Supporting Information

Versatile Asymmetric Thiophene/Benzothiophene Flanked Diketopyrrolopyrrole Polymers with Ambipolar Properties for OFETs and OSCs

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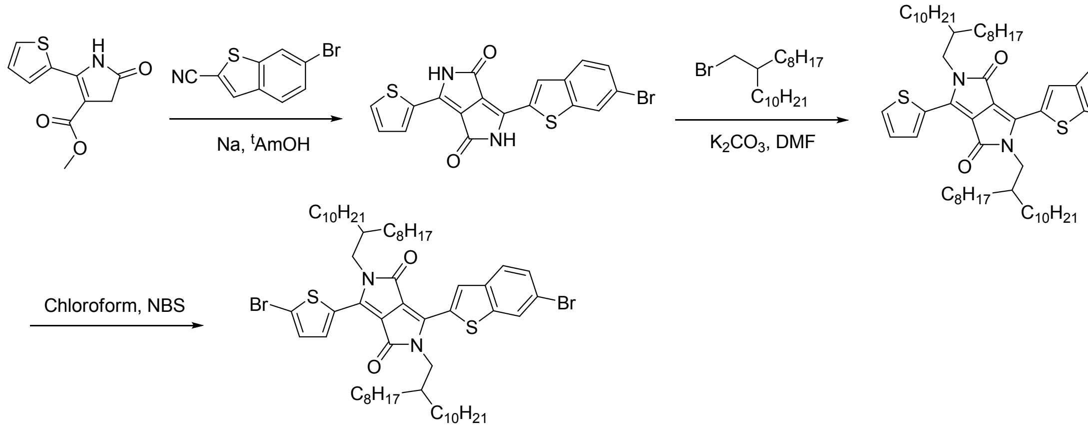

Figure S1 Synthetic route of BTTDPP.

3-(6-bromobenzo[*b*]thiophen-2-yl)-6-(thiophen-2 -yl)pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione

Sodium (0.68 g, 29.6 mmol) was added to a stirred solution of iron chloride (3 mg) in 2-methylbutan-2-ol (30 mL) and heated to reflux until the complete consumption of sodium. The solution was cooled to 80°C and 6-bromobenzo[*b*]thiophene-2-carbonitrile (2.4 g, 10.1 mmol) was added dropwise. and 5-oxo-2-(thiophen-2-yl)-4,5-dihydro-1*H*-pyrrole-3-carboxylate (1.88 g, 8.4 mmol) was added in one portion. The resulting mixture was stirred at 120°C for 2 h. The reaction was quenched by the addition of glacial acetic acid (5 mL) in methanol (20 mL) and the mixture stirred at 90 °C for 10 min. The precipitate was collected by filtration and washed with water and methanol and dried in vacuum. The 3-(6-bromobenzo[*b*]thiophen-2-yl)-6-(thiophen-2 -yl)pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione was obtained in 46% yield and used without further purification.

3-(6-bromobenzo[*b*]thiophen-2-yl)-2,5-bis(2-octyldodecyl)-6-(thiophen-2-yl)pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione

To a solution of 3-(6-bromobenzo[*b*]thiophen-2-yl)-6-(thiophen-2-yl)pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione (2.6 g, 6.1 mmol) and 18-crown-6 (5 mg) in DMF (50 ml) was added K_2CO_3 (8.8 g, 24.4 mmol) and heated to 120 °C for 1 h, then 2-octyldodecylbromide (3.4 g, 24.4 mmol) was added dropwise. After being stirred for another 12 h at 120 °C, the reaction mixture was poured into water and extracted with chloroform. The combined organic layers were washed with water, dried over Na_2SO_4, and concentrated in vacuum. The residue was purified by column chromatography over silica gel using a mixture of petroleum ether and dichloromethane as eluent. Finally, the result product was recrystallized from ethanol.

