

## Supporting Information for

Mechanochemical synthesis of three

double perovskite:  $\text{Cs}_2\text{AgBiBr}_6$ ,

$(\text{CH}_3\text{NH}_3)_2\text{TlBiBr}_6$  and  $\text{Cs}_2\text{AgSbBr}_6$

## **Materials and Methods**

### **Reactants.**

CsBr (Alfa Aesar, 99.9 %), MABr (DyeSol), AgBr (Alfa Aesar, 99.5 %), TIBr (Alfa Aesar, 99.999 %), BiBr<sub>3</sub> (Alfa Aesar, 99 %) and SbBr<sub>3</sub> (Alfa Aesar, 99.999 %) were commercially available and used as received without further purification.

### **Mechanochemical synthesis of the perovskite powders.**

The powders of the double perovskites were synthesized by grinding the corresponding bromide-based salt, i.e.: CsBr, AgBr and BiBr<sub>3</sub> for Cs<sub>2</sub>AgBiBr<sub>6</sub>; MABr, TIBr and BiBr<sub>3</sub> for MATiBiBr<sub>6</sub>; and CsBr, AgBr and SbBr<sub>3</sub> for Cs<sub>2</sub>AgSbBr<sub>6</sub>. They were introduced into a Retsch Emax high-energy ball mill for 30 min at 900 rpm, employing two 125 mL reaction chambers and fourteen 10 mm stainless steel balls in each chamber. The total mass of the precursors in each reaction chamber was around 1-2 g, with a molar ratio of 2:1:1 regarding the A, B and B' cations, respectively.

### **Characterization.**

X-ray diffraction (XRD) data of perovskite powders were collected on a Bruker D8 Discover diffractometer operating at 40 kV and 40 mA and using Cu-K<sub>α</sub> radiation (1.54059 Å).

X-ray photoelectron spectroscopy (XPS) measurements of powders were carried out in a PHOIBOS 150 MCD (SPECS) spectrometer with a non-monochromatic X-ray source (Aluminum K<sub>α</sub> line of 1486.6 eV energy and 300 W), placed perpendicular to the analyzer axis. All measurements were made in an ultra-high vacuum (UHV) chamber.

Diffuse-reflectance spectra of perovskite powders were performed using a Cary 5000 spectrometer with a Pb Smart NIR detector for extended photometric range (200 to 1000 nm). BaSO<sub>4</sub> was used as non-absorbing reflectance reference.

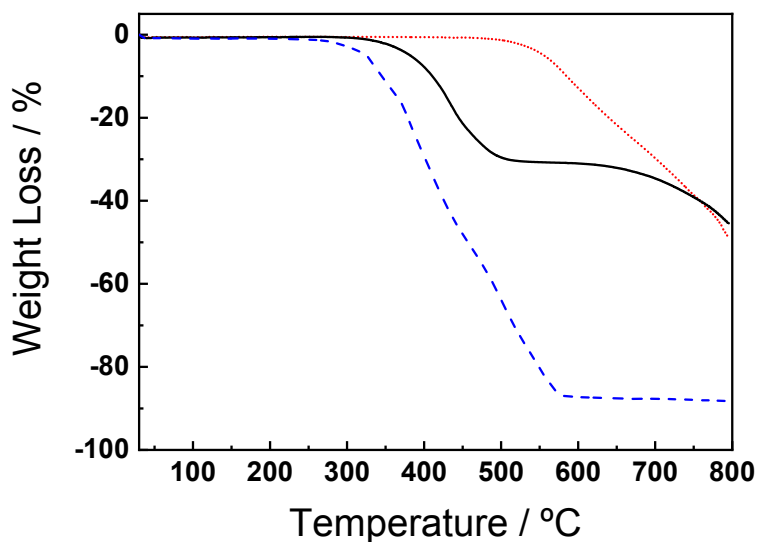
Thermal analysis of the powders was performed by simultaneous TG-DSC measurements using a System Setaram Setsys 12 TGA instrument. Samples were heated at a rate of 5 °C min<sup>-1</sup> in N<sub>2</sub> (40 mL min<sup>-1</sup>) at the temperature range 30-800 °C.

