

Supporting Information

Systematic Investigation of Benzodithiophene- Benzothiadiazole Isomers for Organic Photovoltaics

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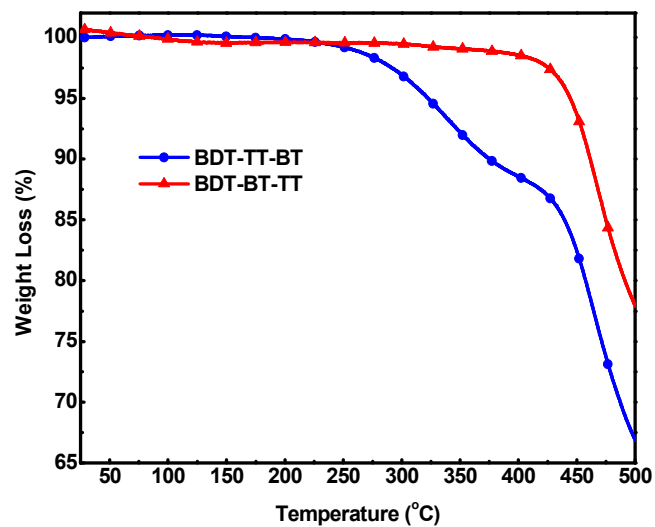


Figure S1. TGA thermograms of BDT-TT-BT and BDT-BT-TT

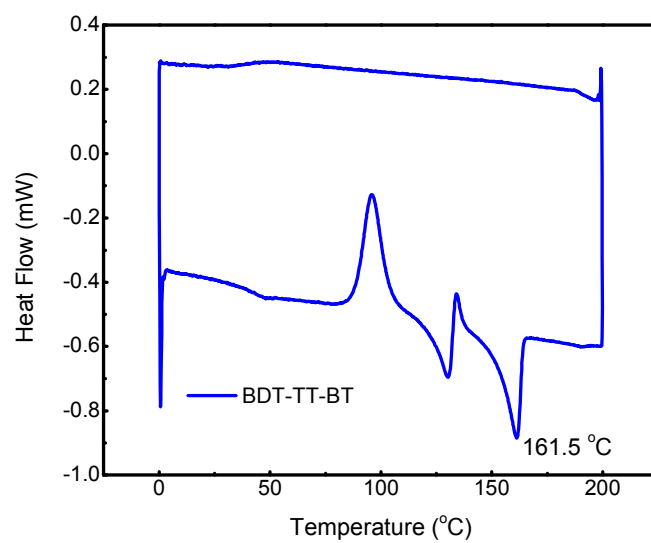


Figure S2. DSC thermograms of BDT-TT-BT

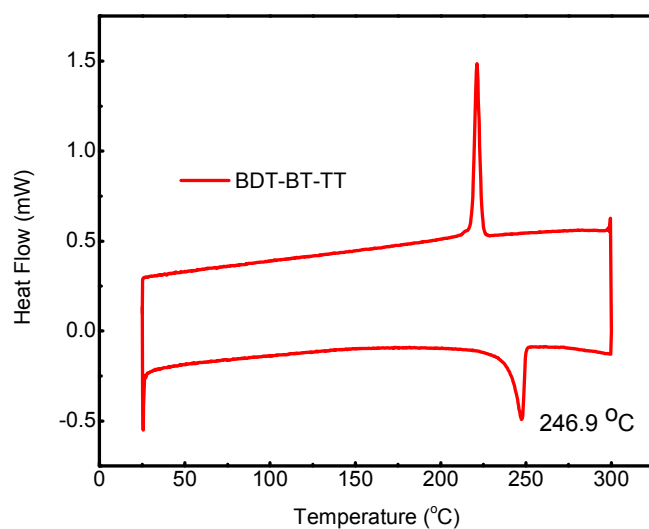


Figure S3. DSC thermograms of BDT-BT-TT

Table S1. Physical Properties of BDT-TT-BT and BDT-BT-TT

Compound	T _d (°C)	T _m (°C)	T _c (°C)	Solubility (mg/mL)
BDT-TT-BT	322	131/161	96	15
BDT-BT-TT	433	247	221	10

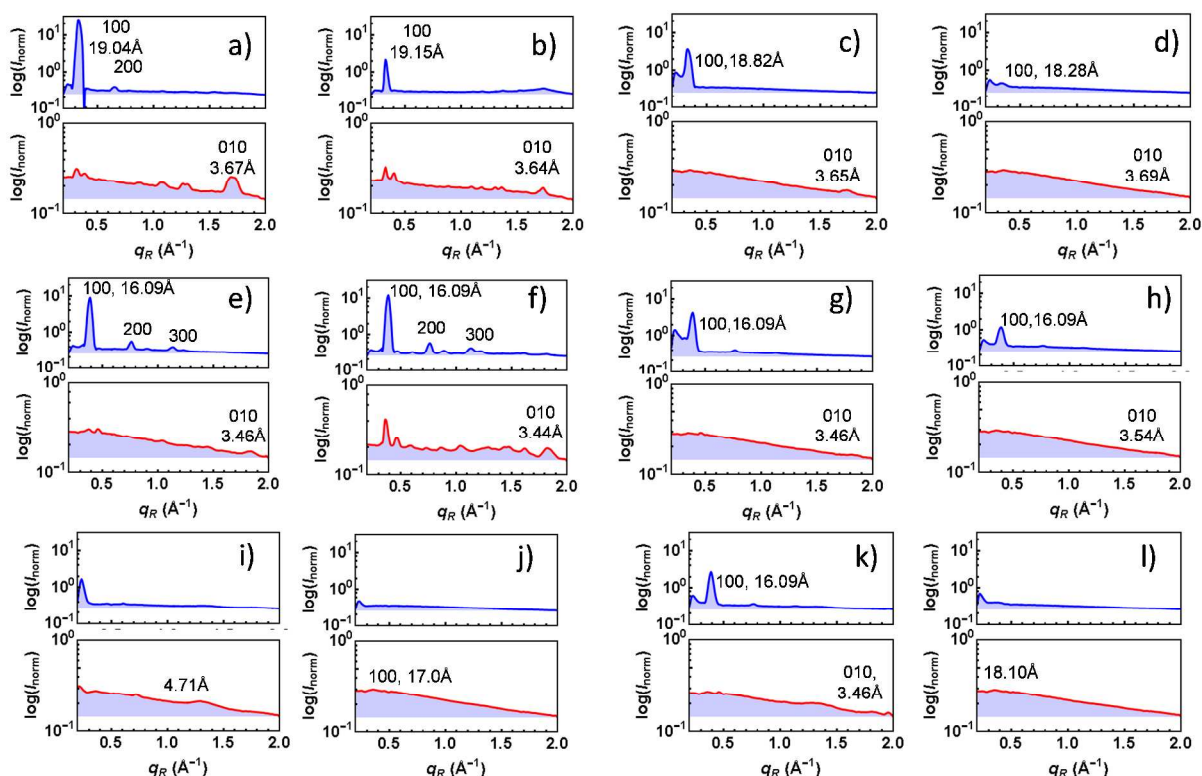


Figure S4. Line-cut profiles in the out-of-plane (q_z , blue) and in-plane (q_{xy} , red) directions of GIWAXS (a) BDT-TT-BT neat film drop-casted from CF, (b) BDT-TT-BT neat film drop-casted from DCB, (c) BDT-TT-BT neat film spin-casted from CF, (d) BDT-TT-BT neat film spin-casted from DCB, (e) BDT-BT-TT neat film drop-casted from CF, (f) BDT-BT-TT neat film drop-casted from DCB, (g) BDT-BT-TT neat film spin-casted from CF, (h) BDT-BT-TT neat film spin-casted from DCB, (i) BDT-TT-BT and PC₇₁BM blend film spin-casted from CF, (j) BDT-TT-BT and PC₇₁BM blend film spin-casted from DCB, (k) BDT-BT-TT and PC₇₁BM blend film spin-casted from CF, (l) BDT-BT-TT and PC₇₁BM blend film spin-casted from DCB. (All the films prepared were annealed at 90 °C for 10 minutes)

Table S2. Photovoltaic Characterization of BDT-TT-BT or BDT-BT-TT and PC₇₁BM at different ratio

