



## Supporting Information

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Unveiling the Effects of Hydrolysis-Derived DMAI/DMAPbI<sub>x</sub>  
Intermediate Compound on the Performance  
of CsPbI<sub>3</sub> Solar Cells

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### **Unveiling the Effects of Hydrolysis-Derived DMAI/DMAPb<sub>x</sub> Intermediate Compound on Performance of CsPbI<sub>3</sub> Solar Cells**

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## Experimental

### *Solution Preparation Section*

*Materials preparation:* Dimethyl formamide (DMF), Dimethyl sulfoxide (DMSO), 4-tert-butylpyridine (TBP), bis (trifluoromethylsulfonyl) imidelithium salt (Li-TFSI), and chlorobenzene were purchased from Sigma-Aldrich.  $\text{PbI}_2$ , CsI, and  $\text{PbBr}_2$  were purchased from Xi'an Polymer Light Technology Corp. All materials were used as received without further purification.

*Precursor solution preparation:* The syn- $\text{PbI}_2$  was prepared by using  $\text{PbI}_2$  (1.2 g) dissolved in 2.5 mL DMF at 80 °C under active stirring for 30 min in air atmosphere. Immediately after, different volumes of HI (2.5 mL, 5 mL, 7.5 mL, 10 mL, 12.5 mL) were added to the solution for 2 h and dry overnight using a vacuum oven. Finally, 0.7022 g syn- $\text{PbI}_2$ , 0.1468 g  $\text{PbBr}_2$  and 0.3638 g CsI were added to the solution of 2 mL DMF and DMSO (9:1) under active stirring for 1 h. The  $\text{CsPbI}_3$  precursor solutions were prepared. For comparison, we prepared the same ratio of solutions using  $\text{PbI}_2$  purchased directly.

*HTL solution preparation:* A solution was prepared by dissolving PTAA (36 mg), a sulfonyl imide (Li-TFSI, 22  $\mu\text{L}$ , 520 mg Li-TFSI in 1 mL acetonitrile), and tert-butylpyridine (TBP, 36  $\mu\text{L}$ ) in 1 mL of CB solution.

### *Device Fabrication Section*

*Preparation of  $\text{TiO}_2$ -blocking layer:* FTO-coated glass was washed and  $\text{O}_2$ -plasma-treated for 15 min before the deposition of  $\text{TiO}_2$ . The clean substrates were immersed in a 40 mM  $\text{TiCl}_4$  aqueous solution for 1h at 70 °C and washed with distilled water and ethanol, followed by annealing at 200 °C for 30 min in air to form a compact  $\text{TiO}_2$  layer.

*Growth of the  $\text{CsPbI}_3$  film:* The  $\text{CsPbI}_3$  layer was fabricated via one-step spin-coating. The mixed solution was spin-coated on top of  $\text{O}_2$ -plasma-treated  $\text{TiO}_2$  substrate at 1000 rpm for 10 s. The speed was then increased to 3500 rpm and maintained 40 s. Finally, the films were annealed at 180 °C for 15min to form the films.

*Assembly of the solar cells:* An HTL film was prepared by spin-coating the HTL solution onto the  $\text{CsPbI}_3$  film at 5000 rpm for 30 s. A 70-nm-thick gold electrode was then thermally evaporated onto the HTL-coated film.

### *Characterization Section*

*SEM and AFM:* The film surface morphology, elemental distribution, and cross-sectional images were characterized by field emission scanning electron microscope (FESEM, Jeol SU-8020). Atomic force microscope (AFM, Bruker Dimension 5000 Scanning Probe Microscope) was used to measure surface roughness of the perovskite film in “tapping” mode.

