Electronic Supplementary Material (ESI) for Chemical Communications.

Direct Arylation Polycondensation towards Water/Alcohol-Soluble Conjugated Polymers as Electron Transporting Layers for Organic Solar Cells

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1. General Experimental Details

Methods and Materials: The monomers of $NDIBr_2$ was synthesized according to the reported procedures[1-2] and ProDOTN was purchased from SunaTech Inc.. All the other WSCPs were prepared as the following procedures as below.

^1H and ^{13}C NMR were characterized with Bruker-500 spectrometer in deuterated chloroform or methanol solution (PNDI-ProDOTNBr) at 298 K. Chemical shifts were recorded as δ values (ppm) with the internal standard of tetramethylsilane (TMS). The number-average (M_n) and weight-average (M_w) molecular weights were determined with Waters GPC 2410 in THF using a calibration curve with standard polystyrene as a reference. Thermogravimetric analyses (TGA) were performed on a Netzsch TG 209 under nitrogen at a heating rate of 10 ^oC min^{-1}. Differential scanning calorimetry (DSC) was performed on a Netzsch DSC 204 under nitrogen flow at heating/cooling rates of 10/20 ^oC min^{-1}. UV-vis absorption spectra were recorded on a HP 8453 pectrophotometer. Cyclic voltammetry (CV) was performed on a CHI600D electrochemical workstation with an ITO-coated glass working electrodeand a Pt wire counter electrode at a scanning rate of 50 mV s^{-1} against an a saturated calomel electrode reference electrode with a nitrogen saturated anhydrous solution of tetra-*n*-butylammonium hexafluorophosphate in acetonitrile (0.1 mol L^{-1}).

2. Synthetic Procedures

The synthetic route for WSCPs are showed in Scheme 1. the synthesis of PNDI-ProDOTN is carried out by using ProDOTN and $NDIBr_2$ as the starting material, using catalyst of $Pd(dba)_3.CHCl_3$, ligand of $P(o\text{-}CH_3Ph)_3$, pivalic acid and $CsCO_3$ in o-Xylene for 24 h at 110 °C. After pouring into methanol, PNDI-ProDOTN was collected by filtration and then successively purified by Soxhlet extraction with methanol, hexane and dichloromethane. The PNDI-ProDOTN of dichloromethane is we need.

Synthesis of PNDI-ProDOTN.

In an oven-dried, magnetic-stirred, 5 mL pressure flask, $NDIBr_2$ (97.27 mg, 0.15 mmol), ProDOTN (40.5 mg, 0.15 mmol), $Pd_2(dba)_3.CHCl_3$ (6.79 mg, 7.64 μmol), $P(o\text{-}CH_3Ph)_3$ (4.9 mg, 15

μmol), pivalic acid (7.07 mg, 0.07 mmol), and $CsCO_3$ (184 mg) were added and the pressure flask evacuated and refilled with argon for three cycles. Then o-Xylene (1.5 mL) was added and the mixture was heated at 110 °C for 24 hours. After that, the dark blue solution was precipitated in methanol. The crude polymer was collected by filtration and then successively purified by Soxhlet extraction with methanol, hexane, and dichloromethane. The final product was obtained by precipitation into methanol. The product was then dried under vacuum for 1 day to get the NDI-ProDOTN as a blue floccule.

Synthesis of PNDI-ProDOTNBr.

In an oven-dried, magnetic-stirred, 25 mL round-bottom flask, PNDI-ProDOTN (100 mg) was added and the round-bottom flask evacuated and refilled with argon for three cycles. Excess bromoethane (2.5 ml) was added in chloroform and methanol mixed solution (10 ml) in darkness for 2 days. The product was dried under vacuum for 1 day to get the PNDI-ProDOTNBr as a blue solid.

