Electronic Supplementary Material (ESI) for Dalton Transactions.

Electronic Supplementary Information (ESI) – Table of Contents

A macrocyclic tetraamine bearing four phenol groups: a new class of heptadentate ligands to provide an oxygen-sensitive luminescent Tb(III) complex with an extendable phenol pendant arm

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Experimental details

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Experimental details

General: All experiments were performed under a dry nitrogen or argon atmosphere using standard Schlenk techniques or a glovebox. $Tb(OTf)_3$ was purchased from Aldrich. Standard gas mixtures containing 0, 30, 50, 75 and 100% of O_2 balanced with N_2 (100, 70, 50, 25 and 0%, respectively) were purchased from Sumitomo Seika Chemicals Co., Ltd. All other chemicals were obtained from commercial sources and used as received unless otherwise noted.

^{1}H and ^{13}C NMR spectra were recorded on a JEOL JNM-AL300 FT-NMR spectrometer in $CDCl_3$. Chemical shifts were referenced to *protio* solvent impurities (^{1}H: δ 7.26, ^{13}C: δ 77.2 ppm) and are reported in ppm. Electrospray ionisation mass spectrometry data were obtained by a JEOL JMS-T100ESI AccuTOF LC-plus. UV-vis absorption spectra were measured in a JASCO V-670 UV-visible-NIR Spectrophotometer (cell length = 10.0 mm). Elemental analyses were performed using a Yanaco CHN-coder MT-5.

Luminescence properties (corrected luminescence and excitation spectra, luminescence lifetimes and luminescence quantum yields) were measured using a Horiba Jobin Yvon FluoroMax-4P Spectrofluorometer. Luminescence quantum yields were measured by the relative comparison method with quinine bisulfate in 0.5 M H_2SO_4 ($\Phi = 0.60$) chosen for the standard (The error in the reported values is within ±10% which is confirmed by the cross-calibration of the standard).[1] The general equation used for determination of relative quantum yields is given as $Q_x/Q_{st} = [A_{st}(\lambda)/A_x(\lambda)][I_x/I_{st}][n_x^2/n_{st}^2]$, where A is absorbance at excitation wavelength, I is integrated luminescence intensity and n is the refractive index. The subscripts x and st represent sample and standard, respectively.

For measuring oxygen-sensing properties, the standard gas mixtures (0, 30, 50, 75 and 100% of O_2) and air were passed through the cuvette to equilibrate the oxygen content to the respective concentrations (flow rate = 5 mL min^{-1}; time > 5 min). The oxygen concentrations (1.01, 0.75, 0.50, 0.30 and 0.00 × 10^{-2} M at 100, 75, 50, 30 and 0% of O_2, respectively) reported in Fig. S4 and S10 were calculated from the mole fraction solubility of oxygen in THF at 101.325 kPa partial pressure of gas (8.16 × 10^{-4} at 298.15 K).[2]

X-ray crystallography: All measurements were made on a Rigaku/MSC Saturn CCD diffractometer with confocal monochromated Mo Kα radiation (λ = 0.71070 Å). Data were collected and processed using CrystalClear[3] software (Rigaku). The data were corrected for Lorentz and polarisation effects. Empirical absorption corrections were applied. The structures were solved by a direct method: SIR-2011[4] and expanded using a Fourier technique. All calculations were performed using the CrystalStructure[5,6] crystallographic software package except for refinement, which was performed using SHELXL2013[7]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model.

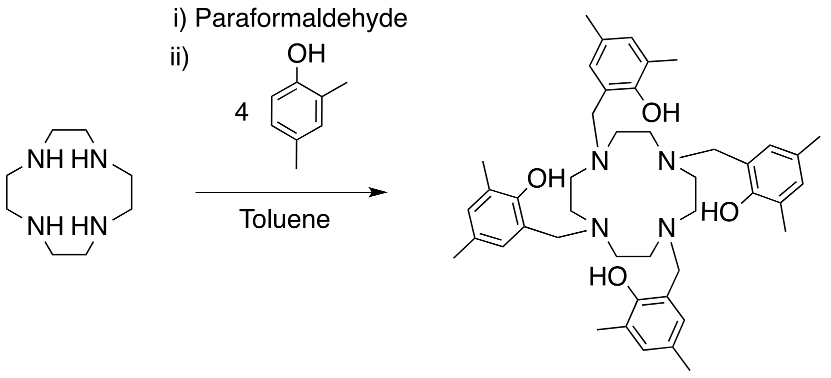
{(^{MeMe}ArOH)$_4$cyclen}: the EtOH molecules were treated by SQUEEZE program as diffuse contributions. In the resulting void space, a contribution of 96 e^- per unit cell (4 x 24) was found and taken to represent four molecules (calc. 4 x 26 = 104 e^-), giving one EtOH per one molecule (Z = 4).

2^{cyclen}: one H_2O (disordered at two positions) and one CH_3CN molecules with partial occupancies are included. The optimal result was obtained with 60%, 20% and 80% occupancies for O(6A) of H_2O, O(6B) of H_2O and CH_3CN, respectively.

