

Luminescent lanthanoid complexes of a tetrazole-functionalised calix[4]arene

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Electronic Supplementary Information

General considerations

All of the reagents were obtained from Sigma Aldrich and used as received without any further purification. All solvents were purified by standard procedures before use; dry solvents were stored over molecular sieves. All reactions were carried out under a nitrogen atmosphere. IR spectra were recorded on solid samples using a diamond ATR Perkin Elmer Spectrum 100 FT-IR. Nuclear magnetic resonance spectra (consisting of ^1H , ^{13}C , DEPT, ^1H - ^1H COSY, HSQC and HMBC experiments) were recorded using a Bruker Avance 400 spectrometer (400.1 MHz for ^1H , 100 MHz for ^{13}C) at room temperature. ^1H and ^{13}C chemical shifts were referenced to residual solvent resonances. Elemental analyses were performed by CMAS (Melbourne, Australia). The absorption spectra were collected on a Perkin Elmer Lambda 35 UV/Vis spectrometer. Steady-state emission spectra were recorded on an Edinburgh FLSP920 spectrofluorimeter equipped with a 450 W Xenon arc lamp, double excitation and single emission monochromators, a peltier cooled (253.15K) Hamamatsu R928P photomultiplier tube (185-850 nm) and a liquid nitrogen cooled (193.15K) Hamamatsu R5509-72 photomultiplier tube (350-1700 nm). The excitation spectra were recorded by monitoring the maximum of the corresponding emission peak. Emission and excitation spectra were corrected for source intensity (lamp and grating) and emission spectral response (detector and grating) by calibration curve supplied with the instrument. Emission lifetimes were determined on the same Edinburgh instrument with: i) the single photon counting technique (TCSPC) using pulsed picosecond LEDs (ELED 295 or ELED 360, FWHM <800 ps, repetition rates between 10 kHz and 1 MHz) as the excitation source; or, ii) by the multichannel scaling (MCS) technique using a μF900 Microsecond Flashlamp (60 W) as the excitation source, by irradiating the sample at $\lambda_{\text{ex}}=306$ nm with a frequency of 100.0 Hz and, in each case, the above-mentioned R928P or R5509-72 PMT as detector. The goodness of fit was assessed by minimizing the reduced χ^2 function and visual inspection of the weighted residuals. To record the 77 K luminescence spectra, the samples were put in glass tubes (2 mm diameter) and inserted in a special quartz dewar, filled up with liquid nitrogen. Melting points were measured with a BI Barnsted Electrothermal 9100 apparatus and are uncorrected.

Synthesis

5,11,17,23-Tetra-tert-butyl-25,27-dicyanomethoxy-26,28-dihydroxycalix[4]arene, **2**.

This method was derived from the literature¹ with some modifications. Potassium iodide (9.617 g, 57.9 mmol) was added to dry THF (150 cm³) and allowed to stir for five minutes. To this, chloroacetonitrile (7.0 cm³, 111.7 mmol) was added and stirred overnight. This resulted in a bright yellow solution with a white precipitate. The white solid was filtered off and calixarene **1** (13.03 g, 20.1 mmol) along with potassium carbonate (10.04 g, 72.6 mmol) were added to the clear yellow solution. This was refluxed overnight producing a brown solution with a dark brown precipitate. The solution was allowed to cool and then filtered through celite. The celite was washed with dichloromethane (3×50 cm³) producing a brown filtrate which was dried over magnesium sulfate. The solvent was removed under reduced pressure and recrystallised from chloroform/methanol (1:2) which furnished the nitrile **2** as a white powder. (8.754 g, 79%), m.p. > 310°C (decomp.) (lit. > 290 °C (decomp)). ¹H NMR (CDCl₃, δ, ppm) 7.12 (s, 2H, Ar-**H**), 6.73 (s, 2H, Ar-**H**), 5.54 (s, 2H, Ar-OH), 4.81 (s, 2H, Ar-O-CH₂), 4.23 (d, 2H, *axial* Ar-CH₂-Ar, J=13.4 Hz), 3.45 (d, 2H, *equatorial* Ar-CH₂-Ar, J=13.5 Hz), 1.33 (s, 9H, Ar-CCH₃), 0.88 (s, 9H, Ar-CCH₃). ¹³C NMR (CDCl₃, δ, ppm) 150.0, 148.8, 148.6, 142.6, 131.9, 127.9, 126.3, 125.4, 115.2, 60.5, 34.1, 34.0, 32.1, 31.8. IR (ATR): ν/cm⁻¹ 3502 (m), 2956 (s), 2905 (m), 2868 (m), 1598 (w), 1479 (s), 1430 (m), 1362 (m), 1190 (m), 1014 (m), 872 (w).

5,11,17,23-Tetra-tert-butyl-25,27-dihydroxy-26,28-ditetrazolylcalix[4]arene, **1H₄**.

Toluene (65 cm³) was placed into a round bottom flask immersed in an ice bath. To the cold solvent, triethylamine (5.0 cm³, 35.8 mmol) and hydrochloric acid (2.5 cm³, 25.0 mmol) was added and the flask stoppered immediately. A white gas was evolved but upon stirring the solution for ten minutes this dissolved into solution resulting in a white residue on the walls of the flask. The dinitrile **2** (5.09 g, 7.0 mmol) was then added to the solution along with sodium azide (2.01 g, 30.9 mmol) and refluxed for 12 hours. The solution was cooled to room temperature and the solvent was removed under reduced pressure yielding a white solid. The residue was dissolved in ethyl acetate resulting in a cloudy white solution which was filtered and then washed with hydrochloric acid (1M, 3×100 cm³). The organic was dried over magnesium sulfate and solvent removed by reduced pressure evaporation. The residue was recrystallised from a dichloromethane/hexane mixture furnishing tetrazole calixarene **1** as a white semi crystalline solid (3.761 g, 66%) m.p. = 253°C (decomp.). Anal. Calculated for C₄₈H₆₀O₄N₈.0.4CH₂Cl₂: C, 68.63; H, 7.24; N, 13.23. Found C, 68.45; H, 7.14; N, 13.27. ¹H NMR (CDCl₃, δ, ppm) 7.08 (s, 2H, Ar-**H**), 7.00 (s, 2H, Ar-**H**), 5.50 (s, 2H, Ar-O-CH₂), 4.10 (d, 2H, *axial* Ar-CH₂-Ar, J=13.4 Hz), 3.50 (d, 2H, *equatorial* Ar-CH₂-Ar,

$J=13.5$ Hz), 1.23 (s, 9H, Ar-CCH₃), 1.08 (s, 9H, Ar-CCH₃). ¹³C NMR (CDCl₃, δ, ppm) 149.3, 149.1, 149.0, 143.7, 132.5, 127.4, 126.6, 125.9, 68.5, 53.52, 34.4, 34.1, 32.5, 31.7, 31.1. IR (ATR): ν/cm^{-1} 3390 (m), 3135 (w), 3050 (w), 2951 (s), 2904 (m), 2869 (m), 1600 (w), 1558 (w), 1483 (s), 1361 (m), 1193 (s), 736 (m).

