Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Electronic Supplementary Information

N-type polymers as electron extraction layer in hybrid perovskite solar cells with improved ambient stability

S. Shao,[a] Z. Chen,[b] H.-H. Fang,[a] G. H. ten Brink[a], D. Bartesaghi,[a] S. Adjokatse,[a] L. J. A. Koster,[a] B. J. Kooi,[a] A. Facchetti,[b] and M. A. Loi[a*]

[a]Zernike Institute for Advanced Materials, University of Groningen, Nijenborgh 4, 9747 AG, Groningen, The Netherlands. Email: m.a.loi@rug.nl.

[b]Polyera Corporation, 8045 Lamon Avenue, Skokie, Illinois 60077, USA.

Experimental Section

Materials: CH_3NH_3I was bought from Luminescence Technology Corporation. PEDOT:PSS water dispersion (Clevios VP AI 4083) was acquired from Heraeus. P(NDI2OD-T2), P(NDI2DT-T2) and P(NDI2OD-TET) were provided by Polyera Corporation. $PbCl_2$ (99.99%), DMF (99.8%) and o-xylene (97%) were acquired from Sigma-Aldrich. All of these materials were used as received without further purification.

Synthesis of the polymers:

5,5'-bis(trimethylstannyl)-2,2'-bithiophene,*N*,*N'*-bis(2-decyltetradecyl)-2,6-dibromonaphthalene-1,4,5,8-bis(dicarboximide) (NDI2DT-Br2),[49] polymer P(NDI2OD-T2),[50] P(NDI2OD-TET)[51] were prepared according to literature reports, respectively. P(NDI2OD-T2): (GPC: M_n = 32.9K Da, PDI = 3.3. Elemental Analysis (calc. C, 75.26; H, 8.96; N, 2.83): found C, 74.93; H, 8.86; N, 2.88). P(NDI2OD-TET): (GPC: M_n = 18.2K Da, PDI = 1.8. Elemental Analysis (calc. C, 75.54; H, 9.11; N, 2.75): found C, 75.27; H, 8.82; N, 2.84). P(NDI2DT-T2) was synthesized by the following procedure: a mixture of NDI2DT-Br2 (293.9 mg, 0.27 mmol), 5,5'-bis(trimethylstannyl)-2,2'-bithiophene (120.0 mg, 0.24 mmol), and $PdCl_2(PPh_3)_2$(6.8 mg, 0.0097 mmol) in anhydrous toluene (30 mL) was stirred at 90 °C for 18 hours. Bromobenzene (0.3 mL) was then added and the reaction mixture was maintained at 90 °C for an additional 5 hours. Upon cooling to room temperature, the reaction mixture was precipitated in methanol (100 mL). The precipitate was collected by filtration, washed with methanol. This crude product was dissolved in chloroform (40 mL), and this solution was precipitated in acetone (100 mL), followed by collection by filtration and washing with acetone. The obtained solid was then purified by Soxhlet extraction with methanol (19 h), acetone (21 h), and hexane (17 h). The remaining solid residue was re-dissolved in chloroform (40 mL) and the resulting mixture was heated to boil. Upon cooling to room temperature, the chloroform solution was filtered, and the filtrate was precipitated in methanol (100 mL). The precipitates were collected by filtration, washed with methanol, and dried in vacuum, leading to a dark blue solid as the product (256.0 mg, 95.2%). GPC: M_n = 32.6K Da, PDI = 2.9. Elemental Analysis (calc. C, 76.31; H, 9.51; N, 2.54): found C, 76.25; H, 9.38; N, 2.60.All other reagents and solvents were purchased from Aldrich and VWR and they were used without further purification. Unless otherwise stated, all reactions were carried out under inert atmosphere using standard Schlenk line techniques.

Cyclic voltammetry measurements: Electrochemical measurements were carried out using a Epsilon Electrochemical Workstation equipped with BAS Epsilon software (Bioanalytical Systems, Inc., Lafayette, IN) in a 3-electrode cell configuration (VC-2 voltammetry cell), using 1.0 mm diameter platinum disk working electrode and a platinum wire counter electrode, and Ag wire was used as the pseudo-reference electrode. Polymer sample films were deposited onto working electrode by drop-casting. Cyclic voltammetry measurements were performed in 0.1 M tetrabutylammoniumhexafluorophosphate ($Bu4N^+PF6^-$) acetonitrile solution at a scan rate of 50 mV S^{-1}. Ferrocene/Ferrocinium (Fc/Fc^+, 0.54 V vs. SCE) was used as an internal reference for all measurements. LUMO energy levels were estimated from reduction onsets (E_{LUMO} = -4.44 – E_{red}), and HOMO energy levels were calculated accordingly from LUMO and optical band gap ($E_{HOMO} = E_{LUMO} – E_{opt}$).

