Supporting Information

Structural tuning of Quinoxaline-Benzodithiophene copolymers *via* alkyl side chain manipulation: Synthesis, Characterization and Photovoltaic Properties

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Synthetic procedures for monomers and polymers

*Synthesis of 4,8-bis(5-octylthiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene (**2**).* 2-Octyl thiophene (**1**) (5.22 g, 26.56 mmol) was dissolved in THF (118 mL) and cooled with an ice bath and stirred under nitrogen atmosphere. *n*-BuLi, 2.5 M (10.63 mL, 26.6 mmol) was added drop-by-drop to the reaction mixture. The mixture was stirred in an ice bath for 90 minutes and then heated at 50 ^{o}C for 90 minutes. Benzo[1,2-b:4,5-b']dithiophene-4,8-dione (1.95 g, 8.85 mmol) suspended in THF was added into the reaction flask and heated at 50 ^{o}C for 90 minutes. The reaction mixture was cooled to room temperature and $SnCl_2.2H_2O$ (11.8 g, 52.2 mmol) dissolved in 10% HCl (27 mL) was added gradually and stirred at room temperature overnight. The reaction mixture was poured on water and extracted with diethyl ether. The ether extract was dried with anhydrous sodium sulfate and the solvent was removed to give a crude product which was purified with silica gel column chromatography using chloroform:hexane (1:9) mixture as eluent to yield 4,8-bis(5-octylthiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene (**2**) as a yellow solid (3.31 g, 64.6%).

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.65 (1H, d, *J*= 4Hz), 7.45 (1H, d, *J*= 4Hz), 7.29 (1H, d, *J*= 4Hz), 6.91 (1H, d, *J*= 4Hz), 2.93 (2H, t), 1.82 (2H, m), 1.47 (10H, m), 0.91 (3H, t).

^{13}C NMR (100 MHz, $CDCl_3$, δ): 147.13, 138.98, 136.96, 136.50, 127.75, 127.41, 124.24, 124.05, 123.41, 31.86, 31.61, 30.27, 29.34, 29.24, 22.67, 14.11.

*Synthesis of (4,8-bis(5-octylthiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis (trimethylstannane) (**3**).* 4,8-Bis(5-octylthiophen-2-yl)benzo[1,2-b:4,5-b']dithiophenecompound (**2**) (3.64 g, 6.28 mmol) was dissolved in THF (100 mL) and stirred in an ice bath for 30 minutes. *n*-BuLi, 2,5 M (6.71 mL, 16.8 mmol) was added drop-by-drop with a syringe over 25 minutes. The reaction mixture was stirred in the ice bath for 90 minutes. The bath was removed and stirred at room temperature for 90 minutes. Trimethyl tin chloride, 1M in hexanes (23 mL, 23 mmol) was added in one portion and stirred overnight. The reaction mixture was poured on water and extracted with diethyl ether. The ether extract was washed with distilled water. The ether extract was dried with anhydrous sodium sulfate and the solvent was removed to yield a crude product which was purified by recrystallization from isopropanol-THF mixture to yield compound **3** as a yellow solid (4.64 g, 81.3%).

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.69 (1H, s), 7.32 (1H, d, *J*= 4 Hz), 6.93 (1H, d, *J*= 4 Hz), 2.95 (2H, t), 1.82 (2H, m), 1.47 (10H, m), 0.92 (3H, t), 0.47 (9H, s).

^{13}C NMR (100 MHz, $CDCl_3$, δ): 146.78, 143.26, 142.22, 137.74, 137.30, 131.14, 127.61, 124.15, 122.38, 31.88, 31.56, 30.28, 29.38, 29.31, 29.27, 22.67, 14.12, -8.33.

*Synthesis of 4,8-bis(4,5-dihexylthiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene (**5**)*. 2,3-Dihexyl thiophene (**4**) (4 g, 15.8 mmol) was dissolved in THF (50 mL) and cooled with an ice bath and stirred under nitrogen atmosphere. *n*-BuLi, 2.5 M (6.4 mL, 16.0mmol) was added drop-by-drop to the reaction mixture. The mixture was stirred for 45 minutes in the ice bath and then heated at 50 ^{o}C for 2 hours. Benzo[1,2-b:4,5-b']dithiophene-4,8-dione (0.99 g, 4.5 mmol) suspended in THF was added into the reaction flask and heated at 50 ^{o}C for 2 hours and 30 minutes. The reaction mixture was cooled to room temperature and $SnCl_2.2H_2O$ (8.4 g, 37.2 mmol) dissolved in 10% HCl (18 mL) was added gradually and stirred at room temperature overnight. The reaction mixture was poured on to water and extracted with diethyl ether. The ether extract was dried with anhydrous sodium sulfate and the solvent was removed to give a crude product which was purified with silica gel column chromatography, using hexane as eluent, to yield **5** (2.01 g, 64.6%).

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.69 (1H, d, *J*= 4Hz), 7.45 (1H, d, *J*= 8 Hz), 7.21 (1 H, s), 2.84 (2H, t), 2.62 (2H, t), 1.77 (4H, m), 1.45 (12 H, m), 0.94 (6H, m).

^{13}C NMR (100 MHz, $CDCl_3$, δ):140.14, 138.80, 138.08, 136.31, 135.03, 129.82, 127.25, 124.09, 123.56, 31.81, 31.77, 31.64, 30.79, 29.19, 29.14, 28.31, 28.00, 22.68, 22.62, 14.13, 14.10.

*Synthesis of (4,8-bis(4,5-dihexylthiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis (trimethylstannane) (**6**)*. 4,8-Bis(4,5-dihexylthiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene (**5**) (1.0 g, 1.45 mmol) was dissolved in THF (45 mL) and stirred in an ice bath for 30 minutes. *n*-BuLi, 2.5 M (1.45 mL, 3.63 mmol) was added drop-by-drop with a syringe over 10 minutes. The reaction mixture was stirred in the ice bath for 1 hour and 30 minutes. The bath was removed and stirred for 90 minutes at room temperature. Trimethyl tin chloride, 1M in hexane (4.4 mL, 4.4 mmol) was added in one portion and stirred overnight. The reaction mixture was poured on water and extracted with diethyl ether. The ether extract was washed with distilled water. The ether extract was dried with anhydrous sodium sulfate and solvent removed to yield a crude product which was purified by recrystallization from ethanol (x2) and isopropanol (x2). The solid was dried to give compound **6** as a yellow solid (0.54 g, 36.7%).

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.72 (1H, s), 7.23 (1H, s), 2.85 (2H, t), 2.64 (2H, t), 1.76 (4H, m), 1.46 (12, m), 0.92 (6H, m), 0.4 (9H, s).

^{13}C NMR (100 MHz, $CDCl_3$, δ): 143.06, 141.90, 139.78, 137.96, 137.13, 135.70, 131.37, 129.78, 122.45, 31.84, 31.76, 31.66, 30.77, 29.15, 28.30, 28.01, 22.69, 22.65, 14.16, 14.11, -8.37.

