

Supporting Information

Low Band-Gap Weak Donor-Strong Acceptor Conjugated Polymer for Organic Solar Cell

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EXPERIMENTAL SECTION

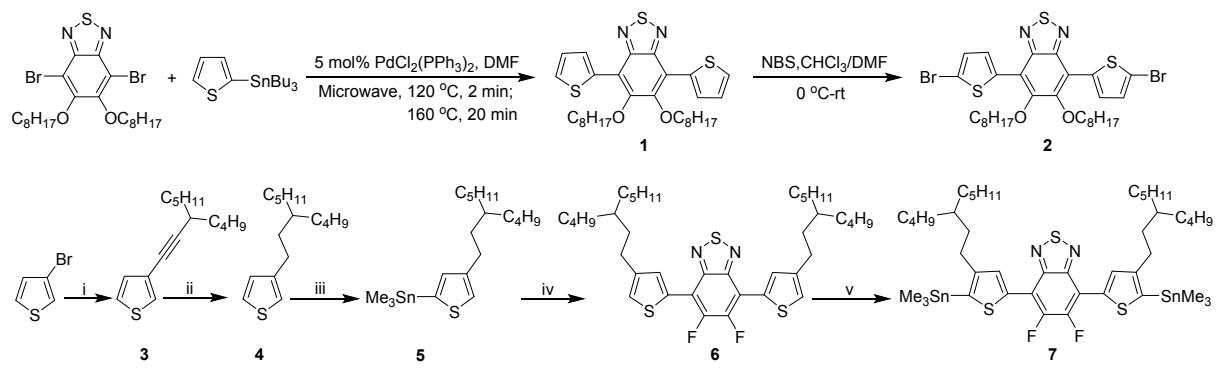
¹H NMR data were acquired on a Bruker DPX 400 MHz spectrometer. Differential scanning calorimetry (DSC) was carried out under nitrogen on a TA Instrument DSC Q100 instrument (scanning rate of 10 °C min⁻¹). Thermogravimetric analysis (TGA) was carried out using a TGA Q500 instrument (heating rate of 10 °C min⁻¹). Molecular weight determinations were carried out in hot chlorobenzene solution on a Shimadzu Prominence CBM-20A series HPLC using an Agilent PLGel 5 micrometer Mixed-C column (79911 GP-MXC) with polystyrene calibration standards. Cyclic voltammetry experiments were performed using an Autolab potentiostat (model PGSTAT30) by Echochimie. A glassy carbon disk was used as working electrode, a platinum wire as counter electrode and a silver wire as reference electrode. Ferrocene was used for potential calibration. UV-Vis-NIR spectra were recorded on a Shimadzu model 2501-PC.

All chemicals and reagents were used as purchased unless stated otherwise. Monomer 4,7-bis(5-bromothiophen-2-yl)-5,6-bis(octyloxy)benzo[*c*][1,2,5]thiadiazole (**2**) and 4,7-bis(4-(3-butyloctyl)-5-(trimethylstannyl)thiophen-2-yl)-5,6-difluorobenzo[*c*][1,2,5]thiadiazole (**7**) were prepared following below synthetic routes (Scheme **S1**).

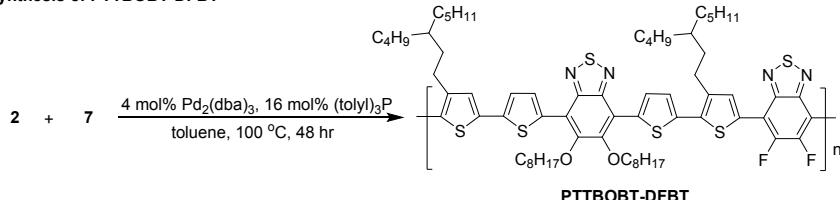
Scheme S1. Synthetic route to weak donor-strong acceptor copolymer **PTTBOBT-DFBT**. i)

