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Impact of Side-Chain Fluorination on Photovoltaic Properties : Fine Tuning of Microstructure and Energy Levels of 2D-Conjugated Copolymers

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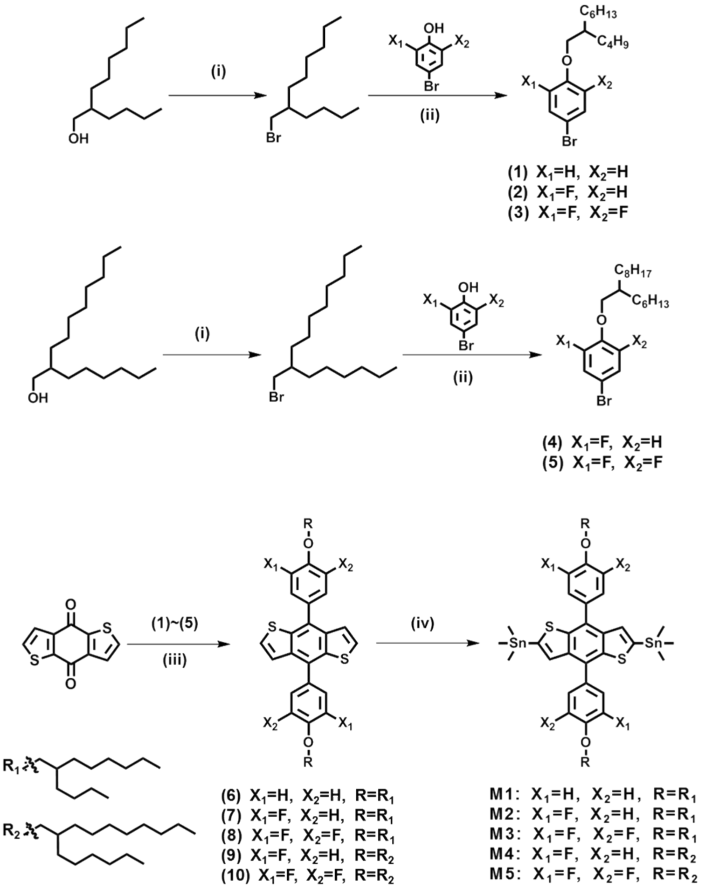
Experimental

Materials

All chemicals and reagents from commercial sources were used without further purification. All anhydrous solvents for the synthesis and fabrication of device were purchased from Sigama-Aldrich. 5,6-difluoro-4,7-bis(5-bromo-4-(2-ethylhexyl)-2-thienyl)-2,1,3-benzothiadiazole, was synthesized according to reference with modified schemes.[1] Monomers were synthesized as shown in Scheme S1. To probe the effect of fluorination by quantity in side chain and chain length attached to polymer backbone, five corresponding polymers with alkoxyphenyl-substituted benzo[1,2-b:3,4-b′]dithiophenes (BDTs) were synthesized as shown in Scheme S2.

Synthesis of Monomers



Scheme S1. Synthetic procedures of electron donating monomers; BDT-Ph-0F-BO, BDT-Ph-1F-BO, BDT-Ph-2F-BO, BDT-Ph-1F-HD, and BDT-Ph-2F-HD. i) PPh_3, Br_2, AcOH, r.t., 12h, ii) K_2CO_3, DMSO, r.t., 48 h, iii) n-butyl lithium, $SnCl_2$, THF, 55 ºC, overnight, iv) n-butyl lithium, trimethyltin chloride, THF, -75 ºC, overnight.

1-Bromo-4-(2'-butyloctyloxy)benzene (1). Under nitrogen atmosphere, 4-bromophenol (8.0 g, 46 mmol), K_2CO_3 (7.03 g, 51 mmol) were put into three-neck round bottom flask with 100ml DMSO. 1-Bromo-butyloctane (2) (12.7 g, 51 mmol) was added dropwise in room temperature. The mixture was stirred 48h and the mixture was poured into 200 ml ice cold water and then extracted with ethylacetate three times. Organic layer was washed with water and dried over magnesium sulfate and evaporated to get crude product. The crude product was purified on a silica gel column with hexane. Clear oil is obtained (14.8 g, 85 %). ^{1}H NMR ($CDCl_3$, 400 MHz), δ (ppm): 7.36 (d, 2H); 6.78 (d, 2H); 3.80 (d, 2H); 1.77 (m, 1H); 1.54–1.25 (m, 16H); 0.92 (s, 6H).

4,8-Bis(4-butyloctyloxy-1-phenyl)-benzo[1,2-b:4,5-b']-dithiophene (6). Under nitrogen atmosphere, 1-bromo-4-(2-butyloctyloxy) benzene (3) (7.87 g, 27.6 mmol) was dissolved in dry THF (40 mL) and then n-butyllithium solution (18 mmol, 11.25 mL, 1.6 M in n-hexane) was added dropwise at -78 °C. After addition, the reaction mixture was maintained at -78 °C for 2 h, followed by the addition of benzo[1,2-b:4,5-b′]dithiophene-4,8-dione (4) (1.32 g, 6 mmol) and allowed to warm to 55 °C for 2 h. The solution was cooled down and then $SnCl_2 \cdot 2H_2O$ (10.83 g, 48 mmol) in 10 % aqueous HCl (12.5 mL) was added. The solution was refluxed for 6 h and then the cooled the mixture was poured into water and extracted with dichloromethane, the organic extraction was washed successively with water and sodium bicarbonate solution twice and the combined organic phase was dried over magnesium sulfate and evaporated to afford the crude product. The crude product was purified on a silica gel column, eluting with pure hexane. White crystals were obtained (2.13 g, 50 % yield). ^{1}H NMR ($CDCl_3$, 400 MHz), δ (ppm): 7.62 (d, 4H), 7.36 (m, 4H), 7.09 (d, 4H), 3.95 (d, 4H), 1.84 (m, 2H), 1.56–1.28 (br, 32H), 0.92 (m, 12H).

2,6-Bis(trimethyltin)-4,8-Bis(4-butyloctyloxy-1-phenyl)-benzo[1,2-b:4,5-b']-dithiophene (M1). A solution of compound (6) (1.2g, 1.7 mmol) in dry THF (20 ml) was stirred under nitrogen gas for 30 min, and then 2.5 M n-butyllithium solution in hexane (2 ml) was added dropwise at -78 °C. Then the solution was kept at -78 °C for 1 h, and 1.0 M trimethyltin chloride solution in THF (5 ml) was added. Then the solution was allowed to warm up to room temperature and stirred overnight. The mixture was poured into water and extracted with ether. The organic phase was evaporated, and the crude product was purified by recrystallization in ethanol to afford pale yellow needles (1.25 g, yield 71 %). ^{1}H NMR ($CDCl_3$, 400 MHz), δ (ppm): 7.65 (d, 4H), 7.38 (s, 2H), 7.10 (d, 4H), 3.96 (d, 4H), 1.83 (m, 2H), 1.58-1.28 (br, 32H), 0.93 (m, 12H), 0.35 (t, 18H). ^{13}C NMR ($CDCl_3$, 100 MHz), δ (ppm): 159.06, 141.61, 137.07, 132.05, 130.56, 128.45, 114.65, 70.91, 38.09, 31.90, 29.74, 29.15, 26.91, 23.11, 22.71, 14.14, 8.37. Elemental analysis: calcd : $C_{48}H_{74}O_2S_4Sn_2$: C, 60.24 ; H, 7.58 ; S, 6.19 found : C, 60.59 ; H, 7.45 ; S, 6.16 MALDI TOF MS: m/z 1036.26

1-Bromo-4-(2'-butyloctyloxy)-3-fluorobenzene (2). Under nitrogen atmosphere, 4-bromo-2-fluorophenol (8.0 g, 42 mmol), K_2CO_3 (6.4 g, 46 mmol) were put into three-neck round bottom flask with 100 ml DMSO. 1-Bromo-butyloctane (2) (11.5 g, 46 mmol) was added dropwise in room temperature. The mixture was stirred 48 h and the mixture was poured into 200 ml ice cold water and then extracted with ethylacetate three times. Organic layer was washed with water and dried over magnesium sulfate and evaporated to get crude product. The crude product was purified on a silica gel column with hexane. Clear oil is obtained (12.7 g, 84 %). ^{1}H NMR ($CDCl_3$, 400 MHz), δ (ppm): 7.22 (d, 1H), 7.16 (d, 1H), 6.82 (t, 1H), 3.86 (d, 2H), 1.80 (m, 1H), 1.48-1.27 (m, 16H), 0.91-0.87 (m, 6H).

