Electronic Supplementary Material (ESI) for Chemical Communications

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

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Electronic Supporting Information

Characterisation of 1:

HRMS: Calculated for $C_{31}H_{29}N_5O_6Na$: $[L+Na]^+$ *m/z* = 590.2016; Found: 590.2019. δ_H (400 MHz, MeOD-D_4): 8.22 (d, J = 5.54 Hz, 2H, Pyr-H), 8.12 (t, J = 5.52 Hz, 1H, Pyr-H), 7.56 (d, J = 5.28 Hz, 2H, Tryp-H), 7.32 (d, J = 5.52 Hz, 2H, Tryp-H), 7.07 (t, J = 4.76 Hz, 2H, Tryp-H), 7.02 (s, 2H, Tryp-H), 6.98 (t, J = 4.76 Hz, 2H, Tryp-H), 5.00 (t, J = 3.72 Hz, 2H, -CH), 3.77 (s, 6H, $-CH_3$), 3.52 (d, J = 3.48 Hz, 4H, $-CH_2$) δc (100 MHz, MeOD-D_4): 172.7, 164.4, 148.9, 139.5, 137.1, 127.6, 125.3, 123.6, 121.6 118.9, 118.2, 111.4, 109.7, 54.1, 51.9, 27.5. IR ν_{max}: 3329.2, 1752.9, 1731.9, 1686.2, 1661.6, 1523.0, 1458.6, 1437.4, 1349.3, 1214.0, 1190.9, 1168.3, 1106.8, 1000.4, 925.7, 843.8, 752.7, 739.8, 683.7.

Characterisation of 2:

HRMS: Calculated for $C_{31}H_{29}N_5O_6Na$: $[L+Na]^+$ *m/z* = 590.2016; Found: 590.2021. δ_H (400 MHz, MeOD-D_4): 8.23 (d, J = 5.52 Hz, 2H, Pyr-H), 8.12 (t, J = 5.52 Hz 1H, Pyr-H), 7.55 (d, J = 5.28 Hz, 2H, Tryp-H), 7.32 (d, J = 5.52 Hz, 2H, Tryp-H), 7.07 (t, J = 4.48 Hz, 2H, Tryp-H), 7.02 (s, 2H, Tryp-H), 6.96 (t, J = 4.48 Hz, 2H, Tryp-H), 5.01 (t, J = 3.52 Hz, 2H, -CH), 3.77 (s, 6H, $-CH_3$), 3.52 (d, J = 3.48 Hz, 4H, $-CH_2$) δc (100 MHz, MeOD-D_4): 172.8, 164.5, 148.9, 139.5, 137.1, 127.6, 125.3, 123.7, 121.6 118.9, 118.2, 111.4, 109.7, 54.1, 52.0, 27.5. IR ν_{max}: 3330.2, 1753.3, 1731.9, 1686.6, 1661.6, 1523.8, 1458.7, 1437.9, 1357.3, 1214.3, 1191.2, 1166.6, 1073.4, 1000.6, 925.2, 844.0, 780.9, 752.9, 739.8.

General procedure for the synthesis of the complexes L_3.Tb:

Ligands **1 or 2** (3 equivalents) and $Tb(CF_3SO_3)_3$ (1.1 equivalents) were refluxed for 12 hours in acetonitrile. The resulting mixture was poured onto diethyl ether and the resulting of white solids isolated by filteration under reduced pressure. The resulting complexes were recrystalised from methanol.

