

Electronic Supplementary Information

Long-Term Thermally Stable Organic Solar Cells Based on Cross-linkable Donor-Acceptor Conjugated Polymers

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1. Experimental details

1.1 Materials and methods

All reagents from commercial sources were used as received. All reactions were carried out under argon atmosphere using solvents dehydrated following standard methods. ^1H NMR (400 MHz) and ^{13}C NMR (100 MHz) were recorded on a Varian Mercury spectrometer with tetramethylsilane (TMS) as an internal reference. The spectra of small molecular compounds were measured in CDCl_3 at room temperature, while those of polymers were recorded in *o*-dichlorobenzene- d_4 at 110 °C. Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectroscopy was carried out on a Shimadzu Biotech Axima Mass Spectrometer using dithranol or *a*-cyano-4-hydroxycinnamic acid as a matrix. Polymer average molecular weight and polydispersity (PDI) were estimated by high-temperature gel permeation chromatography (GPC) operating at 150 °C using 1,3,5-trichlorobenzene as an eluent and monodispersed polystyrenes as standards. Elemental analyses on carbon, hydrogen and nitrogen contents of polymer samples were carried out on an Elementar vario EL III elemental analyser. Thermogravimetric analysis (TGA) was carried out by a TGA Q500 instrument with a temperature rate of 10 °C min^{-1} under a nitrogen atmosphere. Differential scanning calorimetry (DSC) was performed on a Q2000 modulated DSC instrument with a heating rate of 10 °C min^{-1} and a cooling rate of 15 °C min^{-1} under a nitrogen atmosphere. UV-vis absorption spectroscopy was performed on the Hitachi U-3310 spectrophotometer. Cyclic voltammetry (CV) measurements were performed on a CHI 660C instrument with a three-electrode cell using glass carbon as a working electrode, platinum wire as a counter electrode, and Ag/AgNO_3 as a reference electrode. Samples were prepared by casting their chlorobenzene solutions onto glass carbon electrodes. And, the measurements were carried out in dehydrated acetonitrile solutions containing 0.1 M Bu_4NPF_6 electrolyte and under a scan rate of 50 mV s^{-1} . Atomic force microscopy (AFM) was performed on a JPK NanoWizard AFM system under a tapping mode. Benzo[1,2-*b*:4,5-*b'*] dithiophene-4,8-dione,¹ thiophene-3,4-dicarboxylic acid,² and 1*H*,3*H*-thieno[3,4-*c*] furan-1,3-dione² were synthesized according to previously reported methods.

1.2 Photovoltaic device fabrication and characterization

All solar cell devices were fabricated with a structure of ITO/PEDOT:PSS/active layer/Ca/Al. First at all, ITO-coated glass substrates were subsequently cleaned by deionized water, acetone and isopropanol. Then, the substrates were dried with pressurized nitrogen and exposed to UV–ozone plasma for 15 min. A thin layer (25 nm) of filtered PEDOT:PSS (Heraeus Clevios PVP. Al 4083) was spin-coated on the top of cleaned ITO at 4000 rpm and baked at 140 °C for 15 min. Afterwards, the substrates were transferred into a dry nitrogen glovebox ($\text{O}_2 < 1$ ppm, $\text{H}_2\text{O} < 1$ ppm) for active layer deposition. The active layer solutions were prepared by dissolving the checked polymer and PC_{71}BM in a weight ratio of 1:1.5 in chlorobenzene with a total concentration of 20 mg ml^{-1} . The solvent also contained 1-chloronaphthalene (CN) additive in a volume fraction of 5%. After the solutions were stirred at 120 °C for 8 h,

they were spin-coated on top of PEDOT:PSS layer at 110 °C. After 3 hours standing, the substrates containing **PBDTTPD-V_x** were thermally annealed at 150 °C for 30 min for thermal cross-linking. Finally, the devices were finished by thermal deposition of a 7 nm-thick Ca and 120 nm-thick Al cathode under a vacuum of 10⁻⁵ mbar. The thicknesses of all the films were measured by a Veeco Dektak 150 profilometer. Current density–voltage (J–V) curves were recorded with a Keithley 2420 source meter. Photocurrent was acquired upon irradiation using an AAA solar simulator (Oriel 94043A, 450 W) with AM 1.5G filter. Light intensity was adjusted to 100 mW cm⁻² using a standard NREL-certified silicon cell. External quantum efficiency (EQE) was detected with a 75 W Xe lamp, an Oriel monochromator (74125), an optical chopper, a lock-in amplifier, and a NREL-calibrated crystalline silicon cell. For stability checking, the devices were heated at 150 °C in dark in the above dry nitrogen glovebox (O₂ < 1 ppm, H₂O < 1 ppm) for different times (from 30 min to 40 h), and then subjected to J–V characteristic measurement under the illumination of AM 1.5 G with a light density of 100 mW cm⁻².

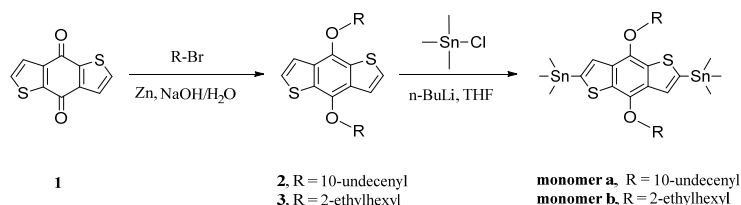
1.3 Hole mobility measurement

Hole-only devices were fabricated with a structure of ITO/PEDOT:PSS/polymer:PC₇₁BM (1:1.5 wt/wt)/Au. The mobility was determined by fitting the dark current to single carrier SCLC, as described by the following equation:

$$J = \frac{9}{8} \epsilon_0 \epsilon_r \mu_h \frac{(V_a - V_{bi})^2}{d^3}$$

where *J* is the current density, μ_h is the hole mobility, ϵ_0 and ϵ_r are the permittivity of free space and the relative permittivity of the materials, respectively, *d* is the thickness of the active layer, *V_a* is the applied voltage and *V_{bi}* is the built-in voltage.

