Synthesis of α-amino acid derived (1,2,3-triazol-4-yl)-picolinamide (tzpa) ligands and their corresponding luminescent Tb(III) complexes

Isabel N. Hegarty, Chris S. Hawes, and Thorfinnur Gunnlaugsson

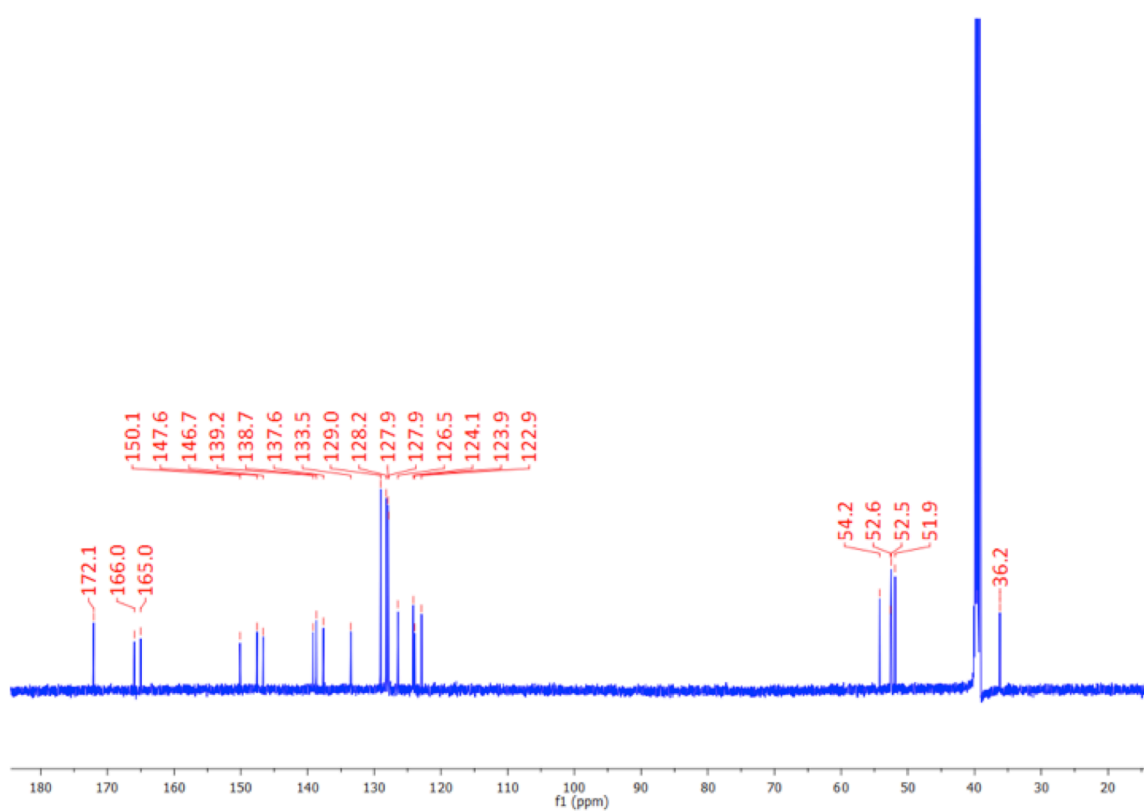**Electronic Supplementary Information (ESI)**

