Supporting information

Highly chemical and thermal stable luminescent Eu_xTb_{1-x} MOF materials for broad-range pH and temperature sensors

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Table S1 Crystallographic data and structure refinement details for **1** and **2**

Compound	**1**	**2**
Formula	$C_{20}H_{22}N_4O_{14}Eu_2$	$C_{20}H_{22}N_4O_{14}Tb_2$
fw	846.36	860.28
Cryst syst	Orthorhombic	Orthorhombic
space group	*P*na2$_1$	*P*na2$_1$
a, Å	13.1154(16)	13.149(2)
β, Å	6.6813(5)	6.6803(12)
c, Å	29.007(3)	29.165(5)
V, Å^3	2541.8(4)	2561.8(7)
Z	4	4
μ, mm^{-1}	4.969	5.555
D_{calcd},g cm^{-3}	2.212	2.230
Flack	0.46(5)	0.47(4)
GOF	1.125	1.083
R_1	0.0705	0.0442
wR_2	0.1679	0.1035

[a] $R_1 = \Sigma||F_0| - |Fc||/\Sigma|F_0|$, $wR_2 = [\Sigma w(F_0^2 - Fc^2)^2/\Sigma w(F_0^2)^2]^{1/2}$

Table S2 ICP of compound **3**

	3-1	**3**-2	**3**-3	**3**-4	**3**-5	**3**-6
Tb (%)	11.30	11.20	10.93	10.79	11.26	11.28
Eu (%)	22.54	22.79	22.86	21.55	22.97	22.86

Table S3 Selected bond lengths (Å) and bond angles (º) of compounds **1** and **2**

Compound **1**			
Eu1—O6	2.347 (12)	Eu2—O4^{iii}	2.234 (15)
Eu1—O7^{i}	2.344 (15)	Eu2—O2^{iv}	2.333 (14)
Eu1—O9	2.353 (15)	Eu2—O1	2.384 (12)
Eu1—O8^{ii}	2.388 (14)	Eu2—O3^{iv}	2.414 (18)
Eu1—O10	2.399 (17)	Eu2—O5	2.404 (14)
Eu1—O14	2.424 (17)	Eu2—O12	2.372 (19)
Eu1—O13	2.486 (19)	Eu2—O11	2.448 (16)
Eu1—N3^{i}	2.71 (2)	Eu2—N1	2.48 (2)
O6—Eu1—O7^{i}	139.8 (5)	O4^{iii}—Eu2—O2^{iv}	80.8 (5)
O6—Eu1—O9	74.6 (5)	O4^{iii}—Eu2—O1	127.0 (5)
O7^{i}—Eu1—O9	74.9 (5)	O2^{iv}—Eu2—O1	140.3 (5)
O6—Eu1—O8^{ii}	75.8 (5)	O4^{iii}—Eu2—O3^{iv}	148.5 (5)
O7^{i}—Eu1—O8^{ii}	124.2 (5)	O2^{iv}—Eu2—O3^{iv}	70.7 (5)
O9—Eu1—O8^{ii}	148.4 (5)	O1—Eu2—O3^{iv}	73.6 (5)
O6—Eu1—O10	78.7 (5)	O4^{iii}—Eu2—O5	82.3 (5)
O7^{i}—Eu1—O10	72.5 (6)	O2^{iv}—Eu2—O5	83.3 (5)
O9—Eu1—O10	83.8 (6)	O1—Eu2—O5	74.6 (5)
O8^{ii}—Eu1—O10	79.7 (6)	O3^{iv}—Eu2—O5	81.4 (6)
O6—Eu1—O14	76.2 (5)	O4^{iii}—Eu2—O12	123.3 (6)
O7^{i}—Eu1—O14	135.9 (6)	O2^{iv}—Eu2—O12	105.0 (6)
O9—Eu1—O14	101.9 (6)	O1—Eu2—O12	83.8 (5)
O8^{ii}—Eu1—O14	81.5 (6)	O3^{iv}—Eu2—O12	78.1 (6)
O10—Eu1—O14	151.6 (6)	O5—Eu2—O12	153.7 (6)
O6—Eu1—O13	109.1 (5)	O4^{iii}—Eu2—O11	75.9 (5)
O7^{i}—Eu1—O13	85.9 (6)	O2^{iv}—Eu2—O11	74.3 (6)
O9—Eu1—O13	72.7 (6)	O1—Eu2—O11	134.3 (5)
O8^{ii}—Eu1—O13	128.4 (6)	O3^{iv}—Eu2—O11	107.8 (6)
O10—Eu1—O13	151.7 (6)	O5—Eu2—O11	150.8 (5)
O14—Eu1—O13	52.6 (6)	O12—Eu2—O11	53.5 (6)
O6—Eu1—N3^{i}	149.3 (6)	O4^{iii}—Eu2—N1	71.8 (6)
O7^{i}—Eu1—N3^{i}	64.0 (6)	O2^{iv}—Eu2—N1	152.1 (6)
O9—Eu1—N3^{i}	135.9 (6)	O1—Eu2—N1	65.3 (6)
O8^{ii}—Eu1—N3^{i}	73.5 (6)	O3^{iv}—Eu2—N1	137.2 (6)
O10—Eu1—N3^{i}	98.0 (6)	O5—Eu2—N1	98.0 (5)
O14—Eu1—N3^{i}	96.8 (6)	O12—Eu2—N1	86.1 (6)

