# Supporting Information

Optimizing energy levels and crystallinity of 2, 2'-bithiophene-3, 3'-dicarboximide-based polymer donors enables high-performance non-fullerene organic solar cells

Yi Tang , ‡[a] Lan Xie, ‡[b] Dingding Qiu,[b] Chen Yang,[b] Yanan Liu,[b] Yanan Shi,[b] Ziyun Huang,[b] Jianqi Zhang,[b] Jiawen Hu,*[a] Kun Lu, *[b] and Zhixiang Wei *[b]

Contents

1. Materials and synthesis

2. Characterization

3. Cyclic voltammograms of Poymers

4. UV-vis absorption

5. GIWAXS and TEM images of different post-treatment of PDTBDT-T-Cl:Y6 system

6. Mobility for Polymer: Y6 blend films

7. Device optimization

8. References

1. Materials and synthesis
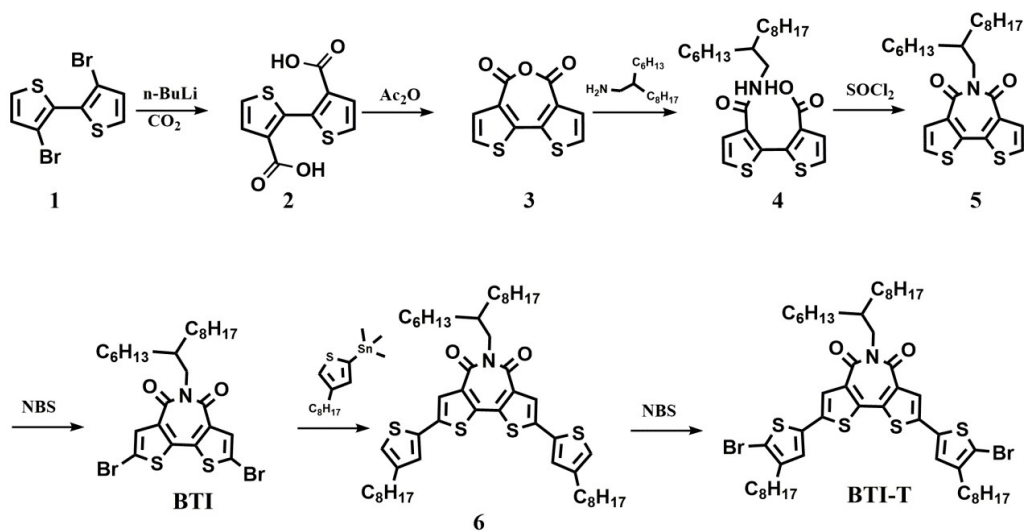
Scheme S1. The synthetic routes of **BTI-T**

Compound 2   [2, 2'-bithiophene]-3,3'-dicarboxylic acid

A solution of compound 1 (19.44 g, 60.0 mmol) in 150 mL of diethyl ether was added dropwise over 1 hour to a stirring solution of n-BuLi (82.5 mL, 1.6 M in hexanes) in 900 mL of ethyl ether at -78 ^{o}C. The reaction mixture was then allowed to stir for 1 hour at -78 ^{o}C before dry CO_2 was bubbled into the reaction mixture for 30 minutes. The reaction mixture was then allowed to stir for an additional 30 minutes before 1 mL of methanol was added, and the reaction was filtered cold to afford a colorless solid. The solid was dried overnight in vacuo at 100 ^{o}C dissolved in 200 mL of water, acidified with 6 M HCl (aq), and the resulting colorless precipitate isolated by filtration. This diacid was dried overnight in vacuo at 100 ^{o}C to yield 14.1 g (92% yield) of a colorless powder. ^{1}H NMR (400 MHz, CDCl$_3$, ppm): δ 7.45 (d, 2H), 7.10 (d, 2H). MS (EI): m/z (%) 253.79 (100) [M+].

Compound 3   Dithieno[3,2-c:2',3'-e]oxepine-4,6-dione

Diacid 2 (12.6 g, 49.4 mmol) was stirred in 100 mL of acetic anhydride at reflux for 6 hours. Upon cooling to 0 ^{o}C, the solid was collected by filtration, washed with 20 mL of cold acetic anhydride, and dried in vacuo at 120 ^{o}C overnight. The resulting light yellow crystals (11.4 g, 98% yield) were used without further purification. ^{1}H NMR (400 MHz, CDCl$_3$, ppm): δ 7.68 (d, 2H), 7.40 (d, 2H). MS (EI): m/z (%) 235.96 (100) [M+].

Compound 4   3'-((2-hexyldecyl) carbamoyl)-[2,2'-bithiophene]-3- carboxylic acid

A solution of 2-hexyldecyl amine solution (8.26 g, 34.2 mmol) in 500 mL of dichloromethane was added dropwise to a solution of compound 3 (8.08 g, 34.2 mmol) in 500 mL of dichloromethane. After the addition, the reaction was stirred under reflux for 2 hours. Upon removal of the solvent, the residue was purified by column chromatography using ethyl acetate as eluent to give product 4 as yellow oil (15.68 g, 96% yield). ^{1}H NMR (400 MHz, CDCl$_3$, ppm): δ 7.49 (d, 1H), 7.40 (d, 1H), 7.37 (d, 1H), 7.27 (d, 1H), 6.02 (s, 1H), 3.27 (m, 2H), 1.48 (m, 1H), 1.22 (m, 24H), 0.85 (m, 6H).

Compound 5   5-(2-hexyldecyl)-4H-dithieno[3,2-c:2',3'-e]azepine-4, 6(5H)-dione

A solution of compound 4 (15.68 g, 32.8 mmol) in 100 mL of thionyl chloride was heated under reflux for 2 hours. Next, all of the thionyl chloride was removed under vacuum. The residue was purified by column chromatography using dichloromethane: hexane (1:1) as eluent, to give the product 5 (13.28 g, 88% yield) as a pale yellow oil. ^{1}H NMR (400 MHz, CDCl$_3$, ppm): δ 7.72 (d, 2H), 7.23 (d, 2H), 4.24 (d, 2H), 1.92 (m, 1H), 1.28 (m, 24H), 0.87 (m, 6H).

