Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Synergistic Interface and Compositional Engineering of Inverted Perovskite Solar Cells Enable Highly Efficient and Stable Photovoltaic Device

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Experimental section

Device fabrication:

ITO glasses were cleaned by immersing them in the following batches and ultrasonic for 20 min: Triton X100 (1%vol in deionized (DI) water, DI water, acetone, and isopropanol. Before deposition of NiO HTL, the ITO glasses were further treated by oxygen plasma for 10 min. Then, NiO was deposited by spin-coating a solution (1 M) of nickel (II) nitrate hexahydrate ($Ni(NO_3)_2.6H_2O$, Sigma Aldrich) dissolved in ethylene glycol with ethylenediamine (Sigma Aldrich) and lithium slat additives at 3000 rpm for 100 s, followed by annealing in air at 300 ˚C for 1h. Before deposition of perovskite film, the surface of NiO film was treated with either oxygen plasma (10 min) or a solution of PFN-P2 (0.5 mg/1 mL methanol). The triple-A cation perovskite solution was prepared from a precursor solution of FAI (1.05 M, Dyesol), PbI_2 (1.10 M, TCI), MABr (0.185 M, Dyesol) and $PbBr_2$ (0.185 M, TCI) dissolved in mixed solvents of DMF:DMSO = 4:1 (volume ratio) with 5

vol% excess amount of CsI (1.5 M in DMSO). In order to study the role of DI water in perovskite film, different amount of DI water (1,2,3,4 vol%) was added to the as-prepared perovskite solution. The perovskite solution was deposited on the substrates in two-step: 1000 rpm for 10 s and 6000 rpm for 30 s (ramp rate: 2000 rpm/s). 10 second before end of spinning, 60 µL of chlorobenzene (CB) as an anti-solvent was dropped on the film. Then, all the films were annealed at 105 °C for 40 min in a nitrogen-filled glovebox. Afterward, the device structure was completed by thermal evaporation of C60 (23 nm) as an ETL, BCP (8 nm) as a buffer layer, and Ag (100 nm) as an electrode, respectively.

Film characterization

Film characterization was performed by scanning electron microscopy (SEM, ZEISS Merlin) and atomic force microscopy (AFM, NanoScope IIIa/Dimension 3100) to investigate morphology, x-ray diffraction (XRD, Bruker D8 X-ray Diffractometer (USA)) to study crystallinity, UV–visible (Varian Cary 5) and photoluminescence (PL, a Fluorolog 322 (Horiba Jobin Ybon Ltd); PL excitation at λ=460 nm) measurements to observe the optical properties of films. To evaluate lifetime of perovskite films, TRPL was measured by a picosecond pulsed diode laser (EPL-405, with excitation wavelength of λ=405 nm and pulse width of 49 ps), followed by curve fitting using biexponential formula of $I(t) = A_i \exp(-t/\tau_i)$, ($A_i$ and τ_i are the amplitude and the lifetime, respectively). An omicron ultrahigh vacuum system was utilized to measure ultraviolet photoelectron spectroscopy (UPS). To study the Fermi level and valence bands of different layers, a He I line (21.2 eV) of a helium discharge lamp was used.

Device measurement

To characterize PV properties of the PSCs, a 450 W xenon lamp (Oriel, USA) together with a digital source meter (Keithley model 2400, USA) were employed to simulate the sunlight according to the standard AM 1.5 G conditions. A Schott K113 Tempax sunlight filter (Präzisions Glas & Optik GmbH, Germany) was used as a filter for simulated light. During the J-V measurement, the voltage scan rate and the dwell time were 10 mV/s and 15 s, respectively. Hysteresis indices (HIs) were calculated by the following equation: $HI = ((PCE_{backward}-PCE_{forward})/PCE_{backward})*100$. For external quantum efficiency measurement, a commercial apparatus (Arkeo-Ariadne, Cicci Research s.r.l.) with a 300 Watts Xenon lamp was used.

In order to evaluate the stability, we performed the experiment in a nitrogen-filled glovebox. The devices were exposed to sunlight (simulated standard AM 1.5G condition using an array of white LED lamp) for 300 h. The devices were measured over time under illumination and maximum power point tracking (MPPT). For EIS measurement, autolab with a frequency range from 200 mHz to1 MHz was used.

