Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

A stable europium metal-organic framework as a dual-functional luminescent sensor for quantitatively detecting temperature and humidity

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Experimental Details

All the reagents were commercially available and used as provided without further purification.

Fourier transform infrared (FTIR) spectra (KBr disk method) were collected with a TENSOR 27 FT-IR spectrophotometer in the wavenumber range from 4000 to 450 cm^{-1}. PXRD was carried out on an EMPY-REAN PANALYTICAL apparatus. TGA was carried out on a SDTQ600 thermal analyser; the samples were analysed under an N_2 atmosphere and at a heating rate of 10°C min^{-1} over the temperature range 40–800°C. Room-temperature photoluminescence(PL) spectra for the powdered solid samples were collected on a Hitachi F-7000 fluorescence spectrophotometer. The PMT voltage was 700 V, the excitation slit was 2.5 nm and the emission slit was 5 nm. The temperature-dependent emission spectra were recorded on a Horiba Fluorolog-3-tau spectrophotometer.

Synthesis of $\{[Eu_2(L)_3\cdot(H_2O)_2\cdot (DMF)_2]\cdot 16H_2O\}_n$

A mixture containing $Eu(NO_3)_3\cdot 6H_2O$(0.0446 g, 0.1 mmol), H_2L (0.0398 g, 0.1 mmol), H_2O (5 mL), and DMF (3 mL) was placed in a Teflon-lined stainless steel vessel (23 ml). After being sonicated in air for 10 min, the resulting suspension was heated at 120 °C for 3 days and then cooled to room temperature at a rate of 5°C/h. Rod-shaped yellow crystals suitable for single-crystal X-ray diffraction were collected by filtration, washed with water and dried in air to afford 42 mg of product. Anal. Calcd. for $C_{72}H_{86}Eu_2N_{14}O_{32}$: C, 44.04; H, 4.42; N, 9.98. Found: C, 43.74; H, 4.53; N, 9.87. IR (cm^{-1}, KBr): 3368(vs), 1661(vs), 1590(s), 1537(s), 1497 (vs), 1467(m), 1399(vs), 1323(s), 1254(s), 956(m), 818 (s), 784(m).

Crystal data collection and refinement

Diffraction intensity data were collected at 293 K on a Bruker APEX II diffractometer equipped with a CCD area detector and graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Empirical absorption corrections were applied using the SADABS program.[1]The structure was solved by direct methods and was refined by the full-matrix least-squares method on F^2 using the SHELXTL-97 program; with all non-hydrogen atoms were refined with anisotropic thermal parameters.[2]Crystallographic data for **1** have been deposited at the Cambridge Crystallographic Data Center with the deposition number of CCDC 1436108. Experimental details for the structure analysis of **1** are given in Table 1. Selected bond lengths and angles are given in Table 2.

Table 1 Crystal data and structure refinements for compound **1**

Compound	**1**
Formula	$C_{72}H_{86}Eu_2N_{14}O_{32}$
Mr	1963.45
Crystal system	Monoclinic
Space group	P2/c
a, Å	8.1737 (5)
b, Å	15.0092 (10)
c, Å	37.574 (2)
α, deg	90
β, deg	101.828 (2)
γ, deg	90
Volume, $Å^3$	4511.7(5)
Z	4
D_c,mg/m^3	1.445
μ,mm^{-1}	1.463
F(000)	1996
Reflections collected	72739
Independent reflections	7782
Data/restraints/parameters	7782 / 1345 / 543
Goodness-of-fit on F^2	1.033
Final R indices [I>2σ (I)]	R1 = 0.0640, wR2 = 0.1437
Final R indices [all data]	R1 = 0.1218, wR2 = 0.1671
Largest diff. peak / hole,e. $Å^{-3}$	1.619/ -1.280

