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Supplementary Information

Addition of Adamantylammonium Iodide to Hole Transport Layers Enables Highly Efficient Perovskite Solar Cells

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This file includes:

- Fig. S1. Perovskite film characterization.
- Fig. S2. TOF-SIMS depth profile of iodide specie.
- Fig. S3. Electron beam penetration and EBIC images.
- Fig. S4. ^{13}C CP solid-state MAS NMR spectra at 21.1 T, 100 K and 12 kHz MAS of bulk mechanochemical (A) δ-$FAPbI_3$ and (B) α-$FAPbI_3$.
- Fig. S5. Statistical photovoltaic parameters of devices based on modified spiro with different concentrations
- Fig. S6. Statistical photovoltaic parameters of devices based on modified spiro and passivation.
- Fig. S7. Statistical photovoltaic parameters of devices based on modified spiro HTL with ADA, ADAHCl, ADAHBr, and ADAHI additives.
- Fig. S8. Statistical photovoltaic parameters of $MAPbI_3$ PSC devices.
- Fig. S9. Statistical photovoltaic parameters of double A-cation PSC devices.
- Fig. S10. Statistical photovoltaic parameters of triple A-cation PSC devices.
- Fig. S11. Urbach energy measurement of modified device.
- Fig. S12. *J-V* curves of the devices treated by addition of alternative agents into HTL.
- Table S1. Figures of merit for champion reference cell and modified device

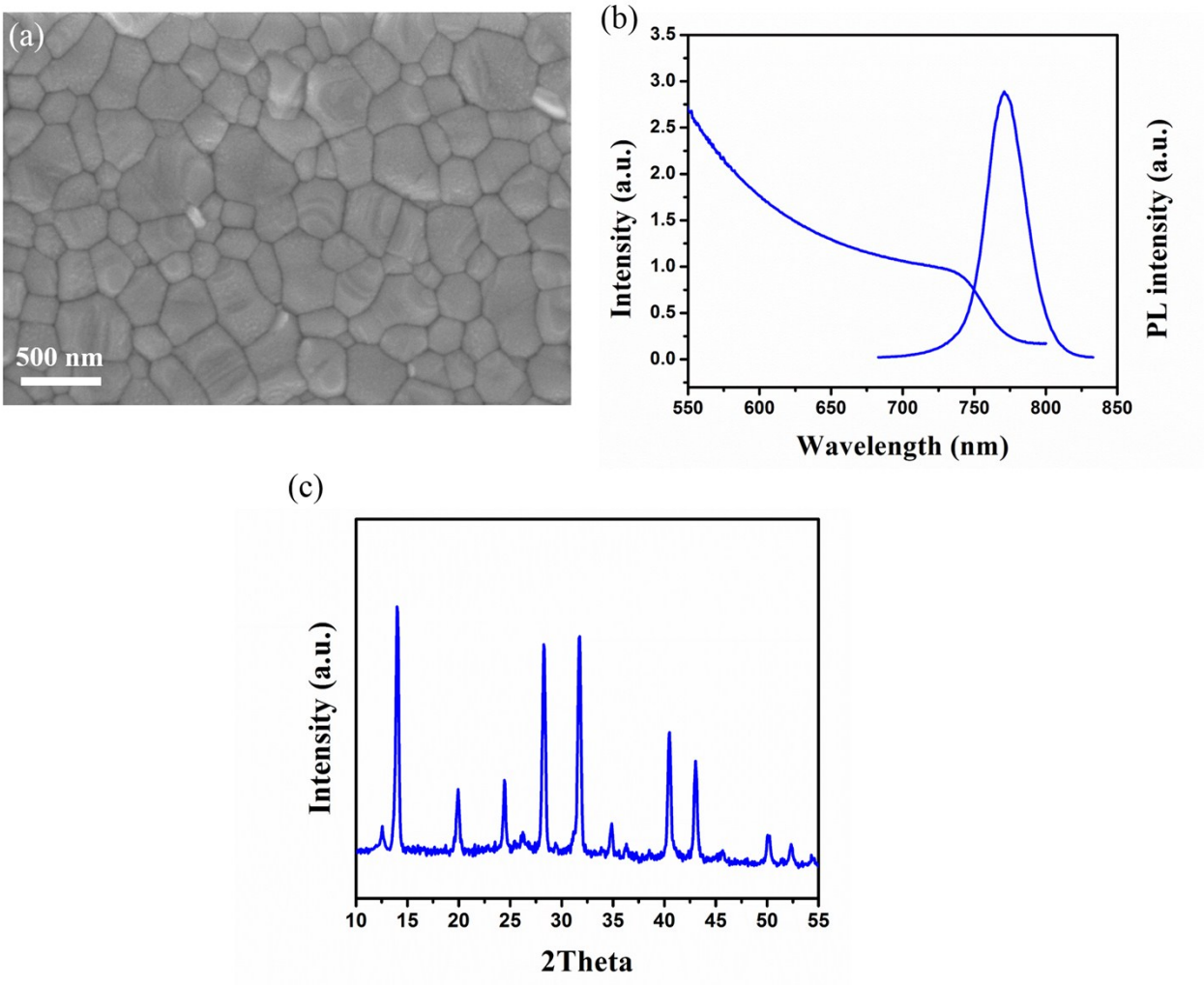

Figure S1. (a) Top-view SEM image, (b) UV-visible and photoluminescence spectra, and (c) x-ray diffraction pattern of triple A-cation perovskite film.

