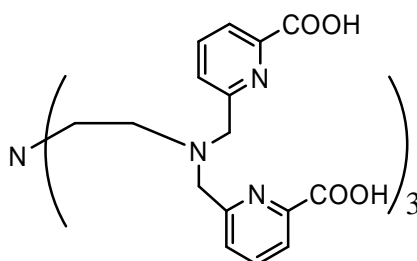


Supporting Information for the manuscript :

Title: “A Flexible Tripodal Ligand Linking Octametallc Terbium Rings into Luminescent Polymeric Chains”.

Authors: Xiao-Yan Chen, Claire Marchal, Yaroslav Filinchuk, Daniel Imbert, and Marinella Mazzanti

N,N,N',N',N'',N''-hexakis[(6-carboxypyridin-2-yl)methyl]-tris(2-aminoethyl)amine
(*H₆trenpa*)



Experimental Section

Materials and Methods. Solvents and starting materials were obtained from Aldrich, Fluka and Acros and used without further purification if nothing else is stated.

Elemental analyses were either performed by the Service Central d'Analyses (Vernaison, France) or by the Pr. Malissa & Reuteur Laboratory (Lindlar, Germany) when done under controlled atmosphere of argon.

Synthesis of the ligand *N,N,N',N',N'',N''-hexakis[(6-carboxypyridin-2-yl)methyl]-tris(2-aminoethyl)amine (H₆trenpa)*

The decadentate ligand *N,N,N',N',N'',N''-hexakis[(6-carboxypyridin-2-yl)methyl]-tris(2-aminoethyl)amine (H₆trenpa)* is readily obtained in five steps from commercially available 2,6-dipicolinic acid and tris(2-aminoethyl)amine (tren) in a yield of 36%.

Detailed description of the synthesis of the ligand *N,N,N',N',N'',N''-hexakis[(6-carboxypyridin-2-yl)methyl]-tris(2-aminoethyl)amine (H₆trenpa)*

6-chloromethylpyridine-2-carboxylic acid ethyl ester (3.2 g, 16 mmol) was dissolved in anhydrous acetonitrile (140 mL). Tris(2-aminoethyl)amine (345 μ L, 2.46 mmol), KI (2.65 g, 16 mmol) and K_2CO_3 (2.56 g, 18.5 mmol) were added into the above solution under argon atmosphere. After refluxing for 26 hours, the mixture was filtered. The solvent was evaporated to get a yellow solid, which was dissolved in dichloromethane. The undissolved white solid was removed by filtration. The resulting solution was washed with water (2×100 mL), and then dried over anhydrous Na_2SO_4 . After evaporation of the solvent, we get brown oil, which was used directly without further purification. The crude product (2.13 g) was refluxed over night in 6 M HCl solution (40 mL). The solvent was evaporated to 5 mL, then redissolved in 100 mL of water, the pH value was adjusted to 2. The solution was stored at 5 $^\circ$ C for 14 hours to get light-yellow crystals, which was filtered, washed with 6 M HCl and dried under vacuum to yield $H_6trenpa \cdot 4HCl$ (1.0g, 36%).

Elemental analysis: Calc. for $H_6trenpa \cdot 4HCl$, $C_{48}H_{52}N_{10}O_{12}Cl_4$, C 52.28, H 4.75, N 12.70%; Found C 52.37, H 4.64, N 13.11%

1H NMR (D_2O , 400 MHz, 298 K, pD = 6) δ = 3.56 (s, 12H, NCH_2CH_2N), 4.45 (s, 12H, NCH_2py), 7.51 (d, 4H, CH), 7.80 (d, 4H, CH), 7.92 (t, 4H, CH).

