Supplementary Information (SI) for Green Chemistry.

Supporting Information

Efficient Tin Halide Perovskite Solar Cells with Extended Processing Window

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Experiment Section

Materials preparation

Isopropanol (IPA, 99.5%, Adamas-beta), dimethyl sulfoxide (DMSO, 99.9%, Sigma-Aldrich), N,N-diethylformamide (DEF, 99%, Adamas-beta), anisole (AS, >99%, Adamas-beta), chlorobenzene (CB, 99.8%, Sigma-Aldrich), poly (3,4-ethylene dioxythiophene)-poly (styrene sulfonate) (PEDOT: PSS, 4083, CleviousTM HTL Solar), tin fluoride (SnF_2, 99%, Sigma-Aldrich), methylammonium bromide (MABr, 99.9%, Great-Cell), formamidinium iodide (FAI, 99.9%, Great-Cell), tin (Ⅱ) iodide (SnI_2, 99.99%, Adamas-beta), tin powder (Sn, 99.8%, Sigma-Aldrich), phenethylammonium iodide (PEAI, >99.5%, Xi'an Polymer Light Technology Corp.), bathocuproine (BCP, >98%, Adamas-beta), acetone (99.5%, Cdkelong), ethanol (99.7%, Reagent), indium tin oxide (ITO, 7-9 Ω sq^{-1}, Advanced Election Technology CO.Ltd), silver (Ag, 99.9%, Trillion Metals). All the materials were used directly without any purification.

Device fabrication

First of all, ITO glass was carefully cleaned with detergent, deionized water, ethanol, acetone, and isopropyl for 20 min, sequentially. Then, the cleaned ITO substrates were blown dry with N_2 and exposed to UV light for 15 min. 100 µL PEDOT: PSS solution was spin-coated on the ITO substrate at 4000 rpm for 50 s followed with 30 min annealing at 140 ℃ under ambient conditions. For the perovskite precursor solution (1M) with a chemical composition of $FA_{0.75}MA_{0.25}SnI_{2.75}Br_{0.25}$, 129.0 mg FAI, 28.0 mg MABr, 372.5 mg SnI_2 together with 5 mg Sn^0 and 16.7 mg SnF_2 were dissolved in DEF: DMSO (600 µL: 400 µL) and then stirred overnight. In addition, 12% PEAI was added and stirred for 1 h before spin-coating. After filtered with 0.22 µm PTFE filters, 45 µL precursor solution was spin-coated on the prepared substrate at 8000 rpm for 60 s. For the CB device and AS device mentioned in the manuscript, CB and AS was dropped on the substrate at 10s and 25 s respectively after spin-coating started. And then the film was annealed at 80 ℃ for 10 min. Next, 50 µL C_{60}-ETPA (20 mg mL^{-1} in CB) was coated on the film at 2000 rpm for 30 s followed by annealed at 70 ℃ for 10 min. Then 90 µL BCP

(5 mg mL^{-1} in IPA) was spin-coated at 6000 rpm for 30 s and annealed at 70 ℃ for 10 min. Finally, the Ag electrode (100 nm) was evaporated at a speed of 2 Å s^{-1} under a high vacuum level.

Characterization

The Fourier transform infrared (FTIR) spectra were detected by a Fourier transform infrared spectroscopy (Bruker). Obtaining the X-ray photoelectron spectroscopy (XPS) by PHI-5000 VersaProbe III instrument with a non-monochromated He Iα photon source (hv= 21.2 eV, with 50 meV energy resolution). To minimize the effect of oxygen, we firstly encapsulated our samples in an airtight box with N_2. Then, we delivered the samples to test center in an hour. The samples were stored overnight in a vacuum chamber through the built-in vacuum chamber of XPS and then tested. X-ray diffraction (XRD) analysis was measured by a MiniFlex 600 (Rigaku) X-ray diffractometer with Cu Kα radiation (λ = 0.15406 nm, 40 kV, 100 mA). *J-V* characteristics were performed by solar simulator (San-EI Electric, 3A) under standard AM 1.5G (1000 W m^{-2}) illumination in N_2 atmosphere (calibration with silicon wafer (AK-200, KONICA MINOLTA, INC) before testing). The devices were measured in a forward scan from -0.1 V to 0.85 V with a 200 mV/s scan speed and 20 ms setting time. The external quantum efficiency (EQE) was measured by QE-R (Enlitech). The UV-vis absorption spectra were probed by UV-2600 (Shimadzu). The steady photoluminescence (PL) and time-resolved photoluminescence (TRPL) were collected by PTI QuantaMaster 8000 (HORIBA) with a pulsed source at 510 nm laser. The space charge limited current (SCLC) measurement was conducted by Keithley 2400 source meter in the voltage range of −0.1~3 V. The effective area of the device is 0.096 cm^2. The instrument model used to measure the contact angle is the JY-82B Kruss DSA. The FTIR tests were conducted by comparing pure AS with a mixture of AS and DMSO. The in-situ PL was measured in real-time during the film spin-coating and annealing processes. Films annealed at 80 °C for 10 minutes were subjected to XRD/UV/SEM/XPS, and contact angle measurements. In addition to the tests mentioned above, all other tests were performed on complete devices.

