

Supplementary information

A NbO-type mixed lanthanide metal-organic framework for cryogenic temperature sensing

Yi Li,^a Xiaoman Zhang,^b Huizhen Wang,^c Lin Zhang,^{b*} Hongjun Li^{a*} and
Dian Zhao^{b*}

^a Department of Physics, Zhejiang Normal University, Jinhua 321004, China.

^b Key Laboratory of the Ministry of Education for Advanced Catalysis Materials, College of Chemistry and Materials Science, Zhejiang Normal University, Jinhua 321004, China.

^c State Key Laboratory of Silicon and Advanced Semiconductor Materials, School of Materials Science and Engineering, Zhejiang University, Hangzhou 310027, China.

Corresponding Author:

linzhang@zjnu.edu.cn (Lin Zhang); hongjunli@zjnu.edu.cn (Hongjun Li); dzhao@zjnu.edu.cn (Dian Zhao).

Experimental Section

1. Materials and characterization

The ligand H₄PDDI was synthesized according to the previous literature.¹ All other relevant chemicals and solvents were obtained from commercial sources and used without further purification. Powder X-ray diffraction (XRD) patterns were acquired on a Maxima_X XRD-7000 diffractometer with Cu K_α ($\lambda = 1.542 \text{ \AA}$) radiation and gathered within 2θ range of 3 to 50° with a rate of 5°/min under room temperature. Thermogravimetric analyses (TGA) were obtained in the temperature range of 303-1073 K by a Netzsch TG209F3 analyzer under nitrogen atmosphere with a heating rate of 5 K min⁻¹. Fourier transform infrared (FTIR) spectra was recorded on a Thermo Fisher Nicolet iS10 spectrophotometer with KBr pellet technique and collected at range from 4000 to 400 cm⁻¹. The pellets were manufactured by mixing and grinding KBr with the sample thoroughly. Then, the mixture was compressed under the pressure to obtain a transparent pellet. Eu_{0.26}Tb_{0.74}PDDI crystalline powders were dissolved in nitric acid aqueous solution and sonicated until clarification. The solution was tested by inductively coupled plasma optical emission spectra (ICP-OES), which was recorded on an Agilent ICP-OES720ES system to determine the molar ratios of Eu³⁺ and Tb³⁺ in this mixed lanthanide MOFs. N₂ adsorption data were collected by using a fully automated gas adsorption meter (Micromeritics ASAP 2020HD88) via a liquid N₂ bath and a circulating thermostatic water bath (Julabo F12) under 77 K. Before the test, MOF samples were solvent exchanged with ethanol and activated by vacuum drying at 373 K for 10 h. The temperature-dependent luminescence spectra and decay curves of the MOF samples were recorded by an Edinburgh Instrument F920 spectrometer with a He closed-cycle cryostat system with a Lakeshore 331 temperature controller, and the slits for the excitation and emission are fixed at 1 nm.

The molecular geometry optimization and frequency analysis of H₄PDDI were performed using density functional theory (DFT) at the B3LYP/6-31+G(d,p) level (Fig. S6)². Based on the optimized result, the energy of the lowest triplet excited state of the H₄PDDI were calculated to be 2.851 eV (22995 cm⁻¹) by the time-dependent DFT approach³. All calculations were performed using Gaussian 09 software⁴.

The single-crystal XRD data of TbPDDI were measured on a Bruker Smart Apex II diffractometer with Mo K_α ($\lambda = 0.71073 \text{ \AA}$) radiation. The crystal structure data of TbPDDI was collected by SHELX-2013 program package on the strength of the full-matrix least-squares on F^2 method. Crystallographic data of TbPDDI was listed in Table S1. The morphology and size of as-prepared crystals were observed by virtue of Olympus IX73 inverted microscope.