Compound	Ratio	V _{oc} (V)	J _{sc} (mA cm ⁻²)	FF	PCE (%)
BDT-TT-BT ^a	1: 1.0	0.84 ± 0.01 (0.86)	5.67 ± 0.12 (5.89)	0.33 ± 0.01 (0.34)	1.56 ± 0.06 (1.64)
	1: 1.5	0.91 ± 0.02 (0.93)	7.02 ± 0.22 (7.37)	0.37 ± 0.01 (0.38)	2.36 ± 0.12 (2.51)
	1: 2.0	0.93 ± 0.03 (0.97)	7.31 ± 0.28 (7.58)	0.37 ± 0.02 (0.39)	2.50 ± 0.32 (2.84)
	1: 2.5	0.97 ± 0.01 (0.97)	5.57 ± 0.21 (5.67)	0.31 ± 0.01 (0.31)	1.68 ± 0.08 (1.74)
BDT-BT-TT ^b	1: 1.0	0.90 ± 0.01 (0.90)	7.96 ± 0.21 (8.18)	0.40 ± 0.01 (0.40)	2.82 ± 0.10 (2.96)
	1: 1.5	0.88 ± 0.01 (0.89)	9.24 ± 0.36 (9.79)	0.43 ± 0.01 (0.44)	3.46 ± 0.06 (3.56)
	1: 2.0	0.89 ± 0.01 (0.89)	9.11 ± 0.19 (9.36)	0.41 ± 0.01 (0.42)	3.32 ± 0.08 (3.39)
	1: 2.5	0.88 ± 0.01 (0.88)	8.71 ± 0.23 (8.87)	0.40 ± 0.01 (0.40)	3.08 ± 0.06 (3.12)

^a 30 mg/mL in CB, spin-coated at 2500 rpm, ^b 20 mg/mL in CB, spin-coated at 2000 rpm

Table S3. Photovoltaic Characterization of BDT-TT-BT at ratio of 1:2 with different thickness (CB)

V_{oc} (V)	J_{sc} (mA cm ⁻²)	FF	PCE (%)	Thickness (nm)	Spin Rate (rpm)
0.95 ± 0.01 (0.96)	5.93 ± 0.30 (6.09)	0.32 ± 0.01 (0.33)	1.81 ± 0.01 (1.95)	104.3	2000
0.95 ± 0.01 (0.96)	7.07 ± 0.17 (3.50)	0.35 ± 0.01 (0.36)	2.36 ± 0.08 (2.43)	96.3	2500
0.96 ± 0.01 (0.97)	7.08 ± 0.17 (7.33)	0.37 ± 0.01 (0.37)	2.53 ± 0.08 (2.65)	95.5	2750
0.97 ± 0.01 (0.98)	7.41 ± 0.06 (7.50)	0.37 ± 0.01 (0.37)	2.67 ± 0.02 (2.70)	92.6	3000
0.96 ± 0.02 (0.98)	7.81 ± 0.18 (8.03)	0.37 ± 0.01 (0.37)	2.72 ± 0.16 (2.89)	87.6	3250
0.97 ± 0.01 (0.98)	7.67 ± 0.37 (8.10)	0.38 ± 0.02 (0.39)	2.78 ± 0.26 (2.99)	83.7	3500
0.97 ± 0.02 (0.98)	7.66 ± 0.48 (8.07)	0.39 ± 0.02 (0.41)	2.87 ± 0.26 (3.22)	80.9	3750
0.97 ± 0.01 (0.98)	7.55 ± 0.04 (7.58)	0.39 ± 0.01 (0.39)	2.88 ± 0.04 (2.91)	77.9	4000
0.99 ± 0.01 (0.99)	7.13 ± 0.33 (7.63)	0.42 ± 0.01 (0.42)	2.91 ± 0.11 (3.06)	77.0	5000

Table S4. Photovoltaic Characterization of BDT-BT-TT at ratio of 1:1.5 with different thickness (CB)

V_{oc} (V)	J_{sc} (mA cm ⁻²)	FF	PCE (%)	Thickness (nm)	Spin Rate (rpm)
0.88 ± 0.01 (0.89)	9.20 ± 0.33 (9.36)	0.43 ± 0.01 (0.44)	3.47 ± 0.21 (3.65)	65.1	1750
0.89 ± 0.01 (0.90)	8.80 ± 0.33 (9.17)	0.45 ± 0.01 (0.46)	3.50 ± 0.20 (3.71)	61.3	2000
0.89 ± 0.01 (0.89)	8.52 ± 0.13 (8.68)	0.46 ± 0.01 (0.47)	3.49 ± 0.08 (3.57)	59.4	2250
0.89 ± 0.01 (0.90)	8.36 ± 0.08 (8.43)	0.47 ± 0.01 (0.47)	3.47 ± 0.04 (3.51)	57.0	1750

Table S5. Photovoltaic Characterization of BDT-TT-BT at ratio of 1:2 with different thickness (CF)

V_{oc} (V)	J_{sc} (mA cm ⁻²)	FF	PCE (%)	Thickness (nm)	Spin Rate (rpm)
0.92 ± 0.01 (0.93)	6.72 ± 0.14 (6.91)	0.34 ± 0.01 (0.34)	2.09 ± 0.05 (2.14)	111.6	2000
0.91 ± 0.01 (0.92)	7.10 ± 0.38 (7.33)	0.36 ± 0.01 (0.36)	2.34 ± 0.11 (2.41)	106.2	2500
0.92 ± 0.01 (0.93)	6.60 ± 0.34 (7.14)	0.38 ± 0.01 (0.39)	2.30 ± 0.05 (2.34)	102.5	3000
0.92 ± 0.01 (0.93)	6.78 ± 0.20 (7.00)	0.40 ± 0.01 (0.40)	2.50 ± 0.08 (2.53)	97.4	3500
0.93 ± 0.01 (0.93)	6.67 ± 0.19 (6.82)	0.41 ± 0.01 (0.42)	2.56 ± 0.04 (2.59)	90.2	4000

Table S6. Photovoltaic Characterization of BDT-BT-TT at ratio of 1:1.5 with different thickness (CF)

V_{oc} (V)	J_{sc} (mA cm^{-2})	FF	PCE (%)	Thickness (nm)	Spin Rate (rpm)
0.88 ± 0.01 (0.89)	8.76 ± 0.25 (9.04)	0.44 ± 0.01 (0.44)	3.34 ± 0.10 (3.45)	96.5	1500
0.88 ± 0.01 (0.89)	7.72 ± 0.14 (7.91)	0.48 ± 0.01 (0.49)	3.32 ± 0.06 (3.42)	90.2	2000
0.88 ± 0.01 (0.88)	7.43 ± 0.24 (7.64)	0.50 ± 0.01 (0.50)	3.25 ± 0.11 (3.40)	85.2	2500
0.87 ± 0.01 (0.88)	6.61 ± 0.19 (6.80)	0.51 ± 0.01 (0.52)	2.97 ± 0.11 (3.12)	78.3	3000
0.88 ± 0.01 (0.89)	5.37 ± 0.17 (5.60)	0.53 ± 0.01 (0.54)	2.54 ± 0.06 (2.61)	70.8	4000

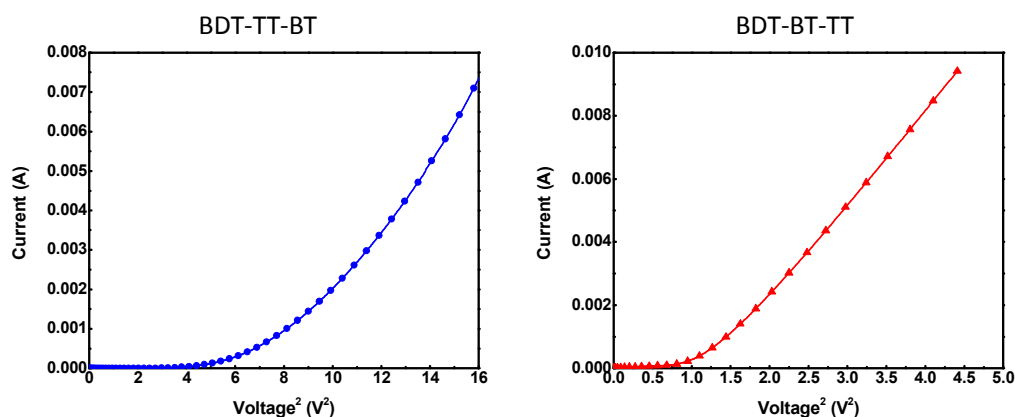


Figure S5. J-V curve of BDT-TT-BT and BDT-BT-TT measured from probe station with SCLC model

Synthesis:

5-bromo-2, 2'-bithiophene

2, 2'-Bithiophene (4.00 g, 24.1 mmol) was dissolved in 100 mL THF. N-Bromosuccinimide (4.29 g, 24.1 mmol) was added slowly to the solution. The reaction was kept at room temperature for 4 hours. After the reaction was completed, the reaction mixture was poured into water. THF was removed by rotary evaporation before extraction with hexane. The organic phase was dried over anhydrous MgSO_4 . The solvent was evaporated and the crude product was further purified by column chromatography with hexane as eluting solvent. Light yellow oil was finally obtained as pure product. Yield: 50% (2.96g). ^1H NMR (CDCl_3 , 500 MHz), δ : 7.22 (d, 1H), 7.11 (d, 1H), 7.00 (dd, 1H), 6.96 (d, 1H), 6.91 (d, 1H). ^{13}C NMR (CDCl_3 , 125 MHz) δ : 138.90, 136.41, 130.60, 127.88, 124.83, 124.06, 123.86, 110.91.

