Supporting Information

Exploring a Fused 2-(Thiophen-2-yl)thieno[3,2-*b*]thiophene (T-TT) Building Block to Construct n-Type Polymer for High-Performance All-Polymer Solar Cells

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Methods

^{1}H NMR spectra were obtained using Bruker 400 MHz and 500 MHz nuclear magnetic resonance (NMR). Molecular weights of the polymers were measured on Angilent Technologies PL-GPC 220 High Temperature Chromatograph at 150 °C using a calibration curve of polystyrene standards and 1,2,4-trichlorobenzene as the eluent. UV-vis absorption spectra of pristine and blend films were acquired with a Hitachi (model U-3010) UV–vis spectrophotometer. Cyclic voltammetry (CV) measurements were performed under nitrogen at a scan rate of 100 mV s^{-1} using a Zahner IM6e Electrochemical workstation. A platinum plate coated with sample film, a platinum wire and a saturated Ag/AgCl electrode were employed as a working electrode, a counter electrode and a reference electrode, respectively. 0.1 M tetra-nbutylammonium hexafluorophosphate (Bu_4NPF_6) dissolved in anhydrous acetonitrile solution was employed as a supporting electrolyte and Ferrocene/ferrocenium (Fc/Fc^+) is used as an internal standard. Atomic force microscopy (AFM) measurements were performed using a Dimension Icon AFM (Bruker) in the tapping mode. 2D-GIWAXS were conducted on a Xeuss SAXS/WAXS system with X-ray wavelength of 1.5418 Å. The

film samples were irradiated at a fixed angle of 0.2°. Transmission electron microscopy (TEM) measurements were performed on a Tecnai G2 F20 U-TWIN instrument (FEI Company, Hillsboro).

Organic Solar Cell Fabrication and Characterization

Organic solar cells with inverted device configurations of ITO/ZnO/PBDB-T:PNDIs/MoO_3/Ag and ITO/ZnO/J71:PNDIs/MoO_3/Ag were fabricated. The ITO-coated glass substrates were firstly cleaned by ultrasonic treatment in detergent, deionized water, acetone and isopropyl alcohol for 30 minutes, respectively. After drying for one night, ZnO precursor solution was spin coated at 4000 rpm and the ZnO layer was generated at 200 °C for 15 min in ambient atmosphere. The active layers were spin-coated from a solution of PBDB-T:**PNDI-T-TT** with weight ratio of 2:1 in chlorobenzene, while the active layers were spin-coated from a solution of PBDB-T:**PNDI-TVT** with weight ratio of 1.5:1 in chlorobenzene. Solution with 0.5%, 0.75 % DPE was stirred overnight prior to cast. Other active layers were spin-coated from a solution of J71:**PNDI-T-TT** with weight ratio of 1.5:1 in chlorobenzene, while the active layers were spin-coated from a solution of J71:**PNDI-TVT** with weight ratio of 2:1 in chlorobenzene. Solution with 2% DPE was stirred overnight prior to cast. After spinning active layers, the blending films were annealed at 120°C for 10 minutes. The MoO_3 were deposited by sequential thermal evaporation of 3 nm followed by 90 nm of Ag. Current density voltage (*J*-*V*) characteristics were measured using a Keithley 2400 Source Measure Unit. The currents were measured under 100 mW cm^{-2} simulated 1.5 Global (AM 1.5G) solar simulator (Enli Technology Co., Ltd, SS-F5-3A). The light intensity was calibrated by a standard Si solar cell (SRC-2020, Enli Technology Co., Ltd). EQE spectra were performed by using a QEX10 Solar Cell IPCE measurement system (PV Measurements, Inc.).

Space-Charge Limited Current Measurement

The charge transport properties were investigated by space charge limited current (SCLC) measurement. The electron-only devices were fabricated with structures of ITO/ZnO/PBDB-T:PNDIs/ZrAcac/Al and ITO/ZnO/J71:PNDIs/ZrAcac/Al). The hole-only devices were fabricated with structures of: ITO/PEDOT:PSS/PBDB-T:PNDIs /MoO_3/Ag and ITO/PEDOT:PSS/J71:PNDIs/MoO_3/Ag). The *J*–*V* curves of devices were fitted by using the Mott–Gurney equation: $J = 9\varepsilon_o\varepsilon_r\mu V^2/8L^3$, in which *J* is the

current density, ε_0 is the permittivity of free space, ε_r is the permittivity of the active layer, μ is the hole mobility or electron mobility, V is the internal voltage of the device ($V = V_{appl} - V_{bi}$), where V_{appl} is the applied voltage, V_{bi} is the offset voltage (V_{bi} is 0 V here), and L is the film thickness of the active layer. The electron mobility could be estimated from the slope of the Log(J)-Log(V) curve.