O13—Eu1—N3^{i}	88.4 (6)	O11—Eu2—N1	93.4 (6)
Symmetry codes: (i) *x*+1/2, −*y*+1/2, *z*; (ii) *x*, *y*+1, *z*; (iii) *x*−1/2, −*y*+3/2, *z*; (iv) *x*−1/2, −*y*+1/2, *z*.			
Compound **2**			
Tb1—O19^{i}	2.321 (10)	Tb2—O21^{i}	2.329 (9)
Tb1—O15^{ii}	2.353 (9)	Tb2—O13^{ii}	2.350 (8)
Tb1—O30	2.390 (12)	Tb2—O20	2.362 (10)
Tb1—O11^{ii}	2.396 (11)	Tb2—O17^{ii}	2.375 (10)
Tb1—O22	2.386 (8)	Tb2—O18	2.388 (11)
Tb1—O16	2.397 (9)	Tb2—O12	2.397 (13)
Tb1—O14	2.447 (15)	Tb2—O31	2.453 (10)
Tb1—N1	2.609 (12)	Tb2—N2	2.598 (14)
O19^{i}—Tb1—O15^{ii}	78.0 (3)	O19^{i}—Tb1—O14	126.4 (4)
O19^{i}—Tb1—O30	79.2 (4)	O15^{ii}—Tb1—O14	106.0 (4)
O15^{ii}—Tb1—O30	73.6 (4)	O30—Tb1—O14	53.1 (4)
O19^{i}—Tb1—O11^{ii}	148.8 (4)	O11^{ii}—Tb1—O14	74.6 (5)
O15^{ii}—Tb1—O11^{ii}	73.6 (4)	O22—Tb1—O14	83.6 (4)
O30—Tb1—O11^{ii}	104.4 (4)	O16—Tb1—O14	151.5 (4)
O19^{i}—Tb1—O22	125.9 (3)	O19^{i}—Tb1—N1	73.0 (4)
O15^{ii}—Tb1—O22	142.3 (4)	O15^{ii}—Tb1—N1	150.5 (4)
O30—Tb1—O22	133.9 (4)	O30—Tb1—N1	95.7 (4)
O11^{ii}—Tb1—O22	74.2 (3)	O11^{ii}—Tb1—N1	135.9 (4)
O19^{i}—Tb1—O16	81.8 (4)	O22—Tb1—N1	63.8 (4)
O15^{ii}—Tb1—O16	81.5 (4)	O16—Tb1—N1	99.1 (4)
O30—Tb1—O16	151.2 (4)	O14—Tb1—N1	87.6 (5)
O11^{ii}—Tb1—O16	81.6 (4)	O17^{ii}—Tb2—O12	76.6 (5)
O22—Tb1—O16	74.9 (3)	O18—Tb2—O12	155.5 (5)
O21^{i}—Tb2—O13^{ii}	78.3 (4)	O21^{i}—Tb2—O31	77.6 (4)
O21^{i}—Tb2—O20	125.5 (4)	O13^{ii}—Tb2—O31	77.5 (4)
O13^{ii}—Tb2—O20	138.1 (4)	O20—Tb2—O31	136.1 (4)
O21^{i}—Tb2—O17^{ii}	148.2 (4)	O17^{ii}—Tb2—O31	105.8 (4)
O13^{ii}—Tb2—O17^{ii}	71.9 (4)	O18—Tb2—O31	151.0 (4)
O20—Tb2—O17ii	74.2 (4)	O12—Tb2—O31	51.9 (5)
O21i—Tb2—O18	79.7 (5)	O21i—Tb2—N2	73.2 (4)
O13ii—Tb2—O18	80.5 (4)	O13ii—Tb2—N2	151.4 (4)
O20—Tb2—O18	72.4 (4)	O20—Tb2—N2	65.1 (4)
O17ii—Tb2—O18	84.6 (4)	O17ii—Tb2—N2	136.6 (4)
O21i—Tb2—O12	124.1 (5)	O18—Tb2—N2	96.8 (4)
O13ii—Tb2—O12	107.9 (4)	O12—Tb2—N2	86.4 (5)
O20—Tb2—O12	87.2 (4)	O31—Tb2—N2	93.7 (5)
Symmetry codes: (i) *x*−1/2, −*y*+3/2, *z*; (ii) *x*−1/2, −*y*+1/2, *z*.			

Table S4 Hydrogen Bond of compound **1**

Donor---H···Acceptor	D···A	D---H···A
N(2)---H(2C)···O(11)	2.837(19)	154
N(4)---H(4B)···O(14)	3.10(2)	163
O(5)---H(5A)···O(7)	2.697(19)	158
O(10)---H(10B)···O(1)	2.642(18)	150
C(3)---H(3B)···O(11)	2.65(2)	119
C(8)---H(8B)···O(13)	2.80(3)	136
C(18)---H(18A)···O(13)	3.44(2)	160

