

## Supporting Information (SI)

# Extending Absorption of Cs<sub>2</sub>AgBiCl<sub>6</sub> Double Perovskite to Near Infra-Red Region by Doping Copper

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## Experimental Section

### Chemicals:

$\text{BiCl}_3$  ( $\geq 98\%$ , Sigma Aldrich),  $\text{AgCl}$  (99%, Sigma Aldrich),  $\text{CsCl}$  (99.9%, Spectrochem),  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  (99.9%, SRL),  $\text{HCl}$  (37%, Sigma Aldrich),  $\text{C}_2\text{H}_5\text{OH}$  (absolute, Merck). All these chemicals were used as received without any further purification.

### Synthesis of Pristine $\text{Cs}_2\text{AgBiCl}_6$ Crystals by hydrothermal method (HT):

Solid  $\text{CsCl}$  (168.4 mg, 1.00 mmol),  $\text{BiCl}_3$  (157.7 mg, 0.5 mmol),  $\text{AgCl}$  (71.7 mg, 0.5 mmol) were dissolved in 6 ml of 37%  $\text{HCl}$  and then transferred into a 50 ml Teflon-lined autoclave. Then autoclave was properly sealed and placed in the oven where it was heated to  $180\text{ }^\circ\text{C}$  for 24 hours. After 24 hours slow cooling was started and it was cooled down to room temperature within next 48 hours, it results in the formation of yellow crystals. **Image S1** shows the crystals of pristine  $\text{Cs}_2\text{AgBiCl}_6$  in mother liquor in an autoclave, along with dry crystals.

**Image S1:** Synthesized crystals of pristine  $\text{Cs}_2\text{AgBiCl}_6$  (HT-0) DP.



### **Synthesis of Cu-doped Cs<sub>2</sub>AgBiCl<sub>6</sub> Crystals by hydrothermal method (HT):**

To prepare Cu doped Cs<sub>2</sub>AgBiCl<sub>6</sub> crystals, equimolar ratio of AgBr and BiBr<sub>3</sub> was replaced by total 10%, 30%, and 50% of CuCl<sub>2</sub>.2H<sub>2</sub>O in the precursor solution, respectively. The Synthesis, strategy is same as that of the pristine Cs<sub>2</sub>AgBiCl<sub>6</sub>.

**Image S2.** Synthesized crystals of HT-50 DP.



**Image S2** shows the crystals of HT-50 in mother liquor in a teflon autoclave, along with dry crystals.

### **Preparation of Cu-doped Cs<sub>2</sub>AgBiCl<sub>6</sub> by Postsynthetic grinding method (PSG):**

Pristine Cs<sub>2</sub>AgBiCl<sub>6</sub> synthesized by hydrothermal method as mentioned above was used in the ground form. 100 mg of powdered Cs<sub>2</sub>AgBiCl<sub>6</sub> was weighed in an agate pestal mortar. Then 54 mg of CuCl<sub>2</sub>.2H<sub>2</sub>O was weighed, 54 mg of this salt will provide 50% Cu compared to (Ag+Bi) present in 100 mg of pristine Cs<sub>2</sub>AgBiCl<sub>6</sub>. Then both of these were properly mixed and ground for 10 minutes at room temperature in ambient conditions. The yellow coloured pristine Cs<sub>2</sub>AgBiCl<sub>6</sub> converts into dark brown or black coloured powder with time. Then, obtained product was characterized with and without washing by collecting PXRD pattern and absorbance spectra. The pure CuCl<sub>2</sub>.2H<sub>2</sub>O is highly soluble in ethanol, hence ethanol was used for washing the obtained product to remove excess of CuCl<sub>2</sub>.2H<sub>2</sub>O precursor present in the product. **Image S3** shows the synthesis and washing steps for PSG -50 DP.

**Image S3:** Synthesis of PSG -50 and steps for washing.

**Precursors ( $\text{Cs}_2\text{AgBiCl}_6$  (100 mg) MCs+  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  (54 mg) After grinding of 10 minutes**



**Preparation of  $\text{Cs}_2\text{AgBiCl}_6$  by mechanochemical synthesis (MCS):**

Solid  $\text{CsCl}$  (168.4 mg, 1.00 mmol),  $\text{AgCl}$  (71.7 mg, 0.5 mmol),  $\text{BiCl}_3$  (157.7 mg, 0.5 mmol) were transferred into an agate pestal mortar. Then all of these precursors were mixed properly and then ground for 60 minutes at room temperature in ambient conditions, forming yellow coloured  $\text{Cs}_2\text{AgBiCl}_6$  double perovskite.

