A "plug-and-play" approach to the preparation of transparent luminescent hybrid materials based on poly(methyl methacrylate), a calix[4]arene crosslinking agent and terbium ions.

Electronic Supplementary Information

General considerations

All of the reagents and solvents were obtained from Sigma Aldrich and used as received without any further purification. IR spectra were recorded on solid samples using a diamond ATR Perkin Elmer Spectrum 100 FT-IR. Nuclear magnetic resonance spectra (consisting of ^{1}H, ^{13}C, DEPT, ^{1}H-^{1}H COSY, HSQC and HMBC experiments) were recorded using a Bruker Avance 400 spectrometer (400.1 MHz for ^{1}H, 100 MHz for ^{13}C) at room temperature. ^{1}H and ^{13}C chemical shifts were referenced to residual solvent resonances. Elemental analyses were performed by CMAS (Melbourne, Australia). The absorption spectrum of **1**H was collected on a Perkin Elmer Lambda 35 UV/Vis spectrometer. Steady-state emission spectra were recorded at room temperature using a Hitachi F7000 fluorimeter. The coupled excitation/emission spectra for a section (of ca. 3 mm thickness) of the crosslinked PMMA, containing Tb coordinated to **1**H, was performed with the use of an Edinburgh FLS920P spectrofluorimeter equipped with a Xe900 450 W Xe arc lamp. The excitation spectrum was recorded by monitoring the emission peak at λ_{em}=545 nm. Corrected spectra were obtained via a calibration curve supplied with the instrument. Emission lifetimes were determined on the same Edinburgh instrument with the multichannel scaling (MCS) technique, by monitoring the decaying of the signal intensity at λ_{em}=545 nm. A μF900 Microsecond Flashlamp (60 W) was used as the excitation source, by irradiating the sample at λ_{ex}=320 nm with a frequency of 100.0 Hz. The Tb-doped polymer displayed a lifetime of τ=0.774 ms with a contribution corresponding to 80% of the entire signal. The remaining 20% was fitted with τ'=0.350 ms. Further investigation to confirm the origin of τ' is currently underway. Melting points were measured with a

BI Barnsted Electrothermal 9100 apparatus and are uncorrected.

Synthesis of 1H

Following the procedure published for the synthesis of **2**H,[i] BaO (1.75 g, 11.4 mmol) and

Ba(OH)$_2$.8H$_2$O (1.72 g, 5.45 mmol) were slurried in DMF (30 mL) for 15 minutes. The *p*-

allylcalix[4]arene[ii] (0.90 g, 1.54 mmol) was added and the mixture stirred for 30 mins at ambient

temperature. A solution of 2-chloro-(N.N)-diethylacetamide (1.86 g, 12.4 mmol) in DMF (10 mL)

was added dropwise and the reaction mixture stirred for 3 hours. The reaction was quenched by

pouring into hydrochloric acid (200 mL, 5 M) and the product extracted with ethyl acetate (3 x 50

mL). The organic extracts were combined and washed with 1M HCl (5 x 50 mL) and the solution

was filtered. Removing the solvent at reduced pressure left a yellow oil which was purified by

column chromatography on silica eluting with chloroform/methanol/acetic acid/water (CMAW)

60:30:3:5. The solvent was removed at reduced pressure and the product was reprecipitated from

methanol/water to give the product as a white powder in 35% yield. Melting point; 82 – 84 ˚C.

Elemental analysis. Found: C, 73.40; H, 7.86; N, 4.58. Calcd for C$_{58}$H$_{73}$N$_3$O$_7$.^{3}/2H$_2$O; C, 73.23; H,

8.05; N, 4.42 %.

IR (diamond ATR, cm^{-1}): ν 3382 w br(phenol OH), 3077 w, 2975 m, 2931 m, 1639 s (CO amide),

1471 s, 1430 s, 1380 w, 1358 w, 1303 w, 1267 m, 1217 s, 1143 m, 1098 w, 1059 m, 993 m, 948 w,

906 m, 863 m, 761 w. ^{1}H NMR (400 MHz, CDCl$_3$, ppm): δ 7.45 (s, 1H, OH), 6.74 (2, 2H, Ar CH),

6.69 (s, 2H, Ar CH), 6.44 (d, J = 1 Hz, 2H, Ar CH), 6.42 (d, J = 1 Hz, 2H, Ar CH), 5.85-5.95 (m,