1.4 Material synthesis



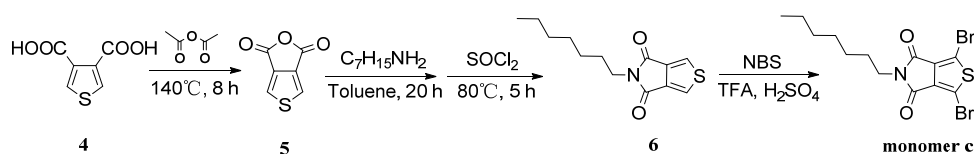
4,8-Bis(undec-10-en-1-yloxy)benzo[1,2-*b*:4,5-*b'*]dithiophene (2). A mixture of benzo [1,2-*b*:4,5-*b'*]dithiophene-4,8-dione (Compound **1**, 440 mg, 2 mmol), zinc powder (307 mg, 4.8 mmol), NaOH (1.2 g, 30 mmol) was put into a 25 mL flask under the protection of argon. After addition of 8 mL deionized water, the reaction mixture was heated to reflux for 1 h under vigorous stirring. During the reaction, the color changed from yellow, to dark red, and then to orange. Next, a catalytic amount of tetrabutylammonium bromide and 10-Undecenyl Bromide (1.114 g, 4.8 mmol) were added into the reaction mixture. After refluxing for additional 2 h, the reaction mixture was poured into cold water and extracted with dichloromethane. Organic layers were combined, washed with brine, dried over anhydrous MgSO₄, and concentrated under vacuum. The crude product was finally purified by silica column chromatography using hexane as eluent to afford compound **2** as colorless oil (741 mg, yield 70%). ¹H NMR

(400 MHz, CDCl₃): δ (ppm): 7.48 (d, J = 5.4 Hz, 2H), 7.36 (d, J = 5.4 Hz, 2H), 5.83 (m, 2H), 4.98 (m, 4H), 4.28 (t, J = 6.4 Hz, 4H), 2.06 (t, J = 6.8 Hz, 4H), 1.89 (t, J = 7.0 Hz, 4H), 1.58 (t, J = 7.2 Hz, 4H), 1.39-1.28 (m, 16H), 1.89 (t, J = 4.8 Hz, 4H).

4,8-bis((2-ethylhexyl)oxy)benzo[1,2-b:4,5-b']dithiophene (3). Compound **3** was obtained as colorless oil (7.6 g, yield 85%) following the same method for compound **2**. ¹H NMR (400 MHz, CDCl₃): δ (ppm): 7.46 (d, J = 5.6 Hz, 2H), 7.34 (d, J = 5.6 Hz, 2H), 4.16 (d, J = 4.5 Hz, 4H), 1.81-1.34 (m, 16H), 0.99 (t, J = 7.6 Hz, 6H), 0.92 (t, J = 7.2 Hz, 6H).

4,8-Bis(undec-10-en-1-yloxy)benzo[1,2-b:4,5-b']dithiophene-2,6-diylbis(trimethylstannane (monomer a). Compound **2** (710 mg, 1.35 mmol) was dissolved in 20 mL dry THF under the protection of argon. After the solution was cooled down to -78 °C using a dry ice-acetone bath, *n*-butyllithium (2.2 mL, 1.6 M in *n*-hexane, 3.4 mmol) was added dropwise. Then, the reaction mixture was slowly warmed up to room temperature, stirred for 2 h, cooled down to -78 °C again, and then added with trimethyltin chloride (4.05 mL, 1 M in *n*-hexane, 4.05 mmol) in one portion. Afterward, the reaction mixture was allowed to slowly warm to room temperature and stirred overnight. The reaction was terminated by pour of cool water (20 mL), and resulted mixture was extracted with diethyl ether. Organic layers were combined, washed with brine, dried over anhydrous MgSO₄, and concentrated under vacuum. The crude product was recrystallized from isopropanol to afford monomer **a** as colorless needles (697 mg, yield 58%). ¹H NMR (400 MHz, CDCl₃): δ (ppm): 7.50 (s, 2H), 5.82 (m, 2H), 4.97 (m, 4H), 4.30 (t, J = 6.4 Hz, 4H), 2.05 (m, 4H), 1.88 (m, 4H), 1.58-1.33 (m, 20H), 0.45 (s, 18H). ¹³C NMR (100 MHz, CDCl₃): δ (ppm): 143.1, 140.5, 139.2, 134.0, 133.0, 128.0, 114.1, 73.6, 33.8, 30.5, 29.6, 29.5, 29.5, 29.2, 28.9, 26.1, -8.15. LRMS (MALDI, *m/z*): [M + H]⁺ calcd. for C₃₈H₆₂O₂S₂Sn₂, 854.2235; found, 851.8.

4,8-Bis((2-ethylhexyl)oxy)benzo[1,2-b:4,5-b']dithiophene-2,6-diylbis(trimethylstannane (monomer b). Monomer **b** was obtained as colorless needles. (3.028 g, yield 65%) following the similar method for monomer **a**. ¹H NMR (400 MHz, CDCl₃): δ (ppm): 7.51 (s, 2H), 4.18 (d, J = 6.8 Hz, 4H), 1.42-1.38 (m, 16H), 1.02 (t, J = 10.0 Hz, 6H), 0.94 (t, J = 8.0 Hz, 6H), 0.44 (s, 18H). ¹³C NMR (100 MHz, CDCl₃): δ (ppm): 143.2, 140.4, 133.8, 132.9, 128.0, 75.6, 40.6, 30.5, 29.2, 23.9, 23.2, 14.2, 11.3.



5-heptyl-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione (6). 1*H*,3*H*-thieno[3,4-*c*]furan-1,3-dione (compound **5**, 3.08 g, 20 mmol) was dissolved in 120 mL dry toluene under the protection of argon. Then, *n*-heptylamine (4.605 g, 40 mmol) was added slowly, and the mixture was heated to 120 °C for 20 h under vigorous stirring. Afterwards, toluene was removed under vacuum to afford brown solid. The obtained crude product without any purification was dissolved in thionyl chloride (100 mL) and the mixture was refluxed for 5 h. After the removal of the volatiles by added water slowly, the mixture was extracted with dichloromethane. Organic layers were combined, washed with brine, dried over anhydrous MgSO₄, and concentrated under vacuum. The

crude product was purified by column chromatography using dichloromethane/hexanes (3:1) as the eluent to afford compound **6** as a white solid (2.976 g, yield 59%). ¹H NMR (400 MHz, CDCl₃): δ (ppm): 7.80 (s, 2H), 3.60 (t, *J* = 7.6 Hz, 2H), 1.63 (t, *J* = 7.2 Hz, 2H), 1.34-1.23 (m, 8H), 0.87 (t, *J* = 6.8 Hz, 3H).

1,3-Dibromo-5-heptyl-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione (monomer c).

