Supporting Information For

Dithieno[3,2-*a*:3′,2′-*j*][5,6,11,12]Chrysene Diimides Based Polymers As Electron Transport Layer Enabling Efficient Inverted Perovskite Solar Cells

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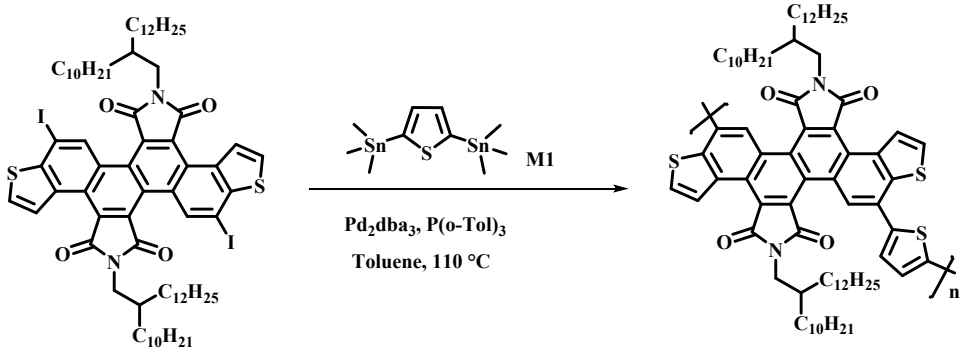
Experimental section

1. Materials and general method

All reagents and solvents were obtained commercially and used as received unless otherwise mentioned. Compounds **1**[1] and **P(DTCDI-2T)**[2] were previously reported by us. ^{1}H NMR (400 MHz) spectra were performed on JEOL NMR (400 MHz) instruments. Elemental analyses were measured on an Elementar Vario EL III elemental analyzer. Optical absorption spectra were conducted on a U-3900 UV-vis spectrophotometer. Thermogravimetric analysis (TGA) measurements were obtained on a TGA Q500 instrument heating from room temperature to 500 ºC under dry nitrogen flow with rate of 10 ºC/min, Differential scanning calorimetry (DSC) measurements were acquired under a dry nitrogen flow heating from room temperature to 350 ºC with rate of 10 ºC/min on a DSC Q2000 instrument. Cyclic voltammetry (CV) was operated using Bu_4NPF_6 (0.1 M) as supporting electrolyte and ferrocene as external reference on CHI610D instruments with a scan rate of 100 mV/s. The CV cell consisted of a platinum wire counter electrode, a platinum button working electrode, and a calomel reference electrode. Photoluminescent (PL) spectra were obtained using a Hitachi F-4600 fluorescent spectrophotometer. The time-resolved PL decay spectra were measured using a Delta flex fluorescence lifetime system. Scanning electron microscopy (SEM) measurements were

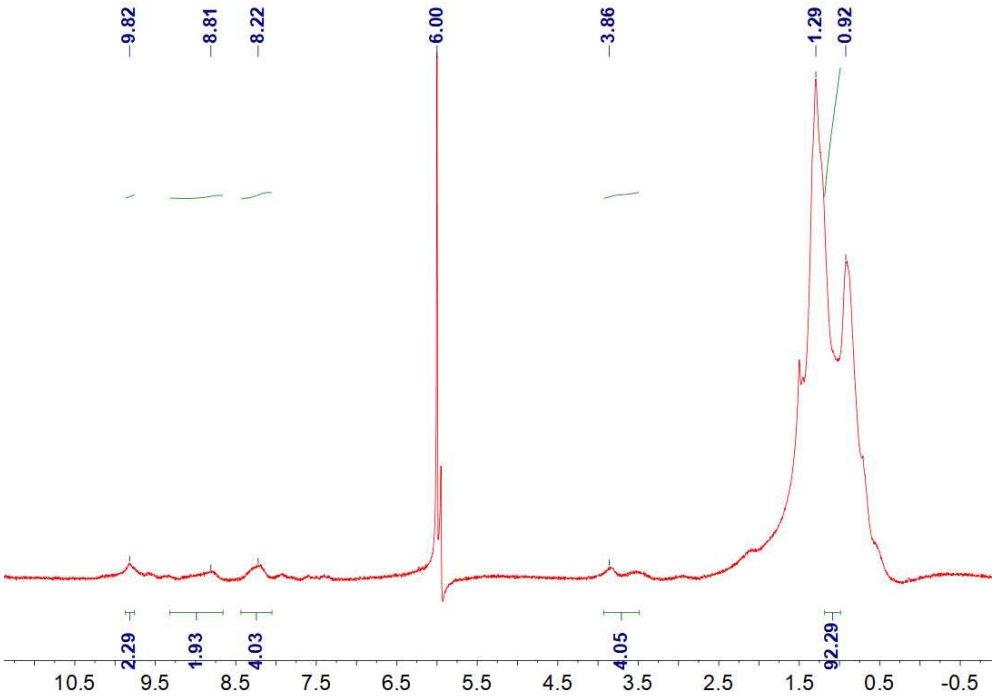
performed in a Hitachi S-4800 instrument. Atomic force microscopy (AFM) was characterized on a Bruker Inova atomic microscope in tapping mode. The current density-voltage (*J–V*) characteristics were tested with a Keithley 2420 measurement source units maintained at room temperature in N_2 filled glovebox. Photocurrent was upon irradiation by an AAA solar simulator (Oriel 94043A, 450 W, USA) with AM 1.5 G filter and light intensity was simulated to be 100 mW cm^{-2} using a NREL-certified standard silicon cell (Oriel reference cell 91150, USA). External quantum efficiency (EQE) was performed with a 75 W xenon lamp equipping with an Oriel monochromator (74125), an optical chopper, a lock-in amplifier and a NREL-calibrated crystalline silicon cell. Water contact angle was performed in a POWEREACH JC2000 machine. X-ray photoelectron spectroscopy (XPS) was performed on an Axis Ultra DLD (Kratos, UK) ultrahigh vacuum photoelectron spectroscopy with a monochromatic Al Kα X-ray (1486.6 eV) as excitation source. Density functional theory (DFT) calculations were conducted using the Gaussian 16 package with the B3LYP hybrid density functional and the 6-31G(d,p) basis set, and the long side chains were replaced by methyl groups.