2,6-di([2,2'-bithiophen]-5-yl)-4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene (M2)

2,6-Bis(trimethyltin)-4,8-bis(5-(2-ethylhexyl)thiophene-2-yl)benzo[1,2-b:4,5-b']dithiophene (1.00 g, 1.1 mmol) and 5-bromo-2,2'-bithiophene (0.54 g, 2.2 mmol) was dissolved in 30 mL toluene with 1 mL DMF under nitrogen. Tetrakis(triphenylphosphine)palladium(0) (0.038 g, 0.033 mmol) was added to the

reaction mixture. The reaction was kept under reflux for 24 hours. After the reaction was completed, the solution was cooled down to room temperature, poured into water, and extracted with methylene chloride. The organic phase was dried over anhydrous MgSO_4 and solvent was removed by rotary evaporation. The crude product was purified by flash column chromatography using methylene chloride and hexane as eluent. Yellow orange solid was obtained. Yield: 57% (0.57 g). ^1H NMR (CDCl_3 , 500 MHz), δ : 7.63 (s, 2H), 7.31 (d, 2H), 7.22 (d, 2H), 7.17 (d, 2H), 7.15 (d, 2H), 7.07 (d, 2H), 7.01 (dd, 2H), 6.94 (d, 2H), 2.91 (t, 4H), 1.72 (m, 2H), 1.45 (m, 16H), 1.00 (t, 6H), 0.96 (t, 6H). ^{13}C NMR (CDCl_3 , 125 MHz) δ : 146.03, 138.64, 137.60, 137.56, 137.32, 137.02, 136.84, 136.19, 127.96, 127.85, 125.92, 125.53, 124.78, 124.40, 123.93, 123.35, 119.04, 41.52, 34.38, 32.57, 29.00, 25.86, 23.11, 14.27, 11.02.

(5',5'''-(4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-*b*:4,5-*b'*])dithiophene-2,6-diyl)bis([2,2'-bithiophene]-5',5-diyl))bis(trimethylstannane) (M3)

2,6-di([2,2'-bithiophene]-5-yl)-4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-*b*:4,5-*b'*]dithiophene (0.35 g, 0.39 mmol) was dissolved in THF under nitrogen. *n*-Butyllithium (0.33 mL, 0.81 mmol) was added dropwise to the solution at -78°C . The reaction was kept at -78°C for 2 hours. Trimethyltin chloride solution in hexane (0.88 mL, 0.88 mmol) was added slowly to the reaction mixture at -78°C before warming to room temperature and kept for another 3 hours. The reaction was quenched in water and extracted with methylene chloride three times. The organic phase was dried over anhydrous MgSO_4 . The crude product was used in the next step without further purification. Yield: 84.0% (0.40 g). ^1H NMR (CDCl_3 , 500 MHz), δ : 7.62 (s, 2H), 7.31 (d, 2H), 7.29 (d, 2H), 7.17 (d, 2H), 7.09 (t, 4H), 6.93 (d, 2H), 2.89 (t, 4H), 1.72 (m, 2H), 1.45 (m, 16H), 0.96 (m, 12H), 0.39 (s, 18H).

4,4'-[(4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-*b*:4,5-*b'*])dithiophene-2,6-diyl)bis(2,2'-bithiophene)-5,5'-diyl]bis(benzo[*c*][1,2,5]thiadiazole) (BDT-TT-BT)

In a three neck flask, (5',5'''-(4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-*b*:4,5-*b'*]dithiophene-2,6-diyl)bis([2,2'-bithiophene]-5',5-diyl))bis(trimethylstannane) **M3** (0.48 g, 0.39 mmol) and 4-bromobenzo[*c*][1,2,5]thiadiazole (0.17 g, 0.81 mmol) was dissolved in 15 mL toluene with 1 mL DMF under nitrogen. Tetrakis(triphenylphosphine)palladium(0) (0.014 g, 0.012 mmol) was added to the reaction mixture. The reaction was heated at 110°C for 24 hours. After reaction was cooled to room temperature, the solution was poured into water and extracted with methylene chloride. The organic phase was dried over anhydrous MgSO_4 . The solvent was removed and the crude product was purified by flash column chromatography on silica gel with methylene chloride and hexane as eluent. The collected product was then dissolved in chloroform and precipitate out in methanol. After that, the collected solid was washed with hexane, acetone and dried in vacuum oven. Dark red solid was obtained as final product. Yield: 58% (0.26 g). ^1H NMR (CDCl_3 , 500 MHz), δ : 8.00 (d, 2H), 7.88 (d, 2H), 7.92 (d, 2H), 7.61 (s, 2H), 7.59 (t, 2H), 7.32 (d, 2H), 7.22 (d, 2H), 7.16 (dd, 4H), 6.95 (d, 2H), 2.93 (m, 4H), 1.73 (m, 2H), 1.46 (m, 16H), 1.00 (m, 12H). ^{13}C NMR (CDCl_3 , 125 MHz) δ : 155.49, 151.93, 145.92, 138.56, 138.28, 138.16, 137.34, 137.24, 137.18, 136.86, 136.57, 129.57, 128.51, 127.85, 127.05, 125.89, 125.50, 124.79, 124.57, 124.47, 123.20, 119.97, 119.07, 41.52, 34.39, 32.59, 29.02, 25.87, 23.14, 14.29, 11.04.

[M]: m/z 1174.16. Found: m/z 1174.91

4-([2,2'-bithiophen]-5-yl)-7-bromobenzo[c][1,2,5]thiadiazole (M4)

In a three neck flask, 5-tributylstannyl-2,2'-bithiophene (1.55 g, 3.41 mmol) and 4,7-dibromobenzo[c][1,2,5]thiadiazole (1.00 g, 3.41 mmol) was dissolved in 40 mL toluene with 1 mL DMF under nitrogen. Tetrakis(triphenylphosphine)palladium(0) (197 mg, 0.17 mmol) was added to the reaction mixture. The reaction was heated at 110 °C for 24 hours. After reaction was cooled to room temperature, the solution was poured into water and extracted with methylene chloride. The organic phase was dried over anhydrous MgSO₄. The solvent was removed and the crude product was purified by flash column chromatography on silica gel with methylene chloride and hexane as eluent. Red solid was obtained as final product. Yield: 32% (0.42 g). ¹H NMR (CDCl₃, 500 MHz), δ: 8.00 (d, 1H), 7.83 (d, 1H), 7.68 (d, 1H), 7.28 (t, 1H), 7.23 (d, 1H), 7.06 (d, 1H), 7.05 (d, 1H). ¹³C NMR (CDCl₃, 125 MHz) δ: 153.82, 151.66, 139.32, 137.10, 137.02, 132.27, 128.84, 128.04, 126.78, 125.26, 125.08, 124.60, 124.26, 112.25.

4,4'-(4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-*b*:4,5-*b'*]dithiophene-2,6-diyl)bis(7-([2,2'-bithiophen]-5-yl)benzo[c][1,2,5]thiadiazole) (BDT-BT-TT)

In a three neck flask, 4-([2,2'-bithiophen]-5-yl)-7-bromobenzo[c][1,2,5]thiadiazole **M4** (0.26 g, 0.70 mmol) and 2,6-Bis(trimethylstannyl)-4,8-bis(5-(2-ethylhexyl)thiophene-2-yl)benzo[1,2-*b*:4,5-*b'*] dithiophene **M1** (0.31 g, 0.35 mmol) was dissolved in 20 mL toluene with 0.5 mL DMF under nitrogen. Tetrakis(triphenylphosphine)palladium(0) (20 mg, 0.02 mmol) was added to the reaction mixture. The reaction was heated at 110 °C for 24 hours. After reaction was cooled to room temperature, the solution was poured into water and extracted with methylene chloride. The organic phase was dried over anhydrous MgSO₄. The solvent was removed and the crude product was purified by flash column chromatography on silica gel with methylene chloride and hexane as eluent. The collected product was then dissolved in chloroform and precipitate out in methanol. After that, the collected solid was washed with hexane, acetone and dried in vacuum oven. Dark purple solid was obtained as final product. Yield: 39% (0.16 g). ¹H NMR (CD₂Cl₄, 500 MHz), δ: 8.70 (s, 2H), 7.82 (d, 2H), 7.71 (d, 2H), 7.65 (d, 2H), 7.40 (d, 2H), 7.15 (m, 4H), 7.06 (d, 2H), 7.65 (m, 4H), 2.92 (d, 4H), 1.76 (m, 2H), 1.46 (m, 16H), 0.99 (t, 6H), 0.90 (t, 6H). ¹³C NMR (CD₂Cl₄, 125 MHz) δ: 152.69, 152.49, 146.05, 139.98, 139.12, 138.78, 138.06, 137.94, 137.26, 137.17, 128.61, 128.32, 128.13, 127.21, 126.36, 125.72, 125.53, 125.11, 124.96, 124.71, 124.33, 124.10, 41.79, 34.57, 32.91, 29.23, 26.19, 23.25, 14.40, 11.37 (Two aromatic carbon overlapped). [M]: m/z 1174.16. Found: m/z 1174.54

