Supporting Information

Effect of the Substitution Pattern of Alkyl Side Chain in a Benzodithiophene Core π -System on Intra- and Inter-Molecular Charge Carrier Mobility

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Prparation of Compound 10

1,4-Phenylenediacrylic acid (**3**, 14.5 g, 66 mmol), thionyl chloride (41 m³, 569 mmol), and pyridine (1.2 m³, 15 mmol) were placed in a 200 mL two-necked reaction flask equipped with a reflux condenser. The resulting mixture was stirred at 140 °C for 5 h, during which hydrogen chloride and sulfur dioxide gasses evolved from the top of the reflux condenser were absorbed by a water trap. After completion of the reaction, the residual thionyl chloride was removed under reduced pressure. The yellow precipitate was collected, washed with CHCl₃, and dried under vacuum to afford 3,7-dichlorobenzo[1,2-*b*;4,5-*b'*]dithiophene-2,6-dicarbonyl dichloride^{S1} (**4**, 17.1 g, 45 mmol) in 68 % yield.

In a 100 m³ two-necked flask were added 3,7-dichlorobenzo[1,2-*b*;4,5-*b'*]dithiophene-2,6-dicarbonyl dichloride (**4**, 5.6 g, 14.6 mmol), *n*-butanol (5.2 m³, 58 mmol), pyridine (4.7 m³, 58 mmol), and chlorobenzene (25 m³). The resulting mixture was stirred at 100 °C for 6 h. After cooling, the reaction mixture was filtered through a filter paper with ether as an eluent followed by evaporation of the solvent. The resulting solid was washed with water and dried under vacuum. The corresponding diester, dibutyl 3,7-dichlorobenzo[1,2-*b*;4,5-*b'*]dithiophene-2,6-dicarboxylate^{S2} (**5**, 4.4 g, 9.5 mmol, 65 %) was isolated as a pale yellow solid by recrystallization from toluene/hexane.

The above **5** (2.6 g, 5.6 mmol), 1-dodecyne (5.0 g, 30 mmol), PdCl₂(PhCN)₂ (44 mg, 0.11 mmol), dicyclohexylphosphino-2',4',6'-triisopropylbiphenyl (XPhos, 160 mg, 0.34 mmol), Cs₂CO₃ (15 g, 45 mmol), and CH₃CN (30 m³) were placed in a 100 m³ reaction flask, which was then filled with nitrogen. After being stirred for 24 h at 100 °C, the mixture was poured into water. The organic layer was extracted with Et₂O and dried over Na₂SO₄. Concentration in vacuo followed by column chromatography on silica gel with hexane/ethyl acetate (95/5, v/v) furnished dibutyl 3,7-bis(1-dodecynyl)benzo[1,2-*b*;4,5-*b'*]dithiophene-2,6-dicarboxylate (**6**, 2.4 g, 3.4 mmol) in 61 % yield.

In a 50 m³ autoclave reactor, Pd/C (10 %, 390 mg, 0.19 mmol) was placed, and the reactor was flushed with hydrogen. After the completion of prior activation of Pd under hydrogen (1 atm, ca. 1 h), **6** (2.2 g, 3.1 mmol), anhydrous ethanol (7 m³), and dioxane (6 m³) were added. The resulting mixture was stirred at room temperature under pressurized hydrogen (1.4 MPa). After 48 h, the mixture was filtered through a pad of Celite to remove Pd/C and concentrated under reduced pressure. The hydrogenated product, dibutyl 3,7-didodecylbenzo[1,2-*b*;4,5-*b'*]dithiophene-2,6-dicarboxylate (**7**, 2.3 g, 3.1 mmol) was obtained in a quantitative yield.

