Formation of lanthanide luminescent di-metallic helicates in solution using a bis-tridentate (1,2,3-triazol-4-yl)-picolinamide (tzpa) ligand

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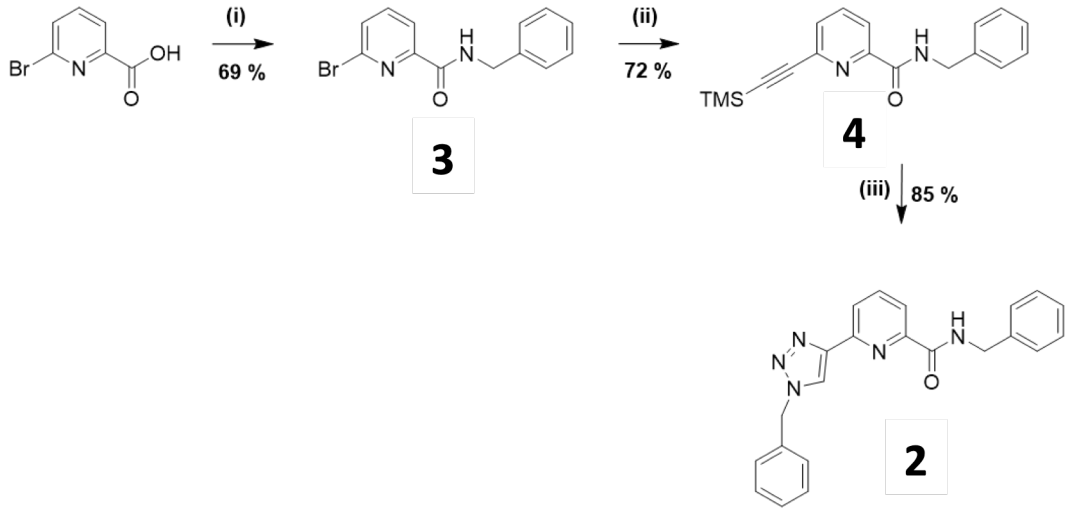
Electronic Supplementary Information (ESI)

Characterisation of Ligand **1**.

*N,N'-(*1,3-phenylenebis(methylene))bis(6-(1-((S)-1-phenylethyl)-1H-1,2,3-triazol-4-yl)picolinamide)

Obtained as white solid (48 mg, 0.012 mmol, 62%).; m.p. 118 – 123 ºC; HRMS (*m/z*) (ESI+): $C_{40}H_{37}N_{10}O_2^+$ *m/z* = 689.3101 $[M+H]^+$. Found *m/z* = 689.3109; ^{1}H NMR (600 MHz, DMSO-d_6): δ (ppm) = 9.41 (t, 2H, NH), 8.98 (s, 2H, triazolyl H), 8.18 (dd, *J* = 7.8, 1.0 Hz, 2H, pyr CH-triazole), 8.02 (t, 2H, *ortho* pyr CH), 7.91 (dd, *J* = 7.7, 1.0 Hz, 2H, pyr CH-Ar), 7.45 – 7.09 (m, 14H, Ar CH), 6.05 (q, *J* = 7.1 Hz, 2H, *CH*-CH_3), 4.55 (d, *J* = 6.5 Hz, 4H, CH_2), 1.95 (d, *J* = 7.1 Hz, 6H, CH_3); ^{13}C NMR (150 MHz, DMSO-d_6): δ (ppm) = 163.75, 149.53, 148.78, 146.79, 140.98, 139.59, 138.79, 128.82, 128.37, 128.05, 126.09, 125.61, 123.03, 121.57, 120.73, 64.90, 59.51, 42.28, 21.29; IR ν_{max} (cm^{-1}): 3326, 2934, 2165, 1664, 1660, 1518, 1444, 1241, 1172, 1076, 995, 830, 765, 697.

Synthesis



Scheme S1. Synthesis of ligand **2**.

