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Supplementary Information

Well-Defined Alternative Polymer Semiconductor using Large Size Regioregular Building Block as Monomer: Electrical and Electrochemical Properties

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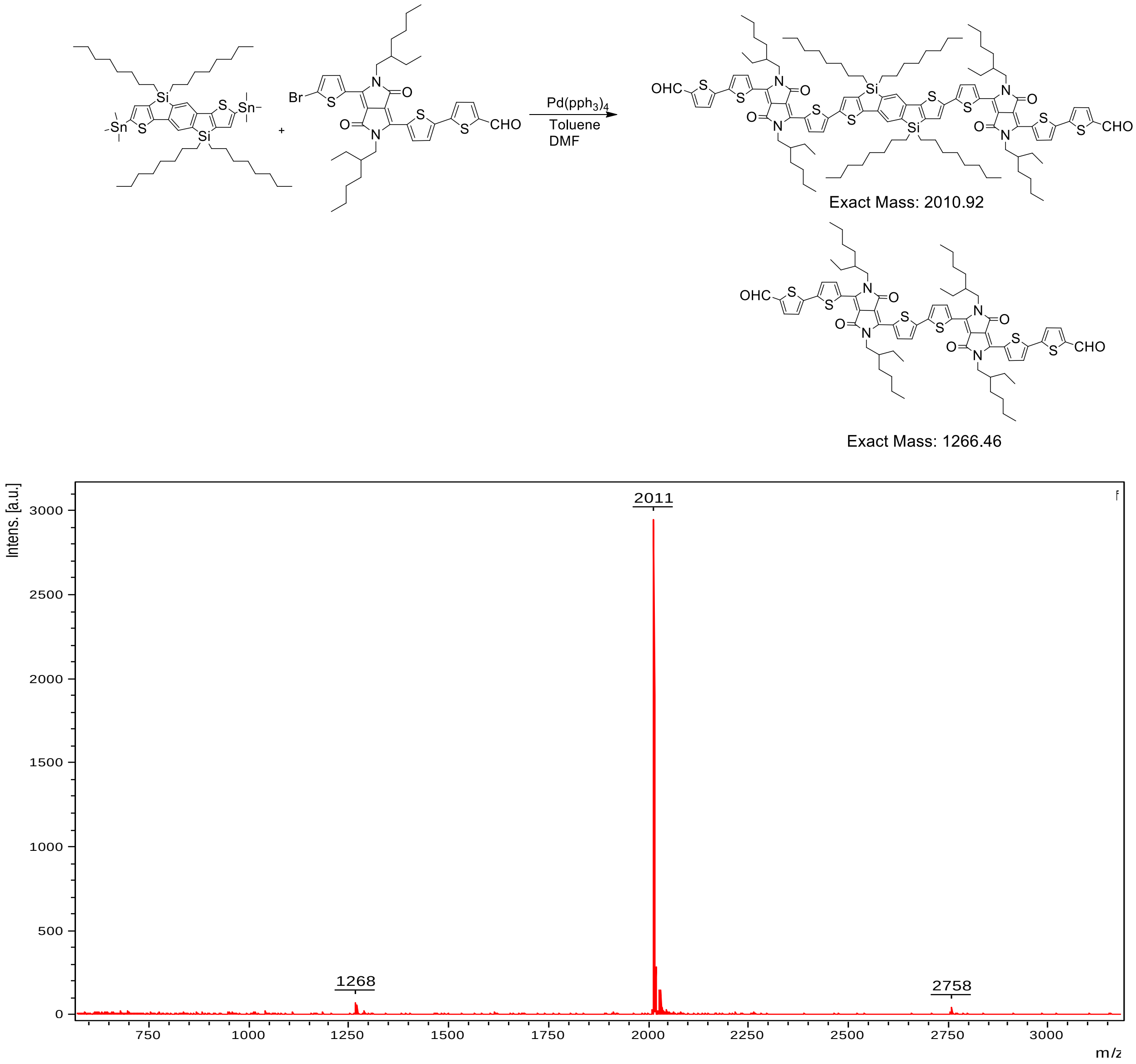


Figure S1. (a) Synthesis scheme for intermediate compound for LGC-D050 using Stille coupling[1], and (b) MALDI-TOF spectrum for corresponding crude product before purification.

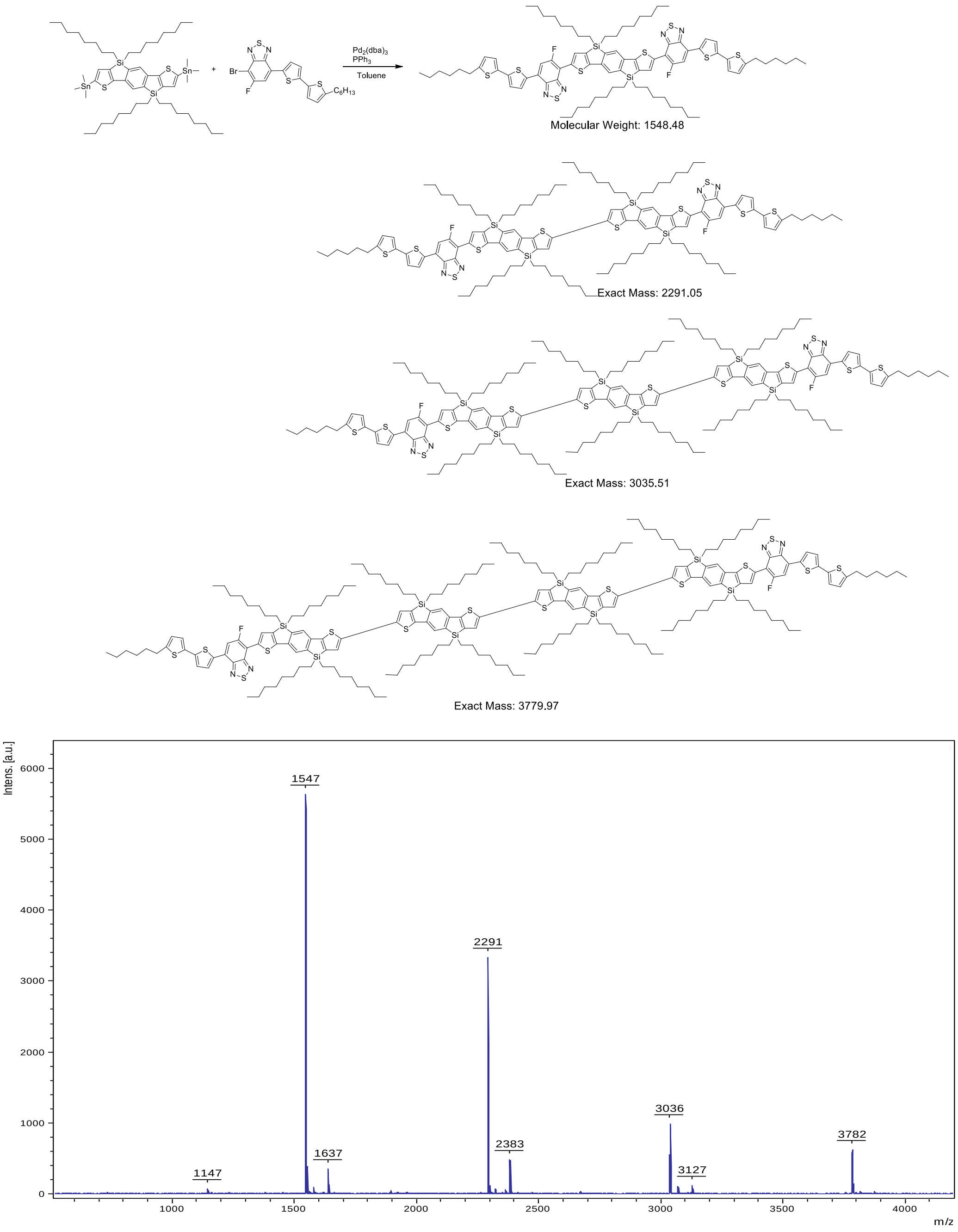


Figure S2. (a) Synthesis scheme for Stille coupling between silaindacenodithiophene and benzothiadiazole derivative, and (b) MALDI-TOF spectrum for corresponding crude product before purification.