5 mol% $\text{PdCl}_2(\text{PPh}_3)_2$, 10 mol% CuI , toluene:triethyl amine = 1:1, 80 $^{\circ}\text{C}$, 12h; ii) $\text{Pd}(\text{OH})_2$, THF/EtOH, 60 $^{\circ}\text{C}$, 24h; iii) LTMP, THF, Me_3SnCl , 78 $^{\circ}\text{C}$ to rt, 12h; iv) 4,7-dibromo-5,6-difluorobenzo[*c*][1,2,5]thiadiazole, 5 mol% $\text{PdCl}_2(\text{PPh}_3)_2$, Microwave, 120 $^{\circ}\text{C}$, 2 min, then 160 $^{\circ}\text{C}$, 20 min; v) LTMP, THF, Me_3SnCl , -78 $^{\circ}\text{C}$ to rt, 12h.

1) Synthesis of monomer **2** and **7**



2) Synthesis of **PTTBOBT-DFBT**



5,6-bis(octyloxy)-4,7-di(thiophen-2-yl)benzo[*c*][1,2,5]thiadiazole (1)

To a 20 mL microwave reactor vial, 4 mmol 4,7-dibromo-5,6-bis(octyloxy)benzo[*c*][1,2,5]thiadiazole and 10 mmol tributyl(thiophen-2-yl)stannane were added, then the vial was transferred into glove box. Anhydrous degassed DMF (10 mL) and 0.2 mmol $\text{PdCl}_2(\text{PPh}_3)_2$ were added. Reaction vial was sealed, and heated at 120 $^{\circ}\text{C}$ for 2 minutes then at 160 $^{\circ}\text{C}$ for 20 mins in a microwave reactor. After reaction was completed, it was quenched with 100 mL water, and then extracted with dichloromethane, dried over magnesium sulphate. Subsequent column chromatography gave pure product in 90% yield.

^1H NMR is identical with literature.⁴⁸

4,7-bis(5-bromothiophen-2-yl)-5,6-bis(octyloxy)benzo[c][1,2,5]thiadiazole (2)

To a 100 mL round bottom flask, 3.4 mmol 5,6-bis(octyloxy)-4,7-di(thiophen-2-yl)benzo[c][1,2,5]thiadiazole (**1**) and 20 mL chloroform were added. 6.8 mmol *N*-bromosuccinimide in 10 mL DMF was slowly dropwise into the reaction vial with ice-water bath. Reaction was kept stirring overnight at room temperature. After reaction was completed, it was quenched with 100 mL water, and then extracted with dichloromethane, dried over magnesium sulphate. Subsequent column chromatography and recrystallization from ethanol gave yellow crystal product in 89% yield. ¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.36 (d, *J* = 4 Hz, 2H), 7.17 (d, *J* = 4 Hz, 2H), 4.12 (q, *J* = 7.2 Hz, 4H), 1.96-1.90 (m, 4H), 1.46-1.30 (m, 18H), 0.89 (t, *J* = 6.8 Hz, 6H).

3-(3-butyloct-1-yn-1-yl)thiophene (3)

To a solution of 3-bromothiophene (20 mmol) and 5-ethynyldecane (22 mmol) in triethylamine- Toluene (1:1, 80 mL) were added dichlorobis(triphenylphosphine) palladium(II) (1 mmol) and copper(I) iodide (1 mmol). The reaction mixture was stirred at 80 °C overnight. Solvent removal by evaporation gave a residue that was purified by flash column chromatography using hexane as eluent. The pure product was collected as light yellow oil in 75% yield. ¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.35 (s, 1H), 7.27 (d, *J* = 4.8 Hz, 1H), 7.08 (d, *J* = 4.8 Hz, 1H), 2.52 (m, 1H), 1.54 -1.35 (m, 14H), 0.93 (t, *J* = 6.4 Hz, 6H).

