

## Supporting Information

### Stabilizing black-phase CsPbI<sub>3</sub> under over 70% humidity

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## **Experimental**

### **Materials**

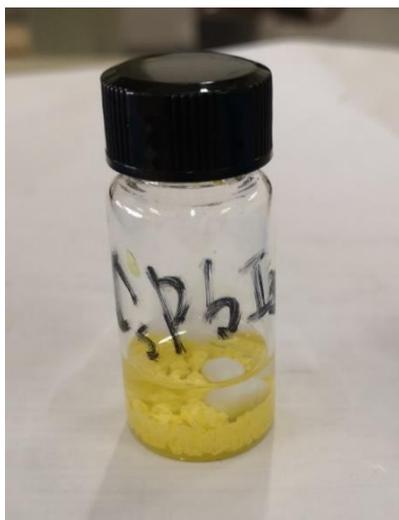
Unless stated otherwise, all materials and solvents were purchased from Sigma-Aldrich. Lead iodide ( $\text{PbI}_2$ , 99.999%) and Cesium iodide (CsI) purchased from Xi'an Polymer Light Technology Corp. 4-N, N-dimethylamino-4'-N'-methyl-stilbazolium tosylate (DAST) was purchased from Sekisui Medical Co. Ltd. All chemicals were used as received without further purification.

### **Perovskite ink preparation and film fabrication**

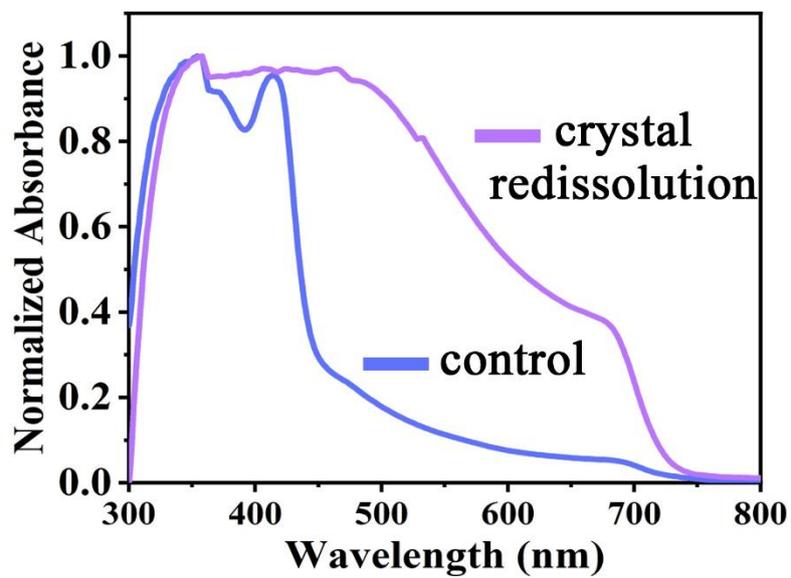
Firstly, an equal molar ratio of CsI and  $\text{PbI}_2$  was dissolved in a DMSO/DMF mixed solvent (1:4 in volume ratio). Then, it was quickly injected into the methanol antisolvent under vigorous stirring, which enabled the precipitation of  $\text{CsPbI}_3$  crystals immediately. Due to the poor solubility of  $\text{CsPbI}_3$  in methanol, the  $\text{CsPbI}_3$  crystals precipitated immediately. After centrifuging, the  $\text{CsPbI}_3$  powders were dried at 90 °C for 4 hours and then redissolved in the above-mentioned DMF/DMSO mixed solvent for preparing  $\text{CsPbI}_3$  perovskite ink. For the DAST-modified sample, 0.24 mM DAST was incorporated into the above-mentioned perovskite ink. The  $\text{CsPbI}_3$  perovskite films were fabricated by spin-coating the 70 °C pre-heated perovskite ink onto the 70 °C pre-heated substrate at a spin rate of 4000 rpm for 50 s in ambient air, and no antisolvent and subsequent annealing process were required.

