Supplementary Information

A hydrophobic hole transporting oligothiophene for planar perovskite solar cells with improved stability

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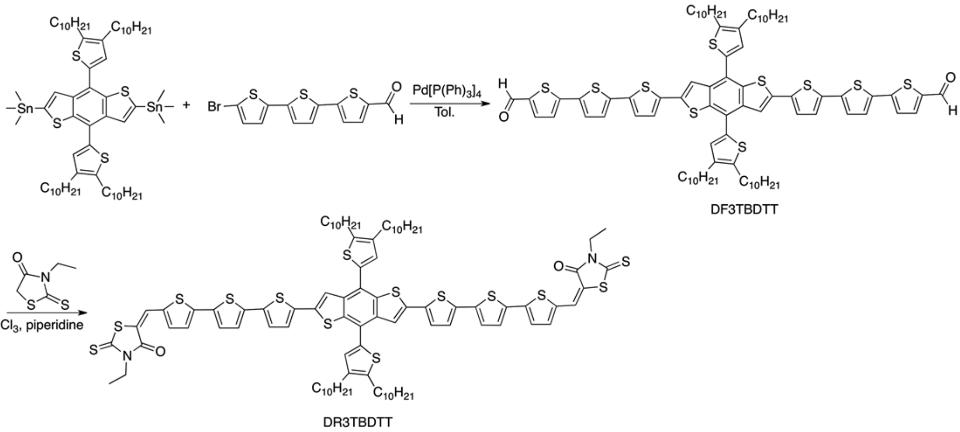
1. Synthesis of HTM



Scheme S1. Synthetic route of DR3TBDTT.

As shown in **Scheme S1**, the DR3TBDTT was synthesized according to the literature procedures.[30] All starting materials were obtained from commercial suppliers without further purification. 2,6-Bis(trimethyltin)-4,8-bis(4,5-didecylthiophen-2-yl)benzo[1,2-b:4,5-b′]dithiophene (BDTT) was purchased from Suna Tech Inc. 5''-bromo-[2,2':5',2''-terthiophene]-5-carbaldehyde (Br3TCHO) and 3-ethylrhodanine were purchased from TCI.

Synthesis of DF3TBDTT

To a solution of BDTT (1 g, 0.81 mmol) and Br3TCHO (0.7156 g, 2.01 mmol) in 100 mL toluene, $Pd(PPh_3)_4$ (186 mg, 0.16 mmol) was added after degassing three times with nitrogen. The resultant mixture was refluxed for 24 hrs under nitrogen before quenching by water. Then, the solution was extracted with chloroform for three times and the organic layer was dried with Na_2SO_4 overnight. After removal of solvent, the crude product was purified by column chromatography on silica gel using firstly a mixture of chloroform and petroleum ether (2:1) and then pure chloroform as the eluent, followed by recrystallization from chloroform and petroleum ether. DF3TBDTT was obtained as a red solid (0.86 g, 73%).

^1H NMR (500 MHz, $CDCl_3$): δ 9.87 (s, 2H), 7.70 (m, 2H), 7.67 (d, 2H), 7.30-7.27 (m, 4H), 7.24-7.21 (m, 4H), 7.15-7.13 (m, 4H), 2.86 (t, 4H), 2.65 (t, 4H), 1.78 (m, 4H), 1.70 (t, 4H), 1.52-1.21 (m, 56H), 0.89-0.88 (m, 12H) ppm.

MS (MALDI-TOF) *m/z*: calculated for $C_{84}H_{102}O_2S_{10}$, $[M]^+$, 1462.5081; found, 1462.5064.