21% yield; purple solid; TLC (PE: DCM, 4:1 v/v): $R_f = 0.20$; ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.01 (s, 1H), 8.96 (dd, J = 1.0, 3.9 Hz, 1H), 8.01-7.99 (m, 1H), 7.81 (d, J = 8.6 Hz, 1H), 7.66 (dd, J = 1.0, 5.0

Hz, 1H), 7.53 (dd, $J = 1.7, 8.6$ Hz, 1H), 7.29 (dd, $J = 4.0, 5.0$ Hz, 1H), 4.04 (dd, $J = 3.9, 7.6$ Hz, 4H), 1.91, (br s, 2H), 1.44-1.08 (m, 64H), 0.94-0.78 (m, 12H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 161.81, 161.51, 142.41, 141.53, 139.62, 137.61, 135.93, 131.19, 131.14, 129.71, 129.65, 128.81, 128.52, 126.21, 124.50, 120.70, 109.74, 108.01, 46.33, 37.92, 37.72, 31.90, 31.86, 31.20, 31.12, 29.98, 29.62, 29.55, 29.49, 29.34, 29.28, 26.21, 26.15, 22.66, 14.10; HRMS (MALDI-TOF-MS) calcd. for $C_{58}H_{89}BrN_2O_2S_2Na^+$ ($[M+Na]^+$): 1011.5441, found 1011.5448.

3-(6-bromobenzo[*b*]thiophen-2-yl)-6-(5-bromothiophen-2-yl)-2,5-bis(2-octyldodecyl)pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione

3-(6-bromobenzo[*b*]thiophen-2-yl)-2,5-bis(2-octyldodecyl)-6-(thiophen-2-yl)pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione (0.99 g, 1.0 mmol) was dissolved in 15 mL chloroform. The solution was purged with argon for 5 min and then *N*-bromosuccinimide (0.392 g, 2.2 mmol) was added in small portions. After stirring at room temperature overnight, the mixture was poured into 100 mL methanol and filtered. The residue was subsequently recrystallized from ethanol.

80% yield; black solid; TLC (PE: DCM, 5:1 v/v): $R_f = 0.30$; ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.02 (s, 1H), 8.70 (dd, $J = 1.0, 4.2$ Hz, 1H), 8.01 (s, 1H), 7.81 (d, $J = 8.6$ Hz, 1H), 7.53 (dd, $J = 1.6, 8.6$ Hz, 1H), 7.23 (d, $J = 4.2$ Hz, 1H), 4.04 (d, $J = 7.7$ Hz, 2H), 3.95 (d, $J = 7.7$ Hz, 2H), 1.89, (br s, 2H), 1.42-1.07 (m, 64H), 0.93-0.76 (m, 12H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 161.48, 161.35, 142.47, 140.05, 139.98, 137.53, 135.74, 131.45, 131.04, 129.58, 128.85, 126.22, 124.48, 120.56, 119.41, 109.53, 108.16, 46.36, 37.90, 37.73, 31.90, 31.87, 31.20, 31.11, 29.98, 29.63, 29.55, 29.49, 29.35, 29.28, 26.20, 26.14, 22.66, 14.10; HRMS (MALDI-TOF-MS) calcd. for $C_{58}H_{88}Br_2N_2O_2SS_2^+$ ($[M]^+$): 1066.4648, found 1066.4644.

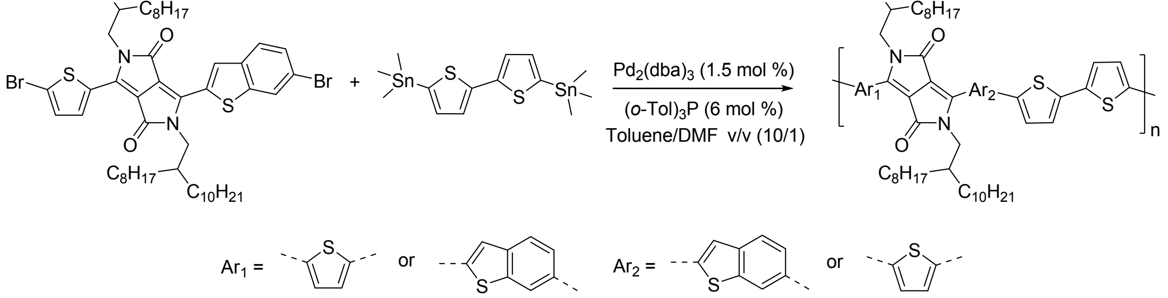

Figure S2 Polymerization route of PBTTDPP-BT.