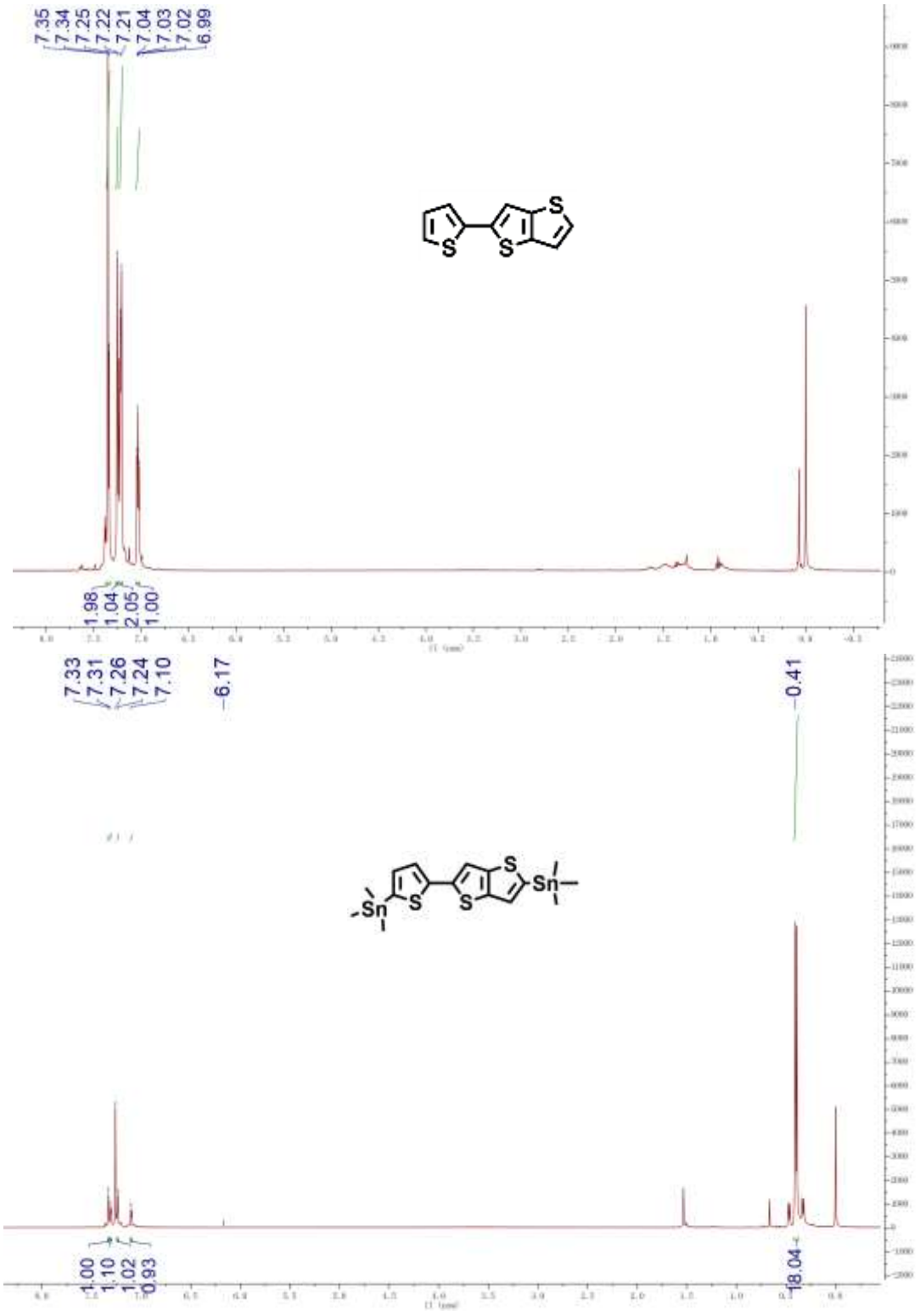


Figure S1. ^{1}H NMR spectra of T-TT and T-TT-Sn (in $CDCl_3$ at 25 °C).

