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Supporting Information

Elucidating the Impact of Molecular Weight on Morphology, Charge Transport, Photophysics and Performance of All-Polymer Solar Cells

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Synthesis of 2,2’-biselenophene. In a 100 mL round bottom flask previously burn and purged, add 1g (7.63 mmol. 1eq) of selenophene, 20 mL of ethyl ether and put at 0 °C. Then, add dropwise 3,5 mL of *n*-buthyllithium (2.5M) (7.63 mmol, 1eq) and let stir for 1h while letting it goes back to room temperature. Put the reaction at -78 ^{o}C and add 1.33 g (9.92 mmol, 1.3eq) of $CuCl_2$ portion wise. Let stir at -78 °C for 5 minutes before letting it come back to room temperature and stir for 16h. Add about 10 mL of ethyl ether before filtering over celite. Then, wash with a solution of 1M HCl, 5% $NaHCO_3$ and then water. Dry the organic phase with Na_2SO_4, filter and evaporate to obtain 543 mg (2.088 mmol) of white crystals for a yield of 55%. (If the crystals are yellow, filter it over activated charcoal with ethyl ether). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.87(dt, 2H, *J*= 5.6-0.9 Hz); 7.31-7.25 (m, 2H); 7.23(dd, 2H, *J* = 5.5-3.8 Hz) (Figure S1). ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.77; 130.23; 129.68; 129.12; 126.72.

Synthesis of 5,5’-bistrimethylstannyl-2,2’-biselenophene. In a 100 mL round bottom flask previously burn and purged, add 500 mg (1.92 mmol. 1eq) of 2,2’-biselenophene, 27 mL of dry THF and put at -78 °C. Then, add dropwise 1.77 mL of *n*-buthyllithium (2.5M) (4.42 mmol, 2.3eq) and let stir for 2h at -78 °C and then let it goes back to room temperature for another hour. Put the reaction at -78 ^{o}C and add 4.6 mL (4.6mmol, 2.4eq) of Me_3SnCl one shot. Let stir at -78 °C for 5 minutes before letting it come back to room temperature and stir for 16h. Pour the solution on water and extract with ethyl ether. Dry the organic phase with Na_2SO_4, filter and evaporate. A recrystallization in isopropanol was performed, however this caused the degradation of the monomer and only 47mg (0.08mmol) of yellowish crystals was obtain for a yield of 4%. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.40-7.31(m, 6H); 0.31-0.44 (t, 24H, *J*=0.5 Hz). (Figure S2). ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.50; 128.26; 7.90.

DHAP Synthesis of poly[[N,N′-bis(2-octyldodecyl)-naphthalene-1,4,5,8-bis(dicarboximide)-2,6-diyl]-alt-5,5′-biselenophene] (PNDIBS). In a 10 mL oven dry biotage microwave vial with a magnetic stirring bar, 189.4 mg (0.192 mmol, 1 eq) of N,N'-bis(2-octyldodecyl)-2,6-dibromo-1,4,5,8-naphtalenediimide, 50 mg (0.192 mmol, 1eq) of 2,2'-biselenophene, 1.8 mg (0.0019 mmol, 1 %mol) of $Pd_2(dba)_3$, 19.6 mg (0.192 mmol, 1eq) of pivalic acid and 79.7 mg (0.577 mmol, 3eq) of anhydrous potassium carbonate are added. The vial was sealed and purged by vacuum and filled with argon three times. Then, 0.4 mL of degassed dry chlorobenzene was added and the solution stirred at room temperature for 15 min to dissolve the monomers. The vial was placed in a preheated oil bath at 100 °C for 18 hr. The reaction was cooled at 50 °C and 20 mL of chloroform and 5 mL of *o*-dichlorobenzene were added prior to precipitation of the polymer in methanol. The precipitate was filtered and Soxhlet extraction using acetone and followed by hexanes was performed to remove catalyst residues and low molecular weight material. Chloroform was then used to recover the polymer. The solvent was reduced to about 10 mL and precipitated into methanol, filtered through 0.45 μm nylon filter and air-dried to afford the deep blue polymer PNDIBS with a yield of 95%.

Stille Synthesis of poly[[N,N′-bis(2-octyldodecyl)-naphthalene-1,4,5,8-bis(dicarboximide)-2,6-diyl]-alt-5,5′-biselenophene] (PNDIBS). In a 10 mL oven dry biotage microwave vial with a magnetic stirring bar, 75.7 mg (0.077 mmol, 1 eq) of N,N’-bis(2-octyldodecyl)-2,6-dibromo-1,4,5,8-naphtalenediimide, 45 mg (0.077 mmol, 1eq) of 5,5’-bistrimethylstannyl-2,2’-biselenophene, 2.46 mg (0.0027 mmol, 3.5 %mol) of $Pd_2(dba)_3$ and 4.2 mg (0.0138 mmol, 18 %mol) of tri(*o*-tolyl)phosphine were added. The vial was sealed and purged by vacuum and filled with argon three times. Then, 3.5 mL of degassed dry chlorobenzene was added and the solution stirred at room temperature for 15 min to dissolve the monomers. The vial was placed in a preheated oil bath at 120 °C for 4 days. Then 0.05mL of 2-trimethylstannylthiophene and bromobenzene were added at 8h interval. The reaction was cooled at 50 °C and 4.5 mL of chloroform was added prior to precipitation of the polymer in methanol. The precipitate was filtered and Soxhlet extraction using acetone followed by hexanes was performed to remove catalyst residues and low molecular weight material. Chloroform was then used to recover the polymer. The solvent was reduced to about 10 mL and precipitated into methanol, filtered through 0.45 μm nylon filter and air-dried to afford the deep blue polymer PNDIBS with a yield of 93%.

