# **Supplementary Information**

# Color-Tunable X-ray Scintillation Based on a Series of Isotypic

## Lanthanide-Organic Frameworks

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#### **S1. EXPERIMENTAL SECTION**

**Materials**:  $Ln(NO_3)_3 \cdot 6H_2O$  (Ln = Eu, Tb) (99.99%, Budweiser), oxalic acid (99%, Vetec), 1, 10-phenanthroline (98%, Tci), DMF (Analytical reagent, Sinopharm), and ethanol (Analytical reagent, Sinopharm) were used as received.

Synthesis: 0.1 mmol Ln(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (44.6 mg for Eu(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O, 45.3 mg for Tb(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O), oxalic acid (ox) (9.0 mg, 0.1 mmol) and 1, 10-phenanthroline (19.8 mg, 0.1 mmol) were dissolved in a mixture of 2 mL DMF and 3 mL H<sub>2</sub>O. The mixture was sealed in a 20 mL glass vial and heated at 100 °C for 7 d. The reaction system was then cooled gradually to ambient temperature. After filtration and subsequent washing three times with ethanol. colorless block-shaped crystals (1 for  $Eu(ox)(COO)(phen)(H_2O)$  and 2 for  $Eu(ox)(COO)(phen)(H_2O))$  suitable for characterization measurements were collected. Yields of 1 and 2 are 56% and 58%, respectively, based on Ln.

When the pure Eu(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O or Tb(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O were replaced by the mixture of Eu(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O and Tb(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (ratio from 0.1% : 99.9% to 10% : 90%) with other conditions unchanged, we obtained the doped crystals Dc-1 to Dc-12, in which the doping ratio of Eu<sup>3+</sup> and Tb<sup>3+</sup> are 10% : 90%, 8% : 92%, 5% : 95%, 3% : 97%, 2% : 98%, 1% : 99%, 0.9% : 99.1%, 0.8% : 99.2%, 0.5% : 99.5%, 0.3% : 99.7%, 0.2% : 99.8%, 0.1% : 99.9%, respectively.

#### **S1.1 Characterizations and Methods**

**S1.1.1 X-ray Crystallography Studies**. Single crystal X-ray diffraction (SCXRD) was performed using a Bruker D8-Venture single crystal X-ray diffractometer equipped with a digital camera. The collection of diffraction data was accomplished in a Turbo X-ray Source (Mo K $\alpha$  radiation,  $\lambda = 0.71073$  Å) equipped with the direct-drive rotating anode technique and a CMOS detector under a temperature of 168 K. Data frames were collected using the program APEX3, while processed using the SAINT routine. Integration of data as well as multi-scan absorption corrections were applied using the program embedded within AEPX3. The structures were analyzed through a direct method and refined on  $F^2$  by full-matrix least-squares methods using SHELXTL-2014.<sup>[1]</sup> Furthermore, symmetry of space group was checked by PLATON to ensure if the possible high symmetry was exist.<sup>[2]</sup> Selected crystallographic information are listed in Table S1, while the crystal structure information are provided in Figure S1. Atomic coordinates and additional structure information are provided in the CIF (CCDC No. 1850378).

**S1.1.2 UV-Vis spectra analysis.** The UV-vis spectra were measured using a Craic Technologies microspectrophotometer. Crystals were placed on quartz slide, and data was collected after auto-set optimization. The emission spectra of **1**, **2**, doped crystals and phen were all collected. Moreover, we obtained the adsorption spectra of **1**, **2** and phen.

S1.1.3 X-ray emission luminescence (XEL) analysis. X-ray emission luminescence (XEL) were also performed on a Bruker D8 X-ray diffractometer with Cu K $\alpha$  radiation

 $(\lambda = 1.54056 \text{ Å})$  equipped with a Lynxeye one-dimensional detector. The controlled dose for these samples used was 13, 29, 53 Gy, respectively. Subsequently, the XEL spectra of samples were recorded.

**S1.1.4 Powder X-ray diffraction (PXRD) Studies.** PXRD were performed on a Bruker D8 X-ray diffractometer with Cu K $\alpha$  radiation ( $\lambda = 1.54056$  Å) equipped with a Lynxeye one-dimensional detector.

**S1.1.5 Hygroscopy hardness experiments.** Hygroscopy hardness was also tested for these samples (**Figure S8**). The control samples were placed in a relative humidity (RH)-controlled chamber. The XEL spectra of **1**, **2** and CsI:Tl were recorded after the samples were exposed under different RH (40%, 60%, 95%) for 2 hours. Both of materials were in the range from 140 to 325 mesh, 24~27 mg, and 0.4 cm<sup>2</sup>.

**S1.1.6 Radiation hardness experiments.** Radiation hardness was probed using a RS-2000 Pro Biological Irradiator equipped with a Cu K $\alpha$  radiation source at a dose rate of 72 Gy / hour.