2H, 2 × C*H*=CH$_2$), 5.64 (m, 2H, 2 × C*H*=CH$_2$), 5.06 (s, 2H, OCH$_2$), 5.05 (d, J = 13 Hz, 2H, 2 ×

ArC*H*HAr), 4.94 (d, J = 14 Hz, 2H, 2 × OC*H*H), 4.75-5.00 (m, 8H, 4 × CH=C*H*$_2$), 4.49 (2

coincident doublets, J = 14 Hz, 4H, 2 × OCH*H* and 2 × ArC*H*HAr), 3.29 - 3.47 (m, 12H, 6 ×

NCH$_2$), 3.12-3.27 (m, 8H, 2 × C*H*$_2$CH=CH$_2$ and 4 × ArCH*H*Ar), 4.44 (d, J = 6.5 Hz, 4H, 2 ×

C*H*$_2$CH=CH$_2$), 1.04-1.24 (m, 18H, 6 × NCH$_2$C*H*$_3$). ^{13}C NMR (100 MHz, CDCl$_3$, ppm): δ 169.5

(C=O), 168.0 (C=O), 155.0 (Ar C-OR), 153.9 (Ar C-OR), 151.7 (Ar COH), 139.0 (*C*H=CH$_2$),

138.4 (CH=CH$_2$), 137.9 (CH=CH$_2$), 135.1 (Ar C), 134.7 (Ar C), 134.1 (Ar C), 133.7 (Ar C), 133.6 (Ar C, 129.4 (Ar CH), 129.1 (Ar C), 128.9 (Ar C), 128.8 (Ar CH), 128.51 (Ar CH), 128.48 (Ar CH), 115.1 (CH=CH$_2$), 114.7 (CH=CH$_2$), 72.8 (OCH$_2$), 71.1 (OCH$_2$), 41.2, 41.1, 40.1, 40.1 (NCH$_2$), 39.54 (CH$_2$CH=CH$_2$), 39.49 (CH$_2$CH=CH$_2$), 39.4 (CH$_2$CH=CH$_2$), 32.1 (ArCH$_2$Ar), 31.5 (ArCH$_2$Ar), 14.5, 13.3, 13.2 (CH$_3$). UV/Vis absorption (dichloromethane solution): λ_{max}=285 nm (ε=6144 cm^{-1}M^{-1}).

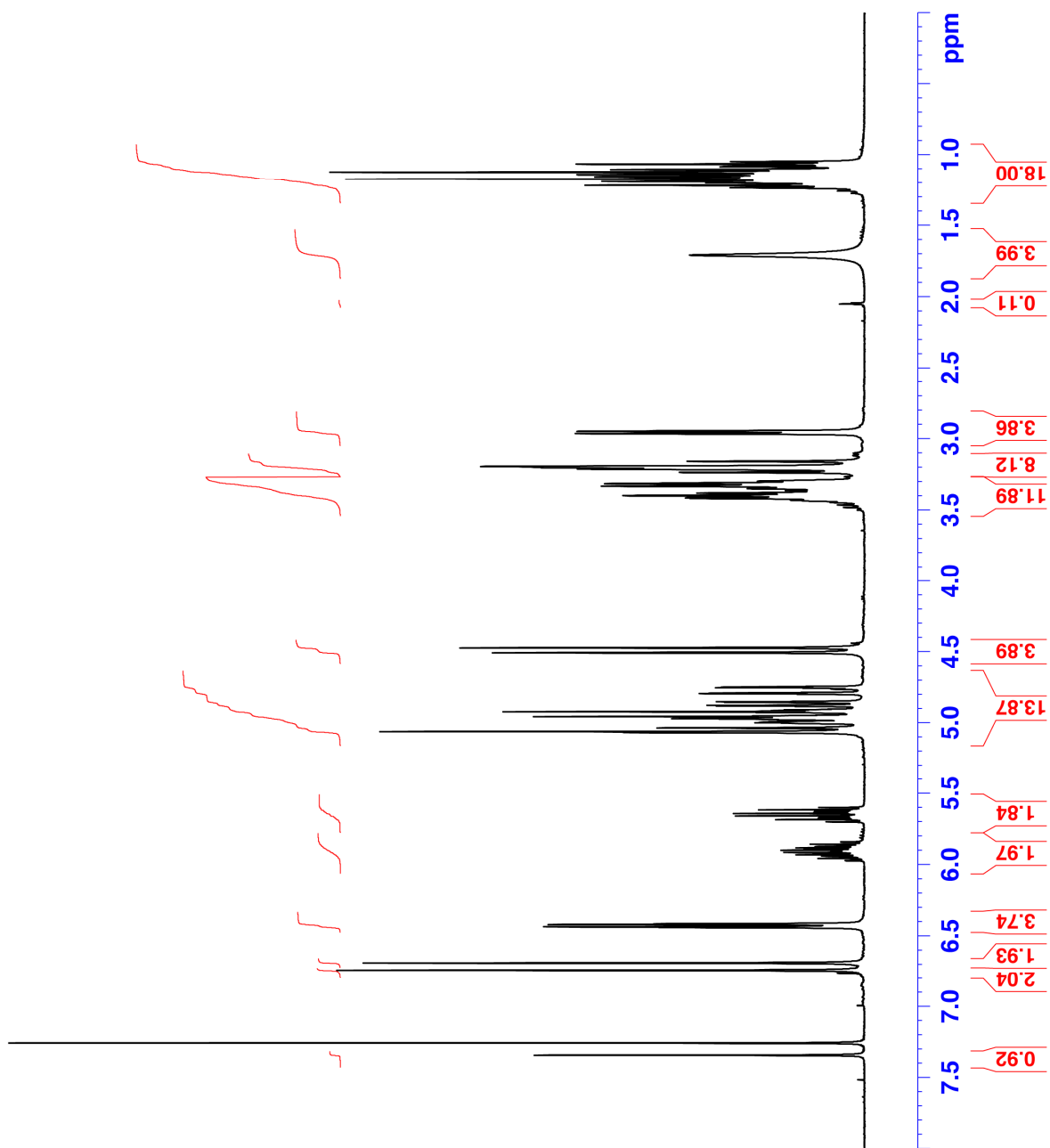**Figure S1 ^{1}H-NMR spectrum of the calix[4]arene 1H in CDCl$_3$**