N-Benzyl-6-bromopicolinamide (3)

Compound **3** was synthesized from 6-bromopyridine-2-carboxylic acid (2.0 g, 9.9 mmol) and benzylamine (1.1mL, 10.8 mmol) in a DMF:DCM (4:1) solvent mixture. Under argon, then to this solution was added HOBt (1 equivalent), NEt_3 (1.2 equivalents), and the reaction mixture was left to stirr for 30 mins, after which it was cooled to 0 °C. EDC·HCl (1.5 equivalents) was then added to the suspension and the rsulting mixture stirred at 0 °C for a further 30 mins. The mixture was then allowed to warm to room temperature and stirred for a further 48 hrs. The product was dried under reduced pressure and taken up in CH_2Cl_2, washed with 1M HCl, sat. $NaHCO_3$ and H_2O dried over magnesium sulfate and concentrated under reduced pressure to yield orange oil. This resulting oil was dried to a solid by repeated evaporation under reduced pressure with toluene to give compound **3** in 69% yield. m.p. 167 - 174 ºC; HRMS (*m/z*) (ESI+): $C_{13}H_{11}BrN_2O^+$ *m/z* = 291.0133 $[M+H]^+$. Found *m/z* = 291.0127; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) = 8.20 (d, *J* = 7.7 Hz, 1H, Ha), 8.14 (s, *J* = 6.2 Hz, 1H, NH), 7.72 (t, *J* = 7.7 Hz, 1H, Hb), 7.61 (d, *J* = 7.7 Hz, 1H, Hc), 7.36 (dd, *J* = 8.3, 5.5 Hz, 4H, Hd & He), 7.33 – 7.27 (m, 1H, *J* = 8.3, 5.5 Hz, Hf), 4.67 (d, *J* = 6.2 Hz, 2H, CH_2); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) = 162.9, 151.1, 140.7, 139.8, 138.1, 130.9, 128.9, 128.1, 127.8, 121.6, 43.7; IR ν_{max} (cm^{-1}): 3354, 3318, 3166, 3033, 2942, 1736, 1639, 1603, 1568, 1527, 1502, 1451, 1374, 1278, 1247, 1222, 1161, 1089, 1049, 972, 865, 819, 764, 743, 728, 687, 631, 606.

N-benzyl-6-((trimethylsilyl)ethynyl)picolinamide (4)

To a solution of **3** (1 g, 3.43 mmol) in THF/NEt_3 stirring at 0 °C (4:1, 40 mL), CuI (0.2 mmol) and $Pd(PPh_3)_4$ (0.2 mmol) were added under an argon atmosphere. Ethynyltrimethylsilane (0.5 mL, 3.43 mmol) was added dropwise and left to stir at room temperature for 48 hrs. The resulting solution was concentrated under reduced pressure and filtered through a plug of celite to yield a brown solid which was purified by flash column chromatography (RediSep® 24g, gradient elution 0 → 20 % EtOAc in Hexane) to yield **4** as a brown solid in 63% yield. m.p. 187 - 191 ºC; HRMS (*m/z*) (ESI+): $C_{18}H_{21}N_2OSi^+$ *m/z* = 309.1418 $[M+H]^+$. Found *m/z* = 309.1418; ^{1}H NMR (600 MHz, DMSO-d_6): δ (ppm) = 9.22 (t, 1H, *J* = 6.4 Hz, NH), 8.02 (m, *J* = 7.5, 1.1 Hz, 2H, pyr H), 7.74 (dd, *J* = 7.5, 1.1 Hz, 1H, pyr H), 7.37 – 7.25 (m, 4H, Ar H), 7.27 – 7.18 (m, 1H, Ar H), 4.49 (d, *J* = 6.4 Hz, 2H, CH_2), 0.26 (s, 9H, CH_3-Si); ^{13}C NMR (150 MHz, DMSO-d_6): δ (ppm) = 163.8, 151.0, 141.2,139.9, 139.0, 130.6, 128.7, 127.9, 127.3, 122.5, 104.0, 95.7, 43.0, 0.1; IR ν_{max} (cm^{-1}): 3371.0, 1674.1, 1520.7, 1442.9, 1248.4, 841.6, 762.4, 645.7, 610.3

