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Supporting Information

Simple synthesis of novel terthiophene-based D-A1-D-A2 polymers for polymer solar cells

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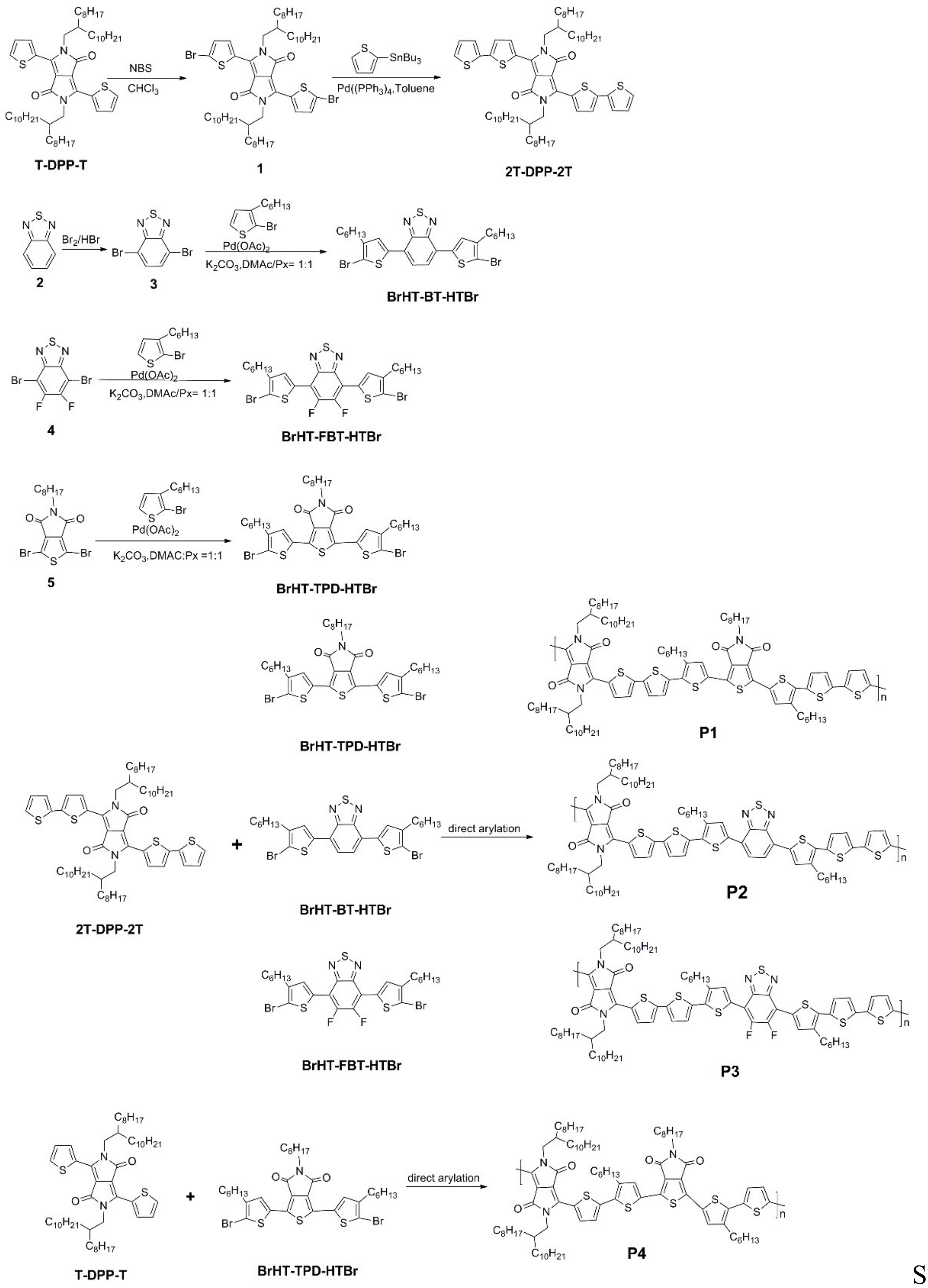
1. Synthesis of monomers and polymers

All reagents and starting materials were purchased from commercial sources. 2,5-bis(2-octyldodecyl)-3,6-di(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4 (2H,5H)-dione (T-DPP-T, purity: >98%), and 1,3-dibromo-5-octyl-4H-thieno[3,4-c]pyrrole-4,6 (5H)-dione (5, purity: >98%) was purchased from Derthon. 4,7-dibromo-5,6-difluorobenzo[c][1,2,5]thiadiazole (4, purity: >98%) was purchased from Suna Tech Inc. Benzo[c][1,2,5]thiadiazole (2, purity: >97%) was purchased from Sinopharm Chemical Reagent Co. Ltd. All reagents were put to use without further purification. The solvent must be corresponding treatment with distillation in order to being in the free-water and free-oxygen conditions.