Time resolved fluorescence measurements were accomplished through the time-correlated single photon counting (TCSPC) technique, by using a FLS980 (Edinburgh Instruments) photoluminescence spectrometer. Samples were excited at 406.4 nm with a 86.8 ps pulse width diode laser. As detector, a R2658P photomultiplier was employed.

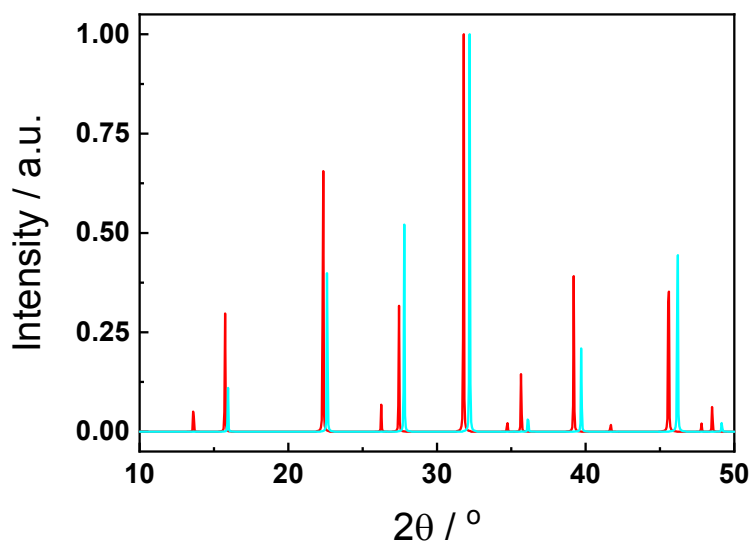
X-ray fluorescence measurements were performed using a Rigaku ZSX Primus IV sequential wavelength dispersive X-ray fluorescence spectrometer with 6 diffraction

crystals. The X-ray generator tube consists of a Rh-anode working at 3-4 kW and 60 kV. Heavy and light elements are detected with a scintillation counter and a flow proportional counter, respectively.

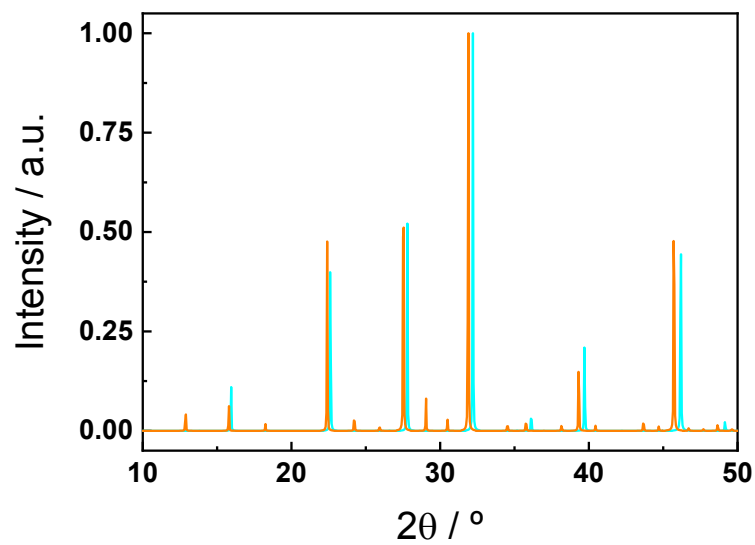
All measurements were collected at room temperature except if indicated otherwise.



