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Supporting Information

Low Band Gap Benzothiophene-Thienothiophene Copolymers with Conjugated Alkylthiothieyl and Alkoxycarbonyl Cyanovinyl Side Chains for Photovoltaic Applications

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1. Synthetic details

1.1 Materials and methods

All reagents were purchased from Aladdin Co., Adamas Co. and Aldrich Chemical Co., and used without further purification. Compounds **1**, **2**, **3**, and monomers TT-CN, BDT-T, BDT-ST were synthesized according to the previous reported procedures.[1-3] ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance-400 spectrometer with *d*-chloroform as solvent and tetramethylsilane as internal standard. The elemental analysis was performed on a Thermo Electron SPA Flash EA 1112 series analyzer. Molecular weights of the copolymers were determined by using a Waters 1515 GPC instrument with chloroform as the eluent and polystyrene as a standard. Thermogravimetric analysis was conducted on a TA Instrument Model SDT Q600 simultaneous TGA/DSC analyzer at a heating rate of 10 °C min^{-1} and under a N_2 flow rate of 90 mL min^{-1}. UV-vis spectra were obtained on a carry 300 spectrophotometer. Cyclic voltammetry measurements were made on an CHI660 potentiostat/galvanostat electrochemical workstation at a scan rate of 50 mV s^{-1}, with a platinum wire counter electrode and a Ag/AgCl reference electrode in an anhydrous and nitrogen-saturated 0.1 mol L^{-1} acetonitrile solution of tetrabutylammonium perchlorate. The copolymers were coated onto the platinum plate working electrodes from dilute chloroform solutions. The energy level of the Ag/AgCl reference electrode was calibrated against the Fc/Fc$^+$ system to be 4.34 eV in this work. The powder X-ray diffraction was detected with a Philips X-ray diffractometer operated in reflection geometry at 30 mA, 40 kV with CuKa radiation. The AFM measurements were performed on a Veeco Nanoscope V microscope in tapping mode.

1.2 Synthesis of monomers

4,6-Dibromothieno[3,4-b]thiophene-2-carboxyaldehyde (**4**)

To a solution of **3** (0.15 g, 0.89 mmol) in 7 mL DMF was added drop-wise a solution of NBS (0.396 g, 2.2 mmol) in 7 mL DMF under nitrogen protection at dark and the mixture was stirred for 25 min at room temperature. The mixture was quenched with 20 mL of 5% sodium thiosulfate solution in an ice bath and extracted three times with diethyl ether. The combined organic fractions were dried over magnesium sulfate and the solvent was removed under reduced pressure. The residue was purified with column chromatography (silica gel) using petroleum ether / dichloromethane (1:1) as an eluent to afford 0.2325 g (yield: 80.1%) of **4** as a orange solid. ^{1}H NMR(400 MHz, $CDCl_3$, δ/ppm): 9.97 (s, 1H, CHO), 7.53 (s, 1H, thiophene-H,). ^{13}C NMR (100 MHz, $CDCl_3$, δ/ppm): 184.90, 150.45, 145.59, 139.97, 127.32, 104.81, 98.05. Anal. Calcd for $C_7H_2OS_2Br_2$ (%): C, 25.79; H, 0.62. Found: C, 25.70; H, 0.59.

2-Cyano-3-(4,6-dibromothieno[3,4-b]thiophen-2-yl) acrylic octyl Ester (**TT-CN**)

Compound **4** (0.242 g, 0.742mmol) was dissolved in a solution of 60 mL dry $CHCl_3$; three drops of triethylamine and then octyl cyanoacetate (0.272, 1.484 mmol) were added, and the resulting solution was stirred for 24 h under argon at room temperature. The reaction mixture was then extracted with CH_2Cl_2, washed with water, and dried over Na2SO4. After removal of solvent, it was purified by chromatography (silica gel) using petroleum ether/ dichloromethane (3:1) as an eluent to afford 0.2732 g (yield: 72.8%) of 6 as a brown solid. ^{1}H NMR(400 MHz, $CDCl_3$, δ/ppm): 8.24 (s, 1H, C=CH), 7.41(s, 1H, thiophene-H), 4.33-4.30(t, 2H, OCH_2), 1.78-1.74(m, 2H, CH_2), 1.41-1.25(m, 12H, CH_2), 0.87-0.90(t, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$, δ/ppm): 161.96, 147.26, 145.05, 142.85, 140.39, 128.12, 114.71, 103.92, 103.46, 97.51, 67.17, 31.77, 29.15, 28.47, 25.78, 22.65, 14.10. Anal. Calcd for $C_{18}H_{19}O_2N_2S_2Br_2$ (%): C, 42.79; H, 3.79; N, 2.77. Found: C, 42.19; H, 3.77; N, 2.59.