4,8-Bis(4-butyloctyloxy-3-fluroro-1-phenyl)-benzo[1,2-b:4,5-b']-dithiophene (7). Under nitrogen atmosphere, 1-bromo-4-(2'-butyloctyloxy)-3-fluorobenzene (3) (8.0 g, 22 mmol) was dissolved in dry THF (40 ml) and then n-butyllithium solution (22 mmol, 8.9 mL, 2.5 M in n-hexane) was added dropwise at -78 °C. After addition, the reaction mixture was maintained at -78 °C for 2 h, followed by the addition of benzo[1,2-b:4,5-b′]dithiophene-4,8-dione (4) (1.37 g, 7.4 mmol) and allowed to warm to 55 °C for 2 h. The solution was cooled down and then $SnCl_2 \cdot 2H_2O$ (13.6 g, 60 mmol) in 10 % aqueous HCl (30 mL) was added. The solution was refluxed for 6 h and then the cooled the mixture was poured into water and extracted with dichloromethane, the organic extraction was washed successively with water and sodium bicarbonate solution twice and the combined organic phase was dried over magnesium sulfate and evaporated to afford the crude product. The crude product was purified on a silica gel column, eluting with pure hexane. White crystals were obtained (2.76 g, 50 % yield). ^{1}H NMR ($CDCl_3$, 400 MHz), δ (ppm): 7.47 (m, 6H), 7.38 (d, 2H), 7.16 (t, 2H), 4.08 (d, 4H), 1.94 (m, 2H), 1.58-1.28 (br, 32H), 0.93 (m, 12H). ^{13}C NMR (400 MHz, $CDCl_3$), δ (ppm): 153.75, 152.11, 147.54, 147.46, 138.32, 136.21, 132.04, 131.99, 129.24, 127.34, 125.26, 125.24, 122.75, 117.38, 117.26, 115.39, 77.15, 76.93, 76.72, 72.85, 38.20, 31.81, 31.45, 31.12, 29.64, 29.11, 26.85, 23.00, 22.61, 13.96, 13.93

2,6-Bis(trimethyltin)-4,8-Bis(4-butyloctyloxy-3-fluoro-1-phenyl)-benzo[1,2-b:4,5-b']-dithiophene (M2). A solution of compound (6) (0.64 g, 0.8 mmol) in dry THF (10 ml) was stirred under nitrogen gas for 30 min, and then 2.5 M n-butyllithium solution in hexane (1 ml) was added dropwise at -78 °C. Then the solution was kept at -78 °C for 1 h, and 1.0 M trimethyltin chloride solution in THF (2.5 ml) was added. Then the solution was allowed to warm up to room temperature and stirred overnight. The mixture was poured into water and extracted with ether. The organic phase was evaporated, and the crude product was purified by recrystallization in ethanol to afford pale yellow needles (0.73 g, yield 85 %). ^{1}H NMR ($CDCl_3$, 400 MHz), δ (ppm): 7.46 (d, 4H), 7.38 (s, 2H), 7.18 (t, 2H), 4.06 (d, 4H), 1.94 (m, 2H), 1.57-1.35 (br, 32H), 0.93 (m, 12H), 0.39 (t, 18H). ^{13}C NMR ($CDCl_3$, 100 MHz), δ (ppm): 153.47, 151.84, 147.25, 147.19, 142.53, 142.35, 136.97, 132.46, 130.45, 127.57, 125.32, 125.30, 117.39, 117.27, 114.80, 77.01, 76.80, 72.35, 38.08, 31.88, 31.36, 31.05, 29.71, 29.10, 26.86, 23.08, 22.70, 14.13, 14.12. Elemental analysis: calcd : $C_{52}H_{76}F_2O_2S_2Sn_2$: C, 58.22 ; H, 7.14 ; S, 5.98 found : C, 58.87 ; H, 6.69 ; S, 5.83. MALDI TOF MS: m/z 1072.19

1-Bromo-4-(2'-butyloctyloxy)-3,5-difluorobenzene (3). A stirred mixture of 4-bromo-2,6-

difluorophenol (5.7 g, 27 mmol), K_2CO_3 (4.15 g, 30 mmol) were put into three-neck round bottom flask with 100 ml DMSO. 1-Bromo-butyloctane (2) (7.48 g, 30 mmol) was added dropwise in room temperature. The mixture was stirred 48h and the mixture was poured into 200 ml ice cold water and then extracted with ethylacetate three times. Organic layer was washed with water and dried over magnesium sulfate and evaporated to get crude product. The crude product was purified on a silica gel column with hexane. Clear oil is obtained (8.25 g, 81 %). ^{1}H NMR ($CDCl_3$, 400 MHz), δ (ppm): 7.01 (d, 2H), 3.99 (d, 2H), 1.72 (m, 1H), 1.58-1.30 (m, 16H), 0.92-0.86 (m, 6H).

4,8-Bis(4-butyloctyloxy-3,5-difluroro-1-phenyl)-benzo[1,2-b:4,5-b']-dithiophene (8). Under nitrogen atmosphere, 1-bromo-4-(2'-butyloctyloxy)-3,5-difluorobenzene (3) (8.2 g, 22 mmol) was dissolved in dry THF (40 mL) and then n-butyllithium solution (22 mmol, 8.7 mL, 2.5 M in n-hexane) was added dropwise at -78 °C. After addition, the reaction mixture was maintained at -78 °C for 2 h, followed by the addition of benzo[1,2-b:4,5-b′]dithiophene-4,8-dione (4) (1.33 g, 7.2 mmol) and allowed to warm to 55 °C for 2 h. The solution was cooled down and then $SnCl_2 \cdot 2H_2O$ (13.2 g, 58 mmol) in 10 % aqueous HCl (15 mL) was added. The solution was refluxed for 6 h and then the cooled the mixture was poured into water and extracted with dichloromethane, the organic extraction was washed successively with water and sodium bicarbonate solution twice and the combined organic phase was dried over magnesium sulfate and evaporated to afford the crude product. The crude product was purified on a silica gel column, eluting with pure hexane. White crystals were obtained (2.88 g, 51 % yield). ^{1}H NMR ($CDCl_3$, 400 MHz), δ (ppm): 7.49 (d, 2H), 7.36 (d, 2H), 7.26 (d, 4H), 4.18 (d, 4H), 1.85 (m, 2H), 1.59–1.33 (br, 32H), 0.90 (m, 12H). ^{13}C NMR ($CDCl_3$, 100 MHz), δ (ppm): 157.04, 156.99, 155.38, 155.34, 138.06, 136.13, 135.95, 133.40, 128.47, 128.00, 122.47, 113.42, 113.30, 113.27, 77.64, 38.92, 31.93, 31.88, 31.01, 30.05, 29.71, 29.62, 29.35, 26.80, 26.76, 22.70