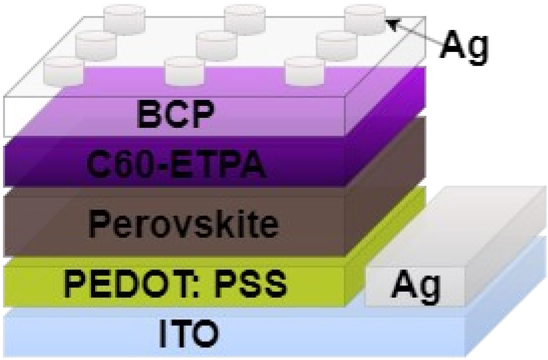

Fig. S1. The device architecture of tin-based perovskite solar cells.

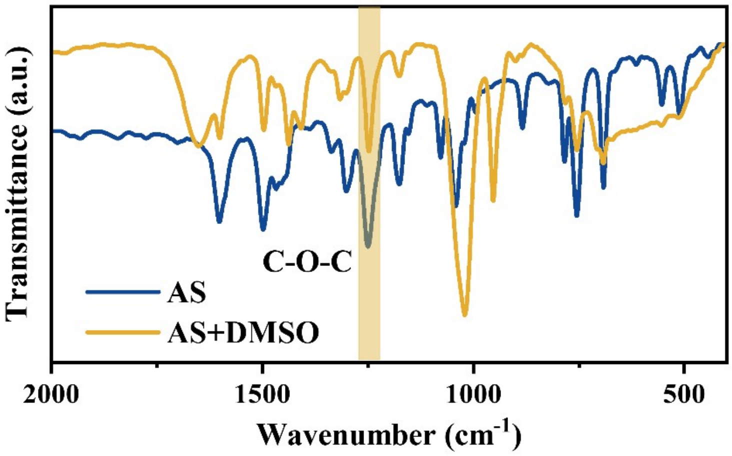

Fig. S2. The FTIR plot of AS and AS+DMSO solutions.

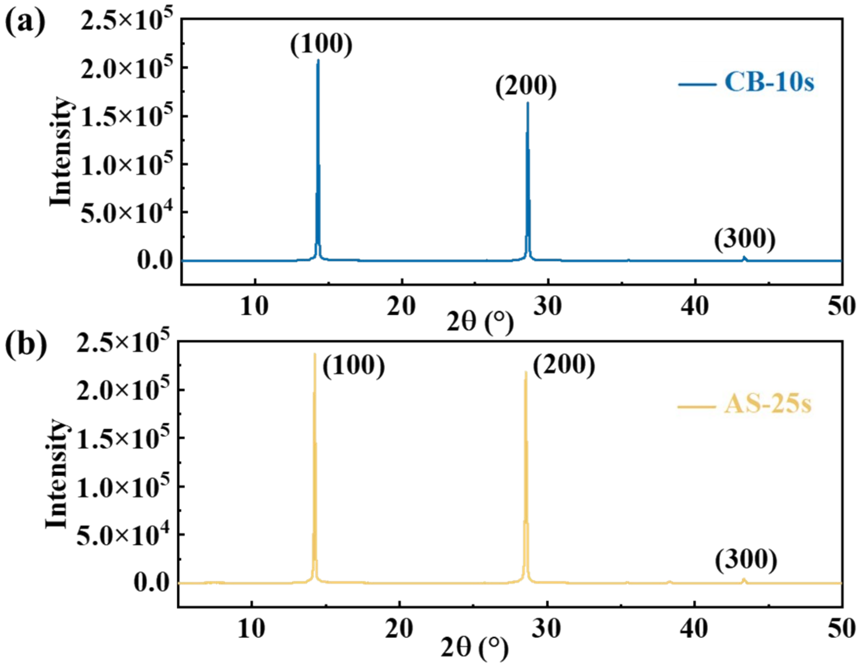

Fig. S3(a-b) The comparative XRD spectra of CB-10s and AS-25s films.