2. Synthesis

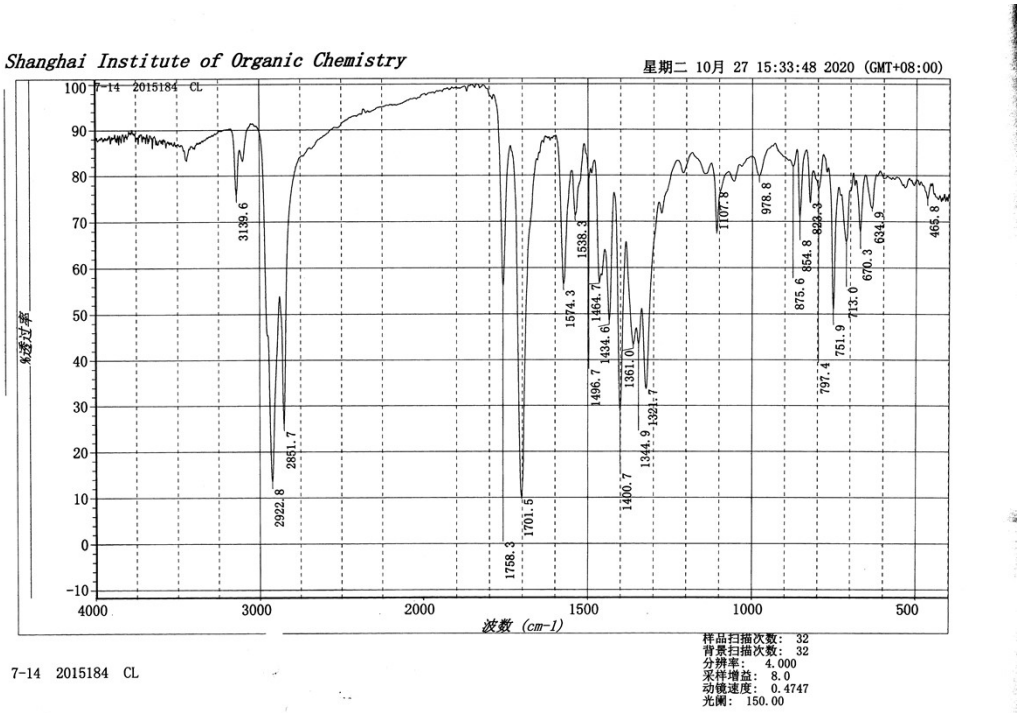


P(DTCDI-T): a mixture of compound **1** (210.5 mg, 0.15 mmol), M1 (61.5 mg, 0.15 mmol), Pd_2dba_3 (8.4 mg, 0.009 mmol), $P(o\text{-}Tol)_3$ (8.0 mg, 0.026 mmol) and Toluene (5 mL) was stirred at 110 ºC under N_2 atmosphere for 72 hours. After cooling, the mixture was dropped into 100 mL methanol and filtered to get dark precipitate. The precipitate was dried and extracted successively with acetone and ethyl acetate using Soxhlet extraction. The ethyl acetate extract was collected, and