Scheme S1 Synthetic routes of the monomers and polymers

1.1 The synthesis of monomers

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

The monomer **T-DPP-T** (0.5 g, 0.58 mmol) and N-Bromosuccinimide (0.26 g, 1.45 mmol) was transferred to a 50mL single-neck bottle in which the mixed solution of $CHCl_3$ (20 mL) in darkness. The mixture was stirred 24 hours at room temperature. The reaction mixture was poured into water, and the product was extracted with dichloromethane. The organic layer was washed several times with water and dried over $MgSO_4$, and the solvent was removed by rotary evaporation. Recrystallization from methanol afforded desired products as purplish red crystals (0.51 g, yield 87.1%). ^{1}H NMR (400 MHz, CDCl3) δ 8.62 (d, 2H), 7.22 (d, 2H), 3.93 (d, 4H), 1.88 (s, 2H),1.54 (s, 4H), 1.29-1.22 (m, 60H), 0.87 (q, 12H). ^{13}C NMR (101 MHz, CDCl3) δ 161.41, 139.41, 135.30, 131.43, 131.18, 118.95, 108.03, 46.36, 37.77, 31.93, 31.89, 31.19, 29.98, 29.64, 29.56, 29.50, 29.36, 29.29, 26.19, 22.69, 22.67, 14.12. ESI-MS (m/z): M_{calcd} =1018.5, M_{found}=1018.3.

*3,6-di([2,2'-bithiophen]-5-yl)-2,5-bis(2-octyldodecyl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione(**2T-DPP-2T**)*

The compound **1** (0.5 g, 0.49 mmol) and catalyst ($Pd(PPh_3)_4$, 5 mol%) were transferred to a 25mL single-neck round-bottom flask. And the mixture was degassed for 20 min. Then 2-tributylstannyl-thiophene(0.46 g, 1.23 mmol) was added. Dry toluene which was degassed with argon for 20 min was added. The flask equipped with a condenser was then degassed and filled with argon three times. The reaction mixture was refluxed at 100 ^{0}C for 24 h under nitrogen. After cooling down to room temperature, the reaction mixture was poured into water, and the product was extracted with dichloromethane. The solvent was removed, and 0.41 g purple red solid was obtained in 81% yield by silica gel column chromatography (1:3 dichloromethane/ petroleum ether as eluent, R_f = 0.3). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.90 (d, 2H), 7.37 (m, 6H), 7.11 (dd, 2H), 4.04 (m, 4H), 1.92 (m, 2H), 1.31 (m, 16H), 0.89 (m, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.49, 142.67, 139.45, 136.56, 136.26, 128.16, 126.20, 125.11, 124.76, 108.28, 46.33, 37.94, 31.90, 31.36, 30.06, 29.65, 29.30, 26.37, 22.68, 14.10. ESI-MS (m/z): M_{calcd} =1024.6, M_{found}=1024.1.

*4,7-dibromobenzo[c][1,2,5]thiadiazole (**3**)*

Benzothiadiazole (0.5 g, 0.37 mmol) and HBr (48%) (2 mL) were transferred to single-neck bottle, and the mixture of bromine (1.6 g, 10 mmol) and HBr (3 mL) was slowly added. After refluxing at 100 ^{0}C for 6 h, an orange solid precipitated was formed. After cooling to room temperature, the mixture was washed with saturated $NaHCO_3$ and was filtered. The solid was washed with cold diethyl ether and 0.91 g pale yellow acicular crystal was obtained in 84.3% yield after recrystallization from methanol. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08 (s, 2H).

*4,7-bis(5-bromo-4-hexylthiophen-2-yl)benzo[c][1,2,5]thiadiazole(**BrHT-BT-HTBr**)*

The compound **3** (0.66 g, 2.24 mmol), 2-bromo-3-hexylthiophene (1.16 g, 4.68 mmol), catalyst $Pd(OAc)_2$ (5 mol%), tricyclohexylphosphonium tetrafluoroborate (10 mol%), K_2CO_3 (0.32 g, 2.34 mmol) and pivalic acid (0.18 g, 1.17 mmol) were transferred to single-neck bottle under an atmosphere of nitrogen. DMAc (8 mL) and p-xylene (8 mL) were added and the mixture was refluxed at 110 ^{0}C for 48 h. After cooling to room temperature, the solvent was removed, and 0.37 g yellow solid was obtained in 26.1% yield by silica gel column chromatography (1:3 dichloromethane/ petroleum ether as eluent, $R_f = 0.5$). ^{1}H NMR (400 MHz, $CDCl_3$): δ7.89 (d, 2H), 6.76 (s, 2H), 2.26 (m, 4H), 1.29-1.59 (m, 16H), 0.88 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.01, 143.06, 138.34, 128.05, 125.05, 124.76, 111.35, 31.66, 29.75, 28.99, 22.63, 14.11. ESI-MS (m/z): M_{calcd} =625.99, M_{found}=626.69.