Table 2 The selected bond lengths and angles

Eu(1)-O(8)	2.321(6)	O(5)-Eu(1)-O(1)	125.33(19)
Eu(1)-O(4)#1	2.388(5)	O(6)-Eu(1)-O(1)	72.60(19)
Eu(1)-O(5)	2.412(5)	O(3)-Eu(1)-O(1)	52.18(18)
Eu(1)-O(6)	2.419(6)	O(8)-Eu(1)-O(7)#2	78.0(2)
Eu(1)-O(3)	2.470(5)	O(4)#1-Eu(1)-O(7)#2	117.15(19)
Eu(1)-O(1)	2.500(5)	O(5)-Eu(1)-O(7)#2	87.7(2)
Eu(1)-O(7)#2	2.501(6)	O(6)-Eu(1)-O(7)#2	79.3(2)
Eu(1)-O(2)	2.547(6)	O(3)-Eu(1)-O(7)#2	147.0(2)
Eu(1)-O(4)#2	2.576(5)	O(1)-Eu(1)-O(7)#2	147.0(2)
O(4)-Eu(1)#1	2.388(5)	O(8)-Eu(1)-O(2)	78.1(2)
O(4)-Eu(1)#3	2.576(5)	O(4)#1-Eu(1)-O(2)	124.61(18)
O(7)-Eu(1)#3	2.501(6)	O(5)-Eu(1)-O(2)	52.38(19)
O(8)-Eu(1)-O(4)#1	154.5(2)	O(6)-Eu(1)-O(2)	147.5(2)
O(8)-Eu(1)-O(5)	130.5(2)	O(3)-Eu(1)-O(2)	76.34(19)
O(4)#1-Eu(1)-O(5)	73.01(19)	O(1)-Eu(1)-O(2)	125.72(19)
O(8)-Eu(1)-O(6)	79.7(2)	O(7)#2-Eu(1)-O(2)	73.2(2)
O(4)#1-Eu(1)-O(6)	83.24(19)	O(8)-Eu(1)-O(4)#2	122.2(2)
O(5)-Eu(1)-O(6)	143.9(2)	O(4)#1-Eu(1)-O(4)#2	66.4(2)
O(8)-Eu(1)-O(3)	83.8(2)	O(5)-Eu(1)-O(4)#2	78.57(19)
O(4)#1-Eu(1)-O(3)	90.46(18)	O(6)-Eu(1)-O(4)#2	66.94(18)
O(5)-Eu(1)-O(3)	83.55(19)	O(3)-Eu(1)-O(4)#2	154.01(18)
O(6)-Eu(1)-O(3)	124.25(19)	O(1)-Eu(1)-O(4)#2	127.23(18)
O(8)-Eu(1)-O(1)	80.2(2)	O(7)#2-Eu(1)-O(4)#2	51.14(18)
O(4)#1-Eu(1)-O(1)	76.70(18)	O(2)-Eu(1)-O(4)#2	106.36(18)

Symmetry transformations used to generate equivalent atoms: #1: -x, y, -z+1/2; #2 : x+1, -y, z-1/2 ; #3: x-1, -y, z+1/2; #4 : -x+3, -y+1, -z.

