Electronic supplementary information (ESI)

Effect of branched versus linear alkyl side chains on the bulk heterojunction photovoltaic performance of small molecules containing both benzodithiophene and thienopyrroledione

Yu Jin Kim[a‡], Kwang Hun Park[b‡], Jong-jin Ha[b], Dae Sung Chung[d*], Soon-Ki Kwon[b*], Yun-Hi Kim[c*] and Chan Eon Park[a*]

[a] POSTECH Organic Electronics Laboratory, Department of Chemical Engineering, Pohang University of Science and Technology, Pohang, 790-784, Republic of Korea

[b] School of Materials Science & Engineering and Research Institute for Green Energy Convergence Technology (REGET), Gyeongsang National University, Jin-ju, 660-701, Republic of Korea

[c] Department of Chemistry & Research Institute of Natural Science, Gyeongsang National University, Jin-ju, 660-701, Republic of Korea

[d] School of Chemical Engineering and Material Science Chung-Ang University, Seoul, 156–756, Republic of Korea

1. Experimental section

1.1. Materials

4,8-Dehydrobenzo[1,2-*b*:4,5-*b'*]dithiophene-4,8-dione (compound 1), 5-octyl-4H-thieno[3,4-*c*]pyrrole-4,6(5H)-dione (compound 6), 1-bromooctane, 2-ethylhexyl bromide, N,N-dimethylformamide (DMF), tetrahydrofuran (THF), N-bromosuccinimide (NBS), n-BuLi, toluene, chloroform, $Pd(PPh_3)_2Cl_2$, zinc powder and trimethyltin chloride were purchased from Aldrich, Alpha, and Langchem Inc. All of these chemicals were used without further purification.

1.2. Synthesis of monomers and small molecules

1.2.1. Synthesis of 4,8-Bis((2-ethylhexyl)oxy)benzo[1,2-b:4,5-b']dithiophene (2)

Compound 1 (2 g, 9.08 mmol), zinc powder (1.3 g, 19.88 mmol), and 25 mL of distilled water were added to a 100 mL flask. To this flask 5.5 g of NaOH was added and the mixture of heated to reflux for 1 h. During the reaction, the color of the mixture changed from yellow to red to orange. Then, 3-(bromomethyl)heptane (5.26 g, 27.23 mmol) and a catalytic amount of tetrabutylammonium bromide were added to the flask, and the reaction mixture was refluxed for 12 h. The reaction mixture was then poured into cold water and extracted two times with diethyl ether. The combined extracts were dried with anhydrous $MgSO_4$, and then evaporated. The crude product was purified by column chromatography on silica gel with ethyl acetate/hexane (1:20) as eluent followed by recrystallization from ethanol to afford compound 2 (3.2 g, 7.17 mmol, 79%) as colorless crystals. ^{1}H NMR (300 MHz, $CDCl_3$), δ = 7.49 (d, 2H), 7.37 (d, 2H), 4.19 (d, 4H), 1.86-1.34 (m, 18H), 1.02 (t, 6H), 0.94 (t, 6H). HRMS(EI) : m/z for $C_{26}H_{38}O_2S_2$, [M]+ : 446.2313; found, 446.2305.

1.2.2. Synthesis of 4,8-Bis(octyloxy)benzo[1,2-b:4,5-b']dithiophene (3)

Compound 1 (2 g, 9.08 mmol), zinc powder (1.3 g, 19.88 mmol), and 25 mL of distilled wat

er were added to a 100 mL flask. To this flask 5.5 g of NaOH was added and the mixture of h eated to reflux for 1 h. During the reaction, the color of the mixture changed from yellow to r ed to orange. Then, 1-bromooctane (5.26 g, 27.23 mmol) and a catalytic amount of tetrabutyl ammonium bromide were added into the flask, and the reaction mixture was refluxed for 12 h . The reaction mixture was then poured into cold water and extracted two times with diethyl e ther. The combined extracts were dried with anhydrous $MgSO_4$ and then evaporated. The cru de product was purified by column chromatography on silica gel with ethyl acetate/hexane (1 :20) as eluent followed by recrystallization from ethanol to afford compound 3 (3.3 g, 7.35 m mol, 81%) as colorless crystals. ^{1}H NMR (300 MHz, $CDCl_3$), δ = 7.66 (d, 2H), 7.47 (d, 2H), 4.26 (t, 4H), 1.87 (q, 4H), 1.53 (m, 4H), 1.37-1.27 (m, 16H), 0.88 (t, 6H). HRMS(EI) : m/z fo r $C_{26}H_{38}O_2S_2$,[M]+ : 446.2313; found, 446.2305.

1.2.3. Synthesis of (4,8-Bis((2-ethylhexyl)oxy)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(tri methylstannane) (4)

In a dry two-neck 50 mL nitrogen purged flask, compound 2 (1.00 g, 2.23 mmol) was dissol ved in 15 mL of anhydrous THF. The solution was cooled to 0 °C, and a solution of n-BuLi (1.79 mL, 2.5 M in hexane, 4.47 mmol) was added dropwise with stirring, after which the reac tion mixture was stirred for 2 h at room temperature. Next, the reaction mixture was cooled to 0 °C and chlorotrimethylstannane (0.89 g, 4.47 mmol) was added in one portion. The reaction mixture was stirred at 0 °C for 30 min and then warmed to room temperature for 2 h. Subsequ ently, the reaction mixture was quenched by the addition of 10 mL distilled water, and the mi xture was extracted with diethyl ether. Finally, the combined organic phase was dried with an hydrous $MgSO_4$ and concentrated to obtain a yellow viscous crude product. Further purificati on by recrystallization with ethanol afforded pure compound 4 (1.26 g, 1.63 mmol, 73%) as a yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$), δ = 7.51 (s, 2H), 4.19 (d, 4H), 1.81 (d, 2H), 1.73-1