Synthesis of DR3TBDTT

Under the protection of argon, to a solution of DF3TBDTT (200 mg, 0.14 mmol) 3-ethylrhodanine (228 mg, 1.37 mmol) in 50 mL chloroform, 3 drops of piperidine was added and refluxed for 24 hrs under stirring. After quenching by water, the solution was extracted with chloroform for three times and the organic layer was dried with Na_2SO_4 overnight. After removal of solvent, the crude product was purified by column chromatography on silica gel using firstly a mixture of chloroform and petroleum ether (3:1) and then pure chloroform as the eluent, followed by recrystallization from chloroform twice. The product was further purified by Soxhlet extraction using methanol, petroleum ether, and chloroform. DR3TBDTT was precipitated from methanol as a shiny black solid (122 mg, 51%).

^1H NMR (500 MHz, $CDCl_3$): δ 7.80 (s, 2H), 7.66 (s, 2H), 7.31-7.26 (m ,2H), 7.22-7.18 (m, 8H), 7.14-7.09 (m, 4H), 4.20-4.15 (m, 4H), 2.87 (t, 4H), 2.67 (t, 4H), 1.82-1.76 (m, 4H), 1.72-1.68 (m, 4H), 1.52-1.21 (m, 62H), 0.89-0.83 (m, 12H) ppm.

^{13}C NMR (600 MHz, $CDCl_3$): δ 191.78, 167.20, 144.78, 140.60, 138.63, 138.31, 138.06, 137.30, 137.25, 137.16, 136.64, 136.49, 135.05, 134.94, 126.17, 125.96, 124.96, 124.89, 124.78, 124.71, 123.55, 120.75, 39.90, 31.93, 31.84, 30.80, 29.74, 29.68, 29.57, 29.55, 29.49, 29.39, 29.36, 29.24, 28.93, 28.36, 28.12, 27.21, 22.68, 14.07, 12.24, ppm.

Anal. Calcd. for $C_{94}H_{112}N_2O_2S_{14}$: C, 64.48; H, 6.45; N, 1.60. Found: C, 64.47; H, 6.19; N, 1.58%.

MS MALDI-TOF) *m/z*: calculated for $C_{94}H_{112}N_2O_2S_{14}$, [M]+, 1748.4808; found, 1748.4800.

2. Preparation of CH_3NH_3I

Based on the literature,[34] hydroiodic acid (114 mmol, 15 mL, 57 wt%) and methylamine (140 mmol, 70 mL, 2 M in methanol) were reacted at 0 ^oC with stirring under N^2 for 120 min.

The resultant solution was evaporated to give a white precipitate, then washed with diethyl ether and dried under vacuum and used for the following step without further purification.

3. Device Fabrication.

Fluorine doped tin oxide (FTO) glass was cleaned sequentially via detergent, water, acetone, and ethanol under ultrasonication for 15 min, and then treated with O_2 plasma for 15 min. The following procedure was modified based on literature.[34] A compact TiO_2 layer on the FTO glass was prepared by spin-coating at 4,000 r.p.m. for 30 s using 0.15 M of titanium diisopropoxide bis(acetylacetonate) (75 wt. % in isopropanol, Aldrich) in 1-butanol, dried at 125 ^oC for 5 min, then repeated with 0.3 M of titanium diisopropoxide bis(acetylacetonate) solution, finally baked at 500 ^oC for 15 min. Then, the resultant TiO_2 film was immersed into a 40 mM $TiCl_4$ aqueous solution at 70 ^oC for 30 min, washed with deionized water and ethanol, then baked at 500 ^oC for 15 min. Precursor films were deposited by spin-coating of 1M PbI_2 (99.999%, Alfa Aesar) /$PbCl_2$ (99.999%, Aldrich) (1:1) mixed solution in DMF at 4000 r.p.m. that was kept at 70 ^oC. After drying at 70 ^oC, the films were dipped into a 10mg/mL solution of CH_3NH_3I in 2-propanol (99%, Fisher) kept at 50 ^oC for tens of seconds, then rinsed with 2-propanol and dried. Oligothiophene HTMs were spin-coated on the perovskite at 1,700 r.p.m. for 60s using DR3TBDTT/chlorobenzene (99.9%, Alfa Aesar) (10mg/ml), or DR3TBDTT/chlorobenzene (10mg/ml) with 0.1mg/mL PDMS (trimethylsiloxy terminated, M_r= 14000, Alfa Aesar), or DR3TBDTT/chlorobenzene (10mg/ml) with 6.8 μL lithium bis(trifluoromethylsulphonyl)imide (Li-TFSI) (98%, Alfa Aesar)/acetonitrile (28.3 mg/mL) and 3.4 μL 4-*tert*-butylpyridine (96%, Aldrich). A solution of 2,2',7,7'-tetrakis(*N*,*N*-di-*p*-methoxyphenylamine)-9,9'-spirobifluorene (spiro-MeOTAD)/chlorobenzene (72.3 mg/mL) with 28.8 μL 4-*tert*-butylpyridine, and 17.5 μL Li-TFSI/ acetonitrile (520 mg/mL) was spin-coated at 2000 r.p.m. for 60 s as the standard HTM. Finally, 80 nm Au was thermally evaporated under vacuum to act as the cathode. The effective area was defined by a shadow mask (0.0314 cm^2).