Metal Complexes of 1H₄

The synthesis of the terbium complex of **1H₄** was attempted by crystallisation from a solution of ligand **1H₄** (31.5 mg, 0.004 mmol) in dichloromethane (50 mL), to which was added Tb(NO₃)₃(DMSO)₄ (35 mg, 0.006 mmol) and four equivalents of triethylamine (3.4 μL). Clear rhombohedral crystals evolved upon standing the solution overnight, and these were characterised by single crystal X-ray structure determination.

The europium complex of **1** was crystallised by the slow evaporation of a 1:1 methanol/acetonitrile solution (5 mL) of **1H₄** (40 mg, 0.05 mmol) and Eu(NO₃)₃(DMSO)₄ (34 mg, 0.06 mmol) along with eight equivalents of triethylamine (65 μL). Yellow/orange needle crystals suitable for single crystal X-ray structure determination were deposited in ~15% yield. Anal. Calculated for C₄₈H₆₀O₄N₈Eu.H₂O: C, 56.74; H, 6.25; N, 11.02. Found C, 56.93; H, 6.74; N, 11.20

X-ray Crystallography

Structure of $1H_4$

The crystal data for $1H_4$ are summarized in Table S-1 with the structure depicted in Figure S-1 and Figure 2 where ellipsoids have been drawn at the 20% probability level. Hydrogen bonding geometries are listed in Table S-2. Crystallographic data for the structures were collected at 100(2) K on an Oxford Diffraction Xcalibur diffractometer fitted with Mo $K\alpha$ radiation. Following analytical absorption corrections and solution by direct methods, the structure was refined against F^2 with full-matrix least-squares using the program SHELXL-97.² One tetrazolyl group is disordered over two sets of sites with occupancies constrained at 0.5 after trial refinement. All hydrogen atoms were added at calculated positions and refined by use of a riding model with isotropic displacement parameters based on those of the parent atoms. Anisotropic displacement parameters were employed for the non-hydrogen atoms.

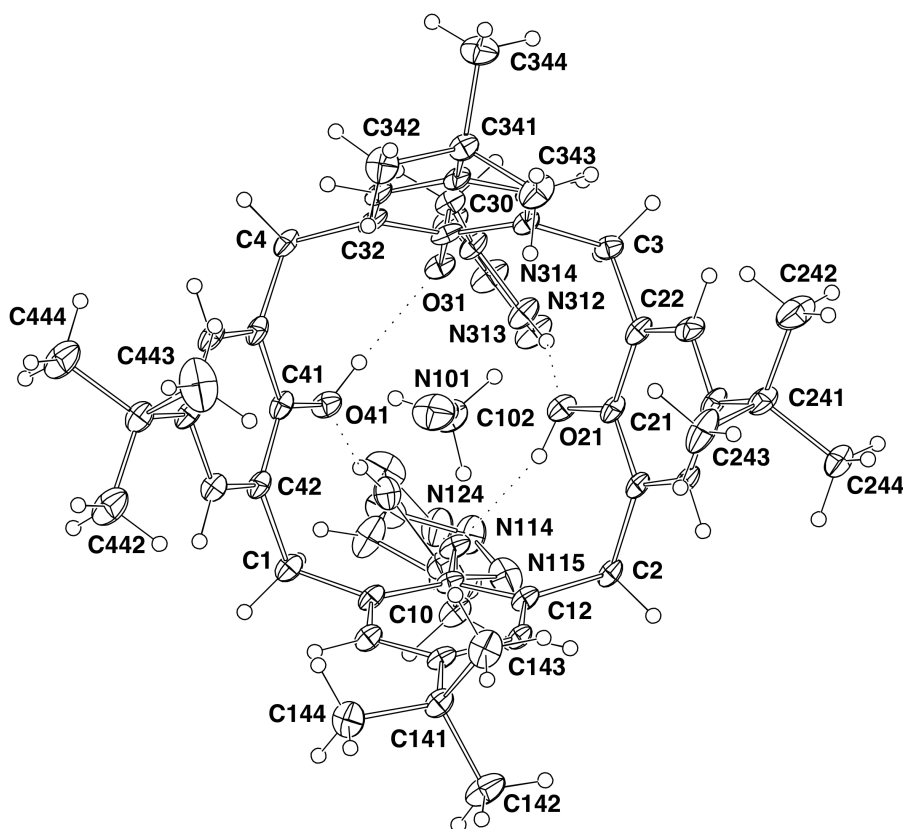


Figure S-1 Molecular structure of $1H_4$ projected onto the plane of the methylene groups and showing the intra-molecular hydrogen bonding. Ellipsoids have been drawn at the 20% probability level.

Table S-1 Crystal data and structure refinement for **1H₄**.

Identification code	modd17
Empirical formula	C ₅₂ H ₆₆ N ₁₀ O ₄
Formula weight	895.15
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	C2/c
Unit cell dimensions	a = 23.526(5) Å b = 11.962(2) Å c = 37.255(6) Å β = 110.96(2)°
Volume	9790(3) Å ³
Z	8
Density (calculated)	1.215 Mg/m ³
Absorption coefficient	0.079 mm ⁻¹
F(000)	3840
Crystal size	0.25 x 0.20 x 0.06 mm ³
θ range for data collection	2.77 to 25.00°.
Index ranges	-27 ≤ h ≤ 26, -14 ≤ k ≤ 14, -44 ≤ l ≤ 44
Reflections collected	71629
Independent reflections	8627 [R(int) = 0.135]
Completeness to θ = 25.00°	99.8 %
Absorption correction	Semi-empirical from equivalents
Max./min. transmission	1.00/0.81
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	8627 / 24 / 636
Goodness-of-fit on F ²	1.015
Final R indices [I > 2σ(I)]	R1 = 0.0785, wR2 = 0.1427
R indices (all data)	R1 = 0.1340, wR2 = 0.1677
Largest diff. peak and hole	0.232 and -0.262 e.Å ⁻³

Table S-2 Hydrogen bonds for **1H₄** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(112)-H(112)...N(201)	0.88	2.01	2.808(10)	150
N(122)-H(122)...O(41)	0.88	2.15	3.028(8)	171
O(21)-H(21)...O(11)	0.84	1.94	2.757(3)	164
N(312)-H(312)...O(21)	0.88	2.17	3.015(3)	162
O(41)-H(41)...O(31)	0.84	1.98	2.816(3)	171

