Supplementary Information

The Integrated Adjustment of Chlorine Substitution and Two-Dimensional Side Chain of Low-Band-Gap Polymers in Organic Solar Cells

Zhen Yang, [a,†] *Hui Chen,*[a,b, †] *Huan Wang,* [a] *Daize Mo,* [a] *Yulin Zhu,* [a] *Chuanjun Liu,* [b] *Wei Chen* [c,d]* and *Feng He* [a] *

[a]Department of Chemistry, Southern University of Science and Technology, Shenzhen, 518055, P. R. China

[b]Department of Chemistry, Wuhan University, Wuhan, 430072, P. R. China

[c]Materials Science Division, Argonne National Laboratory, 9700 Cass Avenue, Lemont, Illinois, 60439, United States

[d]Institute for Molecular Engineering, The University of Chicago, 5640 South Ellis Avenue, Chicago, Illinois, 60637, United States

[†] Z. Yang and H. Chen contributed equally to this work.

Author to whom correspondence should be addressed: hef@sustc.edu.cn (F.H.); wchen@anl.gov (W.C.).

Materials and Synthesis

All reagents and chemicals were purchased from commercial sources and used as received without further purification. The solvents for chemical syntheses were dried over Na/benzophenone and freshly distilled prior to use. Poly(3,4-ethylenedioxy-thiophene): poly(styrenesulfonate) (PEDOT:PSS) (Clevios PVP AI 4083) was purchased from H.C. Stark and passed through a 0.45 µm PVDF syringe filter before spin-coating. [6,6]-Phenyl-C71-butyric acid methyl ester (PC71BM) was obtained from Nano-C. Reagents **5**-**7** were prepared according to the previously published literatures.[1-3]

*Synthesis of the 4,8-bis(5'-(2-octyldodecyl)-[2,2'-bithiophen]-5-yl)benzo[1,2-b:4,5-b']dithiophene (**3**).* Under nitrogen atmosphere, n-BuLi (1.2 ml, 2.4M in THF) was added dropwise to a solution of **1** **(**1.2g, 2.7 mmol**)** in dry THF at 0 °C. The mixture was then warmed to 50 °C and stirred for 2 h. Subsequently, 4,8-dihydrobenzo[1,2-b:4,5-b′]-dithiophen-4,8-dione **(**0.237g, 1.07 mmol**)** was added to the reaction mixture, which was then stirred for another 1 h at 50 °C. Cooling the mixture down to ambient temperature, $SnCl_2 \cdot 2H_2O$ (2.3 g, 10 mmol) in 4 mL HCl (10%) was added, and the mixture was stirred for another 4 h. The mixture was subsequently poured into ice water and extracted with CH_2Cl_2 (100 mL × 3). The combined extracts were dried with anhydrous $MgSO_4$ and evaporated. The crude product was purified by column chromatography (hexane) on silica gel to give pure product as a pale yellow liquid (yield 61%). ^{1}H NMR (400 MHz, Chloroform-d): δ (ppm) 7.70 (d, J = 5.7 Hz, 2H), 7.49 (d, J = 5.7 Hz, 2H), 7.39 (d, J = 3.7 Hz, 2H), 7.24 (d, J = 3.7 Hz, 2H), 7.09 (d, J = 3.5 Hz, 2H), 6.70 (d, J = 3.5 Hz, 2H), 2.77 (d, J = 6.6 Hz, 4H), 1.67 (m, 2H), 1.31 (d, J = 16.1 Hz, 64H), 0.89 (dt, J = 6.9, 3.3 Hz, 12H). ESI-TOF-HRMS (M_w =1079.80): m/z = 1079.57 [M^+].

*Synthesis of the 4,8-bis(5''-(2-octyldodecyl)-[2,2':5',2''-terthiophen]-5-yl)benzo[1,2-b:4,5-b']dithiophene (**4**).* Under nitrogen atmosphere, n-BuLi (2.12 ml, 2.4 M in THF) was added dropwise to the solution of **2** (2.4g, 4.5 mmol) in dry THF at 0 °C. The mixture was then warmed to 50 °C and stirred for 2 h. Subsequently, 4,8-dihydrobenzo[1,2-b:4,5-b′]-dithiophen-4,8-dione (0.28 g, 1.27 mmol) was added to the reaction mixture, which was then stirred for another 1 h at 50 °C. Cooling the mixture down to ambient temperature, $SnCl_2{\cdot}2H_2O$ (2.3 g, 10 mol) in 4 mL HCl (10%) was added, and the mixture was stirred for another 4 h. The mixture was subsequently poured into ice water and extracted with CH_2Cl_2 (100 mL × 3). The combined extracts were dried with anhydrous $MgSO_4$ and evaporated. The crude product was purified by column chromatography (hexane) on silica gel to give pure product as a yellow solid (yield: 67%). ^{1}H NMR (400 MHz, Chloroform-d): δ (ppm) 7.71 (d, J = 5.7 Hz, 2H), 7.52 (d, J = 5.7, 1.5 Hz, 2H), 7.42 (d, J = 3.7 Hz, 2H), 7.30 (d, J = 3.7 Hz, 2H), 7.16 (d, J = 3.7 Hz, 2H), 7.05 (d, J = 3.7 Hz, 2H), 7.03 (d, J = 3.5 Hz, 2H), 6.68 (d, J = 3.5 Hz, 2H), 2.74 (d, J = 6.6 Hz, 4H), 1.64 (m, 2H), 1.29 (d, J = 15.0 Hz, 64H), 0.92 – 0.84 (m, 12H). ESI-TOF-HRMS (M_w =1244.09): m/z =1243.55 [M^+].

*Synthesis of the (4,8-bis(5'-(2-octyldodecyl)-[2,2'-bithiophen]-5-yl)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(trimethylstannane) (**D1**).* Compound 3 (630mg, 0.51mmol) was dissolved in dry THF in a nitrogen purged flask. The solution was cooled to −78 °C before LDA (2.5ml, 1.6 M in THF) was added dropwise. After the reaction was stirred at −78 °C for 90 min, trimethyltin chloride (5.1 ml, 1 M in hexane) was added in one portion. The solution was allowed to warm to room temperature slowly and stirred overnight. After the reaction, the solution was diluted with dichloromethane (200 mL), washed with water (150 mL × 3), dried over anhydrous $MgSO_4$, and evaporated. The crude product was purified by recrystallization in 2-propanol to give pure distannylated BDT-Tin as a yellow solid (yield: 89%). ^{1}H NMR (400 MHz, Chloroform-d): δ (ppm) 7.71 (s, 1H), 7.39 (d, J = 3.5 Hz, 2H), 7.26 (s, 2H), 7.10 (d, J = 3.2 Hz, 2H), 6.70 (d, J = 3.0 Hz, 2H), 2.76 (d, J = 6.4 Hz, 4H), 1.66 (m, 1H), 1.30 (d, J = 16.0 Hz, 64H), 1.02 – 0.80 (m, 12H), 0.41 (s, 18H). ESI-TOF-HRMS (M_w = 1405.46): m/z =1406.50 [M^+].

*Synthesis of the (4,8-bis(5''-(2-octyldodecyl)-[2,2':5',2''-terthiophen]-5-yl)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(trimethylstannane) (**D2**).* Compound 4 **(**800 mg, 0.74 mmol**)** was dissolved in dry THF in a nitrogen purged flask. The solution was cooled to −78 °C before LDA (3 ml, 1.6 M in THF) was added dropwise. After the reaction was stirred at −78 °C for 90 min, trimethyltin chloride (6.3 ml, 1 M in hexane) was added in one portion. The solution was allowed to warm to room temperature slowly and stirred overnight. After the reaction, the solution was diluted with dichloromethane (200mL), washed with water (150 mL × 3), dried over anhydrous $MgSO_4$, and evaporated. The crude product was purified by recrystallization in 2-propanol to give pure distannylated BDT-Tin as a yellow solid (yield: 85%). ^{1}H NMR (400 MHz, Methylene Chloride-d2): δ (ppm) 7.75 (s, 2H), 7.45 (d, J = 3.7 Hz, 2H), 7.34 (d, J = 3.7 Hz, 2H), 7.20 (d, J = 3.7 Hz, 2H), 7.08 (d, J = 3.8 Hz, 2H), 7.06 (d, J = 3.5 Hz, 2H), 6.72 (d, J = 3.5 Hz, 2H), 2.76 (d, J = 6.6 Hz, 4H), 1.66 (m, 2H), 1.30 (d, J = 18.6 Hz, 64H), 0.95 – 0.76 (m, 12H), 0.58 – 0.26 (m, 18H). ESI-TOF-HRMS (M_w = 1569.70): m/z = 1570.48 [M^+].

Synthesis of the BTs. A mixture of BT-Br (1.0 equiv), tributyl(4-dodecylthiophen-2-yl)stannane (2.2 equiv), $Pd_2(dba)_3$ (4% equiv) and $P(o\text{-}tol)_3$ (16% equiv) was degassed and recharged with N_2 in a flask. After the addition of toluene and DMF (4/1, by volume), the reaction mixture was heated to 145 °C and stirred for 24 h. The solution was diluted with ethyl ether, washed with water three times, dried over anhydrous $MgSO_4$, and evaporated. The residue was chromatographically purified on silica gel eluting (PE/DCM).

