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Supplementary Information for

Emergence of a bismuth-based metal–organic framework as an X-ray scintillator

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Experimental Procedures

Materials and synthesis

Materials. $Bi(NO_3)_3 \cdot 5H_2O$ (99.9%, Shanghai Aladdin Biochemical Technology Co., Ltd.), 1,1,2,2-tetra(4-carboxylphenyl)ethylene (H_4TCPE) (95%, Shanghai Adamas Reagent Co., Ltd.), HNO_3 (GR, 96%, Sinopharm Chemical Reagent Co., Ltd.), and dimethylformamide (99.5%, Shanghai Macklin Biochemical Co., Ltd) were used as received from commercial suppliers without further purification.

Synthesis. Bi-TCPE. A mixture of $Bi(NO_3)_3 \cdot 5H_2O$ (0.001 mmol), H_4TCPE (0.001 mmol), HNO_3 (45 μL), and DMF (1000 μL) was loaded into a 7 mL glass vial. The vial was sealed and heated at 100 °C for 48 h, then cooled to room temperature under ambient conditions. Yellow, tablet-shaped single crystals of **Bi-TCPE** were obtained, washed with ethanol, and dried under ambient conditions.

Characterizations

Single-crystal X-ray diffraction (SCXRD) analysis was performed on a Bruker D8-Venture single-crystal X-ray diffractometer equipped with an IμS 3.0 microfocus X-ray source (Mo Kα radiation, λ = 0.71073 Å) and a CMOS detector at 298 K. Data collection and reduction were carried out using the APEX3 program. The crystal structure was solved by intrinsic phasing using ShelXT and refined by full-matrix least-squares techniques with ShelXL, as interpreted by the Olex2 software.

Powder X-ray diffraction (PXRD) patterns were collected on a Bruker D8 Advance diffractometer (40 kV, 40 mA) with Cu Kα radiation (λ = 1.54060 Å) at a step size of 0.02°. The simulated PXRD pattern of **Bi-TCPE** was generated from its crystallographic information file (CIF) using Materials Studio.

Photoluminescence (PL) spectra, time-resolved PL lifetimes, and photoluminescence quantum yields (PLQYs) were measured at room temperature using an Edinburgh FLS980 fluorescence spectrometer.

X-ray-induced radioluminescence (RL) spectra were obtained under a tungsten (W) Kα radiation source (70 kV, 12 W), and the emission was recorded using a NOVA cooled fiber optic spectrometer.

Thermogravimetric analysis (TGA) was conducted using a Waters SDT650 simultaneous thermal analyzer under a dry nitrogen atmosphere from 30 to 800 °C at a heating rate of 10 °C/min.

Fourier-transform infrared (FTIR) spectra were recorded on a Nicolet iS50 FTIR spectrometer in the range of 640–4000 cm^{-1}.

Fabrication of flexible Bi-TCPE⊂PDMS scintillator film

A 10:1 weight ratio of polydimethylsiloxane (PDMS) base to curing agent (SYLGARD 184) was thoroughly mixed. Subsequently, **Bi-TCPE** powder (20 wt%) was incorporated and uniformly dispersed through vigorous stirring. The homogenous mixture was then cast onto a flat glass surface, leveled using a blade, and thermally cured at 100 °C for 1 h to produce the **Bi-TCPE**⊂PDMS scintillator film.

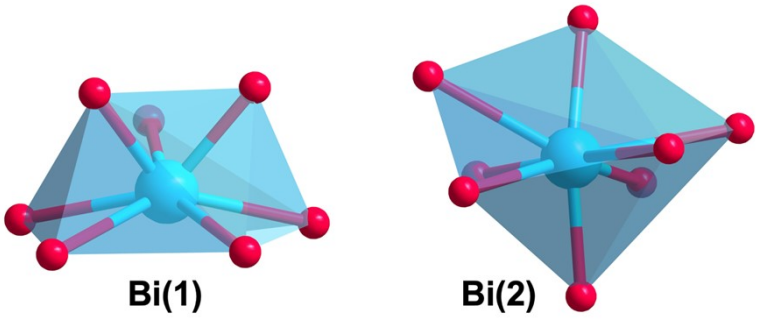

Fig. S1 Coordination environments of Bi(1) and Bi(2) in **Bi-TCPE**.