To a mixture of **7** (1.7 g, 2.3 mmol) and KOH (760 mg, 14 mmol), water (6 m^3) and ethanol (25 m^3) were sequentially added, and the suspension was then heated at 100 °C for 8 h. The resulting mixture was allowed to cool to room temperature, and the ethanol was evaporated. The precipitate formed by addition of diluted aq. HCl to the residual was collected and dried under high vacuum to provide 3,7-didodecylbenzo[1,2-*b*;4,5-*b'*]dithiophene-2,6-dicarboxylic acid (**8**, 1.3 g, 2.2 mmol) in 97 % yield.

The dicarboxylic acid **8** (1.5 g, 2.5 mmol), Cu powder (320 mg, 5.0 mmol), and quinoline (10 m^3) were placed in a 100 mL two-necked flask, and the suspension was then heated at 260 °C for 4 h. After the completion of the reaction, the mixture was poured into diluted aq. HCl and extracted with Et₂O. The combined organic layer was dried over Na₂SO₄, concentrated, and purified by silica gel column chromatography with hexane as an eluent to give 3,7-didodecylbenzo[1,2-*b*;4,5-*b'*]dithiophene (**9**, 1.2 g, 2.2 mmol) in 88 % yield.

To a solution of **9** (300 mg, 0.58 mmol) in DMF (5 m^3), *N*-bromosuccinimide (NBS, 310 mg, 1.7 mmol) was added in one portion. After being stirred for 5 h at room temperature, the resulting mixture was quenched with water and extracted with Et₂O. The combined organic layer was dried over Na₂SO₄. Concentration followed by purification by column chromatography with hexane produced 2,7-dibromo-3,7-didodecylbenzo[1,2-*b*;4,5-*b'*]dithiophene (**10**, 360 mg, 0.54 mmol) in 93 % yield.

XRD Measurements

To obtain information about the molecular orientation and intermolecular interaction, we have preliminarily investigated X-ray diffraction (XRD) measurements of FET devices based on **1** and **2** (See the following figures).

Figure S1. X-ray diffractogram for **1**-based device after ODTS surface treatment and annealing (entry 2 in Table 5)

Figure S2. X-ray diffractogram for **2**-based device after annealing (entry 5 in Table 5)

Characterization Data for Compounds

^1H and ^{13}C NMR spectra for all compounds are attached in the last part. Compounds **4**^{S1} and **5**^{S2} are found in the literature.

3,7–Didodecyl-2,6-bis(5-phenyl-2-thienyl)benzo[1,2-*b*:4,5-*b'*]dithiophene (1)

^1H NMR (400 MHz, CDCl_3) δ 7.68 – 7.62 (m, 6H), 7.45–7.37 (m, 4H), 7.44–7.34 (m, 4H), 7.26–7.23 (m, 2H), 3.10 (t, J = 7.6 Hz, 4H), 1.81–1.70 (m, 4H), 1.55–1.45 (m, 4H), 1.42–1.20 (m, 32H), 0.88 (t, J = 6.8 Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 145.2, 138.7, 135.8, 134.7, 134.3, 132.2, 129.8, 129.2, 128.0 (2C), 126.0, 123.7, 119.3, 32.2, 30.4, 30.1, 29.93 (2C), 29.89, 29.88, 29.69, 29.59, 28.1, 22.9, 14.3; HRMS (EI): m/z (M^+) calcd for $\text{C}_{54}\text{H}_{66}\text{S}_4$: 842.4047, found: 842.4055; m.p. 99 °C

4,8 –Didodecyl-2,6-bis(5-phenyl-2-thienyl)benzo[1,2-*b*:4,5-*b'*]dithiophene (2)

^1H NMR (400 MHz, CDCl_3) δ 7.66–7.58 (m, 4H), 7.48 (s, 2H), 7.44–7.34 (m, 4H), 7.33–7.26 (m, 6H), 3.11 (t, J = 7.6 Hz, 4H), 1.88–1.78 (m, 4H), 1.55–1.45 (m, 4H), 1.42–1.20 (m, 32H), 0.86 (t, J = 6.4 Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 144.5, 137.4, 137.3, 137.1, 136.6, 134.2, 129.2, 128.8, 128.0, 126.1, 125.9, 124.1, 117.9, 33.6, 32.2, 30.2, 29.96 (2C), 29.90, 29.84, 29.77 (2C), 29.59, 22.9, 14.3; HRMS (EI): m/z (M^+) calcd for $\text{C}_{54}\text{H}_{66}\text{S}_4$: 842.4047, found: 842.4061; m.p. 157 °C