*4,7-bis(5-bromo-4-hexylthiophen-2-yl)-5,6-difluorobenzo[c][1,2,5]thiadiazole(**BrHT-FBT-HTBr**)*

The compound **4** (0.5 g, 1.52 mmol), 2-bromo-3-hexylthiophene (0.75 g, 3.04 mmol), catalyst $Pd(OAc)_2$ (5 mol%), tricyclohexylphosphonium tetrafluoroborate (10 mol%), K_2CO_3 (0.52 g, 3.79 mmol) and pivalic acid (0.24 g, 1.52 mmol) were transferred to single-neck bottle under an atmosphere of nitrogen. DMAc (8 mL) and p-xylene (8 mL) were added and the mixture was refluxed at 110 ^{0}C for 48 h. After cooling to room temperature, the solvent was removed, and 0.25 g yellow solid was obtained in 25.2% yield by silica gel column chromatography (1:5 dichloromethane/ petroleum ether as eluent, $R_f = 0.7$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.76 (s, 2H), 2.26(m, 4 H), 1.29-1.59(m, 16 H), 0.88 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.01, 143.06, 138.34, 128.05, 125.05, 124.76, 111.35, 31.66, 29.75, 28.99, 22.63, 14.11. ESI-MS (m/z): M_{calcd} =661.97, M_{found}=662.51.

*1,3-bis(5-bromo-4-hexylthiophen-2-yl)-5-octyl-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione(**BrHT-TPD-HTBr**)*

The compound 5 (0.55 g, 1.30 mmol), 2-bromo-3-hexylthiophene (0.64 mg, 2.60 mmol), catalyst $Pd(OAc)_2$ (5 mol%), tricyclohexylphosphonium tetrafluoroborate (10 mol%), K_2CO_3 (0.36 g, 2.60 mmol) and pivalic acid (0.13 g, 1.30 mmol) were transferred to single-neck bottle under an atmosphere of nitrogen. DMAc (8 mL) and p-xylene (8 mL) were added and the mixture was refluxed at 110 ^{0}C for 48 h. After cooling to room temperature, the solvent was removed, and 0.30 g orange-yellow solid was obtained in 30 % yield by silica gel column chromatography (1:5 dichloromethane/ petroleum ether as eluent, Rf = 0.5). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, 2H), 3.42 (d, 2H), 2.62 (d, 4H), 1.59-0.88 (m, 37H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.47, 143.75, 135.51, 131.87, 130.28, 128.37, 113.52, 38.69, 31.78, 31.57, 29.62, 29.53, 29.16, 28.91, 28.50, 26.98, 22.61, 14.07. ESI-MS (m/z): M_{calcd} =755.10, M_{found}= 757.04.