Complex formed of 1 with Tb(III)

The synthesis of **1_2.Tb** was performed following the general procedure with ligand **1** (31.7 mg, 0.056 mmol) and $Tb(CF_3SO_3)_3$ (12.4 mg, 0.020 mmol). The resulting complex was obtained (25.4 mg, 0.011 mmol) in 72 % yield. Calculated for $C_{64}H_{58}F_6N_{10}O_{18}S_2Tb$: $[L_2.Tb + 2\times CF_3SO_3]^+$ *m/z* = 1591.2529; Found: 1591.2505. δ_H (400 MHz, MeOD-D_4) 33.2, 30.9, 26.8, 25.0, 11.6, 10.2, 9.5, 8.2, 7.6, 7.3, 7.0, 4.9, 3.7, 3.5, 3.3, 1.4, -10.4, -15.6. IR ν_{max}: 3333.3, 2947.2, 1732.6, 1662.1, 1522.8, 1438.1, 1349.7, 1216.0, 1168.6, 1105.5, 1073.8, 1029.8, 1008.3, 844.1, 752.13, 740.3, 685.2.

Complex formed from 2 with Tb(III)

The synthesis of **2_2.Eu** was performed following the general procedure with ligand **4** (17.1 mg, 0.03 mmol) and $Tb(CF_3SO_3)_3$ (6.7 mg, 0.01 mmol). The resulting complex was obtained (15.7 mg, 0.007 mmol) in 90%. Calculated for $C_{64}H_{58}F_6N_{10}O_{18}S_2Tb$: $[L_2.Tb + 2\times CF_3SO_3]^+$ *m/z* = 1591.2529; Found: 1591.2590. δ_H (400 MHz, MeOD-D_4) 33.3, 31.1, 26.8, 25.0, 11.7, 10.2, 9.5, 8.2, 8.1, 7.6, 7.3, 7.1, 6.9, 4.9, 3.8, 3.5, 3.3, 2.2, 1.3, 0.9, -10.5, -15.6. IR ν_{max}: 3327.3, 2949.9, 2445.0, 1732.6, 1662.0, 1521.8, 1438.3, 1342.6, 1235.4, 1169.8, 1105.4, 1074.5, 1029.7, 1001.4, 917.0, 843.6, 751.5, 739.3, 688.2.

