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A photochromic and scintillation Eu-MOF with visual X-ray detection in bright and dark environments

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Content

1.Experimental section

General Information. All the reagents and solvents employed were commercially available and used without further purification. The $Hipbp^+$ ligand was synthesized by following previously reported literature.[1]

Synthesis of $[Eu_3(ipbp)_4(OH)_2(COO)_3(H_2O)_2]\cdot xH_2O$ (PMOF-2). Eu $(NO_3)_3\cdot 6H_2O$（0.089 g, 0.2 mmol）and H_2ipbpCl (0.037 g, 0.1 mmol) were dissolved in a mixture of H_2O (2 mL) that was transferred into a solution with PH in 4-5 by Hydrochloric acid and DMF (2 mL) and ethanol (2 mL), and the Hydrochloric acid was diluted 1 mol/L in advance. The finally solution was sealed in a 20 mL vial, this moment the vial would has slight fever during neutralization reaction then it's mixed well through ultrasound, heated at 100 °C for 24 hours. Yellow plate crystals were collected.

X-ray crystallography Single-crystal X-ray diffractions of **PMOF-2** was performed by a Rigaku PILATUS CCD diffractometer equipped with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å) at 293 K. The structures were solved by direct methods, and the subsequent successive difference Fourier syntheses yielded other nonhydrogen atoms. All atoms except hydrogen atoms were performed through the anisotropic refinement. The final structures were refined using a full-matrix least-squares refinement on F^2 with the SHELXL-97 program package.[2]-[4] There is disorder with C73, we refined it with C73 and C73B for an occupancy of 63% and 37%, respectively. Pertinent crystal data and structure refinements are summarized in **Table S1**. The bond lengths are listed in **Tables S2**.

Powder X-Ray Diffraction Powder X-ray diffraction patterns (PXRD) were recorded with a Miniflex 600 at 40 kV, 40 mA for Cu-K_α with a scan speed of 0.10 s per step and a step size of 0.02°, the data were collected within 2θ range of 5–50°. The Mercury Version 4.1.0 software was utilized to achieve simulated PXRD patterns dependent on the X-ray crystallographic structure.

UV–Vis Spectroscopy Solid state UV-vis diffuse reflectance spectrum was taken by PerkinElmer Lambda 950 at room.

Electron Spin Resonance Spectroscopy The ESR signal at X band was recorded using polycrystalline samples on the Brucker A300 spectrometer.

Fluorescence measurements The photoluminescence spectra were recorded on an Edinburgh FL920 phosphorimeter using a 450W Xenon lamp as excitation source.

X-ray stimulated Fluorescence measurements The self-built scintillating measurement equipment. The whole backbone of the X-ray stimulated Fluorescence Spectrometer was from FLS920 Spectrometer, except that the excitation Xe lamp is replaced by a highly purified tungsten target.

FT-IR The spectra of **PMOF-2**were measured on a PerkinElmer Spectrum One FT-IR spectrometer (**Figure S11**): 3212(w), 2983 (w), 2830 (w), 1637 (w), 1604 (m), 1558 (m), 1490 (w), 1467 (w), 1438 (w), 1396 (m), 1369 (m), 1214 (w), 1074 (w), 823 (m), 781 (m), 738 (m), 709 (m).

Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC) The data were collected on a METTLER TOLEDO analyzer and heated in an Al_2O_3 crucible under N_2 atmosphere at a heating rate of 10 K min^{-1}.

Nuclear Magnetic Resonance Spectrometer (NMR) The data of ligand were collected on a AVANCE III HD spectrometer (**Figure S13**). 1H (D2O): δ 9.26 (d, J = 7.2 Hz, 2H); 8.88 (dd, J1 = 1.5 Hz, J2 = 5.7 Hz, 2H); 8.67 (t, J = 1.5 Hz, 1H); 8.57 (d, J = 6.6 Hz, 2H); 8.40 (d, J = 1.5 Hz, 2H); 8.36 (dd, J1 = 1.5 Hz, J2 = 5.4 Hz, 2H).