Synthesis of polymer PFQBDT-TR$_1$. ((4,8-bis(5-octylthiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(trimethylstannane) (**3**) (0.151 g, 0.167 mmol) and 5,8-bis(5-bromothiophen-2-yl)-6,7-difluoro-2,3-bis(3-(octyloxy)phenyl)quinoxaline (**7**) (0.1 g, 0.116 mmol) were dissolved in toluene (9 mL) and N_2 gas was bubbled for 10 minutes. $Pd_2(dba)_3$ (6.8 mg, $7.4x10^{-3}$ mmol) and P(o-Toly)$_3$ (11.4 mg, $3.7x10^{-2}$ mmol) were added and N_2 gas was bubbled for 25 minutes. The reaction mixture was heated at 90 ^oC for 25 minutes under nitrogen atmosphere. The viscous polymer solution was precipitated by adding on methanol and the solid was collected by filtration. The solid was re-dissolved in chloroform by heating at 60 ^oC (1 hr) and 85 ^oC (1 hr) and 10% sodium diethyldithiocarbamate trihydrate (100 mL) (aq) was added and stirred at room temperature overnight. The chloroform soluble portion was separated and washed with distilled water (x4). The chloroform solution was reduced to small volume and then added to methanol. The solid formed was collected by filtration and then purified by Soxhlet extraction using methanol hexane, diethyl ether and dichloromethane. Finally, the polymer remaining in the thimble was extracted with chloroform. After reducing the chloroform extract to a small volume, the polymer was precipitated by adding on methanol. The solid was collected by filtration and dried in vacuum oven at 40 ^oC, yielding PFQBDT-TR$_1$ as a brown solid (71 mg, 32.4%).

^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.0-7.0 (Aromatic protons), 2.0-1.0 (Aliphatic protons)

Synthesis of polymer PFQBDT-T2R$_2$. (4,8-bis(4,5-dihexylthiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(trimethylstannane) (**6**) (0.15 g, 0.147 mmol) and 5,8-bis(5-bromothiophen-2-yl)-6,7-difluoro-2,3-bis(3-(octyloxy)phenyl)quinoxaline (**7**) (0.132 g, 0.147 mmol) were dissolved in toluene (8 mL) and degassed with N_2 gas for 10 minutes. $Pd_2(dba)_3$ (6 mg, $6.6x10^{-3}$mmol) and P(*o*-Toly)$_3$ (10 mg, $3.28x10^{-2}$ mmol) were added and the mixture was purged with nitrogen gas for 25 minutes. The reaction mixture was heated at 90 ^oC for 1 hour under nitrogen atmosphere. The viscous polymer solution was precipitated by adding on methanol and the solid was collected by filtration. The solid was re-dissolved in chloroform by heating at 60 ^oC for 1 hour and 10% sodium diethyldithiocarbamate trihydrate (100 mL) (aq) was added and stirred at room temperature overnight. The chloroform soluble portion was separated and washed with distilled water (x4). The chloroform solution was reduced to small volume and then added to methanol. The solid formed was collected by filtration and then purified by Soxhlet extraction using methanol, hexane and diethyl ether. Finally, the polymer remaining in the thimble was extracted with chloroform. After reducing the chloroform extract to small volume, the polymer was precipitated by adding on methanol. The

solid was collected by filtration and dried in vacuum oven at 40 °C overnight, yielding PFQBDT-T2R$_2$ as a brown solid (170 mg, 80.6%).

^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.0-7.0 (Aromatic protons), 3.79 (-OCH_2), 2.89-2.67 (-CH_2 attached to thiophene), 2.0-1.0 (aliphatic protons).

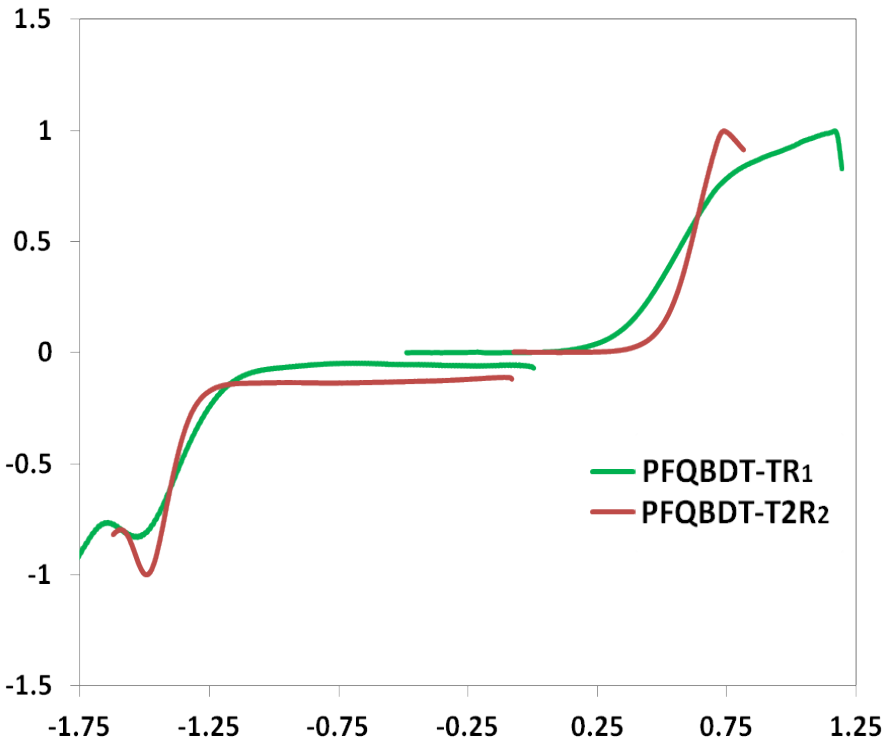

Figure S1. Square-wave voltammograms of the polymers in thin films.

Table S1. OPV characteristics of **PFQBDT-TR$_1$ / PFQBDT-T2R$_2$** : PC$_{XX}$BM based solar cells.