*Synthesis of the 4,7-bis(4-dodecylthiophen-2-yl)-5-fluorobenzo[c][1,2,5]thiadiazole (**8**).* Compound **8** was the yellow solid (yield: 92.5%). ^{1}H NMR (400 MHz, Chloroform-d): δ (ppm) 8.09 (s, 1H), 7.98 (d, J = 1.3 Hz, 1H), 7.73 (d, J = 13.0 Hz, 1H), 7.15 (d, J = 1.1 Hz, 1H), 7.09 (d, J = 1.0 Hz, 1H), 2.70 (q, J = 8.1 Hz, 4H), 1.70 (p, J = 6.8 Hz, 4H), 1.26 (s, 36H), 0.93 – 0.80 (m, 6H). ESI-TOF-HRMS (Mw = 655.05): m/z = 655.36 [M^+].

*Synthesis of the 5-chloro-4,7-bis(4-dodecylthiophen-2-yl)benzo[c][1,2,5]thiadiazole (**9**).* Compound **9** was the yellow solid (yield: 91.2%). ^{1}H NMR (400 MHz, CDCl3) δ 7.98 (d, J = 1.3 Hz, 1H), 7.92 (s, 1H), 7.61 (d, J = 1.3 Hz, 1H), 7.18 (d, J = 1.1 Hz, 1H), 7.09 (s, 1H), 2.81 – 2.54 (m, 4H), 1.81 – 1.59 (m, 4H), 1.46 – 1.18 (m, 37H), 0.88 (t, J = 6.8 Hz, 6H). ESI-TOF-HRMS (M_w = 671.50): m/z = 671.65 [M^+].

*Synthesis of the 5,6-dichloro-4,7-bis(4-dodecylthiophen-2-yl)benzo[c][1,2,5]thiadiazole (**10**).* Compound **10** was the yellow solid (yield: 81.3%). ^{1}H NMR (500 MHz, Chloroform-d): δ (ppm) 7.49 (d, J = 1.4 Hz, 2H), 7.21 (d, J = 1.2 Hz, 2H), 2.78 – 2.67 (m, 4H), 1.70 (d, J = 7.6 Hz, 4H), 1.44 – 1.15 (m, 36H), 0.88 (t, J = 7.0 Hz, 6H). ESI-TOF-HRMS (M_w = 705.95): m/z = 705.29 [M^+].

Synthesis of the DBT-Br. To a solution of *DBT* (1.0 equiv) in THF was slowly added N-bromosuccinimide (NBS, 10 equiv). After the reaction was carried out in the dark at room temperature for 18 h, the solution was diluted with dichloromethane, washed with water three times, dried over anhydrous $MgSO_4$, and evaporated. The crude product was purified by column chromatography on silica gel and then further recrystallized from CH_2Cl_2 to give the pure product.

*Synthesis of the 4,7-bis(5-bromo-4-dodecylthiophen-2-yl)-5-fluorobenzo[c][1,2,5]thiadiazole (**A1**).* Compound **A1** was red powders (yield: 97%). ^{1}H NMR (400 MHz, Chloroform-d): δ (ppm) 7.95 (s, 1H), 7.75 (s, 1H), 7.64 (d, J = 13.0 Hz, 1H), 2.64 (q, J = 7.4 Hz, 4H), 1.66 (p, J = 7.5 Hz, 4H), 1.31 (d, J = 41.1 Hz, 36H), 0.90 – 0.84 (m, 5H). ^{13}C NMR (101 MHz, CDCl3): δ(ppm) 160.06, 157.53, 152.98, 149.35, 143.23, 142.35, 137.07, 132.19, 131.05, 128.77, 124.92, 116.08, 115.75, 113.07, 110.59, 31.93, 29.79, 29.73, 29.69, 29.67, 29.66, 29.61, 29.60, 29.44, 29.44, 29.36, 29.29, 22.69, 14.11. ESI-TOF-HRMS (M_w = 812.84): m/z = 812.17 [M^+].

Synthesis of the 4,7-bis(5-bromo-4-dodecylthiophen-2-yl)-5-chlorobenzo[c][1,2,5]thiadiazole (A2). Compound **A2** was red powders (yield: 97%). ^{1}H NMR (500 MHz, Chloroform-d): δ (ppm) 7.85 (s, 1H), δ (ppm) 7.76 (s, 1H), 7.60 (s, 1H), 2.65 (q, J = 8.3 Hz, 4H), 1.64 (d, J = 15.5 Hz, 4H), 1.48 – 1.01 (m, 36H), 0.87 (t, J = 6.8 Hz, 6H). ^{13}C NMR (126 MHz, CDCl3): δ (ppm) 154.39, 150.56, 143.20, 141.85, 136.76, 134.05, 133.33, 132.27, 128.90, 127.15, 125.52, 123.05, 113.06, 112.84, 31.93, 29.74, 29.69, 29.65, 29.62, 29.60, 29.58, 29.43, 29.36, 29.27, 22.70, 14.14. ESI-TOF-HRMS (M_w = 829.30): m/z = 829.15 [M^+].

Synthesis of the 4,7-bis(5-bromo-4-dodecylthiophen-2-yl)-5,6-dichlorobenzo[c][1,2,5]-thiadiazole (A3). Compound **A3** was the bright orange (78%: yield). ^{1}H NMR (400 MHz, Chloroform-d): δ (ppm) 7.47 (s, 2H), 2.91 – 2.52 (m, 4H), 1.81 – 1.56 (m, 4H), 1.47 – 1.10 (m, 36H), 0.87 (t, J = 6.8 Hz, 6H). ^{13}C NMR (101 MHz, Chloroform-d): δ (ppm) 152.22, 141.96, 134.03, 132.77, 125.44, 113.18, 31.95, 30.15-28.87 (m), 22.72, 14.15. ESI-TOF-ESI-TOF-HRMS (M_w = 863.74): m/z = 865.11 [$M+H^+$].

*Synthesis of **PBBF1-T2***. **D1** (100 mg, 0.0711 mmol), **A1** (57.8 mg, 0.0711 mmol), and $Pd_2(dba)_3$ (2.60 mg, 0.00284 mmol), $P(o\text{-}tol)_3$ (3.46 mg, 0.0114 mmol) was added into 5mL of anhydrous chlorobenzene under an atmosphere of N_2. The solution was refluxed for 18 h at the temperature of 145 °C. Then the mixture was cooled down and precipitated into 100 mL of methanol. The precipitate was filtered into a Soxhlet extractor; CH_3OH, hexane, CH_2Cl_2 and $CHCl_3$ were used as solvents to remove the residual oligomers and catalyst. Finally, the polymer as extracted by CB. Then the solution was concentrated and poured into 100 mL of CH_3OH. The polymer was collected as a dark green solid (100 mg). Yield 84%. ^{1}H NMR (500 MHz, 1,1,2,2-Tetrachloroethane-d): δ (ppm) 8.11-6.55 (br, ArH), 3.01-2.54 (CH_2), 1.76-1.6 (CH, CH_2), 1.67-1.03 (CH_2), 1.03-0.57 (CH_3). Elemental analysis calcd (%) for $C_{104}H_{147}FN_2S_9$: C, 72.08; H, 8.55; N, 1.62; S, 16.65. Found: C, 72.10; H, 8.56; N, 1.61; S, 16.60.

*Synthesis of **PBBCl1-T2***. **PBBCl1-T2** (150 mg) was prepared using the same procedure as **PBBF1-T2**. Yield 88%. ^{1}H NMR (500 MHz, 1,1,2,2-Tetrachloroethane-d): δ (ppm) 8.21 – 7.59 (m, 5H), 7.43 (s, 2H), 7.23 (s, 2H), 7.07 (s, 2H), 6.66 (s, 2H), 2.81 (d, J = 70.2 Hz, 8H), 1.68 (d, J = 36.0 Hz, 6H), 1.26 (d, J = 22.0 Hz, 100H), 0.83 (s, 18H). Elemental analysis calcd (%) for $C_{104}H_{147}ClN_2S_9$: C, 71.41; H, 8.47; N, 1.60; S, 16.50. Found: C, 71.38; H, 8.45; N, 1.58; S, 16.50.

*Synthesis of **PBBF1-T3***. **PBBF1-T3** (150 mg) was prepared using the same procedure as **PBBF1-T2**. Yield 83%. ^{1}H NMR (500 MHz, 1,1,2,2-Tetrachloroethane-d): δ (ppm) 7.86-6.27 (br, ArH), 2.91-2.56 (CH_2), 1.82-1.65 (CH, CH_2), 1.56-1.00 (CH_2), 1.00-0.40 (CH_3). Elemental analysis calcd (%) for $C_{112}H_{151}FN_2S_{11}$: C, 70.91; H, 8.02; N, 1.48; S, 18.59. Found: C, 70.89; H, 8.02; N, 1.47; S, 18.62.

