Supporting Information

High Efficiency Perovskite Solar Cells with PTAA Hole Transport Layer enabled by PMMA:F4-TCNQ Buried Interface Layer

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Experimental section

Materials

CH_3NH_3I (MAI, 99%), PbI_2 (99.99%), PTAA (Mn < 6000), F4-TCNQ, phenyl-C61-butyric acid methyl ester ($PC_{61}BM$, 99.5%) and bathocuproine (BCP) were purchased from Xi'an Polymer Light Technology Corp. Ag was purchased from Zhongnuo Advanced Material (Beijing) Technology Co., Ltd. PMMA, N,N-dimethyl forma-mide (DMF), dimethyl sulfoxide (DMSO), chlorobenzene (CB, 99.5%), toluene, ethyl acetate and isopropanol were obtained from Shanghai Aladdin biotechnology co., LTD.

Device fabrication

The F4-TCNQ precursor solutions with different concentrations of 0.015, 0.025, and 0.035 mg mL^{-1} were prepared by dissolving F4-TCNQ in ethyl acetate solvent. The PMMA precursor solutions with different concentrations of 0.5, 1.0, and 1.5 mg mL^{-1} were prepared by dissolving PMMA in ethyl acetate solvent. PMMA:F4-TCNQ mixture solution was

prepared by dissolving F4-TCNQ in PMMA precursor solution. The PTAA solution with a concentration of 5 mg mL^{-1} was prepared by dissolving PTAA in toluene solvent. The F4-TCNQ solution with a concentration of 0.15 mg mL^{-1} was prepared by dissolving F4-TCNQ in toluene solvent. A 20 nm thick ETL was prepared by spin-coating using $PC_{61}BM$ solution with a concentration of 20 mg mL^{-1}, formulated by dissolving $PC_{61}BM$ in chlorobenzene solvent. The cathode buffer layer was fabricated by spin-coating using BCP solution with a concentration of 0.5 mg mL^{-1}, prepared by dissolving BCP in isopropanol solvent. The $MAPbI_3$ layer was prepared using the two-step process, (1) spin-coating using the $MAPbI_3$ precursor solution, containing PbI_2 (1.3 mol) and MAI (0.3 mol) in DMSO and DMF (1:9), (2) spin-coating using the MAI precursor solution, prepared by dissolving MAI (40 mg mL^{-1}) in isopropanol.

The pre-patterned indium tin oxide (ITO)/glass substrates were cleaned by ultrasonication sequentially in deionized water, ethanol, acetone and isopropanol each for 15 min. The wet cleaned ITO/glass substrates were dried by the pure N_2 gas stream and then exposed to the ultraviolet-ozone treatment for 5 min. A 30 nm thick PTAA HTL was prepared on the ITO surface by spin-coating PTAA solution, filtered by a 0.45 μm pore size filter, with a rotation speed of 4000 rpm for 30 s, following an annealing at 100°C for 15 min in glove box. The F4-TCNQ-, PMMA- and PMMA:F4-TCNQ-modified PTAA HTLs were prepared by spin-coating at a rotation speed of 6000 rpm for 30 s using different solutions of F4-TCNQ, PMMA and PMMA:F4-TCNQ on the surface of the PTAA layers separately forming PTAA/F4-TCNQ, PTAA/PMMA and PTAA/PMMA:F4-TCNQ HTLs. The modified PTAA HTLs were then annealed at 100°C for 10 min in glove box. The perovskite active layer was prepared using a two-step process, (1) spin-coating using a 60 μL of the mixture precursor solution of PbI_2 (1.3 mol) and MAI (0.3 mol) in DMSO and DMF (1:9) on the HTL surface at 6000 rpm for 15 s, (2) then using a 70 μL MAI solution (40 mg mL^{-1} in isopropanol) at 4000 rpm for 45 s. A 20 nm thick $PC_{61}BM$ ETL was formed on the perovskite layer by spin-coating using $PC_{61}BM$ solution (25 μL) at a rotation speed of 2700 rpm. The BCP cathode buffer layer was formed on the $PC_{61}BM$ ETL by spin-coating using BCP solution (25 μL) at a rotation speed of 6000 rpm for 30 s. Finally, a 100 nm thick Ag electrode was deposited on the BCP cathode buffer layer by thermal evaporation in an adjacent vacuum chamber with a base pressure of $< 5.0\times10^{-4}$ Pa.

