

Supporting Information

Ethanol purification enables high-quality α -phase FAPbI₃ perovskite microcrystals for commercial photovoltaic applications

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Methods

Chemicals

All materials were purchased from Sigma-Aldrich unless otherwise noted. Tin oxide (SnO₂) nanoparticles colloidal dispersion (21 wt% in water) was purchased from Sukgyung AT. Formamidinium iodide (FAI) and lead iodide (PbI₂) were purchased from LKCHEM. 4-methoxy-phenethylammonium-iodide (MeO-PEAI) was purchased from GreatCell Solar. Ethanol, ethyl acetate, and toluene were purchased from DUKSAN. The 2,2',7,7'-tetrakis-(N,N-di-4-methoxyphenylamino)-9,9'-spirobifluorene (spiro-OMeTAD) was purchased from MS Solution.

Device fabrication

Perovskite solar cells were fabricated with a configuration of indium-doped tin oxide (ITO)/SnO₂/perovskite/MeO-PEAI/spiro-OMeTAD/Au. ITO substrates were cleaned by successive ultrasonic bathing in detergent, DI water, acetone, and isopropyl alcohol (IPA) followed by drying in a convection oven. Afterward, the substrates were treated with Ar plasma to remove organic residues and improve the wetting of solutions. The SnO₂ solution was diluted with distilled water at a volumetric ratio of 1:5 and spin-coated onto an ITO substrate at 3000 rpm for 30 sec, followed by thermal annealing at 150°C for 10 min. The perovskite solution was prepared by dissolving 800 mg of FAPbI₃, 30 mg of MAPbBr₃, and 30 mg of MACl in 0.8 ml of N,N-dimethylformamide (DMF) and 0.1 ml of dimethyl sulfoxide (DMSO), followed by filtration using 0.2 μm PTFE filters. After Ar plasma treatment, the perovskite layer was formed by multi-step spin-coating at 500 rpm, 1000 rpm, and 5000 rpm. In the final step, 1 ml of diethyl ether was sprayed onto the rotating film. The perovskite layer was then thermally annealed at 100°C for 40 min and 150°C for 5 min. The 13 mM mPEAI solution in IPA was spin-coated onto the perovskite surface at 3000 rpm for 30 s and heat-treated at 100°C for 1 min. 100 mg of spiro-OMeTAD was dissolved in 1.1 ml of chlorobenzene and then doped with 23 μl of a bis(trifluoromethylsulfonyl)amine lithium salt (Li-TFSI) solution (540 mg in 1 ml of acetonitrile, ACN), 39 μl of tert-butyl pyridine (tBP), and 10 μl of an FK 209 (Lumtec) solution (376 mg in 1 ml of ACN). The solution was filtered through a PTFE filter and spin-coated for 30 s at 3000 rpm. Finally, gold (Au) was deposited as an electrode by thermal evaporation.

Characterization

The scanning electron microscope (SEM) images were obtained by using field-emission SEM (Mira 3 LMU FEG, Tescan). The X-ray diffraction (XRD) spectra of the perovskite films were recorded by using X-ray diffractometer (SmartLab, Rigaku) using a Cu-K α radiation source. Film thickness was measured by Alpha step (D-600, KLA Tencor). UV-Vis spectra were recorded using UV-Vis spectrophotometer (UV-2600, Shimadzu). Steady-state photoluminescence (PL) spectra were acquired by home-made PL measurement apparatus comprised of a 532 nm diode laser (Thorlabs) and an Ocean Optics Spectrometer. Time-resolved PL (TRPL) spectra were obtained by using a lifetime fluorometer (FluoTime 250, PicoQuant) that is equipped with a 470 nm pulsed laser with a time-correlated single photon counting (TCSPC) technique. Transient photovoltage (TPV) and photocurrent (TPC) measurements were carried out by using a characterization platform (Paivos, Fluxim). Nyquist plots obtained from Potentio/Galvanostat-Impedance spectroscopy system (Autolab, Metrohm). Current density-voltage (J-V) curves were recorded using a solar simulator (Oriel Class AAA, 91195A, Newport) and a source meter voltage-current sourcemeter (Keithley 2420, Keithley Instruments) under AM 1.5G with illumination of 100 mW/cm² calibrated using a calibrated silicon reference cell. EQE measurement was conducted by using a quantum efficiency measurement system (QuantX-300, Newport). The active area was defined by using a metal mask, having an area of 0.084 cm². H-NMR spectra were measured by a nuclear magnetic resonance spectrometer (Avance 700MHz, Bruker).