2,6-Bis(trimethyltin)-4,8-Bis(4-butyloctyloxy-3,5-difluoro--1-phenyl)-benzo[1,2-b:4,5-b']-dithiophene (M3). A solution of compound (7) (1.0 g, 1.2 mmol) in dry THF (20 ml) was stirred under nitrogen gas for 30 min, and then 1.6M n-butyllithium solution in hexane (2.3 ml) was added dropwise at -78 °C. Then the solution was kept at -78 °C for 1 h, and 1.0 M trimethyltin chloride solution in THF (3.7 ml) was added. Then the solution was allowed to warm up to room temperature and stirred overnight. The mixture was poured into water and extracted with ether. The organic phase was evaporated, and the crude product was purified by recrystallization in ethanol to afford pale yellow needles (0.98 g, yield 74 %). ^{1}H NMR ($CDCl_3$, 400 MHz), δ (ppm): 7.35 (s, 2H), 7.28 (d, 4H), 4.20 (d, 4H), 1.86 (m, 2H), 1.56-1.31 (br, 32H), 0.93 (m, 12H), 0.37 (t, 18H). ^{13}C NMR ($CDCl_3$, 100 MHz), δ (ppm): 157.02, 156.97, 155.37, 155.32, 143.24, 142.33, 136.76, 135.87, 134.15, 129.96, 126.83, 113.48, 113.44, 113.35, 113.32, 77.22, 77.01, 76.79, 38.95, 31.92, 31.88, 31.05, 30.05, 29.72, 29.61, 29.35, 26.82, 26.78, 22.69, 14.12. Elemental analysis: calcd : $C_{52}H_{74}F_4O_2S_2Sn_2$: C, 56.33 ; H, 6.73 ; S, 5.83 found : C,56.90 ; H, 6.45 ; S, 5.83. MALDI TOF MS: m/z 1108.13

1-Bromo-4-(2'-hexyldecyloxy)-3-fluorobenzene (4). Under nitrogen atmosphere, 4-bromo-2-fluorophenol (8.0 g, 42 mmol), K_2CO_3 (6.4 g, 46 mmol) were put into three-neck round bottom flask with 100 ml DMSO. 1-Bromo-hexyldecane (2) (14.0 g, 46 mmol) was added dropwise in room temperature. The mixture was stirred 48 h and the mixture was poured into 200 ml ice cold water and then extracted with ethylacetate three times. Organic layer was washed with water and dried over magnesium sulfate and evaporated to get crude product. The crude product was purified on a silica gel column with hexane. Clear oil is obtained (14.5 g, 83 %). ^{1}H NMR ($CDCl_3$, 400 MHz), δ (ppm): 7.22 (d, 1H), 7.15 (d, 1H), 6.83 (t, 1H), 3.86 (d, 2H), 1.82 (m, 1H), 1.48-1.25 (m, 24H), 0.90-0.86 (m, 6H).

4,8-Bis(4-hexyldecyloxy-3-fluroro-1-phenyl)-benzo[1,2-b:4,5-b']-dithiophene (9). Under nitrogen atmosphere, 1-bromo-4-(2'-hexyldecyloxy)-3-fluorobenzene (3) (9.0 g, 22 mmol) was dissolved in dry THF (40 ml) and then n-butyllithium solution (22 mmol, 8.9 mL, 2.5 M in n-hexane) was added dropwise at -78 °C. After addition, the reaction mixture was maintained at -78 °C for 2 h, followed by the addition of benzo[1,2-b:4,5-b′]dithiophene-4,8-dione (4) (1.37 g, 7.4 mmol) and allowed to warm to 55 °C for 2 h. The solution was cooled down and then $SnCl_2·2H_2O$ (13.6 g, 60 mmol) in 10 % aqueous HCl (30 mL) was added. The solution was refluxed for 6 h and then the cooled the mixture was poured into water and extracted with dichloromethane, the organic extraction was washed successively with water and sodium bicarbonate solution twice and the combined organic phase was dried over magnesium sulfate and evaporated to afford the crude product. The crude product was purified on a silica gel column, eluting with pure hexane. White crystals were obtained (3.05 g, 48 % yield). ^{1}H NMR ($CDCl_3$, 400 MHz), δ (ppm): 7.45 (m, 6H), 7.37 (d, 2H), 7.16 (t, 2H), 4.07 (d, 4H), 1.94 (m, 2H), 1.59-1.29 (br, 48H), 0.92 (m, 12H).

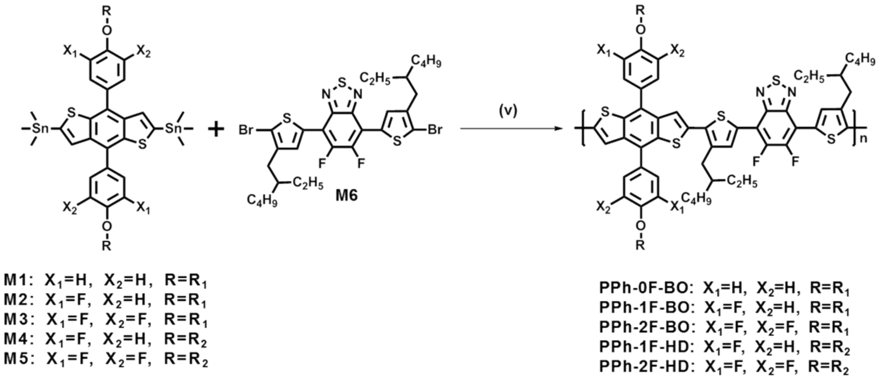
2,6-Bis(trimethyltin)-4,8-Bis(4-hexyldecyloxy-3-fluoro-1-phenyl)-benzo[1,2-b:4,5-b']-dithiophene (M4). A solution of compound (6) (1.38 g, 1.6 mmol) in dry THF (14 ml) was stirred under nitrogen gas for 30 min, and then 2.5 M n-butyllithium solution in hexane (2 ml) was added dropwise at -78 °C. Then the solution was kept at -78 °C for 1 h, and 1.0 M trimethyltin chloride solution in THF (5 ml) was added. Then the solution was allowed to warm up to room temperature and stirred overnight. The mixture was poured into water and extracted with ether. The organic phase was evaporated, and the crude product was purified by recrystallization in ethanol to afford pale yellow needles (1.56 g, yield 82 %). ^{1}H NMR ($CDCl_3$, 400 MHz), δ (ppm): 7.44 (d, 4H), 7.38 (s, 2H), 7.18 (t, 2H), 4.04 (d, 4H), 1.94 (m, 2H), 1.57-1.36 (br, 48H), 0.92 (m, 12H), 0.39 (t, 18H). ^{13}C NMR ($CDCl_3$, 100 MHz), δ (ppm): 153.47, 151.84, 147.31, 147.19, 142.53, 142.31, 136.97, 132.42, 130.45, 127.52, 125.32, 125.30, 117.37, 117.25, 114.80, 77.03, 76.80, 72.32, 38.06, 31.92, 31.51, 31.36, 31.02, 29.71, 29.91, 29.31, 29.10, 27.02, 26.86, 23.08, 22.70, 14.13, 14.12. Elemental analysis: calcd : $C_{60}H_{92}F_2O_2S_2Sn_2$: C, 60.82 ; H, 7.83, S, 5.41 found : C, 60.55 ; H, 7.26, S, 5.27. MALDI TOF MS: m/z 1185.22

1-Bromo-4-(2'-hexyldecyloxy)-3,5-difluorobenzene (5). A stirred mixture of 4-bromo-2,6-difluorophenol (9.0 g, 43 mmol), K_2CO_3 (6.4 g, 46 mmol) were put into three-neck round bottom flask with 100 ml DMSO. 1-Bromo-hexyldecane (2) (14.0 g, 46 mmol) was added dropwise in room temperature. The mixture was stirred 48h and the mixture was poured into 200 ml ice cold water and then extracted with ethylacetate three times. Organic layer was washed with water and dried over magnesium sulfate and evaporated to get crude product. The crude product was purified on a silica gel column with hexane. Clear oil is obtained (15.1 g, 81 %). ^1H NMR ($CDCl_3$, 400 MHz), δ (ppm): 7.02 (d, 2H), 3.97 (d, 2H), 1.72 (m, 1H), 1.58-1.30 (m, 24H), 0.90-0.85 (m, 6H).