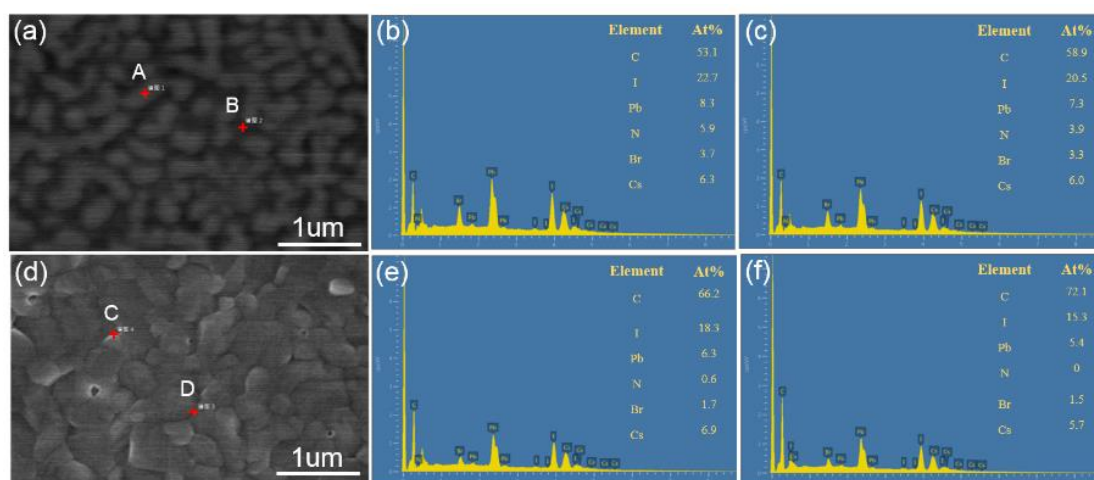
*Absorbance and PL:* Absorbance spectra were collected using a Shimadzu UV-3600 double beam spectrometer using the slowest scanning rate with one-second integration and a 2 nm slit width. The PL spectra were measured using a PicoQuant FluoTime 300.

The source light was a xenon short arc lamp. PL (excitation at 532 nm) spectra were measured using a FLS980 spectrometer (Edinburgh Instruments Ltd)

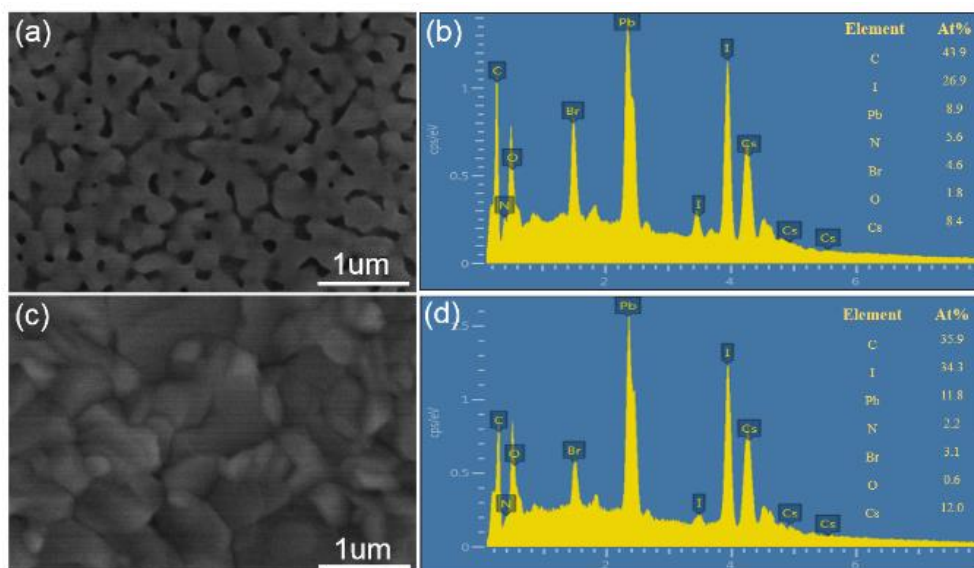
**XRD, FTIR, NMR and XPS:** XRD patterns of the samples were obtained using a Bruker D8 GADDS Diffractometer with the Cu K $\alpha$  line. FTIR spectra were measured with a Bruker Vertex 70. NMR was performed by using JNM-ECZ400S/L1 with a frequency of 400 MHz and deuterated DMSO was used as solvent. The XPS measurements were performed in a VG ESCALAB MK2 system with monochromatized Al K $\alpha$  radiation at a pressure of  $5.0 \times 10^{-7}$  Pa. XPS was carried out by using a photoelectron spectrometer (ESCALAB250Xi, Thermo Fisher Scientific).