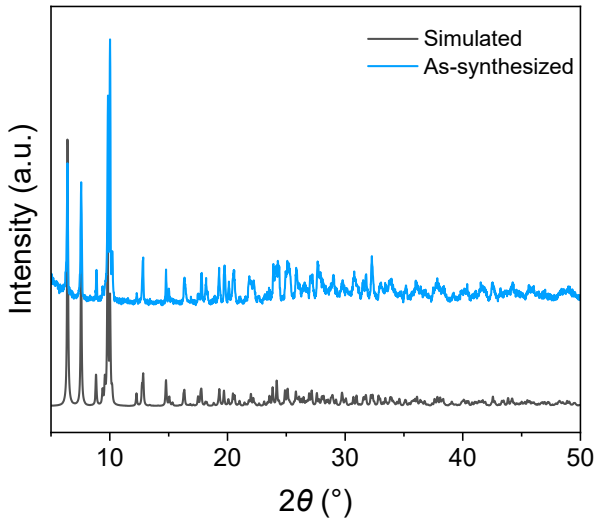

Fig. S2 Simulated and as-synthesized PXRD patterns of **Bi-TCPE**.

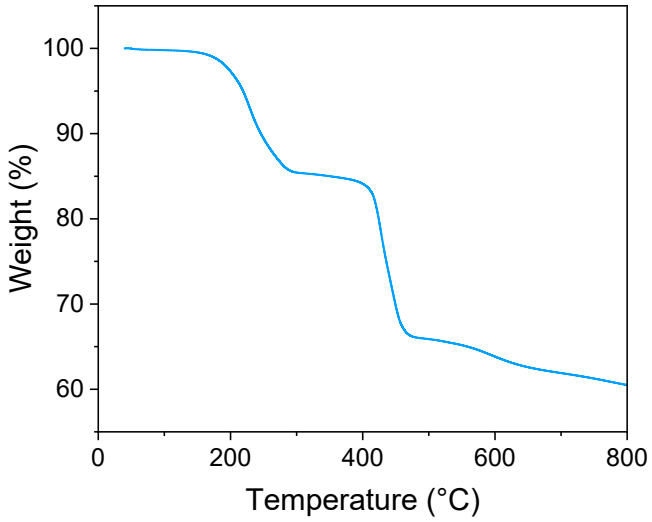

Fig. S3 Thermogravimetric analysis (TGA) curve of **Bi-TCPE**.

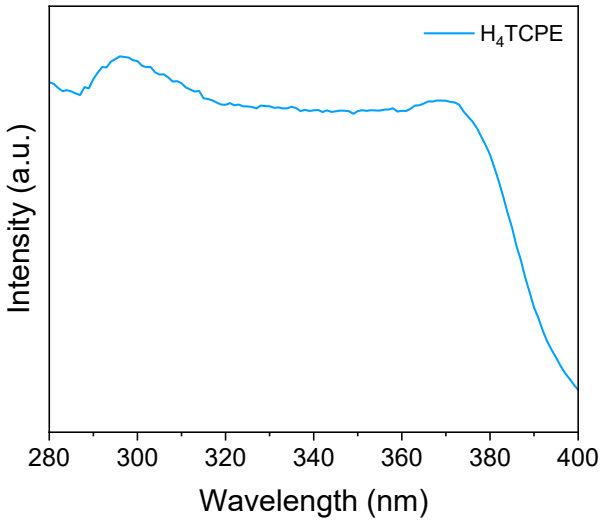

Fig. S4 Excitation spectrum of H_4TCPE.

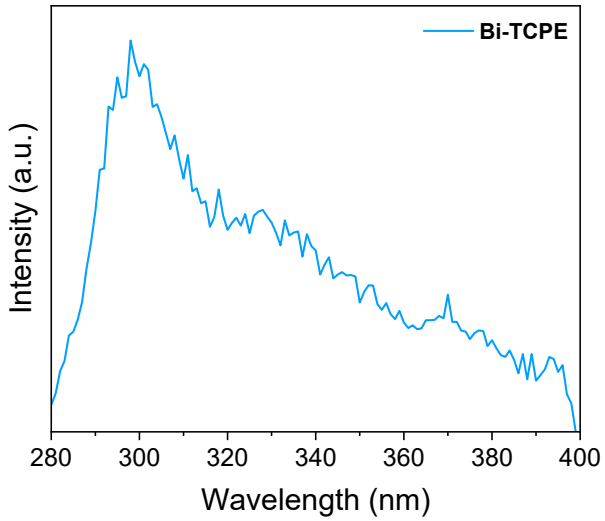

Fig. S5 Excitation spectrum of **Bi-TCPE**.

