

## Supplementary information

### Large-area, High-resolution, Flexible X-Ray Scintillator Film Based on a Novel 0D Hybrid Cuprous Halide

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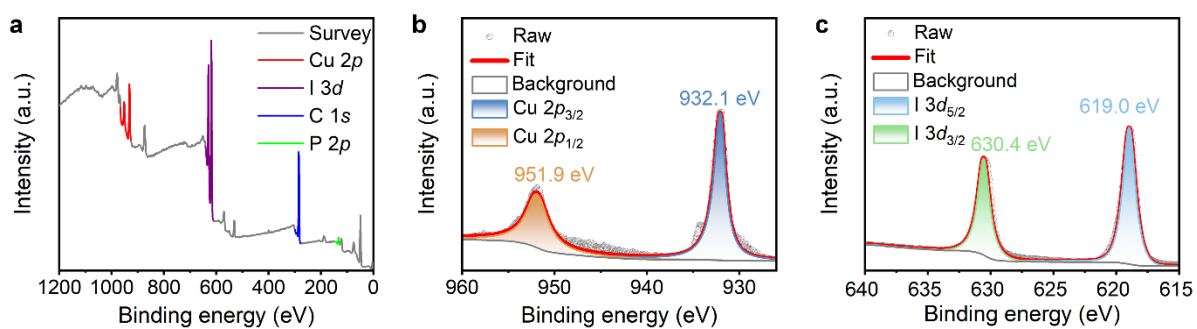
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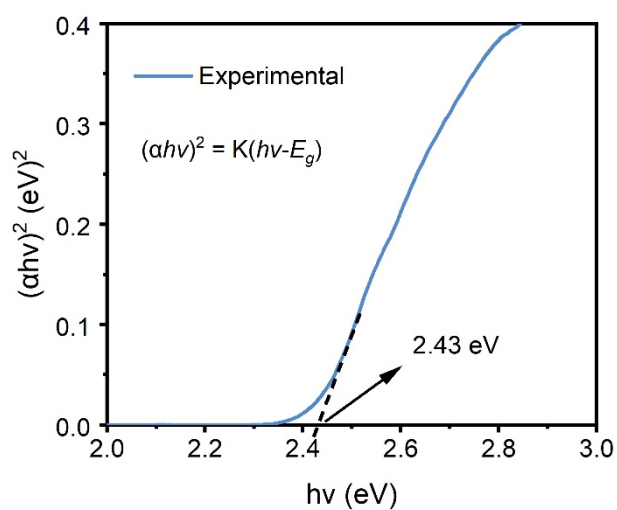
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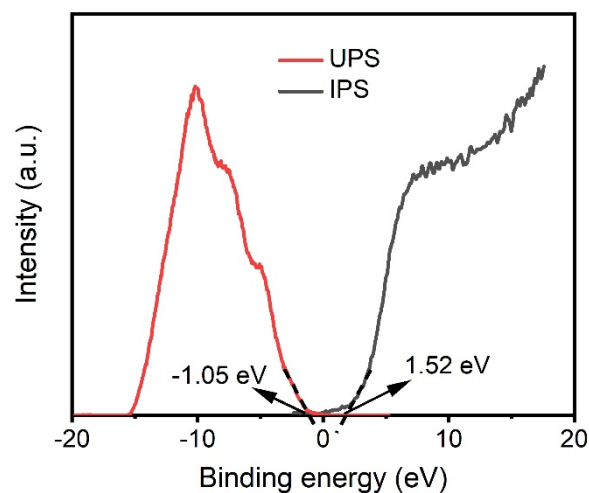
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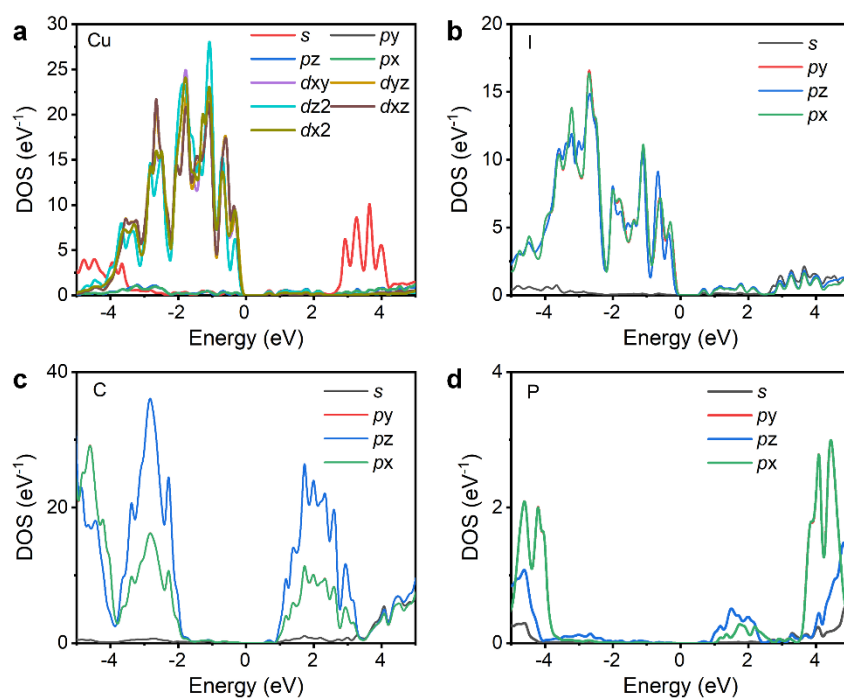
**Fig. S1** X-ray photoelectron spectroscopy (XPS) spectra of  $(\text{MTP})_2\text{Cu}_4\text{I}_6$ . **a**  $(\text{MTP})_2\text{Cu}_4\text{I}_6$  survey, **b** Cu 2p, and **c** I 3d.