Structure of Eu-1

The crystal data for Eu-1 are summarized in Table S-3 with the structure depicted in Figure S-2 where ellipsoids have been drawn at the 30% probability level, and also in Figure 3. Coordination geometries are listed in Table S-4. Crystallographic data for the structures were collected at 100(2) K on an Oxford Diffraction Xcalibur diffractometer fitted with Mo K α radiation. Following analytical absorption corrections and solution by direct methods, the structure was refined against F^2 with full-matrix least-squares using the program SHELXL-97.² The molecule is situated on a crystallographic mirror plane. As a result, the tetrazole group, the two coordinated water molecules, and two of the tert-butyl groups are disordered over two sets of sites with occupancies constrained to 0.5. The geometries and displacement parameters of the tert-butyl groups were restrained to realistic values. Despite many attempts, the residual electron density could not be modelled as a possible nitrate anion or as any of the solvents used. This electron density was effectively removed by use of the program Squeeze. Refinement in a space group of lower symmetry did not improve the model. Water molecule/hydroxyl and the possible hydrogen atoms on the tetrazole groups were not located. All remaining hydrogen atoms were added at calculated positions and refined by use of a riding model with isotropic displacement parameters based on those of the parent atoms. Anisotropic displacement parameters were employed for the non-hydrogen atoms.

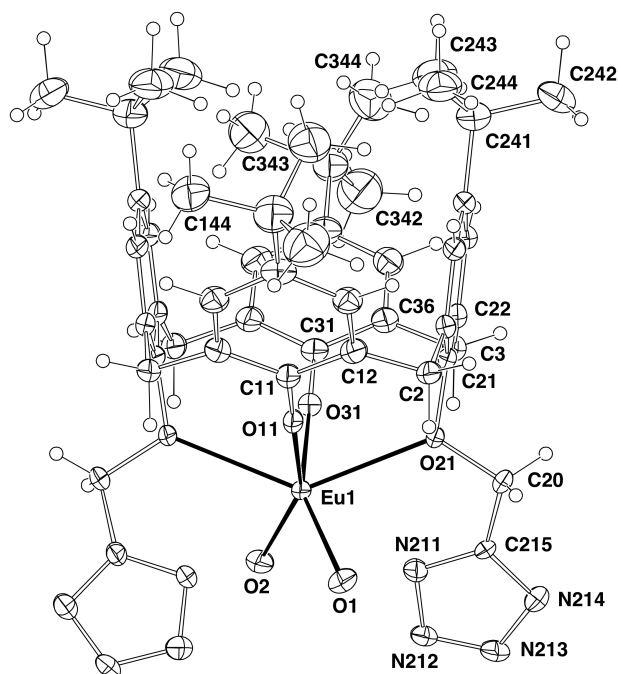


Figure S-2 Molecular structure of Eu-1 projected oblique to the plane of the methylene groups. Only one set of the disordered atoms is shown. Ellipsoids have been drawn at the 30% probability level.

Table S-3 Crystal data and structure refinement for Eu-1.

Identification code	modd17eub4
Empirical formula	C ₄₈ H ₆₁ EuN ₈ O ₆
Formula weight	998.01
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	C2/m
Unit cell dimensions	a = 20.852(3) Å b = 12.9596(12) Å c = 24.4175(19) Å β = 103.649(11)°
Volume	6412.2(11) Å ³
Z	4
Density (calculated)	1.034 Mg/m ³
Absorption coefficient	1.019 mm ⁻¹
F(000)	2064
Crystal size	0.59 x 0.48 x 0.21 mm ³
θ range for data collection	2.94 to 27.50°
Index ranges	-27 ≤ h ≤ 27, -16 ≤ k ≤ 16, -22 ≤ l ≤ 31
Reflections collected	31105
Independent reflections	7685 [R(int) = 0.0435]
Completeness to θ = 27.50°	99.8 %
Absorption correction	Analytical
Max. and min. transmission	0.821 and 0.641
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	7685 / 120 / 388
Goodness-of-fit on F ²	1.121
Final R indices [I > 2σ(I)]	R1 = 0.0838, wR2 = 0.2084
R indices (all data)	R1 = 0.0884, wR2 = 0.2109
Largest diff. peak and hole	1.915 and -3.956 e.Å ⁻³

Table S-4 Selected bond lengths [Å] and angles [°] for Eu-1.

Eu(1)-O(11)	2.156(7)
Eu(1)-O(31)	2.201(7)
Eu(1)-O(2)	2.453(9)
Eu(1)-O(1)	2.499(11)
Eu(1)-O(21)	2.565(4)
Eu(1)-N(211)	2.604(10)
Eu(1)-N(221)	2.619(10)
<hr/>	
O(11)-Eu(1)-O(31)	101.9(3)
O(11)-Eu(1)-O(2)	158.6(2)
O(31)-Eu(1)-O(2)	78.4(3)
O(11)-Eu(1)-O(1)	78.8(3)
O(31)-Eu(1)-O(1)	159.0(3)
O(2)-Eu(1)-O(1)	108.7(3)
O(11)-Eu(1)-O(21)	76.37(12)
O(31)-Eu(1)-O(21)	76.39(13)
O(2)-Eu(1)-O(21)	83.0(3)
O(1)-Eu(1)-O(21)	123.5(3)
O(1) ¹ -Eu(1)-O(21)	83.5(3)
O(2)-Eu(1)-O(21) ¹	123.6(3)
O(21)-Eu(1)-O(21) ¹	136.10(18)
O(11)-Eu(1)-N(211)	128.3(2)
O(31)-Eu(1)-N(211)	95.5(3)
O(1)-Eu(1)-N(211)	100.4(4)
O(1) ¹ -Eu(1)-N(211)	69.1(4)
O(21)-Eu(1)-N(211)	61.1(2)
O(21) ¹ -Eu(1)-N(211)	155.3(3)
O(2)-Eu(1)-N(211) ¹	72.4(3)
N(211)-Eu(1)-N(211) ¹	97.2(5)
O(2)-Eu(1)-N(221) ¹	101.1(3)
O(21)-Eu(1)-N(221) ¹	155.1(3)
N(211)-Eu(1)-N(221) ¹	110.7(3)
O(11)-Eu(1)-N(221)	95.4(3)
O(31)-Eu(1)-N(221)	128.5(3)
O(2)-Eu(1)-N(221)	69.3(4)
O(1)-Eu(1)-N(221)	71.8(4)
O(21)-Eu(1)-N(221)	61.2(3)
N(221) ¹ -Eu(1)-N(221)	97.0(5)
C(11)-O(11)-Eu(1)	177.4(7)
C(21)-O(21)-Eu(1)	120.5(3)
C(20)-O(21)-Eu(1)	125.1(3)
C(215)-N(211)-Eu(1)	119.1(8)
N(212)-N(211)-Eu(1)	135.6(8)
C(225)-N(221)-Eu(1)	120.2(9)
N(222)-N(221)-Eu(1)	134.7(8)
C(31)-O(31)-Eu(1)	176.8(7)