4,8-Bis(4-hexyldecyloxy-3,5-difluroro-1-phenyl)-benzo[1,2-b:4,5-b']-dithiophene (10). Under nitrogen atmosphere, 1-bromo-4-(2'-hexyldecyloxy)-3,5-difluorobenzene (3) (9.5 g, 22 mmol) was dissolved in dry THF (40 mL) and then n-butyllithium solution (22 mmol, 8.7 mL, 2.5 M in n-hexane) was added dropwise at -78 °C. After addition, the reaction mixture was maintained at -78 °C for 2 h, followed by the addition of benzo[1,2-b:4,5-b′]dithiophene-4,8-dione (4) (1.33 g, 7.2 mmol) and allowed to warm to 55 °C for 2 h. The solution was cooled down and then $SnCl_2 \cdot 2H_2O$ (13.2 g, 58 mmol) in 10 % aqueous HCl (15 mL) was added. The solution was refluxed for 6 h and then the cooled the mixture was poured into water and extracted with dichloromethane, the organic extraction was washed successively with water and sodium bicarbonate solution twice and the combined organic phase was dried over magnesium sulfate and evaporated to afford the crude product. The crude product was purified on a silica gel column, eluting with pure hexane. White crystals were obtained (3.22 g, 50 % yield). ^1H NMR ($CDCl_3$, 400 MHz), δ (ppm): 7.49 (d, 2H), 7.36 (d, 2H), 7.27 (d, 4H), 4.15 (d, 4H), 1.85 (m, 2H), 1.59–1.33 (br, 48H), 0.89 (m, 12H).

2,6-Bis(trimethyltin)-4,8-Bis(4-hexyldecyloxy-3,5-difluoro--1-phenyl)-benzo[1,2-b:4,5-b']-dithiophene (M5). A solution of compound (7) (1.61 g, 1.8 mmol) in dry THF (20 ml) was stirred under nitrogen gas for 30 min, and then 1.6M n-butyllithium solution in hexane (3.5 ml) was added dropwise at -78 °C. Then the solution was kept at -78 °C for 1 h, and 1.0 M trimethyltin chloride solution in THF (5.6 ml) was added. Then the solution was allowed to warm up to room temperature and stirred overnight. The mixture was poured into water and extracted with ether. The organic phase was evaporated, and the crude product was purified by recrystallization in ethanol to afford pale yellow needles (1.54 g, yield 70 %). ^1H NMR ($CDCl_3$, 400 MHz), δ (ppm): 7.37 (s, 2H), 7.28 (d, 4H), 4.18 (d, 4H), 1.86 (m, 2H), 1.57-1.30 (br, 48H), 0.93 (m, 12H), 0.37 (t, 18H). ^{13}C NMR ($CDCl_3$, 100 MHz), δ (ppm): 157.02, 156.97, 155.37, 155.32, 143.24, 142.32, 136.76, 135.85, 134.15, 128.02, 126.83, 113.47, 113.44, 113.35, 113.32, 77.22, 77.01, 76.79, 38.95, 31.92, 31.71, 31.51, 31.05, 30.05, 29.92, 29.72, 29.61, 29.35, 26.82, 23.78, 22.69, 14.12. Elemental analysis: calcd : $C_{52}H_{74}F_4O_2S_2Sn_2$: C, 59.03 ; H, 7.43 ; S, 5.25 found C, 59.42, H, 7.11, S, 5.25. MALDI TOF MS: m/z 1219.13

Synthesis of Polymers



Scheme S2. Synthetic procedures of polymers; PPh-0F-BO, PPh-1F-BO, PPh-2F-BO, PPh-1F-HD, and PPh-2F-HD.v) Polymerization condition: M1~M5, $Pd(PPh_3)_4$, toluene/DMF (9:1), 110 °C reflux, 48 h.

PPh-0F-BO. M1 (311.0 mg, 0.3 mmol) and M6 (215.6 mg, 0.3 mmol) in 9 mL of anhydrous toluene and 1mL of DMF were put into a two-necked flask. The solution was refluxed at 110 °C for 48 h under nitrogen, followed by end-capping using 2-tributyltinthiophene and 2-bromothiophene, successively. After cooling down to room temperature, the solution was quenched in methanol, filtered, and then purified by Soxhlet extraction successively with methanol, acetone, hexane, chloroform and CB. Finally, the CB fraction was concentrated, and then the concentrate was precipitated in methanol. The dark blue solid was obtained after filtering and dried overnight in 70 % yield. ^{1}H NMR (500 MHz, *o*-dichlorobenzene-d_5): δ 8.59-8.49 (br, 2H), 8.13-8.10 (br, 4H), 8.10-8.03 (br, 2H), 7.55-7.50 (br, 4H), 4.38-4.31 (br, 4H), 3.28-3.11 (br, 4H), 2.23-1.71 (br, 48H), 1.41-1.13 (br, 24H), GPC (o-DCB, 80 °C): M_n = 14.1 kDa, PDI= 1.17

PPh-1F-BO. M2 (321.8 mg, 0.3 mmol) and M6 (215.6 mg, 0.3 mmol) in 9 mL of anhydrous toluene and 1mL of DMF were put into a two-necked flask. The solution was refluxed at 110 °C for 48 h under nitrogen, followed by end-capping using 2-tributyltinthiophene and 2-bromothiophene, successively. After cooling down to room temperature, the solution was quenched in methanol, filtered, and then purified by Soxhlet extraction successively with methanol, acetone, hexane, chloroform and CB. Finally, the CB fraction was concentrated, and then the concentrate was precipitated in methanol. The dark blue solid was obtained after filtering and dried overnight in 62 % yield. ^{1}H NMR (500 MHz, *o*-dichlorobenzene-d_5): δ 8.29-8.19 (br, 2H), 7.63-7.51 (br, 6H), 6.90-6.88 (br, 2H), 4.12-4.01 (br, 4H), 3.02-2.80 (br, 4H), 1.88-1.31 (br, 48H), 0.90-0.82 (br, 24H), GPC (o-DCB, 80 °C): M_n = 12.3 kDa, PDI= 2.33