Fabrication of the device: The fabrication of the device started with cleaning the ITO coated substrates, which were sonicated sequentially in detergent, deionized water, acetone, and isopropanol for 20 minutes, respectively. After spin-drying, the cleaned ITO substrates were further dried at 140 degree for 10 min. The following step was to expose the ITO substrates to the UV ozone cleaning treatment for 20 min. A 45 nm thick PEDOT:PSS layer was then spin coated onto the ITO substrates and dried at 140 degree for 10 min. A precursor solution (40% wt) of CH_3NH_3I and $PbCl_2$ with a 3:1 molar ratio was spin-coated on top of PEDOT:PSS and then the substrates were stored in high vacuum ($<10^{-6}$ mbar) for 12 h. The annealing step was performed on the aforementioned substrates at 100 degree for 1 h in a nitrogen-filled glove box, in this way films of 210 nm thick

$CH_3NH_3PbI_{3-x}Cl_x$were obtained. Then, a 40 nm thick electron extraction layer was spin-coated on top of the perovskite layer from a solution of P(NDI2OD-T2), P(NDI2DT-T2) or P(NDI2OD-TET) in o-oxylene. The device structure was completed by evaporating 100 nm thick Al on top of the n-type polymers; the evaporation is performed in high vacuum < 1×10^{-6} mbar.

Characterization of the perovskite solar cells: The illuminated current density-voltage characteristics of the perovskite solar cells were measured under simulated AM 1.5 G solar illumination using a Steuernagel Solar constant 1200 metal halide lamp in a nitrogen filled glove box. The light intensity was calibrated to be 100 mW cm^{-2} by using a calibrated Si cell. The external quantum efficiency data were measured under monochromatic conditions at short circuit condition using a 250 w quartz tungsten halogen lamp (6334NS, Newport) as light source. Monochromatic light was achieved using narrow band pass filters (Thorlabs) with a full width half maximum (FWHM) of 10±2 nm from 400 nm to 1250 nm and a FWHM of 12±2.4 nm from 1300 nm to 1400 nm, respectively. Light intensity was determined by calibrated PD300 and PD300IR photodiodes (Ophir Optics).

Steady state and time resolved PL measurement: The samples for the PL experiments were prepared in the same way as the devices, but without the deposition of the top electrode. These samples were excited at 400 nm by the second harmonic of a mode locked Ti:sappire (Mira 900) laser delivering pulses of 150 fs. Time resolved traces were recorded with a Hamamatsu streak camera working in a single sweep mode.

Fabrication and characterization of the electron only device: The substrates were cleaned using the same procedure as for the ITO substrates. A layer of 80 nm thick Al was evaporated on top of clean glass substrate under vacuum <10^{-6} mbar. These substrates were exposed to ambient conditions for 1 min and then transferred into the glove box for spin-coating the n-type polymers. The film thicknesses of the P(NDI2OD-T2), P(NDI2DT-T2) and P(NDI2OD-TET) were 140, 130 and 155 nm, respectively. The device was completed by evaporation of 1 nm LiF and 100 nm Al sequentially under vacuum <10^{-6} mbar.

AFM measurement: The samples were prepared in the same way as the samples for PL experiments. AFM topographical images were recorded in tapping mode using a Bruker MultiMode 8 microscope with TESP probes.

SEM measurements: SEM images were recorded on a XL 30 ESEM microscope under operating voltage of 5 KV.