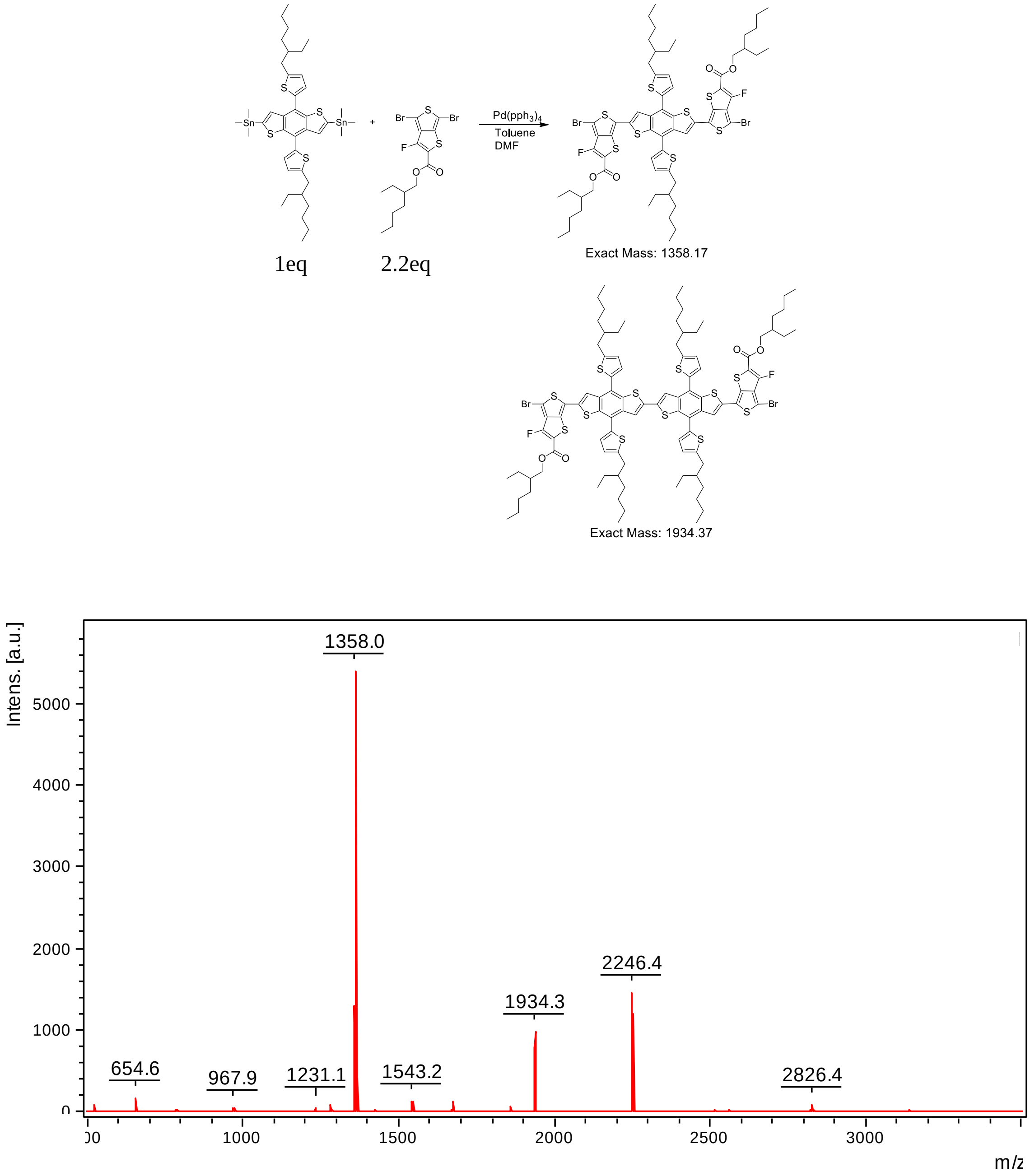
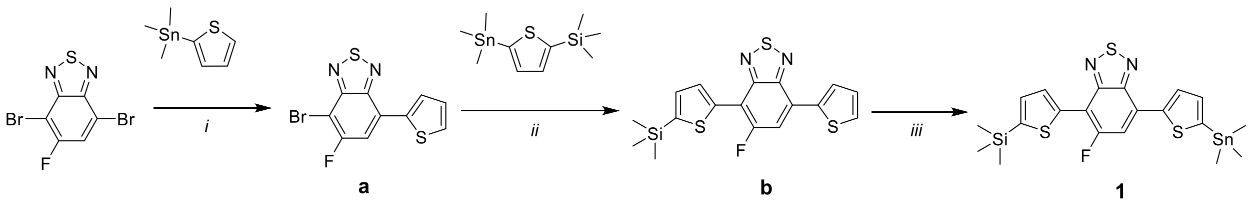


Figure S3. (a) Synthesis scheme for Stille coupling between benzodithiophene (1 eq.) and thienothiophene derivative (2.2 eq.) following previously details procedure[2,3], and (b) MALDI-TOF spectrum for corresponding crude product before purification.



Scheme S1. Synthesis routes for intermediate compound 1. Reagents and conditions: *(i)* Pd(pph$_3$)$_4$, toluene, 80 °C for 48 h, *(ii)* Pd(pph$_3$)$_4$, toluene/DMF, 100 °C for 48 h, *(iii)* LDA, THF, $(CH_3)_3SnCl$, -78 °C.

Compound a preparation

4-bromo-5-fluoro-7-(5′-hexyl-[2,2′-bithiophene]-5-yl)benzo[*c*][1,2,5]thiadiazole (7.80 g, 25.0 mmol), 2-(trimethyltin)thiophene (6.17 g, 25.0 mmol), tetrakis(triphenylphosphine)palladium (1.15 g, 1.0 mmol), and toluene (250 ml) were placed in a 100 ml flask, then was heated to 80 °C for 48 h. After cooling, the reaction mixture was poured into methanol and filtered, and the precipitate recrystallized with dichloromethane and methanol. The product was filtered to produce a yellow solid (Yield: 6.50 g, 83%). ^{1}H NMR (CDCl$_3$, 500 MHz, [ppm]): δ 8.119 (d, 1H, J=2.5 Hz), 7.724 (d, 1H, J=10.0 Hz), 7.534 (d, 1H, J=5 Hz), 7.224 (t, 1H, J=8.5 Hz); MALDI-TOF: m/z 315.5, calcd 313.90.

Compound b preparation

Compound a (13.0 g, 4.09 mmol), trimethyl[5-(trimethylsilyl)-2-thienyl]stannane (4.47 g, 14.0 mmol), toulene (75 ml), and DMF (25 ml) were mixed in a flask, then tetrakis(triphenylphosphine)palladium (0.60 g, 0.52 mmol)was added, and the mixture was heated to 100 °C for 48 h. After cooling, the reaction mixture was poured into methanol and filtered. The precipitate was recrystallized with dichloromethane and hexane and filtered. The solid was washed with copious hexane and methanol, and then dried under vacuum for 24 h, producing an orange solid (Yield: 4.6 g, 91%).^{1}H NMR (CDCl$_3$, 500 MHz, [ppm]): δ 8.284 (d, 1H, J=3.0 Hz), 8.141 (d, 1H, J=3.5 Hz), 7.801 (d, 1H, J=12 Hz), 7.513(d, 1H, J=5.0 Hz), 7.373

(d, 1H, J=2.0 Hz), 7.231 (t, 1H, J=8.0 Hz), 0.399 (s, 9H); MALDI-TOF: m/z 390.0, calcd 390.02.

Intermediate compound 1 preparation

A 5.75 ml (11.5 mmol) of LDA solution (2.0 M) at -78 °C was added dropwise to a solution of compound b (4.09 g, 10.5 mmol) in 300 ml of THF under nitrogen atmosphere. The mixture was stirred for 1 h at -78 °C, and then 12 ml (12 mmol) of trimethyltinchloride solution in hexane (1.0 M) was added. After stirring for 1 h, the ice bath was removed and the mixture allowed to warm gradually to room temperature. The reaction mixture was extracted with dichloromethane, washed with water, dried with anhydrous $MgSO_4$, and the solvent was removed. The crude product was recrystallized with dichloromethane and hexane and filtered. The solid was washed with copious hexane and methanol, and then dried under vacuum for 24 h to produce an orange solid (Yield: 5.1 g, 88%). ^{1}H NMR ($CDCl_3$, 500 MHz, [ppm]): δ 8.274 (d, 1H, J=3.0 Hz), 8.206 (d, 1H, J=2.5 Hz), 7.788 (d, 1H, J=12.5 Hz), 7.369 (d, 1H, J=3.0 Hz), 7.302 (d, 1H, J=3.5 Hz), 0.442 (s, 9H), 0.396 (s, 9H); MALDI-TOF: m/z 553.7, calcd 553.98.