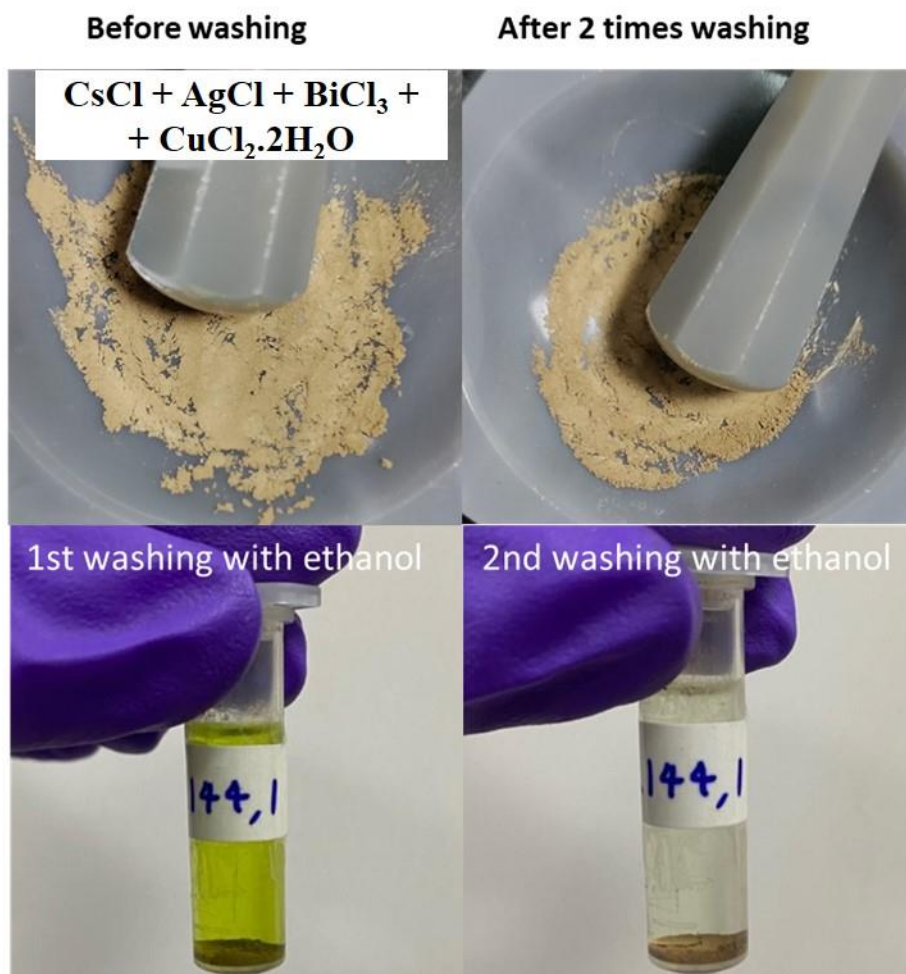
**Image S4:** Synthesis of Pristine  $\text{Cs}_2\text{AgBiCl}_6$  (MCS-0).



**Synthesis of Cu doped  $\text{Cs}_2\text{AgBiCl}_6$  by mechanochemical synthesis (MCS):**

To Synthesize Cu-doped  $\text{Cs}_2\text{AgBiCl}_6$ , Solid CsCl (168.4 mg, 1.00 mmol), AgCl (71.7 mg, 0.5 mmol),  $\text{BiCl}_3$  (157.7 mg, 0.5 mmol),  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  (42.7mg, 0.25 mmol) were transferred, mixed and then ground properly for 60 minutes in the agate pestal mortar. it results in the formation of dark brown coloured Cu doped  $\text{Cs}_2\text{AgBiCl}_6$  double perovskite. **Image S5** shows the synthesized MCS-50 DP, before washing it contains  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  impurity, and after 2 times washing it with ethanol, it shows pure MCS-50. **Image S5** also shows the washing steps of synthesized MCS-50 DP.

**Image S5:** Synthesis of MCS-50.



### **Characterization Techniques**

Percentage reflectance measurements were performed using Perkin Elmer (UV/Visible/NIR) Lambda 1050 double-beam spectrophotometer equipped with an integrating sphere operating in reflectance mode, with slit widths of 2 nm in the visible region and variable slit widths in the NIR range. Barium sulphate (BaSO<sub>4</sub>) powder was used as a reference for reflectance measurements. powdered samples were mixed with BaSO<sub>4</sub> and then mounted in the sample holder to collect the spectra. The percentage reflectance spectra were transformed to pseudo absorption data by using the Kubelka–Munk transformation,<sup>1</sup> which gives pseudo absorbance

as a function of reflectance from the equation:  $F(R) = \alpha S = (1 - R) / 2R$  where  $R$  is the reflectance and  $\alpha$  is the optical absorption coefficient and  $S$  is the scattering coefficient.

PL spectra were recorded using Edinburgh instrument FLSP 920 with constant monochromator bandwidths of 15 and 15 nm for excitation and emission, respectively. The excitation wavelength for pristine HT-0 and Cu doped (HT-10, HT-30, HT-50) was 400 nm. Photoluminescence life time decay (TRPL) curves were collected by using time-correlated single photon counting (TCSPC) at room temperature using Edinburgh instruments FLSP920. The excitation light source used for these measurements is a laser, emitting at 375 nm. Optical characterization of these materials was done at room temperature using the sample in powder form.

Powder X-ray diffraction (PXRD) was performed on Bruker D8 Advance X-ray diffractometer equipped with Cu  $K\alpha$  ( $K\alpha_1 = 1.540598 \text{ \AA}$ ,  $K\alpha_2 = 1.544426 \text{ \AA}$ ,  $K\alpha$  ratio 0.5,  $K\alpha_{av} = 1.541874 \text{ \AA}$ ) X-ray tubes. The XRD measurements of these samples by placing the powdered sample onto the glass holder. The diffraction patterns were collected in the ambient conditions in the range of 10-70  $2\theta^\circ$ . To check the thermal stability of HT-50, its powder was heated at increasing temperatures (100 to 500  $^\circ\text{C}$ ) in a crucible in a furnace for 30 minutes at each temperature. And then the PXRD pattern was collected after cooling it to room temperature.

Horiba Raman spectrophotometer coupled with Olympus microscope and objective 10x, 1800gr, CCD as detector, laser 785 nm was used to perform Raman spectroscopic measurements. 1-2 mg of powder samples were used to collect the Raman spectrum.

X-band electron paramagnetic resonance (EPR) measurement was done by using Bruker A300-9.5/12/S/W System consists of X-band, Q-band, ENDOR, and Dual-mode resonator.

Undoped and Cu doped  $\text{Cs}_2\text{AgBiCl}_6$  (15-20 mg) in powder form was used to collect the XPS spectrum. Axis Supra (Kratos Analytical. Ltd) equipped with Monochromatic X-ray source: Al  $K\alpha - 1486.6 \text{ eV}$  was used to obtain XPS spectrum. For fitting the data, the least-squared-

error-fit method was employed. A minimum number of components were chosen to describe the experimental data. Shirley method was used to describe the background.