3. NMR Spectra

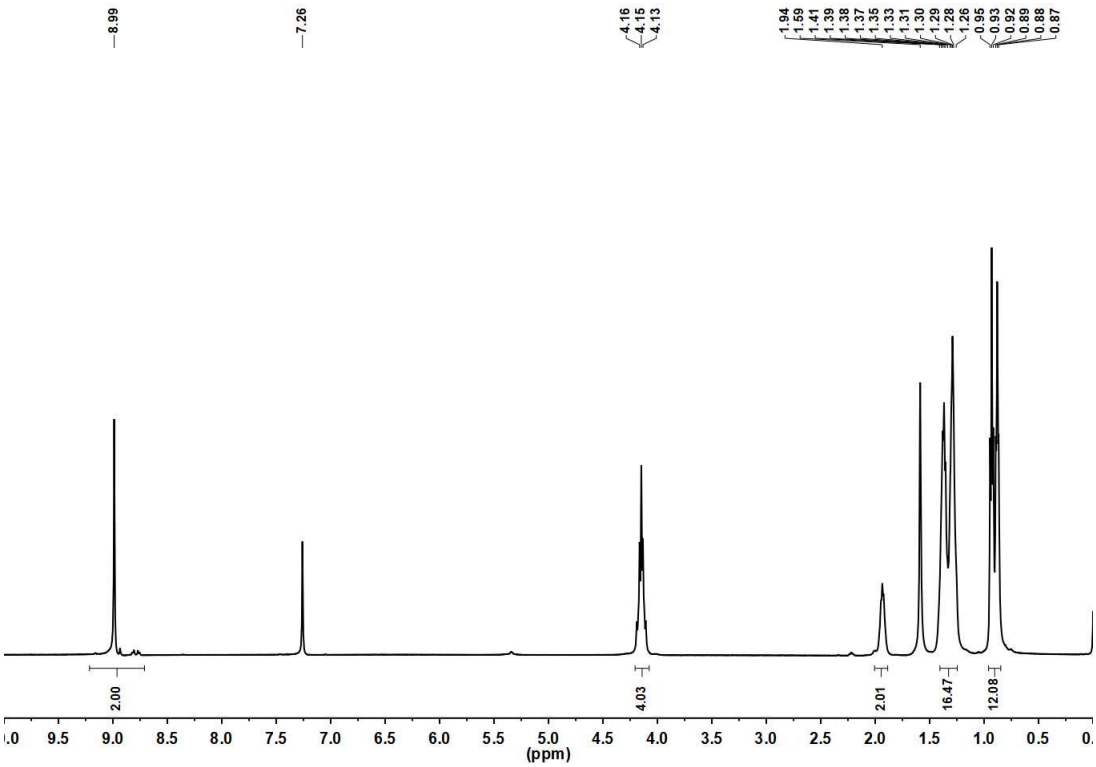

Figure S1. ^{1}H NMR spectrum of $NDIBr_2$.

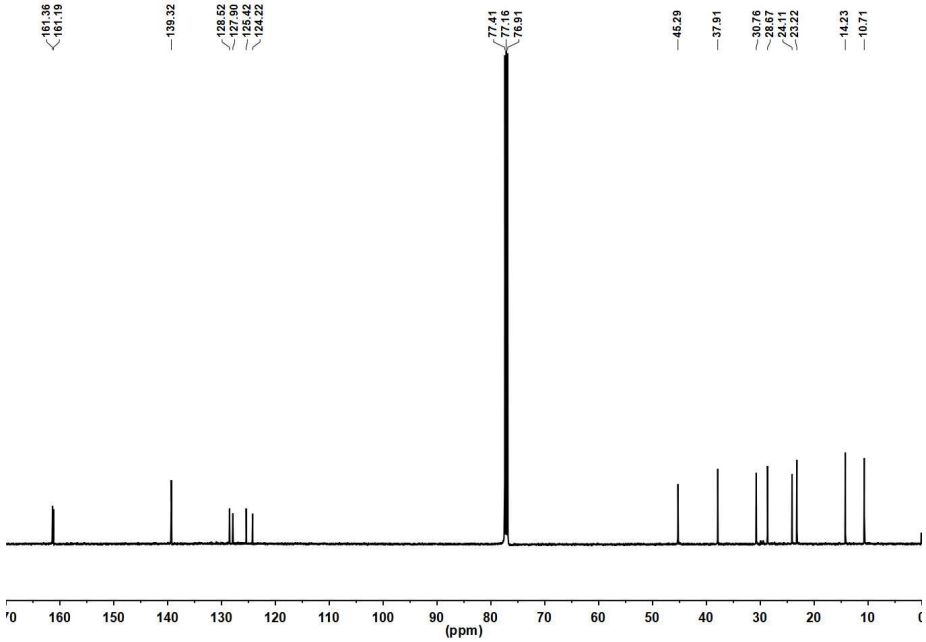

Figure S2. ^{13}C NMR spectrum of $NDIBr_2$.