Dibutyl 3,7-bis(1-dodecynyl)benzo[1,2-*b*:4,5-*b'*]dithiophene-2,6-dicarboxylate (6)

^1H NMR (400 MHz, CDCl_3) δ 7.99 (s, 2H), 4.39 (t, J = 6.4 Hz, 4H), 2.62 (t, J = 6.8 Hz, 4H), 1.83–1.71 (m, 8H), 1.58–1.48 (m, 8H), 1.43–1.18 (m, 24H), 1.00 (t, J = 7.6 Hz, 6H), 0.88 (t, J = 6.0 Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 162.1, 140.4, 133.9, 133.1, 125.4, 122.2, 101.5, 74.2, 65.7, 32.1, 30.9, 29.8, 29.7, 29.5, 29.4, 29.3, 29.0, 22.9, 20.3, 19.5, 14.3, 14.0; HRMS (FAB): m/z (M^+) calcd for $\text{C}_{44}\text{H}_{62}\text{O}_4\text{S}_2$: 718.4090, found: 718.4083; m.p. 44.5–45.5 °C

Dibutyl 3,7-didodecylbenzo[1,2-*b*:4,5-*b'*]dithiophene-2,6-dicarboxylate (7)

^1H NMR (400 MHz, CDCl_3) δ 7.78 (s, 2H), 4.36 (t, J = 7.2 Hz, 4H), 3.32 (t, J = 7.6, 4H), 1.82–1.75 (m, 4H), 1.72–1.64 (m, 4H), 1.58–1.42 (m, 10H), 1.37–1.13 (m, 30H), 1.01 (t, J = 7.6 Hz, 6H), 0.88 (t, J = 6.4 Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 163.1, 147.1, 139.0, 135.1, 126.7, 120.4, 65.4, 32.1, 31.0, 30.7, 30.2, 29.9, 29.88, 29.84, 29.83, 29.7, 29.6, 28.0, 22.9, 19.5, 14.3, 14.0; HRMS (EI): m/z (M^+) calcd for $\text{C}_{44}\text{H}_{70}\text{O}_4\text{S}_2$: 726.4716, found: 726.4720; m.p. 36.5–37.5 °C.

3,7–Didodecylbenzo[1,2-*b*:4,5-*b'*]dithiophene-2,6-dicarboxylic acid (8)

¹H NMR (400 MHz, DMSO-*d*₆) δ 7.90 (s, 2H), 3.28 (t, *J* = 7.5 Hz, 4H), 1.64–1.54 (m, 4H), 1.35–1.11 (m, 36H), 0.81 (t, *J* = 6.4 Hz, 6H); HRMS (EI): *m/z* (*M*⁺) calcd for C₃₄H₅₄O₄S₂: 614.3464, found: 614.3478; m.p. 244–245 °C. The clear ¹³C NMR spectrum of **8** was not obtained due to poor solubility in DMSO.

3,7–Didodecylbenzo[1,2-*b*:4,5-*b'*]dithiophene (9)

¹H NMR (400 MHz, CDCl₃) δ 7.70 (s, 2H), 7.02 (s, 2H), 2.88 (t, *J* = 7.6 Hz, 4H), 1.88–1.73 (m, 4H), 1.70–1.30 (m, 36H), 0.92 (t, *J* = 7.3 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 138.4, 136.7, 134.8, 118.9, 118.4, 32.2, 29.9, 29.89, 29.87, 29.85, 29.80, 29.7, 29.6 (2C), 29.2, 22.9, 14.3; HRMS (EI): *m/z* (*M*⁺) calcd for C₃₄H₅₄S₂: 526.3667, found: 526.3658; m.p. 46.8–48.0 °C.