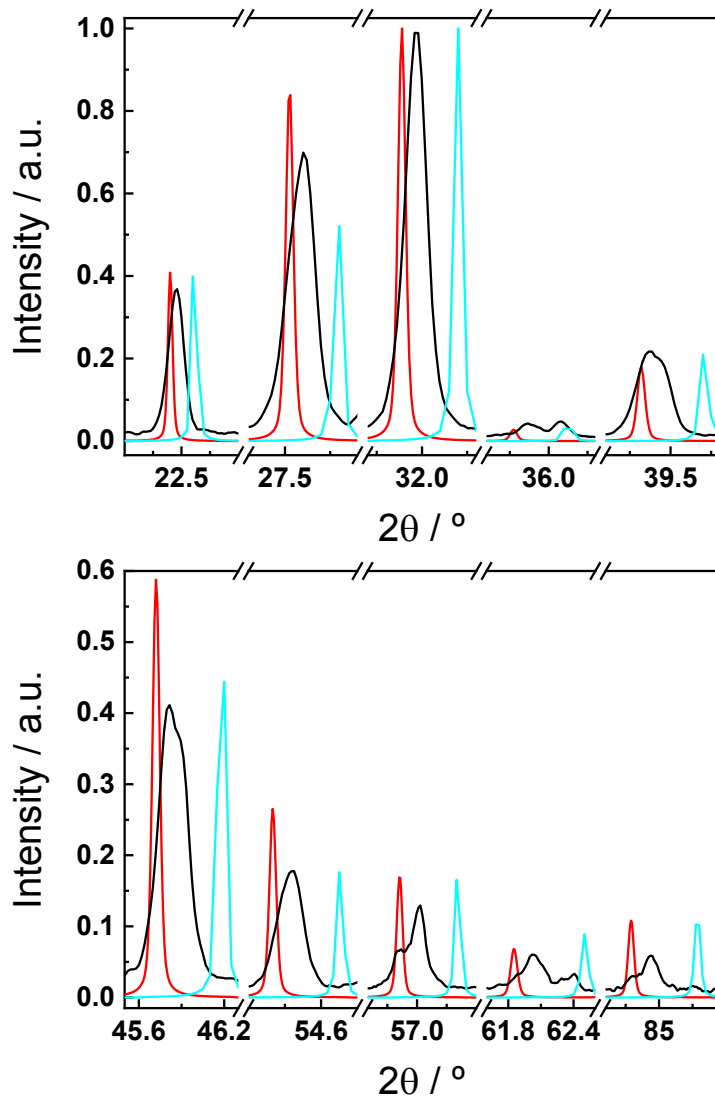
**Figure S1.** TGA curves of the synthesized powders **1** (red dotted line), **2** (black solid line) and **3** (blue dashed line).



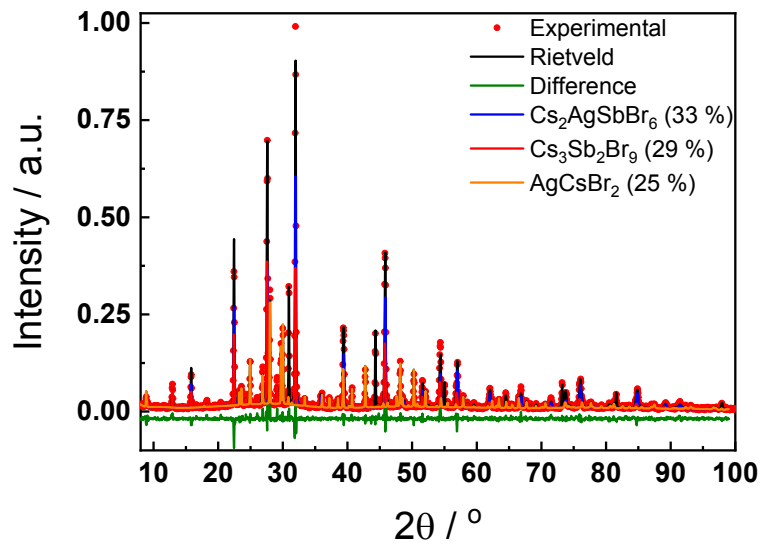
**Figure S2.** Simulated diffractogram of the Cs<sub>2</sub>AgBiBr<sub>6</sub> structure obtained from the literature (red line) and of the Cs<sub>2</sub>AgSbBr<sub>6</sub> structure obtained by replacement of Bi with Sb in Cs<sub>2</sub>AgBiBr<sub>6</sub> and subsequent theoretical optimization of the geometry (light blue line).



