Supporting Information

Inter-crosslinking Through Both Donor and Acceptor with Unsaturated Bonds for Highly Efficient and Stable Organic Solar Cells

Lie Chen[1,2], Xuee Li[1], Yiwang Chen*[1,2]

[1]Institute of Polymers/Department of Chemistry, Nanchang University, 999 Xuefu Avenue, Nanchang 330031, China; [2]Jiangxi Provincial Key Laboratory of New Energy Chemistry, Nanchang University, 999 Xuefu Avenue, Nanchang 330031, China

Experiment section:

Materials: 4,8-Dihydrobenzo[1,2-b:4,5-b']dithiophen-4,8-dion, 2,6-bis(trimethyltin)-4,8-di(2-ethylhexyloxyl)benzo[1,2-b:4,5-b']dithiophene, 1-(4,6-dibromothieno[3,4-b]thiophen-2-yl)-2-ethylhexan-1-one were purchased from Solarmer Materials Inc.; 8-bromo-1-octene, tetrakis(triphenylphosphine)palladium, LiF (99.99%), Al (99.998%), $PC_{61}BM$ (99.9%) and other materials are purchased from Alfa or Aldrich and used without further purification. Tetrahydrofuran (THF) and toluene were dried over sodium, and N,N-Dimethylformamide (DMF) was dried in CaH_2. Indium-tin oxide (ITO) glass was purchased from Delta Technologies Limited, whereas PEDOT:PSS (Baytron PAl4083) was obtained from Bayer Inc. The following compounds were synthesized according to the procedure in the literature: PBDTTT[1], PCBA[2].

Synthetic Procedures

4,8-Bis(oct-7-en-1-yloxy)benzo[1,2-b:4,5-b']dithiophene (2)

4,8-Dihydrobenzo[1,2-b:4,5-b']dithiophen-4,8-dion (2.2 g, 10 mmol), zinc powder (1.56 g, 24 mmol), and 30 mL of water were put into a 100 mL flask, then 6 g of NaOH was added into the mixture. The mixture was well stirred and heated to reflux for 1 h. Then, 8-bromo-1-octene (5.73 g, 30 mmol) and a catalytic amount of tetrabutylammonium bromide were added into the flask, and the reactant was heated to reflux for 12 h. Then, the reactant was poured into cold water and extracted by 200

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* Corresponding author. Tel.: +86 791 83969562; fax: +86 791 83969561. *E-mail address*: ywchen@ncu.edu.cn (Y. Chen).

mL of diethyl ether two times. The ether layer was dried over anhydrous $MgSO_4$. After solvent was removed, the crude product was purified by silica gel chromatography, using *n*-hexane/CH_2Cl_2=3/1 as eluent. A yield of 3.45 g of compound **2** (yield 78%) was obtained as a colorless sticky oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.47 (d, 2H), 7.35 (d, 2H), 5.82 (m, 2H), 4.97 (q, 4H), 4.27 (t, 4H), 2.07 (q, 4H), 1.87 (m, 4H), 1.58 (m, 4H), 1.34 (m, 8H).

2,6-Bistrimethyltin-4,8-di(oct-7-en-1-yloxy)benzo[1,2-b:4,5-b']dithiophene (3)

To a solution of **2** (0.88 g, 2.0 mmol) in 30 mL THF, 2.5 M solution of n-BuLi in hexane (2.0 mL, 5.0 mmol) was added dropwise at -78 °C under N_2. The solution was stirred at -78 °C for 1 h. Then trimethyltin chloride (6.0 mL, 6 mmol, 1.0 M) in THF was added dropwise and kept stirring at room temperature for overnight. The resulting mixture was quenched with 100 mL of water and extracted with diethyl ether. The organic layer was dried over anhydrous $MgSO_4$. After removing solvent, the crude product was purified by recrystallization from isoprapanol two times. 1.10 g of **3** (yield 71.6%) was obtained as colourless needles. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.51 (s, 2H), 5.83 (m, 2H), 4.98 (q, 4H), 4.29 (t, 4H), 2.09 (q, 4H), 1.88 (m, 4H), 1.60 (m, 4H), 1.44 (m, 8H), 0.45 (s, 18H).