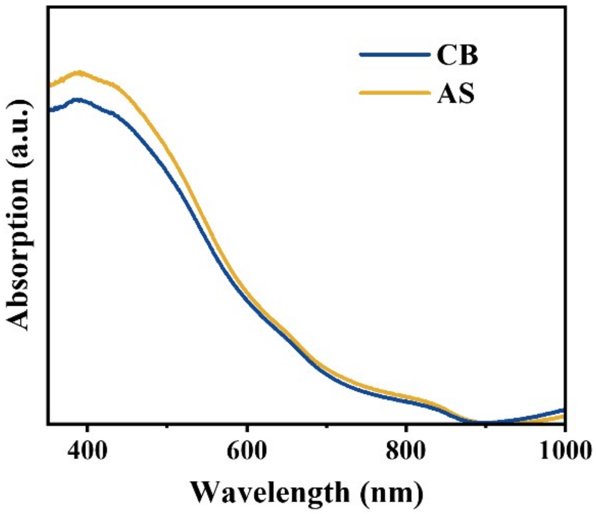

Fig. S4. UV-vis absorption curves for CB and AS films.

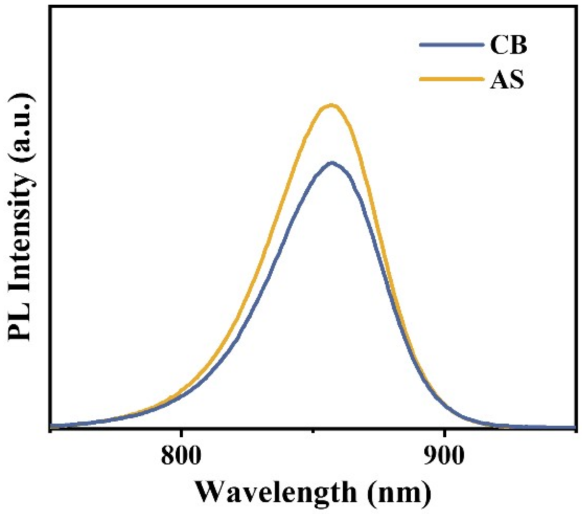

Fig. S5. PL curves for CB and AS films.

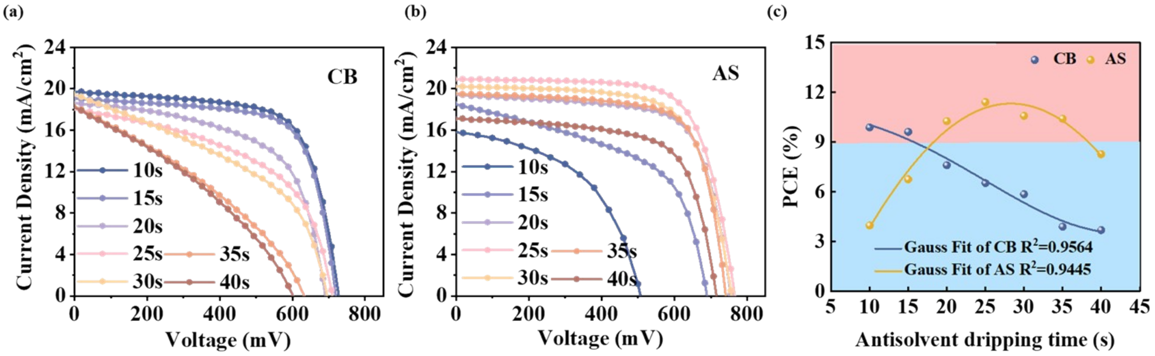

Fig. S6. J-V curves of (a) CB and (b) AS devices prepared with different antisolvent dripping time; (c) PCE of CB and AS devices.