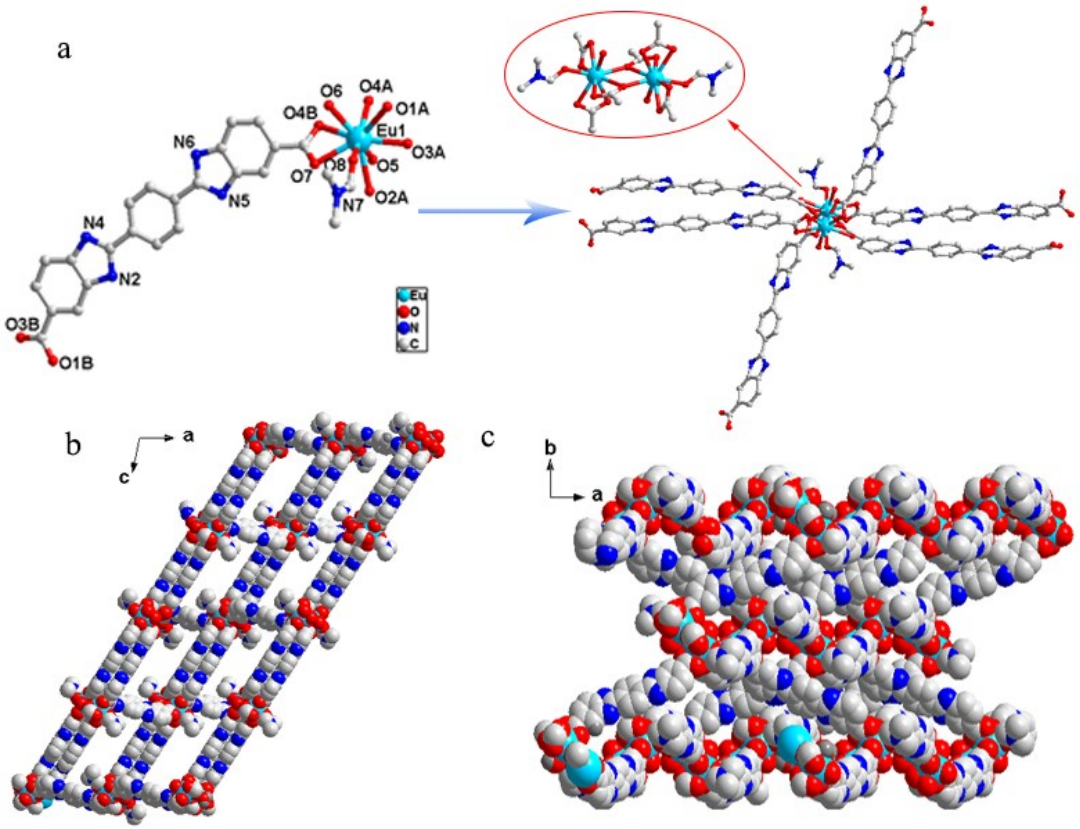

Fig. S1 (a) Coordination environment of Eu^{3+} in **1**; (b) Space fill model of **1** along *b*-axis ; (c) Space fill model of **1** along *c*-axis . Symmetry codes: A: 1 + x , -y, -1/2 + z; B: -x, y, -1/2 - z.

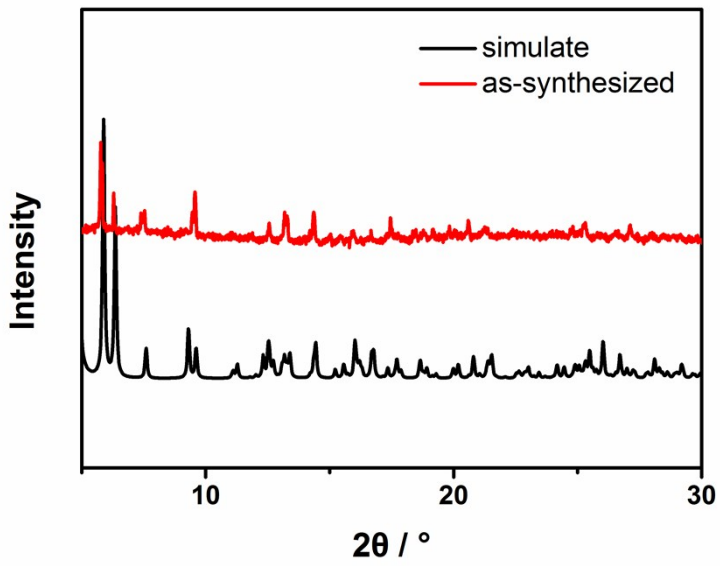

Fig. S2 The simulated patterns and experimental powder XRD patterns of **1**.

Object 1	Object 2	Length
O6	O1	2.726
N2	O9	2.861
N5	O12	2.736
O9	O7	2.964
O10	N6	2.811
O11	N1	3.084
O13	O11	2.863
O13	O2	2.912
O15	O9	2.735
O15	O13	2.888
O16	O14	2.783
O16	N4	3.059

Fig. S3 The hydrogen bonding table of **1**.

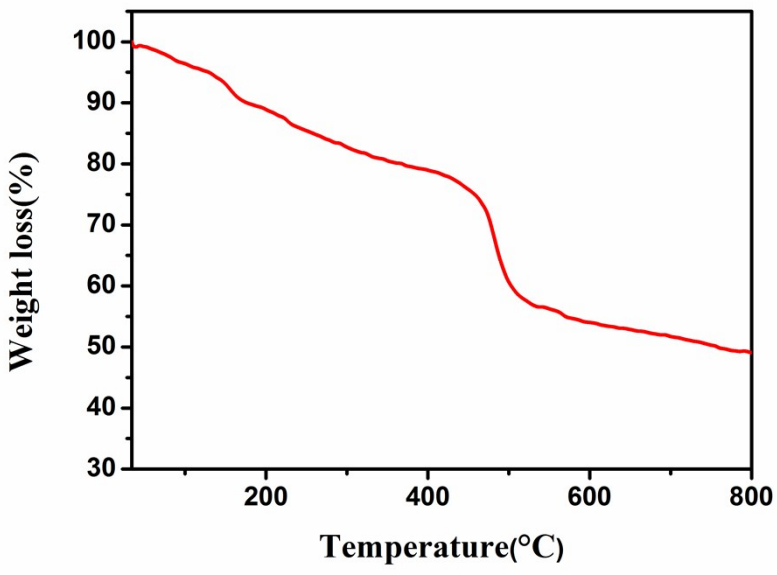

Fig. S4 Thermogravimetric analyses trace of **1**.