**J-V and EQE:** The active area of solar cell was restrained by a 9 mm<sup>2</sup> metal mask. The J–V characteristics of the PSCs were collected by using a digital source meter (Keithley Model 2400) under an illumination of an AM 1.5 solar simulator (100 mW cm<sup>-2</sup>, SS-F5-3A, Enlitech), as calibrated by a NREL-traceable KG5-filtered silicon reference cell. This used reverse scan mode (from V<sub>OC</sub> to I<sub>SC</sub>) and forward scan mode (from I<sub>SC</sub> to V<sub>OC</sub>) with a scan rate of 30 mV/s. The external quantum efficiency (EQE) data were obtained by solar-cell spectral-response measurement system (QE-R3011, Enlitech). The monochromatic light intensity for EQE was calibrated using a reference silicon detector.

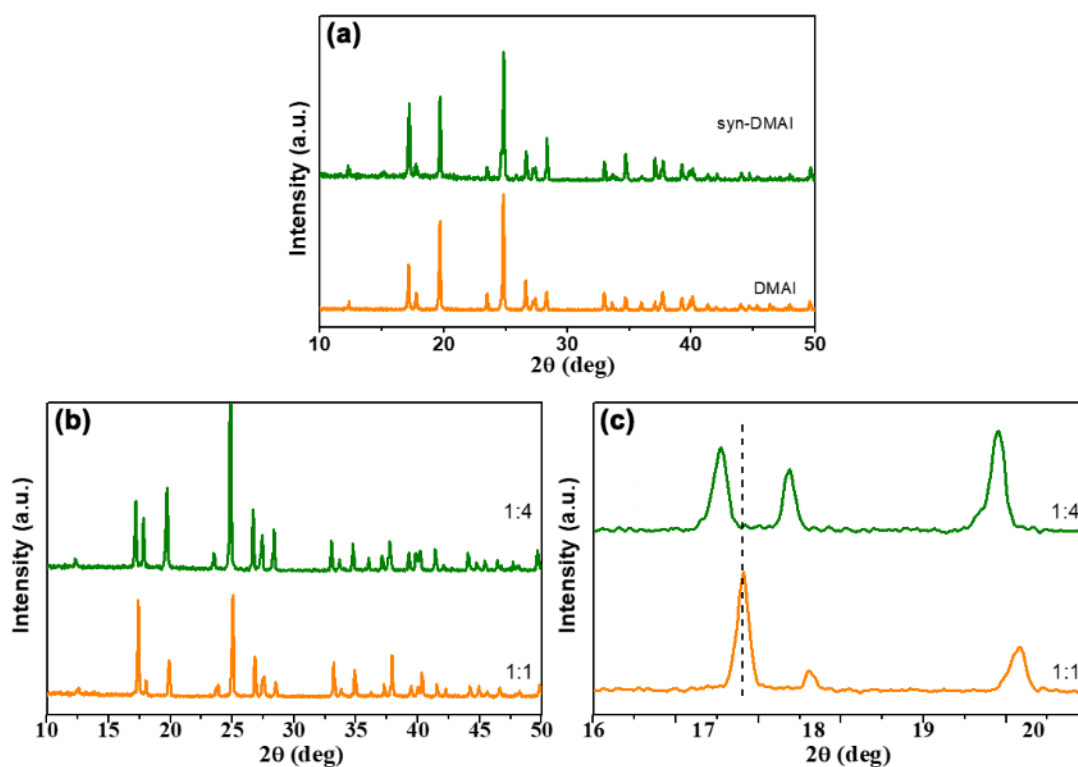
**Long-term stability analysis:** The steady photocurrent and PCE were measured at the maximum power point. The long-term stability was measured after storage in air (relative humidity of 30%-40% at 25 °C) over 7 days without any encapsulation. To test the device heat stability, we put the unencapsulated device in a nitrogen glovebox with 80 °C for 30 days.



