

Supporting Information

A Breathing Europium-Terbium co-doped Luminescent MOF as Broad Range Ratiometric Thermometer with Contrary Temperature-Intensity Relationship

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Table S1. Crystal data and refinement parameters for **1**-Eu and **1'**-Eu.

Identification code	1 -Eu	1' -Eu
Empirical formula	C ₄₈ H ₃₀ Eu ₂ N ₁₂ O ₁₂	C ₄₈ H ₃₀ Eu ₂ N ₁₂ O ₁₂
T/K	293(2)	293(2)
Formula weight	1270.76	1270.76
Crystal system	monoclinic	monoclinic
Space group	P2 ₁ /c	P2 ₁ /c
a/Å	27.609(3)	32.159(3)
b/Å	23.570(3)	16.9564(14)
c/Å	15.2364(16)	15.0477(12)
$\alpha/^\circ$	90.00	90.00
$\beta/^\circ$	104.257(3)	102.061(2)
$\gamma/^\circ$	90.00	90.00
Volume/Å ³	9609.8(18)	8024.4(12)
Z	4	4
ρ_{calc} /(mg cm ⁻³)	0.878	1.052
μ/mm^{-1}	1.332	1.595
Crystal size (mm)	0.2 × 0.1 × 0.09	0.79 × 0.232 × 0.043
F(000)	2496.0	2496.0
Reflections	23933	19874
R _{int}	0.0519	0.656
Theta range for data collection	4.422 to 56.872	4.56 to 56.64
Data/parameters	23993/0/667	19874/0/667
Goodness-of-fit on F ₂	1.071	1.099
R ₁ ^a , wR ₂ ^b [I > 2(I)]	0.0790, 0.2220	0.0973, 0.2830
R ₁ , wR ₂ (all data)	0.0866, 0.2272	0.1119, 0.2913

$$^a R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|, \quad ^b wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$$

Table S2. Selected bond length and bond angle for compounds **1-Eu**.

Compound 1-Eu			
Eu(1)-O(8)	2.552(10)	Eu(2)-O(8)	2.398(10)
Eu(1)-O(7)	2.434(11)	Eu(2)-O(5)	2.401(9)
Eu(1)-O(5)	2.536(9)	Eu(2)-O(10d)	2.307(12)
Eu(1)-O(6)	2.422(11)	Eu(2)-O(2f)	2.612(11)
Eu(1)-O(9b)	2.315(14)	Eu(2)-O(11g)	2.503(9)
Eu(1)-O(2c)	2.402(9)	Eu(2)-O(12g)	2.438(10)
Eu(1)-O(4a)	2.289(12)	Eu(2)-O(3a)	2.313(13)
Eu(1)-O(11d)	2.419(9)	Eu(2)-O(1f)	2.392(12)
O(7)-Eu(1)-O(8)	51.0(4)	O(2c)-Eu(1)-O(7)	155.0(4)
O(7)-Eu(1)-O(5)	115.2(3)	O(2c)-Eu(1)-O(6)	80.2(4)
O(7)-Eu(1)-O(6)	123.4(5)	O(2c)-Eu(1)-O(5)	84.9(3)
O(5)-Eu(1)-O(8)	64.9(3)	O(2c)-Eu(1)-O(11d)	74.2(3)
O(6)-Eu(1)-O(8)	85.8(4)	O(11d)-Eu(1)-O(8)	130.9(3)
O(6)-Eu(1)-O(5)	52.2(3)	O(11d)-Eu(1)-O(7)	81.6(4)
O(9b)-Eu(1)-O(7)	76.0(6)	O(11d)-Eu(1)-O(5)	151.5(3)
O(9b)-Eu(1)-O(5)	123.0(4)	O(11d)-Eu(1)-O(6)	138.5(4)
O(9b)-Eu(1)-O(6)	74.4(4)	O(4a)-Eu(1)-O(8)	84.3(4)
O(9b)-Eu(1)-O(2c)	106.3(6)	O(4a)-Eu(1)-O(7)	86.7(5)
O(9b)-Eu(1)-O(11d)	82.1(4)	O(4a)-Eu(1)-O(5)	78.0(4)
O(2c)-Eu(1)-O(8)	149.1(3)	O(4a)-Eu(1)-O(6)	128.4(4)
O(4a)-Eu(1)-O(9b)	157.1(5)	O(8)-Eu(2)-O(12g)	75.5(3)
O(4a)-Eu(1)-O(2c)	83.1(4)	O(5)-Eu(2)-O(2f)	135.3(3)
O(4a)-Eu(1)-O(11d)	80.5 (4)	O(5)-Eu(2)-O(11g)	125.9 (3)
O(8)-Eu(2)-O(5)	69.4(3)	O(5)-Eu(2)-O(12g)	75.5(3)
O(8)-Eu(2)-O(2f)	153.9 (3)	O(10d)-Eu(2)-O(8)	83.3 (4)
O(8)-Eu(2)-O(11g)	89.3(3)	O(10d)-Eu(2)-O(5)	144.1(5)
O(10d)-Eu(2)-O(2f)	76.8(3)	O(12g)-Eu(2)-O(2f)	94.6(4)

