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A thermostable terbium(III) complex with high fluorescence quantum yields

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Synthesis and characterization:

All of the chemicals are commercially available and used without further purification. All the reactions were carried out under aerobic conditions. The addition of $Tb(NO_3)_3 \cdot 6H_2O$ (453 mg, 1.0 mmol) to a stirred solution of salicylic acid (414 mg, 3.0 mmol) and triethylamine (303 mg, 3.0 mmol) in ethanol (20 mL) produces colorless solution. After stirring at room temperature for one hour, white precipitates were formed and the solution was filtered and the filtrate was evaporated slowly at room temperature. After two weeks, colorless block crystals of complex **1** (168 mg, 23% based on Tb) isolated from the solution. UV-vis (C_2H_5OH) $\lambda_{max}[\varepsilon/(10^3\ mol^{-1} \bullet L \bullet cm^{-1})]$: 305(16), 236 (32) (Fig. S1).Anal. calcd for $C_{40.5}H_{69.5}N_9O_{28.75}Tb_2$ (**1**$\cdot(C_2H_5OH)_{0.75} \cdot H_2O$): C, 33.31; H, 4.80; N, 8.63%. Found: C, 33.51; H, 4.324; N, 8.14%. Elemental analyses for C, H and N were performed using a Elementar Vario EL elemental analyzer. IR (ν, cm^{-1}): ν(OH)-3142 w, ν(C=O)-1625 w, ν(Ar=C)-1595 w, ν(OH in -COOH)-1546 w/865 s, $\nu(NO_3)$-1459 s/1383 s/1030 s, ν(C-O)-1292 s, ν(C-O)- 1241 m, ν(C-N)-1145 m, ν(Ar-H)-816 m/756 s/702 s/660 s, ν(Tb-O)-577 w/551 w/533 m (Fig. S2). Anal. calcd for $C_{40.5}H_{69.5}N_9O_{28.75}Tb_2$ (**1**$\cdot(C_2H_5OH)_{0.75} \cdot H_2O$): C, 33.31; H, 4.80; N, 8.63%. Found: C, 33.51; H, 4.324; N, 8.14%. Elemental analyses for C, H and N were performed using a Elementar Vario EL elemental analyzer. TG analysis were performed on a Netzsch TG 209 instrument under nitrogen atmosphere with a heating rate of 10 °C/min. PXRD patterns were obtained on a Bruker D2 Phaser with Cu-Kα radiation (λ = 1.54178 Å) at 30 kV and 10 mA. Data were recorded in the range of 5–40° (2θ) in a continuous scan mode using a step size of 0.014° (2θ) and a scan speed of 0.1 s per step.

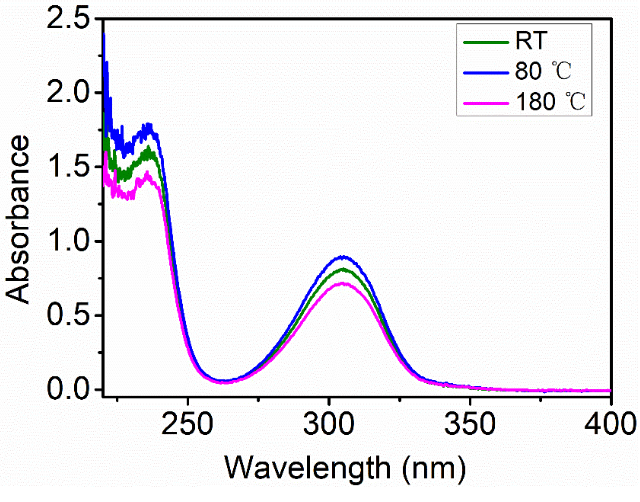

Fig. S1. Normalized UV–vis absorption spectra of complex **1** (0.5 μM) at room temperature (green), and after heating at 80 °C (blue) or 180 °C (purple) in C_2H_5OH.

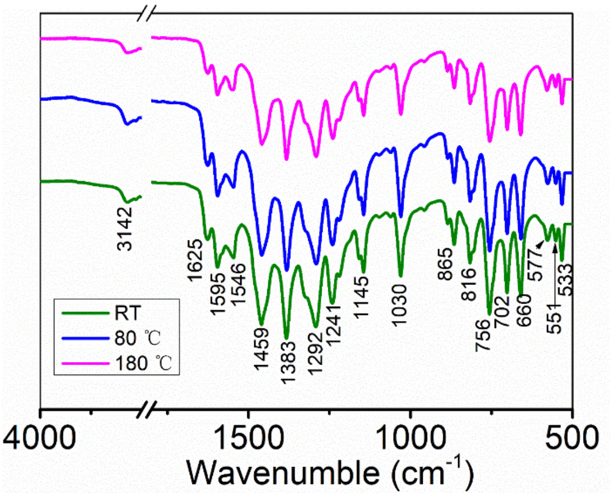

Fig. S2. FTIR spectra for complex **1** at room temperature (green), and after heating at 80 °C (blue) or 180 °C (purple).

