Supporting information

Efficient two-dimensional $Cs_2PbI_2(SCN)_2$ perovskite solar cells via intermediate-modulated crystallization

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Methods for fitting and numerical calculation:

(a) Time-resolved photoluminescence (TRPL)

The TRPL curves were fitted with a bi-exponential decay function to describe the process of charge extraction.

$$I(t) = A_1 e^{(-t/\tau_1)} + A_2 e^{(-t/\tau_2)} + \gamma_0 \tag{1}$$

τ_1 is the rapid decay of charge transfer from perovskite to adjacent layers through the boundary, τ_2 is the slow recombination of charges in the perovskite layer.

(b) Space charge limited current

The trap density can be calculated from the following equation (2):

$$V_{TFL} = \frac{q N_t L^2}{2\varepsilon_r \varepsilon_0} \tag{2}$$

where L is the thickness of the perovskite film, ε_r is the relative dielectric constant of perovskite, ε_0 is the vacuum permittivity (8.854×10^{-12} F/m), q is the unit charge with the value of 1.602×10^{-19} C, and N_t is the trap density. Through the capacitance (C) – voltage (V) measurement and equation (3) the perovskite dielectric constant (ε_r) is calculated:

$$C = \frac{\varepsilon_r \varepsilon_0 S}{d} \tag{3}$$

where C, ε_0, S, and D represent capacitance, vacuum dielectric constant, device area, and perovskite film thickness, respectively.

(c) Density functional theory (DFT) calculations

In this work, the DFT calculations were performed by the Cambridge serial total energy package (CASTEP)[1] code, in which a plane wave basis set was used. The exchange and correlation interactions were modeled using the generalized gradient approximation (GGA) and the Perdew–Burke–Ernzerhof (PBE)[2] functional. The Vanderbilt ultrasoft pseudopotential[3] was used with a cutoff energy of 450 eV. Geometric convergence tolerances were set for maximum force of 0.03 eV/ Å, maximum energy change of 10^{-5} eV/atom, maximum displacement of 0.001 Å and maximum stress of 0.5 GPa. The sampling in the Brillouin zone was set with $3\times3\times1$ by the Monkhorst-Pack method.

The substitution energy of iodine for chlorine is defined as:

$$E_s = E_{SCNCsPbI(x+1)Cl(y-1)} - E_{SCNCsPbIxCly} + E_{FAI(z-1)Cl(z+1)} - E_{FAI(z+1)Cl(z-1)} \tag{4}$$

The incorporation energy of iodine into the SCNCsPbICl/SCNCsPbI system is defined as:

$$E_{Incorporation} = E_{SCNCsPbI(x+1)Cly} - E_{SCNCsPbIxCly} - E_I \tag{5}$$
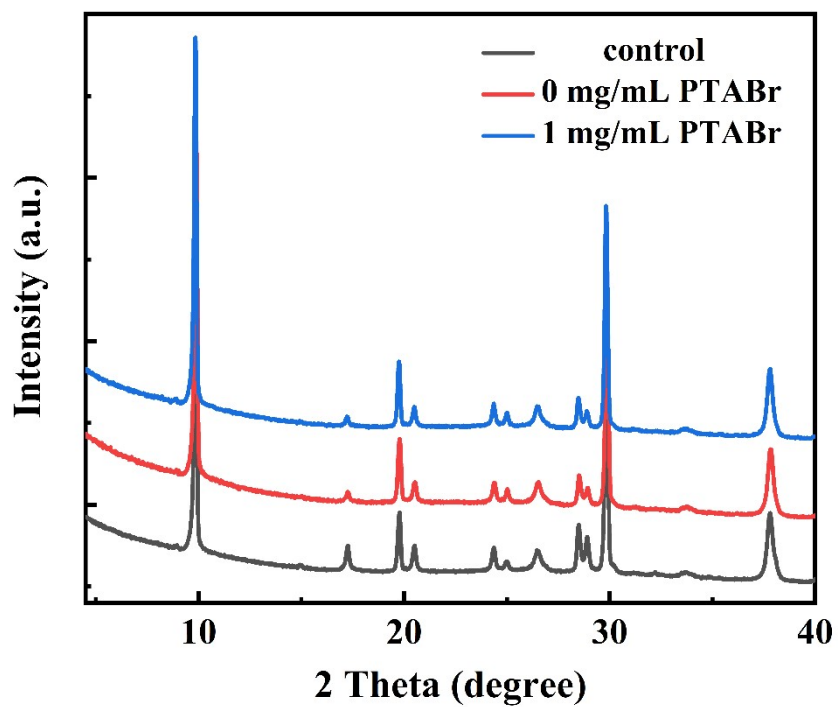
Figure S1. XRD patterns of $Cs_2PbI_2(SCN)_2$ control film without any post-treatment, film after post-treatment with neat isopropanol solution, i.e., containing 