^1H NMR and ^{13}C NMR

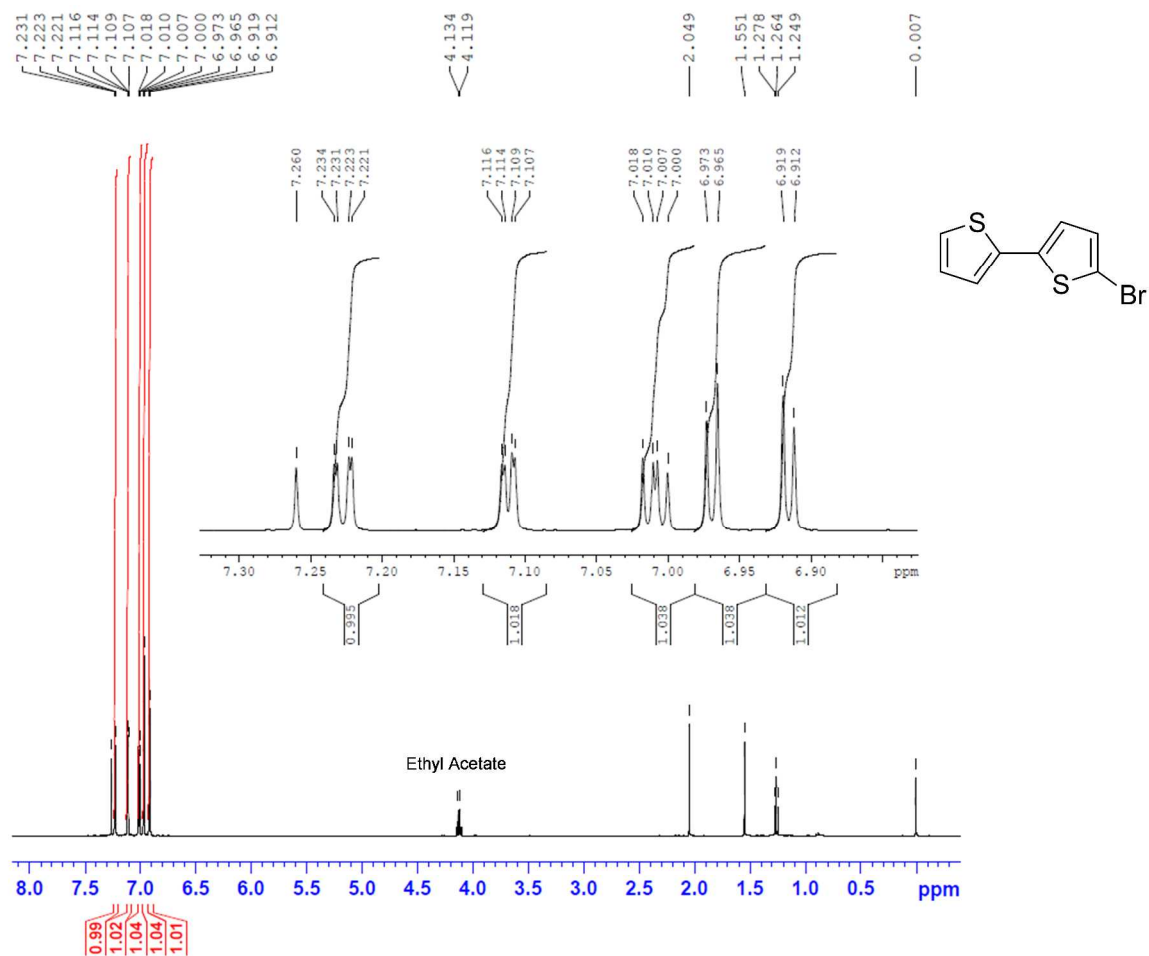


Figure S6. ^1H NMR of 5-bromo-2,2'-bithiophene

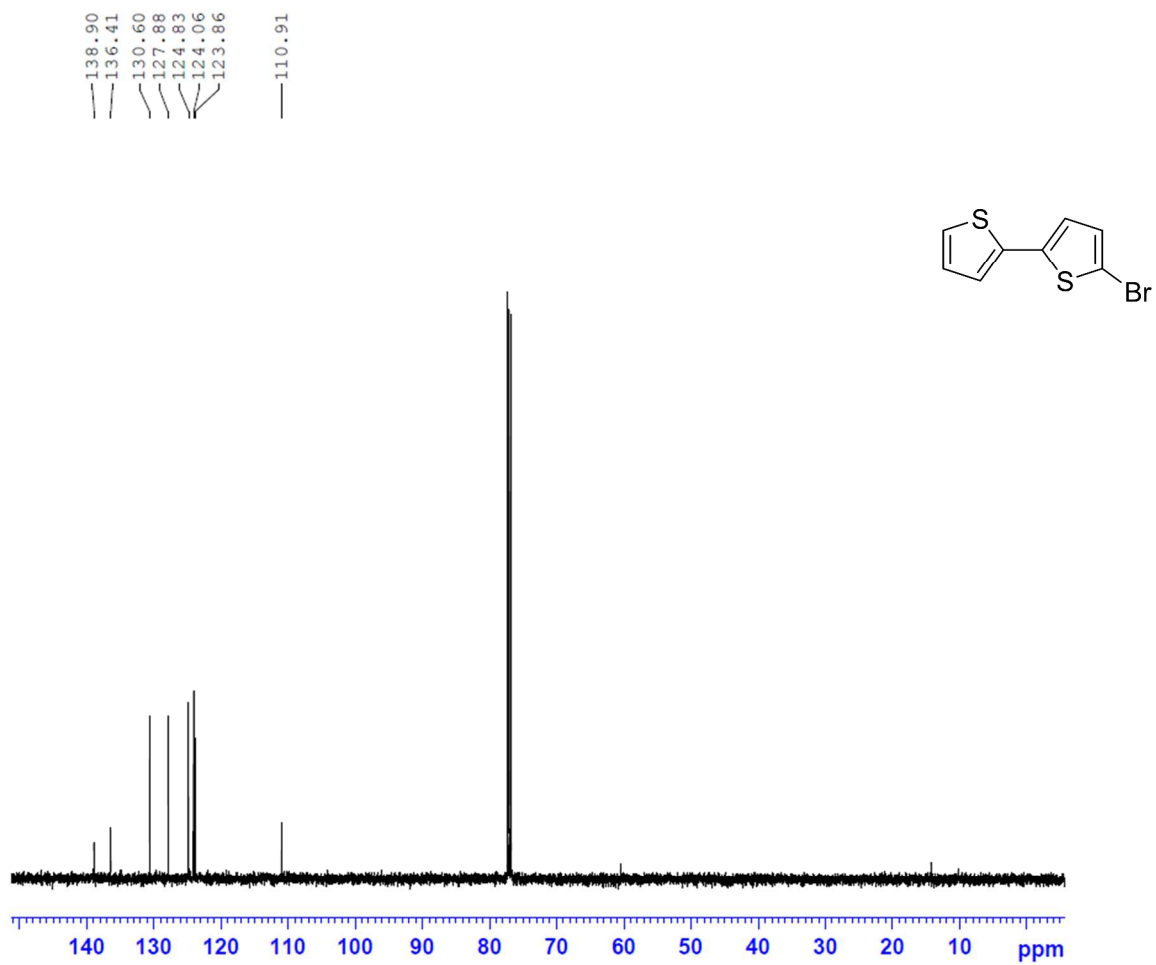


Figure S7. ^{13}C NMR of 5-bromo-2, 2'-bithiophene

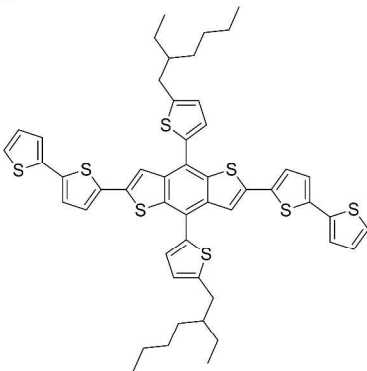


Figure S8. ¹H NMR of 2,6-di([2,2'-bithiophen]-5-yl)-4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-*b*:4,5-*b'*]dithiophene (**M2**)