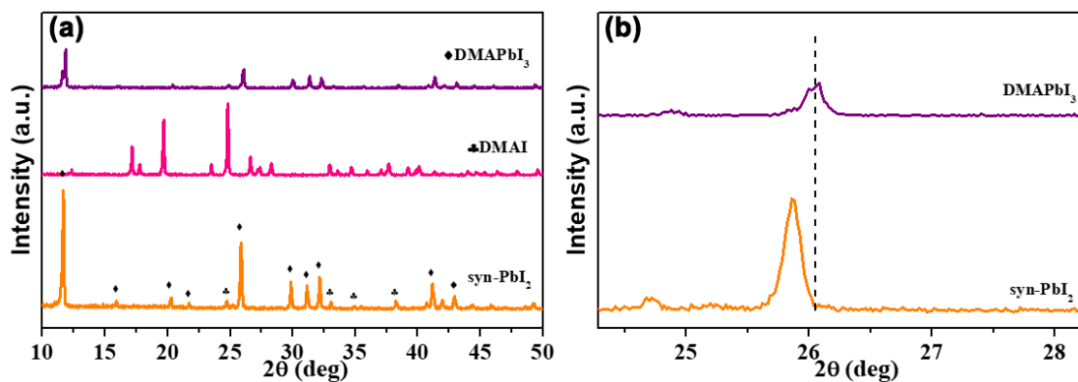
**Figure S1. Characterization of the Syn-CsPbI<sub>3</sub> Film** (a) The SEM image of unannealed syn-CsPbI<sub>3</sub> film. (b) and (c) are the EDX spectra of points A and B in **Figure S1a**, respectively. (d) The SEM image of annealed syn-CsPbI<sub>3</sub> film. (e) and (f) are the EDX spectra of points C and D in **Figure S1d**, respectively.



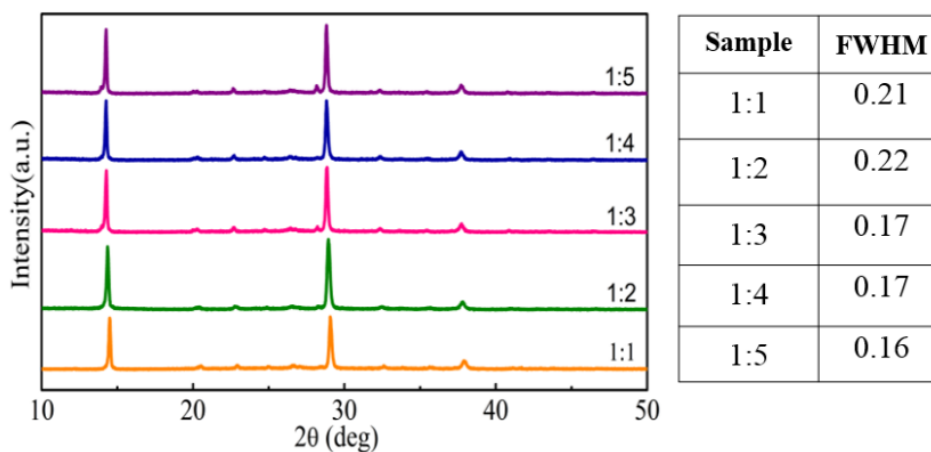
**Figure S2. Characterization of the Syn-CsPbI<sub>3</sub> Film.** The SEM image and EDX spectra of (a)-(b) unannealed syn-CsPbI<sub>3</sub> film. (c)-(d) annealed syn-CsPbI<sub>3</sub> film.