Figures

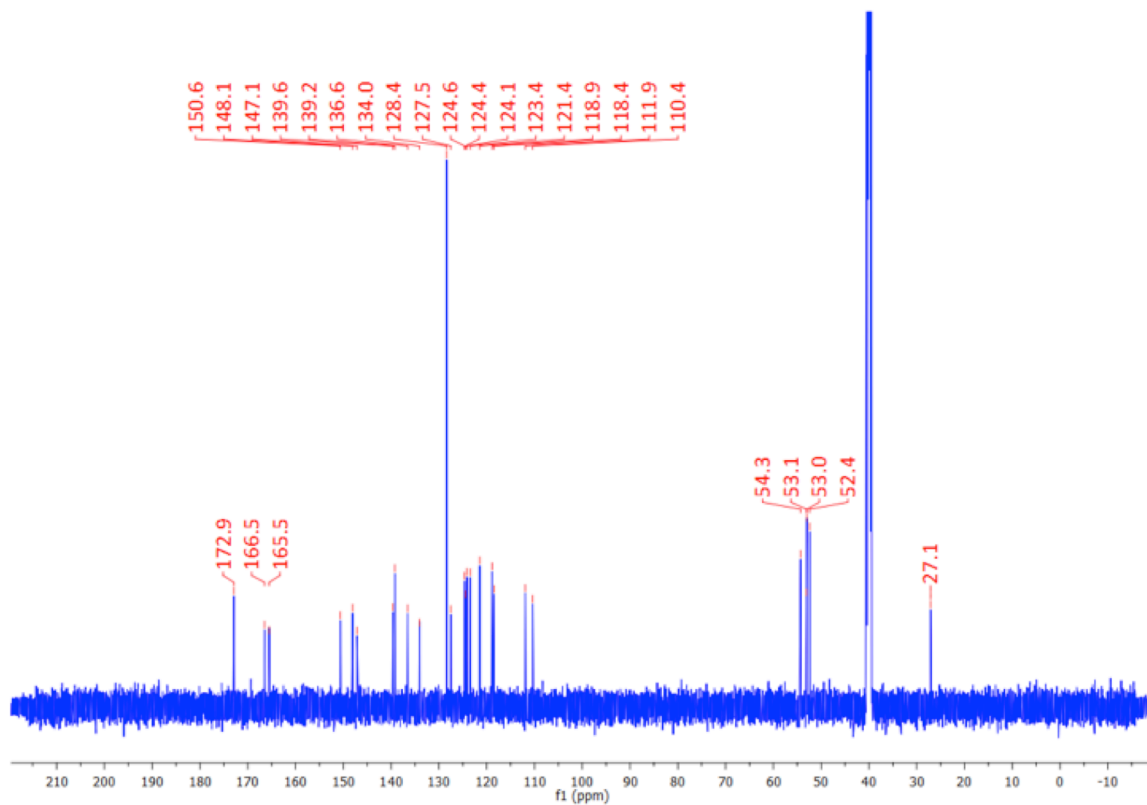***Figure S1.*** *^{13}C NMR spectrum (150 MHz, DMSO) of **4**.*

Figure S2. ^{13}C NMR spectrum (150 MHz, DMSO) of **5**.
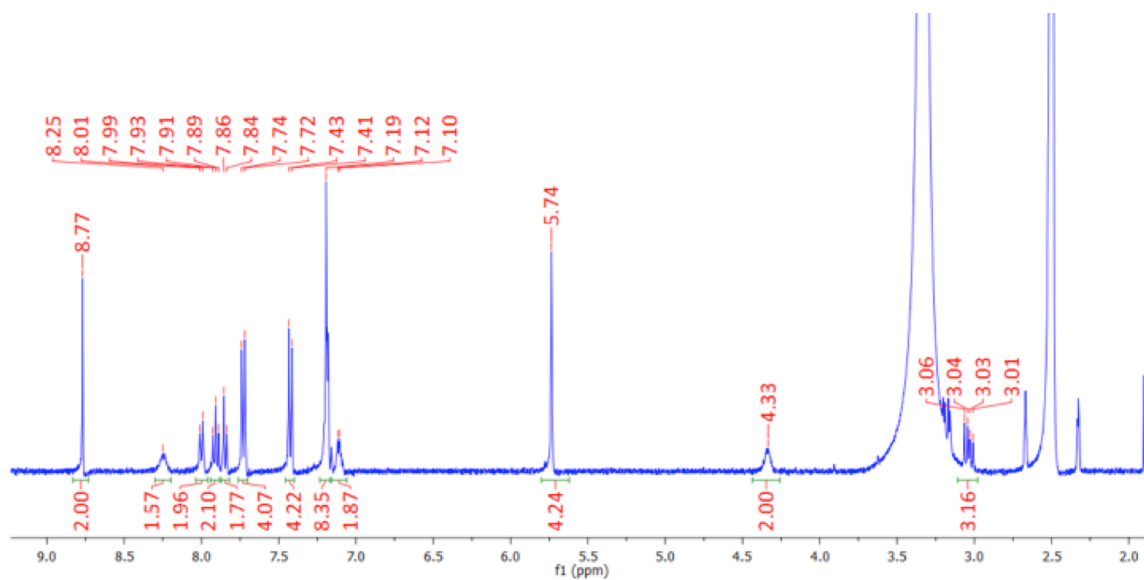