3-(3-butyloctyl)thiophene (4)

To a solution of 3-(3-butyloct-1-yn-1-yl)thiophene (**3**) (14 mmol) in THF/EtOH (20ml/ 40ml) was added Pd(OH)₂/C (20 wt% dry basis on activated carbon) (1.4 g, 40% by weight) with a hydrogen balloon and the mixture stirred 12 hrs at 60°C. The reaction was monitored by ¹HNMR, another batch of Pd(OH)₂/C (0.7g, 20% by weight) was added to the mixture after

24 hours. The solution was filtered through Celite, the solvent was removed by evaporation and the residue was purified by chromatography using hexane as eluent to give product in 85% yield as light yellow oil. ^1H NMR (400MHz, CDCl_3) δ (ppm) 7.27 (s, 1H), 6.97 (t, J = 4.8 Hz, 1H), 2.63 (t, J = 8.0 Hz, 2H), 1.62-1.58 (m, 2H), 1.30 (m, 14H), 0.93-0.90 (m, 6 H).

(4-(3-butyloctyl)thiophen-2-yl)trimethylstannane (5)

To a solution of 3-(3-butyloctyl)thiophene (**4**) (9.5 mmol) in 20 mL THF was added dropwise freshly prepared tetramethylpiperidine lithium THF solution (11.4 mmol) under dry ice/acetone bath, after the mixture stirred at same temperature for 1 hour, trimethyl stanyl chloride (11.4 mmol) was added one portion. The reaction was slowly warmed to room temperature and stirred overnight. Reaction was quenched with H_2O , extracted with dichloromethane, washed with brine, dried over MgSO_4 , filtered through Celite, the solvent was removed by evaporation to give light yellow oil in 95% yield. ^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.21 (s, 1H), 7.05 (s, 1H), 2.65 (t, J = 8.0 Hz, 2H), 1.66-1.57 (m, 4H), 1.31-1.30 (m, 13H), 0.92 (t, J = 3.2 Hz, 6H), 0.38 (s, 9H).

4,7-bis(4-(3-butyloctyl)thiophen-2-yl)-5,6-difluorobenzo[c][1,2,5]thiadiazole (6)

To a solution of (4-(3-butyloctyl)thiophen-2-yl)trimethylstannane (**5**) (9 mmol) and 4,7-dibromo-5,6-difluorobenzo[c][1,2,5]thiadiazole (1.0g, 3 mmol) in degassed DMF (10 mL) was added $\text{PdCl}_2(\text{PPh}_3)_2$ (0.15 mmol). The reaction mixture was heated under 120 °C under microwave for 2 minutes, and then stirred at 160 °C for 20 minutes. The reaction mixture was extracted with dichloromethane, washed with brine, dried over MgSO_4 , filtered through Celite, the solvent was removed by evaporation and the residue was purified by chromatography and recrystallization from ethanol to give product in 80% yield as yellow

solid. ^1H NMR (400MHz, CDCl_3) δ (ppm) 8.16 (s, 2H), 7.25 (s, 2H), 2.72 (t, J = 8.0 Hz, 4H), 1.67 (t, J = 5.6 Hz, 4H), 1.41-1.33 (m, 30 H), 0.91 (t, J = 6.8 Hz, 12 H).

4,7-bis(4-(3-butyloctyl)-5-(trimethylstannyl)thiophen-2-yl)-5,6-difluorobenzo[c][1,2,5]thiadiazole (7)

To a solution of 4,7-bis(4-(3-butyloctyl)thiophen-2-yl)-5,6-difluorobenzo[c][1,2,5]thiadiazole (**6**) (2.4 mmol) in 20 mL THF was added dropwise freshly prepared tetramethylpiperidine lithium THF solution (7.2 mmol) under dry ice/acetone bath, after the mixture stirred at same temperature for 2 hour, trimethyl stanyl chloride (6 mmol) was added one portion. The reaction was slowly warmed to room temperature and stirred overnight. Reaction was quenched with H_2O , extracted with dichloromethane, washed with brine, dried over MgSO_4 , filtered through Celite, the solvent was removed by evaporation, recrystallization from ethanol in dry ice-acetone bath to give red solid product in 83% yield. ^1H NMR (400 MHz, CDCl_3) δ (ppm) 8.24 (s, 2H), 2.73 (d, J = 8.0 Hz, 4H), 1.63 (t, J = 5.6 Hz, 4H), 1.34 (m, 30 H), 0.92 (t, J = 7.2 Hz, 12H), 0.47 (s, 18 H).