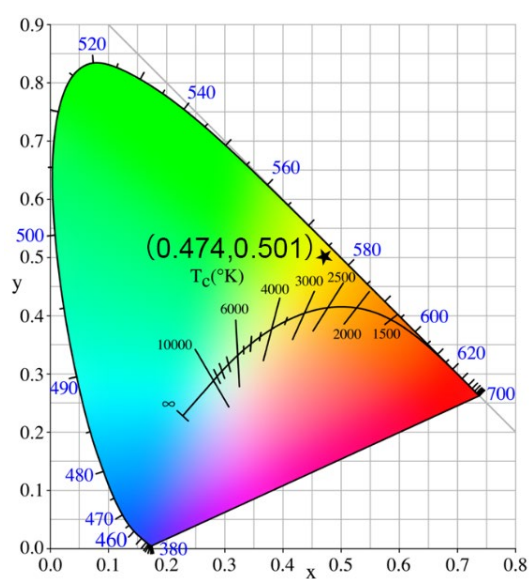
**Fig. S2**  $(\text{MTP})_2\text{Cu}_4\text{I}_6$  bandgap derived from the Tauc plot.



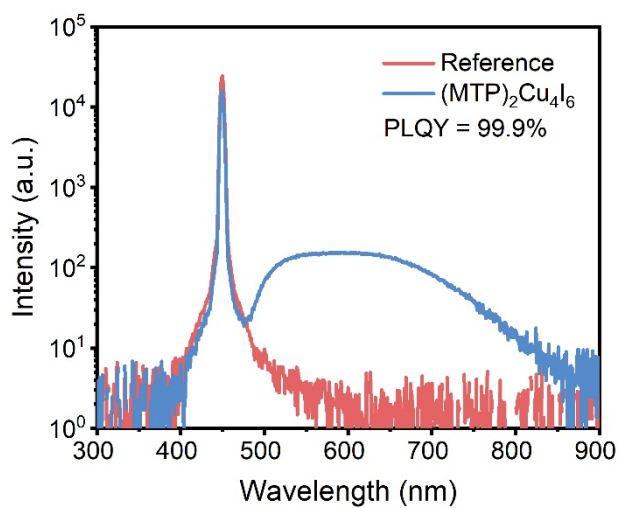
**Fig. S3** Ultraviolet photoelectron spectroscopy and inverse photoelectron spectroscopy spectra of the  $(\text{MTP})_2\text{Cu}_4\text{I}_6$ .