O(10d)-Eu(2)-O(1f)	123.8(4)	O(12g)-Eu(2)-O(11g)	52.3(3)
O(10d)-Eu(2)-O(11g)	74.6 (5)	O(3a)-Eu(2)-O(8)	101.9 (5)
O(10d)-Eu(2)-O(12g)	125.1(4)	O(3a)-Eu(2)-O(5)	82.4(4)
O(1f)-Eu(2)-O(8)	152.3 (4)	O(3a)-Eu(2)-O(10d)	80.8 (6)
O(1f)-Eu(2)-O(5)	83.6(3)	O(3a)-Eu(2)-O(2f)	91.7(4)
O(1f)-Eu(2)-O(11g)	102.6 (4)	O(3a)-Eu(2)-O(1f)	79.4 (6)
O(1f)-Eu(2)-O(12g)	84.8(4)	O(3a)-Eu(2)-O(11g)	151.7(4)
O(1f)-Eu(2)-O(2f)	51.9(3)	O(3a)-Eu(2)-O(12g)	154.1(3)
O(11g)-Eu(2)-O(2f)	69.3(5)		

¹1-Y,+X,2-Z; ²1/2-Y,1/2-X,+Z; ³+Y,1-X,1-Z; ⁴3/2-X,-1/2+Y,1-Z; ⁵1-Y,+X,1-Z; ⁶1/2+Y,-1/2+X,+Z;
⁷+Y,1-X,2-Z; ⁸-1/2+X,1/2-Y,1-Z

Table S3. Selected bond length and bond angle for compounds **1'-Eu**.

Compound 1'-Eu			
Eu(1)-O(1)	2.510(5)	Eu(2)-O(1)	2.442(4)
Eu(1)-O(2)	2.403(5)	Eu(2)-O(7)	2.646(4)
Eu(1)-O(4d)	2.426(4)	Eu(2)-O(8)	2.403(5)
Eu(1)-O(11b)	2.307(5)	Eu(2)-O(4a)	2.620(4)
Eu(1)-O(10c)	2.592(4)	Eu(2)-O(3a)	2.391(5)
Eu(1)-O(9c)	2.384(5)	Eu(2)-O(12b)	2.356(5)
Eu(1)-O(6f)	2.302(5)	Eu(2)-O(10c)	2.408(4)
Eu(1)-O(7)	2.382(4)	Eu(2)-O(5d)	2.296(4)
O(1)-Eu(1)-O(10c)	68.62(13)	O(9c)-Eu(1)-O(10c)	51.79(14)
O(7e)-Eu(1)-O(1)	152.72(13)	O(6f)-Eu(1)-O(1)	100.78(17)
O(7e)-Eu(1)-O(2)	153.45(17)	O(6f)-Eu(1)-O(7e)	95.59(18)
O(7e)-Eu(1)-O(4)	71.77(14)	O(6f)-Eu(1)-O(2)	83.7(2)
O(7e)-Eu(1)-O(10c)	87.35(13)	O(6f)-Eu(1)-O(4d)	81.38(17)
O(2)-Eu(1)-O(1)	51.31(15)	O(6f)-Eu(1)-O(9c)	153.75(19)
O(2)-Eu(1)-O(4d)	81.93(16)	O(6f)-Eu(1)-O(10c)	154.37(18)

