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Supporting Information for

High Charge Mobility Polymers Based on a New Di(thiophen-2-yl)thieno[3,2b]thiophene for Transistors and Solar Cells

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Experimental Section

The synthesis procedures of corresponding materials:

2,5-dioctylthieno[3,2-b]thiophene (TT(R))

A solution of TT (2.00 g, 14.28 mmol, 1 equiv) in anhydrous THF (80 mL) was degassed through argon for 15 min and then an n-BuLi solution (2.4 M in hexanes, 14.88 mL, 2.5 equiv) was added at -78 °C dropwised. The resulting solution was kept at -78 °C for 10 min and then room temperature for 2 h. After dropping of 1-bromooctane solution (6.07g, 31.43 mmol, 2.2 equiv) at -78 °C, it was kept at room temperature for overnight. Then the solution was poured into brine and extracted with ethyl ether twice, which was combined and dried over sodium sulfate. The solvent was removed and the crude product was subjected to silica gel chromatography (n-hexane) to give TT(R) as colorless oil (4.17 g, 11.43 mmol, 80%). ¹H-NMR (CDCl₃,

400 MHz): δ (ppm) 6.86 (s, 1H), 2.85 (t, 2H), 1.86 (m, 2H), 1.70 (m, 2H), 1.29 (m, 15H), 0.90 (m, 5H). ¹³C-NMR (CDCl₃, 400 MHz): δ (ppm) 146.44, 136.35, 116.30, 33.76, 32.65, 31.86, 31.55, 31.03, 29.08, 28.74, 28.19, 22.48, 14.01.

3,6-dibromo-2,5-dioctylthieno[3,2-b]thiophene (TT(R)-Br)

To a solution of thus obtained TT(R) (2.00 g, 5.48 mmol, 1 equiv) was dropwise added Br₂ (0.62 ml, 12.06 mmol, 2.2 equiv). After being stirred for 2 h in dark, the reaction was quenched by 10 ml of water and the organic phase was washed with aqueous solution of NaOH three times and dried over MgSO₄. The crude product was purified by chromatography on silica gel with hexanes to afford the titled compound (2.15 g, 4.11 mmol, 75%) as light yellow oil. ¹H-NMR (CDCl₃, 400 MHz): δ (ppm) 2.84 (t, 1H), 1.62 (m, 2H), 1.69 (m, 1H), 1.27 (m, 6H), 0.88(m, 2H). ¹³C-NMR (CDCl₃, 400 MHz): δ (ppm) 141.00, 135.97, 101.02, 31.72, 30.70, 29.99, 29.26, 28.97, 22.64, 14.05.

2,5-dioctyl-3,6-di(thiophen-2-yl)thieno[3,2-b]thiophene (DTTT)

The TT(R)-Br (2.15 g, 4.11 mmol, 1 equiv), Pd(PPh₃)₄ (100 mg), and 2-tributhyltinthiophene (3.83 g, 10.28 mmol, 2.5 equiv) were weighed into a 100 mL round-bottom flask. The flask was vacuumed and protected with N₂ and then toluene (20 mL) was added. The reaction was carried out at 110 °C for 24 h, after which the solution was diluted with dichloromethane. The solvent was removed and the crude product was purified through chromatography on silica gel with hexanes to give the product TT(R)-T (1.85 g, 3.49 mmol, 85%) as white solid. ¹H-NMR (CDCl₃, 400 MHz): δ (ppm) 7.35 (d, 1H), 7.27 (d, 1H), 7.15 (t, 1H), 3.03 (t, 2H), 1.62 (m, 2H), 1.35 (m, 10H), 0.92 (t, 3H). ¹³C-NMR (CDCl₃, 400 MHz): δ (ppm) 142.02, 136.55, 135.53, 127.31, 125.80, 124.83, 123.66, 123.58, 31.82, 29.69, 29.31, 28.33, 26.82, 22.64, 17.17, 14.15, 13.53.