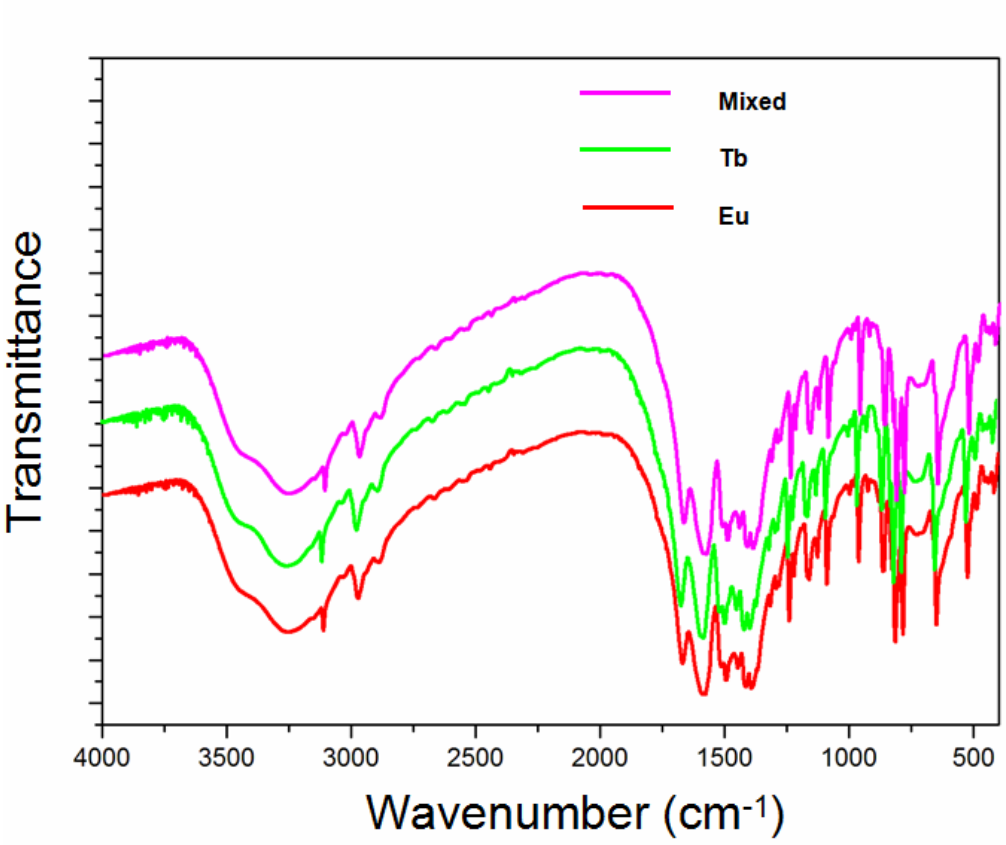


Figure S1 The IR spectra of **1**–**3**.

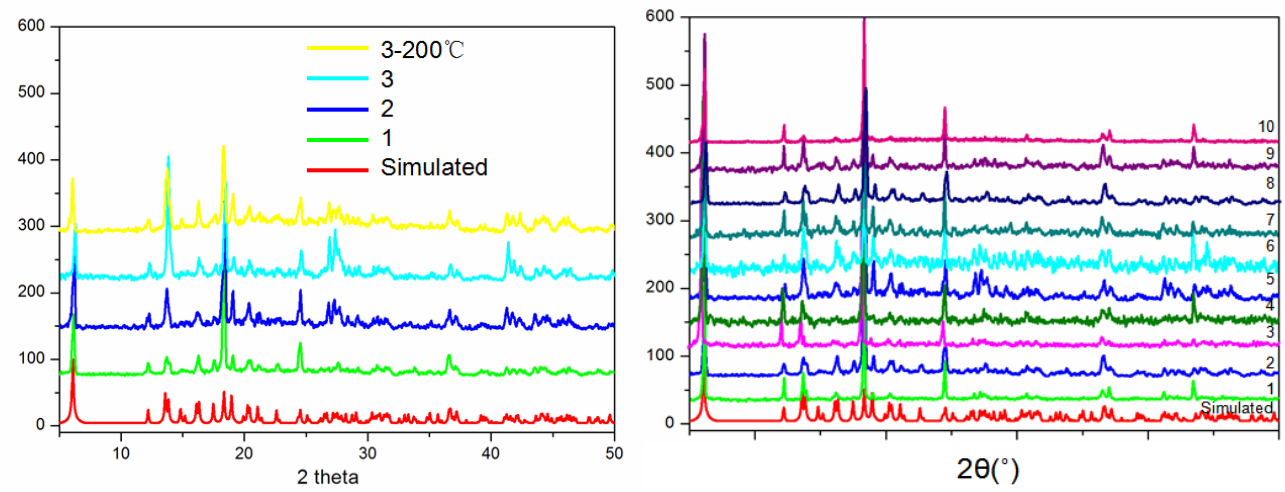


Figure S2 PXRD patterns (Left) for the as-synthesized **1–3** and the simulated patterns from single-crystal X-ray data, and the PXRD patterns (Right) of sample **1** after immersed in solutions with different metal ions (1: Fe^{3+}, 2: Cr^{3+}, 3:Zn^{2+}, 4: Cd^{2+}, 5: Cu^{2+}, 6: Co^{2+}, 7: Ni^{2+}, 8: Mn^{2+}) PBS (9) and HEPES (10) buffer solutions for one week.