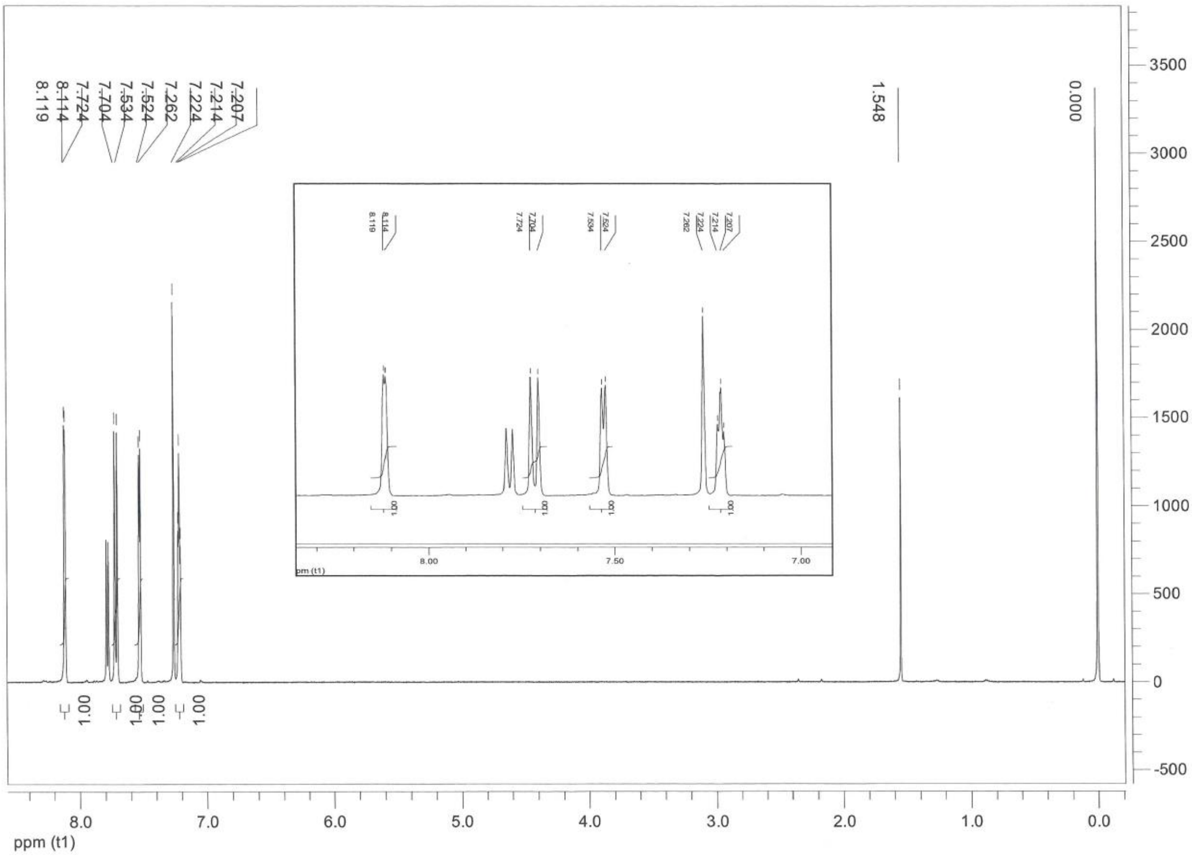


Figure S4. ^{1}H NMR spectrum for compound a.

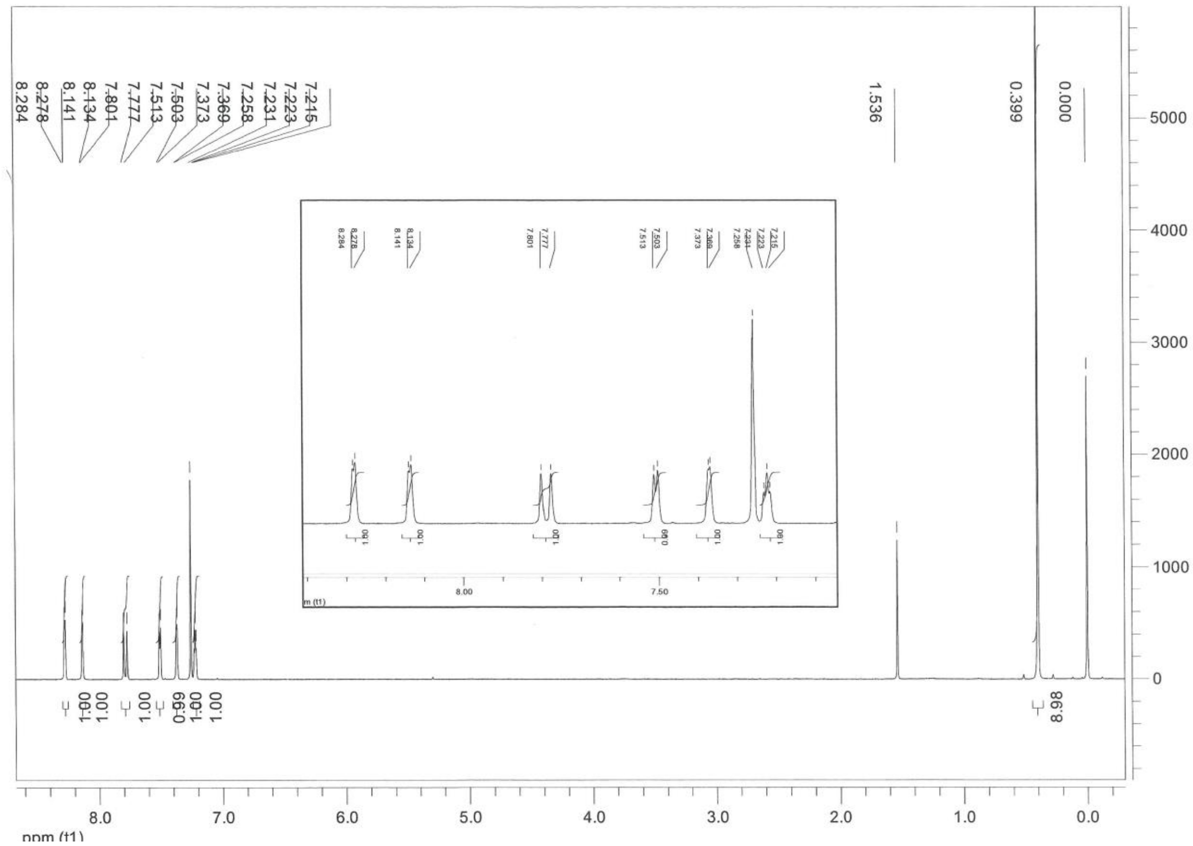


Figure S5. ^{1}H NMR spectrum for compound b.