3,6-bis(5-bromothiophen-2-yl)-2,5-dioctylthieno[3,2-b]thiophene (2Br-DTTT)

To a stirred solution of TT(R)-T (1.85 g, 3.49 mmol, 1 equiv) in 50 mL chloroform in dark, was added NBS (1.55 g, 8.72 mmol, 2.5 equiv) in batches. After being stirred for 5 h in dark, the reaction was quenched by 10 ml of water and the organic phase was washed with water three times and dried over MgSO₄. After column chromatograph with hexanes, the product TT(R)-T-Br was obtained as white solid (1.92 g, 2.79 mmol, 80%). ¹H-NMR (CDCl₃, 400 MHz): δ (ppm) 7.08 (d, 1H), 7.00 (d, 1H), 2.98 (t, 2H), 1.71 (m, 2H), 1.36 (dd, 10H), 0.87 (t, 3H). ¹³C-NMR (CDCl₃, 400 MHz): δ (ppm) 142.85, 18.00, 135.37, 130.01, 126.32, 122.68, 111.57, 31.88, 29.78, 29.15, 22.64, 14.14.

Synthetic procedure for PDTTT-DPP_3/7 and PDTTT-DPP_4/6

The monomer DTTT, 3,6-di- (thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (DPP) and 2,5-bis(tributylstannyl)thiophene (T) were polymerized to afford two polymers with different feeding ratios (DTTT to DPP to T being 3:7:10 and 4:6:10 to yield PDTTT-DPP_3/7 and PDTTT-DPP_4/6 respectively) (Scheme 1). A typical procedure is described as follow:

The comonomers were weighed with each molar ratio and added to a reaction vial equipped with a magnetic stirrer. The vial was then transferred to a glovebox where tris(dibenzylideneacetone)dipalladium(0) (2 mol%), tri(o-tolyl)phosphine (8 mol%) and anhydrous chlorobenzene (6 mL) were added. The vial was then stirred at 130 °C for 72 hours using an oil bath. The reaction mixture was poured into 150 mL of methanol and 10 mL of concentrated hydrochloric acid and stirred overnight to remove the stannylated end-groups. The polymers were subjected to Soxhlet extraction with acetone, hexanes and chloroform for 24 h each. Then poured into 150 ml of molecular methanol, obtain dark solid after suction filtration.

Synthetic procedure for PDTTT-DPP

A mixture of $Pd(OAc)_2$ (7.5 mg, 0.034 mmol), K_2CO_3 (176 mg, 1.27 mmol), 2,5dioctyl-3,6-di(thiophen-2-yl)thieno[3,2-b]thiophene (450 mg, 0.85 mmol), and 4,4di(2-ethylhexyl)-cyclopenta[2,1-b:3,4-b']dithiophene, (866 mg, 0.85 mmol) was stirred in anhydrous dimethylacetamide (DMAc) (10 mL) for 48 h under N₂ atmosphere. After cooling to room temperature the reaction was quenched by addition of 5 mL of 6 M aqueous HCl, poured into chloroform, and stirred for further 30 min. separation the organic layer was washed with After phase aqueous ethylenediaminetetraacetic acid (EDTA) disodium salt, 2 M aqueous HCl, saturated aqueous Na₂CO₃ solution, and brine and finally dried over anhydrous magnesium sulfate. After removing the solvent the crude polymer was precipitated from CHCl3 into acidified MeOH and purified by Soxhlet extraction with methanol and hexane before collecting the black polymer. PDTTT-T-DPP 3/7 ¹H-NMR (CDCl₃, 400 MHz): 8.91 (m, 4H), 7.51 (m, 1H), 7.02 (m, 2H), 4.01 (m, 2H), 3.04 (m, 1H), 1.53-0.85 (m, 74H). PDTTT-T-DPP_4/6 ¹H-NMR (CDCl₃, 400 MHz): 8.90 (m, 2H), 7.50 (m, 1H), 7.00 (m, 2H), 4.03 (m, 2H), 3.05 (m, 2H), 1.54-0.85 (m, 52H).