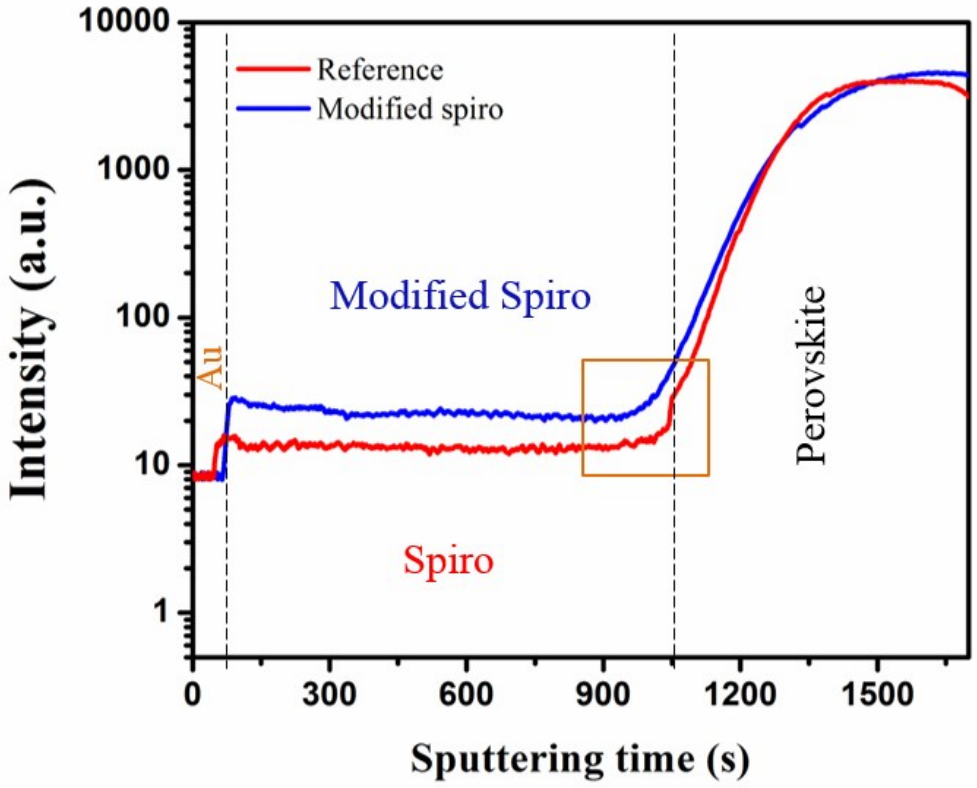

Figure S2. TOF-SIMS depth profile of iodide species for PSC devices without and with ADAHI.

