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A highly luminescent and highly oxygen-sensitive Tb(III) complex with a tris-aryloxy functionalised 1,4,7-triazacyclononane ligand

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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 O₂ balanced with N₂ (100, 70, 50, 25 and 0%, respectively) were purchased from Sumitomo Seika Chemicals Co., Ltd. $\{(\text{MeMeArOH})_3\text{tacn}\} = \{(\text{CH}_2(\text{CH}_3)_2\text{C}_6\text{H}_2\text{OH})_3\text{C}_6\text{H}_{12}\text{N}_3\}$ was prepared according to the literature procedures.¹ All other chemicals were obtained from commercial sources and used as received unless otherwise noted.

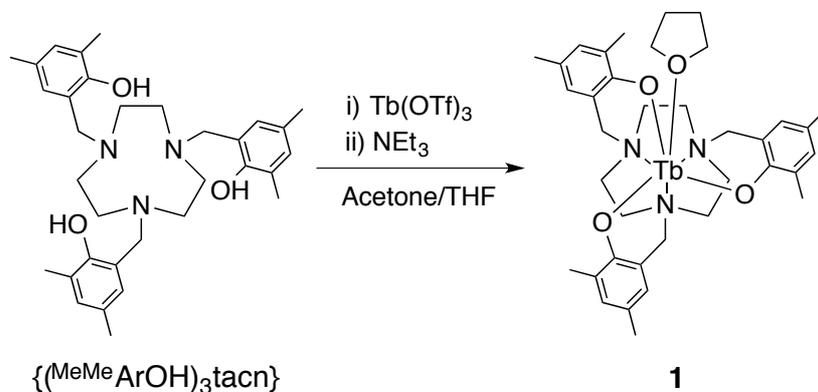
UV-vis absorption spectra were measured in a JASCO V-670 UV-visible-NIR Spectrophotometer (cell length = 10.0 mm). Electrospray ionisation mass spectrometry data were obtained by a JEOL JMS-T100ESI AccuTOF LC-plus. Elemental analyses were performed using a Yanaco CHN-coder MT-5.

Luminescence properties (corrected luminescence and excitation spectra, luminescence lifetimes and luminescence quantum yields) were measured using a Horiba Jobin Yvon FluoroMax-4P Spectrofluorometer. Low temperature (77 K) spectra were obtained using a quartz tube cell (1 mm inner diameter) placed in a quartz-walled Dewar flask filled with liquid nitrogen. Luminescence quantum yields were measured by the relative comparison method with quinine bisulfate in 0.5 M H₂SO₄ ($\Phi = 0.60$) chosen for the standard (The error in the reported values is within $\pm 10\%$ which is confirmed by the cross-calibration of the standard).² 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 O₂) 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 $\times 10^{-2}$ M at 100, 75, 50, 30 and 0% of O₂, respectively) reported in Fig. 3 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).³

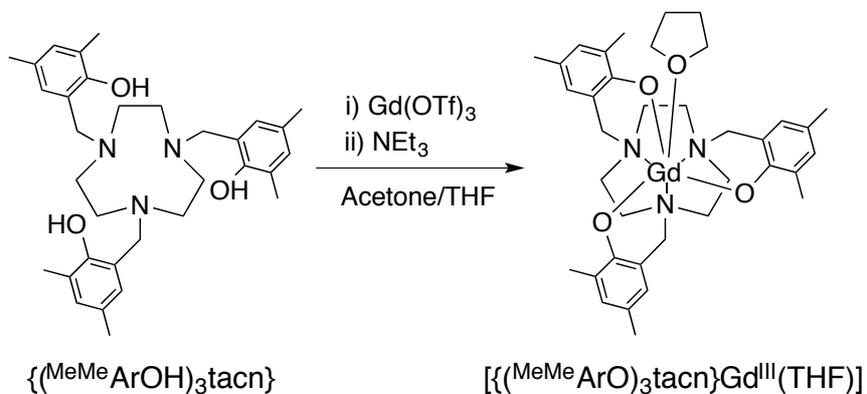
X-ray crystallography: All measurements were made on a Rigaku/MSK Saturn CCD diffractometer with confocal monochromated Mo K α radiation ($\lambda = 0.71070 \text{ \AA}$). Data were collected and processed using CrystalClear⁴ software (Rigaku). The data were corrected for Lorentz and polarisation effects. Empirical absorption corrections were applied. The structures were solved by a direct method: SIR-2011⁵ and expanded using a Fourier technique. All calculations were performed using the CrystalStructure⁶ crystallographic software package except for refinement, which was performed using SHELXL2013⁷. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. Crystallographic data has been deposited with the Cambridge Crystallographic Data Centre (CCDC). CCDC reference number: 1026622 (**1**).