N-benzyl-6-(1-benzyl-1H-1,2,3-triazol-4-yl)picolinamide (2)

Ligand **2** was synthesised from benzylbromide (0.13 mL, 1.135 mmol) and sodium azide (1.135 mmol) which were added to a mixture of DMF/H_2O (4:1)

(15 mL) and stirred for an hour. To the mixture $CuSO_4.5H_2O$ sodium ascorbate (0.9 mmol), and K_2CO_3 (1.135 mmol) were added and the mixture was degassed. Finally **4** (0.35 g, 1.13 mmol) in DMF (2 ml) was added. The reaction was stirred at r.t. under Ar for 48 hrs and dried under reduced pressure. A solution of EDTA/NH_4 (15 mL) was added and the product was extracted into DCM, washed with H_2O (3x30 mL) and dried over $MgSO_4$. The solution was concentrated under reduced pressure to yield a white solid (85% yield) HRMS (*m/z*) (ESI+): $C_{22}H_{20}N_5O^+$ *m/z* = 370.1662 $[M+H]^+$. Found *m/z* = 370.1662; ^1H NMR (600 MHz, DMSO-d_6): δ (ppm) = 9.47 (t, 1H, *J* = 6.5 Hz, NH), 8.98 (s, 1H, triazole H), 8.21 (d, *J* = 7.8, 0.6 Hz, 1H, pyr H), 8.09 (t, 1H, *J* = 7.8 Hz, pyr H), 7.99 (d, 1H, *J* = 7.8, 0.6 Hz, Pyr H), 7.39 – 7.23 (m, 10H, Ar H), 5.73 (s, 2H, CH_2-triazole), 4.56 (d, *J* = 6.5 Hz, 2H, CH_2-NH); ^{13}C NMR (150 MHz, DMSO-d_6): δ (ppm) = 163.8, 149.7, 148.8, 147.2, 139.5, 138.9, 135.9, 128.9, 128.3, 128.2, 127.7, 127.1, 126.8, 124.5, 121.7, 120.9, 53.2, 42.3; IR ν_{max} (cm^{-1}): 3322.8, 1654.9, 1601.8, 1571.5, 1521.9, 1545.6, 1420.3, 1354.1, 1257.3, 1232.6, 1168.8, 1042.9, 995.4, 977.0, 820.2, 750.7, 716.7, 696.3, 582.9.

Figures

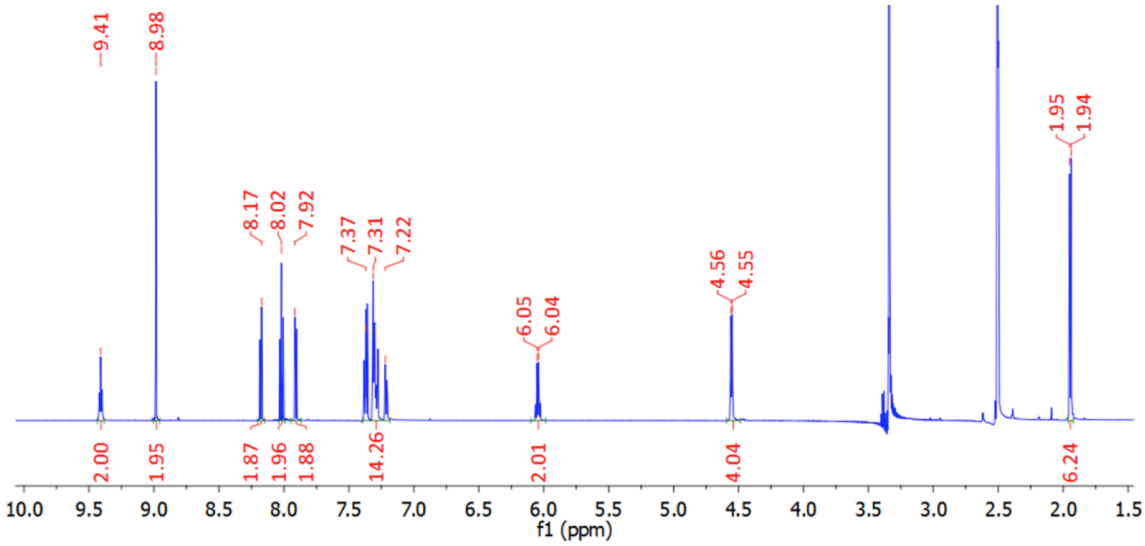


Figure 1S. The ^1H NMR spectrum (600 MHz, DMSO-d_6) of **1**.