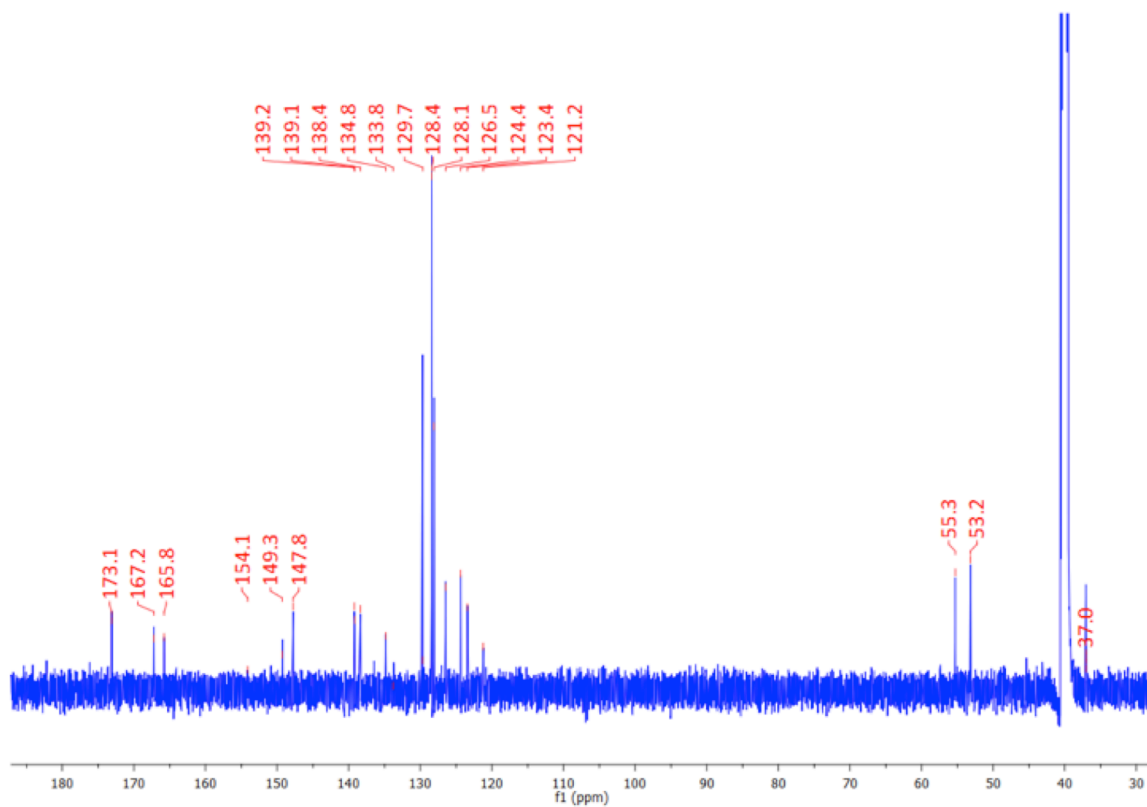*Figure S3.* ^{1}H NMR spectrum (600 MHz, DMSO) of **6**.

Figure S4. ^{13}C NMR spectrum (150 MHz, DMSO) of **6**.
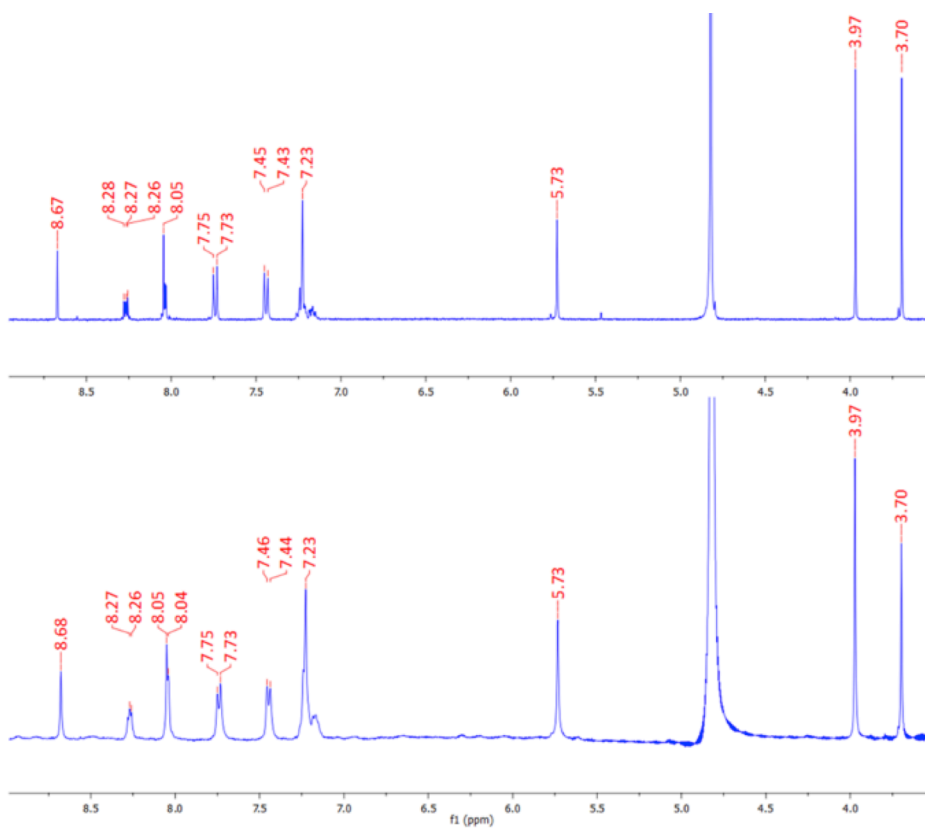