.31 (d, 16H), 1.02 (t, 6H), 0.94 (m, 6H), 0.44 (s, 18H). ^{1}C NMR (500 MHz, $CDCl_3$), δ = 142. 9, 140.0, 133.5, 132.5, 127.6, 75.3, 40.3, 30.2, 28.9, 23.6, 22.8, 13.9, 11.0, 8.7. HRMS(EI) : m/z for $C_{32}H_{54}O_2S_2Sn_2$, [M]+ : 774.1609; found, 774.1595.

1.2.4. Synthesis of (4,8-Bis(octyloxy)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(trimethylstannane) (5)

In a dry two-neck 50 mL nitrogen purged flask, compound 3 (1.00 g, 2.23 mmol) was dissolved in 15 mL of anhydrous THF. The solution was cooled to 0 °C, and a solution of n-BuLi (1.79 mL, 2.5 M in hexane, 4.47 mmol) was added dropwise with stirring, after which the reaction mixture was stirred for 2 h at room temperature. Next, the reaction mixture was cooled to 0 °C and chlorotrimethylstannane (0.89 g, 4.47 mmol) was added in one portion. The reaction mixture was stirred at 0 °C for 30 min and then warmed to room temperature for 2 h. Subsequently, the reaction mixture was quenched by the addition of 10 mL distilled water, and the mixture was extracted with diethyl ether. Finally, the combined organic phase was dried with anhydrous $MgSO_4$ and concentrated to obtain a yellow viscous crude product. Further purification by recrystallization with ethanol afforded pure compound 5 (1.16 g, 1.50 mmol, 67%) as a yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$), δ = 7.62 (s, 2H), 4.15 (d, 4H), 1.79 (d, 2H), 1.53 (m, 4H), 1.33-1.28 (m, 18H), 0.87 (t, 6H), 0.43 (s, 18H). ^{1}C NMR (500 MHz, $CDCl_3$), δ = 143 .15, 140.49, 134.09, 133.01, 129.10, 128.04, 73.63, 31.97, 30.58, 29.76, 29.71, 29.55, 29.40, 26.16, 22.73, 14.16, 8.31. HRMS(EI) : m/z for $C_{32}H_{54}O_2S_2Sn_2$, [M]+ : 774.16; found, 774.15.

1.2.5. Synthesis of 1,3-dibromo-5-octyl-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione (7)

Compound 6 (4.90 g, 18.46 mmol) was dissolved in 27.6 mL of concentrated sulfuric acid and 92.4 mL of trifluoroacetic acid. N-bromosuccinimide (9.86 g, 55.39 mmol) was added in one portion and the reaction mixture was stirred overnight at room temperature. The resulting

brown solution was diluted with 500 mL of water and extracted with dichloromethane. The organic phase was dried over anhydrous $MgSO_4$ and evaporated to afford the crude product as orange crystals. Purification by column chromatography on a silica gel with dichloromethane/hexane (1:1) as eluent followed by recrystallization from aqueous ethanol afforded compound 7 (6.41 g, 15.14 mmol, 82%) as white crystals. Mp: 104-105 °C (760 torr) ^{1}H NMR (300 MHz, $CDCl_3$) : δ = 3.60 (t, 2H), 1.62 (q, 2H), 1.31 (m, 10H), 0.89 (t, 3H).

1.2.6. Synthesis of 5-octyl-1, 3-di(thiophen-2-yl)-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione (8)

Compound 7 (7.50 g, 17.72 mmol) and trimethyl(thiophen-2-yl)stannane (16.53 g, 44.31 mmol) were dissolved in 300 mL of toluene in a pressure tube. The solution was then degassed with nitrogen for 30 min. $Pd(PPh_3)_2Cl_2$ (0.37 g, 0.53 mmol) was then added to the solution and the tube was capped and heated to 110 °C overnight. Once cooled, the mixture was extracted with dichloromethane. The combined organic layer was dried over anhydrous $MgSO_4$. After removing the solvent, the residue was purified by column chromatography on silica gel with hexane/dichloromethane (4:1) as eluent. Recrystallization from hexane afforded compound 8 (4.87 g, 11.34 mmol, 64%) as a yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.00 (s, 2H), 7.45 (s, 2H), 7.15 (t, 2H), 3.68(t, 2H), 1.72 (m, 2H), 1.32 (m, 10H), 0.88 (t, 3H).

1.2.7. Synthesis of 1-(5-bromothiophen-2-yl)-5-octyl-3-(thiophen-2-yl)-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione (9)

Compound 8 (5.50 g, 12.79 mmol) was added to 100 mL of DMF and 100 mL of $CHCl_3$, to which NBS (2.27 g, 12.79 mmol) was added dropwise over 30 min. After 2 h, the reaction mixture was poured into water and extracted with chloroform three times. The organic phase was combined and dried over anhydrous $MgSO_4$. After the removal of the solvent, the crude product was purified by column chromatography on silica gel with dichloromethane/hexane (1:4

) as eluent. Recrystallization from hexane afforded compound 9 (3.45 g, 6.78 mmol, 53%) as a yellow solid. ^{1}H NMR (300 MHz, DMSO): δ = 7.99 (s, 1H), 7.83 (s, 1H), 7.70 (t, 1H), 7.35 (d, 1H), 7.24(d, 1H), 3.51(t, 2H), 1.50 (s, 2H), 1.27 (m, 10H), 0.84 (m, 3H).