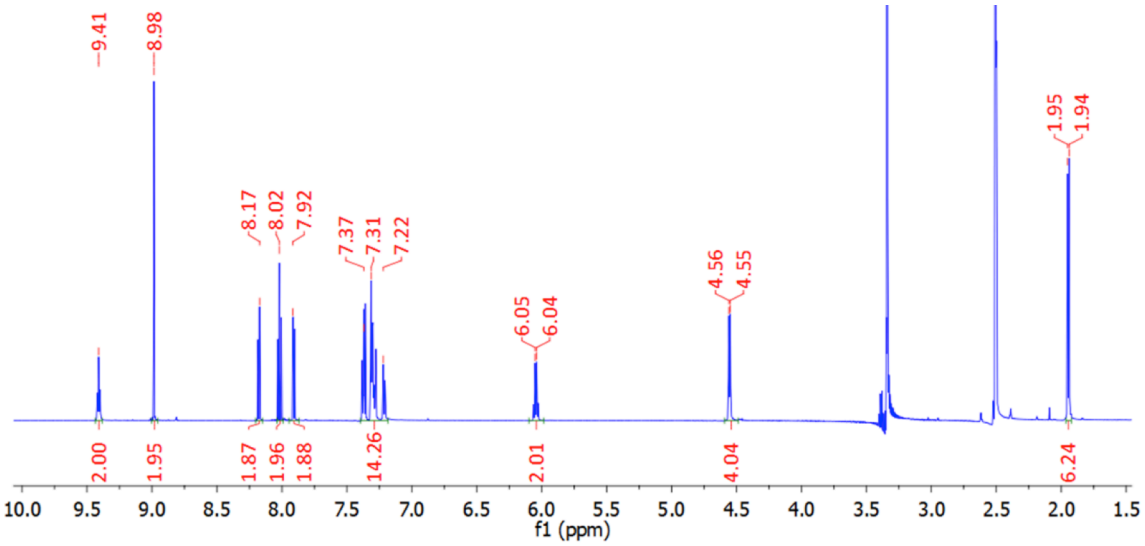


Figure 2S. The ^{1}H NMR spectrum (600 MHz, DMSO-d_6) of **2**.

