Supplemental information

Experimental Methods

Preparation of perovskite solar cells

All reagents including materials were used without further purification. ITO (Indium Tin Oxide) Coated Glass (Liaoning Yike Precision New Energy Technology Co.,Ltd.) and flexible substrates PET/IMI (purchased from OPVIUS GmbH) were ultrasonically cleaned sequentially for 10 minutes in acetone and isopropanol. Then, the substrates were treated under UV-Ozone box for 10 minutes to remove organic residues and to enable better wetting. For the standard device an aqueous SnO_2 nanoparticle solution (Alfa Aesar) was used to prepared the electron transport layer (ETL). The solution was diluted to 5.0 wt.% SnO_2 and treated in the ultrasonic bath for 10 minutes followed by filtering using a 0.45 μm PP filter. The solution was then doctor bladed at 60 °C with 10 mm/s and a gap height of 100 μm. Next, the film was annealed at 150 °C for 30 minutes to form a compact layer. For a simplified device, bis-(1-Methoxy-3-(6-phosphonic acid hexyloxy)-methano)-1,2-dihydro fullerene (FAPA in short, purchased from Nano-C which is dark brown powder can partially dissolve in alcohol) layer was blade-coated by using a filleted 1 mg/ml solution in (1-butanol, Aldrich, 99.8 %) at 10 mm/s and a gap height of 250 μm and following anneal at 100 °C for 5 min. Same solution and coating parameters applied on top of perovskite. Equal molar ratio of MAI (Sigma, 98 %) and PbI_2 (TCI, 99.99%) were dissolved in anhydrous N,N-Dimethylformamide (DMF, Aldrich, 99.8%) with1-methyl-2-pyrrolidinone (NMP, Aldrich, 99.8%), (DMF: NMP, 9:1) to prepare 1.25 M $MAPbI_3$ precursor solution and ultrasonication at room temperature for 10 mins. 1.25M FAPbI3 with 10% CsCl inside was prepared for mixing with MAPbI3 by 7:3 volume ratio. The precursor solution was doctor bladed onto the substrate at 4 mm/s and a gap height of 150 μm. The substrate with the still wet film was treated by air blowing for 5 seconds to get a dark brown perovskite intermediate film followed an annealing process at 120 °C for 10 minutes to get the final perovskite film. For the reference device, PEDOT (poly(3,4-ethylenedioxythiophene)) (HTL solar 3, purchased from Ossila) is being used as the hole transport layer. A gap height of 250 μm and a volume of 30 μl was used for doctor blading. The blade-coating temperature and speeds for PEDOT were 60 °C with 10 mm/s, following with annealed at 100°C for 5 minutes. For the simplified device a thin layer of FAPA on the top of perovskite with the same coating parameters of the layer on the ITO. Finally, the Carbon back electrode was printed by stencil method following by annealing on a hot plate at 120°C for 10 minutes.

Preparation of flexible perovskite solar modules

The preparation of flexible perovskite solar modules begins with the patterning of a flexible PET/IMI foil using a femtosecond laser to create P1 lines prior to coating with SnO_2 or FAPA.

Subsequently, the patterned conductive flexible foils undergo cleaning via a CO_2 laser. The layer of SnO_2 (3wt%) is then applied onto the clean, patterned PET/IMI using a roll-to-roll slot die at a flow rate of 0.3 ml/min. The resulting SnO_2 film undergoes transfer to an oven for annealing at 130ºC for a few minutes. Next, the printed SnO_2 substrates are cut into small pieces for the subsequent printing of perovskite and PEDOT complex via doctor blading within a dry air glove box. The simplified stack consisting of PET/IMI/FAPA/Perovskite/FAPA/Carbon was printed all by doctor blading. The layer stack before printing carbon is then subjected to patterning of P2 lines using a femtosecond laser power of 850mW. Finally, carbon electrodes are printed onto the substrate using a stencil mask to create P3 lines, followed by transfer to a hotplate for annealing for 10 minutes at 120ºC.

Characterization

Photoluminescence measurement: Steady-state PL was measured using a 402 nm laser diode as the excitation source in a back-scattering configuration. The transient PL test was performed with a Fluotime 300 system. The samples were excited through the glass substrate.