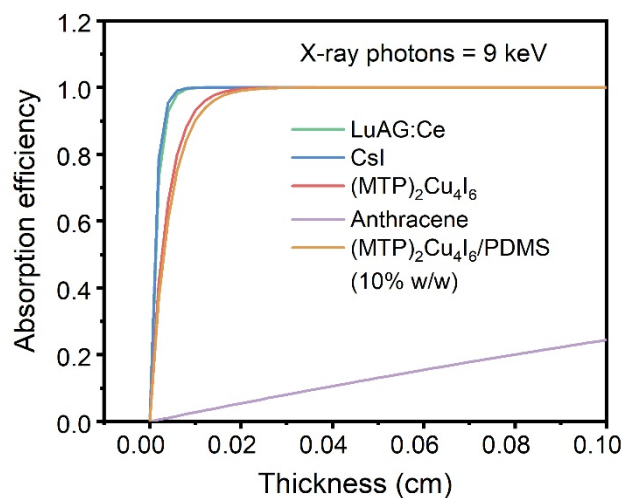
**Fig. S4** Density of states of **a** Cu, **b** I, **c** C, and **d** P elements with energies from -5 to 5 eV.



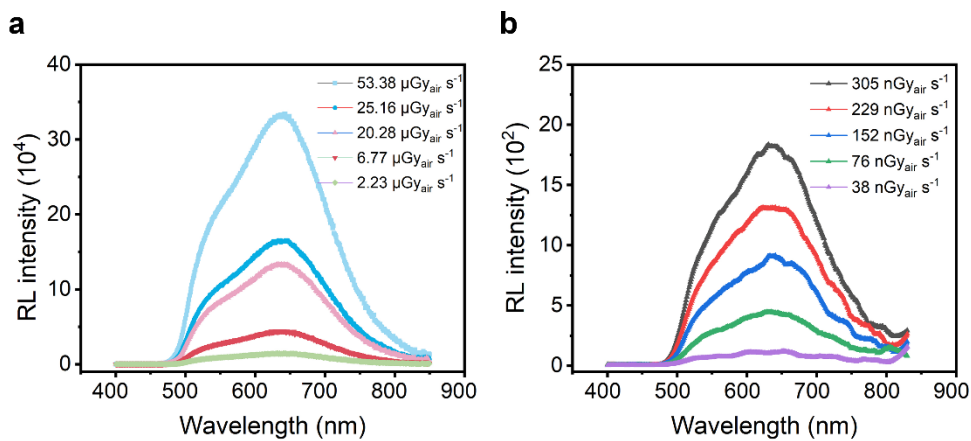
**Fig. S5** Commission Internationale de l'Eclairage (CIE) chromaticity coordinates (black star) of emissions measured for  $(\text{MTP})_2\text{Cu}_4\text{I}_6$  samples in the CIE1931.



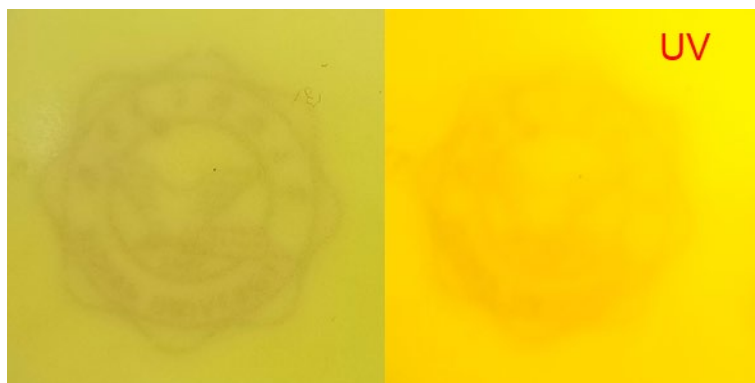
**Fig. S6** Photoluminescence quantum yield (PLQY) curve of  $(\text{MTP})_2\text{Cu}_4\text{I}_6$  crystals. The reference curve is measured by placing a blank quartz plate in the integrating sphere.