General procedure for the Stille cross-coupling polymerization

PDBTTT-V: The monomer **3** (0.031 g, 0.04 mmol), monomer **4** (0.15 g, 0.2 mmol) and monomer **5** (0.10 g, 0.24 mmol) were mixed in 10 mL of toluene and 2 mL of DMF. After being purged with argon for 5 min, $Pd(PPh_3)_4$ (15 mg) was added as the catalyst, and the mixture was then purged with argon for 25 min. The reaction mixture was stirred and heated to reflux for 16 h. Then the reaction mixture was cooled to room temperature, and the polymer was precipitated by addition of 50 mL methanol, filtered through a Soxhlet thimble. The precipitate was then subjected to Soxhlet extraction with methanol, hexanes, and chloroform. The polymer was recovered as solid from the chloroform fraction by precipitation from methanol. The solid was dried under vacuum. Yield 0.085 g (50%).

Synthesis of PCBM derivates PCBD

PCBA (72 mg, 0.08 mmol), dec-9-en-1-ol (mg, 0.10 mmol), and dichlorobenzene (10 ml) were mixed in a 50 mL round-bottom Schlenk flask under the atmasphere of N_2. The mixture was stirred in room temperature for 2 h, then cooled down to 0 ºC in an ice/water bath. Then, dimethylaminopyride (DMAP) (24 mg, 0.20 mmol) and dicyclohexylcardbodiimide (DCC) (43 mg, 0.20 mmol) were added quickly to the reaction flask. The mixture was continuously stirred at 0 ºC for 30 min, followed by warming to the room temperature and being continuously stirred overnight. Then, the solvent was removed under the reduced pressure; the residue was purified by silica gel chromatography using *n*-hexane then toluene as eluent gradients to give a brown solid. Finally, the sediment was washed with MeOH and dried in vacuum. Yield: 50 mg (64%). ^{1}H NMR ($CDCl_3$, 600 MHz): δ (ppm) 7.93 (d, 2H), 7.55 (t, 2H), 7.47 (t, H), 5.81 (m, 1H), 4.96 (q, 2H), 4.06 (t, 2H), 2.91 (m, 2H), 2.51 (t, 2H), 2.19 (m, 2H), 2.04 (q, 2H), 1.40-1.24 (m, 12H).

Characterizations

The nuclear magnetic resonance (NMR) spectra were collected on a Bruker ARX 400 NMR spectrometer with deuterated chloroform as the solvent and with tetramethylsilane (δ=0) as the internal standard. Thermogravimetric analysis (TGA) was performed on a PerkinElmer TGA 7 for thermogravimetry at a heating rate of 10 °C/min under nitrogen with a sample size of 8 - 10 mg. The ultraviolet-visible (UV) spectra of the samples were recorded on a PerkinElmer Lambda 750 spectrophotometer. The X-ray diffraction (XRD) study of the samples was carried out on a Bruker D8 Focus X-ray diffractometer operating at 30 kV and 20 mA with a copper target (λ=1.54 Å) and at a scanning rate of 1 º/min. The cyclic voltammetry (CV) was performed on a CHI660C potentiostat in an acetonitrile solution of 0.1 mol/L of Bu_4NBF_4 at a potential sweep rate of 0.05 V/s at room temperature under the protection of dry N_2. A platinum electrode coated with a thin film of polymers was used as the working electrode. A Pt wire and an Ag wire were used as the counter electrode and quasi reference electrode, respectively. The electrochemical potential was calibrated against Fc/Fc^+. The HOMO energy level of polymers was determined from the oxidation onset of the second scan from CV data. It is assumed that the redox potential of Fc/Fc^+ has an absolute energy level of -4.80 eV to vacuum. The energy of HOMO and LUMO levels were calculated according to the eqs1 and 2; the electrochemically determined band gaps were deduced from the difference between onset potentials from oxidation and reduction of copolymers as depicted in eq 3[3, 4]