PLQY: Tt was collected by an integrating sphere with a 405nm laser diode as the excitation source. The laser intensity was controlled by a step beam attenuator. The intensity of 1 sun illumination was subject to the photo flux equal to AM1.5 spectrum.

XPS: X-ray is used to irradiate a solid surface for obtaining the kinetic energy of electrons that emitted from the top several nanometres of the samples.

UPS: UPS refers to the measurement of kinetic energy spectra of photoelectrons emitted by molecules which have absorbed ultraviolet photons (He 1=21.2eV), in order to determine molecular orbital energies in the valence region.

Scanning Kelvin Probe measurement: The Kelvin probe measures the contact potential difference between a sample and a tip-not the work function (WF) of the sample. The WF of the sample can be calculated by determining the WF of the tip calibrated against a known surface.

STEM imaging, a cross-sectional sample lamella was prepared with an FEI Helios Nanolab Dualbeam Focused Ion Beam (FIB)/SEM. The lamella was immediately transferred into an FEI Tecnai Osiris 80–200 TEM, minimizing air exposure to ~2 min. The electron beam acceleration voltage was set at 200 kV. STEM high-angle annular dark-field images were acquired using a beam current of 250 pA and a dwell time of 1 µs per pixel.

Characterization of devices: Solar cells were characterized by measuring their current–voltage (JV)-characteristics with a AAA solar simulator, which provides AM1.5G illumination and source measurement system from LOT-Quantum Design, calibrated with a certified silicon solar module. The sweeping ranges for solar cells are -0.2 V to 1.5 V in steps of 20 mV.
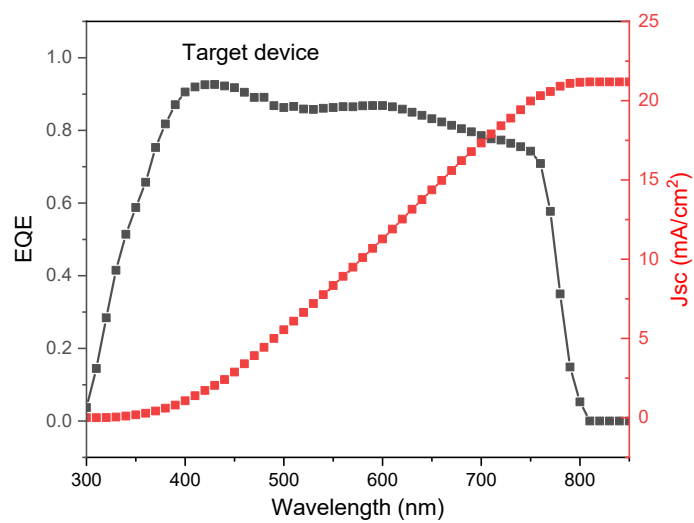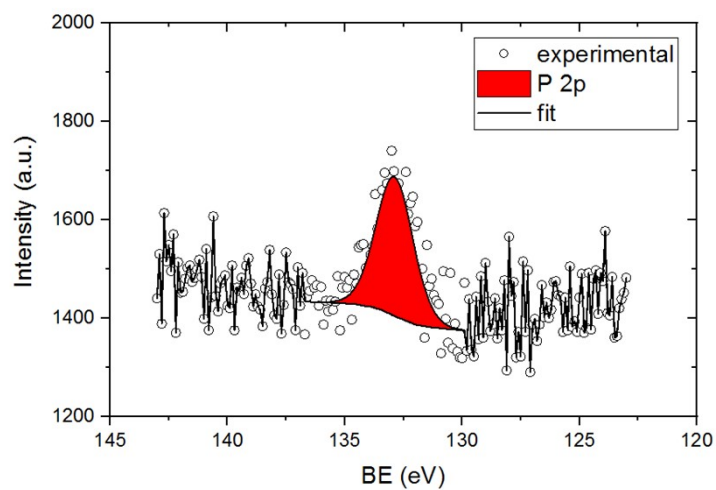
Figure S1. EQE spectrum of target device of ITO/FAPA/Pero/FAPA/Carbon and corresponding integrated photocurrent.
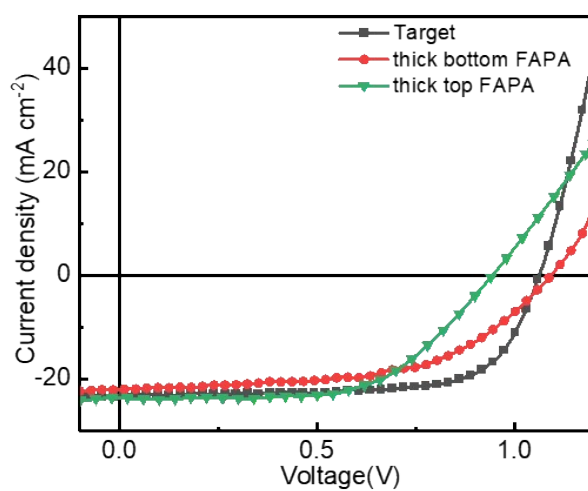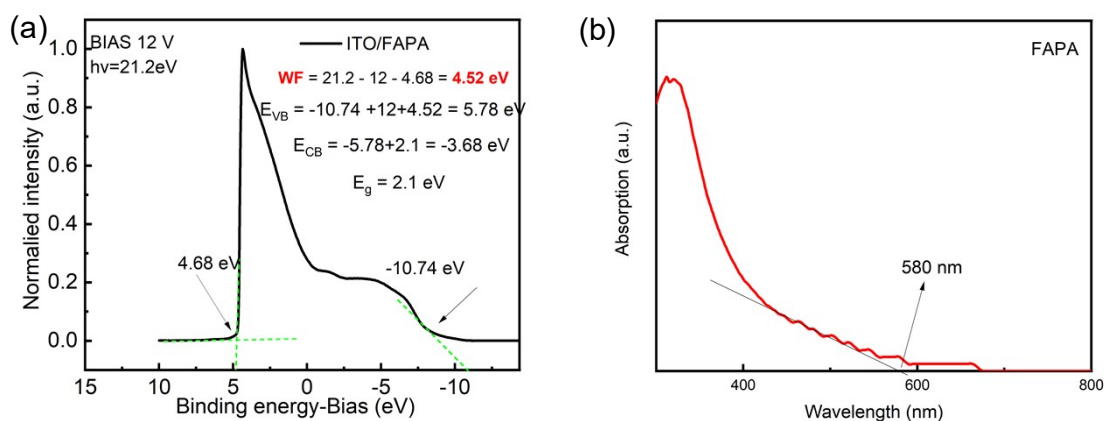