Symmetry transformations used to generate equivalent atoms: ¹ x, 1-y, z

Structure of $Tb(H_2O)(dmsO)_2(NO_3)_3$

The crystal data for $Tb(H_2O)(dmsO)_2(NO_3)_3$ are summarized in Table S-5 with the structure depicted in Figure S-3 where ellipsoids have been drawn at the 50% probability level. Selected geometries are listed in Table S-6. Crystallographic data for the structures were collected at 100(2) K on an Oxford Diffraction Gemini diffractometer fitted with Mo $K\alpha$ radiation. Following analytical absorption corrections and solution by direct methods, the structure was refined against F^2 with full-matrix least-squares using the program SHELXL-97.² Water hydrogen atoms were refined with restrained O-H distances. All remaining hydrogen atoms were added at calculated positions and refined by use of a riding model with isotropic displacement parameters based on those of the parent atoms. Anisotropic displacement parameters were employed for the non-hydrogen atoms.

Structural Description

The formula of the molecule is $Tb(H_2O)(dmsO)_2(NO_3)_3$. The Tb atom is nine coordinate. The coordination sphere could be described as a distorted capped square antiprism with the nitrate oxygen atom O32 being the capping atom. One hydrogen atom of the water molecule hydrogen atom, H1B, forms a hydrogen bond to this atom of the molecule related by an inversion centre forming a hydrogen-bonded dimer (Table S-7). There is a further hydrogen bond from the other water molecule hydrogen atom, H1A, to the uncoordinated oxygen atom O33 of the same nitrate group of the molecule translated one unit cell along the b axis thus forming a one-dimensional hydrogen-bonded polymer (Figure S-4). To our knowledge, this combination of ligands has not been observed to date for any metal, with $Ln(dmsO)_n(NO_3)_3$ ($n = 4$, La–Sm; $n = 3$, Eu–Lu, Y) being the typical formulation for the lanthanoids.³

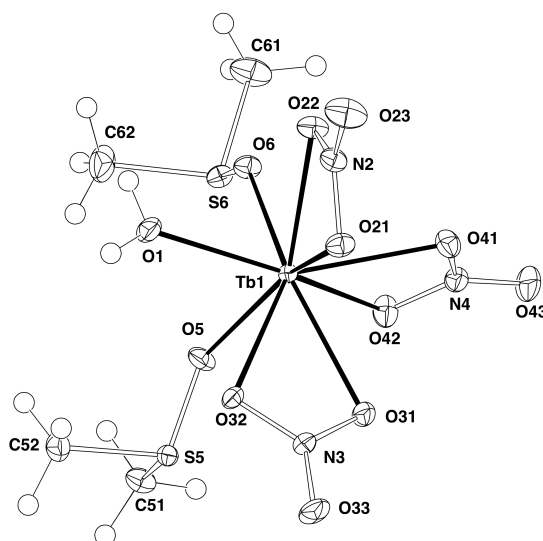


Figure S-3 Molecular structure of $Tb(H_2O)(dmsO)_2(NO_3)_3$. Ellipsoids have been drawn at the 50% probability level.

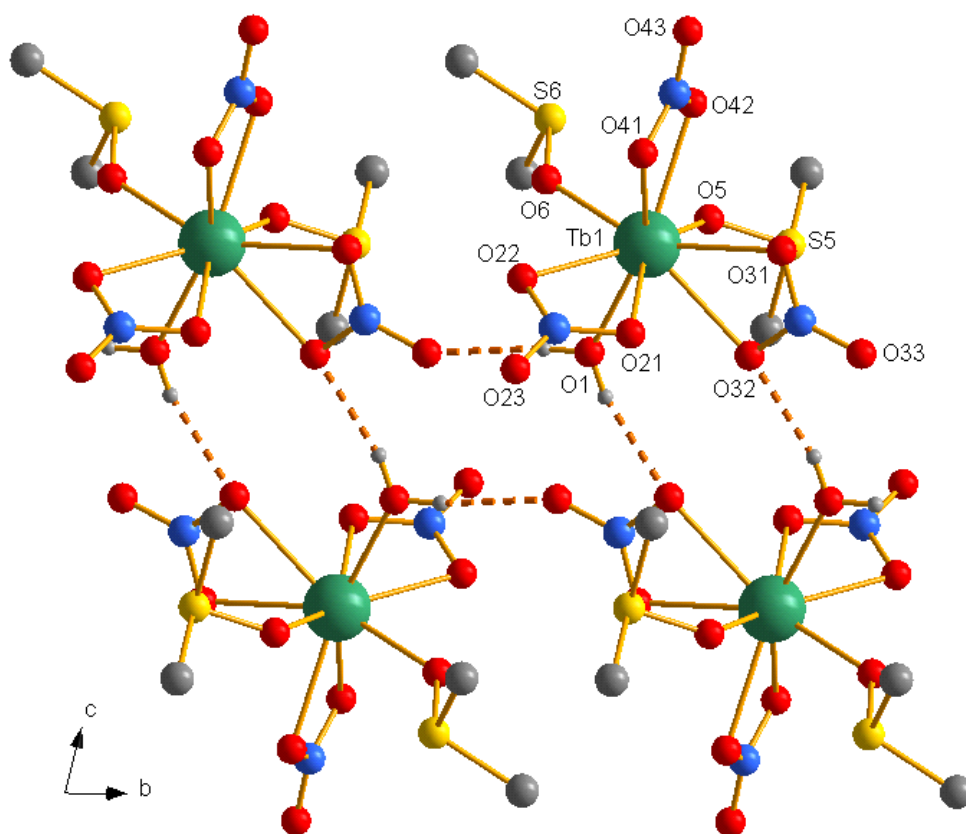


Figure S-4 The hydrogen bonded polymer of Tb(H₂O)(dmsO)₂(NO₃)₃.

Table S-5 Crystal data and structure refinement for $\text{Tb}(\text{H}_2\text{O})(\text{dmsO})_2(\text{NO}_3)_3$.