$$\mathrm{E}_{\mathrm{HOMO}} = -(E_{onset}^{ox} + 4.82)\ (\mathrm{eV}) \qquad (1)$$

$$\mathrm{E}_{\mathrm{LUMO}} = -(E_{onset}^{red} + 4.82)\ (\mathrm{eV}) \qquad (2)$$

$$E_{gap}^{ec} = (E_{onset}^{ox} - E_{onset}^{red})\ (\mathrm{eV}) \qquad (3)$$

AFM images were measured on a Nanoscope III A (Digital Instruments) scanning probe microscope using the tapping mode. The surfaces of the organic layers were observed using a Nikon E600POL polarizing optical microscope.

Device Fabrication and Characterization

The polymer photovoltaic cells (PVCs) were fabricated with the active layer consisting of the copolymer PBDTTT:PCBM, PBDTTT-V:PCBM and PBDTTT-V:PCBD in a 1:1.5 wt/wt ratio, and PBDTTT-V:PCBM:PCBD in a 6:5:1 wt/wt ratio. ITO-coated glasses were cleaned with acetone and isopropyl alcohol. After the substrates were dried with air, they were treated with UV ozone for 10 min. PEDOT:PSS (Baytron AI 4083) was spin-cast on the cleaned ITO as received and baked at 140 ºC for 20 min. The copolymer was dissolved in dichlorobenzene to make 10 mg/mL solutions, and PCBM (purchased from Lumtec. Corp) was added to reach the desired ratio. The active layer was obtained by spin-coating the blend solution at 1000 rpm for 30 s. Subsequently, LiF (0.8 nm) and Al (100 nm) electrodes were deposited via thermal evaporation in vacuum (<10^{-6} Torr) in thickness of approximately. The thicknesses of all the films were measured by a Dektak profiler. Current-voltage (J-V) characteristics were recorded using Keithley 2400 Source Meter in the dark and under 100 mW/cm^2 simulated AM 1.5 G irradiation (Abet Solar Simulator Sun2000). All the measurements were performed under ambient atmosphere at room temperature.