Donor : PC$_{61}$BM ratio [wt/wt][a]	**DIO**[b] [% v/v]	**Annealing** [°C]	**J_{SC}** [mA/cm^2]	**V_{OC}** [V]	**FF** [%]	**PCE** [%]
PFQBDT-TR$_1$: PC$_{61}$BM **(1:1)**	-	110°C / 5 min	10.0	0.81	64	5.2
PFQBDT-TR$_1$: PC$_{61}$BM **(1:1)**	-	80°C / 5 min	9.5	0.84	61	5.0
PFQBDT-TR$_1$: PC$_{61}$BM **(1:1)**	3	-	9.5	0.75	56	4.0
PFQBDT-TR$_1$: PC$_{71}$BM **(1:1)**	-	-	11.7	0.82	55	5.3
PFQBDT-TR$_1$: PC$_{71}$BM **(1:1)**	-	110°C / 10 min	10.5	0.81	60	5.1
PFQBDT-TR$_1$: PC$_{71}$BM **(1:1)**	3	-	11.7	0.82	55	5.3
PFQBDT-TR$_1$: PC$_{71}$BM **(1:1)**	3	110°C / 10 min	10.5	0.81	60	5.1
PFQBDT-TR$_1$: PC$_{61}$BM **(1:2)**	3	-	9.7	0.70	45	3.0
PFQBDT-TR$_1$: PC$_{61}$BM **(1:2)**	3	110°C / 10 min	9.5	0.73	50	3.3
PFQBDT-T2R$_2$: PC$_{61}$BM **(1:1)**	-	80°C / 5 min	6.7	0.99	44	3.0
PFQBDT-T2R$_2$: PC$_{61}$BM **(1:1)**	3	-	7.1	0.97	41	2.9
PFQBDT-T2R$_2$: PC$_{61}$BM **(1:1)**	3	110°/10 min	7.1	0.96	44	3.0
PFQBDT-T2R$_2$: PC$_{61}$BM **(1:2)**	3	-	5.1	0.96	47	2.3
PFQBDT-T2R$_2$: PC$_{71}$BM **(1:2)**	-	-	7.0	0.98	47	3.3
PFQBDT-T2R$_2$: PC$_{71}$BM **(1:2)**	-	110°C / 10 min	6.3	0.93	48	2.8
PFQBDT-T2R$_2$: PC$_{71}$BM **(1:2)**	3	-	3.2	0.90	52	1.5
PFQBDT-T2R$_2$: PC$_{71}$BM **(1:2)**	3	110°C / 10 min	3.2	0.94	47	1.4
PFQBDT-T2R$_2$: PC$_{61}$BM **(1:3)**	-	-	5.8	0.95	49	2.7
PFQBDT-T2R$_2$: PC$_{61}$BM **(1:3)**	-	110°C / 10 min	5.6	0.91	38	1.9
PFQBDT-T2R$_2$: PC$_{61}$BM **(1:3)**	3	-	2.9	0.94	48	1.3
PFQBDT-T2R$_2$: PC$_{61}$BM **(1:3)**	3	110°C / 10 min	3.8	0.94	52	1.9

a) ODCB solutions; *b*)1,8-diiodooctane

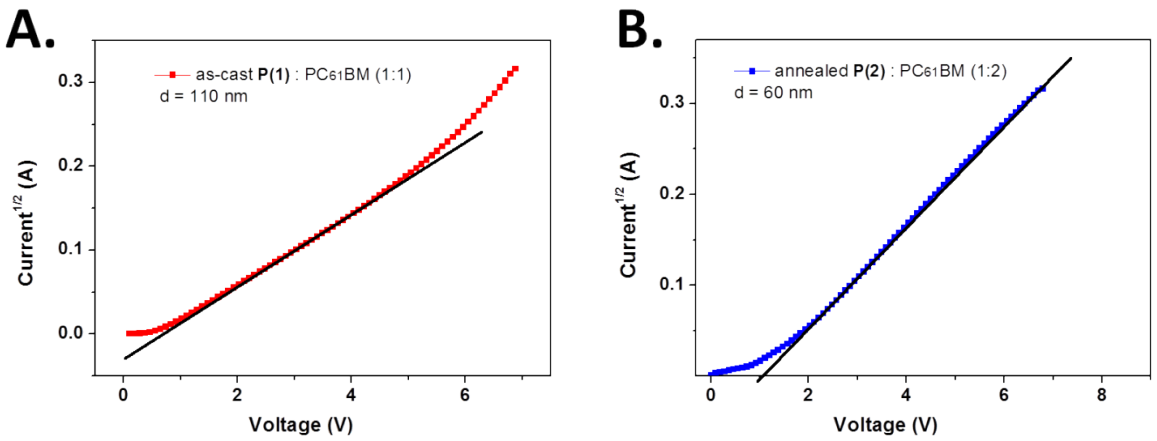

Figure S2. Dark $I^{1/2}$-V curves of *hole-only devices* based on the best performing active blends (*d*: thickness of the blend).

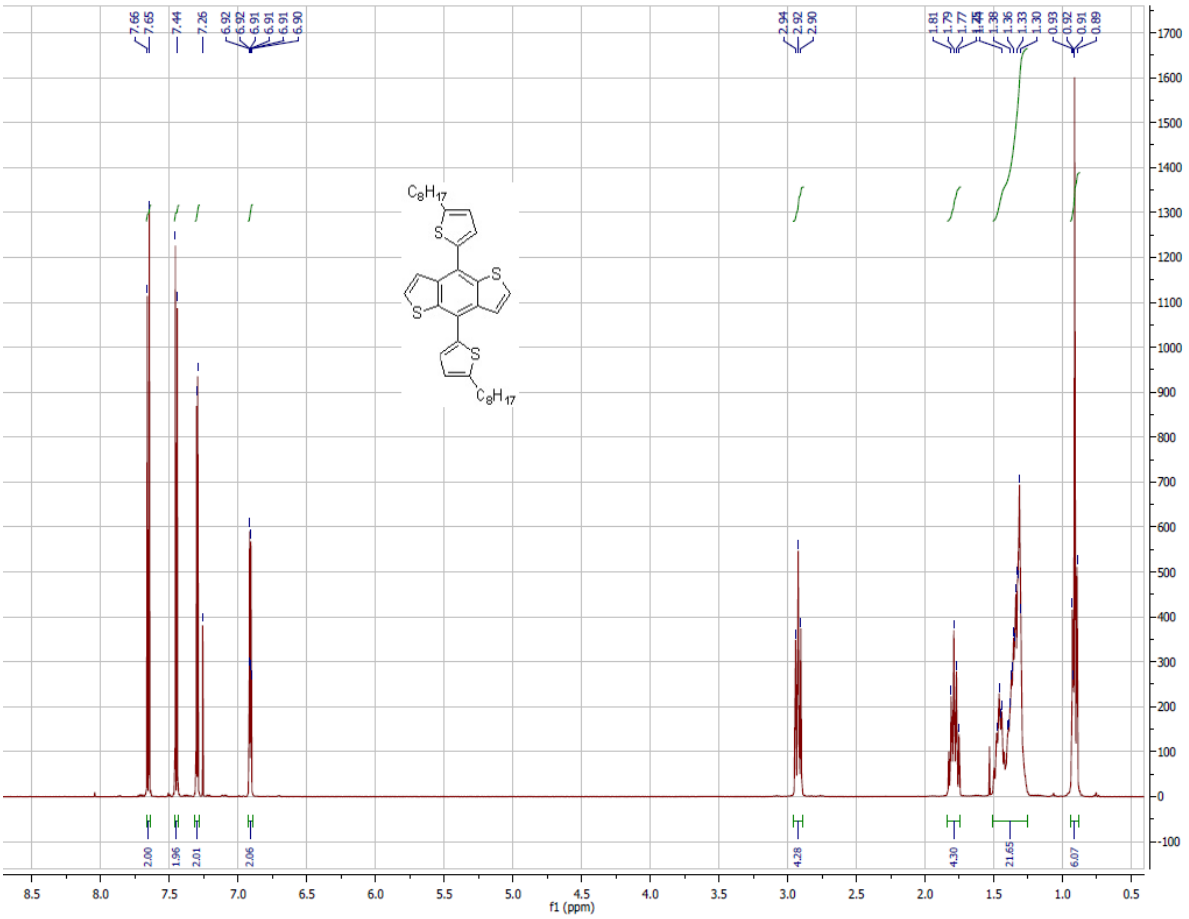

Figure S3. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound 2.