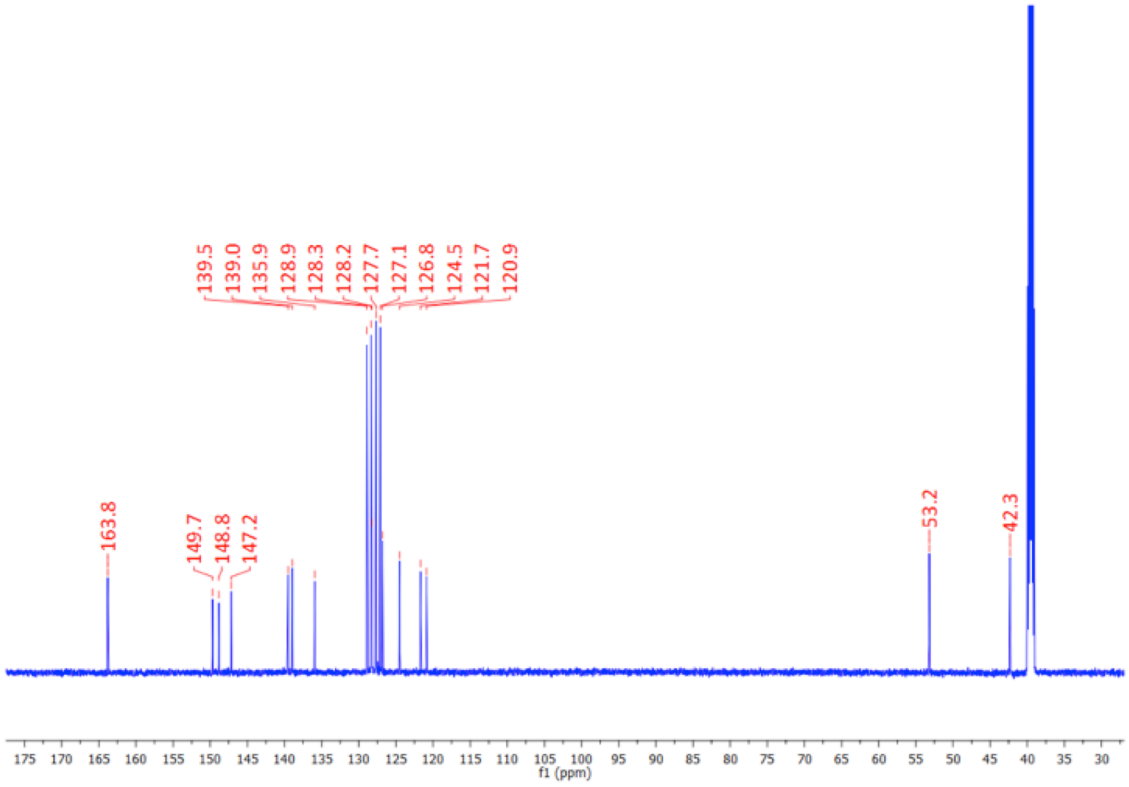


Figure 3S. The ^{13}C NMR spectrum (150 MHz, DMSO) of **2**.

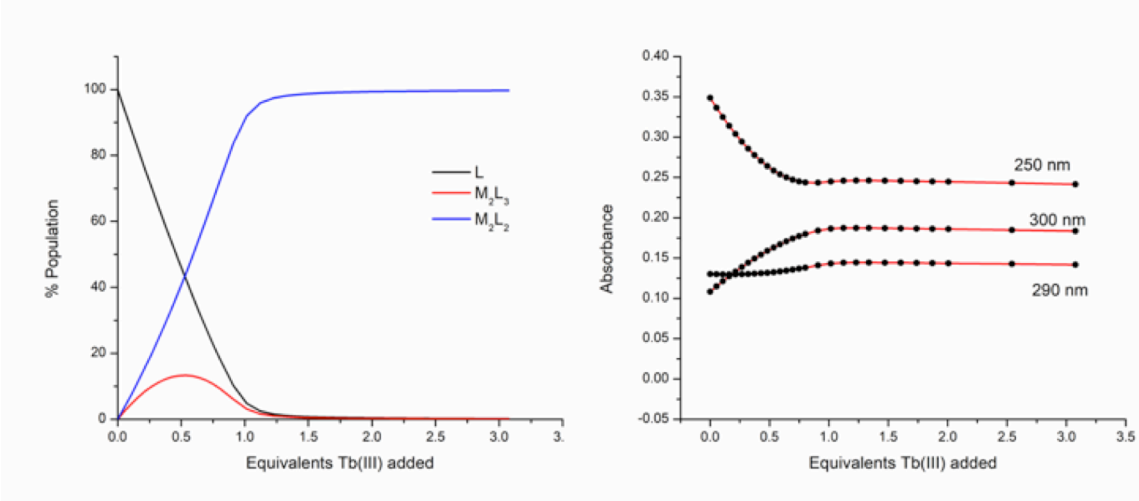


Figure 4S. (left) The speciation distribution diagram obtained from the fit of the UV-visible absorption titration data of ligand **1** against $Tb(CF_3SO_3)_3$ in CH_3CN. (right) The fit of the experimental binding isotherms using non-linear regression analysis software ReactLab.