Device characterization

The ultraviolet-visible (UV-vis) absorption spectra of the function layers were measured using a UV-Visible spectrometer with an integrating sphere (Shimadzu UV-2600). Photocurrent density-voltage (*J*−*V*) characteristics were measured using a Keithley 2400 source meter under AM1.5G illumination (100 mW cm^{-2}) using a calibrated xenon-lamp-based solar simulator (ABET Sun 3000). The active area of PSCs is 0.04 cm^2. X-ray diffraction (XRD) patterns of the perovskite layers were measured using the X-ray diffractometer (D2 PHASER 2nd Gen Flyer DOC-H88-EXS 063 V6 high). Steady-state and transient-state (PL) spectra of the functional layers were measured using a transient fluorescence spectrometer (FLS980, Edinburgh Instruments, E I). The surface morphologies of the perovskite layer and the modified HTLs were measured using scanning electron microscopy (SEM) (Jeol JSM-7100F) and atomic force microscopy (AFM) (NX10). Contact angles of the different surface modified HTL layers were measured using a contact angle tester (AST Optima). The surface electronic properties of the functional layers were analyzed using the ultraviolet photoelectron spectroscopy (UPS) spectra (Thermo ESCALAB XI+). Fourier transform infrared spectrum (FTIR) of the samples were measured using an infrared spectrometer (Thermo Scientific, NICOLET iS10).

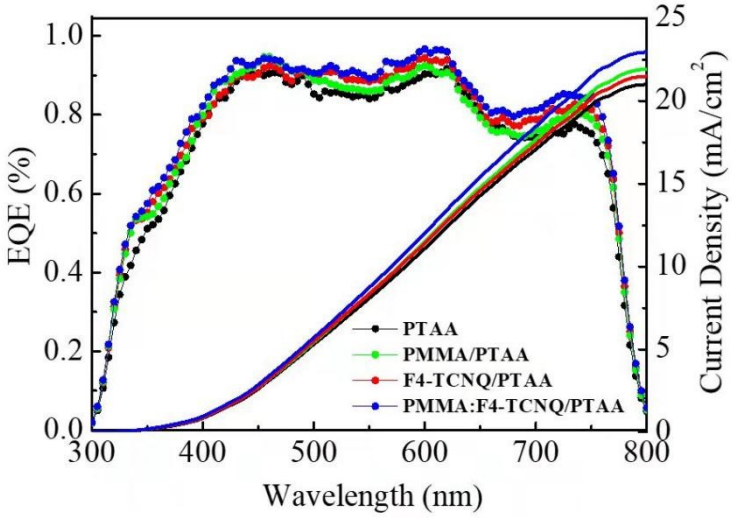

Fig. S1 EQE spectra measured for the champion PSCs prepared using different HTLs of PTAA, PMMA-modified PTAA, F4-TCNQ-modified PTAA and PMMA:F4-TCNQ-modified PTAA.