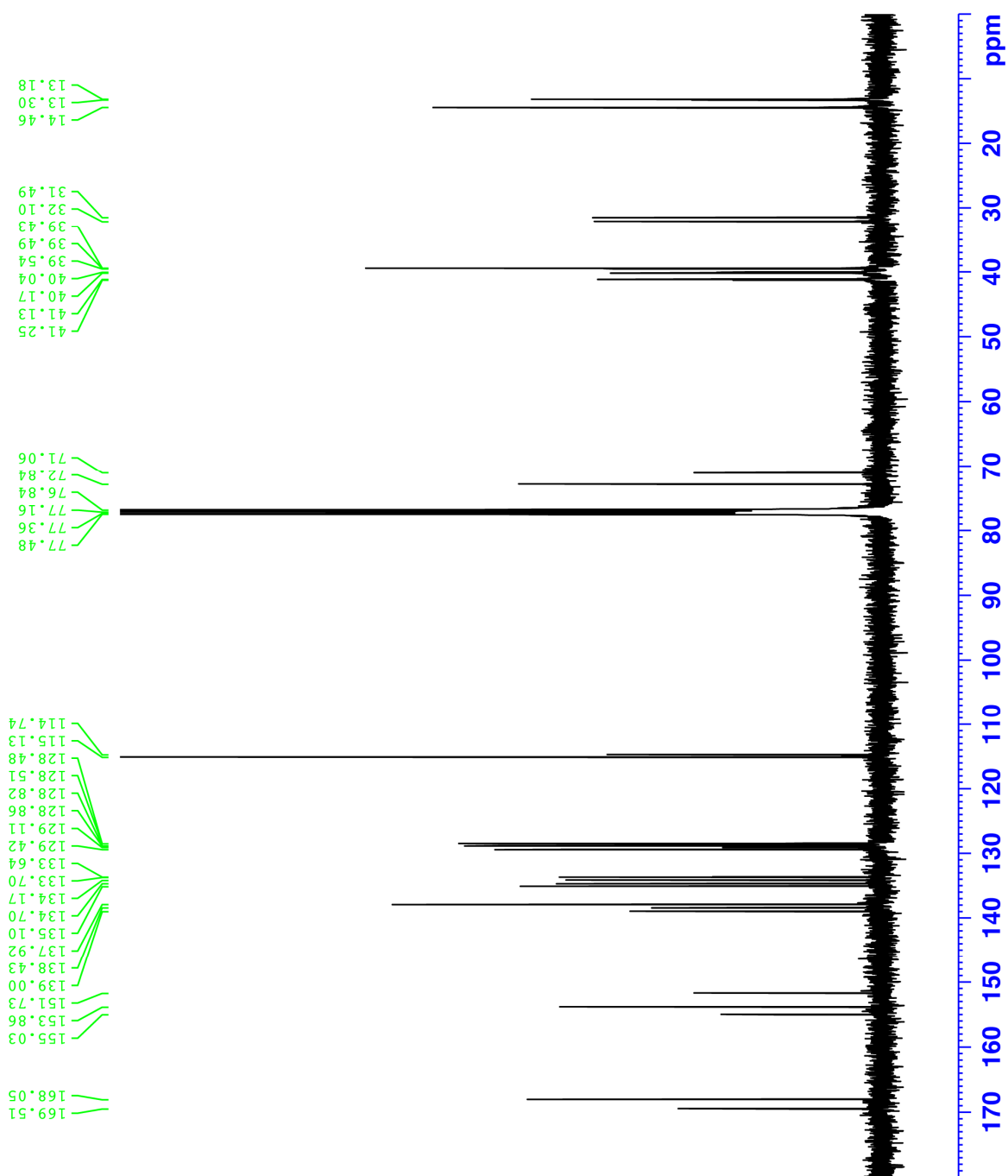**Figure S2 ^{13}C-NMR spectrum of the calix[4]arene 1H in CDCl$_3$**