Synthesis of PTTBOBT-DFBT

Tris(dibenzylideneacetone)palladium (0.04 mmol) and tri(o-tolyl)phosphine (0.032 mmol) were added to a solution of a mixture of 0.1 mmol 4,7-bis(5-bromothiophen-2-yl)-5,6-bis(octyloxy)benzo[c][1,2,5]thiadiazole (**2**) and 0.1 mmol 4,7-bis(4-(3-butyloctyl)-5-(trimethylstannyl)thiophen-2-yl)-5,6-difluorobenzo[c][1,2,5]thiadiazole (**7**) in anhydrous toluene (10 mL) in glove box. The mixture was stirred at 100°C for 48h. Subsequently, the mixture was precipitated into 200 mL methanol and 15 mL concentrated hydrochloric acid, after stirring overnight, polymer was collected by suction filtration and subjected to Soxhlet extraction with methanol (12h), ethyl acetate (12h), hexane (12h), and chloroform (12h). The

chloroform fraction was then concentrated, precipitated into 150 mL methanol, filtered and dried over vacuum oven to obtain the final product.

Copolymer **PTTBGBT-DFBT** 82% yield, ¹H NMR (400 MHz, C₂D₂Cl₄): δ (ppm) 8.64 (s, 2H), 8.29 (s, 2H), 7.49 (s, 2H), 4.31 (s, 4H), 3.06 (s, 2H), 2.08 (s, 4H), 1.85 (s, 2H), 1.48 (br, 56H), 0.94 (s, 18H). Molecular weight: Mn = 12.2 kDa, PDI = 2.2. Anal. Calcd for C₆₈H₉₂F₂N₄O₂S₆; C, 66.52; H, 7.55; N, 4.56; S, 15.67. Found: C, 66.94; H, 7.41; N, 4.49; S, 16.15.

PhotoCELIV Test

The charge mobility in the device was measured using the photoinduced charge extraction by linearly increasing voltage (PhotoCELIV) technique. The experimental detail of the PhotoCELIV measurement was described elsewhere.^{2,3} The device was excited with pulsed laser of wavelength 630nm, pulse width <5ns, and 1Hz repetition rate. The delay between the laser pulse and voltage ramp was fixed to 5 μ s. The PhotoCELIV transients were measured by varying the ramp voltage is shown in figure S4 (a). It was found that the PhotoCELIV transients show single peak for all the voltage ramps, indicating balanced charge mobility. The charge mobility was calculated for different applied ramp voltages and plotted with respect to the electric field shown in figure S4 (b). The charge mobility was found to be 1.3x10⁻⁴ cm²/Vs at an applied electric field of 2.7x10⁴ V/cm. The charge mobility was almost independent of the applied electric field which is similar to the charge transport characteristics in most of the organic photovoltaic blends.