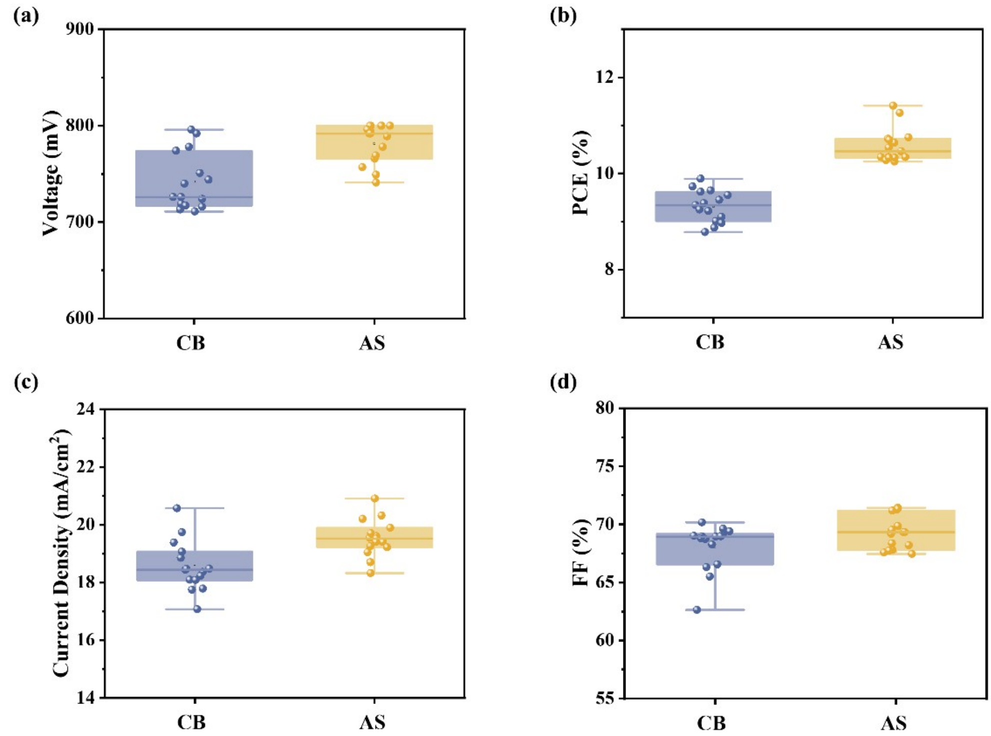

Fig. S7. The box diagram of (a) V_{oc}, (b) PCE (c) J_{sc} and (d) FF for 15 independent devices.

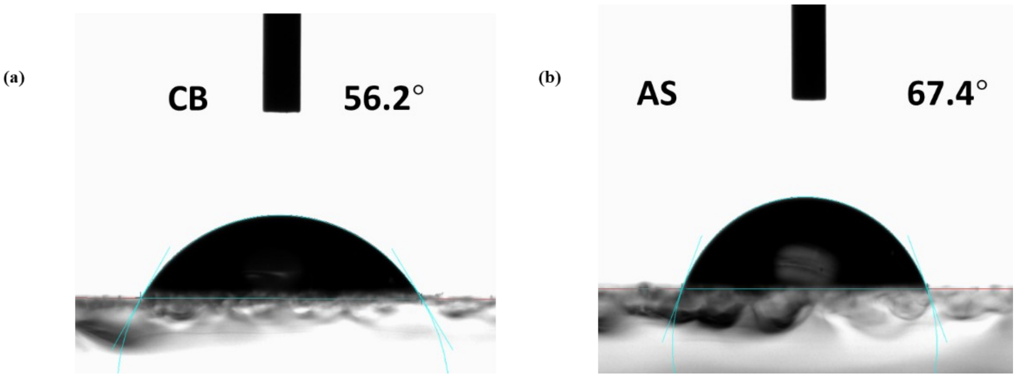

Fig. S8. Water-contact angle images of the (a) CB, (b) AS treated perovskite films.

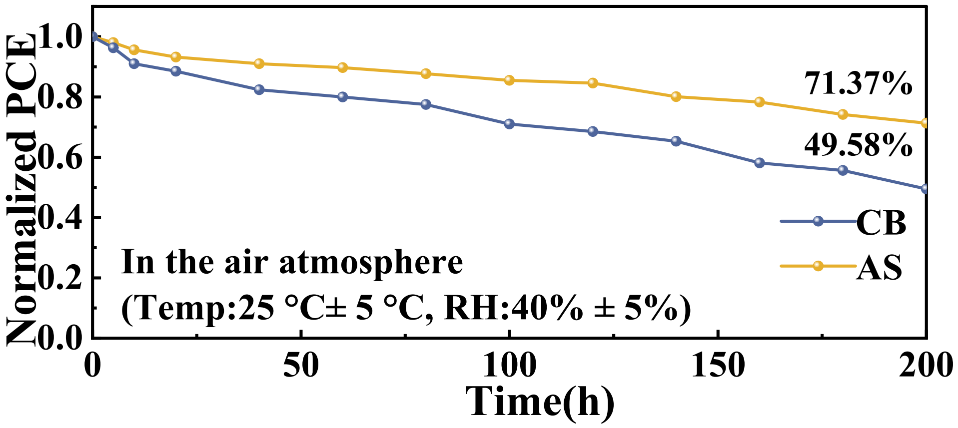

Fig. S9. Normalized PCE revolutions of unencapsulated CB and AS devices in air environment for 200 hours.