Identification code	modd17tbb
Empirical formula	$\text{C}_4\text{H}_{14}\text{N}_3\text{O}_{12}\text{S}_2\text{Tb}$
Formula weight	519.22
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	$a = 7.9696(2)$ Å $b = 7.9761(2)$ Å $c = 13.9627(3)$ Å $\alpha = 75.947(2)^\circ$ $\beta = 87.082(2)^\circ$ $\gamma = 66.169(2)^\circ$
Volume	786.47(3) Å ³
Z	2
Density (calculated)	2.193 Mg/m ³
Absorption coefficient	4.823 mm ⁻¹
F(000)	504
Crystal size	0.30 x 0.21 x 0.06 mm ³
θ range for data collection	3.63 to 41.00°.
Index ranges	-14 ≤ h ≤ 14, -14 ≤ k ≤ 14, -25 ≤ l ≤ 25
Reflections collected	35729
Independent reflections	10211 [R(int) = 0.0321]
Completeness to $\theta = 41.00^\circ$	98.6 %
Absorption correction	Analytical
Max. and min. transmission	0.768 and 0.394
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	10211 / 2 / 211
Goodness-of-fit on F^2	1.097
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0237$, $wR2 = 0.0537$
R indices (all data)	$R1 = 0.0287$, $wR2 = 0.0544$
Largest diff. peak and hole	2.197 and -1.621 e.Å ⁻³

Table S-6 Selected bond lengths [\AA] and angles [$^\circ$] for $\text{Tb}(\text{H}_2\text{O})(\text{dmsO})_2(\text{NO}_3)_3$.

Tb(1)-O(6)	2.2832(12)
Tb(1)-O(5)	2.2983(12)
Tb(1)-O(1)	2.3694(13)
Tb(1)-O(21)	2.4383(13)
Tb(1)-O(41)	2.4551(13)
Tb(1)-O(22)	2.4687(13)
Tb(1)-O(31)	2.4752(13)
Tb(1)-O(42)	2.4931(14)
Tb(1)-O(32)	2.5409(12)
Tb(1)-N(2)	2.8821(15)
Tb(1)-N(4)	2.9036(15)
Tb(1)-N(3)	2.9351(14)
O(6)-Tb(1)-O(5)	80.39(4)
O(6)-Tb(1)-O(1)	79.82(5)
O(5)-Tb(1)-O(1)	83.49(5)
O(6)-Tb(1)-O(21)	125.58(4)
O(5)-Tb(1)-O(21)	147.70(4)
O(1)-Tb(1)-O(21)	83.13(5)
O(6)-Tb(1)-O(41)	93.31(5)
O(5)-Tb(1)-O(41)	125.60(5)
O(1)-Tb(1)-O(41)	148.86(5)
O(21)-Tb(1)-O(41)	76.32(4)
O(6)-Tb(1)-O(22)	73.34(4)
O(5)-Tb(1)-O(22)	147.68(5)
O(1)-Tb(1)-O(22)	73.73(5)
O(21)-Tb(1)-O(22)	52.27(4)
O(41)-Tb(1)-O(22)	75.20(5)
O(6)-Tb(1)-O(31)	152.60(5)
O(5)-Tb(1)-O(31)	86.66(5)
O(1)-Tb(1)-O(31)	122.76(4)
O(21)-Tb(1)-O(31)	76.24(4)
O(41)-Tb(1)-O(31)	74.78(4)
O(22)-Tb(1)-O(31)	124.90(4)
O(6)-Tb(1)-O(42)	78.37(5)
O(5)-Tb(1)-O(42)	74.35(5)
O(1)-Tb(1)-O(42)	151.07(5)
O(21)-Tb(1)-O(42)	125.24(5)
O(41)-Tb(1)-O(42)	51.64(4)
O(22)-Tb(1)-O(42)	117.12(5)

O(31)-Tb(1)-O(42)	74.91(5)
O(6)-Tb(1)-O(32)	145.12(4)
O(5)-Tb(1)-O(32)	76.85(4)
O(1)-Tb(1)-O(32)	71.68(4)
O(21)-Tb(1)-O(32)	71.06(4)
O(41)-Tb(1)-O(32)	121.44(4)
O(22)-Tb(1)-O(32)	115.69(4)
O(31)-Tb(1)-O(32)	51.18(4)
O(42)-Tb(1)-O(32)	119.43(4)
O(6)-Tb(1)-N(2)	99.38(4)
O(5)-Tb(1)-N(2)	158.76(5)
O(1)-Tb(1)-N(2)	75.62(5)
O(21)-Tb(1)-N(2)	26.20(4)
O(41)-Tb(1)-N(2)	75.64(4)
O(22)-Tb(1)-N(2)	26.16(4)
O(31)-Tb(1)-N(2)	101.29(4)
O(42)-Tb(1)-N(2)	126.64(4)
O(32)-Tb(1)-N(2)	92.71(4)
O(6)-Tb(1)-N(4)	85.78(4)
O(5)-Tb(1)-N(4)	99.93(5)
O(1)-Tb(1)-N(4)	164.45(4)
O(21)-Tb(1)-N(4)	100.80(5)
O(41)-Tb(1)-N(4)	25.84(4)
O(22)-Tb(1)-N(4)	96.62(4)
O(31)-Tb(1)-N(4)	72.73(4)
O(42)-Tb(1)-N(4)	25.81(4)
O(32)-Tb(1)-N(4)	123.85(4)
N(2)-Tb(1)-N(4)	101.24(4)
O(6)-Tb(1)-N(3)	162.48(4)
O(5)-Tb(1)-N(3)	82.11(4)
O(1)-Tb(1)-N(3)	97.31(4)
O(21)-Tb(1)-N(3)	70.64(4)
O(41)-Tb(1)-N(3)	97.62(4)
O(22)-Tb(1)-N(3)	122.72(4)
O(31)-Tb(1)-N(3)	25.45(4)
O(42)-Tb(1)-N(3)	97.79(4)
O(32)-Tb(1)-N(3)	25.79(4)
N(2)-Tb(1)-N(3)	96.58(4)
N(4)-Tb(1)-N(3)	98.18(4)

Table S-7 Hydrogen bonds for Tb(H₂O)(dmsO)₂(NO₃)₃ [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(1)-H(1A)...O(33) ¹	0.823(18)	2.126(19)	2.9436(19)	172(4)
O(1)-H(1B)...O(32) ²	0.833(18)	2.053(19)	2.8680(18)	166(3)

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

Figure S-5. Absorption profiles for **1H₄** (black line), [Ln(**1**)](NO₃)₃ (red line), and (Et₃NH)[Ln(**1**)] (blue line) measured in diluted (ca. 10⁻⁵ M) MeOH solutions. The spectra shown with Ln = Gd are representative for all the lanthanoid ions used in this work.