^{13}C NMR (D_2O , 400 MHz, 298 K, pD = 6) δ = 49.64 (CH_2); 50.75 (CH_2); 59.86 (CH_2); 123.06 ($CHpy$); 125.87 ($CHpy$); 138.75 ($CHpy$); 153 (Cpy); 156.43 (Cpy); 172.57 ($COOH$)

Mass spectrum shows the peak of $(L+2H)/2^+$ at 479.6

Synthesis of $[Ln_4(Htrenpa)(trenpa)(H_2O)_2]Cl$

A solution of $TbCl_3 \cdot 6H_2O$ (0.10 mmol) in a mixture DMF/water (1:3) (2 mL) was added to a solution of $H_6trenpa$ (0.05 mmol) in a mixture DMF/water (1:5) (10mL) in presence of KOH (350 μ L solution 1M in water). Acetonitrile was allowed to slowly diffuse into the resulting solution to afford white crystals of **1** (66%).

Elemental analysis (%): Calc. for $[Ln_4(Htrenpa)(trenpa)(H_2O)_2]Cl \cdot 24H_2O + 2.6KCl$, $C_{96}H_{137}N_{20}O_{50}Cl_{3.6}K_{2.6}Tb_4$, C, 35.63; H, 4.27; N, 8.66; Found C, 35.71; H, 4.20; N, 8.66.

Elemental analysis showed that some KCl co-crystallised with the complex.

Dried sample : The terbium complex was dried under vacuum at 130 $^\circ$ C for 6 days to remove all the water molecules.

Elemental analysis (%): Calc. for $[Ln_4(Htrenpa)(trenpa)]Cl + 2.6 KCl$, $C_{96}H_{85}N_{20}O_{24}Cl_{3.6}K_{2.6}Tb_4$, C, 41.66; H, 3.10; N, 10.12; Found C, 41.52; H, 3.28; N, 10.27.

X-ray Data collections and Structure Determination

A crystal has been selected from the bulk sample and measured at the Swiss-Norwegian Beam Lines (SNBL) at the European Synchrotron Radiation Facility (ESRF). Diffraction data were collected at 100K using the MAR345 Image Plate detector, at the wavelength 0.71076 Å and the crystal-to-detector distance of 150 mm. 300 frames with exposure time 30 sec and 0.8° rotation step have been collected. Diffraction intensities were integrated using CrysAlis software [1]. The data were corrected for Lorentz factor and polarization effects. Absorption correction and scaling of frames for the decaying intensity of the synchrotron beam were performed using SADABS [2]. The structure was solved using SHELXS and refined anisotropically using SHELXH (structure refinement program for huge structures) [3]. The H-atom at site N21 was located from the difference Fourier map and refined independently. 42 positions of water molecules were identified from difference Fourier maps. Occupation factors has been refined for 13 of them. The occupancies suggest 37 water molecules per asymmetric unit. Hydrogen atoms of water molecule were not located. Hydrogen atoms bonded to carbon atoms were refined using the riding model. All peaks of residual electron density higher than 0.85 e/Å³ are located in the close vicinity of the oxygen atoms of water molecules and the terbium atoms. PLATON [4] did not detect higher metric or crystallographic symmetry, but revealed a number of voids of up to ~210 Å³ in volume, which however in total occupy less than 5% of the crystal volume.

Experimental details for X-ray data collections of the terbium complex are given in Table 1. Selected bond distances are given in Table 2.

[1] Oxford Diffraction. CrysAlis Software Package. Oxfordshire, UK, 2006.

[2] G.M. Sheldrick, SHELXS97 and SHELXL97. University of Göttingen, Germany, 1997.

[3] G.M. Sheldrick, SADABS. University of Göttingen, Germany, 1997.

[4] A.L. Spek, PLATON. University of Utrecht, The Netherlands, 2006.

Spectroscopic measurements

The photoluminescence measurements were carried out on powder samples inside capillary tubes on a Fluorolog FL 3-22 spectrometer from Spex-Jobin Yvon-Horiba. Quantum yields were determined by an absolute method using a home-built integration sphere.

Thermogravimetric Analysis:

TGA experiments were carried out on a SETARAM TGA92 under an argon flow in the temperature range 25-700°C at a heating rate of 10°C / min.

A thermogravimetric analysis of hydrated Tb complex displays the first weight loss of 7.60% between 30 and 130°C corresponding to the removal of 14 water molecules (calculated: 7.79 %). Then the weight continues to decrease up to a temperature of 330°C and the loss observed corresponds to the loss of the other water molecules, following by decomposition of the complex. (Figure S8).