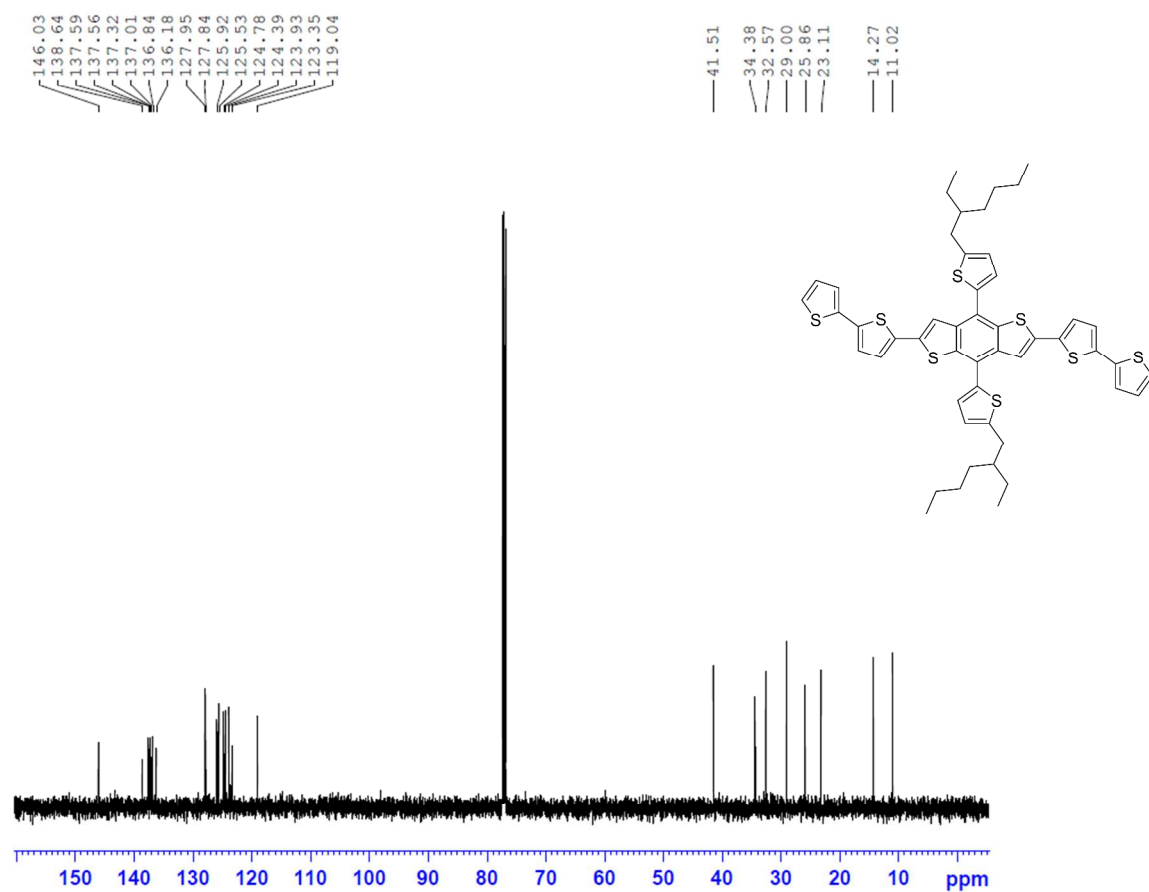


Figure S9. ^{13}C NMR of 2,6-di([2,2'-bithiophen]-5-yl)-4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-*b*:4,5-*b'*]dithiophene (**M2**)

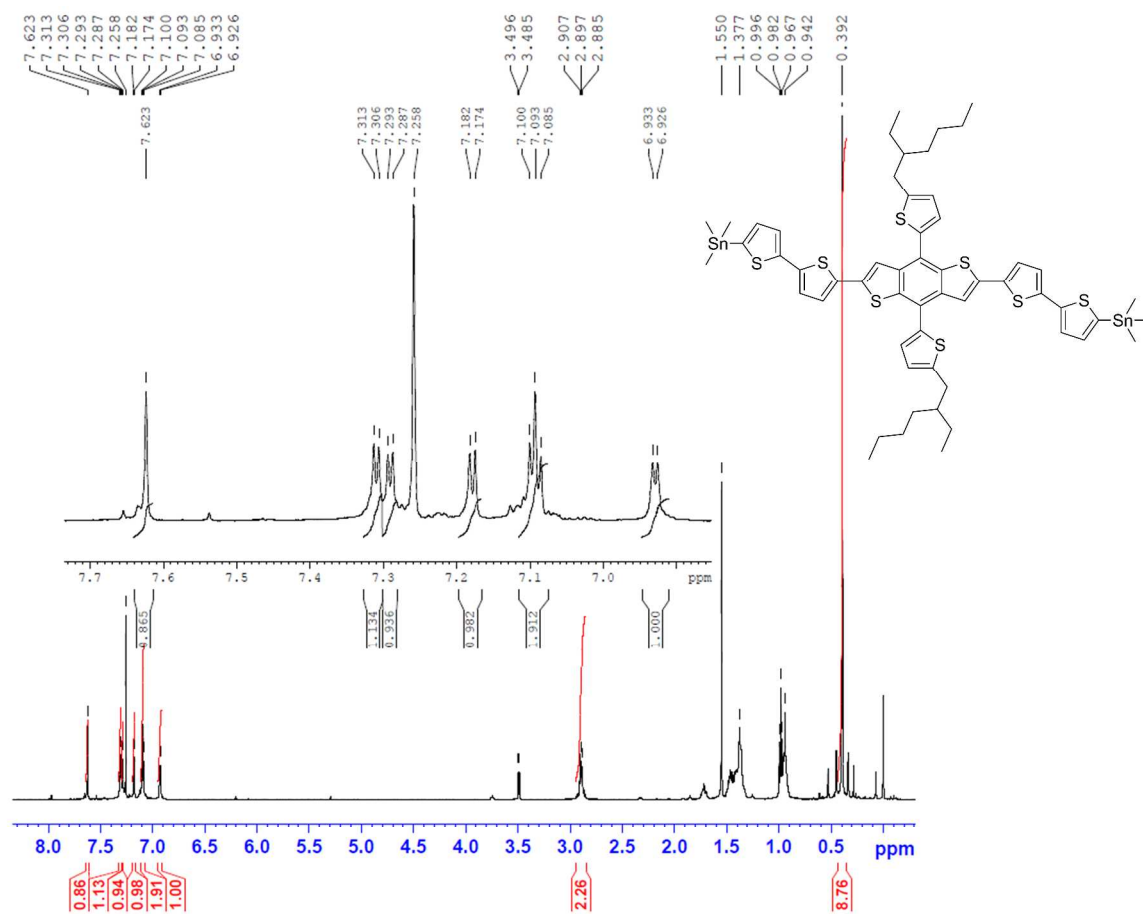


Figure S10. ¹H NMR of (5',5''-(4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-*b*:4,5-*b'*]dithiophene-2,6-diyl)bis([2,2'-bithiophene]-5',5-diyl))bis(trimethylstannane) (**M3**)

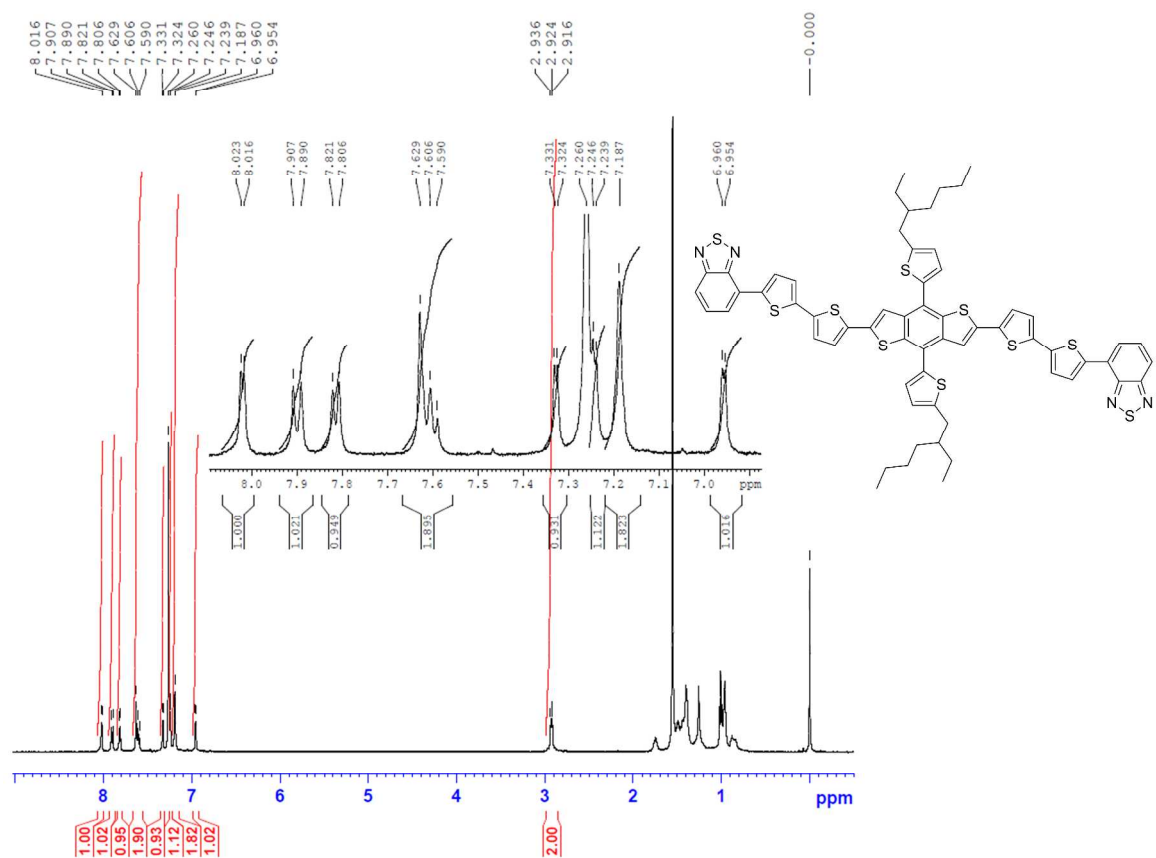


Figure S11. ^1H NMR of 4,4'-[(4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-*b*:4,5-*b'*]dithiophene-2,6-diyl)bis(2,2'-bithiophene)-5,5'-diyl]bis(benzo[*c*][1,2,5]thiadiazole) (**BDT-TT-BT**)