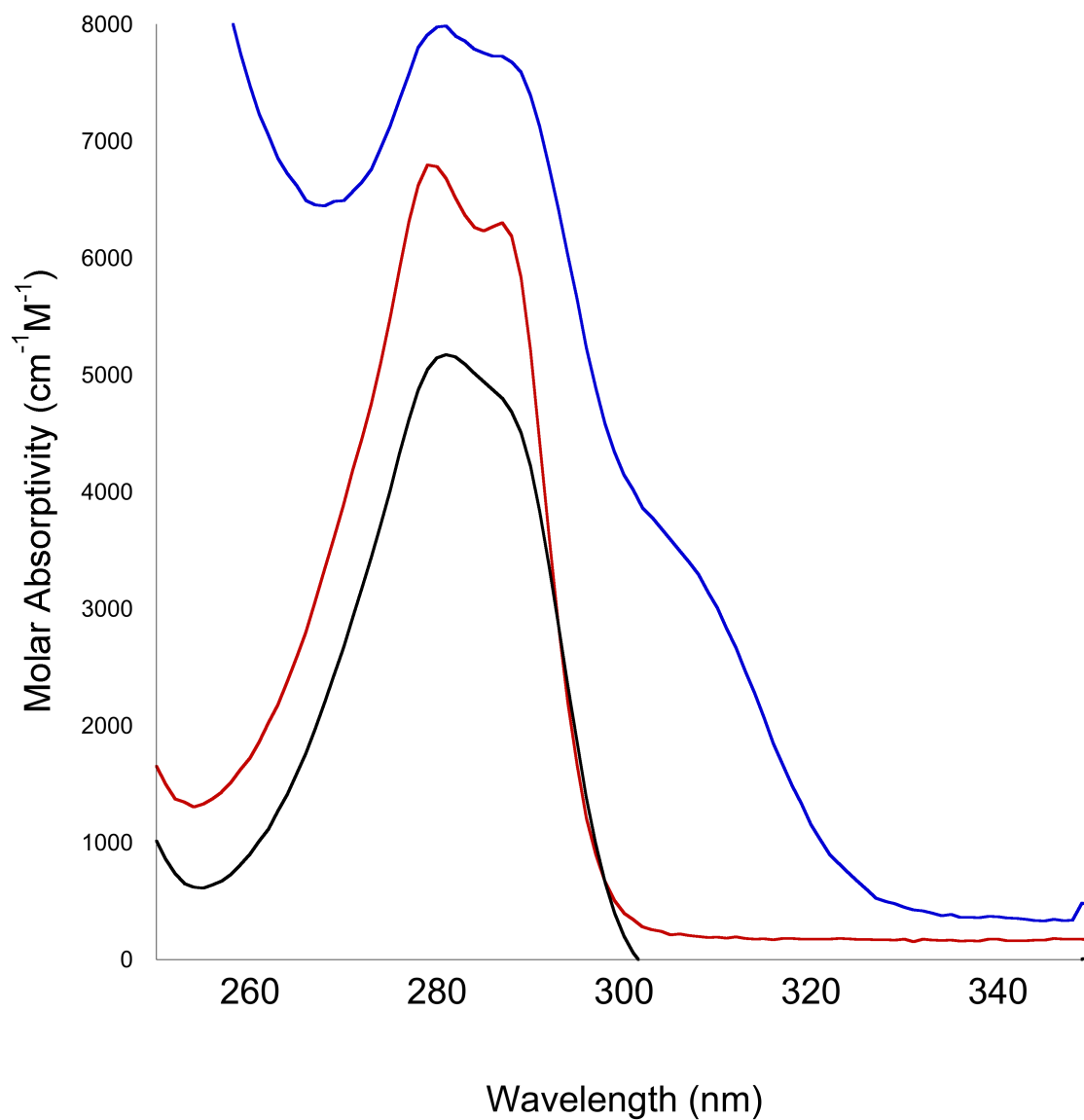


Figure S-6. Excitation (red line) and emission profiles (black line) of $(Et_3NH)[Gd(1)]$ in glassy MeOH at 77 K.