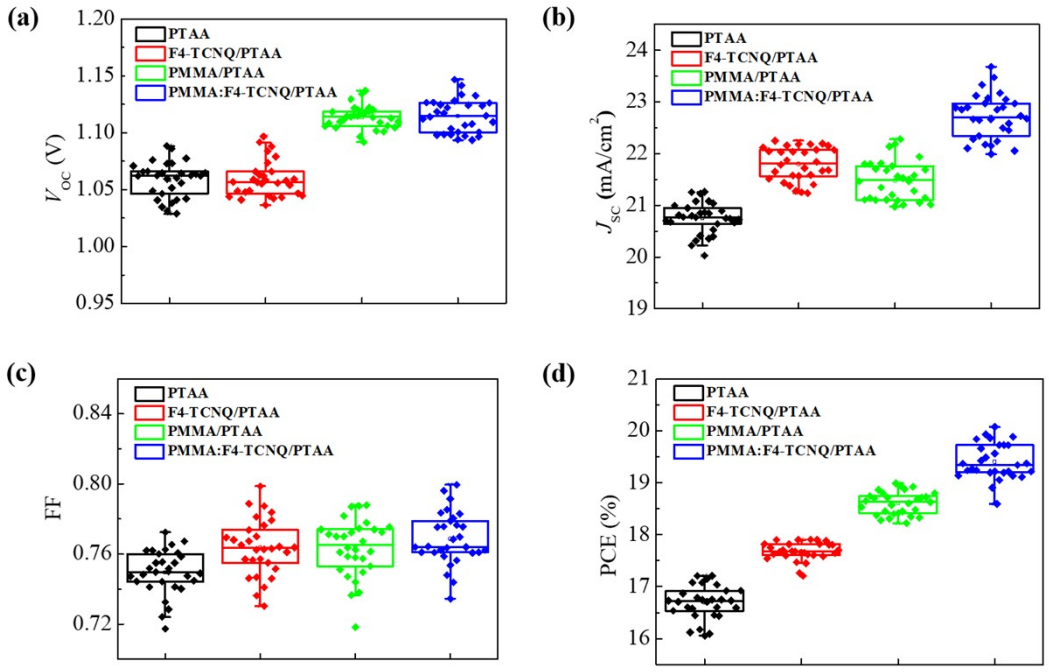

Fig. S2 Distributions of (a) *V*oc, (b) *J*sc, (c) FF and (d) PCE measured for a set of 30 PSCs each, prepared using different HTLs of PTAA, PMMA-modified PTAA, F4-TCNQ-modified PTAA and PMMA:F4-TCNQ-modified PTAA.

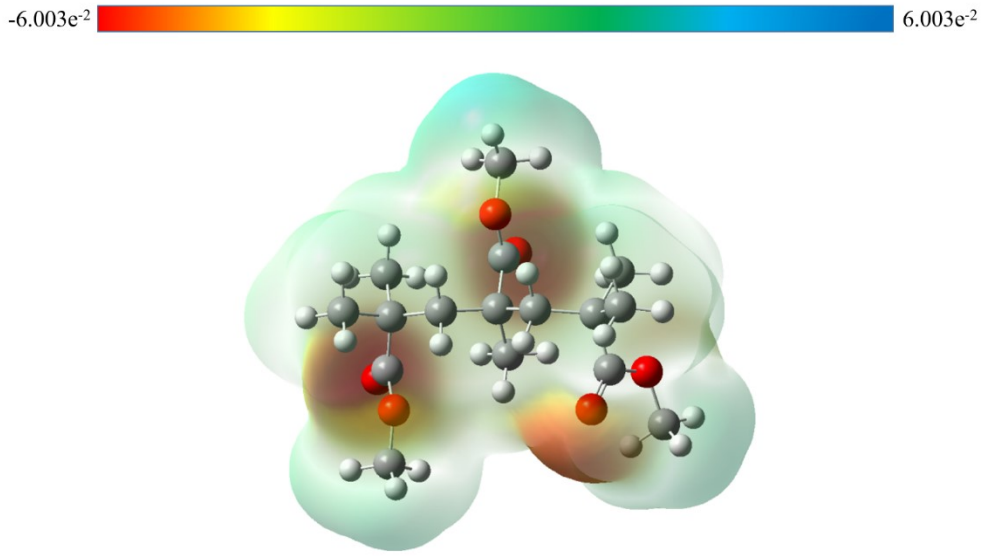

Fig. S3 Molecular structure and calculated electrostatic potential (ESP) profile of PMMA.