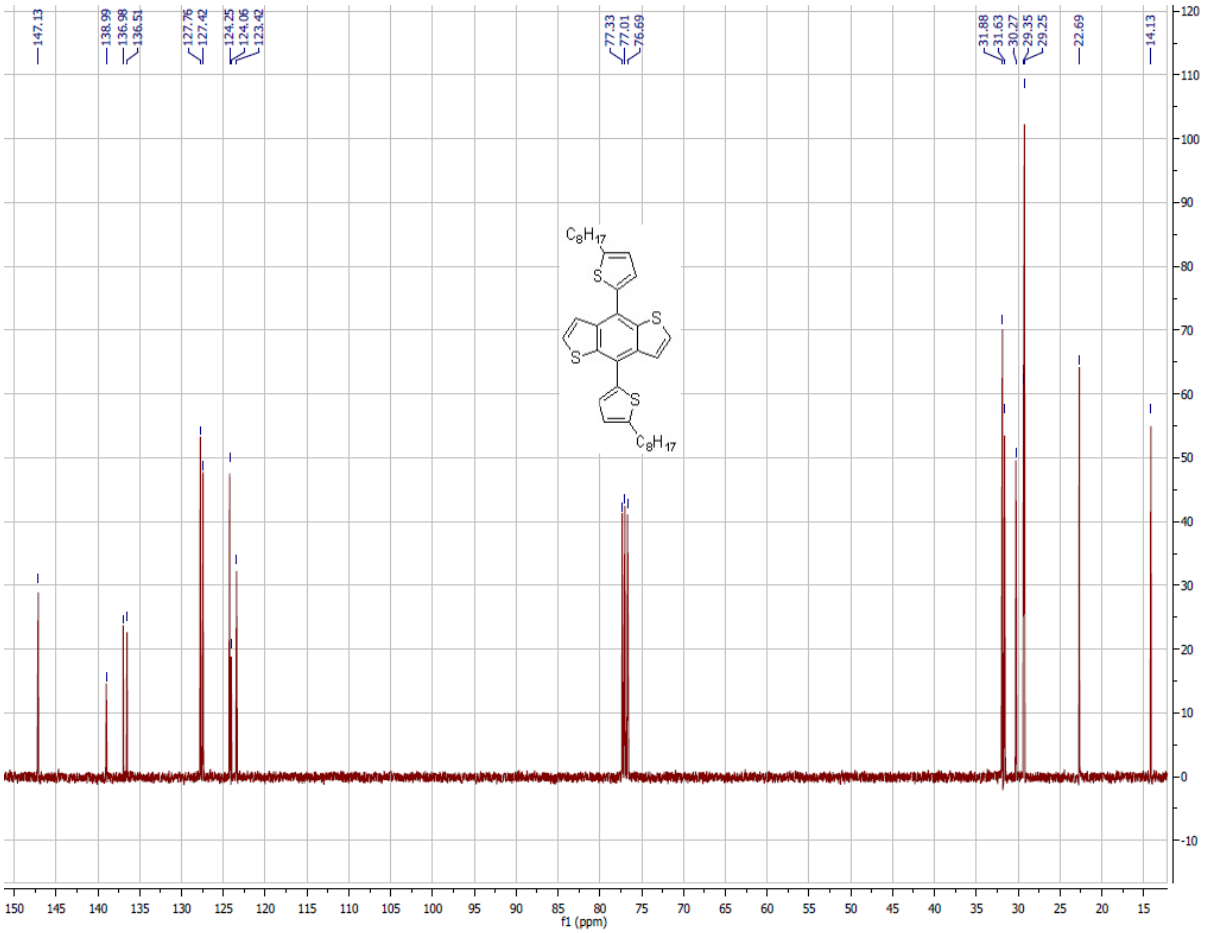

Figure S4. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound 2.