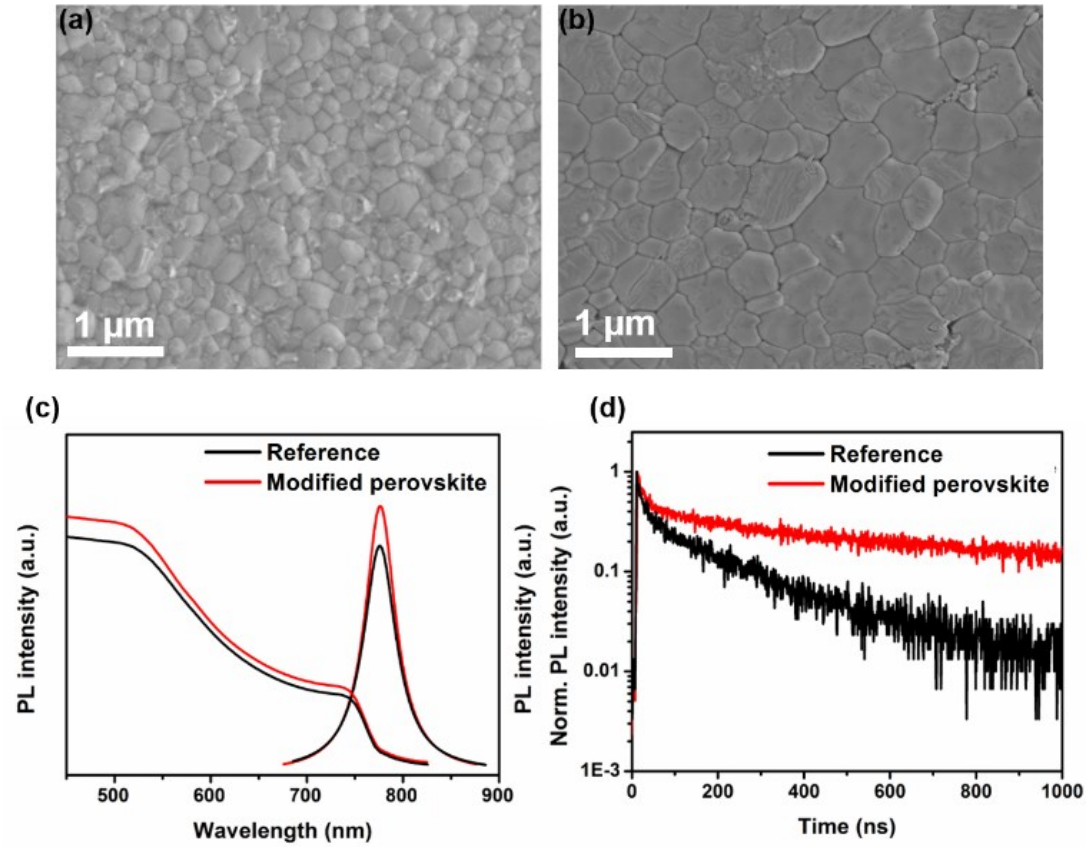

Figure S1. Top-view SEM images of perovskite films, (a) reference and (b) modified perovskite by DI water. (c) UV-visible and PL spectra and (d) TRPL curves of the corresponding perovskite films.

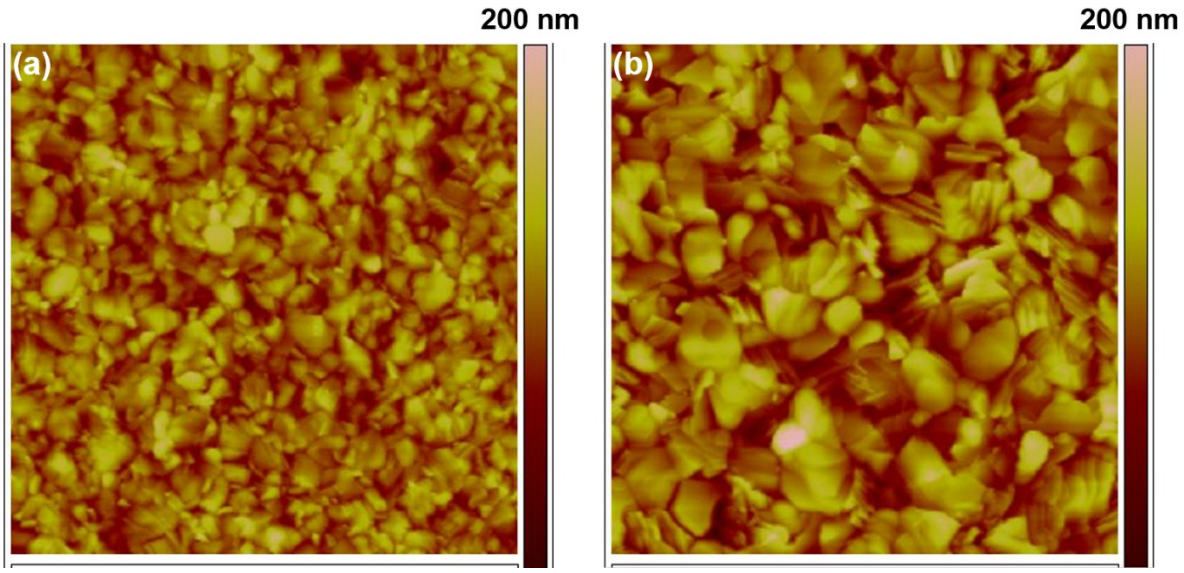

Figure S2. AFM images of reference (a) and modified perovskite films by DI water (b). Note that the area of image is 10×10 μm^2.