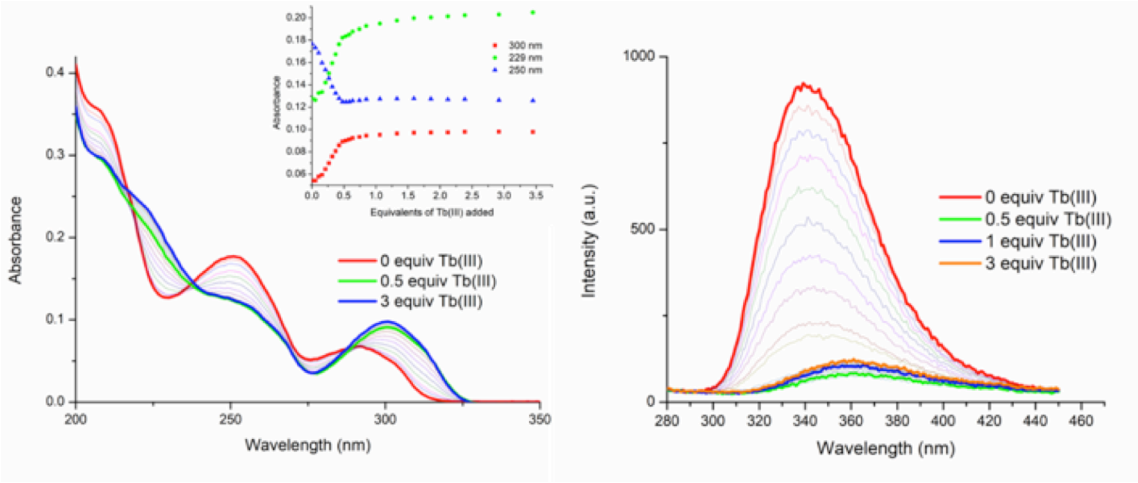


Figure 5S. The overall changes in the (left) UV-visible absorption spectra and (right) fluorescence emission spectra (excitation wavelength λ = 250 nm) upon titrating **2** (1×10^{-5} M) against $Tb(CF_3SO_3)_3$ (0→3 equiv.) in CH_3CN at RT. **Inset**: Corresponding experimental binding isotherms of absorbance at λ = 300, 230 and 250 nm.

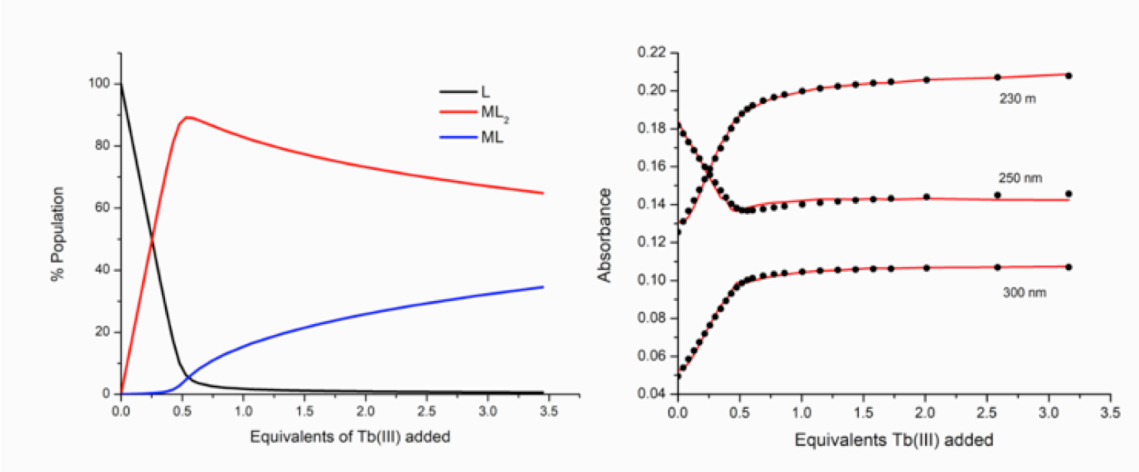


Figure 6S. (left) The speciation distribution diagram obtained from the fit of the UV-visible absorption titration data of ligand **2** against $Tb(CF_3SO_3)_3$ in CH_3CN. (right) The fit of the experimental binding isotherms using non-linear regression analysis software ReactLab.