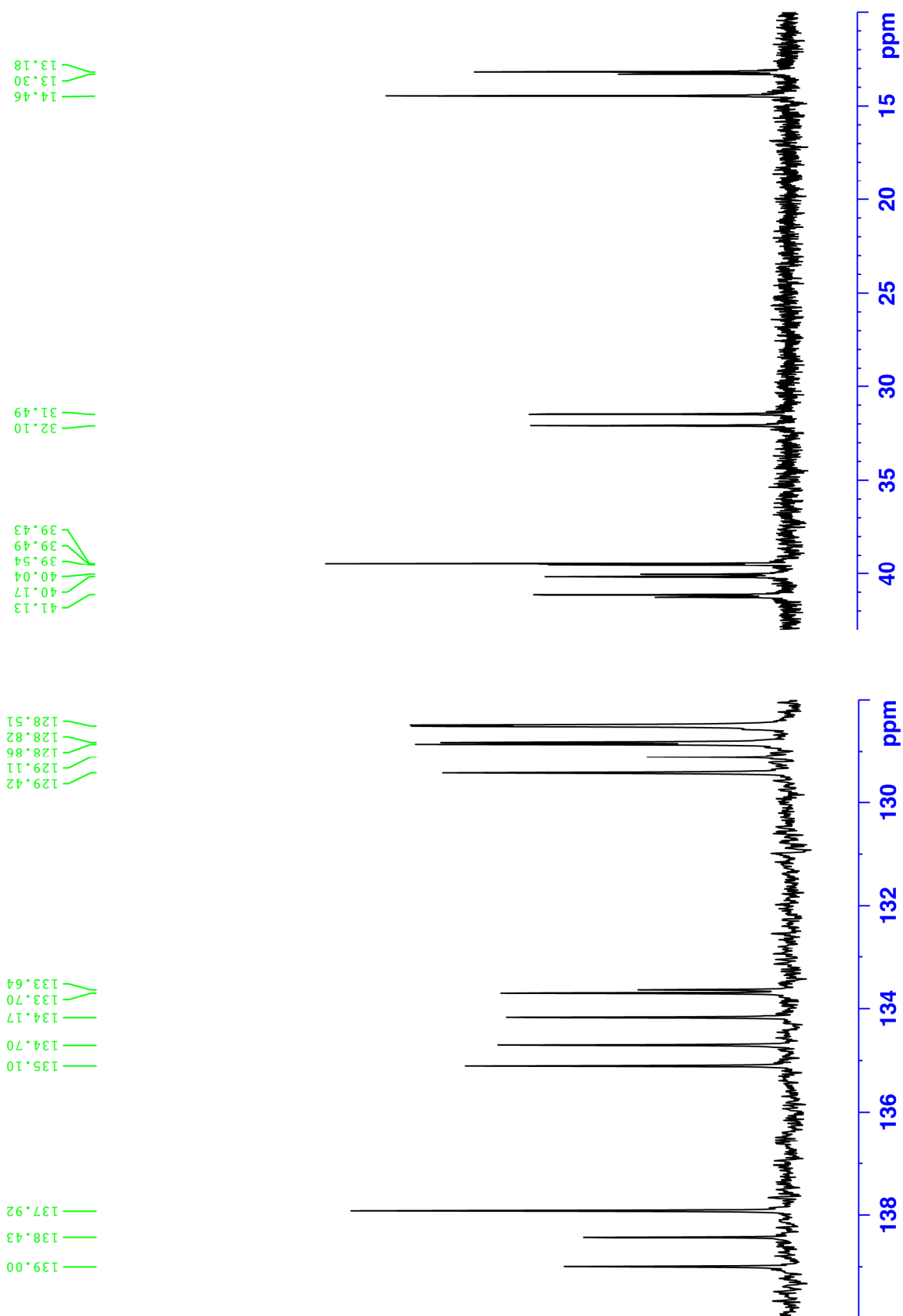**Figure S3 ^{13}C-NMR spectrum of the calix[4]arene 1H in CDCl$_3$ (expansions)**