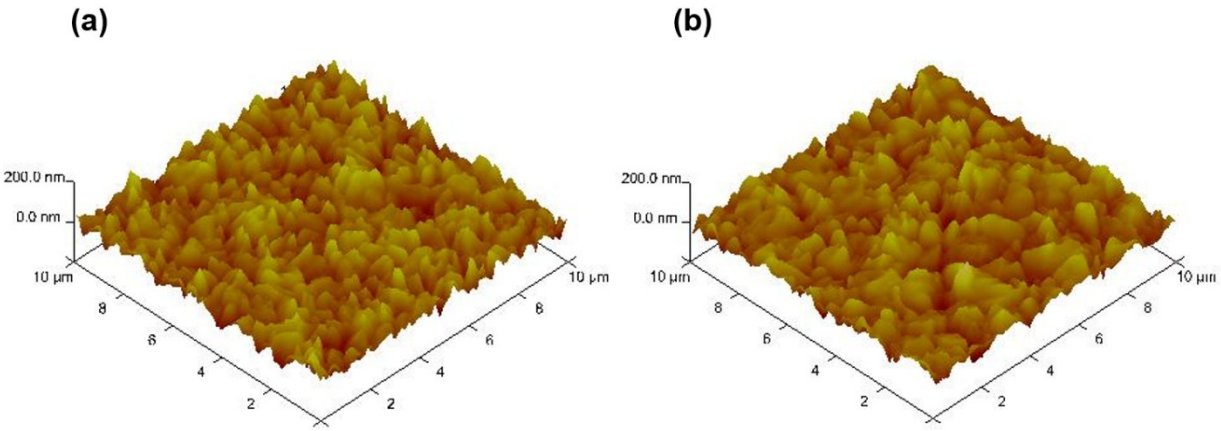

Figure S3. 3D-AFM images of reference (a) and modified perovskite films by DI water (b).

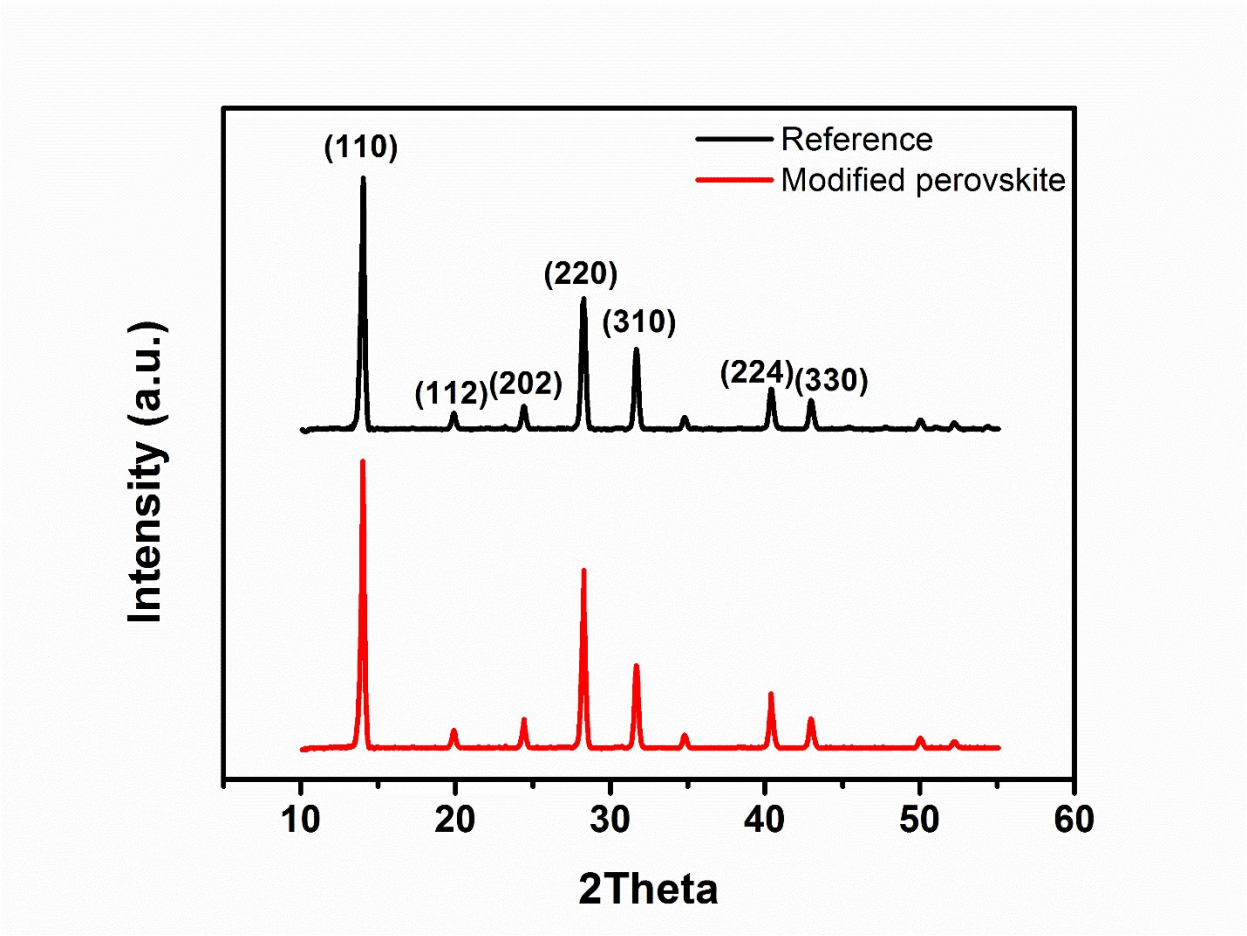

Figure S4. XRD patterns of the perovskite films without and with water additive.