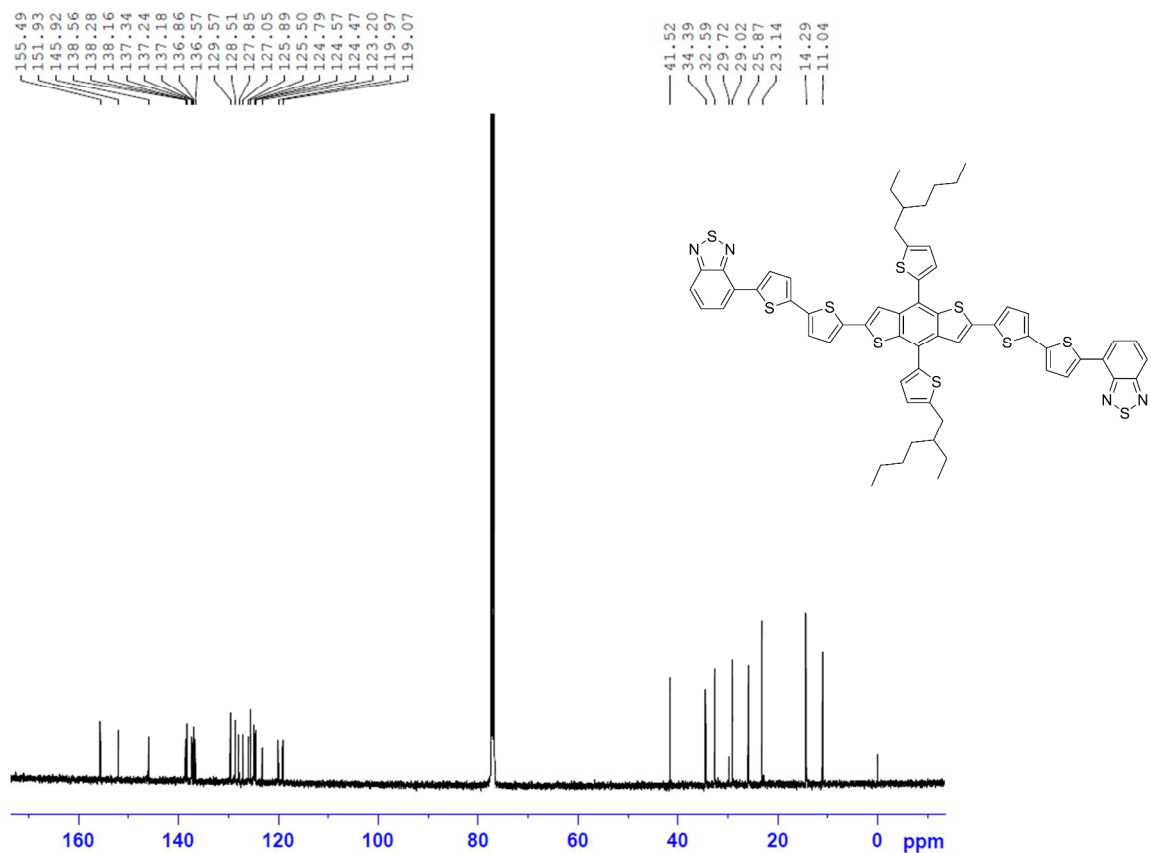


Figure S12. ^{13}C NMR of 4,4'-[(4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-*b*:4,5-*b'*]dithiophene-2,6-diyl)bis(2,2'-bithiophene)-5,5'-diyl]bis(benzo[*c*][1,2,5]thiadiazole) (BDT-TT-BT)

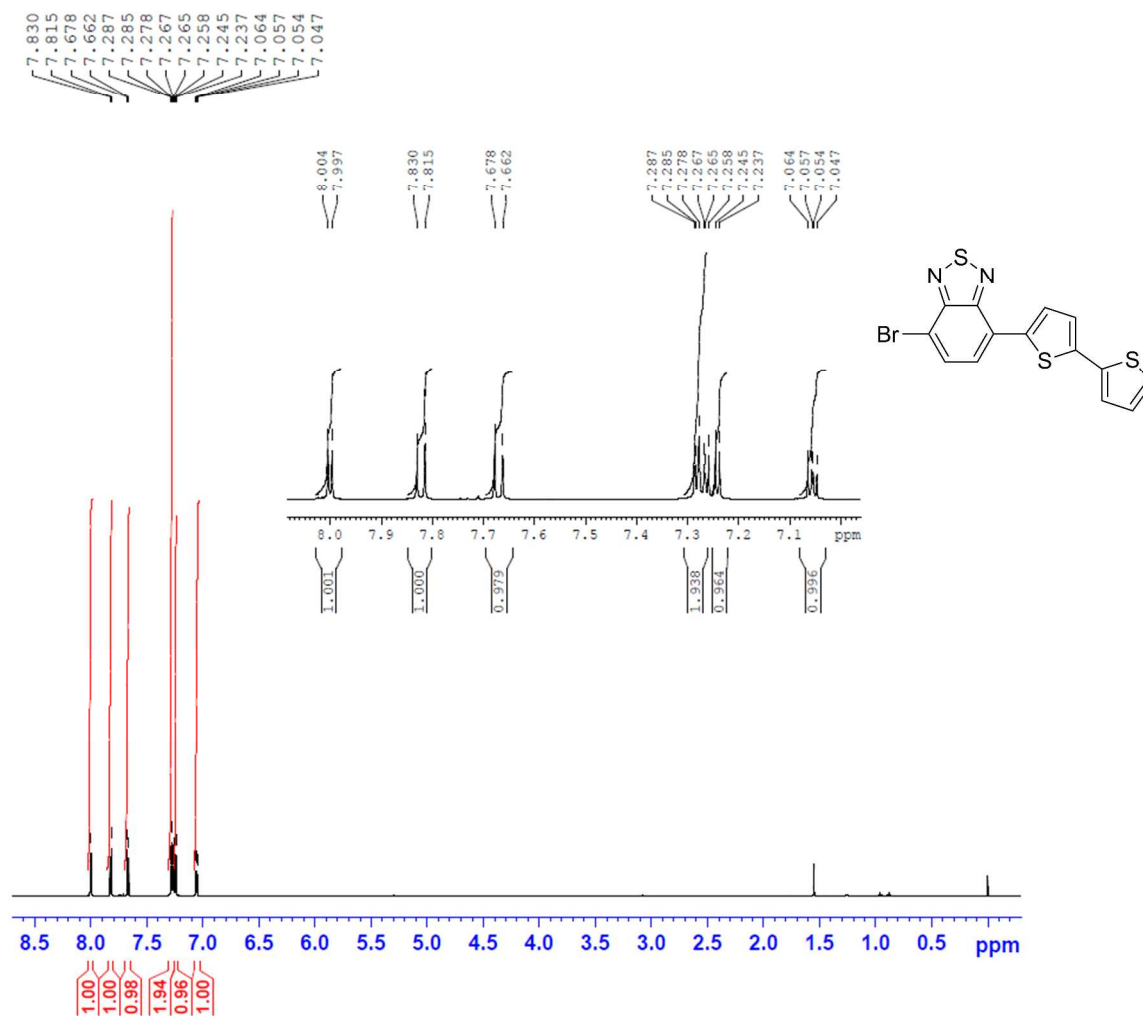


Figure S13. ¹H NMR of 4-([2,2'-bithiophen]-5-yl)-7-bromobenzo[c][1,2,5]thiadiazole (**M4**)

