

A Random Copolymer Approach to Develop Nonfullerene Acceptors for All-polymer Solar Cells

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Supplementary Information

Instrumentation and characterization:

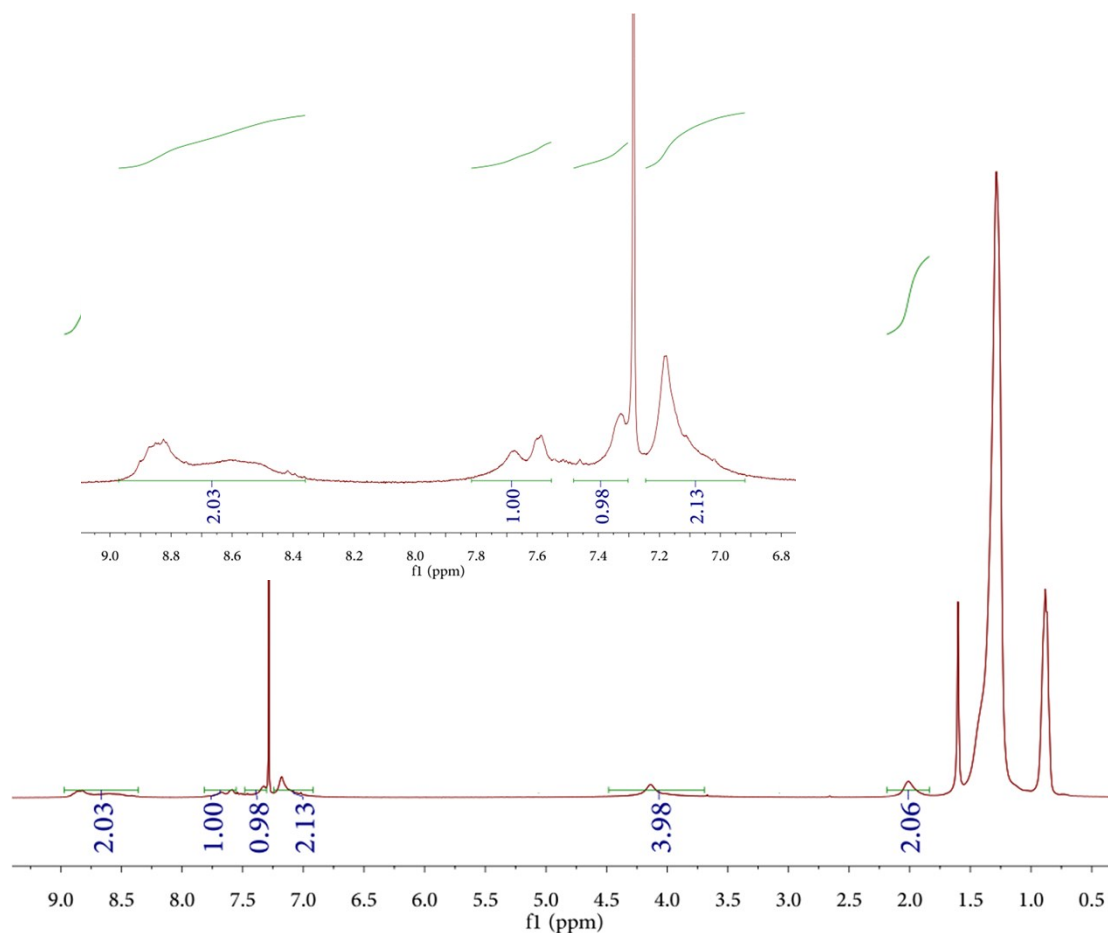
¹H NMR data were acquired on a Bruker DPX 400 MHz spectrometer. Differential scanning calorimetry (DSC) was carried out under nitrogen on a TA Instrument DSC Q100 instrument (scanning rate of 10 °C min⁻¹). Thermogravimetric analysis (TGA) was carried out using a TGA Q500 instrument (heating rate of 10 °C min⁻¹). Molecular weight determinations were carried out in hot dichlorobenzene solution on a Shimadzu Prominence CBM-20A series HPLC using Agilent PLGel 5 micrometer Mixed-C column (79911 GP-MXC) with polystyrene calibration standards. Cyclic voltammetry experiments were performed using an Autolab potentiostat (model PGSTAT30) by Echochimie. A glassy carbon disk was used as working electrode, a platinum wire as counter electrode and a silver wire as reference electrode. Ferrocene was used for potential calibration. UV-Vis-NIR spectra were recorded on a Shimadzu model 2501-PC. The nanoscale morphology of the blended films was observed using a Veeco Nanoscope V atomic force microscope (AFM) in the tapping mode. Deionized water droplets (about 2 μL) were dropped carefully onto the surface.