2.Figure and Table

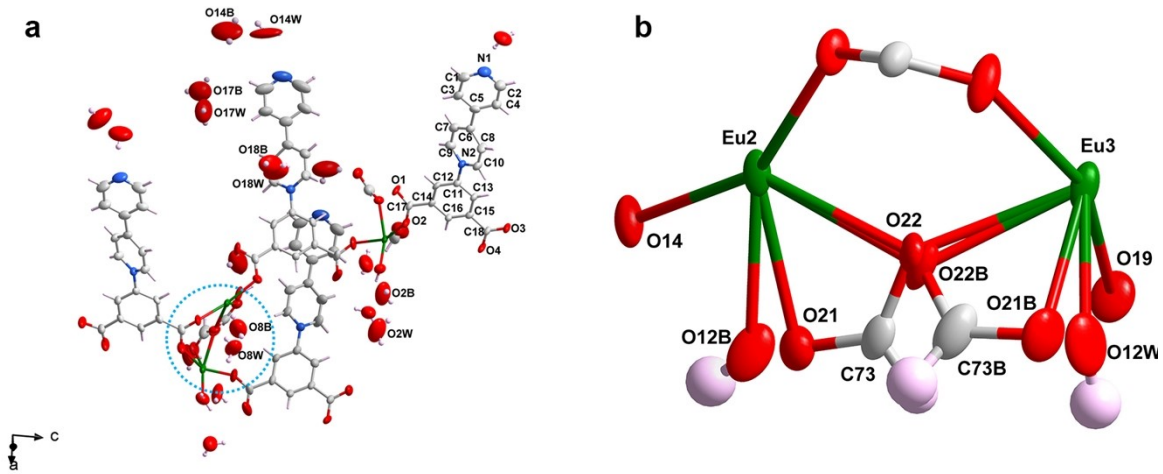

Figure S1. Crystal structure of **PMOF-2.** (a) Asymmetric unit with 30% thermal ellipsoids (H atoms are shrunk for clarity); (b) Enlarged image of the blue circle in (a): Part1, the occupancy of 63%: C73, O21, O22, O12W; Part2, the occupancy of 37%: C73B, O21B, O22B, O12B. Color scheme: Eu green, O red, N blue, C gray, H pink.

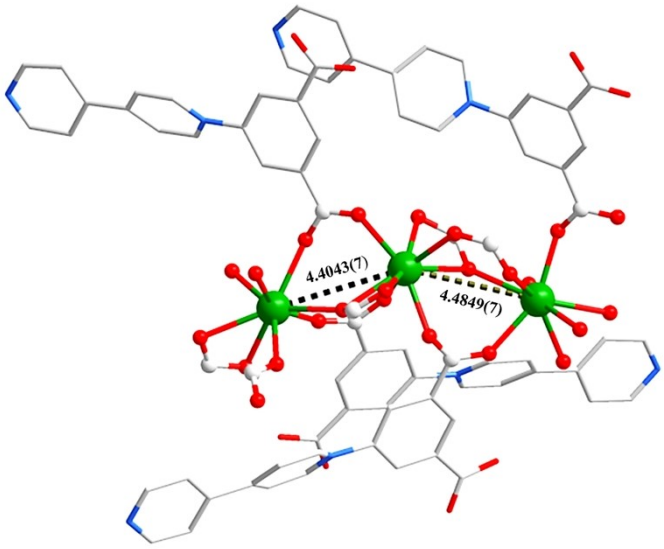

Figure S2. The distance between Eu atoms in the crystal structure.