2. Synthesis of LnPDDI (Ln = Eu, Tb, Tb_{1-x}Eu_x)

Take TbPDDI as an example, H₄PDDI (20.0 mg, 0.0491 mmol) and Tb(NO₃)₃·6H₂O (133 mg, 0.294 mmol) were dissolved into a mixed solvent of N,N-dimethylformamide (DMF, 4 mL), methylbenzene (8 mL), deionized water (100 μ L) in a screw-capped glass vial (25 mL), and then nitric acid (3.5 M, 50 μ L) were added, sealed and placed in an oven at 358 K for 12 h. After cooling to room temperature naturally, transparent rhombus crystals were acquired, collected by filtration and washed with DMF several times. Yield: 71%. Additionally, the synthesis of EuPDDI and Tb_{1-x}Eu_xPDDI were similar to TbPDDI except for replacing the Tb(NO₃)₃·6H₂O with Eu(NO₃)₃·6H₂O and the mixture of Tb(NO₃)₃·6H₂O and Eu(NO₃)₃·6H₂O as the initial reactants,

respectively. The as-synthesized microcrystals were placed in an 353 K oven for 6 hours to ensure complete drying, and the dried samples were the used for further measurements.

3. Tables and figures

Table S1. Crystallographic Data collection and Refinement result for TbPDDI.

TbPDDI	
Chemical formula	$C_{222}H_{298}N_{43}O_{110}Tb_{12}$
Formula weight	7236.169
Temperature (K)	247.15
Wavelength (Å)	0.71073
Crystal system	Trigonal
Space group	$P3_221$
a (Å)	19.9247(18)
b (Å)	19.9247(18)
c (Å)	68.595(9)
α (°)	90
β (°)	90
γ (°)	120
V (Å ³)	23583(5)
Z	3
Density (calculated g/cm ⁻³)	1.529
Absorbance coefficient (mm ⁻¹)	2.747
$F(000)$	10782.0
R(int)	0.0522
Goodness of fit on F^2	1.029
R_1, wR_2 ($I > 2\sigma(I)$)	0.0544, 0.1424
R_1, wR_2 (all data)	0.0576, 0.1448
Largest difference peak and hole (e/Å ³)	1.68, -2.33
CCDC 2205669	

Table S2. The molar ratio of the starting Tb/Eu salt and that in the synthesized product calculated by ICP-OES analysis.

sample	The molar ratio of the starting Tb/Eu salt	The Tb/Eu ratio calculated by ICP analysis
NbO-Tb_{0.74}Eu_{0.26}	0.75:0.25	0.74:0.26

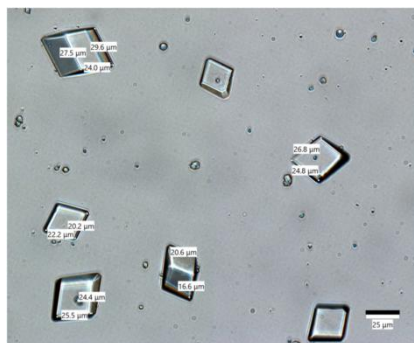


Fig. S1 The optical images of TbPDDI crystals.