Figure S1 ^{1}H and ^{13}C NMR of **1**

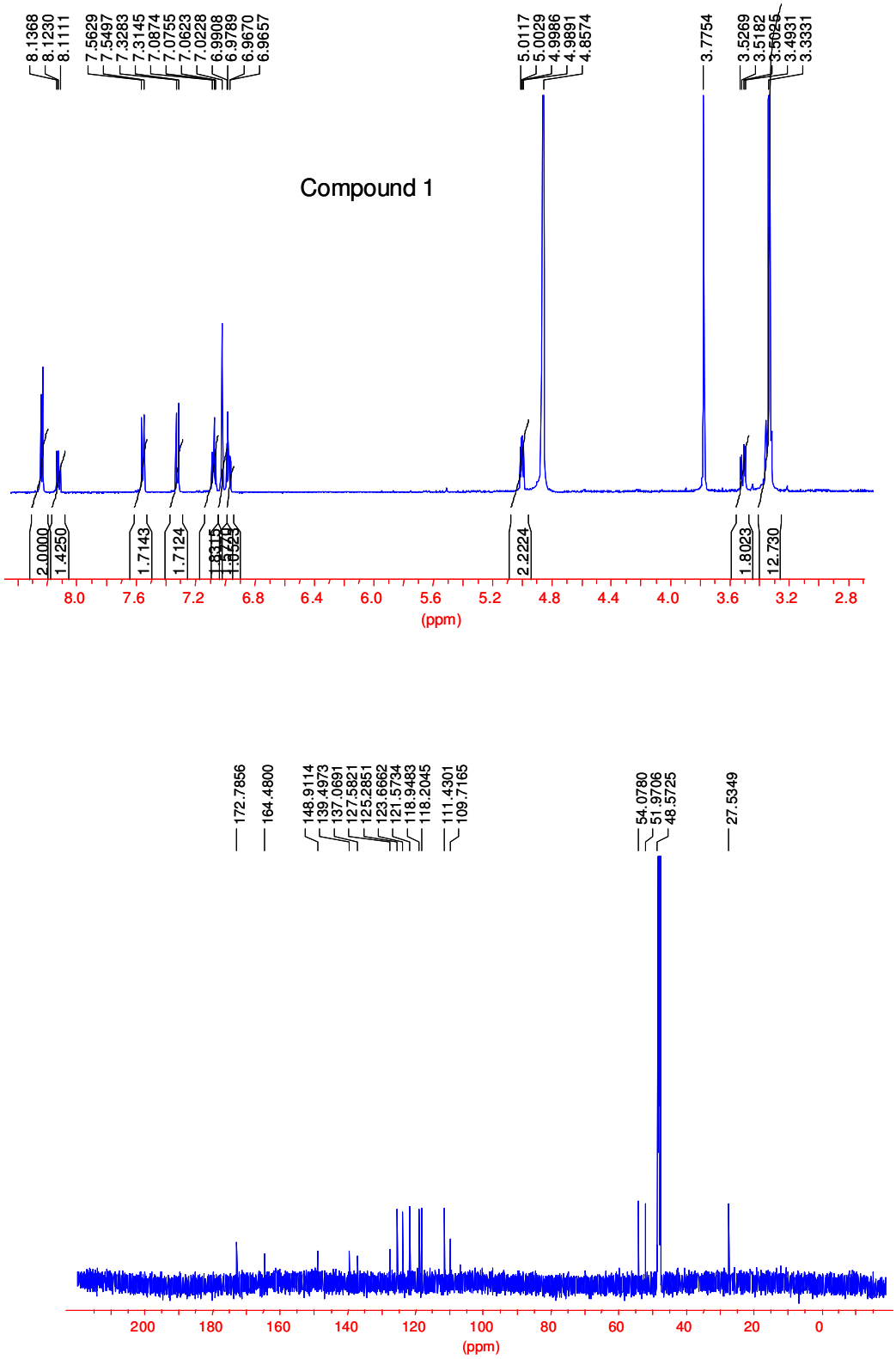

Figure S2 ^{1}H and ^{13}C NMR of **2**

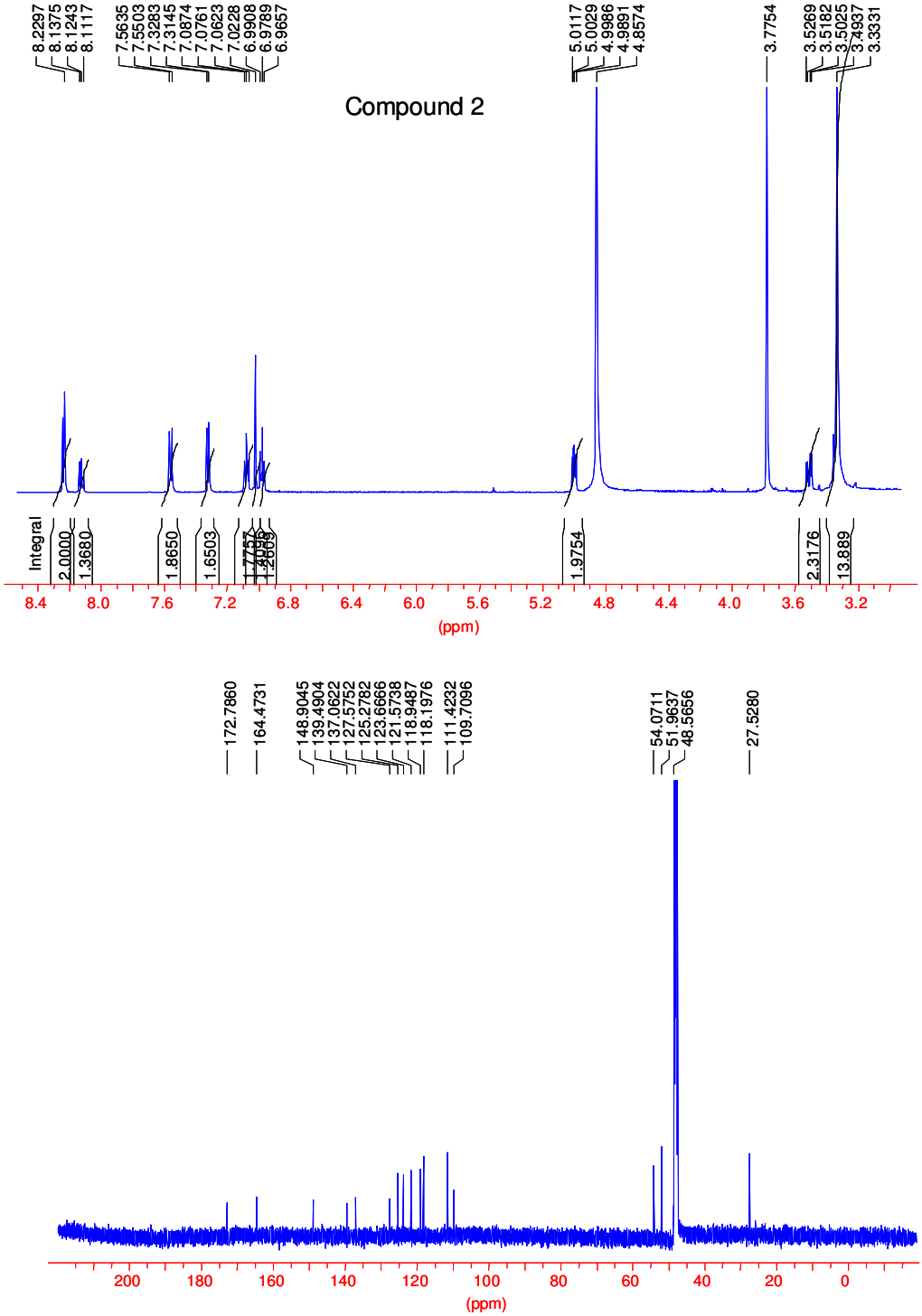