O(2)-Eu(1)-O(10c)	104.7 (16)	O(1)-Eu(2)-O(7)	149.91(15)
O(4d)-Eu(1)-O(1)	132.06(13)	O(1)-Eu(2)-O(4a)	87.59(14)
O(4d)-Eu(1)-O(10c)	123.39(13)	O(8)-Eu(2)-O(1)	151.55(16)
O(11b)-Eu(1)-O(1)	73.80(17)	O(8)-Eu(2)-O(7)	51.21(14)
O(11b)-Eu(1)-O(7e)	86.71(17)	O(8)-Eu(2)-O(4a)	115.69(14)
O(11b)-Eu(1)-O(2)	119.40(19)	O(8)-Eu(2)-O(10c)	79.77(15)
O(11b)-Eu(1)-O(4d)	152.11(19)	O(4a)-Eu(2)-O(7)	64.70(12)
O(11b)-Eu(1)-O(10c)	71.4 (2)	O(3a)-Eu(2)-O(1)	82.6 (2)
O(11b)-Eu(1)-O(9c)	122.9(2)	O(3a)-Eu(2)-O(7)	88.14(19)
O(9c)-Eu(1)-O(1)	89.15 (17)	O(3a)-Eu(2)-O(8)	124.4 (2)
O(9c)-Eu(1)-O(2)	83.8(2)	O(3a)-Eu(2)-O(4a)	50.59(15)
O(9c)-Eu(1)-O(4d)	74.06(15)	O(3a)-Eu(2)-O(10c)	139.17(18)
O(12b)-Eu(2)-O(1)	108.62(19)	O(10c)-Eu(2)-O(1)	153.56(13)
O(12b)-Eu(2)-O(7)	95.67 (18)	O(5d)-Eu(2)-O(1)	83.35 (16)
O(12b)-Eu(2)-O(8)	75.4(2)	O(5d)-Eu(2)-O(7)	80.48(16)
O(12b)-Eu(2)-O(4a)	119.02 (16)	O(5d)-Eu(2)-O(8)	85.0 (2)
O(12b)-Eu(2)-O(3a)	72.84(19)	O(5d)-Eu(2)-O(4a)	79.81(17)
O(12b)-Eu(2)-O(10c)	84.68 (17)	O(5d)-Eu(2)-O(3a)	129.02 (19)
O(10c)-Eu(2)-O(1)	72.77(14)	O(5d)-Eu(2)-O(12b)	157.2(2)
O(10c)-Eu(2)-O(7)	128.48(13)	O(5d)-Eu(2)-O(10c)	80.47(17)

¹1-Y,+X,2-Z; ²1/2-Y,1/2-X,+Z; ³+Y,1-X,1-Z; ⁴3/2-X,-1/2+Y,1-Z; ⁵1-Y,+X,1-Z; ⁶1/2+Y,-1/2+X,+Z;
⁷+Y,1-X,2-Z; ⁸-1/2+X,1/2-Y,1-Z

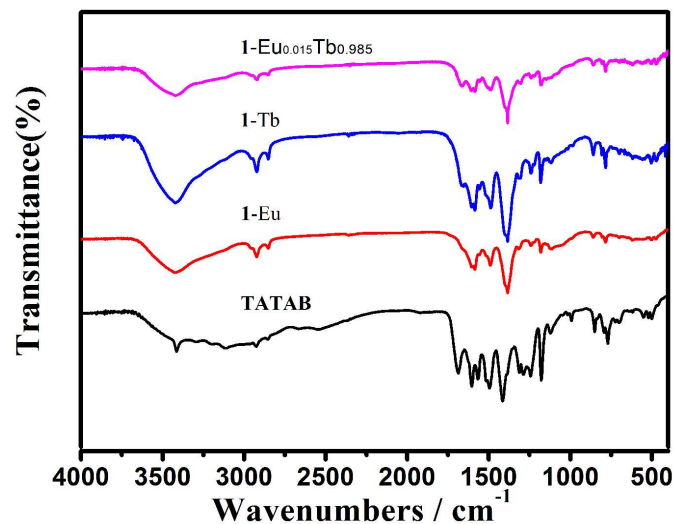


Figure S1. The IR spectrum of TATAB, 1-Eu, 1-Tb and 1-Eu_{0.015}Tb_{0.985}.