Table S1 X-ray diffraction data for [Tb(1)(DMSO)]|[ClO₄]₂·2(CH₃CH₂OH)

Empirical formula	$C_{68}H_{106}Cl_2N_3O_{18}STb$
Formula weight	1515.44
Temperature	100(2) K
Wavelength	1.54178 Å
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	a = 12.3105(17) Å
	b = 12.8395(16) Å
	c = 27.754(3) Å
	α= 81.545(10)°
	β= 80.603(10)°
	γ = 61.860(13)°
Volume	3804.0(8) Å^3
Z	2
Density (calculated)	1.323 Mg/m^3
Absorption coefficient	6.011 mm^{-1}
F(000)	1588
Crystal size	0.48 x 0.31 x 0.22 mm^3
θ range for data collection	3.24 to 67.64°.
Index ranges	-14<=h<=14, -15<=k<=14, -32<=l<=33
Reflections collected	37342
Independent reflections	13517 [R(int) = 0.1742]
Completeness to θ = 67.64°	98.1 %
Absorption correction	Analytical
Max./min. transmission	0.477/0.193
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	13517 / 48 / 906
Goodness-of-fit on F^2	0.852
Final R indices [I>2σ(I)]	$R_1 = 0.0778$, $wR_2 = 0.1749$
R indices (all data)	$R_1 = 0.1555$, $wR_2 = 0.2074$
Largest diff. peak and hole	2.568 and -0.991 e.Å^{-3}

Structure refinement details

Crystallographic data for the structures were collected at 100(2) K on an Oxford Diffraction Gemini diffractometer fitted with Cu Kα 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. One tert-butyl group of the calixarene was modelled as being disordered

over two sites with occupancies refined to 0.812(14) and its complement. One solvent ethanol molecule was disordered about a crystallographic inversion centre with another refined with site occupancies of 0.5 as a result of molecular interactions. Geometries of all ethanol molecules were restrained to ideal values and with ADP's also restrained. Although no significant electron density was located in the voids of lattice, the use of the program Squeeze resulted in a significant reduction of the R-factors. Hydroxyl hydrogen positions were obtained from the best fit to electron density. 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 all the non-hydrogen atoms.

One ethanol molecule is situated in the cavity formed by the calixarene ligand. The Tb atom is 8 coordinate, the coordination sphere approximating to a square anti-prism consisting of the four calixarene oxygen atoms forming one plane of the square anti-prism, the three amide oxygen atoms and an oxygen atom from the dmso molecule forming the other plane. The unique phenyl ring of the calixarene is displaced further from this axis than the remaining three. The dihedral angles between this axis and each of the Ph rings (1n)-(4n) being 111.1(2), 114.4(2), 109.8(2) and 137.0(2)°. The angles between opposite Ph rings are 40.9(3) (rings 1 and 3) and 71.4(2)° (rings 2 and 4).
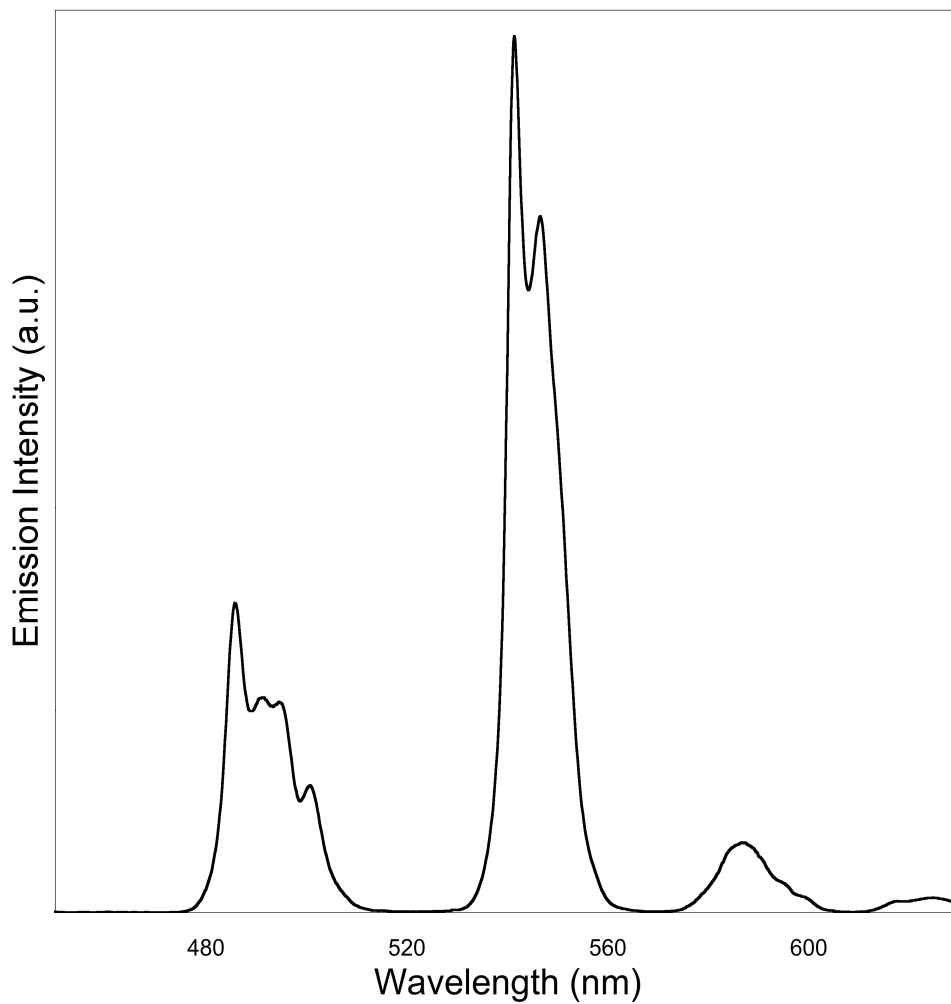
Table S2 Selected bond lengths and angles for $[Tb(\mathbf{1})(DMSO)][ClO_4]_2 \cdot 2(CH_3CH_2OH)$