Supplementary Tables and Figures

Solvent	Dielectric constant	D_N
Tol	2.4	0.1
CB	5.62	3.27
EtOAc	6.02	17.05
EtOH	29.4	19.2
ACN	37.5	14
2ME	16.93	22

Table S1. The list of dielectric constant (ϵ_f) and Gutmann donor number (D_N) of solvents investigated in this work.

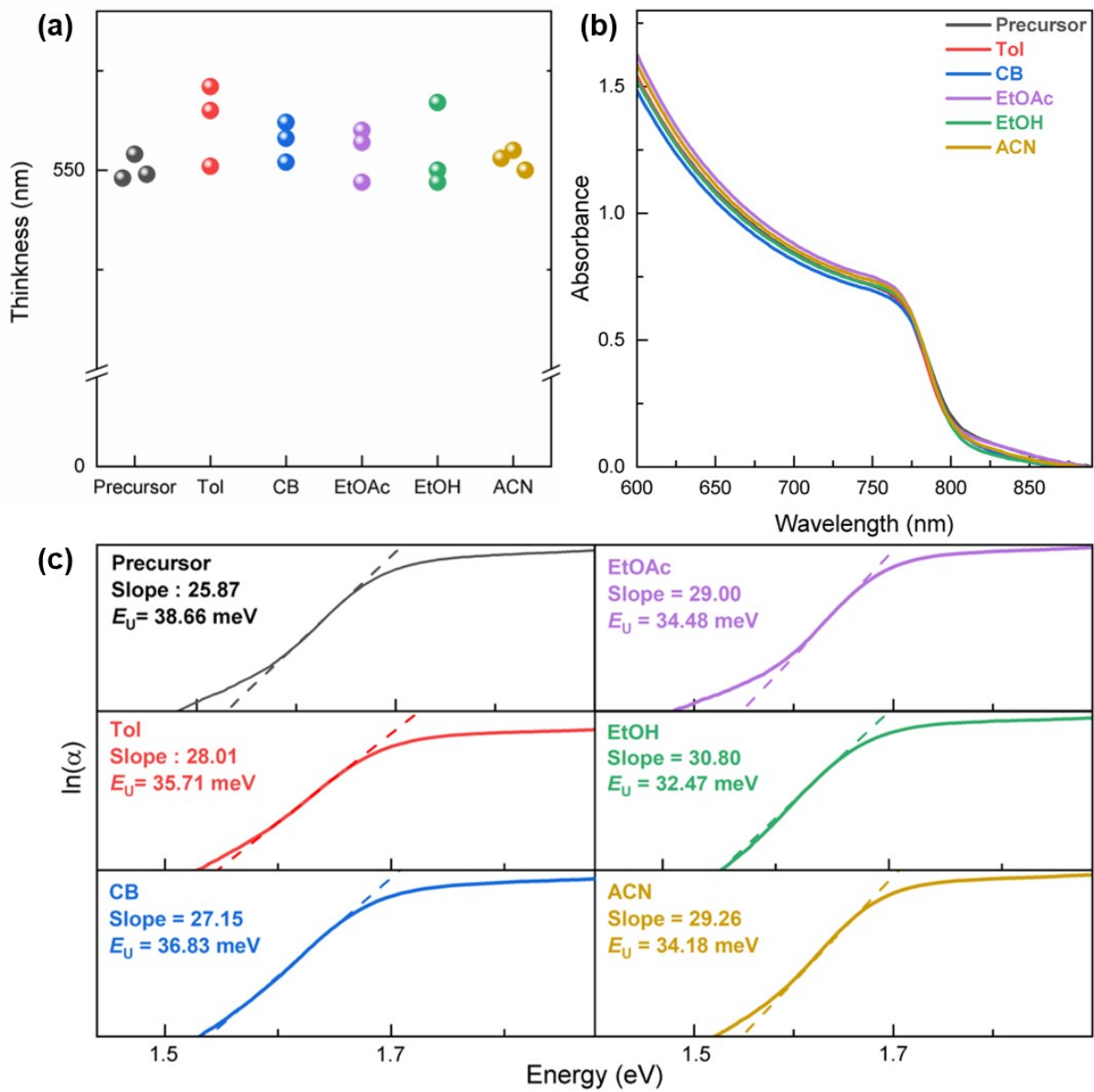


Fig. S1. (a) Thickness of the as-deposited perovskite thin films measured by Alpha step (KLA Tencor). (b) The UV absorption spectrum of perovskite varies depending on the cleaning solvent used. (c) The Urbach energy of the perovskite film for each sample is estimated at the onset of the corresponding spectrum.