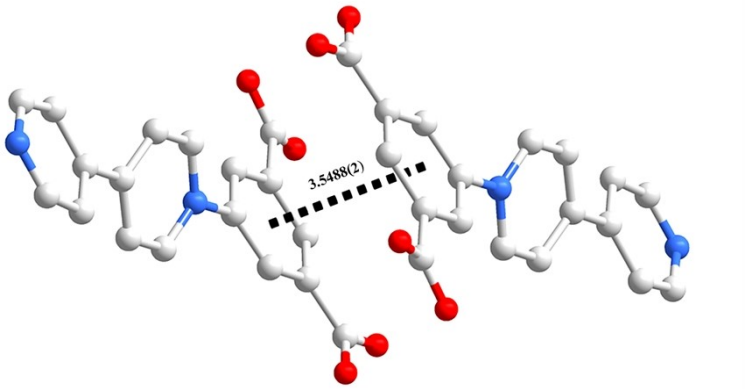

Figure S3. The closest π-π stacking distance between the ligand and the ligand in the crystal structure.

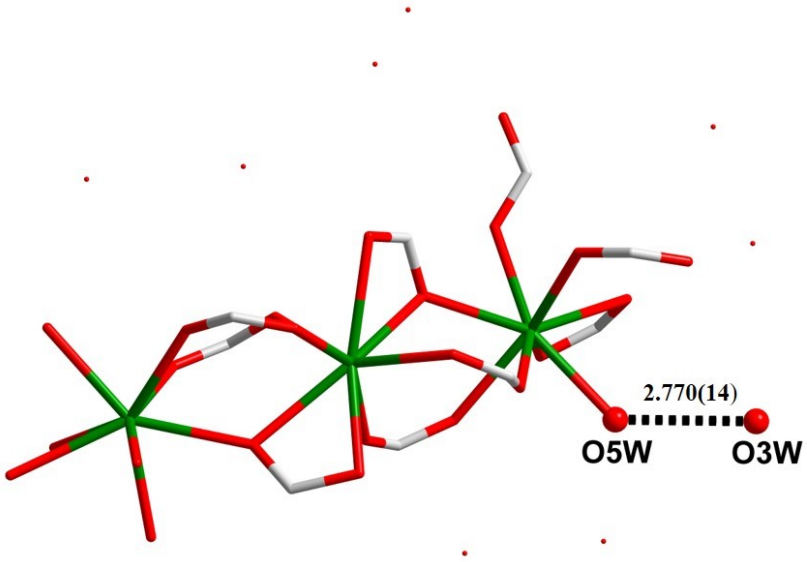

Figure S4. The closest distance between the oxygen atom and the oxygen atom in the crystal structure.

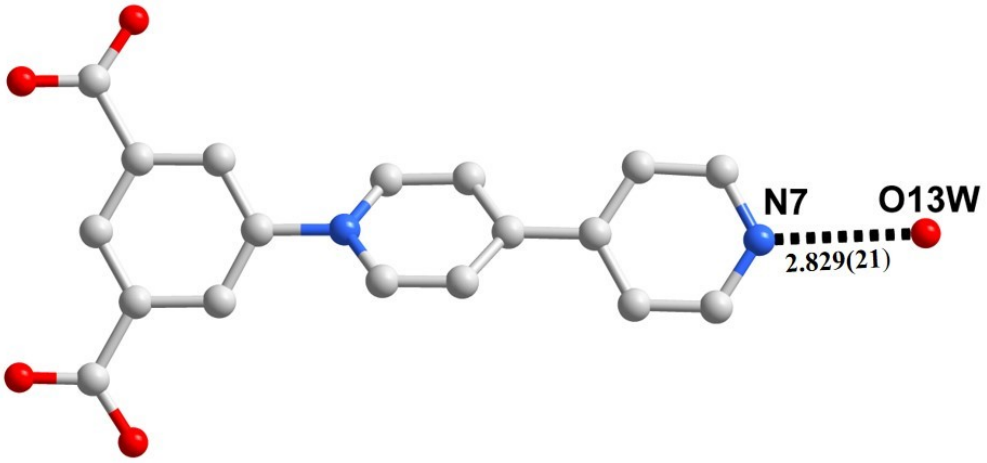

Figure S5. The closest distance between the nitrogen atom and the oxygen atom in the crystal structure.