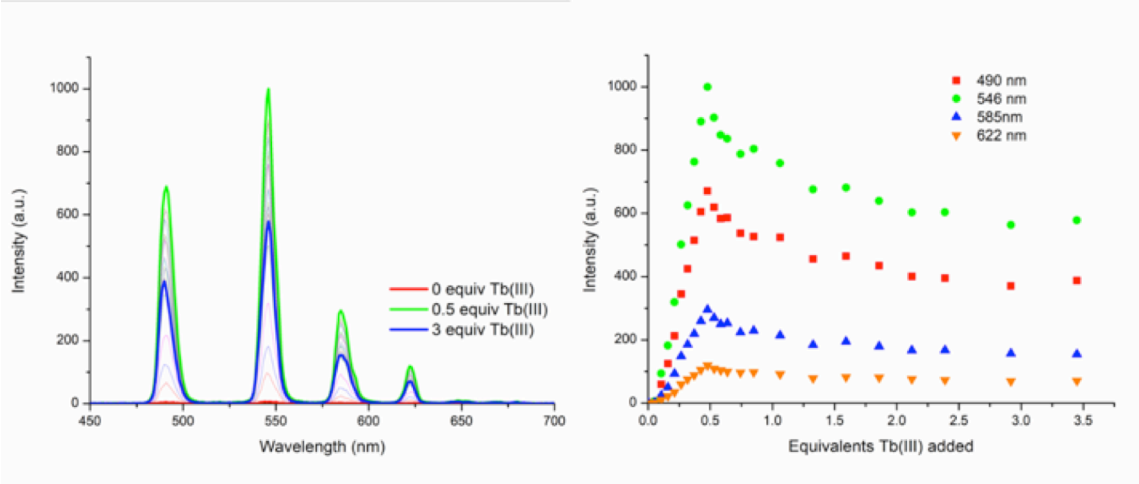


Figure 7S. The overall changes in the (left) UV-visible absorption spectra and (right) fluorescence emission spectra (excitation wavelength λ = 250 nm) upon titrating **2** (1×10^{-5} M) against $Tb(CF_3SO_3)_3$ (0→3 equiv.) in CH_3CN at RT. **Inset**: corresponding experimental binding isotherms of absorbance at λ = 300, 230 and 250 nm.

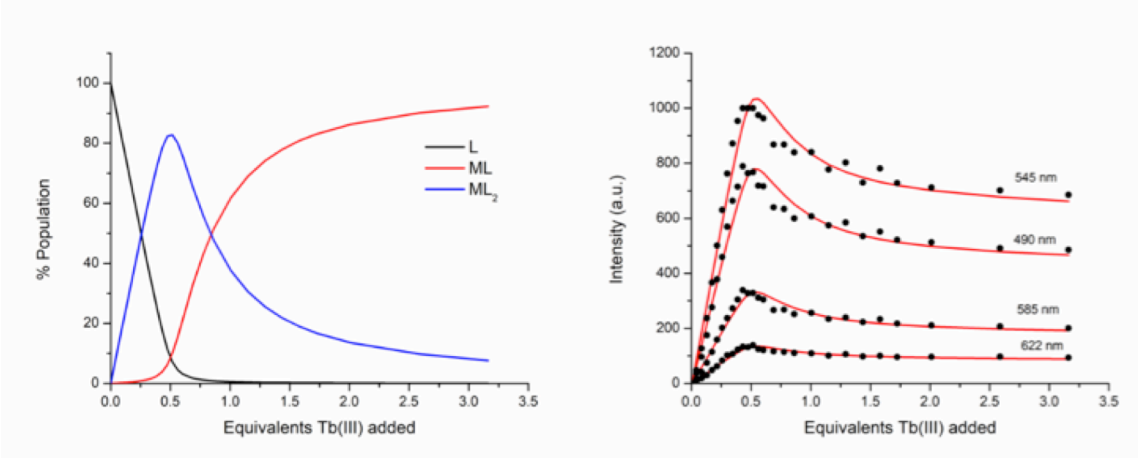


Figure 8S. (left) The speciation distribution diagram obtained from the fit of the time-gated luminescence titration data of ligand **2** against $Tb(CF_3SO_3)_3$ in CH_3CN. (right) The fit of the experimental binding isotherms using non-linear regression analysis software ReactLab.