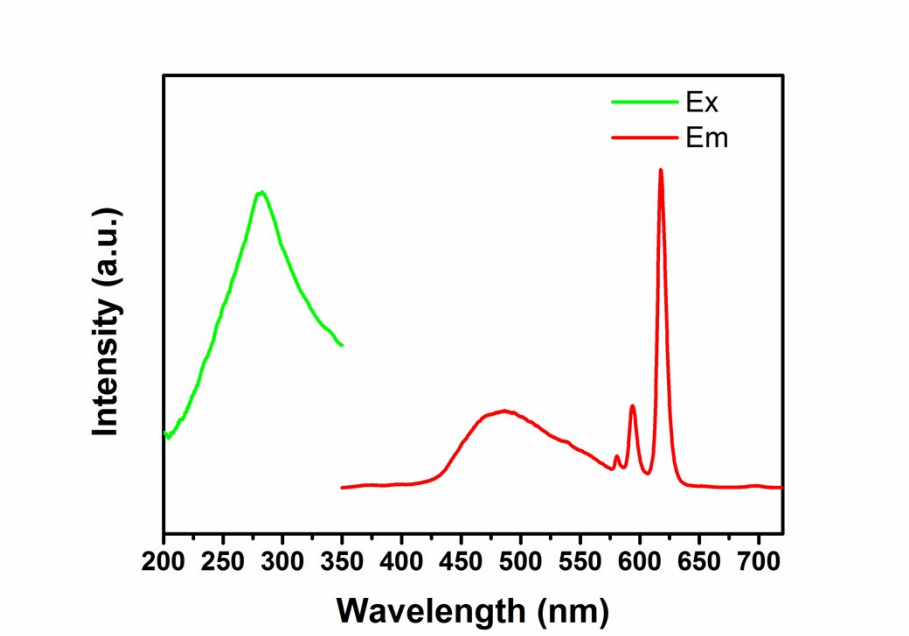

Fig. S5 The excitation spectra and emission spectra upon excitation at 280 nm for **1**.

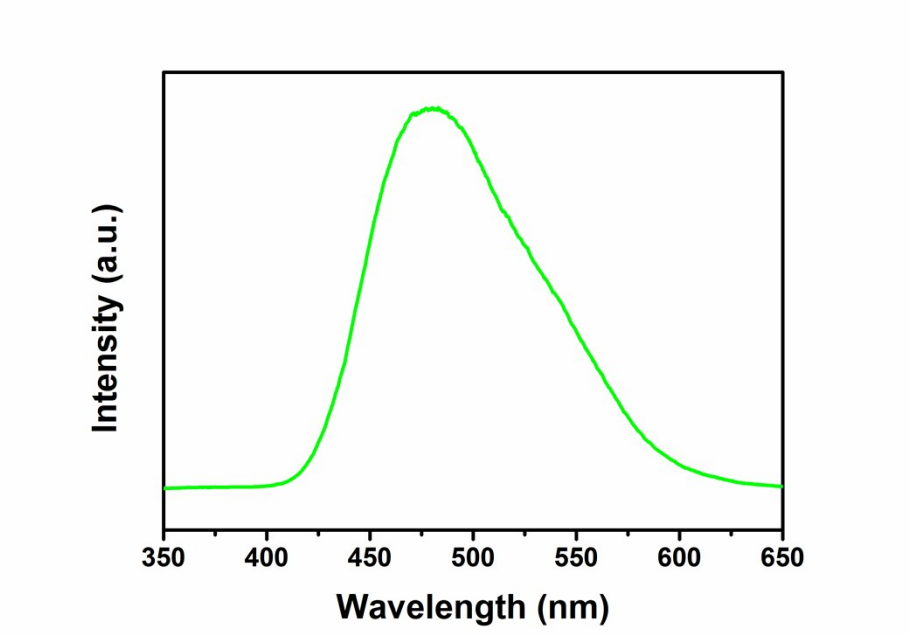

Fig. S6 The emission spectra for ligand H_2L upon excitation at 280 nm.