Crystallographic data has been deposited with the Cambridge Crystallographic Data Centre (CCDC). CCDC reference number: 1041014 ({(^{MeMe}ArOH)$_4$cyclen}), 1041015 (**1**^{cyclen}) and 1041016 (**2**^{cyclen}).

Synthesis

{($\{(^{MeMe}ArOH)_4cyclen\}$



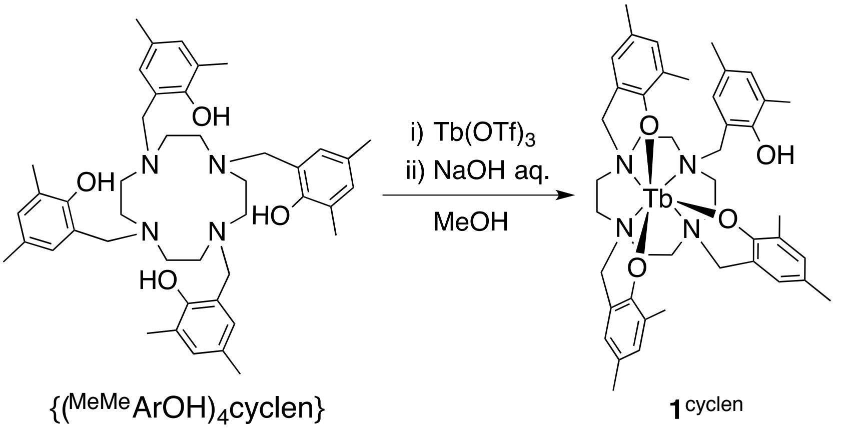
Cyclen

$\{(^{MeMe}ArOH)_4cyclen\}$

A mixture of 1,4,7,10-tetraazacyclododecane (2.18 g, 12.7 mmol) and paraformaldehyde (1.91 g, 63.5 mmol) in toluene (90 mL) was stirred for 5 h at 50 °C. To the resulting pale yellow solution was added 2,4-dimethylphenol (7.85 g, 63.5 mmol). The mixture was stirred for 3 days at room temperature. The white precipitate was isolated by filtration and washed with MeOH. Yield: 5.77 g (64%). Single crystals suitable for X-ray diffraction analysis were obtained from a saturated solution of $\{(^{MeMe}ArOH)_4cyclen\}$ in AcOEt/EtOH (3/1) at room temperature.

^{1}H NMR (300 MHz, $CDCl_3$): δ 9.72 (4H, s, $\{(CH_2(CH_3)_2C_6H_2O\mathit{H})_4C_8H_{16}N_4\}$), 6.85 (4H, s, $\{(CH_2(CH_3)_2C_6\mathit{H}_2OH)_4C_8H_{16}N_4\}$), 6.52 (4H, s, $\{(CH_2(CH_3)_2C_6\mathit{H}_2OH)_4C_8H_{16}N_4\}$), 3.51 (8H, s, $\{(C\mathit{H}_2(CH_3)_2C_6H_2OH)_4C_8H_{16}N_4\}$), 2.79 (16H, s, $\{(CH_2(CH_3)_2C_6H_2OH)_4C_8\mathit{H}_{16}N_4\}$), 2.19 (24H, s, $\{(CH_2(C\mathit{H}_3)_2C_6H_2OH)_4C_8H_{16}N_4\}$). ^{13}C NMR (75 MHz, $CDCl_3$): δ 152.73, 130.82, 127.96, 127.39, 125.10, 120.98, 59.10, 50.79, 20.37, 15.70. UV-vis (THF): λ_{max}/nm (ε/M^{-1}cm^{-1}) = 285 (10000). Anal. calcd. for $\{(^{MeMe}ArOH)_4cyclen\}$ ($C_{44}H_{60}N_4O_4$): C, 74.54; H, 8.53; N, 7.90%. Found: C, 74.70; H, 8.57; N, 8.00%.

*[{(^{MeMe}ArOH)(^{MeMe}ArO)$_3$cyclen}Tb^{III}] (**1**^{cyclen})*

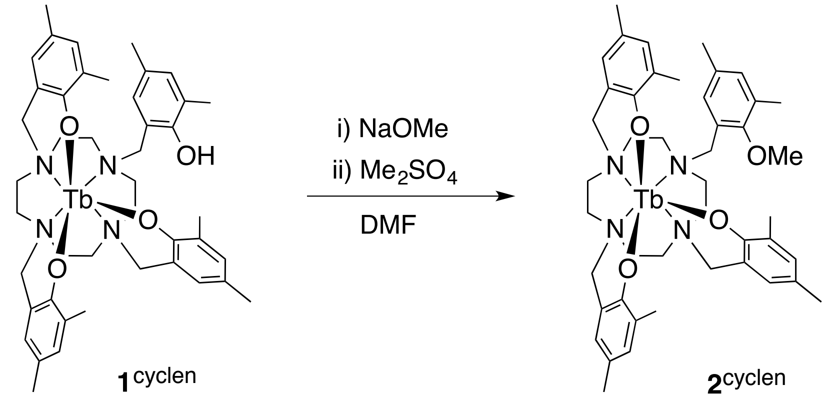


A mixture of {(^{MeMe}ArOH)$_4$cyclen} (300 mg, 0.42 mmol) and Tb(OTf)$_3$ (256 mg, 0.42 mmol) in MeOH (90 mL) was stirred for 5 min at room temperature. To the mixture was added dropwise a 7.5 M NaOH aq. solution (180 μL, 1.4 mmol). The resulting solution was stirred for 3 h at room temperature. The solvent was removed under reduced pressure and the product was extracted with CH_2Cl_2. The CH_2Cl_2 was removed under reduced pressure. The obtained white microcrystalline solid was washed with a small amount of MeOH. Yield: 238 mg (65%). Single crystals suitable for X-ray diffraction analysis were obtained from a saturated solution of **1**^{cyclen} in MeOH at room temperature.