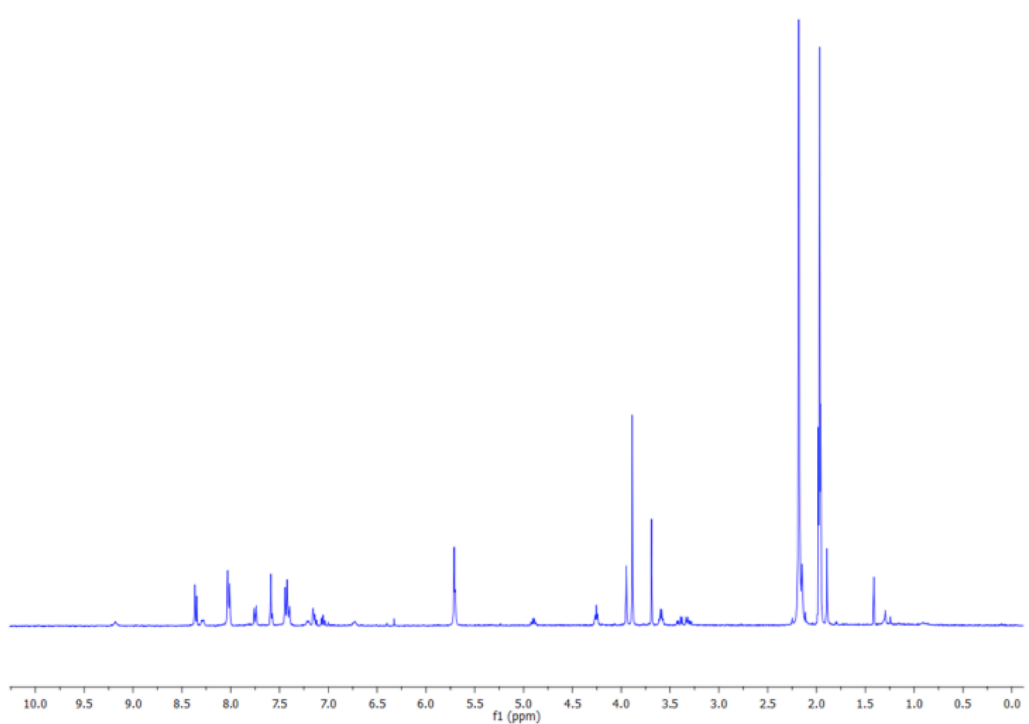**Figure S5.** ^1H NMR spectra of (top) **4** and (bottom) [Tb(**4**)$_3$]$^{3+}$ (400 MHz, CD$_3$CN).

Figure S6. *¹H NMR spectrum (400 MHz, CD₃CN) of Tb.**5**₃.*
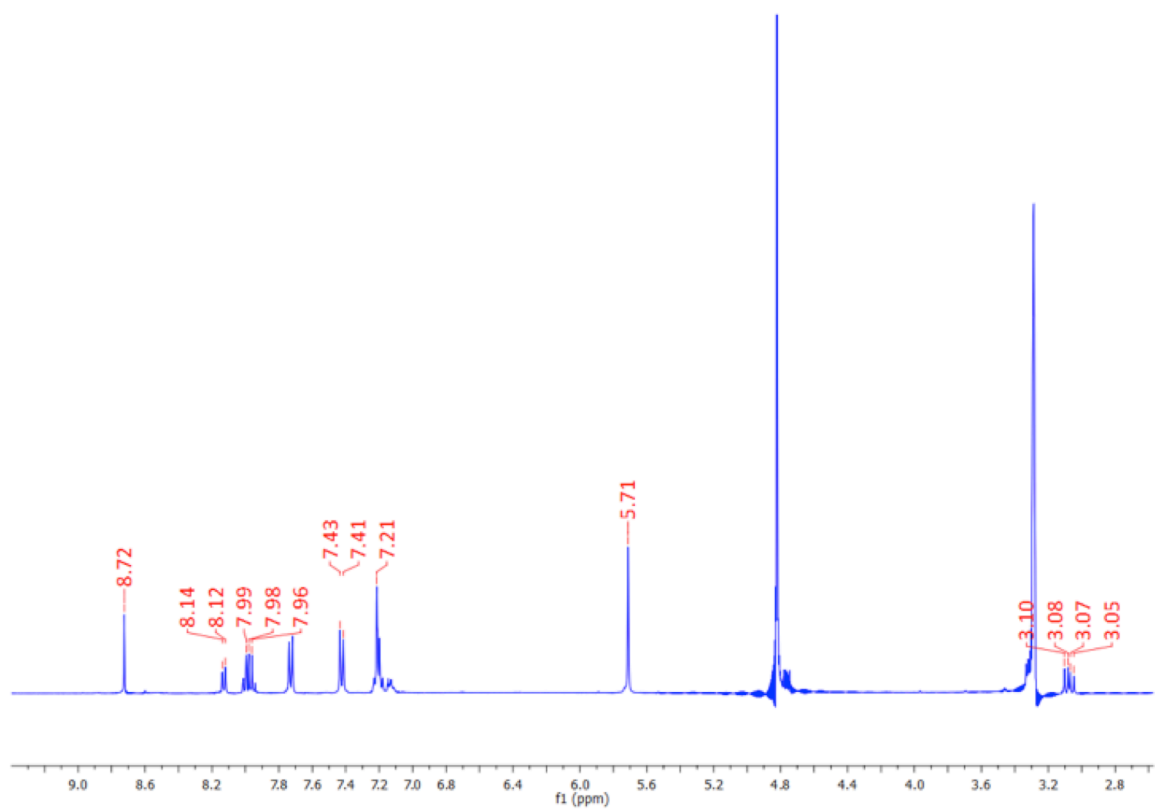
Figure S7. *¹H NMR spectrum (400 MHz, CD₃CN) of Tb.**6**₃.*