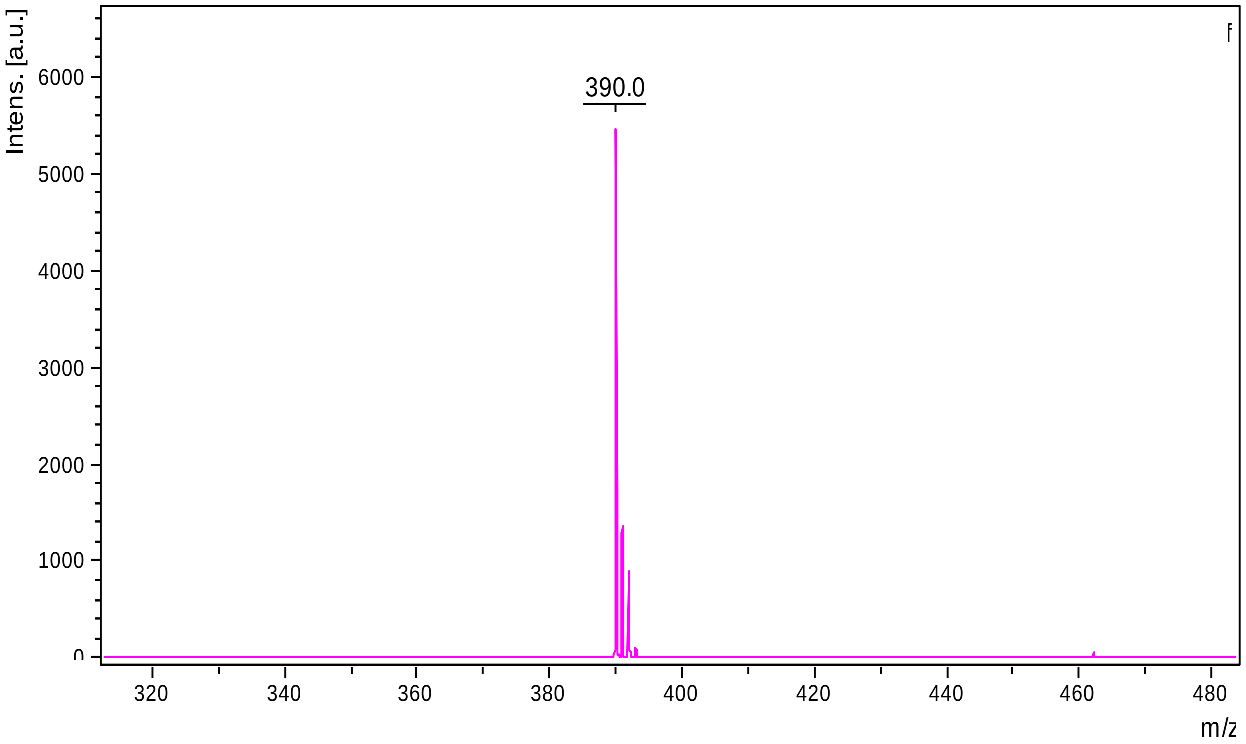


Figure S6. MALDI-TOF spectrum for compound b.

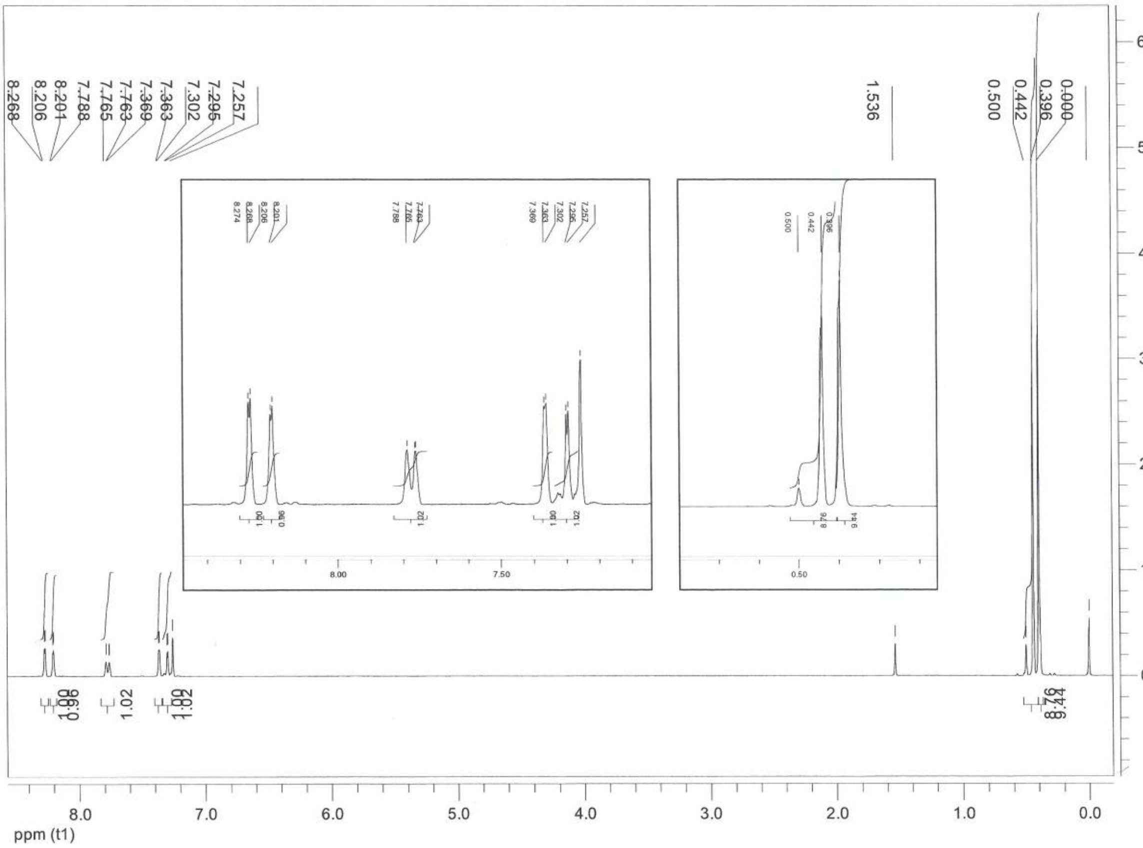


Figure S7. ^{1}H NMR spectrum for compound 1.

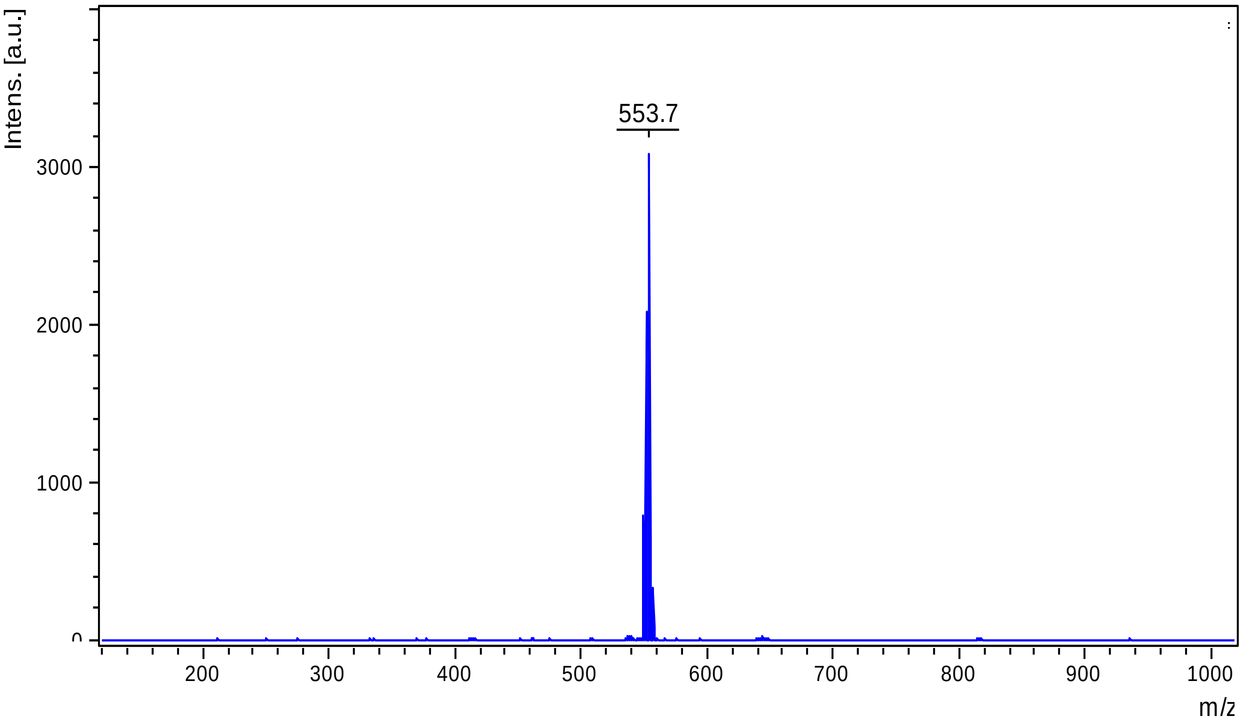
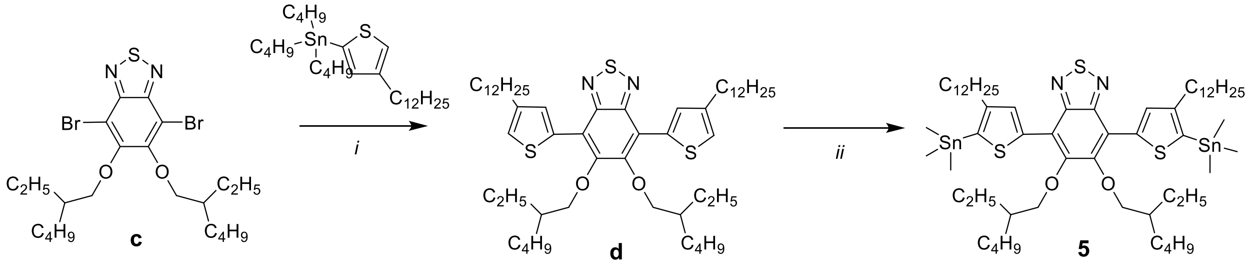


Figure S8. MALDI-TOF spectrum for compound 1.