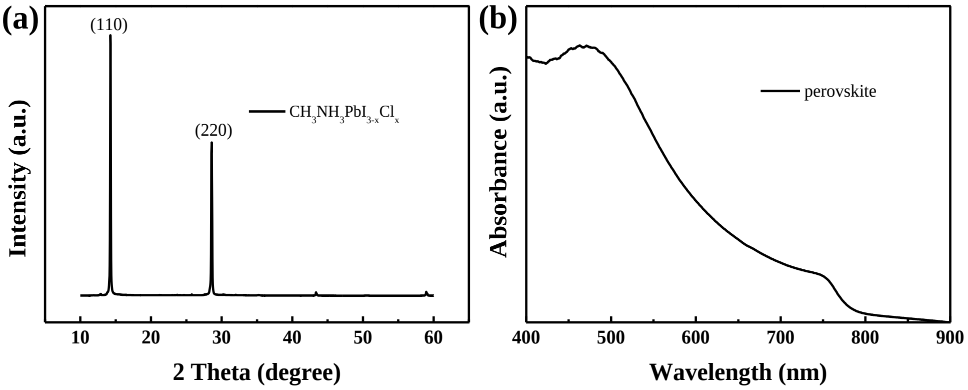

Fig. S1. (a) XRD pattern and (b) UV-vis absorption of the perovskite film.

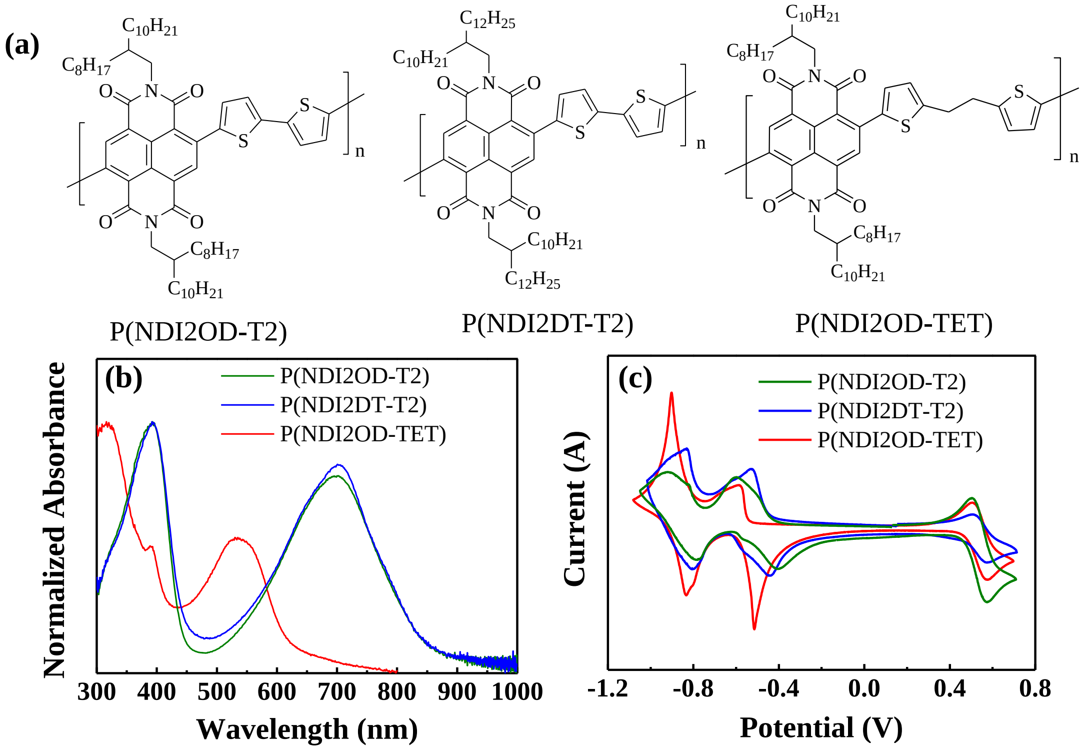

Fig. S2 (a) Chemical structures, (b) absorbance and (c) CV measurements of the three n-type polymers used in this work.