Figure S3 ^{1}H of **1_2Tb**

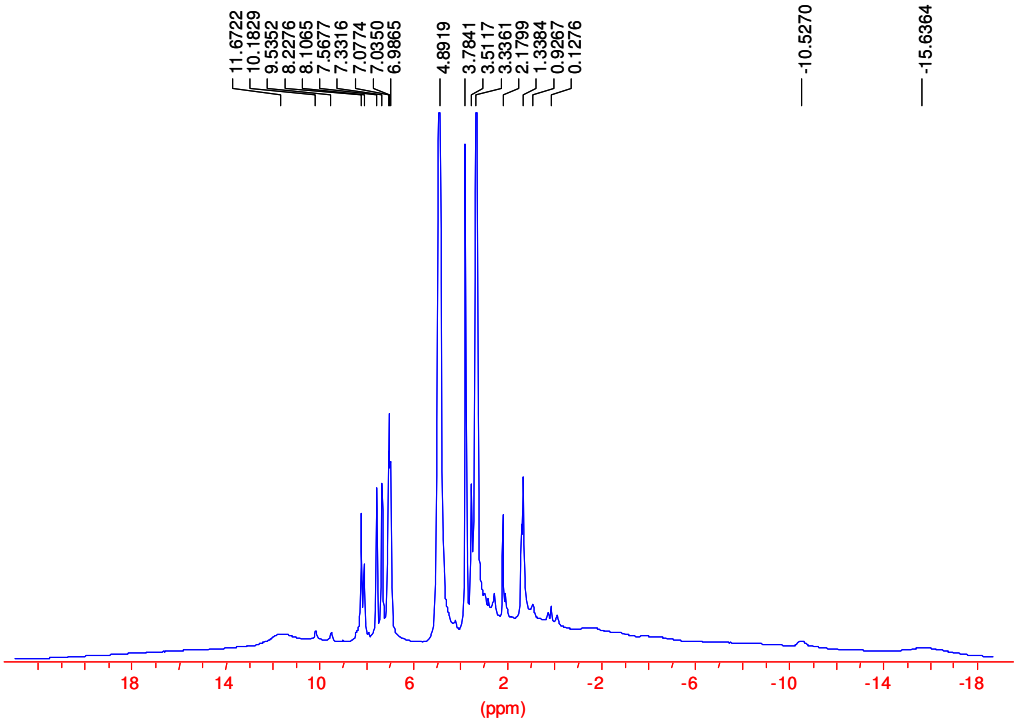

Figure S3 ^{1}H of **2_2Tb**

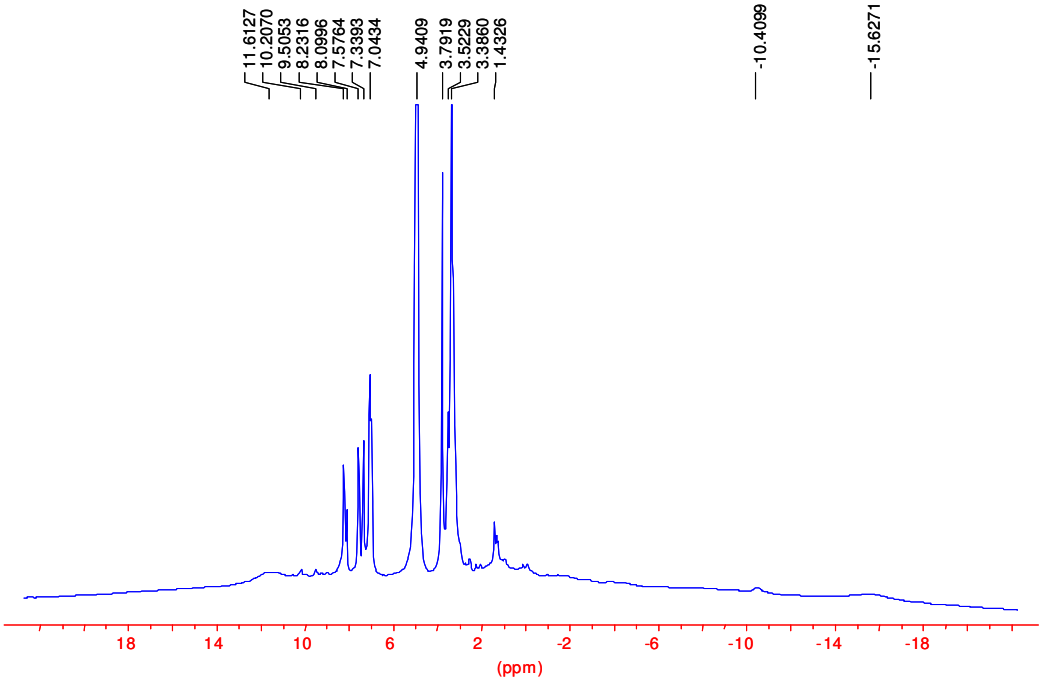