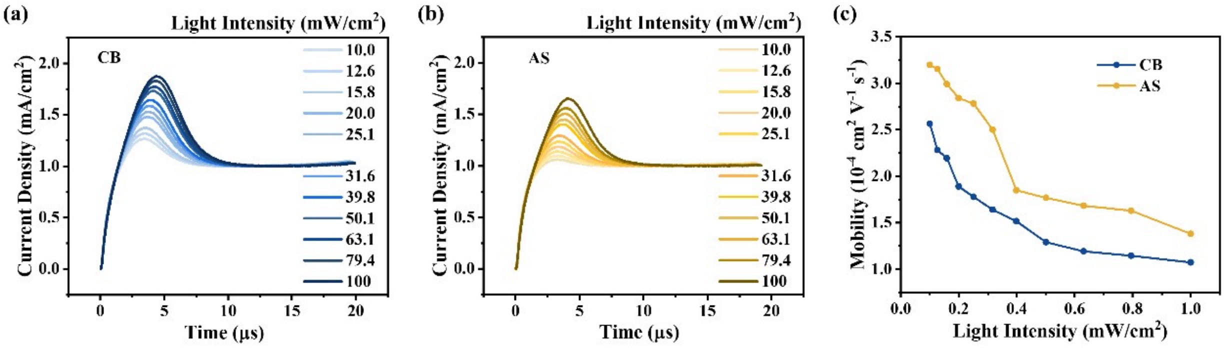

Fig. S10. Photo-CELIV plots of the (a) CB and (b) AS device. (c) and the calculated electron mobility.

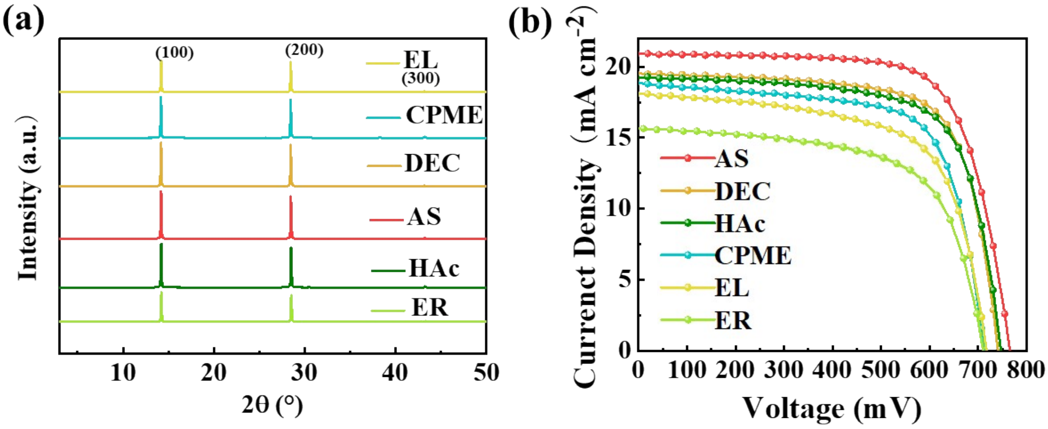

Fig. S11 (a) The XRD spectra of the annealed films using six different antisolvents; (b) the JV curves for the devices with different antisolvent.

Table S1. The FWHM values of the (100) crystal plane of the perovskite films prepared with CB and AS at different application times.

FWHM	**10s**	**15s**	**20s**	**25s**	**30s**	**35s**	**40s**
CB	0.1071 (0.1081 ± 0.0013)	0.1114 (0.1120 ± 0.0013)	0.1153 (0.1159 ± 0.0010)	0.1156 (0.1147 ± 0.0014)	0.1175 (0.1185 ± 0.0012)	0.1176 (0.1176 ± 0.0012)	0.1175 (0.1164 ± 0.0011
AS	0.1160 (0.1062 ± 0.0016)	0.1152 (0.1156 ± 0.0015)	0.1135 (0.1138 ± 0.0016)	0.1051 (0.1058 ± 0.0013)	0.1076 (0.1072 ± 0.0013)	0.1095 (0.1100 ± 0.0012)	0.1184 (0.1189 ± 0.0012

Table S2. The fitted PL lifetime from TRPL spectra of CB and AS perovskite films.