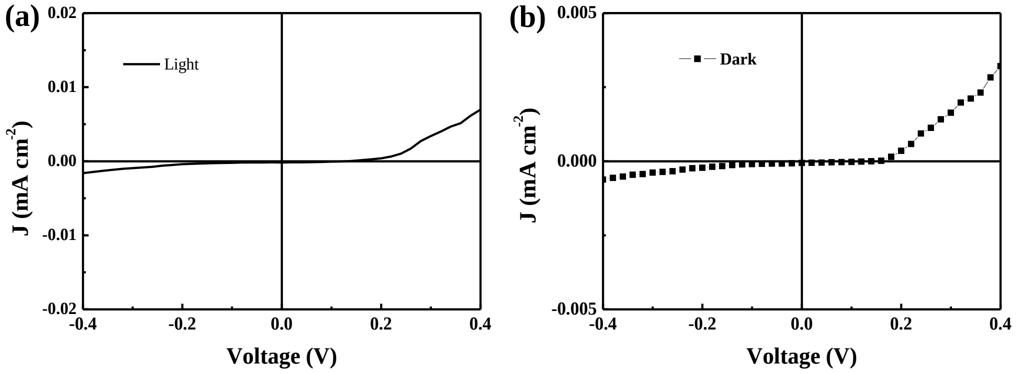

Fig. S3. JV characteristics of the perovskite solar cell without any electron extraction layer (a) under illumination and (b) in the dark.

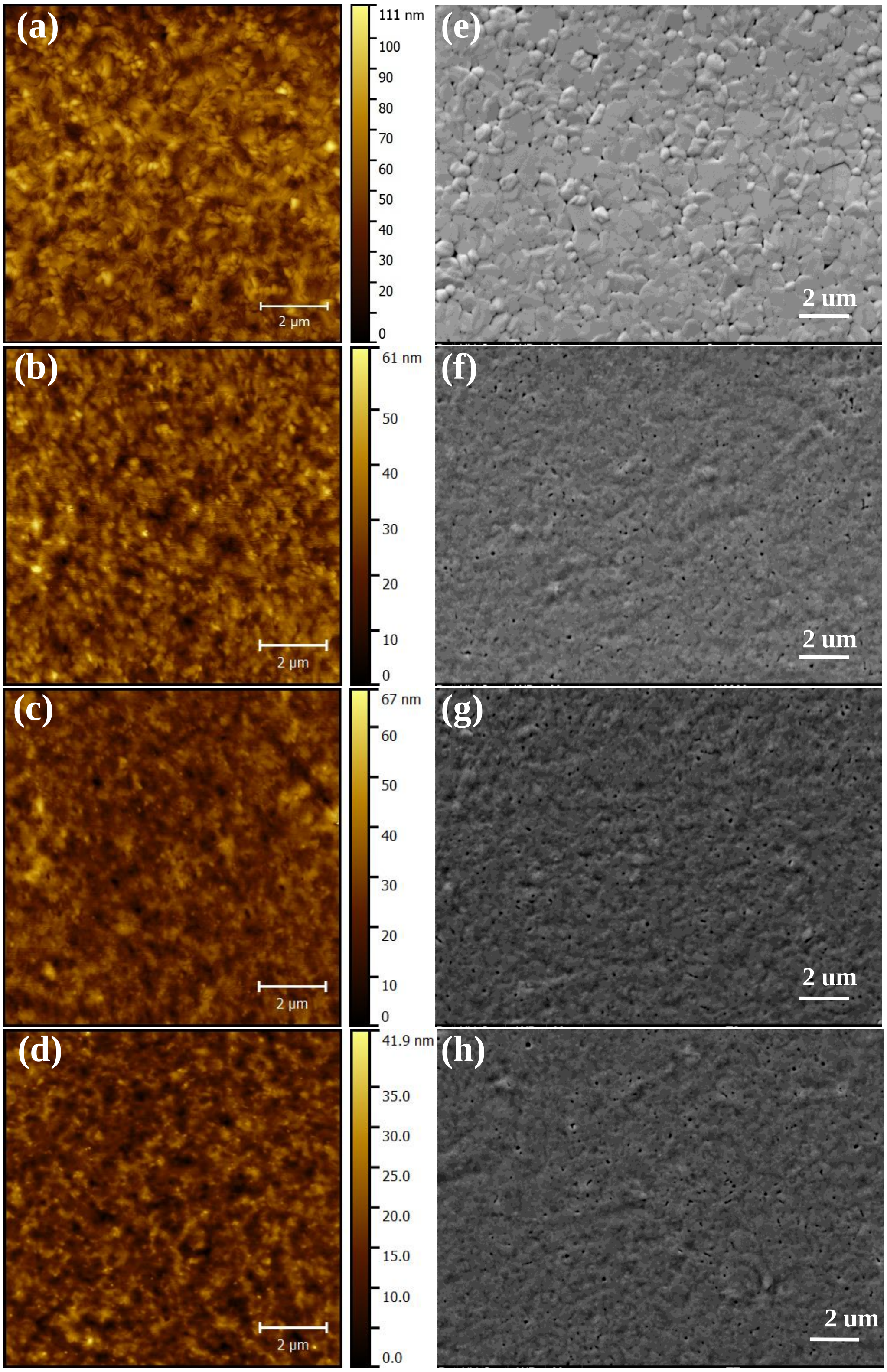

Fig. S4. AFM topography and SEM micrographs for the bare perovskite film (a and e), perovskite/P(NDI2OD-T2) (b and f), perovskite/P(NDI2DT-T2) (c and g), and perovskite/P(NDI2OD-TET) film (d and h).