*Synthesis of **PBBCl1-T3***. **PBBCl1-T3** (90 mg) was prepared using the same procedure as **PBBF1-T2**. Yield 73%. ^{1}H NMR (500 MHz, 1,1,2,2-Tetrachloroethane-d): δ (ppm) 8.01-6.27 (br, ArH), 2.99-2.28 (CH_2), 1.84-1.56 (CH, CH_2), 1.56-1.04 (CH_2), 1.04-0.56 (CH_3). Elemental analysis calcd (%) for $C_{112}H_{151}ClN_2S_{11}$: C, 70.30; H, 7.95; N, 1.46; S, 18.43. Found: C, 70.31; H, 7.93; N, 1.44; S, 18.45.

*Synthesis of **PBBCl2-T3***. **PBBCl2-T3** (100 mg) was prepared using the same procedure as **PBBF1-T2**. Yield 81%.^{1}H NMR (500 MHz, 1,1,2,2-Tetrachloroethane-d): δ (ppm) 7.75 (s, 2H), 7.66 (s, 2H), 7.44 (s, 2H), 7.27 (s, 2H), 7.11 (d, J = 2.0 Hz, 2H), 6.96 (d, J = 6.9 Hz, 4H), 6.61 (s, 2H), 2.89 (s, 4H), 2.66 (s, 4H), 1.71 (s, 4H), 1.58 (s, 2H), 1.20 (t, J = 18.5 Hz, 100H), 0.81 (s, 18H). Elemental analysis calcd (%) for $C_{112}H_{150}Cl_2N_2S_{11}$: C, 69.05; H, 7.76; N, 1.44; S, 18.11. Found: C, 69.12; H, 7.74; N, 1.42; S, 18.09.

Table S1. GPC number-averaged molecular weight (Mn), weight-averaged molecular weight (Mw) and PDI of **PBBF1-T2**, **PBBCl1-T2**, **PBBF1-T3**, **PBBCl1-T3** and **PBBCl2-T3** polymers.

	PBBF1-T2	**PBBCl1-T2**	**PBBF1-T3**	**PBBC1-T3**	**PBBCl2-T3**
Mn (kDa)	30.9	29.2	47.0	26.3	20.1
Mw (kDa)	78.4	67.2	100.8	51.3	37.9
PDI	2.54	2.30	2.14	1.95	1.82

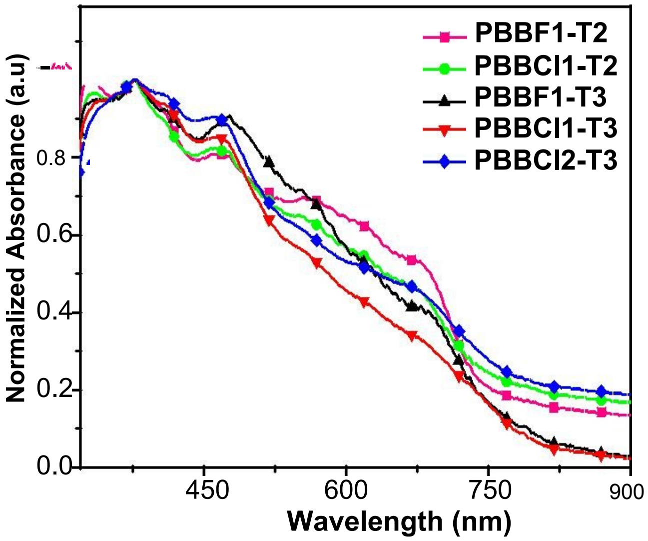


Figure S1. The Normalized UV−vis absorption spectra of PBBF1-T2, PBBCl1-T2, PBBF1-T3, PBBCl1-T3 and PBBCl2-T3 film blending with $PC_{71}BM$.

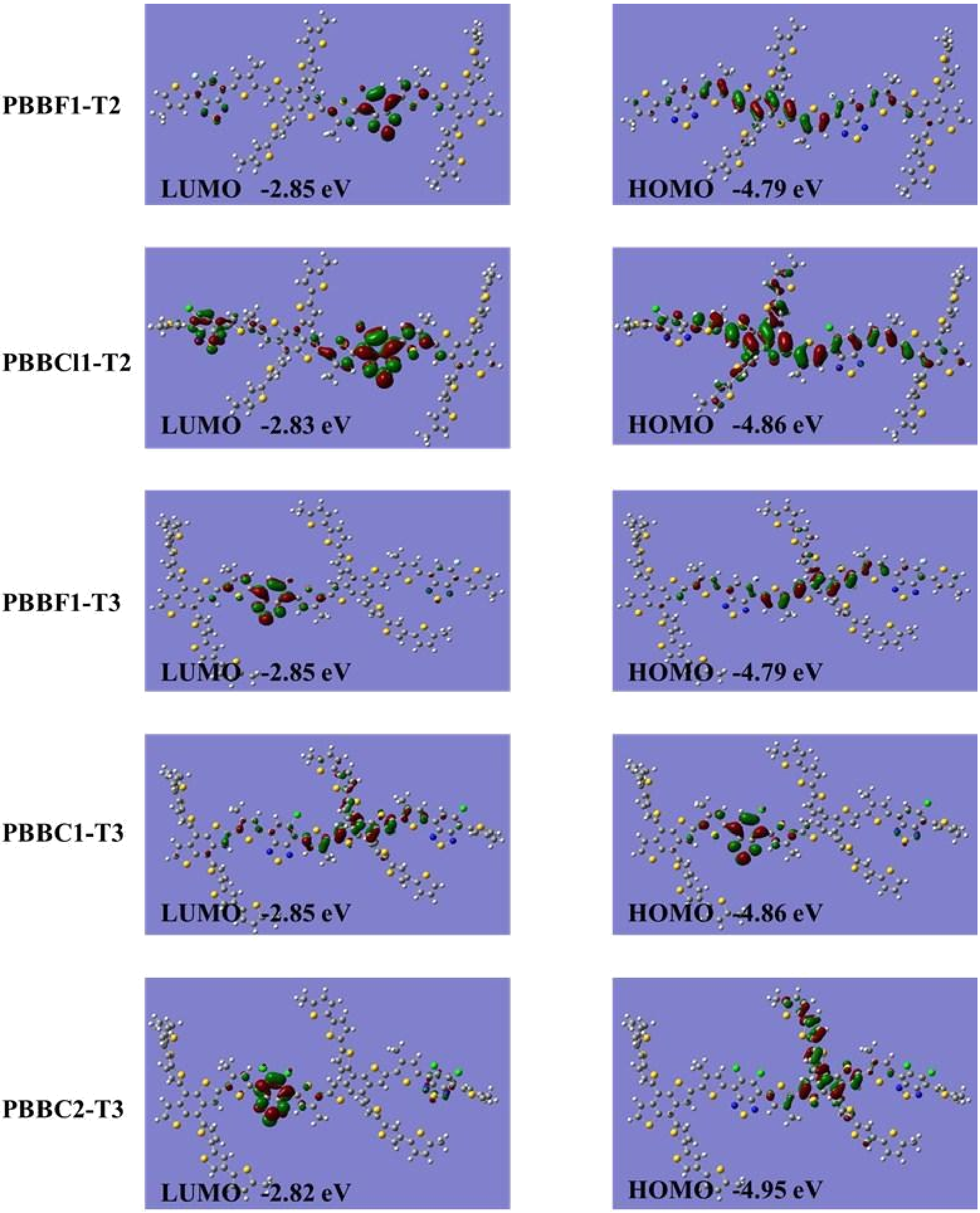


Figure S2. The Optimized geometry and molecular frontier orbitals of PBBF1-T2, PBBCl1-T2, PBBF1-T3, PBBCl1-T3 and PBBCl2-T3 obtained using DFT calculation.

Table S2. The performance parameters of the PSCs devices without DIO as an additive under 100 mW cm^{-2} AM 1.5 G irradiation.

Polymer	V_{OC} (V)	J_{SC} (mA cm^{-2})	FF (%)	PCE (%)
PBBF1-T2	0.84	8.49	40.20	2.86
PBBCl1-T2	0.88	7.89	45.36	3.15
PBBF1-T3	0.76	9.85	58.03	4.33
PBBCl1-T3	0.77	10.12	60.25	4.68
PBBCl2-T3	0.88	7.91	48.62	3.39

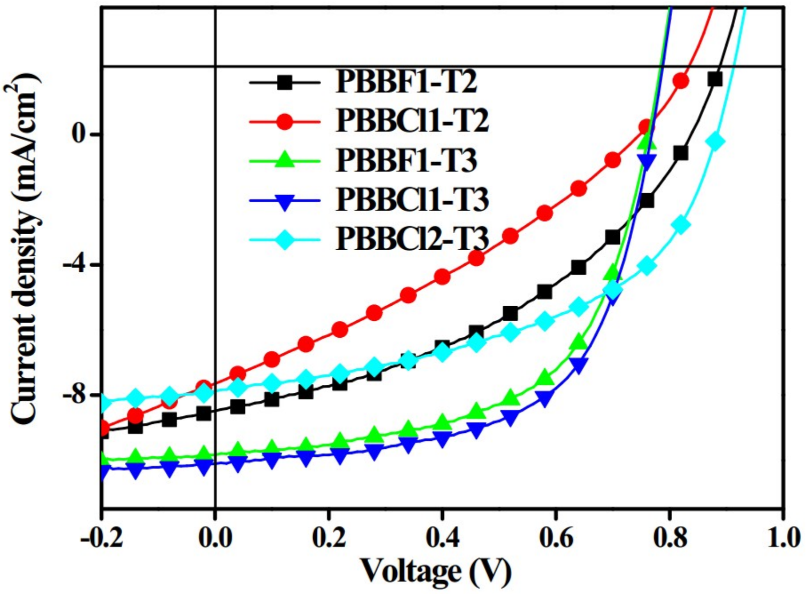


Figure S3. *J*-*V* curves of the PSCs devices without DIO as an additive under 100 mW cm^{-2} AM 1.5 G irradiation.