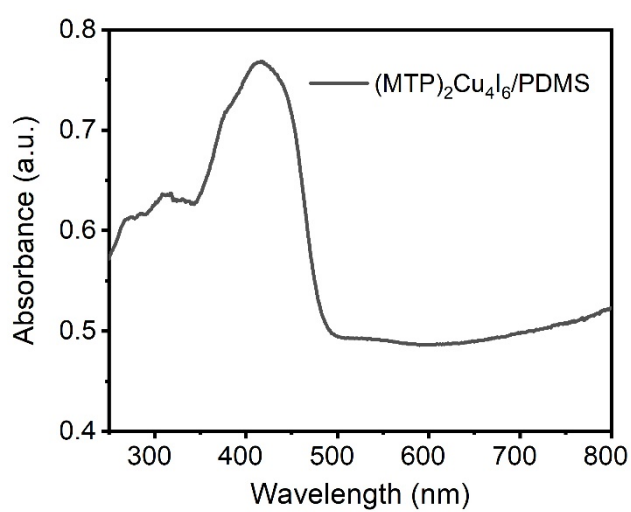
**Fig. S7** Absorption efficiency of  $(\text{MTP})_2\text{Cu}_4\text{I}_6$ ,  $(\text{MTP})_2\text{Cu}_4\text{I}_6/\text{PDMS}$  (10% w/w), CsI, LuAG:Ce, and anthracene as a function of thickness.



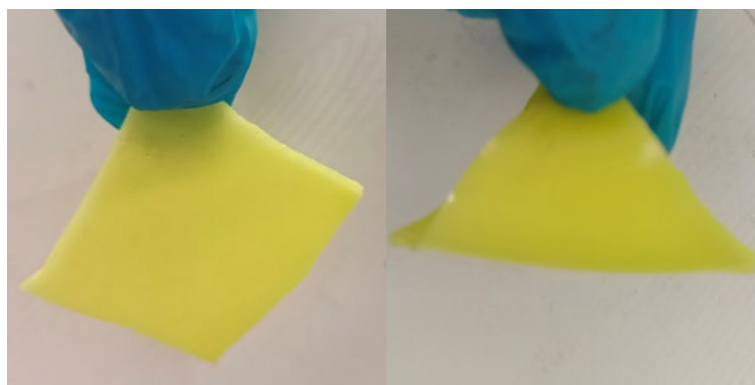
**Fig. S8** Radioluminescence spectra of  $(\text{MTP})_2\text{Cu}_4\text{I}_6$  single crystals under **a** high, and **b** low-dose rate conditions.



**Fig. S9** Photographs of  $(\text{MTP})_2\text{Cu}_4\text{I}_6$ /polydimethylsiloxane (PDMS) composite film under ambient light and 365 nm ultraviolet (UV) irradiation.



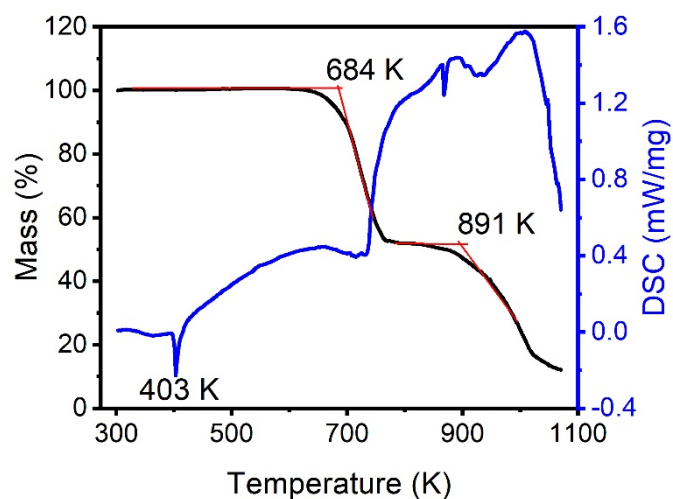
**Fig. S10** UV-visible absorption spectrum of  $(\text{MTP})_2\text{Cu}_4\text{I}_6$ /PDMS composite film.