Materials Synthesis

General, most organic and inorganic chemicals in this chapter were obtained from Sigma-Aldrich and used without further purification. PTB7-Th and PDIN were purchased from 1-Materials and Sunatech Inc, respectively.

Synthesis

PNDI-TT-TVT: 4,9-dibromo-2,7-bis(2-octyldodecyl)benzo[*lmn*][3,8]phenanthroline-1,3,6,8(2H,7H)-tetraone (197.0 mg, 0.2 mmol), 2,5-bis(trimethylstannyl) thieno[3,2-*b*]thiophene (46.6mg, 0.10 mmol), (E)-1,2-bis(5-(trimethylstannyl) thiophen-2-yl)ethene (51.8 mg, 0.10 mmol), Pd(PPh₃)₄ (9.3 mg, 0.0080 mmol) were added into a 25 mL reaction vial. The flask equipped with a condenser was then degassed and filled with argon three times. Afterwards, toluene (5.0 mL) was added and degassed and filled with argon three times. The reaction mixture was refluxed for 16 h under argon. After cooling down to room temperature, the polymerization mixture was poured into the mixture of methanol (200.0 mL) and hydrochloric acid (5.0 mL) and stirred for 3 h. The polymer precipitated was collected by filtration using a filter paper. The solid was then washed with hot methanol, acetone, and hexane in a sequence in a Soxhlet apparatus. Finally, CHCl₃ was used to extract the materials. The chloroform extracts were concentrated under reduced pressure and the residue was precipitated by dropwise addition to methanol (200.0 mL). PNDI-TT-TVT was then obtained by filtration and dried under vacuum. ¹H NMR (CDCl₃, 400 MHz): d (ppm) 8.83-8.61 (br, 2H), 7.68-7.55 (br, 1H), 7.33-7.29 (br, 1H), 7.23-7.05 (br, 2H), 4.24-4.05 (br, 4H), 2.14-1.85 (br, 2H), 1.64-1.06 (br, 64H), 0.99-0.78 (br, 12H).



^1H NMR spectrum of PNDI-TT-TVT

PNDI-TT: ^1H NMR (CDCl_3 , 400 MHz): d (ppm) 8.91 (s, 2H), 7.62-7.37 (br, 2H), 4.15 (m, 4H), 2.12-1.97 (br, 2H), 1.50-1.14 (br, 64H), 0.95-0.88 (br, 12H).

PNDI-TVT: ^1H NMR (CDCl_3 , 400 MHz): d (ppm) 8.80-8.50 (br, 2H), 7.26-7.15 (br, 2H), 7.14-6.99 (br, 4H), 4.18-4.10 (br, 4H), 2.12-1.97 (br, 2H), 1.50-1.16 (br, 64H), 0.90-0.80 (br, 12H).

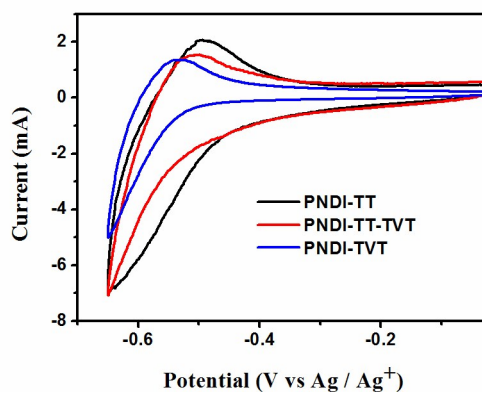


Fig. S1 Cyclic voltammetry spectra of PNDI-TT, PNDI-TT-TVT and PNDI-TVT.