Compound **6** (2.511 g, 10 mmol) was dissolved in a mixture of sulfuric acid (20 mL) and trifluoroacetic acid (60 mL) under the protection of argon, and then NBS (5.34 g, 30 mmol) was added under the ice-water bath. The reaction mixture was stirred at room temperature overnight. 80 mL of cool water was poured into the flask to dilute the solution, and the solution was extracted with dichloromethane. Organic layers were combined, washed with brine, dried over anhydrous MgSO₄, and concentrated under vacuum. The crude product was purified by column chromatography using dichloromethane/hexanes (1:1) as the eluent to afford monomer **c** as a white solid (2.851 g, yield 70.1%). ¹H NMR (400 MHz, CDCl₃): δ (ppm): 3.59 (t, *J* = 7.2 Hz, 2H), 1.62 (t, *J* = 6.4 Hz, 2H), 1.34-1.22 (m, 8H), 0.87 (t, *J* = 7.2 Hz, 3H). ¹³C NMR (100MHz, CDCl₃): δ (ppm): 160.4, 134.8, 112.9, 38.8, 31.6, 28.8, 28.2, 26.7, 22.6, 14.0.

General procedure for polymer synthesis. A mixture of Monomer **a**, monomer **b** and monomer **c** in a desired molar ratio was dissolved in dry chlorobenzene under the protection of Ar atmosphere. After the solution was freeze-dried by liquid nitrogen, tris(dibenzylideneacetone)dipalladium (0) (Pd₂(dba)₃) and tri-*o*-tolylphosphine (P(*o*-tol)₃) were added quickly into the flask. The resulted mixture was then subjected to thoroughly degassing with three freeze-pump-thaw cycles and filled back with Ar. After stirring at 110 °C for 36 h, the reaction mixture was poured into 150 mL methanol to precipitate the produced polymer. The crude product was dissolved in chloroform and reprecipitated with MeOH for several times, and finally purified by SEC column with S-X1 Biobeads using chloroform as an eluent.

PBDTTPD-V₀. **PBDTTPD-V₀** was synthesized following the general method using monomer **b** (464.5 mg, 0.6 mmol) and monomer **c** (244.2 mg, 0.6 mmol) in the presence of Pd₂(dba)₃ (17 mg) and P(*o*-tol)₃ (22.7 mg) in a yield of 77.3% (323 mg). *M_n* = 16.1 kDa, PDI = 3.13. Anal. Calcd. for (C₃₉H₅₁NO₄S₃)_n: C, 67.30; H, 7.68; N, 2.01. Found: C, 67.57; H, 7.32; N, 1.61.

PBDTTPD-V_{0.0125}. **PBDTTPD-V_{0.0125}** was synthesized following the general method using monomer **a** (6.4 mg, 0.0075mol), monomer **b** (458.7 mg, 0.5925 mmol) and monomer **c** (244.2 mg, 0.6 mmol) in the presence of Pd₂(dba)₃ (17 mg) and P(*o*-tol)₃ (22.7 mg) in a yield of 69% (291 mg). *M_n* = 12.0 kDa, PDI = 2.73. Anal. Calcd. for (C₃₉H₅₁NO₄S₃)_{0.9875}(C₄₅H₅₉NO₄S₃)_{0.0125}: C, 67.33; H, 7.68; N, 2.01. Found: C, 67.34; H, 7.47; N, 1.79.

PBDTTPD-V_{0.025}. **PBDTTPD-V_{0.025}** was synthesized following the general method using monomer **a** (12.8 mg, 0.015 mmol), monomer **b** (452.8 mg, 0.585 mmol) and monomer **c** (244.2 mg, 0.6 mmol) in the presence of Pd₂(dba)₃ (17 mg) and P(*o*-tol)₃ (22.7 mg) in a yield of 80.6% (337 mg). *M_n* = 13.7 kDa, PDI = 3.21. Anal. Calcd. for (C₃₉H₅₁NO₄S₃)_{0.975}(C₄₅H₅₉NO₄S₃)_{0.025}: C, 67.36; H, 7.68; N, 2.00. Found: C, 67.39; H, 7.55; N, 1.68.

PBDTTPD-V_{0.05}. **PBDTTPD-V_{0.05}** was synthesized following the general method using monomer **a** (25.6 mg, 0.03 mmol), monomer **b** (441 mg, 0.57 mmol) and monomer **c** (244.2 mg, 0.6 mmol) in the presence of Pd₂(dba)₃ (17 mg) and P(*o*-tol)₃ (22.7 mg) in a yield of 76% (318 mg). $M_n = 16.2$ kDa, PDI = 3.28. Anal. Calcd. for (C₃₉H₅₁NO₄S₃)_{0.95}(C₄₅H₅₉NO₄S₃)_{0.05}: C, 67.41; H, 7.69; N, 2.00. Found: C, 67.19; H, 7.55; N, 1.70.

PBDTTPD-V_{0.10}. **PBDTTPD-V_{0.10}** was synthesized following the general method using monomer **a** (21.4 mg, 0.025 mmol), monomer **b** (174.2 mg, 0.225 mmol) and monomer **c** (101.7 mg, 0.25 mmol) in the presence of Pd₂(dba)₃ (7.1 mg) and P(*o*-tol)₃ (9.4 mg) in a yield of 76% (133 mg). $M_n = 14.0$ kDa, PDI = 2.76. Anal. Calcd. for (C₃₉H₅₁NO₄S₃)_{0.90}(C₄₅H₅₉NO₄S₃)_{0.10}: C, 67.53; H, 7.70; N, 1.99. Found: C, 67.19; H, 7.51; N, 1.77.

1.5 References

- (1) J. Hou, M. H. Park, S. Zhang, Y. Yao, L. M. Chen, J. H. Li, Y. Yang, *Macromolecules* 2008, **41**, 6012.
- (2) Y. Zou, A. Najari, P. Berrouard, P. S. Beaupre, R. A. Badrou, Y. Tao, M. Leclerc, *J. Am. Chem. Soc.* 2010, **132**, 5330.