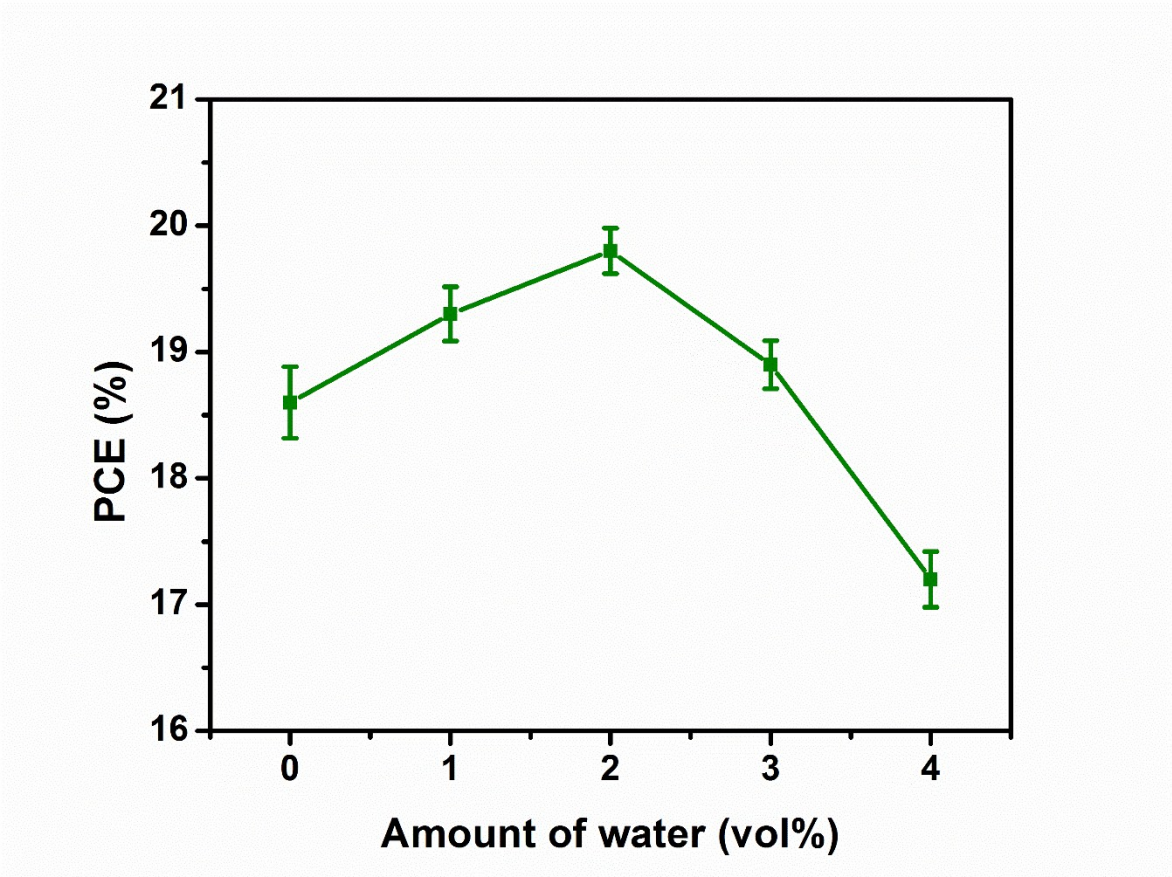

Figure S5. Variation of PCE with the amount of water additive inside of the perovskite solution.