PPh-2F-BO. M3 (332.6 mg, 0.3 mmol) and M6 (215.6 mg, 0.3 mmol) in 9 mL of anhydrous toluene and 1mL of DMF were put into a two-necked flask. The solution was refluxed at 110 °C for 48 h under nitrogen, followed by end-capping using 2-tributyltinthiophene and 2-bromothiophene, successively. After cooling down to room temperature, the solution was quenched in methanol, filtered, and then purified by Soxhlet extraction successively with methanol, acetone, hexane, chloroform and CB. Finally, the CB fraction was concentrated, and then the concentrate was precipitated in methanol. The dark blue solid was obtained after filtering and dried overnight in 60 % yield. ^{1}H NMR (500 MHz, *o*-dichlorobenzene-d_5): δ 8.25-8.22 (br, 2H), 7.68-7.52 (br, 2H), 7.42-7.36 (br, 4H), 6.92-6.82 (br, 4H), 4.24-4.14 (br, 4H), 2.98-2.82 (br, 4H), 1.91-1.40 (br, 48H), 0.90-0.80 (br, 24H), GPC (o-DCB, 80 °C): M_n = 12.2 kDa, PDI= 2.85

PPh-1F-HD. M4 (355.5 mg, 0.3 mmol) and M6 (215.6 mg, 0.3 mmol) in 9 mL of anhydrous toluene and 1mL of DMF were put into a two-necked flask. The solution was refluxed at 110 °C for 48 h under nitrogen, followed by end-capping using 2-tributyltinthiophene and 2-bromothiophene, successively. After cooling down to room temperature, the solution was quenched in methanol, filtered, and then purified by Soxhlet extraction successively with methanol, acetone, hexane, chloroform and CB. Finally, the CB fraction was concentrated, and then the concentrate was precipitated in methanol. The dark blue solid was obtained after filtering and dried overnight in 72 % yield. ^{1}H NMR (500 MHz, *o*-dichlorobenzene-d_5): δ 8.47-8.44 (br, 2H), 7.92-7.73 (br, 6H), 7.50-7.45 (br, 2H), 4.31-4.23 (br, 4H), 3.61-3.49 (br, 2H), 3.21-3.08 (br, 4H), 2.25-2.20 (br, 4H), 1.91-1.40 (br, 64H), 1.17-1.10 (br, 24H), GPC (o-DCB, 80 °C): M_n = 16.2 kDa, PDI= 1.94

PPh-2F-HD. M5 (366.3 mg, 0.3 mmol) and M6 (215.6 mg, 0.3 mmol) in 9 mL of anhydrous toluene and 1mL of DMF were put into a two-necked flask. The solution was refluxed at 110 °C for 48 h under nitrogen, followed by end-capping using 2-tributyltinthiophene and 2-bromothiophene, successively. After cooling down to room temperature, the solution was quenched in methanol, filtered, and then purified by Soxhlet extraction successively with methanol, acetone, hexane, chloroform and CB. Finally, the CB fraction was concentrated, and then the concentrate was precipitated in methanol. The dark blue solid was obtained after filtering and dried overnight in 64 % yield. ^{1}H NMR (500 MHz, *o*-dichlorobenzene-d_5): δ 8.48-8.43 (br, 2H), 7.88-7.84 (br, 2H), 7.67-7.60 (br, 4H), 4.47-4.38 (br, 4H), 3.21-3.09 (br, 4H), 2.14-2.03 (br, 4H) 1.88-1.28 (br, 64H), 1.18-1.02 (br, 24H), GPC (o-DCB, 80 °C): M_n = 15.8 kDa, PDI= 2.06

Analysis

Electrochemistry. Electrochemical cyclic voltammetry (CV) was conducted on a PowerLab/AD instrument model system with glassy carbon disk as working electrode, Pt wire as counter electrode, Ag/AgCl as reference electrode, repectivly in a 0.1 M tetrabutyl ammonium hexafluorophosphate (n-Bu_4NPF_6)-anhydrous acetonitrile solution at a potential scan rate of 50 mV s^{-1}. Thin films of polymers were deposited using drop cast onto the glassy carbon working electrode from a 2.0 mg mL^{-1} hot CB solution and dried under nitrogen prior to measurements. The electrochemical onsets were determined at the position where the current starts to differ from the baseline. The potential of the Ag/AgCl reference electrode was internally calibrated using the ferrocene/ferrocenium redox couple (Fc/Fc+). The energy levels were estimated: HOMO = – (4.80 + $E_{\text{onset, ox}}$), and LUMO = – (4.80 + $E_{\text{onset, red}}$).[2] UV-Vis spectra were measured by using Varian CARY-5000 UV-Vis spectrophotometer. For the measurements of thin films, materials were spin coated onto the glass substrates from hot chlorobenzene solutions (10 mg mL^{-1}). Optical band gap (Eg^{opt}) was calculated from the absorption edge of thin film sample.

Computational Studies. Density functional theory (DFT) calculations were performed using Gaussian 09 software package to obtain an in-depth understanding of the electronic structure of the polymer.[3] Hybrid three-parameter B3LYP functional combined with the 6-31G (d) basis set was used to obtain the optimized structures at the singlet ground state.[4] For simplicity, the 2-hexyldecyl-, 2-butyloctyl- and 2-ethylhexyl chains appended to the conjugated backbone and phenyl side chains were trimmed with methyl chains at the branch positions. HOMO and LUMO energy levels were analyzed using minimized singlet geometries to approximate the ground state.

Grazing Incidence Wide Angle X-ray Scattering (GIWAXS) analysis. Grazing incidence X-ray Wide Angle X-ray Scattering (GIWAXS) measurements were performed using Beamline 3C, 9A at the Pohang Accelerator Laboratory (PAL). The two dimensional GIXS images from the films were analyzed according to the relationship $q = 2\pi/d$ between the scattering vector q and the d spacing. The GIWAXS images shown are normalized with respect to exposure time.

Fabrication and Characterization of Organic Solar Cells

ITO glasses were used as the anodes and cleaned stepwise in detergent aqueous solution, deionized water, isopropyl alcohol, and acetone. The cleaned ITO glasses were exposed on UV-ozone. For photovoltaic devices with a MoO_3 interlayer, a MoO_3 film (9 nm) was thermally evaporated with a rate of 0.1 nm s^{-1} on UV-treated ITO substrates. PPhs and $PC_{71}BM$ were dissolved in o-DCB and the blend solutions were kept at a high temperature (90 °C) for more than one day. All processes were carried out in a glovebox with nitrogen. All blend films had to be processed from hot solutions in order to prevent premature aggregation of the polymers. Polymer/$PC_{71}BM$ solutions were spin-coated onto MoO_3 substrates, and then the films were left in a N_2 atmosphere to dry. To deposit the electrodes, the samples were transferred into a vacuum chamber, and then LiF (0.6 nm)/ Al(100 nm) were deposited. The current density−voltage ($J-V$) characteristics of the OSCs were measured a source/measure unit (Keithley 4200) in the dark and under 100 mW cm^{-2} AM 1.5 G solar illumination in a N_2 -filled glove box. Light was generated with an Oriel 1-kW solar simulator referenced using a Reference Cell PVM 132 calibrated at the US National Renewable Energy Laboratory. A photo modulation spectroscopic set-up was used to measure the incident photon-to-current conversion efficiency as a function of light wavelength.

SCLC measurement. The electron-only devices with (ITO/Al/polymers:$PC_{71}BM$/Al) architecture and the hole-only devices with (ITO/MoO_3/PPhs:$PC_{71}BM$/MoO_3/Ag) architecture were fabricated. The electrical characteristics were measured with a source/measure unit (Keithley 4200) in a N_2-filled glove box. I-V curves were fitted by using the Mott-Gurney square law. $J = (9/8)\ \varepsilon\ \mu\ (V^2/L^3)$, where ε is the static dielectric constant of the medium and μ is the carrier mobility.