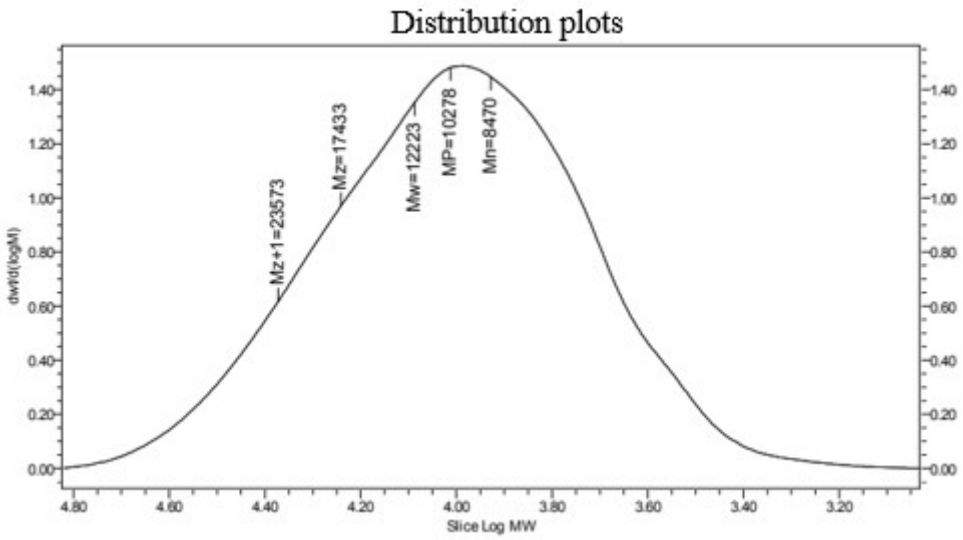
the solvent was removed using a rotavapor to obtain 146 mg dark solid (yield 83%). M_n = 8.4 kDa, PDI = 1.44. ^{1}H NMR (400 MHz, $CDCl_2CDCl_2$) δ (ppm) 9.67-9.99 (br, 4H), 8.66-9.32 (br, 2H), 8.05-8.43 (br, 4H) 3.30-3.93 (br, 4H), 0.44-1.44 (br, 92 H). IR (cm^{-1}): 3139.6, 2922.8, 2851.7,1758.3, 1701.5, 1574.3, 1496.7, 1400.7, 1321.7, 1107.8, 854.8, 751.9, 713.0, 670.3; Anal. Calcd for $C_{78}H_{106}N_2O_4S_3$: C, 76.05; H, 8.67; N, 2.27; Found: 76.34; H, 8.82; N, 1.95.