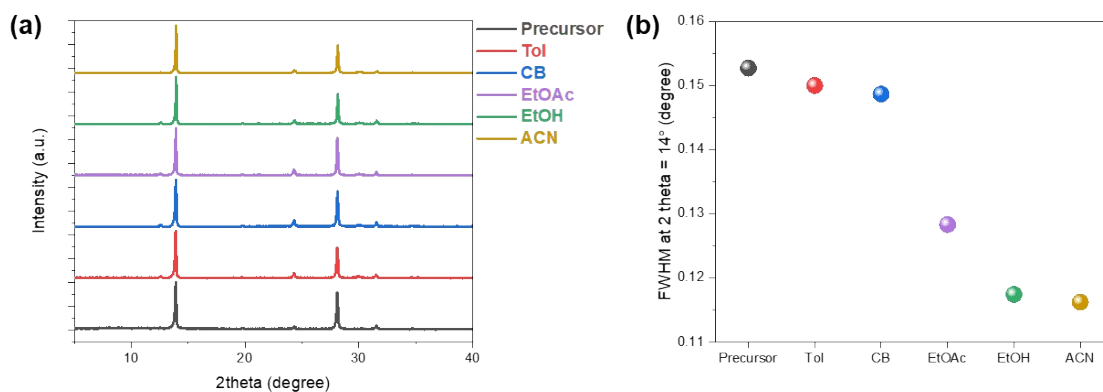


Fig. S2. (a) X-ray diffraction (XRD) patterns of perovskite films engineered with different washing solvents. (b) FWHM values of (001) peak for perovskite films from their XRD patterns in Fig. S2a.

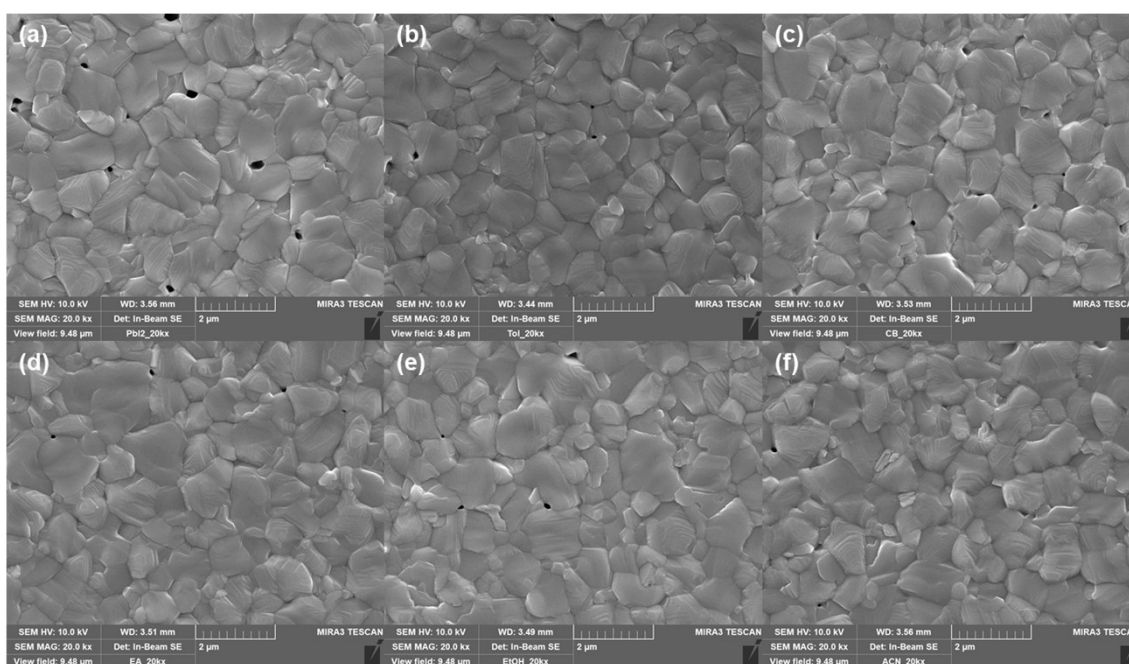


Fig. S3. Surface SEM image of the glass/SnO₂/perovskite thin films. There is scarcely a distinguishable difference by processing solvents. (a) Mixture of precursors. (b) Toluene. (c) Chlorobenzene. (d) Ethyl acetate. (e) Ethanol. (f) Acetonitrile.