**S1.1.7 X-Ray Attenuation length spectrum.** The attenuation length is defined as the depth into the material where the intensity of the X-rays has decreased to about 37% (1/e) of the value at the surface. The calculation formula is  $x = 1/(\mu\rho)$ , where  $\mu$  (mass absorption coefficient) is related to material's photoabsorption and inelastic scattering cross sections, and  $\rho$  is the density for the material. The data in this work is extracted from reference 3. Grazing angle is fixed at 90 degree, and the photon energy range is from 30 eV to 30 KeV. An available calculation is free from the center for X-ray optics at http://henke.lbl.gov/optical\_constants/atten2.html.

**S1.1.8 Thermogravimetric analysis.** Thermalgravimetric analysis was carried out on a NETZSCH STA 449F3 instrument in the range of 30 - 900 °C under a nitrogen flow at a heating rate of 10 °C / min.

# **S2. FIGURES AND TABLES**



Figure S1. a) The coordination environment of  $Eu^{3+}$  and  $Tb^{3+}$  centers. b) The onedimensional chain structure. c) The Z-shaped building unit in **1** and **2**. d) The pseudo-2D framework viewed along the *a*-axis. Color code: Eu and Tb in orange, O in cyan, C in light gray, and N in mauve. All hydrogen atoms have been omitted for clarity.



Figure S2. Emission spectra of 1 under UV and X-ray excitation.



Figure S3. Emission spectra of 2 under UV and X-ray excitation.



Figure S4. Experimental setup for X-ray excited luminescence (XEL). All XEL data were recorded through a spectrometer embedded within a laboratory X-ray source (Bruker D8 advance with Cu K $\alpha$  radiation).



Figure S5. (a and b) The luminescence spectra of doped crystals. Dc-1, Dc-2, Dc-3, Dc-4, Dc-5, Dc-6, Dc-7, Dc-8, Dc-9, Dc-10, Dc-11, Dc-12 represent the doped ratio of Eu<sup>3+</sup> and Tb<sup>3+</sup> were 10% : 90%, 8% : 92%, 5% : 95%, 3% : 97%, 2% : 98%, 1% : 99%, 0.9% : 99.1%, 0.8% : 99.2%, 0.5% : 99.5%, 0.3% : 99.7%, 0.2% : 99.8%, 0.1% : 99.9%, respectively. (c) Linear CIE chromaticity diagram of UV luminescence for Dc-1 to Dc-12. (d) Corresponding photographs of luminescence excited by UV irradiation.



Figure S6. The UV-Vis absorption spectra for 1 at 298 K.



Figure S7. The UV-Vis absorption spectra for **2** at 298 K.



Figure S8. The UV-Vis adsorption spectra for phen at 298 K.



Figure S9. Emission spectra for phen under UV excitation.



Figure S10. PXRD patterns of 1 and 2.



Figure S11. Simulated and experimental PXRD patterns for compound Dc-1 to Dc-12, confirming the phase purity.



Figure S12. Hygroscopy hardness measurements of 1.



Figure S13. Hygroscopy hardness measurements of 2.



Figure S14. Hygroscopy hardness measurements of CsI:Tl.



Figure S15. Radiation hardness measurements of CsI:Tl.



Figure S16. X-ray attenuation length spectrum of **1** and **2**.



Figure S17. TG curves for 1 and 2.



Figure S18. The PXRD of 1 and 2 after a 53 Gy X-ray irradiation.

	2
Formula	Tb(ox)(COO)(phen)(H <sub>2</sub> O)
Formula weight (mol g <sup>-1</sup> )	490.19
Crystal system	Monoclinic
<i>a</i> (Å)	11.0348(19)
<i>b</i> (Å)	9.2759(17)
<i>c</i> (Å)	14.386(3)
α (°)	90
β (°)	97.876(5)
γ (°)	90
$V(Å^3)$	1458.6(5)
Ζ	4
$D_{\rm c} ({\rm g}{\rm cm}^{-3})$	2.232
$\mu$ (mm <sup>-1</sup> )	4.894
F (000)	944
T (K)	168(2)
GOF on $F^2$	1.033
R1, <sup>a</sup> wR2 <sup>b</sup> ( $I > 2\sigma(I)$ )	0.0206, 0.0512
R1, <sup>a</sup> wR2 <sup>b</sup> (all data)	0.0272, 0.0537
${}^{a}R_{I} = \Sigma   F_{o}  -  F_{c}   / \Sigma  F_{o} . {}^{b}wR_{2} = [\Sigma w (F_{o}^{2} - F_{c}^{2})^{2} / \Sigma w (F_{o}^{2})^{2}]^{1/2}$	

Table S1. Crystallographic data for 2.

## **S3. REFERENCE**

- [1] G. Sheldrick, P. SHELXTL, Madison, WI 1990.
- [2] A. L. Spek, *Acta Crystallographica Section D: Biological Crystallography*, 2009, 65, 148-155.
- [3] B. L. Henke, E. M. Gullikson, J. C. Davis, *Atomic Date Nucl. Date.*, 1993, 54, 181-342.