Figure S1. ¹H NMR spectra of the TT(R)



Figure S2. ¹³C NMR spectra of the TT(R)



Figure S3. ¹H NMR spectra of the TT(R)-Br



Figure S4. ¹³C NMR spectra of the TT(R)-Br



Figure S5. ¹H NMR spectra of the DTTT



Figure S6. ¹³C NMR spectra of the DTTT







Figure S8. ¹³C NMR spectra of the 2Br-DTTT



Figure S9. ¹H NMR spectra of the polymer PDTTT-T-DPP_3/7



Figure S10. ¹H NMR spectra of the polymer PDTTT-T-DPP_4/6



Figure S11. ¹H NMR spectra of the polymer PDTTT-DPP

General Measurement and Characterization

¹H NMR spectra were recorded in deuterated solvents on a Bruker ADVANCE 400 NMR Spectrometer Spectrometer. ¹H NMR chemical shifts were reported in ppm downfield from tetramethylsilane (TMS) reference using the residual protonated

solvent as an internal standard. Molecular weights of the polymers were determined using a Waters 2410 gel permeation chromatograph (GPC) with a refractive index detector in tetrahydrofuran (THF) using a calibration curve of polystyrene standards. Thermo gravimetric analysis (TGA) was performed on a TA-600 for thermal analysis at a heating rate of 10 °C/min under nitrogen with a sample weight of 5-8 mg. UV-vis absorption spectra were measured with Perkin Elmer Lambda 750 UV-Vis spectrophotometer. Cyclic voltammetry (CV) was performed with a Zahner IM6e electrochemical workstation. 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 ($\lambda = 1.54$ Å) and at a scanning rate of 1°/min. The three polymers were measured under the same condition with similar substrate, and all the film thickness were between 800 nm to 950 nm. Atomic force microscopic (AFM) images were measured on a Nanoscope III A (Digital Instruments) scanning probe microscope using the tapping mode. Current-voltage (J-V) characteristics were recorded using a Keithley 2400 Source Meter in the dark and under 100 mW/cm² simulated AM 1.5 G irradiation (Abet Solar Simulator Sun2000).

Thermal properties

Thermogravimetry analysis (TGA) and differential scanning calorimetry (DSC) of polymers have been carried out to evaluate their thermal properties. The three polymers PDTTT-T-DPP_3/7, PDTTT-T-DPP_4/6 and PDTTT-DPP displayed a decomposition temperature (5% weight loss, T_d) of 400, 398, and 390 °C, respectively (**Figure S12**). The results exhibit these polymers have sufficient thermal stability for PSC applications and polymerization pattern have no significant effect on the polymer thermal stability because of the little difference of T_d values of these polymers. Besides, as shown in **Figure S13**, no endothermic or exothermic behavior was found between 50 °C and 250 °C according to the DSC curves, implying that these polymers are amorphous.

Table S	Molecular	Weight and	Thermal Properties	of these polymers
		0	1	1 2

Copolymer	Molar	ratio	M _w (kg/mol)	M _n (kg/mol)	PDI	$T_d(^{\circ}C)$
	(DTTT/DPP))				

	Feed	Actual				
	ratio	ratio				
PDTTT-T-	0.428	0.581	37.5	17.6	2.13	400
DPP_3/7						
PDTTT-T-	0.667	0.716	34.2	14.7	2.32	398
DPP_4/6						
PDTTT-DPP	-	-	17.8	10.8	1.65	390



Figure S12. Thermogravimetry analysis (TGA) of polymers



Figure S13. Differential scanning calorimetry (DSC) curves of polymers

CV measurements

The CV measurements were conducted in a 0.1 M Bu_4PF_6/CH_3CN solution, using a three-electrode cell with a platinum disc working electrode, a platinum wire counter

electrode, and an Ag/Ag⁺ reference electrode. The working electrode was coated with the polymer thin films prepared by drop-casting the polymer solutions in chlorobenzene.