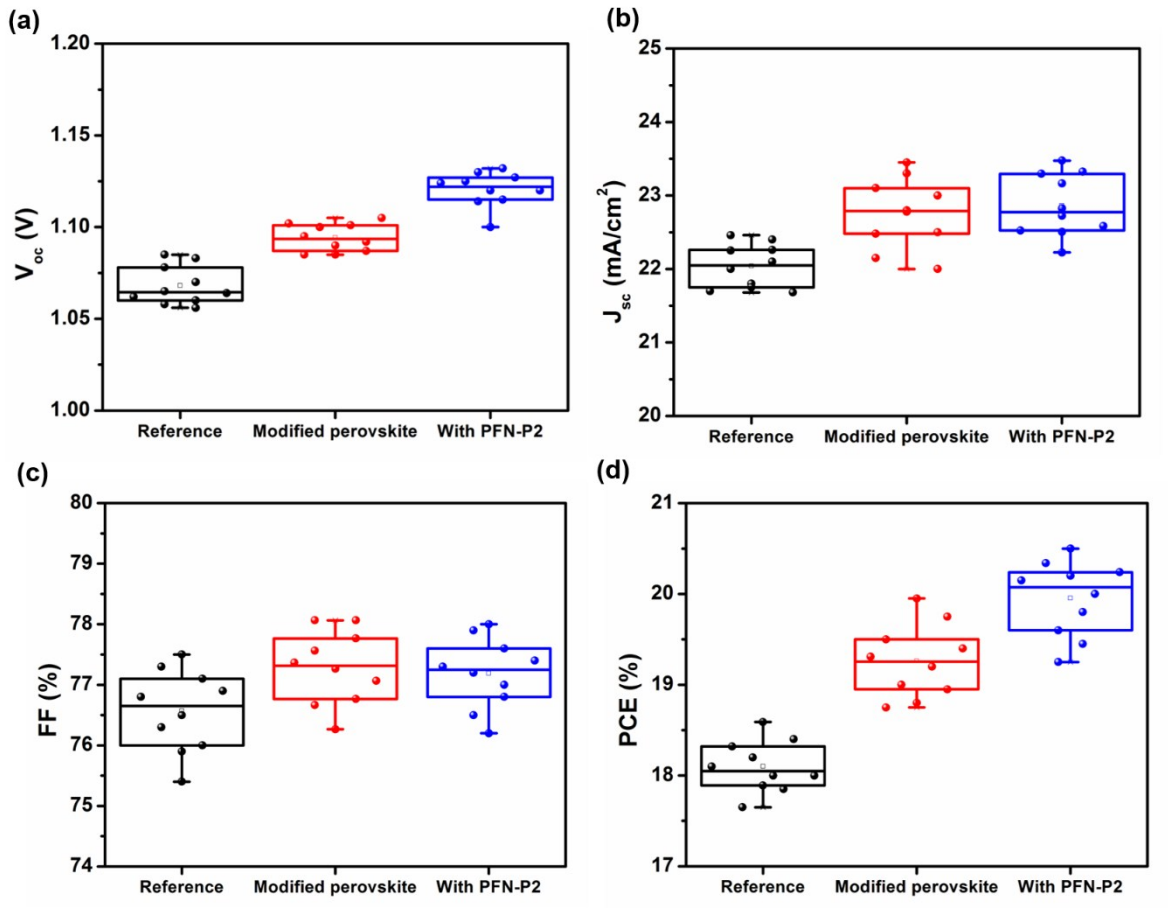

Figure S6. Statistics of the PV parameters for the reference device and the modified PSCs without and with PFN-P2.

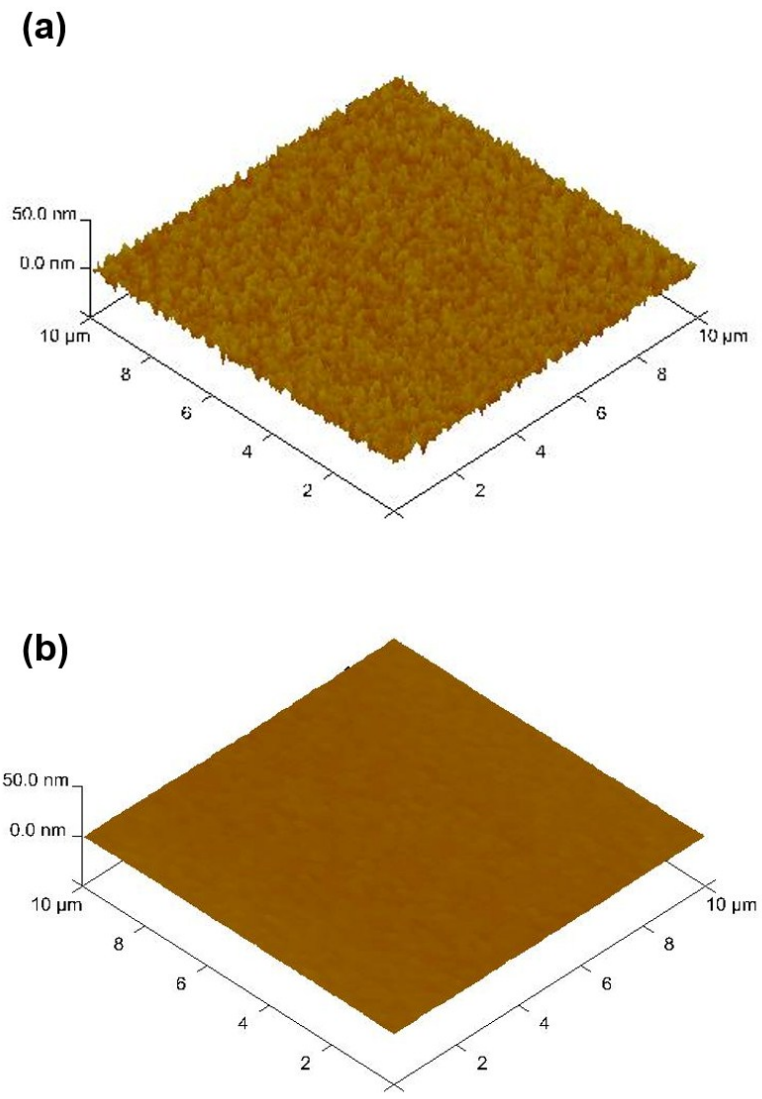

Figure S7. 3D AFM images of NiO (a) and NiO/PFN-P2 HTLs.