1.2 ^{1}H NMR and ^{13}C NMR spectra of the monomers and polymers

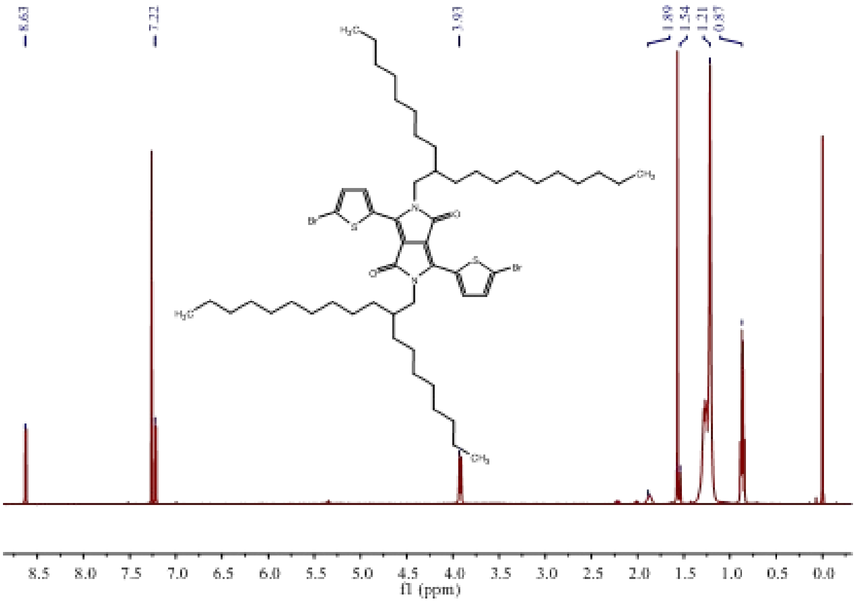


Fig. S1 ^{1}H NMR spectra of monomer 1

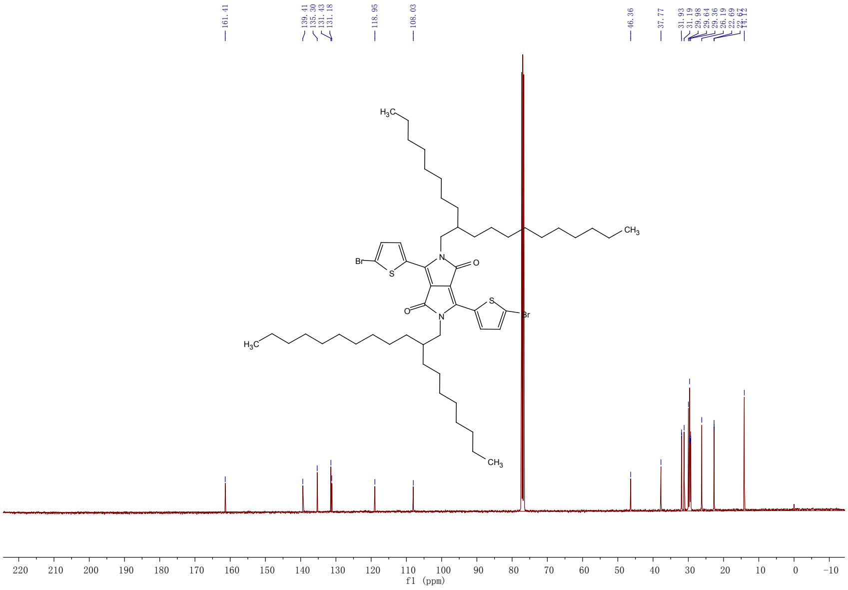


Fig. S2 ^{13}C NMR spectra of monomer 1

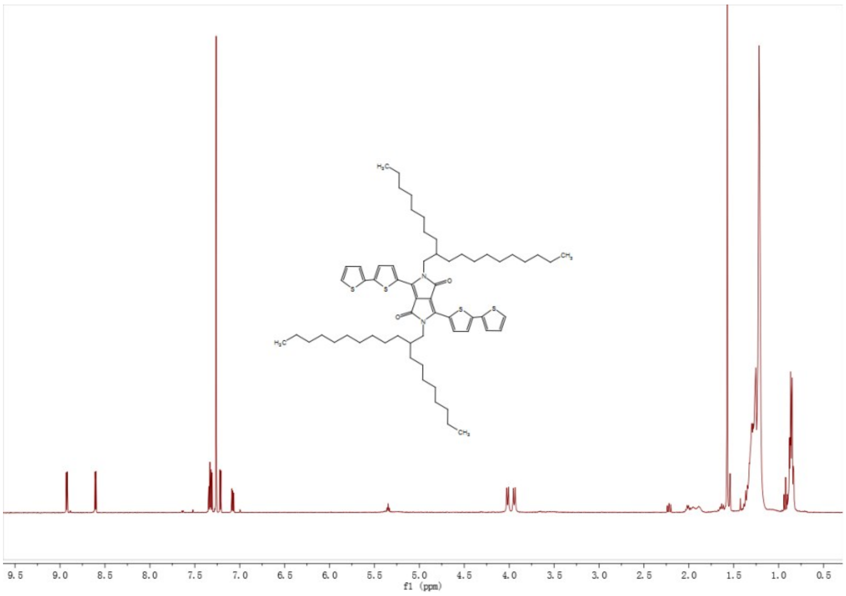


Fig. S3 ^{1}H NMR spectra of monomer 2T-DPP-2T

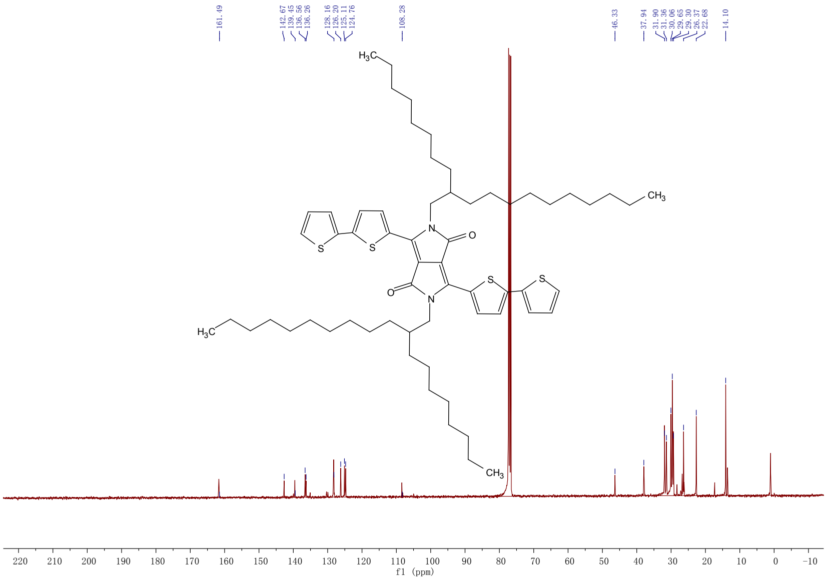