Polymerization of ***PBTTDPP-BT***:

Under an argon atmosphere, a mixture of 3-(6-bromobenzo[*b*]thiophen-2-yl)-6-(5-bromothiophen-2-yl)-2,5-bis(2-octyldodecyl)pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione (0.10 mmol, 107 mg), 5,5'-bis(trimethylstannyl)-2,2'-bithiophene (0.10 mmol, 49.2 mg), $Pd_2(dba)_3$ (1.4 mg, 0.0015 mmol, 1.5

mol %) and (o-Tol)$_3$P (1.8 mg, 0.006 mmol, 6 mol %) were dissolved in a mixture solution of toluene (5 mL) and DMF (0.5 mL) in a Schlenk tube. The reaction was stirred at 110 °C for 2 h, followed by addition of 2-bromothiophene (0.5 mL) to react with the trimethylstannyl end group. The mixture was further stirred at 100 °C for 1 h. After cooling to room temperature, the mixture was precipitated into chilled methanol (20 mL). Then the crude polymer was collected by filtration and purified by Soxhlet extraction with acetone, hexane and the remaining product was dissolved with refluxing 1,2-dichlorobenzene. The 1,2-dichlorobenzene solution was then concentrated by evaporation and precipitated into methanol, dried over vacuum. Finally, the desired polymer was obtained.

96% yield; GPC(1,2-dichlorobenzene, 120 °C): Mn = 66.2 KDa, Mw= 153.2 KDa, PDI = 2.31; Anal. Calcd. for $C_{60}H_{88}N_2O_2S_3Se$, C, 68.99; H, 8.49; N, 2.68, Found: C, 68.31; H, 8.31; N, 2.78.

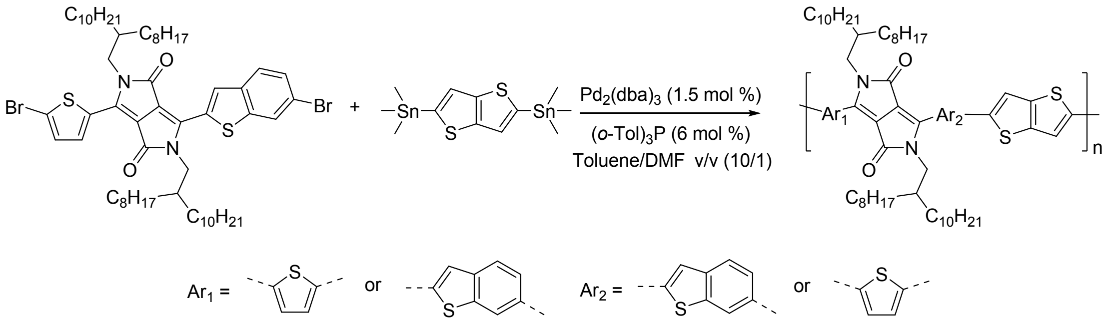

Figure S3 Polymerization route of PBTTDPP-TT

Polymerization of ***PBTTDPP-TT***:

Under an argon atmosphere, a mixture of 3-(6-bromobenzo[*b*]thiophen-2-yl)-6-(5-bromothiophen-2-yl)-2,5-bis(2-octyldodecyl)pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione (0.10 mmol, 107 mg), 2,5-bis(trimethylstannyl)thieno[3,2-*b*]thiophene (0.10 mmol, 46.6 mg), Pd$_2$(dba)$_3$ (1.4 mg, 0.0015 mmol, 1.5 mol %) and (o-Tol)$_3$P (1.8 mg, 0.006 mmol, 6 mol %) were dissolved in a mixture solution of toluene (5 mL) and DMF (0.5 mL) in a Schlenk tube. The reaction was stirred at 110 °C for 1 h, followed by addition of 2-bromothiophene (0.5 mL) to react with the trimethylstannyl end group. The mixture was further stirred at 100 °C for 1 h. After cooling to room temperature, the mixture was precipitated into chilled methanol (20 mL). Then the crude polymer was collected by filtration and purified by Soxhlet extraction with acetone, hexane and the remaining product was dissolved with refluxing 1,2-dichlorobenzene. The 1,2-dichlorobenzene solution was then concentrated by evaporation and precipitated into methanol, dried over vacuum. Finally, the desired polymer was obtained.

99% yield; GPC(1,2-dichlorobenzene, 120 °C): Mn = 44.3 KDa, Mw= 118.6 KDa, PDI = 2.67; Anal.