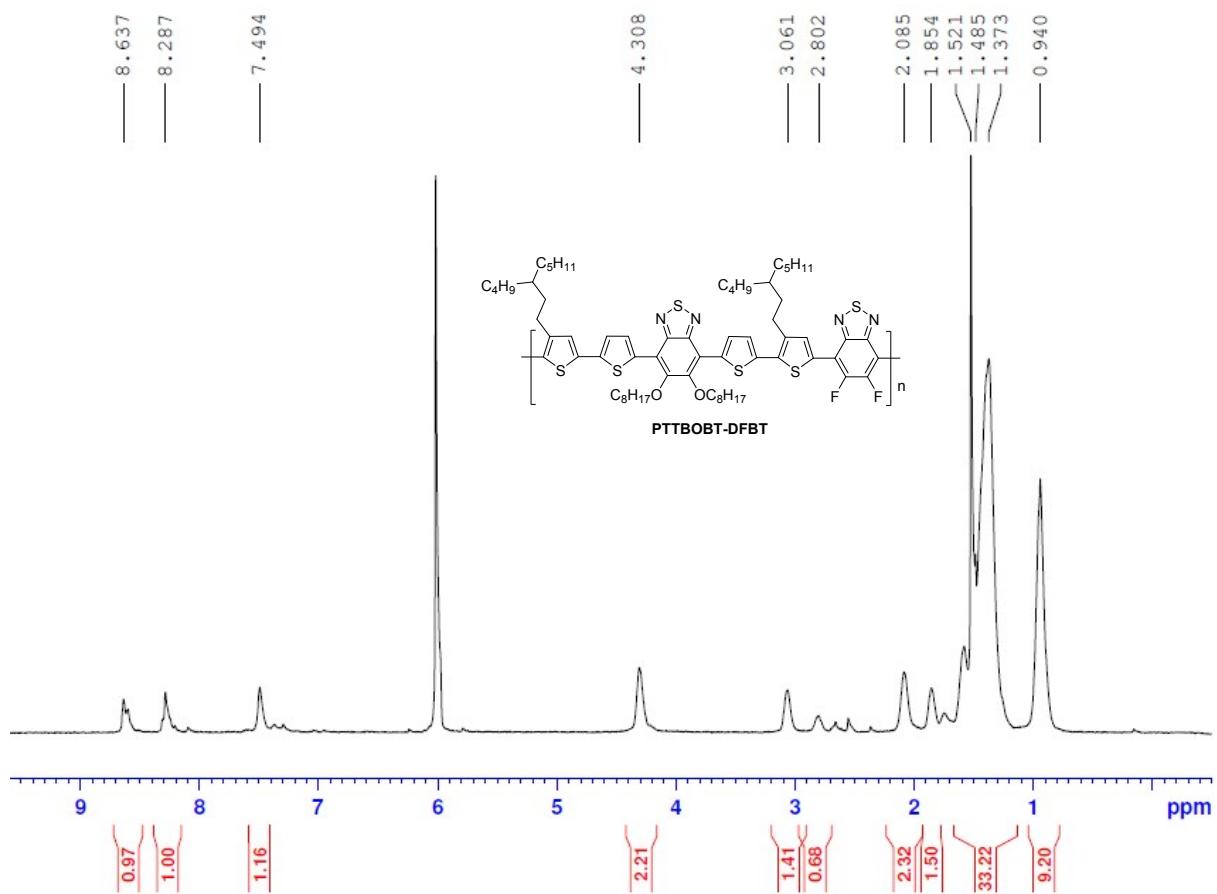


Figure S1. ¹H NMR spectrum of PTTBOBT-DFBT.

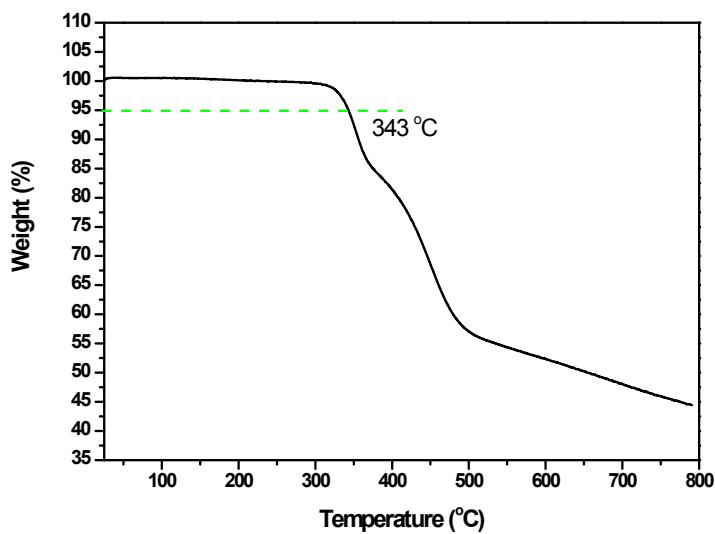


Figure S2. TGA plot of **PTTBOBT-DFBT** with a heating rate of 20 °C/min under an inert atmosphere.