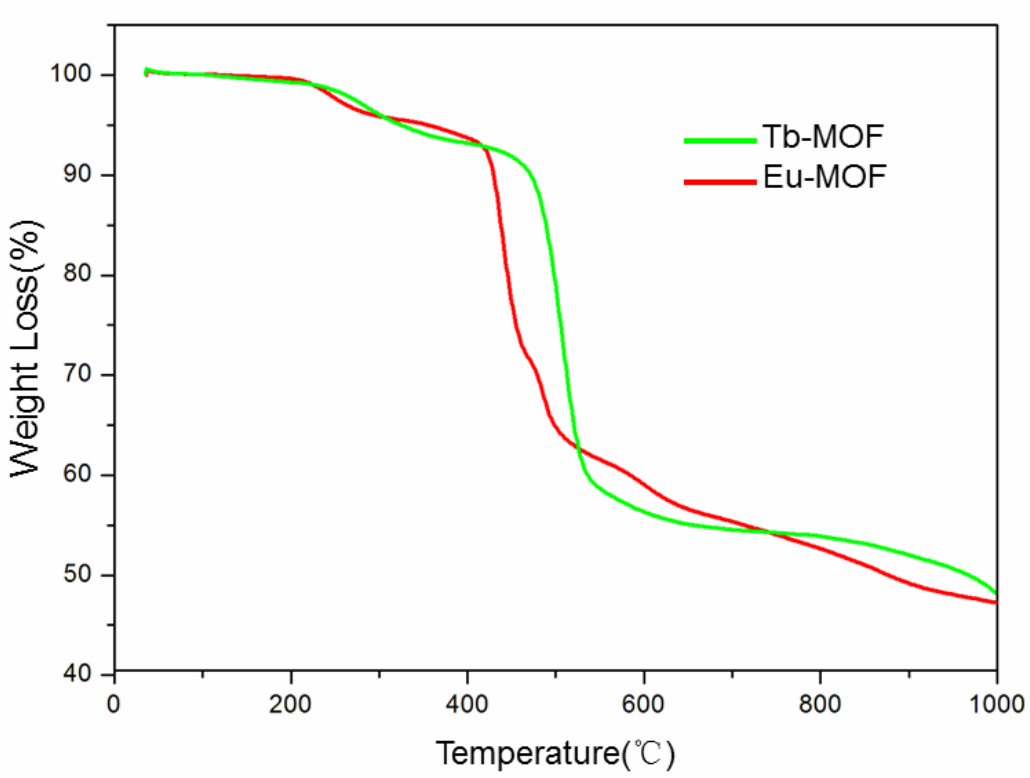


Figure S3 The TGA curves of **1–2**.

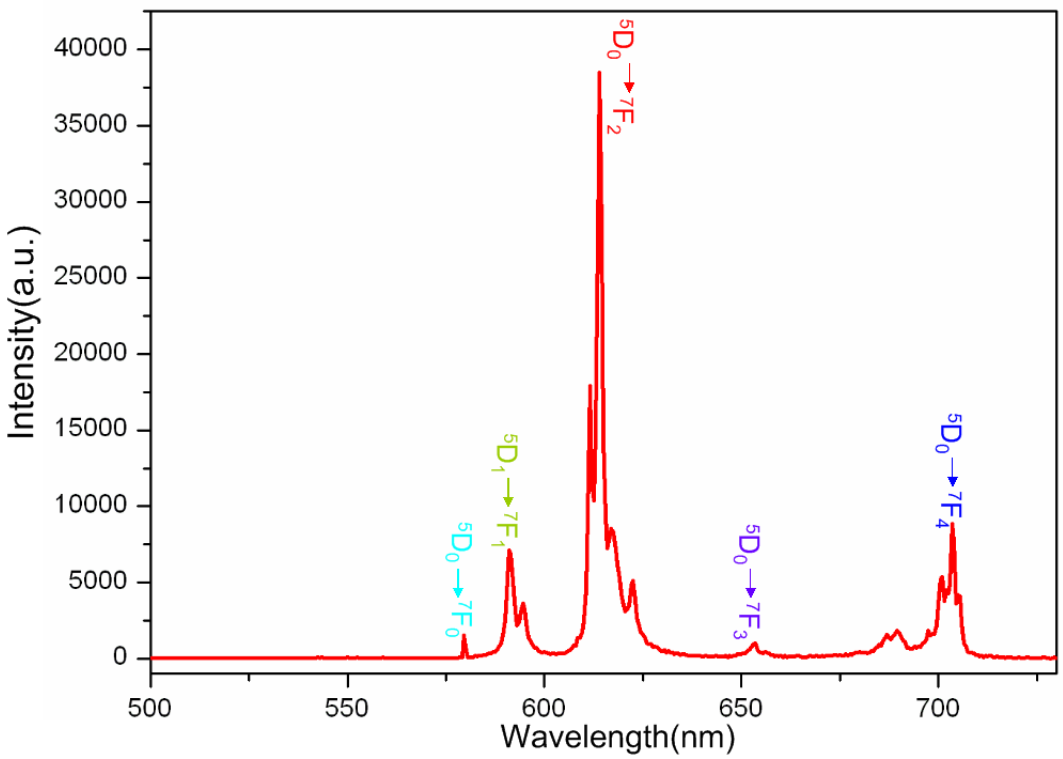


Figure S4 The emission spectrum of **1** at temperature.