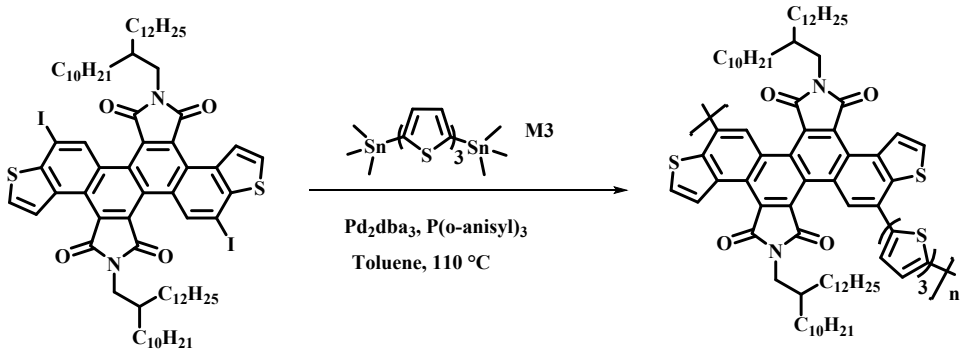
^{1}H NMR of **P(DTCDI-T)**



IR of **P(DTCDI-T)**

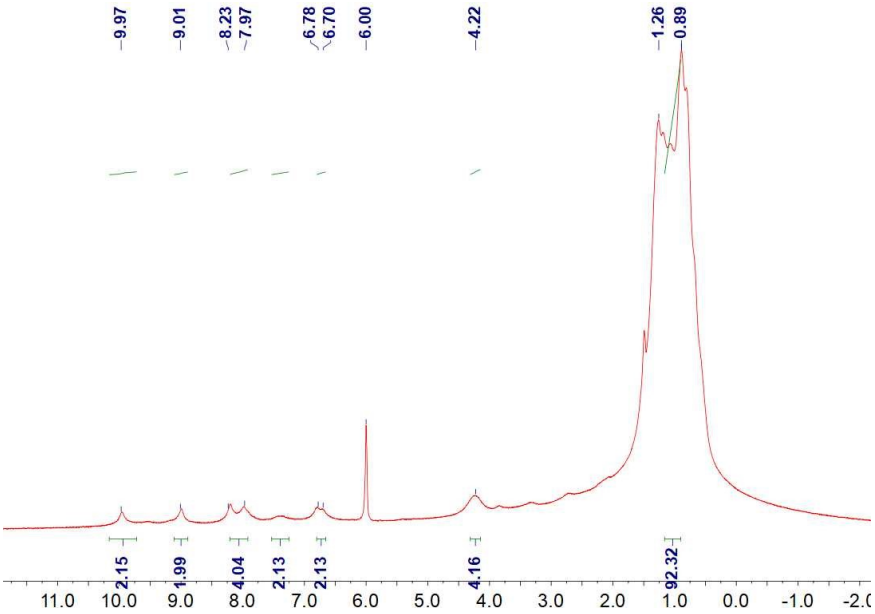


GPC distribution plots of **P(DTCDI-T)**

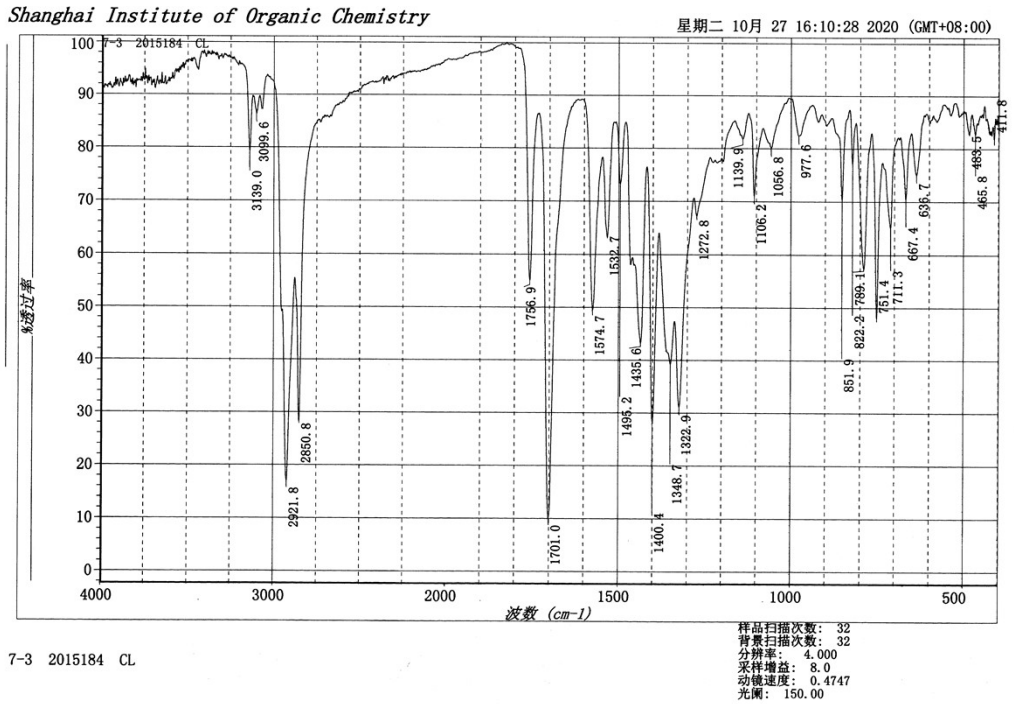


1 **P(DTCDI-3T), 98%**

P(DTCDI-3T): a mixture of compound **1** (210.5 mg, 0.15 mmol), M3 (86.1 mg, 0.15 mmol), Pd_2dba_3 (8.3 mg, 0.009 mmol), P(*o*-Tol)$_3$ (8.4 mg, 0.024 mmol) and Toluene (5 mL) was stirred at 110 ºC under N_2 atmosphere for 72 hours. After cooling, the mixture was dropped into 100 mL methanol and filtered to get dark precipitate. The precipitate was dried and extracted successively with acetone, ethyl acetate, petroleum ether and chloroform using Soxhlet extraction. The chloroform extract was collected, and the solvent was removed using a rotavapor to obtain 204 mg dark solid (yield 98%). Mn = 48.1 kDa, PDI = 3.46. ^{1}H NMR (400 MHz, $CDCl_2CDCl_2$, 100 ° C) δ (ppm) 9.72-10.16 (br, 2H), 8.89-9.11 (br, 2H), 7.92-8.27 (br, 4H), 7.25-7.53 (br, 2H), 6.66-6.80 (br, 2H), 4.14-4.44 (br, 4H), 0.37-1.43 (br, 92 H). IR (cm^{-1}): 3139.0, 2921.8, 2850.8, 1756.9, 1701.0, 1574.7, 1495.2, 1400.4, 1322.9, 1106.2, 851.9, 789.1, 751.4, 711.3, 677.4. Anal. Calcd for $C_{86}H_{110}N_2O_4S_5$: C, 73.99; H, 7.94; N, 2.01; Found: 74.07; H, 7.98; N, 1.75.



^{1}H NMR of **P(DTCDI-3T)**



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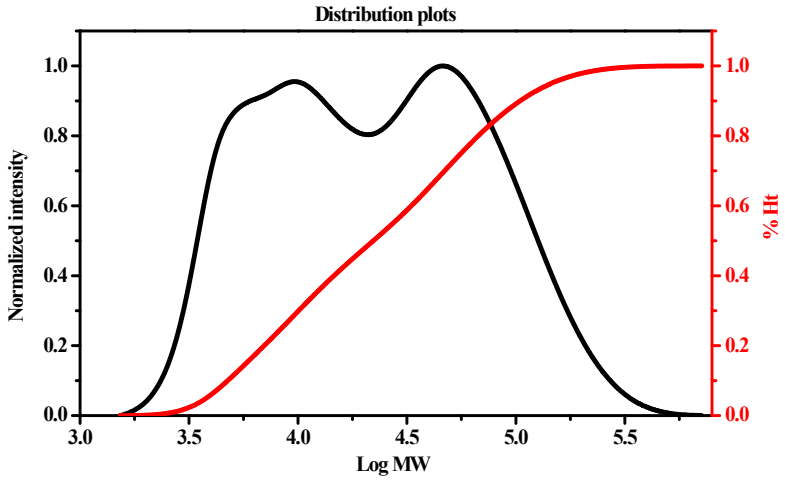
IR of **P(DTCDI-3T)**