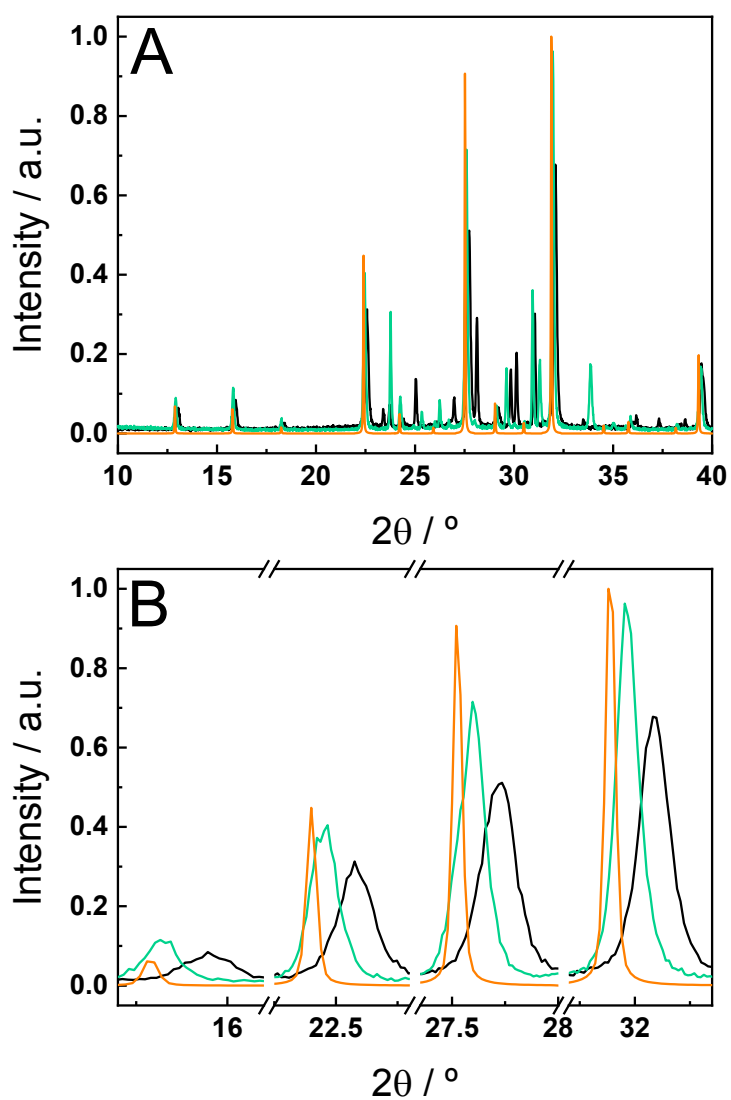
**Figure S3.** Simulated diffractogram of the Cs<sub>3</sub>Sb<sub>2</sub>Br<sub>9</sub> layered structure obtained from the literature (orange line) and of the Cs<sub>2</sub>AgSbBr<sub>6</sub> structure obtained by replacement of Bi with Sb in Cs<sub>2</sub>AgBiBr<sub>6</sub> and subsequent theoretical optimization of the geometry (light blue line).