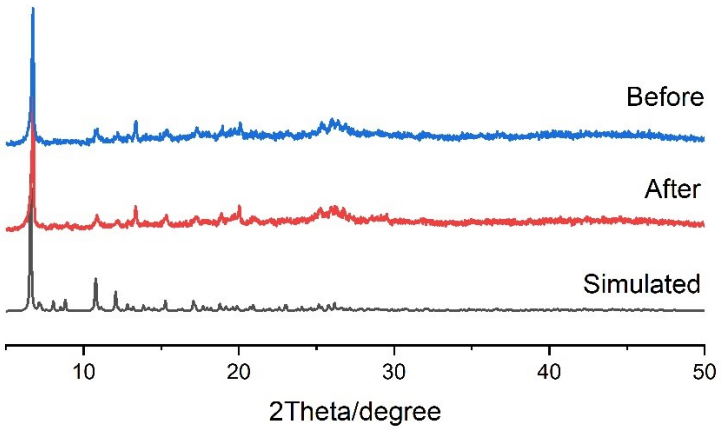

Figure S6. The PXRD patterns of **PMOF-2** simulated, before and after (Cu-K_α X-ray) irradiation at 25℃.

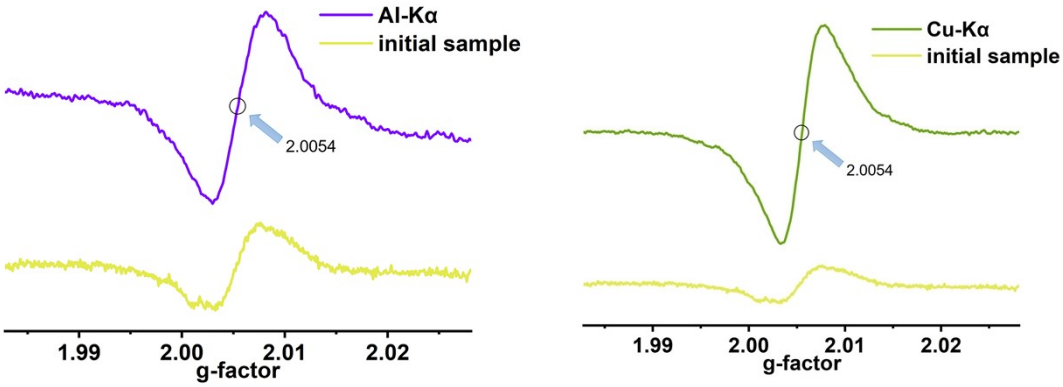

Figure S7. EPR signals of the Al-K_α and Cu-K_α X-ray irradiated samples for compound **PMOF-2**.

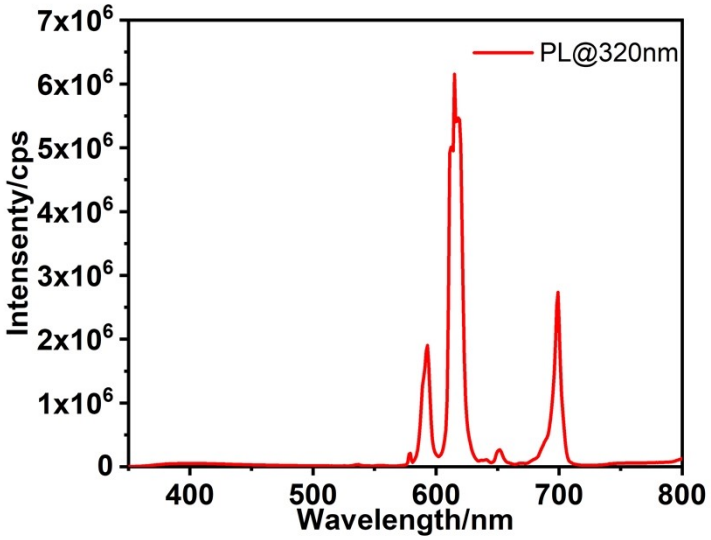

Figure S8. Solid-state photoluminescence (PL; excitation wavelength, 320 nm) spectra of **PMOF-2** at room temperature.