UV-vis (THF): λ_{max}/nm (ε/M^{-1}cm^{-1}) = 299 (15000). ESI-MS (CsOH/MeOH): *m*/*z* 997.3 [**1**^{cyclen} + Cs]$^+$ {relative intensity (*I*) = 100% in the range of *m*/*z* 200-2000}. The molecular ion, *m*/*z* 865.3 [**1**^{cyclen} + H]$^+$, can be observed without the cationic additives (Cs$^+$, K$^+$ or Na$^+$): the cationic additives help soft ionisation of **1**^{cyclen}. The molecular ion, *m*/*z* 863.4 [**1**^{cyclen} – H]$^-$ {relative intensity (*I*) = 100% in the range of *m*/*z* 200-2000}, can also be observed in the negative-ion electrospray ionisation mass spectrum in MeOH. Anal. calcd. for **1**^{cyclen} + 3MeOH ($C_{47}H_{69}N_4O_7Tb$): C, 58.74; H, 7.24; N, 5.83%. Found: C, 58.74; H, 7.08; N, 6.00%.

The ^{1}H NMR spectrum of **1** in $CDCl_3$ at room temperature shows severe broadening. This may be attributed to the dynamic motions of the cyclen-based ligand: D. Parker, R. S. Dickins, H. Puschmann, C. Crossland and J. A. K. Howard, *Chem. Rev.*, 2002, **102**, 1977.

$[\{(^{MeMe}ArOMe)(^{MeMe}ArO)_3cyclen\}Tb^{III}]$ (2^{cyclen})



A mixture of $\mathbf{1}^{cyclen}$ (180 mg, 0.21 mmol) and sodium methoxide (12 mg, 0.23 mmol) in DMF (10 mL) was stirred for 0.5 h at room temperature. To the mixture was added dropwise dimethyl sulfate (Me_2SO_4) (22 μL, 0.23 mmol). The resulting solution was stirred for 2 h at room temperature. The solvent was removed under reduced pressure and the product was extracted with AcOEt. The AcOEt was removed under reduced pressure. The obtained white microcrystalline solid was washed with a small amount of MeCN. Yield: 113 mg (62%). Single crystals suitable for X-ray diffraction analysis were obtained from a saturated solution of $\mathbf{2}^{cyclen}$ in MeOH/MeCN (2/1) at room temperature.

UV-vis (THF): λ_{max}/nm (ε/M^{-1}cm^{-1}) = 301 (15000). ESI-MS (CsOH/MeOH): *m*/*z* 1011.4 [$\mathbf{2}^{cyclen}$ + Cs]$^+$ {relative intensity (*I*) = 100% in the range of *m*/*z* 200-2000}. The molecular ion, *m*/*z* 879.4 [$\mathbf{2}^{cyclen}$ + H]$^+$, can be observed without the cationic additives (Cs$^+$, K$^+$ or Na$^+$): the cationic additives help soft ionisation of $\mathbf{2}^{cyclen}$. Anal. calcd. for $\mathbf{2}^{cyclen}$ ($C_{45}H_{59}N_4O_4Tb$): C, 61.50; H, 6.77; N, 6.37%. Found: C, 61.26; H, 7.00; N, 6.25%.

References

1 K. Suzuki, A. Kobayashi, S. Kaneko, K. Takehira, T. Yoshihara, H. Ishida, Y. Shiina, S. Oishi and S. Tobita, *Phys. Chem. Chem. Phys.*, 2009, **11**, 9850.

2 R. Battino, T. R. Rettich and T. Tominaga, *J. Phys. Chem. Ref. Data*, 1983, **12**, 163.

3 *CrystalClear*: Data collection and Processing Software, Rigaku Corporation (1998-2014). Tokyo 196-8666, Japan.

4 M. C. Burla, R. Caliandro, M. Camalli, B. Carrozzini, G. L. Cascarano, C. Giacovazzo, M. Mallamo, A. Mazzone, G. Polidori and R. Spagna, *J. Appl. Cryst.*, 2012, **45**, 357.

5 *CrystalStructure 4.1*: Crystal Structure Analysis Package, Rigaku Corporation (2000-2014). Tokyo 196-8666, Japan.