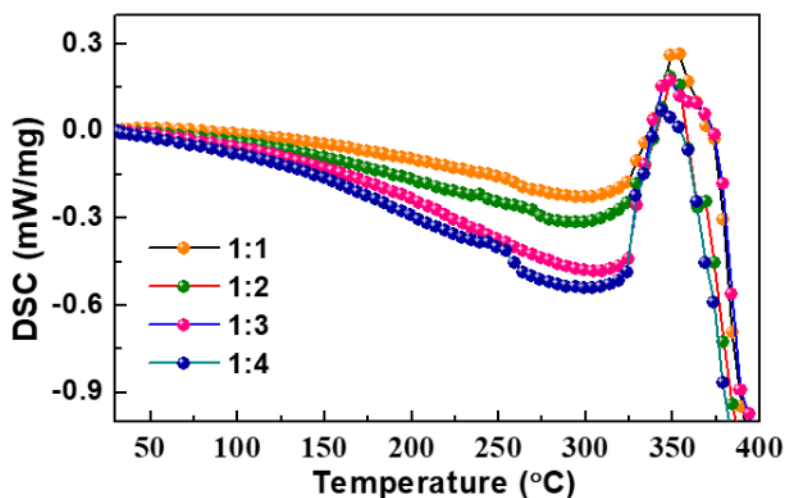
**Figure S3. Characterization of Syn-DMAI Powder.** (a) XRD patterns of purchased DMAI and syn-DMAI; (b) XRD patterns of syn-DMAI using different HI ratios; (c) corresponding magnification of a portion of the XRD patterns.



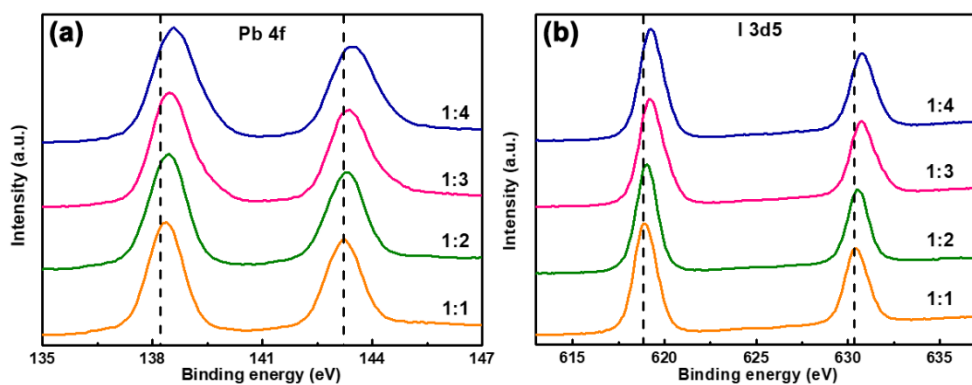
**Figure S4. Films and Powders Component Studies.** XRD patterns of (a) the syn-PbI<sub>2</sub> powder, DMAI and DMAPbI<sub>3</sub>; (b) the corresponding magnification of a portion for syn-PbI<sub>2</sub> powder and DMAPbI<sub>3</sub>.