4. Measurements.

The ^1H NMR spectra were recorded on a Bruker AVANCE III 500M Hz Spectrometer. The ^{13}C NMR spectra were recorded on a Bruker AVANCE DRX 600M Hz Spectrometer. Elemental analysis was taken on a Vario EL-III elemental analyzer. Matrix assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF) were performed on a Bruker Daltonics Inc. Autoflex III instrument. The thermogravimetric analysis (TGA) and Differential Scanning Calorimetry (DSC) were carried out with a TA SDT Q600 thermal analyzer under purified nitrogen gas flow with a 10 °C min^{-1} heating rate. HOMO levels were determined by photoelectron spectroscopy (Rikken Keiki AC-2). The absorption spectrum was recorded with UV–visible spectrophotometer (Agilent 8453). The morphology was measured using scanning electron microscope (SEM) (HITACHI 4300). The EDS spectra were recorded on Nova_NanoSEM430. Photovoltaic performances were measured by using Keithley 2611 source meter under simulated sunlight from Oriel 300 solar simulator. All the current density-voltage curves were tested from forward bias to short-circuit. IPCE was measured by using a lock-in amplifier coupled with a monochromator and 500 W xenon lamp (Crowntech, Qtest Station 2000). Both the systems were calibrated against a certified reference solar cell. All the measurements of the solar cells were performed under ambient atmosphere at room temperature without encapsulation. Water contact angles were measured on a Dataphysics OCA20 contact angle measuring system at ambient temperature. XRD was carried out in a PANalytical X'Pert PRO X-ray diffractometer.

5. Additional Information.

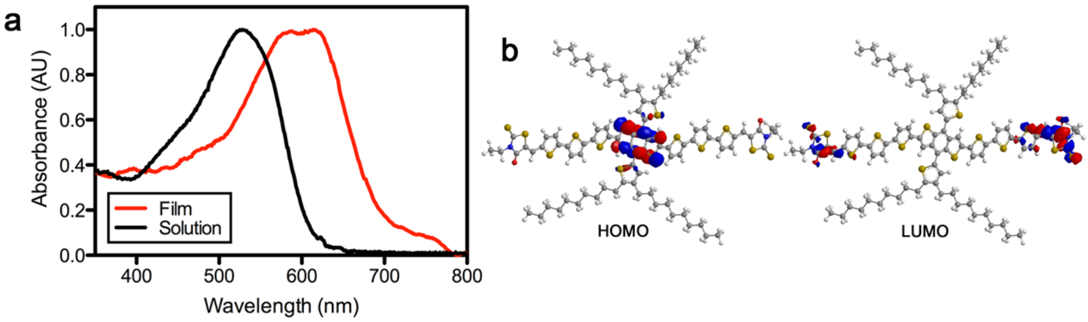


Figure S1. a) Normalized UV-vis absorption spectra in $CHCl_3$ solution and solid film of DR3TBDTT. b) Calculated distributions of the HOMO and LUMO energy densities using Gaussian suite of programs (Gaussian 09) with B3LYP/6-311G+(d,p) basis set.