Figure S2. (a) JV curves with thick bottom or top FAPA compared to target device.
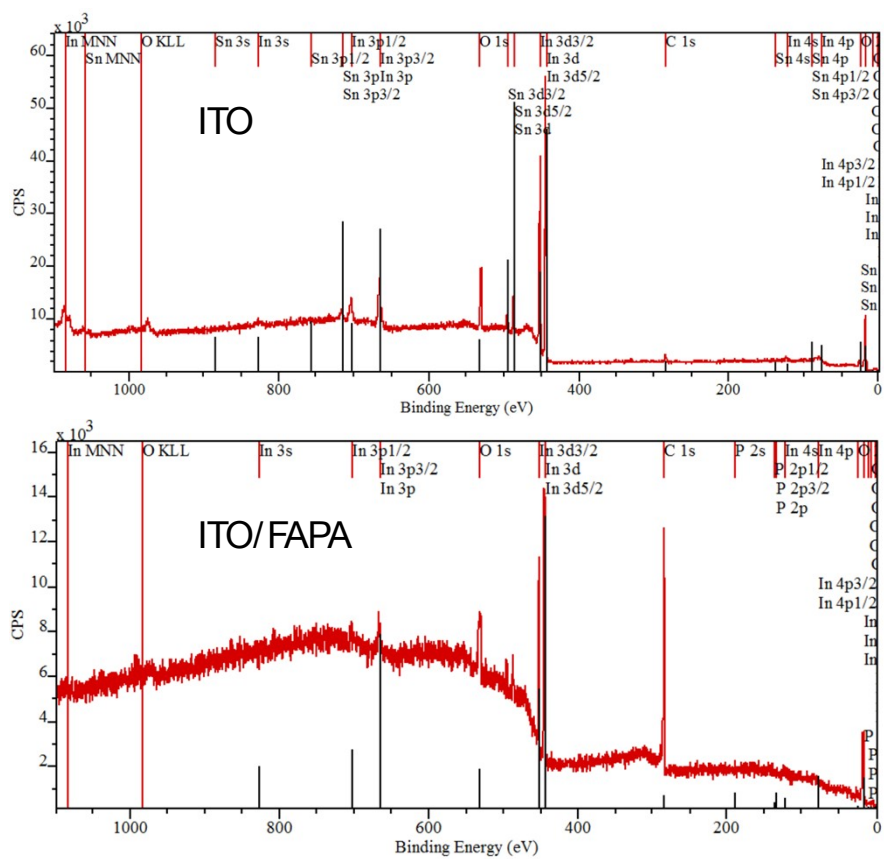
**Figure S3.** Full XPS spectroscopy of sample ITO wi/wo FAPA layer.