2. Supporting Figures

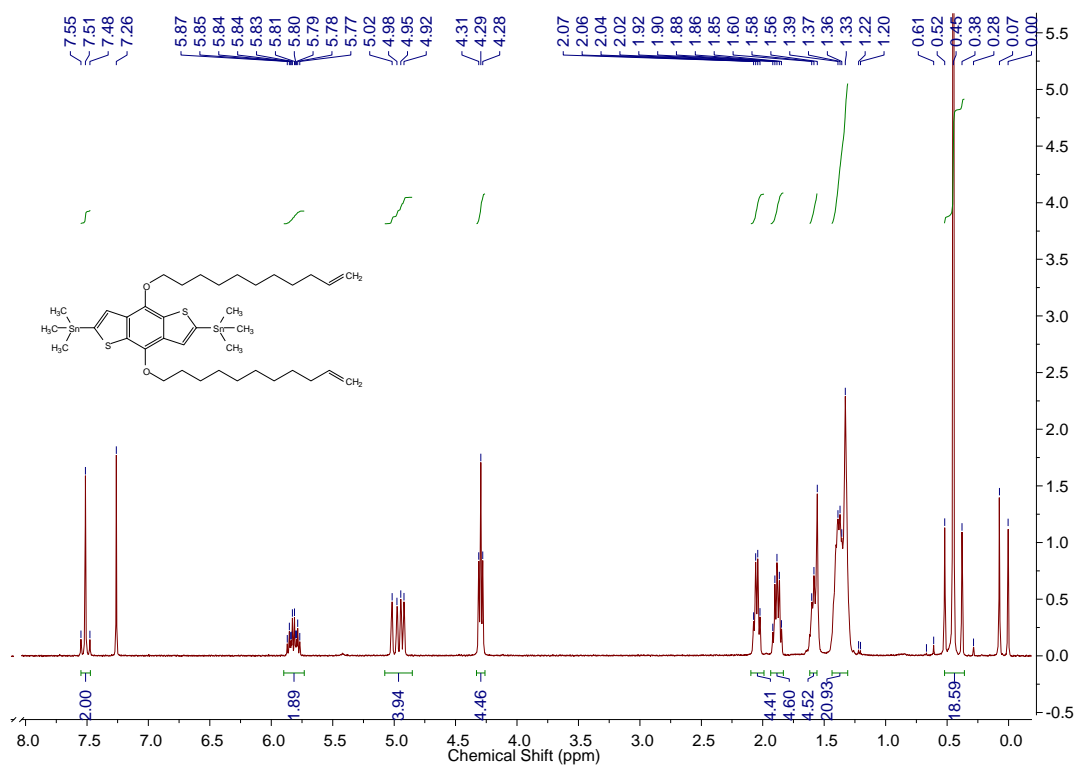


Fig. S1 ¹H NMR of monomer **a** in CDCl₃ at room temperature.

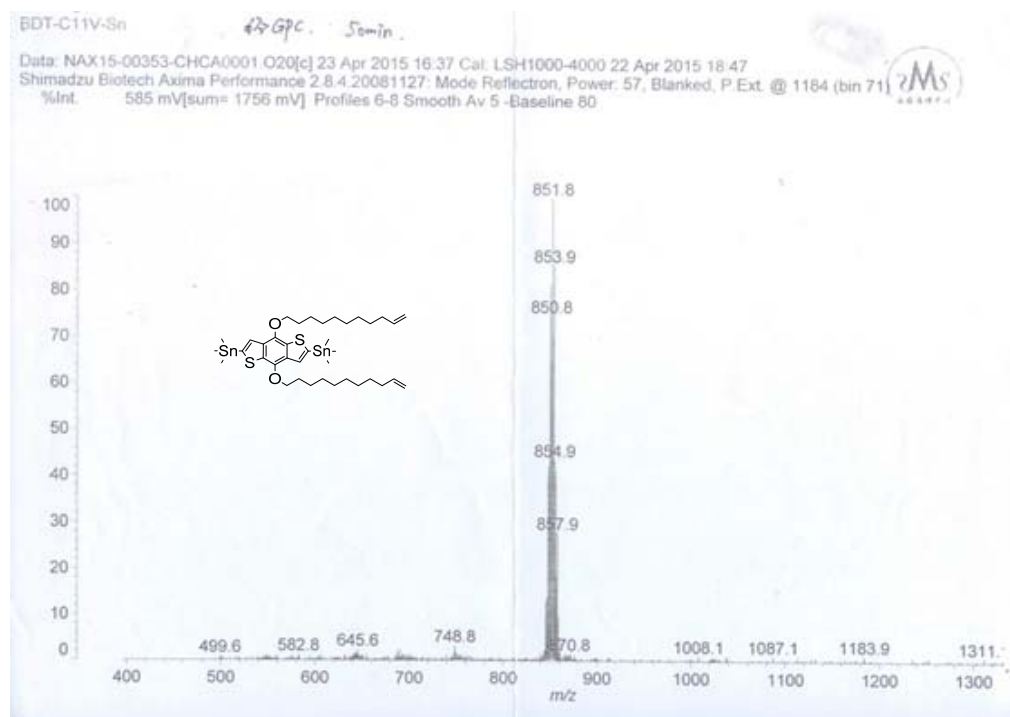


Fig. S2 MALDI-TOF mass spectrum of monomer **a**.