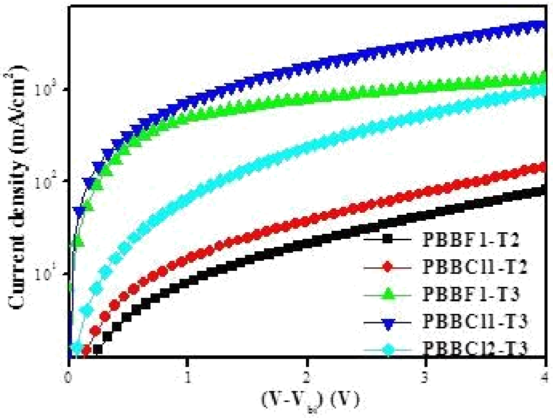


Figure S4. The *J-V* curves of hole-only **PBBF1-T2**, **PBBCl1-T2**, **PBBF1-T3**, **PBBCl1-T3** and **PBBCl2-T3:**PC$_{71}$BM blend films in dark.

Table S3. Hole mobilities extracted from J-V curves of hole-only **PBBF1-T2**, **PBBCl1-T2**, **PBBF1-T3**, **PBBCl1-T3** and **PBBCl2-T3**:PC$_{71}$BM blend films from SCLC model.

Polymers	μ（cm^2 V^{-1} s^{-1}）
PBBF1-T2	1.8×10^{-6}
PBBCl1-T2	2.7×10^{-6}
PBBF1-T3	8.3×10^{-5}
PBBCl1-T3	2.5×10^{-4}
PBBCl2-T3	3.6×10^{-5}