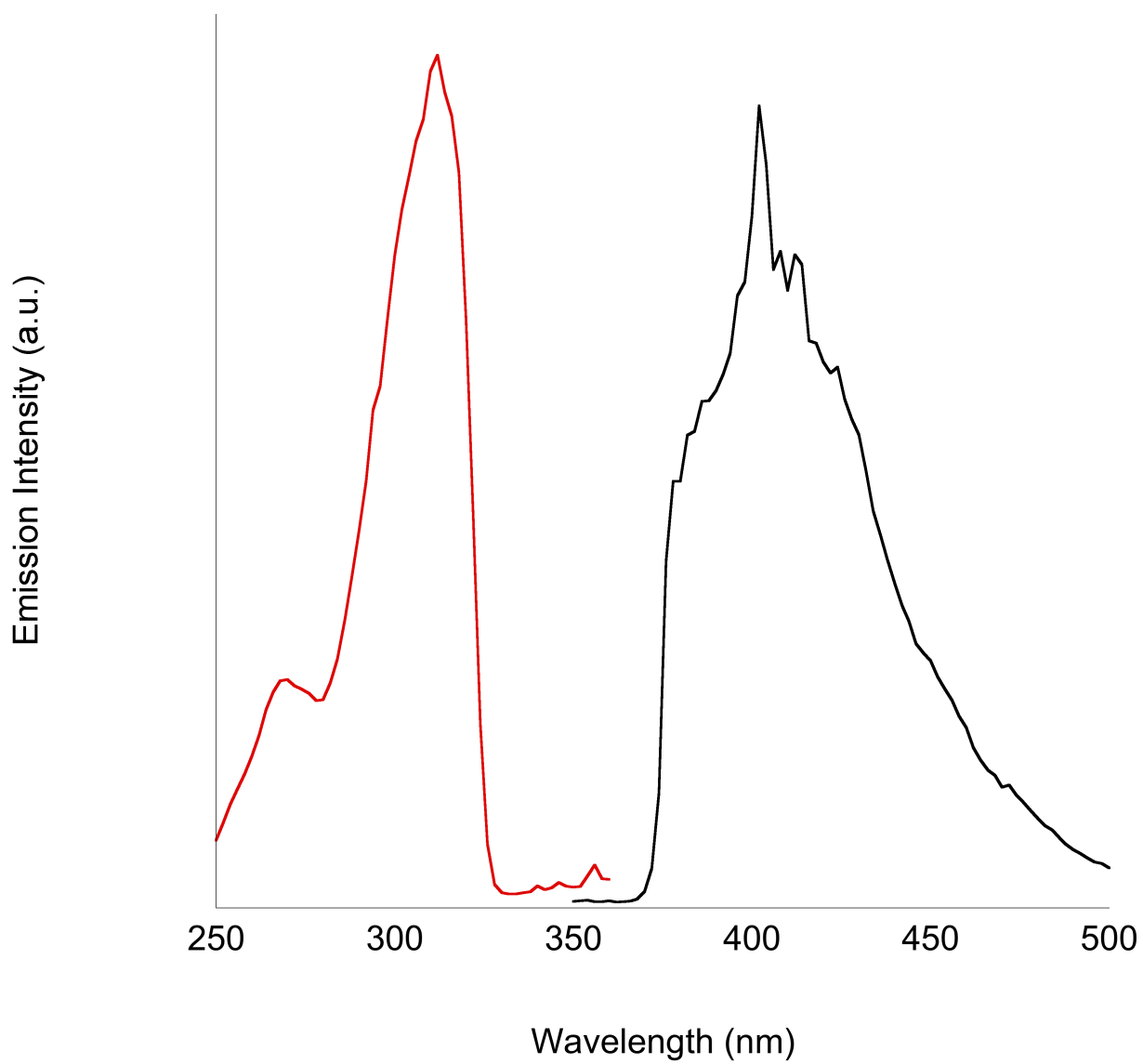


Figure S-7. Normalised excitation and emission profiles of [Tb(**1**)](NO₃)₃ (black and green lines) and (Et₃NH)[Tb(**1**)] (red and blue lines) in air-equilibrated DCM solution.

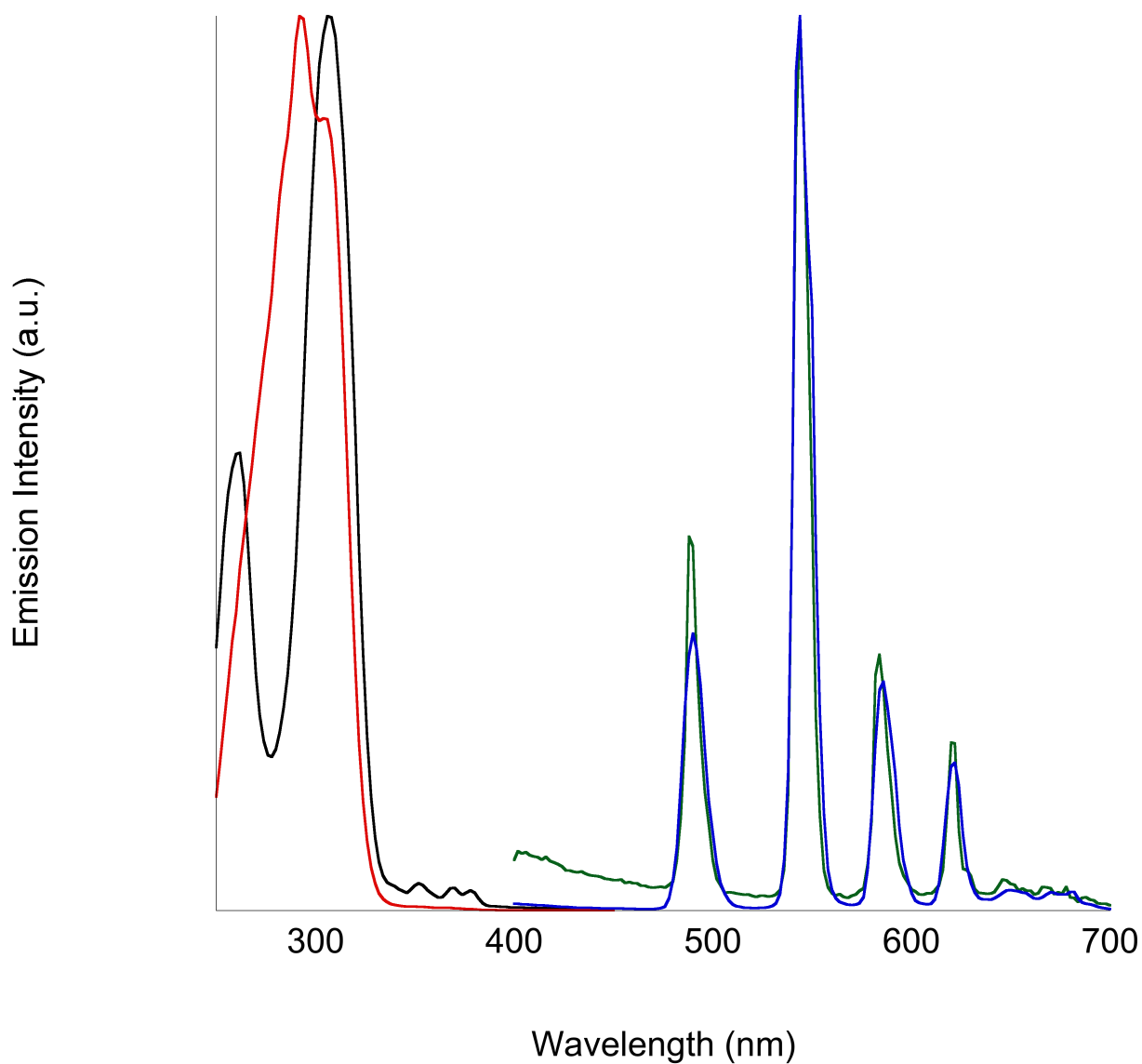


Figure S-8. Normalised excitation and emission profiles of $[\text{Eu}(\mathbf{1})](\text{NO}_3)_3$ (black and red lines) and a solution containing $[\text{Eu}(\mathbf{1})](\text{NO}_3)_3$ and four equivalents of triethylamine (blue and orange lines) in air-equilibrated DCM. The excitation spectra also evidence direct Eu line-like f-f transitions in the region 350-500 nm).