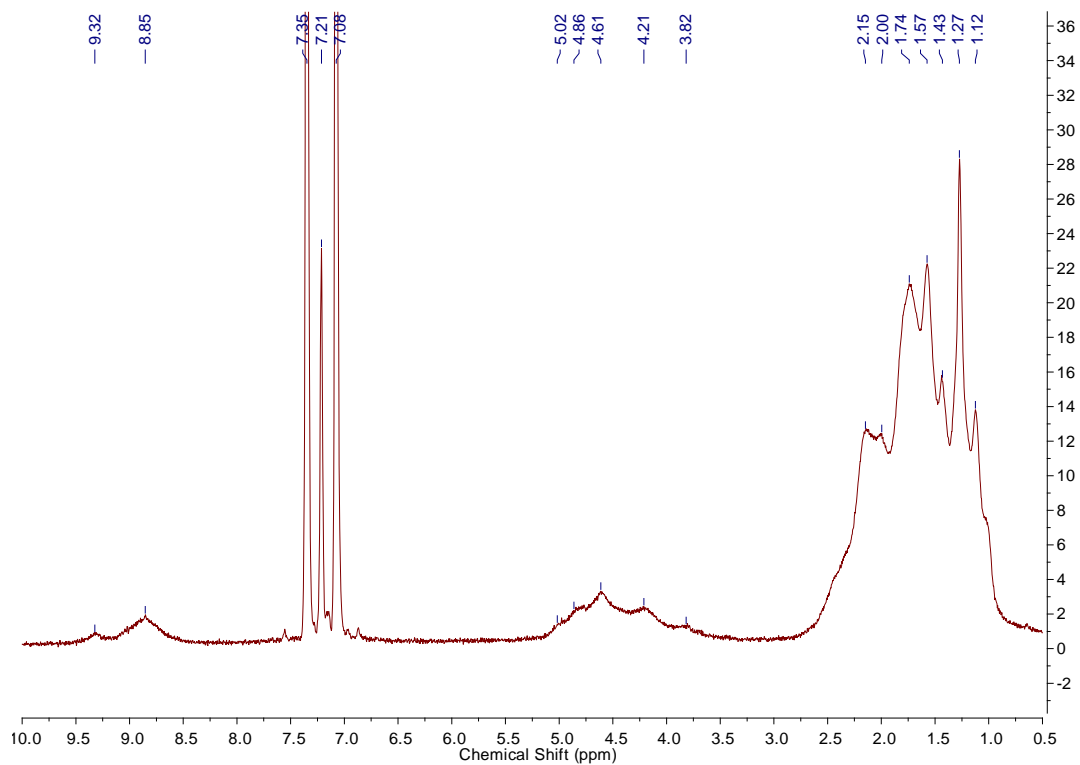


Fig. S3 ^1H NMR of **PBDTTPD- V_0** in o -dichlorobenzene- d_4 at $110\text{ }^\circ\text{C}$

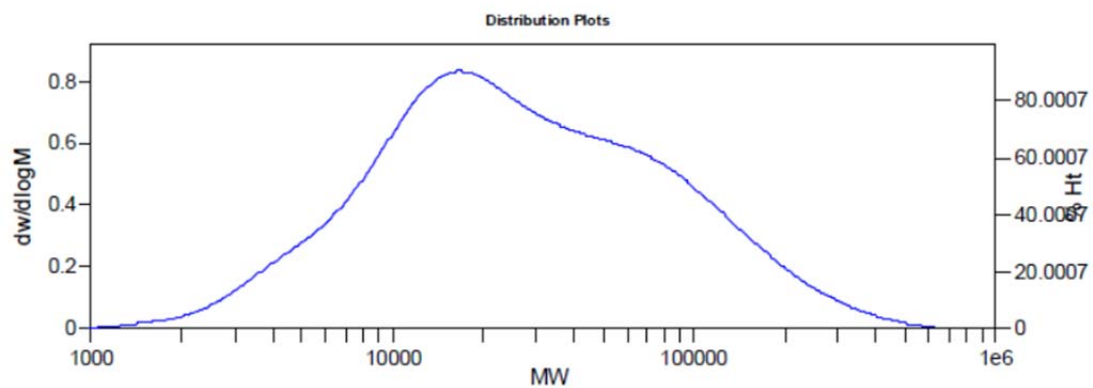


Fig. S4 GPC curve of **PBDTTPD- V_0** with 1,3,5-trichlorobenzene as eluent and monodispersed polystyrenes as standards at $150\text{ }^\circ\text{C}$.