References

(1) Lee, J.; Jo, S. B.; Kim, M.; Kim, H.G.; Shin, J.; Kim, H.; Cho, K. Donor–Acceptor Alternating Copolymer Nanowires for Highly Efficient Organic Solar Cells. *Adv. Mater.* **2014**, *26*, 6706-6714.
(2) Zhou, H.; Yang, L.; Stuart, A. C.; Price, S. C.; Liu, S.; You, W. Development of Fluorinated Benzothiadiazole as a Structural Unit for a Polymer Solar Cell of 7 % Efficiency. *Angew. Chem. Int. Ed.* **2011**, *50*, 2995-2998.
(3) Frisch, M. J.; *Gaussian 09, Revision A.02*, Gaussian, Inc., Wallingford CT, **2009**.
(4) Xu, Y. X.; Chueh, C. C.; Yip, H. L.; Ding, F. Z.; Li, Y. X.; Li, C. Z.; Li, X.; Chen, W. C.; Jen, A. K. Y. Improved Charge Transport and Absorption Coefficient in Indacenodithieno[3,2-b]thiophene-based Ladder-Type Polymer Leading to Highly Efficient Polymer Solar Cells. *Adv. Mater.* **2012**, *24*, 6356-6361.

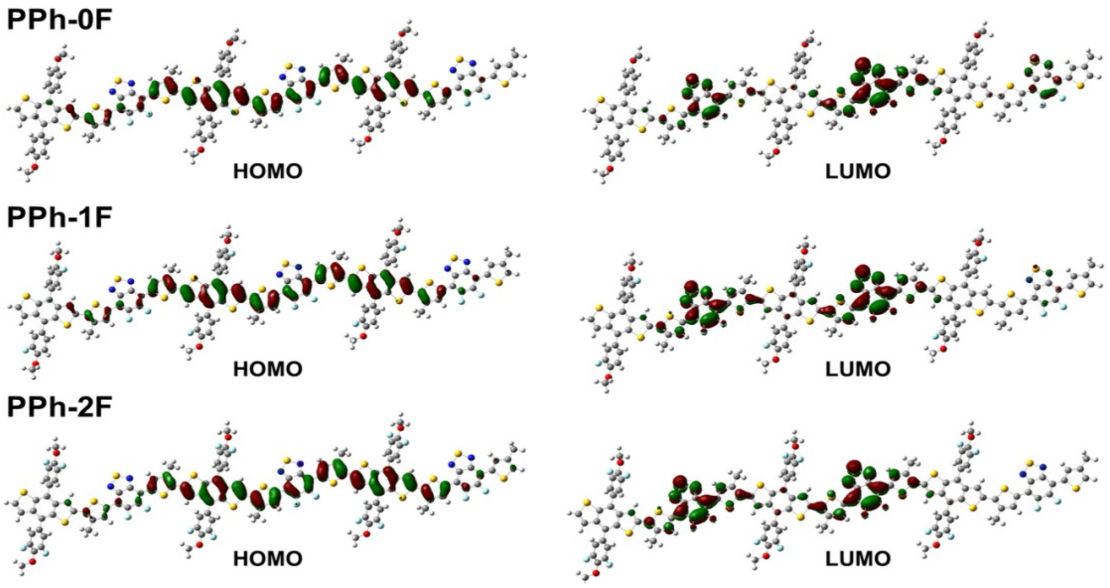
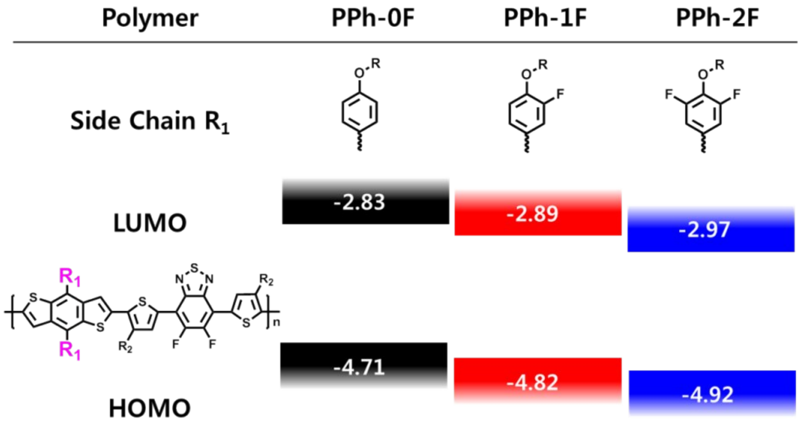


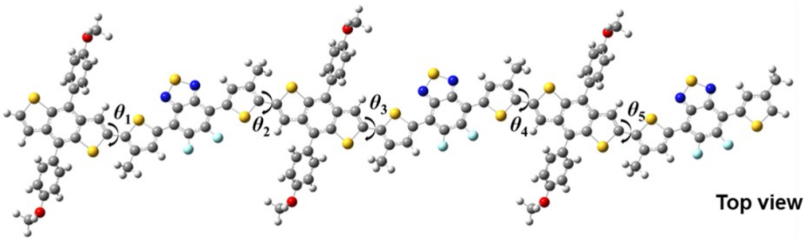
Figure S1. Calculated structure (B3LYP/6–31G) of the HOMO and LUMO of the model compounds. The yellow, red, blue and sky blue symbols represent sulfur, oxygen, nitrogen, and fluorine atoms, respectively.

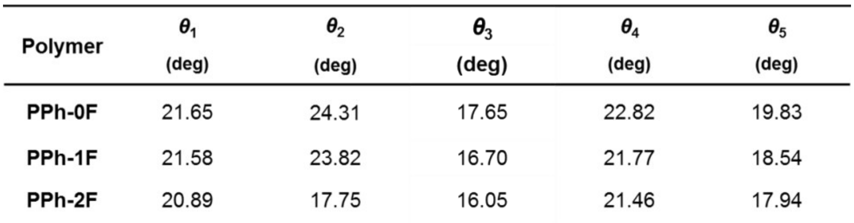


Gaussian 09 Software, Energy-minimized structure (B3LYP/6–31G*)
of the HOMO and LUMO of the model compounds at the bottom and top

Figure S2. Calculated energy levels of polymers with DFT calculation (B3LYP/6–31G).

Table S1. Calculated dihedral angles of PPhs obtained from DFT calculations of energy-minimized structure (B3LYP/6-31G).





Polymer	θ_1 (deg)	θ_2 (deg)	θ_3 (deg)	θ_4 (deg)	θ_5 (deg)
PPh-0F	21.65	24.31	17.65	22.82	19.83
PPh-1F	21.58	23.82	16.70	21.77	18.54
PPh-2F	20.89	17.75	16.05	21.46	17.94

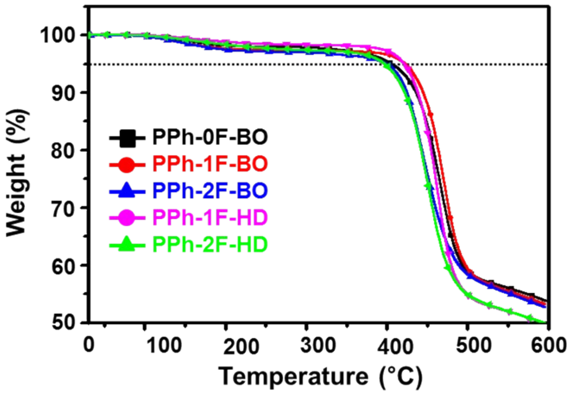


Figure S3. TGA plots of polymers with a heating rate of 10 °C min^{-1}.