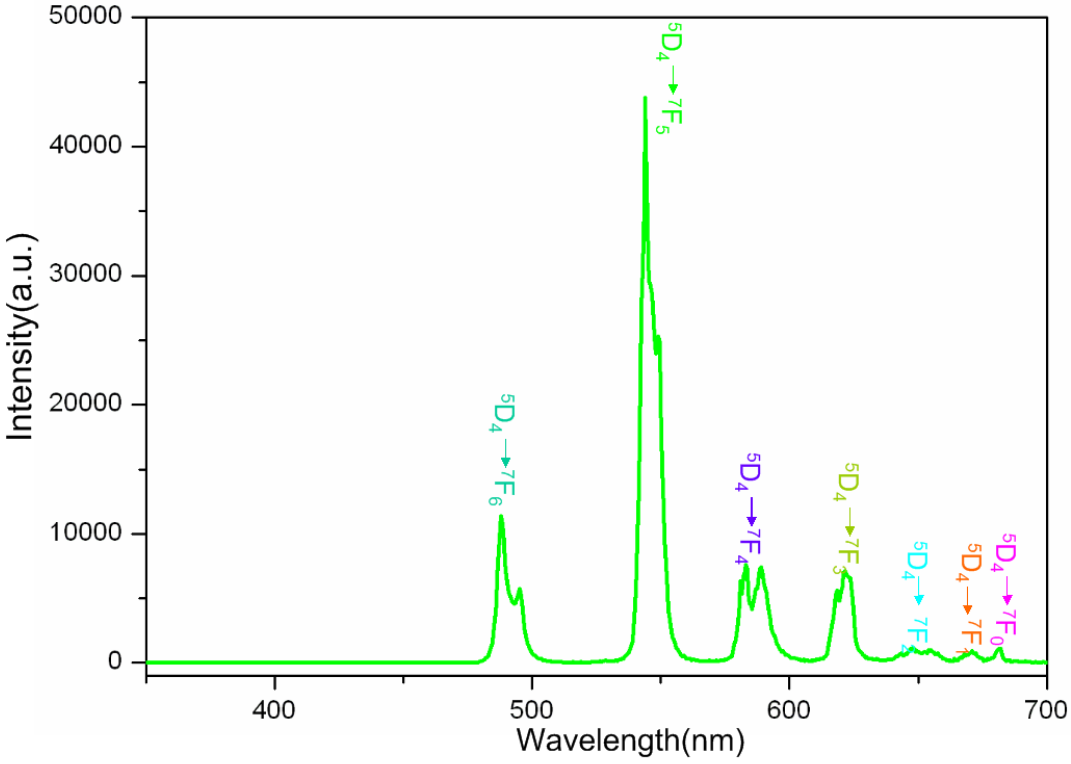
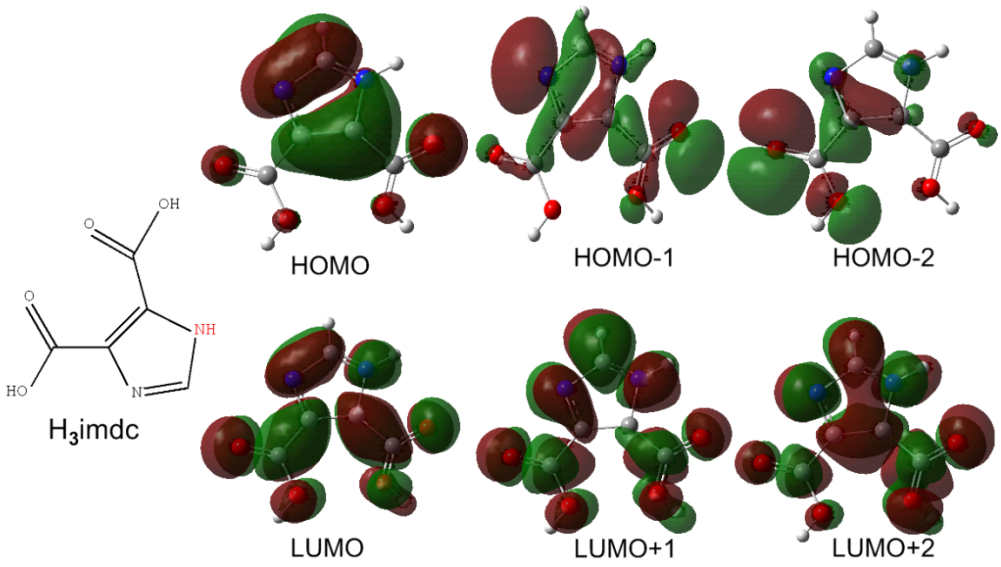
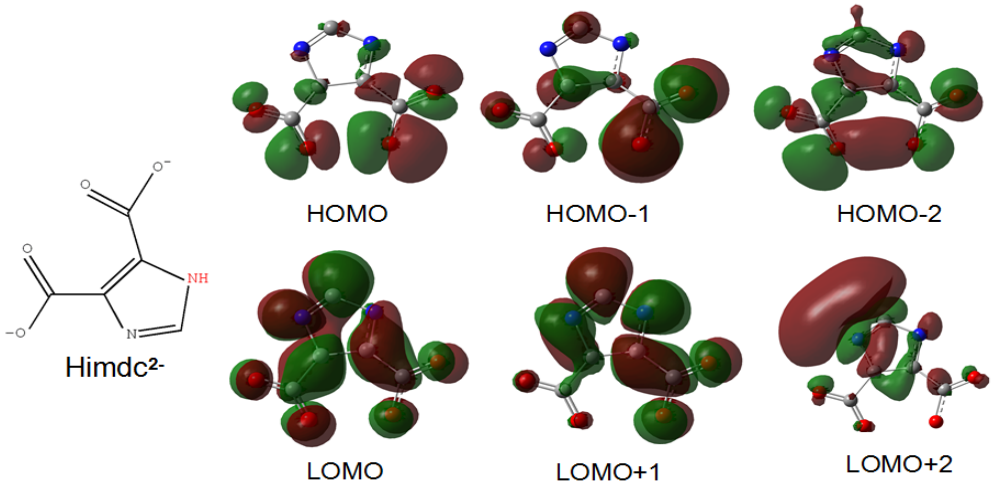


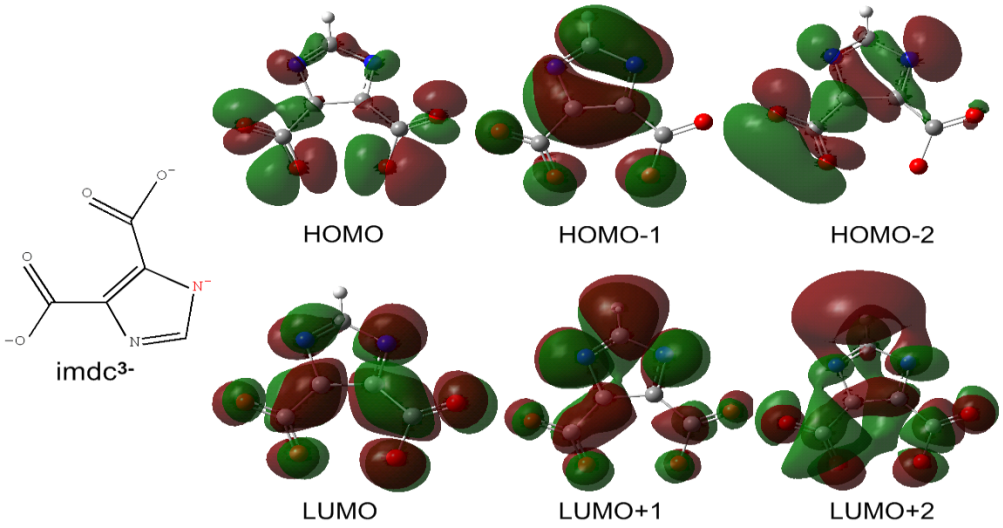
Figure S5 The emission spectrum of **2** at temperature.