Figure S8. The calculated and experimental isotopic distribution patterns for Tb.4_2 showing the 1:2 metal:ligand stoichiometric pattern for a molecular species of the formula $[Tb(\mathbf{4})_2](CF_3SO_3)_2{}^+$

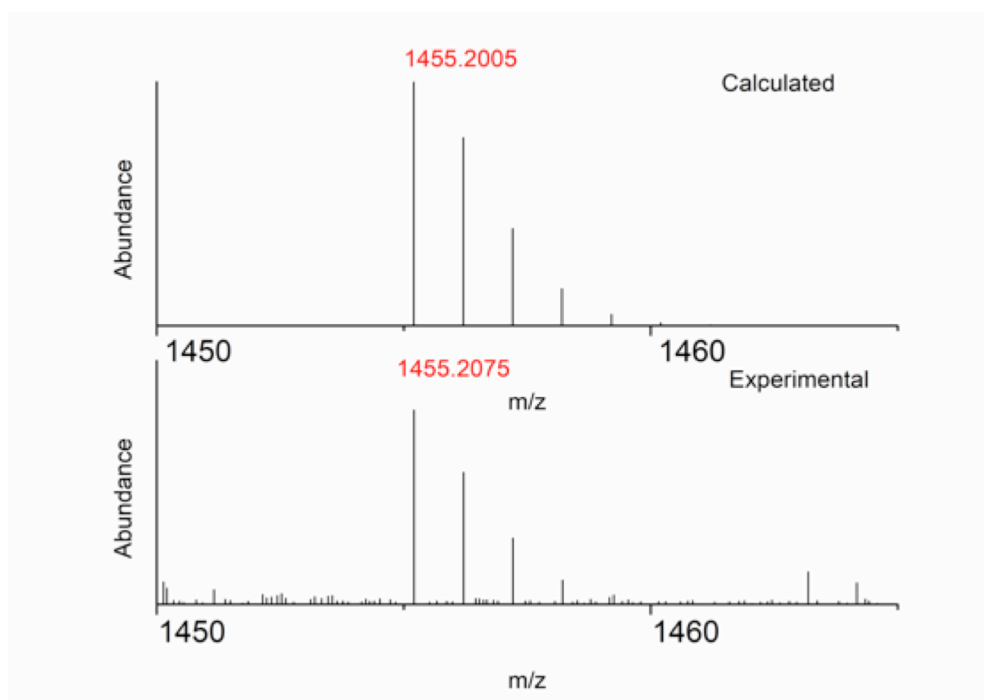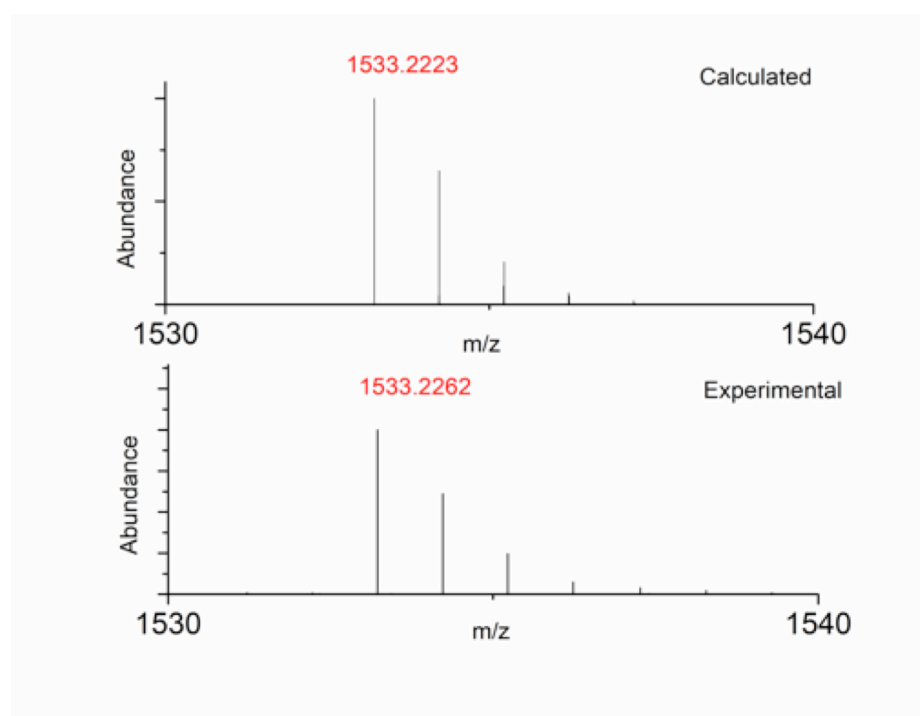**Figure S9.** The calculated and experimental isotopic distribution patterns for Tb.5_2 showing the 1:2 metal:ligand stoichiometric pattern for a molecular species of the formula $[Tb(\mathbf{5})_2](CF_3SO_3)_2{}^+$
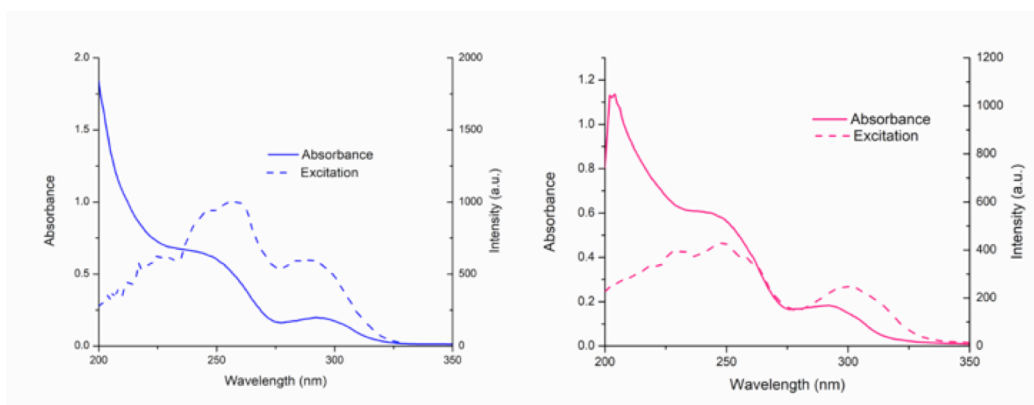