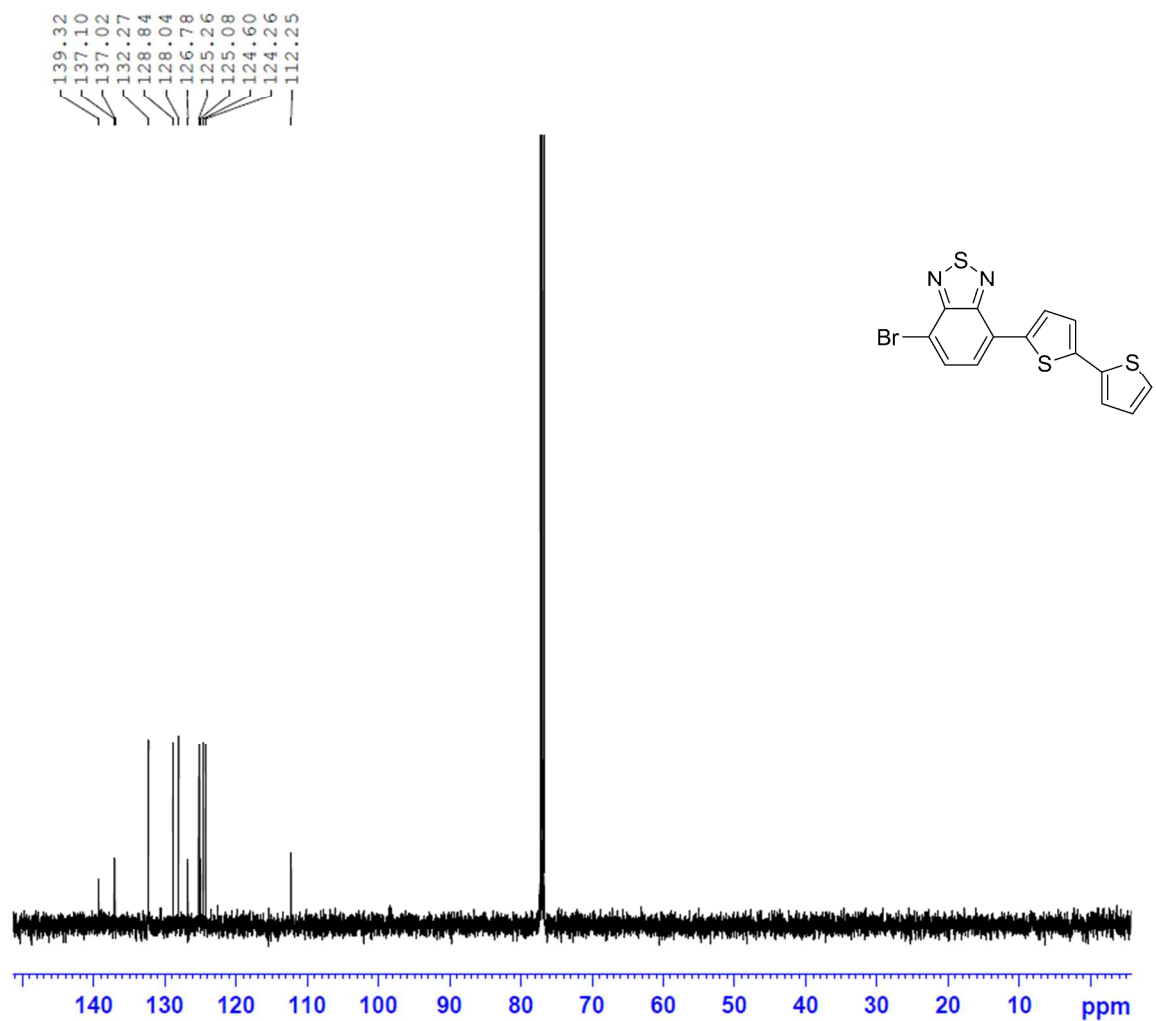
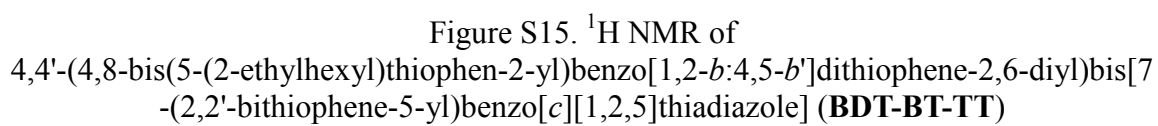


Figure S14. ¹³C NMR of 4-([2,2'-bithiophen]-5-yl)-7-bromobenzo[c][1,2,5]thiadiazole (M4)



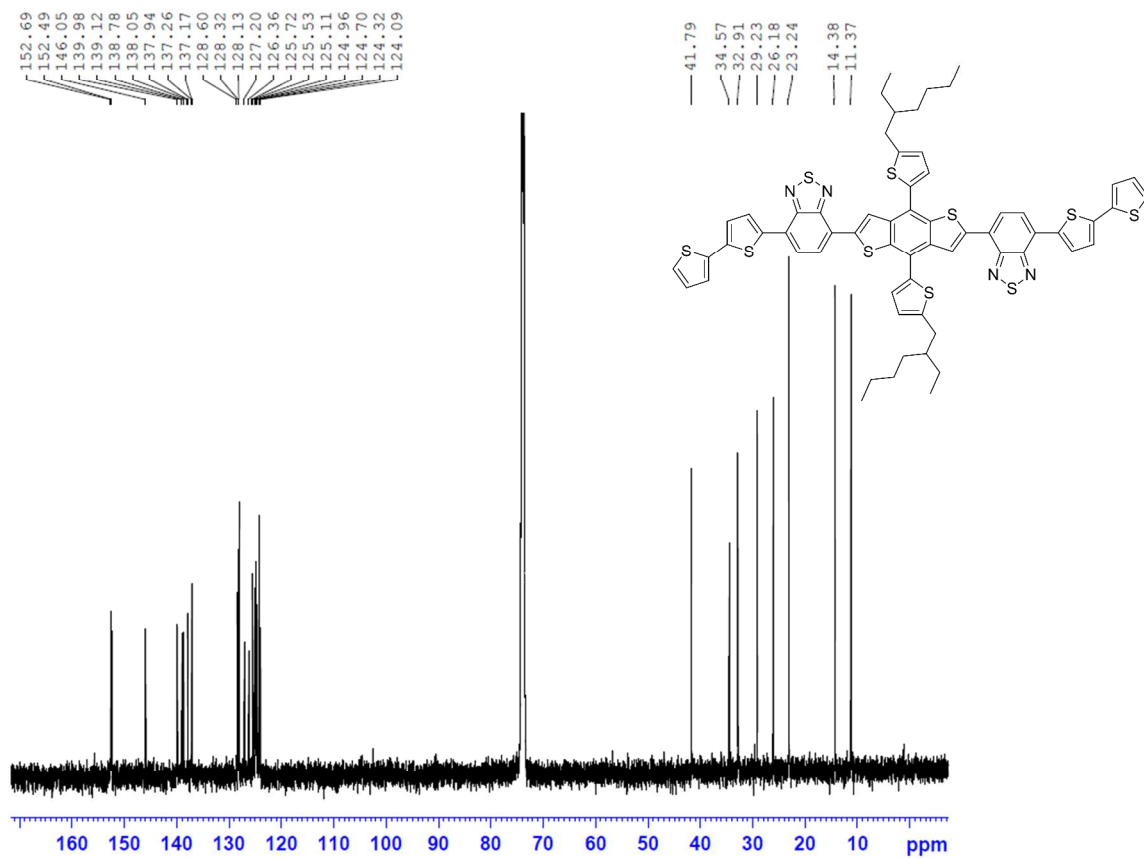


Figure S16. ^{13}C NMR of 4,4'-(4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-*b*:4,5-*b'*]dithiophene-2,6-diyl)bis[7-(2,2'-bithiophene-5-yl)benzo[*c*][1,2,5]thiadiazole] (**BDT-BT-TT**)

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 Shimadzu Biotech Axima Confidence 2.9.2.20100726: Mode Reflectron_HiRes, Power: 76, P.Ext. @ 1647 (bin 75)
 %Int. 1.2 mV[sum= 173 mV] Profiles 1-150 Smooth Av 75

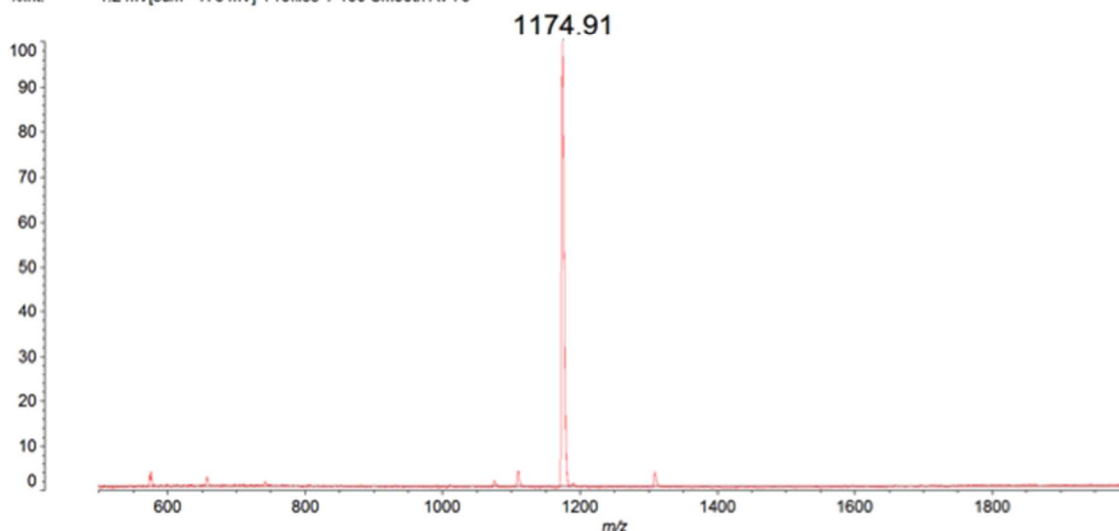


Figure S17. MALDI-TOF mass spectrum of 4,4'-[(4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-*b*:4,5-*b'*]dithiophene-2,6-diyl)bis(2,2'-bithiophene)-5,5'-diyl]bis(benzo[*c*][1,2,5]thiadiazole) (**BDT-TT-BT**)