BTI   2, 8-dibromo-5-(2-hexyldecyl)-4H-dithieno[3,2-c:2',3' -e]azepine-4,6(5H)-dione

N-Bromosuccinimide （NBS） (1.30 g, 7.30 mmol) was added to a solution of imide 5 (1.68 g, 3.65 mmol) in 30 mL of dichloromethane followed by addition of ferric chloride (11.8 mg, 0.07 mmol). The reaction mixture was allowed to stir in the dark for 6 hours before 10 mL of saturated aqueous Na$_2$SO$_3$ was added and stirring continued for an additional 0.5 hour. The reaction mixture was then poured into 300 mL of dichloromethane, washed three times with 200 mL of water and once with 100 mL of brine, and dried over Mg$_2$SO$_4$. The organic solution was next filtered and concentrated by evaporation to give a light yellow solid, which was purified by column chromatography using DCM: hexane (1:1) as eluent to give the product (2.23 g, 98% yield). ^{1}H NMR (500 MHz, CDCl3, ppm): δ 7.66 (s, 2H), 4.17 (d, 2H), 1.86 (m, 1H), 1.24 (m, 24H), 0.87 (m, 6H).

***Compound 6***   5-(2-hexyldecyl)-2,8-bis (4-octylthiophen-2-yl)-4H-dithieno [3,2-c:2',3'-e] azepine- 4,6(5H)- dione

An air-free flask was charged with BTI (2.00g, 3.24 mmol), trimethyl(4-octylthiophen-2-yl)stannane (2.33 g, 6.48 mmol), Pd(PPh$_3$)$_4$ (7.45 g, 6.48 mmol), and 100 mL of THF. The reaction mixture was stirred at 90 °C for 12 hours, then the solvent was removed by evaporation to afford a red solid, which was purified by column chromatography over silica gel with CH$_2$Cl$_2$/hexane (1:3) as eluent to

afford an orange oil as the product (1.31 g, 68% yield). ^{1}H NMR (400 MHz, CDCl$_3$, ppm): δ 8.03 (s, 2H), 7.43 (s, 2H), 7.15 (s, 2H), 3.55 (d, 2H), 1.29 (m, 72H), 0.87 (m, 12H).

BTI-T 2, 8-bis (5-bromo-4-octylthiophen-2-yl)-5-(2-hexyldecyl)-4H-dithieno[3,2-c:2',3'-e] azepine-4,6(5H)-dione

NBS (355.96 mg, 2 mmol) was added to a solution of compound 6 (848.38 mg, 1 mmol) in CHCl3/HOAC (4:1; total volume = 40 mL) in one portion. The reaction mixture was stirred at room temperature for 4 hours, and 50 mL of H$_2$O was then added. Next, the reaction mixture was extracted three times with 50 mL of CH$_2$Cl$_2$, and the combined organic layer was washed with 50 mL of H$_2$O, 50 mL of 10% aqueous KOH solution, 50 mL of brine, and dried over MgSO$_4$. After filtration, the solvent was removed by evaporation to afford an orange solid, which was purified by column chromatography over silica gel with CH$_2$Cl$_2$/hexane (1:3) as eluent. The desired product was obtained as an orange solid (945 mg, 89% yield). [1] H NMR (500 MHz, CDCl$_3$, ppm): δ 7.66 (s, 2H), 6.85 (s, 2H), 4.17 (d, 2H), 2.68 (t, 4H), 1.86 (m, 1H), 1.24 (m, 72H), 0.87 (m, 12H). ^{13}C NMR (400 MHz, CDCl$_3$, ppm): δ 161.53 (s), 136.54 (s), 135.12 (s), 134.89 (s), 133.78 (s), 131.01 (s), 128.90 (s), 125.48 (s), 113.53 (s), 49.56 (s), 36.43 (s), 31.91 (s), 31.84 (s), 31.75 (s), 31.70 (s), 30.08 (s), 29.76 (s), 29.57 (s), 29.34 (s), 26.46 (d, J = 8.0 Hz), 22.67 (d, J = 8.0 Hz), 14.11 (s).