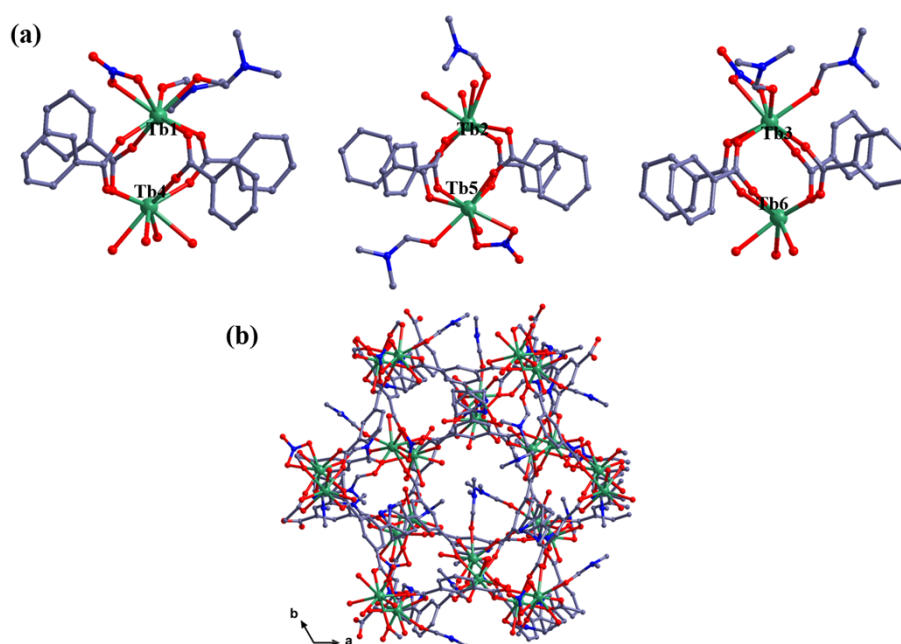


Fig. S2 (a) The three different $Tb_2(COO)_4$ SBUs with the Tb1-Tb4, Tb2-Tb5, and Tb3-Tb6 separations. (b) The structure of TbPDDI with the coordinated solvent molecules and ions in the pores.

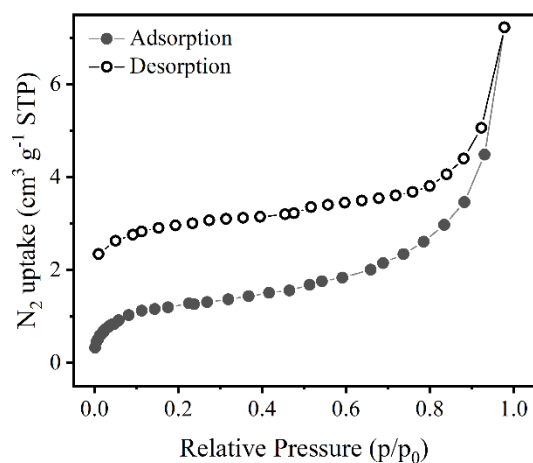


Fig. S3 The N_2 adsorption isotherm curve of pure TbPDDI.

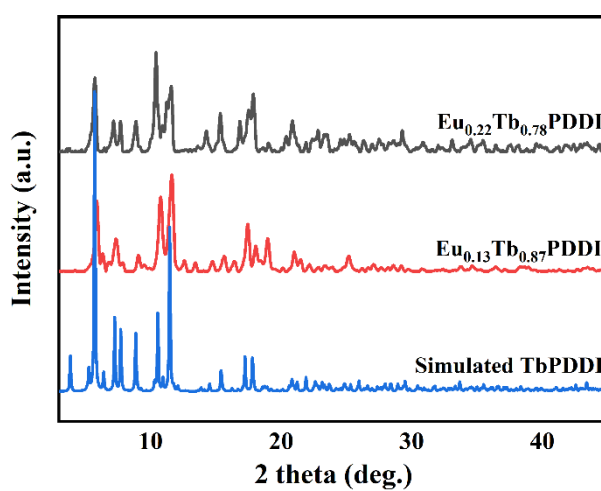


Fig. S4 The powder XRD patterns of $Eu_{0.13}Tb_{0.87}PDDI$ and $Eu_{0.22}Tb_{0.78}PDDI$ compared to simulated crystal data.

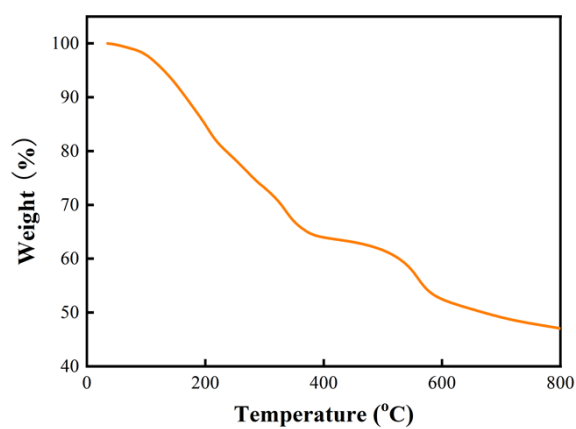


Fig. S5 The TGA curve of TbPDDI.