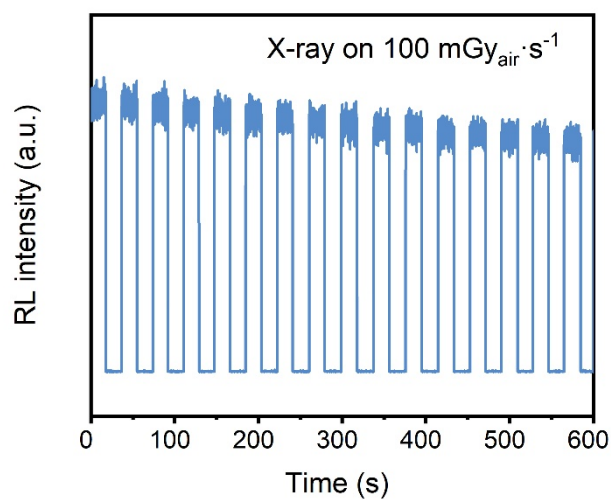
**Fig. S11** Planar and nonplanar  $(\text{MTP})_2\text{Cu}_4\text{I}_6/\text{PDMS}$  scintillator film images under ambient light conditions.



**Fig. S12** Photograph of the standard tungsten edge.



**Fig. S13** Thermogravimetric analysis and differential scanning calorimetry curve of  $(\text{MTP})_2\text{Cu}_4\text{I}_6$  powder.



**Figure S14** Emission photostability at 620 nm for the  $(\text{MTP})_2\text{Cu}_4\text{I}_6/\text{PDMS}$  film following exposure to cyclical X-rays at a dose rate of  $100 \text{ mGy}_{\text{air}} \text{ s}^{-1}$ .

**Table S1.** Crystal information from Checkcif of (MTP)<sub>2</sub>Cu<sub>4</sub>I<sub>6</sub> characterized by single-crystal X-ray diffraction.

| Chemical formula                             | (C <sub>19</sub> H <sub>18</sub> P) <sub>2</sub> Cu <sub>4</sub> I <sub>6</sub> |
|----------------------------------------------|---------------------------------------------------------------------------------|
| Temperature / K                              | 193                                                                             |
| Crystal system                               | Trigonal                                                                        |
| Space group                                  | <i>R3c</i>                                                                      |
| <i>a</i> / Å                                 | 13.91190 (2)                                                                    |
| <i>b</i> / Å                                 | 13.91190 (2)                                                                    |
| <i>c</i> / Å                                 | 39.85970 (10)                                                                   |
| $\alpha$ / °                                 | 90                                                                              |
| $\beta$ / °                                  | 90                                                                              |
| $\gamma$ / °                                 | 120                                                                             |
| <i>V</i> / Å <sup>3</sup>                    | 6680.9392 (3)                                                                   |
| <i>M<sub>r</sub></i>                         | 1570.21                                                                         |
| $\rho_{\text{calc}}$ / (g cm <sup>-3</sup> ) | 2.342                                                                           |
| $\mu$ / mm <sup>-1</sup>                     | 35.679                                                                          |
| <i>Z</i>                                     | 6                                                                               |
| <i>F</i> (000)                               | 4368.0                                                                          |
| Index ranges                                 | -17 ≤ <i>h</i> ≤ 17,<br>-17 ≤ <i>k</i> ≤ 17,<br>-50 ≤ <i>l</i> ≤ 50             |

**Table S2.** Atomic ratios of C, P, Cu, and I in (MTP)<sub>2</sub>Cu<sub>4</sub>I<sub>6</sub> measured by XPS.

| Elements | Atomic % |
|----------|----------|
| C        | 73.01    |
| P        | 4.28     |
| Cu       | 8.92     |
| I        | 13.79    |
| Total    | 100.00   |