DTBDT   BTI   PDTBDT

DTBDT   BTI-T   PDTBDT-T
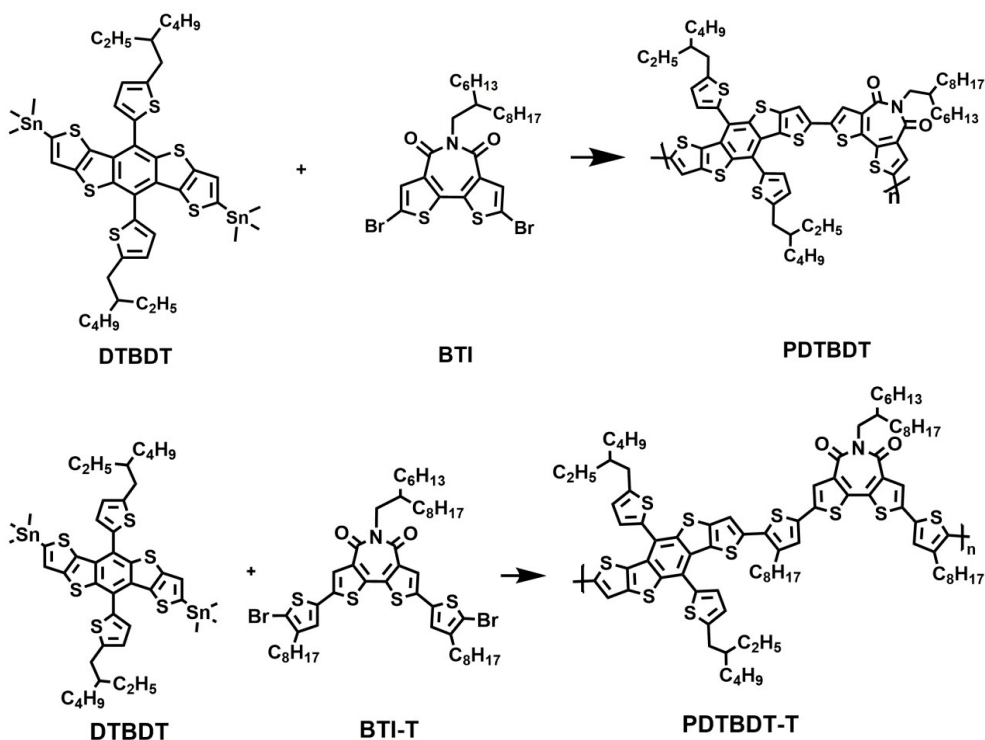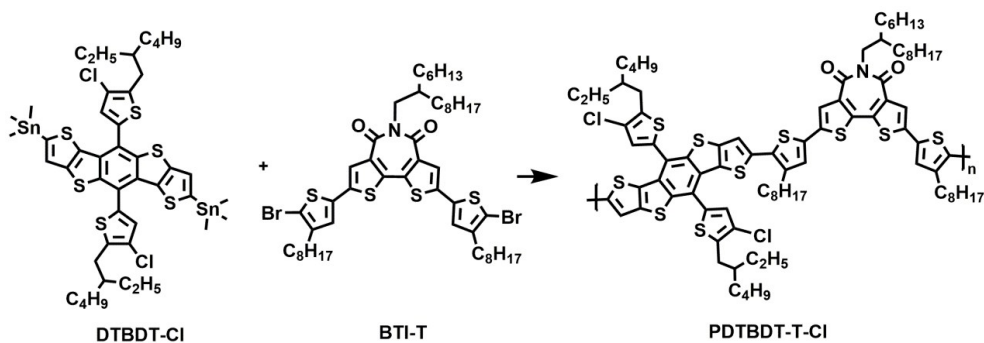
Scheme S2. The synthetic routes of polymers

Synthesis of the polymer PDTBDT This polymer was prepared according to the method of Stille coupling. Pd(PPh$_3$)$_4$ (11.5 mg, 0.01 mmol), compound DTBDT (101.67 mg, 1 mmol) and compound BTI (61.75 mg 1mmol) were put into a three-neck flask. The mixture was flushed with argon for 10 minutes and then 10 mL toluene was added. Under the protection of argon, the reactant was heated to 110 °C reflux for 18 hours. The mixture was cooled to room temperature and a solution of KF (5 g) in water (10 mL) was added and stirred at room temperature for 2 hours to remove the tin impurity. The mixture was extracted with toluene (2 × 150 mL), washed with water (2 × 150 mL), and dried over anhydrous MgSO$_4$. The solution was concentrated to 5 mL and poured into 30 mL of methanol and then filtered into a Soxhlet thimble. Soxhlet extraction was performed with methanol, hexanes, and chloroform. The polymer was recovered from the chloroform fraction by rotary evaporation. Finally, the polymer was further purified by size exclusion column chromatography over Bio-Rad Bio-Beads S = X1 eluting with chloroform and only chosen the medium narrow fraction of the column to afford a solid. The solid was dried under vacuum overnight. ^{1}H NMR (400 MHz, CDCl$_3$, ppm): δ 6.42-7.98 (br, aromatic protons), 4.30 (br, aliphatic protons), 3.01 (br, aliphatic protons), 0.89-1.56 (br, aliphatic protons).

The synthesis of PDTBDT-T and PDTBDT-T-Cl were similar to PDTBDT.

PDTBDT-T ^{1}H NMR (400 MHz, CDCl$_3$, ppm): δ 6.59-7.84 (br, aromatic protons), 4.30 (br, aliphatic protons), 3.01 (br, aliphatic protons), 0.88-1.43 (br, aliphatic protons).