(1)



(2)



(3)

Figure S6 The corresponding molecular orbital diagrams from TD-DFT electronic structure calculations for H_3imdc and the basis transient state (2) and (3).

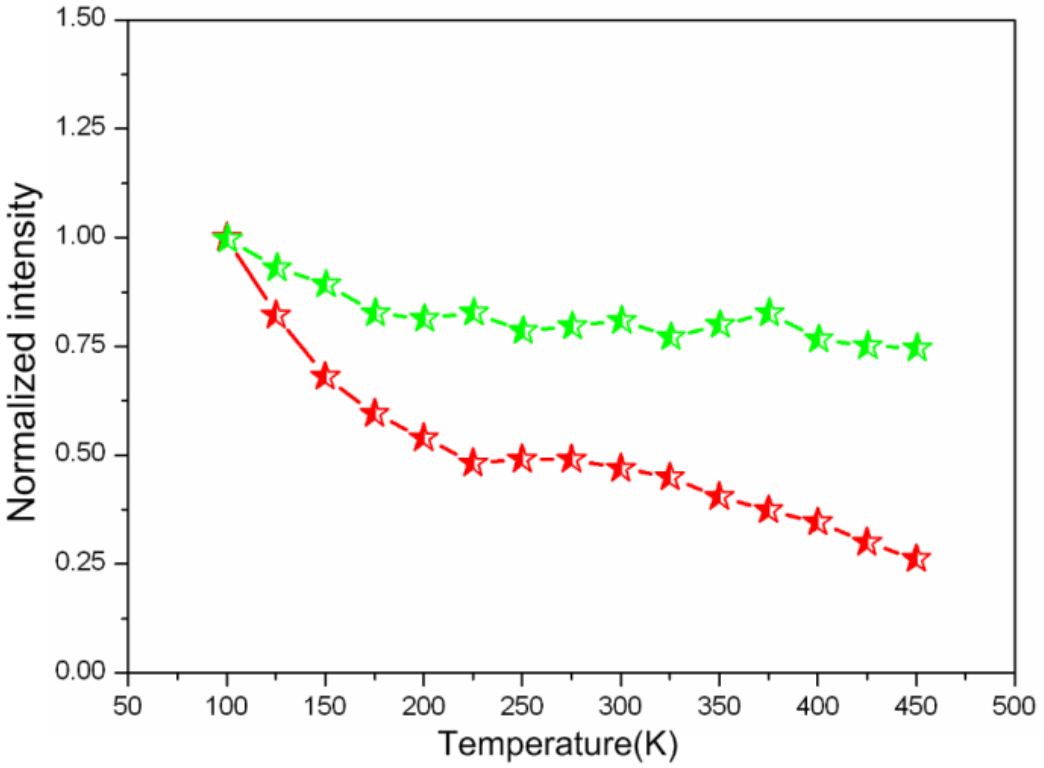


Figure S7 View of the normalized intensities of Eu^{3+}/613 nm (red) and Tb^{3+}/545 nm (green).

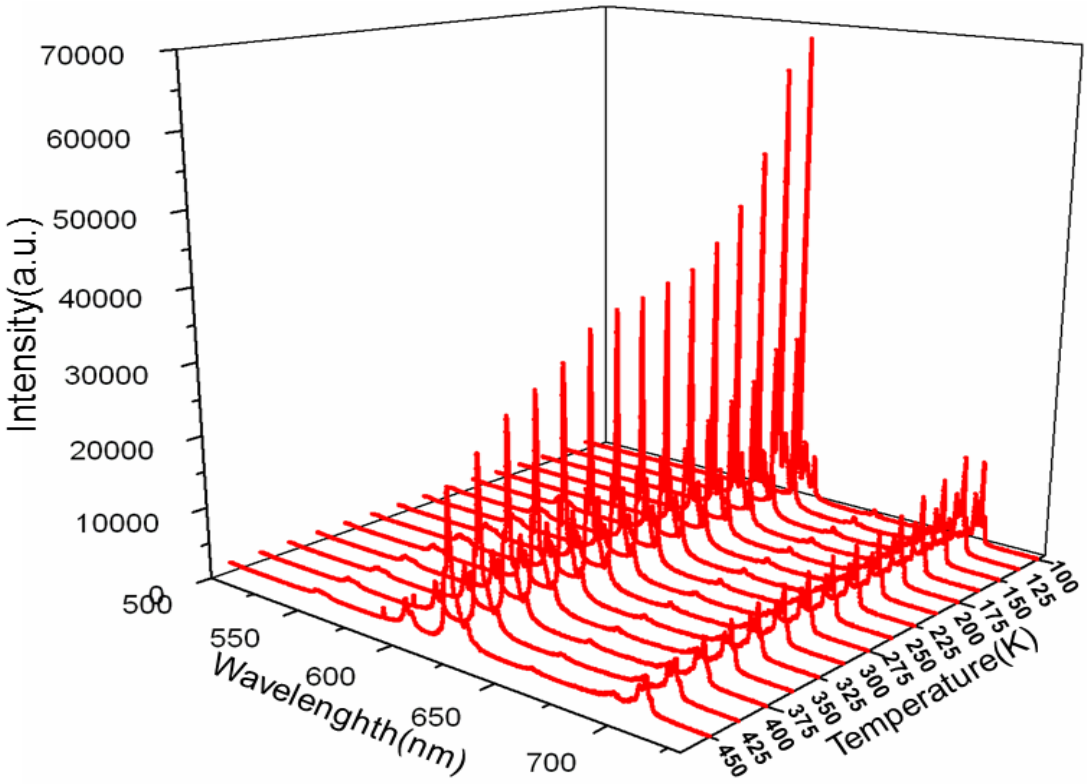


Figure S8 View of the luminescent emissions of different temperature of **1**.