6 G. M. Sheldrick, *Acta Cryst.*, 2008, **A64**, 112.

Tables

Table S1 Crystallographic data for {(^{MeMe}ArOH)$_4$cyclen}, **1**^{cyclen} and **2**^{cyclen}

	{(^{MeMe}ArOH)$_4$cyclen}	**1**^{cyclen}	**2**^{cyclen}
Formula	$C_{44}H_{60}N_4O_4$ $\cdot 2H_2O\cdot EtOH$	$C_{44}H_{57}N_4O_4Tb$ $\cdot 3MeOH$	$C_{45}H_{59}N_4O_4Tb$ $\cdot 1.8H_2O\cdot 0.8CH_3CN$
Fw	791.08	961.01	944.15
Crystal system	tetragonal	monoclinic	monoclinic
Space group	*P*4/*ncc* (No. 130)	*P*2$_1$/*c* (No. 14)	*P*2$_1$/*n* (No. 14)
a (Å)	16.679(3)	9.966(2)	15.798(3)
b (Å)	16.679(3)	23.022(5)	16.162(3)
c (Å)	16.933(3)	19.964(4)	18.914(4)
α (deg)	90	90	90
β (deg)	90	90.782(3)	105.204(3)
γ (deg)	90	90	90
V (Å^3)	4710.3(15)	4580.3(17)	4660.1(16)
Z	4	4	4
μ (cm^{-1})	0.75	15.94	15.67
F(000)	1720.00	2000.00	1958.00
D_{calcd}(g/cm^3)	1.115	1.394	1.346
Temperature (K)	93	93	103
Reflections collected	34536	36868	36921
Independent	2700 (R_{int} = 0.0497)	10337 (R_{int} = 0.0509)	10601 (R_{int} = 0.0459)
Data/parameters	2700/127	10337/544	10601/546
R_1 [$I > 2\sigma(I)$]	0.1020	0.0442	0.0443
wR_2 (all data)	0.2534	0.1003	0.1069
Goodness-of-fit	1.072	1.064	1.102

Table S2 Continuous shape measures (CSM) values calculated for the Tb^{3+} in **1**^{cyclen} and **2**^{cyclen}

	HP–7	HPY–7	PBPY–7	COC–7	CTPR–7	JPBPY–7	JETPY–7
1^{cyclen}	35.837	17.736	7.059	1.670	**1.180**	11.198	20.607
2^{cyclen}	36.212	17.628	6.391	**1.094**	1.724	10.416	21.246

HP-7 (D_{7h})	Heptagon
HPY-7 (C_{6v})	Hexagonal pyramid
PBPY-7 (D_{5h})	Pentagonal bipyramid
COC-7 (C_{3v})	Monocapped octahedron (Capped octahedron)
CTPR-7 (C_{2v})	Monocapped trigonal prism (Capped trigonal prism)
JPBPY-7 (D_{5h})	Johnson pentagonal bipyramid (J13)
JETPY-7 (C_{3v})	Johnson elongated triangular pyramid (J7)

Shape and Symmetry of Heptacoordinate Compounds: D. Casanova, P. Alemany, J. M. Bofill and S. Alvarez, *Chem. Eur. J.* 2003, **9**, 1281.

The CTPR-7 and COC-7 are interconvertible in small translation of two atoms: A. J. Amoroso, P. G. Edwards, S. T. Howard, B. M. Kariuki, J. C. Knight, L. Ooi, K. M. A. Malik, L. Stratford and A.-R. H. Al-Sudani, *Dalton Trans.*, 2009, 8356.

Figures

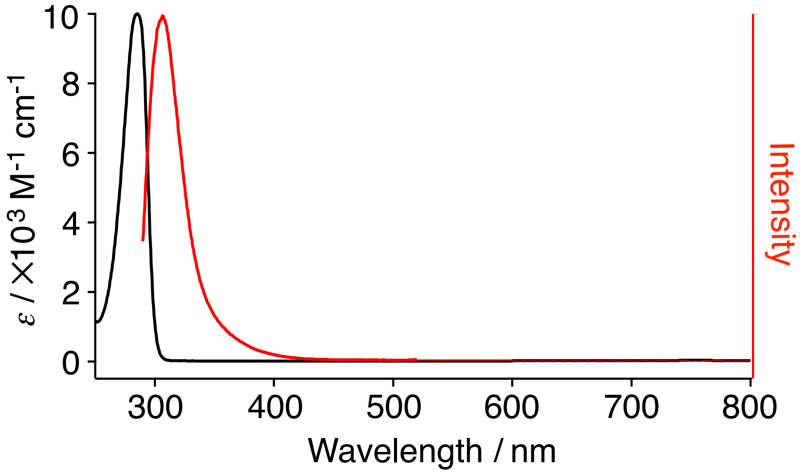


Fig. S1 UV–vis absorption (black) and corrected luminescence spectra (red, λ_{ex} = 270 nm) of $\{(^{MeMe}ArOH)_4cyclen\}$ in THF at room temperature.