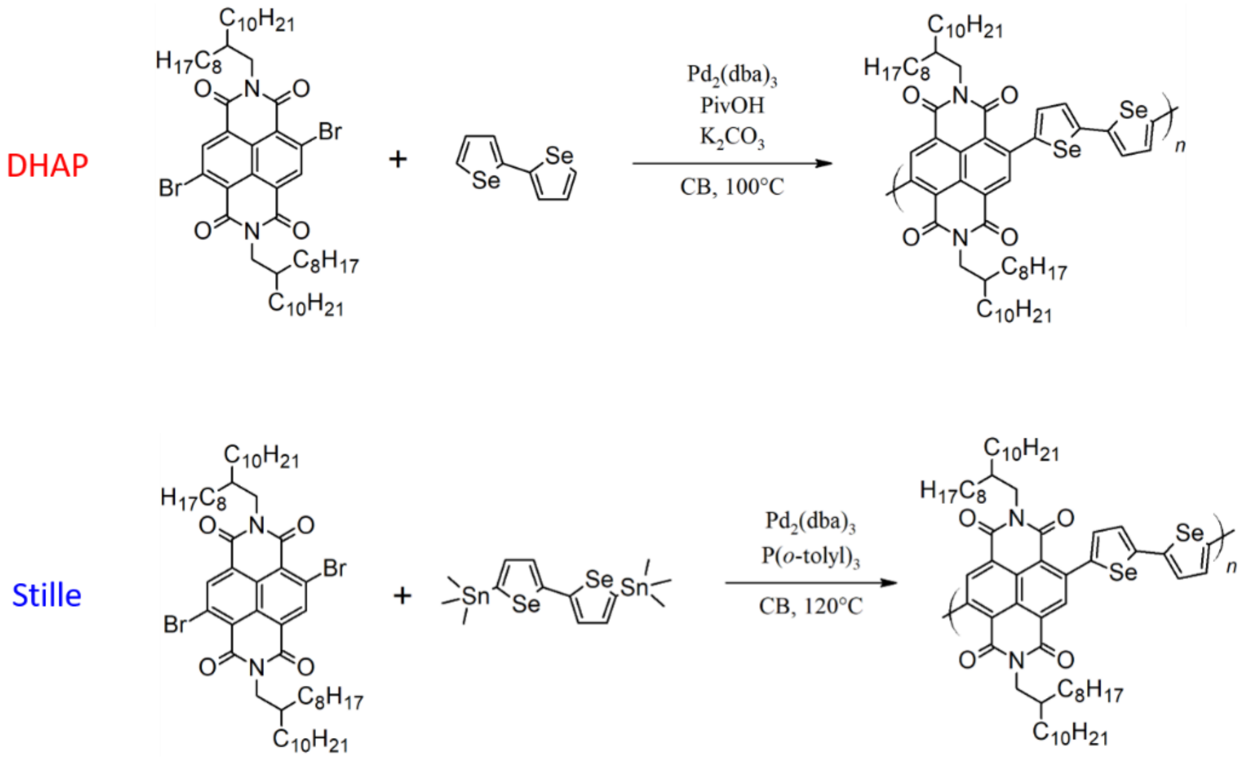
Characterizations. ^1H NMR spectra were recorded using a Varian AS400 in deuterated chloroform at 298 K. Chemicals shifts were reported as δ values (ppm) relative to chloroform value of 7.26 ppm. ^1H spectra of the polymers were recorded on a Varian Agilent DD2 500 MHz apparatus in 1,1,2,2-tetrachloroethane-D_2 at 90 °C. Number-average (M_n) and weight-average (M_w) molecular weights were determined by size exclusion chromatography (SEC) using a high temperature Varian Polymer Laboratories GPC220 equipped with an RI detector and a PL BV400 HT Bridge Viscometer. The column set consists of 2 PL gel Mixed C (300 x 7.5 mm) columns and a PL gel Mixed C guard column. The flow rate was fixed at 1mL/min using 1,2,4-trichlorobenzene

(TCB) (with 0.0125% BHT w/v) as the eluent. The temperature of the system was set to 110 °C. The samples (2 mg) were dissolved in 2 mL of TCB in a 5 mL chromatography vial then stirred and heated to 110 °C for 1 hour for a complete dissolution. Then, a filtration through a 0.45 µm cellulose fiber film in a 5 mL chromatography vial lead to a homogenous polymeric solution. Dissolution of the polymers was performed through a loop of 200 µL with a Varian Polymer Laboratories PL-SP 260VC sample preparation system. The calibration method used to generate the reported data was the classical polystyrene method using polystyrene narrow standards Easi-Vials PS-M from Varian Polymer Laboratories which were dissolved in TCB. Thermogravimetric analyses (TGA) of the polymers were performed with a TGA/SDTA 851e from Metler-Toledo. The acquisitions were recorded under argon with a 10 °C/min scan rate from 50 to 800 °C. While the Stille-prepared had a degradation temperature (T_d) of 416^{o}C, the DHAP-prepared polymer of similar molecular weight showed a markedly higher T_d at 440^{o}C. The higher thermal stability of the DHAP-prepared PNDIBS strongly suggests minimal structural defects in the DHAP-prepared polymer compared to the Stille-prepared one. The reported degradation temperatures (DT) correspond to a 5% mass lost. UV vis-NIR absorption spectra were recorded using a Perkin Elmer model Lambda 900 UV-Vis/near IR spectrophotometer. Polymer solutions in chlorobenzene were spin-coated on untreated glass substrate for solid-state absorption spectra measurements. The optical bandgap was calculated from the onset of the absorption band.

Cyclic voltammetry. Cyclic voltammetry (CV) was performed on an EG&G Princeton Applied Research potentiostat/galvanostat model 273A. A three-electrode cell was used where platinum wires were used as both the working and counter electrodes. The reference electrode contained silver/silver ions (Ag in 0.01M $AgNO_3$ solution). The working electrodes were made by coating the platinum wires with PNDIBS solutions and subsequently dried in oven at 65^{o}C overnight. The

CV measurements were done in a 0.1M tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) electrolyte solution in acetonitrile, which was purged with N_2 gas before use, at a scan rate of 50mV/s. Ferrocene was used as an internal standard. The HOMO and LUMO energy levels were determined from the oxidation onset potential and reduction onset potential following the equations: $E_{\mathrm{HOMO}} = -(eE_{\mathrm{ox}}^{\mathrm{onset}} - E_{\mathrm{Fc/Fc+}} + 4.8)$ and $E_{\mathrm{LUMO}} = -(eE_{\mathrm{red}}^{\mathrm{onset}} - E_{\mathrm{Fc/Fc+}} + 4.8)$, respectively.

Scheme S1. General polymerization conditions for the preparation of acceptor copolymer PNDIBS by DHAP and Stille coupling methods.



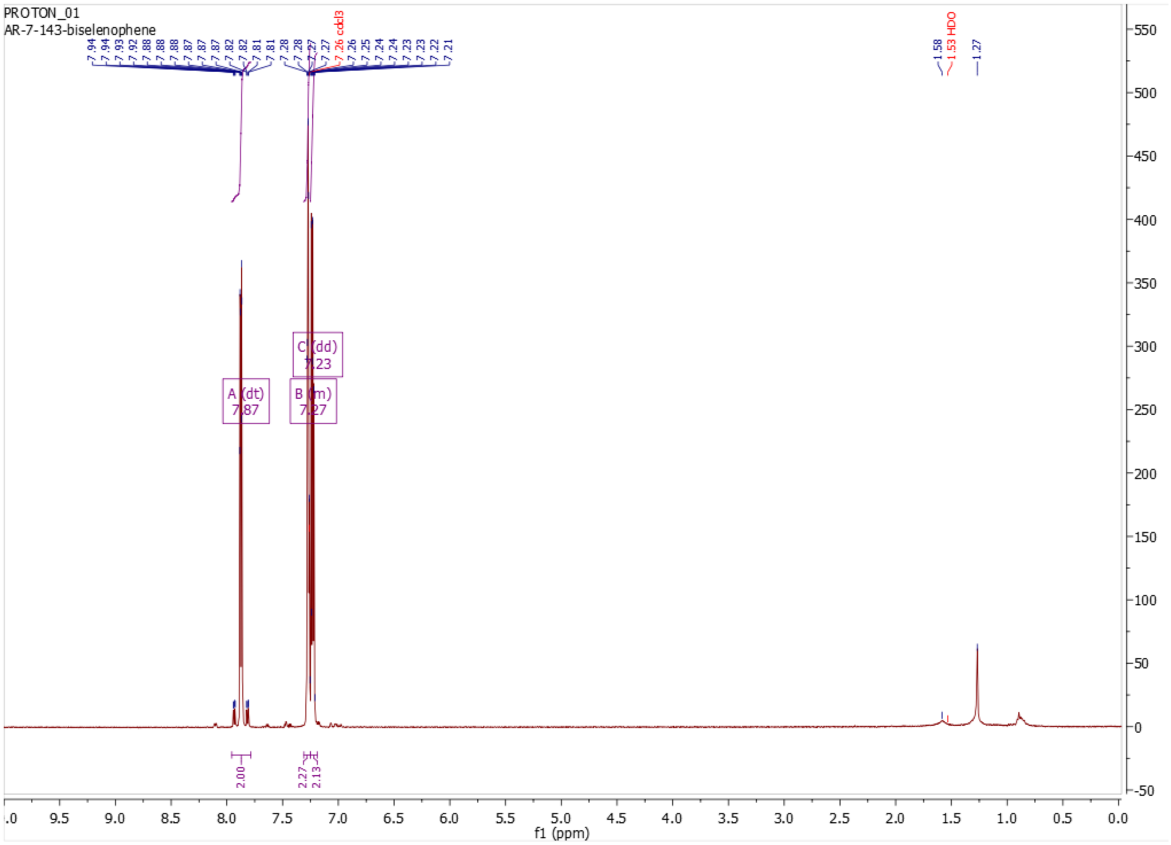


Figure S1. ^{1}H NMR of 2,2’-biselenophene.