**Figure S4.** Charateristic phosphorus element measured by XPS on the surface of ITO with FAPA layer.

Figure S5. (a) Secondary electron cut-off energy edge measured by UPS on the surface of ITO with FAPA layer and (b) The absorotance of the FAPA in 1-butanol measured in a Quartz Cuvette and the aborption peak is located in 275 nm the corresponding optical is around 3.83 eV.
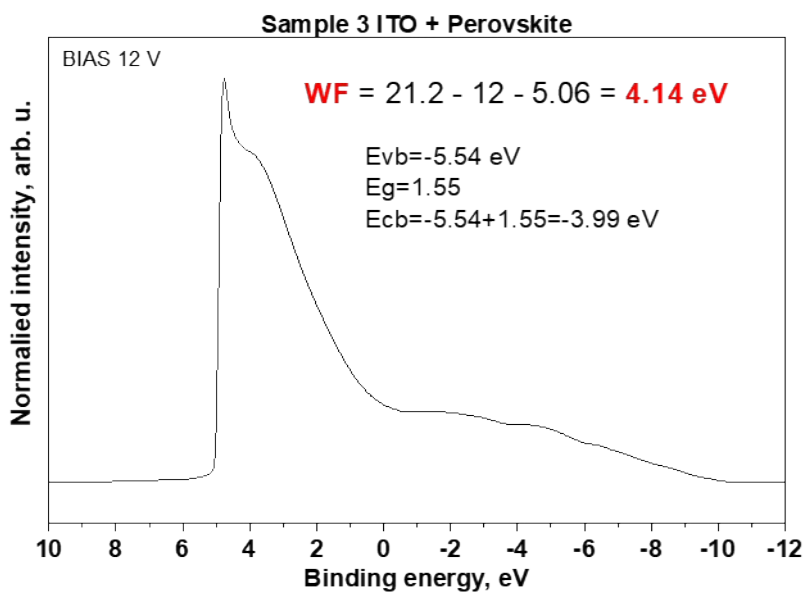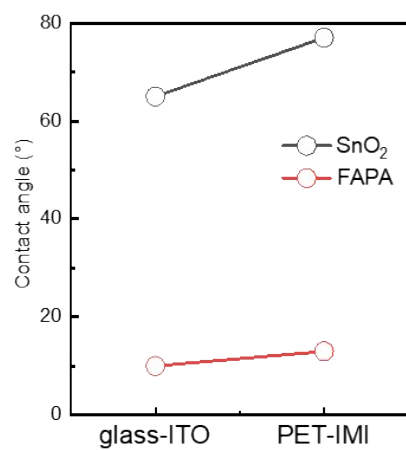