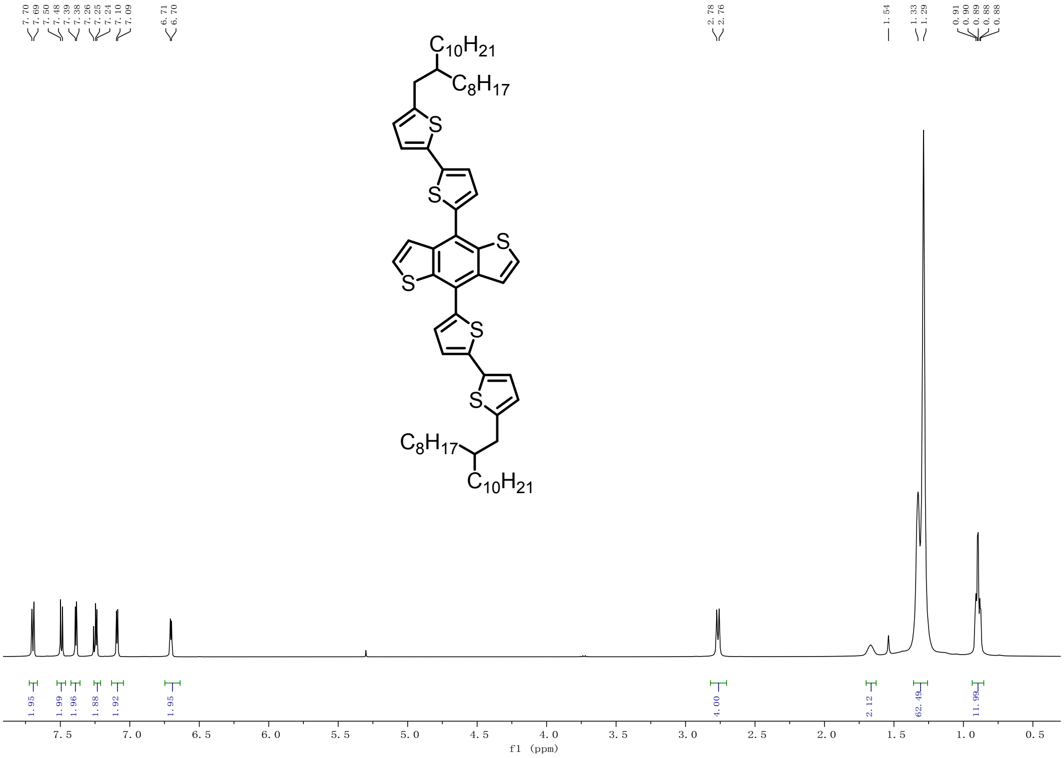


Figure S5. ^{1}HNMR spectrum of **3**

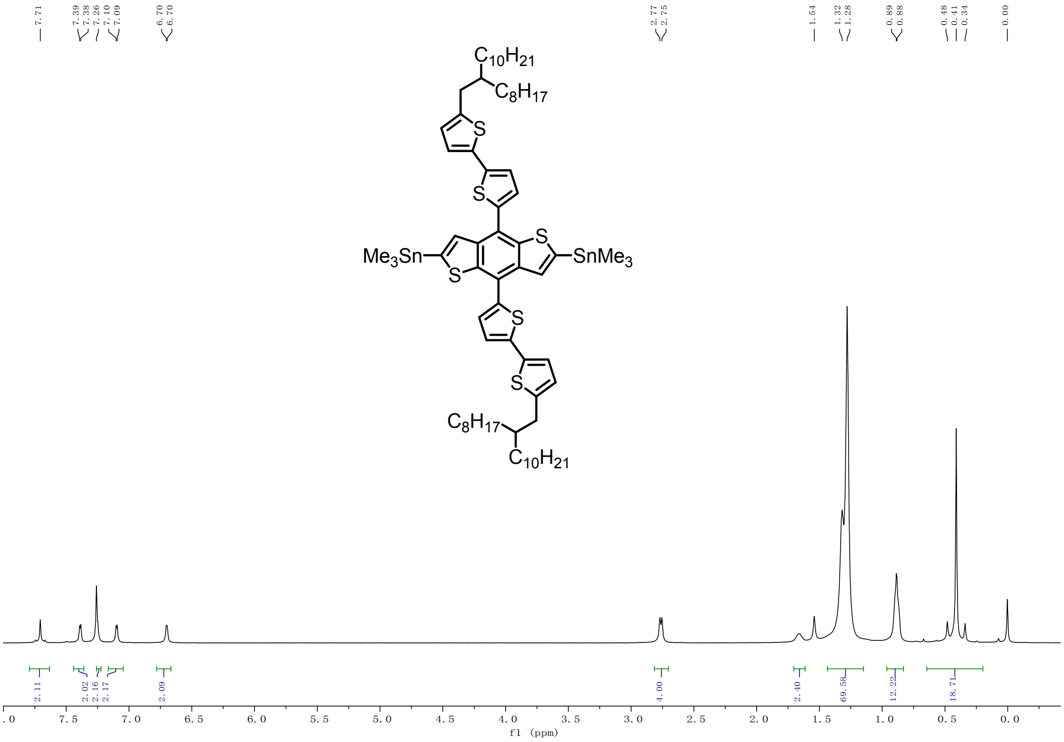


Figure S6. ^{1}HNMR spectrum of **D1**

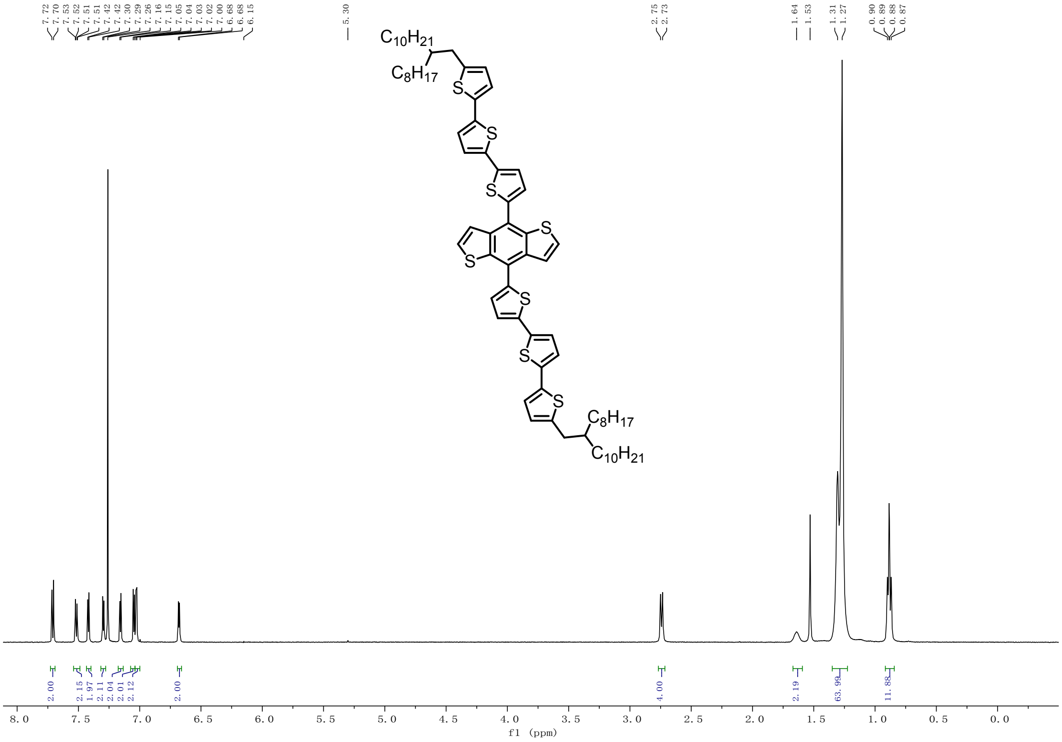


Figure S7. ^{1}HNMR spectrum of **4**

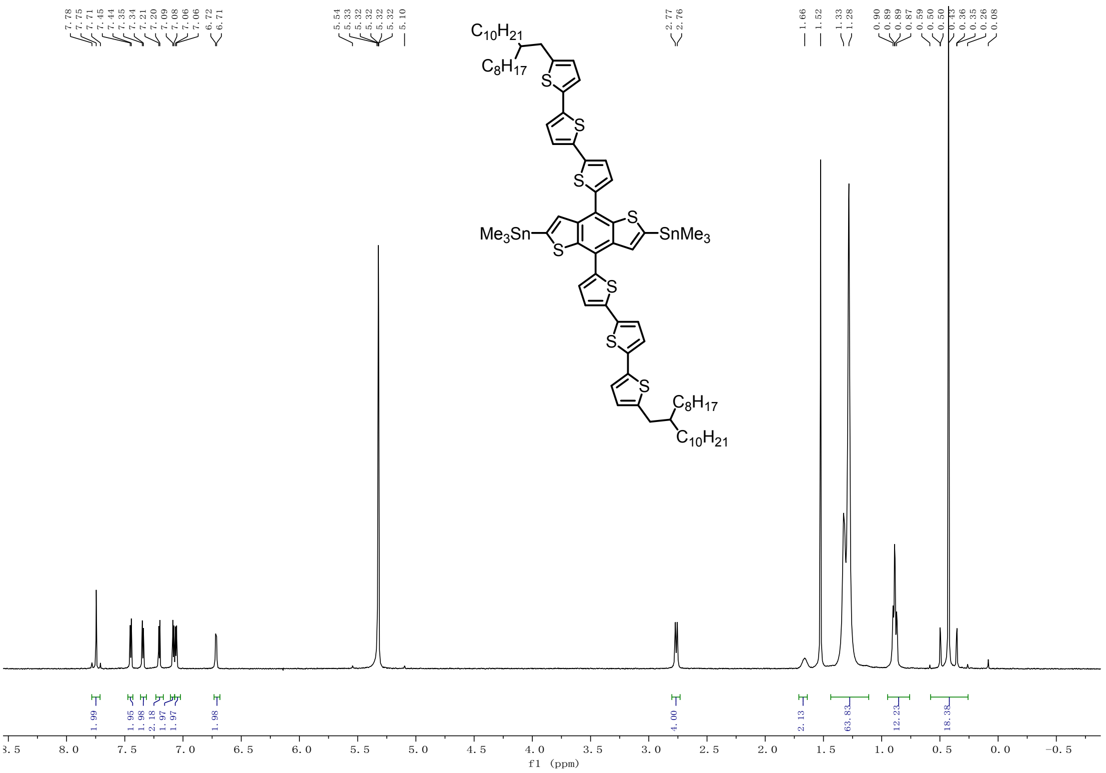


Figure S8. ^{1}HNMR spectrum of **D2**

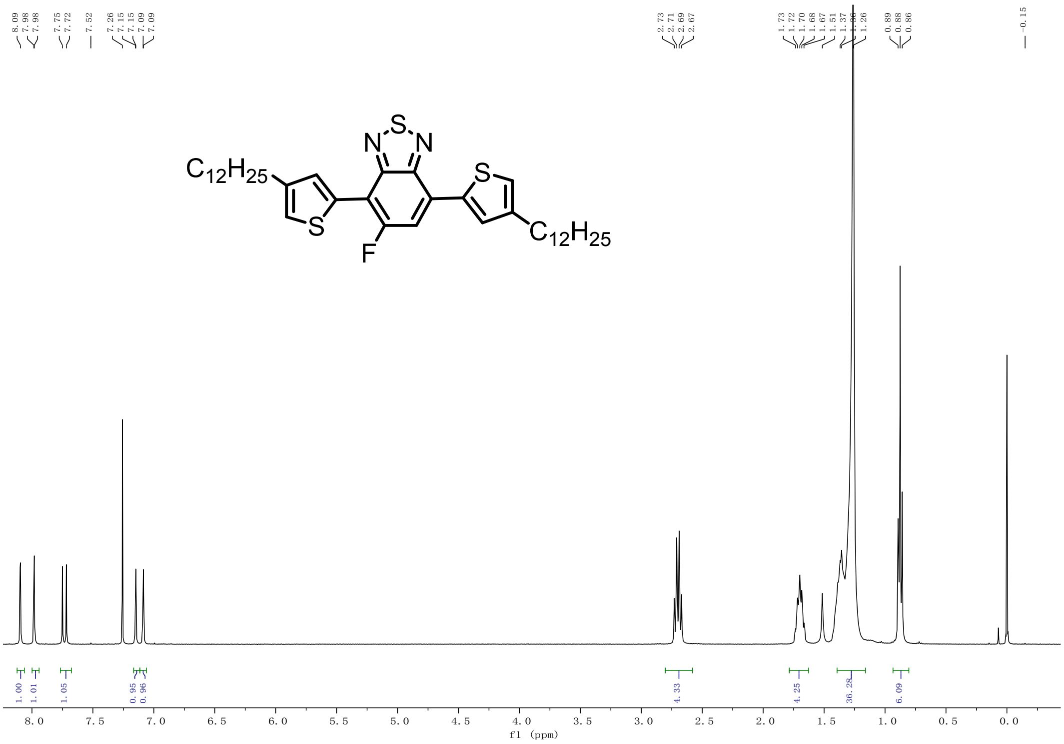