Figure S5 CD- spectra of **1** and **2**

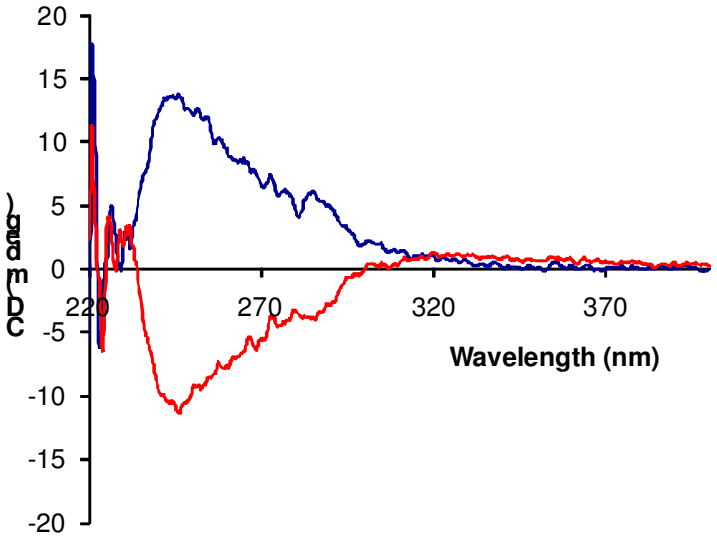

Figure S6 CD-Spectra of $\mathbf{1_2Tb}$ and $\mathbf{2_2Tb}$