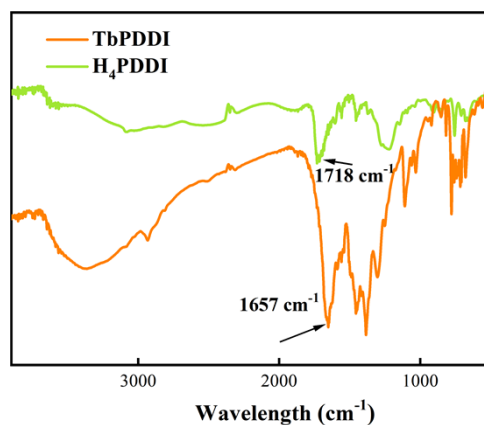


Fig. S6 The FTIR spectra of H₄PDDI and TbPDDI.

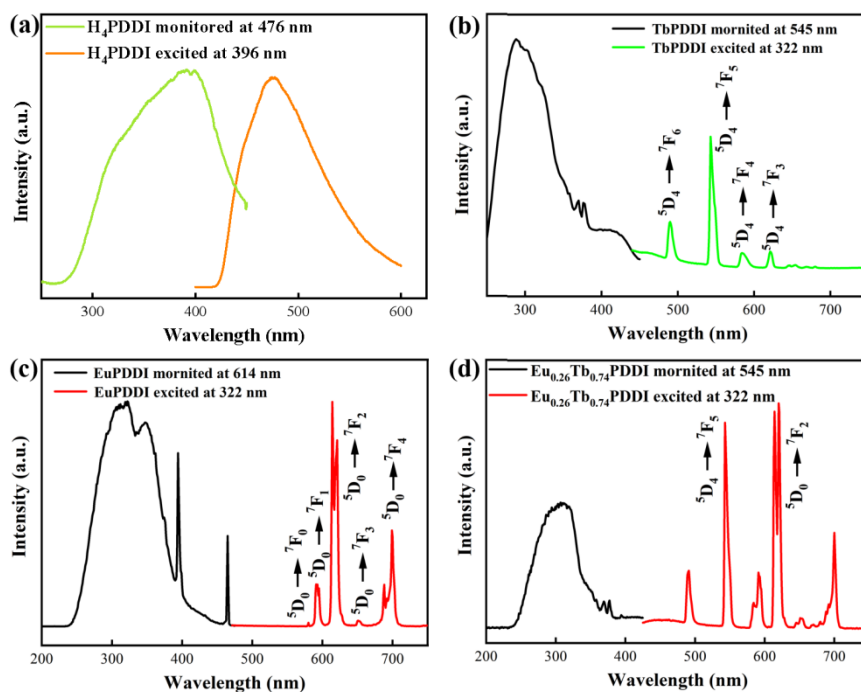


Fig. S7 The excitation and emission spectra of (a) H₄PDDI, (b) TbPDDI, (c) EuPDDI and (d) Eu_{0.26}Tb_{0.74}PDDI.

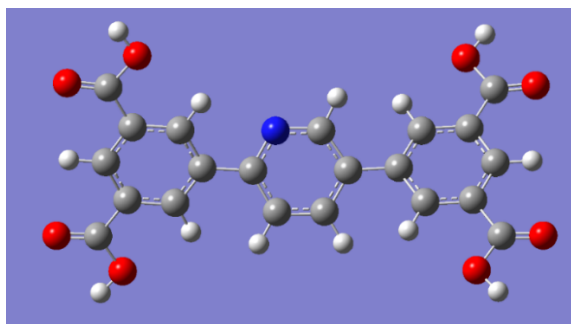


Fig. S8 The optimized geometry of free H₄PDDI ligand.

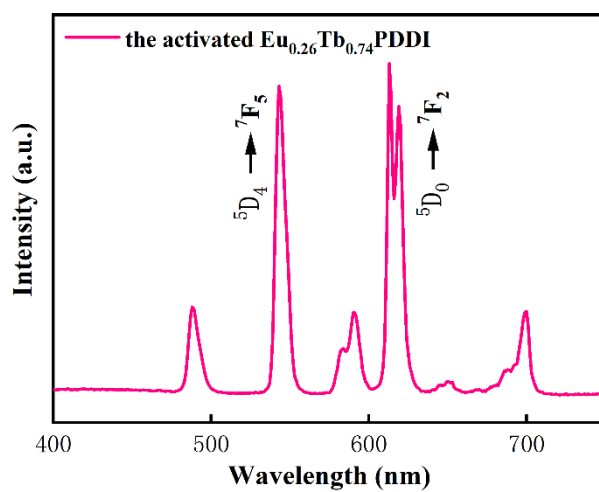


Fig. S9 The emission spectra of activated Eu_{0.26}Tb_{0.74}PDDI when excited at 322 nm.