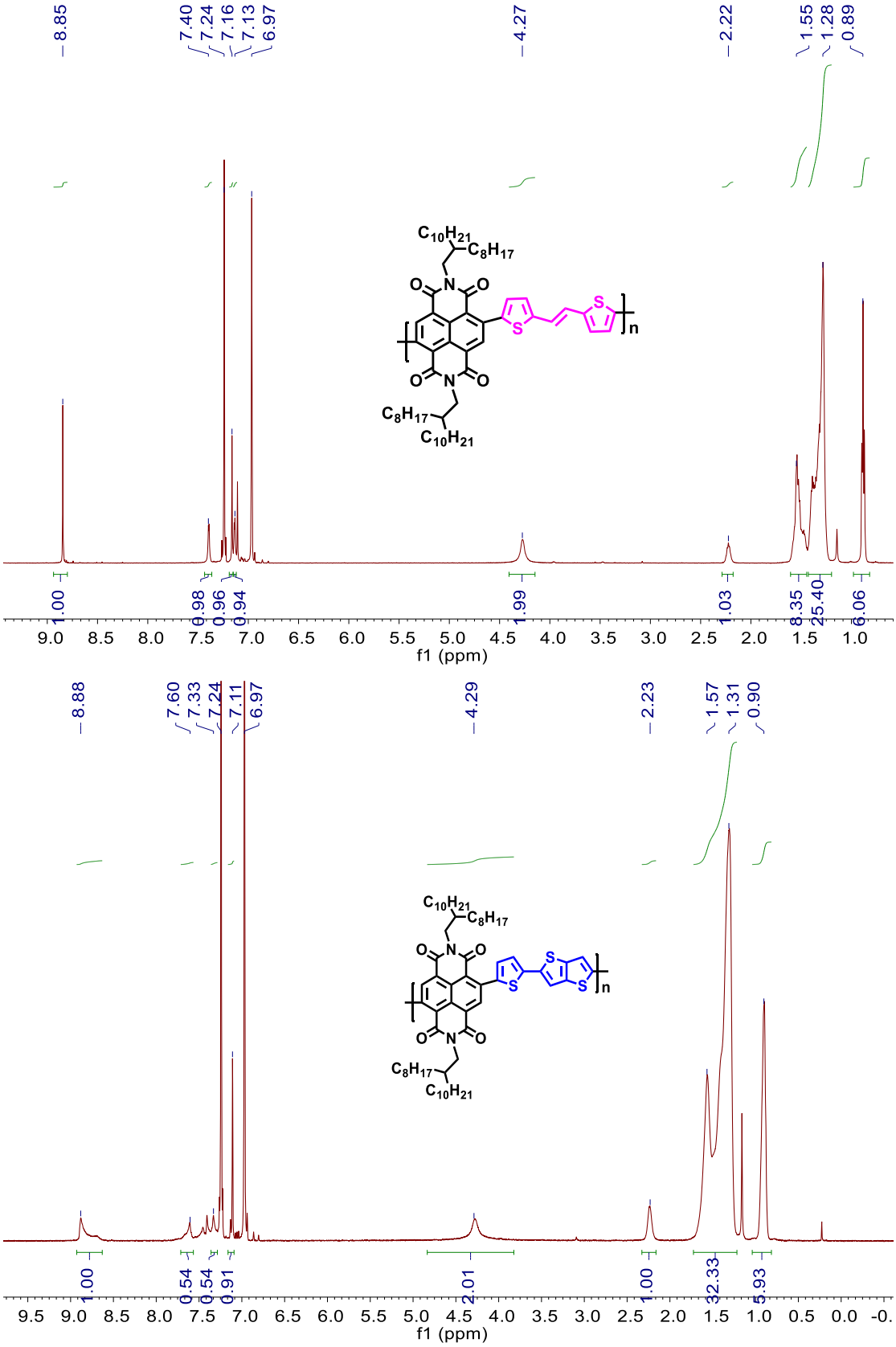


Figure S2. ^{1}H NMR spectra of PNDI-TVT and PNDI-T-TT (in 1,2-dichlorobenzene-d_4 at 120 °C).