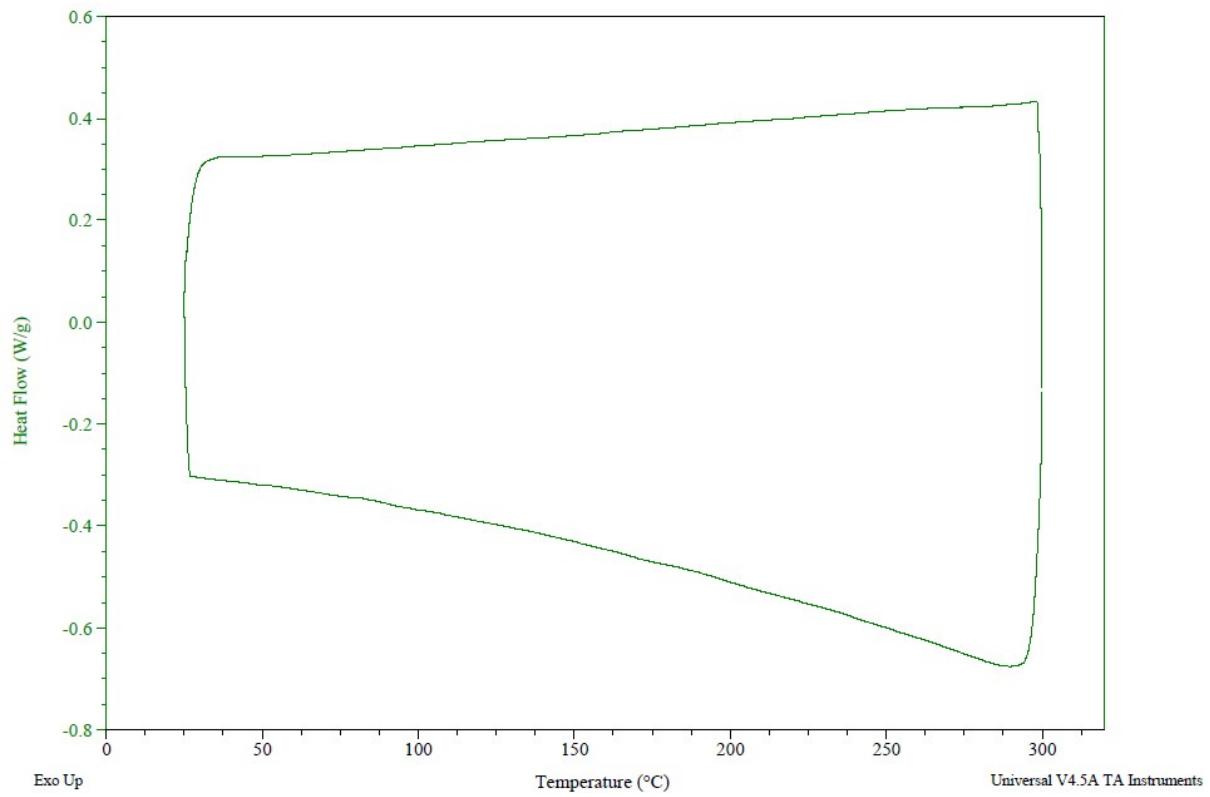


Figure S3. DSC plot of **PTTBOBT-DFBT**.

Table S1. Optical and electrochemical properties of **PTTBOBT-DFBT**.