1.3 Synthesis of copolymers

PBDTT-CN

Monomer **TT-CN** (0.20 g, 0.395 mmol) and **BDT-T** (0.46 g, 0.395 mmol) was dissolved in degassed toluene (15 mL) and then added $Pd_2(dba)_3$ (7.25 mg, 2% mmol) and P(*o*-tol)$_3$ (9.63 mg, 8% mmol) under a Ar atmosphere. The mixture was stirred at 110 °C for 24 h in dark environment. After the reaction the mixture was cooled to room temperature, and dropped into methanol (500 mL). A green precipitate was obtained. The resulting solid was collected by filtered, and then subjected to Soxhlet extraction successively with methanol, acetone, and hexane to remove the oligomers and impurities. The remaining polymer was dissolved with chloroform and precipitated again from methanol to yeild a dark copolymer 0.2502g (yield: 82%) of dark solid. ^{1}H NMR(400 MHz, $CDCl_3$, δ/ppm): 8.71-7.03 (br, 8H, Ar-H, thiohene-H and CH), 4.37 (br, 4H, OCH_2), 2.92 (br, 4H, thiophene-CH_2), 2.03-0.94 (m, 40H, CH_3, CH_2). Anal. Calcd for $(C_{54}H_{63}NO_2S_6)_n$ (%): 67.71, H: 6.45, N:1.52. Found C: 67.80, H: 6.50, N:1.42.

PBDTT-S-CN

Monomer **TT-CN** (0.1915 g, 0.379 mmol) and **BDT-ST** (0.4628 g, 0.379mmol) was dissolved in degassed toluene (15 mL) and then added Pd2(dba)3 (6.94mg, 2% mmol) and P(o-tol)3 (9.2 mg, 8% mmol) under a Ar atmosphere. The mixture was stirred at 110 °C for 24 h in dark environment. After the reaction the mixture was cooled to room temperature, and dropped into methanol (500 mL). A green precipitate was obtained. The resulting solid was collected by filtered, and then subjected to Soxhlet extraction successively with methanol, acetone, and hexane to remove the oligomers and impurities. The remaining polymer was dissolved with chloroform and precipitated again from methanol to yeild a dark copolymer 0.2402g (yield: 82%) of dark solid. ^{1}H NMR (400 MHz, $CDCl_3$, δ/ppm): 8.52-7.09 (br, 8H, ArH, thiophene-H and CH), 4.41 (br, 4H, OCH_2), 3.02 (br, 4H, thiophene-CH_2), 2.13-0.74 (m, 40H, CH_3, -CH_2 and CH). Anal. Calcd for $(C_{52}H_{59}NO_2S_8)_n$ (%): 63.31, H: 6.03, N:1.42. Found C: 62.99, H: 5.97, N:1.40.

2. DSC, TGA and Fig. S1

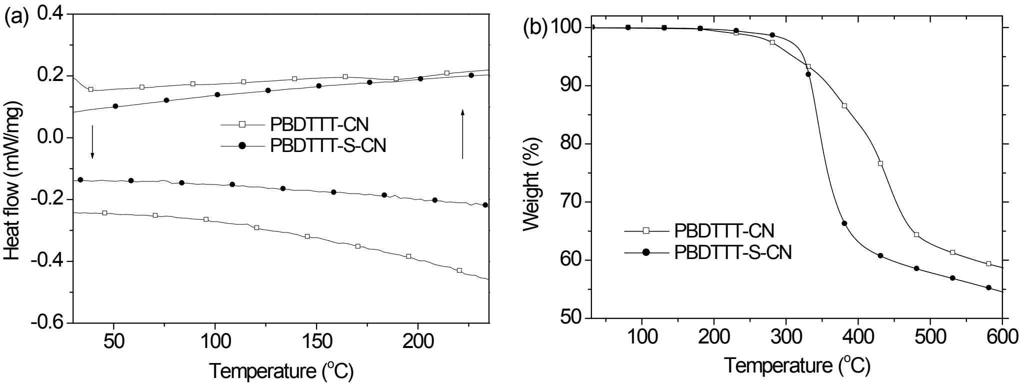

Fig. S1. (a) Differential scanning calorimetry (DSC) curves of PBDTT-CN PBDT-S-CN. (b) Thermogravimetric analysis (TGA) plots of PBDTT-CN PBDT-S-CN.