Cirrus GPC Sample Peak Report

Generated by: yugui 2018年12月21日 15:20
Workbook: E:\Cirrus Workbooks\o-DCB workfunction\20170606-GYT.plw

Sample Details
Sample Name: 6
Acquired: 2018/12/21 15:11:30 By Analyst: yugui
Batch Name: Imported
Filename: E:\Cirrus Workbooks\o-DCB workfunction\imported-1034.cgrm
Concentration: 0.10 mg/ml K of Sample: 14.1000
Injection Volume: 200.0 ul Alpha of Sample: 0.7000
LIMS ID: Bottle ID:

Workbook Details
Eluent: DCB Flow Rate: 1.00 ml/min
Column Set: Column Set Length: 0 mm
Detector: RI Temperature: 140

Analysis Using Method: 20170606-baseline
Comments:

Results File: E:\Cirrus Workbooks\o-DCB workfunction\imported-1034.rst

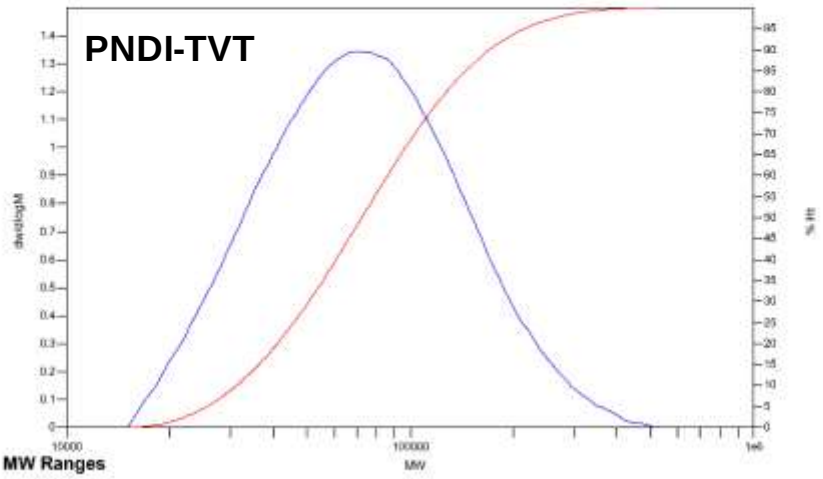
Calibration Used: 2017/6/8 15:43:34
Calibration Type: Narrow Standard Curve Fit Used: 1
Calibration Curve: y = 13.117150 - 0.606883x^1

High Limit MW RT: 11.33 mins Low Limit MW RT: 16.85 mins
High Limit MW: 1734370 Low Limit MW: 778
K: 14.1000 FRM Name:
Alpha: 0.7000 Flow Marker RT: 0.00 mins
FRCF: 1.0000