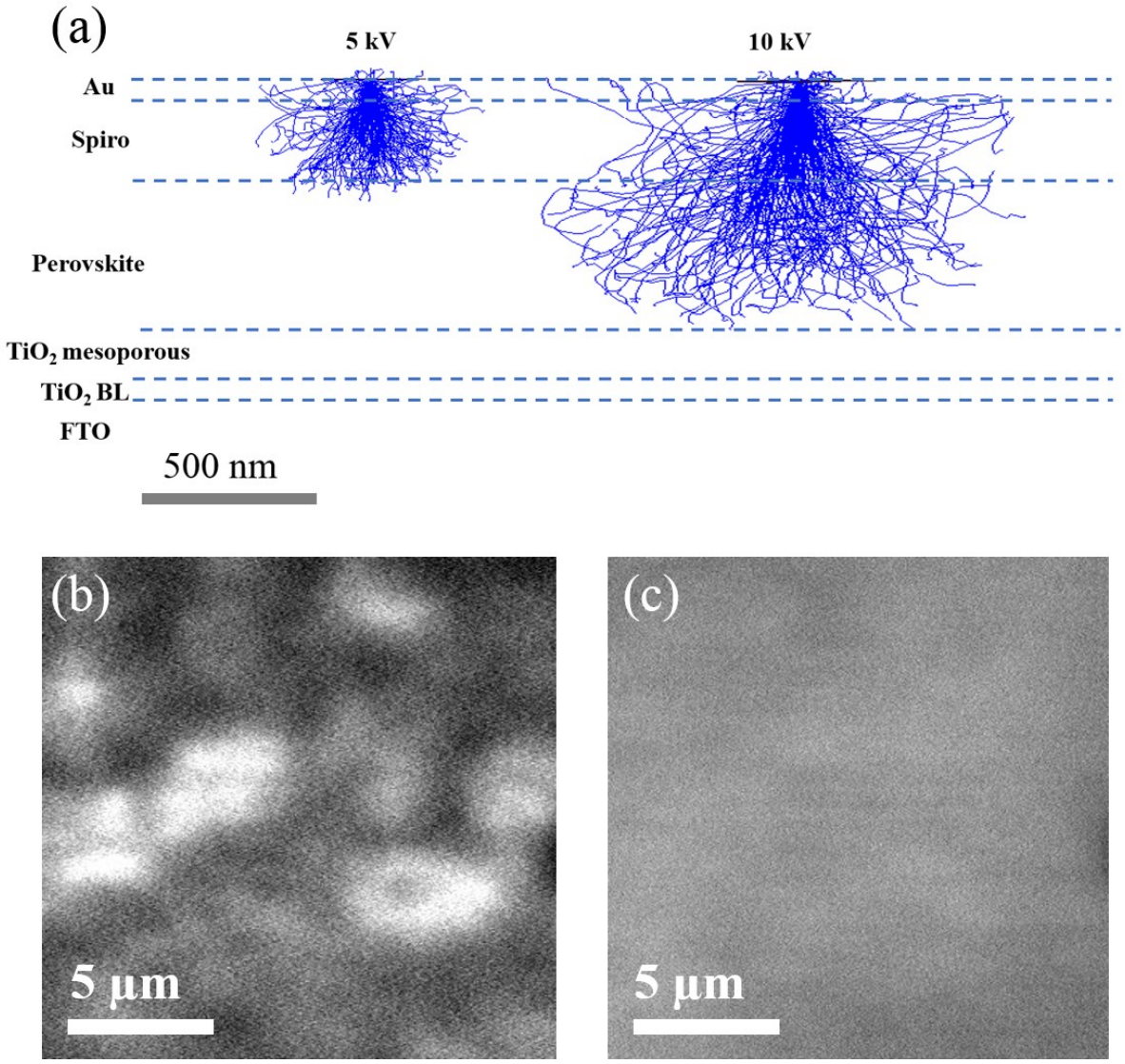

Figure S3. (a) Estimation of the required voltage for EBIC measurement using Monte Carlo simulation performed by CASINO. In this experiment, 5 kV and 10 kV were used as accelerating voltages to study the interaction of electron beam with different layers of PSC device. The original EBIC images of PSC devices for reference (b) and ADAHI containing (c) spiro HTLs.

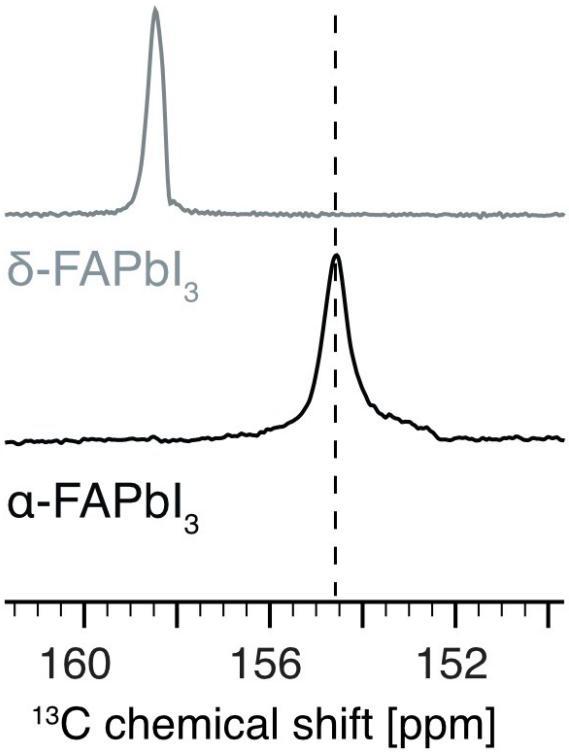

Figure S4. ^{13}C CP solid-state MAS NMR spectra at 21.1 T, 100 K and 12 kHz MAS of bulk mechanochemical (A) δ-$FAPbI_3$ and (B) α-$FAPbI_3$.

