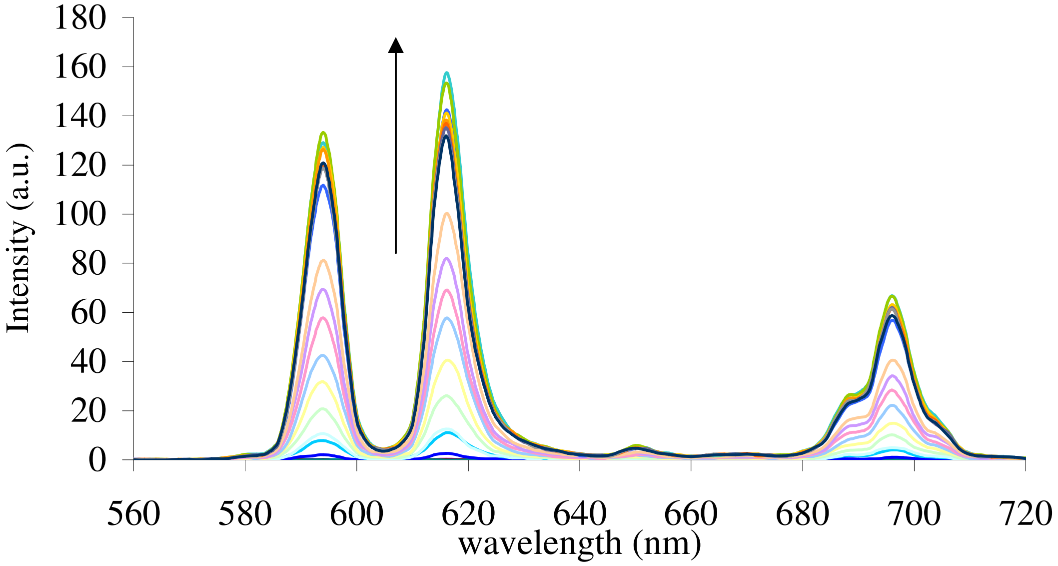


Figure S23. The overall changes observed upon carrying out a Job's plot analysis of **2** with Eu(III).

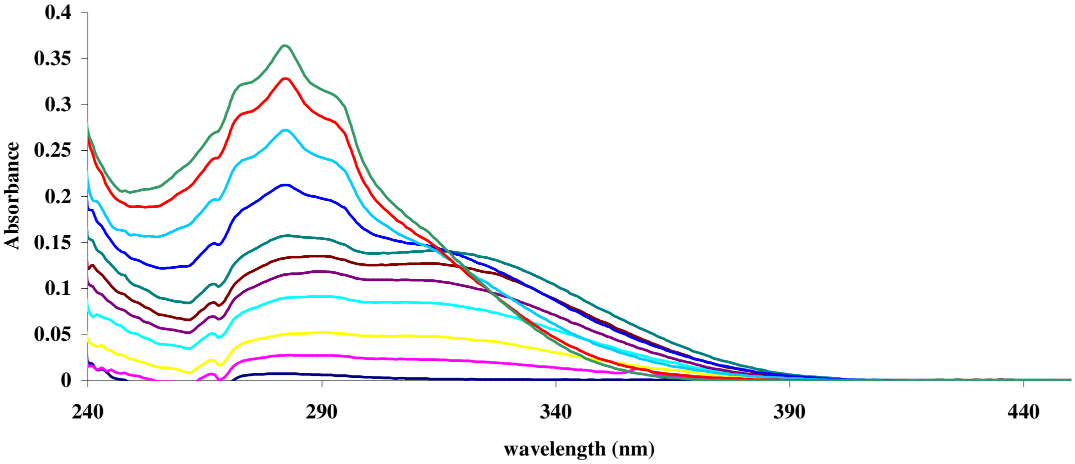
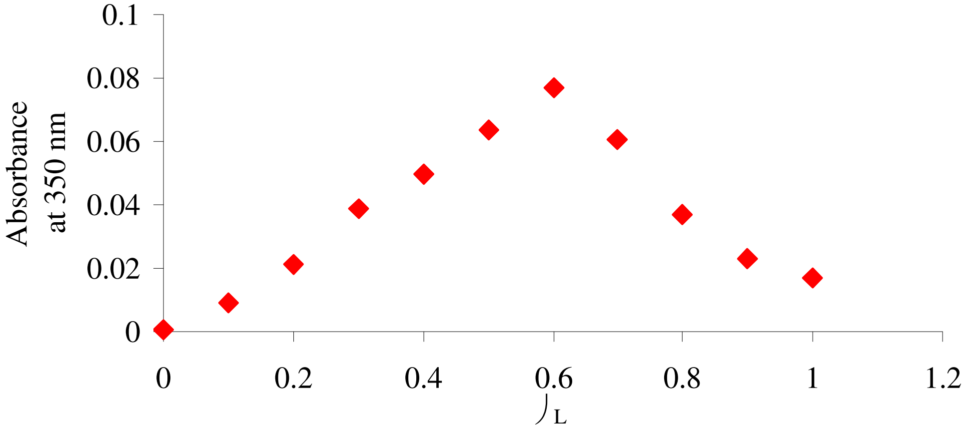


Figure S24. Job's plot for the determination of the stoichiometry of the Eu^{III} complex of ligand **2** *(S,S)*; absorbance at 350 nm measured in $CH_3CN/CHCl_3$ (50:50, v/v) *vs* χ_L ($0 \leq \chi \leq 1$); $[Eu^{III} + 67]_{tot} = 1 \times 10^{-5}$ M



5. Tables

Table S1. Life time measurements and q-value determination for **Eu$_2$:1$_3$**

Solvent	τ_1 (ms)	τ_2 (ms)	A_1	A_2	C	S.D.	q (±0.3)
H_2O	1.513	0.306	1.342	6.976	0.023	0.026	-0.36
D_2O	3.453	∅	5.483	∅	0.017	0.037	

q values in water formula: $q = A (1/\tau_{H2O} - 1/\tau_{D2O} - 0.25 - n_{NH} \times 0.075)$ with A = 1.2

Equation of the fit: $I_{615} = A_1\, e(\tau_1^{-1}) + C$

Table S2. Life time measurements and q-value determination for **Eu$_2$:2$_3$**

Solvent	τ_1 (ms)	τ_2 (ms)	A_1	A_2	C	S.D.	Q (±0.3)
H_2O	1.622	0.316	3.567	14.84	0.073	0.092	-0.44
D_2O	3.125	∅	9.262	∅	0.069	0.060	