Fig. S4 ^{13}C NMR spectra of monomer 2T-DPP-2T

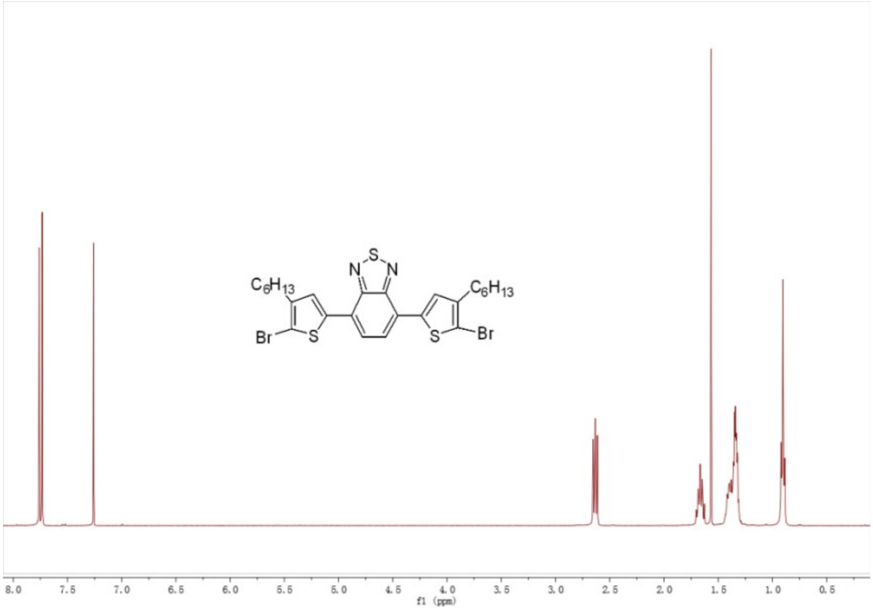


Fig. S5 ^{1}H NMR spectra of monomer BrHT-BT-HTBr

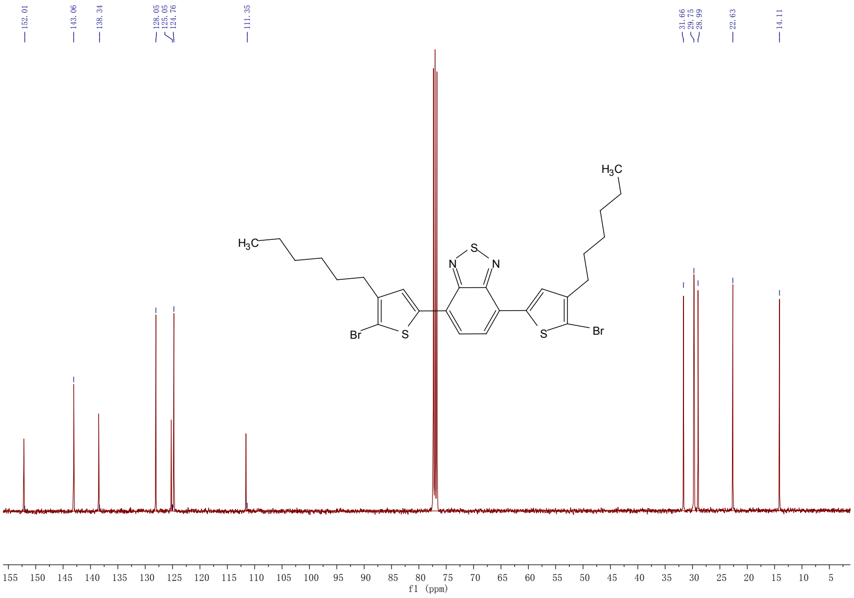


Fig. S6 ^{13}C NMR spectra of monomer BrHT-BT-HTBr

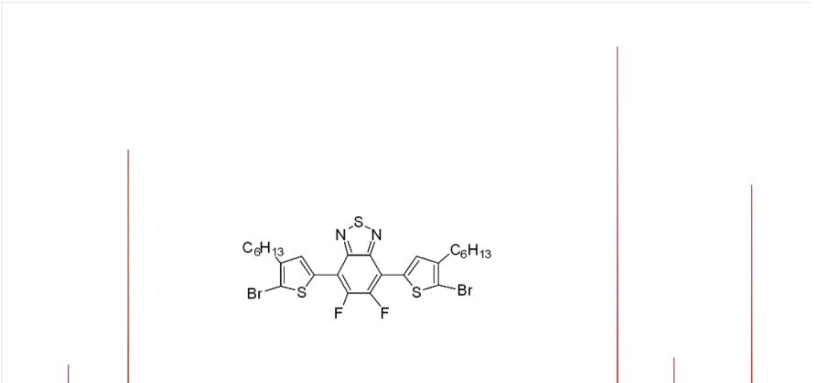


Fig. S7 ^{1}H NMR spectra of monomer BrHT-FBT-HTBr

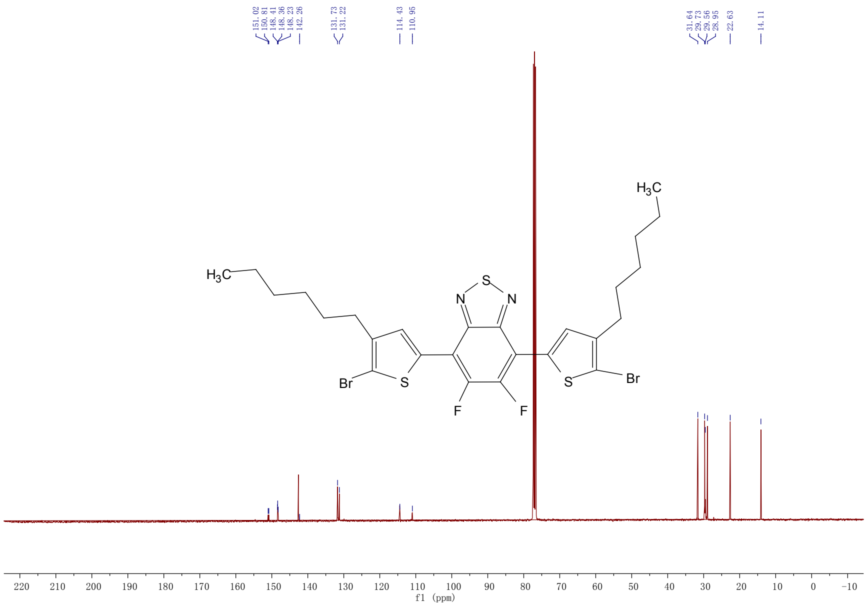