PDTBDT-T-Cl ^{1}H NMR of PDTBDT (400 MHz, CDCl$_3$, ppm): δ 6.58-7.89 (br, aromatic protons), 4.30 (br, aliphatic protons), 3.01 (br, aliphatic protons), 0.67-1.54 (br, aliphatic protons).
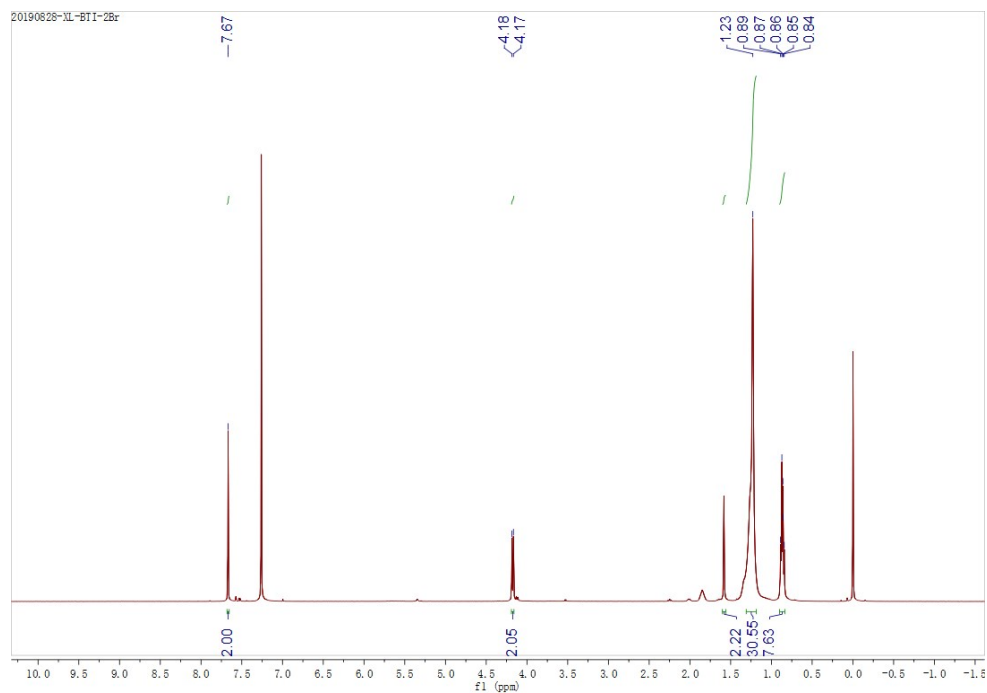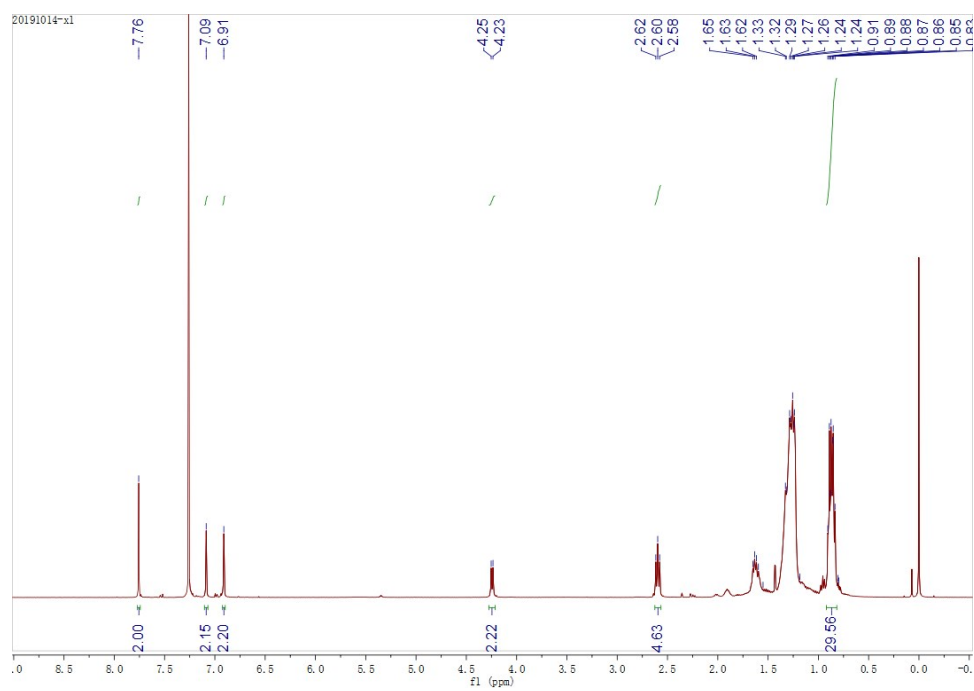
Fig. S1 The ^{1}H NMR of BTI
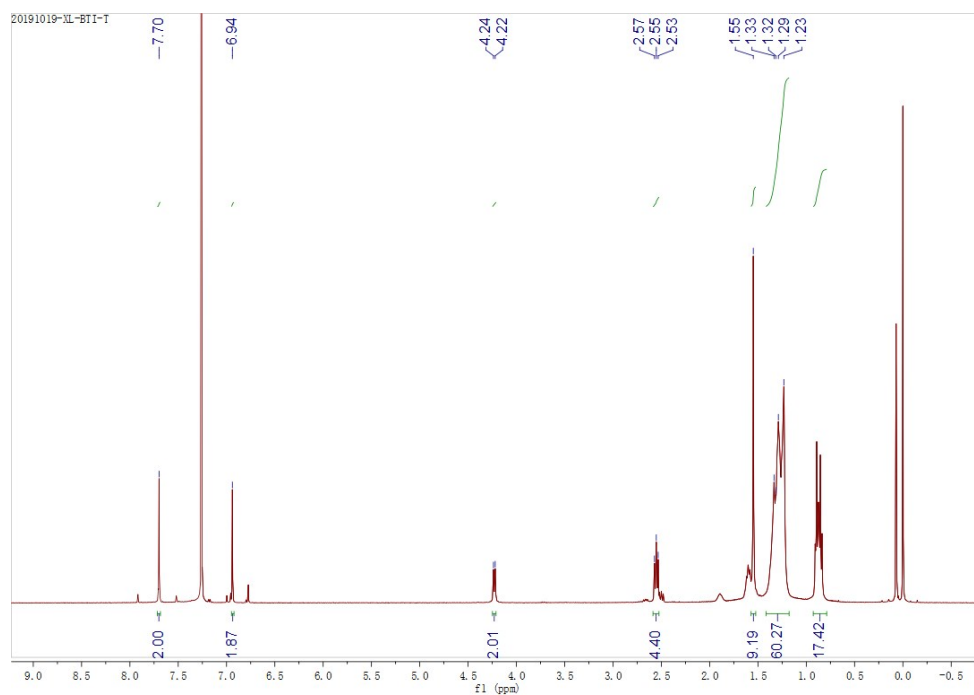