Figure S10. *(Left) The UV-Vis absorbance and excitation (λ_{em} = 545 nm) spectra of [Tb(**4**)$_3$]$^{3+}$ recorded in CH$_3$CN (2.7 × 10^{-5}M), and (Right) of [Tb(**5**)$_3$]$^{3+}$ recorded in CH$_3$CN (2.5 × 10^{-5}M).*
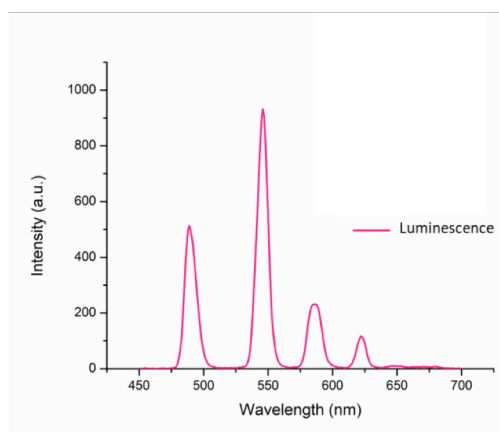
Figure S11. *Delayed luminescence spectra [Tb(**5**)$_3$]$^{3+}$ (2.5 × 10^{-5}M) recorded in CH$_3$CN showing characteristic Tb(III) transitions $^5D_4 \rightarrow {}^7F_{6,5,4,3,2}$.*
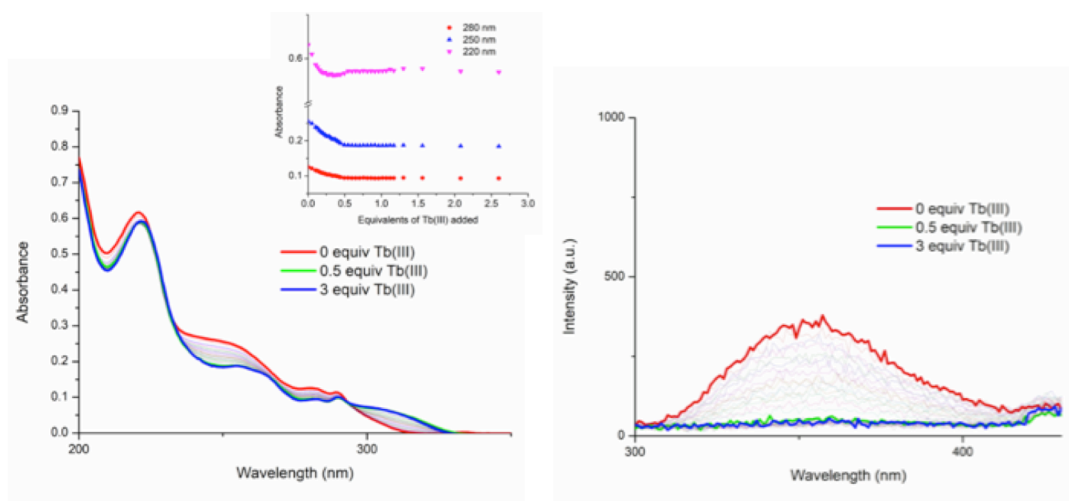
Figure S12. *The overall changes in the (left) UV-visible absorption spectra and (right) fluorescence