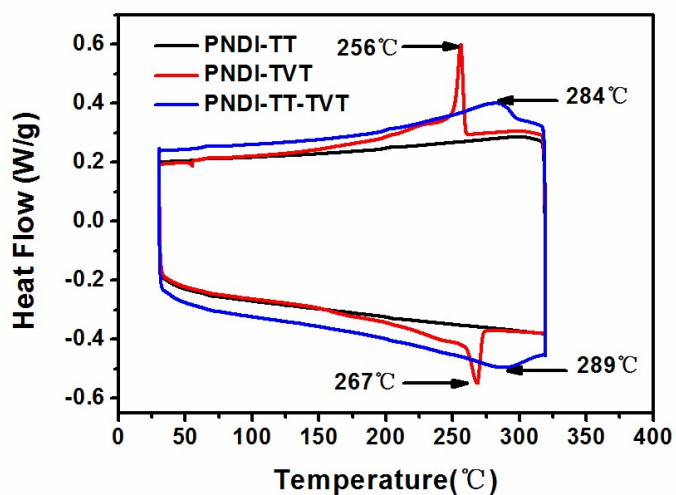
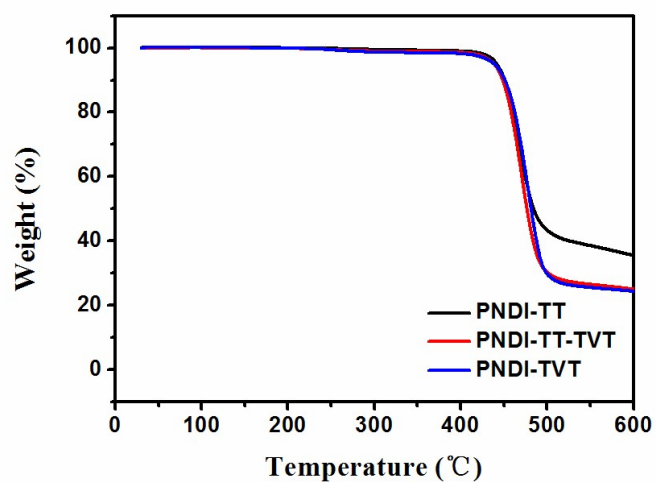


Fig. S2 Thermogravimetric analysis of the polymers heated at rate of 10 °C/min under nitrogen and differential scanning calorimetry of the polymers. In DSC measurement, the samples were heated from room temperature to 320 °C and back to room temperature and then heated to 320 °C at a ramp rate of 10 °C/min.

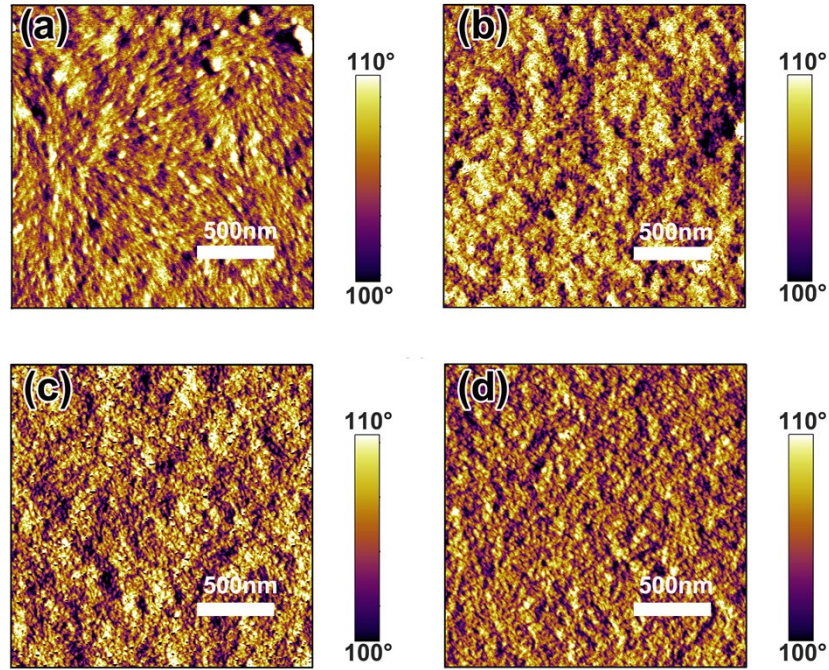


Fig. S3 AFM phase images ($2\mu\text{m}\times 2\mu\text{m}$) of the surfaces of all-polymer solar cells: (a) PTB7-Th:PNDI-TT (b) PTB7-Th:PNDI-TVT (c) PTB7-Th:PNDI-TT-TVT = 2:1 (d) PTB7-Th:PNDI-TT-TVT = 3:1.

