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

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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(PPh₃)₂Cl₂, 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 MgSO₄, 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. ¹H NMR (300 MHz, CDCl₃), 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 C₂₆H₃₈O₂S₂, [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 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 MgSO₄, 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. ¹H NMR (300 MHz, CDCl₃), 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 C₂₆H₃₈O₂S₂, [M]+ : 446.2313; found, 446.2305.
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 MgSO₄ 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. ¹H NMR (300 MHz, CDCl₃), 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 C₂₆H₃₈O₂S₂ ,[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. Subsequen
tly, 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 MgSO₄ 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. ¹H NMR (300 MHz, CDCl₃), δ = 7.51 (s, 2H), 4.19 (d, 4H), 1.81 (d, 2H), 1.73-1
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 MgSO₄ 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. ¹H NMR (300 MHz, CDCl₃), 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). ¹C NMR (500 MHz, CDCl₃), 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 C₃₂H₅₄O₂S₂Sn₂, [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\(_3\))\(_2\)Cl\(_2\) (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
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(PPh₃)₂Cl₂ (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 MgSO₄ 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. ¹H NMR (300 MHz, CDCl₃), 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). ¹³C NMR (500 MHz, CDCl₃): 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 C₇₀H₈₀N₂O₈S₈ : 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\(_3\))\(_2\)Cl\(_2\) (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 BDTO-TTPD (0.53 g, 0.40 mmol, 41%) as a dark red solid. \(^1\)H NMR (300 MHz, CDCl\(_3\)), \(\delta = 7.93\) (d, 4H), 7.36 (d, 2H), 7.10 (s, 2H), 7.06 (d, 4H), 4.11 (t, 4H), 3.61 (t, 4H), 1.88-1.57 (br, 16H), 1.44–1.12 (br, 32H), 1.03–0.88 (m, 12H). \(^1\)\(^3\)C NMR (500 MHz, CDCl\(_3\)): \(\delta (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, 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\(_2\)O\(_6\)S\(_8\); 1300.3782; 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).
**Fig S7.** High Resolution Mass Spectrum of **BDTEH-TTPD** (a) and **BDTO-TTPD** (b).