Synthesis



A mixture of $\{({}^{\text{MeMe}}\text{ArOH})_3\text{tacn}\}$ (300 mg, 0.56 mmol) and $\text{Tb}(\text{OTf})_3$ (339 mg, 0.56 mmol) in Acetone/THF (100/1, 4 mL) was stirred for 5 min at room temperature. To the mixture was added dropwise triethylamine (0.26 mL, 1.85 mmol). The resulting solution was stirred for 3 h at room temperature. The white precipitate was isolated by filtration and washed with acetone. Yield: 323 mg (77%). Single crystals suitable for X-ray diffraction analysis were obtained from a saturated solution of **1** in AcOEt/THF (9/1) at room temperature.

UV-vis (THF): $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{M}^{-1}\text{cm}^{-1}$) = 302 (15000). Anal. calcd. for **1** ($\text{C}_{37}\text{H}_{50}\text{N}_3\text{O}_4\text{Tb}$): C, 58.49; H, 6.63; N, 5.53%. Found: C, 58.40; H, 6.60; N, 5.50%.



A mixture of $\{({}^{\text{MeMe}}\text{ArOH})_3\text{tacn}\}$ (54 mg, 0.10 mmol) and $\text{Gd}(\text{OTf})_3$ (60 mg, 0.10 mmol) in Acetone/THF (100/1, 10 mL) was stirred for 5 min at room temperature. To the mixture was added dropwise triethylamine (0.06 mL, 0.43 mmol). The resulting solution was stirred for 3 h at room temperature. The white precipitate was isolated by filtration and washed with acetone. Yield: 44 mg (70%).

UV-vis (THF): $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{M}^{-1}\text{cm}^{-1}$) = 303 (15000). Anal. calcd. for $[\{({}^{\text{MeMe}}\text{ArO})_3\text{tacn}\}\text{Gd}^{\text{III}}(\text{THF})]$ ($\text{C}_{37}\text{H}_{50}\text{GdN}_3\text{O}_4$): C, 58.62; H, 6.65; N, 5.54%. Found: C, 58.62; H, 6.61; N, 5.52%.

References

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

Table S1 Crystallographic data for **1**

1	
Formula	C ₃₇ H ₅₀ N ₃ O ₄ Tb
<i>F</i> _w	759.75
Crystal system	triclinic
Space group	<i>P</i> -1 (No. 2)
<i>a</i> (Å)	7.901(6)
<i>b</i> (Å)	14.273(10)
<i>c</i> (Å)	16.298(10)
α (deg)	69.07(3)
β (deg)	76.98(4)
γ (deg)	85.52(4)
<i>V</i> (Å ³)	1673(2)
<i>Z</i>	2
μ (cm ⁻¹)	21.53
<i>F</i> (000)	780.00
<i>D</i> _{calcd} (g/cm ³)	1.508
Temperature (K)	93
Reflections collected	19591
Independent reflection	7638
	(<i>R</i> _{int} = 0.048)
Data/parameters	7638/406
<i>R</i> ₁ [<i>I</i> > 2σ(<i>I</i>)]	0.0477
<i>wR</i> ₂ (all data)	0.1203
Goodness-of-fit	1.074

Table S2 Continuous shape measures (CSM) values calculated for the Tb³⁺ in **1**

	HP-7	HPY-7	PBPY-7	COC-7	CTPR-7	JPBPY-7	JETPY-7
1	36.638	20.505	8.442	0.907	2.276	11.239	14.143
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)						

Figures

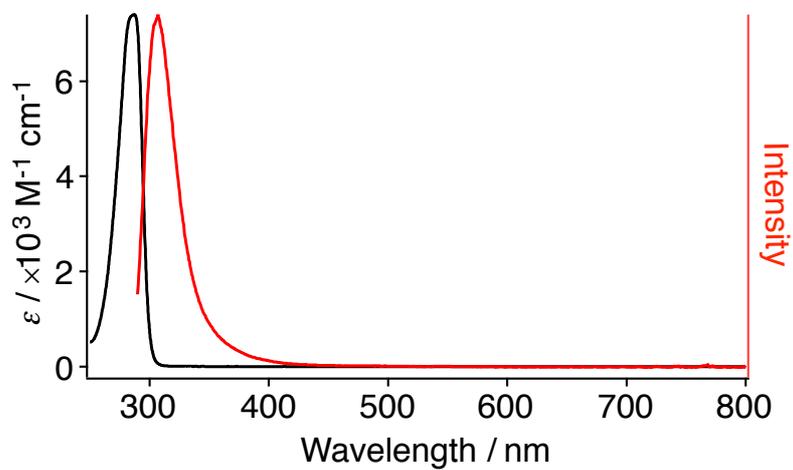


Fig. S1 UV-vis absorption (black) and corrected luminescence (red, $\lambda_{\text{ex}} = 270 \text{ nm}$) spectra of $\{(\text{MeMeArOH})_3\text{tacn}\}$ in THF at room temperature.