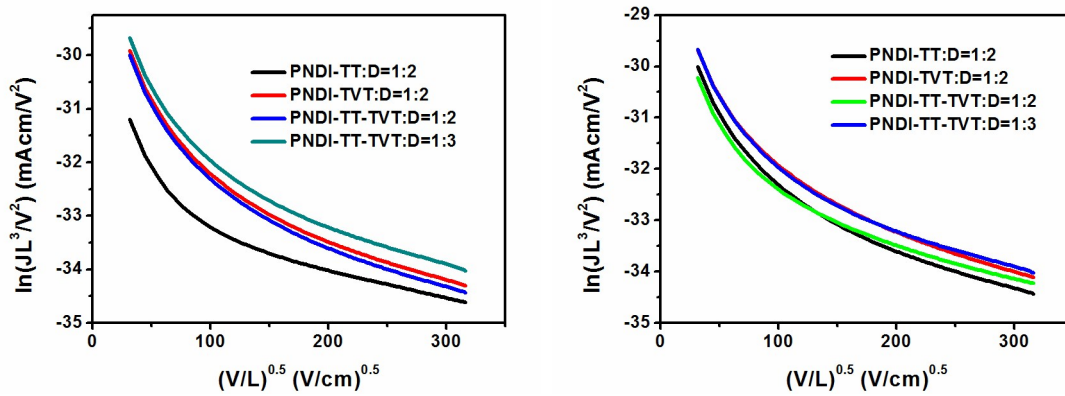


Fig. S4 Space-charge-limited current (SCLC) fittings of devices (left) Hole-only SCLC devices: ITO/PEDOT:PSS/blend/MoO_x/Al. and (right) electron-only devices with the structure of ITO/ZnO/blend/Ca/Al.

Photovoltaic Cells Fabrication and Measurement:

PSCs were fabricated with the structure ITO/PEDOT:PSS/PTB7-Th:PNDI-TT, or PNDI-TT-TVT/PDIN/Al. The patterned ITO glass was precleaned in an ultrasonic bath of acetone and isopropyl alcohol, and treated in an ultraviolet–ozone chamber (Jelight

Company, Irvine, CA) for 20 min. A thin layer (30 nm) of PEDOT:PSS (Clevios VP AI 4083, from H. C. Starck, Leverkusen, Germany) was spin-coated onto the ITO glass and baked at 150 °C for 15 min. A solution (total of 20 mg mL⁻¹) of PTB7-Th:PNDI-TT or PNDI-TVT or PNDI-TT-TVT blend was subsequently spin-coated (2000 rpm) on the PEDOT:PSS layer to form a photosensitive layer (ca.100 nm thick). The thickness of the photosensitive layer was measured using an Ambios Technology (Santa Cruz, CA) XP-2 profilometer. The methanol solution (0.2% acetic acid) of PDIN at a concentration of 1.5 mg mL⁻¹ was deposited on the active layer at 3000 rpm for 30 s, giving a PDIN layer ca. 13 nm thick. An aluminum (ca. 100 nm) layer was subsequently evaporated onto the surface of the PDIN layer under vacuum (ca. 10⁻⁶ Pa) to form the negative electrode. The active area of the device was 0.1 cm². The J-V curve was measured with a computer controlled Keithley (Cleveland, OH) 236 Source Measure Unit. A xenon lamp coupled with AM1.5 solar spectrum filters was used as the light source, and the optical power at the sample was 100 mW cm⁻². The light intensity of the solar simulator was calibrated using a standard silicon solar cell. The IPCE spectrum was measured using a Stanford Research Systems (Sunnyvale, CA) model SR830 DSP lock-in amplifier coupled with a WDG3 monochromator and 500 W xenon lamp.

Table S1 Characteristics of polymers

Polymer	M _n (kDa)	M _w (kDa)	M _w /M _n	E _{onset} ^{red} (V)	HOMO (eV)	LUMO (eV)	E _g ^{opt} (eV)
PNDI-TT	26.7	40.8	1.5	-0.46	-5.59	-3.94	1.65
PNDI-TT-TVT	36.5	56.5	1.6	-0.48	-5.50	-3.92	1.58
PNDI-TVT	31.4	50.7	1.6	-0.56	-5.34	-3.88	1.46

Table S2 Space-charge-limited current (SCLC) measurement of the devices.

Donor : acceptor(w/w)	μ _h [cm ² V ⁻¹ s ⁻¹]	μ _e [cm ² V ⁻¹ s ⁻¹]	μ _h /μ _e
PTB7-Th:NDI-TT(2:1)	1.56 x 10 ⁻⁵	2.89 x 10 ⁻⁵	0.54
PTB7-Th:NDI-TVT(2:1)	3.23 x 10 ⁻⁵	4.23 x 10 ⁻⁵	0.76
PTB7-Th:NDI-TT-TVT(2:1)	2.78 x 10 ⁻⁵	3.45 x 10 ⁻⁵	0.81
PTB7-Th:NDI-TT-TVT(3:1)	4.34 x 10 ⁻⁵	4.26 x 10 ⁻⁵	1.02