GPC distribution plots of **P(DTCDI-3T)**

3. Fabrication and measurement of perovskite solar cells

ITO-coated glasses were respectively cleaned consecutively in detergent, deionized water, acetone and isopropanol ultrasonic baths for 15 min and then treated with UV-Ozone for 30 min. After cleaning, the ITO-coated glasses were transferred to N_2 filled glovebox for device fabrication. PTAA (5 mg mL^{-1} in toluene) was firstly spin-coated onto the ITO at 6000 rpm for 30 s, and annealed at 100 °C for 10 min. Secondly, a mixed solution of PbI_2 and MAI (1.3 M:0.3 M) in mixed solvents of DMF and DMSO (v_{DMF}: v_{DMSO} = 9:1) was spin-coated upon PTAA layer under a condition of 0 to 6000 rpm in 8 s, and keeping 6000 rpm for 15 s, then decelerate to 2700 rpm in 13 s. Subsequently, 50 uL MAI solution (55 mg mL^{-1} in isopropanol) was dropped down spun for another 51 s, and then annealed at 100 °C for 30 min. After cooling down, the ETLs (PCBM (20 mg mL^{-1} in chlorobenzene), P(DTCDI-T) (20 mg mL^{-1} in chlorobenzene), P(DTCDI-2T) (20 mg mL^{-1} in chlorobenzene) and P(DTCDI-3T) (20 mg mL^{-1} in chlorobenzene)) were deposited respectively at 1000 rpm for 30 s and 1500 rpm for 30 s at room temperature, and subsequently BCP (0.5 mg mL^{-1} in isopropanol) layer at 5000 rpm for 30 s. The sample was then transferred to vacuum chamber for deposition of Ag (80 nm) by thermal evaporation under a pressure of 3×10^{-6} mbar to finish the device fabrication process. The active area of the device by the overlap with electrodes was approximately 0.07 cm^2.

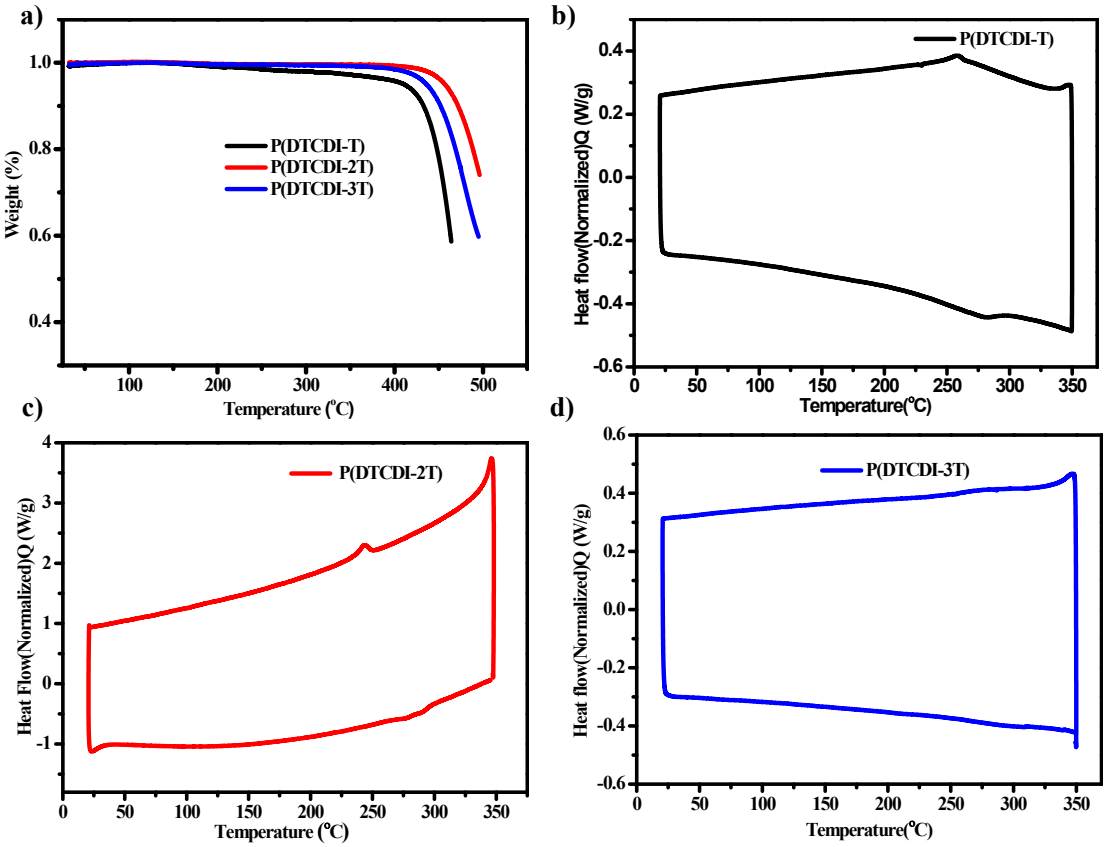


Figure S1 TGA and DSC curve of P(DTCDI-T), P(DTCDI-2T) and P(DTCDI-3T)

