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Supporting Information

A luminescent ratiometric thermometer based on thermally coupled levels of Dy-MOF

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1. Experimental Section

Materials and Methods

All reagents were obtained from commercial sources and used without further purification. Powder X-ray diffraction (PXRD) data were collected in the 2θ = 5-50° range on a PANalytical X'Pert Pro Xray diffractometer using Cu-K_α (λ = 1.542 Å) beam at 293 K. Elemental analyses for C, H, and N were performed on a Thermo Finnigan Flash EA1112 microelemental analyzer. Thermogravimetric analyses (TGA) were carried out on a Netzsch TG209F3 with a heating rate of 5 ^oC min^{-1} under N_2 atmosphere.

Synthesis of Lncpia

$Dy(NO_3)_3$•$6H_2O$ (36 mg, 0.0789 mmol), 5-(4-carboxyphenoxy)isophthalic acid (H_3cpia, 12 mg, 0.0397 mmol) were ultrasonically dissolved in the mixed solvent of DMF (4 mL) and H_2O (1 mL). The mixture was sealed and heated in 80 ^oC oven for 36 hours. After cooling down to room temperature, colorless crystals of **Dycpia** were collected by filtration and washed with DMF three times. **Tbcpia** was synthesized similarly to **Dycpia** except for the use of $Tb(NO_3)_3$•$6H_2O$.

Single Crystal X-ray Crystallography

Single-crystal data were collected on Oxford Xcalibur Gemini Ultra diffractometer with an Atlas detector using graphite-monochromatic Mo K_α radiation (λ = 0.71073 Å) at room temperature. The determination of the unit cells and data collections were performed with CrysAlisPro. The data sets were corrected by empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm. The structure was solved by direct methods, and refined by full-matrix least-squares method with the SHELX-97 program package. All non-hydrogen atoms including solvent molecules were located successfully from Fourier maps and were refined anisotropically. The H atoms on the ligands were placed in idealized positions and refined using a riding model. CCDC 1526828 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Luminescence Sensing Study

All of the emission and excitation spectra for the samples were recorded in solid state. In order to remove DMF molecules in the framework, the MOF **Dycpia** was calcinated at 523 K for 2 hours prior to measurements, and thermogravimetric analyses (TGA) and elemental analyses (EA) were conducted to verify the residual DMF in calcinated **Dycpia**. The emission and excitation spectra of H_3cpia, **Dycpia**, and **Tbcpia** at room temperature were recorded by a Hitachi F4600 fluorescence spectrometer. The temperature-dependent emission spectra for the powders of **Dycpia** were recorded on an Edinburgh Instrument F920 spectrometer using Xe lamp as the light source. The phosphorescence spectrum of **Gdcpia** in 77 K was recorded on an Edinburgh

Instrument F920 spectrometer.

2 Characterization Results

Table S1 Crystallographic Data Collection and Refinement Result for **Dycpia.**

	Dycpia
CCDC number	1526828
Chemical formula	$C_{21}H_{21}N_2O_9Dy$
Formula weight	607.90
Temperature (K)	296(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	P $\bar{1}$
a (Å)	9.3615(3)
b (Å)	10.6240(3)
c (Å)	12.5081(3)
α (º)	79.653(2)
β (º)	89.326(2)
γ (º)	66.439(2)
V (Å^3)	1119.27(5)
Z	2
Density (calculated g·cm^{-3})	1.804
Absorbance coefficient (mm^{-1})	3.393
F(000)	598
R_{int}	0.0651
Crystal size (mm^3)	0.20×0.15×0.10
Goodness of fit on F^2	1.031
R_1, wR_2 [$I>2\sigma(I)$]^a	0.0368, 0.0779
R_1, wR_2 (all data)^a	0.0543, 0.0715

$^aR_1 = \Sigma(|F_o| - |F_c|) / \Sigma|F_o|$; $wR_2 = [\Sigma w(|F_o|-|F_c|^2) / \Sigma wF_o^2]^{1/2}$.

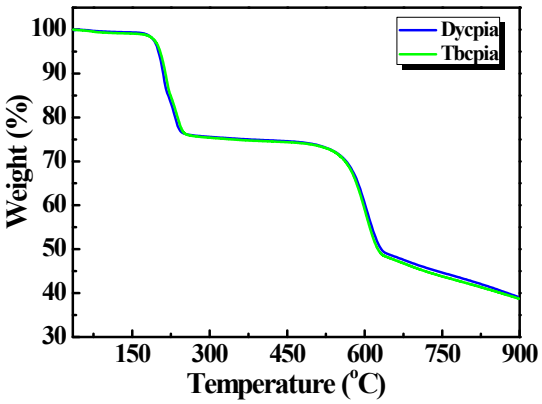

Fig. S1 TGA curves of **Dycpia** and **Tbcpia**.