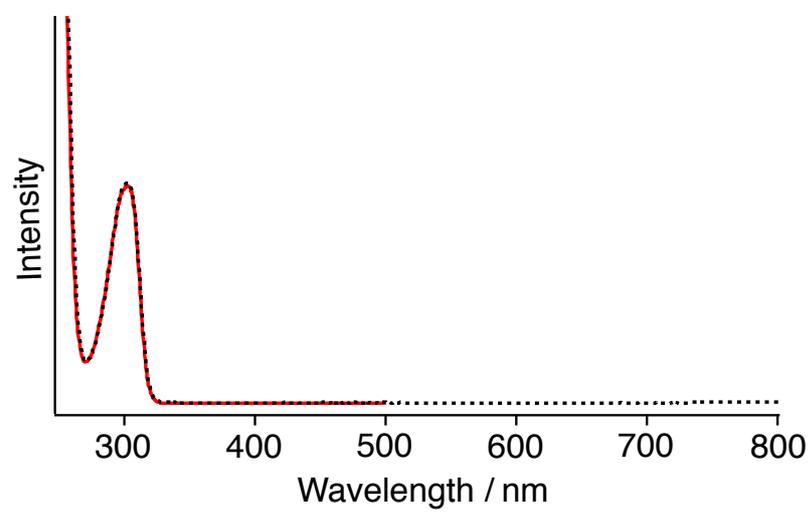


Fig. S2 Absorption (black dot) and excitation (red) spectra of **1** in THF at room temperature. The excitation spectrum was detected at 547 nm.

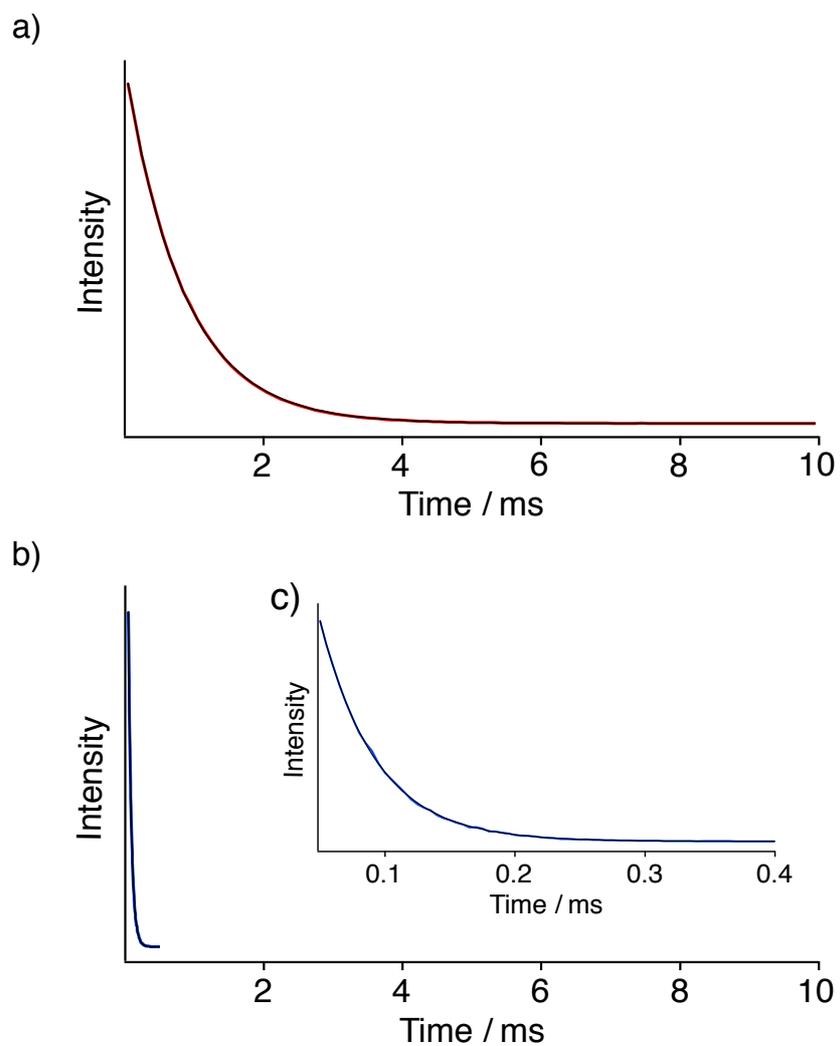


Fig. S3 Luminescence decay curves of **1** under (a) N₂ (red, 840 μ s) and (b and c) air (blue, 40 μ s) in THF at room temperature. The decay was monitored at 547 nm ($\lambda_{\text{ex}} = 300$ nm). Fitted by single exponential curve (black).