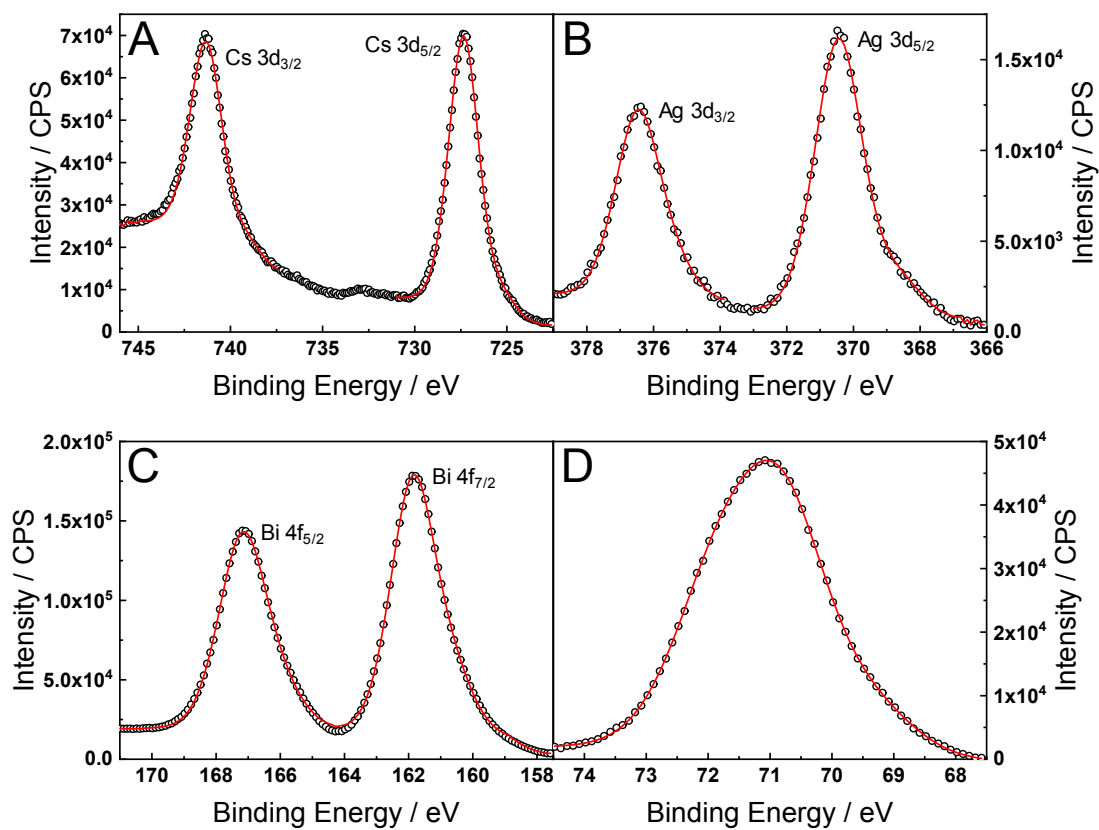
**Figure S4.** Zoom of the experimental diffractogram of powder **2** (black line) and the calculated diffractograms of  $\text{Cs}_3\text{Sb}_2\text{Br}_9$  (red line) and of  $\text{Cs}_2\text{AgSbBr}_6$  (light blue line) obtained by replacing the  $\text{Bi}^{3+}$  with  $\text{Sb}^{3+}$  cations in the crystalline lattice of the related  $\text{Cs}_2\text{AgBiBr}_6$  double perovskite and subsequent relaxation of the structure by keeping fixed the relative positions of all constituent ions.



**Figure S5.** Rietveld refinement analysis of the experimental XRD pattern of **2** (dotted line) showing the percentage of each crystal structure, Cs<sub>2</sub>AgSbBr<sub>6</sub> (blue line), Cs<sub>3</sub>Sb<sub>2</sub>Br<sub>9</sub> (red line) and AgCsBr<sub>2</sub> (orange line).  $R_{wp} = 0.15$  and  $R_p = 0.11$ .