Calcd. for $C_{60}H_{88}N_2O_2S_3Se$, C, 68.99; H, 8.49; N, 2.68, Found: C, 68.31; H, 8.31; N, 2.78.

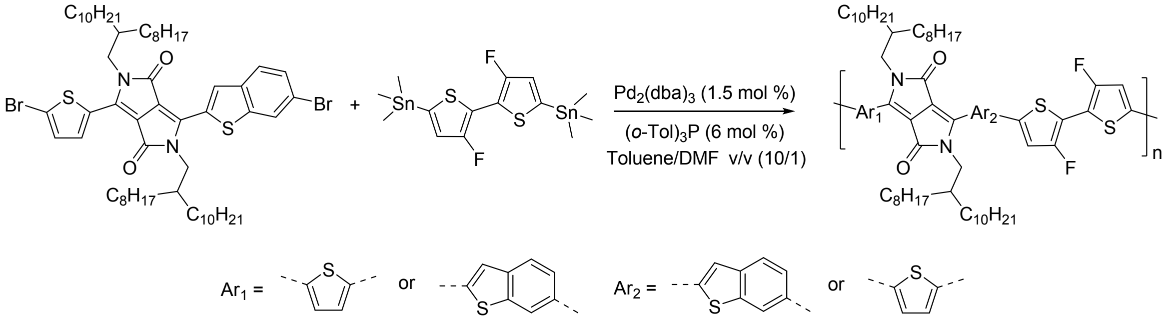

Figure S4 Polymerization route of PBTTDPP-2FBT

Polymerization of ***PBTTDPP-2FBT***:

Under an argon atmosphere, a mixture of 3-(6-bromobenzo[*b*]thiophen-2-yl)-6-(5-bromothiophen-2-yl)-2,5-bis(2-octyldodecyl)pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione (0.10 mmol, 107 mg), (3,3'-difluoro-2,2'-bithiophene-5,5'-diyl)bis(trimethylstannane) (0.10 mmol, 52.8 mg), $Pd_2(dba)_3$ (1.4 mg, 0.0015 mmol, 1.5 mol %) and (*o*-Tol)$_3$P (1.8 mg, 0.006 mmol, 6 mol %) were dissolved in a mixture solution of toluene (5 mL) and DMF (0.5 mL) in a Schlenk tube. The reaction was stirred at 110 °C for 1 h, followed by addition of 2-bromothiophene (0.5 mL) to react with the trimethylstannyl end group. The mixture was further stirred at 100 °C for 1 h. After cooling to room temperature, the mixture was precipitated into chilled methanol (20 mL). Then the crude polymer was collected by filtration and purified by Soxhlet extraction with acetone, hexane and the remaining product was dissolved with refluxing 1,2-dichlorobenzene. The 1,2-dichlorobenzene solution was then concentrated by evaporation and precipitated into methanol, dried over vacuum. Finally, the desired polymer was obtained.

94% yield;GPC(1,2-dichlorobenzene, 120 oC): Mn = 74.7 KDa, Mw= 174.1 KDa, PDI = 2.33; Anal. Calcd. for $C_{60}H_{88}N_2O_2S_3Se$, C, 68.99; H, 8.49; N, 2.68, Found: C, 68.31; H, 8.31; N, 2.78.