Tb(1)-O(41)	2.106(6)
Tb(1)-O(1)	2.322(6)
Tb(1)-O(112)	2.341(6)
Tb(1)-O(212)	2.367(5)
Tb(1)-O(312)	2.376(5)
Tb(1)-O(11)	2.500(5)
Tb(1)-O(31)	2.504(5)
Tb(1)-O(21)	2.529(6)

O(41)-Tb(1)-O(1)	87.9(2)
O(41)-Tb(1)-O(112)	93.3(2)
O(1)-Tb(1)-O(112)	74.9(2)
O(41)-Tb(1)-O(212)	149.3(2)
O(1)-Tb(1)-O(212)	114.2(2)
O(112)-Tb(1)-O(212)	73.8(2)
O(41)-Tb(1)-O(312)	138.3(2)

O(1)-Tb(1)-O(312)	73.8(2)
O(112)-Tb(1)-O(312)	116.4(2)
O(212)-Tb(1)-O(312)	71.11(19)
O(41)-Tb(1)-O(11)	74.8(2)
O(1)-Tb(1)-O(11)	133.83(19)
O(112)-Tb(1)-O(11)	64.06(18)
O(212)-Tb(1)-O(11)	74.47(18)
O(312)-Tb(1)-O(11)	143.29(19)
O(41)-Tb(1)-O(31)	77.1(2)
O(1)-Tb(1)-O(31)	80.4(2)
O(112)-Tb(1)-O(31)	153.8(2)
O(212)-Tb(1)-O(31)	125.5(2)
O(312)-Tb(1)-O(31)	63.29(19)
O(11)-Tb(1)-O(31)	133.59(17)
O(41)-Tb(1)-O(21)	108.3(2)
O(1)-Tb(1)-O(21)	148.24(19)
O(112)-Tb(1)-O(21)	129.1(2)
O(212)-Tb(1)-O(21)	64.2(2)
O(312)-Tb(1)-O(21)	76.22(19)
O(11)-Tb(1)-O(21)	77.66(18)
O(31)-Tb(1)-O(21)	77.04(19)

Figure S4 Emission profile of a solution containing equimolar quantities of TbCl$_3$(H$_2$O)$_6$ and

1H

Spectrum obtained at room temperature from a 1:1 ethanol/dichloromethane solution at λ_{ex}=320 nm