emission spectra (excitation wavelength λ = 230 nm) upon titrating **5** (1×10^{-5} M) against Tb(CF$_3$SO$_3$)$_3$ (0→3 equiv.) in CH$_3$CN at RT. **Inset**: corresponding experimental binding isotherms of absorbance at λ = 220, 250 and 280 nm.*
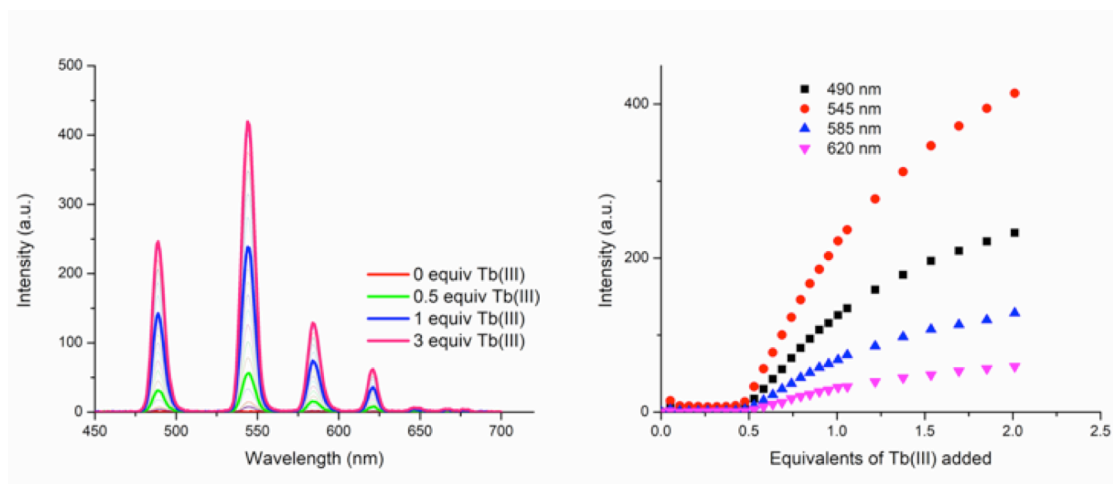
Figure S13. *(left) The overall changes to the Tb(III)-centred phosphorescence spectra upon titrating **5** (1×10^{-5} M) against Tb(CF$_3$SO$_3$)$_3$ (0→3 equiv.) in CH$_3$CN at RT. (right) corresponding experimental binding isotherms of phosphorescence at l = 492, 545, 583 and 620 nm.*