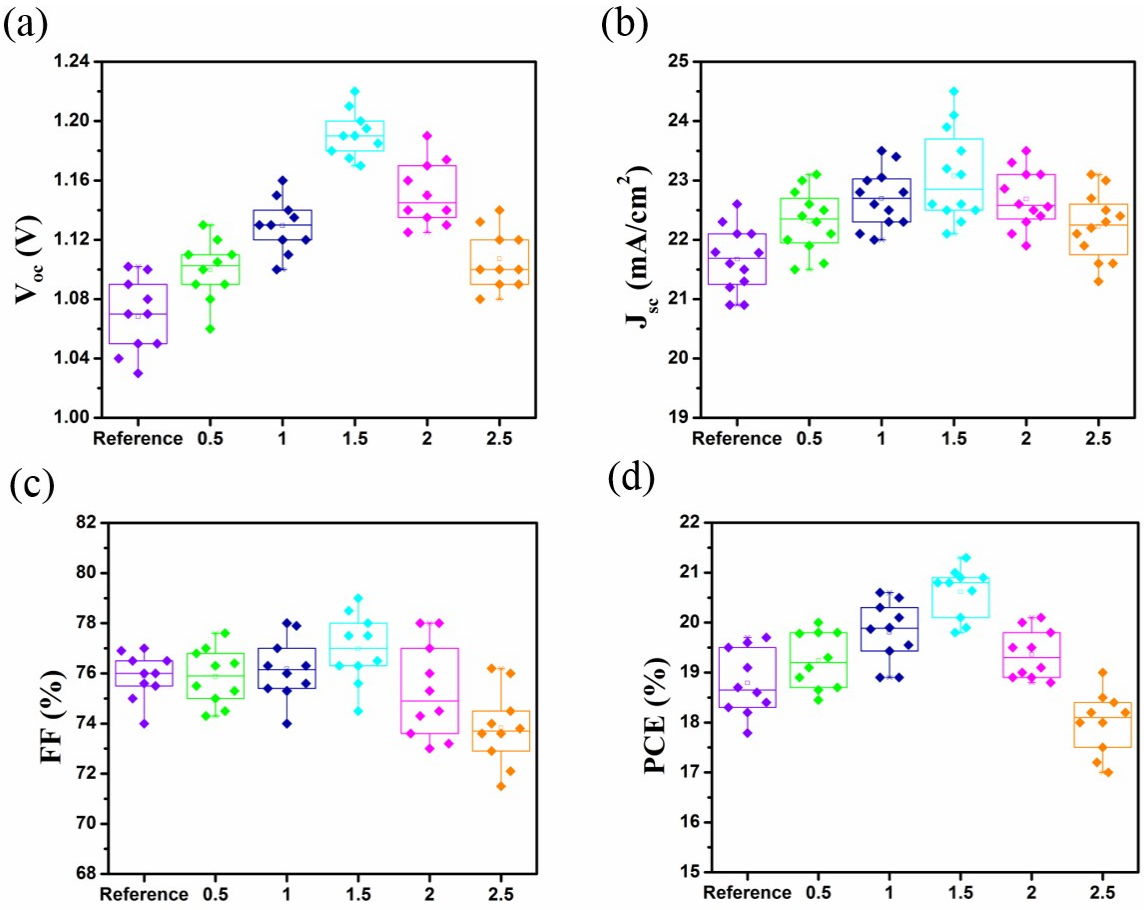

Figure S5. Statistical photovoltaic parameters of triple A-cation PSC devices based on modified spiro with different concentrations of ADAHI (0, 0.5, 1, 1.5, 2, 2.5 mg/0.5 mL solution).

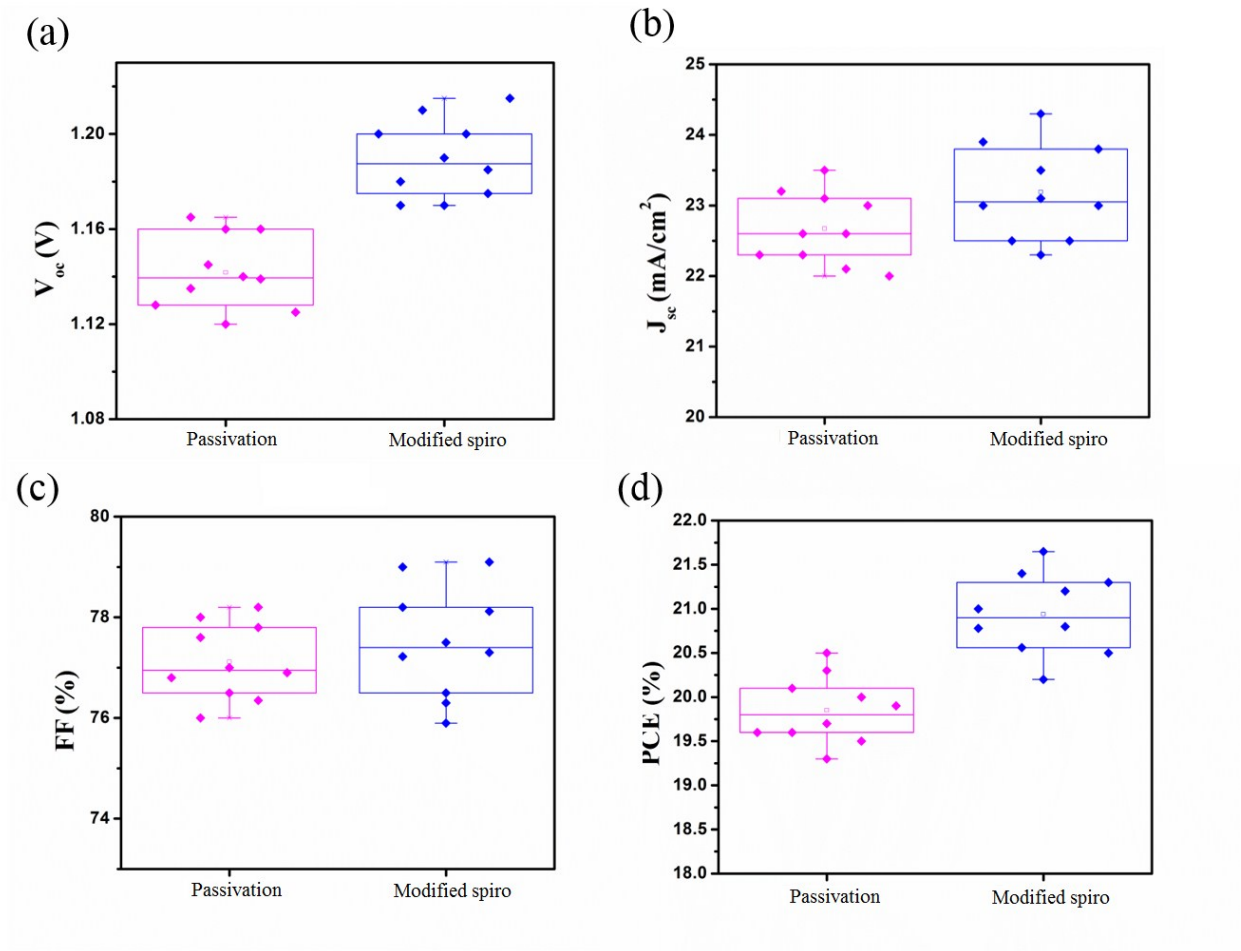

Figure S6. Statistics of photovoltaic parameters of triple A-cation PSC devices based on either modified spiro or passivation of perovskite layer by direct ADAHI deposition from solution on top of perovskite film.