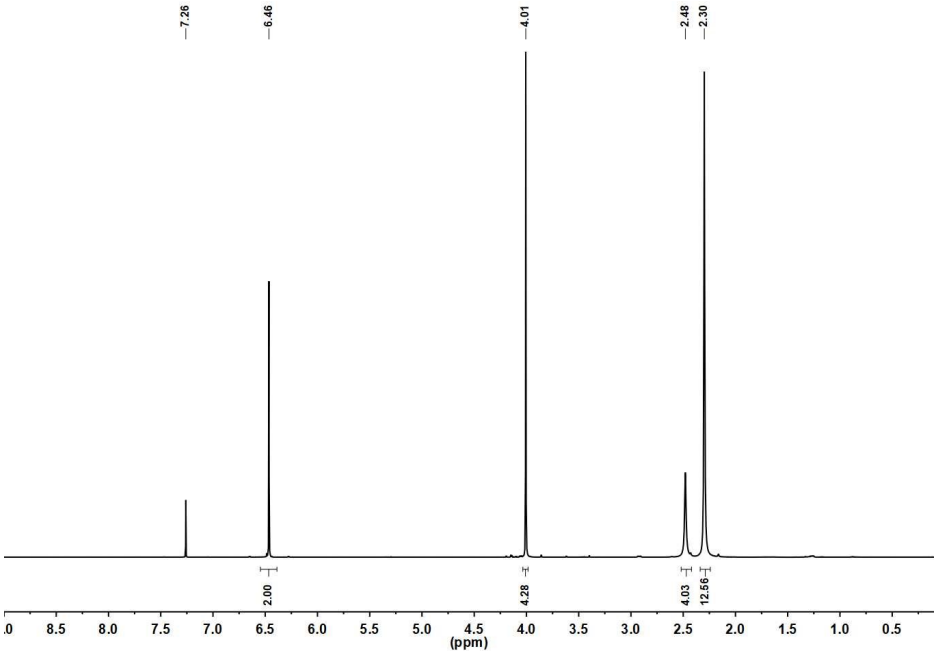

Figure S3. ^{1}H NMR spectrum of ProDOTN.

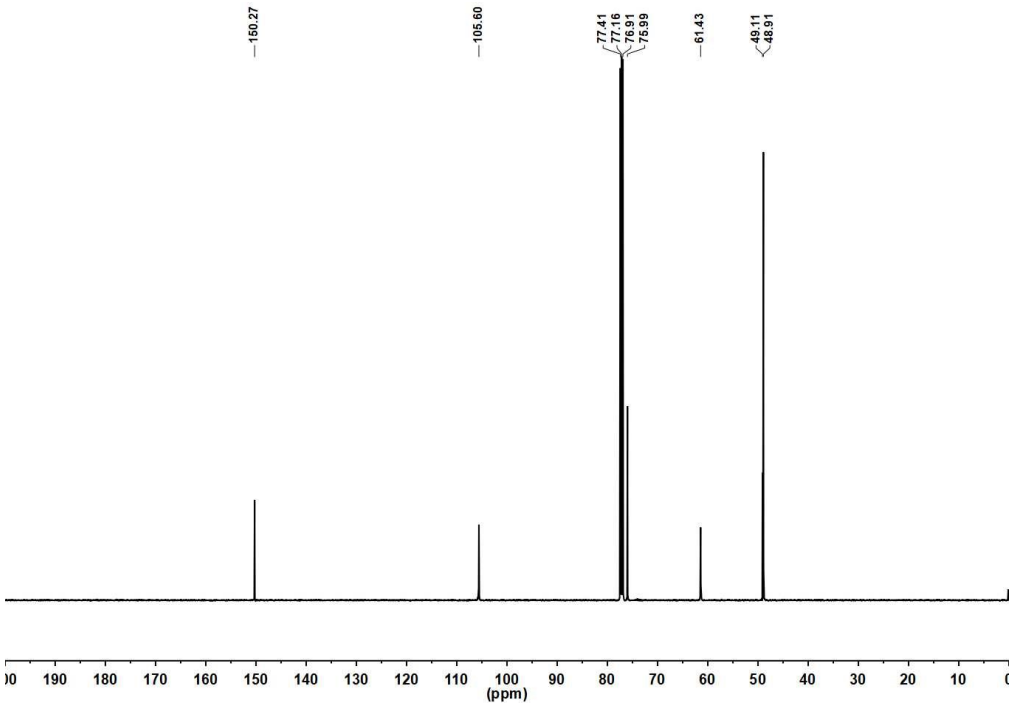

Figure S4. ^{13}C NMR spectrum of ProDOTN.