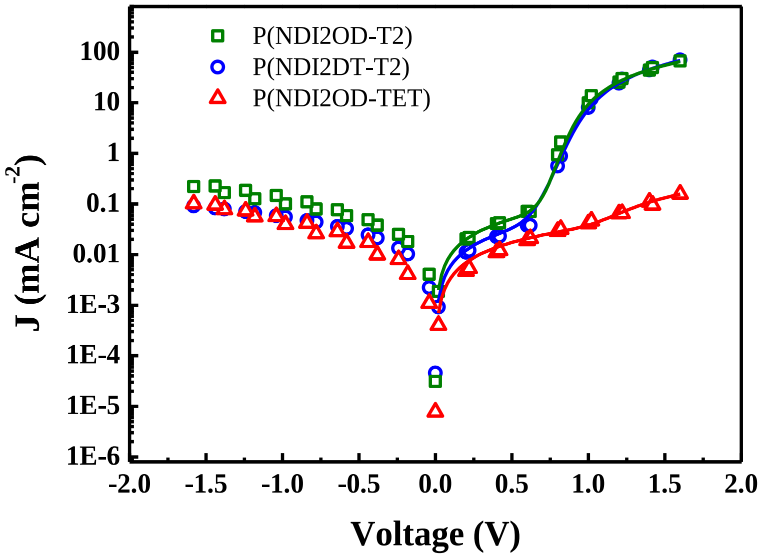

Fig. S5 Dark J-V characteristics for the perovskite solar cells with the three n-type polymers as electron extraction layer. Symbols represent experimental data, solid lines are fitted results using Schottky diode equation for dark conditions.