0 mg/mL PTABr, and film after post-treatment with isopropanol solution containing 1 mg/mL PTABr.
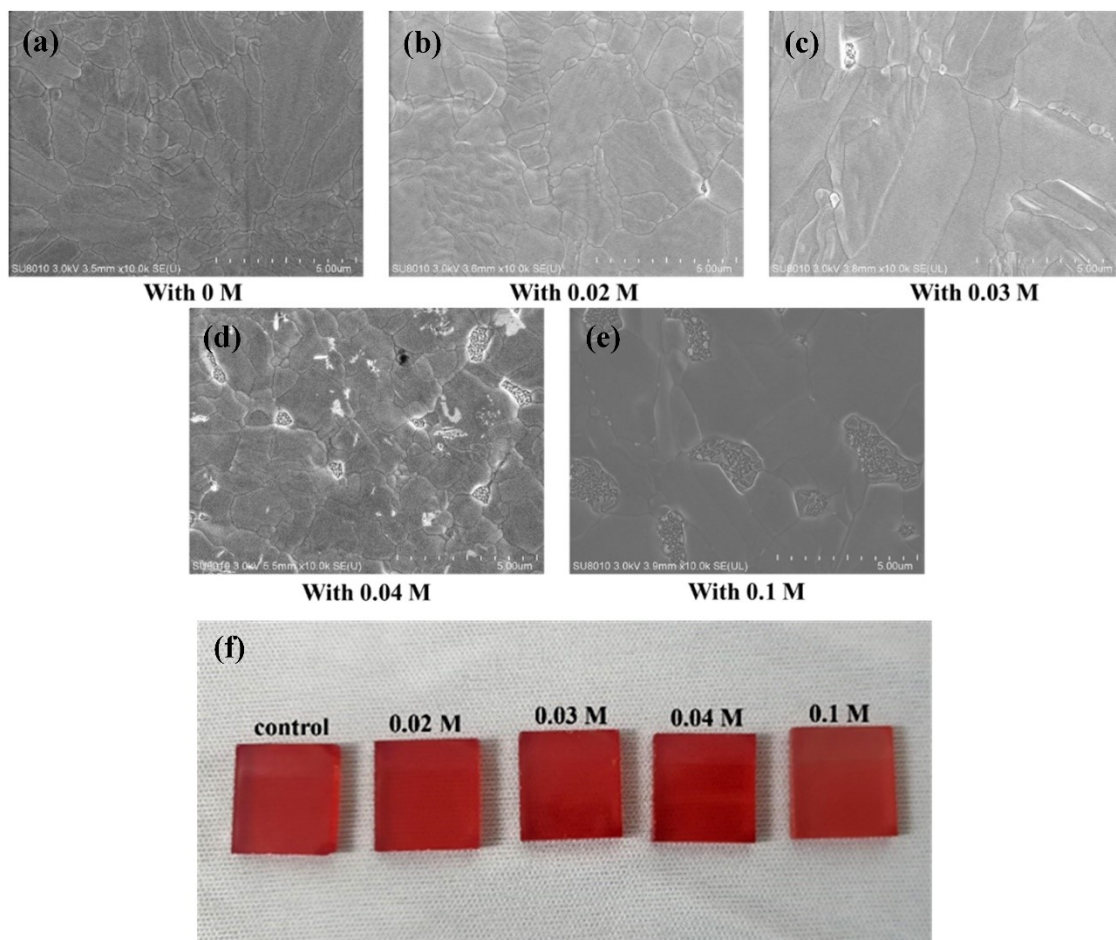
Figure S2. (a)-(e) SEM images of $Cs_2PbI_2(SCN)_2$ thin films prepared by adding different amounts of FACl. (f) Optical photographs