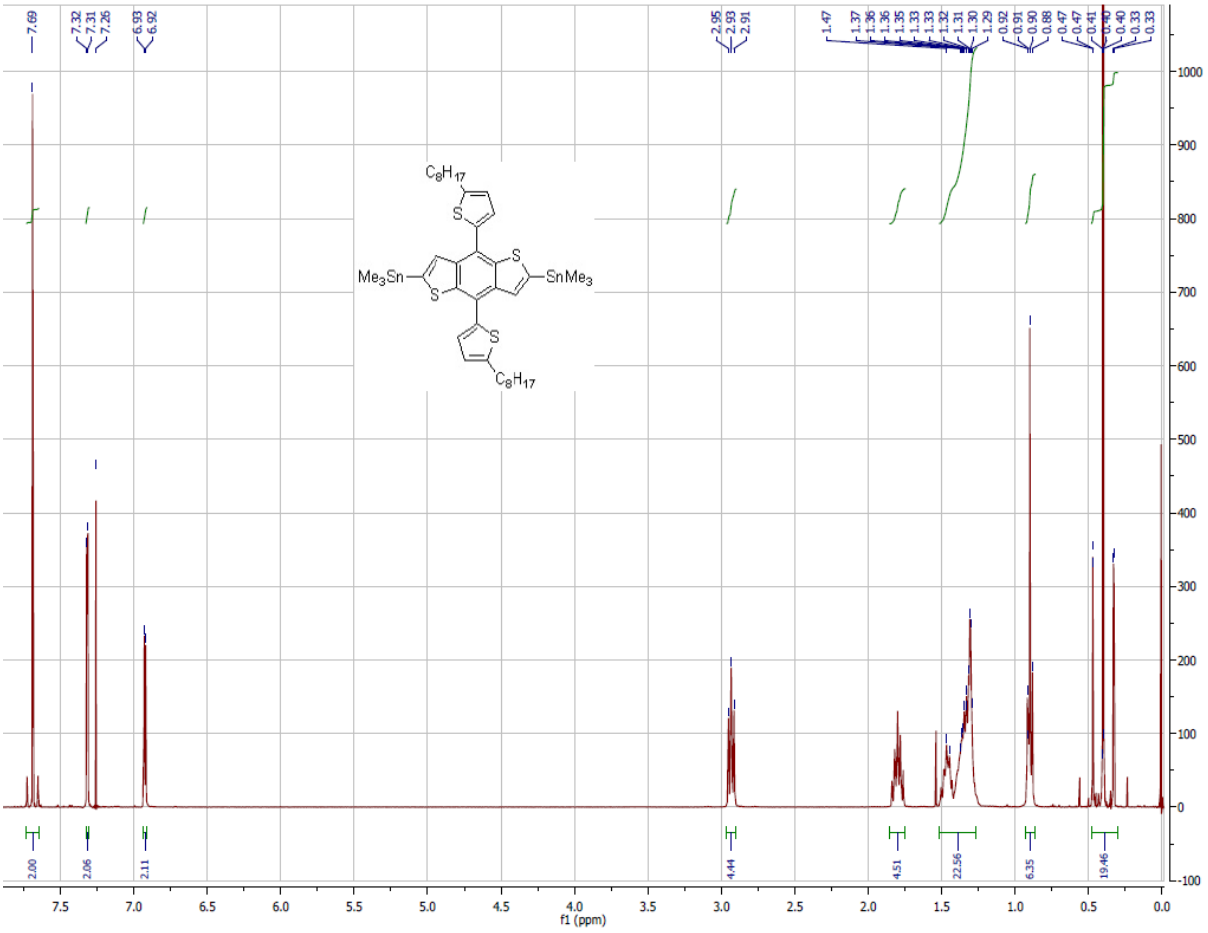

Figure S5. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound 3.

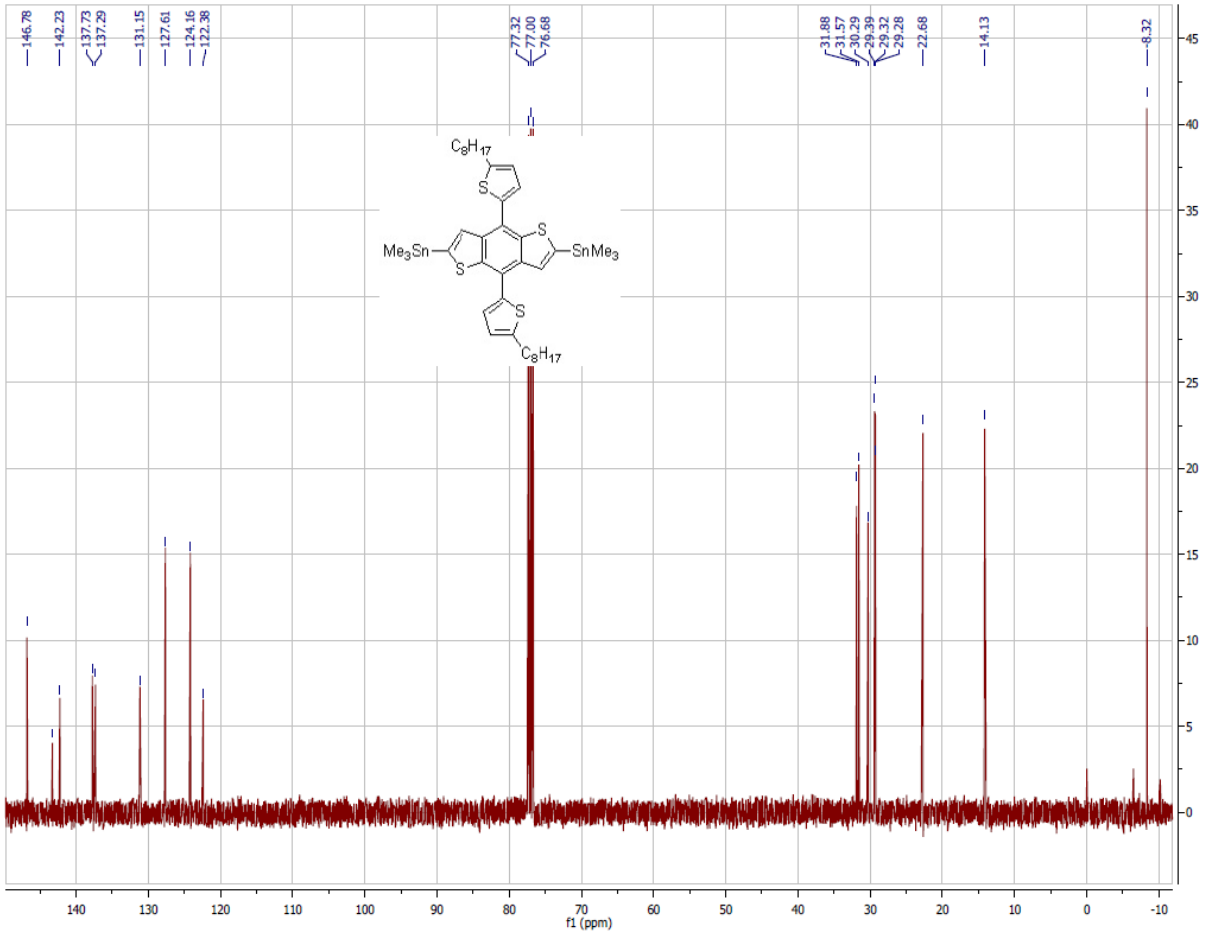

Figure S6. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound 3.