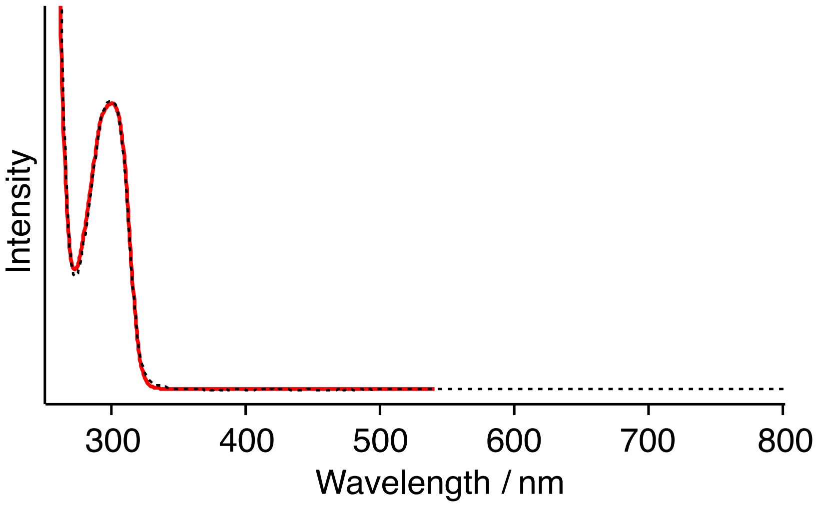


Fig. S2 Absorption (black dot) and excitation (red) spectra of $\mathbf{1}^{cyclen}$ in THF at room temperature. The excitation spectrum was detected at 543 nm.

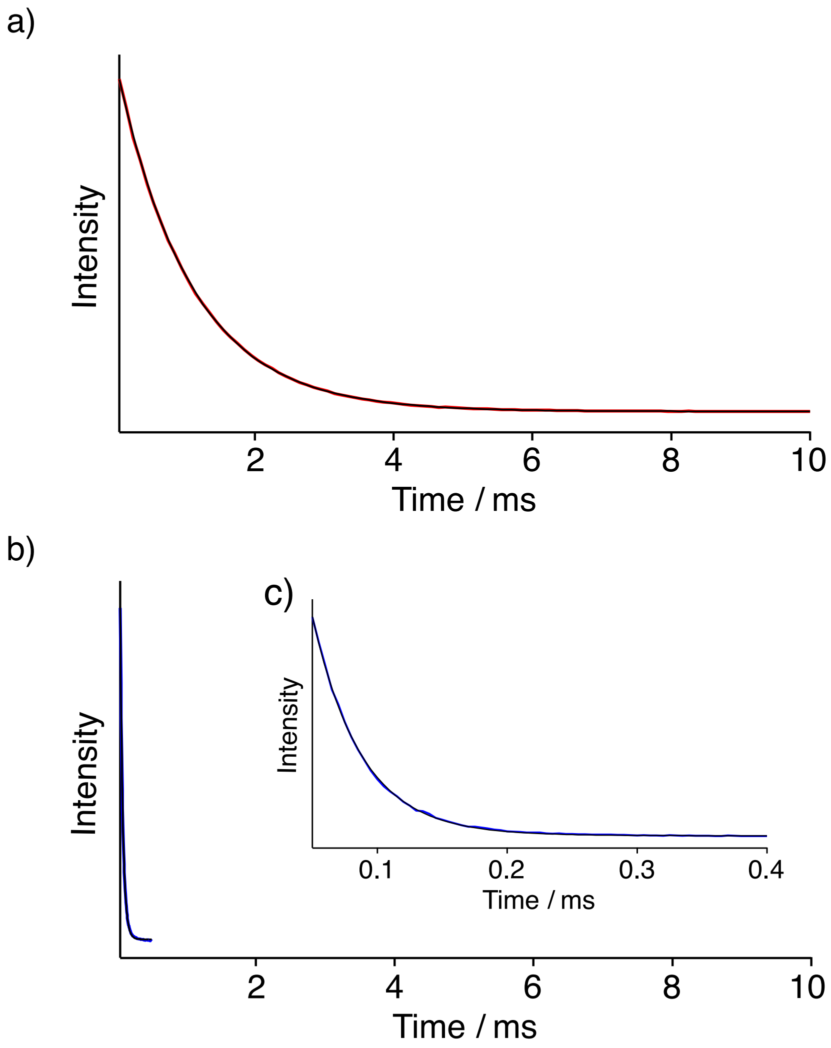


Fig. S3 Luminescence decay curves of $\mathbf{1}^{\text{cyclen}}$ under (a) N_2 (red, 1070 μs) and (b and c) air (blue, 40 μs) in THF at room temperature. The decay was monitored at 543 nm (λ_{ex} = 300 nm). Fitted by single exponential curve (black).