3. UV-vis, Fig. S2 and Table S1

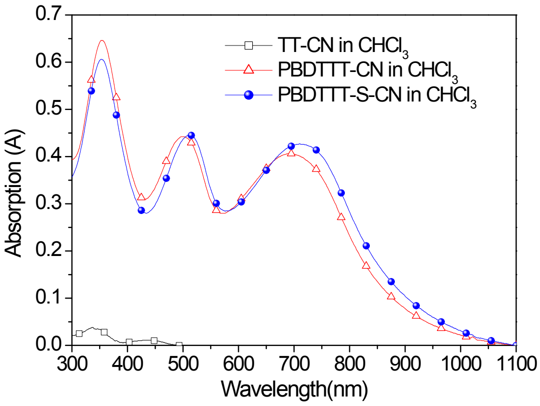

Fig. S2 UV-Vis absorption spectra of the monomer and copolymers in chloroform solutions.

Table S1. Photovoltaic properties of **PBDTTT-CN and PBDTTT-S-CN** based solar cell devices with copolymer/ $PC_{71}BM$ (1:1.5, w/w) blends.

Number	Concentration (M)	Abs. (nm) $\lambda_{\max}^{Sol}$	molar extinction coefficient ($M^{-1}cm^{-1}$)
TT-CN	1×10^{-6}	337, 414	2.95×10^{4} (337 nm) 6.998×10^{4} (414 nm)
PBDTTT-CN	1×10^{-6}	354, 499, 695	3.67×10^{5} (354 nm) 2.51×10^{5} (499 nm) 2.31×10^{5} (695 nm)
PBDTTT-S-CN	1×10^{-6}	353, 508, 711	4.18×10^{5} (353 nm), 3.08×10^{5} (508 nm) 2.94×10^{5} (711 nm)

4. Theoretical calculations and Fig. S3

The electronic properties of **PBDTTT-CN** and **PBDTTT-S-CN** trimers were simulated by density functional theory (DFT) calculations at the B3LYP/6-31G(d) level using the Gaussian 03 program suite.[4] The alkyl chains were replaced by methyl groups to save calculation time and simplify calculations process, which did not significantly affect the equilibrium geometries and the electronic properties.

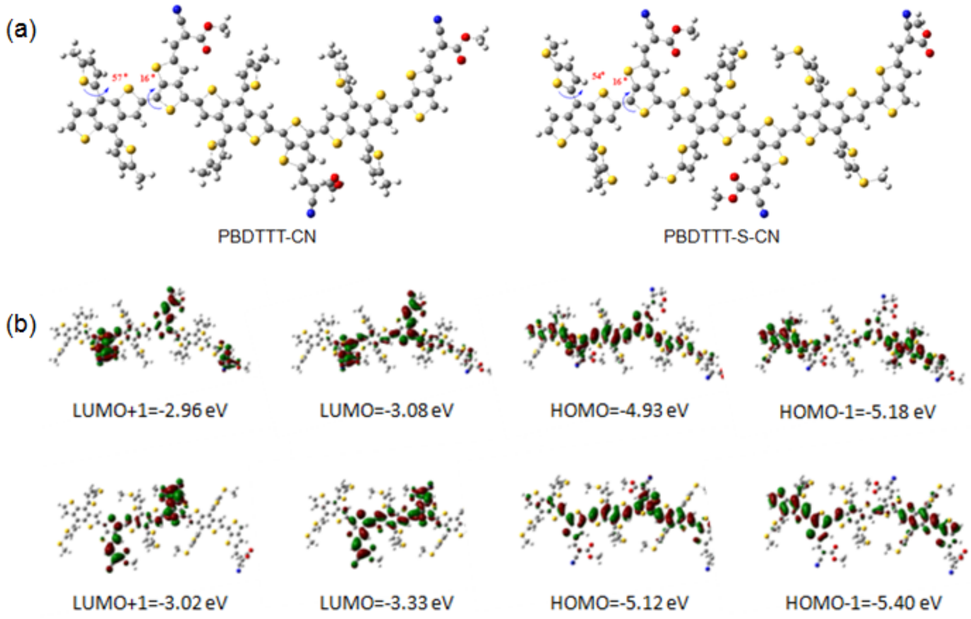

Fig. S3. (a) Optimized molecular structures of PBDTTT-CN and PBDTTT-S-CN. (b) LUMO+1, LUMO, HOMO and HOMO-1 of PBDTTT-CN (top) and PBDTTT-S-CN (bottom), obtained by Gaussian 09 at the B3LYP/6-31G(d) level.