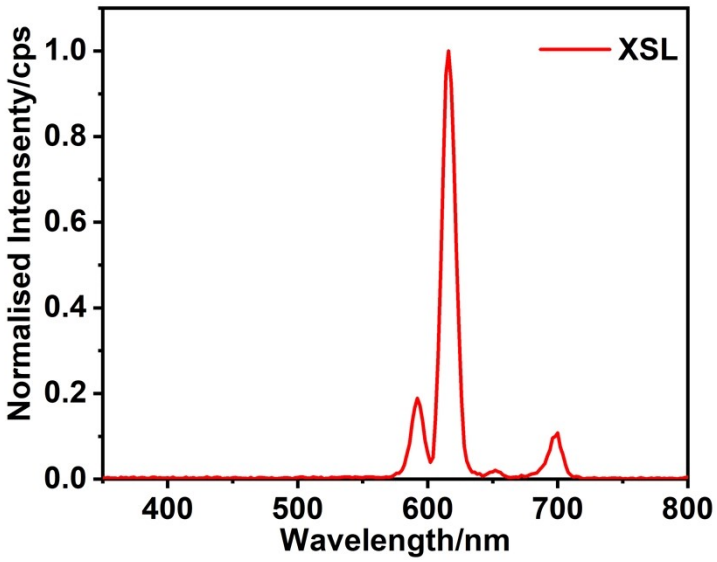

Figure S9. Solid-state XSL (a high-purity tungsten target with a tube voltage of 50 kV and a tube current of 100 μA) spectra of **PMOF-2** at room temperature.

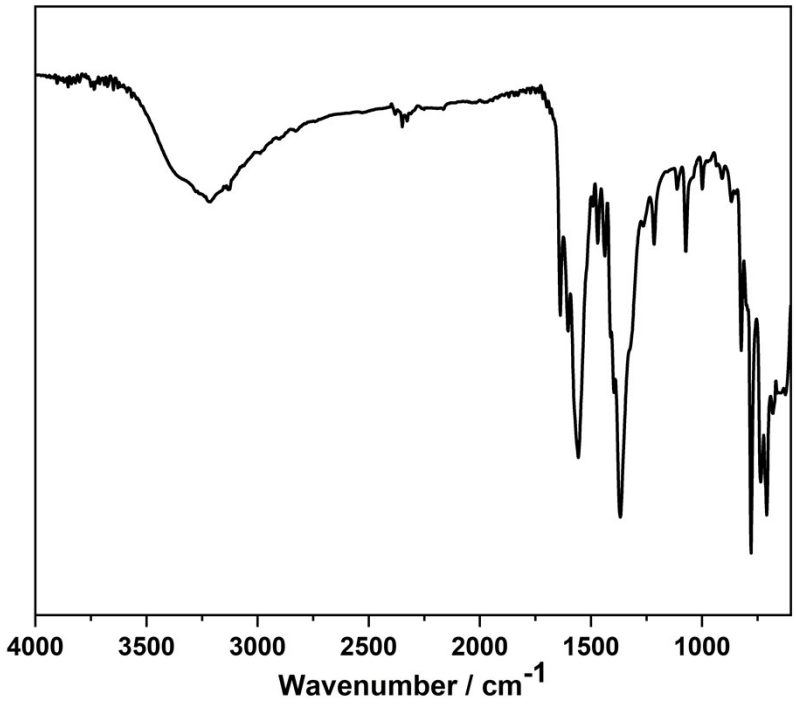

Figure S10. The FT-IR spectra of **PMOF-2** at room temperature.