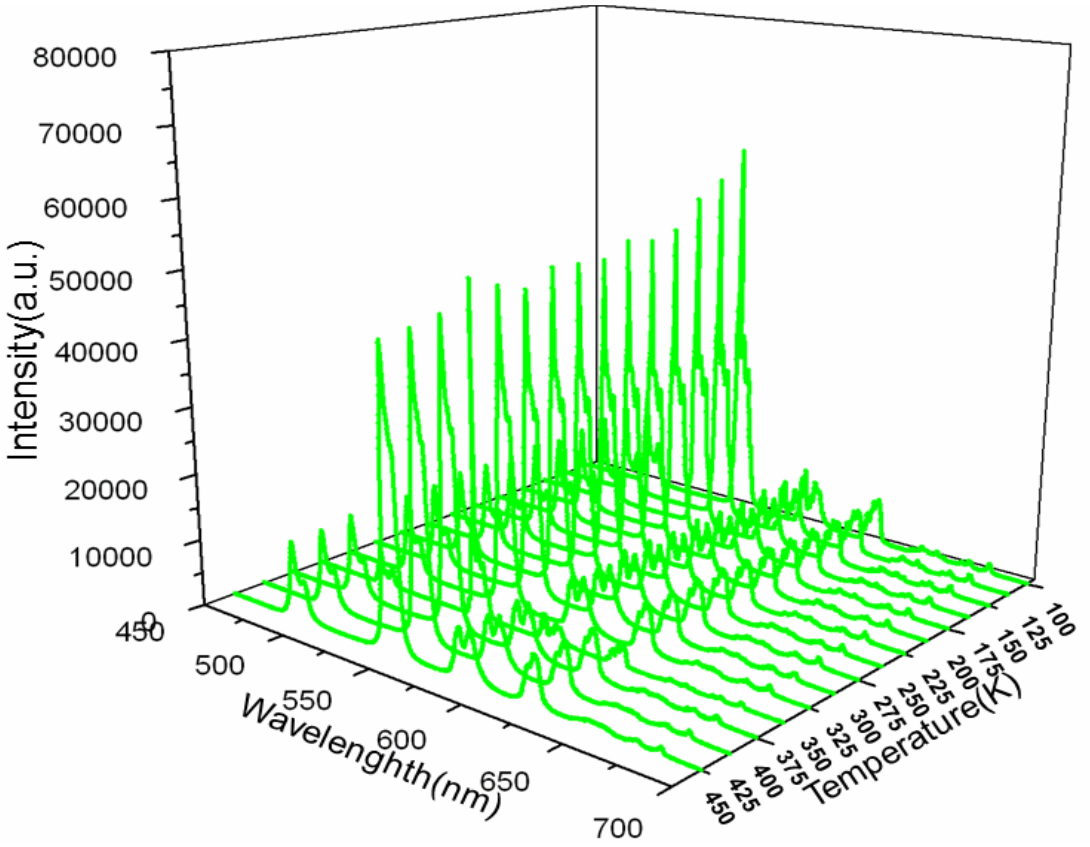


Figure S9 View of the luminescent emissions of different temperature of **2**.

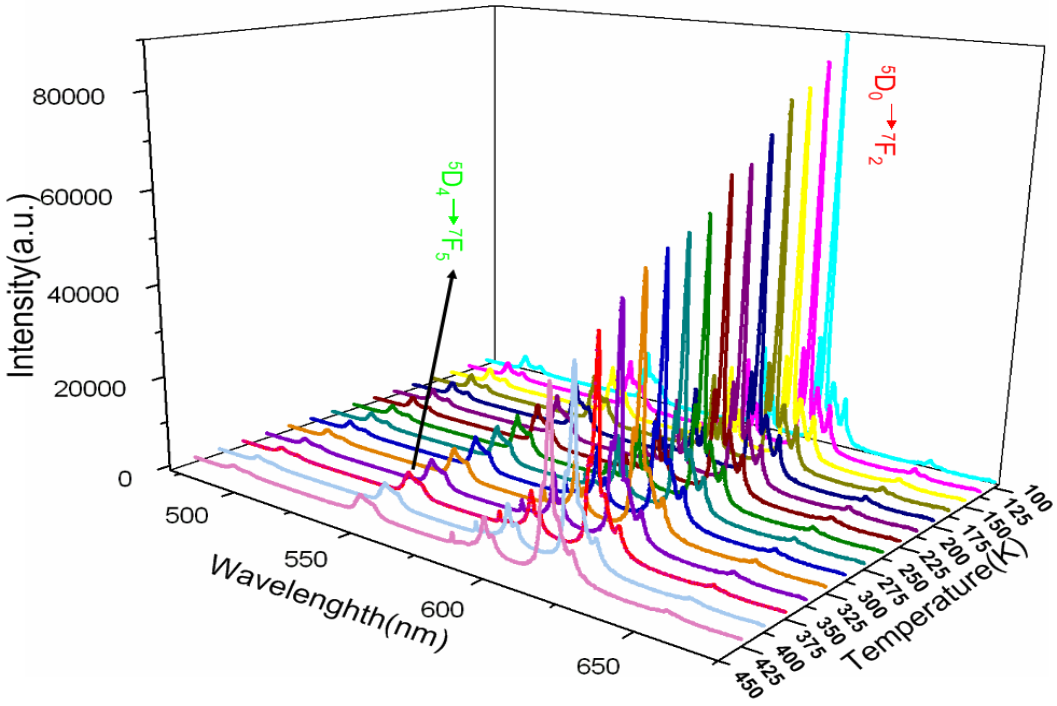


Figure S10 The emission spectra of different temperature of $Eu_{0.02}Tb_{0.98}$-MOF.