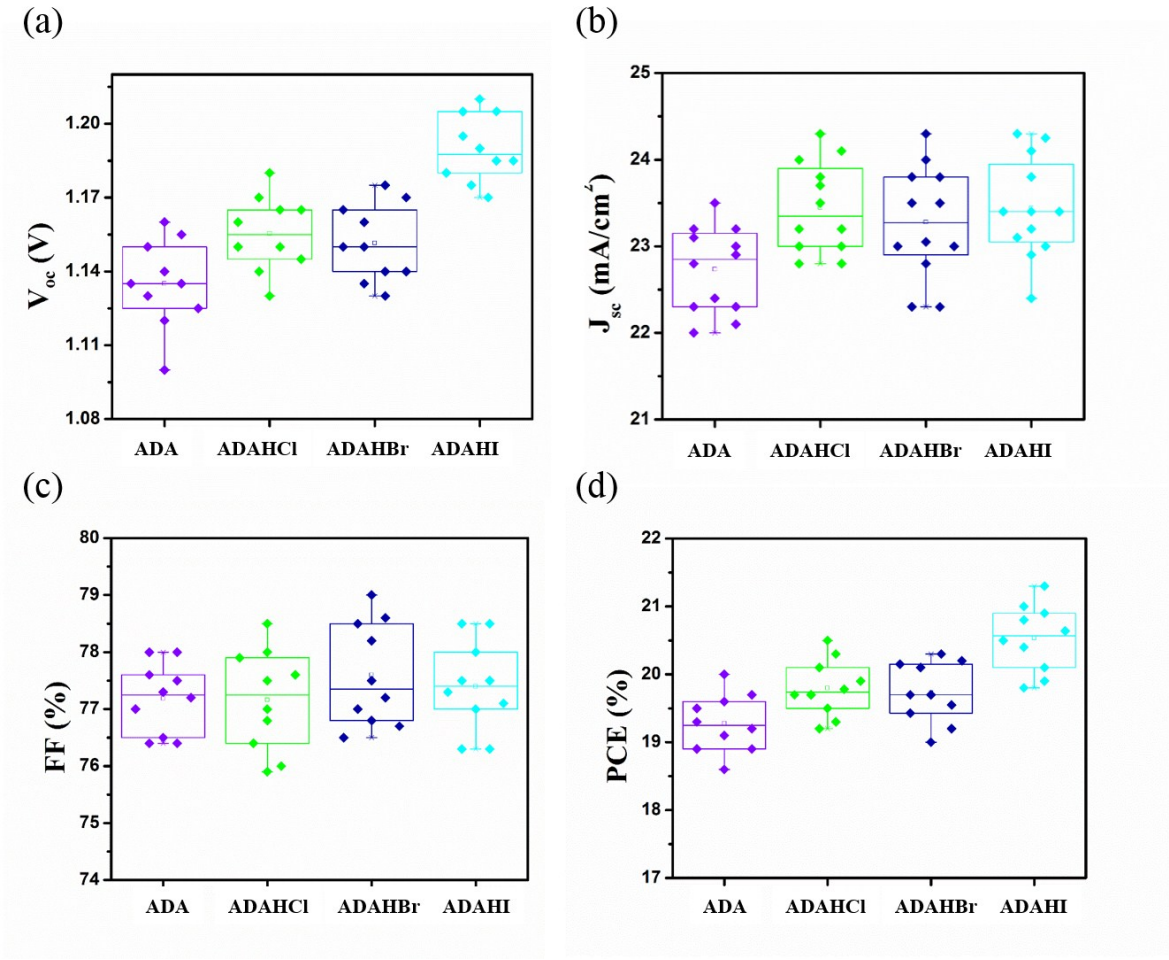

Figure S7. Statistics for photovoltaic parameters of triple A-cation PSC devices based on modified spiro HTL with ADA, ADAHCl, ADAHBr, and ADAHI additives.