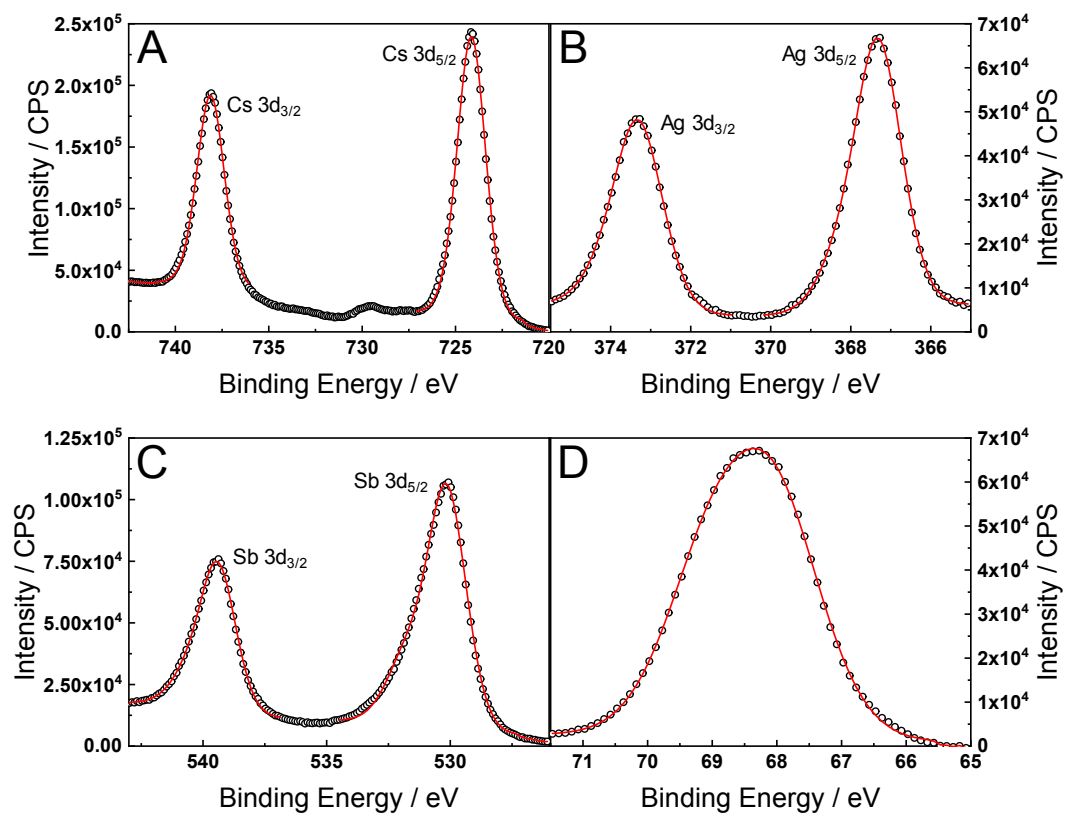


**Figure S6.** A) Simulated diffractogram of the  $\text{Cs}_3\text{Sb}_2\text{Br}_9$  layered structure obtained from the literature (orange line) and experimental diffractogram of powder **2** before (black line) and after (green line) a heating treatment in an oven at ca. 200 °C for 2.5 h. B) Zoom of some regions of the comparison depicted in A).