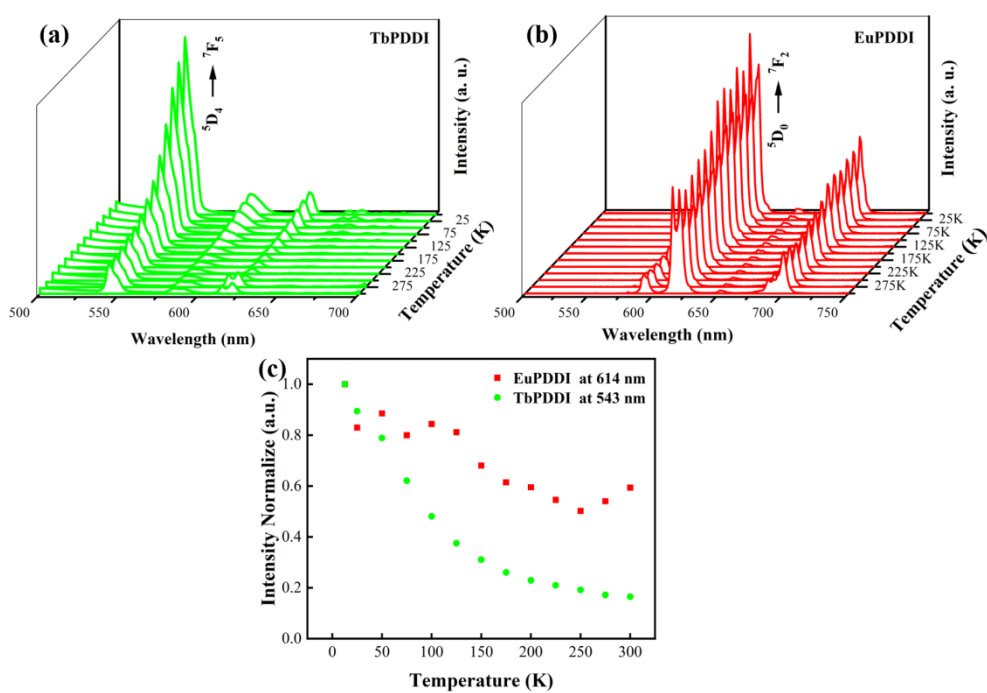


Fig. S10 Emission spectra of (a) TbPDDI and (b) EuPDDI and recorded in the temperature range of 12 and 300 K, excited at 322 nm. (c) The temperature-dependent intensity of Tb³⁺ (543 nm) and Eu³⁺ (614 nm).

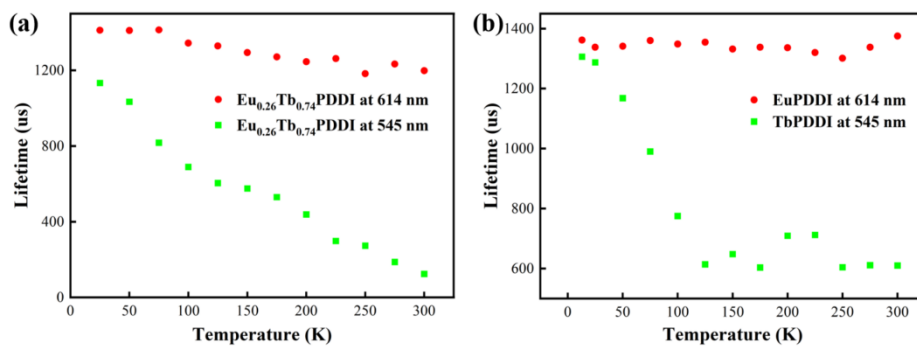


Fig. S11 The lifetime changes of Tb³⁺ (⁵D₄, 545 nm) and Eu³⁺ (⁵D₀, 614 nm) in (a) $\text{Eu}_{0.26}\text{Tb}_{0.74}\text{PDDI}$ and (b) two S' LnMOFs.

Reference

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