Scheme S2. Synthesis routes for monomer 5. Reagents and conditions: *(i)* Pd(pph$_3$)$_4$, toluene/DMF, 100 °C for 48 h, *(ii)* LDA, THF, (CH$_3$)$_3$SnCl, -78 °C.

Compound d preparation

Compound c (4,7-Dibromo-5,6-bis-(2-ethyl-hexyloxy)-benzo[1,2,5]thiadiazole) was prepared according to the procedure from the literature.[4] Compound c (3.03 g, 5.5 mmol), 2-(tributylstannyl)-4-dodecylthiophene (7.58 g, 14.0 mmol), toulene (40 ml) and DMF (20 ml) were mixed in a flask, then tetrakis(triphenylphosphine)palladium (0.29 g, 0.25 mmol) was added, and the mixture was heated to 100 °C for 48 h. After cooling, the reaction mixture was poured into methanol and filtered. The filtered compound was dissolved in dichloromethane and washed with water. After volatiles were removed, the crude compound was purified by flash chromatography using hexane:dichloromethane=9:1eluents, producing a viscous yellow oil (Yield: 4.86 g, 99%). ^{1}H NMR (CDCl$_3$, 500 MHz, [ppm]): δ 7.966 (s, 2H), 7.097 (s, 2H), 3.914 (d, 4H, J=6.5 Hz), 2.713 (t, 4H, J=15,5 Hz), 1.887 (m, 2H), 1.700 (m, 4H), 1.390 (m, 52H), 0.890 (m, 18H); GC-MS: m/z 892.8, calcd 892.60.

Monomer 5 production

A 5.6 ml (11.2 mmol) LDA solution (2.0 M) at -78 °C was added dropwise to a solution of compound d (2.00 g, 2.24 mmol) in THF (50 ml) under nitrogen atmosphere. The mixture was stirred for 2 h at -78 °C, and then 12 ml (12 mmol) of trimethyltinchloride solution in hexane (1.0 M) was added. After stirring for 1 h, the ice bath was removed and the mixture allowed to warm gradually to room temperature. The reaction mixture was extracted with dichloromethane, washed with water, dried with anhydrous $MgSO_4$, and the solvent removed. The crude product was washed with methanol to remove impurities, producing a viscous orange oil and used without further purification (Yield: 1.8 g, 66%). ^1H NMR ($CDCl_3$, 500 MHz, [ppm]): δ 8.086 (s, 2H), 3.912 (d, 4H, J=7 Hz), 2.696 (t, 4H, J=16 Hz), 1.90 (m, 2H), 1.664 (m, 4H), 1.393 (m, 52H), 0.881 (m, 18H), 0.417 (t, 18H).

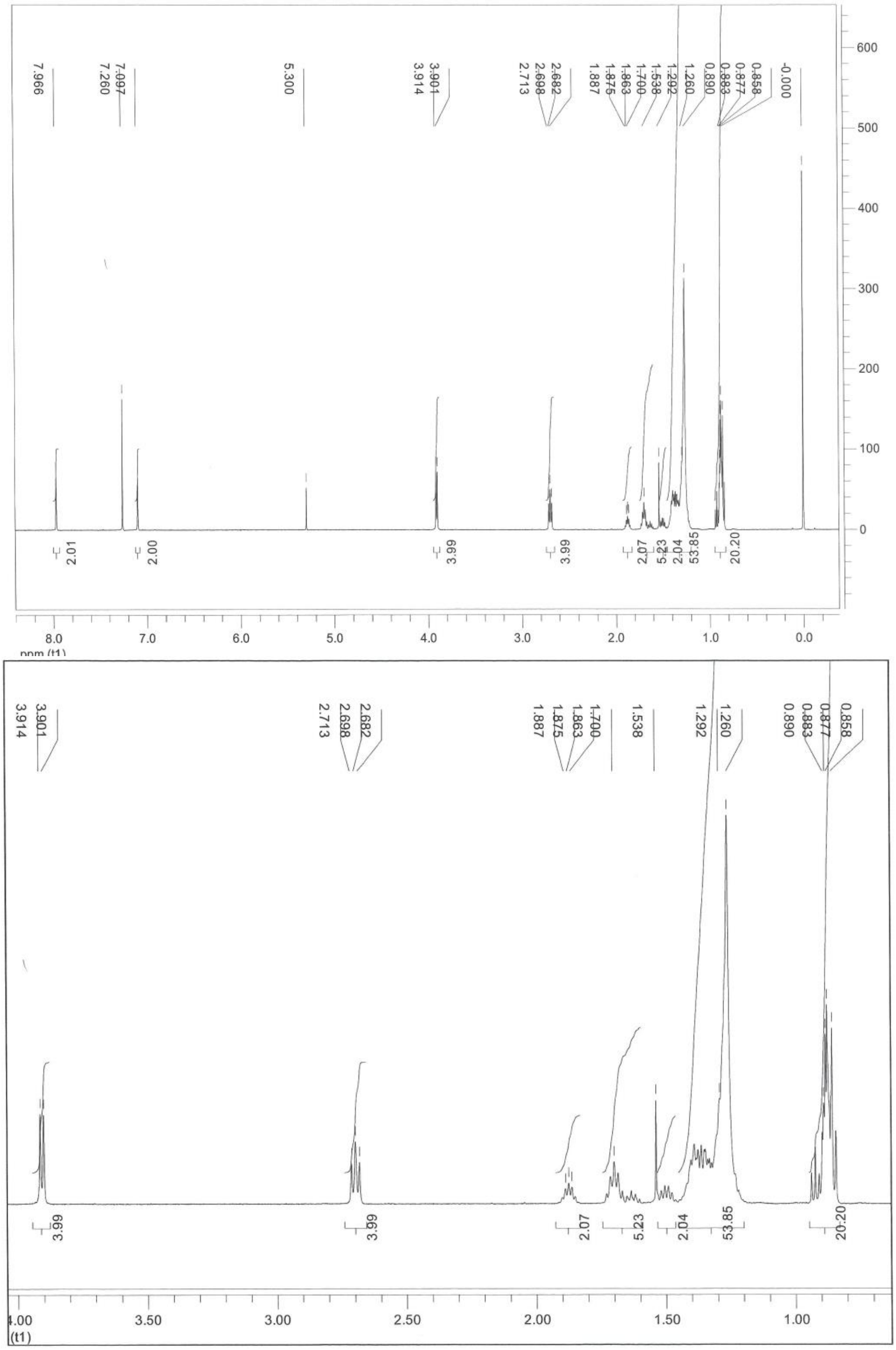


Figure S9. ^{1}H NMR spectrum for compound d.