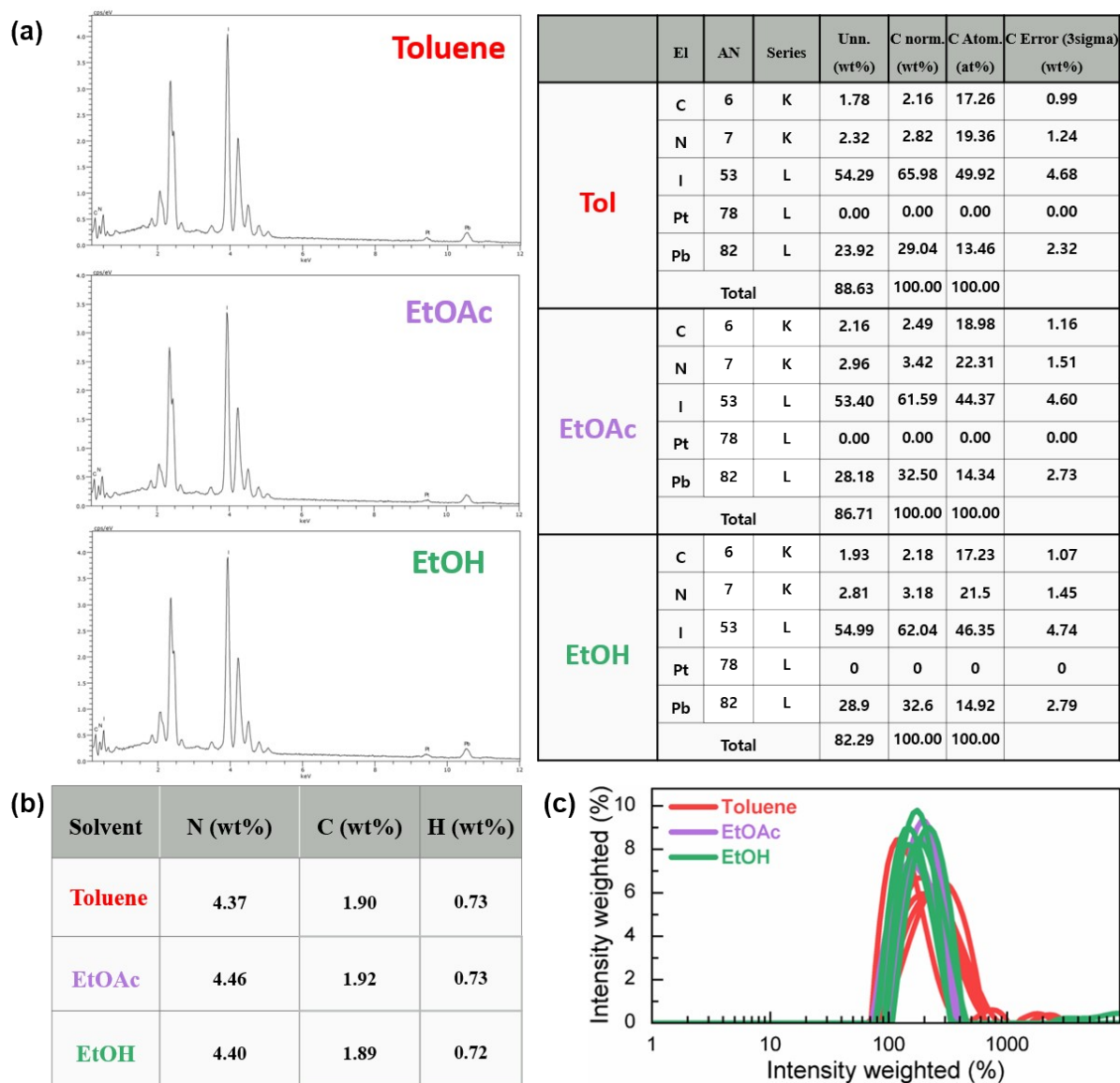


Fig. S4. (a) Energy-dispersive X-ray spectroscopy (EDS, Bruker Quantax 200) of perovskite MCs. (b) Results of the elemental analyzer (EA, Thermo Scientific Flash 2000). (c) Result of dynamic light scattering (DLS) measured by a particle analyzer (Anton Paar Litesizer 500)