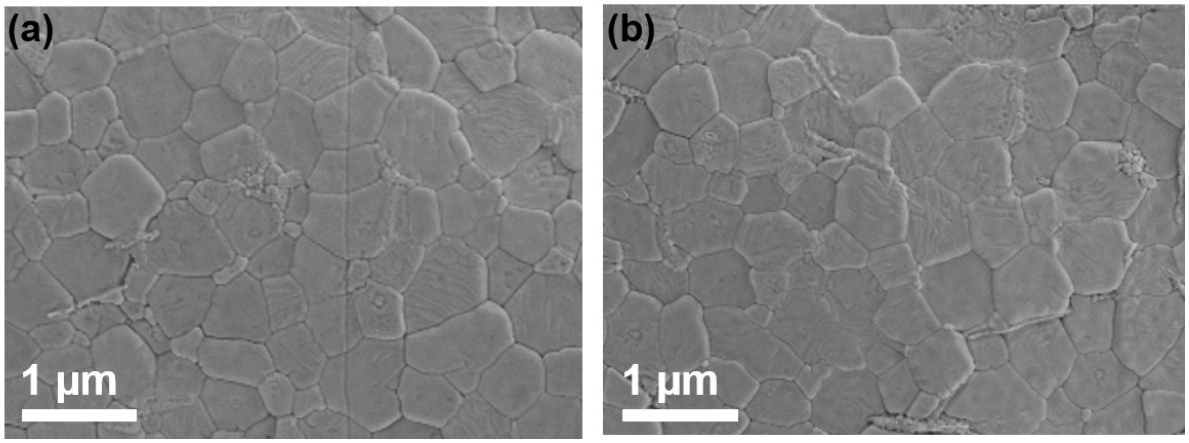

Figure S8. Top-view SEM images of perovskite films deposited on NiO (a) and NiO/PFN-P2 HTLs.