Figure S14. Cyclic voltammograms of these polymers

Space Charge Limited Current (SCLC) measurement

The mobility was determined by fitting the dark current to the model of a single carrier SCLC, described by the equation:

$$J=\frac{9}{8}\varepsilon_0\varepsilon_r\mu_h\frac{V^2}{d^3}$$

where J is the current density, μ_h is the mobility under zero field, ε_0 is the permittivity of free space, ε_r is the material relative permittivity, d is the active layer thickness, 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.

Table S2. The charge mobilities of pure polymers and polymers/PCBM blend films

 by SCLC

	Mobility (cm ² V ⁻¹ s ⁻¹)
PDTTT-T-DPP_3/7-PC ₇₁ BM	4.1×10 ⁻³
PDTTT-T-DPP_3/7-PC ₆₁ BM	2.5×10 ⁻³
PDTTT-T-DPP_4/6-PC71BM	2.6×10 ⁻³

PDTTT-T-DPP_4/6-PC ₆₁ BM	2.0×10 ⁻³
PDTTT-DPP-PC71BM	2.8×10 ⁻⁴
PDTTT-DPP-PC ₆₁ BM	2.1×10 ⁻⁴
PDTTT-T-DPP_3/7	2.3×10 ⁻²
PDTTT-T-DPP_4/6	1.1×10 ⁻²
PDTTT-DPP	7.0×10 ⁻³



Figure S15. J^{1/2}~V curves of the hole-only devices based on these polymers: (a) pure polymer films; (b) blend films of polymer and PCBM

OTFTs Device Fabrication

Si wafers were used as the substrates, and a layer of 200 nm of SiO₂ (grown by thermal oxidation) was used as the gate dielectric. Au layer was evaporated through a shadow mask to obtain the source and drain electrodes. The substrates were cleaned using acetone and isopropanol and dried at 100 °C for 20 min, and then treated with octadecyltrichlorosilane (OTS) at room temperature for 12 h. The semiconductor layers were deposited by spin-coating of a chlorobenzene solution (10 mg/mL) onto substrates at 3000 rpm with 30 s. All the fabrication processes were carried out in a glove box filled with nitrogen. Electrical characterization of the polymers was performed using a Keithley semiconductor parameter analyzer (Keithley 4200-SCS) under nitrogen atmosphere. The device characteristics were measured under ambient conditions.

 Table S3. PTFTs characteristics for PDTTT-DPP_3/7 and PDTTT-DPP thin film

 based on different channel length

Polymer	(W/L) a /	280	140	70	46.7	35	28
	μ (cm ²						
	V ⁻¹ s ⁻¹)						

PDTTT-T-	RT	0.111	0.096	0.0274	0.360	0.285	0.460
DPP_3/7	100 °C	0.475	0.290	0.200	0.296	0.227	0.572
	200 °C	0.354	0.357	0.309	0.463	0.401	0.627
PDTTT-DPP	RT	7.36×10-4	1.47×10-3	4.51×10-3	5.66×10-3	6.43×10 ⁻³	7.55×10-3
	100 °C	1.20×10-3	3.05×10-3	7.08×10-3	6.57×10-3	1.27×10-2	2.11×10-2
	200 °C	3.20×10-3	8.22×10 ⁻³	2.09×10-2	2.31×10-2	3.47×10-2	3.51×10-2

^a W=1400 μm and L=5 μm, 10 μm, 20 μm, 30 μm, 40 μm, 50μm respectively.



Figure S16. The transfer (a, c, e) and output (b, d, f) characteristics of PDTTT-DPP films deposited on substrate (a, b), annealed at 100 °C (c, d) and 200 °C (e, f)