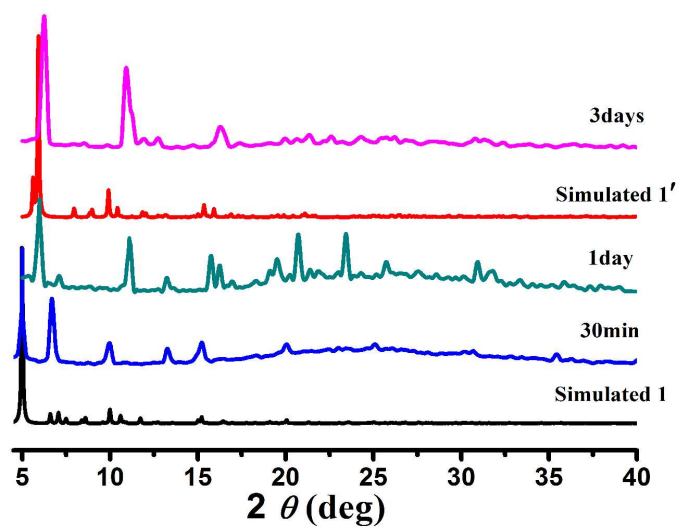


Figure S2. Powder pattern X-ray diffraction measurements taken of samples of the desolvation of as-synthesized 1-Eu to 1'-Eu.

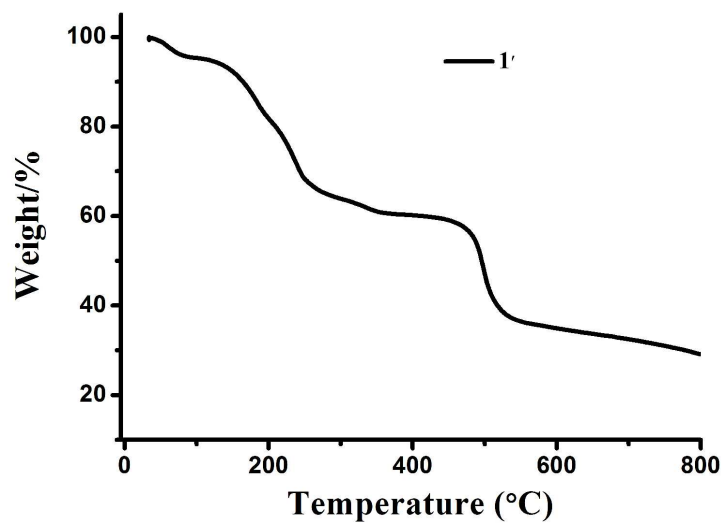


Figure S3. TGA curve of compound 1'-Eu.

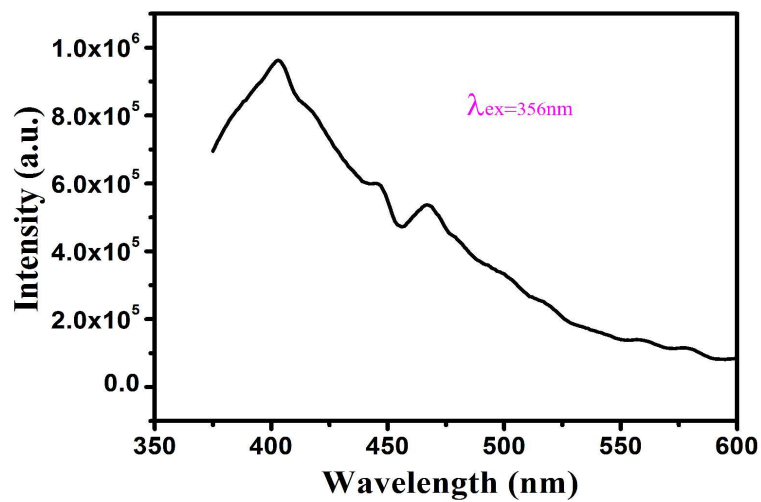


Figure S4. Excitation and emission spectra of TATAB at room temperature.

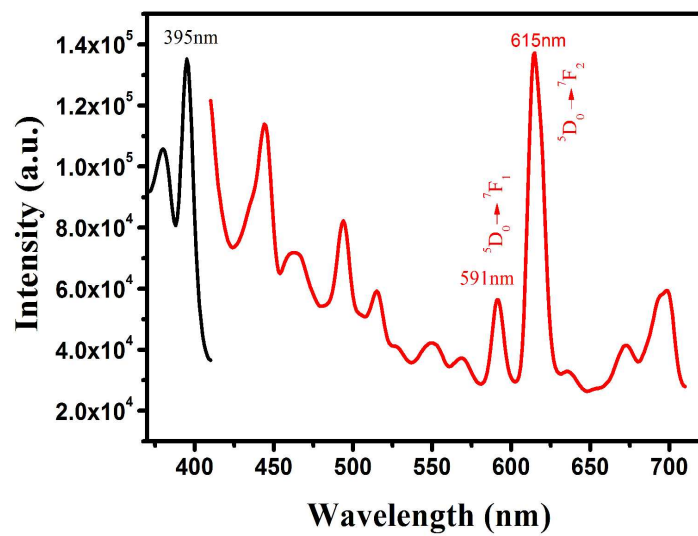


Figure S5. Excitation and emission spectra of **1'-Eu** at room temperature.