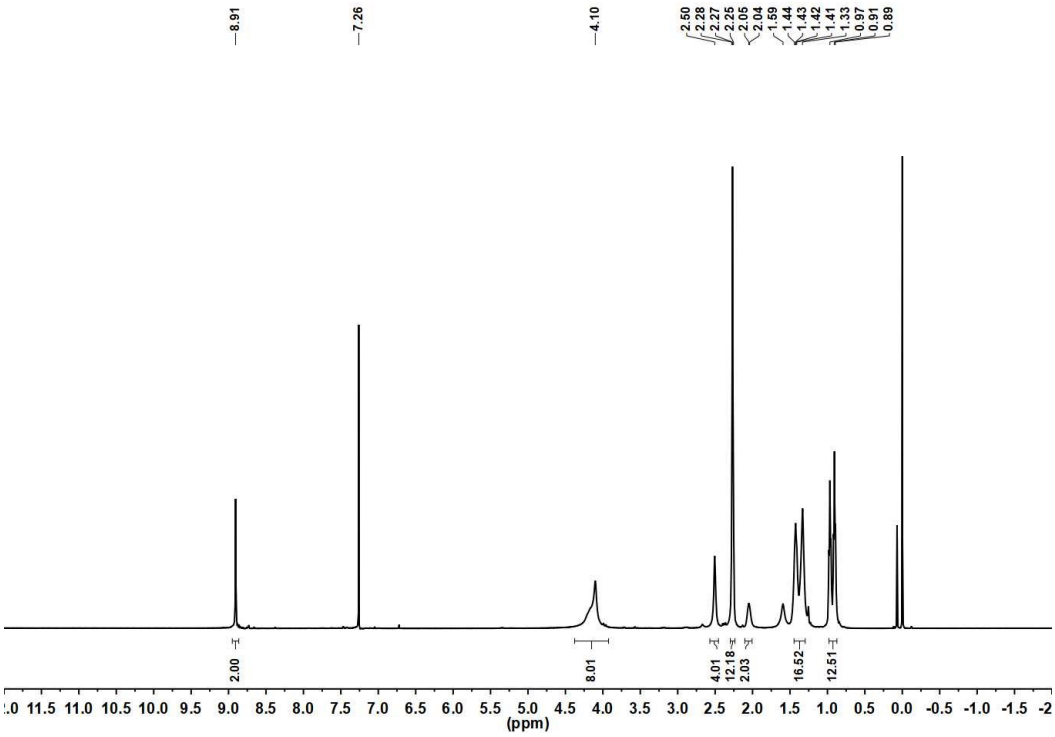

Figure S5. ^{1}H NMR spectrum of PNDI-ProDOTN.

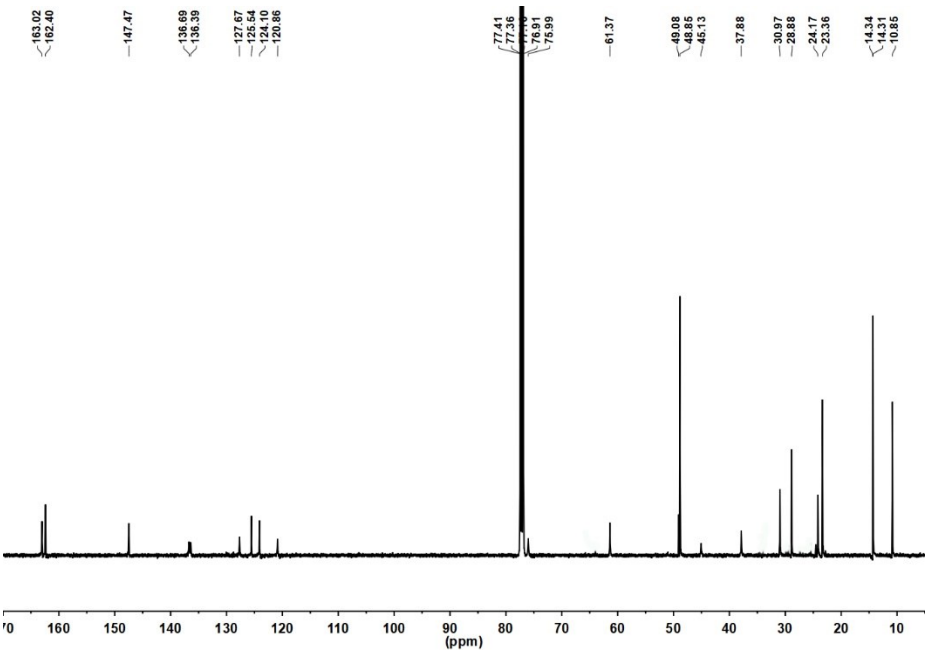

Figure S6. ^{13}C NMR spectrum of PNDI-ProDOTN.