Fig. S8 ^{13}C NMR spectra of monomer BrHT-FBT-HTBr

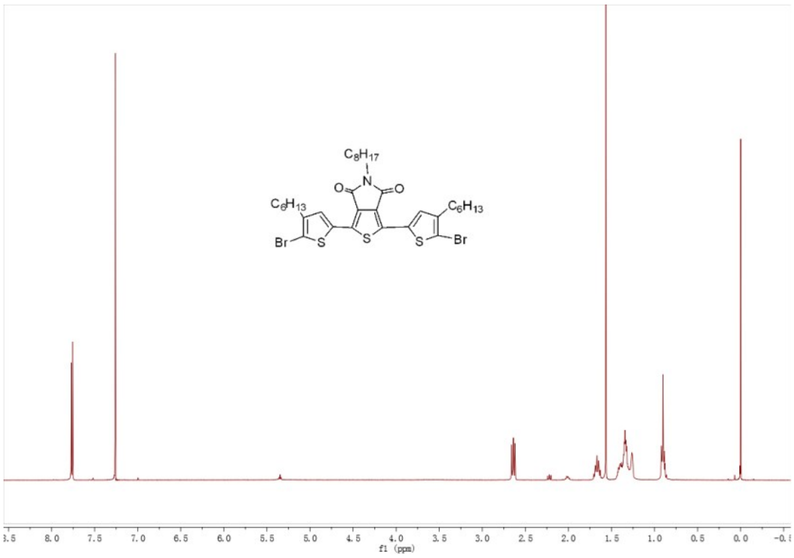


Fig. S9 ^{1}H NMR spectra of monomer BrHT-TPD-HTBr

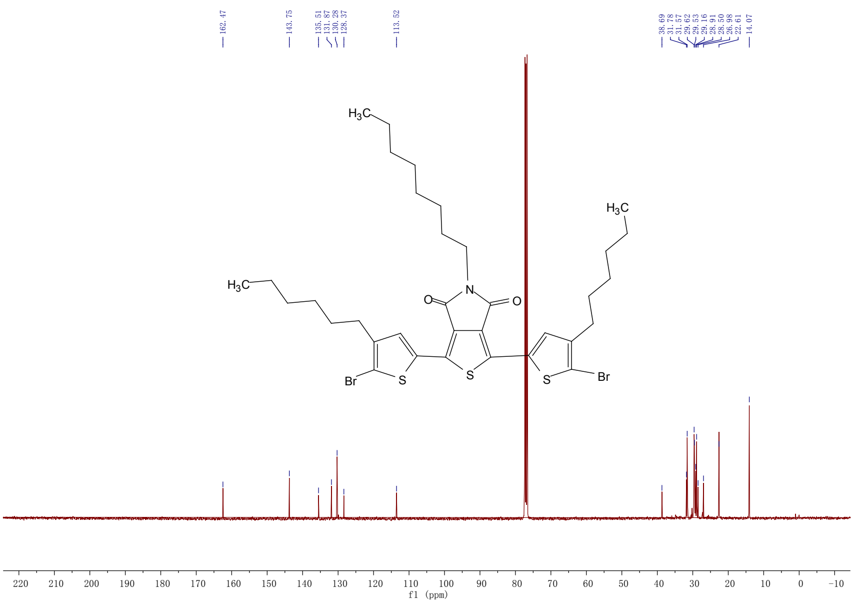


Fig. S10 ^{13}C NMR spectra of monomer BrHT-TPD-HTBr

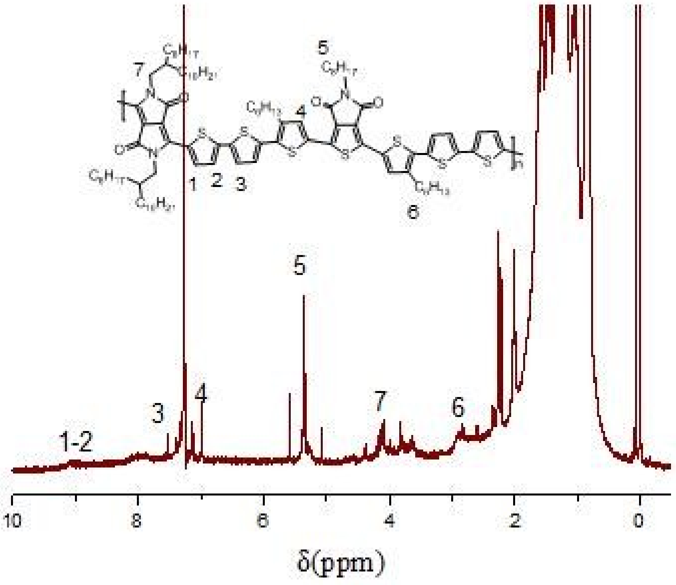


Fig. S11 ^{1}H NMR spectra of polymer P1