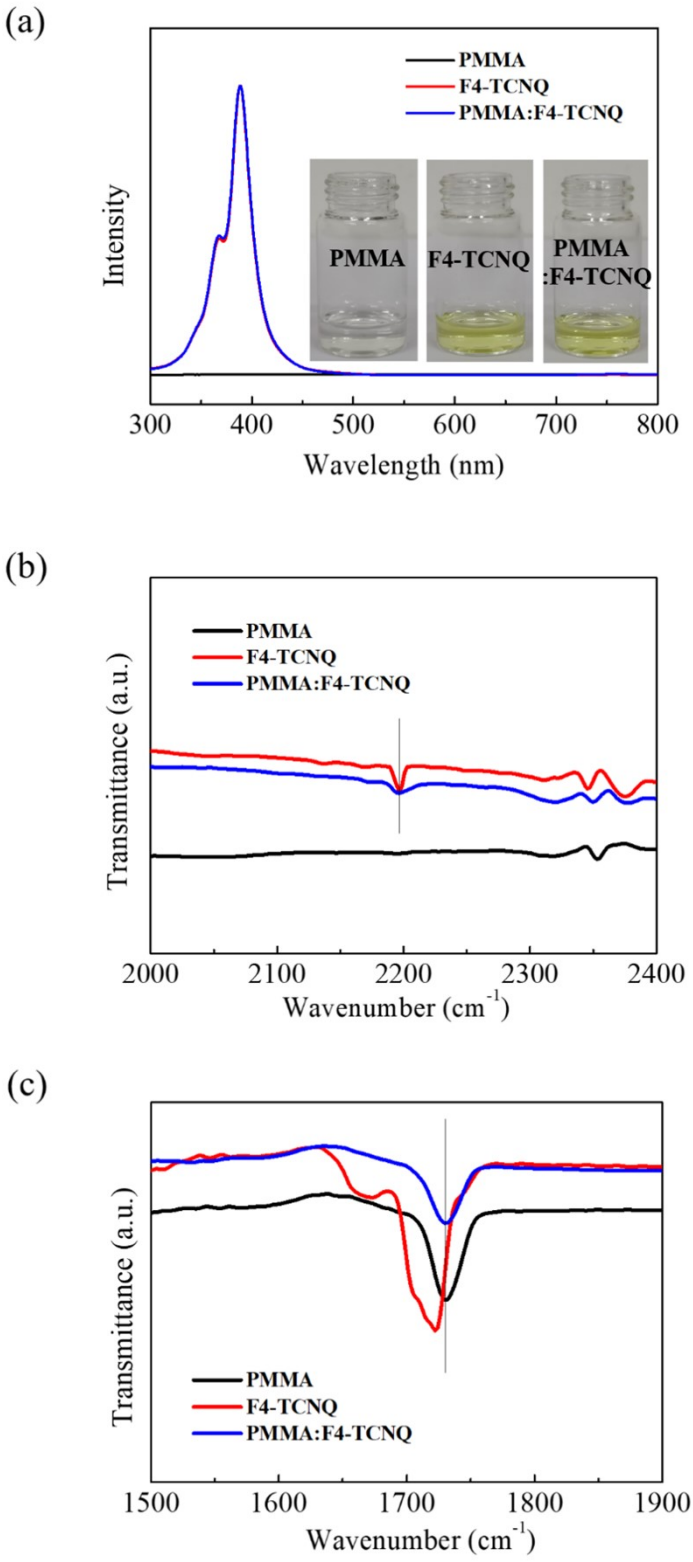

Fig. S4 (a) UV-vis absorption spectra measured for the PMMA, F4-TCNQ, PMMA:F4-TCNQ precursor solutions. FTIR spectra measured for PMMA, F4-TCNQ, PMMA:F4-TCNQ deposited on KBr substrates over different wavenumber ranges of (b) 2000 to 2400 cm^{-1}, and (c) 1500 to 1900 cm^{-1}.