	A_1	τ_1 (ns)	A_2	τ_2 (ns)	τ_{ave} (ns)
CB	0.58	5.40	0.42	11.44	7.95
AS	0.66	8.83	0.34	22.03	13.33

Table S3. The detailed photovoltaic performance parameters of CB devices with different antisolvent dripping time.

CB	V_{oc} (mV)	J_{sc} (mA/cm^2)	FF (%)	PCE (%)
10s	726 (742 ± 28.63)	19.74 (18.56 ± 0.84)	68.97 (68.07 ± 1.92)	9.89 (9.32 ± 0.32)
15s	719 (731 ± 16.90)	19.07 (18.49 ± 0.75)	70.17 (65.31 ± 2.97)	9.62 (8.82 ± 0.50)
20s	690 (656 ± 26.65)	18.61 (18.05 ± 0.51)	59.26 (55.94 ± 3.05)	7.61 (6.62 ± 0.47)
25s	708 (650 ± 29.81)	18.03 (17.79 ± 0.72)	51.13 (51.69 ± 2.63)	6.53 (5.97 ± 0.36)
30s	696 (655 ± 25.23)	19.45 (18.17 ± 0.83)	43.29 (40.39 ± 2.96)	5.86 (4.81 ± 0.45)
35s	630 (621 ± 10.06)	18.31 (17.63 ± 0.58)	33.84 (29.99 ± 3.51)	3.90 (3.28 ± 0.41)
40s	599 (605 ± 15.14)	18.20 (17.68 ± 0.52)	33.99 (29.72 ± 2.62)	3.71 (3.18 ± 0.31)

Table S4. The detailed photovoltaic performance parameters of AS devices with different antisolvent dripping time.

AS	V_{oc} (mV)	J_{sc} (mA/cm^2)	FF (%)	PCE (%)
10s	507 (510 ± 24.77)	15.77 (15.78 ± 0.52)	49.71 (44.86 ± 3.61)	3.97 (3.60 ± 0.27)
15s	690 (692 ± 19.17)	18.50 (18.32 ± 0.43)	53.00 (50.21 ± 2.42)	6.76 (6.36 ± 0.32)
20s	754 (745 ± 29.16)	19.45 (19.38 ± 0.83)	70.03 (69.11 ± 1.23)	10.27 (9.96 ± 0.22)
25s	766 (782 ± 19.57)	20.91 (19.54 ± 0.62)	71.26 (69.30 ± 1.41)	11.41 (10.58 ± 0.34)
30s	755 (753 ± 29.83)	20.23 (19.95 ± 0.45)	69.22 (66.67 ± 3.61)	10.58 (10.01 ± 0.59)
35s	741 (742 ± 30.45)	19.52 (19.38 ± 0.76)	71.96 (65.40 ± 4.42)	10.41 (9.40 ± 0.57)
40s	715 (690 ± 37.02)	17.11 (16.64 ± 0.55)	67.58 (66.01 ± 1.75)	8.27 (7.58 ± 0.51)

Table S5. The detailed photovoltaic performance parameters of devices with different antisolvent

Samples	V_{oc} (mV)	J_{sc} (mA/cm^2)	FF (%)	PCE (%)
AS	761 (766 ± 21.41)	20.79 (20.51 ± 0.43)	71.65 (70.68 ± 2.14)	11.33 (11.16 ± 0.21)
DEC	740 (746 ± 26.18)	19.51 (19.33 ± 0.58)	71.41 (70.12 ± 1.37)	10.32 (10.09 ± 0.38)
HAc	746 (743 ± 25.64)	19.26 (19.17 ± 0.69)	70.02 (68.96 ± 2.52)	10.08 (9.88 ± 0.25)
CPME	719 (725 ± 20.23)	18.67 (18.45 ± 0.52)	68.75 (67.61 ± 2.18)	9.21 (9.03 ± 0.37)
EL	717 (719 ± 30.11)	18.10 (17.99 ± 0.41)	64.68 (62.43 ± 3.56)	8.40 (7.96 ± 0.56)
ER	709 (711 ± 29.34)	15.64 (15.32 ± 0.77)	64.10 (63.97 ± 3.49)	7.13 (6.82 ± 0.61)