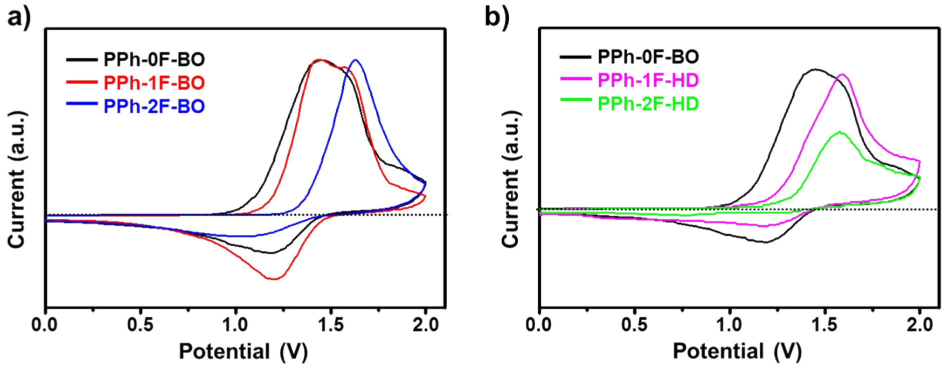


Figure S4. a) Cyclic voltammograms of the PPhs with butyl octyl alkyl chains in the CH_3CN solutions at a scan rate of 50 mVs^{-1}. b) Cyclic voltammograms of the PPhs with hexyl decyl alkyl chains in the CH_3CN solutions at a scan rate of 50 mVs^{-1}

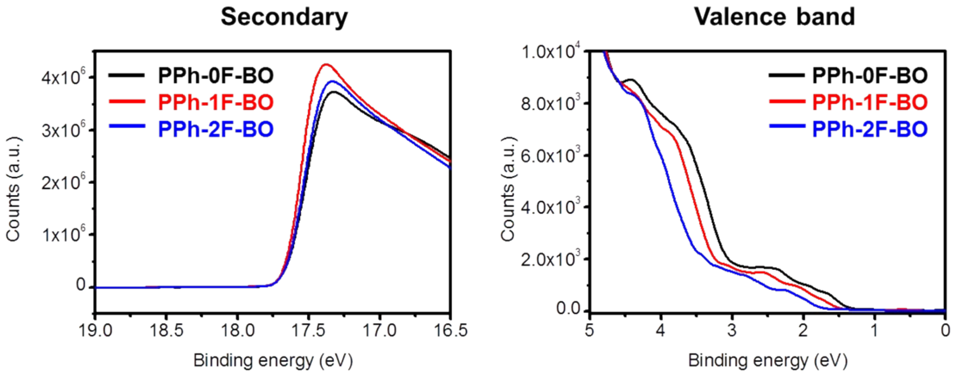


Figure S5. Ultraviolet Photoelectron Spectroscopy (UPS) plots of polymers with fluorine substitution.

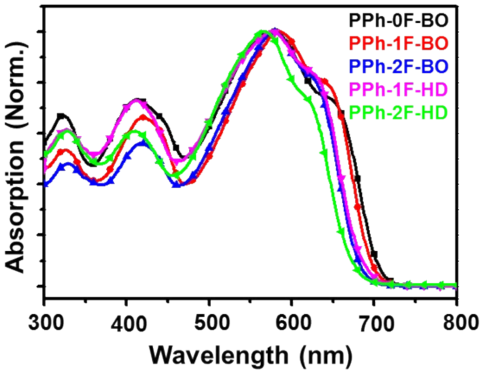


Figure S6. Normalized UV-Vis absorption spectra of the polymers in DCB at a concentration of 0.025 g L^{-1}.

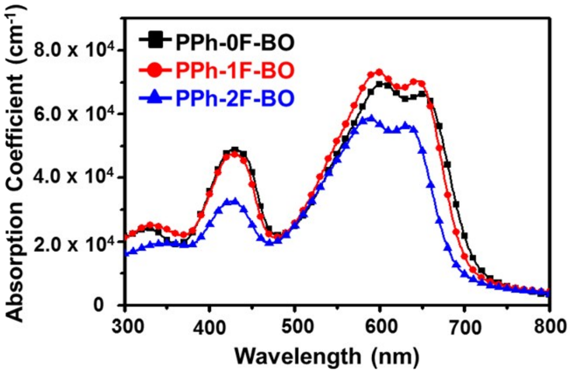


Figure S7. The calculated absorption coefficient of series of polymer films.

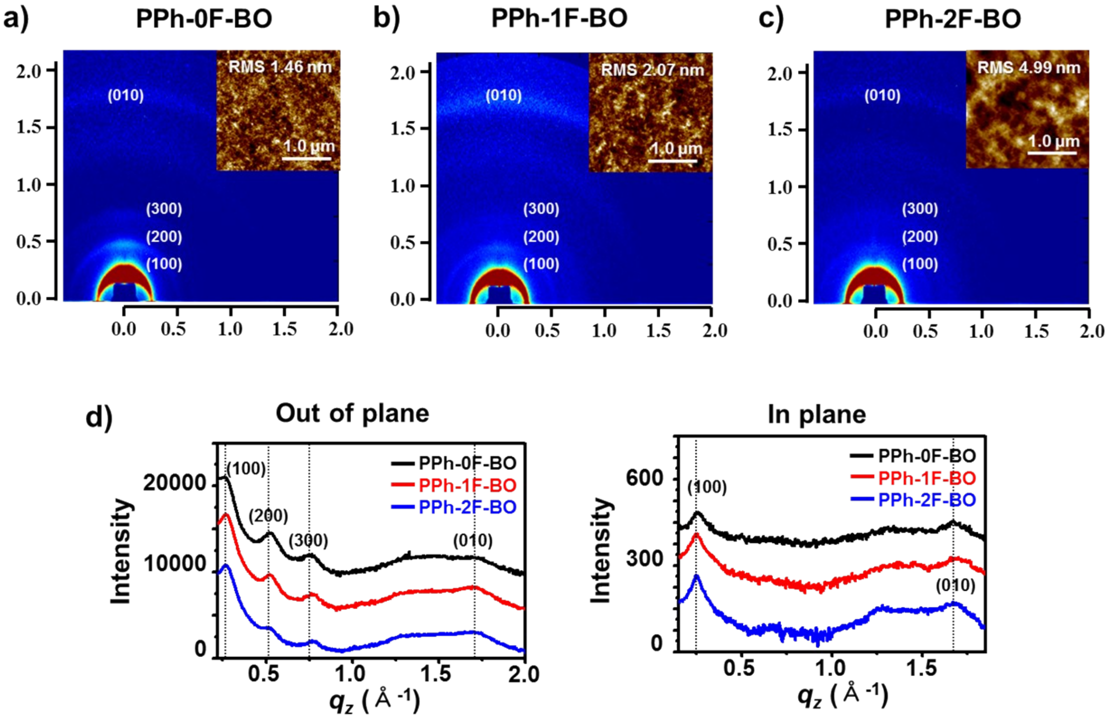


Figure S8. a~c) 2D GIXD data of neat polymer films. The insets are AFM height images of neat polymer films prepared by DCB. d) The corresponding 1D GIXD diffractogram profiles along the out-of-plane direction and in-plane direction.