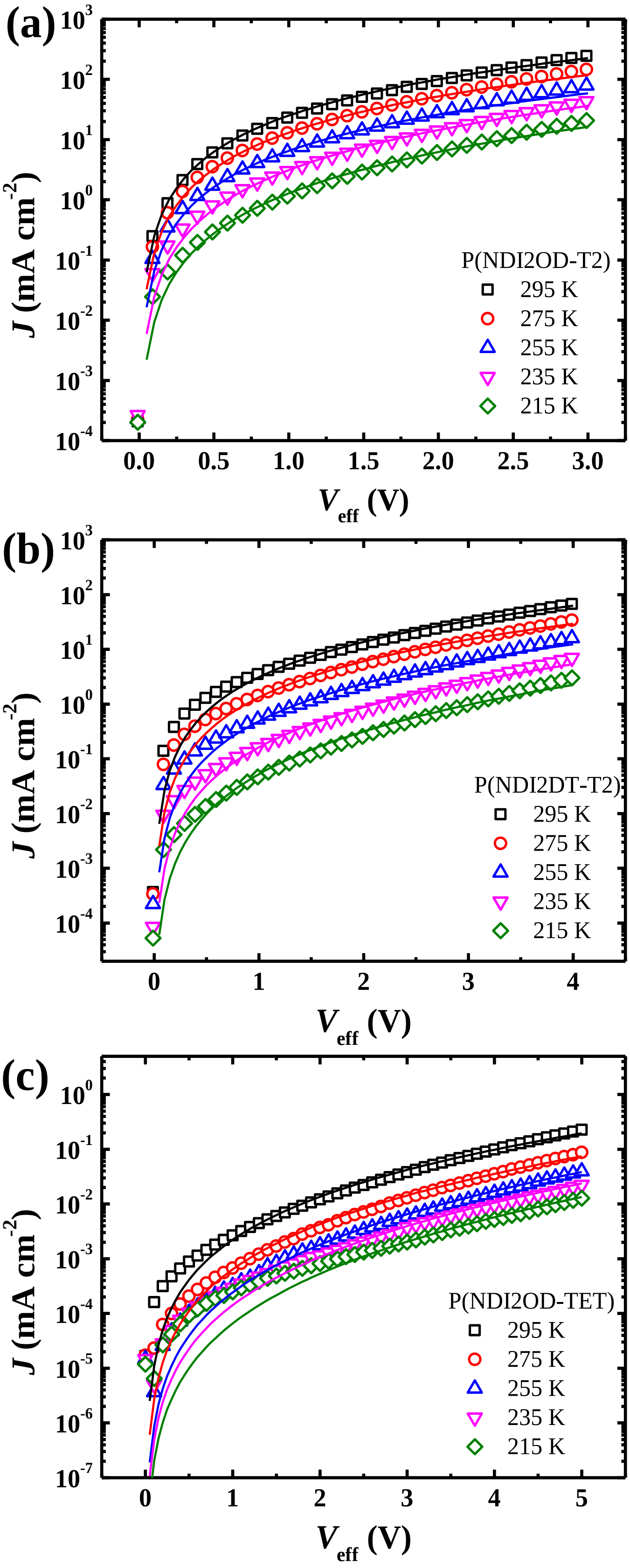

Fig. S6 Dark JV characteristics for the electron only device of structure glass/Al/n-type polymers/LiF/Al measured at different temperatures.

Table S1. Fitting results for zero-field electron mobility (μ_{0n}) and field activation factor (γ_n) of the electron only devices using three n-type polymers at different temperatures. The device thickness is indicated for every polymer.

T [K]	P(NDI2OD-T2) *L* = 140 nm		P(NDI2DT-T2) *L* = 130 nm		P(NDI2OD-TET) *L* = 155 nm	
	μ_{0n} [cm^2 (VS)$^{-1}$]	γ_n [(mV^{-1})$^{1/2}$]	μ_{0n} [cm^2 (VS)$^{-1}$]	γ_n [(mV^{-1})$^{1/2}$]	μ_{0n} [cm^2(VS)$^{-1}$]	γ_n [(mV^{-1})$^{1/2}$]
295	2.3×10^{-4}	0	1.2×10^{-5}	1.0×10^{-4}	1.0×10^{-8}	4.5×10^{-4}
275	1.2×10^{-4}	0	3.4×10^{-6}	2.1×10^{-4}	2.3×10^{-9}	5.5×10^{-4}
255	5.0×10^{-5}	1.0×10^{-4}	1.2×10^{-6}	2.9×10^{-4}	6.8×10^{-10}	6.6×10^{-4}
235	2.0×10^{-5}	1.5×10^{-4}	3.0×10^{-7}	4.2×10^{-4}	3.8×10^{-10}	6.8×10^{-4}
215	7.3×10^{-6}	2.0×10^{-4}	7×10^{-8}	5.3×10^{-4}	1.5×10^{-10}	7.5×10^{-4}

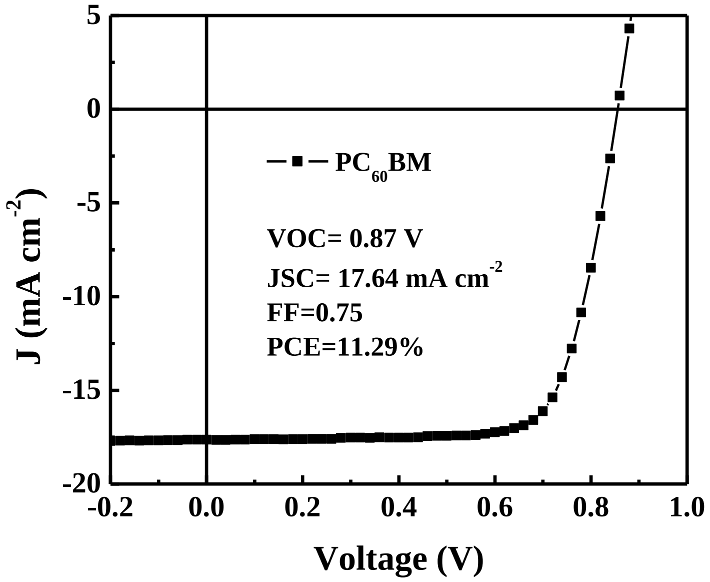

Fig. S7 The illuminated J-V characteristic for the HPSC using PC$_{60}$BM as EEL.