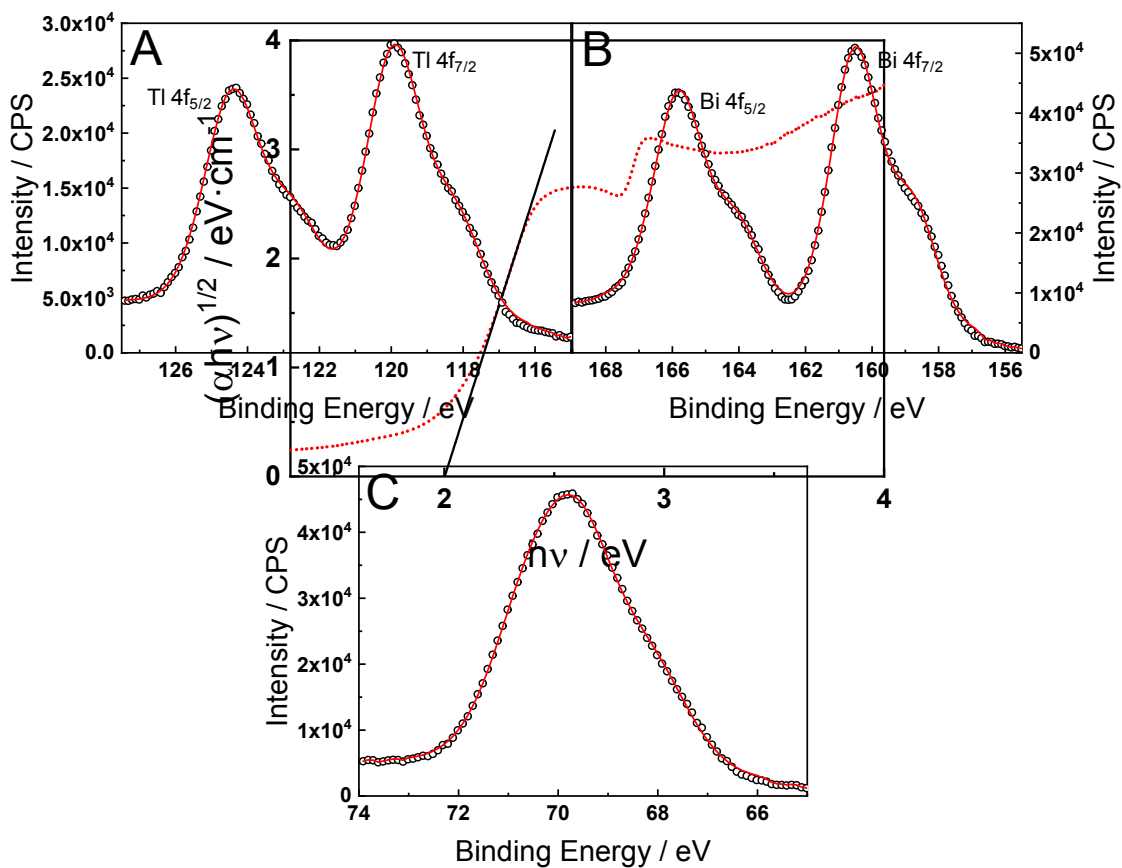


**Figure S7.** XPS spectra of Cs 3d (A), Ag 3d (B), Bi 4f (C) and Br 3d (D) for the synthesized powder by mixing CsBr, AgBr and BiBr<sub>3</sub> (**1**).