Fig. S2 The ^{1}H NMR of compound 6

Fig. S3 The ^{1}H NMR of BTI-T
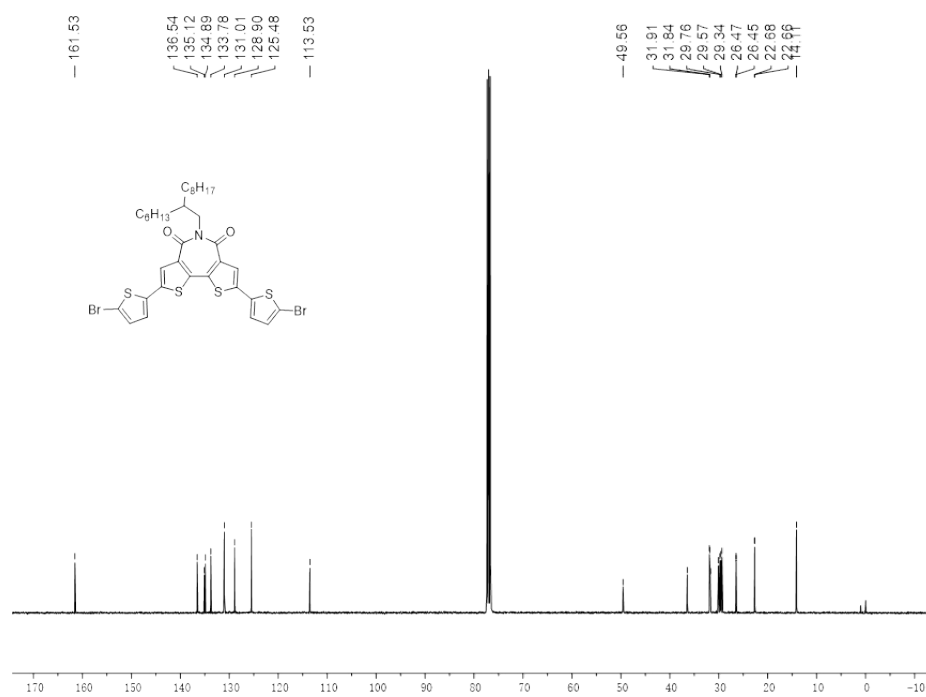

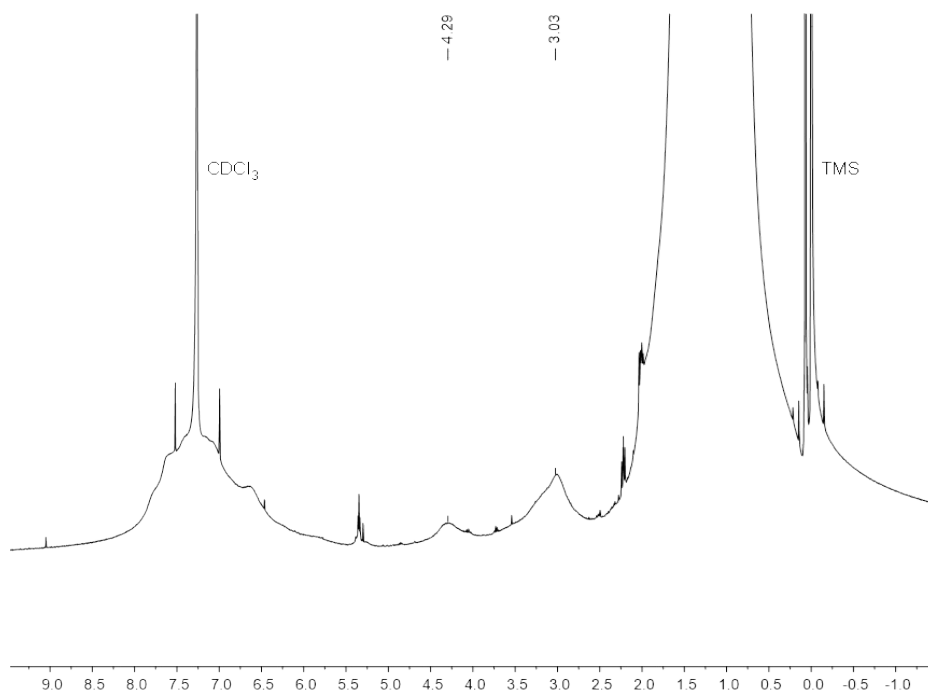**Fig. S4** The ^{13}C NMR of BTI-T

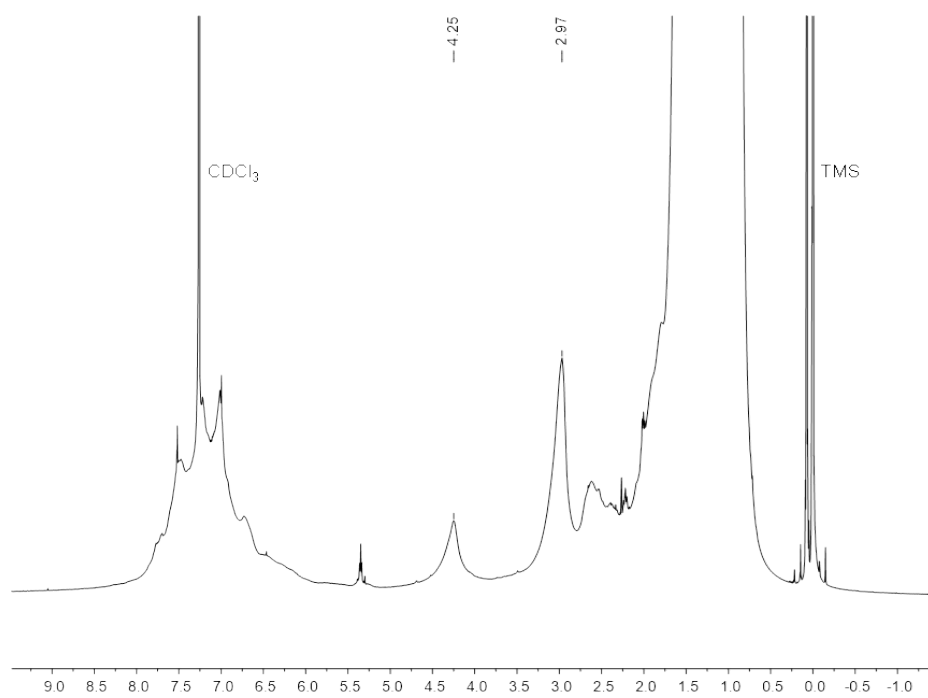**Fig. S5** The ^{1}H NMR of PDTBDT

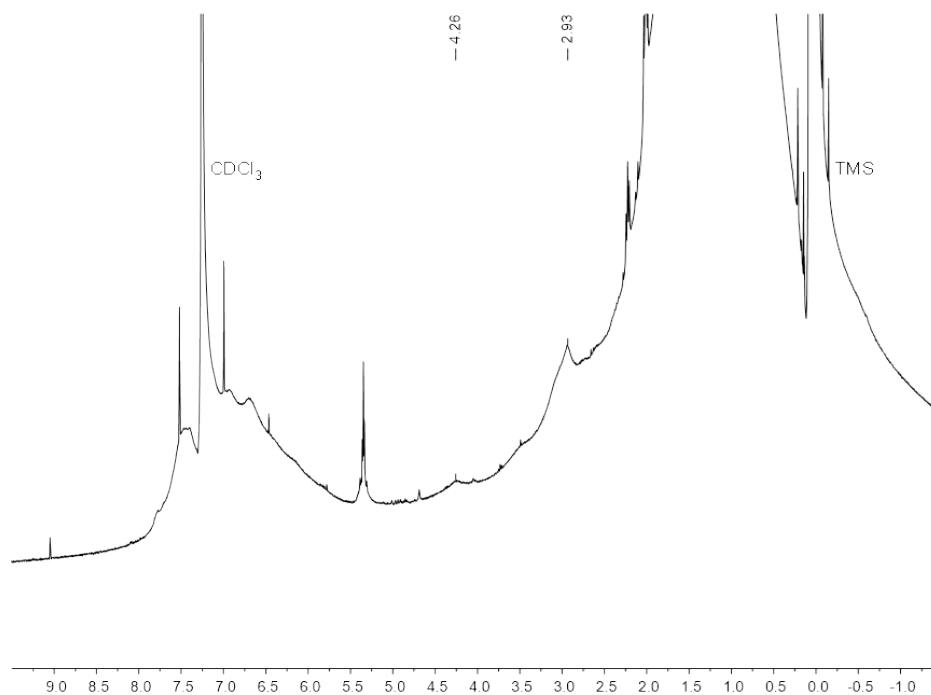**Fig. S6** The ^{1}H NMR of PDTBDT-T

Fig. S7 The ^{1}H NMR of PDTBDT-T-Cl

2. Characterization

UV-vis absorption and molecular energy level test

The UV-Vis spectra in solution and solid-state are determined by Perkin Elmer Lambda 950 spectrophotometer. Cyclic voltammetry (CV) is used to measure the energy level of molecules. The experiment was carried out by an electrochemical workstation (VMP3 Biologic, France), in a 0.1 mol L^{-1} tetrabutylammonium phosphorus hexafluoride (Bu4NPF6) acetonitrile solution, using a Pt electrode coated with target films as the working electrode, Pt plate was used as counter electrode, and Ag/Ag$^+$ electrode was used reference electrode, respectively. Redox potentials were internally calibrated using the ferrocene/ferrocenium (Fc/Fc$^+$) redox couple (-4.8 eV).

Fabrication and characterization of OSCs

All the OSCs were fabricated with a conventional structure of glass/ITO/PEDOT: PSS/active layer/PFN-Br/Ag. The ITO-coated glass ultrasonically cleaned in detergent, deionized water, acetone and isopropanol for 20 minutes in sequence, and then treated by UVO 15 minutes. The PEDOT: PSS layer was placed on the ITO substrate by spin-coating at 3500 rpm for 30 seconds, then annealed at 15 ^{o}C for 15 minutes, and then transferred to a nitrogen-filled glove box. The total concentration of the blend solution of Polymer: Y6 was ca.16 mg/ml. The donor and acceptor materials was dissolved in chloroform at 50 ^{o}C for 1 hour, with 0.5% volume ratio of CN as a solvent additive, and then spin-

coated for 35 seconds at 4000 rpm to form the active layer. Subsequently, thermal annealing at 110 °C for 10 minutes, followed by solvent annealing at THF for 20 seconds to further optimize the morphology of the active layer. Then, the PFN-Br interlayer was deposited onto the active layer by spin-coating the solution for 30 seconds at 3000 rpm. Finally, Ag layer (160 nm) was used as the top electrode by vapor deposition in a high vacuum.