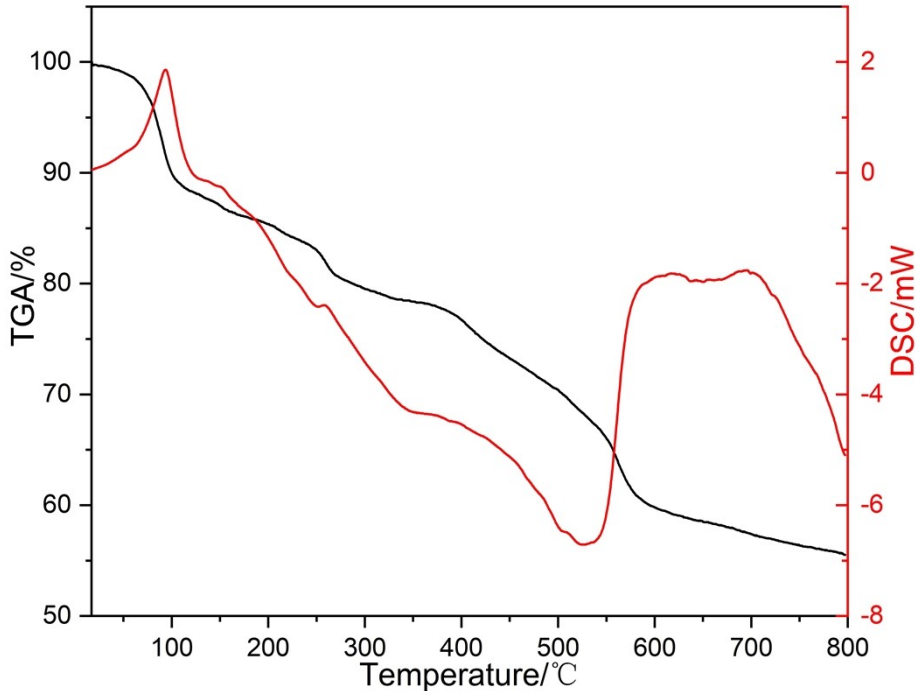

Figure S11. TGA and DSC curves of **PMOF-2**.