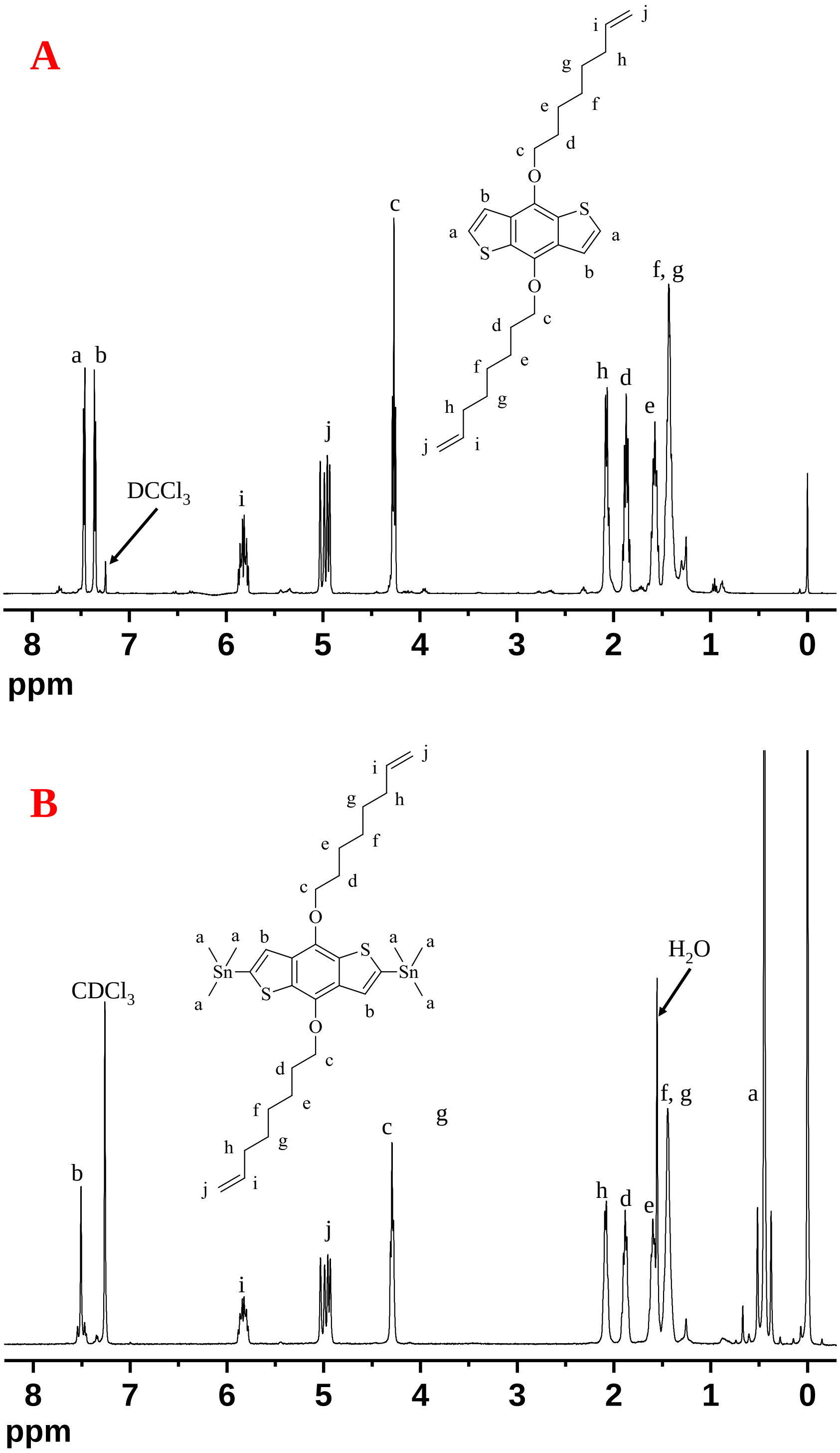

Figure S1. ^{1}H NMR spectra of the monomers (A) **2** and (B) **3**

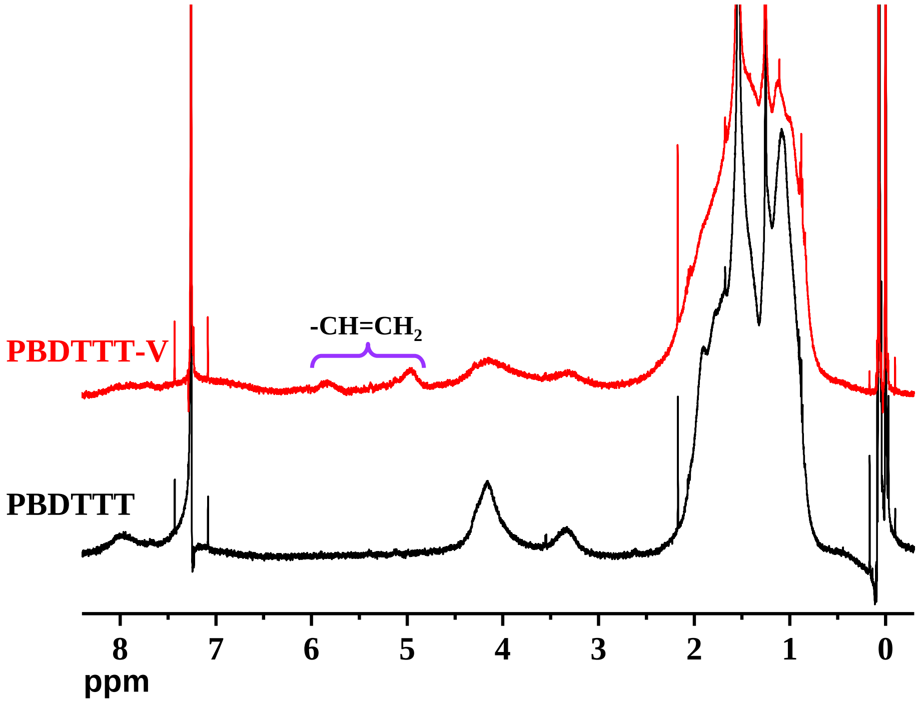

Figure S2. ^{1}H NMR spectra of the copolymers PDTTT and PBDTTT-V