**Figure S6.** The UPS spectra of perovksite on ITO and calculated LUMO and HOMO.
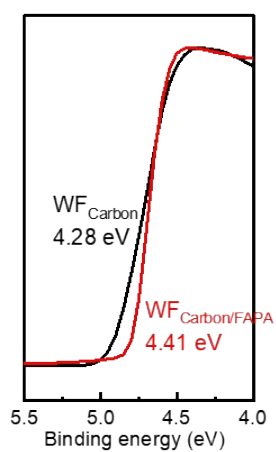
Figure S7. UPS spectra of ITO/Carbon and ITO/Carbon/FAPA surfaces. The WFs of each layer evaluated from the cut-off energies in the spectra are denoted in the figure.
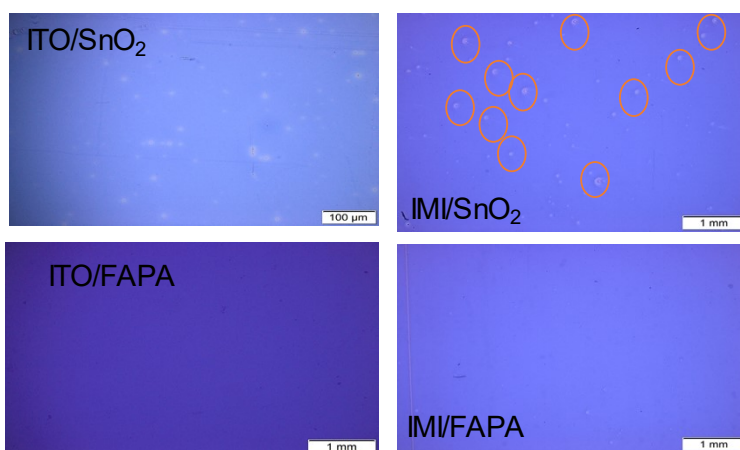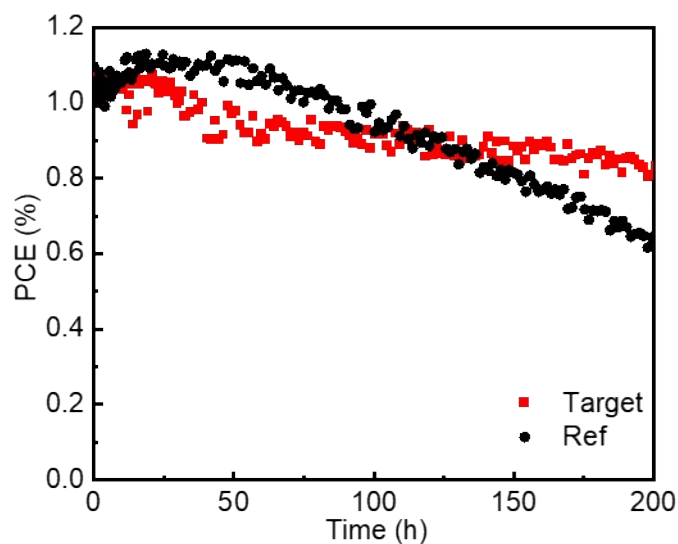

**Figure S8.** The optical images of SnO_2 and FAPA layer on glass-ITO and PET-IMI substrate.

Figure S9. The values of contact angles of SnO$_2$ and FAPA inks on glass-ITO and PET-IMI substrates.
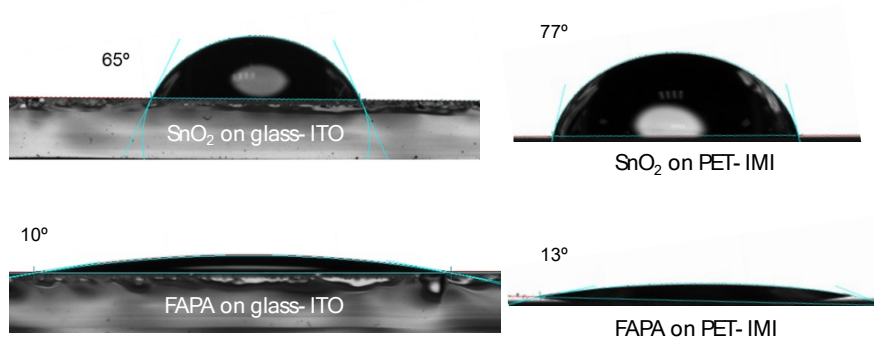
Figure S10. The images of contact angles of SnO$_2$ and FAPA ink deposited on glass-ITO and PET-IMI substrates.