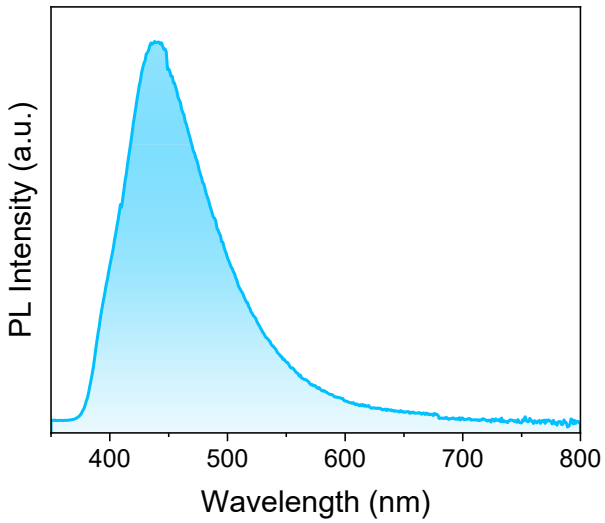

Fig. S6 Photoluminescence spectrum of H_4TCPE.

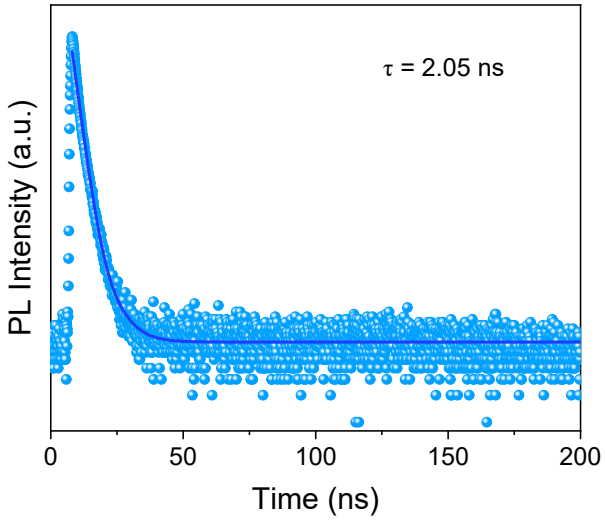

Fig. S7 Time-resolved photoluminescence decay profile of **Bi-TCPE**.

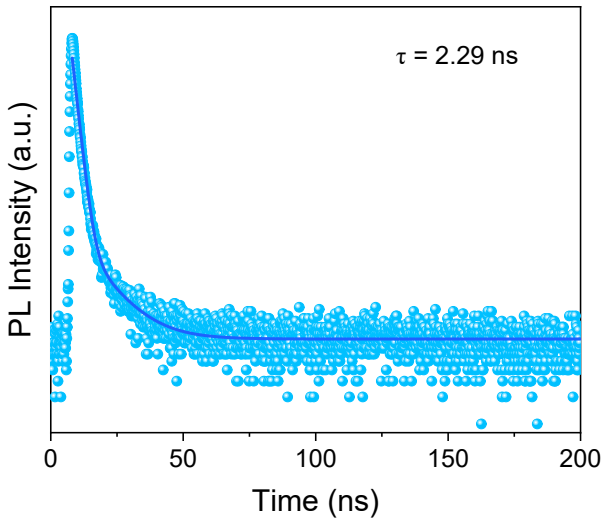

Fig. S8 Time-resolved photoluminescence decay profile of H_4TCPE.

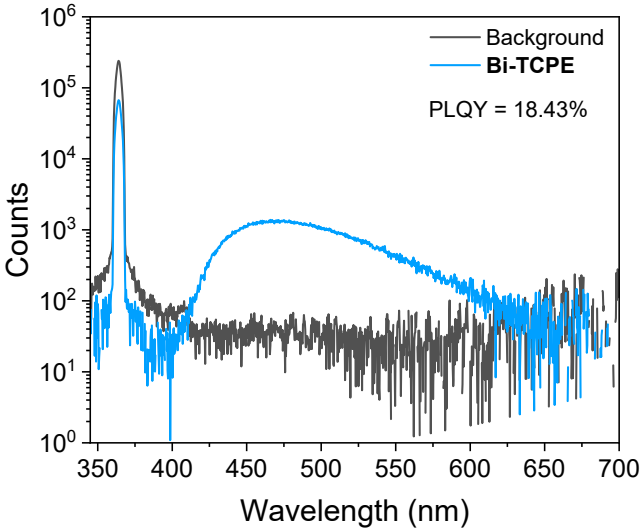

Fig. S9 Photoluminescence quantum yield of **Bi-TCPE**.