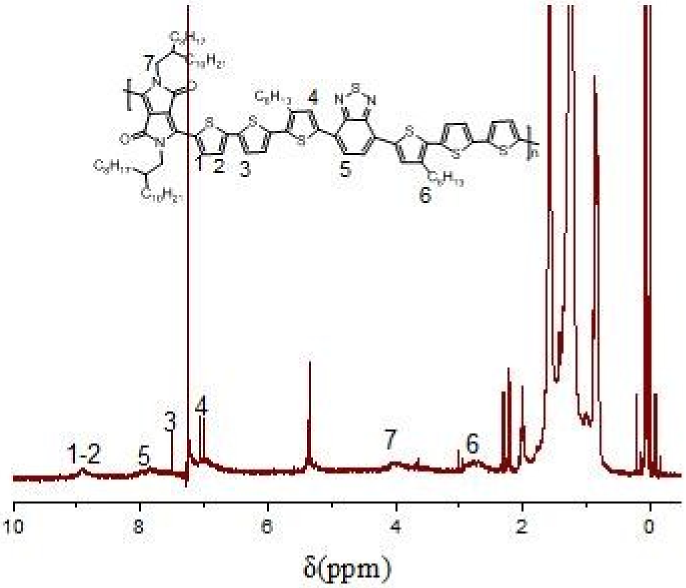


Fig. S12 ^{1}H NMR spectra of polymer P2

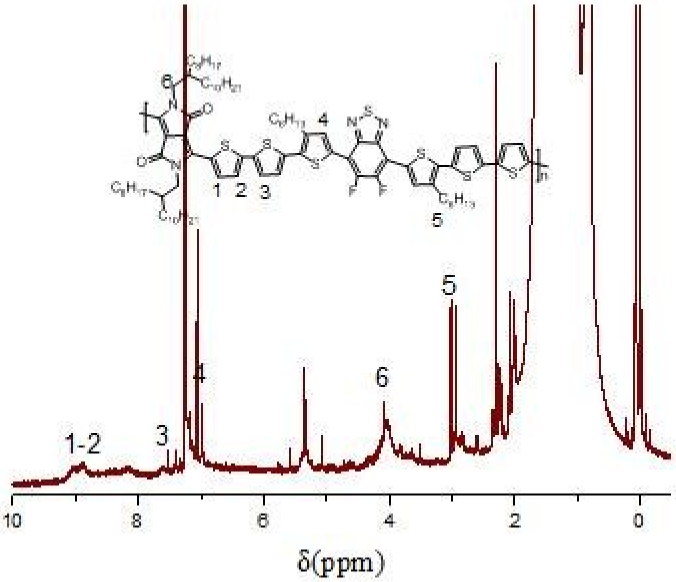


Fig. S13 ^{1}H NMR spectra of polymer P3

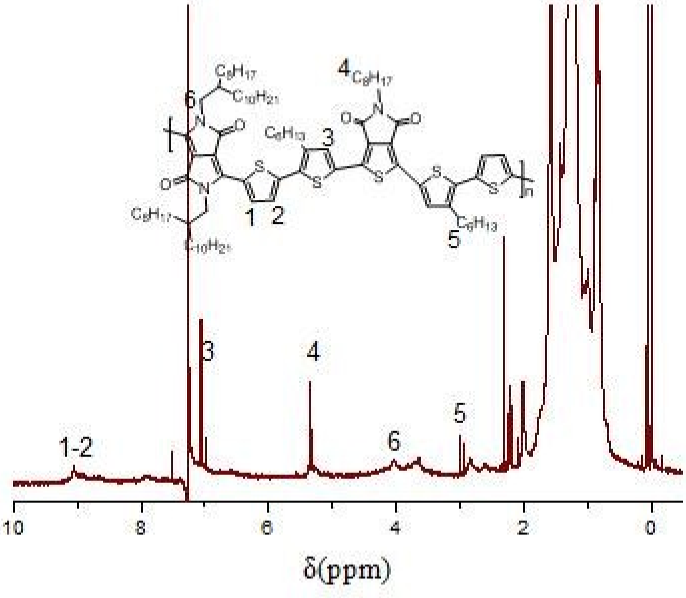


Fig. S14 ^{1}H NMR spectra of polymer P4

Table. S1 the optimization condition of PSCs based on polymer: PC$_{71}$BM

Polymer	D/A ratio	Speed r min^{-1}	Concentration mg/mL	DIO Vol %	solvent