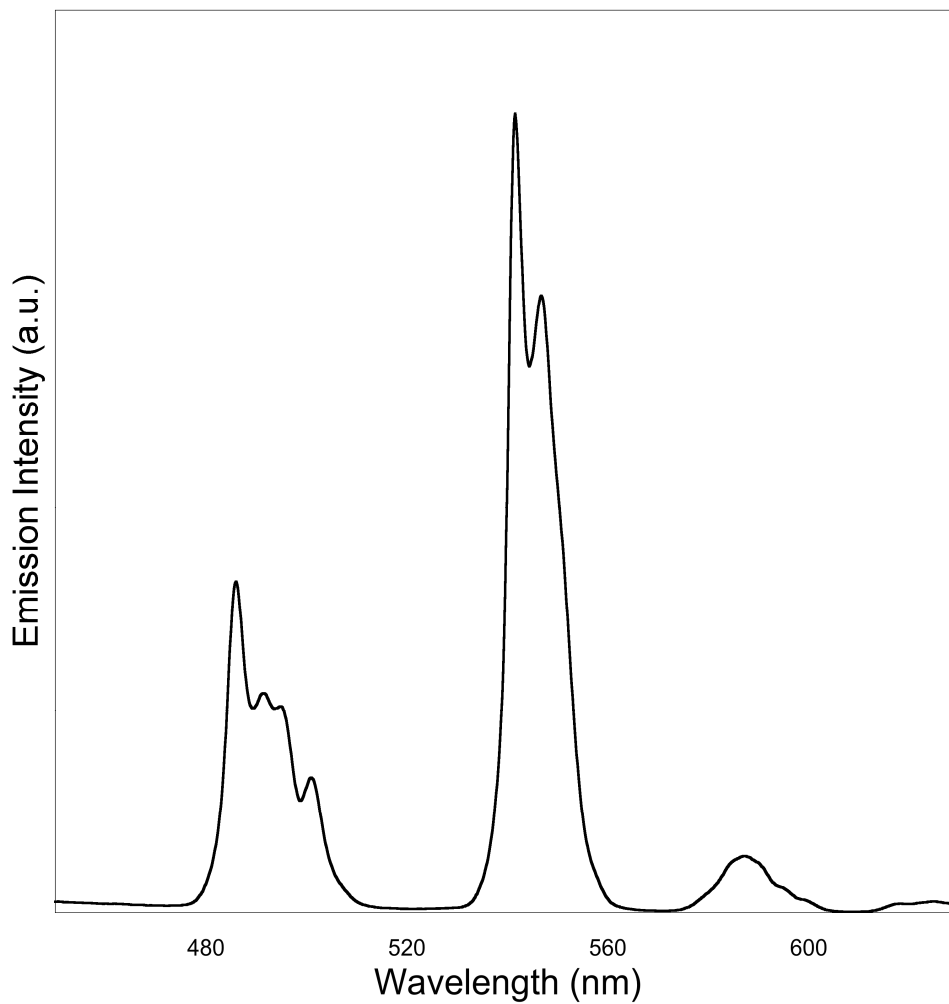**Figure S5 Emission profile of a solution containing equimolar quantities of Tb(NO$_3$)$_3$(DMSO)$_4$**

and 2H (with and without added triethylamine)

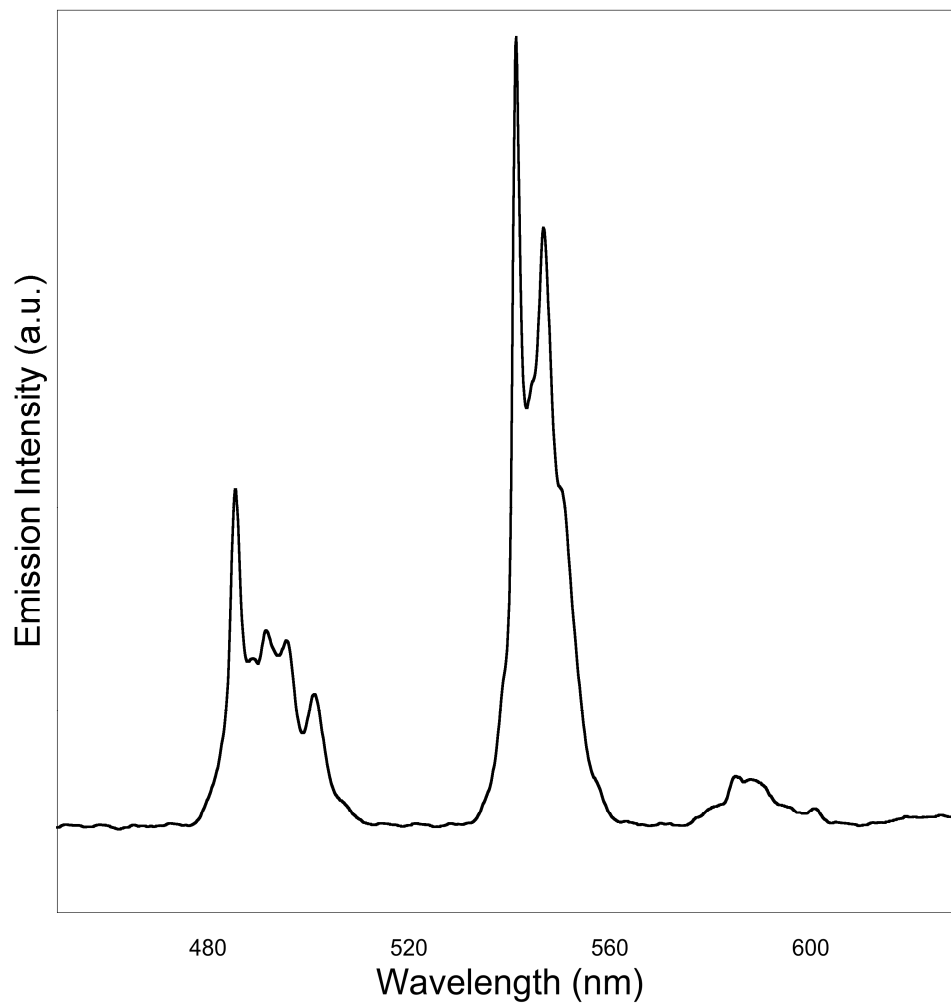Spectra obtained at room temperature from a 1:1 ethanol/dichloromethane solution at λ_{ex}=320 nm