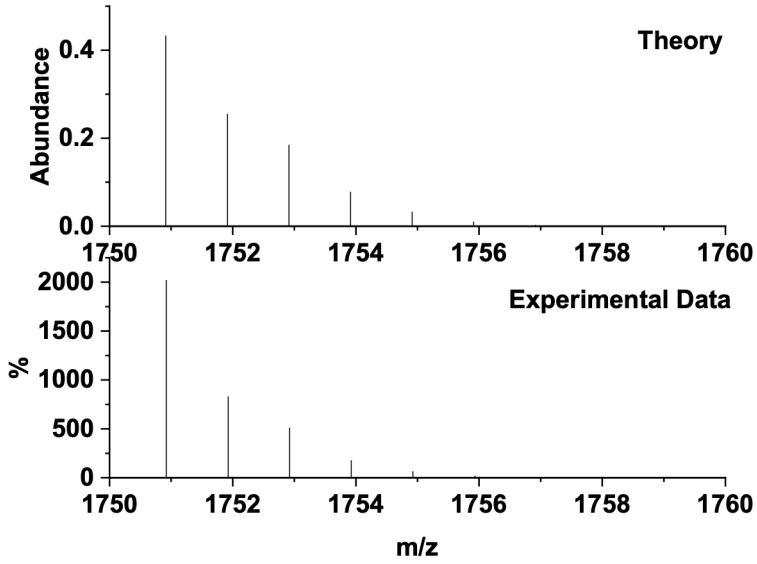


Figure 9S. The HRMS of **1** in the presence of Tb(III) showing the **2M:L**: $C_{45}H_{36}F_{15}N_{10}O_{17}S_5Tb_2$ m/z = 1750.9125, found 1750.9208.

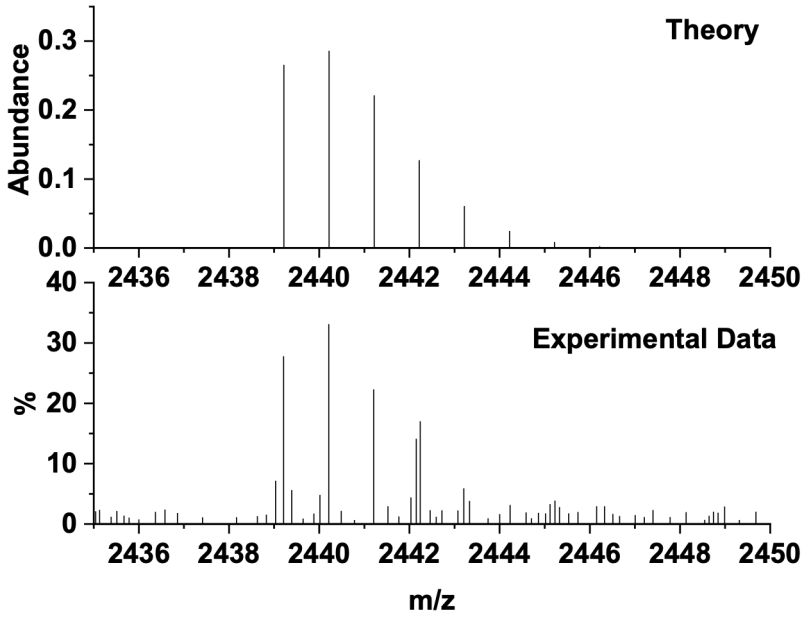


Figure 10S. The HRMS of **1** in the presence of Tb(III) showing the **2M:2L**: $C_{85}H_{72}F_{15}N_{20}O_{19}S_5Tb_2$ m/z = 2439.2148, found 2439.2107.