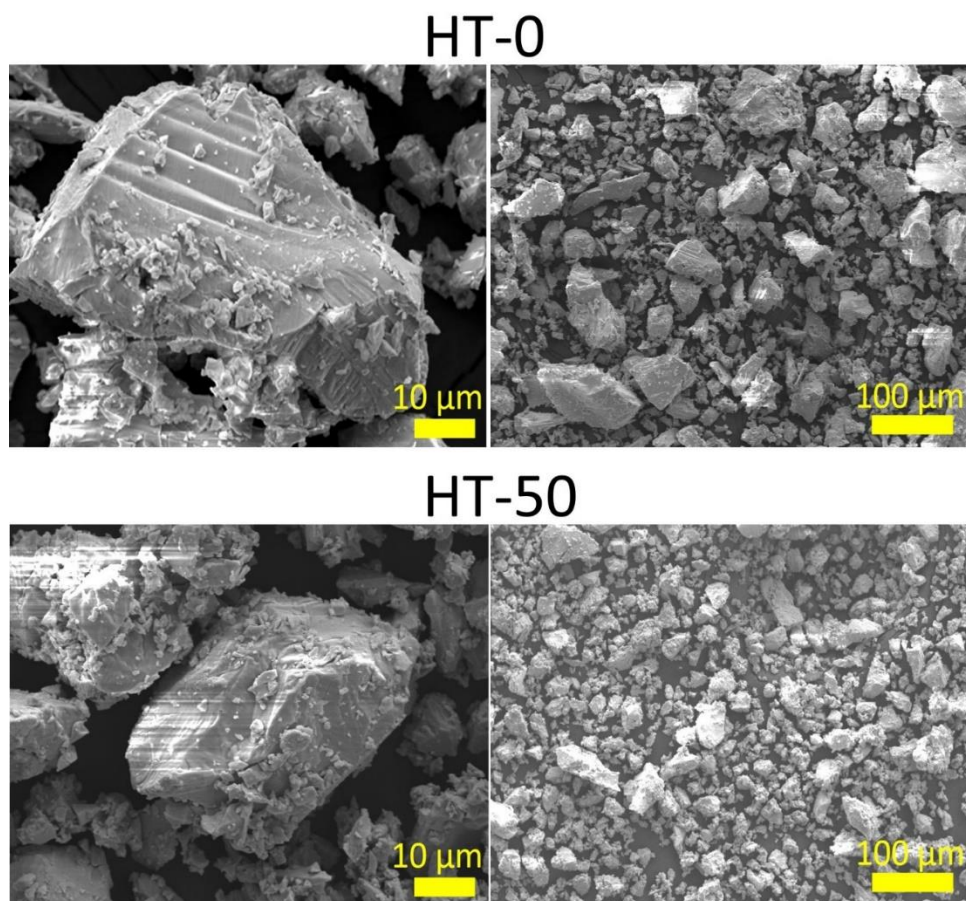
Thermogravimetric analysis (TGA) was carried out in an inert atmosphere provided by nitrogen gas between 50 and 870 °C at a heating rate of 10 °C min<sup>-1</sup> on a PerkinElmer thermal analysis system.

Inductively Coupled Plasmon Mass Spectrometry (ICP-MS) analysis of solid Cu doped samples was performed by digesting the samples in aqua-regia. Agilent ICP-MS 7900 was used for elemental analysis of these samples.

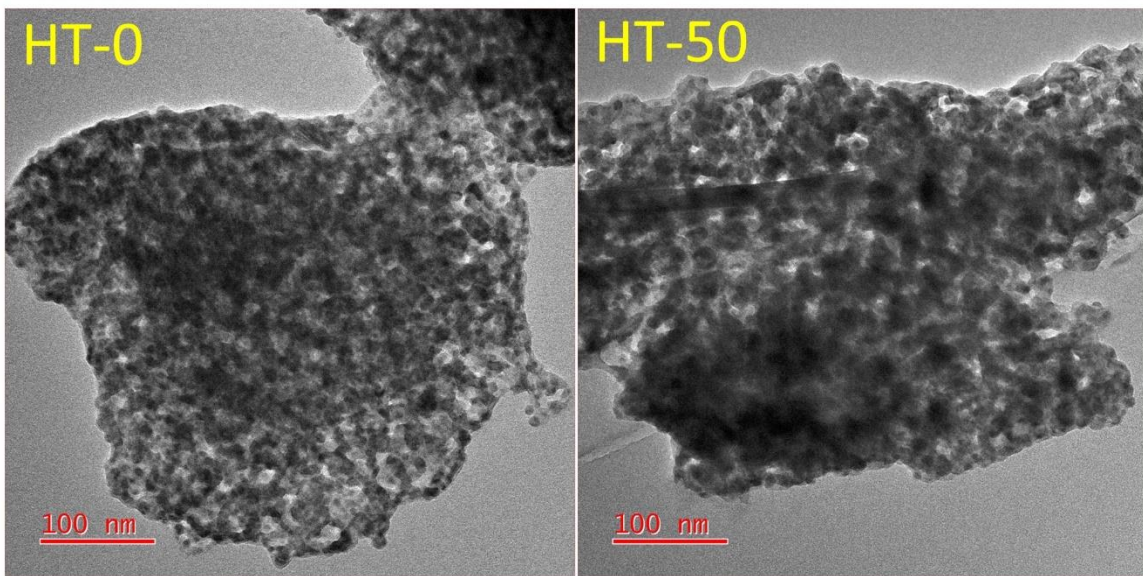
Field Emission Scanning Electron Microscopy (FESEM) images and EDX was collected using TESCAN MAGNA instrument. Transmission electron microscopy (TEM) imaging was carried out using 200 kV Tecnai TF20 instrument.



## Morphological Characterization



**Figure S1.** FESEM images of pristine  $\text{Cs}_2\text{AgBiCl}_6$  (HT-0) and Cu-doped  $\text{Cs}_2\text{AgBiCl}_6$  (HT-50).