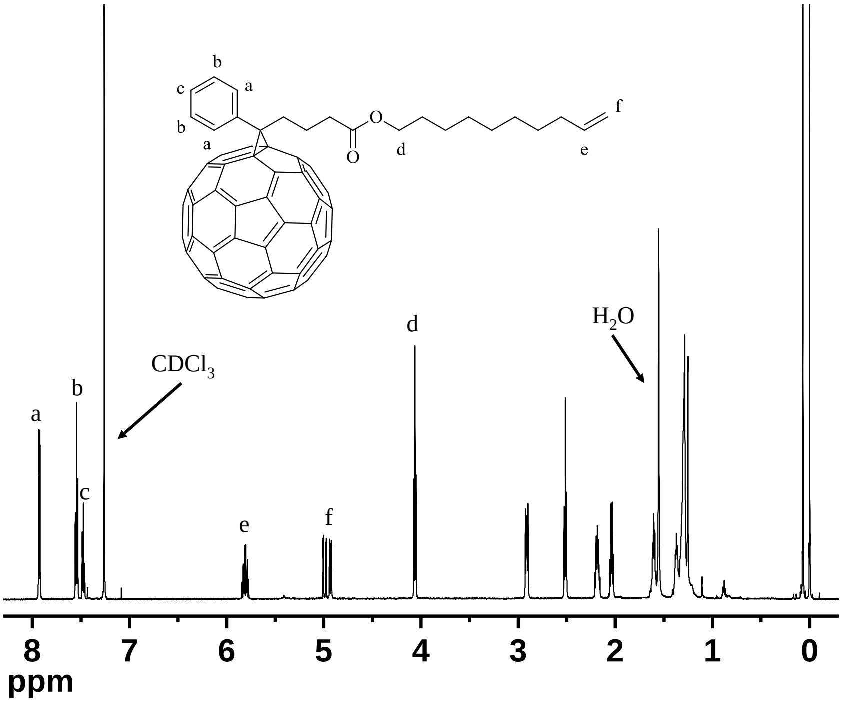

Figure S3. ^{1}H NMR spectra of the monomer PCBD

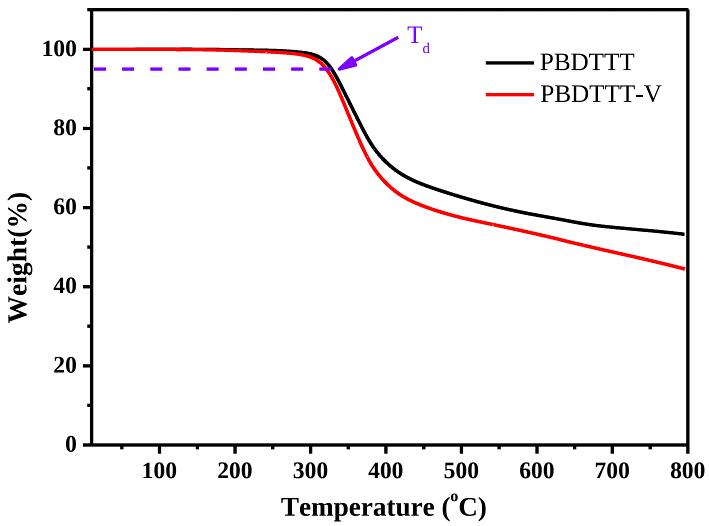

Figure S4. TGA thermogram of the polymers PBDTTT and PBDTTT-V under nitrogen at a heating rate of 20 ºC/min