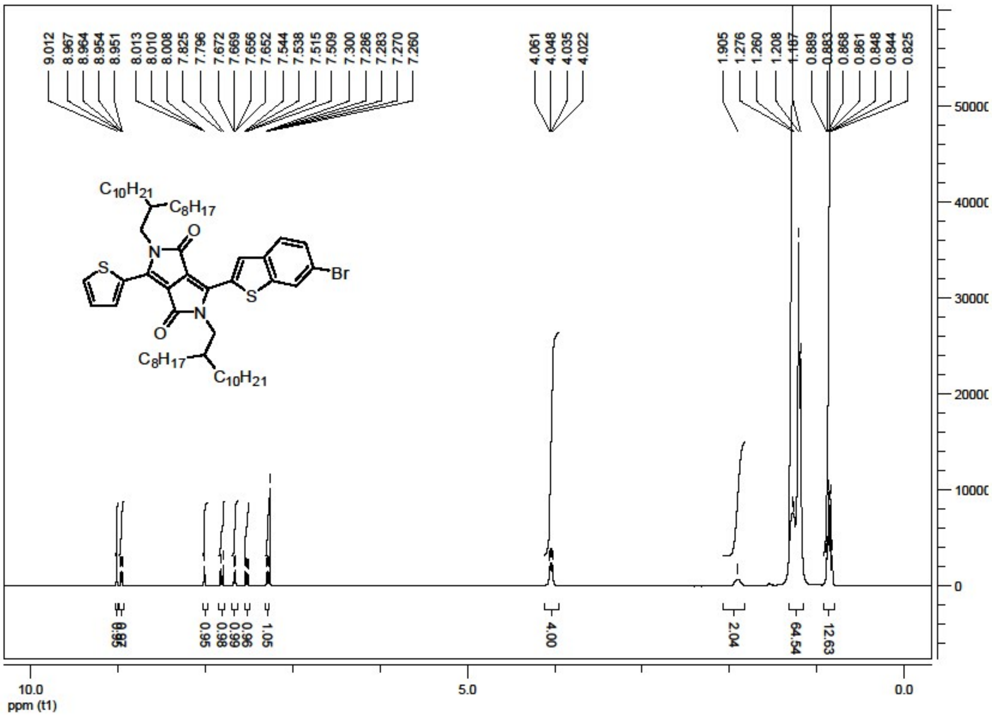

Figure S5 1H NMR of 3-(6-bromobenzo[b]thiophen-2-yl)-2,5-bis(2-octyldodecyl)-6-(thiophen-2-yl)pyrrolo [3,4-c]pyrrole-1,4(2H,5H)-dione

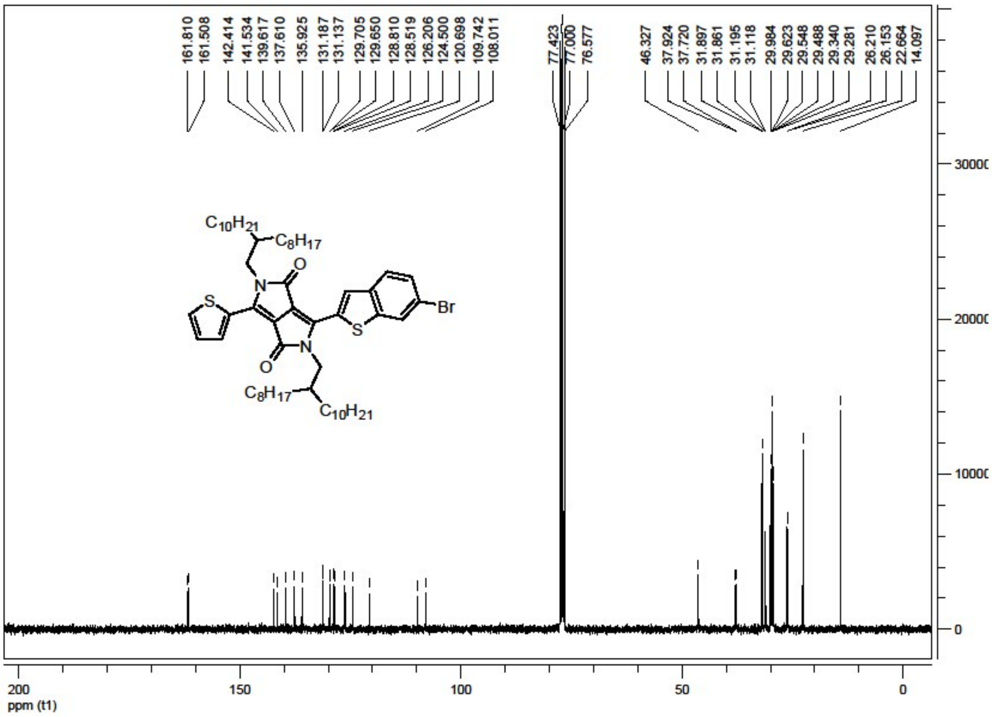

Figure S6 13C NMR of 3-(6-bromobenzo[b]thiophen-2-yl)-2,5-bis(2-octyldodecyl)-6-(thiophen-2-yl)pyrrolo [3,4-c]pyrrole-1,4(2H,5H)-dione