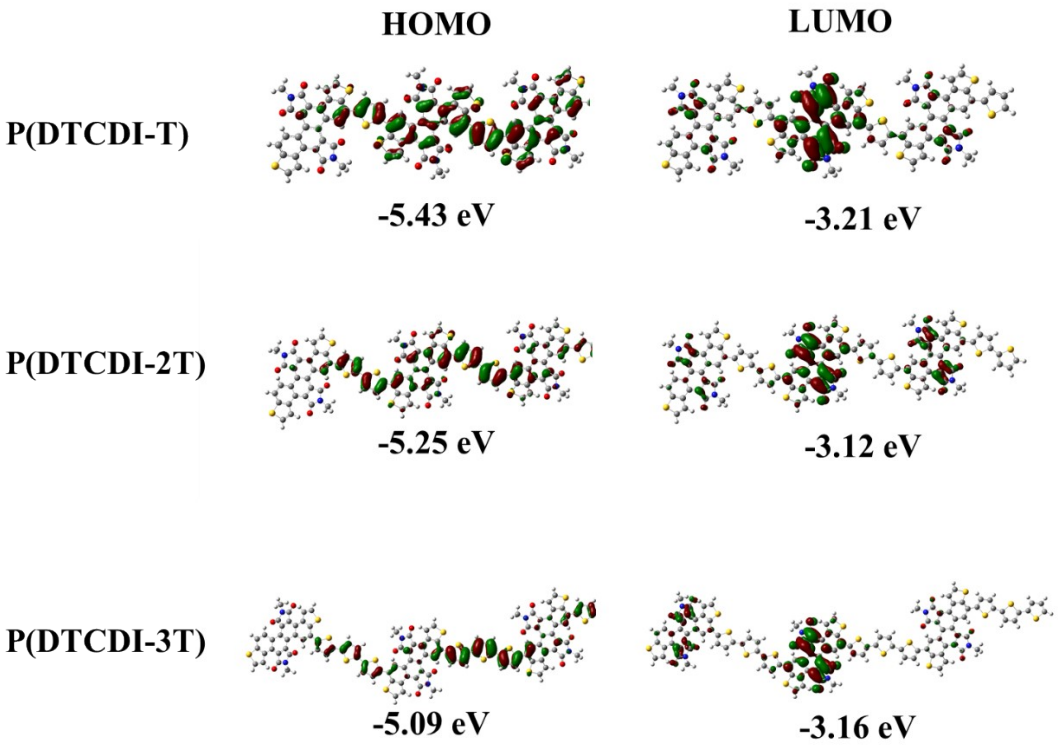


Figure S2. Optimized geometry of frontier molecular orbital diagrams of polymer

Table S1 fitted Parameters of TRPL decay and derived time constants

Sample	A_1	τ_1 (ns)	A_2	τ_2 (ns)	τ_{ave} (ns)
PVSK	0.037	396.6	0.963	340.2	342.6
PVSK/PCBM	0.672	19.9	0.328	345.4	311.0
PVSK/P(DTCDI-T)	0.476	14.9	0.524	221.9	210.0
PVSK/P(DTCDI-2T)	0.352	2.7	0.648	75.8	74.4
PVSK/P(DTCDI-3T)	0.424	3.2	0.576	68.1	65.9