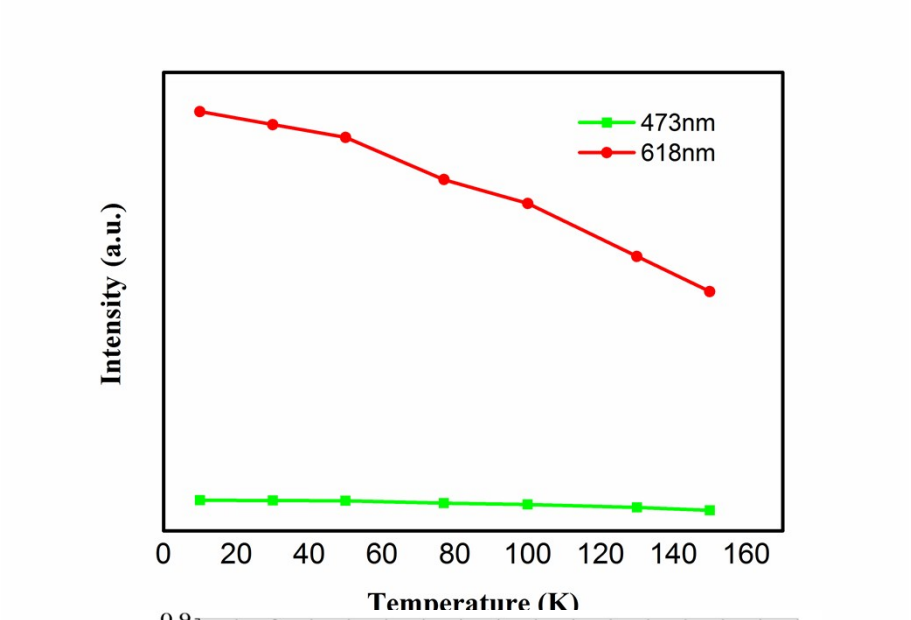

Fig. S7 Different rate of decreasing intensity at 473 nm and 618 nm. luminescent

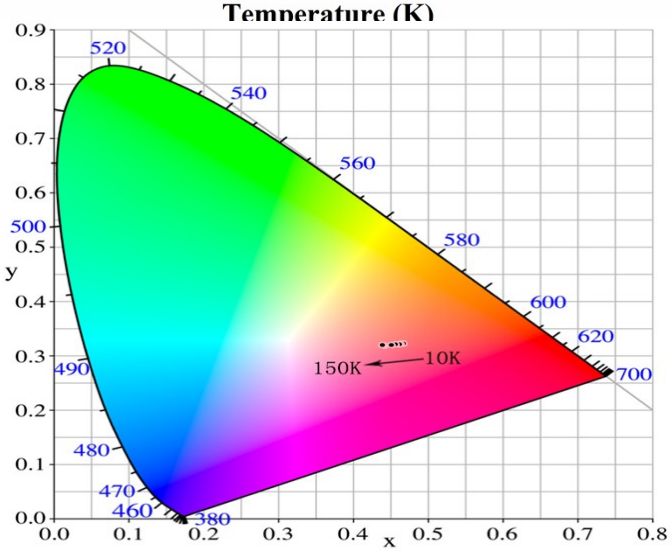

Fig. S8 CIE of temperature-dependent luminescence color of **1**.

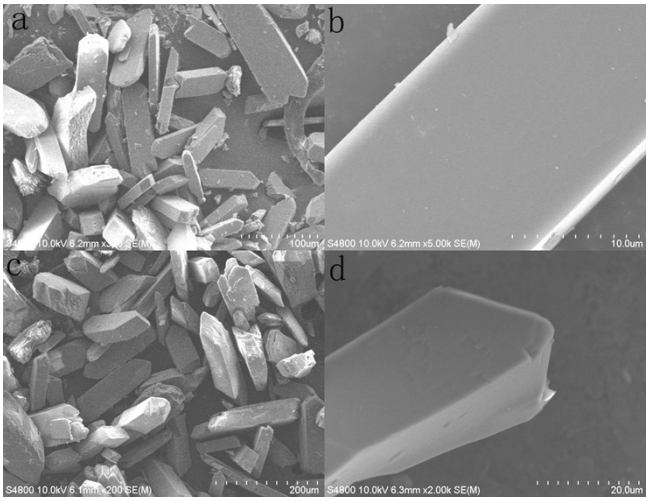

Fig. S9 SEM images of **1** (a, b) and **1** after exposure to moisture (RH 75%) for 3 days(c, d).

References

1. G.M.Sheldrick,*Program for Empirical Absorption Correction of Area Data Detector*, University of Göttingen, Germany, 1996.

2. G.M.Sheldrick, SHELXTL Version 5.1, *Bruker Analytical X-ray Instruments Inc.*, Madis on, Wisconsin, USA, 1998.