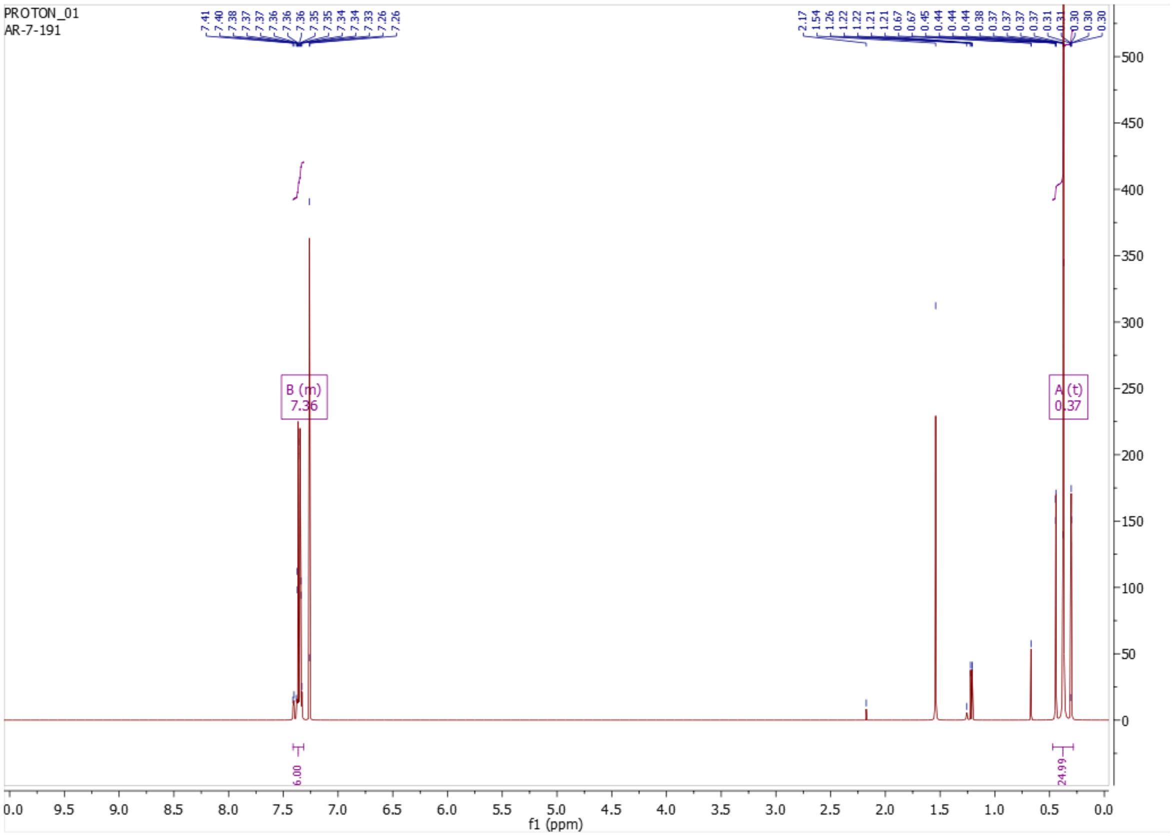


Figure S2. ^{1}H NMR of 5,5’-triméthyl-2,2’-biselenophene.

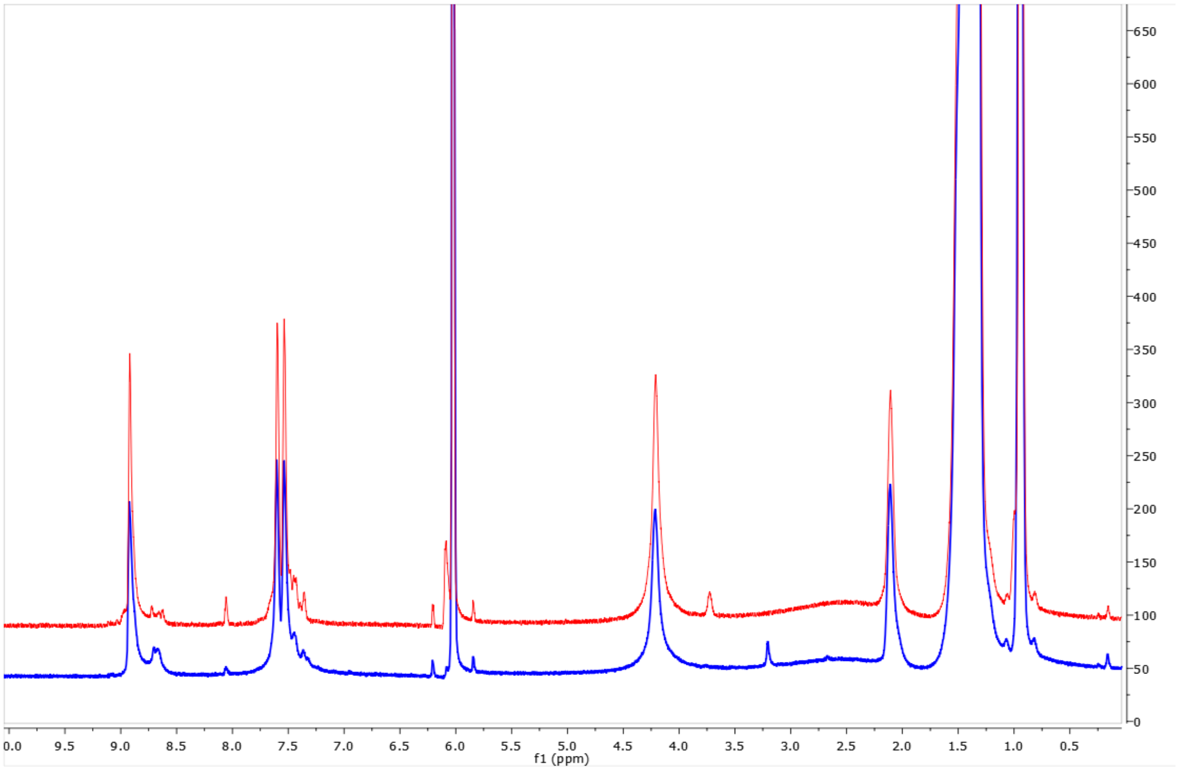


Figure S3. ^{1}H NMR spectrum of DHAP (red) and Stille (blue) prepared PNDIBS samples.