Solvent	A_1	τ_1	A_2	τ_2	τ_{avg} (ns)
Precursor	0.273	27.951	0.727	111.907	104.715
Tol	0.796	46.068	0.204	304.080	208.282
CB	0.666	52.754	0.334	283.212	220.822
EtOAc	0.730	88.205	0.270	529.239	392.288
EtOH	0.513	230.970	0.487	938.968	793.168
ACN	0.617	157.675	0.383	806.608	651.376

Table S2. Fitting parameters for the TRPL decay of as-prepared perovskite thin films. To calculate the average carrier lifetime, TRPL profiles were fitted to a bi-exponential decay equation given by $I(t) = I_0 + a_1 \exp(-t/\tau_1) + a_2 \exp(-t/\tau_2)$, where I_0 is an offset, a_1 and a_2 are weight constants, and τ_1 and τ_2 are time decay constants. From these fitting components, we calculated the average amplitudes A_1 and A_2 and the average carrier lifetime as follows:

$$A_1(\%) = \frac{a_1}{a_1 + a_2} \times 100, \quad A_2(\%) = \frac{a_2}{a_1 + a_2} \times 100$$

. The averaged carrier lifetime is calculated as

$$\tau_{avg} = \frac{A_1 \tau_1^2 + A_2 \tau_2^2}{A_1 \tau_1 + A_2 \tau_2}$$

follows:

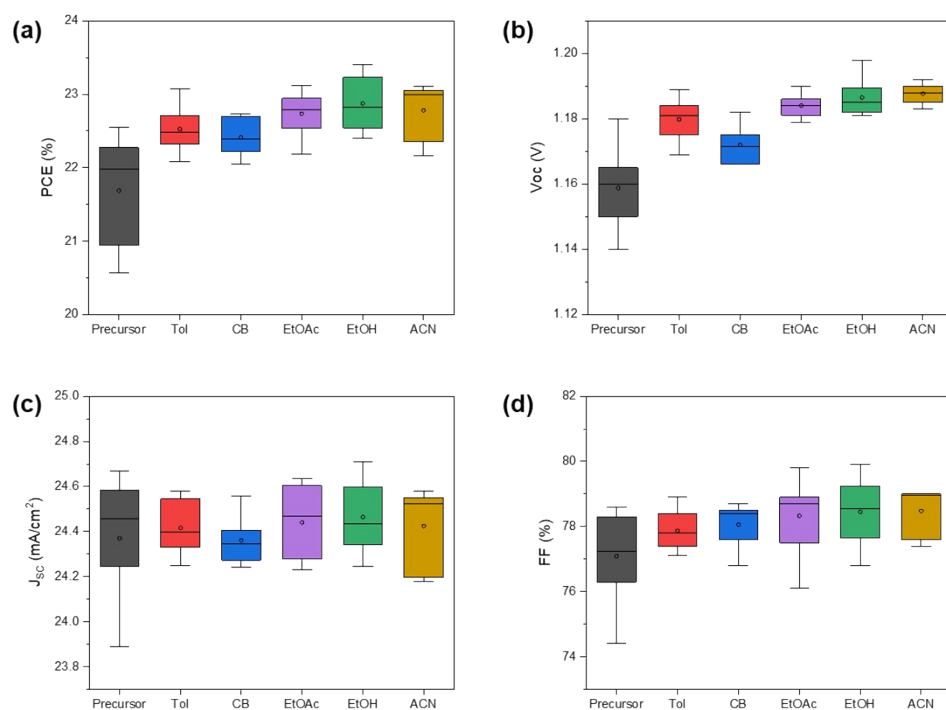


Fig. S5. The box diagrams of statistical photovoltaic parameters of perovskite solar cell by varying washing solvents. (a) Power conversion efficiency (PCE). (b) Open-circuit voltage (V_{OC}). (c) Short-circuit current with antireflective films (J_{SC}). (d) Fill factor (FF).