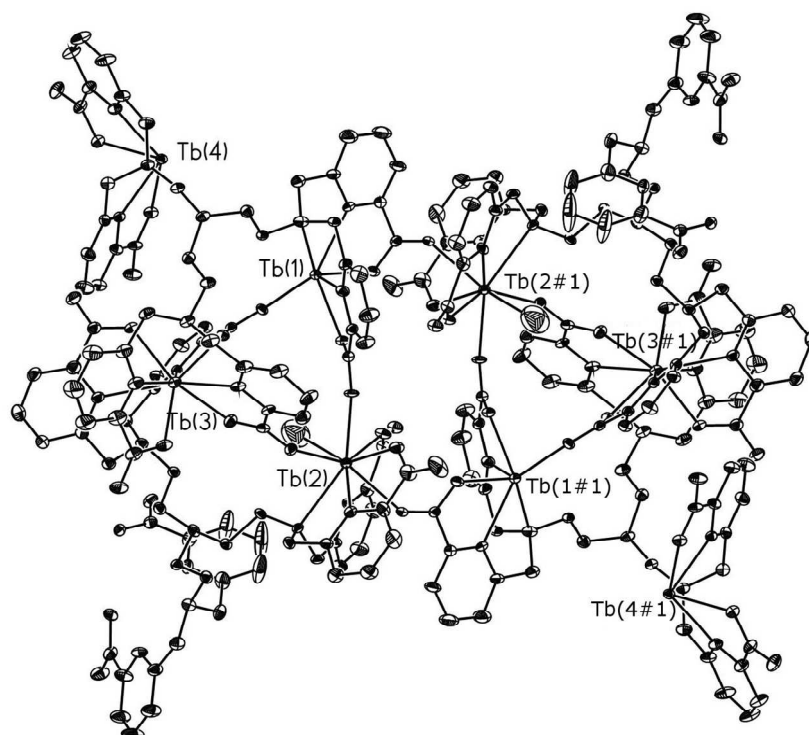


Figure S1. Ortep view of the octameric unit $[\text{Tb}_4(\text{Htrenpa})(\text{trenpa})(\text{H}_2\text{O})_2]_2^{2+}$ in **1**. Ellipsoids are shown at the 50% probability level. H-atoms and water molecules are omitted for clarity. Chlorine atom is shown as an isolated ellipsoid close to Tb(2) atom. The inversion related atoms Tb(n) and Tb(n#1) are at equivalent positions (1-x,-y,-z).