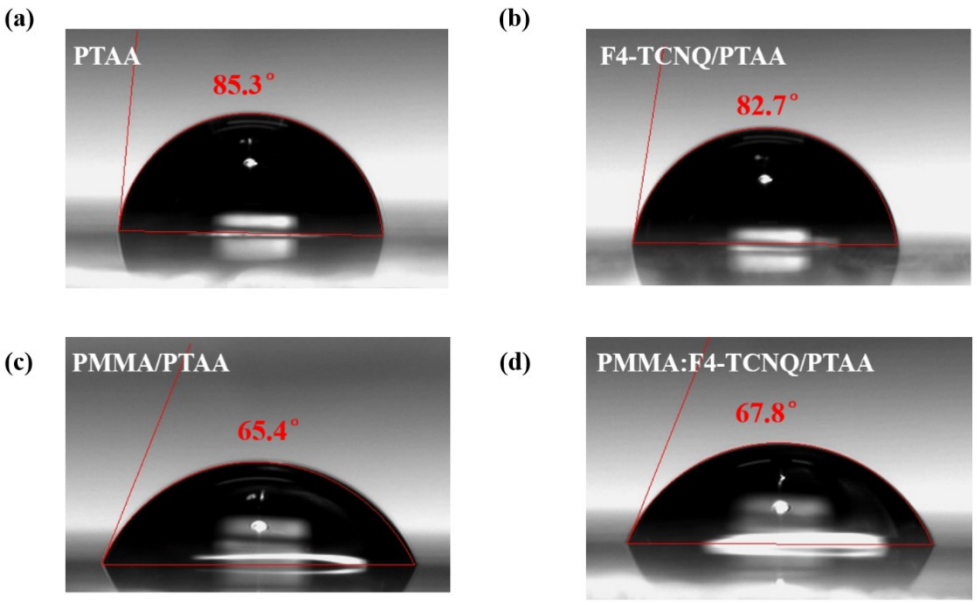

Fig. S5 Water contact angles measured for the surfaces of (a) PTAA, (b) F4-TCNQ-, (c) PMMA-, (d) PMMA:F4-TCNQ-modified PTAA samples.