Figure S9. ^{1}HNMR spectrum of **8**

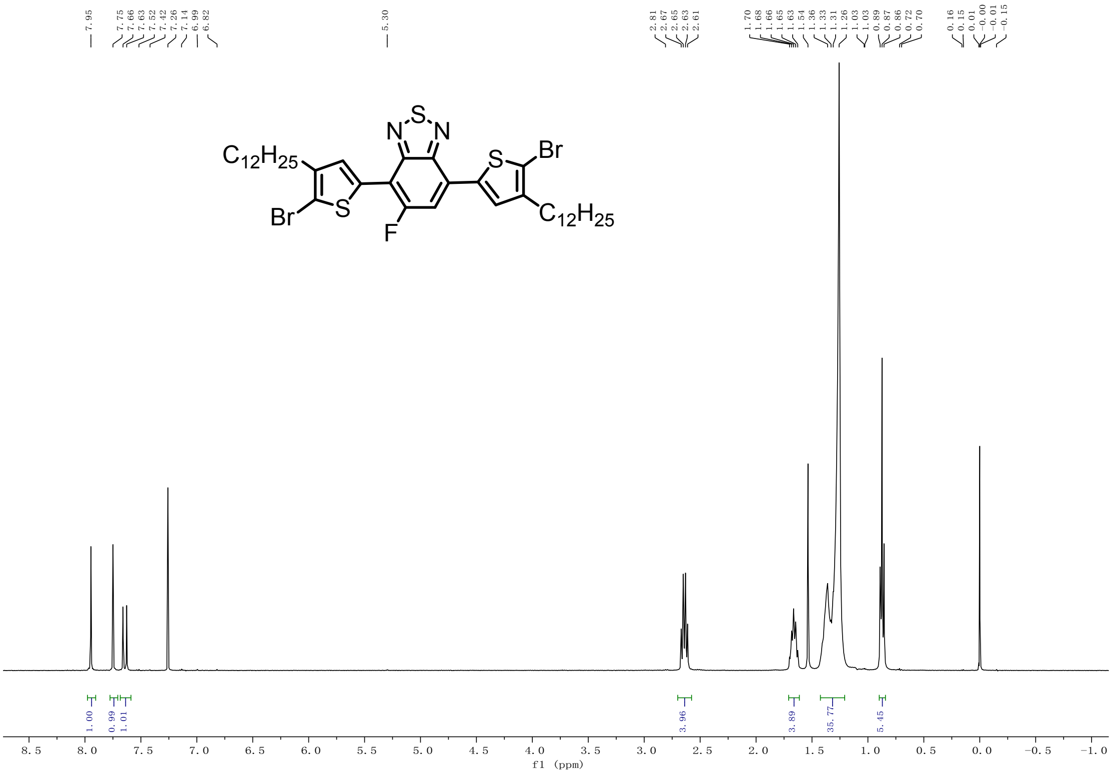


Figure S10. ^{1}HNMR spectrum of **A1**

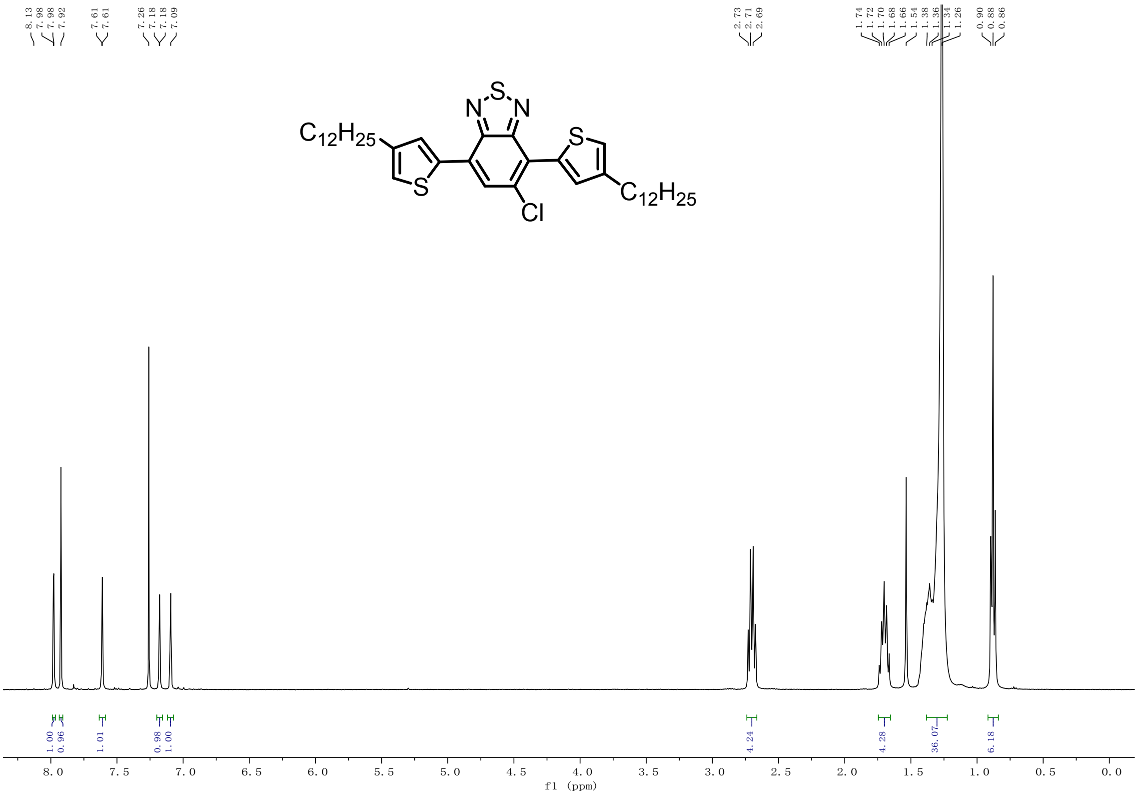


Figure S11. ^{1}HNMR spectrum of **9**

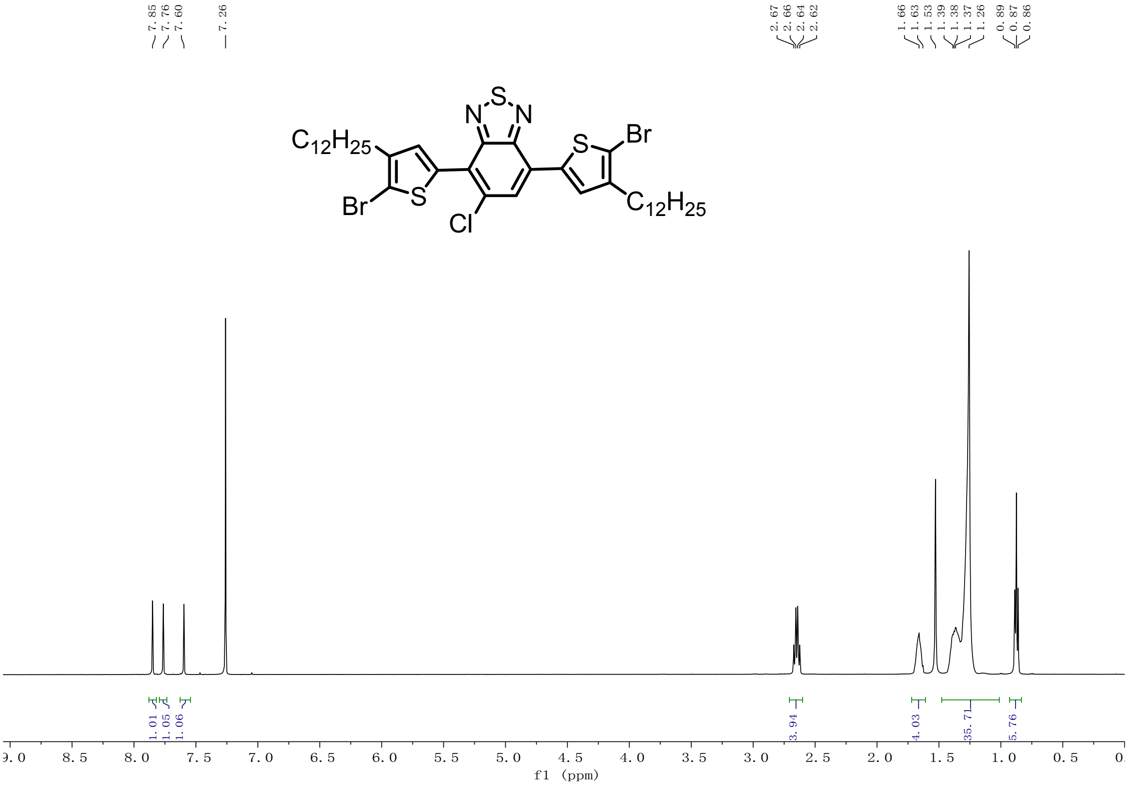


Figure S12. ^{1}HNMR spectrum of **A2**

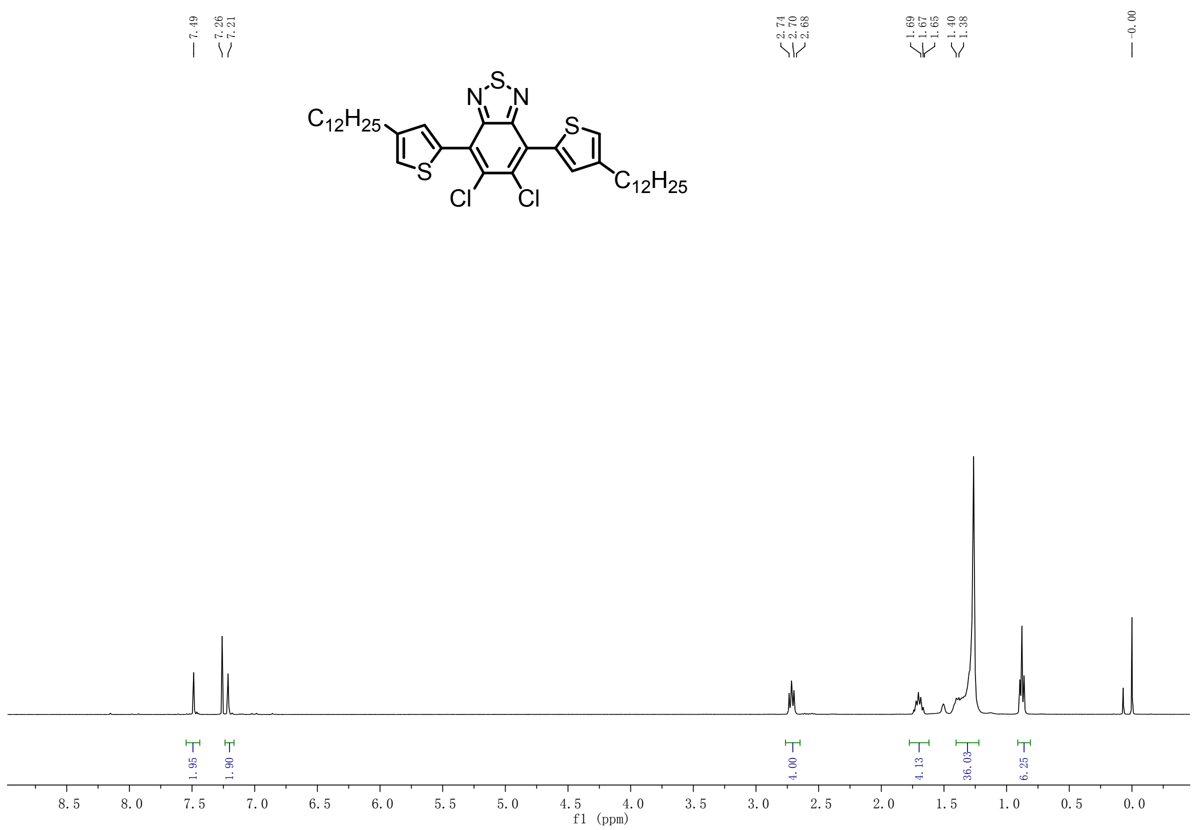