A solar cell device contains four cells, and the effective area of each cell is 4 mm^2. Newport Thermal Oriel 91159A solar simulator was used for J–V curves measurement under AM 1.5 G (100 mW cm^{-2}). Newport Oriel PN 91150 V Si-based solar cell was applied for light intensity calibration. J–V measurement signals were recorded by a Keithley 2400 source-measure unit. Oriel Newport system (Model 66902) was used for external quantum efficiency (EQE) test in a N$_2$-filled glovebox.

Charge carrier mobility

Hole and electron mobility are tested by space-charge limited current (SCLC) method, and the conditions of the active layer are the same as the device preparation. The hole mobility test adopts the structure of ITO/ZnO/active layer/PFN-Br/Al, and the electron mobility adopts the structure of ITO/PEDOT: PSS /active layer/MoO$_x$/Ag.[1,2] The J–V curves in the range of 0 to 5 V were gained by Keithley 2400 source-measure unit in the dark. Use the following formula to fit the J-V curve to get the mobility:

$$J = \frac{9}{8} \varepsilon_0 \varepsilon_r \mu_0 \frac{V^2}{L^3} exp\, (\beta \sqrt{V/L}\,)$$

where J is the current density, L is the thickness of the active layer, μ_0 is the mobility, ε_0 is the vacuum dielectric constant, ε_r is the relative dielectric constant of the transport medium, V (= V_{app} - V_{bi}) is the internal voltage, where V_{app} is the applied voltage and V_{bi} is the built-in voltage.

AFM and TEM characterization

Dimension 3100 is the instrument used by AFM. The preparation method of the sample of the AFM is the same as the preparation method of the active layer, but the size of the substrate is 1×1 cm^2 according to the model of the AFM used. Tecnai G2 F20 U-TWIN is the instrument used by TEM. The conditions for preparing the active layer of the TEM sample are the same as those prepared by the device, spin-coated on ITO, then immerse it in water, and transfer the sample with copper mesh for testing.

GIWAXS

GIWAXS was measured using the beamline of 7.3.3. The blending or neat films for GIWAXS were made by the same method for device active layer except for the substrate as Si/PEDOT: PSS.