MW Averages

Mp: 69712	Mn: 59153	Mv: 83329	Mw: 88654
Mz: 131838	Mz+1: 184095	PD: 1.4987	

Distribution Plots



MW Ranges

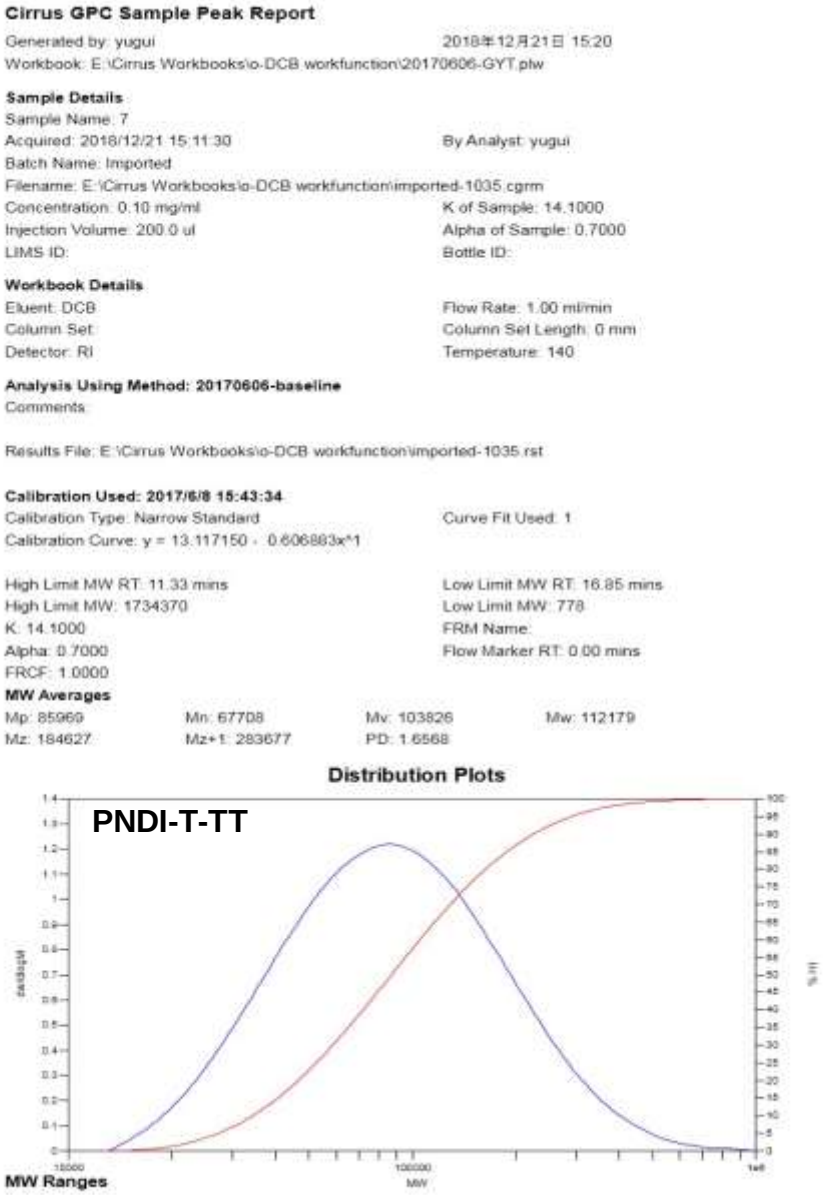


Figure S3. GPC curves of polymer **PNDI-TVT** and **PNDI-T-TT**.

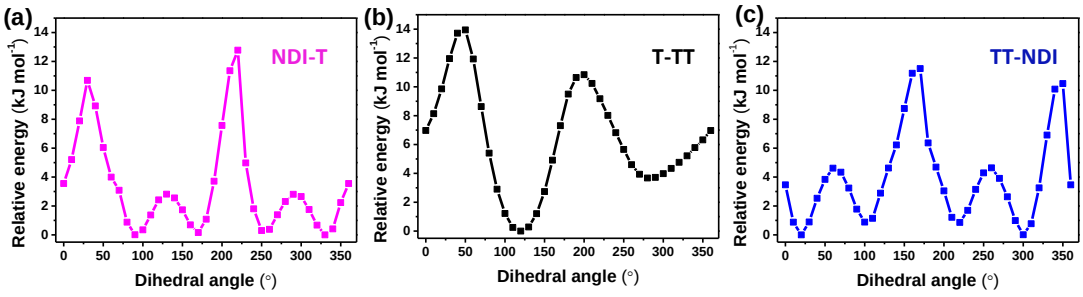


Figure S4. Potential energy surface scan of NDI-T, T-TT and TT-NDI.

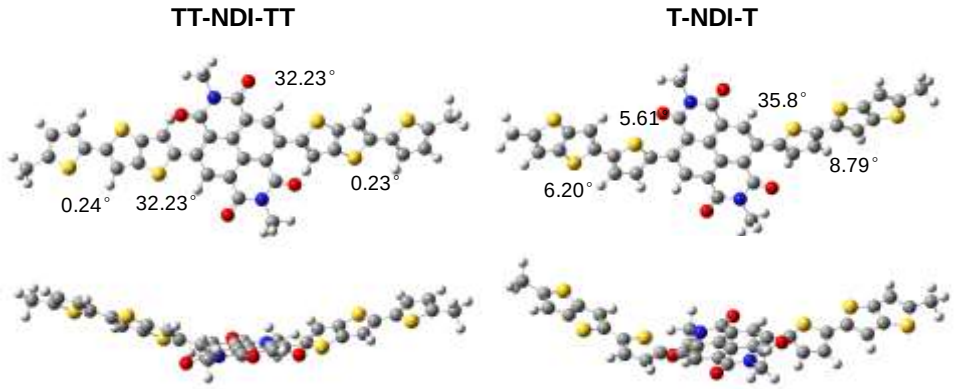


Figure S5. Optimized structures of different connections T-NDI-T and TT-NDI-TT with dihedral angles.