2,6-Dibromo-3,7–didodecylbenzo[1,2-*b*:4,5-*b'*]dithiophene (10)

¹H NMR (400 MHz, CDCl₃) δ 7.59 (s, 2H), 2.86 (t, *J* = 7.6 Hz, 4H), 1.68–1.61 (m, 4H), 1.45–1.12 (m, 36H), 0.88 (t, *J* = 7.2 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 137.6, 136.0, 133.3, 119.8, 110.4, 32.1, 29.88, 29.86, 29.85, 29.78, 29.71, 29.69, 29.57, 29.3, 28.3, 22.9, 14.3; HRMS (EI): *m/z* (*M*⁺) calcd for C₃₄H₅₂Br₂S₂: 682.1857, found: 682.1874; m.p. 37.0–38.0 °C.

2,6-Dibromo-4,8 –didodecylbenzo[1,2-*b*:4,5-*b'*]dithiophene (11)

¹H NMR (400 MHz, CDCl₃) δ 7.40 (s, 2H), 2.97 (t, *J* = 7.8 Hz, 4H), 1.77–1.67 (m, 4H), 1.46–1.23 (m, 36H), 0.88 (t, *J* = 6.8 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 138.8, 135.6, 127.8, 124.9, 115.1, 33.6, 32.2, 30.1, 29.89 (2C), 29.87, 29.78, 29.73, 29.71, 29.59, 22.9, 14.4; HRMS (EI): *m/z* (*M*⁺) calcd for C₃₄H₅₂Br₂S₂: 682.1857, found: 682.1862; m.p. 99.0–100.0 °C.

References

- ^{S1)} Malešević, M.; Karminsky-Zamola, G.; Bajić, M.; Boykin, D. W. *Heterocycles* **1995**, *41*, 2691.
^{S2)} Miyasaka, M.; Hirano, K.; Satoh, T.; Miura, M. *Adv. Synth. Catal.* **2009**, *351*, 2683.

[^1H and ^{13}C NMR spectra of **1**]

1

[^1H and ^{13}C NMR spectra of **2**]

[^1H and ^{13}C NMR spectra of **6**]

[^1H and ^{13}C NMR spectra of **7**]

No.	ppm	Hz	Height	No.	ppm	Hz
1	163.15	16400.4	31.38	13	29.86	3001.3
2	147.14	14791.0	37.36	14	29.84	3000.2
3	139.02	13974.7	31.53	15	29.83	2999.0
4	135.08	13579.5	23.45	16	29.75	2990.2
5	126.66	12733.0	25.35	17	29.56	2971.6
6	120.44	12107.4	30.23	18	28.01	2815.9
7	65.36	6570.0	47.61	19	22.90	2301.7
8	32.13	3230.2	85.50	20	19.53	1963.3
9	30.98	3113.8	69.48	21	14.32	1439.6
10	30.74	3090.2	32.27	22	13.97	1404.5
11	29.88	3004.0	76.23			
12	29.87	3002.5	80.68

[^1H NMR spectrum of **8**]

[^1H and ^{13}C NMR spectra of **9**]

[^1H and ^{13}C NMR spectra of **10**]

No.	ppm	Hz	Height
1	137.62	13833.9	15.93
2	135.99	13670.6	13.38
3	133.26	13396.0	8.06
4	118.77	11939.5	18.25
5	110.40	11097.6	8.60
6	32.14	3231.3	34.05
7	29.88	3004.0	39.13
8	29.86	3002.1	30.92
9	29.85	3000.9	32.49
10	29.78	2994.1	27.07
11	29.71	2986.4	30.24
12	29.69	2984.1	24.96
13	29.57	2972.3	32.77
14	29.31	2946.0	16.00
15	28.28	2842.6	14.37
16	22.92	2303.6	33.42
17	14.34	1441.9	29.67

[^1H and ^{13}C NMR spectra of **11**]