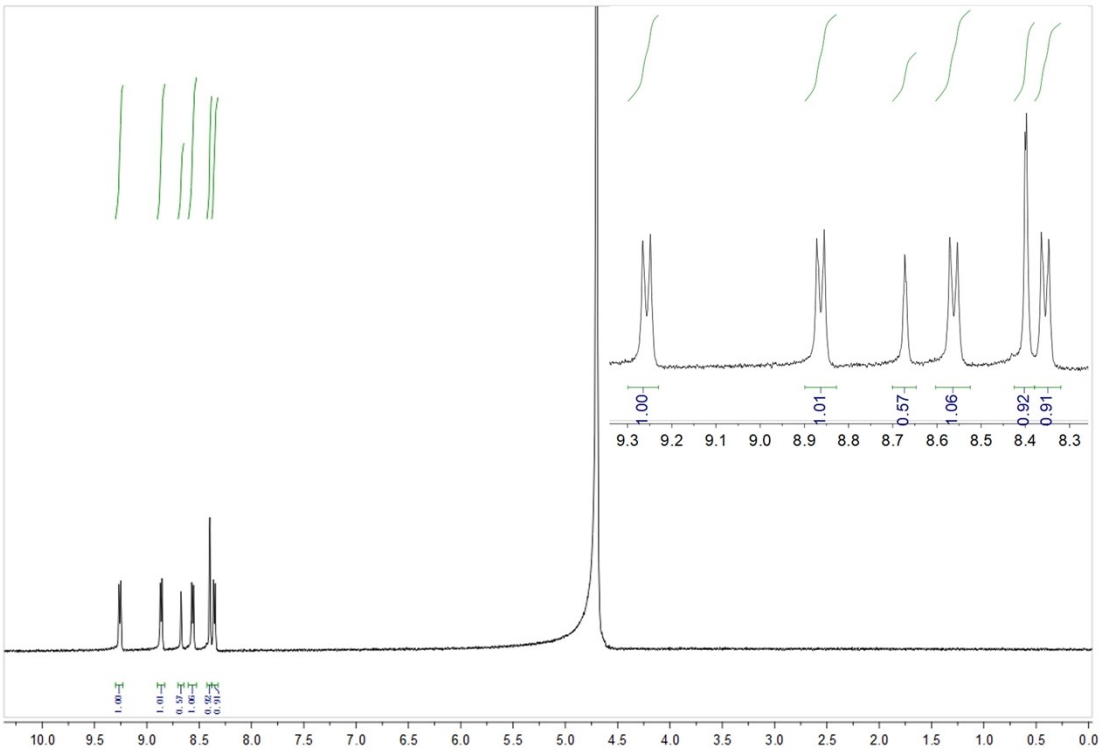

Figure S12. ^{1}H NMR spectra (400 MHz) of **PMOF-2**, recorded in D_2O. Inset: enlarge part around the 9.3-8.3 ppm peak.

Table S1. Crystal data and structural refinements for **PMOF-2**.

Formula	$[Eu_3(ipbp)_4(OH)_2(COO)_3(H_2O)_2]\cdot xH_2O$
CCDC	2126492
Fw	2172.34
Crystal system	triclinic
Space group	P-1
a /Å	14.3027(7)
b /Å	17.1267(5)
c /Å	19.0402(7)
α /°	88.509(3)
β /°	83.110(3)
γ /°	70.595(4)
V /Å^3	4366.9(3)

Z	2
Dc /g.cm^{-3}	1.652
μ /mm^{-1}	2.223
Goodness-of-fit on F^2	1.023
R1, wR2 [I > 2σ(I)]	0.0543, 0.1302
R1, wR2 (all data)	0.0992, 0.1494

$R_1 = \sum||F_o|-|F_c||/\sum|F_o|$, $wR_2 = \{\sum w[(F_o)^2-(F_c)^2]^2/\sum w[(\underline{F}_o)^2]^2\}^{1/2}$.

Table S2. The bond lengths (Å) in **PMOF-2**.

The bond lengths (Å) in **PMOF-2**			
Eu1—O15	2.313(5)	C3—C5	1.381(10)
Eu1—O2	2.357(5)	C4—C5	1.405(10)
Eu1—O7	2.369(6)	C5—C6	1.474(10)
Eu1—O5W	2.420(5)	C6—C8	1.381(10)
Eu1—O5	2.431(4)	C6—C7	1.389(10)
Eu1—O13^1	2.441(5)	C7—C9	1.368(10)
Eu1—O4^2	2.462(4)	C8—C10	1.370(10)
Eu1—O3^2	2.533(4)	C11—C12	1.370(9)
Eu2—O11	2.320(4)	C11—C13	1.385(9)
Eu2—O14	2.358(5)	C12—C14	1.394(9)
Eu2—O1^1	2.363(4)	C13—C15	1.381(9)
Eu2—O18^3	2.365(4)	C14—C16	1.386(8)
Eu2—O21	2.428(14)	C14—C17	1.506(9)
Eu2—O22	2.43(2)	C15—C16	1.392(8)
Eu2—O12B	2.43(3)	C15—C18	1.485(9)
Eu2—O5^1	2.494(5)	C19—C21	1.367(11)
Eu2—O6^1	2.517(6)	C20—C22	1.377(11)
Eu2—O22B	2.63(4)	C21—C23	1.384(11)
Eu3—O19	2.301(5)	C22—C23	1.383(10)
Eu3—O21B	2.34(3)	C23—C24	1.494(10)
Eu3—O12	2.344(5)	C24—C25	1.397(10)
Eu3—O17^3	2.382(5)	C24—C26	1.403(9)
Eu3—O11W	2.403(6)	C25—C27	1.365(10)
Eu3—O22B	2.45(5)	C26—C28	1.355(9)
Eu3—O12W	2.45(2)	C29—C30	1.387(9)
Eu3—O10^4	2.458(5)	C29—C31	1.388(9)
Eu3—O22	2.50(3)	C30—C32	1.369(9)
Eu3—O9^4	2.564(5)	C31—C33	1.391(9)
O1—C17	1.248(7)	C32—C34	1.390(9)
O2—C17	1.241(7)	C32—C35	1.495(9)
O3—C18	1.265(7)	C33—C34	1.391(9)