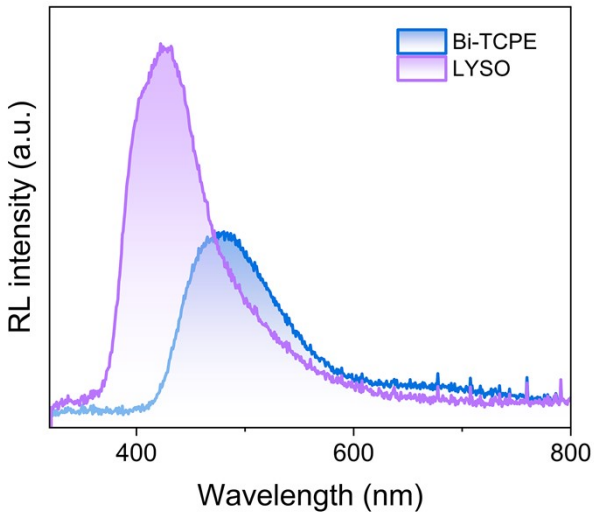

Fig. S10 Radioluminescence spectra of **Bi-TCPE** and LYSO under comparable irradiation condition.

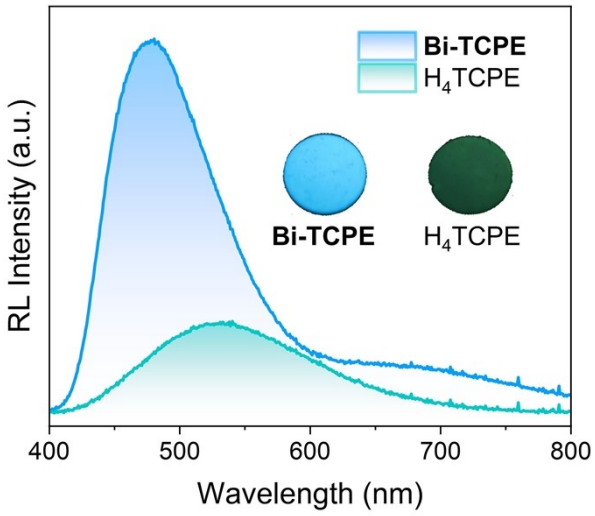

Fig. S11 Radioluminescence spectra and photographs of **Bi-TCPE** and H_4TCPE under comparable irradiation condition.

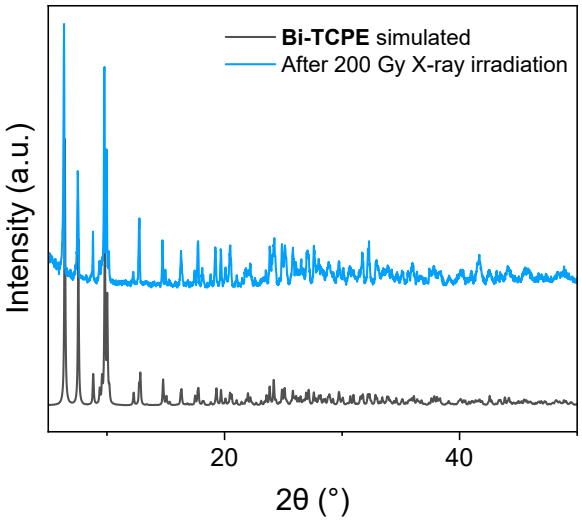

Fig. S12 PXRD patterns of **Bi-TCPE** before and after X-ray irradiation.

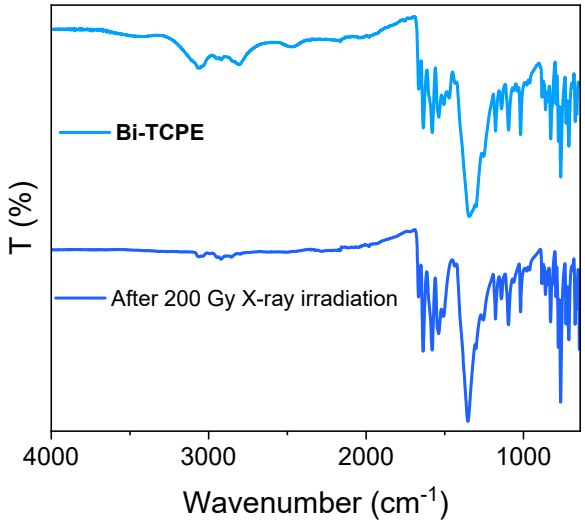

Fig. S13 FTIR spectra of **Bi-TCPE** before and after X-ray irradiation.