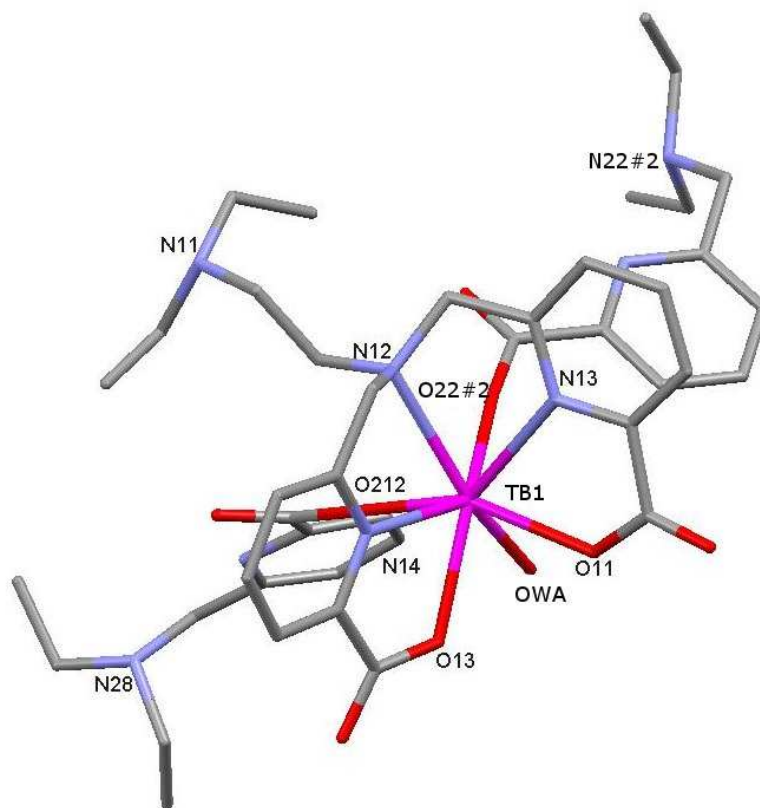


Figure S2. Coordination environment of Tb1. Symmetry transformations used to generate equivalent atoms #2 : $1-x, y, -0.500-z$.