O4—C18	1.276(8)	C33—C36	1.513(9)
O5—C75	1.278(9)	C37—C39	1.380(12)
O6—C75	1.255(9)	C38—C40	1.369(14)
O7—C74	1.246(11)	C39—C41	1.391(12)
O8—C74	1.246(11)	C40—C41	1.392(11)
O9—C35	1.258(8)	C41—C42	1.459(10)
O10—C35	1.251(9)	C42—C43	1.392(10)
O11—C36	1.243(7)	C42—C44	1.403(11)
O12—C36	1.251(8)	C43—C45	1.349(10)
O13—C53	1.250(8)	C44—C46	1.362(10)
O14—C53	1.263(8)	C47—C48	1.379(9)
O15—C54	1.247(8)	C47—C49	1.388(9)
O16—C54	1.203(9)	C48—C50	1.395(9)
O17—C71	1.252(8)	C49—C51	1.381(9)
O18—C71	1.256(8)	C50—C52	1.402(8)
O19—C72	1.261(9)	C50—C53	1.482(9)
O20—C72	1.216(10)	C51—C52	1.391(9)
N1—C2	1.342(11)	C51—C54	1.521(9)
N1—C1	1.363(11)	C55—C57	1.407(11)
N2—C9	1.346(9)	C56—C58	1.405(11)
N2—C10	1.357(8)	C57—C59	1.383(11)
N2—C11	1.470(8)	C58—C59	1.366(11)
N3—C19	1.319(12)	C59—C60	1.467(10)
N3—C20	1.327(12)	C60—C61	1.377(11)
N4—C28	1.334(8)	C60—C62	1.380(11)
N4—C27	1.361(8)	C61—C63	1.349(10)
N4—C29	1.455(8)	C62—C64	1.372(10)
N5—C38	1.317(15)	C65—C67	1.369(9)
N5—C37	1.330(15)	C65—C66	1.369(9)
N6—C45	1.345(9)	C66—C68	1.404(9)
N6—C46	1.350(8)	C67—C69	1.381(9)
N6—C47	1.448(8)	C68—C70	1.380(9)
N7—C55	1.337(13)	C68—C71	1.498(9)
N7—C56	1.344(12)	C69—C70	1.390(9)
N8—C64	1.326(8)	C69—C72	1.507(9)
N8—C63	1.383(9)	O22—C73	1.268(19)
N8—C65	1.462(8)	O21—C73	1.220(13)
C1—C3	1.378(10)	O21B—C73B	1.272(17)
C2—C4	1.382(11)	O22B—C73B	1.234(19)

Symmetry transformations used to generate equivalent atoms: [1]1-X, 1-Y, 1-Z; [2]1-X, 1-Y, 2-Z; [3]1-X, 2-Y, 1-Z; [4]1-X, 2-Y, -Z.

3.Reference:

[1] C.H. Zhang, L.B. Sun, C.Q. Zhang, S. Wan, Z.Q. Liang and J.Y. Li. Novel photo- and/or thermochromic MOFs derived from bipyridinium carboxylate ligands. *Inorg. Chem. Front.,* 2016, **3**, 814–820

[2] O.V. Dolomanov, L.J. Bourhis, R.J. Gildea, J.A.K. Howard and H. Puschmann. OLEX2: a complete structure solution, refinement and analysis program. *J.Appl.Cryst*. 2009, **42**, 339–341.

[3] G.M, Sheldrick. SHELXT-Integrated space-group and crystal-structure determination. *Acta Cryst. A*, 2015, **71**, 3–8.

[4] A.L. Spek. Single-crystal structure validation with the program PLATON. *J. Appl. Cryst.*,2003, **36**, 7–13.