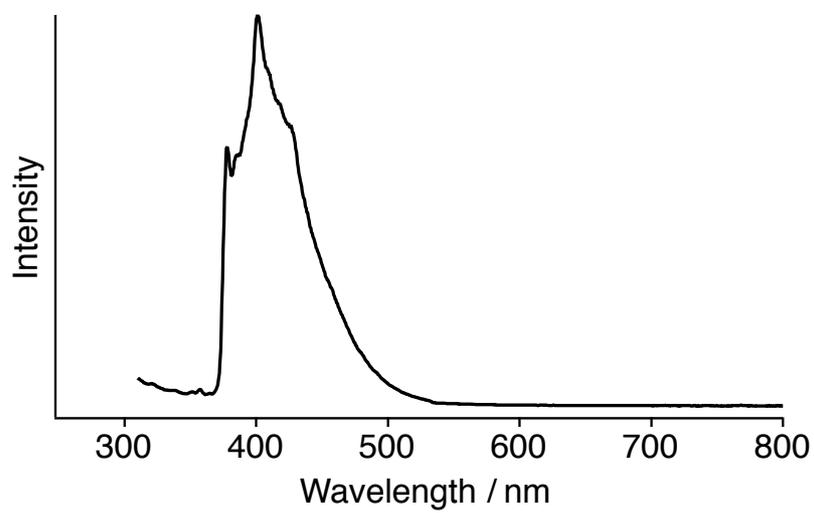


Fig. S4 Corrected luminescence spectrum of [$\{(\text{MeMeArO})_3\text{tacn}\}\text{Gd}^{\text{III}}(\text{THF})\}$] in 2-MeTHF at 77 K ($\lambda_{\text{ex}} = 250$ nm).

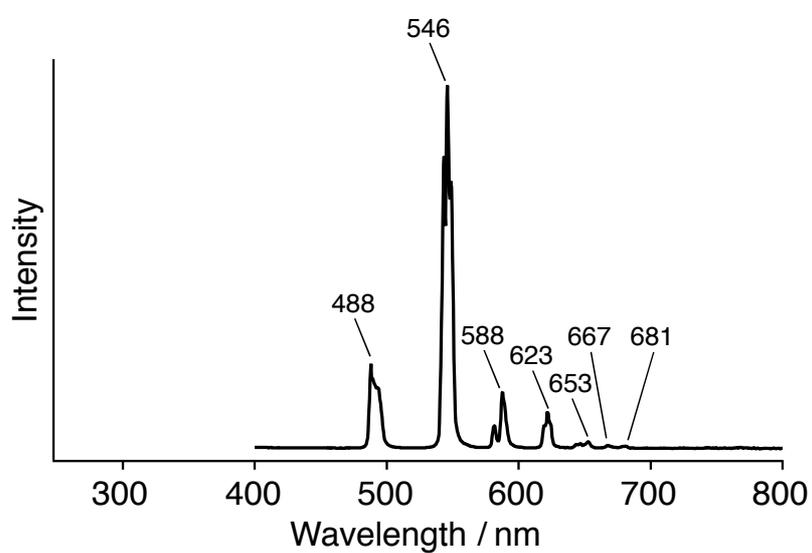


Fig. S5 Corrected luminescence spectrum of **1** in 2-MeTHF at 77 K ($\lambda_{\text{ex}} = 300$ nm).

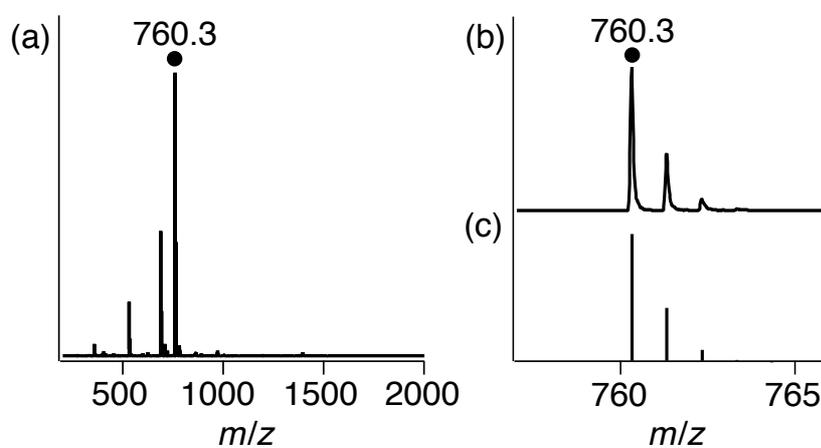


Fig. S6 (a) Positive-ion electrospray ionisation mass spectrum of **1** dissolved in THF/MeOH (7/1). (b) The signal at m/z 760.3 corresponds to $[\mathbf{1} + \text{H}]^+$. (c) Calculated isotopic distribution for $[\mathbf{1} + \text{H}]^+$.