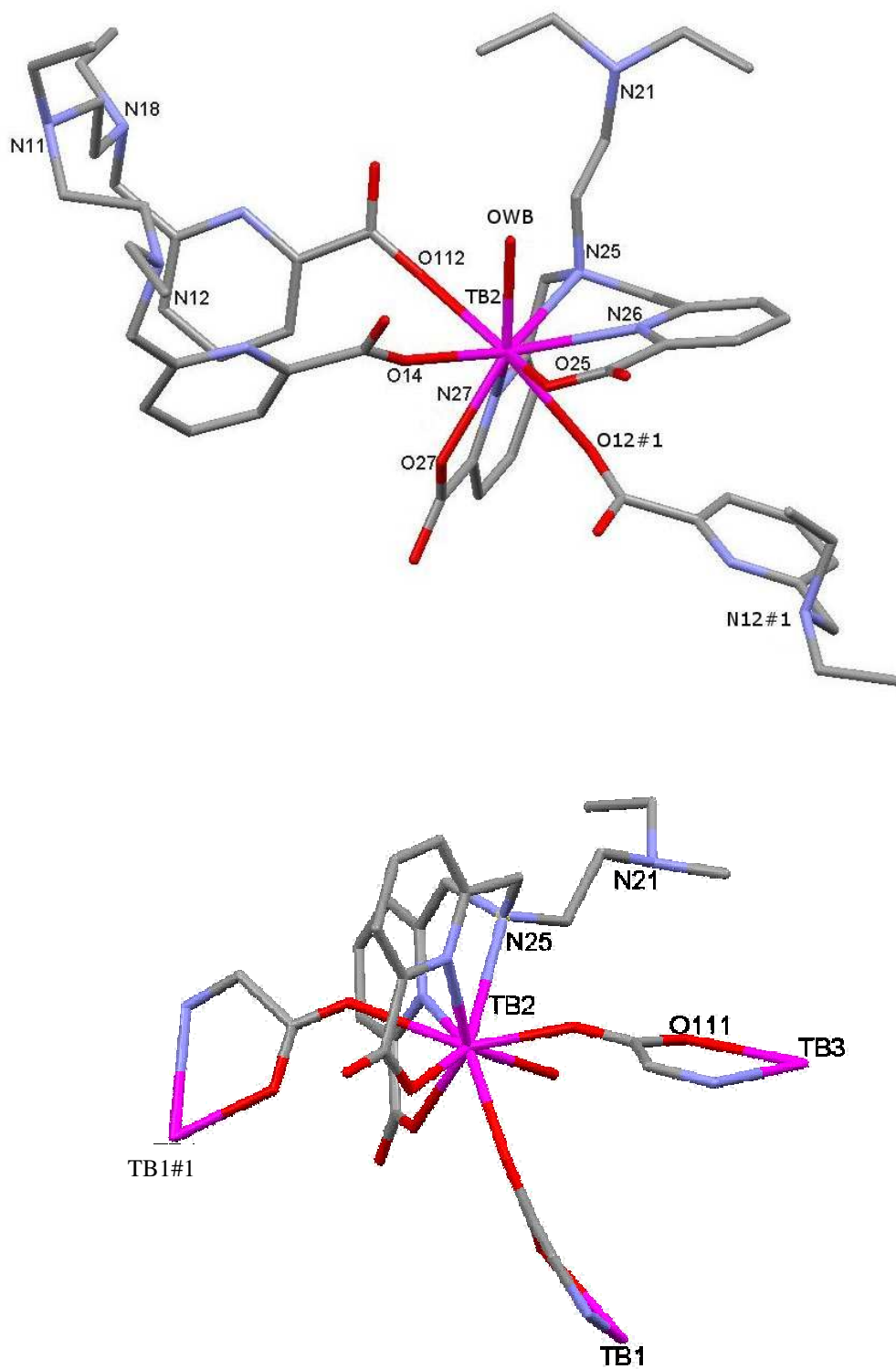


Figure S3. Coordination environment of Tb2. Symmetry transformations used to generate equivalent atoms #1 : 1-x,-y,-z.

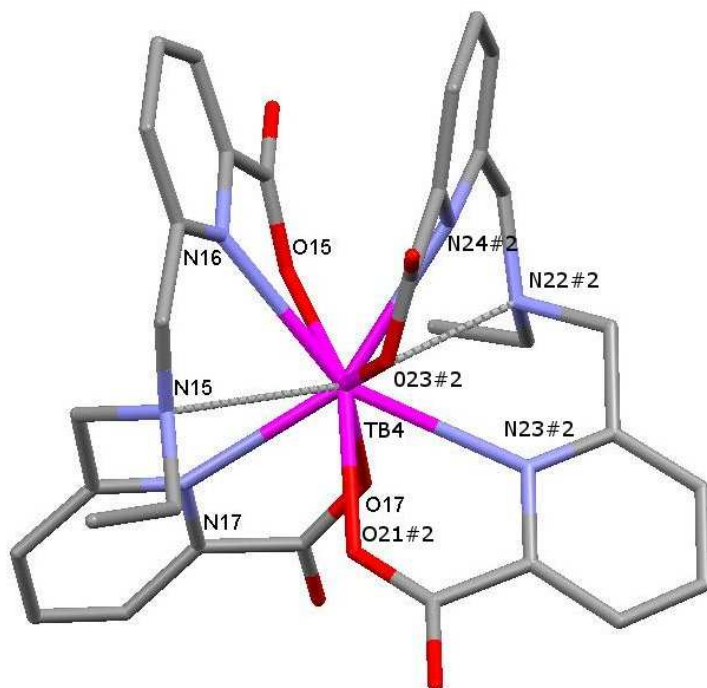


Figure S5. Coordination environment of Tb4. Symmetry transformations used to generate equivalent atoms #2 : $1-x, y, -0.500-z$.

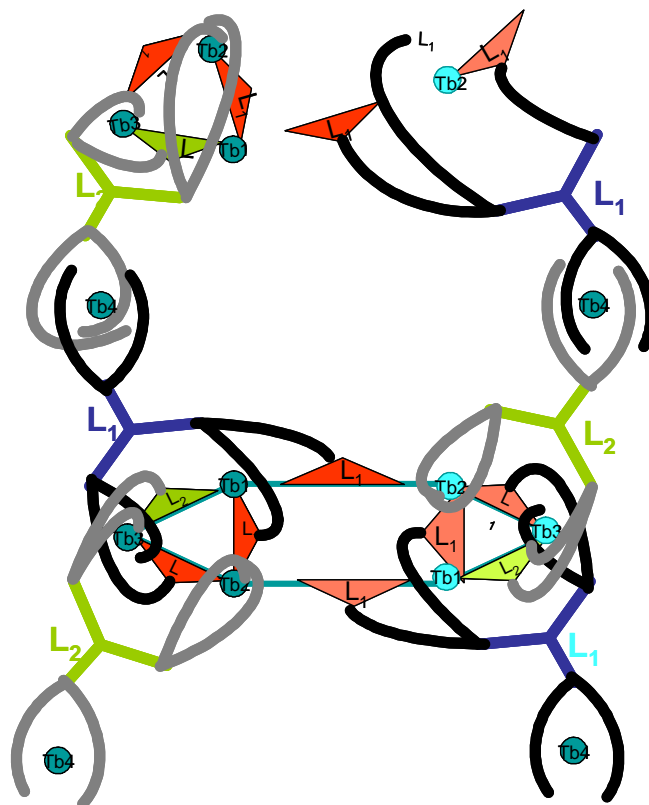


Figure S6. Schematic representation of the polymeric network $[\text{Tb}_4(\text{Htrenpa})(\text{trenpa})(\text{H}_2\text{O})_2]\text{Cl}\cdot 35\text{H}_2\text{O}$ (**1**). The Tb octamers are linked by the symmetry of a two-fold axis parallel to the *b* axis.