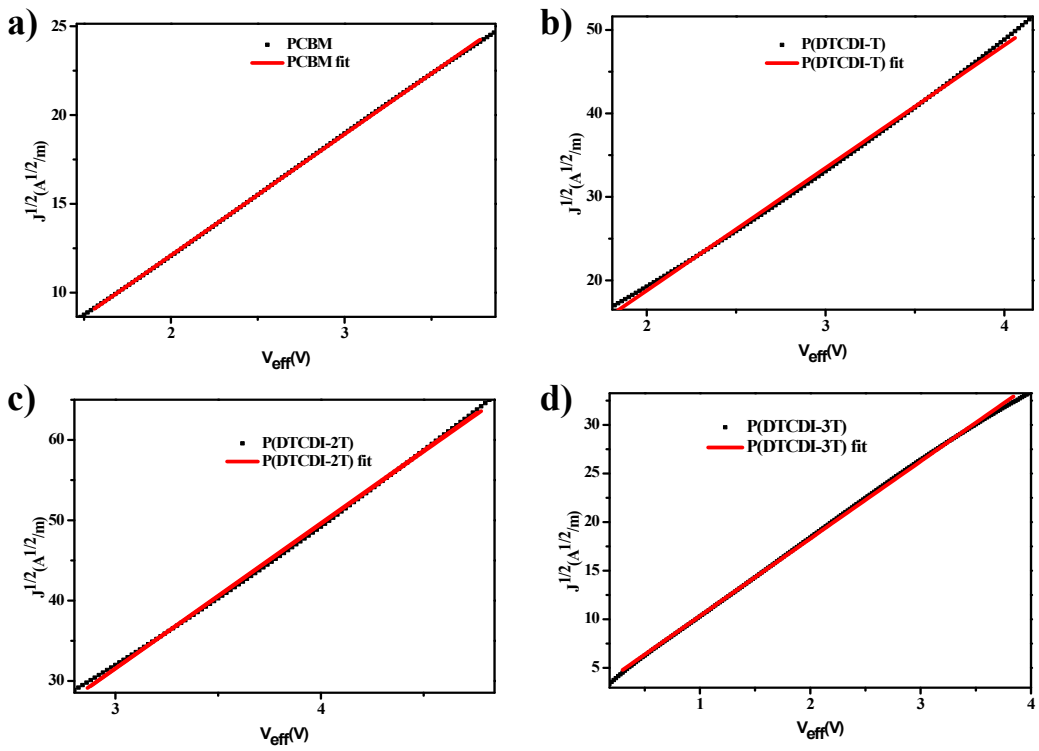


Figure S3 $J^{1/2}$-V curves for electron-only devices with structure of ITO/ ZnO / ETL/ Al, a) PCBM, b) P(DTCDI-T), c) P(DTCDI-2T), d) P(DTCDI-3T)

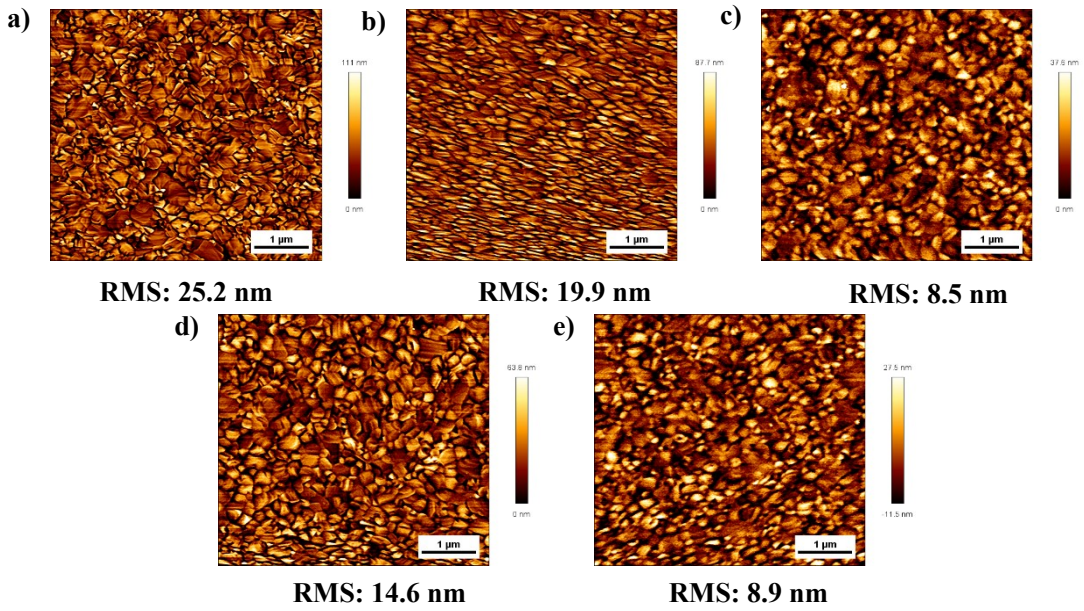


Figure S4 AFM images of a) the as-prepared perovskite film, b) PCBM, c) P(DTCDI-T) d) P(DTCDI-2T), and e) P(DTCDI-3T) covered perovskite film. The scanning size is 5 µm × 5 µm