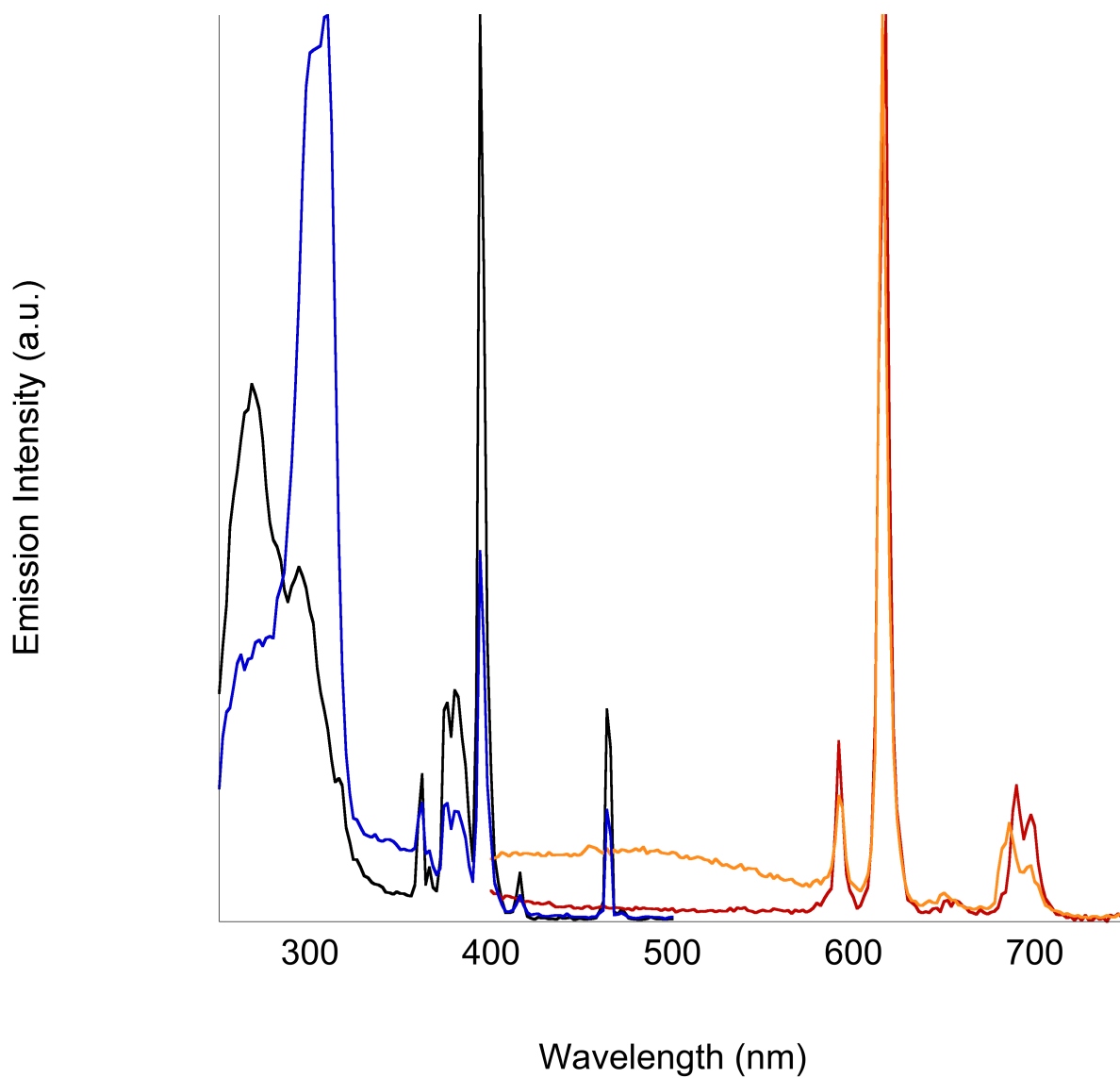
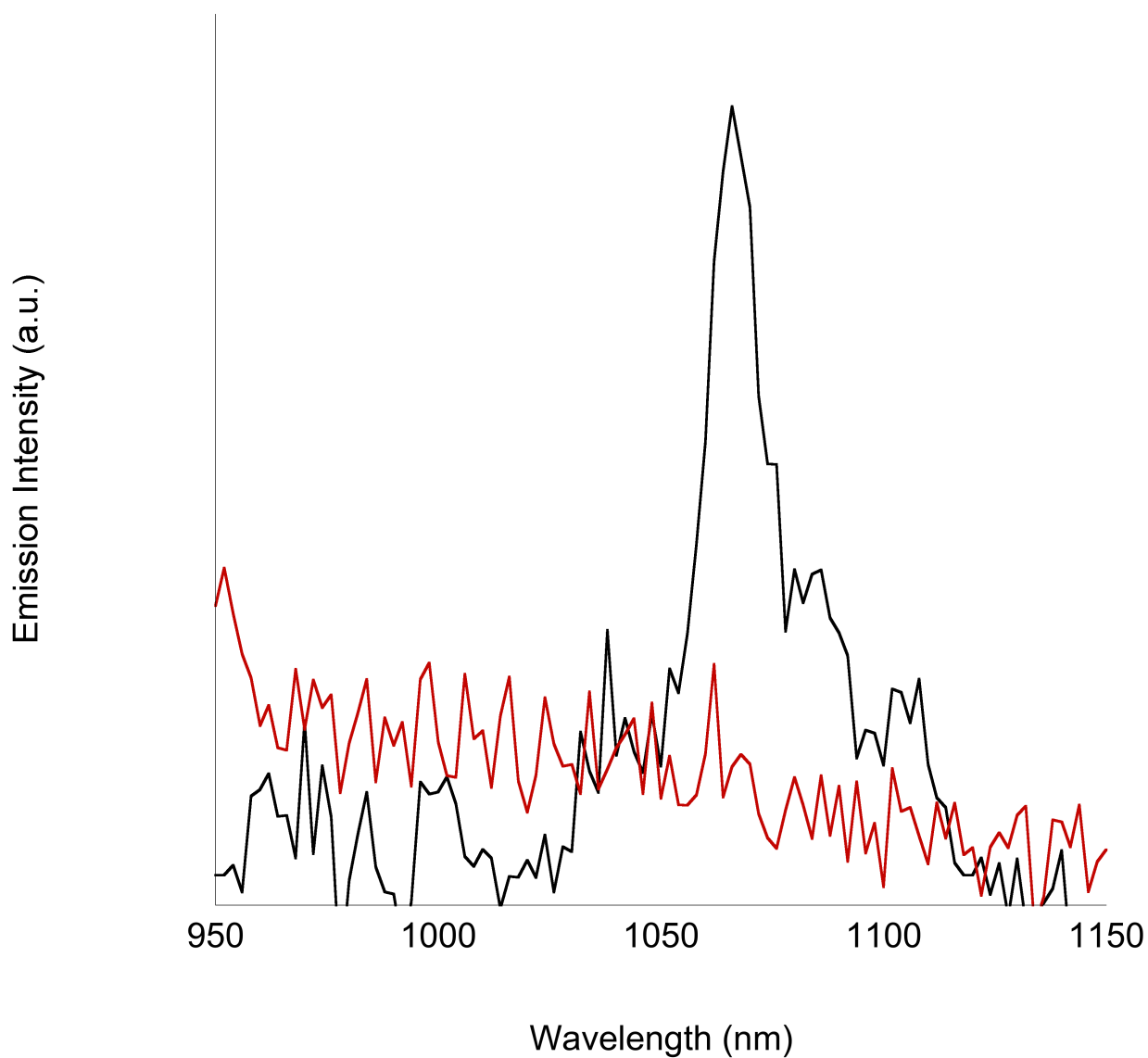


Figure S-9. Emission profiles of [Nd(1)](NO₃)₃ (red line) and (Et₃NH)[Nd(1)] (black line) in air-equilibrated DCM solution.



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