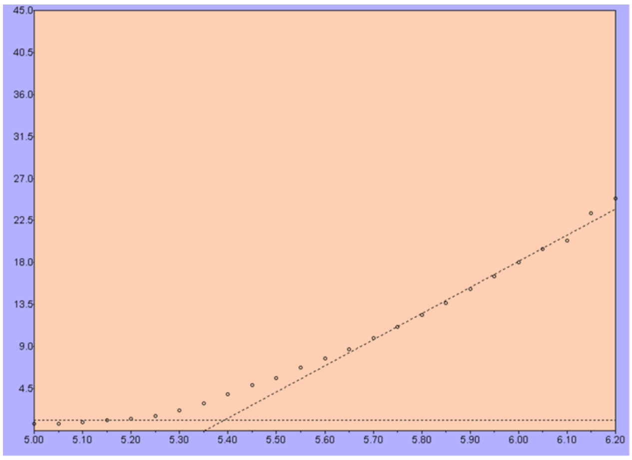


Figure S2. Photoelectron spectrum of DR3TBDTT.

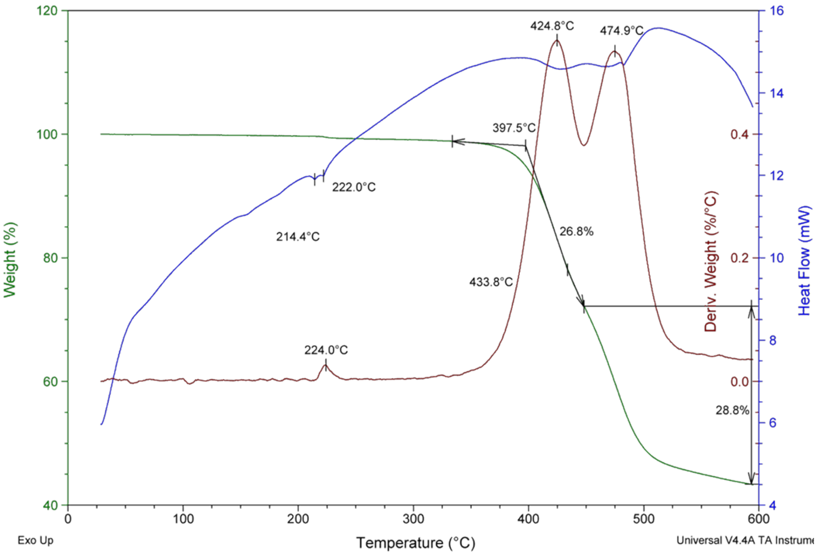


Figure S3. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) analysis of DR3TBDTT with a heating rate of 10 °C min^{-1} under nitrogen atmosphere.

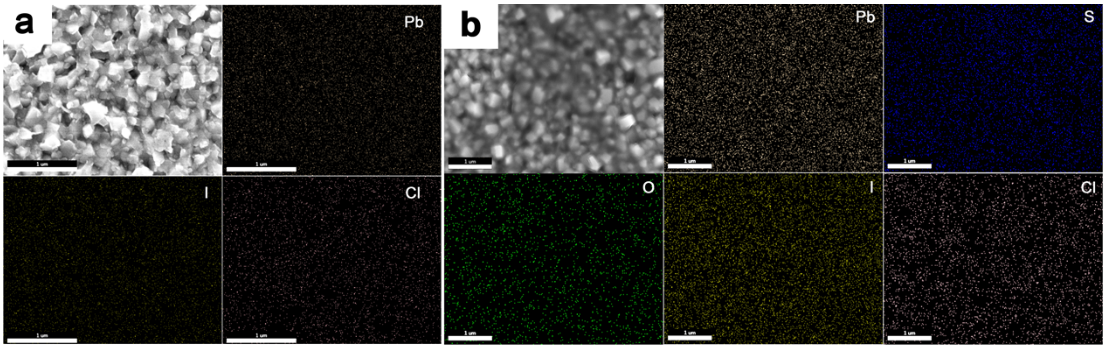


Figure S4. Top-view energy dispersive X-ray spectra (EDS) mapping of a) the Pb, I, Cl elements in the perovskite layer. b) the Pb, I, Cl, S, O elements in the DR3TBDTT-based planar perovskite solar cells.