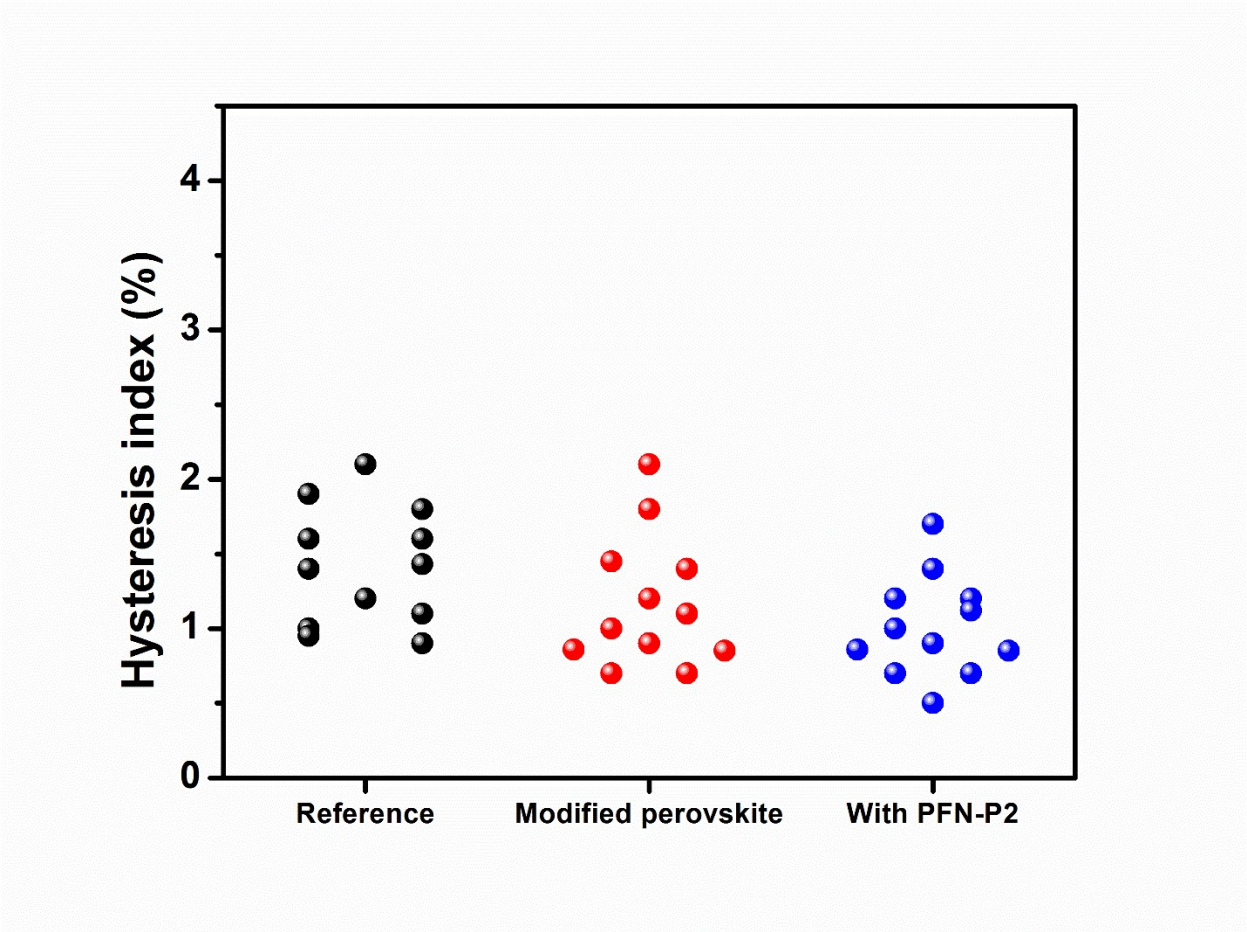

Figure S9. Statistics of the HI parameter for the reference device and the modified PSCs without and with PFN-P2.

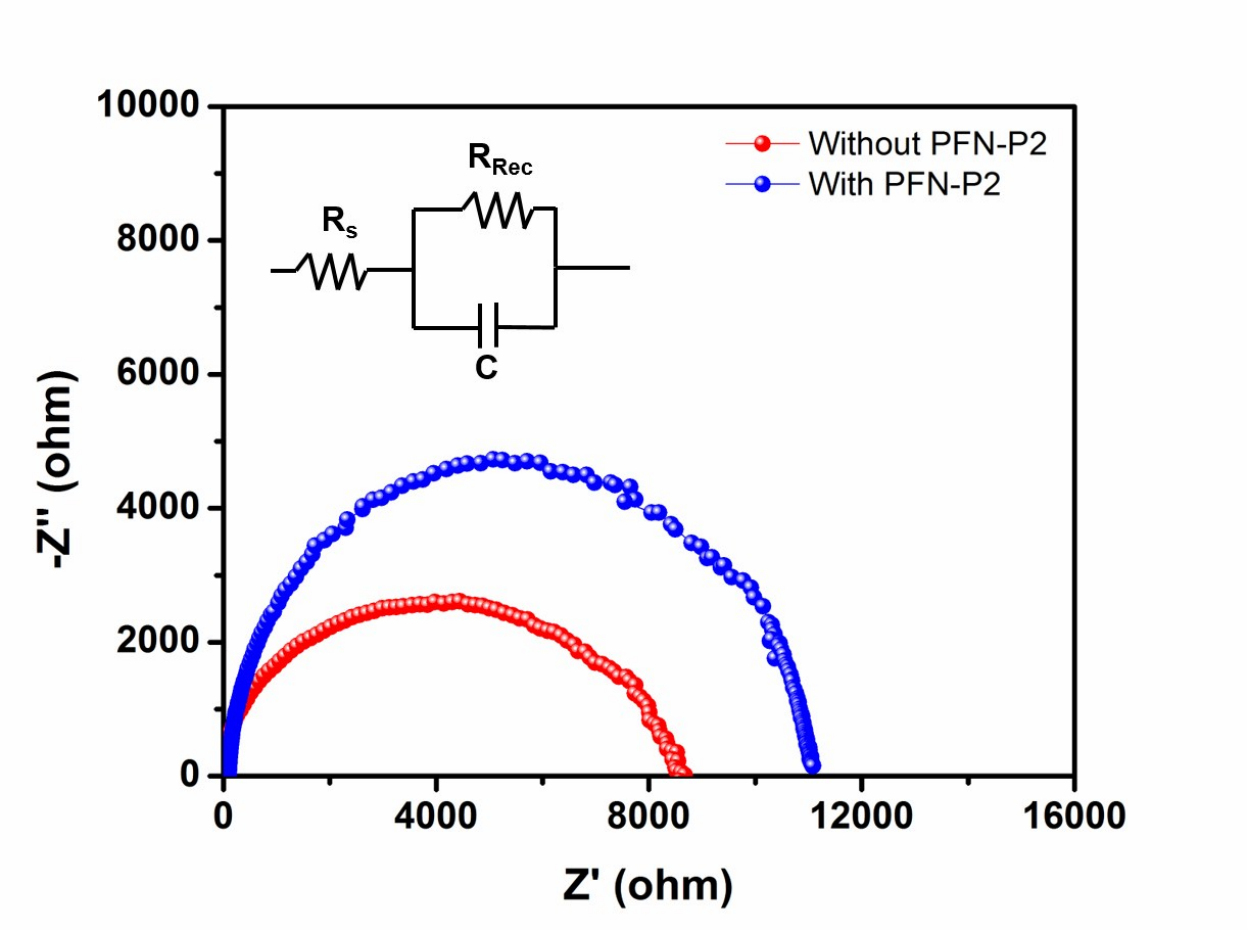

Figure S10. Nyquist plots of the modified PSCs without and with PFN-P2.