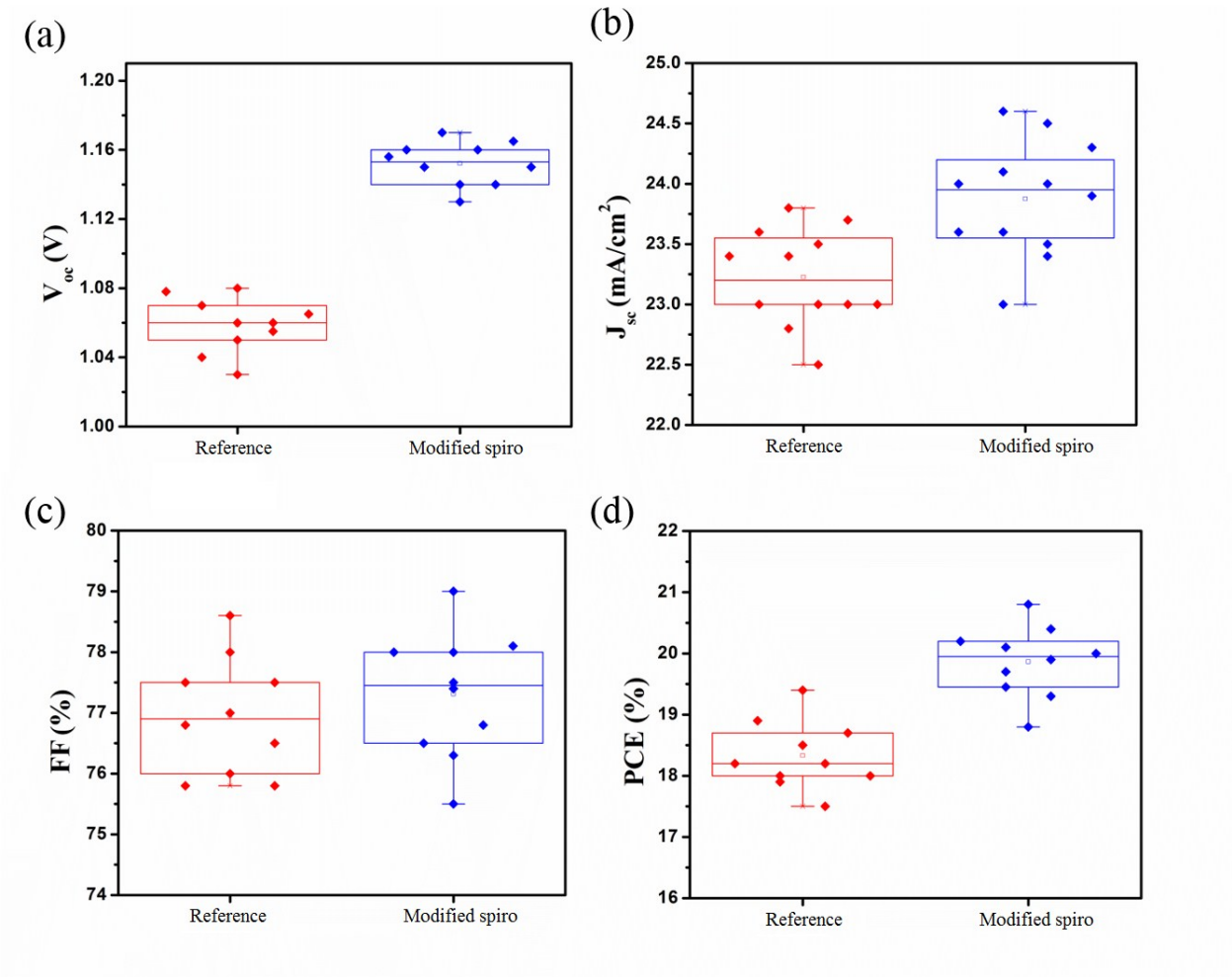

Figure S8. Statistics of photovoltaic parameters of $MAPbI_3$ single A-cation PSC devices based on reference and modified spiro HTL with ADAHI additive.