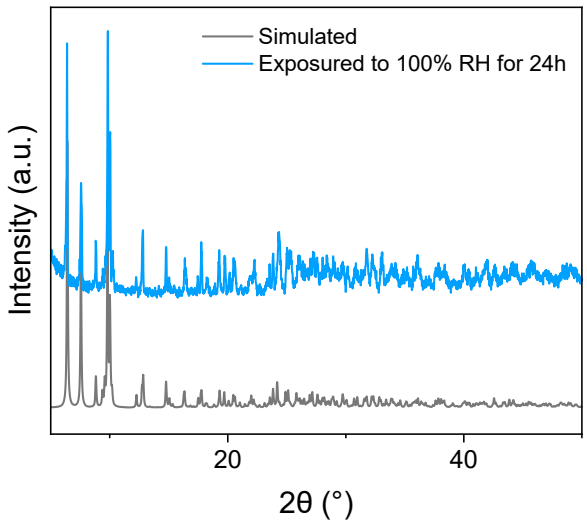

Fig. S14 PXRD patterns of **Bi-TCPE** before and after exposure to 100% relative humidity (RH).

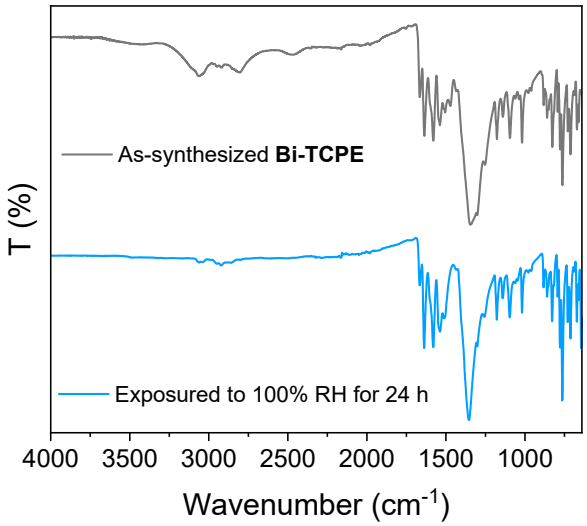

Fig. S15 FTIR spectra of **Bi-TCPE** before and after exposure to 100% relative humidity (RH).

Table S1 Crystallographic data for **Bi-TCPE**.

Compound	**Bi-TCPE**
CCDC	2443648
Formula	$C_{33}H_{23}O_{10}Bi_2$
Formula weight	1011.48
$\rho_{calc.}$ (g cm^{-3})	1.891
μ (mm^{-1})	7.424
Colour	Yellow
Habit	block
Space group	*P*-1
a (Å)	11.032(4)
b (Å)	12.390(4)
c (Å)	14.370(4)
α (deg)	85.718(10)
β (deg)	73.575(10)
γ (deg)	70.606(12)
V (Å^3)	1776.7(10)
Z	2
T (K)	293.00
λ (Å)	0.711
Θ_{max} (deg)	25.027
R_1	0.0418
ωR_2	0.1080
R_{int}	0.0698
GooF	1.013

Table S2 Selected bond distances and bond valence sums of Bi(1) and Bi(2) in **Bi-TCPE**.

	Bond Distance (Å)		Bond Distance (Å)
Bi(1)-O(1)	2.167	Bi2–O1	2.146
Bi(1)-O(1)#1	2.209	Bi2–O8	2.268
Bi(1)-O(3)	2.260	Bi2–O6	2.332
Bi(1)-O(7)	2.540	Bi2–O4	2.472
Bi(1)-O(2)	2.542	Bi2–O9	2.492
Bi(1)-O(10)	2.609	Bi2–O10	2.798
Bi(1)-O(6)	2.762	Bi2–O5	2.886
		Bi2–O5	2.887
Bi(1) BVS	3.167	Bi(2) BVS	3.071