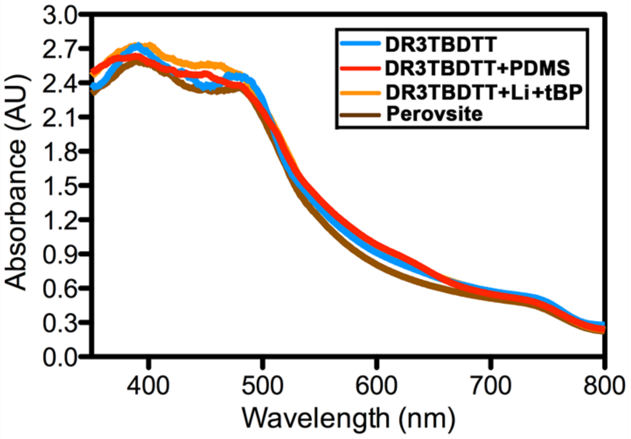


Figure S5. UV-vis absorption spectra of the perovskite layer and the perovskite layer coated by DR3TBDTT with different additive.

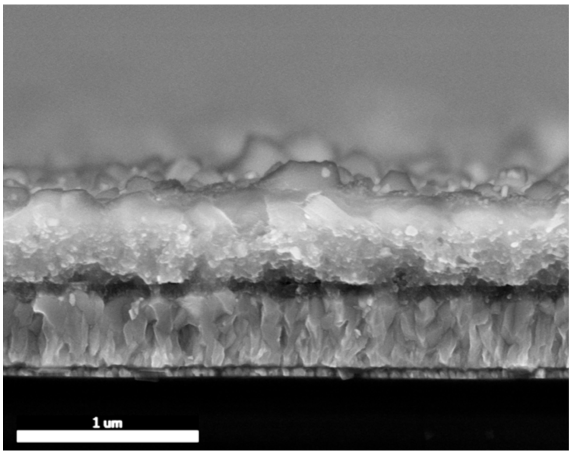
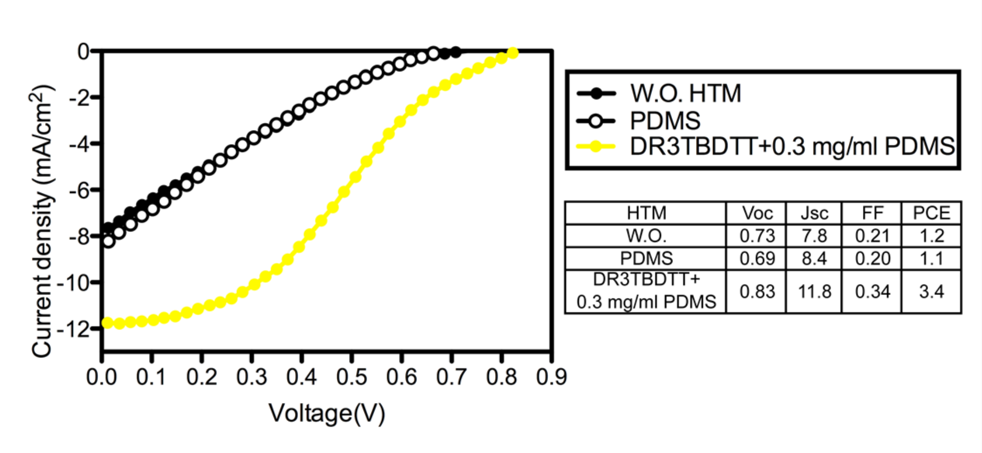


Figure S6. Cross-sectional SEM image of thin DR3TBDTT based HTM coated perovskite layer.