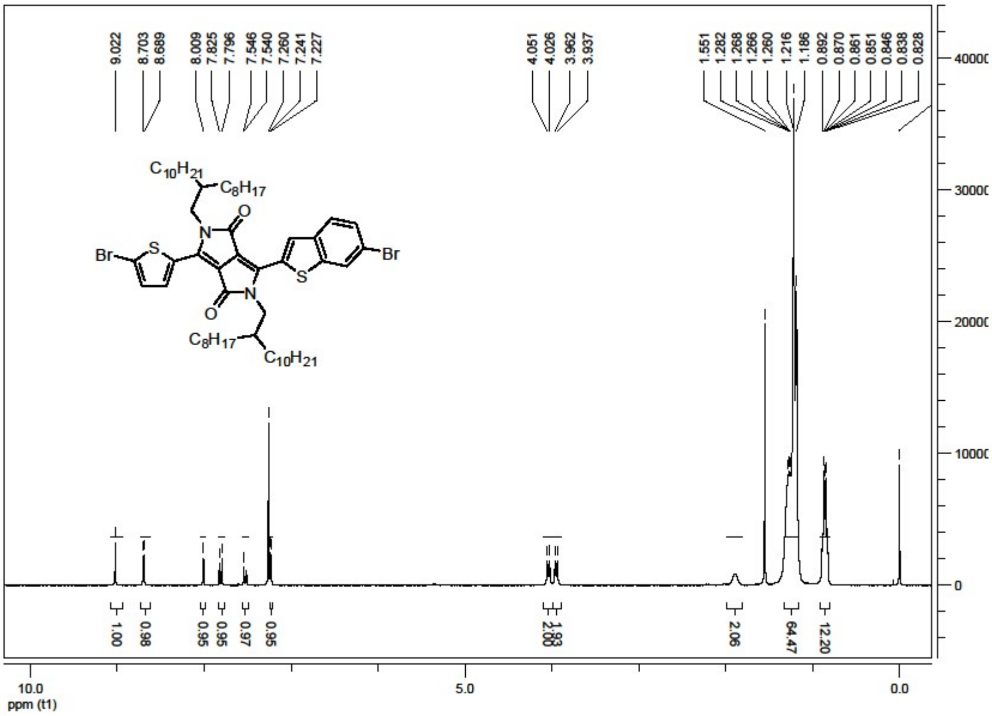

Figure S7 1H NMR of 3-(6-bromobenzo[b]thiophen-2-yl)-6-(5-bromothiophen-2-yl)-2,5-bis(2-octyldodecyl) pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione

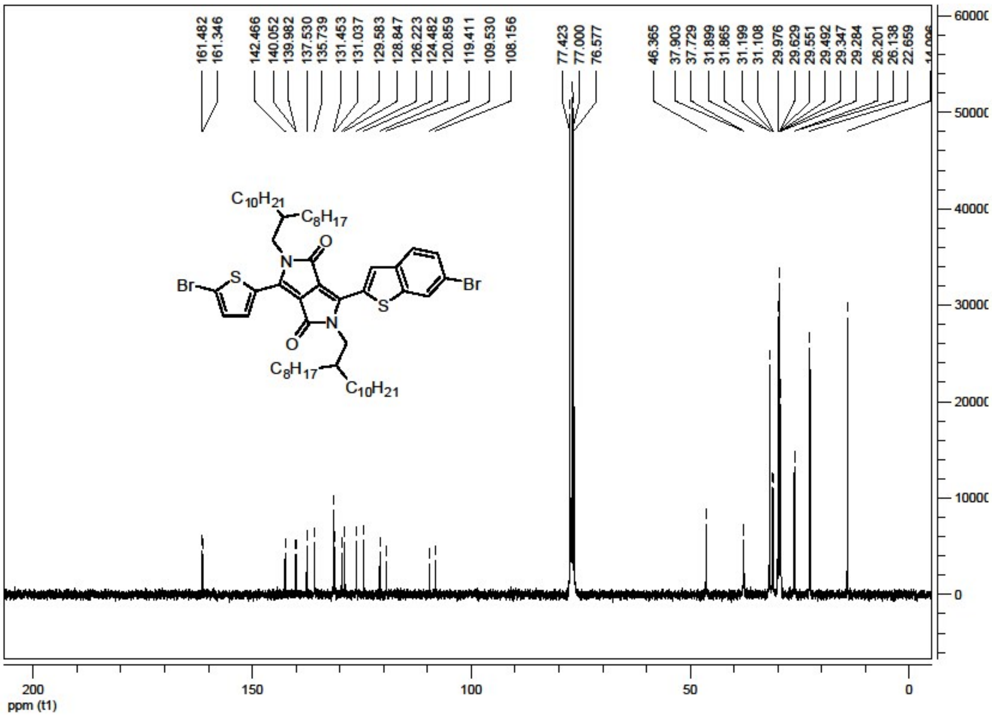

Figure S8 13C NMR of 3-(6-bromobenzo[b]thiophen-2-yl)-6-(5-bromothiophen-2-yl)-2,5-bis(2-octyldodecyl) pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione