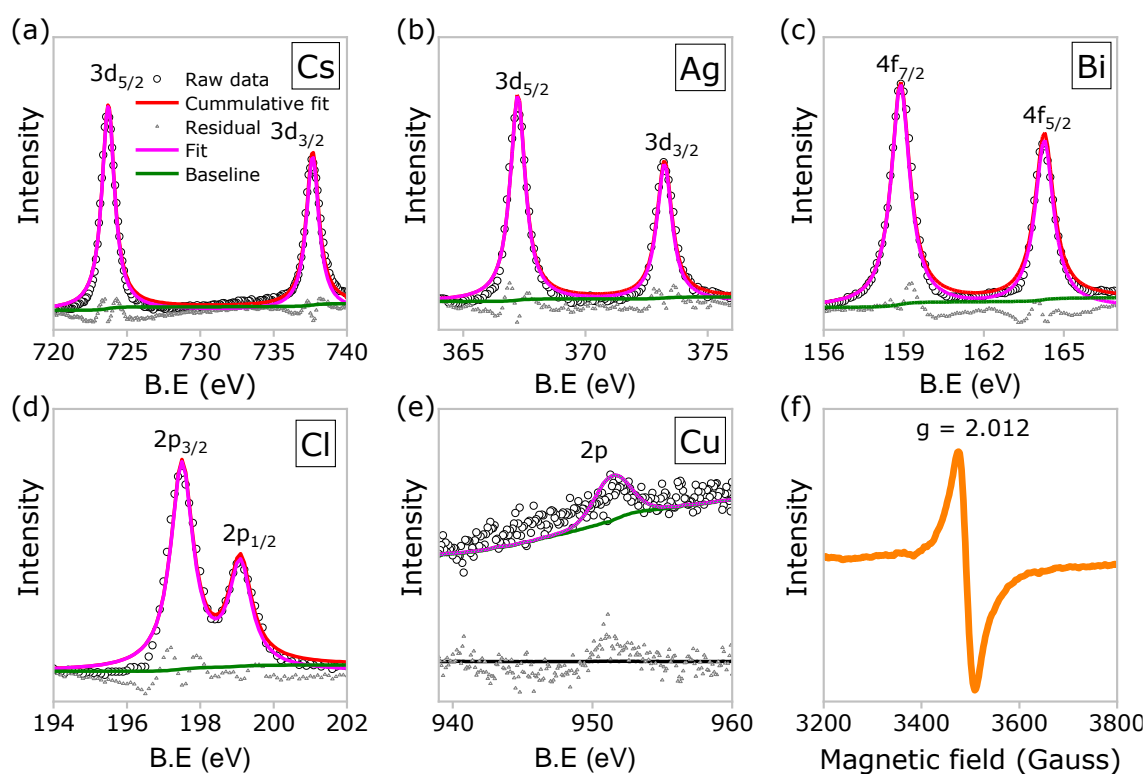
**Figure S2.** TEM images of pristine  $\text{Cs}_2\text{AgBiCl}_6$  (HT-0) and Cu-doped  $\text{Cs}_2\text{AgBiCl}_6$  (HT-50).

### **XPS and EPR analysis of HT-50**

To determine the chemical composition and valence state of the elements present in Cu-doped (HT-50) double perovskite, we performed XPS measurements. We show the high resolution XPS core level spectra of Cs 3d, Ag 3d, Bi 4f, Cl 2p, Cu 2p of the HT-50 double perovskite and their peaks were fitted using pseudo-voigt function in **Figure S3(a-e)**. XPS analysis reveals the presence of all the expected elements in their desired oxidation states. The XPS peak at 723.7 eV and 737.6 eV is due to the Cs 3d<sub>3/2</sub> and Cs 3d<sub>5/2</sub>, respectively. The Ag peaks shown in **Figure S3b** at 367.2 eV and 373.2 eV are due to the Ag 3d<sub>5/2</sub> and Ag 3d<sub>3/2</sub>. The photoelectron peaks at 158.9 eV and 164.2 eV are attributed to the Bi 4f<sub>7/2</sub> and Bi 4f<sub>5/2</sub>. The XPS peaks 197.5 eV and 199.1 eV are due to the Cl 2p<sub>3/2</sub> and Cl 2p<sub>1/2</sub>.