HTM	Voc	Jsc	FF	PCE
W.O.	0.73	7.8	0.21	1.2
PDMS	0.69	8.4	0.20	1.1
DR3TBDTT+ 0.3 mg/ml PDMS	0.83	11.8	0.34	3.4

Figure S7. *J-V* curves and performances of the planar perovskite solar cells using different materials as the HTMs.

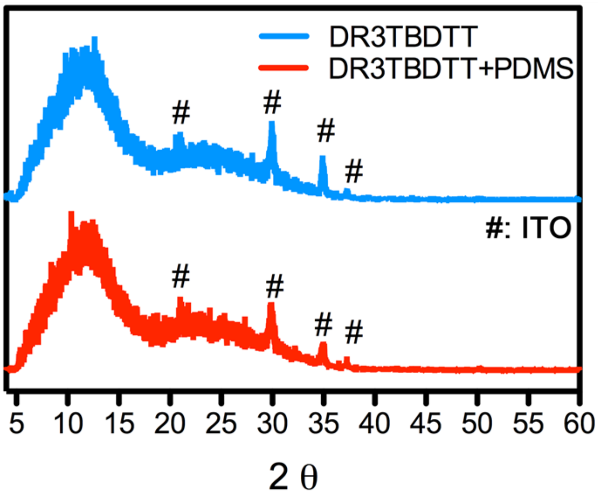


Figure S8. XRD data of DR3TBDTT and DR3TBDTT+PDMS films on ITO glass.

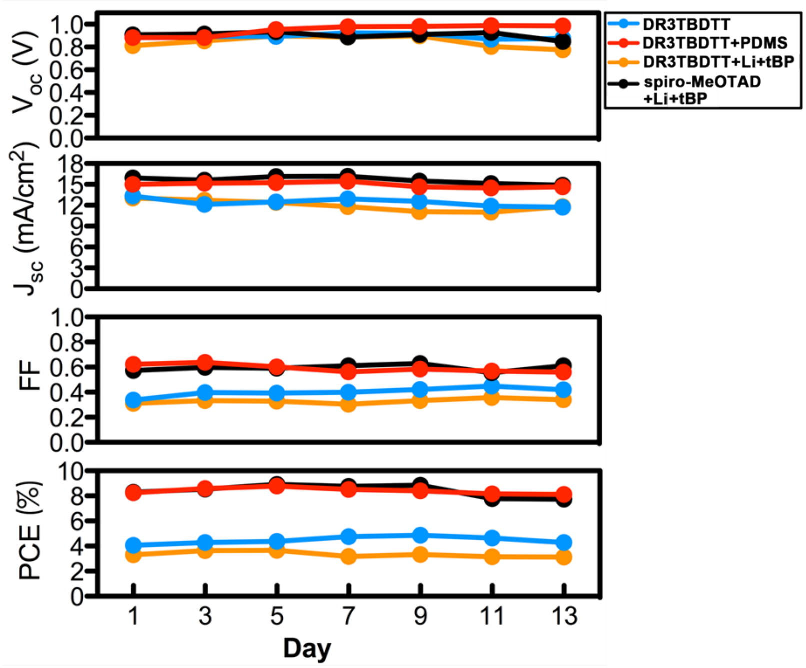


Figure S9. Evolution of photovoltaic parameters of devices under 100 mW cm^{-2} simulated AM1.5G irradiation. Devices were stored in air at room temperature in the dark (humidity <20%) without encapsulation.