Data: JD161_60001.F21[c] 12 Sep 2016 9:34 Cal: 20160310 Hi Res Cal 7 Sep 2016 17:18
 Shimadzu Biotech Axima Confidence 2.9.2.20100726: Mode Reflectron_HiRes, Power: 76, P.Ext. @ 1647 (bin 75)
 %Int. 3.1 mV[sum= 467 mV] Profiles 1-150 Smooth Av 75

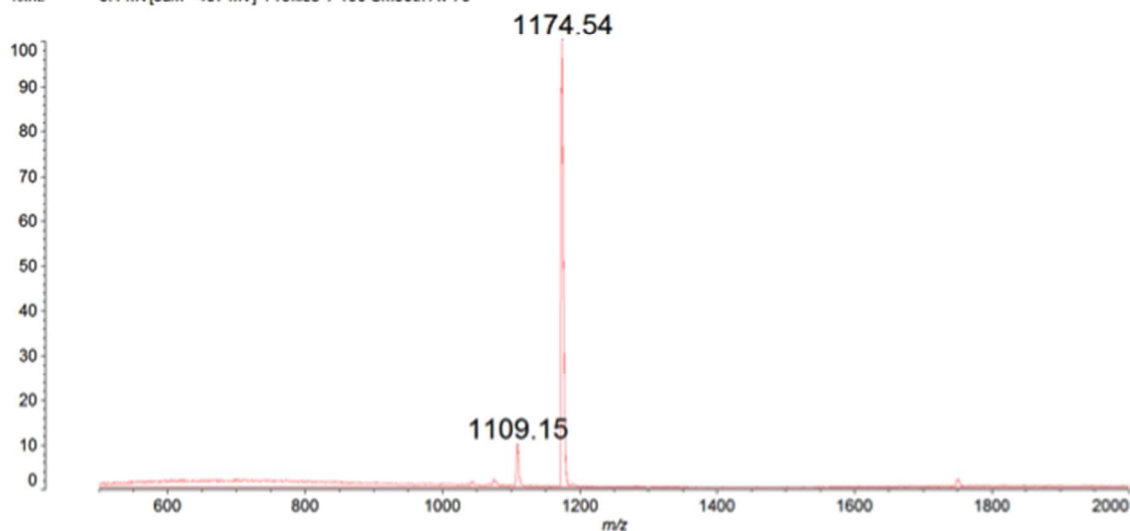


Figure S18. MALDI-TOF mass spectrum of 4,4'-(4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-*b*:4,5-*b'*]dithiophene-2,6-diyl)bis[7-(2,2'-bithiophene-5-yl)benzo[*c*][1,2,5]thiadiazole] (**BDT-BT-TT**)

Details of sample preparation and testing for AFM and GIWAXS

Atomic Force Microscopy. The samples were prepared under a dry nitrogen environment in a glovebox. 1 mg/mL solutions in anhydrous ortho-dichlorobenzene or chloroform (Sigma Aldrich) were casted on 2×2 cm silicon wafers with native oxide. The solutions were heated to 80 °C in glass vials for 30 minutes, filtered through a 0.22 mm PTFE syringe filter using a glass syringe, and re-heated for 10 minutes prior to drop-casting hot solutions onto the wafers. The wafers were cleaned by spraying with fresh acetone and isopropanol and dried under a jet of filtered, dry nitrogen, followed by UV/Ozone treatment at 120 °C for 45 minutes, followed by an incubation period of 45 minutes until cooled to 42 °C (Novascan PSD-UVT). The wafers were then placed under vacuum, 10 mTorr, for 90 min. The as-treated wafers were placed in a petri dish, completely covered with a minimum amount of solution, and allowed to dry under reduced pressure (10 mTorr) for 10 hours. The as-obtained films were imaged with a Bruker Dimension V hybrid AFM in tapping mode.

Grazing-Incidence Wide Angle X-Ray Scattering. Three sets of samples were prepared for analysis. The pure samples were prepared under ambient conditions. All samples were prepared from 2 mg/mL solutions in anhydrous chloroform, anhydrous ortho-dichlorobenzene (ODCB) and anhydrous toluene (Sigma Aldrich) on 2×2 cm silicon wafers with native oxide. The solutions were heated to 50 °C in glass vials for 30 minutes, filtered through a 0.22 mm PTFE syringe filter using a glass syringe, and re-heated for 10 minutes prior to drop-casting hot solutions onto the wafers. The wafers were cleaned by spraying with fresh hexanes, acetone and isopropanol and dried under a jet of filtered, dry nitrogen, followed by UV/Ozone treatment at 120 °C for 45 minutes,

followed by an incubation period of 45 minutes until cooled to 42 °C (Novascan PSD-UVT). The wafers were then placed under vacuum (10 mTorr) for 90 minutes. For the chloroform series, the as-treated wafers were placed in a petri dish and lined with 1 mL of chloroform, completely covered with a minimum amount of solution, and allowed to dry slowly by solvent-vapor annealing. For the toluene series, the as-treated wafers were placed in a petri dish and covered with a minimal amount of solvent and allowed to dry slowly whereas the ODCB samples were placed under reduced pressure (10 mTorr) overnight. The annealed films were heated at 90°C for 30 min prior to measurement.

Spincoat samples were prepared under a dry nitrogen environment in a glovebox. The SiO₂ native oxide wafers were treated in a similar fashion as the dropcast series. The solutions were heated to 50°C for 30 minutes, filtered through a 0.22 mm PTFE syringe filter using a glass syringe, and re-heated for 10 minutes prior to drop-casting hot solutions onto the wafers for each solvent series, including chloroform, toluene and ODCB samples. Thin film samples were prepared from spin-coating conditions consisting of three cycles, a 300 RPM spreading cycle for 5 seconds, a 400 RPM main cycle for 60 seconds and a 1500 RPM wicking cycle for 5 seconds. Annealed films were heated at 90°C for 30 minutes under a nitrogen environment.

PC₇₁BM samples were prepared under a dry nitrogen environment in a glovebox. PC₇₁BM blended samples were mixed in ratios of (1:2) for the (BDT-TT-BT: PC₇₁BM) solution and (1:1.5) for the (BDT-BT-TT: PC₇₁BM) solution. Each component was weighed separately and blended together using the appropriate solvent, either chloroform or ODCB. The solutions were heated to 50°C and 90°C for 1 hour for the chloroform and ODCB samples respectively, filtered through a 0.22 mm PTFE syringe filter using a

glass syringe, and re-heated for 10 minutes prior to drop-casting hot solutions onto the wafers. Thin film samples were prepared from spin-coating conditions consisting of three cycles, a 300 RPM spreading cycle for 5 seconds, a 400 RPM main cycle for 60 seconds and a 1500 RPM wicking cycle for 5 seconds. Annealed films were heated at 90°C for 30 minutes under a nitrogen environment.

GIWAXS measurements were taken at the Cornell High Energy Synchrotron Source (CHESS) D1 ($\lambda = 1.162$ nm) station. A wide bandpass (1.47%) doublebounce multilayer monochromator supplied an intense beam of 10.1 keV photons. GIWAXS intensities were recorded with an area detector (Medoptics) with a resolution of 46.9 μm per pixel and a total area of about 50 mm by 50 mm at a distance of 10.62 cm from the thin film sample. The sample was mounted on a sample goniometer, in order to control the incident angle and the sample azimuth. An accurate calibration of the incident angle was performed in situ by measuring the X-ray reflectivity from the sample using an ion chamber. The measurements were calibrated using a ceria standard. The intense scattering close to the direct beam was blocked with a 1.5-mm-wide tantalum rod. Exposures times under these conditions ranged from 0.1 sec to 3 sec depending on the contrast and sample quality.

Images were post processed using Mathematica Software (Wolfram Research, Inc.) The profiles had all dead pixels removed by the averaging of surrounding points and then the intensity was normalized by exposure time. The scattering wavevector transfer components q_x , q_y and q_z were treated elastically to derive q_{\parallel} and q_{\perp} functions as described in literature.¹ Diffuse scattering outside of the ewald sphere was depicted as a missing edge, thereby any 2D-GIWAXS patterns were representative of the satisfied

Bragg diffraction condition. The azimuthally averaged in plane and out of plane “slices” in q ranging from $80\text{-}90^\circ$ and $5\text{-}15^\circ$ were normalized by the invariant over the entire range of ϕ and q , then interpreted from 2D scattering profiles without the missing wedge.

References:

1. Renaud, G.; Lazzari, R.; Leroy, F., Probing Surface and Interface Morphology with Grazing Incidence Small Angle X-Ray Scattering. *Surf. Sci. Rep* **2009**, 4, 255.