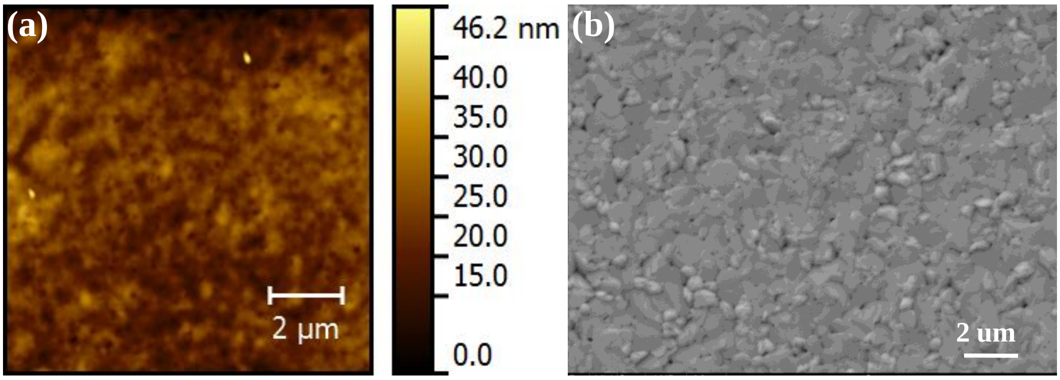

Fig. S8 (a) AFM and (b) SEM mcrographss of the PC$_{60}$BM coated perovskite film on top of PEDOT:PSS/ ITO.

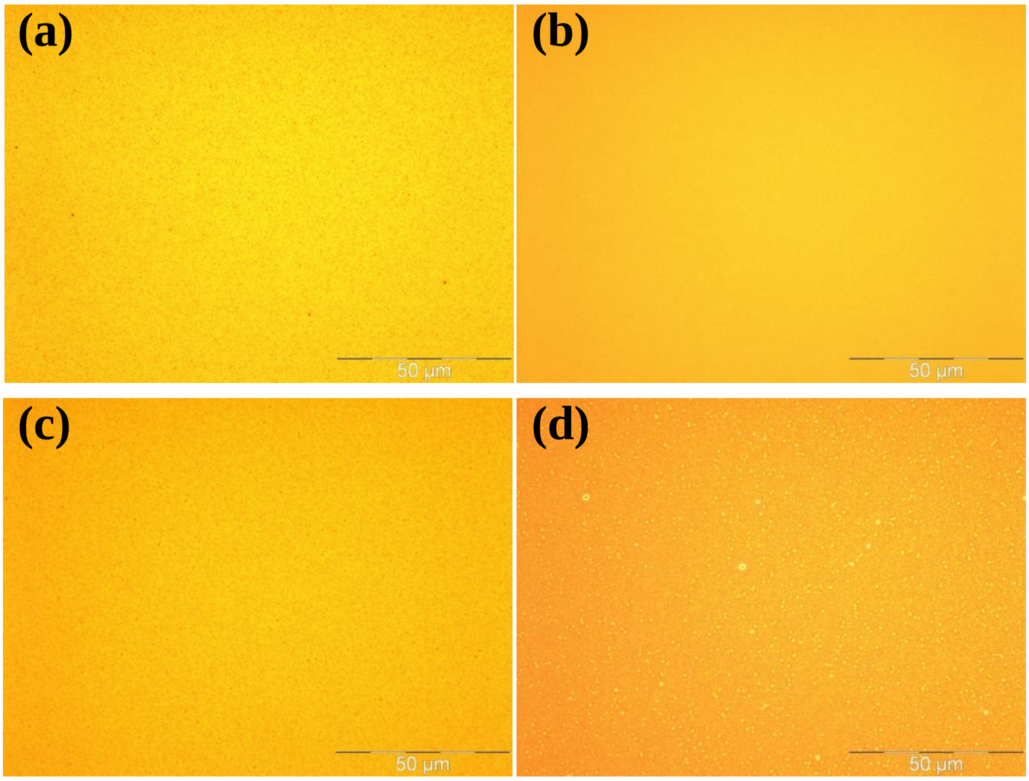

Fig. S9 Optical micrographs of the perovskite films covered with P(NDI2OD-T2) and $PC_{60}BM$ EEL (a), (b) before and (c), (d) after exposure to air, respectively.