PSCs Device Fabrication

Power conversion efficiencies (PCEs) were measured under an AM1.5G solar simulator (Sciencetech SS-0.5K Solar Simulator). The current density-voltage (J-V) characteristics were recorded with a Keithley 2400 source meter. A calibrated Si

photodiode was used to determine the photosensitivity. Patterned ITO-glass substrates were used as the anode in the polymer solar cells. The ITO coated glass substrates were cleaned by sonication in detergent, deionized water, acetone, and isopropyl alcohol and dried in a nitrogen stream, followed by an oxygen plasma treatment. Then the surface of the ITO substrate was modified by spin-coating the conducting ZnO layer, followed by baking at 140 °C for 15 minutes under ambient conditions. The optimal polymer:PC₇₁BM or polymer:PC₆₁BM weight ratios were 1:1.5 or 1:2 and the solid concentration of 15 mg/mL was found to be best. Solutions prepared using different solvents (chlorobenzene, chloronaphthalene, and their mixed solvent). The solutions were then spin-coated onto the ZnO layer at 1200 rpm/min for 40 s. The thicknesses of the active layer were about 100-120 nm. Subsequently, MoO₃ (0.8 nm) and Ag (100 nm) electrodes were deposited via thermal evaporation in vacuum (<10⁻⁶ Torr) in a thickness of approximately. The effective area was measured to be 0.04 cm².



Figure S17. Characteristic J-V curves of the BHJ solar cell based on these polymers fabricated from CB

 Table S4. Maximum photovoltaic performance of polymers in invert BHJ devices

 with different solvents

Polymer	Solvent	Acceptor	Polymer/PCBM	$J_{\rm sc}$ (mA	$V_{\rm oc}({ m V})$	FF	PCE
			(w/w)	cm ⁻²)		(%)	(%)
PDTTT-T-DPP_3/7	СВ	PC ₇₁ BM	1:1.5	2.644	0.562	32.4	0.5
PDTTT-T-DPP_3/7	СВ	PC ₆₁ BM	1:2	5.707	0.615	43.7	1.5
PDTTT-T-DPP_4/6	СВ	PC ₇₁ BM	1:1.5	3.613	0.561	57.3	1.2
PDTTT-T-DPP_4/6	CB	PC ₆₁ BM	1:2	6.119	0.570	53.8	1.9
PDTTT-DPP	CB	PC ₇₁ BM	1:1.5	2.150	0.601	26.7	0.3
PDTTT-DPP	CB	PC ₆₁ BM	1:2	2.570	0.565	31.3	0.5
PDTTT-T-DPP_3/7	CN	PC ₇₁ BM	1:1.5	7.565	0.598	57.9	2.6
PDTTT-T-DPP_3/7	CN	PC ₆₁ BM	1:2	7.638	0.587	59.6	2.7
PDTTT-T-DPP_4/6	CN	PC ₇₁ BM	1:1.5	5.132	0.592	63.8	1.9
PDTTT-T-DPP_4/6	CN	PC ₆₁ BM	1:2	5.252	0.594	62.6	2.0
PDTTT-DPP	CN	PC ₇₁ BM	1:1.5	-	-	-	-
PDTTT-DPP	CN	PC ₆₁ BM	1:2	-	-	-	-
PDTTT-T-DPP_3/7	CN	PC ₆₁ BM	1:1	7.738	0.575	47.3	2.1
PDTTT-T-DPP_3/7	CN	PC ₆₁ BM	1:3	7.724	0.581	56.3	2.5
PDTTT-T-DPP_3/7	CN	PC ₆₁ BM	1:4	8.097	0.580	55.6	2.6
PDTTT-T-DPP_3/7	10%CN	PC ₆₁ BM	1:2	5.744	0.570	51.0	1.7
PDTTT-T-DPP_4/6	10%CN	PC ₆₁ BM	1:2	5.409	0.580	55.8	1.7
PDTTT-T-DPP_3/7	30%CN	PC ₆₁ BM	1:2	5.742	0.577	55.2	1.8
PDTTT-T-DPP_4/6	30%CN	PC ₆₁ BM	1:2	5.375	0.579	62.9	2.0
PDTTT-T-DPP_3/7	50%CN	PC ₆₁ BM	1:2	8.193	0.568	50.6	2.4
PDTTT-T-DPP_4/6	50%CN	PC ₆₁ BM	1:2	6.503	0.567	47.9	1.8



Figure S18. Phase images by AFM of blend films of Polymers:PCBM from different

solvents



Figure S19. Topography in 3D images by AFM of blend films of Polymer:PCBM from different solvents.