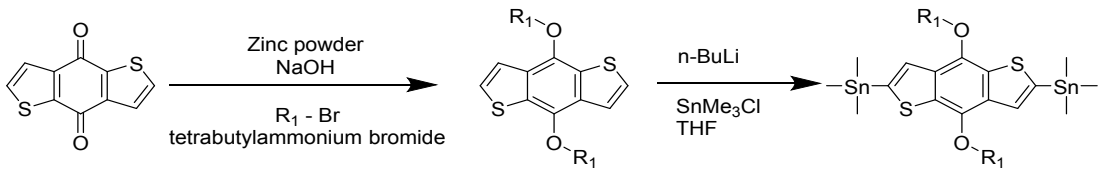
*1.2.8. Synthesis of 3,3'-((4,8-bis((2-ethylhexyl)oxy)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(thiophene-5,2-diyl))bis(5-octyl-1-(thiophen-2-yl)-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione (**BDTEH-TTPD**) (10)*

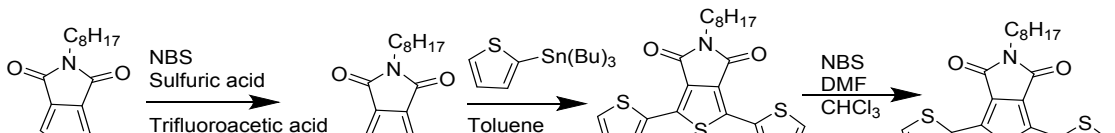
Compound 4 (0.76 g, 0.98 mmol) and compound 9 (1.00 g, 1.96 mmol) were dissolved in 20 mL of dry toluene and degassed with nitrogen for 10 min. $Pd(PPh_3)_2Cl_2$ (0.02 g, 0.03 mmol) was then added and the mixture was stirred at 100 °C overnight under a nitrogen atmosphere. The reaction mixture was then poured into water and extracted with chloroform three times. The organic phase was combined and dried over anhydrous $MgSO_4$ and the residue was purified by column chromatography on silica gel with hexane/dichloromethane (1:1) as eluent to afford **BDTEH-TTPD** (0.57 g, 0.44 mmol, 45%) as a dark red solid. ^{1}H NMR (300 MHz, $CDCl_3$), δ = 7.89 (d, 2H), 7.74 (d, 2H), 7.31 (t, 2H), 7.16 (s, 2H), 7.01(d, 4H), 4.09 (t, 4H), 3.63 (t, 4H), 1.69 (br, 10H), 1.36–1.16 (br, 32H), 1.13–0.88 (m, 18H). ^{13}C NMR (500 MHz, $CDCl_3$): δ(162.7, 162.6, 162.5, 146.2, 140.6, 139.6, 136.9, 135.9, 132.9, 132.7, 132.2, 130.9, 130.2, 128.7, 126.1, 125.9, 125.6, 123.6, 120.3, 41.8, 38.9, 34.8, 33.0, 32.2, 29.6, 29.4, 28.9, 27.5, 27.4, 26.2, 23.5, 23.0, 14.7, 14.4, 11.4). MS (MALDI-TOF/TOF): calculated for $C_{70}H_{80}N_2O_6S_8$: 1300.3782 ; found, 1300.3787.

*1.2.9. Synthesis of 3,3'-((4,8-bis(octyloxy)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(thiophene-5,2-diyl))bis(5-octyl-1-(thiophen-2-yl)-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione (**BDTO-TTPD**) (11)*

Compound 5 (0.76 g, 0.98 mmol) and compound 9 (1.00 g, 1.96 mmol) were dissolved in 20

mL of dry toluene and degassed with nitrogen for 10 min. $Pd(PPh_3)_2Cl_2$ (0.02 g, 0.03 mmol) was then added and the mixture was stirred at 100 °C overnight under a nitrogen atmosphere. The reaction mixture was then poured into water and extracted with chloroform three times. The organic phase was combined and dried over anhydrous $MgSO_4$ and the residue was purifi ed by column chromatography on silica gel with hexane/dichloromethane (1:1) as eluent to af ford **BDTO-TTPD** (0.53 g, 0.40 mmol, 41%) as a dark red solid. ^1H NMR (300 MHz, $CDCl_3$), δ = 7.93 (d, 4H), 7.36 (d, 2H), 7.10 (s, 2H), 7.06 (d, 4H), 4.11 (t, 4H), 3.61 (t, 4H), 1.88-1.5 7 (br, 16H), 1.44–1.12 (br, 32H), 1.03–0.88 (m, 12H). ^{13}C NMR (500 MHz, $CDCl_3$): δ (162.8 , 162.7, 162.6, 144.3, 140.8, 139.7, 136.7, 135.7, 132.8, 132.7, 132.4, 131.0, 130.3, 130.2, 12 8.8, 128.7, 126.3, 125.7, 117.3, 41.1, 39.0, 38.9, 32.2, 30.8, 29.7, 29.6, 28.9, 27.4, 24.2, 23.7, 23.6, 23.0, 14.7, 14.4, 11.8, MS (MALDI-TOF/TOF): calculated for $C_{70}H_{80}N_2O_6S_8$; 1300.37 82 ; found, 1300.3796.