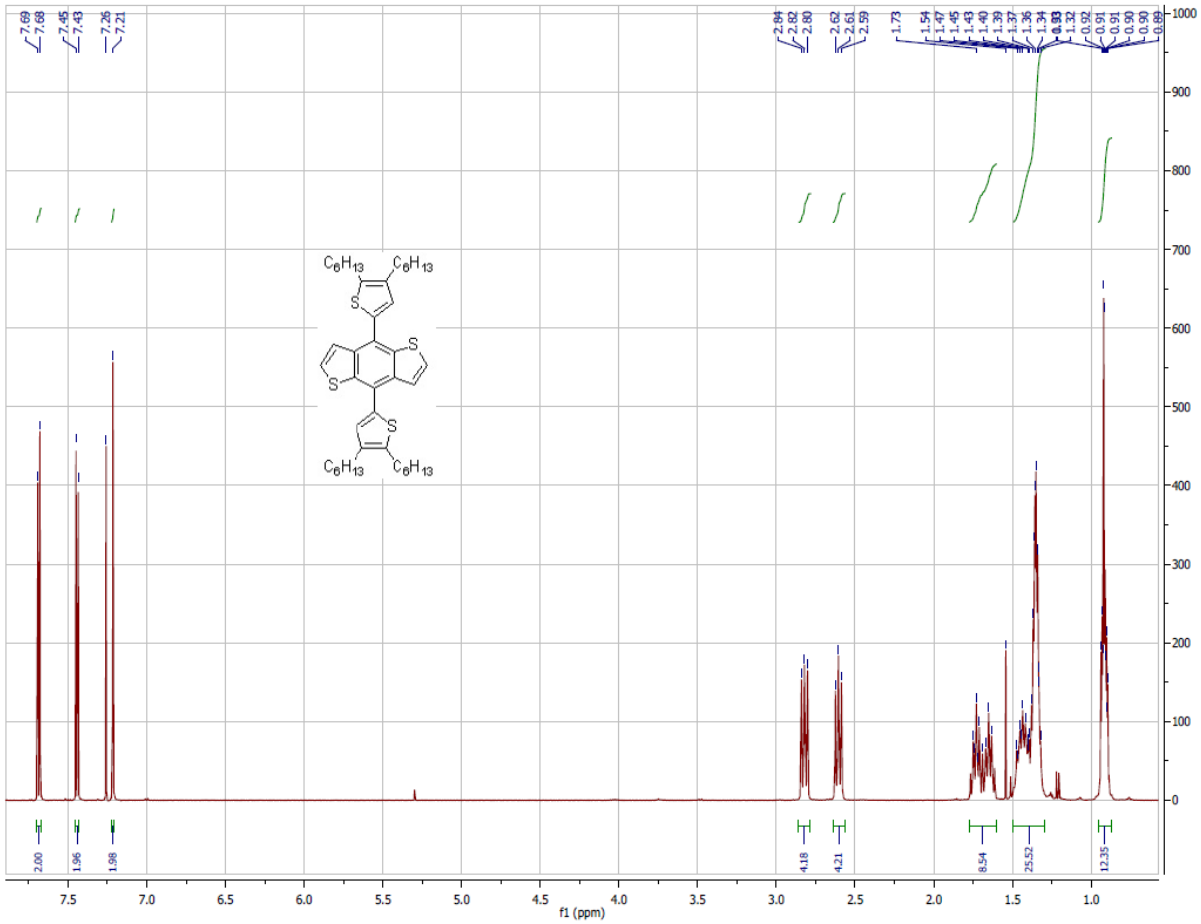

Figure S7. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound 5**.**

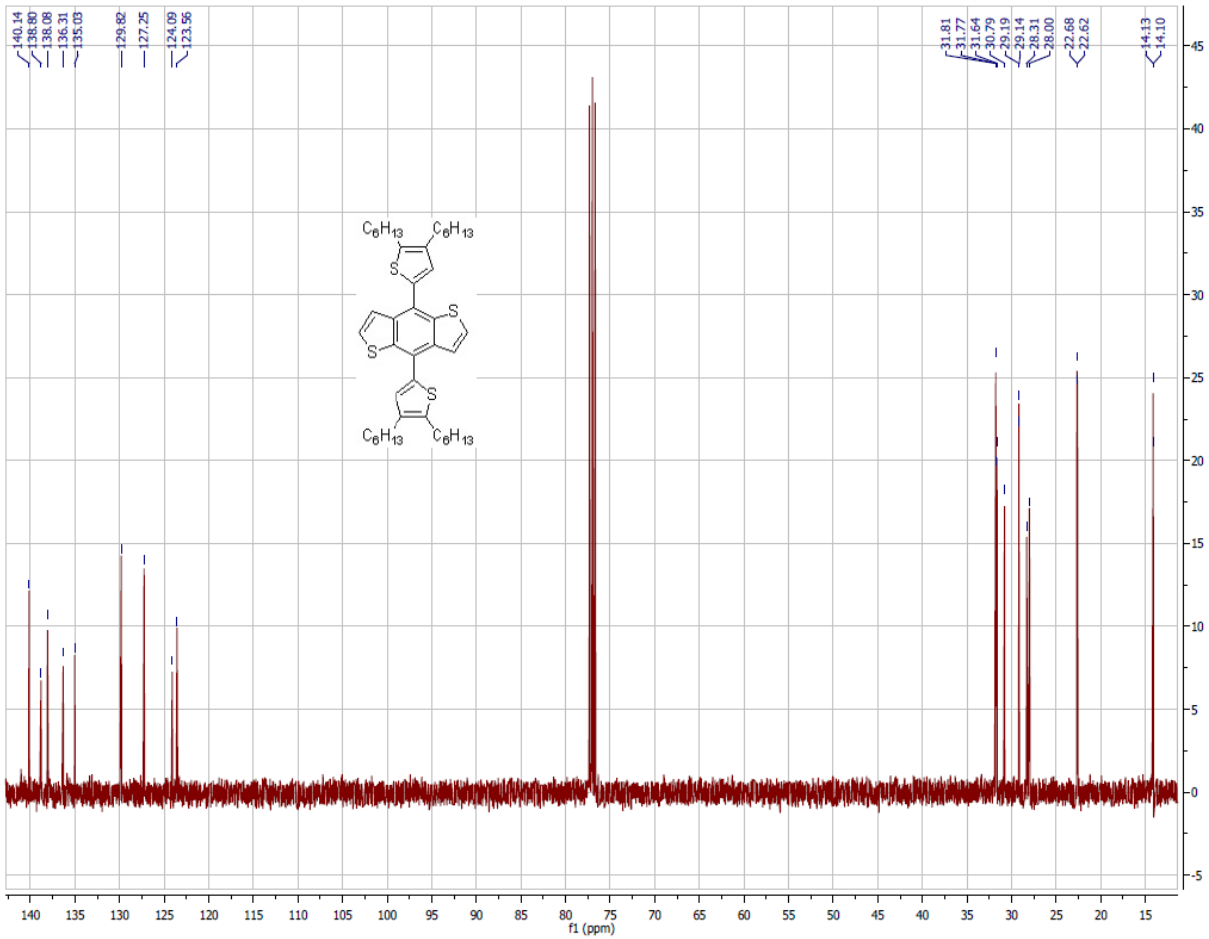

Figure S8. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound 5.