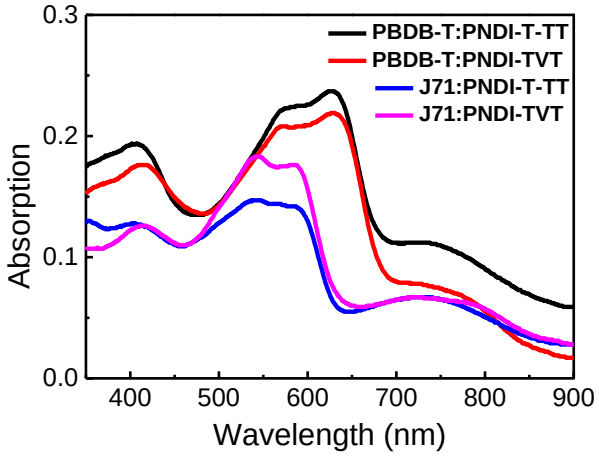


Figure S6. UV-vis absorption spectra of blend films on quartz plates.

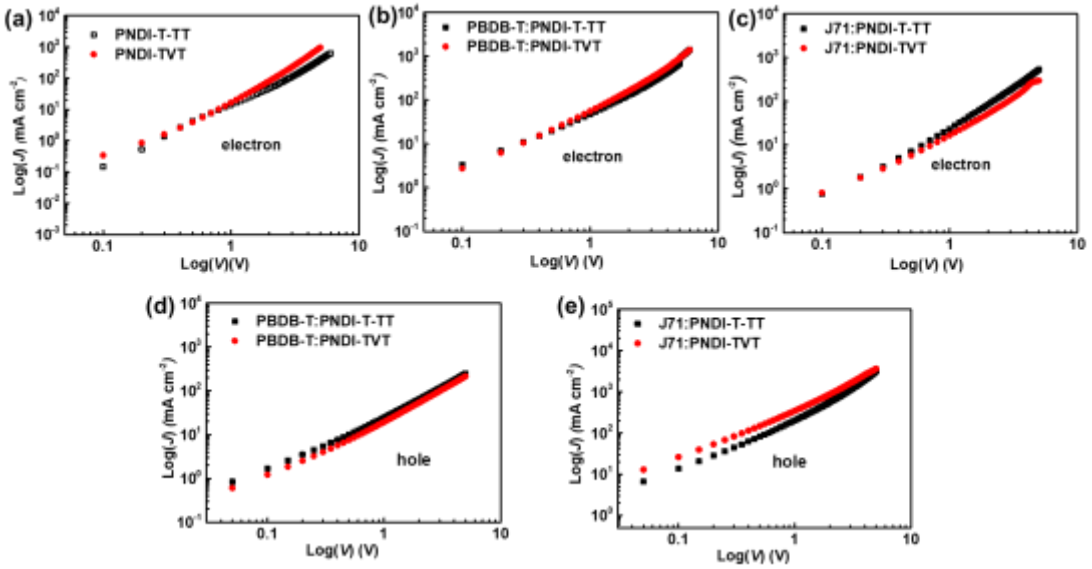


Figure S7. (a) SCLC fittings curves of **PNDI-T-TT** and **PNDI-TVT** electron devices. (b-e) SCLC fittings curves of electron-only and hole-only device based on **PNDI-T-TT** and **PNDI-TVT** blend films with PBDB-T and J71.