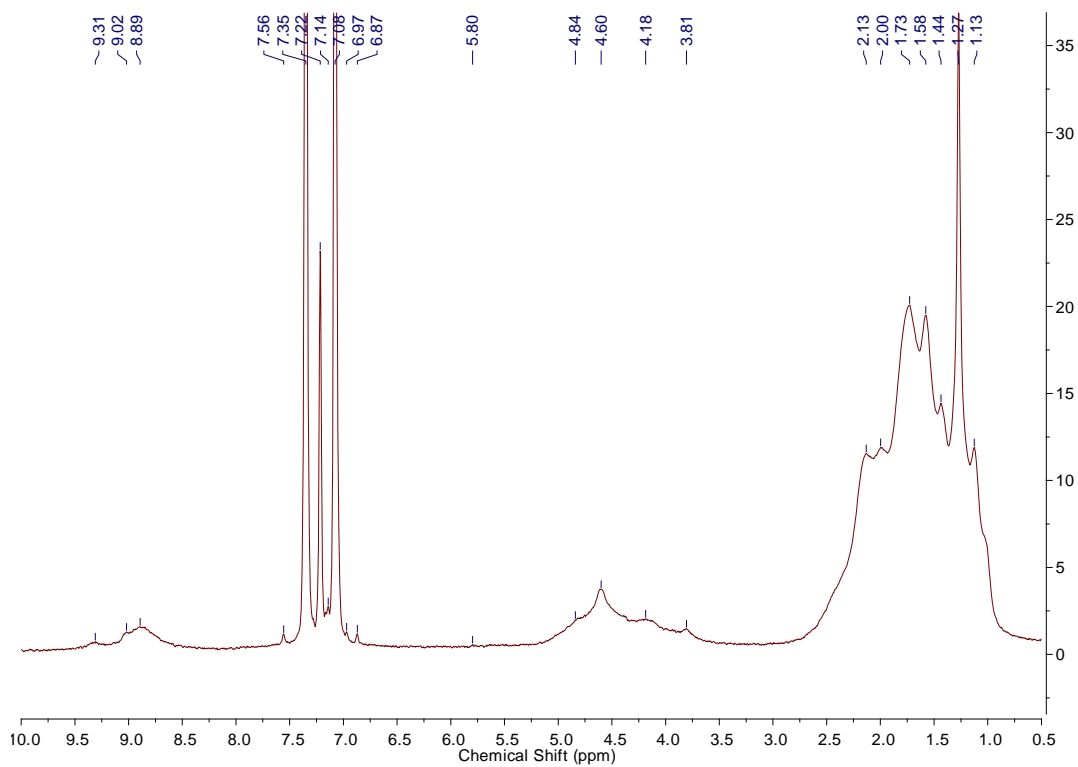


Fig. S5 ^1H NMR of **PBDTTPD-V_{0.0125}** in *o*-dichlorobenzene- d_4 at 110 °C

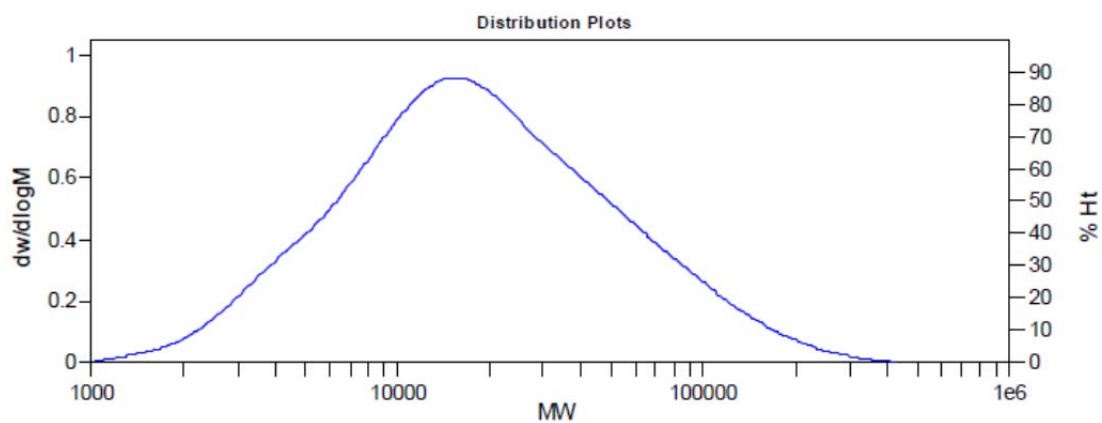


Fig. S6 GPC curve of **PBDTTPD-V_{0.0125}** with 1,3,5-trichlorobenzene as eluent and monodispersed polystyrenes as standards at 150 °C.

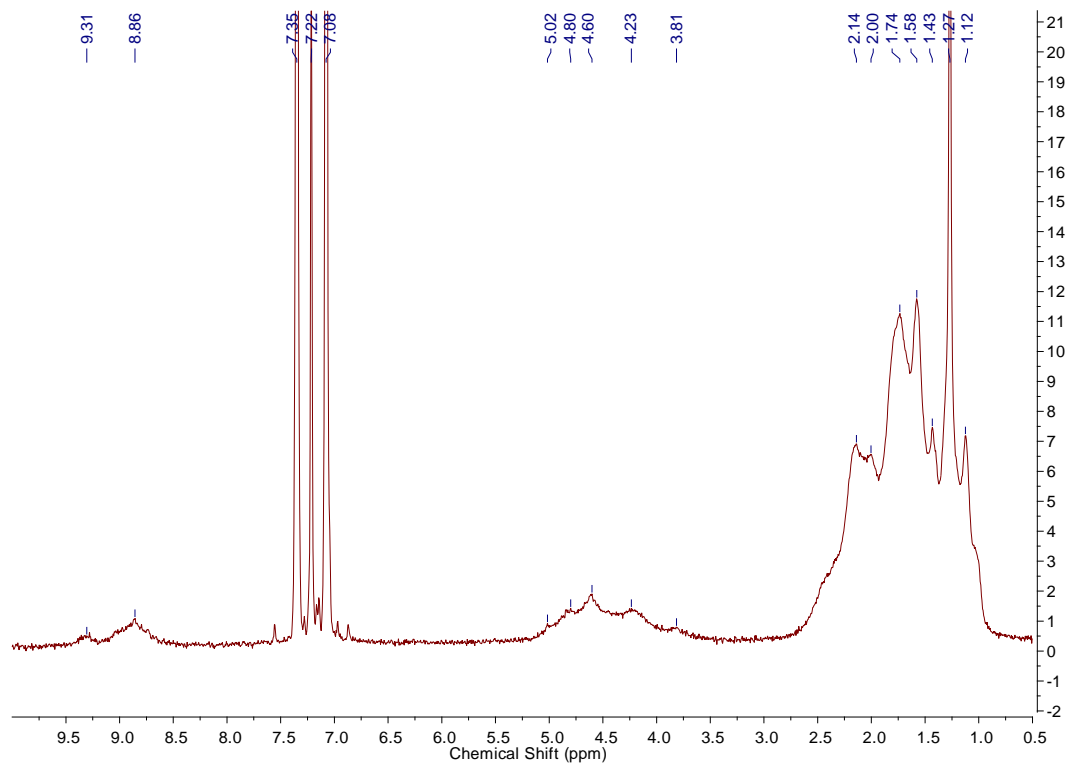


Fig. S7 ¹H NMR of **PBDTTPD-V_{0.025}** in *o*-dichlorobenzene-*d*₄ at 110 °C

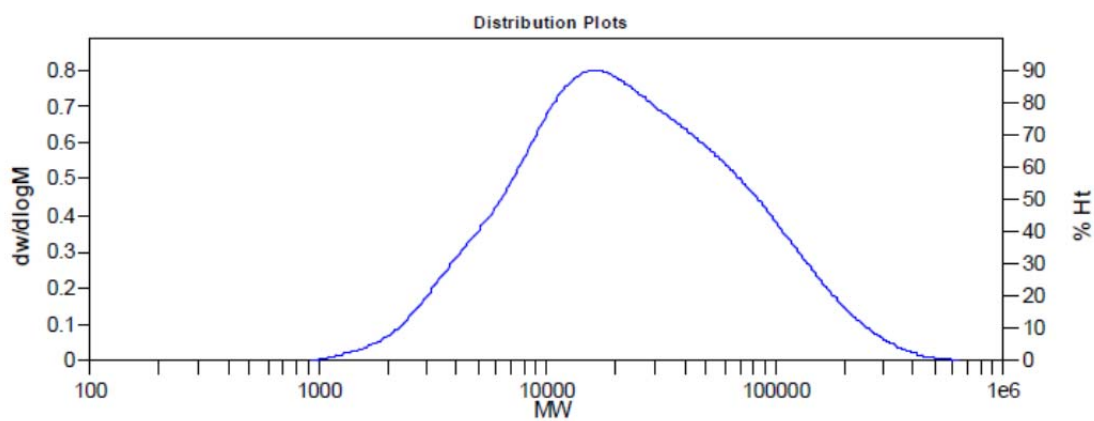


Fig. S8 GPC curve of **PBDTTPD-V_{0.025}** with 1,3,5-trichlorobenzene as eluent and monodispersed polystyrenes as standards at 150 °C.