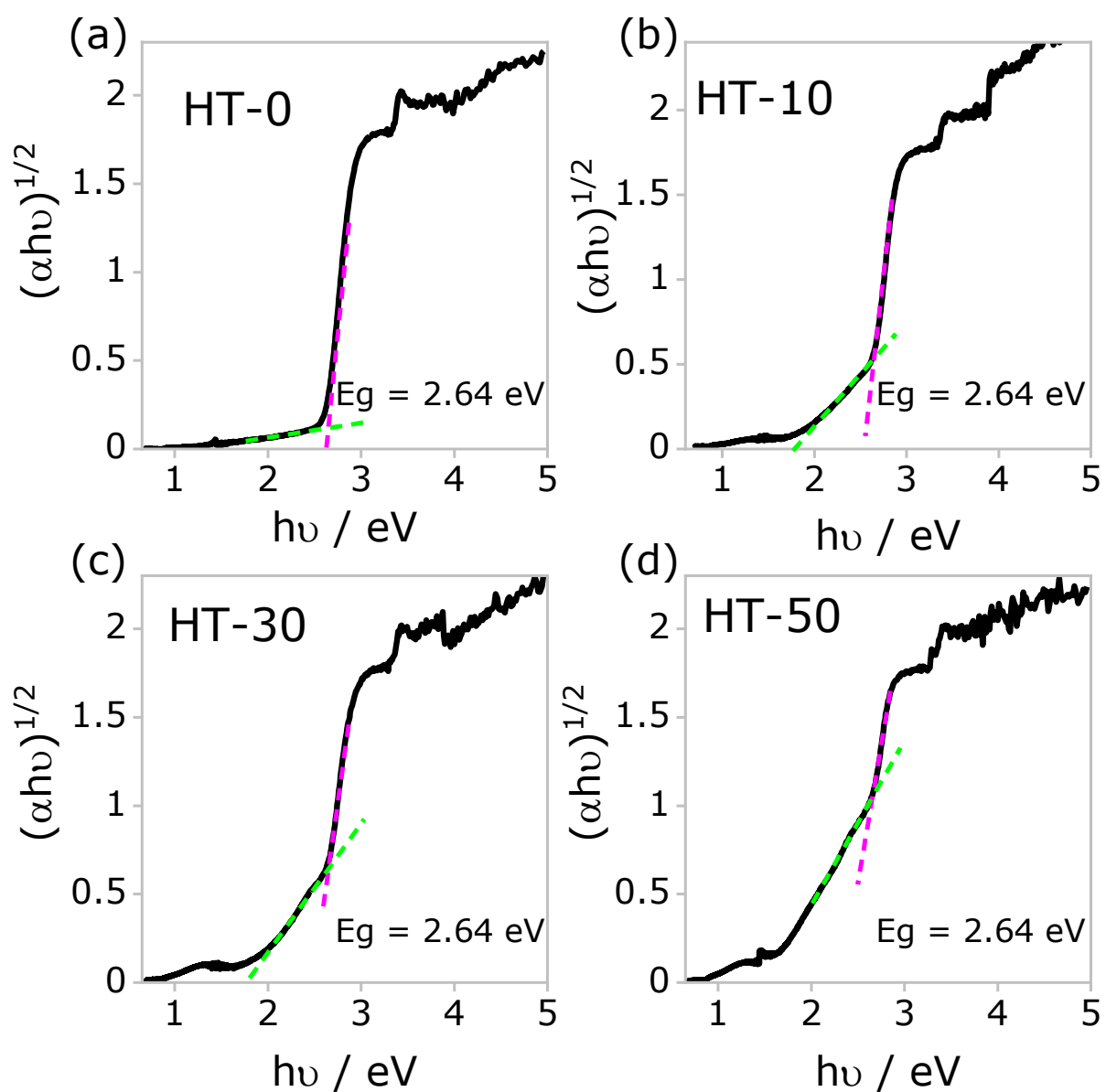
It is quite possible that Cu ions are present with multiple stable valence states (+1 and +2) in these synthesized DPs, which are possibly formed through rich redox reactions during synthesis.<sup>2</sup> To investigate the oxidation state of Cu present in the doped crystals we performed the X-ray photoelectron spectroscopy (XPS) and electron paramagnetic resonance spectroscopy (EPR) measurements. There is presence of weak signal due to Cu 2p at 952 eV which confirms the presence of Cu in the lattice of these doped DPs. However, the satellite peaks are absent in this spectrum which is due the very less doping amount of Cu in these materials (~ 1% w.r.t. Bi in HT-50). The absence of satellite peaks and noise in the Cu 2p spectrum does not enable us to confirm the oxidation state of Cu in these doped materials using XPS spectroscopy. To confirm the presence of Cu<sup>2+</sup> dopant into the Cs<sub>2</sub>AgBiCl<sub>6</sub> double perovskite host lattice we have performed the EPR measurement of doped material (HT-50). EPR spectroscopy is the method of choice to confirm the presence of Cu<sup>2+</sup> paramagnetic cation in the host matrix. **Figure S3f** shows the room temperature X-band spectra of HT-50, which

displayed the characteristic single broad peak with g-factor of 2.012 and hence confirms the doping of  $\text{Cu}^{2+}$  into the double perovskite host lattice. The combination of both XPS and EPR analysis confirmed the presence of Cu in the lattice of doped DPs synthesized by HT method, and peak in EPR spectrum confirms the presence of Cu in +2 oxidation state.



**Figure S3.** Elemental analysis of HT-50. (a-e) High resolution XPS spectrum of Cs-3d, Ag-3d, Bi-4f, Cl-2p, and Cu-2p for HT-50. (f) EPR spectrum of HT-50. All peaks were corrected according to the standard C 1s peak at 284.5 eV.

### Bandgap Calculation of pristine $\text{Cs}_2\text{AgBiCl}_6$ and Cu-doped $\text{Cs}_2\text{AgBiCl}_6$

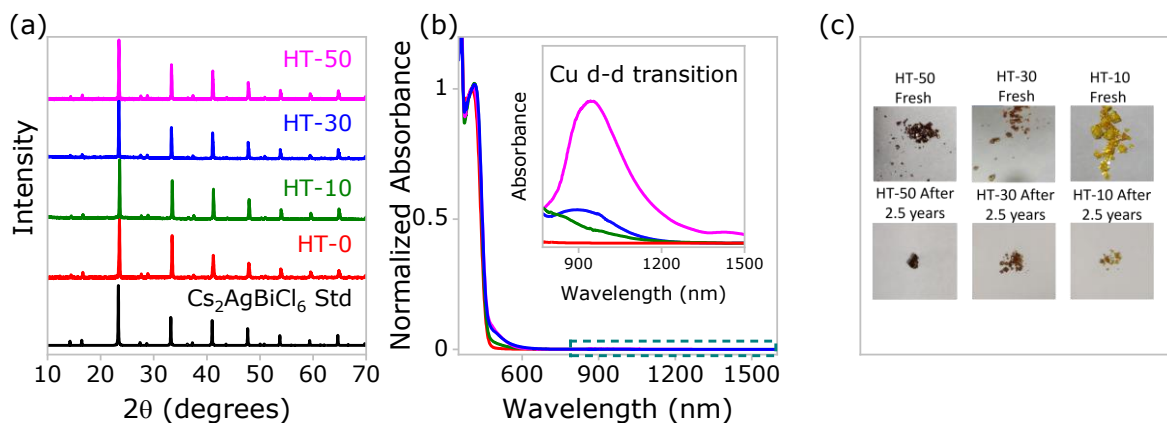


**Figure S4.** (a-d) Tauc analysis of indirect band gaps in pristine  $\text{Cs}_2\text{AgBiCl}_6$  and Cu-doped  $\text{Cs}_2\text{AgBiCl}_6$  (HT-10, HT-30, HT-50).