Table S1. Crystal data and structure refinement for complex **1**.

Molecular formula	$C_{39}H_{63}N_9O_{27}Tb_2$
M_w(g.mol^{-1})	1407.82
Crystal system	Monoclinic
a(Å)	19.3502(3)
b(Å)	11.14440(10)
c(Å)	14.4386(2)
α(°)	90
β(°)	120.5930(10)
γ(°)	90
V(Å^3)	2680.23(6)
Space group	$C2$
Z	1
D_{calc}(g.cm^{-3})	1.744
R_{int}	0.0251
Final R_1 ($I > 2\sigma(I)$)	0.0360
wR_2	0.0972
(GOF) over R_2	1.037

Table S2. Selected bond lengths (Å) and angles (°) for complex **1**.

Tb1—O1	2.521(5)	O6—C8—O6a	124.4(8)
Tb1—O2	2.487(7)	O4—C1—O5	123.1(5)
Tb1—O4	2.283(4)	C8—O6—Tb1	140.7(4)
Tb1—O5a	2.318(4)	C1—O5a—Tb1	137.3(4)
Tb1—O6	2.291(4)	C1—O4—Tb1	145.0(4)
Tb1—O8	2.472(4)	O4—Tb1—O6	86.69(15)
Tb1—O10	2.477(4)	O4—Tb1—O5a	88.24(16)
Tb1—O11	2.442(6)	O6—Tb1—O5a	89.26(15)
Tb1—O13	2.487(5)	Tb…Tb	4.7721(3)

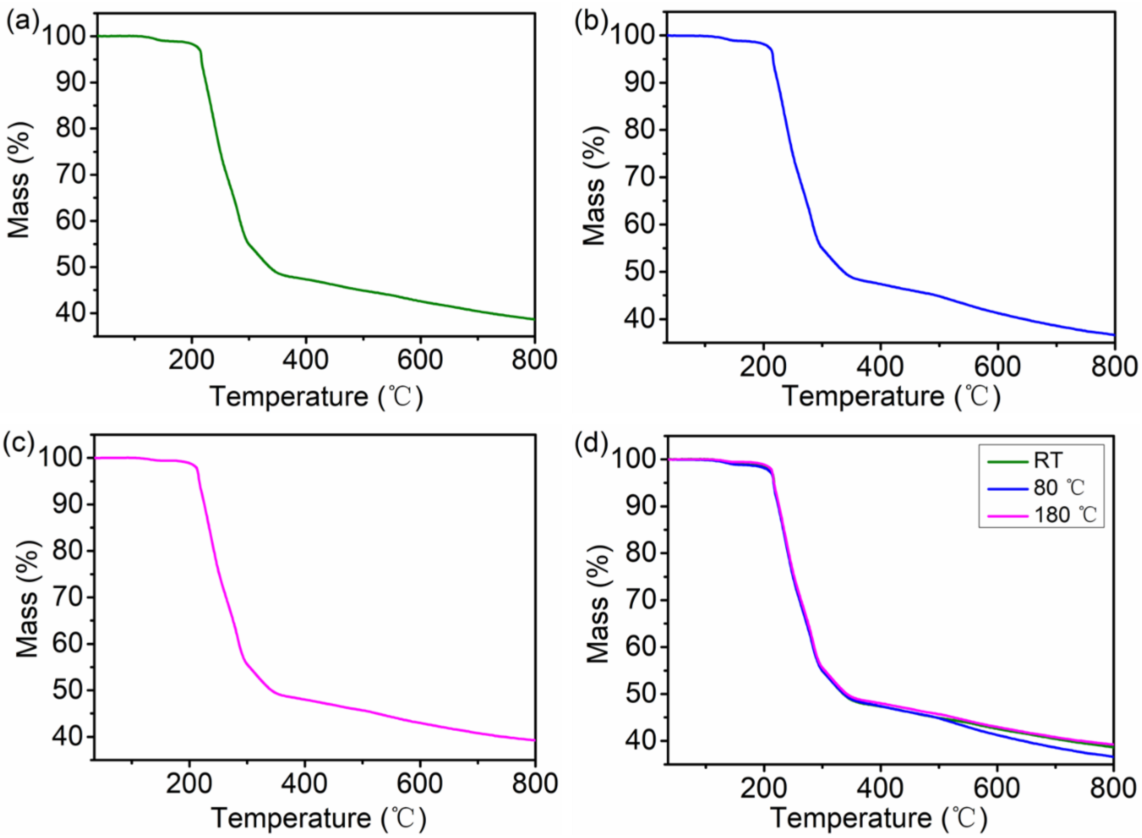

Fig. S3. TGA analyses under air of complex **1**. (a) complex **1** with room temperature, (b) complex **1** after heated at 80 °C, (c) complex **1** after heating at 180 °C, (d) all.