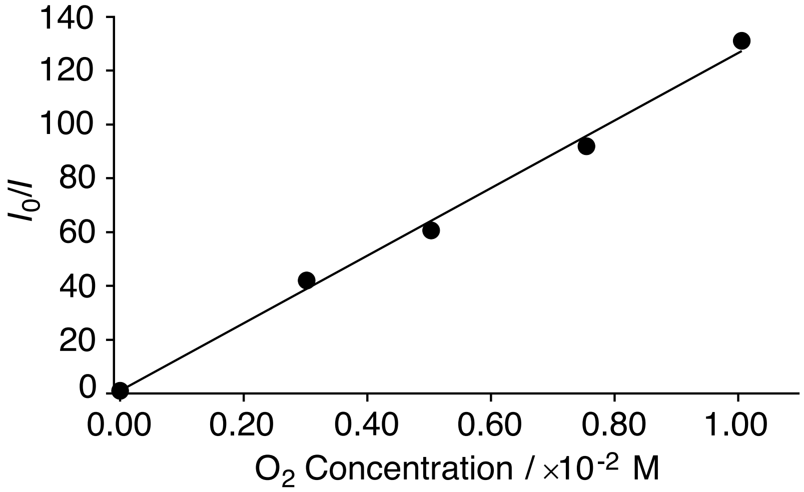


Fig. S4 Stern–Volmer plot of the luminescence intensity (I_0/I) against the oxygen concentration [O_2] for $\mathbf{1}^{\mathrm{cyclen}}$ (5.5×10^{-6} M) ($K_{\mathrm{sv}} = 12600$ M^{-1}, $R^2 = 0.9974$). The I_0 and I are the luminescence intensities at an O_2 concentration of 0.00 M (under N_2) and at the indicated O_2 concentrations, respectively.

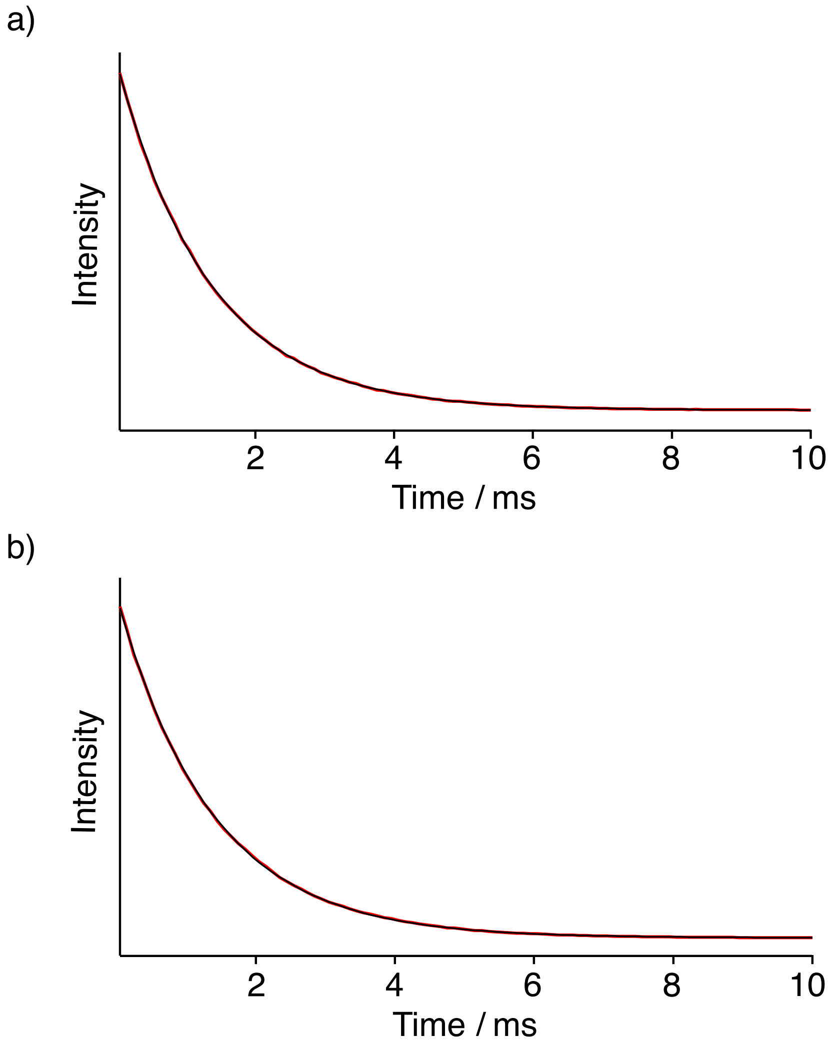


Fig. S5 Luminescence decay curves (red) of $\mathbf{1}^{\mathrm{cyclen}}$ under N_2 in (a) CH_3OH (1350 μs) and (b) CD_3OD (1360 μs) at room temperature. The decay was monitored at 543 nm (λ_{ex} = 300 nm). Fitted by single exponential curve (black).