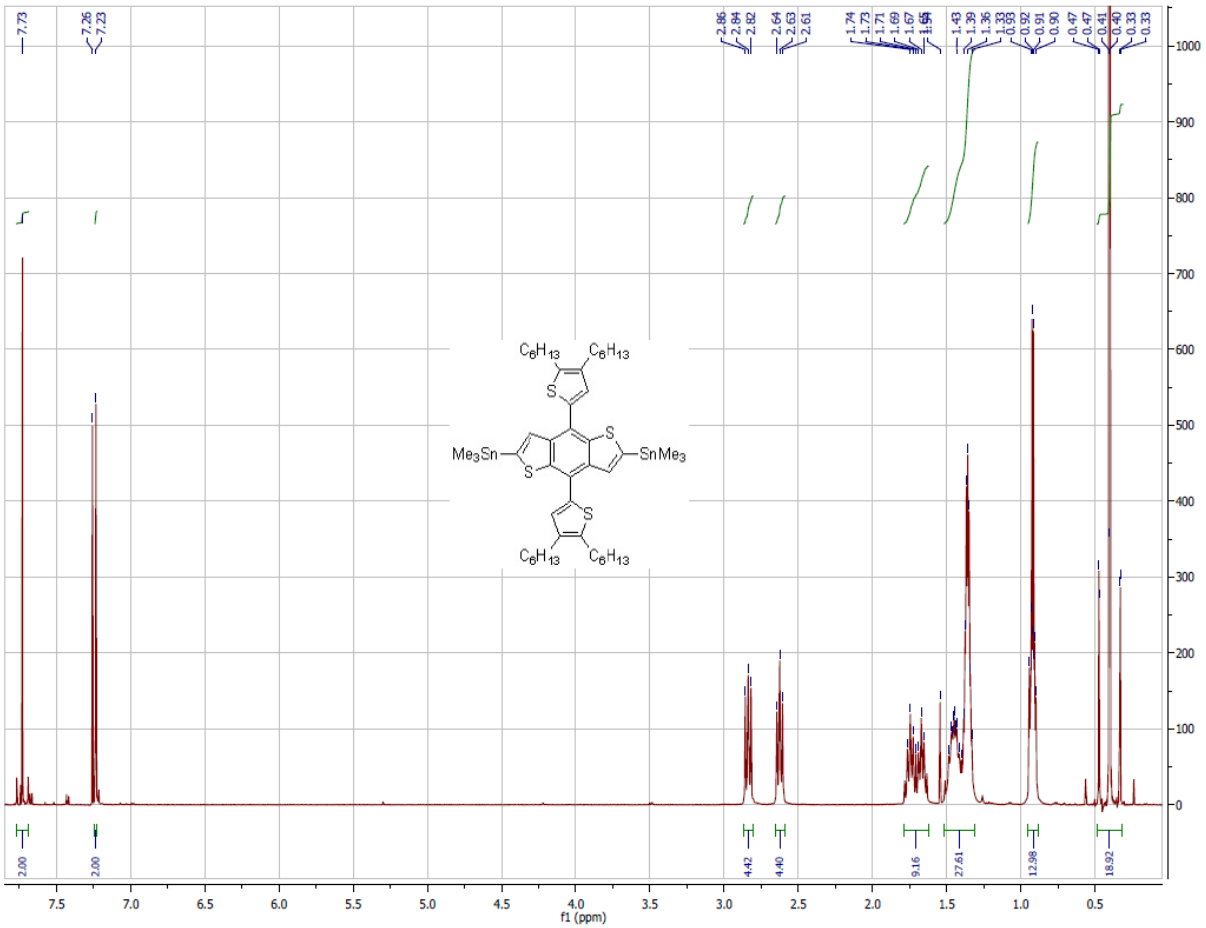

Figure S9. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound 6.