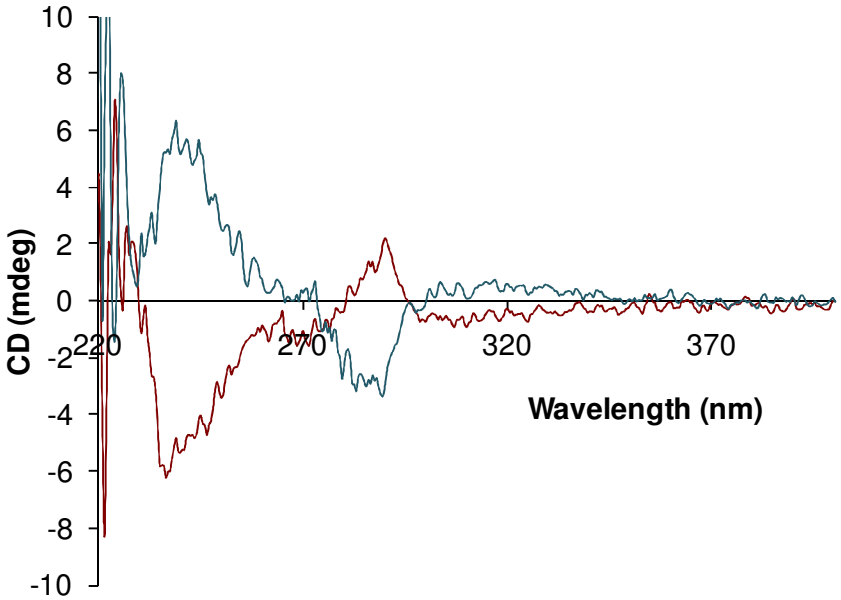

Figure S7 MS of **2_2Tb**

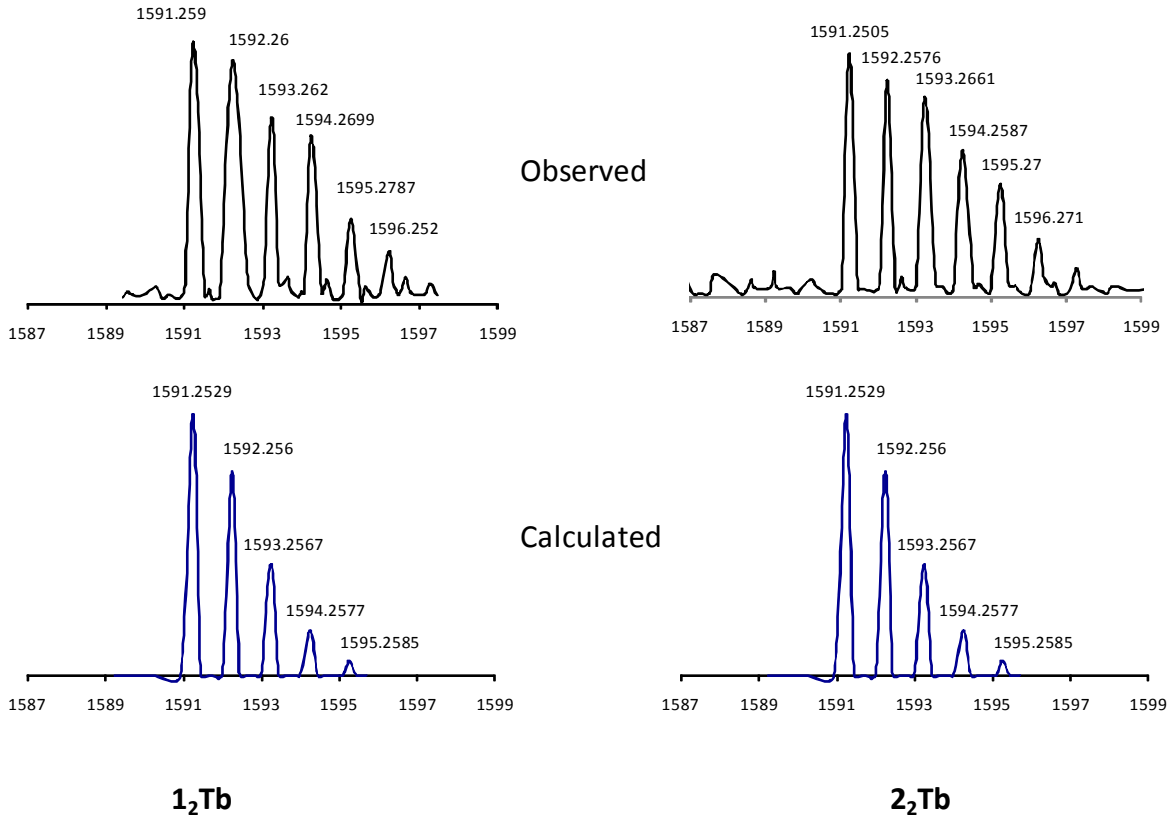

Figure S8 Tb(III) emission from **2_2Tb**