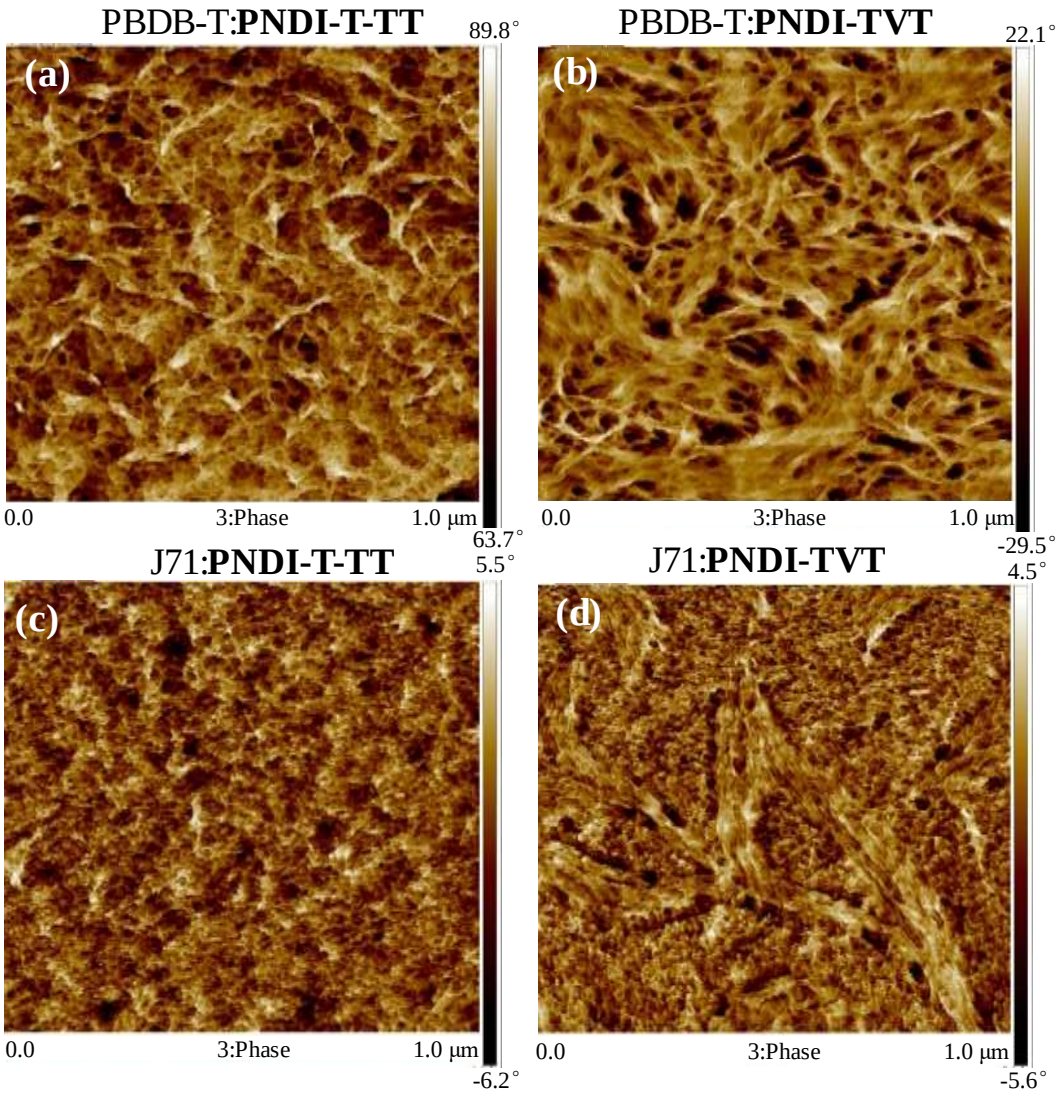


Figure S8. AFM phase images of (a) PBDB-T:**PNDI-T-TT**, (b) PBDB-T:**PNDI-TVT**, (c) J71:**PNDI-T-TT** and (d) J71:**PNDI-TVT**.

Table S1 Photovoltaic performance of **PBDB-T**:**PNDIs** based OSCs under the illumination of AM 1.5 G, 100 $mW \cdot cm^{-2}$ (solvent: chlorobenzene, annealing temperature 120°C). Average values with standard deviation were obtained from measurements of 12 devices measurements of 12 devices.