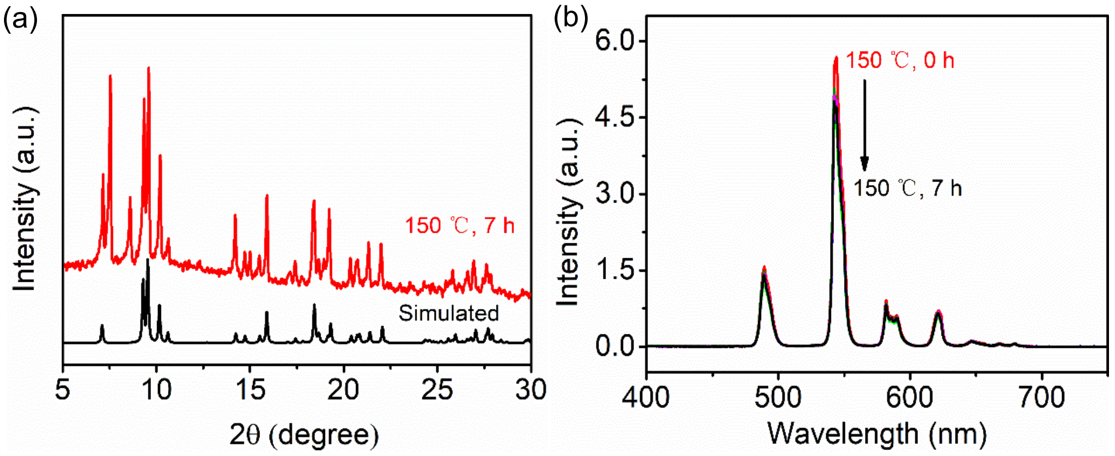

Fig. S4. (a) PXRD patterns and (b) emission spectra of complex **1** after heating at 150 °C for 7 h.

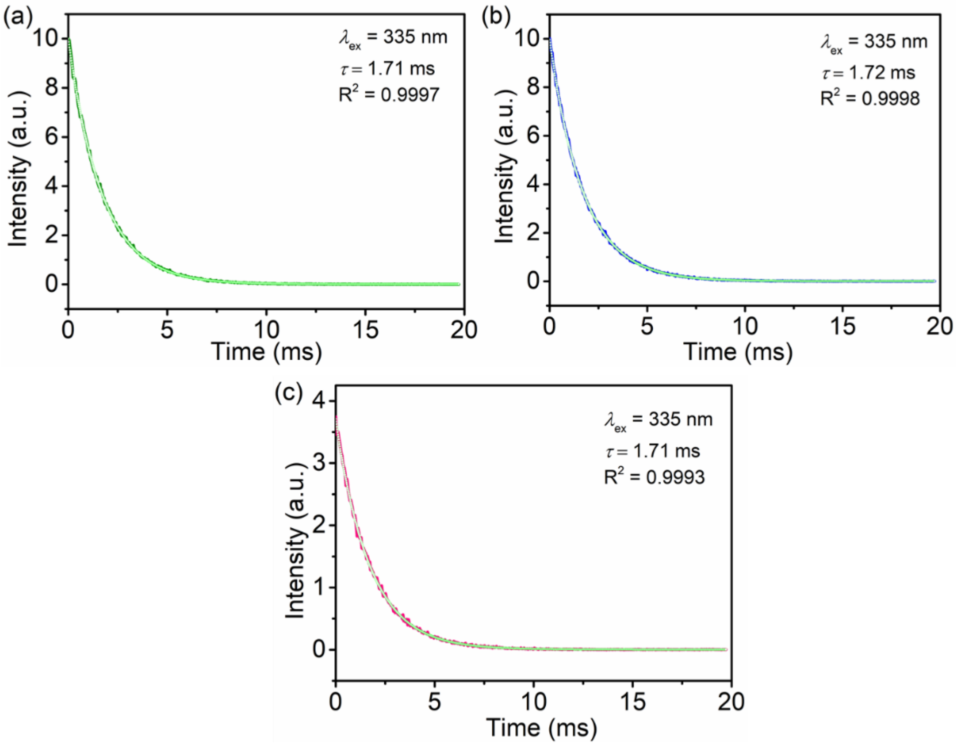

Fig. S5. Luminescence decay of complex **1** at room temperature and their fitting curves. (a) complex **1** with room temperature, (b) complex **1** after heating at 80 °C, (c) complex **1** after heated at 180 °C.