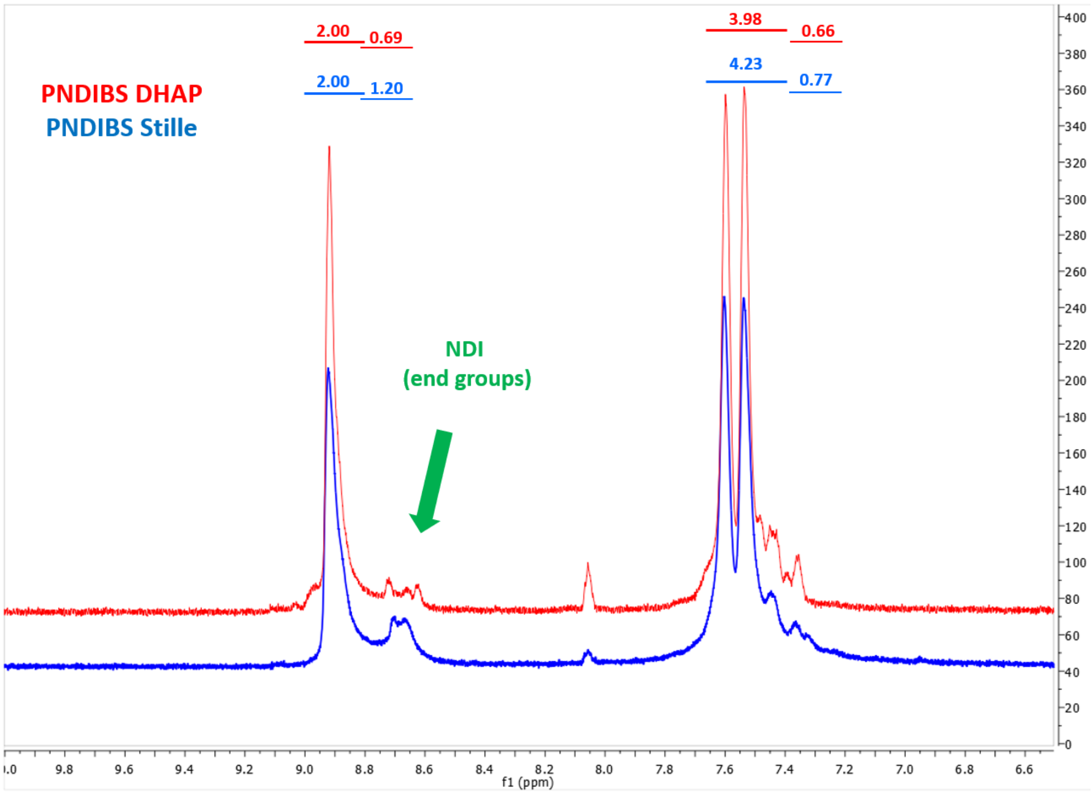


Figure S4. Aromatic region close-up of the ^{1}H NMR of DHAP-prepared (red) and Stille-prepared (blue) PNDIBS samples.

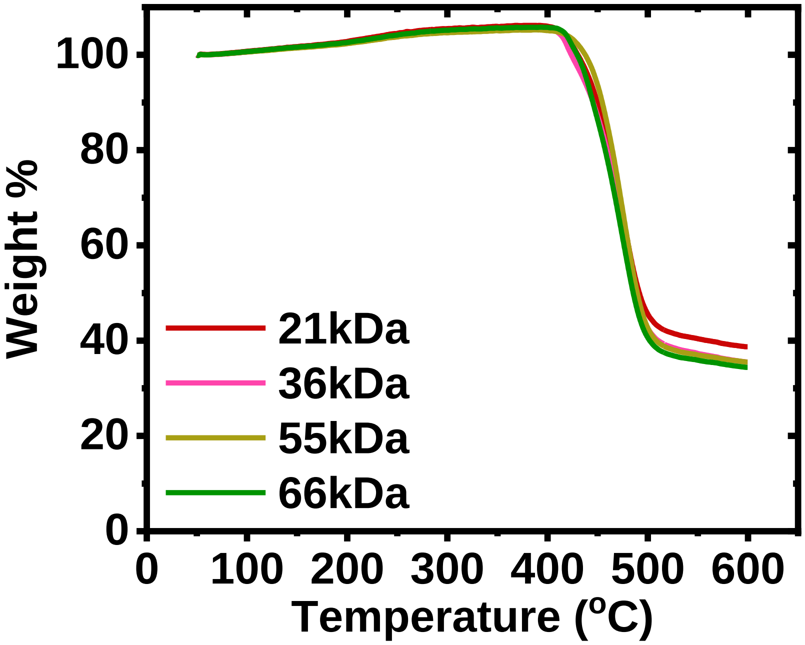


Figure S5. TGA traces of PNDIBS polymer of different M_n heating at 20°C/min.

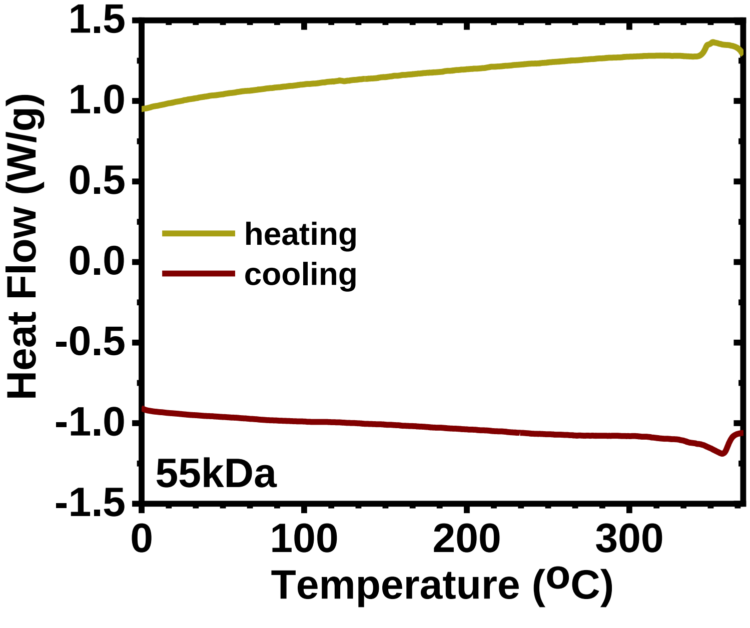


Figure S6. Second heating and cooling DSC scans of PNDIBS of 55kDa at 10°C/min under N_2 flow.