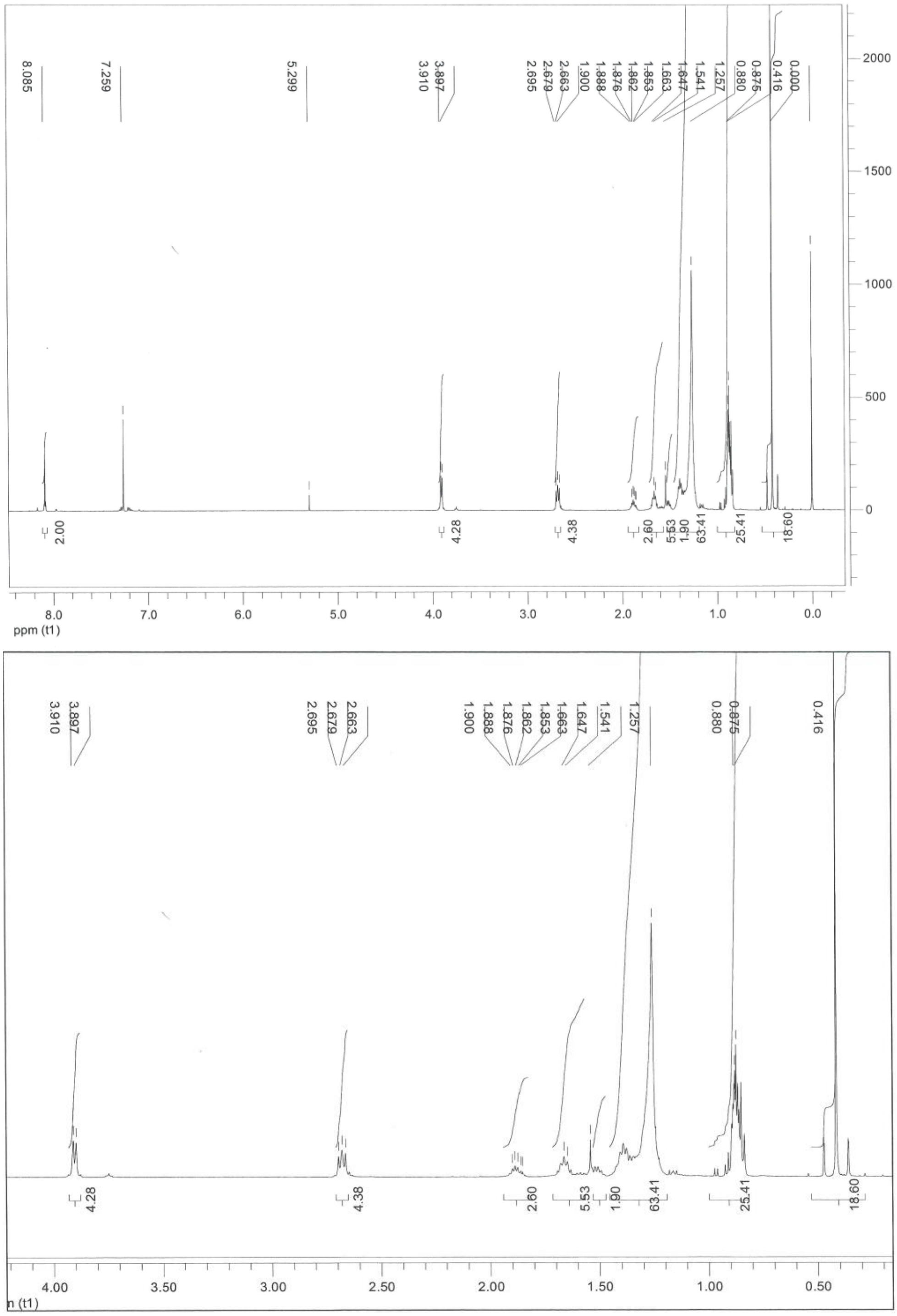


Figure S10. ^{1}H NMR spectrum for compound 5.

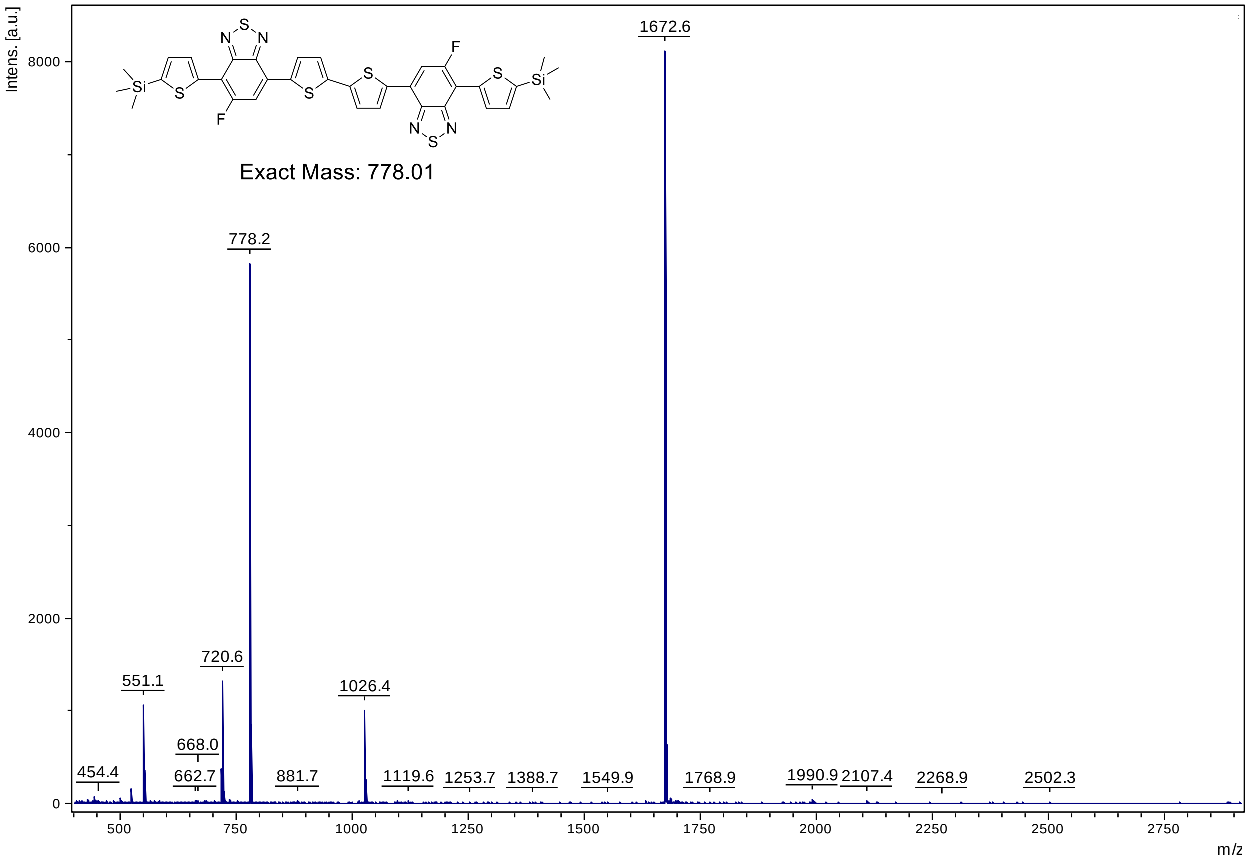


Figure S11. MALDI-TOF spectrum for compound 3.