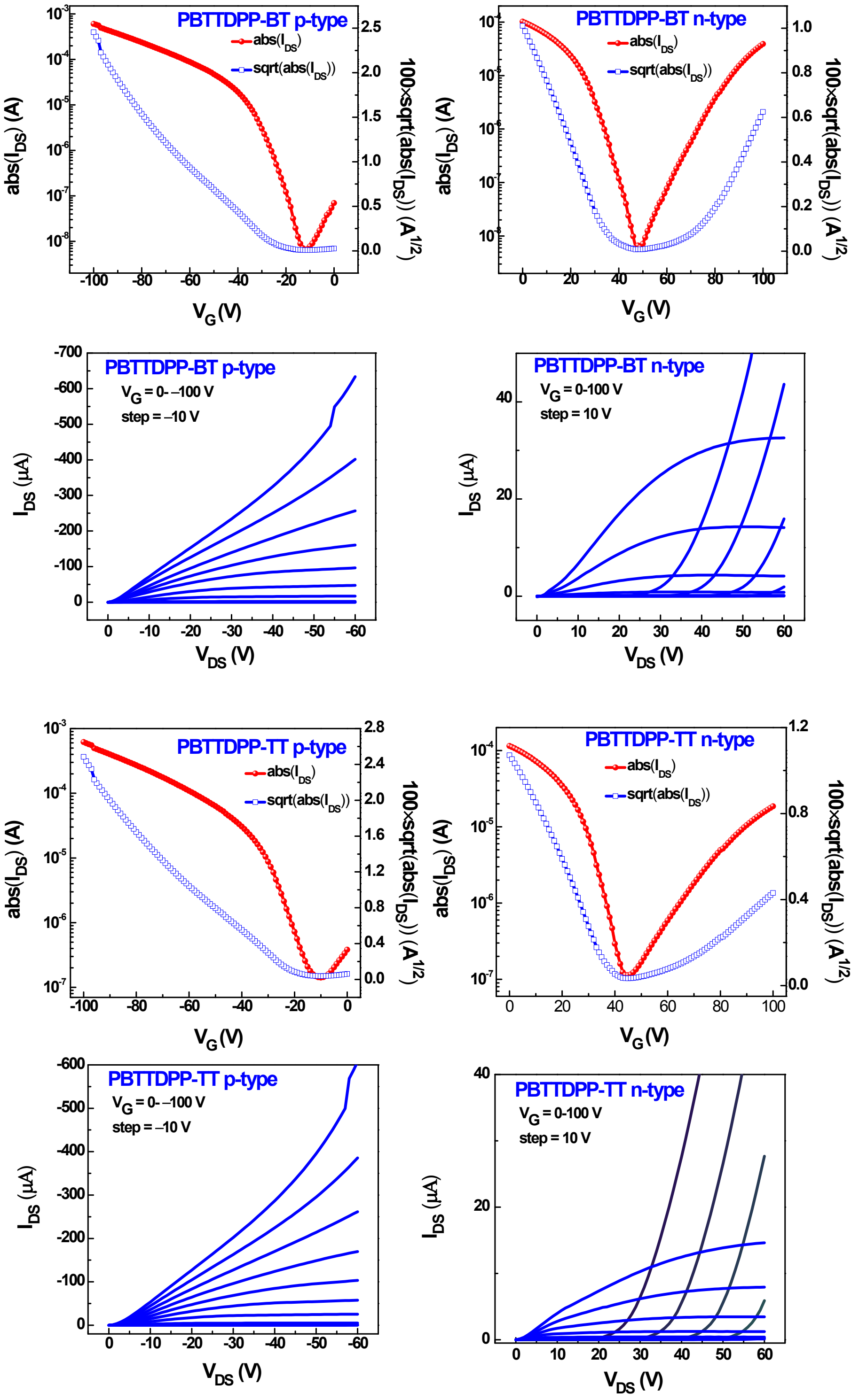

Figure S9 transfer and output characteristics of ambipolar OFETs based on PBTTDPP-BT, PBTTDPP-TT