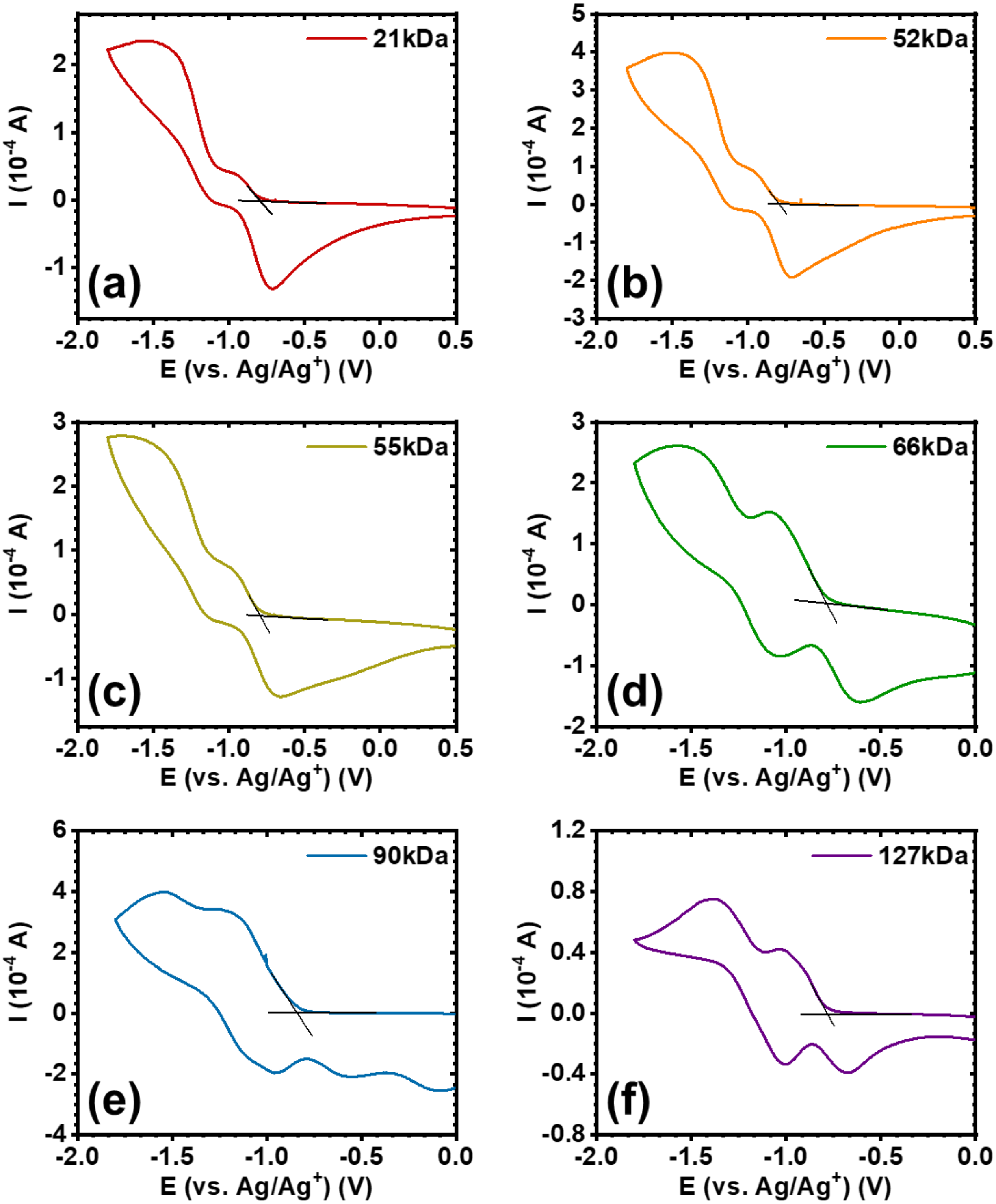


Figure S7. Cyclic voltammogram for reduction of PNDIBS thin film of different molecular weights in 0.1M tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) solution in acetonitrile at a scan rate of 50 mV/s.

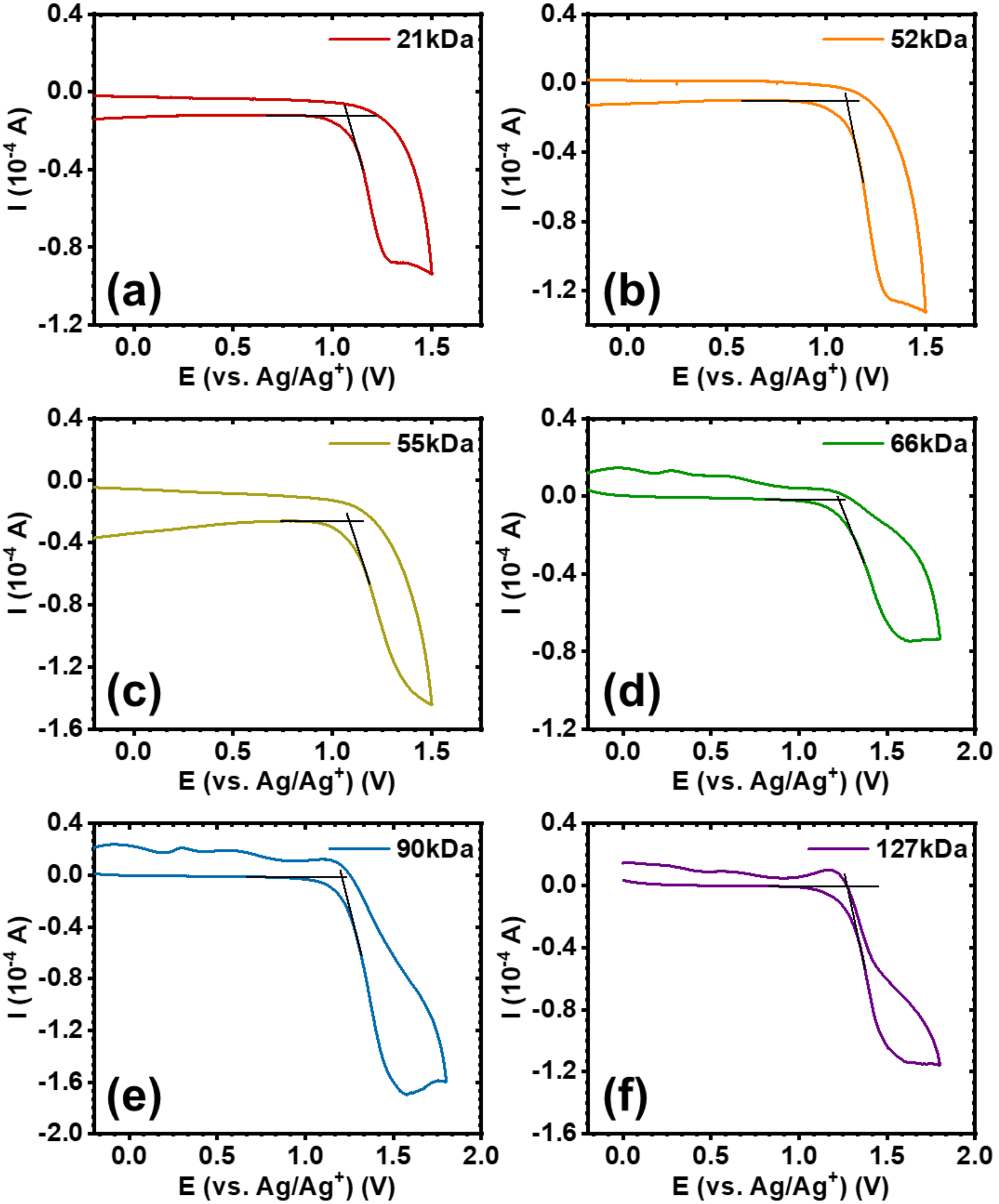


Figure S8. Cyclic voltammogram for oxidation of PNDIBS thin film of different molecular weights in 0.1M tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) solution in acetonitrile at a scan rate of 50 mV/s.