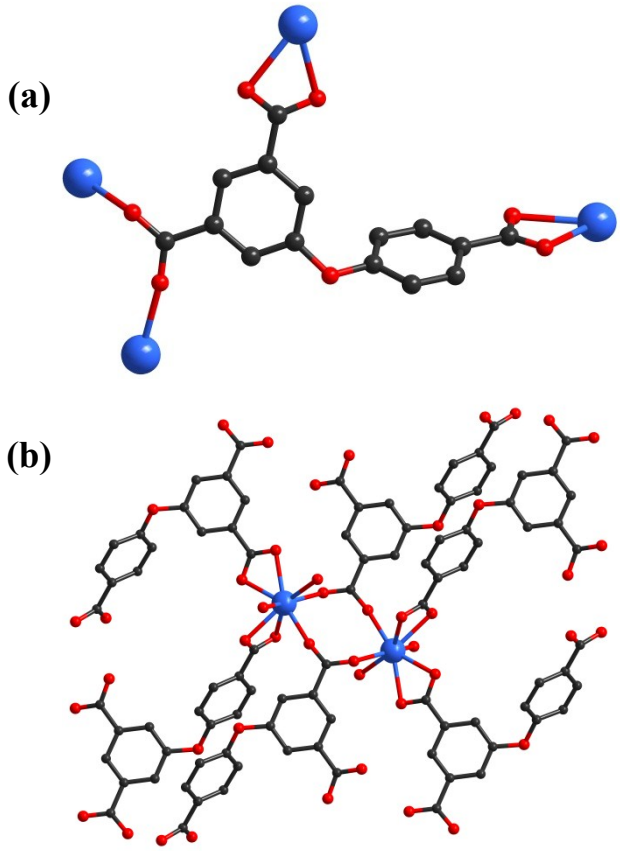

Fig. S2 Coordination environment of (a) $cpia^{3-}$ ligands and (b) Dy^{3+} ions.

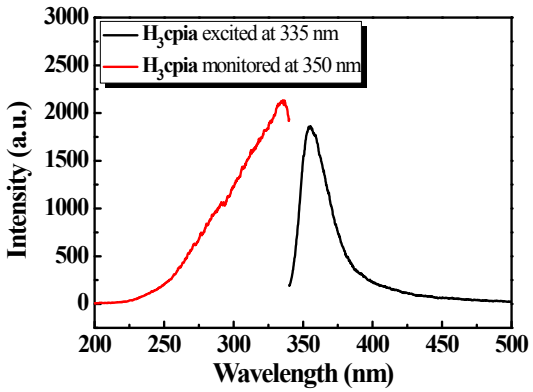

Fig. S3 Excitation (red) and emission (black) spectra of H_3cpia at room temperature.

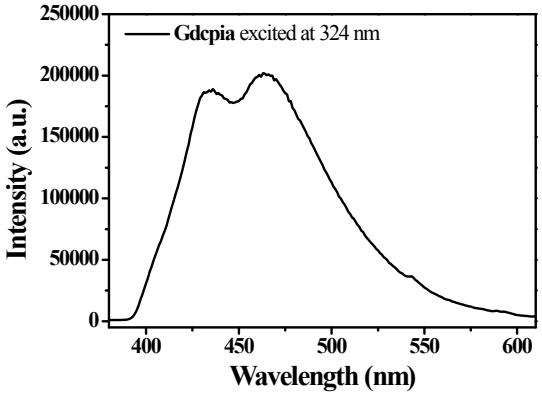

Fig. S4 Fluorescence spectrum of **Gdcpia** at 77 K.

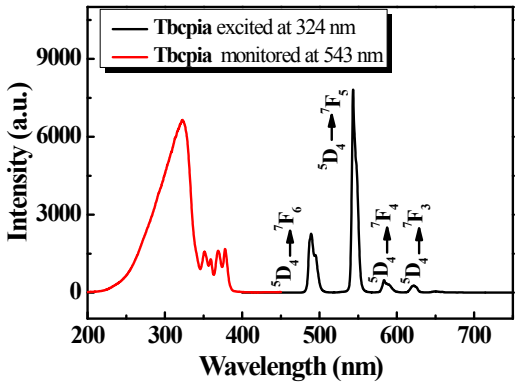

Fig. S5 Excitation (red) and emission (black) spectra of **Tbcpia** at room temperature.