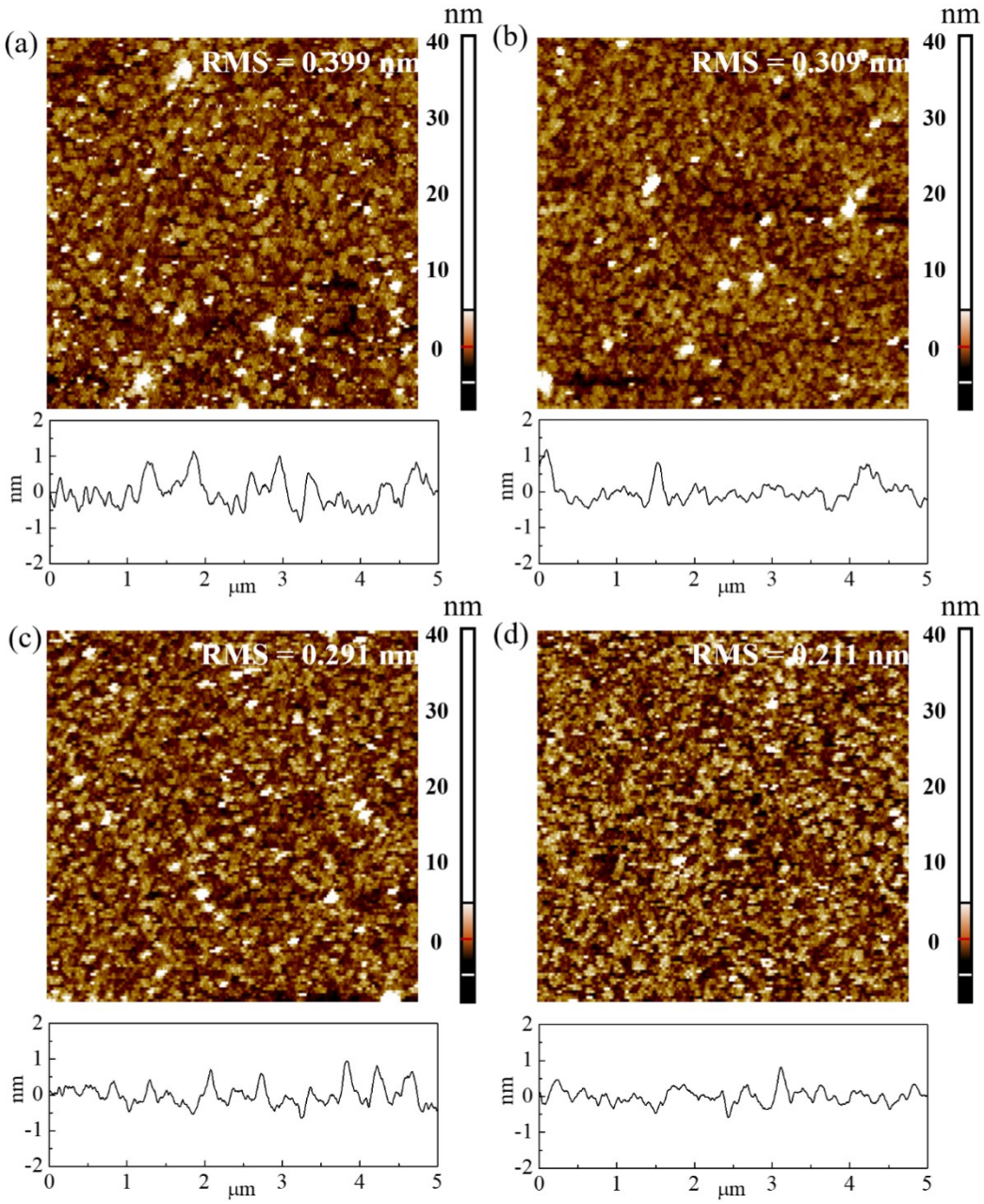

Fig. S6 AFM images measured for the surfaces of (a) PTAA, (b) F4-TCNQ-, (c) PMMA-, (d) PMMA:F4-TCNQ-modified PTAA samples.

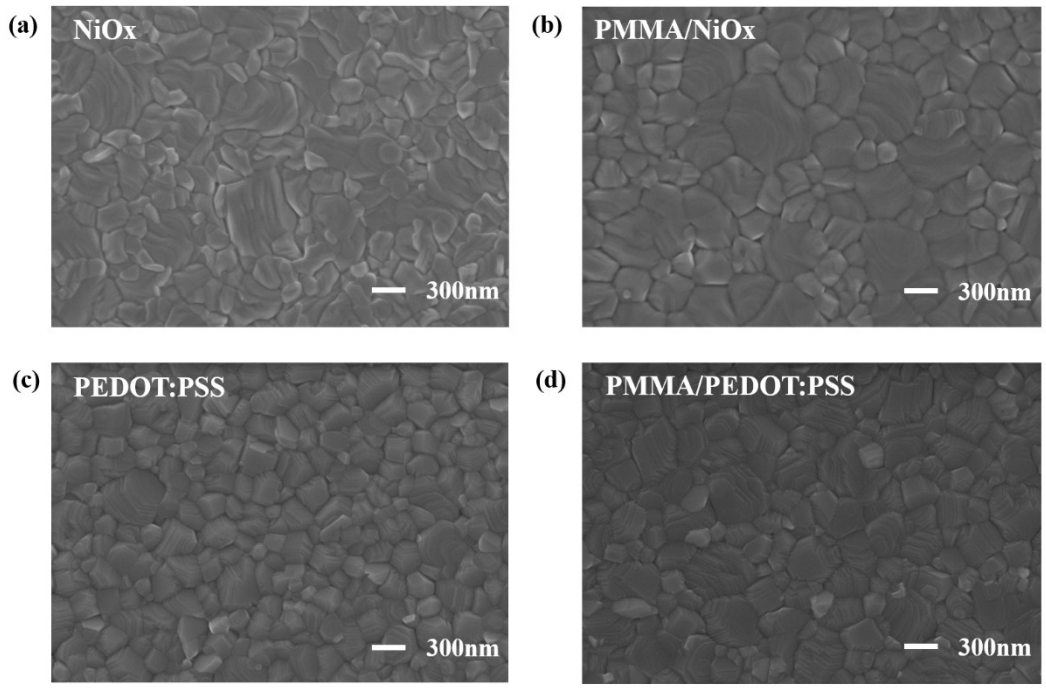

Fig. S7 Top-view SEM images measured for the $MAPbI_3$ perovskite films grown on different substrates of (a) NiOx/ITO/glass, (b) PMMA-modified NiOx/ITO/glass, (c) PEDOT:PSS/ITO/glass, and (d) PMMA-modified PEDOT:PSS/ITO/glass.