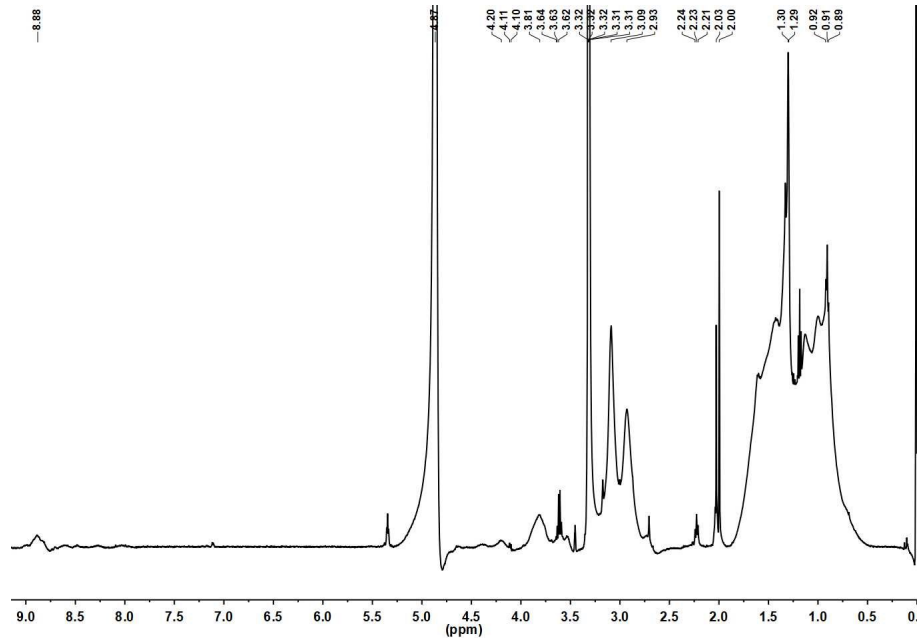

Figure S7. ^{1}H NMR spectrum of PNDI-ProDOTNBr.

4. Molecular Weight and Thermal Properties

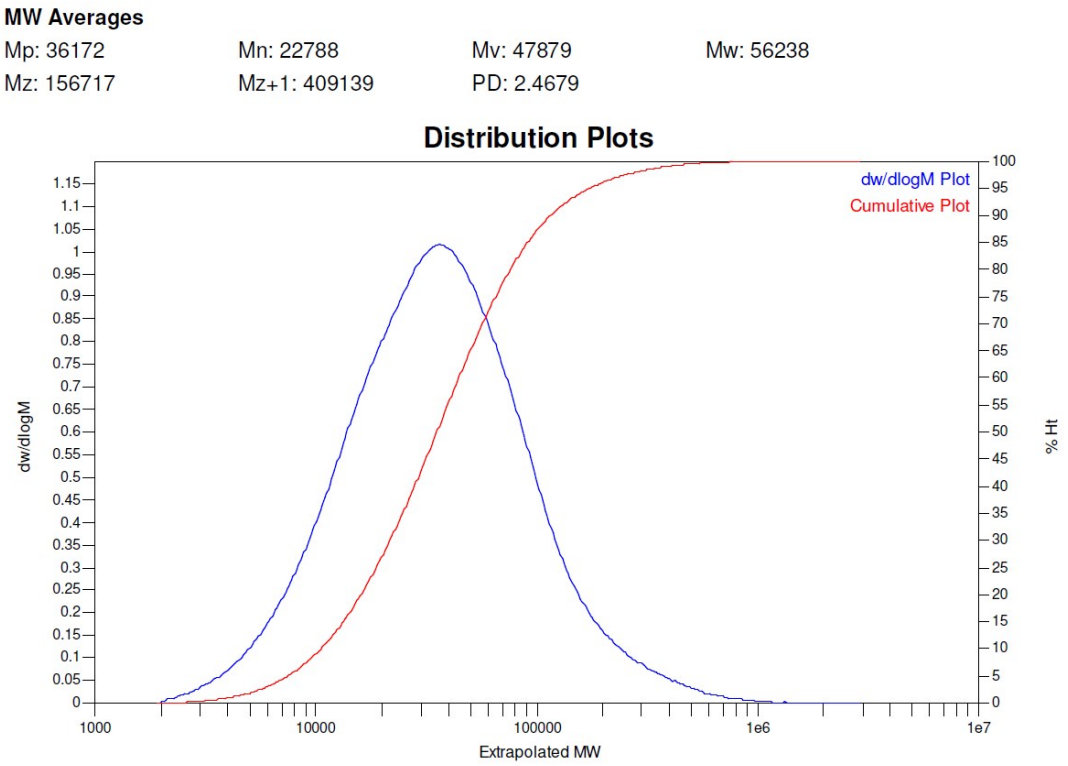

Figure S8. The GPC of PNDI-ProDOTN.