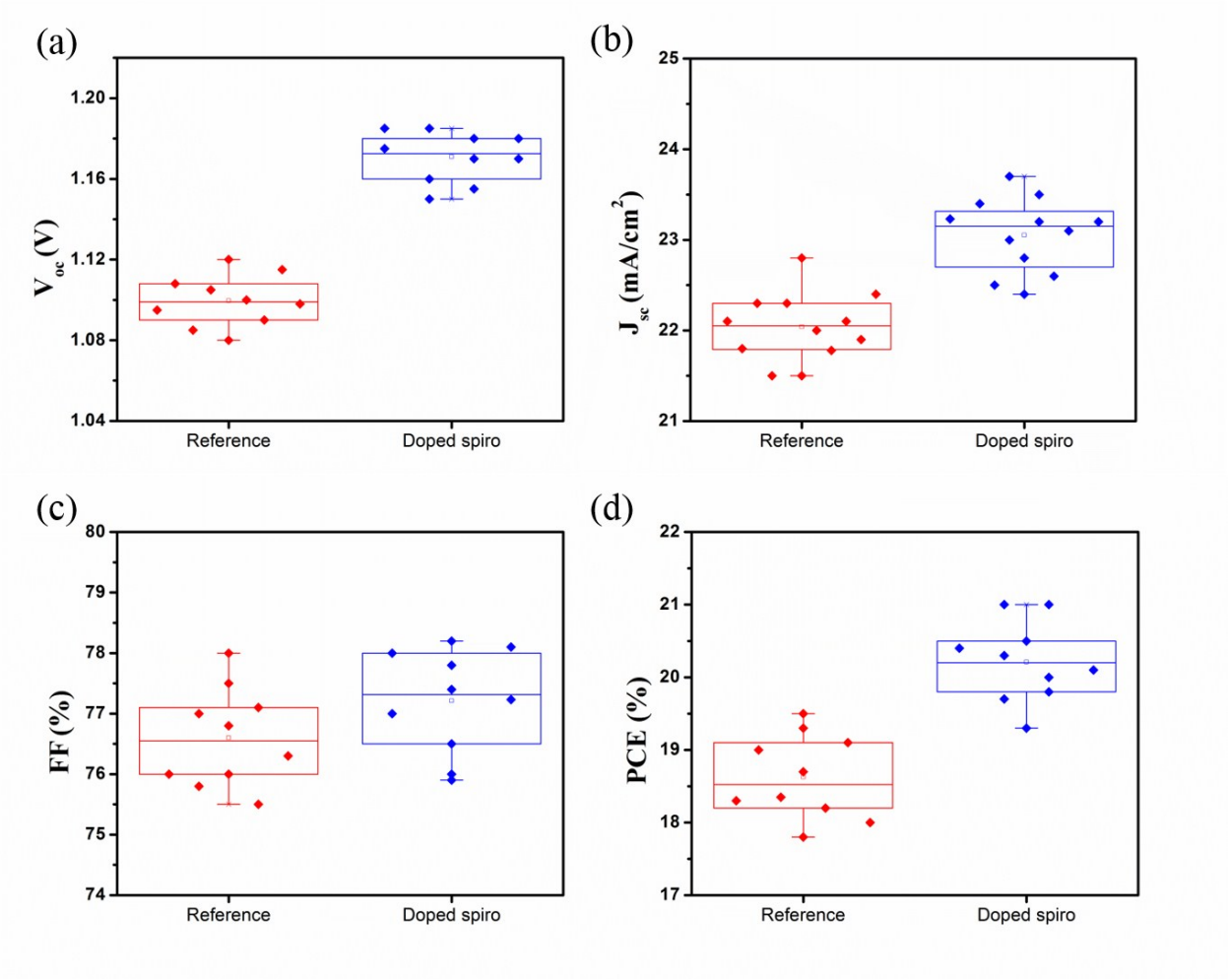

Figure S9. Statistics of photovoltaic parameters of double A-cation (Cs/FA) PSC devices based on reference and modified spiro HTL with ADAHI additive.

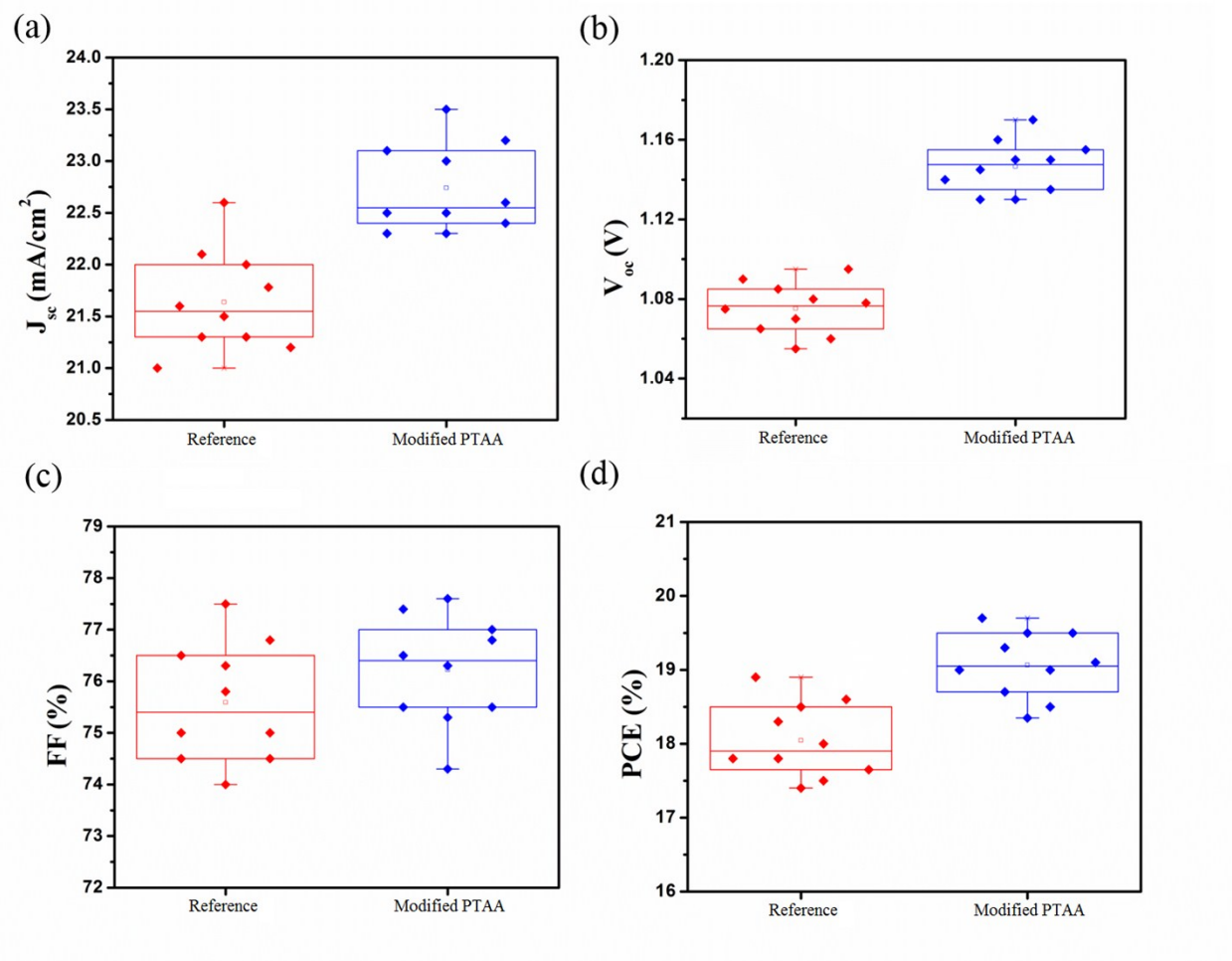

Figure S10. Statistics of photovoltaic parameters of triple A-cation PSC devices based on reference and modified PTAA HTL with ADAHI additive.