Figure S13. ^{1}HNMR spectrum of **10**

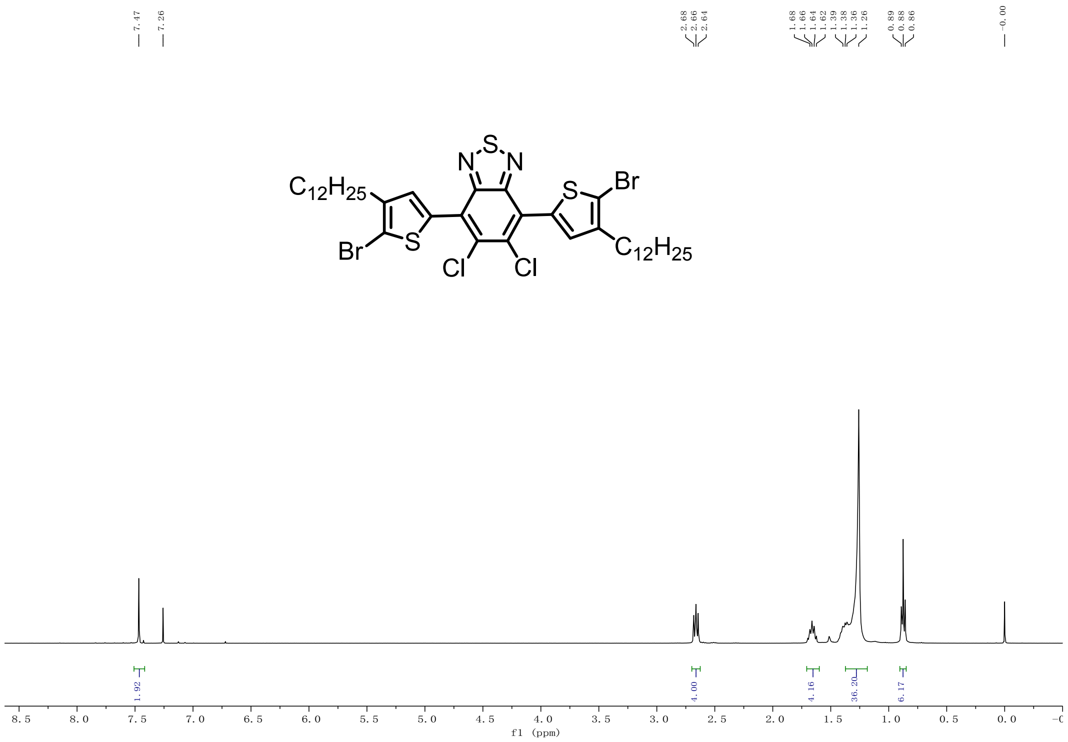


Figure S14. ^{1}HNMR spectrum of **A3**

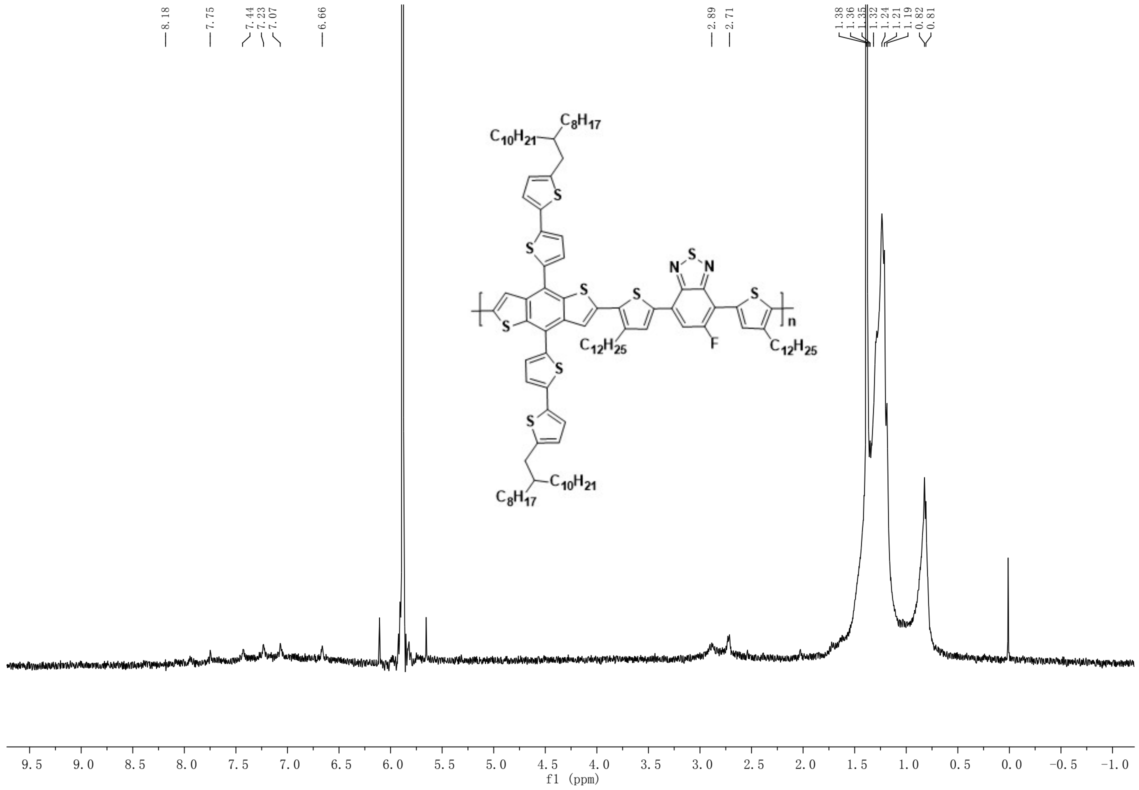
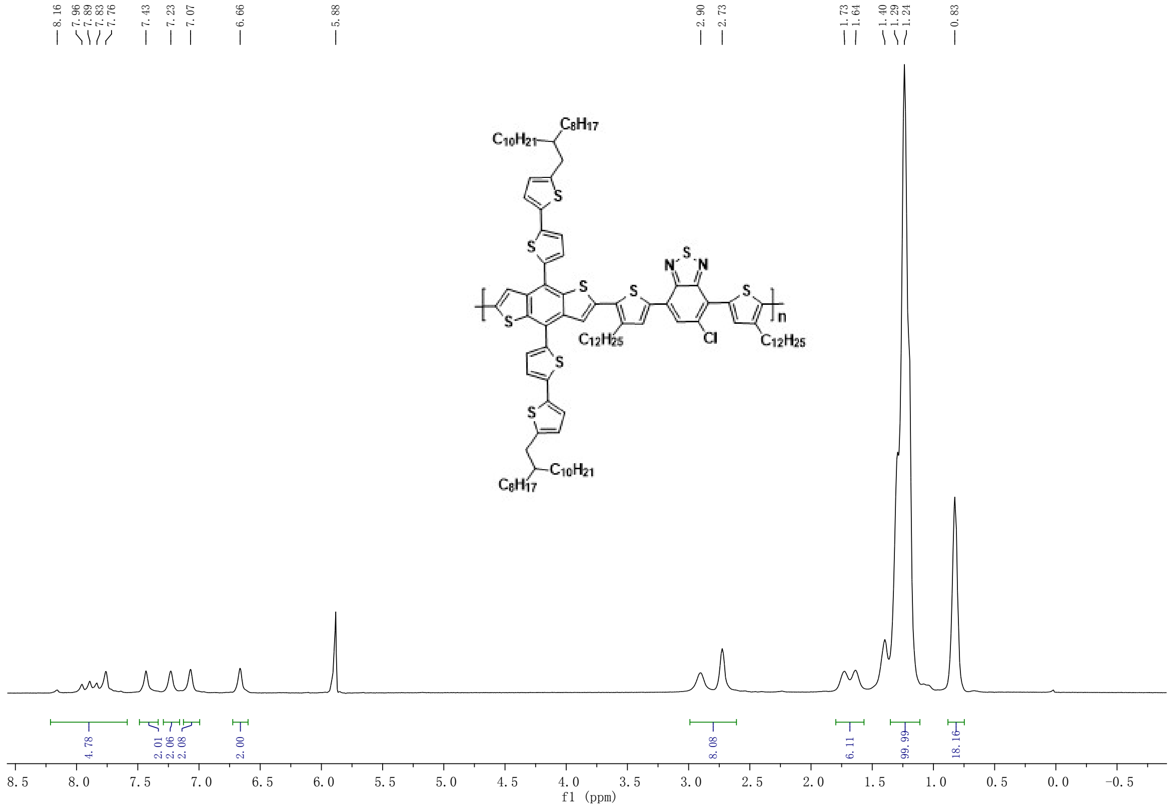


Figure S15. ^{1}HNMR spectrum of **PBBF1-T2**



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igure S16. ^{1}HNMR spectrum of **PBBCl1-T2**