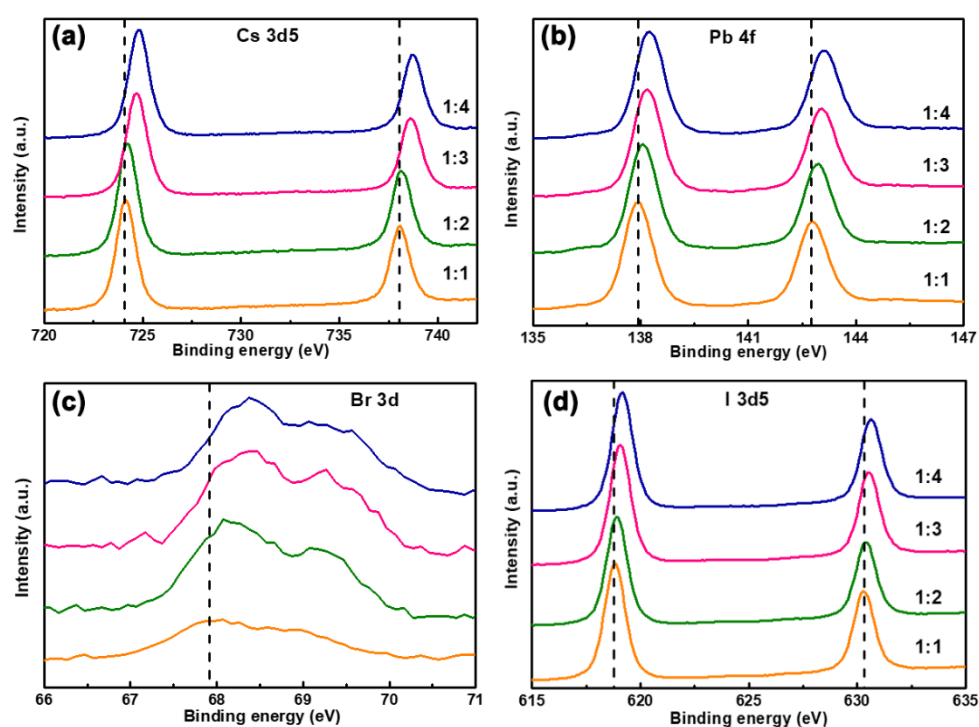
**Figure S5.** XRD patterns of syn-CsPbI<sub>3</sub> films and the corresponding FWHM of the peaks (110).



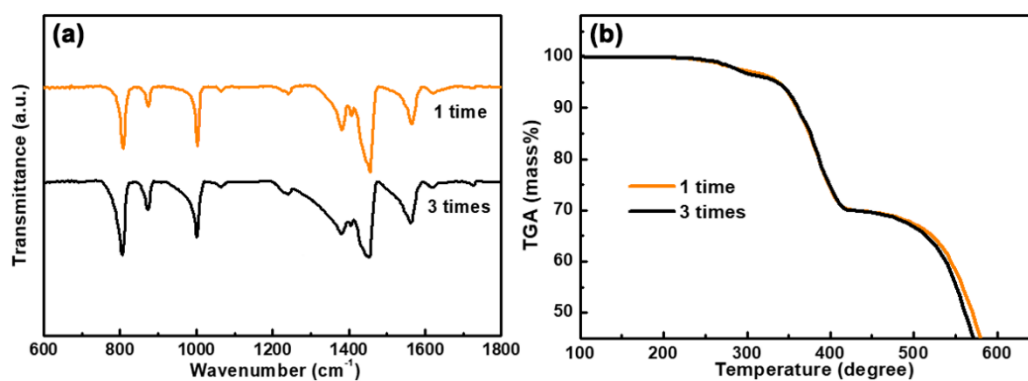
**Figure S6.** DSC curves of Syn-PbI<sub>2</sub> Powder.



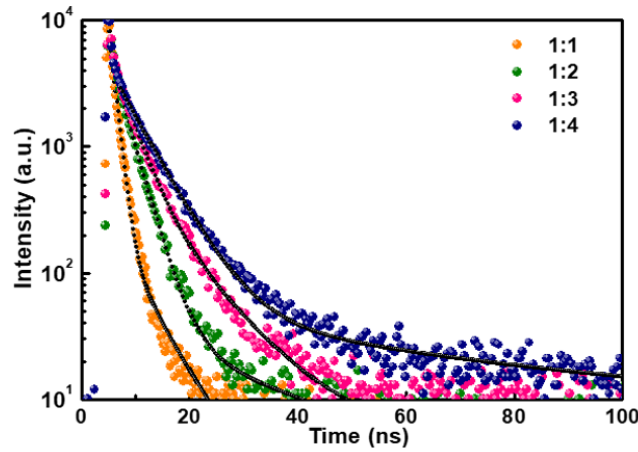
**Figure S7.** XPS spectra of (a) Pb 4f; (b) I 3d5 in syn-PbI<sub>2</sub> powder.