Contact angle measurement

According to the reported literature, calculate the surface tension of each pure material, and calculate the interfacial tension between the two materials from the surface tension of each material. Use two liquids (water and glycerol) to measure the contact angle on various pure films[3].

$$\gamma=\gamma^d+\gamma^p$$

γ is the surface tension of each phase , γ^d is the dispersion component and γ^p the polar component.

$$\gamma_i(1+\cos\theta)= 2(\gamma_i^d \gamma^d)^{1/2} + 2(\gamma_i^p \gamma^p)^{1/2}$$

γ_i is the surface tension of the liquid droplet (water or glycerol), Then, we calculate the Flory-Huggins interaction parameter by

$$\sigma=K(\gamma_{Donor}^{-2}-\gamma_{Acceptor}^{-2})^2$$

γ is the surface energy of the organic material, K is the proportionality constant.

3. UV-vis absorption
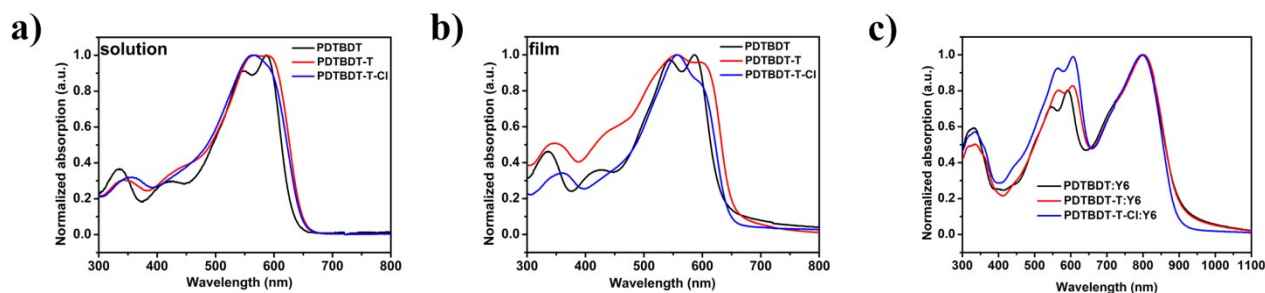
Fig. S8 UV-vis absorption spectra of Polymers. (a) In solution. (b) In film. (c) In blend film.

Table S1. Basic Optical and Chemical Properties of polymers

Polymer	λ_{max} (nm)	λ_{max} (nm)	λ_{edge} (nm)	E_g^{opt}	HOMO	LUMO
	Solution	Film	Film	(eV)	(eV)	(eV)
PDTBDT	585	585	645	1.92	− 5.67	− 3.28
PDTBDT-T	563	555	662	1.87	− 5.40	− 3.21
PDTBDT-T-Cl	562	556	654	1.90	− 5.58	− 3.26

4. Cyclic voltammograms of Polymers
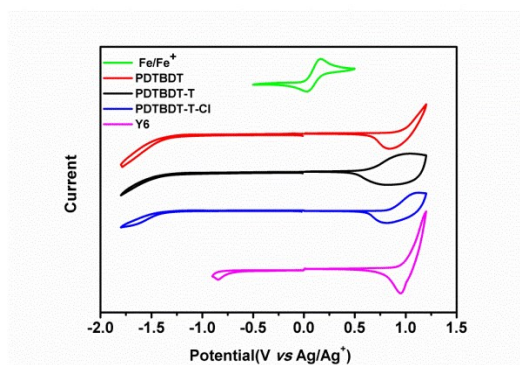
Fig. S9 Molecular energy levels determined by the cyclic voltammetry (CV).

5. GIWAXS and TEM images of different post-treatment of PDTBDT-T-Cl:Y6 system

Fig. S10 (a) 2D GIWAXS graphs of the PDTBDT-T-Cl：Y6 blend film with different post-treatment method.

(b) Corresponding curves of 2D GIWAXS patterns.(c) TEM images.

6. Motilities for Polymer: Y6 blend films

Fig. S11 (a) The hole motilities in Polymer:Y6 films. (b) The electron motilities in Polymer:Y6 films.

7. Device optimization

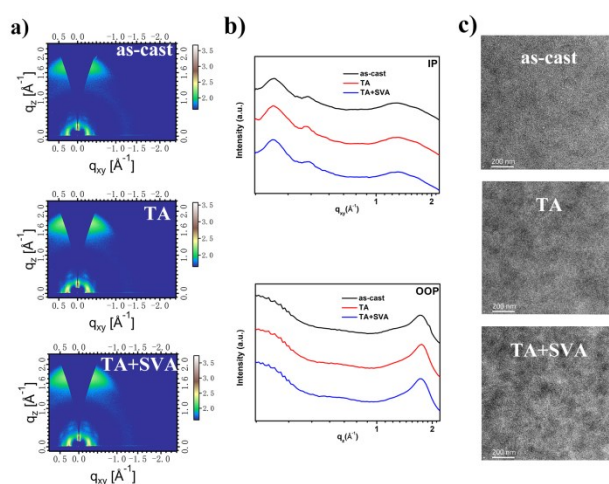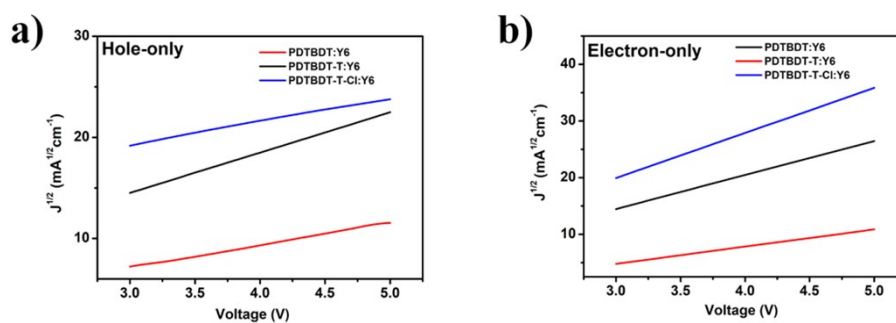Detailed photovoltaic parameters of the PDTBDT-T-Cl: Y6-based devices by varied conditions.