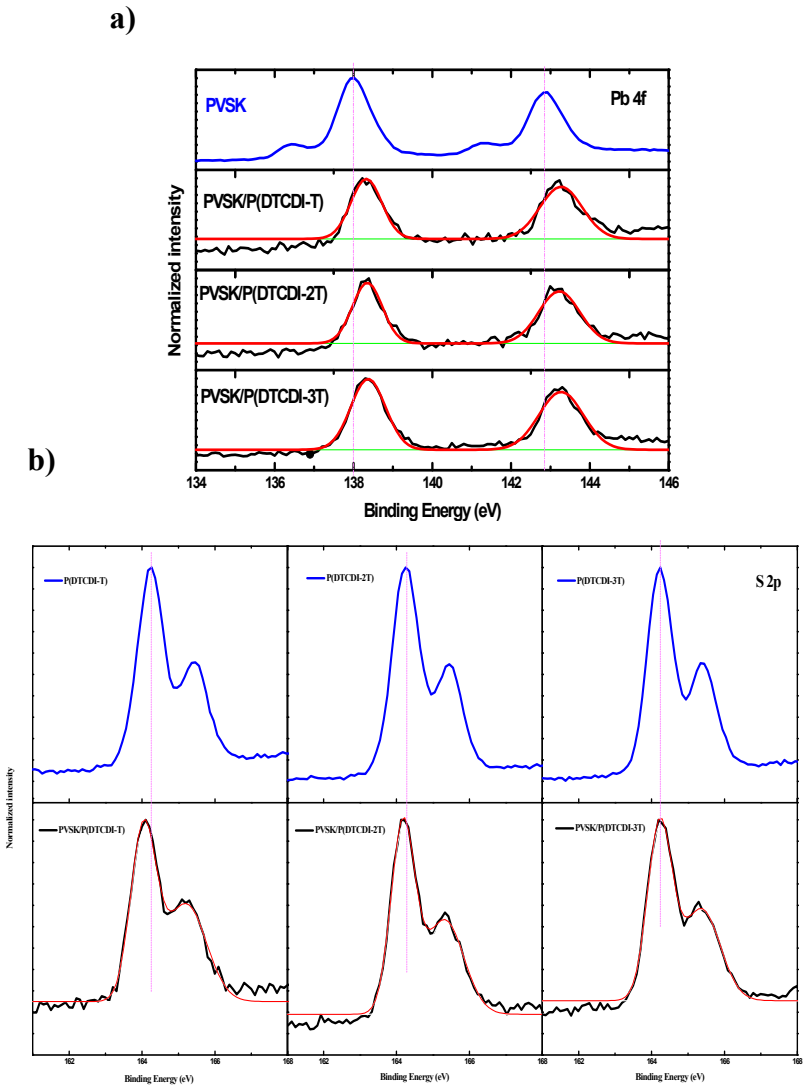


Figure S5 XPS spectra of the perovskite films with and without polymeric ETLs layer for a) Pb 4f, b) S 2p.

Table S2 Impedance data of Nyquist plot

Samples	R_s (Ω)	R_{ct} (Ω)
PCBM	185	2760
P(DTCDI-T)	236	2373
P(DTCDI-2T)	164	1795
P(DTCDI-3T)	215	1970

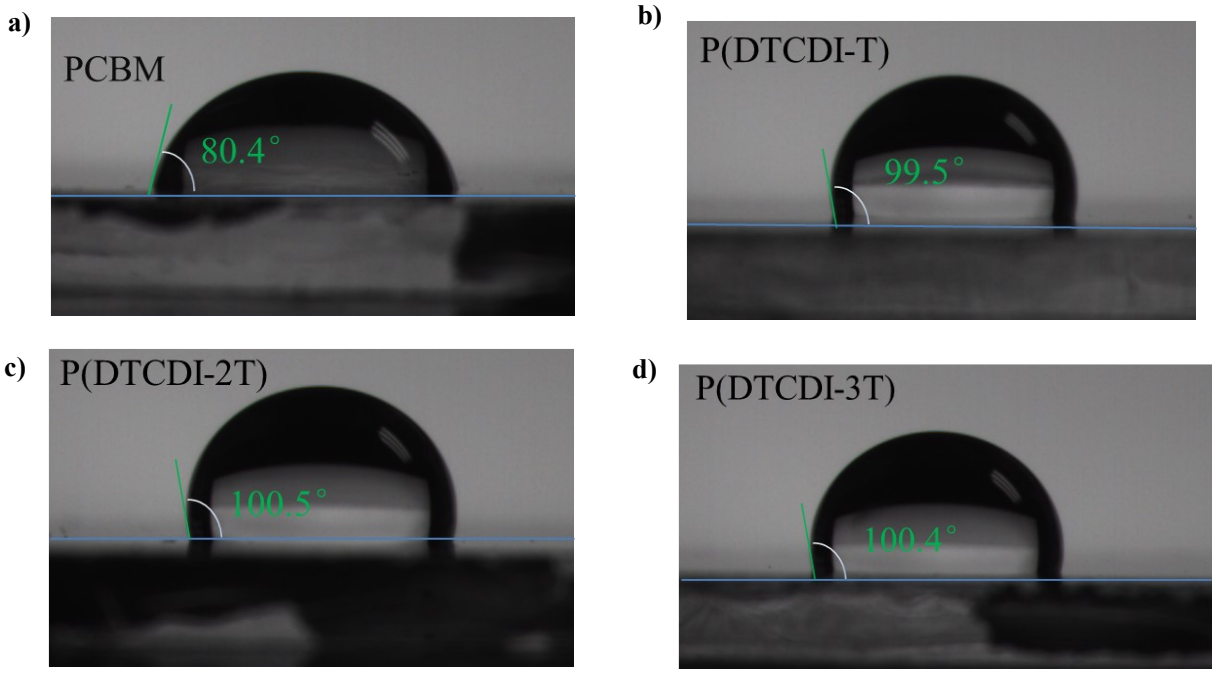


Figure S6 Water contact angle measurement on top of a) PCBM, b) P(DTCDI-T) c) P(DTCDI-2T) and d) P(DTCDI-3T) films.

1. X. Zhao, C. Ge, X. Yang and X. Gao, *Materials Chemistry Frontiers*, 2017, **1**, 1635-1640.
2. X. Zhao, C. Ge, X. Xu, J. Huang, X. Yang, Q. Peng, W.-S. Li and X. Gao, *Chemical Communications*, 2019, **55**, 10234-10237.