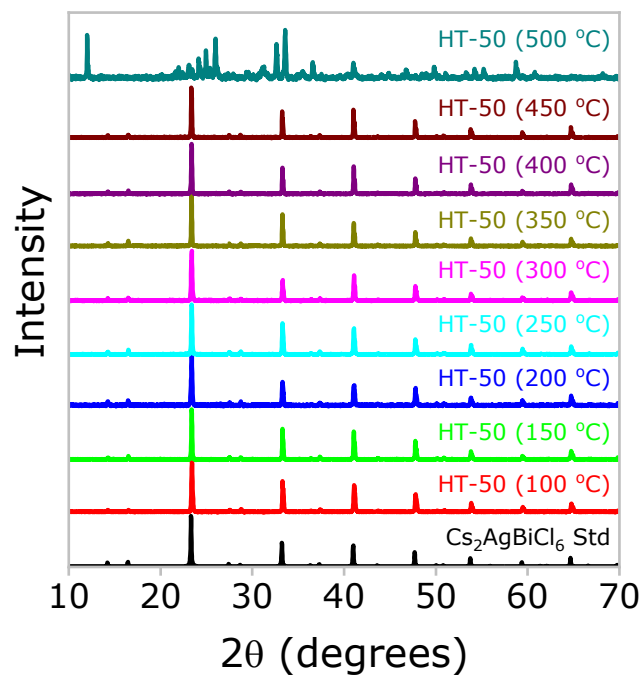
**Table S1:** TRPL decay parameters of undoped and Cu doped Cs<sub>2</sub>AgBiCl<sub>6</sub>,  $\alpha_i$  and  $\tau_i$  are the amplitude and decay time of  $i$ th component.

Double Perovskite	$\tau$ (ns)	$\alpha$
HT-0	$\tau_1 = 0.4405, \tau_2 = 6.22$	$\alpha_1 = 0.962, \alpha_2 = 0.0377$
HT-10	$\tau_1 = 0.297, \tau_2 = 1.776, \tau_3 =$ 14.814	$\alpha_1 = 0.916, \alpha_2 = 0.076, \alpha_3 =$ 0.008
HT-30	$\tau_1 = 0.286, \tau_2 = 1.954, \tau_3 =$ 17.050	$\alpha_1 = 0.926, \alpha_2 = 0.067, \alpha_3 =$ 0.007
HT-50	$\tau_1 = 0.290, \tau_2 = 1.676, \tau_3 =$ 10.660	$\alpha_1 = 0.885, \alpha_2 = 0.099, \alpha_3 =$ 0.015

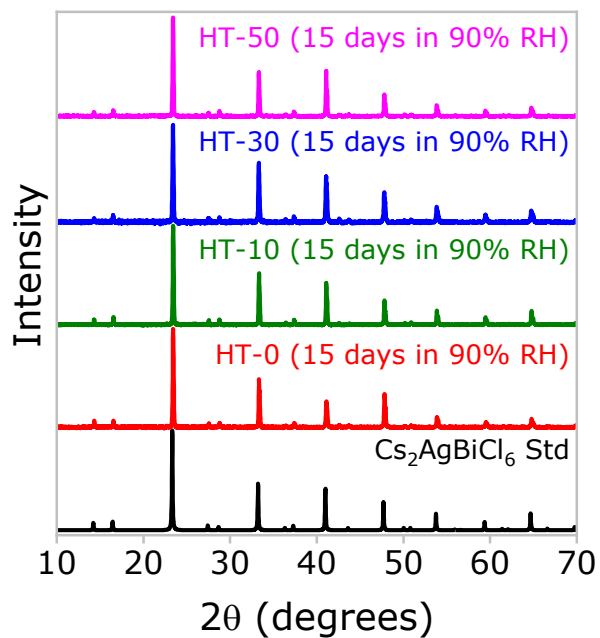
## Stability Analysis After 2.5 Years in Ambient Conditions



**Figure S5.** Stability analysis of pristine Cs<sub>2</sub>AgBiCl<sub>6</sub> and Cu-doped Cs<sub>2</sub>AgBiCl<sub>6</sub> DPs (HT-0, HT-10, HT-30 and HT-50) after 2.5 years. (a) PXRD patterns, color codes given in panel a are same for all the panels of this figure. (b) Absorbance spectra spectra (c) Images of fresh crystal and aged crystals of pristine Cs<sub>2</sub>AgBiCl<sub>6</sub> and Cu-doped Cs<sub>2</sub>AgBiCl<sub>6</sub> DPs after 2.5 years in ambient conditions.