of $Cs_2PbI_2(SCN)_2$ films prepared with different amounts of FACl.
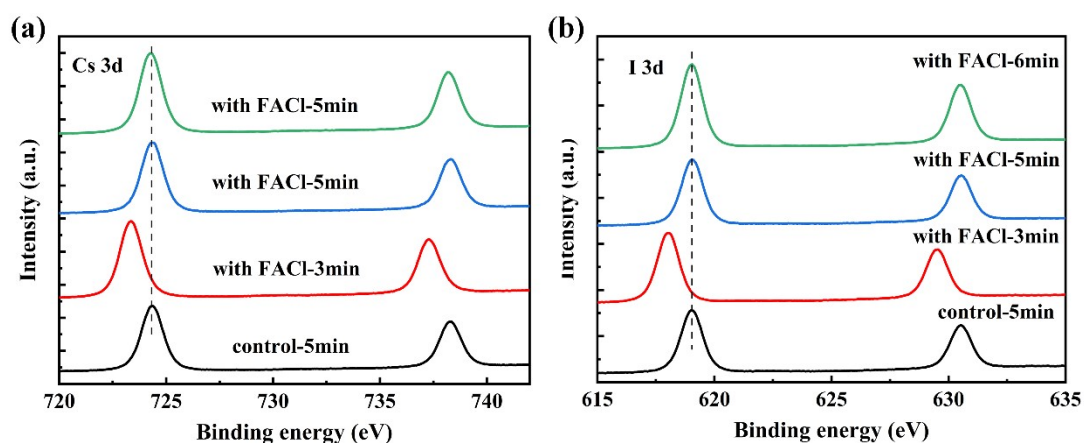
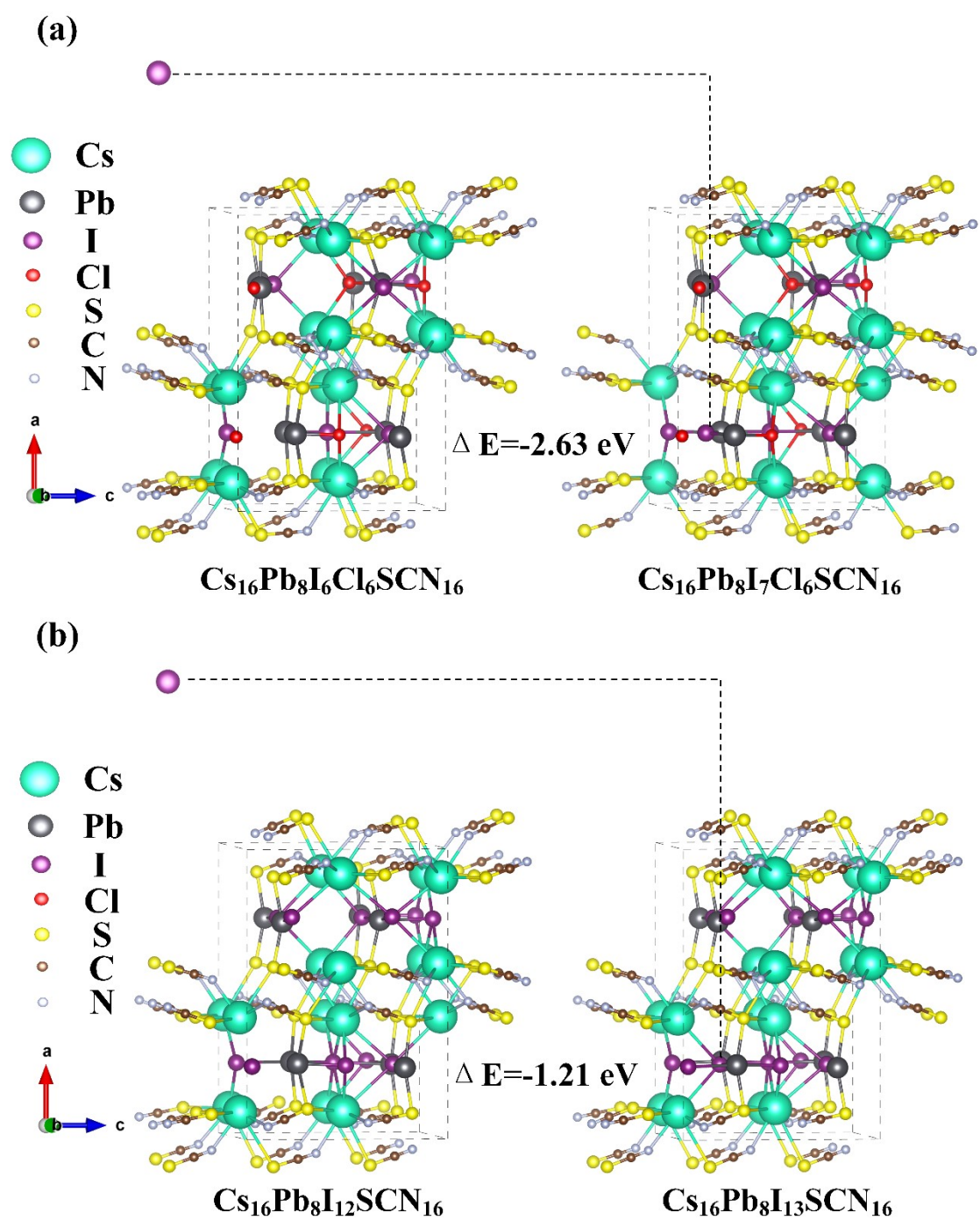**Figure S3.** XPS patterns for (a) Cs $3d$ and (b) I $3d$ for $Cs_2PbI_2(SCN)_2$ control sample, and films prepared with 