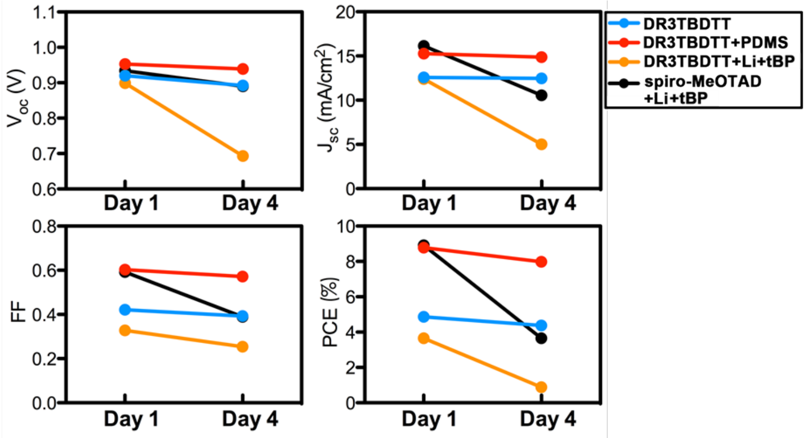


Figure S10. Evolution of photovoltaic parameters of devices under 100 mW cm^{-2} simulated AM1.5G irradiation. Devices were exposured to a relative humidity >50% in air for 3 days at room temperature without encapsulation under illumination.

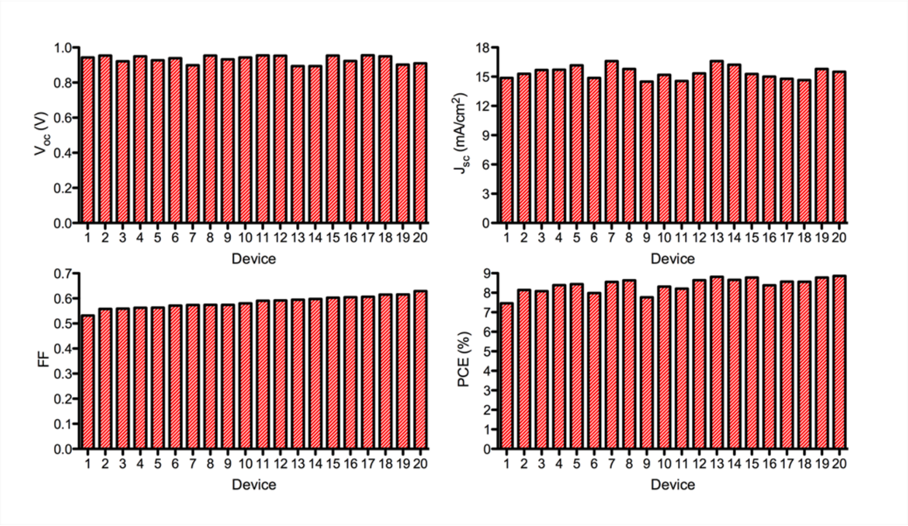


Figure S11. Histogram plots of device performance parameters for 20 individual cells based on the structure: FTO/compact TiO_2/ $CH_3NH_3PbI_{3-x}Cl_x$/DR3TBDTT+PDMS/Au.

Table 1. The best-performing devices with different HTMs and the fitted resistances.[a]

HTM	V_{oc} (V)	J_{sc} (mA cm^{-2})	*FF*	PCE (%)	$R_{series}^{\#}$ (Ω•cm^2)	R_s (Ω•cm^2)	R_{pc} (Ω•cm^2)	R_{series} (Ω•cm^2)
DR3TBDTT	0.92	12.6	0.42	4.9	23.4	1.0	16.8	17.8
DR3TBDTT+PDMS	0.95	15.3	0.60	8.8	8.8	1.0	3.1	4.1
DR3TBDTT+Li+*t*BP	0.90	12.4	0.33	3.7	33.5	1.3	148.1	149.4
Spiro-MeOTAD+Li+*t*BP	0.93	16.1	0.59	8.9				

[a] $R_{series}^{\#}$ calculated from the *J-V* curves and R_s, R_{pc}, R_{series} calculated from the EIS.