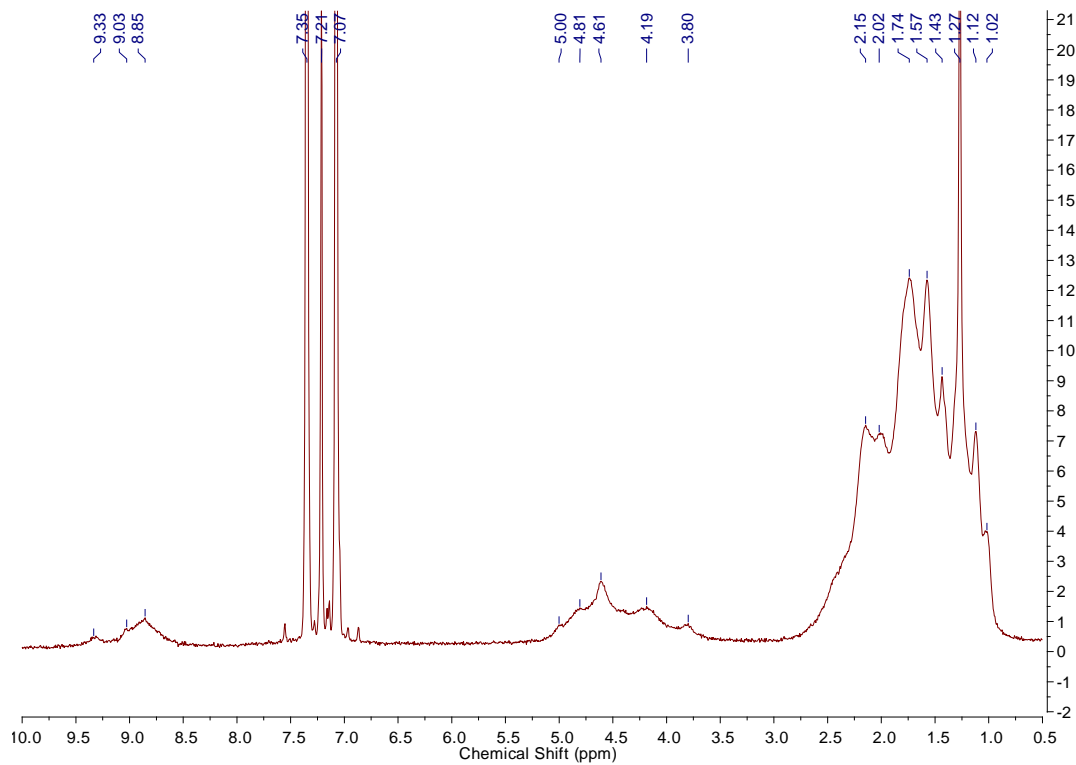


Fig. S9 ¹H NMR of **PBDTTPD-V_{0.05}** in *o*-dichlorobenzene-*d*₄ at 110 °C

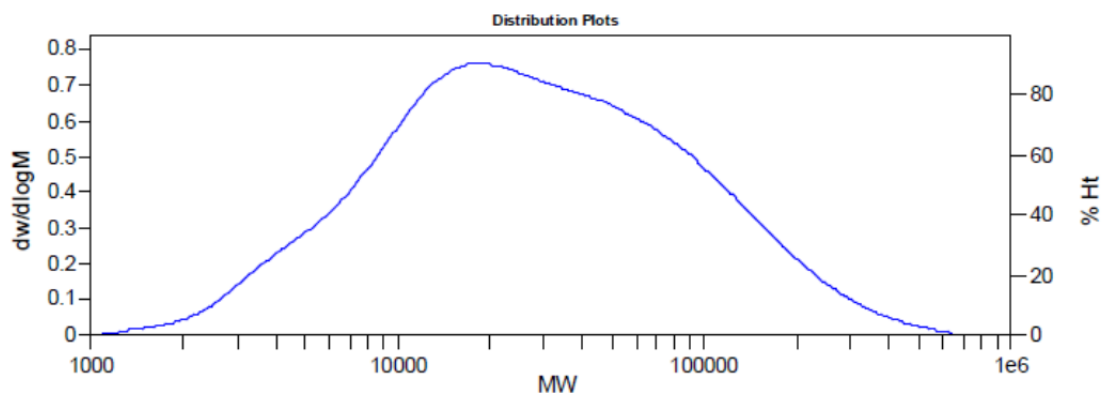


Fig. S10 GPC curve of **PBDTTPD-V_{0.05}** with 1,3,5-trichlorobenzene as eluent and monodispersed polystyrenes as standards at 150 °C.