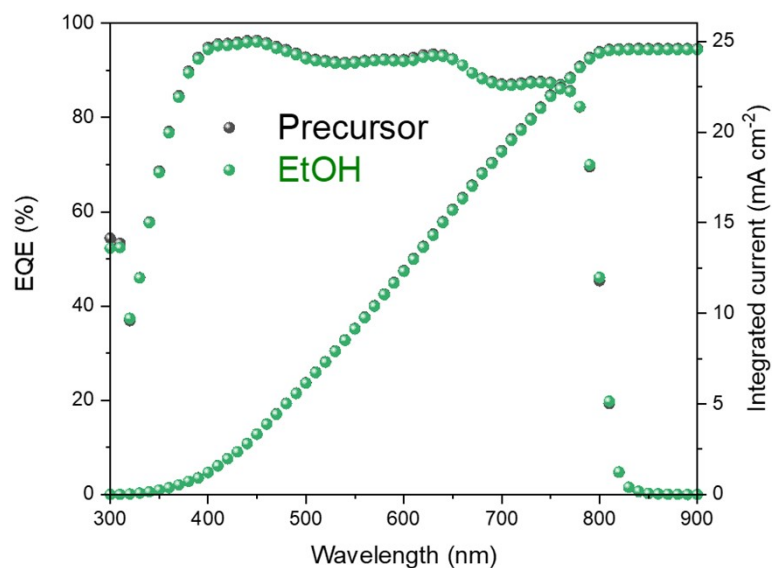


Fig. S6. External quantum efficiency (EQE) spectra and integrated J_{SC} for control and target devices.

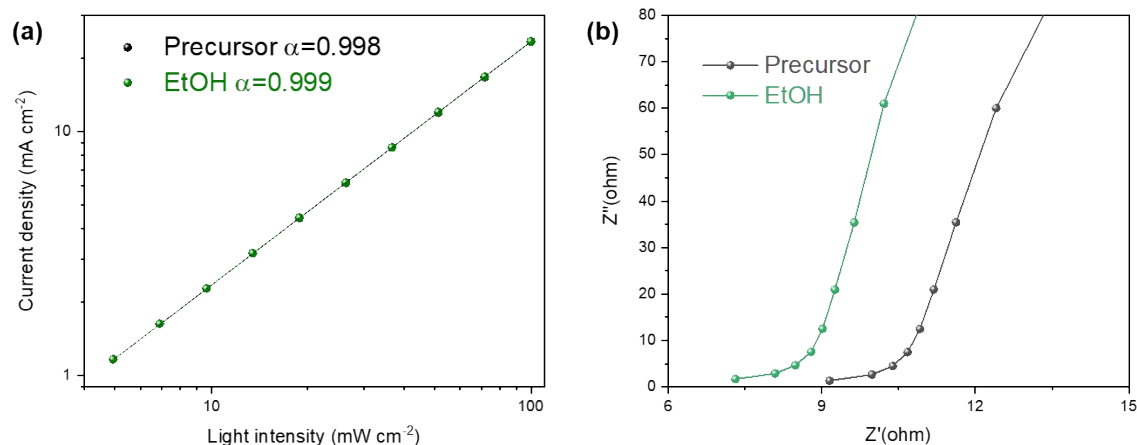


Fig. S7. (a) Light intensity dependence of J_{SC} for PSCs. (b) High-frequency Nyquist plots obtained from electrochemical impedance spectroscopy (EIS) measurements under dark with a bias voltage near V_{OC}

Table S3. Simple techno-economic analysis for synthesis of FAPbI₃ perovskite

Chemical	Usage ^a	Cost/unit	Price (\$)	Unit	Vendor	Cat. No.	Final cost ^b
FAI	0.305	1.26	6,280.71	5,000 g	Greatcell solar	MS150000	0.384
PbI ₂	0.818	2.73	2,727	1,000 g	TCI	L0279	2.231
2ME	0.91	0.04	630.65	16,000 mL	Fisher Scientific	AA31733M6	0.036
EtOH	20	0.053	10,600	200,000 mL	Sigma Aldrich	459844	1.060
Tol	20	0.021	4,150	200,000 mL	Sigma Aldrich	179418	0.415
CB	20	0.096	239	2,500 mL	Sigma Aldrich	319996	1.912
ACN	20	0.081	1,450	18,000 mL	Sigma Aldrich	271004	1.611
EtOAc	20	0.021	4,210	200,000 mL	Sigma Aldrich	319902	0.421

a: Usage for 1g FAPbI₃ synthesis. In the solid cases, those scale is gram and in the liquid cases, those scale is milli-liter; b: Required cost per used unit