D:A	D/A ratio (w/w)	V_{OC} (V)	J_{SC} ($mA \cdot cm^{-2}$)	FF (%)	PCE (%)
PBDBT: **PNDI-T-TT**	2:1	0.84 (0.84±0.00)	10.97 (10.69±0.28)	0.57 (0.57±0.00)	**5.28** (5.10±0.18)
	2.5:1	0.84 (0.84±0.01)	11.00 (10.70±0.30)	0.55 (0.55±0.00)	5.14 (4.90±0.24)
	3:1	0.84 (0.84±0.00)	10.81 (10.61±0.20)	0.55 (0.56±0.01)	5.03 (4.96±0.07)
PBDB-T: **PNDI-TVT**	1:1.5	0.82 (0.83±0.01)	5.18 (5.00±0.18)	0.57 (0.56±0.01)	2.49 (2.47±0.02)
	1:1	0.83 (0.83±0.00)	5.93 (5.83±0.10)	0.53 (0.53±0.01)	2.61 (2.54±0.07)
	1.5:1	0.86 (0.85±0.01)	7.60 (7.22±0.38)	0.56 (0.55±0.01)	**3.51** (3.39±0.12)
D:A	Additives	V_{OC} (V)	J_{SC} ($mA \cdot cm^{-2}$)	FF (%)	PCE (%)
PBDB-T: **PNDI-T-TT**	2% DPE	0.83 (0.820±0.010)	9.33 (9.227±0.103)	0.64 (0.625±0.015)	4.95 (4.72±0.23)
	1% DPE	0.83 (0.829±0.001)	9.86 (9.741±0.119)	0.61 (0.611±0.001)	4.97 (4.93±0.04)
	0.75% DPE	0.84 (0.837±0.003)	11.72 (11.62±0.10)	0.62 (0.837±0.003)	**6.09** (6.091±0.001)
	0.5% DPE	0.84 (0.837±0.003)	11.33 (11.36±0.03)	0.63 (0.623±0.007)	5.95 (5.88±0.07)
PBDB-T: **PNDI-TVT**	2% DPE	0.85 (0.850±0.002)	7.78 (7.84±0.06)	0.61 (0.588±0.013)	3.99 (3.92±0.07)
	1% DPE	0.85 (0.852±0.001)	8.44 (8.39±0.05)	0.58 (0.585±0.005)	4.22 (4.19±0.03)
	0.5% DPE	0.85 (0.850±0.001)	8.70 (8.60±0.10)	0.57 (0.569±0.005)	**4.24** (4.18±0.06)

Table S2 Photovoltaic performance of the OSCs based on the **J71**:**PNDIs** under theillumination of AM 1.5 G, 100 $mW \cdot cm^{-2}$ (solvent: chlorobenzene, annealing temperature 120°C). Average values with standard deviation were obtained from measurements of 12 devices.

D:A	D/A ratio (w/w)	V_{OC} (V)	J_{SC} ($mA \cdot cm^{-2}$)	FF (%)	PCE (%)
J71: **PNDI-T-TT**	1.5:1	0.88 (0.88±0.00)	7.50 (7.45±0.05)	0.56 (0.56±0.01)	3.71 (3.69±0.02)
	1.5:1	0.88 (0.88±0.00)	7.59 (7.34±0.25)	0.56 (0.57±0.01)	**3.74** (3.68±0.06)
	1.5:1	0.88 (0.88±0.00)	7.12 (7.08±0.04)	0.57 (0.57±0.04)	3.57 (3.56±0.01)
J71: **PNDI-TVT**	2:1	0.88 (0.88±0.00)	3.47 (3.43±0.04)	0.46 (0.46±0.00)	**1.41** (1.39±0.02)
	1.5:1	0.86 (0.87±0.01)	3.27 (3.22±0.05)	0.49 (0.49±0.00)	1.37 (1.36±0.01)
	1:1	0.83 (0.85±0.02)	3.08 (2.88±0.20)	0.45 (0.47±0.02)	1.16 (1.13±0.03)
D:A	Additives	V_{OC} (V)	J_{SC} ($mA \cdot cm^{-2}$)	FF (%)	PCE (%)
J71: **PNDI-T-TT**	3% DPE	0.880 (0.879±0.001)	7.53 (7.50±0.03)	0.63 (0.623±0.007)	4.14 (4.09±0.05)
	2% DPE	0.878 (0.879±0.001)	8.21 (8.14±0.07)	0.62 (0.622±0.002)	**4.47** (4.44±0.03)
	1% DPE	0.871 (0.871±0.000)	8.78 (8.62±0.16)	0.55 (0.556±0.006)	4.24 (4.12±0.12)
J71: **PNDI-TVT**	3% DPE	0.882 (0.883±0.001)	4.51 (4.40±0.11)	0.48 (0.487±0.007)	1.99 (1.93±0.06)
	2% DPE	0.881 (0.880±0.001)	5.28 (5.22±0.06)	0.50 (0.499±0.001)	**2.32** (2.29±0.03)
	1% DPE	0.871 (0.873±0.002)	5.23 (5.22±0.01)	0.48 (0.476±0.004)	2.20 (2.17±0.03)