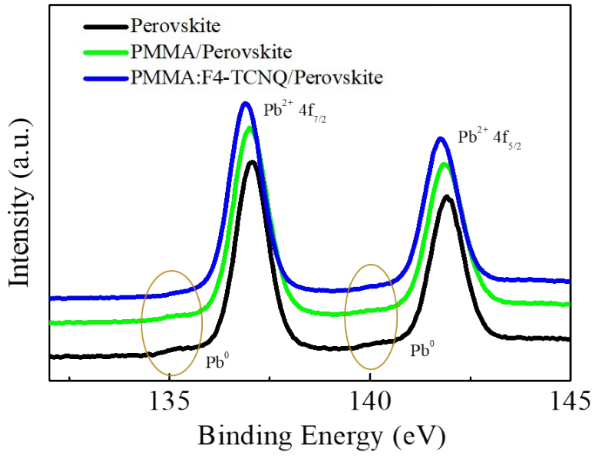

Fig. S8 XPS spectra of perovskite film, PMMA-modified perovskite film and PMMA:F4-TCNQ-modified perovskite film.

Table S1

A summary of the cell parameters measured for a set of 30 PSCs with different F4-TCNQ-modified HTLs, prepared using different concentrations of the F4-TCNQ solutions, under AM 1.5 G illumination (100 mW cm^{-2}).

F4-TCNQ ($mg\ mL^{-1}$)	*V*oc (V)	*J*sc ($mA\ cm^{-2}$)	FF	PCE (%)	Best PCE (%)
0	1.06±0.01	20.75±0.30	0.751±0.01	16.75±0.35	17.21
0.015	1.06±0.02	21.45±0.74	0.752±0.02	17.07±0.04	17.39
0.025	1.06±0.02	21.81±0.46	0.763±0.01	17.68±0.30	17.90
0.035	1.06±0.03	22.42±0.68	0.734±0.02	17.37±0.03	17.71

Table S2

A summary of the cell parameters measured for a set of 30 PSCs with different PMMA-modified HTLs, prepared using different concentrations of the PMMA solutions, under AM 1.5 G illumination (100 mW cm^{-2}).

PMMA ($mg\ mL^{-1}$)	V_{OC} (V)	J_{SC} ($mA\ cm^{-2}$)	FF	PCE (%)	Best PCE (%)
0	1.06±0.01	20.75±0.30	0.751±0.01	16.75±0.35	17.21
0.5	1.10±0.01	21.45±0.56	0.752±0.02	18.06±0.38	18.51
1	1.12±0.02	21.48±0.38	0.770±0.01	18.58±0.41	18.92
1.5	1.12±0.03	21.30±0.58	0.763±0.02	18.30±0.55	18.57

Table S3

A summary of the cell parameters measured for the PSCs with a PEDOT:PSS HTL and a PMMA-modified PEDOT:PSS HTL under AM 1.5 G illumination (100 mW·cm^{-2}).

PMMA (mg mL^{-1})	V_{OC} (V)	J_{SC} (mA cm^{-2})	FF	PCE (%)	Best PCE (%)
0	0.862±0.02	17.07±0.295	0.717±0.02	10.56±0.05	11.31
0.5	0.864±0.02	17.53±0.325	0.725±0.01	10.98±0.05	11.45
1	0.865±0.03	17.76±0.493	0.747±0.01	11.47±0.02	11.73
1.5	0.866±0.01	17.56±0.258	0.735±0.02	11.09±0.08	11.70

Table S4

A summary of the cell parameters measured for the PSCs with a NiOx HTL and a PMMA-modified NiOx HTL under AM 1.5G illumination (100 mW cm^{-2}).

PMMA (mg mL^{-1})	V_{OC} (V)	J_{SC} (mA cm^{-2})	FF	PCE (%)	Best PCE (%)
0	1.05±0.01	19.403±0.301	0.763±0.01	15.58±0.37	15.93
0.5	1.05±0.02	19.851±0.302	0.768±0.03	15.98±0.28	16.22
1	1.05±0.02	20.015±0.362	0.771±0.01	16.17±0.41	16.82
1.5	1.05±0.01	19.901±0.251	0.765±0.03	16.01±0.21	16.48

Table S5

The measured Rrec of the PSCs with different interlayers at the low-frequency region.

HTL	R_{rec} (ohm)
PTAA	1.89×10^3
PTAA/F4-TCNQ	2.48×10^3
PTAA/PMMA	4.42×10^3
PTAA/PMMA:F4-TCNQ	4.85×10^3