**Figure S8.** XPS spectra of (a) Cs 3d5; (b) Pb 4f; (c) Br 3d; and (d) I 3d5 in syn-CsPbI<sub>3</sub> film.



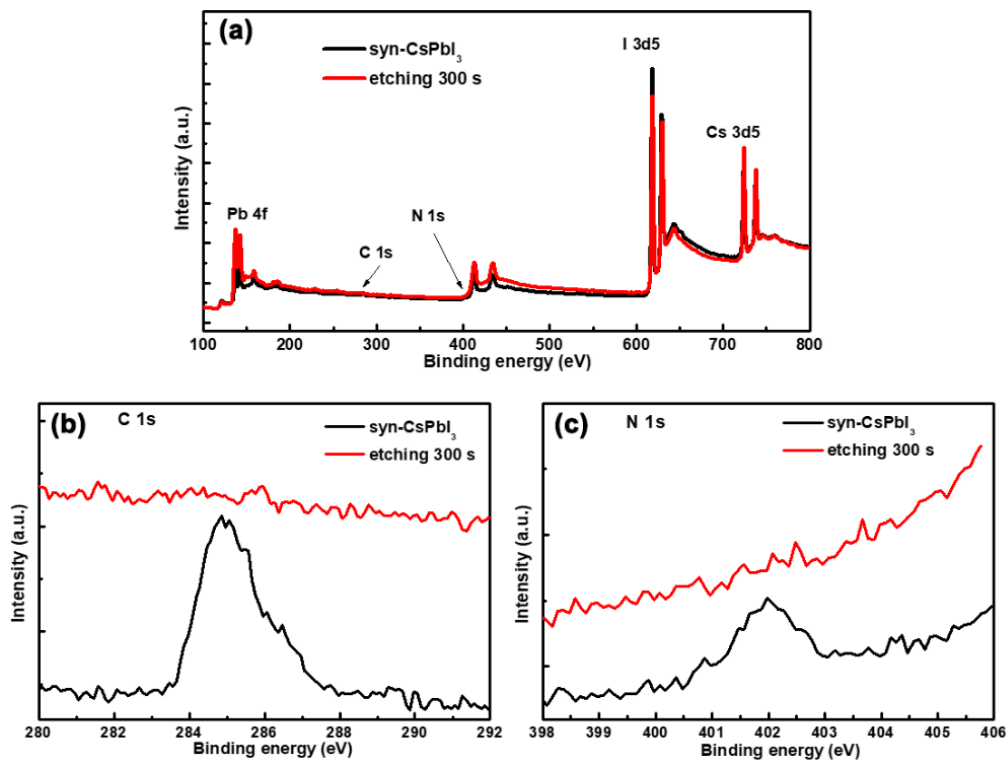
**Figure S9.** Different purification times for syn-PbI<sub>2</sub>: (a) FTIR spectra; (b) TGA curves.