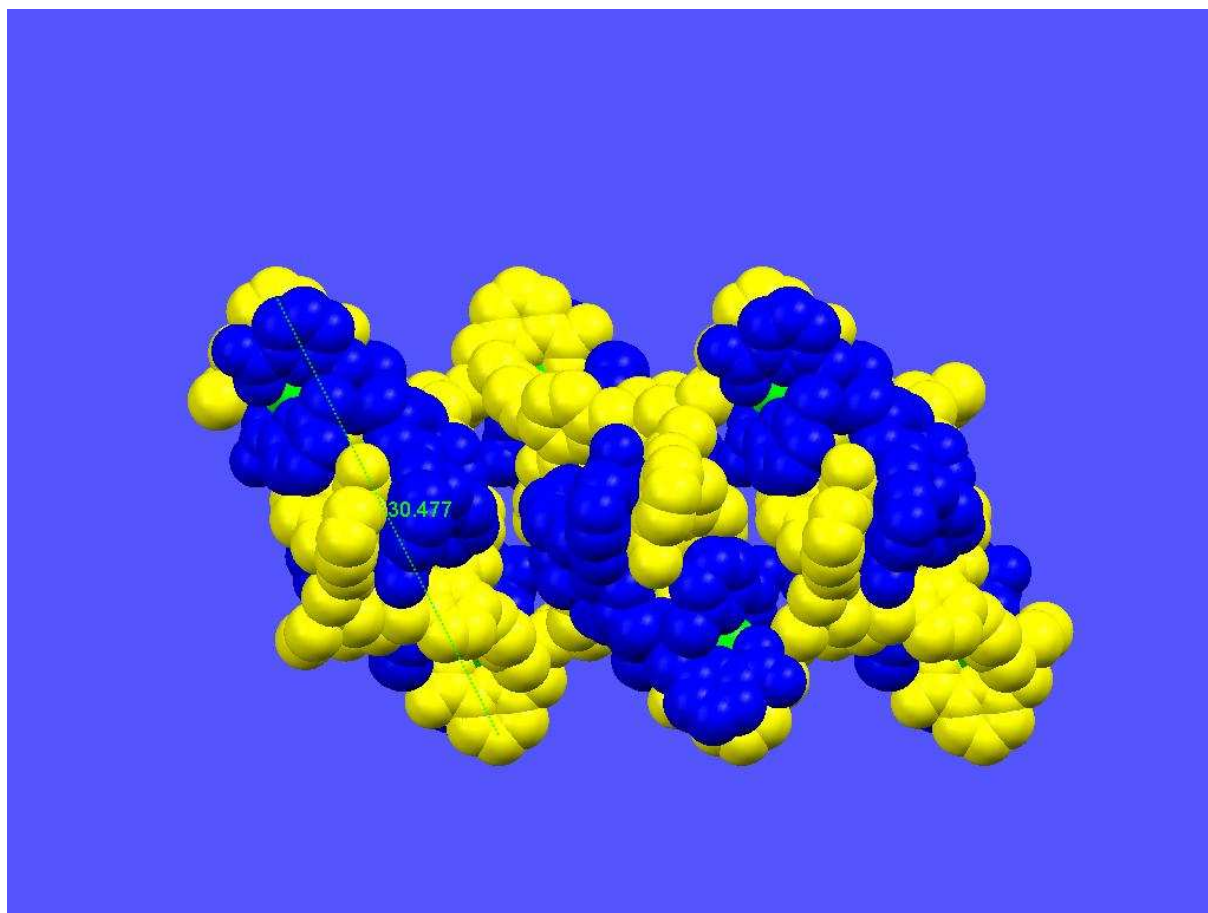


Figure S7. Space-Fill representation of the polymeric network

Table 1. Crystal Data and Structure Refinements [Tb₄(Htrenpa)(trenpa)(H₂O)₂]Cl·35H₂O (**1**).