Copolymer	λ_{\max} (nm)		E_g^{opt} (eV) ^a	HOMO (eV)	LUMO (eV) ^b
	Solution	film			
PTTBOBT-DFBT	386, 576	398, 632	1.64	-5.44	-3.80

^a Optical band gap. ^b Calculated from the difference of HOMO level and optical band gap.

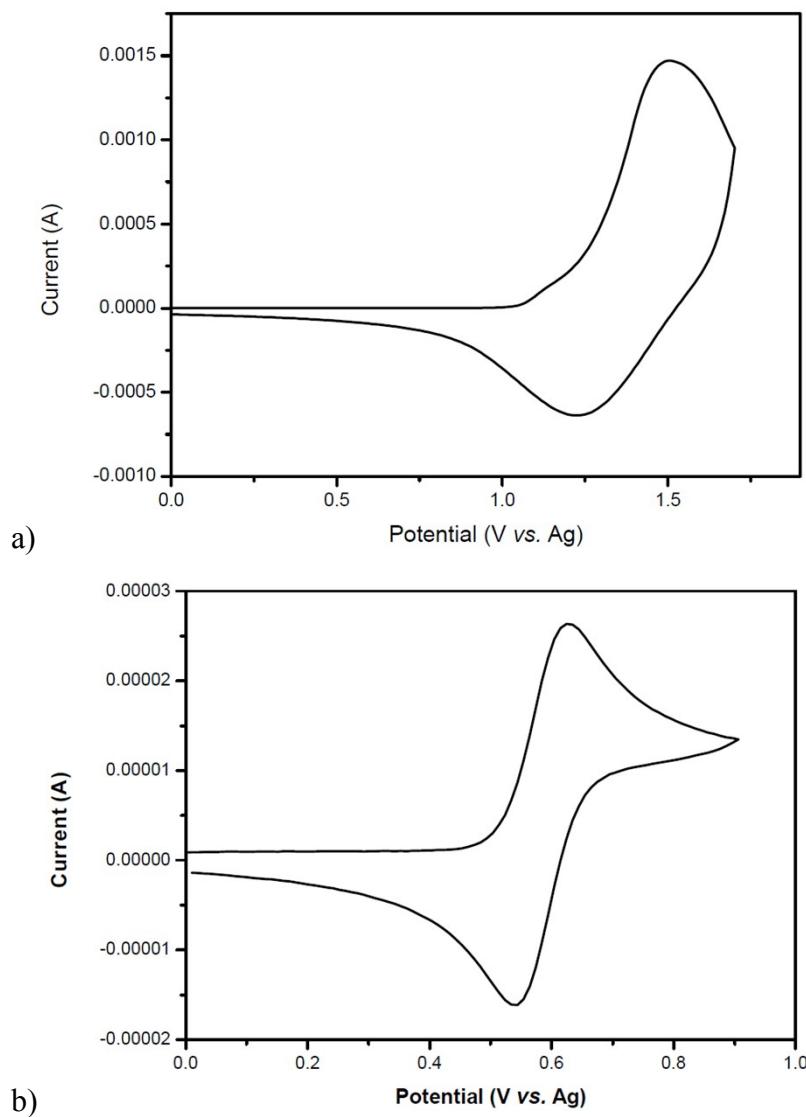


Figure S4. Cyclic voltammogram of **PTTBOBT-DFBT** (a) and Ferrocene (b) in

Bu_4NBF_4 /acetonitrile at a scan rate of 100 mV.s⁻¹.

Scheme S2. PTTBOBT-DFBT and reference polymer FBT-Th₄(1,4) and PQT12oBT.