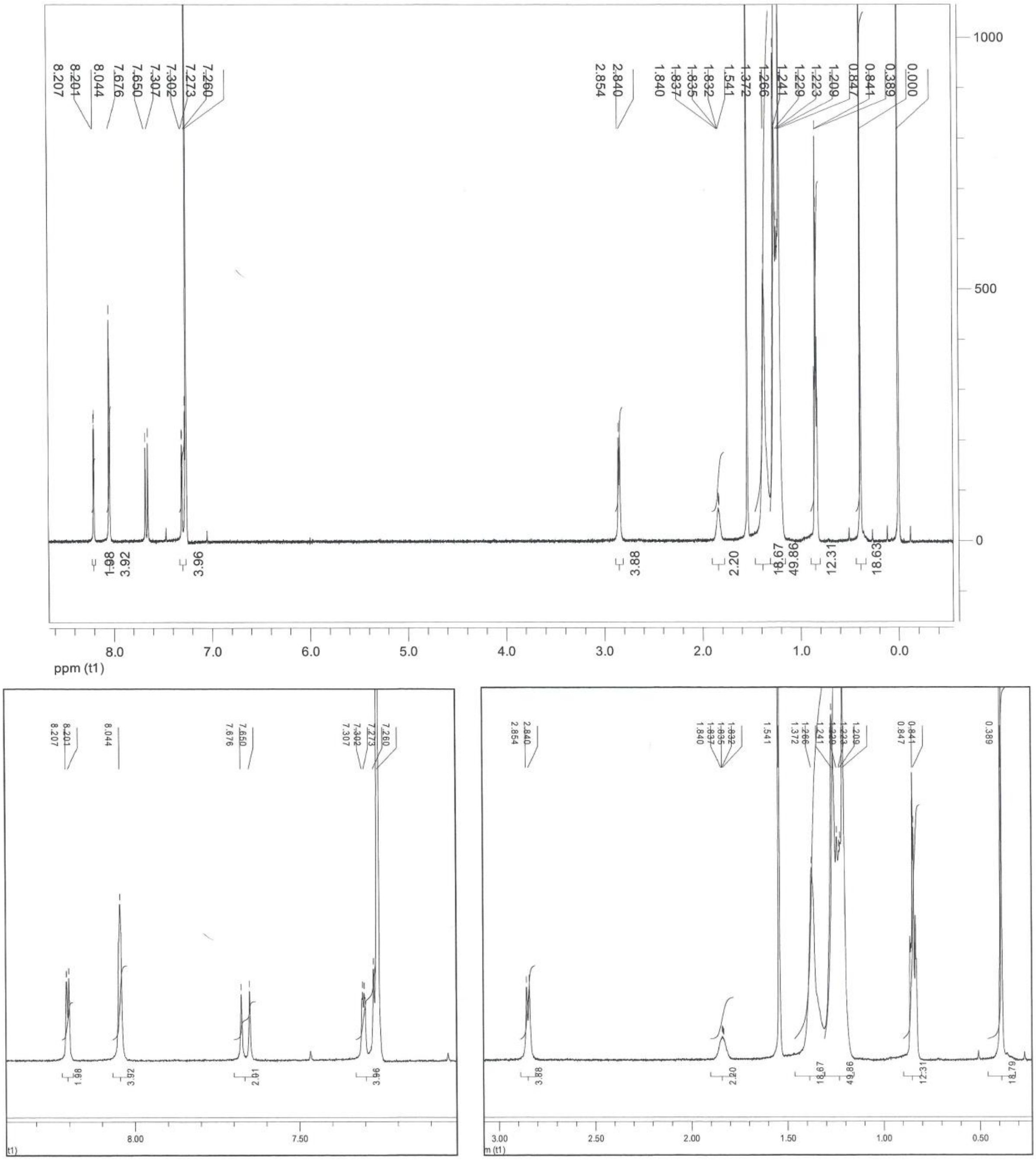


Figure S12. ^{1}H NMR spectrum for compound 3.

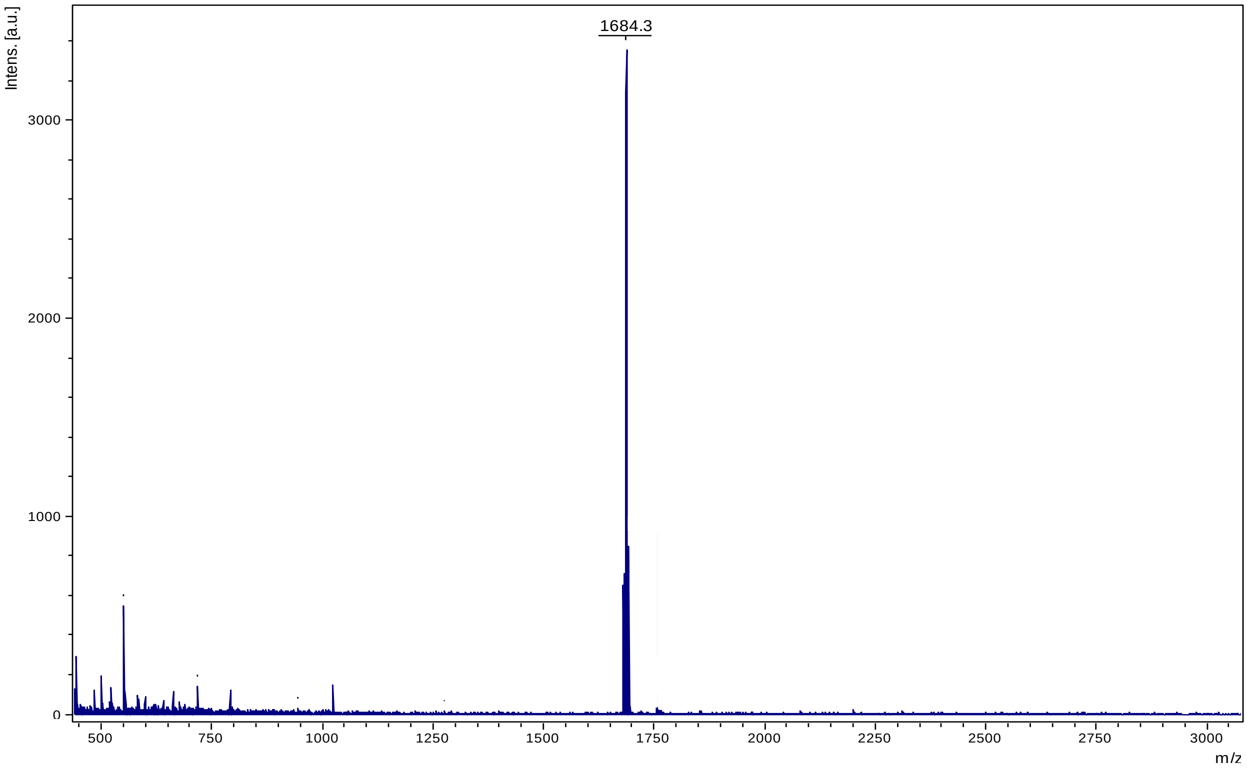


Figure S13. MALDI-TOF spectrum for compound 4.

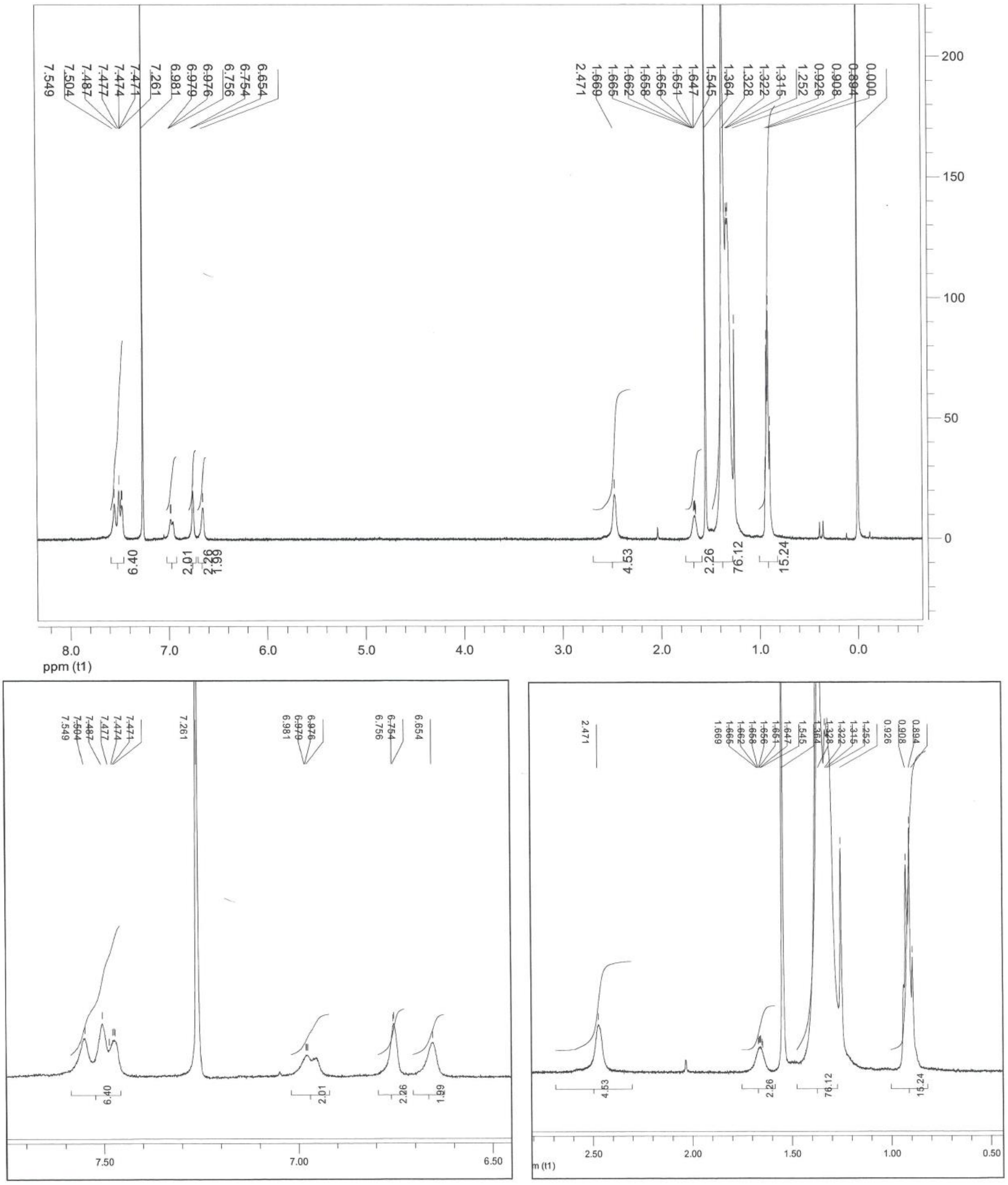


Figure S14. ^{1}H NMR spectrum for compound 4.