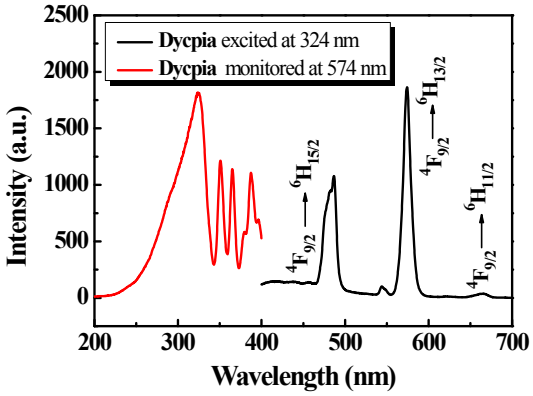

Fig. S6 Excitation (red) and emission (black) spectra of **Dycpia** at room temperature.

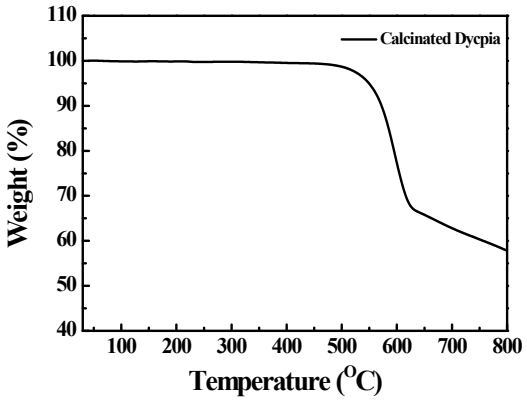

Fig. S7 TGA curves of calcinated **Dycpia** indicate that there is almost no residual

DMF in calcinated **Dycpia.** Elemental analysis found (%) C, 35.08%; H, 2.39%; N, 0.22%.

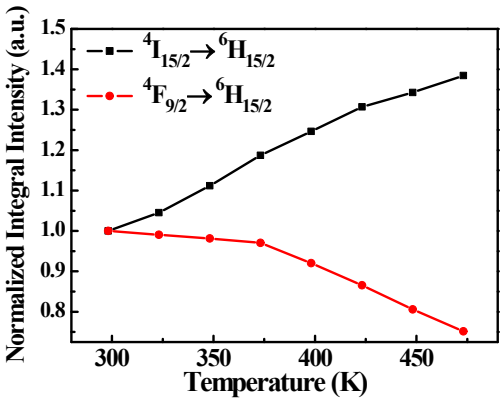

Fig. S8 The temperature-dependent normalized integral intensity of $^4I_{15/2} \rightarrow {}^6H_{15/2}$ and $^4F_{9/2} \rightarrow {}^6H_{15/2}$ transition for calcinated **Dycpia**.

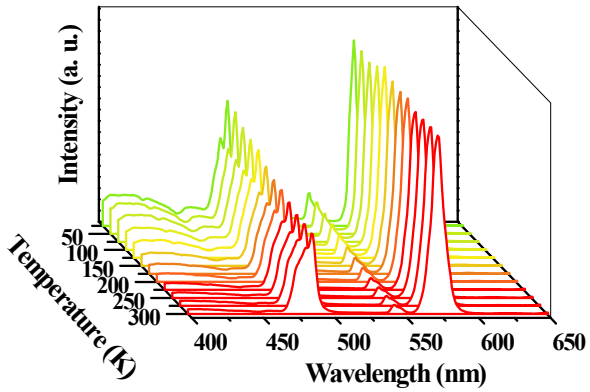

Fig. S9 Temperature-dependent spectra of **Dycpia** in 25-300 K excited at 324 nm.

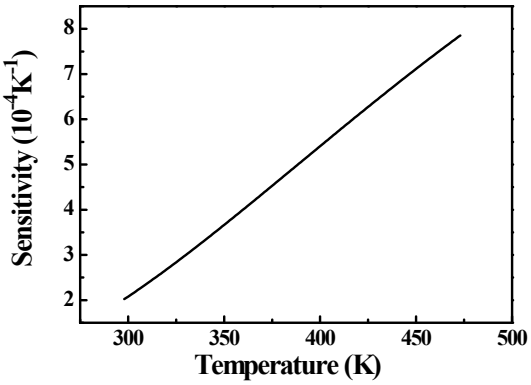

Fig. S10 Sensor sensitivity based on $^4I_{15/2} \rightarrow {}^6H_{15/2}$ and $^4F_{9/2} \rightarrow {}^6H_{15/2}$ transitions of Dy^{3+} as a function of the temperature in the range from 298 K to 473 K.