Scheme S1. Synthetic route to the small molecules **BDTEH-TTPD** (compound 10) and **BDT O-TTPD** (compound 11).

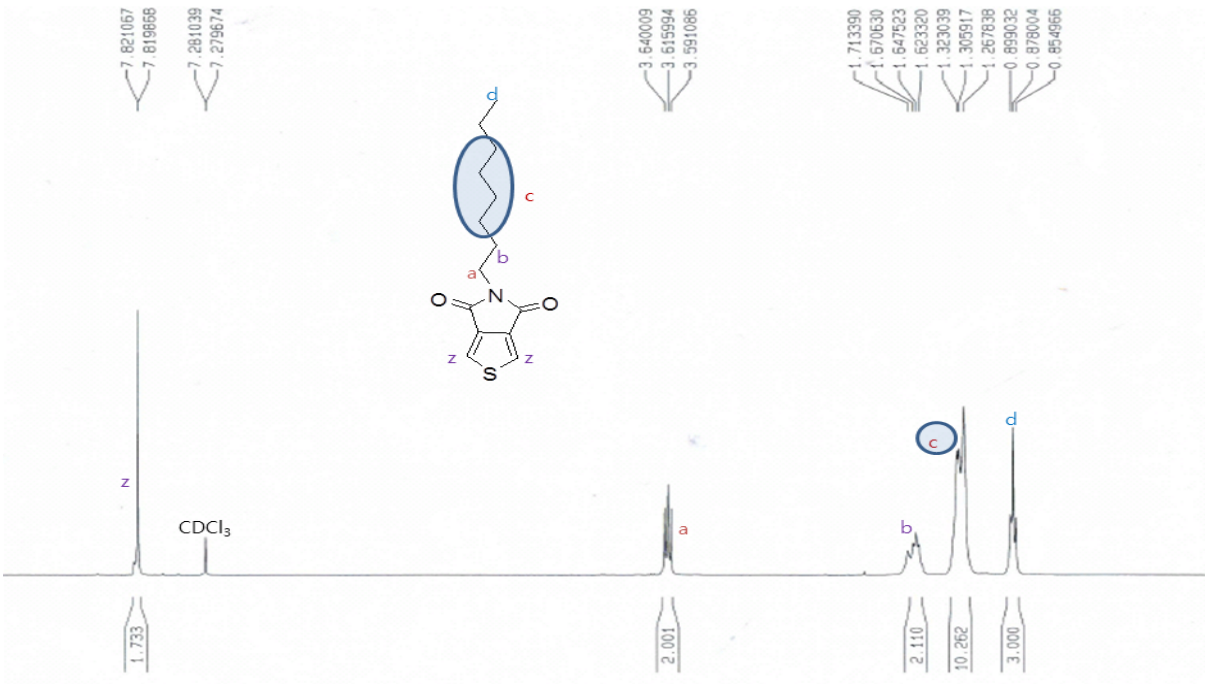


Fig S1. [1]H NMR spectrum of Compound 6.

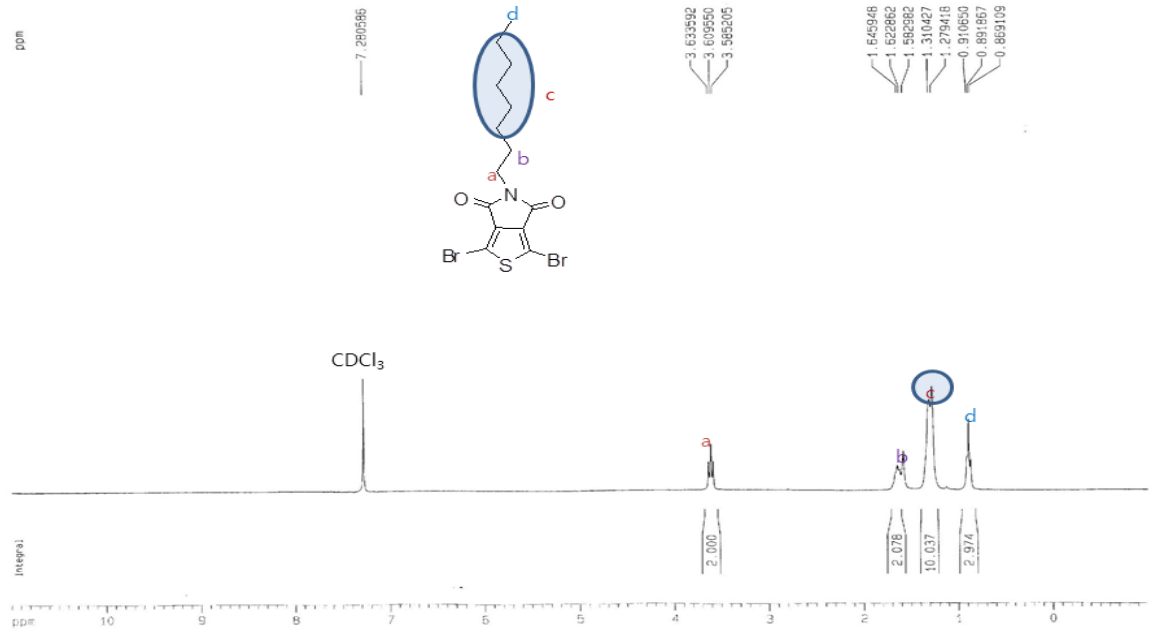


Fig S2. [1]H NMR spectrum of Compound 7.