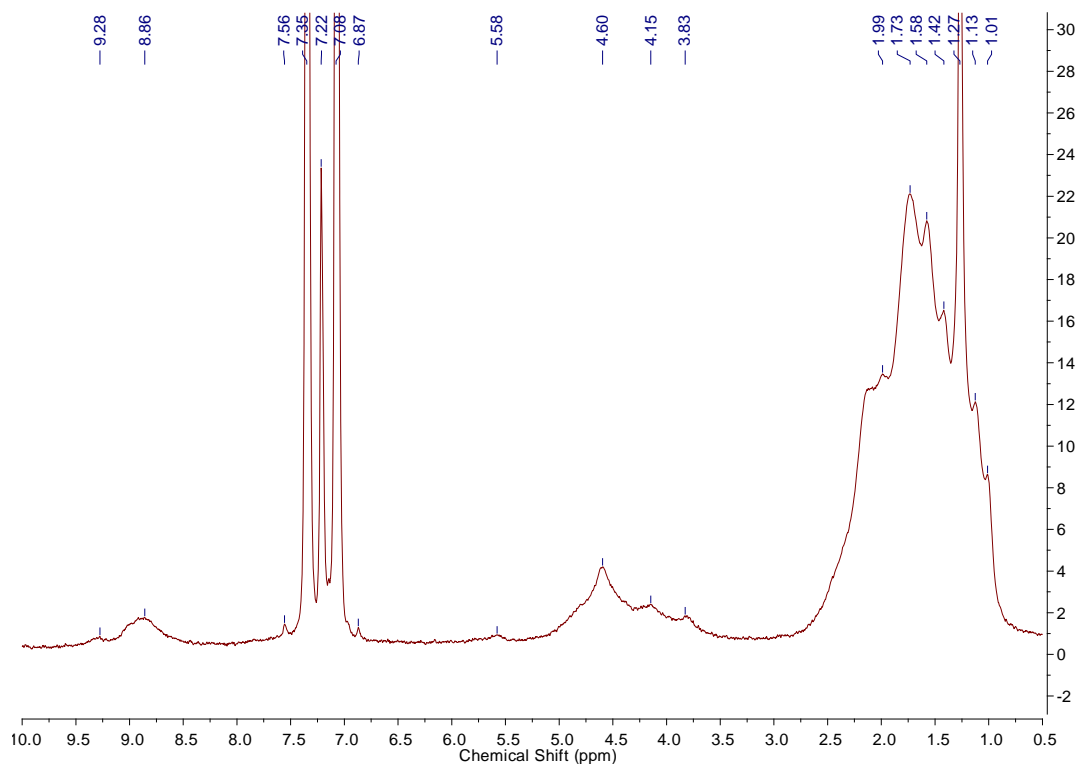


Fig. S11 ¹H NMR of **PBDTTPD-V_{0.10}** in *o*-dichlorobenzene-*d*₄ at 110 °C

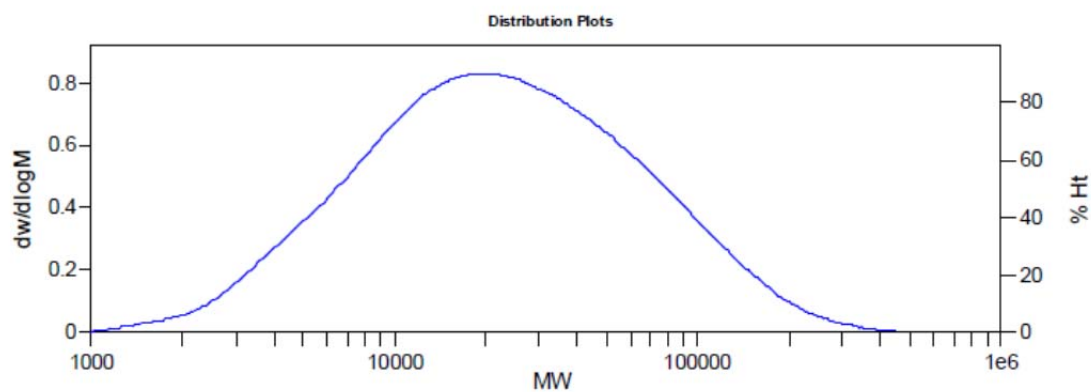


Fig. S12 GPC curve of **PBDTTPD-V_{0.10}** with 1,3,5-trichlorobenzene as eluent and monodispersed polystyrenes as standards at 150 °C.

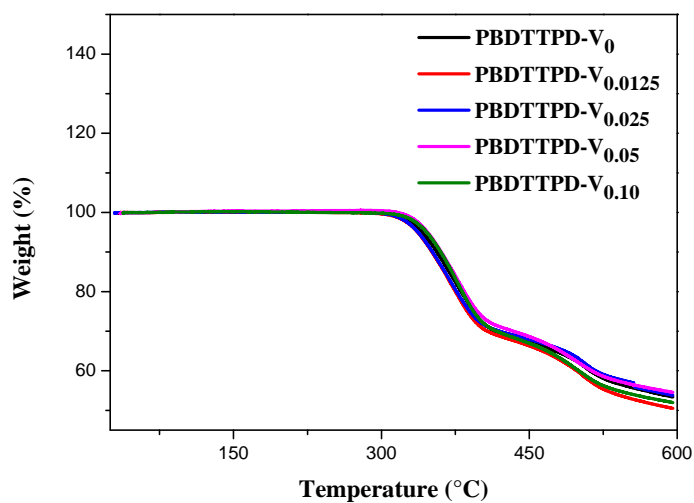


Fig. S13 TGA curves of **PBDTTPD-V_x** with a heating rate of 10 °C min⁻¹ under nitrogen flow.

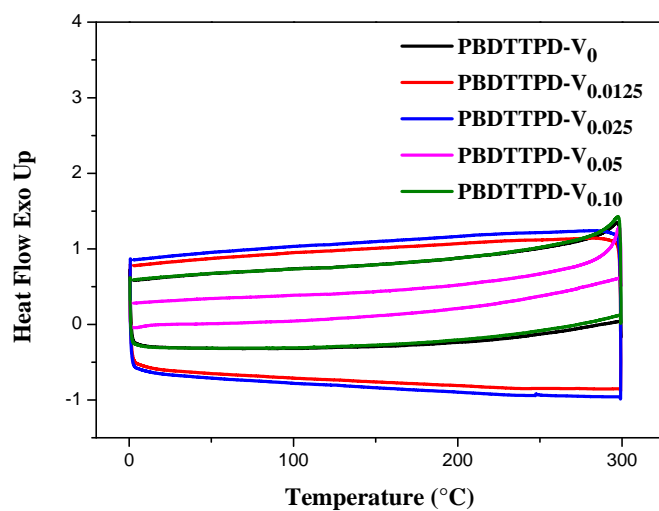


Fig. S14 Second heating and cooling DSC traces of **PBDTTPD-V_x** with a heating rate of 10 °C min⁻¹ and a cooling rate of 15 °C min⁻¹ under nitrogen.

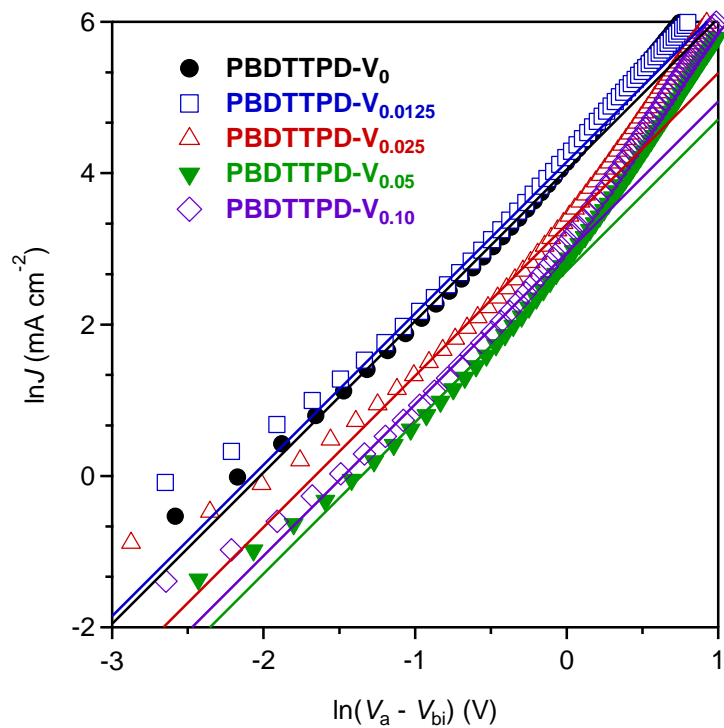


Fig. S15 SCLC fitting on dark J-V characteristics of **PBDTTPD-V_x:PC₇₁BM** blends with hole-only devices.