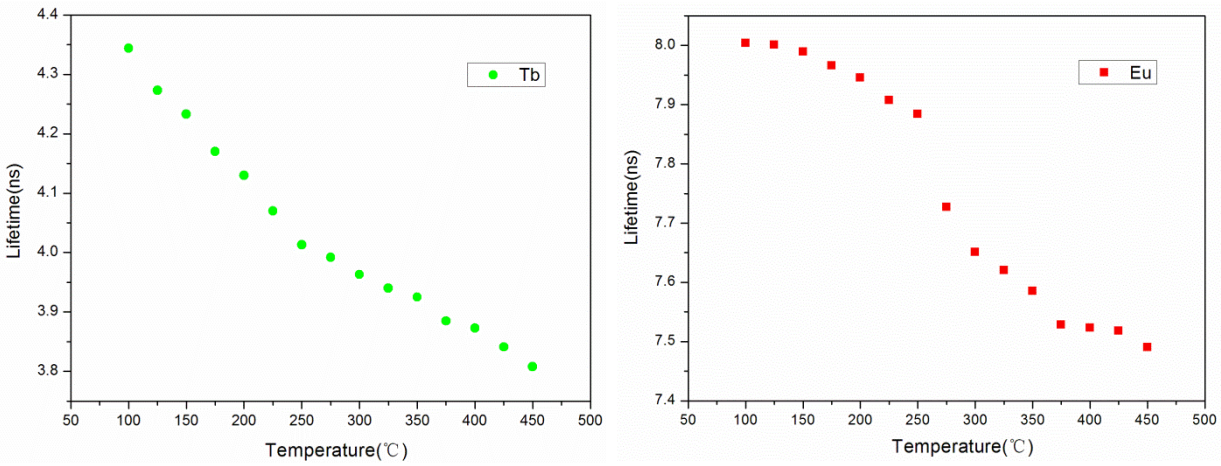


Figure S11 Temperature dependent lifetimes of **2** (545 nm) and **1** (613 nm) (100–450 K). The decay curves are monitored at 545/613 nm and excited at 277 nm.

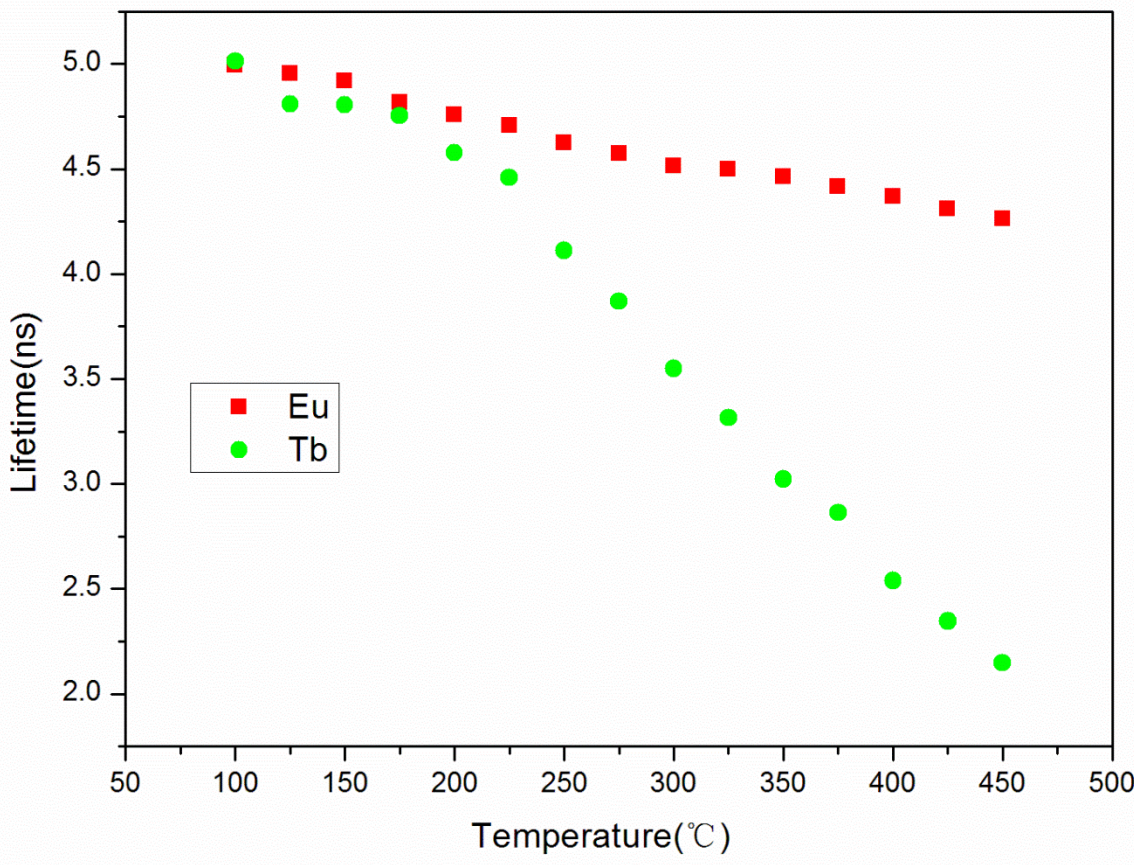


Figure S12 Temperature dependent lifetime of **3** (545/613 nm) (100–450 K). The decay curves are monitored at 545/613 nm and excited at 277 nm.