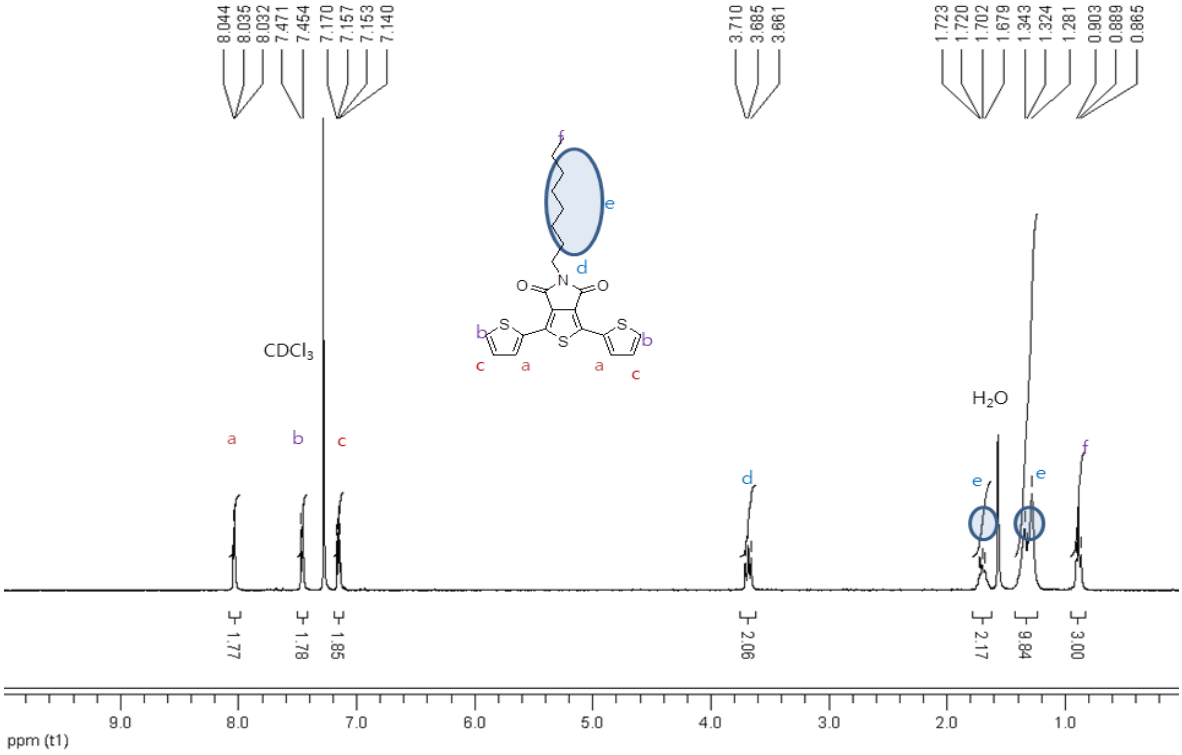


Fig S3. [1]H NMR spectrum of Compound 8.

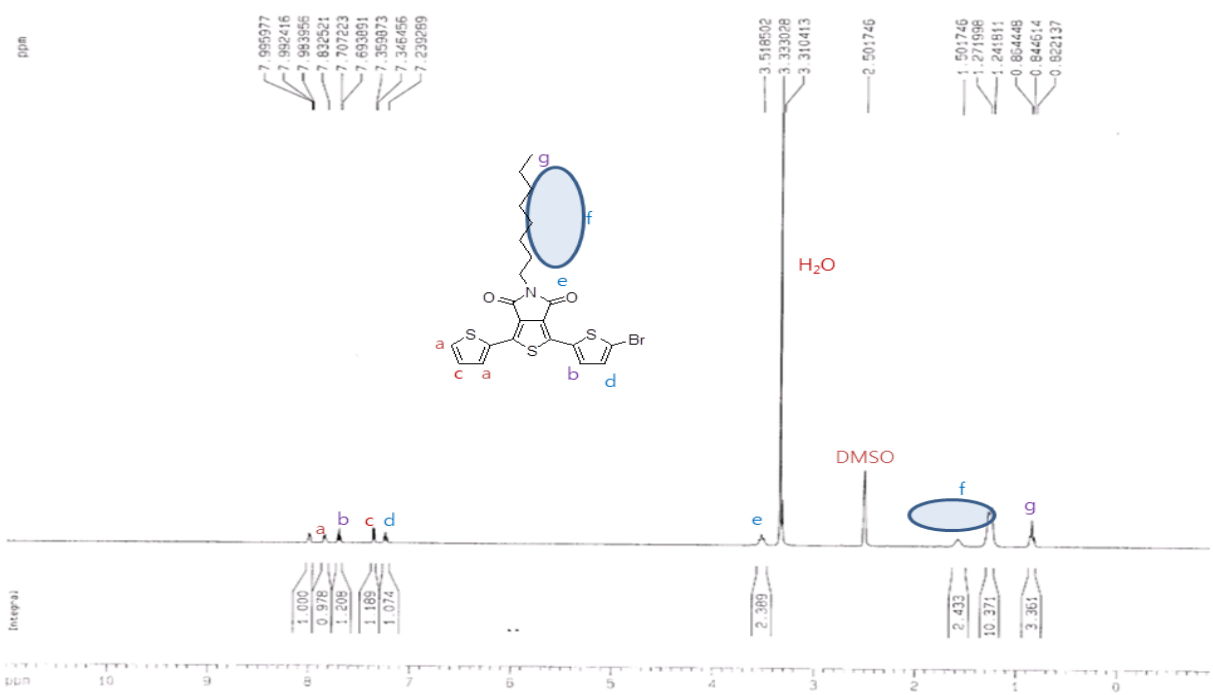


Fig S4. [1]H NMR spectrum of Compound 9.