Figure S11. Normalized PCE of target and reference device under 1 sun illumination at 65ºC.
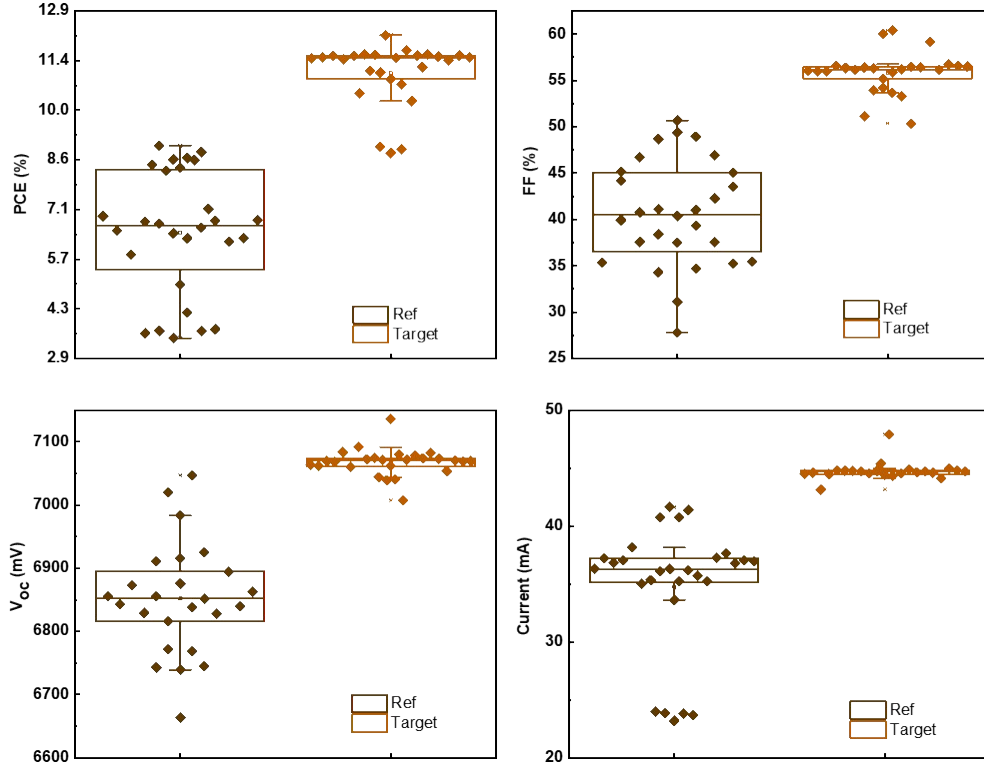
Figure S12. Data for flexible perovskite modules were collected from over 20 devices for both the target and reference groups.

Note 1: It is assumed that the all emission is generated from the direct radiative recombination due to absorbed every photon. According to the detailed balance theory the radiative recombination current density[1] can be written in the following expression:

$$J_{rad} = J_{0,rad}\,exp\left(\frac{\mu}{KT}\right) \tag{1}$$

Where μ represent the QFLS, $J_{0,rad}$ is the radiative thermal equilibrium recombination current density in the dark. k is Boltzmann constant and the temperature T=300K. By transformation of equation (1), the QFLS can be calculated by the equation (2).

$$\mu = KTln\left(\frac{J_{rad}}{J_{0,rad}}\right) = KTln\left(\frac{PLQY \times J_G}{J_{0,rad}}\right) = KTln\left(\frac{J_G}{J_{0,rad}}\right) + KTlnPLQY \tag{2}$$

Where JG is the total free charge generation current density, and PLQY equals the ratio between

J_G and $J_{0,rad}$. The first term of $KTln\left(\dfrac{J_G}{J_{0,rad}}\right)$ indicate the radiative recombination of the solar cells. The latter part is used to quantify non-radiative recombination losses. Where $J_{0,rad}$ can be expressed by equation (3)

$$J_{0,rad} = q \int_0^\infty EQE_{PV}(E)\emptyset_{bb}(E)dE \tag{3}$$

And the black body radiation of solar cells $\emptyset_{bb}$ is equals to:

$$\emptyset_{BB}(E) = \frac{2\pi E^2}{h^3 c^2} \frac{1}{\exp\left(\dfrac{E}{KT}\right) - 1} \approx \frac{2\pi E^2}{h^3 c^2} exp(-E/KT) \tag{4}$$

Where q is the elementary charge, E the photon energy and c light velocity in vacuum.

1. Shockley, W.; Queisser, Detailed balance limit of efficiency of p-n junction solar cells. **1961,** *32* (3), 510-519.