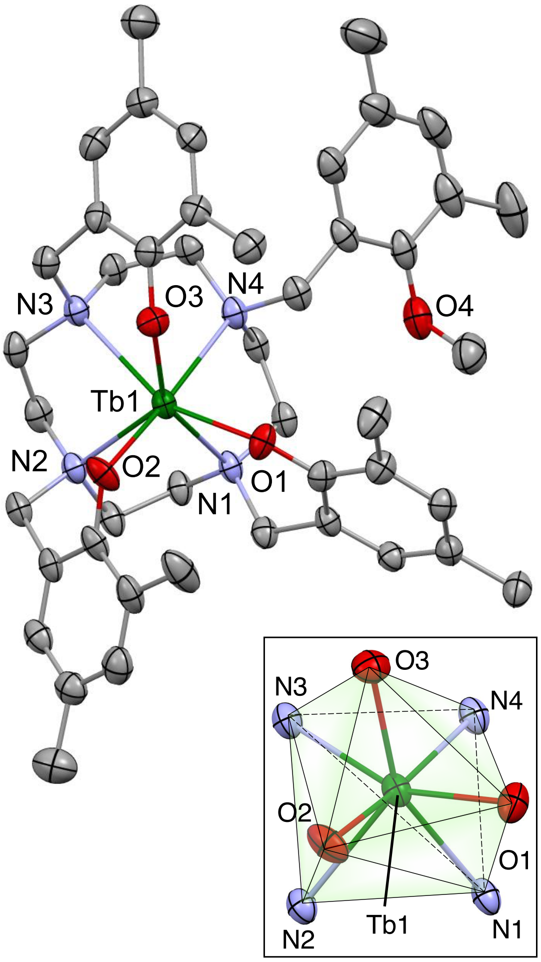


Fig. S6 An ORTEP drawing of $\mathbf{2}^{\text{cyclen}}$ with 50% probability ellipsoids. Hydrogen atoms and co-crystallised solvents are omitted for clarity. Selected bond lengths [Å] and angle [°]: Tb1-N1 = 2.649(3), Tb1-N2 = 2.638(3), Tb1-N3 = 2.631(3), Tb1-N4 = 2.636(3), Tb1-O1 = 2.141(3), Tb1-O2 = 2.207(2), Tb1-O3 = 2.201(3), O1-Tb1-O2 = 91.83(10), O1-Tb1-O3 = 93.40(10), O2-Tb1-O3 = 86.94(10), N1-Tb1-N2 = 68.73(9), N2-Tb1-N3 = 70.27(10), N3-Tb1-N4 = 69.96(10), N4-Tb1-N1 = 68.10(10). Inset: the coordination polyhedron of the Tb^{3+} ion in $\mathbf{2}^{\text{cyclen}}$ (monocapped octahedron, Table S2). The nitrogen atom (N2) caps the triangular face formed by the one oxygen atom (O2) and the two nitrogen atoms (N1 and N3).

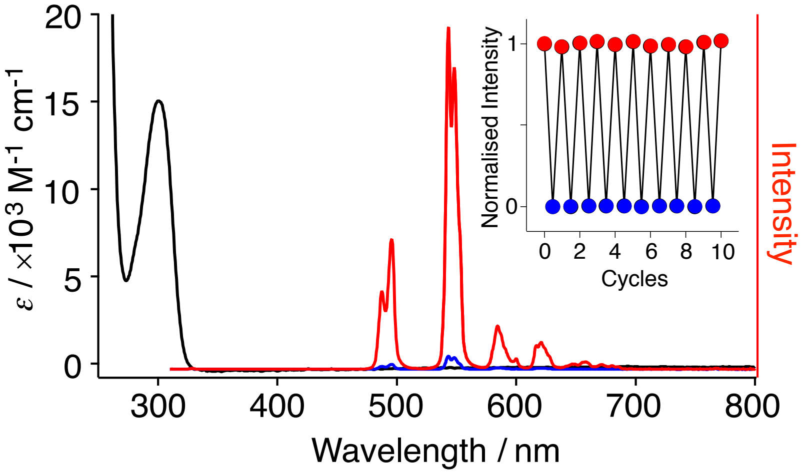


Fig. S7 UV–vis absorption (black) and corrected luminescence spectra of $\mathbf{2}^{\mathrm{cyclen}}$ under N_2 (red) and air (blue) in THF at room temperature (λ_{ex} = 300 nm). Inset: reversible responses of the luminescence intensity of $\mathbf{2}^{\mathrm{cyclen}}$ (3.1×10^{-6} M) to alternating air and N_2 exposures. The luminescence was monitored at 543 nm.

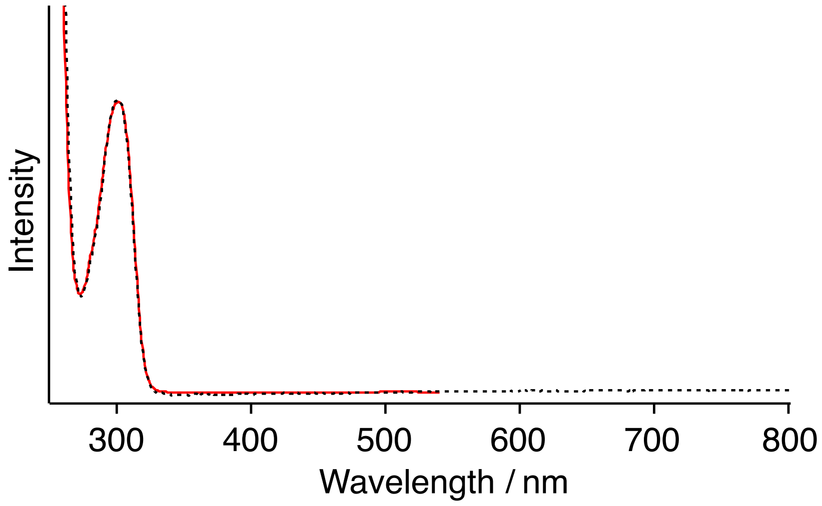


Fig. S8 Absorption (black dot) and excitation (red) spectra of $\mathbf{2}^{\mathrm{cyclen}}$ in THF at room temperature. The excitation spectrum was detected at 543 nm.