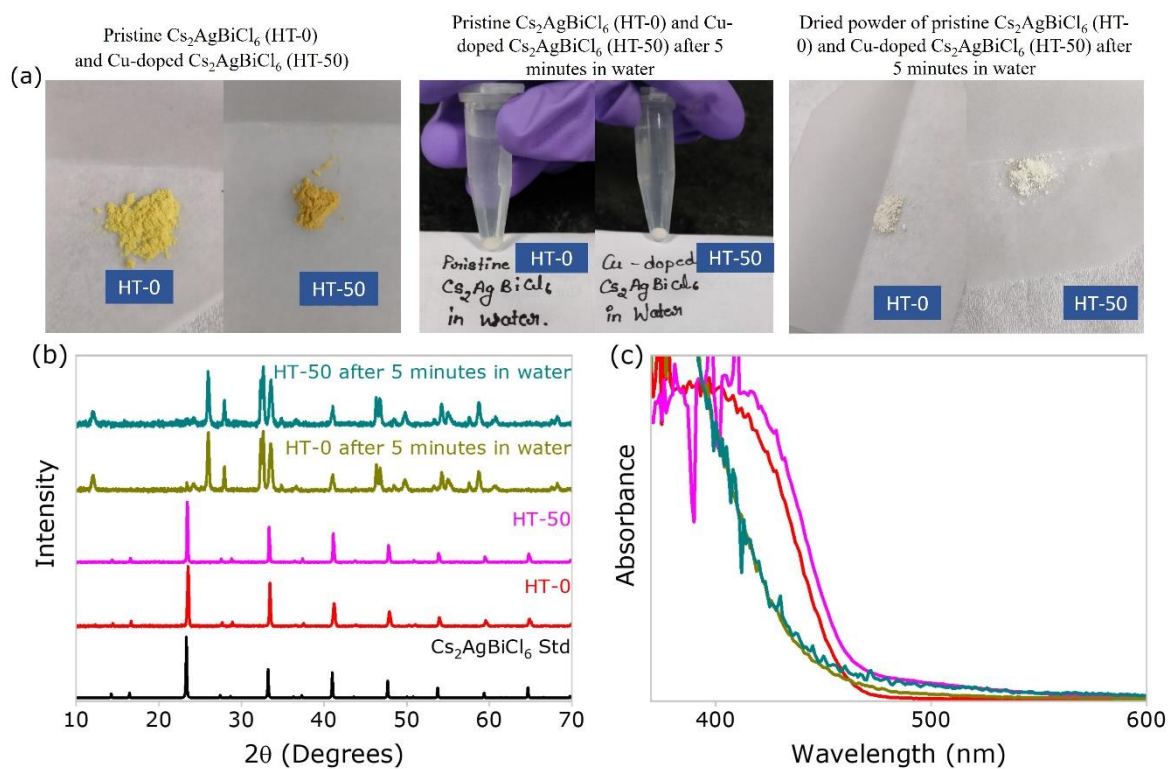


**Figure S6.** PXR D pattern of Cu-doped  $\text{Cs}_2\text{AgBiCl}_6$  (HT-50) DP after annealing it at different temperatures for 30 minutes in ambient conditions.

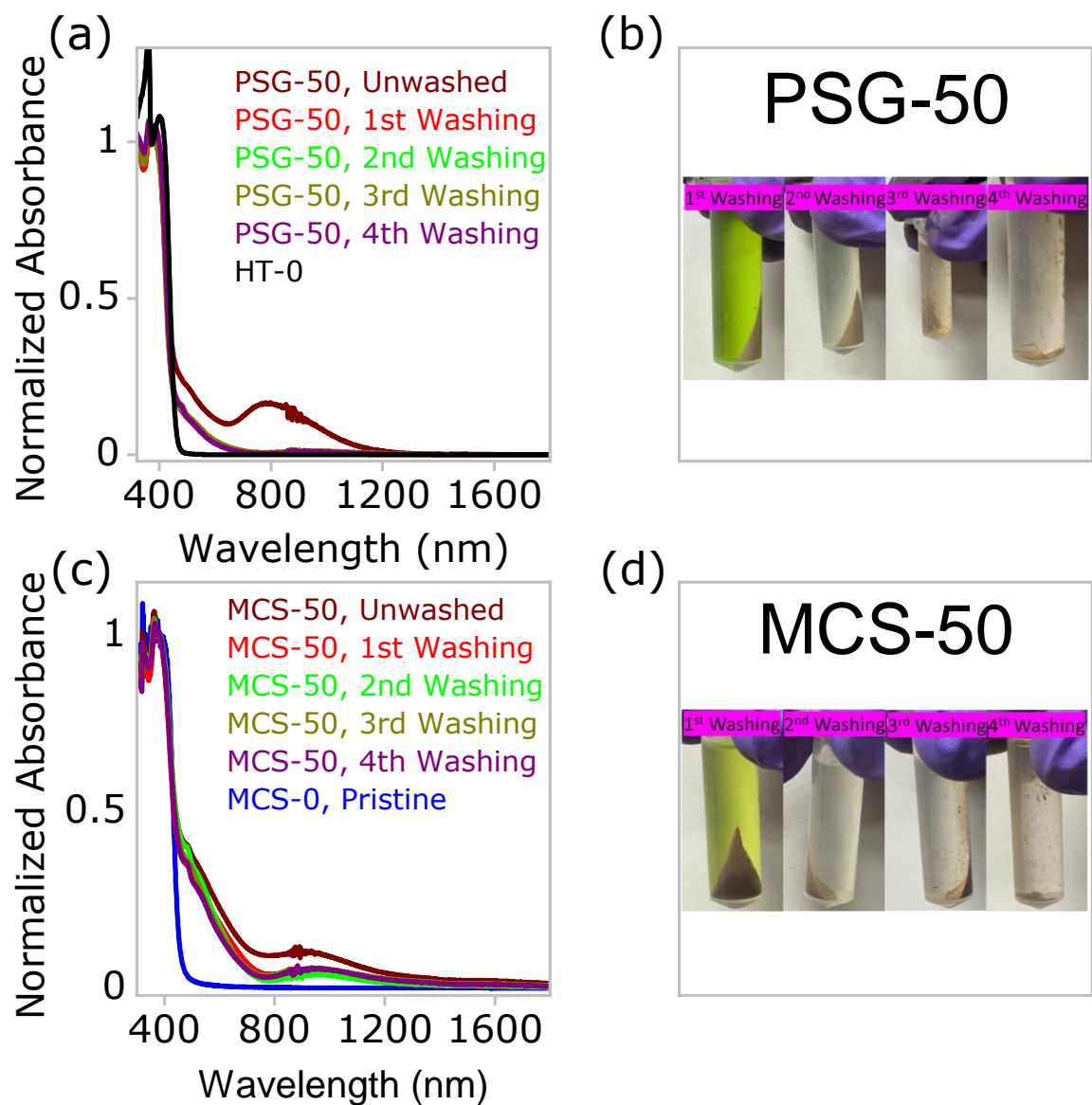


**Figure S7.** PXR D pattern of Cu-doped  $\text{Cs}_2\text{AgBiCl}_6$  (HT-50) DP after exposing it to the environment of 90% RH.