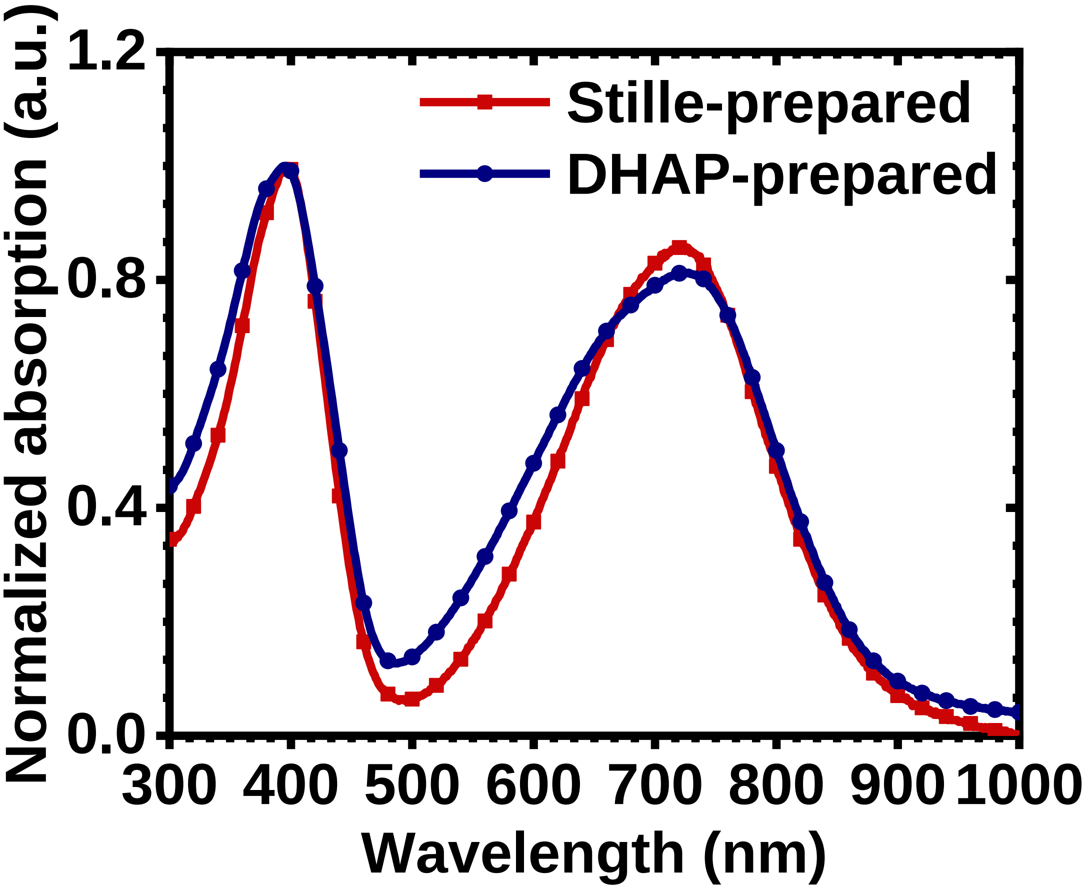


Figure S9. Thin film UV-Visible spectra of PNDIBS synthesized via DHAP and Stille.

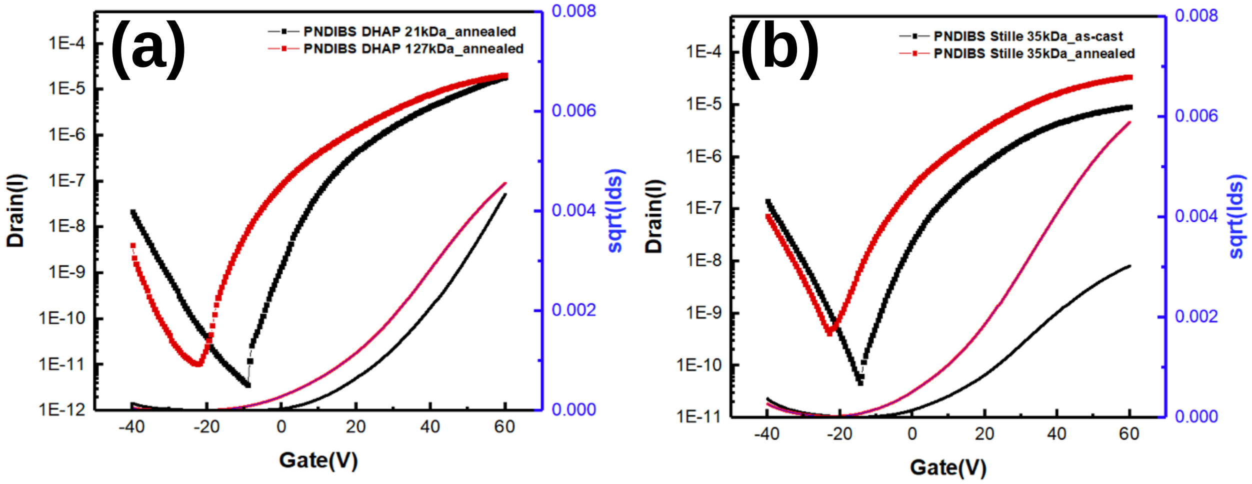


Figure S10. Representative transfer curves for neat PNDIBS films without annealing and annealed at 170◦C (a) PNDIBS DHAP 21kDa and (b) PNDIBS Stille 35kDa.

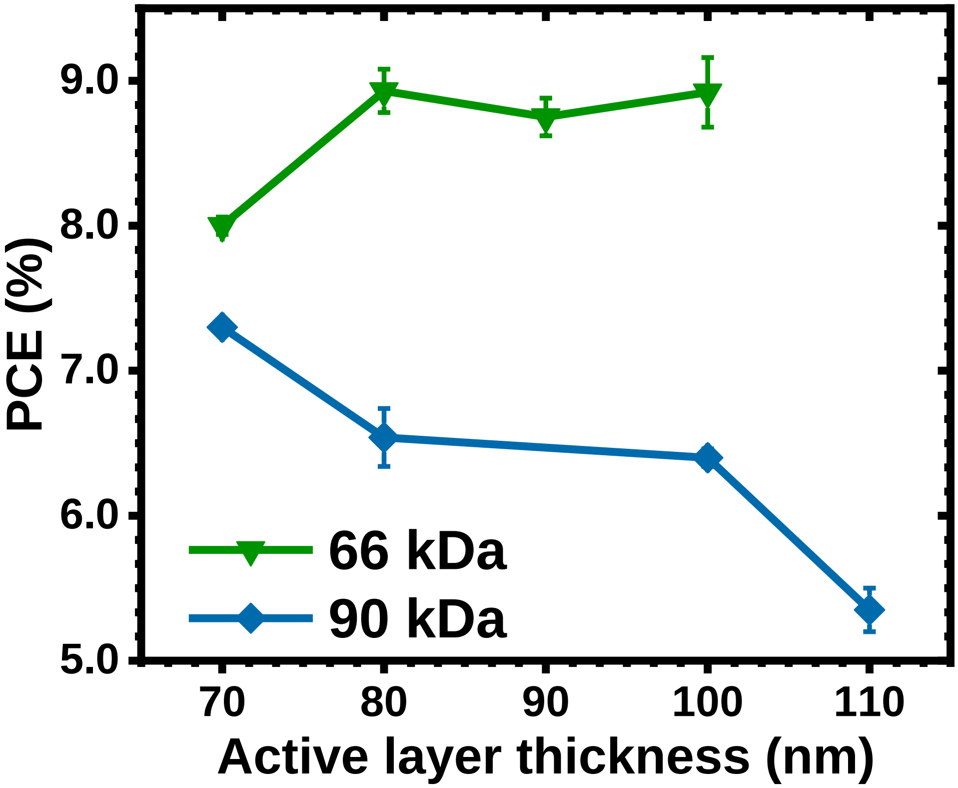


Figure S11. The relationship of the power conversion efficiency (PCE) of the optimized PBDB-T:PNDIBS devices as a function of the active layer thicknesses for the 66kDa and 90kDa molecular weights. The error bars were generated from 8 devices.