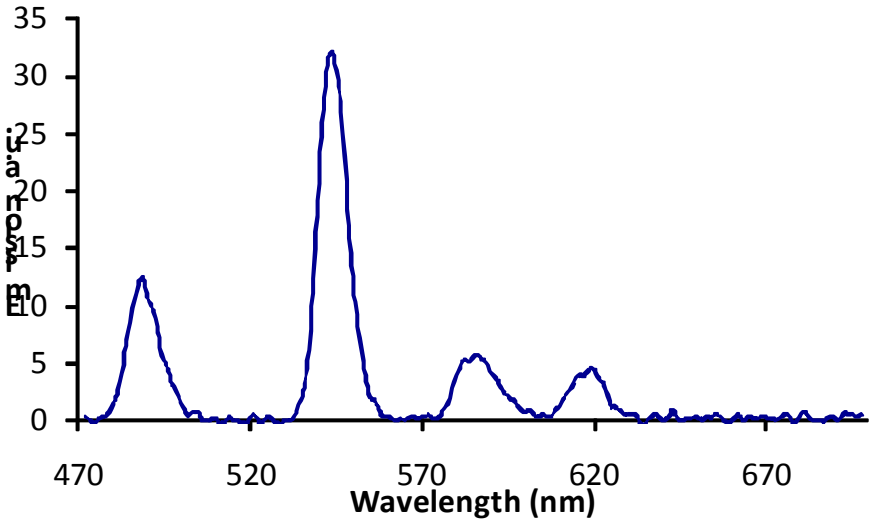

Figure 9 Changes in the fluorescence emission of **1** upon addition of 0 and 05. equivalents of Tb(III)