### **Characterization**

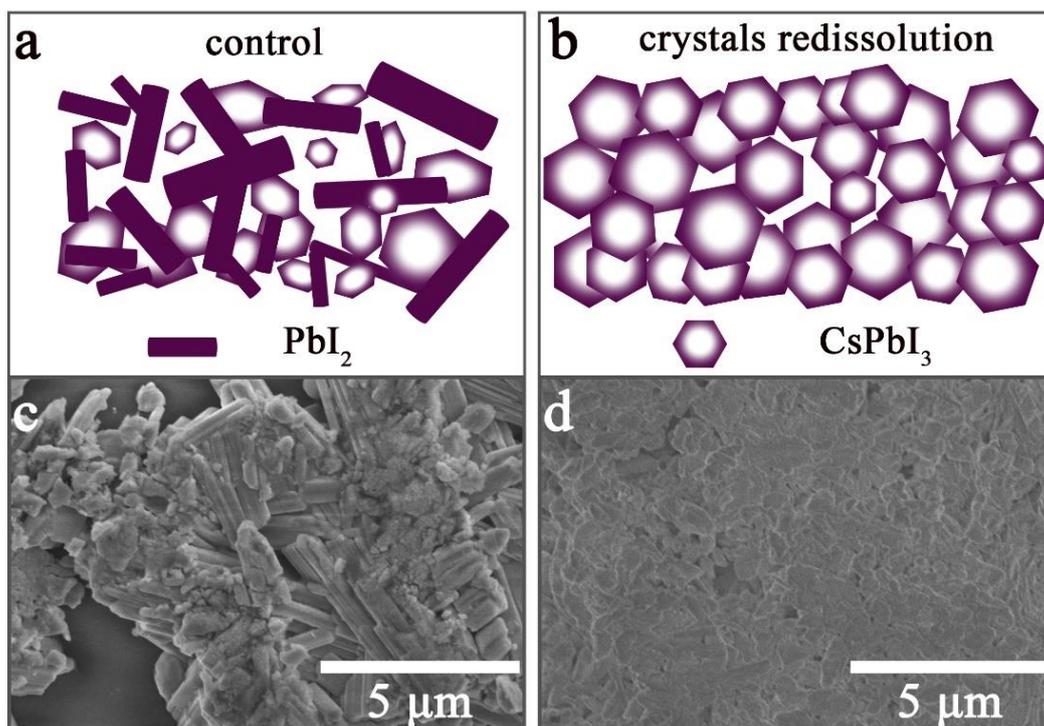
The UV-vis absorption spectra of the  $\text{CsPbI}_3$  films were obtained from the UV-3600 spectrophotometer (Shimadzu). The morphologies and surface coverage of the samples were characterized using a field emission scanning electron microscope (SEM, Hitachi-SU8010). The XRD patterns of the samples were measured on an X-ray diffractometer (Bruker D8 ADVANCE). Fourier-transform-infrared (FTIR) characterization was conducted by using an infrared spectrometer (Frontier, 16A01828).



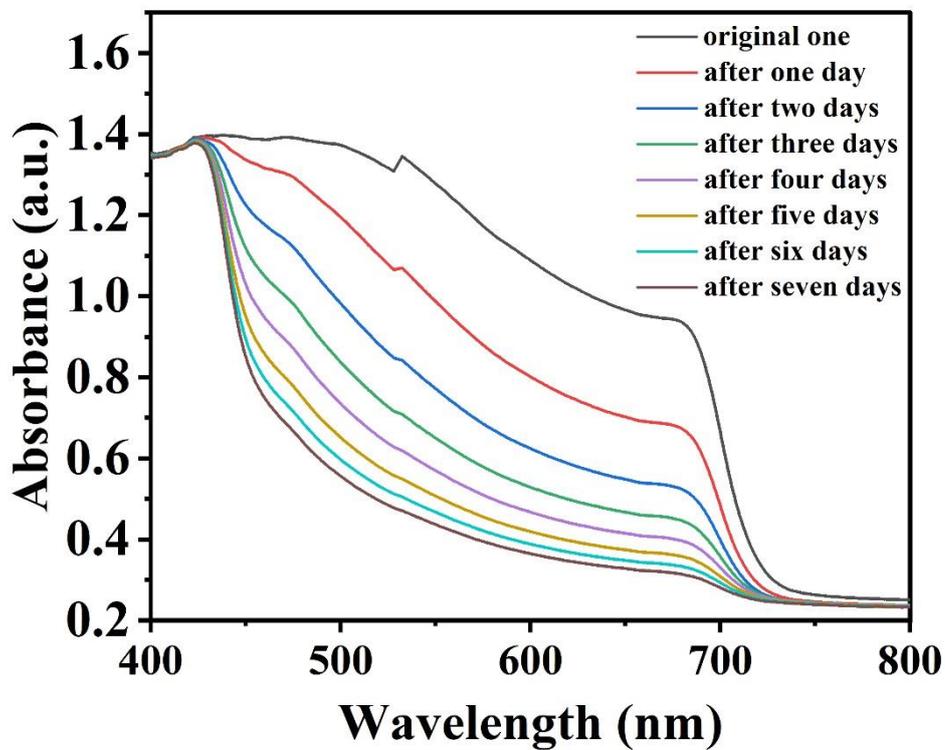
**Figure S1.** The photo of the CsPbI<sub>3</sub> crystals obtained via antisolvent-assisted precipitation strategy.