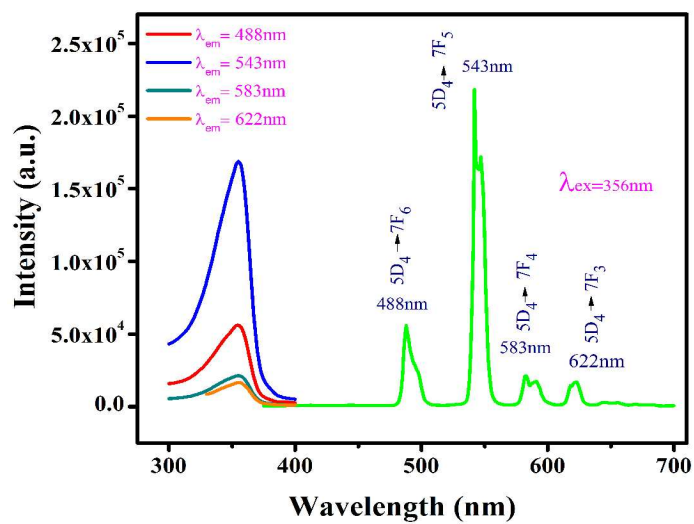


Figure S6. Excitation and emission spectra of **1'-Tb** at room temperature.

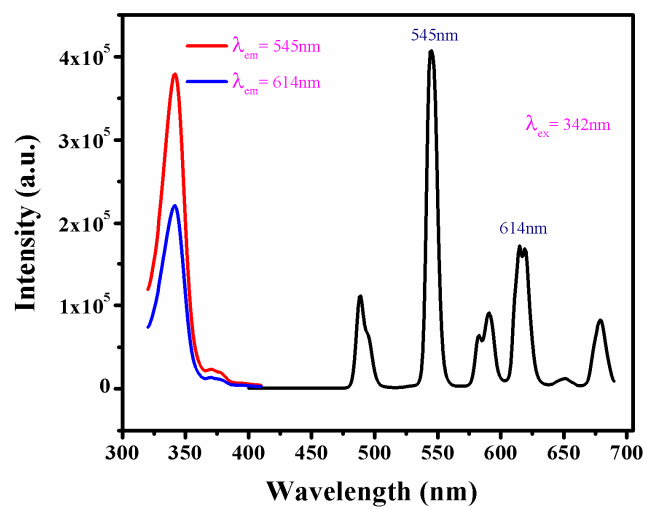


Figure S7. Excitation and emission spectra of **1'**-Eu_{0.015}Tb_{0.985} at room temperature.

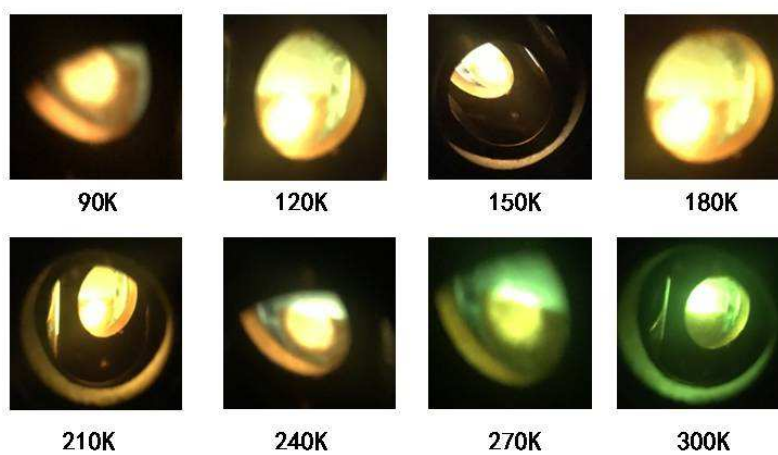


Figure S8. Photograph of luminescent **1'**-Eu_{0.015}Tb_{0.985} at different temperatures.