***Figure S14.*** *The speciation distribution diagram obtained from (Left) the fit of the UV-visible absorption titration data of ligand **5** against Tb(CF$_3$SO$_3$)$_3$ in CH$_3$CN and (Right) the fit of the experimental binding isotherms using non-linear regression analysis software ReactLab.*

Table S1 Crystal data and structure refinement for 4.

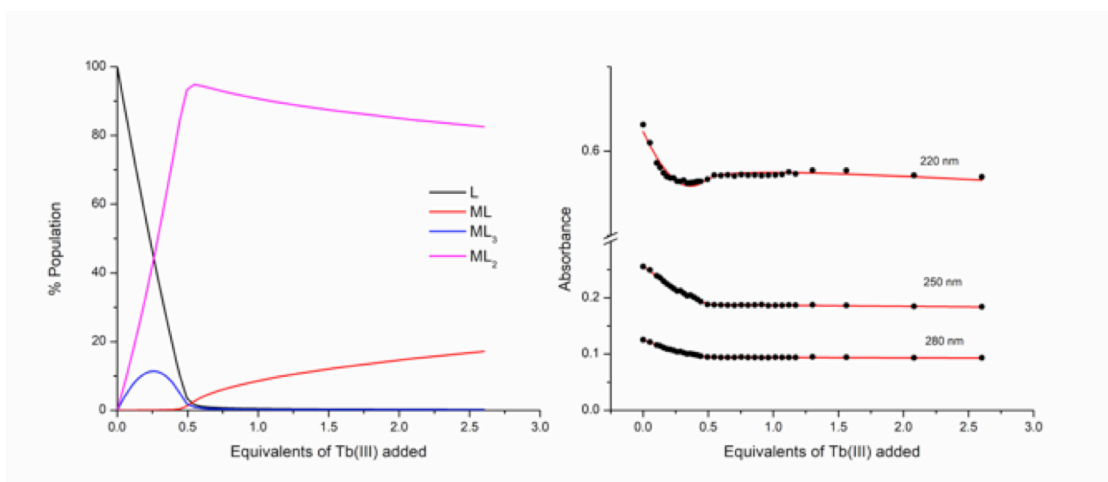|	
Identification code	4
Empirical formula	$C_{27}H_{25}N_5O_5$
Formula weight	499.52
Temperature/K	100(2)
Crystal system	monoclinic
Space group	$P2_1$
a/Å	9.9204(3)
b/Å	9.6670(3)
c/Å	13.2315(4)
α/°	90
β/°	106.3690(10)
γ/°	90
Volume/Å^3	1217.47(6)
Z	2
ρ_{calc}g/cm^3	1.363
μ/mm^{-1}	0.793
F(000)	524.0
Crystal size/mm^3	$0.14 \times 0.13 \times 0.1$
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	9.29 to 136.496
Index ranges	$-11 \le h \le 11, -11 \le k \le 11, -15 \le l \le 15$
Reflections collected	12684
Independent reflections	4398 [R_{int} = 0.0369, R_{sigma} = 0.0383]
Data/restraints/parameters	4398/1/336
Goodness-of-fit on F^2	1.021
Final R indexes [I>=2σ (I)]	R_1 = 0.0275, wR_2 = 0.0716
Final R indexes [all data]	R_1 = 0.0281, wR_2 = 0.0722
Largest diff. peak/hole / e Å^{-3}	0.13/-0.14
Flack parameter	0.04(7)
CCDC No.	2239920

Experimental

Materials and Methods

Solvents and reagents were purchased from purchased from Sigma-Aldrich, Alfa Aesar or TCI Ltd. unless otherwise stated and used without further purification.. NMR spectra were recorded using a Bruker AV-600 instrument operating at 600.1 MHz for ^{1}H NMR and 150.9 MHz for ^{13}C NMR. Chemical shifts are reported in commercially available deuterated solvents; δ in ppm relative to $SiMe_4$ (= 0 ppm) referenced relative to the internal solvent signals. 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 Perkin Elmer Spectrum One FT-IR spectrometer equipped with universal ATR sampling accessory. UV-Visible absorption spectra were measured in 1-cm quartz cuvettes on a Varian Cary 50 spectrophotometer, and emission (fluorescence, phosphorescence and excitation) spectra and lifetimes were recorded on a Varian Cary Eclipse Fluorimeter, with samples dissolved in spectrophotometric grade solvents.

X-ray Crystallography

X-ray data were collected on a Bruker APEX-II DUO diffractometer using microfocus Cu Kα (λ = 1.5405 Å) radiation. All data collections were carried out using standard ω and φ scans at 100 K with temperature control provided by a Cobra cryostream. The data were reduced and multi-scan absorption corrections applied using SADABS[1] within the Bruker APEX3 software suite.[2] Datasets were solved using the intrinsic phasing routine within SHELXT [3] and refined on F^2 using least squares techniques with SHELXL[4] operating within the OLEX-2 GUI.[5] Non-hydrogen atoms were located from their residuals within the Fourier difference map, while hydrogen atoms were either placed in calculated positions with U_{iso} dependencies derived from their carrier atoms, or (where appropriate for hydrogen bonding species) were manually located from the Fourier map and restrained with distance restraints and U_{iso} dependencies manually. CCDC 2239920.

References

1. Bruker APEX-3, Bruker-AXS Inc., Madison, WI, 2016.
2. SADABS, Bruker-AXS Inc., Madison, WI, 2016.
3. G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Adv.,* 2015, **71**, 3–8.
4. G. M. Sheldrick, *Acta Crystallogr., Sect. C: Struct. Chem*., 2015, **71**, 3–8.
5. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Crystallogr.,* 2009, **42**, 339–341.