5. X-ray diffraction (XRD) and Fig. S4

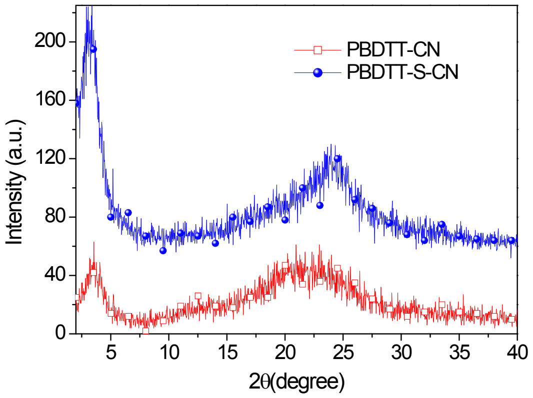

Fig. S4 X-ray diffraction patterns of PBDTTT-CN and PBDTTT-S-CN films on silicon wafers.

6. Hole mobility measurements (SCLC) and Fig. S5

Hole-only devices, with a structure of ITO/PEDOT/polymer/MoO_3/Au, were fabricated to determine the hole mobilities using the space charge limited current (SCLC) method reported previously.[5] The mobility was determined by fitting the dark current to the model of a single carrier SCLC, which is described by the following equation:

where J is the current, μ_h is the zero-field mobility, ε_0 is the permittivity of free space, ε_r is the relative permittivity of the material, d is the thickness of the active layer, and V is the effective voltage. The effective voltage can be obtained by subtracting the built-in voltage (V_{bi}) and the voltage drop (V_s) from the substrate's series resistance from the applied voltage (V_{appl}), $V=V_{appl} - V_{bi} - V_s$. The hole mobility can be calculated from the slope of the $J^{1/2} \sim V$ curves.

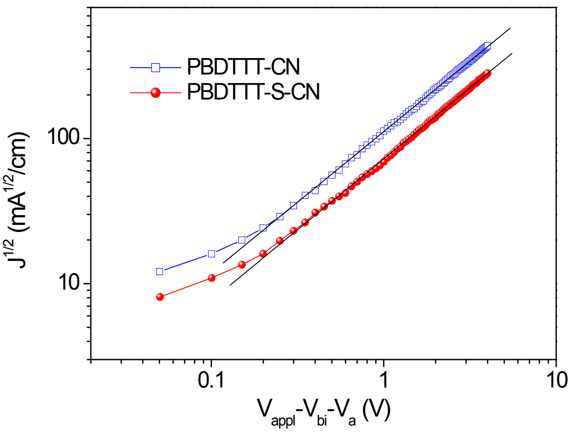

Fig. S5 $J^{1/2}$-V characteristics of PBDTTT-CN and PBDTTT-S-CN hole-only devices measured at ambient temperature.

7. Atomic Force Microscopy (AFM) and Fig. S6

The surface morphology of blended films of copolymer:$PC_{71}BM$ was studied by atom force microscopy (AFM) performed on a Nanoscope IIIa (Digital Instruments, CA) multimode AFM in the tapping mode.