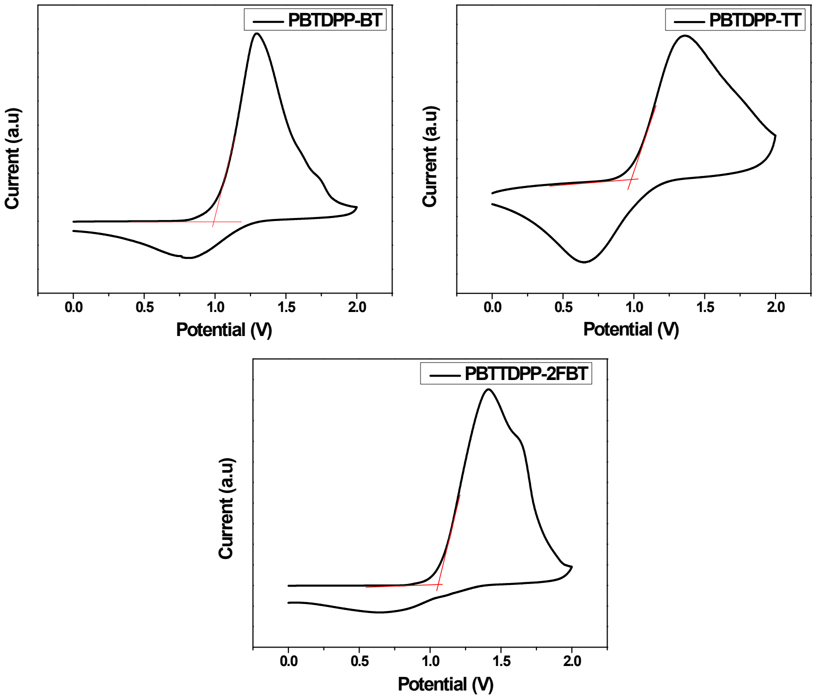

Figure S10 cyclic voltametry data of PBTTDPP-BT, PBTTDPP-TT and PBTTDPP-2FBT

Table S1. cyclic voltametry data of PBTTDPP-BT, PBTTDPP-TT and PBTTDPP-2FBT

Polymer	BTT-TT	BTT-2FBT	BTT-BT
	0.9922	1.07222	1.02222
HOMO	-5.41	-5.49	-5.44
λ_{edge}	852.00	850.00	813.00
Eg^{opt}	1.46	1.46	1.53
LUMO	-3.96	-4.04	-3.92

Table S2. Optimized OPV performances of PBTTDPP-BT, PBTTDPP-TT and PBTTDPP-2FBT after blending with P3HT (1:2, w/w)

Polymer	V_{oc} [V]	J_{sc} [mA/cm^2]	FF [%]	PCE [%]
PBTTDPP-BT	-	-	-	-
PBTTDPP-TT	0.855	0.85	38.4	0.28
PBTTDPP-2FBT	0.851	1.16	44.5	0.44

Table S3. Optimized OPV performances of PBTTDPP-BT, PBTTDPP-TT and PBTTDPP-2FBT after blending with $PC_{71}BM$ (1:3, w/w)

Polymer	weight ratio (w/w)	DIO [%, v/v]	V_{oc} [V]	J_{sc} [mA/cm^2]	FF [%]	PCE [%]
PBTTDPP-TT	1:3	3% DPE	0.666	16.31	59.0	6.41
PBTTDPP-2FBT	1:3	3% DPE	0.796	9.81	70.3	5.49

Table S4. Optimized OPV performances of PBTTDPP-BT, PBTTDPP-TT and PBTTDPP-2FBT after blending with J60 (1:2, w/w)

Polymer	weight ratio (w/w)	DIO [%, v/v]	V_{oc} [V]	J_{sc} [mA/cm^2]	FF [%]	PCE [%]
PBTTDPP-TT	1:2	3% DIO	0.537	0.075	35.67	0.014
PBTTDPP-2FBT	1:2	3%DIO	0.711	0.154	32.76	0.036