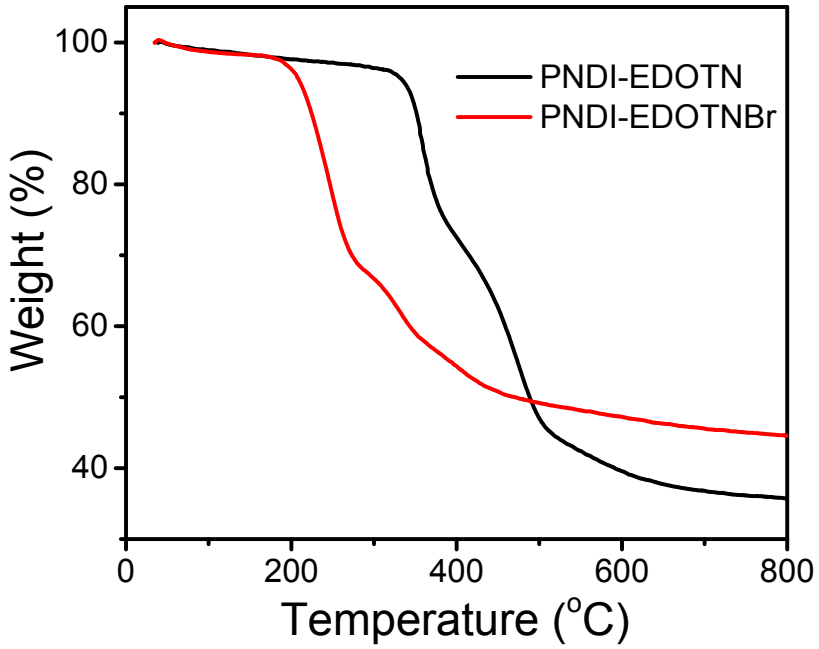

Figure S9. TGA of PNDI-ProDOTN and PNDI-ProDOTNBr.

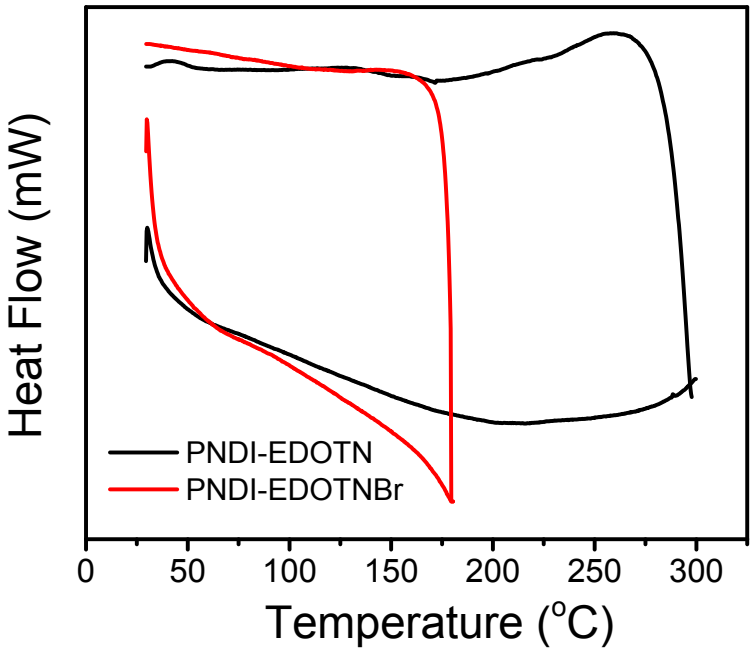

Figure S10. DSC of the PNDI-ProDOTN and PNDI-ProDOTNBr.

5. SCLC Measurements

Electron Mobility Measurement by Space Charge Limited Current (SCLC) Method.

Electron-only devices were fabricated by using the device structure of ITO/ZnO/ WSCPs /Ca/Al. And was measured by using the space-charge-limited current (SCLC) method. The mobility was calculated with the Mott−Gurney equation in the SCLC region: $J = 9\varepsilon_0\varepsilon_r\mu V^2/8d^3$, where J is the space charge limited current, ε_0 is the permittivity of free space, ε_r is the relative permittivity of the material, d is the thickness of the material and V is the effective voltage. The effective voltage was obtained by subtracting the built-in voltage (V_{bi}) and the voltage drop (V_s) from the series resistance of the whole device except for the active layers from the applied voltage (V_{appl}), $V = V_{appl} - V_{bi} - V_s$. The electron mobility can be calculated from the slope of the $J^{1/2}$~V curves.