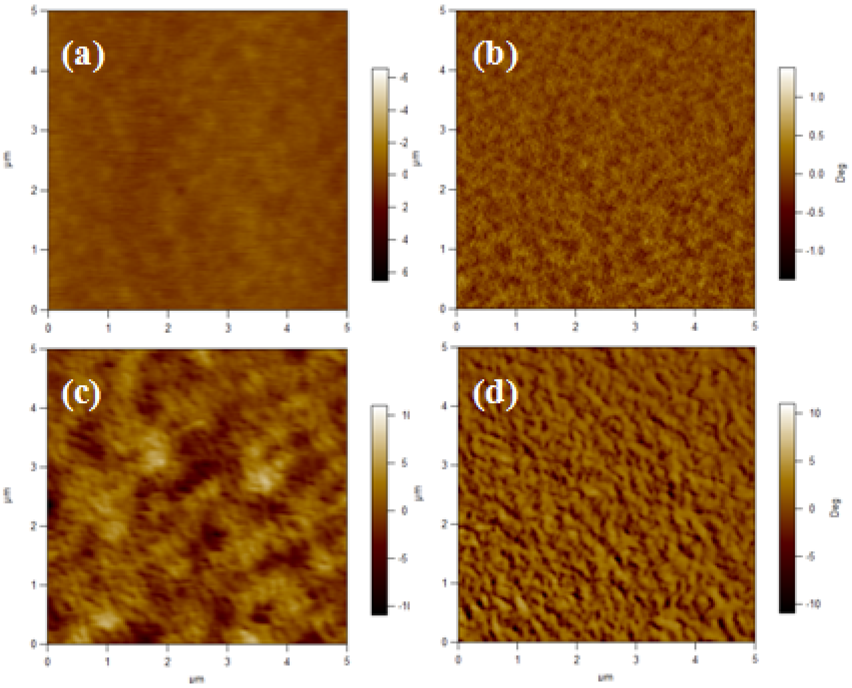

Fig. S6 AFM height and phase images of the active blend films (copolymer:$PC_{71}BM$=1:1.5, w/w) with 2% DIO. (a,b) PBDTTT-CN, (c,d) PBDTTT-S-CN. Image size: 5×5 μm^2.

8. Device fabrication and Table S2

Conventional polymer solar cells were fabricated with ITO glass as an anode, Ca/Al as a cathode, and blend film of the copolymer and $PC_{71}BM$ as a photosensitive layer. After spin-coating a 30 nm layer of PEDOT:PSS onto the pre-cleaned ITO substrate, the photosensitive layer was then prepared by spin-coating a blend solution of the copolymer and $PC_{71}BM$ (1:1.5, w/w) in *o*-dichlorobenzene on the ITO/PEDOT:PSS electrode with a typical concentration of 10 mg mL^{-1}. For the inverted devices, an about 40 nm ZnO thin film was deposited on the surface of ITO glass. The ZnO layer was pretreated with UV-ozone for 10 minutes and the conjugated polyelectrolyte of poly[(9,9-bis(3'-(N,N-dimethylamino)propyl)-2,7-fluorene)-*alt*-2,7-(9,9-dioctylfluorene)] dibromide (PNFBr) (5 nm) was spin-coated on the top of ZnO layer. The photoactive layer of PBDTT-FID:$PC_{71}BM$ composite (1:1.5, w/w) was then spin-coated on the top of above layer from 1,2-dichlorobenzene solution. Subsequently, about 10 nm MoO_3 and 100 nm Ag were deposited in turn through shadow masks by thermal evaporation. The device area was 0.09 cm^2. The current-voltage (I-V) characterization of the devices was carried out on a computer-controlled Keithley 236 Source Measurement system. The EQE was measured at a chopping frequency of 280 Hz with a lock-in amplifier (Stanford, SR830 DSP) during illumination with the monochromatic light from a xenon lamp. A solar simulator was used as the light source, and the light intensity was monitored by a standard Si solar cell. The thickness of films was measured using a Dektak 6 M surface profilometer.

Table S2. Photovoltaic properties of **PBDTTT-CN and PBDTTT-S-CN** based solar cell devices with copolymer/ PC$_{71}$BM (1:1.5, w/w) blends.

Polymer	Thickness [nm]	J_{sc} [mA cm^{-2}]	V_{oc} [V]	FF [%]	PCE$_{max}$ [%]	J_{sc} (calc.) [mA cm^{-2}]
PBDTTT-CN	95	9.65	0.79	0.53	4.06	9.21
PBDTTT-S-CN	100	11.57	0.83	0.57	5.45	11.08
PBDTTT-CN	100	10.68	0.78	0.59	4.94	10.03
PBDTTT-S-CN	105	13.85	0.82	0.62	7.00	13.26

9. References

(1) J. H. Park, Y. G. Seo, D. H. Yoon, Y. Lee, S. Lee, M. Pyo, K. Zong. *Eur. Polym. J.,* 2010, **46**, 1790.

(2) Y. Wang, Y. Liu, S. Chen, R. X. Peng, Z. Y. Ge. *Chem. Mater.,* 2013, **25**, 3196.

(3) C. H. Cui, W. Wong, Y. F. Li. *Energy Environ. Sci.,* 2014, **7**, 2276.