Figure S6 Emission profile of a solution containing equimolar quantities of TbCl$_3$(H$_2$O)$_6$ and

2H

Spectrum obtained at room temperature from a 1:1 ethanol/dichloromethane solution at λ_{ex}=320 nm
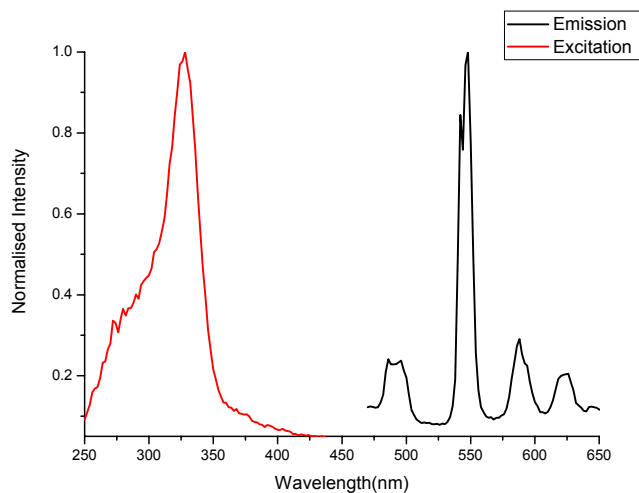
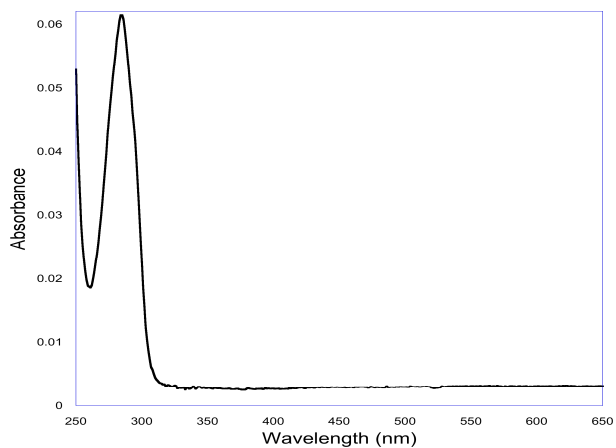**Figure S7 Emission profile of a solution containing equimolar quantities of Tb(ClO₄)₃(DMSO)₄ and 2H**

Spectrum obtained at room temperature from a 1:1 ethanol/dichloromethane solution at λ_{ex}=320 nm

Figure S8 (a) Excitation and emission profiles of a ca. 3 mm thick section of PMMA monolith crosslinked with Tb(1)(NO₃)₂ (b) UV/Vis absorption spectrum of ligand 1H (10⁻⁵ M solution in dichloromethane)

(a)

(b)

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[i] M. I. Ogden, B. W. Skelton and A. H. White, *J. Chem. Soc., Dalton Trans.*, 2001, 3073-3077.

[ii] C. D. Gutsche, J. A. Levine and P. K. Sujeeth, *J Org Chem*, 1985, **50**, 5802-5806.