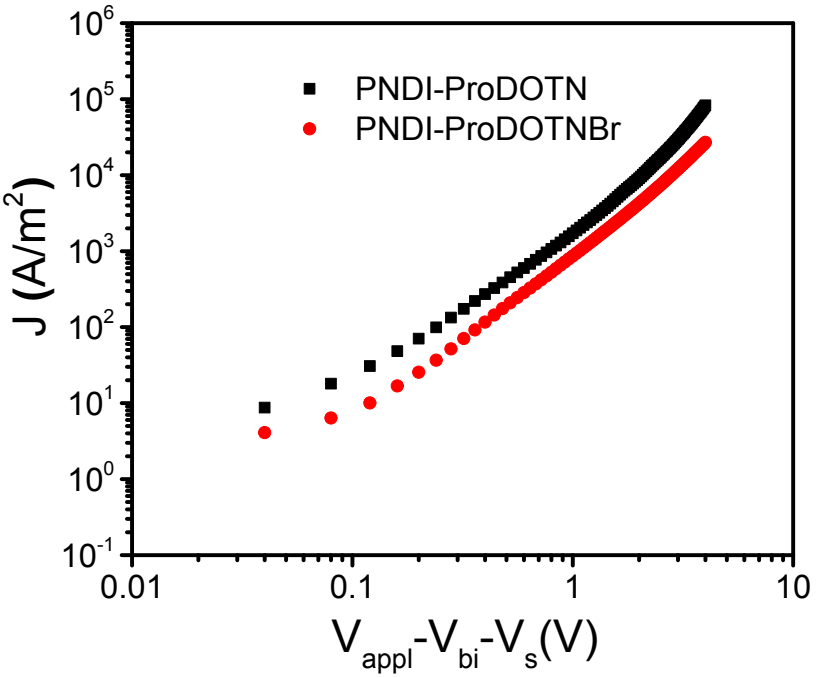

Figure S11. Electron mobilities of PNDI-ProDOTN and PNDI-ProDOTNBr.

6. Devices Fabrication

Before fabrication of the device, the indium tin oxide (ITO)-coated glass substrates were cleaned by ultrasonic treatment in deionized water, acetone, isopropyl alcohol and dried in oven at 80 ^{o}C for 12 h before used. After PEDOT:PSS (30 nm) layer was spin coated onto the substrate, and dried at 150 ^{o}C for 15 min in air. Then, the ITO substrates were transferred into a nitrogen protected glovebox where the H_2O concentration is≤0.5 ppm and O_2 concentration is ≤20 ppm. The thin film of active layer was spin-coated and transferred to a vacuum thermal evaporator. The WSCPs was then spin coated onto the active layer as the cathode interface layer, followed by deposition of the Ag cathode at a pressure of 2×10^{-7} Torr through a shadow mask. Before the *J-V* test, a physical mask with an aperture with precise area of 0.04 cm^2 was used to define the device area. The *J-V* curves were measured on a computer-controlled Keithley 2400 source meter under 1 sun, the AM 1.5 G spectra came from a class solar simulator (Enlitech, Taiwan), and the light intensity was 100 $mWcm^{-2}$ as calibrated by a China General Certification Center-certified reference monocrystal silicon cell (Enlitech). The EQE spectra measurements were performed on a commercial QE measurement system (QE-R3011, Enlitech).