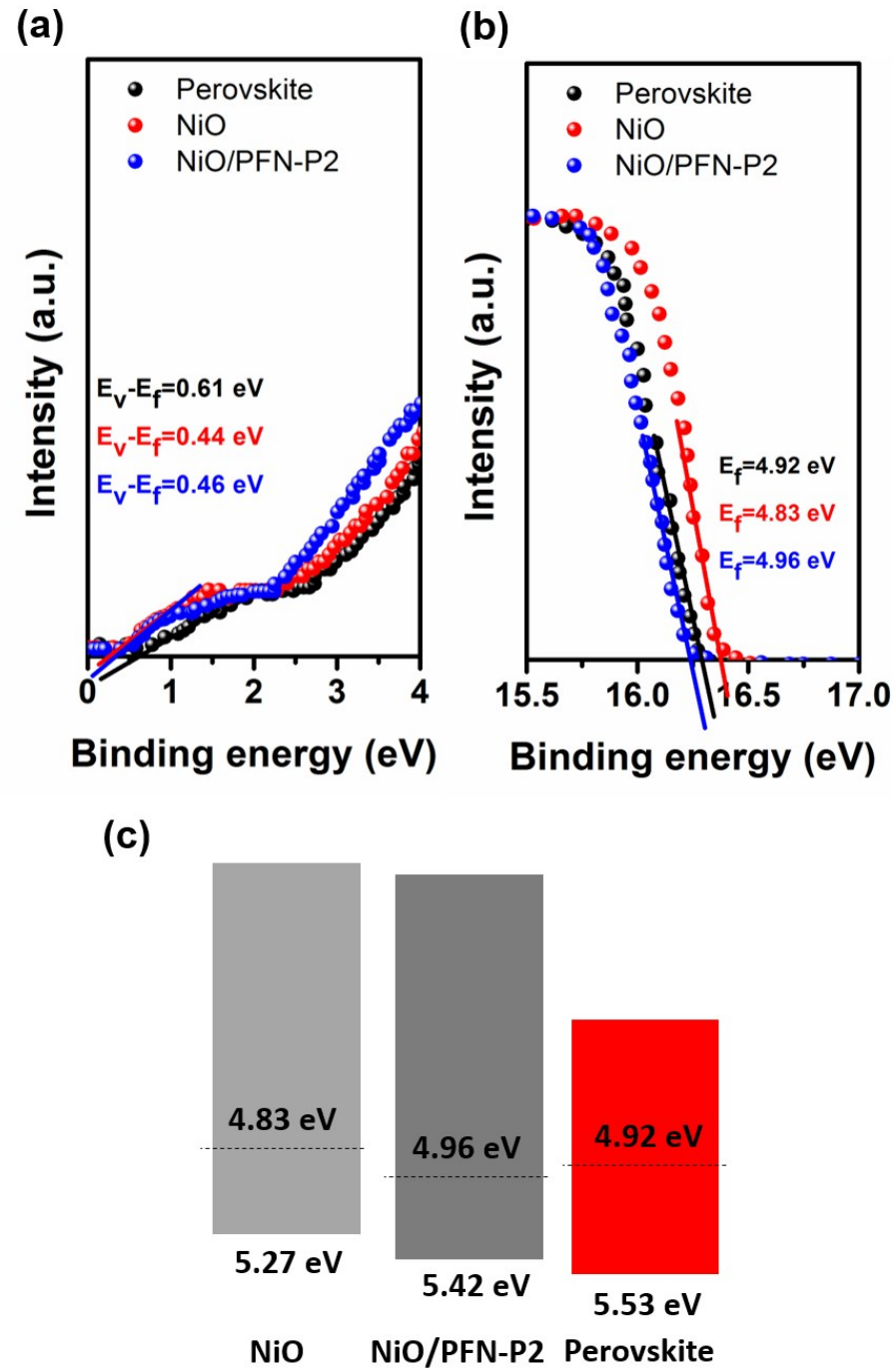

Figure S11. UPS measurement of perovskite, NiO and NiO/PFN-P2 films indicating (a) the difference between valence band and Fermi level and (b) the Fermi level. (c) Band diagram of the perovskite film in contact with HTLs.

Table S1. Fitting parameters of TRPL curves for the perovskite films without and with water deposited on glass

Sample	A_1	τ_1 (ns)	A_2	τ_2 (ns)
Reference	2.8	14.55	0.36	216.3
Modified perovskite	3.5	23.1	0.32	883.4

Table S2. Figures of merit for the reference device and the modified PSCs by water and PFN-P2

Device	V_{oc} (mV)	J_{sc} (mA/cm^2)	FF (%)	PCE (%)	MPP (%)
Reference	**1083**	**22.26**	**77.1**	**18.59**	**18.45**
Modified perovskite	**1101**	**23.3**	**77.8**	**19.95**	**19.73**
Modified perovskite with PFN-P2	**1132**	**23.33**	**77.6**	**20.5**	**20.27**

Table S3. Fitting parameters of TRPL curves for the perovskite films deposited on NiO and PFN-P2/NiO HTLs

Sample	A_1	τ_1 (ns)	A_2	τ_2 (ns)
With PFN-P2	0.87	2.51	0.13	7.95
Without PFN-P2	0.79	3.9	0.2	9.95