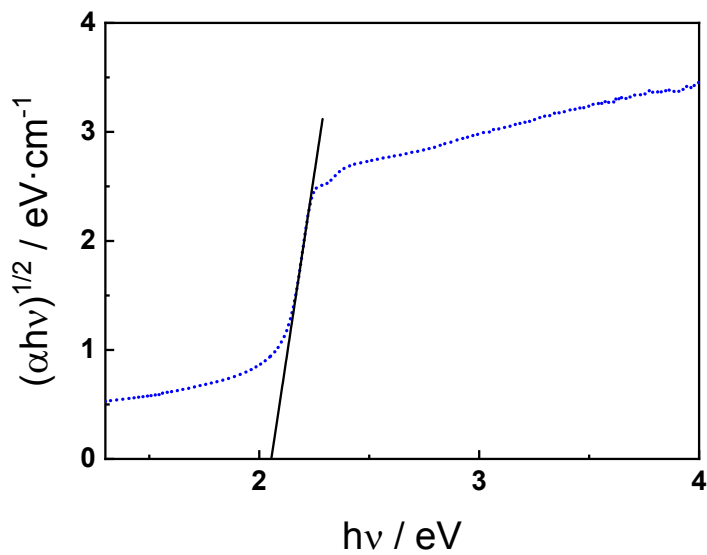


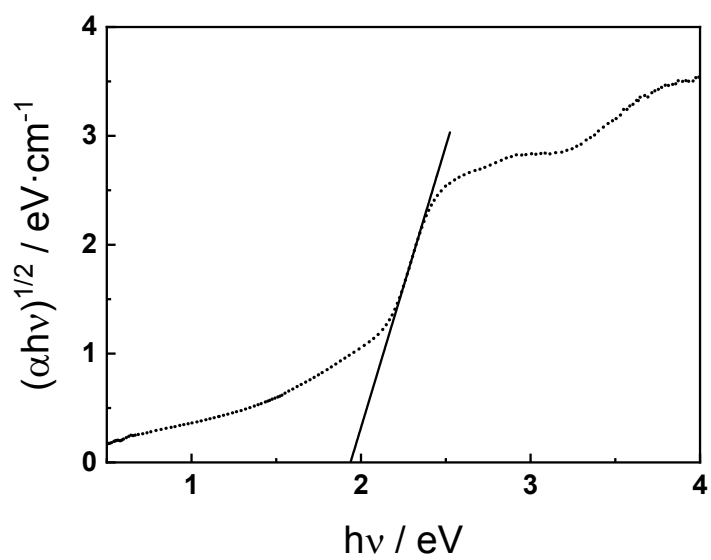


**Figure S8.** XPS spectra of Cs 3d (A), Ag 3d (B), Sb 3d (C) and Br 3d (D) for the synthesized powder by mixing CsBr, AgBr and SbBr<sub>3</sub> (2).

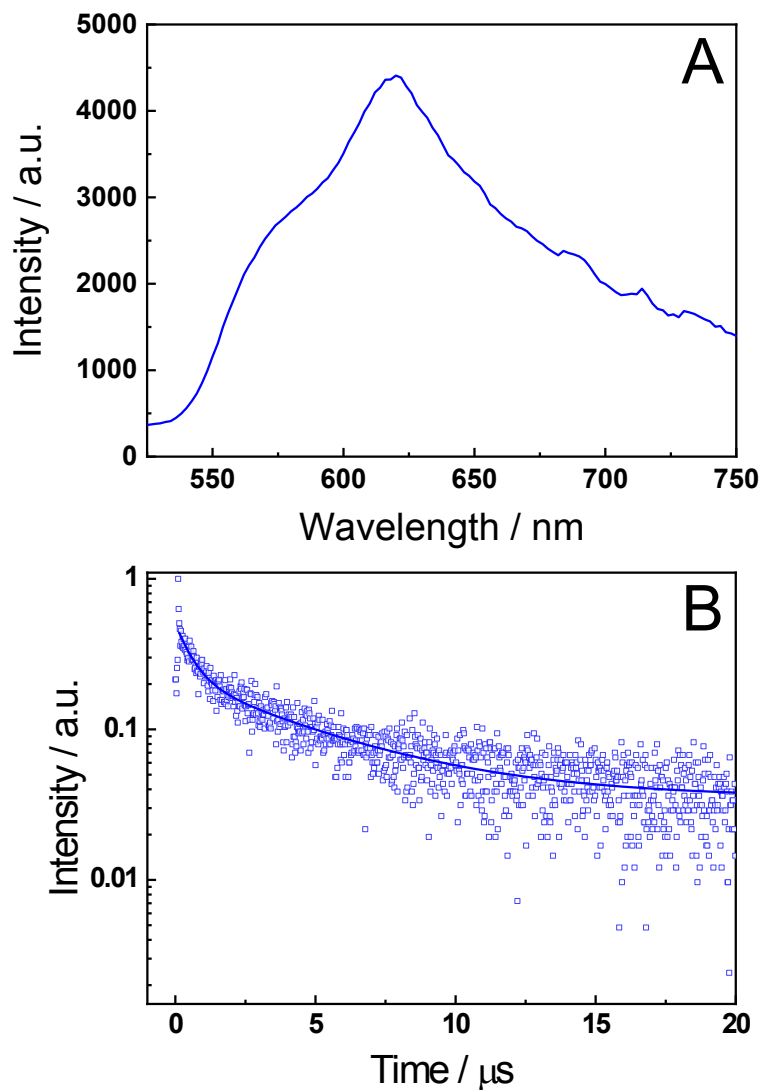


**Figure S9.** XPS spectra of TI 4f (A), Bi 4f (B) and Br 3d (C) for the synthesized powder by mixing MABr, TIBr and BiBr<sub>3</sub> (**3**).





**Figure S10.** Tauc's plot of the synthesized powders **1** (red line), **2** (black line) and **3** (blue line).



**Figure S11.** Steady-state PL spectrum (A) and time decay of the PL signal (B) of MA<sub>2</sub>TlBiBr<sub>6</sub> at  $\lambda_{em} = 570$  nm. The excitation wavelength was 405 nm.