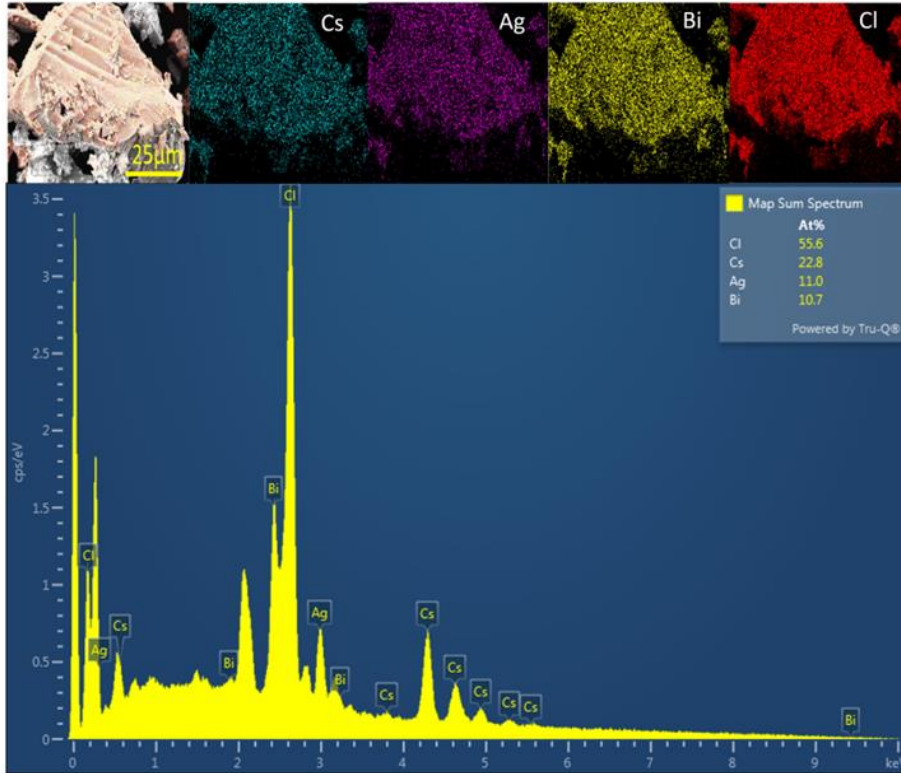
**Figure S8.** Water stability test of HT-0 and HT-50. (a) Images showing the change in colour of HT-0 and HT-50 after suspending in water. (b) PXRD pattern of HT-0 and HT-50 before and after suspending in water. (c) Absorbance spectra of HT-0 and HT-50 before and after suspending in water.



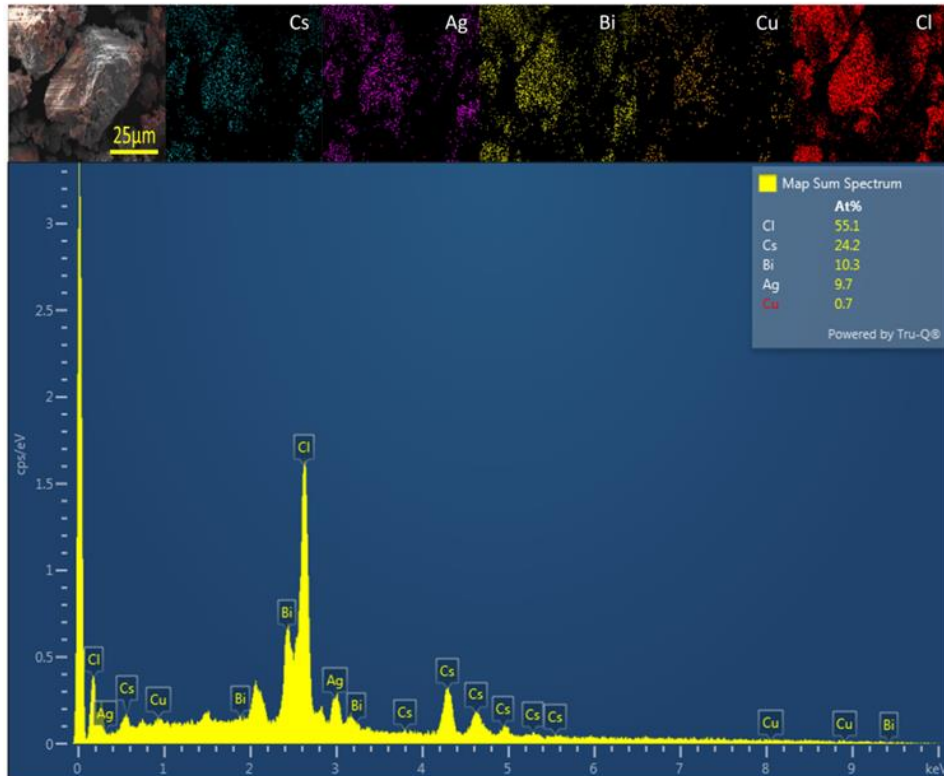
**Figure S9.** Analysis of effect of multiple washing on the PSG -50 and MCS-50. (a) Absorbance spectra of PSG-50. (b) Images showing multiple washing of PSG-50. (c) Absorbance spectra of PSG-50. (d) Images showing multiple washing of MCS-50.

# Elemental Analysis using FESEM.

## HT-0



## HT-50



**Figure S10.** FESEM EDX imaging and EDX of pristine Cs<sub>2</sub>AgBiCl<sub>6</sub> (HT-0) and Cu-doped Cs<sub>2</sub>AgBiCl<sub>6</sub> (HT-50).

## References

- 1 P. Kubelka and F. Munk, *Z. Tech. Phys*, 1931, **12**, 593–601.
- 2 F. Ji, Y. Huang, F. Wang, L. Kobera, F. Xie, J. Klarbring, S. Abbrent, J. Brus, C. Yin, S. I. Simak, I. A. Abrikosov, I. A. Buyanova, W. M. Chen and F. Gao, *Adv. Funct. Mater.*, 2020, **30**, 2005521.