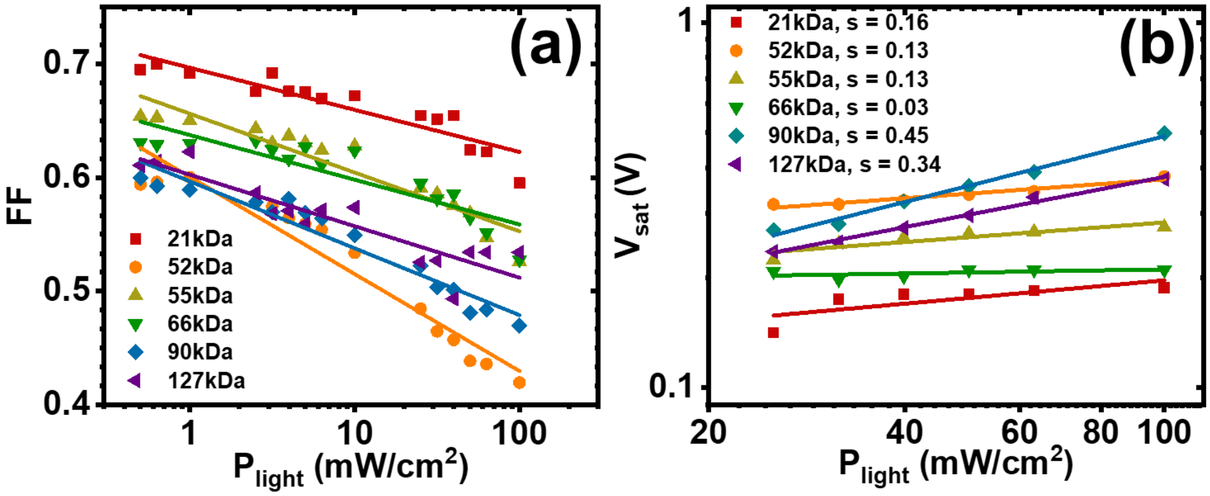


Figure S12. (a) FF dependency on incident light intensity for the optimized PBDB-T:PNDIBS devices of various acceptor polymer molecular weight. (b) Saturation voltage (V_{sat}) vs. incident light intensity (P_{light}) for optimized PNDIBS:PBDB-T devices of various acceptor polymer molecular weights.

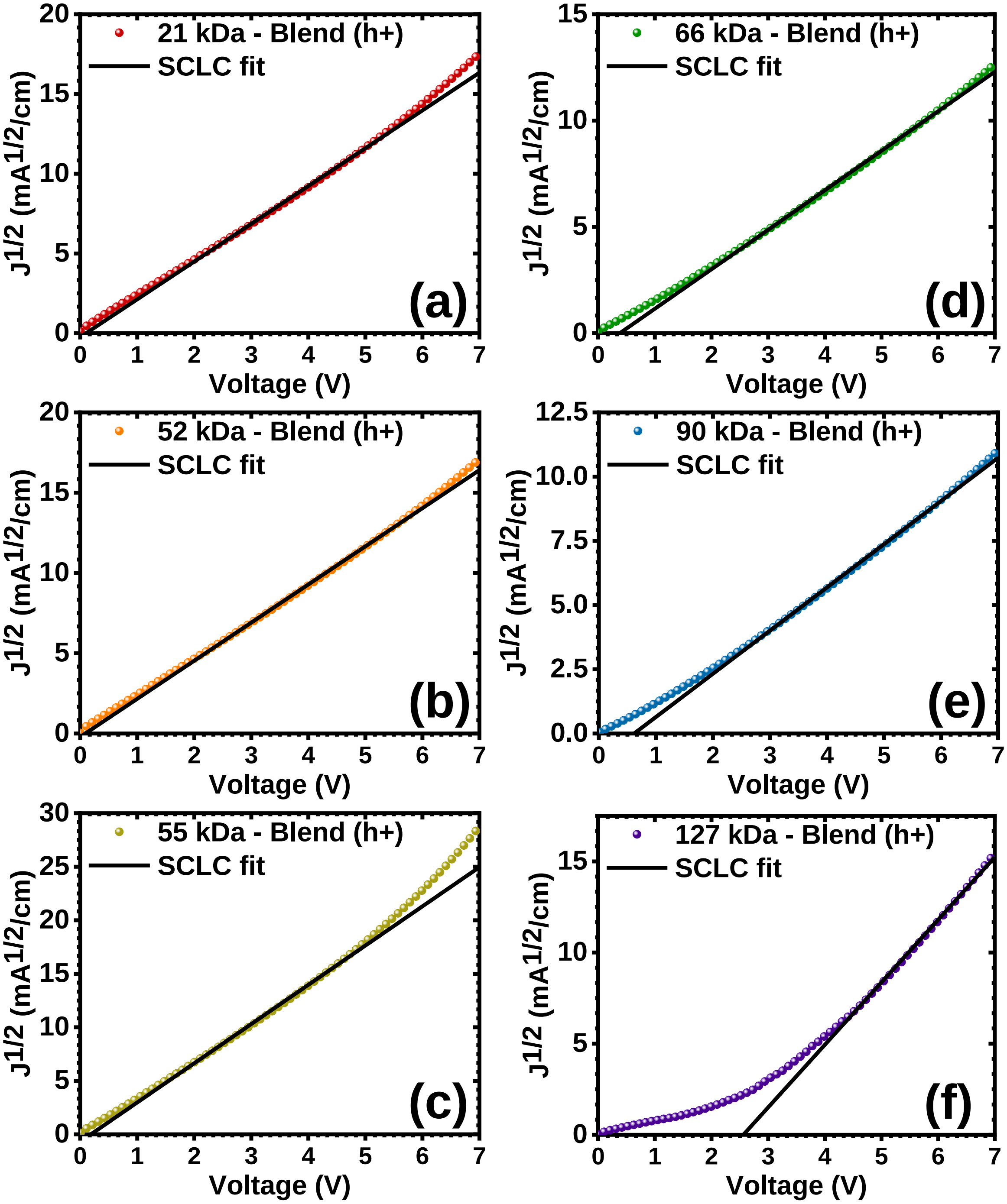


Figure S13. *J-V* curves measured by the space-charge-limited current (SCLC) method of hole-only devices and fitting for PBDB-T:PNDIBS blend films of various acceptor molecular weight. All active layers were processed at optimal conditions.