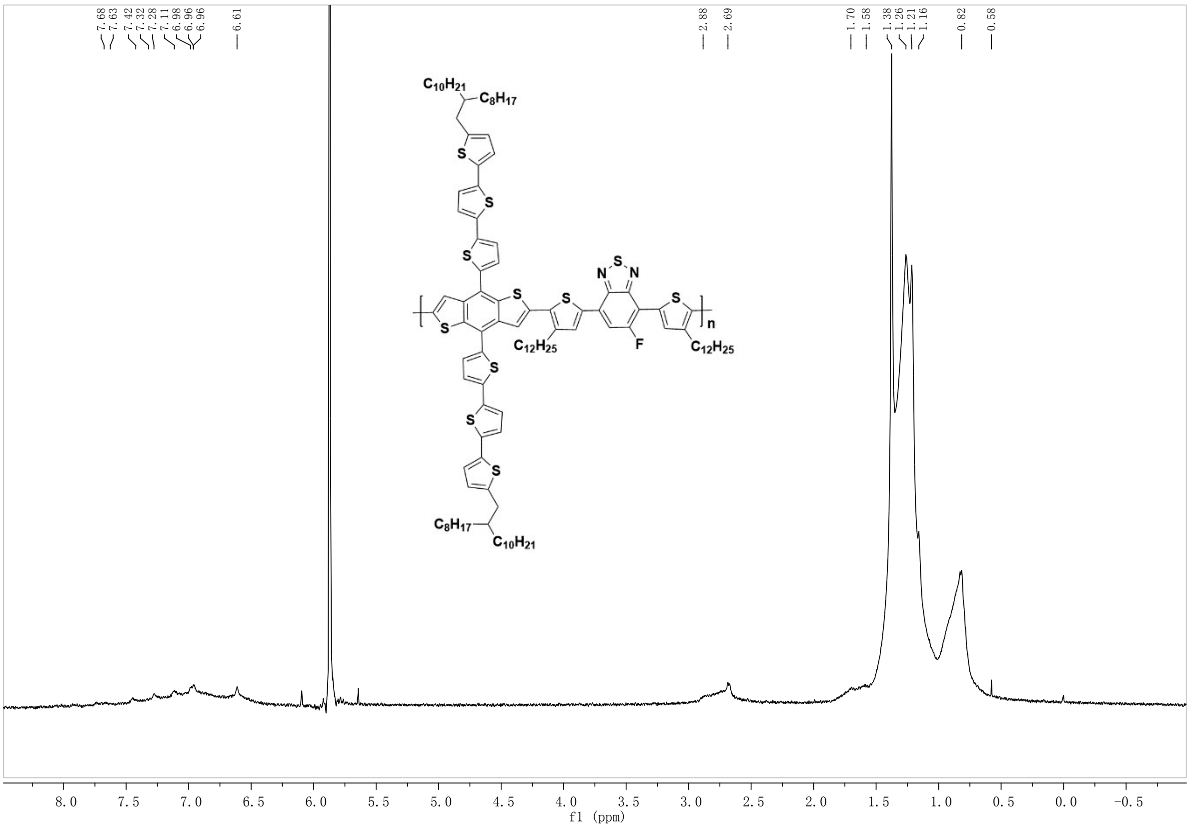

Figure S17. ^{1}HNMR spectrum of **PBBF1-T3**

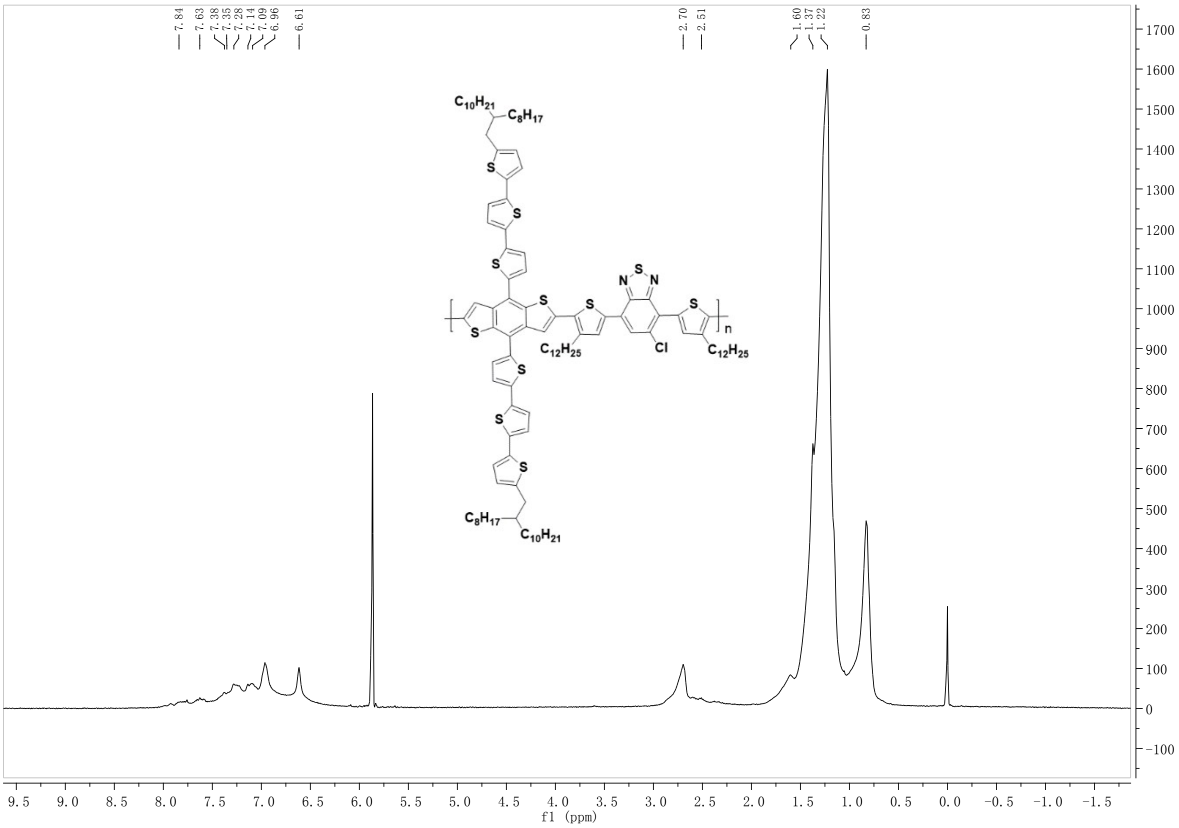

Figure S18. ^{1}HNMR spectrum of **PBBCl1-T3**

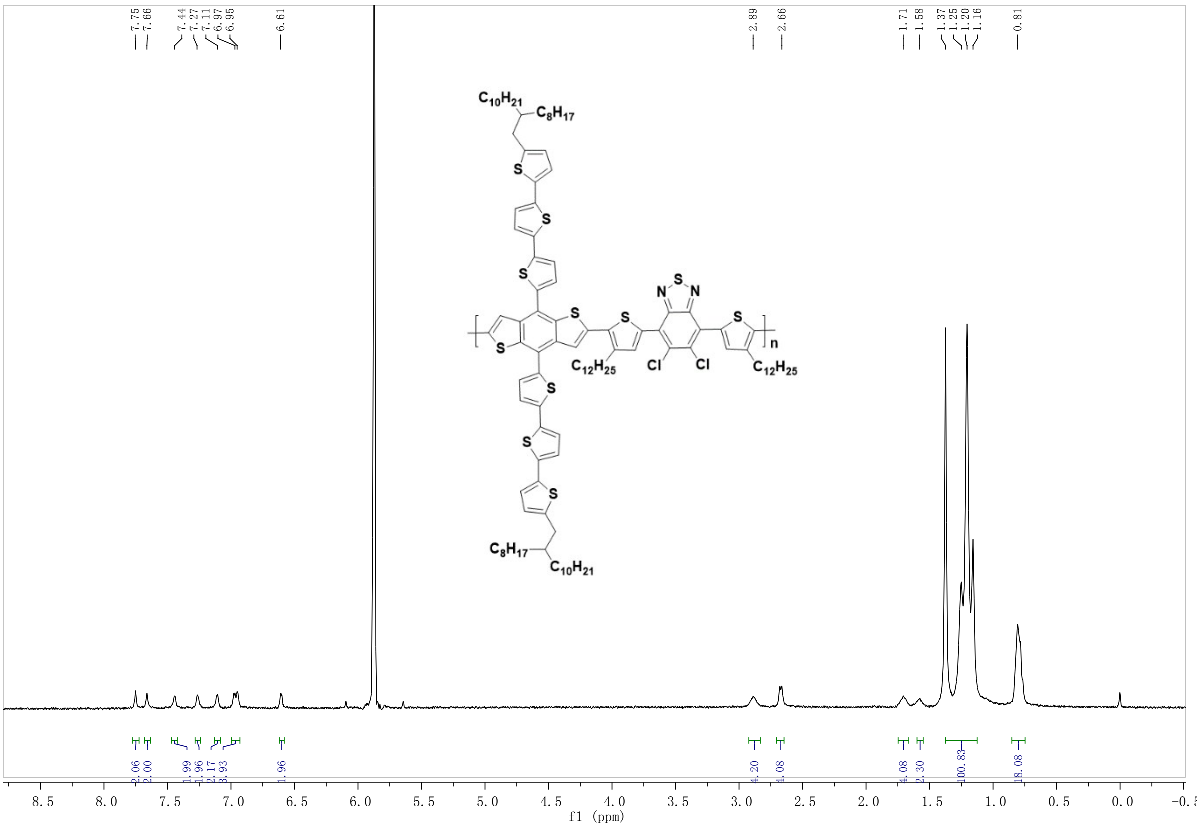

Figure S19. ^{1}HNMR spectrum of **PBBCl2-T3**

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