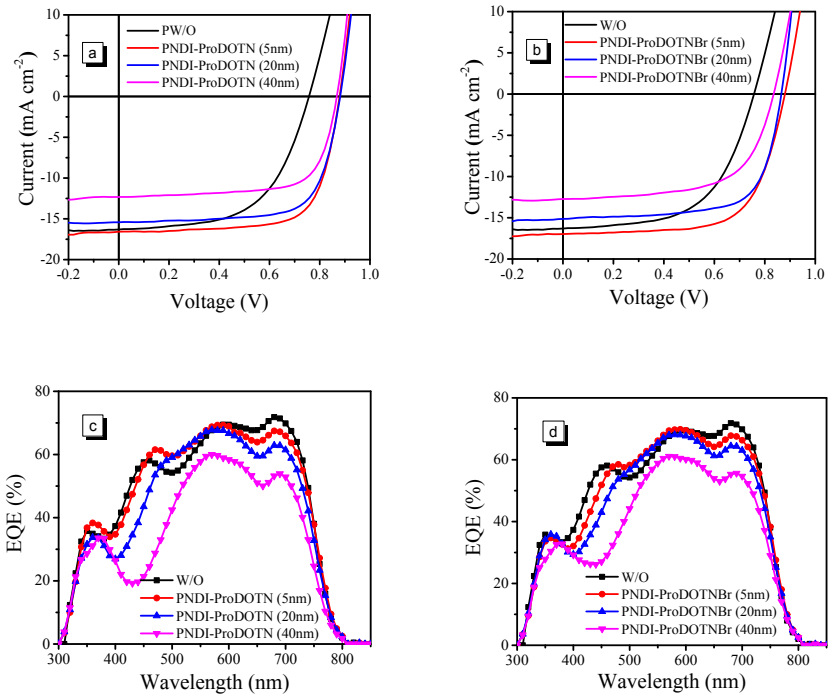

Figure S12. J–V curves of the conventional OSCs based on the active layer of PBDB-T:ITIC without any CILs and with PNDI-ProDOTN (a) and PNDI-ProDOTNBr (b) in various thicknesses. EQE spectra of the conventional OSCs based on the active layer of PBDB-T:ITIC without any CILs and with PNDI-ProDOTN (c) and PNDI-ProDOTNBr (d) in various thickness.

Table S1. Device parameters of the OSCs based on PTB7-Th:PC71BM and PBDB-T:ITIC with 0 nm, 5 nm,20 nm and 40 nm ETLs.

System	ETLs	Thickness (nm)	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF (%)	PCE (%)	PCE$_{max}$ (%)
PTB7-Th: PC71BM	Without	0	0.69	15.79	60.29	6.58	6.71
	NDI-ProDOTN	5	0.78	17.51	68.15	9.35	9.37
		20	0.78	16.24	68.66	8.74	8.77
		40	0.77	11.93	68.21	6.29	6.30
	NDI-ProDOTNBr	5	0.78	17.12	68.21	9.15	9.17
		20	0.79	16.29	67.52	8.69	8.72
		40	0.77	13.88	65.41	6.99	7.01
PBDB-T: ITIC	Without	0	0.74	16.67	56.32	6.95	7.07
	NDI-ProDOTN	5	0.88	16.64	71.13	10.4	10.4
		20	0.88	15.44	70.94	9.65	9.67
		40	0.87	12.32	70.35	7.52	7.55
	NDI-ProDOTNBr	5	0.88	15.98	70.67	9.93	9.97
		20	0.87	15.15	69.27	9.09	9.10
		40	0.83	12.80	61.92	6.57	6.59

7. Contact Angles of Water

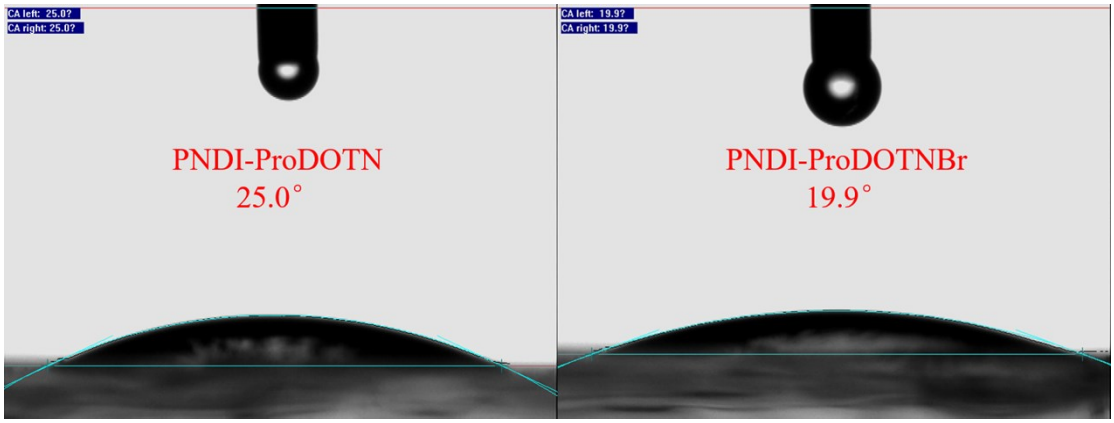

Figure S13. Contact angles of water on the surfaces of PNDI-ProDOTN and PNDI-ProDOTNBr.

8. Supplementary Information References

1 Z. H. Wu, C. Sun, S. Dong, X-F. J, S. P. Wu, H. B. Wu, H-L. Yip, F. Huang and Y. Cao, J. Am. Chem. Soc., 2016, 138, 2004.

2 A. S. Dudnik, T. J. Aldrich, N. D. Eastham, R. P. H. Chang, A. Facchetti and T. J. Marks, J. Am. Chem. Soc., 2016, 138, 15699.