Formula	C ₉₆ H ₁₅₉ N ₂₀ O ₆₁ ClTb ₄
Mw	3240.56
T (K)	100
Cryst. syst.	monoclinic
Space group	<i>C2/c</i>
<i>a</i> (Å)	30.5311(5)
<i>b</i> (Å)	33.6509(3)
<i>c</i> (Å)	27.1283(3)
β (deg)	98.116(1)
<i>V</i> (Å ³)	27592.4(6)
<i>Z</i>	8
ρ (g/cm ³)	1.560
μ (mm ⁻¹)	2.141
θ (deg)	2.34-24.64
reflns collected	75754
independant reflns	22635
parameters	1648
GOF on <i>F</i> ²	1.032
<i>R</i> _{int} , <i>R</i> _σ	0.0554, 0.0516
<i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2σ (<i>I</i>)]	0.0603, 0.1487
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.0734, 0.1593
Δρ, min/max (e/Å ³)	2.8(2), -1.4(2)

Table 2. Selected Bond Lengths (Å) for complex 1

Complex 1			
Tb(1)-O(#2)	2.270 (6)	Tb(2)-O(112)	2.351 (5)
Tb(1)-O(212)	2.287 (5)	Tb(2)-O(14)	2.378 (5)
Tb(1)-O(11)	2.335 (6)	Tb(2)-O(25)	2.377 (6)
Tb(1)-O(13)	2.366 (5)	Tb(2)-O(27)	2.399 (6)
Tb(1)-OW(A)	2.412 (6)	Tb(2)-OWB	2.408 (7)
Tb(1)-N(14)	2.515 (7)	Tb(2)-O(12#1)	2.475 (5)
Tb(1)-N(13)	2.544 (7)	Tb(2)-N(26)	2.540 (6)
Tb(1)-N(12)	2.677 (7)	Tb(2)-N(27)	2.541 (7)
		Tb(2)-N(25)	2.706 (6)
Tb(3)-O(29)	2.348 (5)	Tb(4)-O(17)	2.329 (5)
Tb(3)-O(211)	2.370 (5)	Tb(4)-O(23#2)	2.364 (5)
Tb(3)-O(19)	2.370 (6)	Tb(4)-O(21#2)	2.376 (5)
Tb(3)-O(111)	2.406 (6)	Tb(4)-O(15)	2.381 (5)
Tb(3)-N(210)	2.619 (6)	Tb(4)-N(17)	2.598 (6)
Tb(3)-N(19)	2.625 (7)	Tb(4)-N(24#2)	2.614 (6)
Tb(3)-N(29)	2.635 (7)	Tb(4)-N(23#2)	2.650 (7)
Tb(3)-N(110)	2.651 (7)	Tb(4)-N(16)	2.650 (7)
Tb(3)-N(18)	3.036 (7)	Tb(4)-N(15)	3.005 (6)
Tb(3)-N(28)	3.053 (7)	Tb(4)-N(22#2)	3.080 (7)

Symmetry transformations used to generate equivalent atoms #2 : 1-x, y, -0.500-z; #1 : 1 -x, -y, -z.