**Table S3.** Comparison of PL properties and scintillation performance of reported cuprous halide scintillators.

| Scintillator                                                 | PLQY<br>(%) | Lifetime<br>( $\mu$ s) | Light yield<br>(photons $\text{MeV}^{-1}$ ) | Detection limit<br>( $\text{nGy}_{\text{air}} \text{s}^{-1}$ ) | Ref.             |
|--------------------------------------------------------------|-------------|------------------------|---------------------------------------------|----------------------------------------------------------------|------------------|
| <b>(MTP)<sub>2</sub>Cu<sub>4</sub>I<sub>6</sub></b>          | <b>99.9</b> | <b>2.18</b>            | <b>43800</b>                                | <b>37.6</b>                                                    | <b>This work</b> |
| [BzTPP] <sub>2</sub> Cu <sub>2</sub> I <sub>4</sub>          | 44.2        | 1.93                   | 27700                                       | 352                                                            | 1                |
| [BAPMA]Cu <sub>2</sub> Br <sub>5</sub>                       | 53.4        | 50.2                   | 43700                                       | 74                                                             | 2                |
| [ETPP] <sub>2</sub> Cu <sub>4</sub> Br <sub>6</sub>          | 94.2        | 32.89                  | 53600                                       | --                                                             | 3                |
| [ETPP]CuBr <sub>2</sub>                                      | 65.2        | 2.75                   | 58000                                       | 453                                                            | 3                |
| C <sub>9</sub> H <sub>20</sub> NCuBrI                        | 99.5        | 2.52                   | 25000                                       | 40.4                                                           | 4                |
| (TBA)CuCl <sub>2</sub>                                       | 92.8        | 28.7                   | 23400                                       | --                                                             | 5                |
| (TBA)CuBr <sub>2</sub>                                       | 80.5        | 232.05                 | 24100                                       | --                                                             | 5                |
| (DIET) <sub>3</sub> Cu <sub>3</sub> Cl <sub>3</sub>          | 69.2        | 1.3                    | 6000                                        | --                                                             | 6                |
| (DIET) <sub>3</sub> Cu <sub>3</sub> Br <sub>3</sub>          | 39.3        | 0.6                    | 20700                                       | 189                                                            | 6                |
| [Rb(18-crown-6)] <sub>2</sub> Cu <sub>4</sub> I <sub>6</sub> | 93.4        | 2.4                    | 10600                                       | 458.3                                                          | 7                |
| Rb <sub>2</sub> CuCl <sub>3</sub>                            | 99.4        | 11.3                   | 16600                                       | 88.5                                                           | 8                |
| K <sub>2</sub> CuBr <sub>3</sub>                             | 87.0        | 64.3                   | 23800                                       | 132.8                                                          | 9                |
| Cs <sub>3</sub> Cu <sub>2</sub> I <sub>5</sub>               | 91.2        | 0.97                   | 32000                                       | --                                                             | 10               |

BzTPP = Benzyltriphenylphosphonium; BAPMA = *N,N*-Bis(3-aminopropyl)methylamine; ETPP = Ethyltriphenylphosphonium; TBA = Tetrabutylammonium; DIET = 1,3-Diethyl-2-thiourea.

**Table S4.** Comparison of spatial resolution of reported cuprous halide scintillators.

| Scintillator                                                                          | Spatial resolution<br>(lp mm <sup>-1</sup> ) | Ref.             |
|---------------------------------------------------------------------------------------|----------------------------------------------|------------------|
| <b>(MTP)<sub>2</sub>Cu<sub>4</sub>I<sub>6</sub>/PDMS</b>                              | <b>10.2</b>                                  | <b>This work</b> |
| [BzTPP] <sub>2</sub> Cu <sub>2</sub> I <sub>4</sub> /PVP                              | 4.9                                          | 1                |
| [BAPMA]Cu <sub>2</sub> Br <sub>5</sub> /PDMS                                          | 15.8                                         | 2                |
| C <sub>9</sub> H <sub>20</sub> NCuBrI/PDMS                                            | 5.6                                          | 4                |
| (TBA)CuBr <sub>2</sub> /PVDF                                                          | 3.0                                          | 5                |
| (DIET) <sub>3</sub> Cu <sub>3</sub> Br <sub>3</sub> /PDMS                             | 11.7                                         | 6                |
| (C <sub>8</sub> H <sub>20</sub> N) <sub>2</sub> Cu <sub>2</sub> Br <sub>4</sub> wafer | 9.5                                          | 11               |
| Rb <sub>2</sub> CuBr <sub>3</sub> /PS                                                 | 1.7                                          | 12               |
| Cs <sub>3</sub> Cu <sub>2</sub> I <sub>5</sub> /PDMS                                  | 6.8                                          | 13               |

## References

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