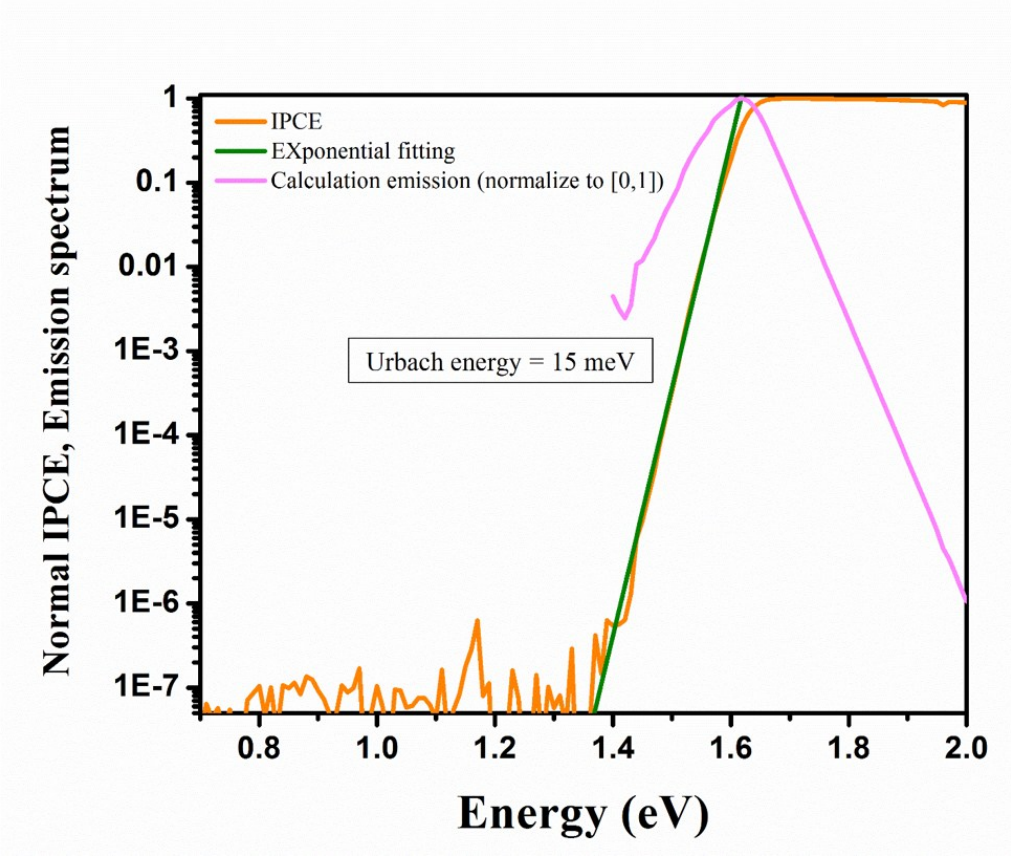

Figure S11. Urbach energy measurement of triple A-cation PSC device based on spiro modified by ADAHI additive.

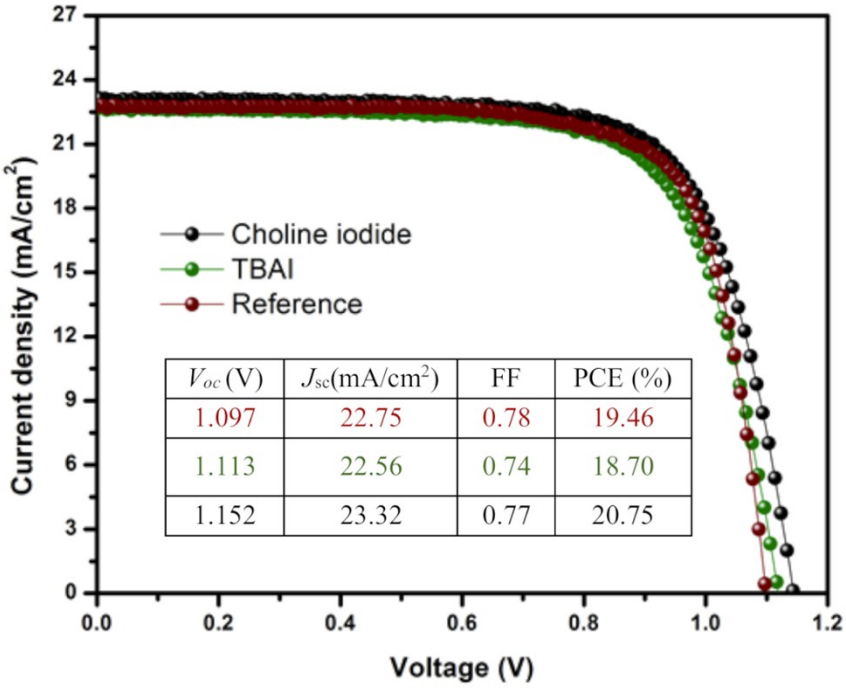

Figure S12. *J-V* curves of the devices treated by addition of alternative agents into HTL, comprising choline iodide (black) and *tert*-butylammonium iodide (TBAI; green), as compared to the reference (red). The corresponding PV metrics is shown in the inset.

Table S1. Figures of merit for champion reference cell and device with modified spiro by ADAHI (forward and backward scan directions)

Sample	V_{oc} (mV)	J_{sc} (mA/cm^2)	FF (%)	PCE (%)	Hysteresis index (%)
Reference-forward	1086	23	76.2	19	4.5
Reference - backward	1105	23.5	76.8	19.9	
ADHI-spire-forward	1156	24.2	76.7	21.5	1.9
ADHI-spire-backward	1164	24.3	77.3	21.9	