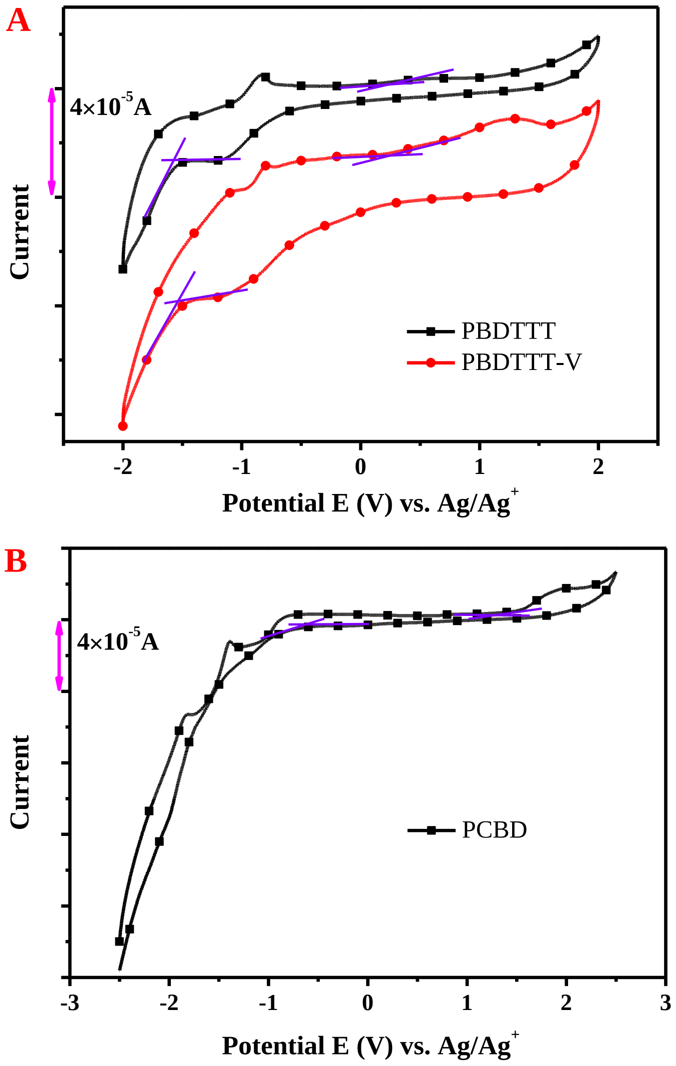

Figure S5. Cyclic voltammograms of (A) polymers PBDTTT and PBDTTT-V, (B) PCBD in thin films at a scan rate of 50 mV/s.

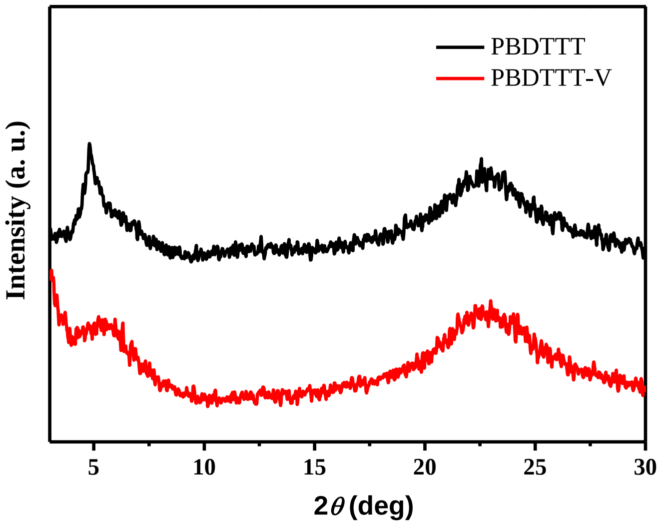

Figure S6. X-ray diffraction patterns of the polymers PBDTTT and PBDTTT-V

References

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