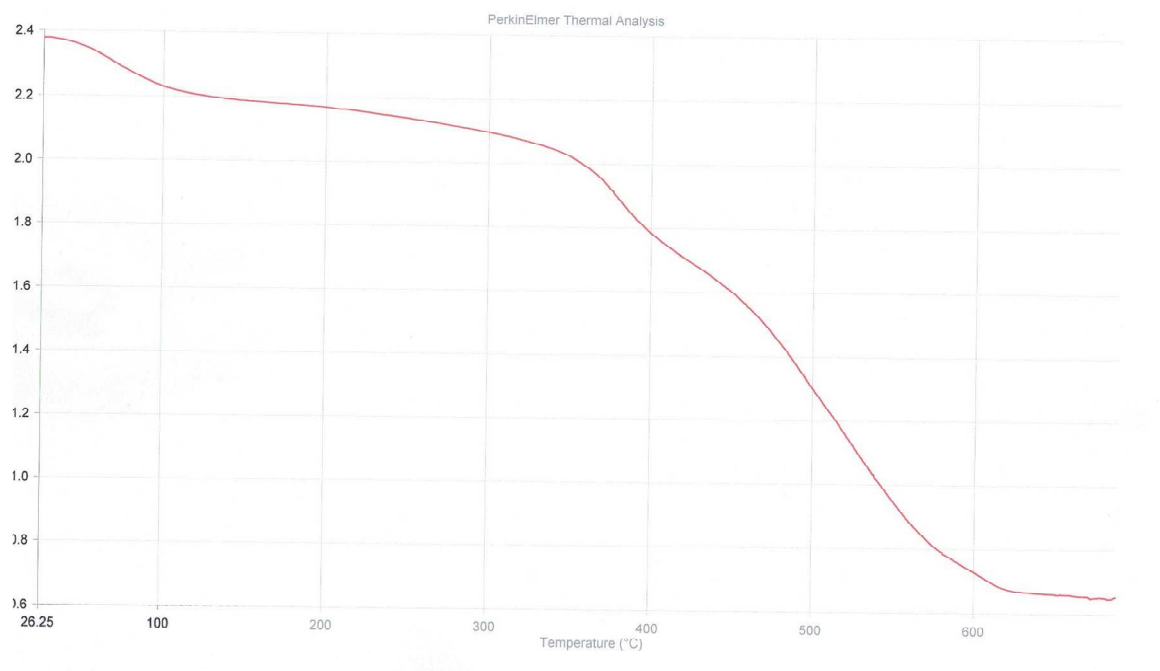


Figure S8. TGA curve of the Tb complex

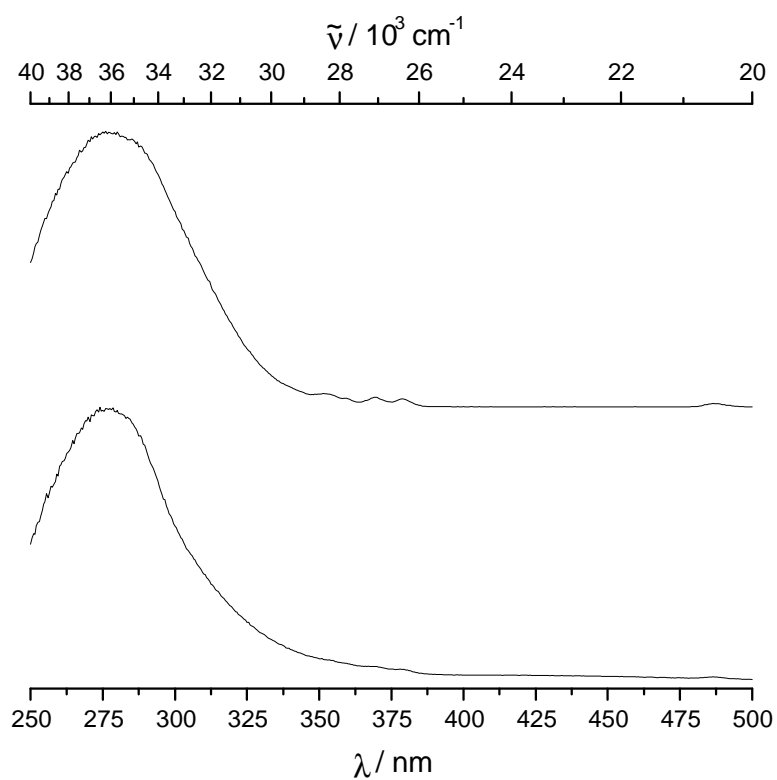


Figure S9. Excitation spectra of the terbium complex (top: hydrated complex; bottom: anhydrous complex) recorded at 295 K.