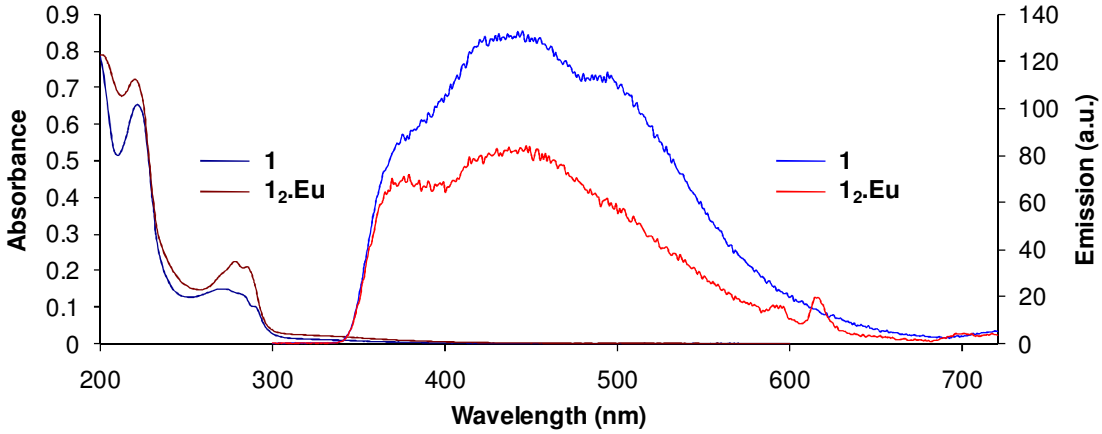

Figure 10 The speciation distribution diagram for the formation of **2_2Tb** from **2**

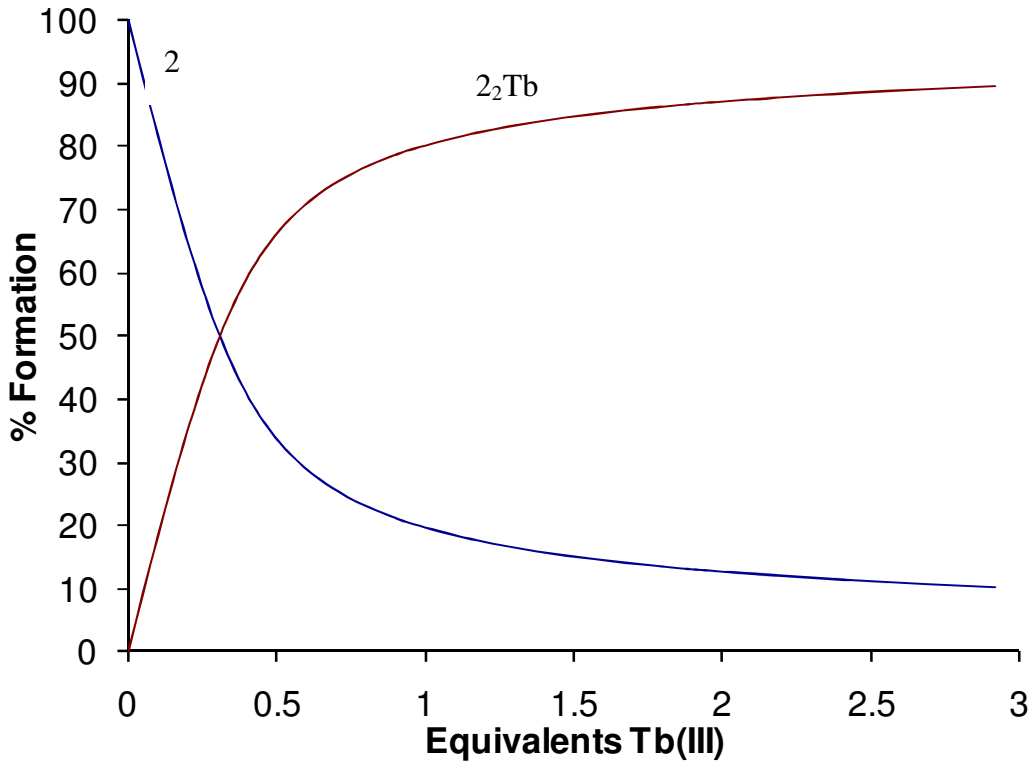

Figure 11 The speciation distribution diagram for the formation of $\mathbf{1_2Eu}$ from **1**