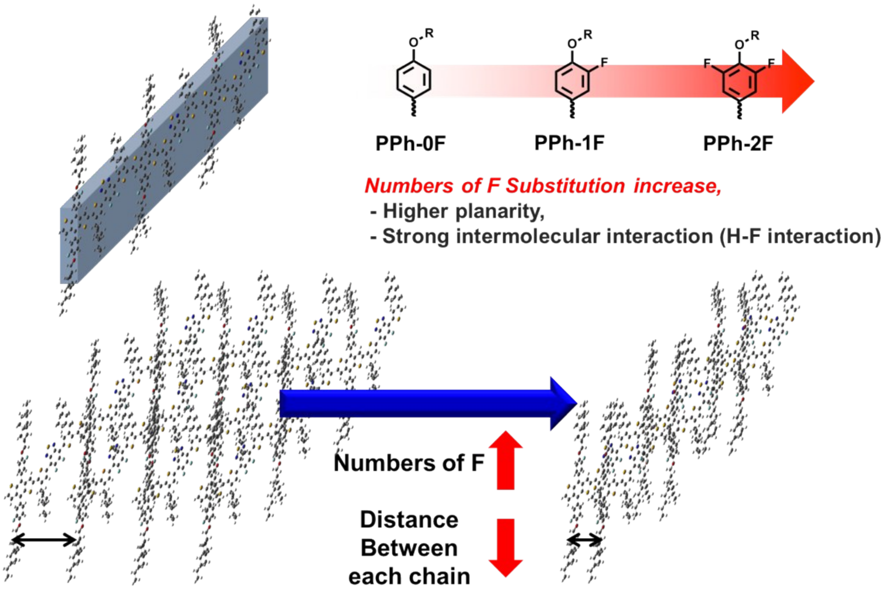


Figure S9. Schematic diagram of intermolecular packing of polymrs.

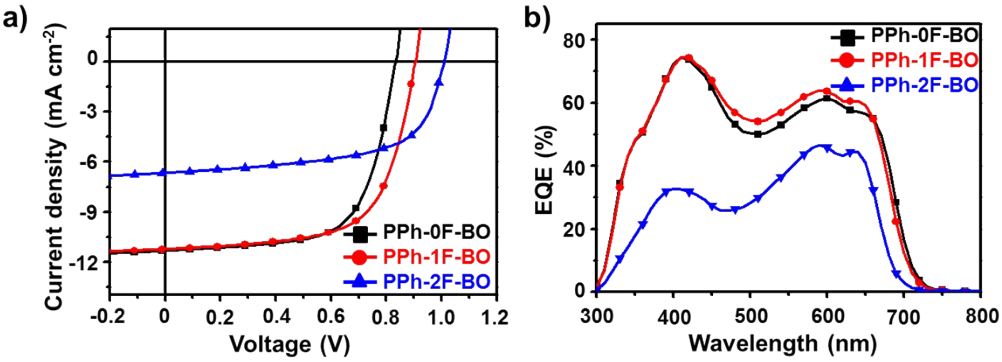


Figure S10. a) *J–V* characteristics of PPhs/PC$_{71}$BM solar cell prepared by DCB with DIO under illumination of AM 1.5 G, 100 mW cm^{-2}. b) EQE curves of the corresponding organic solar cells.

Table S2. Photovoltaic properties of the OSCs based on polymer/PC$_{71}$BM blends including standard deviation.

		V_{oc} [V]	J_{sc} [mA cm^{-2}]	*FF* [%]	*PCE* [%]
PPh-0F-BO	Avg.	0.83	11.92	62.4	6.14
	+/-	0.01	0.28	0.9	0.13
PPh-1F-BO	Avg.	0.91	10.34	67.5	6.36
	+/-	0.01	0.84	3.0	0.22
PPh-2F-BO	Avg.	0.99	6.87	60.5	4.13
	+/-	0.02	0.36	1.3	0.33
PPh-1F-HD	Avg.	0.90	12.60	65.1	7.40
	+/-	0.01	0.40	1.2	0.24
PPh-2F-HD	Avg.	0.99	8.93	57.9	5.14
	+/-	0.01	0.12	0.5	0.12

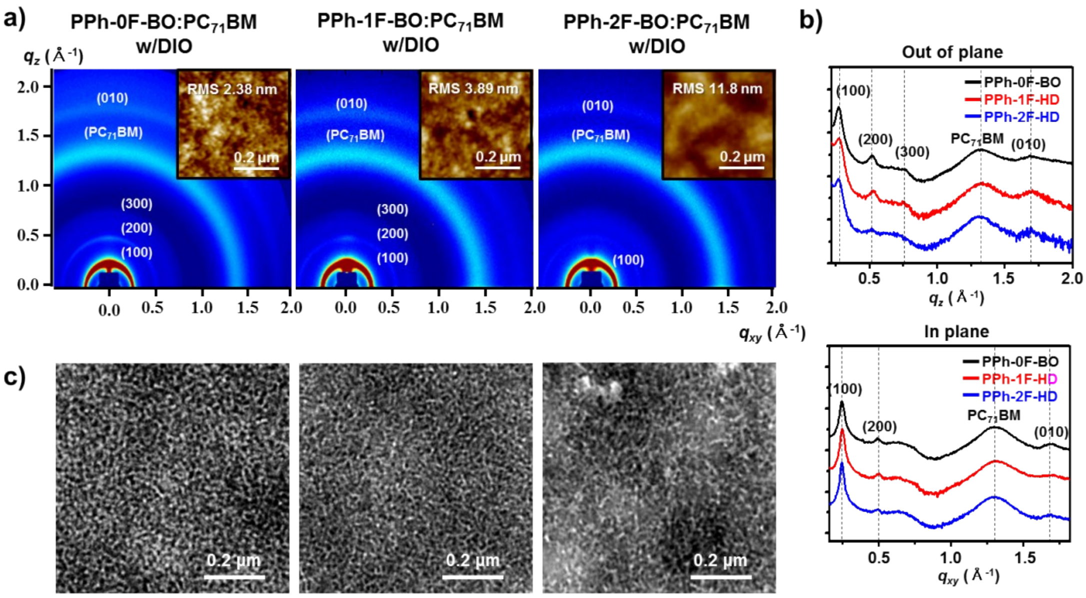
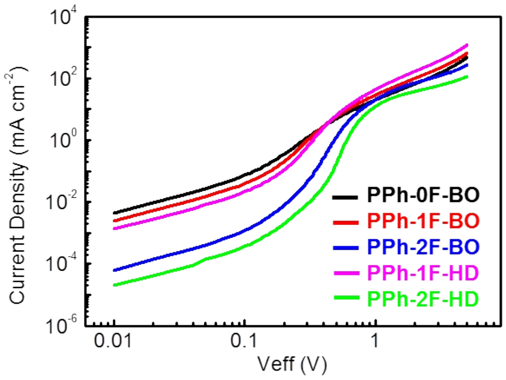


Figure S11. a) 2D GIXD data of polymers/PC$_{71}$BM (DIO) blend films. The insets are AFM height images (2.0 μm x 2.0 μm) of blend fims prepared by DCB with DIO for PPhs:PC$_{71}$BM. b) The corresponding 1D GIXD diffractogram profiles along the out-of-plane direction and in-plane direction. c) TEM images of blends prepared with DIO, PPh-0F-BO:PC$_{71}$BM, PPh-1F-BO:PC$_{71}$BM and PPh-2F-BO:PC$_{71}$BM.



Polymer	Hole mobility ($cm^2 \cdot V^{-1} \cdot s^{-1}$)
PPh-0F-BO	7.58×10^{-4} (±0.11)
PPh-1F-BO	1.07×10^{-3} (±0.16)
PPh-2F-BO	1.92×10^{-3} (±0.08)
PPh-1F-HD	5.01×10^{-4} (±0.21)
PPh-2F-HD	2.27×10^{-4} (±0.15)

Figure S12. Dark current density versus effective voltage characteristics of hole-only devices with photoactive layers based on PPhs:PC71BM blends with DIO (1.5 vol%).