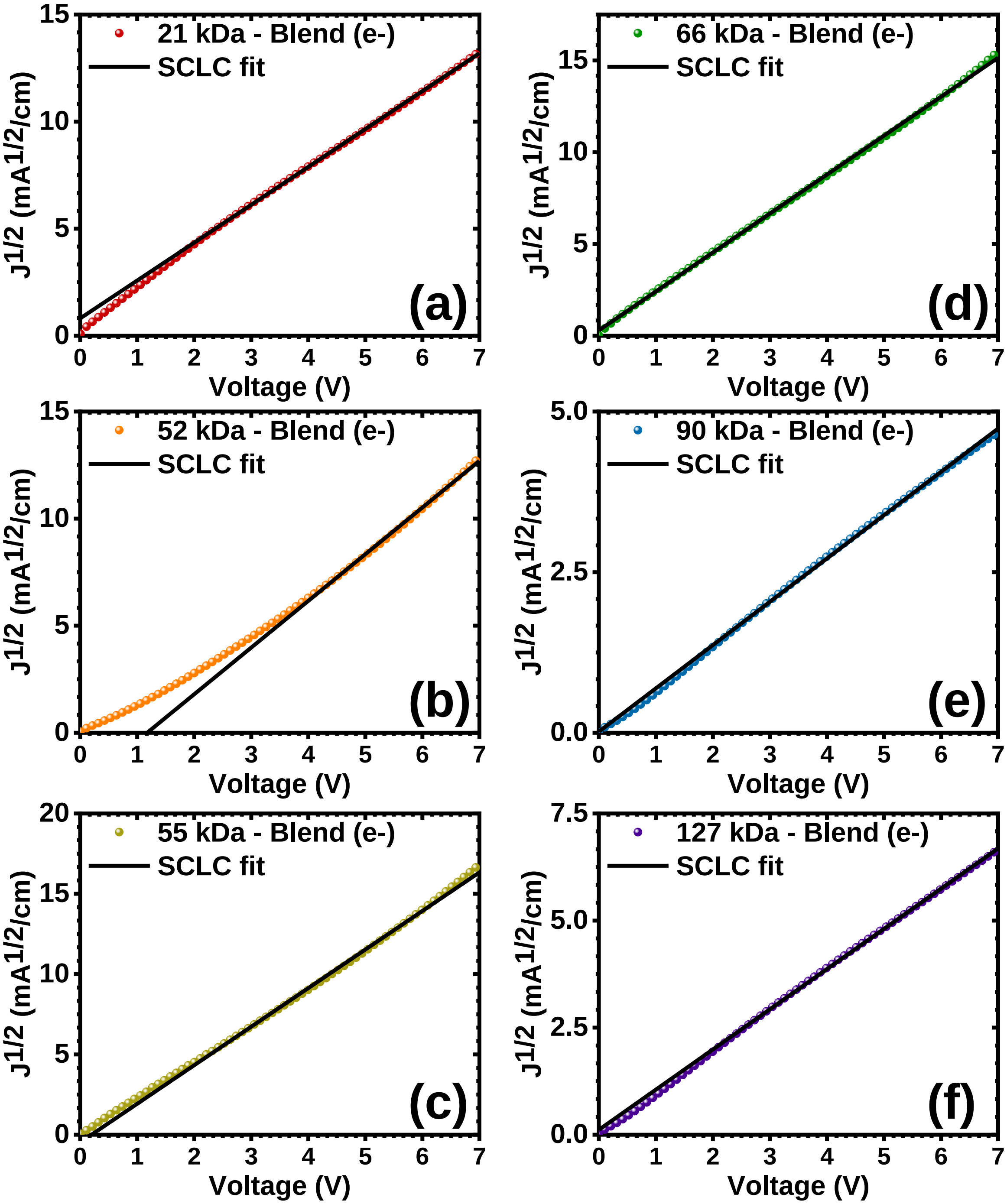


Figure S14. *J-V* curves measured by the space-charge-limited current (SCLC) method of electron-only devices and fitting for PBDB-T:PNDIBS blend films of various acceptor molecular weight. All active layers were processed at optimal conditions.

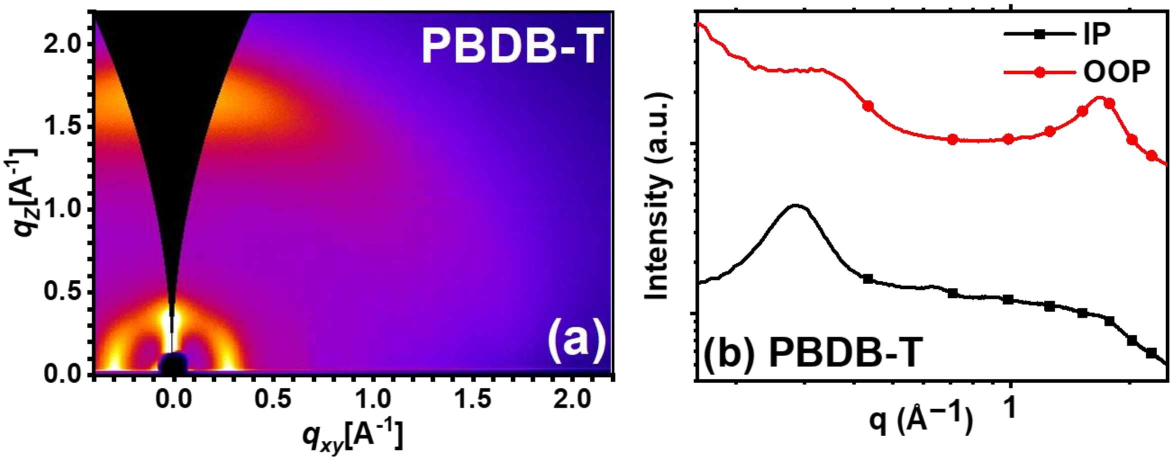


Figure S15. (a) 2D-GIWAXS patterns and (b) 1D line cut in the in-plane (IP) and out-of-plane (OOP) direction of neat PBDB-T film.

Table S1. Direct Hetero(Arylation) Polymerization Conditions for Different Molecular Weight of PNDIBS Acceptor Copolymer.

Polymers	M_n (kDa)	PDI	Polymerization time (hr)
PNDIBS (DHAP) 21 kDa	21	1.7	3
PNDIBS (DHAP) 52 kDa	52	3.3	16
PNDIBS (DHAP) 55 kDa	55	2.4	18
PNDIBS (DHAP) 66 kDa	66	2.6	13
PNDIBS (DHAP) 90 kDa	90	3.0	20
PNDIBS (DHAP) 127 kDa	127	2.3	22

Table S2. Electron Mobility of PNDIBS Acceptor Polymer Measured via Bottom-Gate Top-Contact OFET Architecture.

Polymer	T_{anneal} (°C)	$\mu_{e,\ ave}^{FET}$ (cm^2/Vs)	I_{on}/I_{off}	$V_{threshold}$ (V)
PNDIBS (DHAP) 21 kDa	170	0.16	4×10^6	26
PNDIBS (Stille) 35kDa	25°C	0.04	2×10^5	26
PNDIBS (Stille) 35kDa	170	0.15	1×10^5	31

Table S3. Charge Extraction Probability at Short-Circuit Condition and Maximum Charge Photogeneration Rate of the Optimized PBDB-T:PNDIBS All-PSC Devices for Different Acceptor Polymer Molecular Weight.

Blend	$P_c\ (E,T)$ (%)	$G_{\max}$ ($m^{-3}s^{-1}$)
PBDB-T:PNDIBS (21kDa)	97.24	1.06×10^{28}
PBDB-T:PNDIBS (52kDa)	97.48	1.14×10^{28}
PBDB-T:PNDIBS (55kDa)	94.08	1.21×10^{28}
PBDB-T:PNDIBS (66kDa)	97.25	1.10×10^{28}
PBDB-T:PNDIBS (90kDa)	89.31	1.09×10^{28}
PBDB-T:PNDIBS (127kDa)	93.69	1.09×10^{28}

Table S4. Summary of (100) and (010) Peaks in Both In-Plane (IP) and Out-of-Plane (OOP) Directions in Neat Component and Blend Polymer Thin Films.

Polymer	q_{xy} (Å^{-1}) (100) IP	q_{xy} (Å^{-1}) (200) IP	q_{xy} (Å^{-1}) (300) IP	q_z (Å^{-1}) (010) OOP
PBDB-T	0.29	-	-	1.69
PBDB-T:PNDIBS (21kDa)	0.27	-	-	1.63
PBDB-T:PNDIBS (52kDa)	0.27	-	-	1.66
PBDB-T:PNDIBS (55kDa)	0.27	-	-	1.63
PBDB-T:PNDIBS (66kDa)	0.25	-	-	1.52
PBDB-T:PNDIBS (90kDa)	0.26	-	-	1.63
PBDB-T:PNDIBS (127kDa)	0.25	-	-	1.61