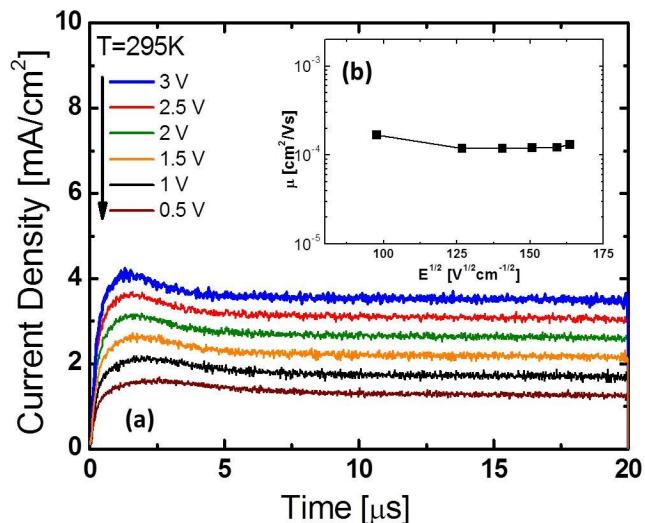
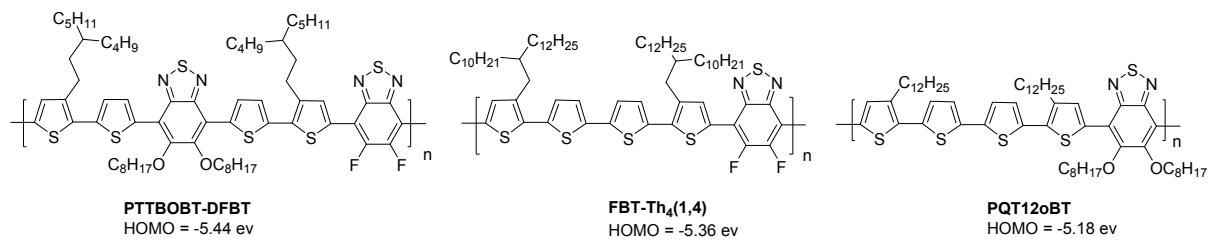


Figure S5. (a) PhotoCELIV transients for various ramp voltages; (b) the variation of charge mobility with applied electric field.

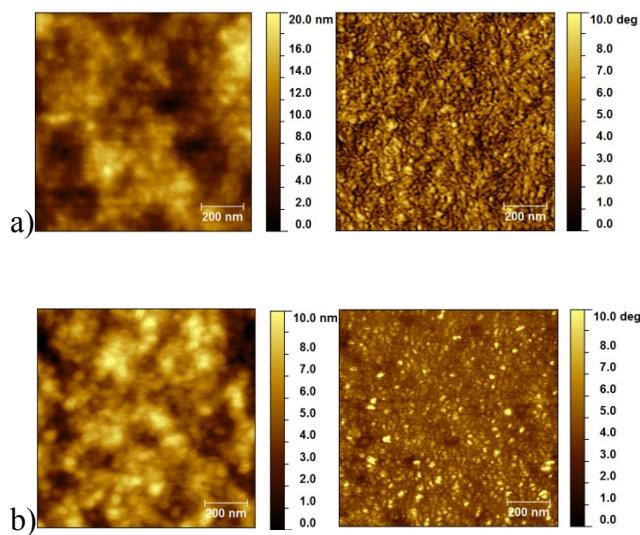


Figure S6. AFM image of PTTBOBT-DFBT/PC₇₁BM blend films: a) non-annealing; b) after annealing at 90 °C.

Reference

- (1) Cardone, A.; Martinelli, C.; Losurdo, M.; Dilonardo, E.; Bruno G.; Scavia, G.; Destri, S.; Cosma, P.; Salamandra, L.; Reale, A.; Carlo, A. D.; Aquirre, A.; Milián-Medina, B.; Gierschner, J.; Farinola, G. M. *J. Mater. Chem. A*, **2013**, *1*, 715.
- (2) Tan, M. J.; Goh, W. P.; Li, J.; Pundir, G.; Vijila, C.; Chen, Z.-K. *ACS Appl. Mater. Interfaces*, **2010**, *2*, 1414.
- (3) Vijila, C.; Ging Meng Ng, G. M.; Tan, M. J.; Goh, W. P.; Zhu, F. *Appl. Phys. Lett.* **2009**, *95*, 263305.