0.02 M FACl additive and annealed for 3, 5 and 6 mins.
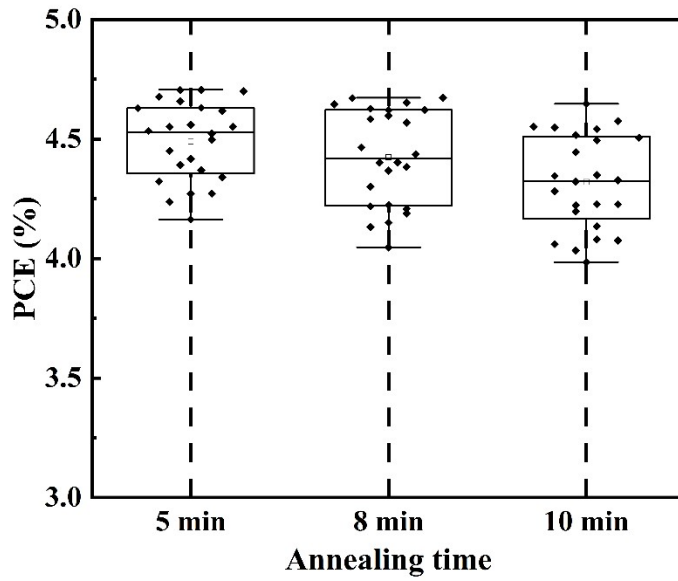
Figure S4. Statistical-results for the PCE values of the devices based on the $Cs_2PbI_2(SCN)_2$ films with prolonged annealing times.
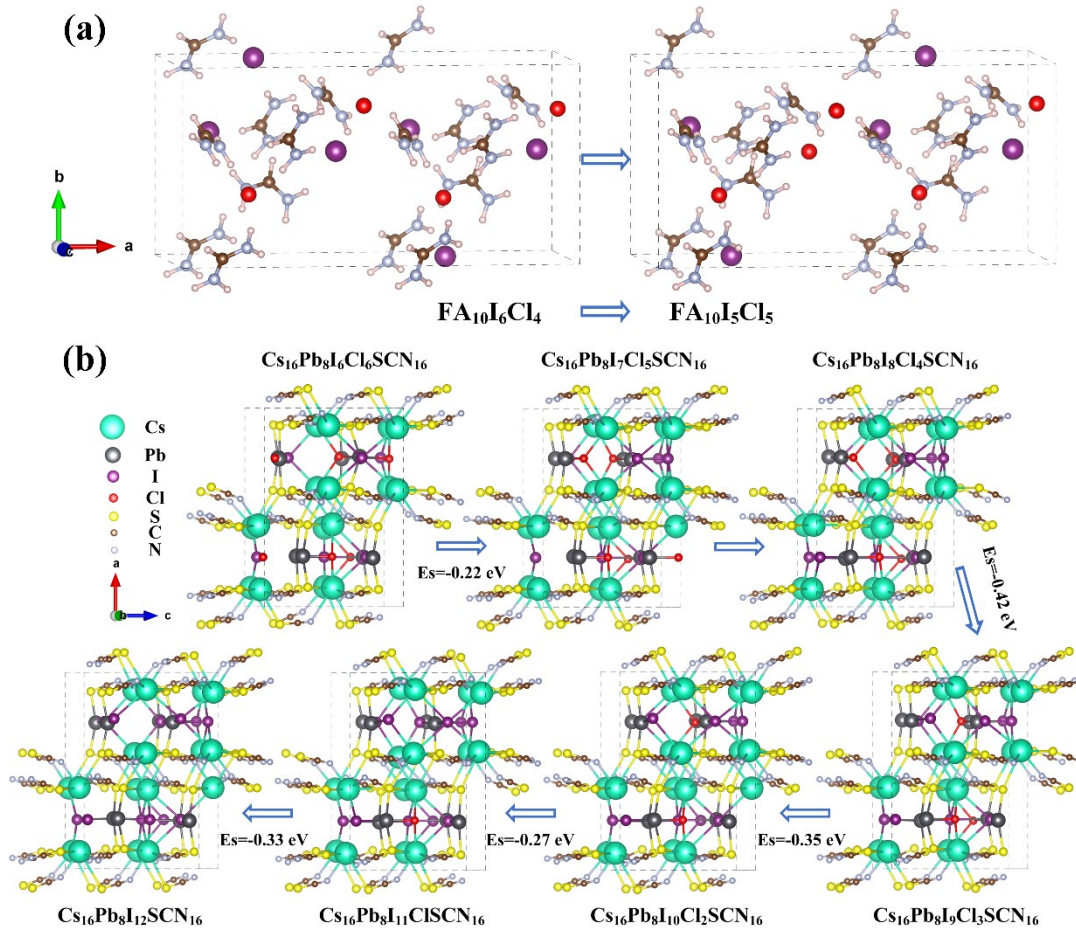