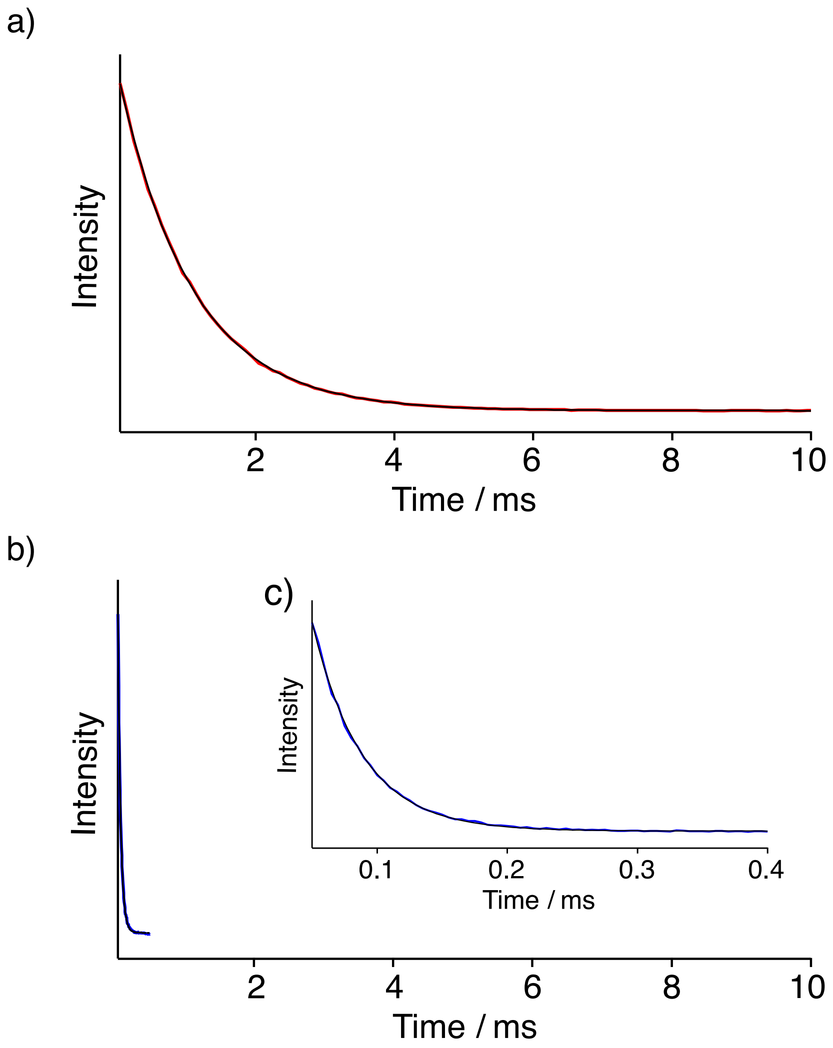


Fig. S9 Luminescence decay curves of **2**$^{\text{cyclen}}$ under (a) N_2 (red, 1060 μs) and (b and c) air (blue, 40 μs) in THF at room temperature. The decay was monitored at 543 nm (λ_{ex} = 300 nm). Fitted by single exponential curve (black).

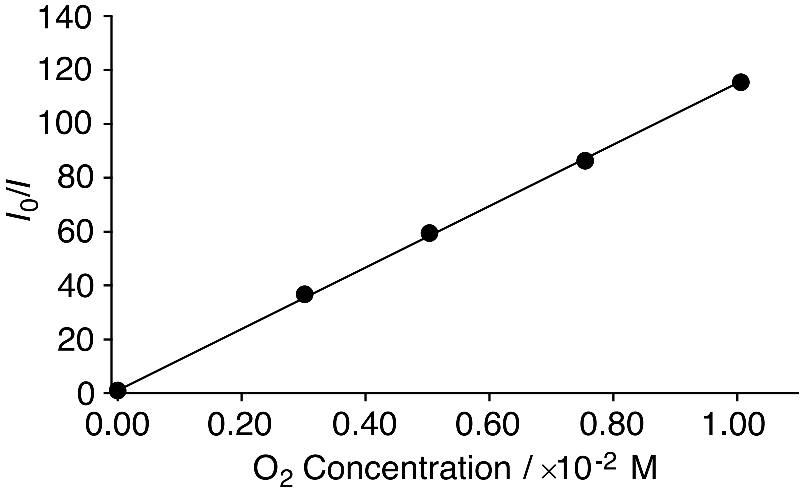


Fig. S10 Stern–Volmer plot of the luminescence intensity (I_0/I) against the oxygen concentration [O_2] for **2**$^{\text{cyclen}}$ (4.9 × 10^{-6} M) (K_{sv} = 11400 M^{-1}, R^2 = 0.9998). The I_0 and I are the luminescence intensities at an O_2 concentration of 0.00 M (under N_2) and at the indicated O_2 concentrations, respectively.