P1	1:2	1500	4	3	chloroform
P2	1:1.5	1800	5	3	chloroform
P3	1:2	1000	5	3	chloroform
P4	1:2	4300	7	2	chloroform

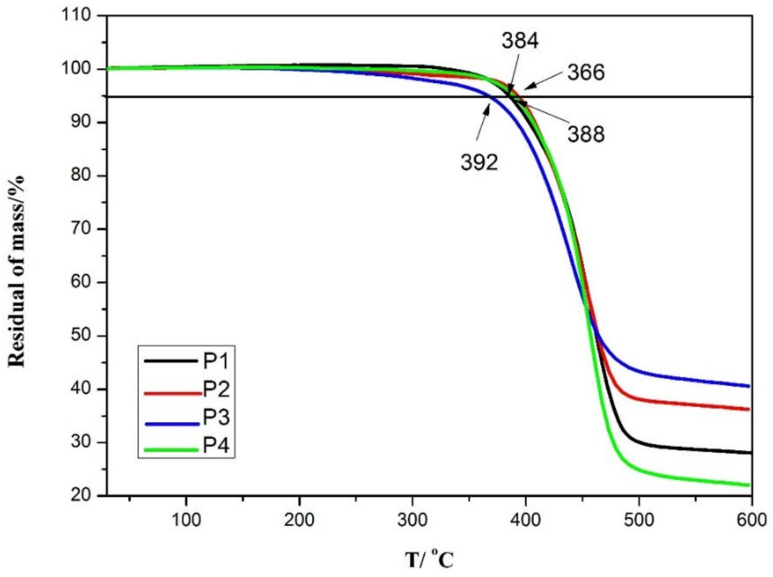


Fig. S15 TGA curves of P1, P2, P3 and P4

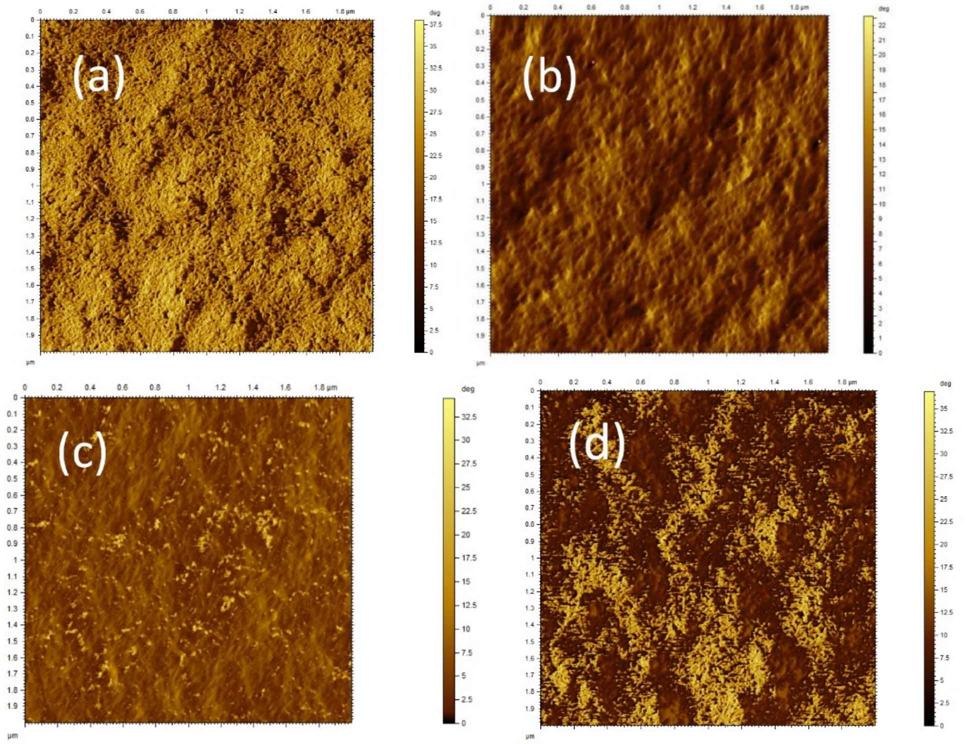


Fig. S16 AFM phase images of polymers : $PC_{71}BM$ blend films: P1 (a), P2 (b), P3 (c) and P4(d).