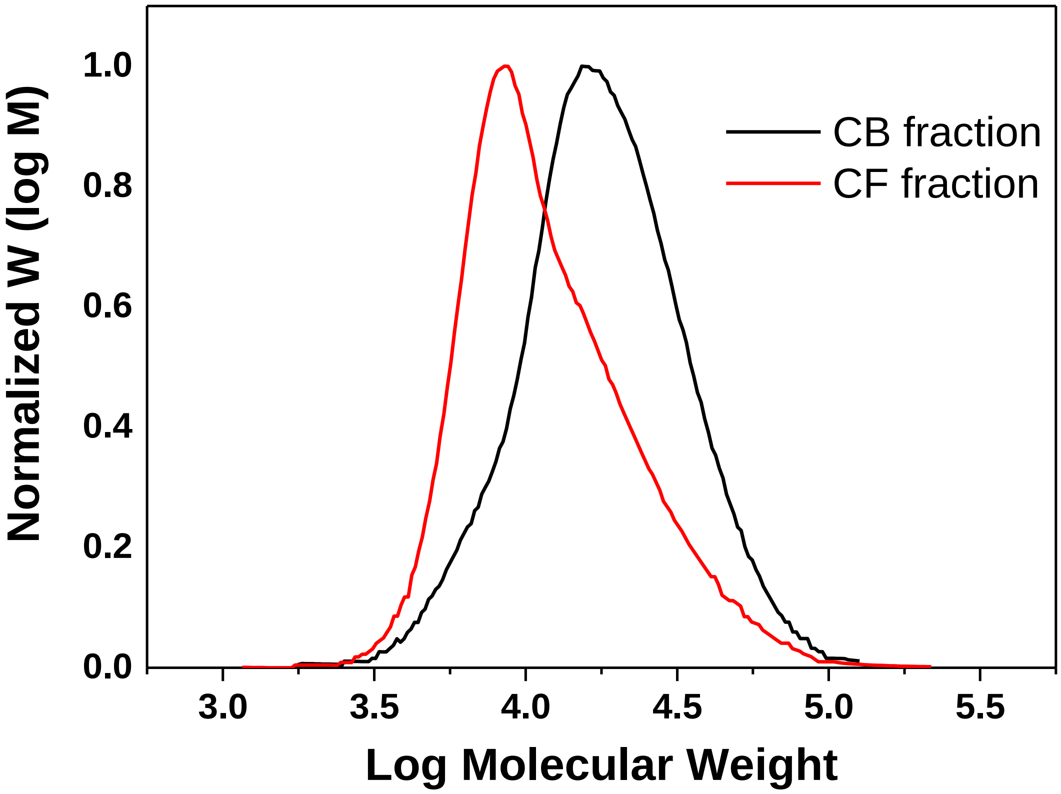


Figure S15. Molar mass distributions of rr-PBTTh chloroform and chlorobenzene fractions (measured by HT-GPC).

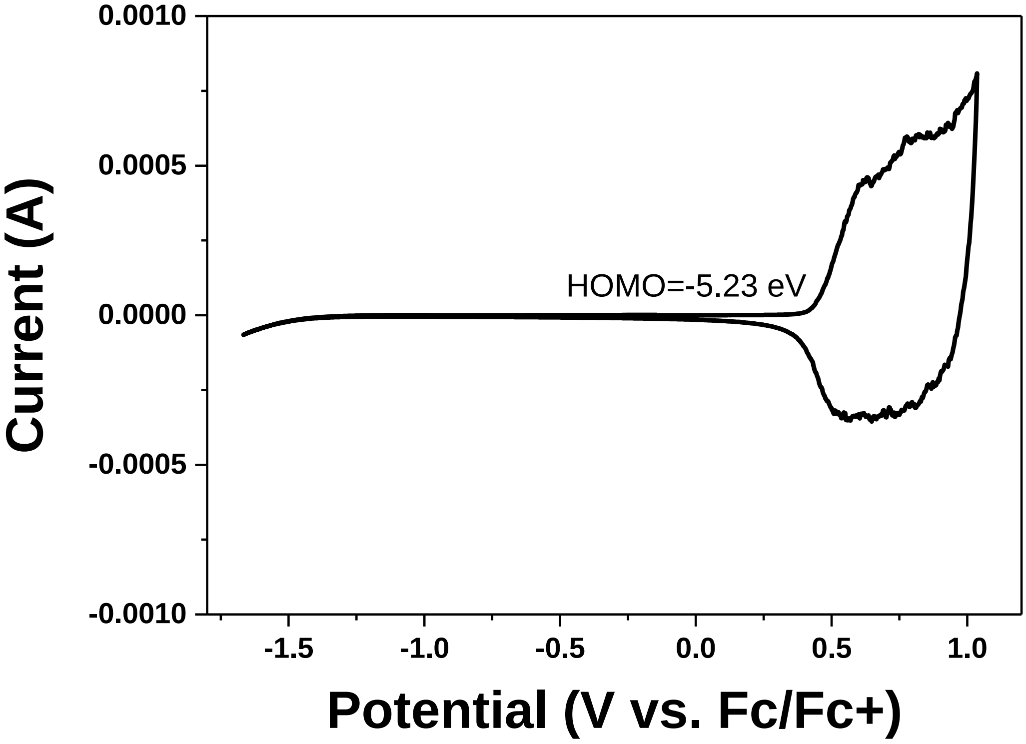


Figure S16. Cyclic voltammogramfor rr-PBTTh.

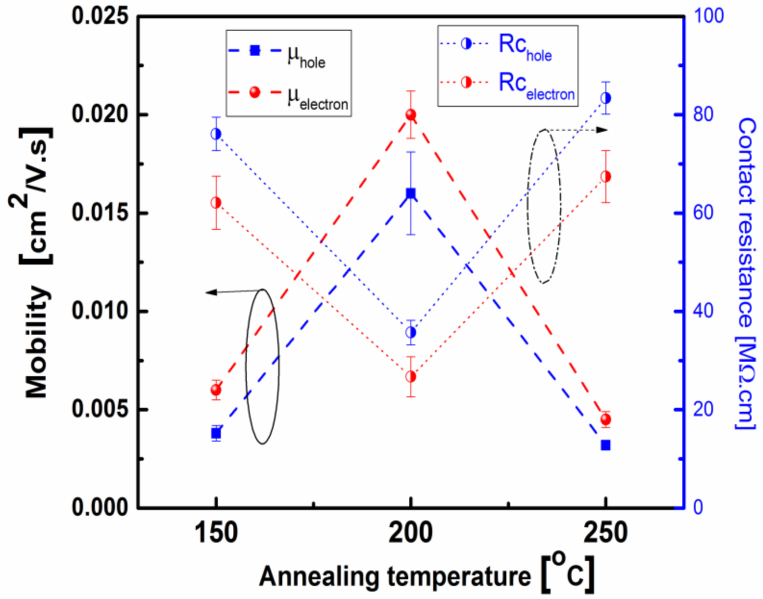


Figure S17. Hole (μ_h) and electron (μ_e) mobilities for rr-PBTTh, and hole (R_h) and electron (R_e) contact resistance for the corresponding devices: extracted from the YFM effect.

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