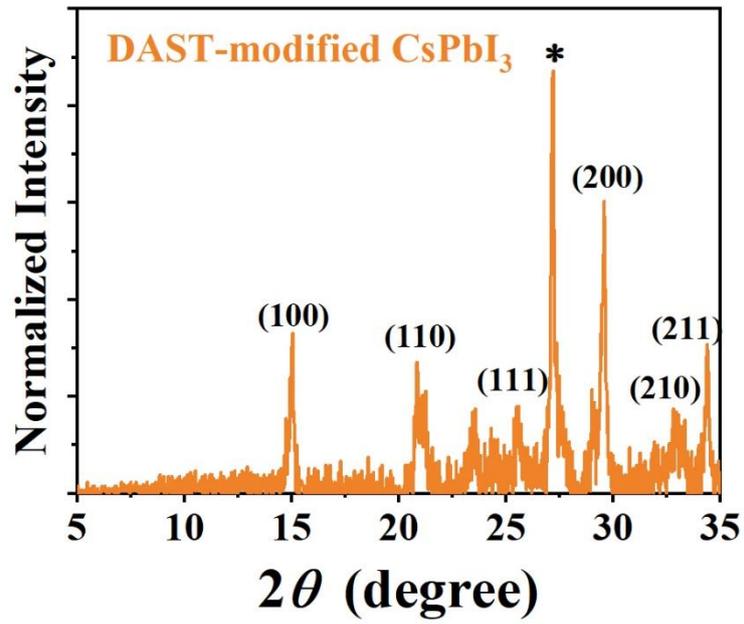
**Figure S2.** The absorbance spectra of the resultant CsPbI<sub>3</sub> films and as indicated.



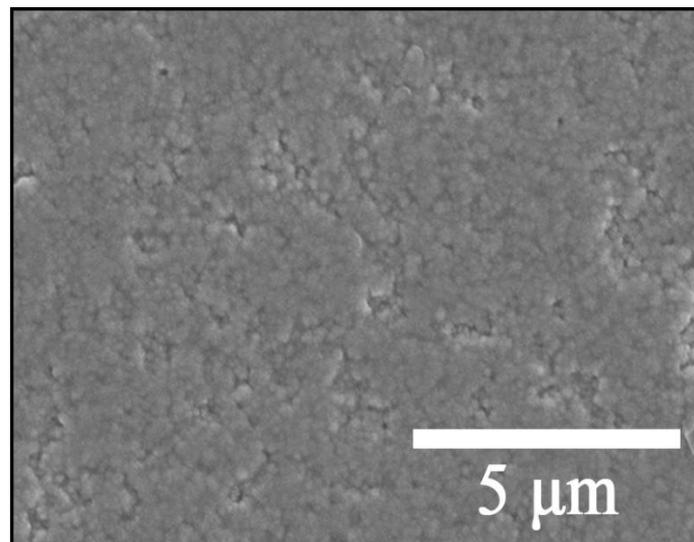
**Figure S3.** Sketch and SEM images of (a, c) control CsPbI<sub>3</sub> film and (b, d) crystal redissolution-derived CsPbI<sub>3</sub> film.



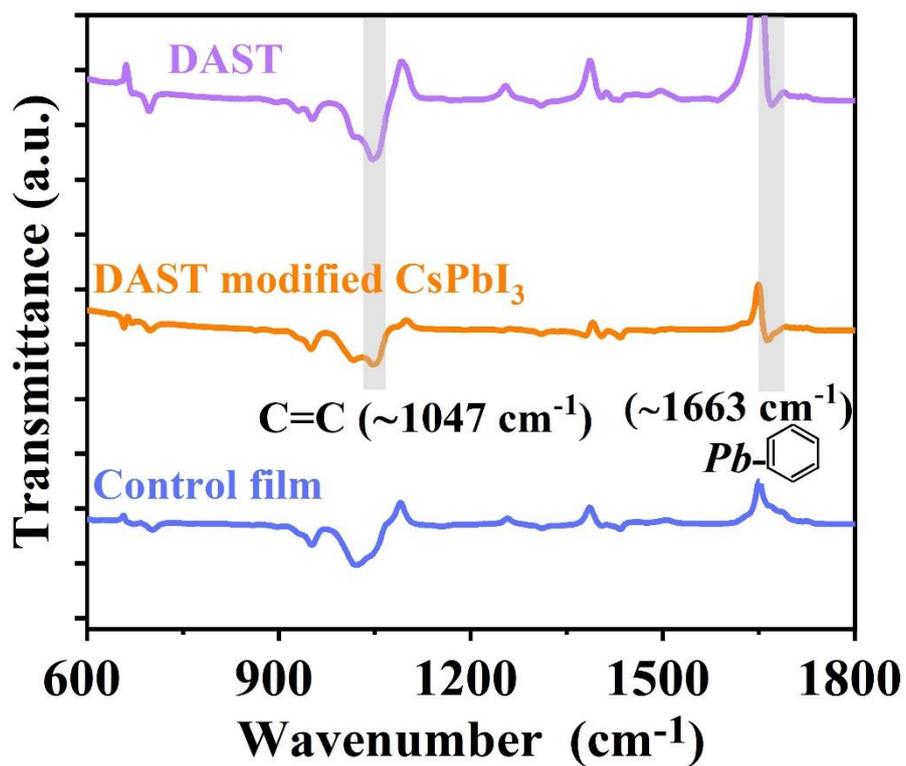
**Figure S4.** The absorbance spectra of the crystal redissolution-derived CsPbI<sub>3</sub> film, which has been stored in air for one week.



**Figure S5.** The XRD pattern of the DAST-modified CsPbI<sub>3</sub>.



**Figure S6.** SEM image of the DAST-modified CsPbI<sub>3</sub> film.



**Figure S7.** FTIR spectra of DAST powder, DAST-modified CsPbI<sub>3</sub> film and pristine CsPbI<sub>3</sub> film.