Figure S5. (a) Presence of elements I and Cl in the form of amorphous structures formed with FA cations. (b) substitution energy for I to replace Cl.

(a)

$Cs_{16}Pb_8I_6Cl_6SCN_{16}$ $\Delta E = -2.63$ eV   **$Cs_{16}Pb_8I_7Cl_6SCN_{16}$**

(b)

$Cs_{16}Pb_8I_{12}SCN_{16}$ $\Delta E = -1.21$ eV   **$Cs_{16}Pb_8I_{13}SCN_{16}$**

Figure S6 (a) Energy difference between I–Cl mixed structure after addition of an I atom from the outside, (b) energy difference between pure I structure after addition of an I atom from outside.
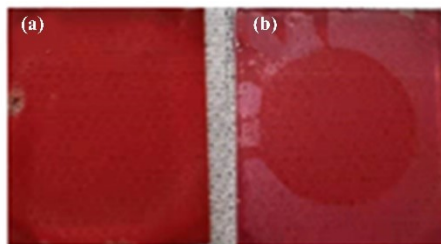
Figure S7. Optical photos of spiro-OMeTAD coated $Cs_2PbI_2(SCN)_2$ film (a) with / (b) without PTABr treatment.
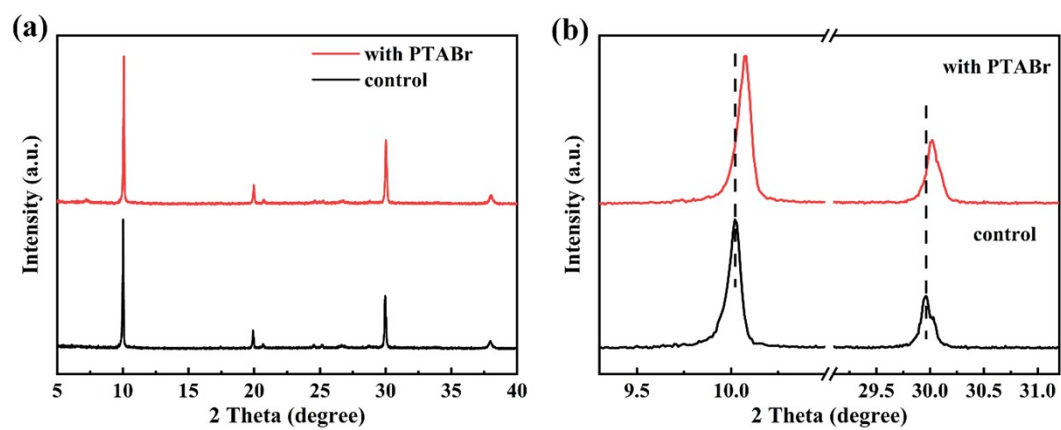
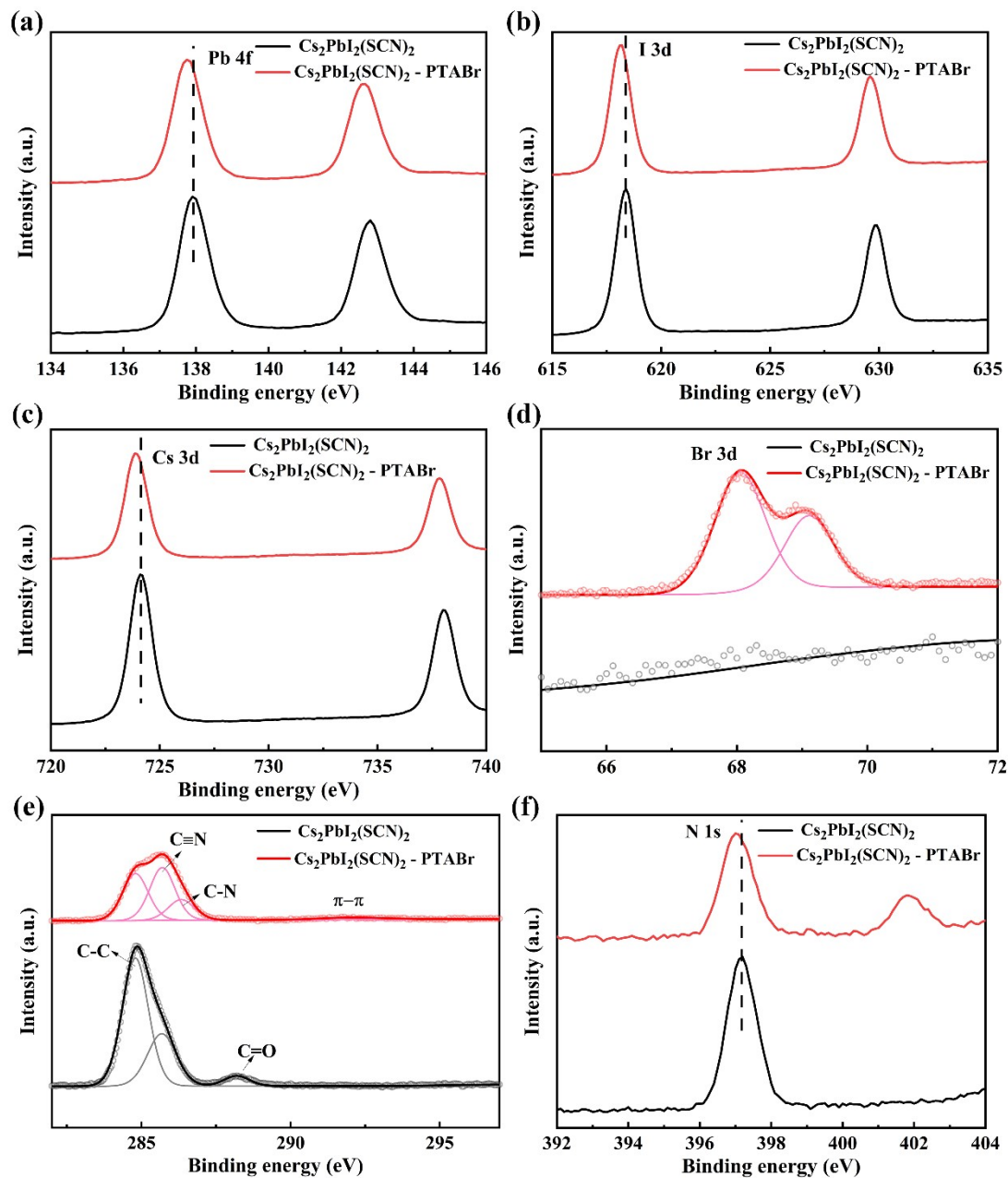**Figure S8.** XRD patterns of $Cs_2PbI_2(SCN)_2$ films with and without PTABr post-treatment.
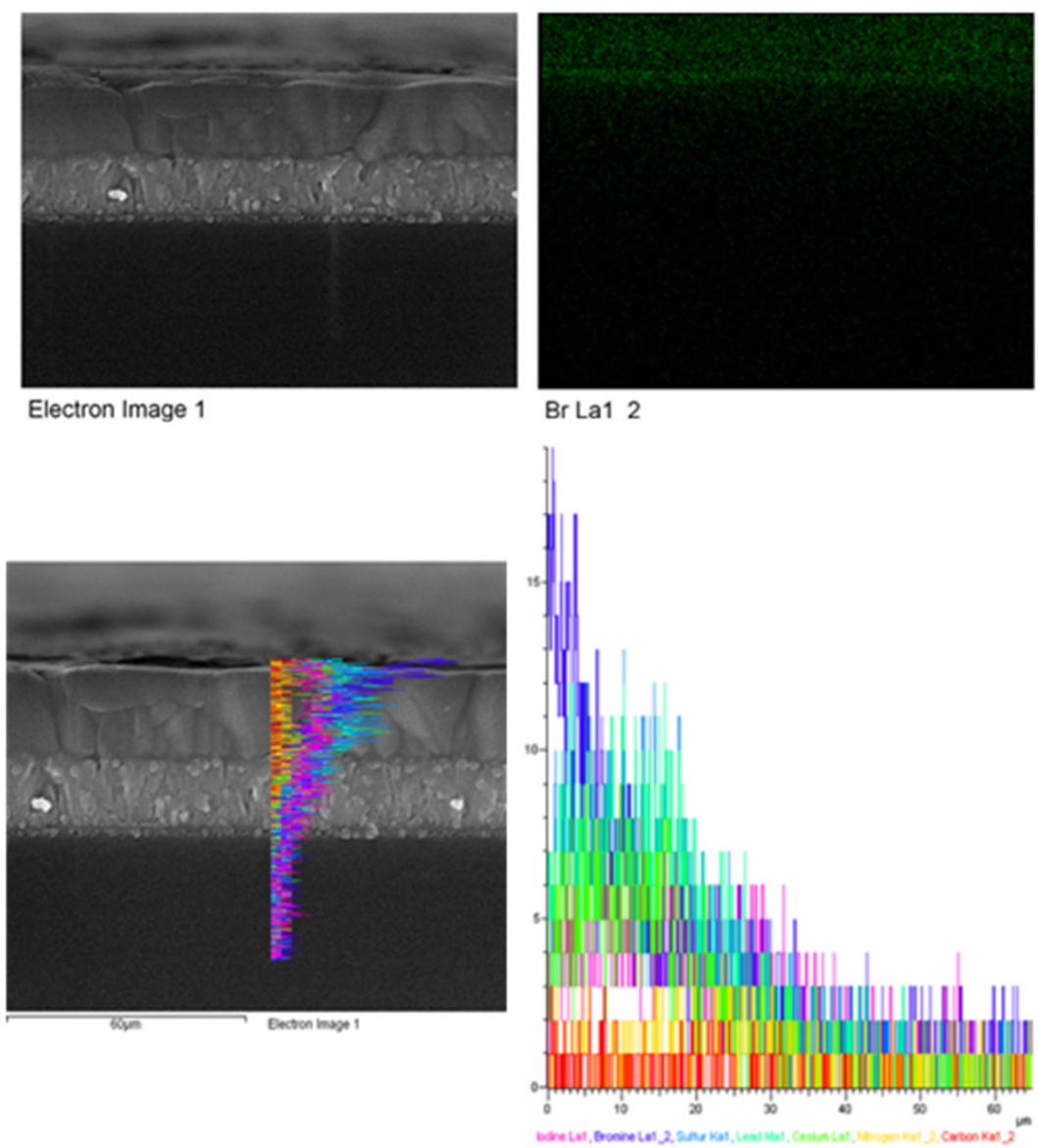
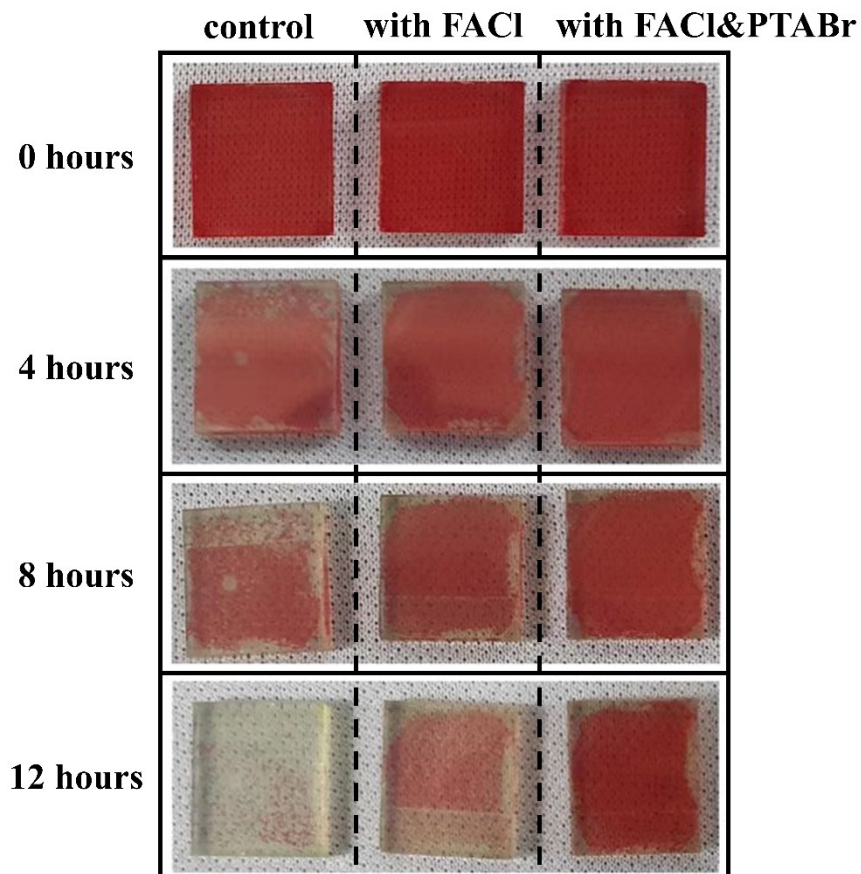**Figure S9.** EDX images of $Cs_2PbI_2(SCN)_2$ film after PTABr post-treatment.

Figure S10. XPS patterns of $Cs_2PbI_2(SCN)_2$ control sample and films with PTABr post-treated.

Figure S11. Photos recorded the changes in the three kinds of $Cs_2PbI_{2(}SCN)_2$ films every 4 hours from when they were freshly prepared to when they were left in the air (RH of 45%) for 12 hours.

Reference

1. M. D. Segall, P. J. D. Lindan, M. J. Probert, C. J. Pickard, P. J. Hasnip, S. J. Clark and M. C. Payne, *Journal of Physics: Condensed Matter*, 2002, **14**, 2717-2744.

2. J. P. Perdew, K. Burke and M. Ernzerhof, *Physical review letters*, 1996, **77**, 3865-3868.

3. D. Vanderbilt, *Physical Review B*, 1990, **41**, 7892-7895.