Table S2. The Optimization of concentrations, the D/A ratio is 1: 1.2; the films are thermally annealed at 110 °C for 10 minutes.

Concentration (mg/ml)	V_{OC} (V)	J_{SC} (mA cm^{-2})	FF (%)	PCE (%)
14	0.865	20.87(21.00±0.14)	67.51(66.35±1.17)	12.13(11.97±0.15)
16	0.868	22.63(22.91±0.27)	67.19(66.28±0.91)	13.13(13.11±0.03)
18	0.864	20.81(22.00±0.23)	63.19(63.78±0.59)	12.07(12.02±0.06)

Table S3. The Optimization of D/A ratios, the total concentration is 16 mg/ml; the films are thermally annealed at 110 °C for 10 minutes.

D/A	V_{OC} (V)	J_{SC} (mA cm^{-2})	FF (%)	PCE (%)
1:1	0.862	22.02(21.12±0.14)	65.64(65.10±1.17)	11.91 (11.85±0.15)
1:1.2	0.868	22.63(22.91±0.27)	67.19(66.28±0.91)	13.13(13.11±0.03)
1:1.4	0.863	21.14 (21.07±0.07)	67.64 (67.95±0.31)	12.35(12.37±0.15)
1:1.6	0.853	20.65 (20.64±0.04)	67.62(66.97±0.64)	11.99(11.87±0.12)

Table S4. The Optimization of thermal annealing temperatures, the D/A ratio is 1: 1.2; the total concentration is 16 mg/ml.

TA (℃)	V_{OC} (V)	J_{SC} (mA cm^{-2})	FF (%)	PCE (%)
-	0.873	21.03(21.02±0.02)	66.56(66.30±0.26)	12.28(12.22±0.07)
90	0.864	22.32(22.29±0.04)	66.76(66.34±0.43)	12.93(12.83±0.11)
110	0.856	23.34(23.19±0.30)	67.42(66.53±0.75)	13.53(13.28±0.15)
130	0.842	22.90(22.70±0.61)	63.90(61.32±0.11)	12.21(11.87±0.21)
150	0.812	23.81(23.65±0.12)	60.72(60.65±1.24)	11.91(11.86±0.11)

Table S5. The optimization by adding CN as additive, the D/A ratio is 1: 1.2, the total concentration is 16 mg/ml, and the films are thermally annealed at 110 °C for 10 minutes.

Additive	V_{OC} (V)	J_{SC} (mA cm^{-2})	FF (%)	PCE (%)
-	0.856	23.34(23.19±0.30)	67.42(66.53±0.75)	13.53(13.28±0.15)
0.5%CN	0.858	24.12(24.05±0.03)	67.75(67.26±0.37)	14.01(13.87±0.12)
1%CN	0.867	20.14(19.95±0.19)	66.35(66.18±0.15)	11.63(11.49±0.14)

Table S6. The optimization of solvent annealing for PDTBDT-T-Cl: Y6 at TA 110 °C.

SVA	V_{OC} (V)	J_{SC} (mA cm^{-2})	FF (%)	PCE (%)
-	0.858	24.12(24.05±0.03)	67.75(67.26±0.37)	14.01(13.87±0.12)
THF(20s)	0.860	24.46(24.49±0.32)	71.65(69.92±0.41)	15.63(14.85±0.32)
THF(40s)	0.859	23.28(23.77±0.48)	66.58(65.95±0.63)	13.35(13.47±0.20)
THF(60s)	0.864	23.49(23.89±0.17)	66.53(65.13±1.4)	13.55(13.48±0.07)
CF(20s)	0.862	22.92(22.82±0.16)	67.39(67.91±0.52)	13.35(13.36±0.01)
CF(40s)	0.858	22.80(22.91±0.10)	67.49(67.44±0.04)	13.25(13.32±0.08)
CF(60s)	0.864	23.34(23.28±0.25)	66.95(67.22±0.29)	13.43(13.50±0.11)

Table S7. Summary of crystal coherence length (CCL) and d-spacing of neat polymer films

		LOCATION (Å^{-1})	FWHM (Å^{-1})	CCL (Å)	d-space (Å)
PDTBDT	IP	0.24	0.082	68.93	26.17
PDTBDT-T	(100)	0.27	0.065	86.95	23.25
PDTBDT-T-Cl		0.28	0.070	80.74	22.43
PDTBDT	OOP	-	-	-	-
PDTBDT-T	(010)	1.67	0.2553	22.14	3.76
PDTBDT-T-Cl		1.67	0.2269	24.91	3.76

Table S8. Summary of crystal coherence length (CCL) and d-spacing of blend films.

		LOCATION ($Å^{-1}$)	FWHM ($Å^{-1}$)	CCL ($Å$)	d-space ($Å$)
PDTBDT:Y6	IP	0.26	0.074	76.38	24.15
PDTBDT-T:Y6	(100)	0.28	0.040	141.30	22.43
PDTBDT-T-Cl:Y6		0.27	0.042	134.57	23.25
PDTBDT:Y6	OOP	1.75	0.048	11.78	3.59
PDTBDT-T:Y6	(010)	1.75	0.045	12.56	3.59
PDTBDT-T-Cl:Y6		1.71	0.027	20.93	3.67

8. References

1 G. G. Malliaras, J. R. Salem, P. J. Brock, and C. Scott, *Phys. Rev. B*, 1998, **58**, 13411.

2 Arnold B. Tamayo, Bright Walker, and Thuc-Quyen Nguyen, *J Phys. Chem. C*, 2008, **112**, 11545−11551.

3 S. Pang, R. Zhang, C. Duan, S. Zhang, X. Gu, X. Liu, F. Huang and Y. Cao, *Adv. Energy Mater.*, 2019, **9**, 1901740.

4 J. Wu, G. Li, J. Fang, X. Guo, L. Zhu, B. Guo, Y. Wang, G. Zhang, L. Arunagiri, F. Liu, H. Yan, M. Zhang and Y. Li, *Nat. Commun.,* 2020, **11**, 4612.