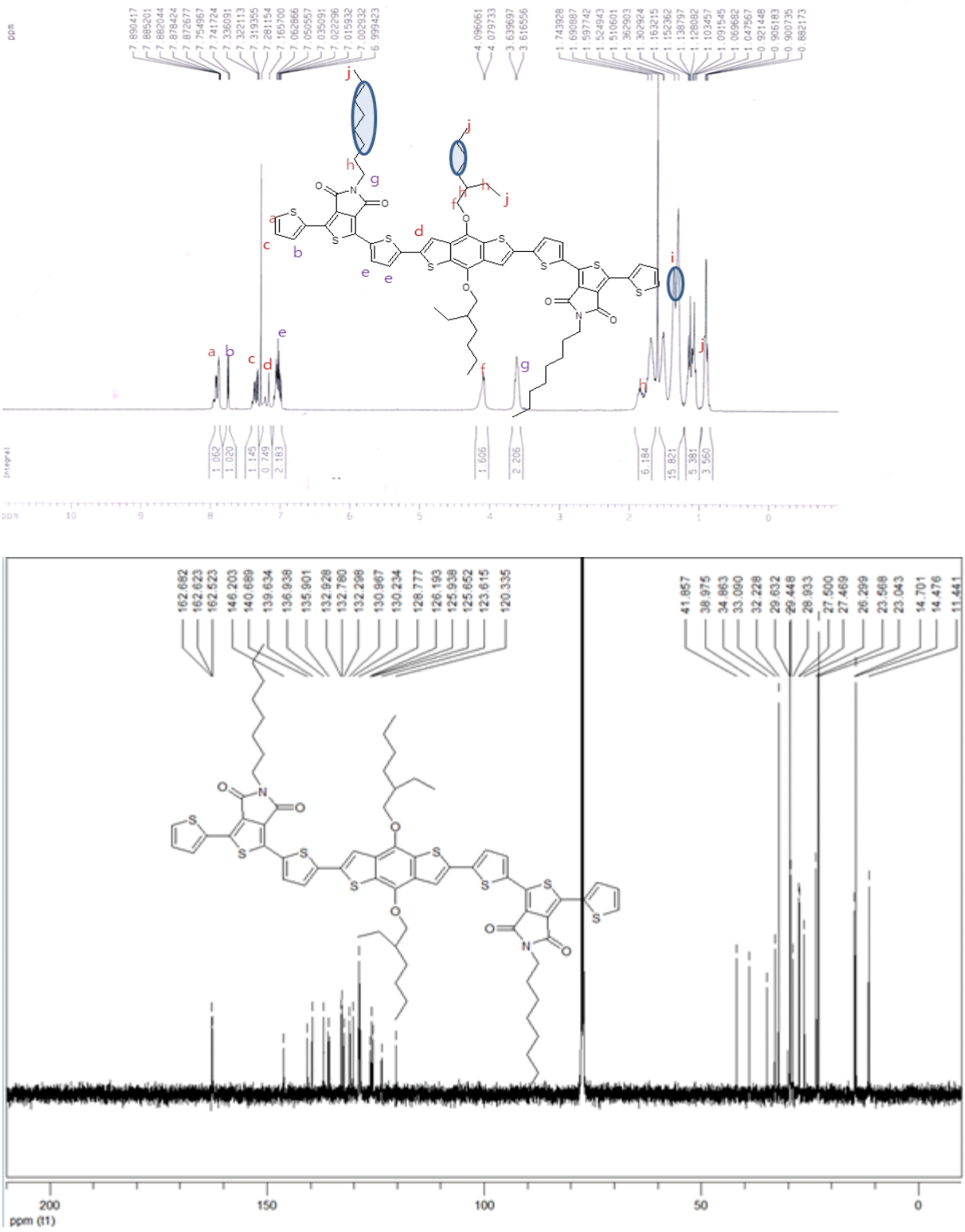
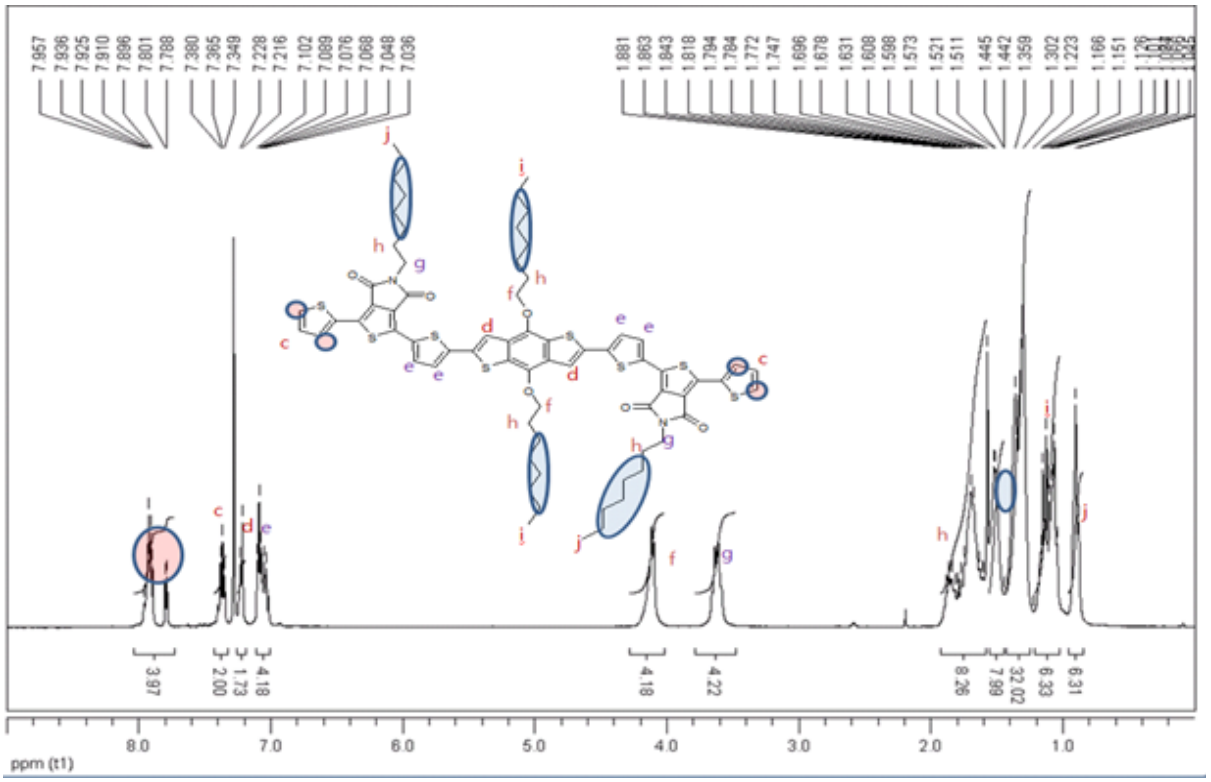