**Figure S10.** TRPL decay curves for syn-CsPbI<sub>3</sub> films.

**Table S1.** TRPL spectroscopy fitting parameters of the syn-CsPbI<sub>3</sub> films (extracted from **Figure S10**).

Sample	$T_{ave}$ (ns)	$T_1$ (ns)	amplitude $\tau_1$ (%)	$T_2$ (ns)	amplitude $\tau_2$ (%)
1:1	1.56	5.63	11.15	1.05	88.85
1:2	4.18	18.76	8.85	2.76	91.15
1:3	4.76	8.9	29.25	3.04	70.75
1:4	10.87	48.01	12.74	5.45	87.26

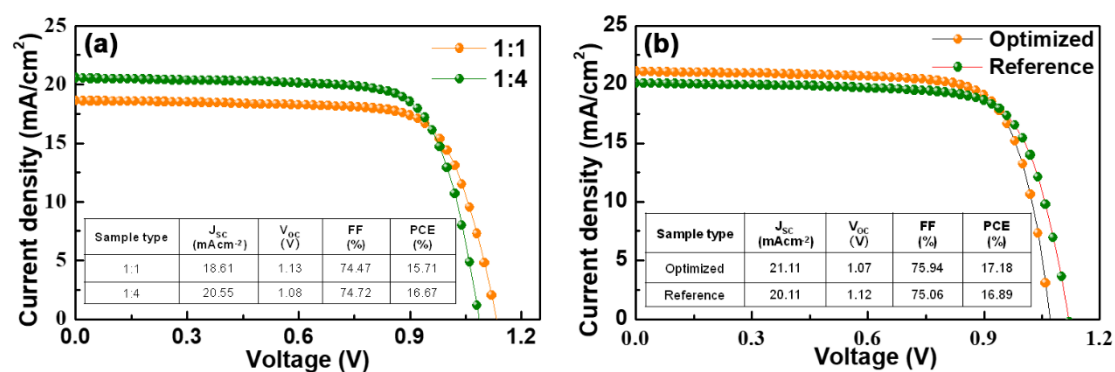


**Figure S11.** (a) XPS spectra of syn-CsPbI<sub>3</sub> film before and after etching 300 s; (b) C 1s; (c) N 1s.

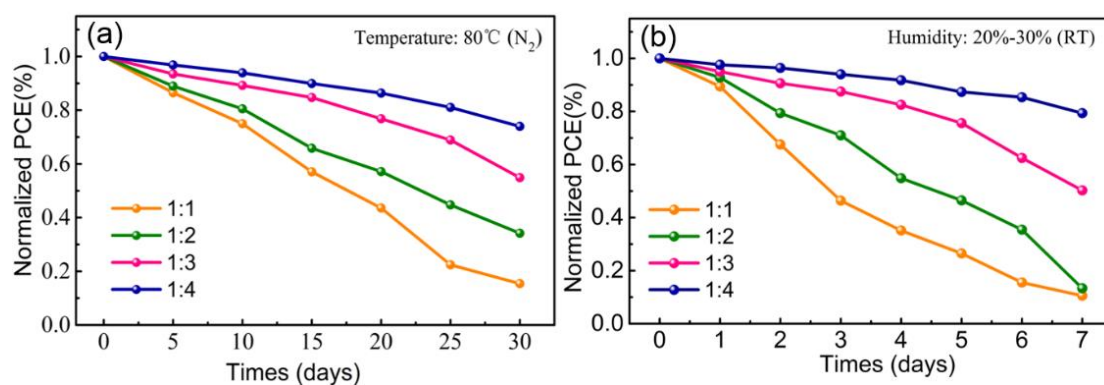


**Table S2.** The measured elements value of the XPS spectra of syn-CsPbI<sub>3</sub> film before and after etching 300 s (extracted from **Figure S11a**).

Element	C	I	Pb	N	Br	O	Cs
At% (0nm)	18.73	43.6	12.94	0.07	3.88	2.19	18.59
At% (0nm)	0	46.85	20.48	0	8.1	0	24.57



**Figure S12. Photovoltaic Performance of Syn-CsPbI<sub>3</sub> PSCs.** (a) J-V curves of 1:1 and 1:4 samples after longer annealing process; (b) J-V curves for 1:4 sample of optimized device and reference device with longer annealing process.



**Figure S13.** Long-term stability of the best-performing device stored: (a) in N<sub>2</sub> atmosphere at 80 °C; (b) in air at relative humidity of 20%-30%.