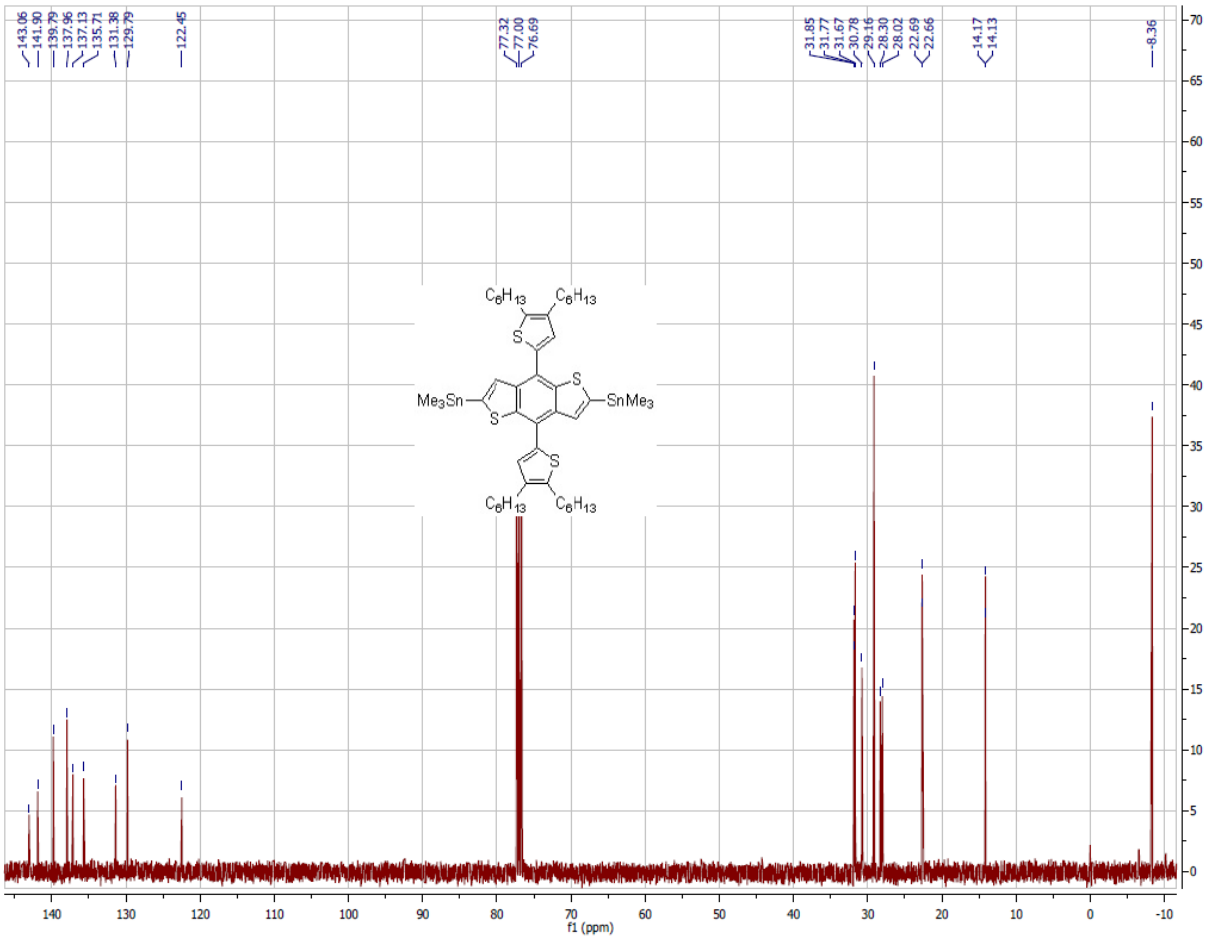

Figure S10. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound 6**.**

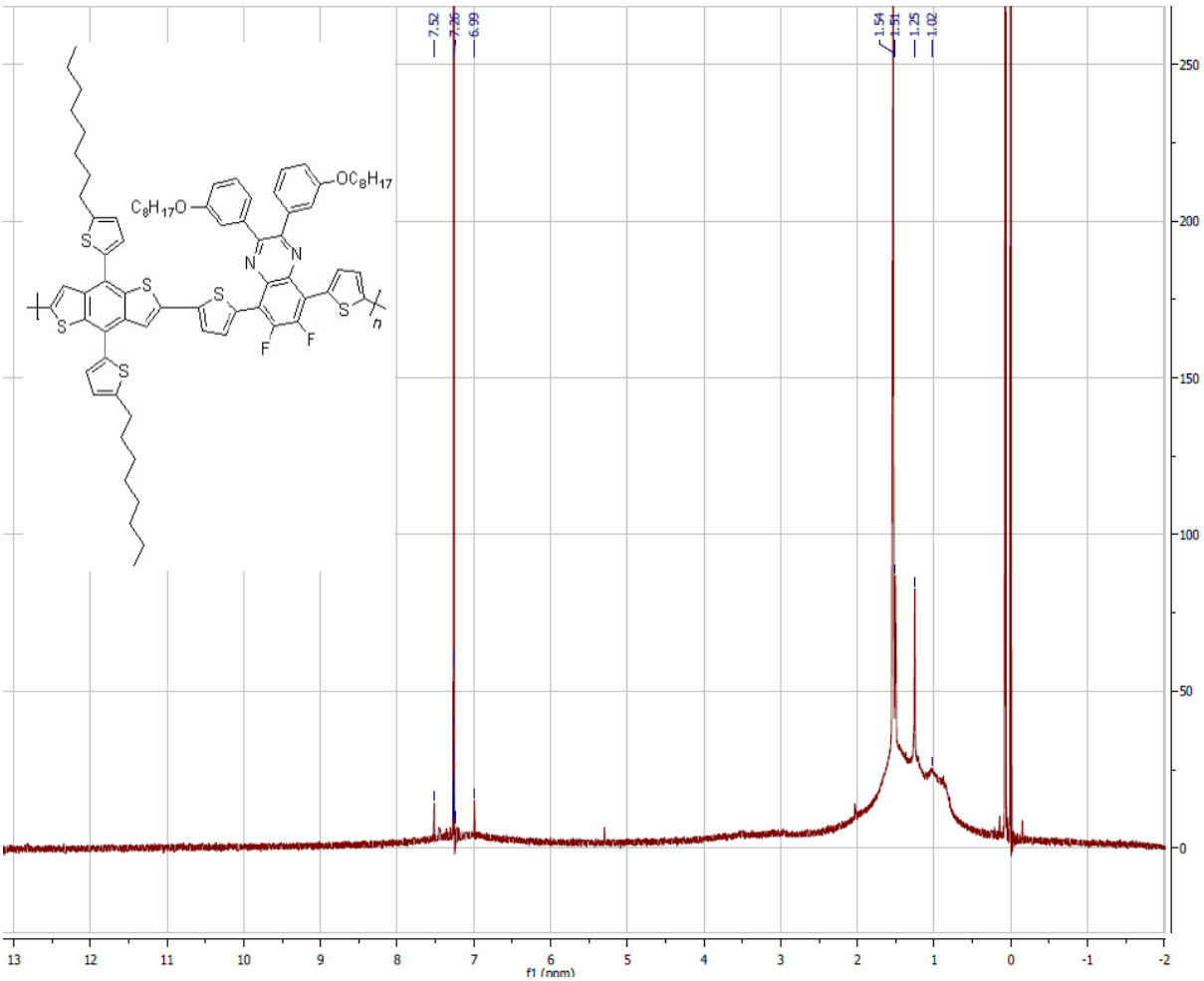

Figure S11. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **PFQBDT-TR$_1$**

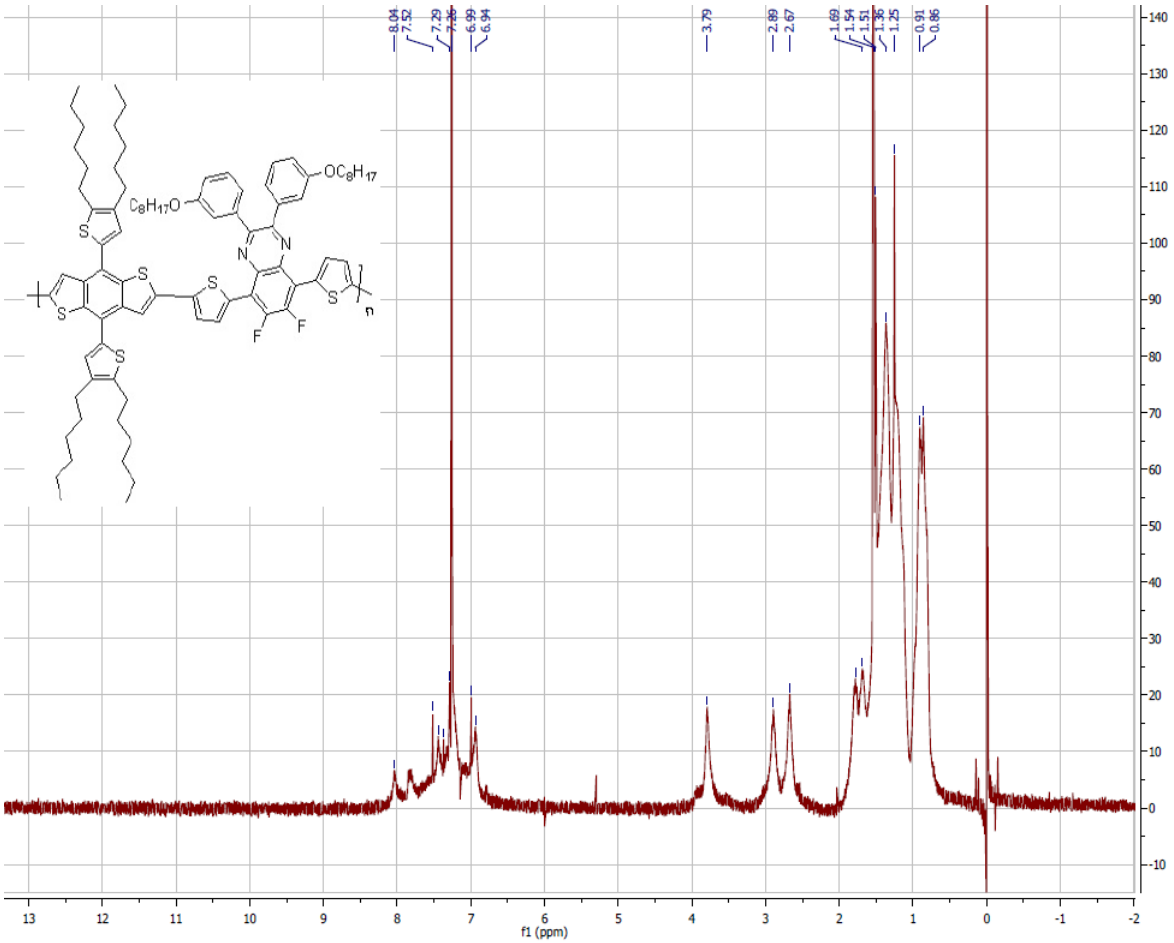

Figure S12. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **PFQBDT-T2R$_2$**