Fig S5. ^{1}H NMR and ^{13}C NMR spectra of compound 10 **(BDTEH-TTPD).**



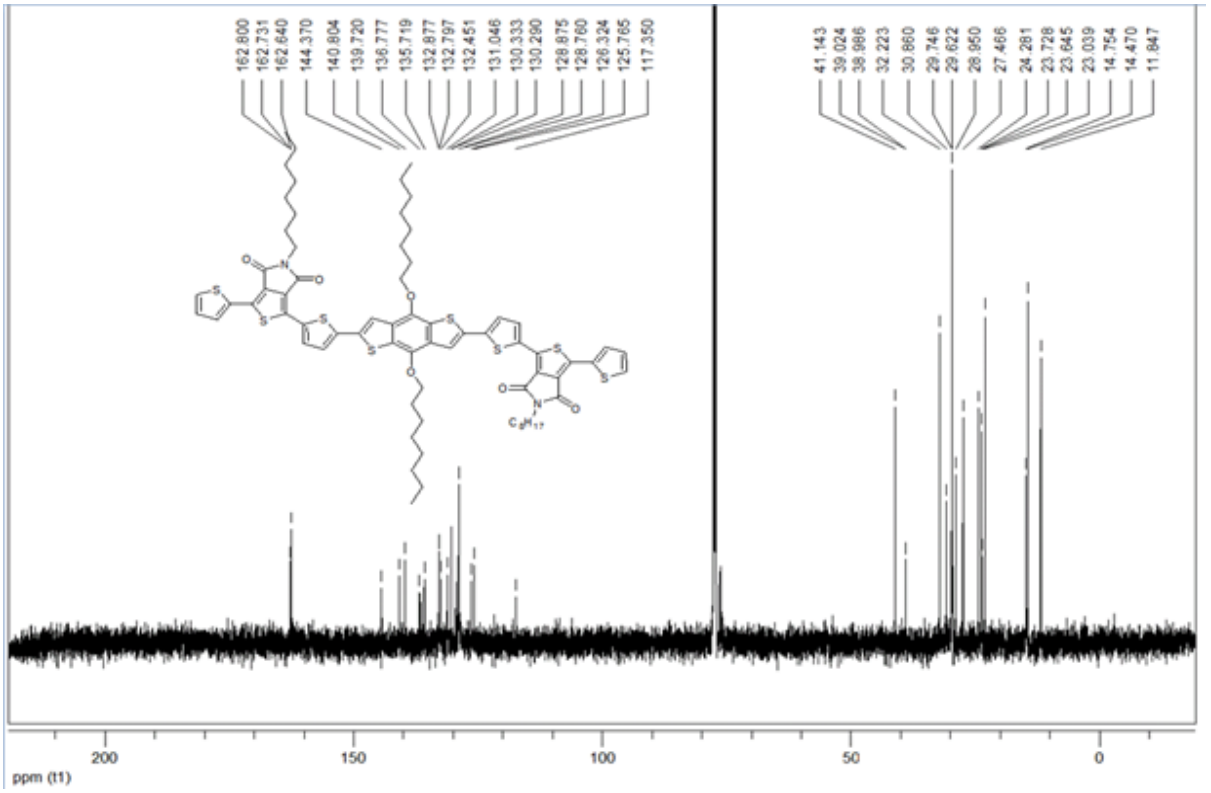
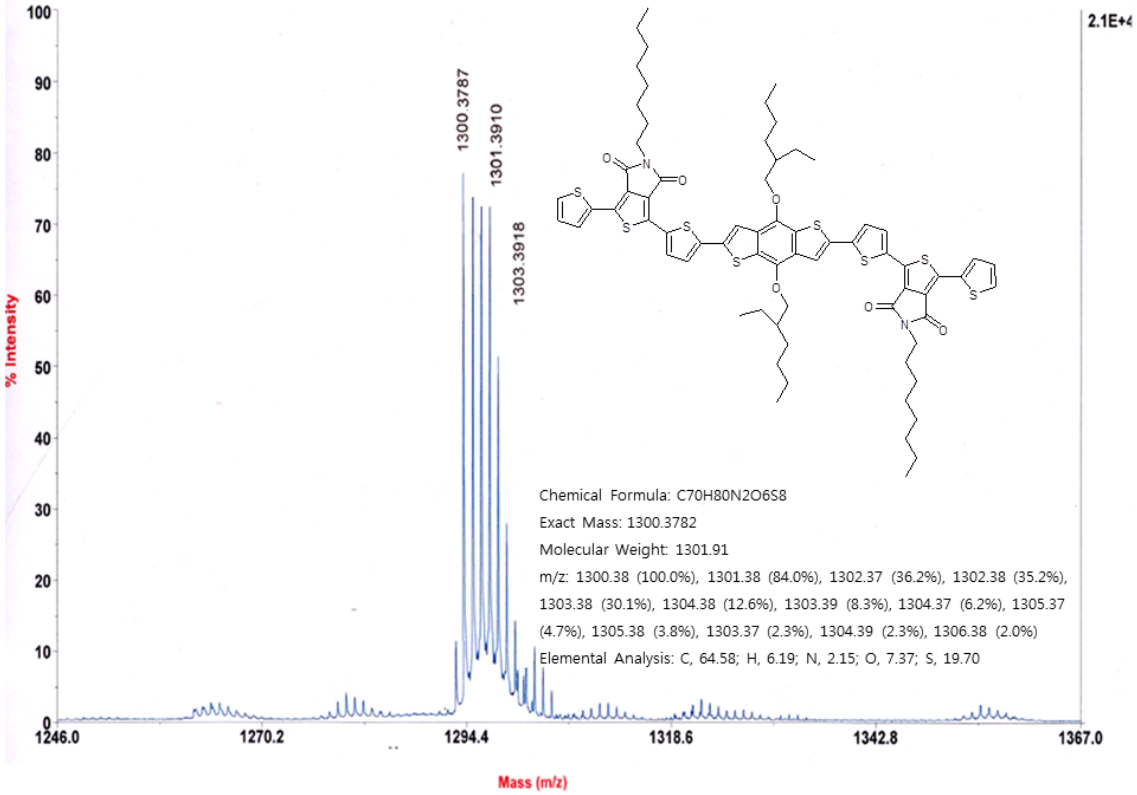


Fig S6. ^{1}H NMR and ^{13}C NMR spectra of compound 11 **(BDTO-TTPD).**

(a)



(b)

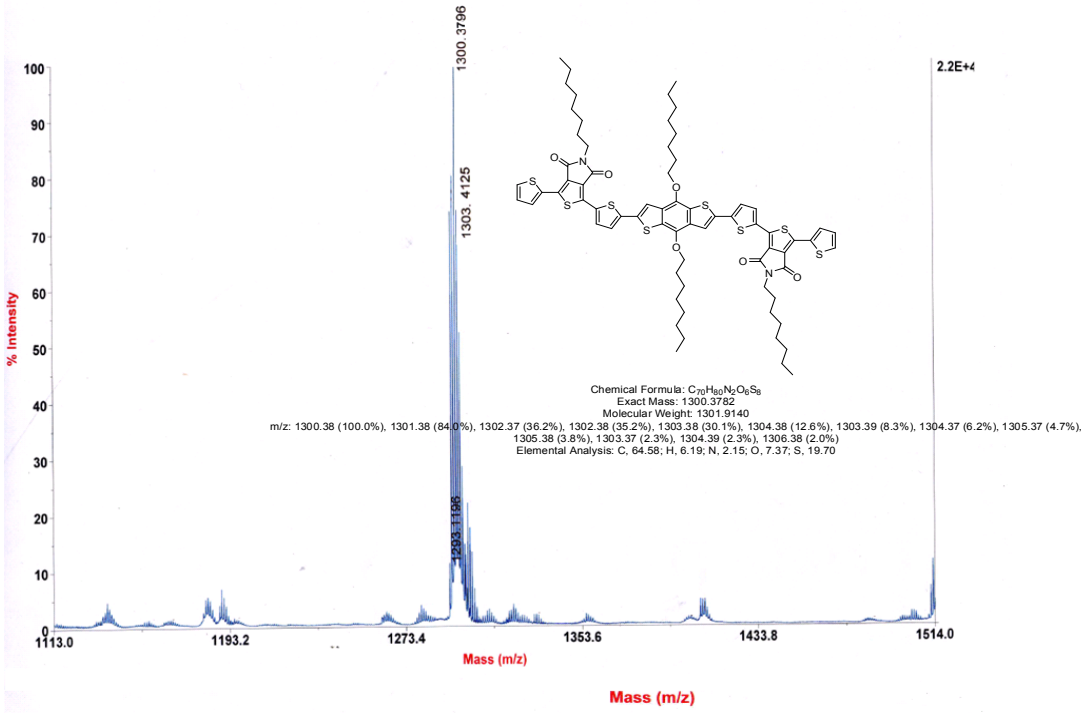


Fig S7. High Resolution Mass Spectrum of **BDTEH-TTPD** (a) and **BDTO-TTPD** (b).