

Synthesis and Application of Dual Electron-Deficient Featured Copolymers and their Sequential Fluorination for Ambipolar Organic Thin Film Transistors

Dhananjaya Patra,¹ Xin Zhan,² Rajkumari Linthoinganbi,¹ Sunita Muduli,³ Sabyashachi Mishra,³ Yao Liu,² Sungjune Park^{1*}

¹Department of Polymer-Nano Science and Technology, Jeonbuk National University, Jeonju 54896, Korea; Department of Nano Convergence Engineering, Jeonbuk National University, Jeonju 54896, Korea

²State Key Laboratory of Chemical Resource Engineering, Beijing Advanced Innovation Center for Soft Matter Science and Engineering, Beijing University of Chemical Technology, Beijing, 100029, China

³Department of Chemistry, Indian Institute of Technology, Kharagpur-721302, India

Corresponding author: s.park@jbnu.ac.kr

1 Experimental Section

1.1 Materials

All chemicals and solvents were purchased in reagent grade from Aldrich, ACROS, and TCI, and, except Pd(PPh₃)₄ which was obtained from Strem Chemical. Tetrahydrofuran (THF), toluene, were distilled over Na/benzophenone; all reagents were used as received. Monomer M2 was obtained from Derthon Shenzhen, China. Compound 5, monomers M1 and M3, were synthesized using a similar or slightly modified process from previously reported works.¹

1.2 Measurements and Characterization

¹H and ¹³C NMR spectra were recorded from CDCl₃ solutions using a Bruker 400 MHz spectrometer; chemical shifts are reported as δ values (7.26 ppm) relative to an internal tetramethylsilane (TMS) standard. UV–Vis absorption spectra were recorded using a Jasco V-670 absorption spectrometer from dilute solutions in chlorobenzene or from solid films that had been spin-coated onto glass substrate from dilute chlorobenzene solutions (5 mg mL⁻¹). The electrochemical measurements were carried out in a deoxygenated solution of tetra-n-butylammoniumhexafluorophosphate (0.1 M) in acetonitrile with a computer-controlled electrochemical workstation. A glassy carbon electrode, a Pt wire, and an Ag/AgCl electrode were used as the working, counter, and reference electrodes, respectively. The corresponding energy levels of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) were calculated from the experimental values of $E_{\text{ox/onset}}$ and $E_{\text{red/onset}}$ for the solid films BDD-BT, BDD-FBT, and BDD-2FBT, formed by drop-casting films at a similar thickness from chlorobenzene solutions (ca. 5 mg mL⁻¹). The onset potentials were determined from the intersections of two tangents drawn at the rising currents and background currents of the CV measurements. The XRD spectra as recorded by using BRUKER (D8

ADVANCE) instrument having Cu X-ray tube (2.2 KW) with a maximum voltage 40 kV and power 40 mA having the 2θ values from 3° to 30° .

The ground electronic states of the monomer, dimer, and trimer of the non-fluorinated and mono- and di-substituted BDD-BT systems were optimized using the density functional theory (DFT) method with B3LYP functional in chlorobenzene solvent under the polarized continuum model (PCM) of implicit solvation. The 6-31G(d,p)^{2,3} basis set was used for C, H, N, and O atoms, while the 6-31G(2df,p)⁴ basis set was used as the basis for the fluorine atom. The vibrational frequencies obtained from the Hessian calculations at the optimized geometries were all positive, confirming the absence of any imaginary frequency and a stable acceptor-acceptor system. The optimized structures were subjected to time-dependent density functional theory (TD-DFT) calculations at the aforementioned theoretical level in order to assess their vertical excitations. In the present work, all electronic structure calculations, and the highest occupied molecular orbital (HOMO)-lowest unoccupied molecular orbital (LUMO) analysis were carried out using the Gaussian16 software package.⁵ The natural transition orbital (NTO) analysis was done by using the Multiwfn software.

2. Devices fabrication and characterizations

For bottom gate-bottom contact (BG-BC) devices, gold (Au) and titanium (Ti) layers were thermally evaporated onto a SiO₂ (300 nm)/p⁺⁺-Si substrate using a shadow mask to form the source and drain contacts with 30 nm in thickness. The channel length (L) and channel width (W) were 5 and 1400 μm , respectively. The substrate was thoroughly cleaned by placing it in piranha solution for about 2 min. After removing the piranha solution and rinsing the substrate with deionized water three times, the substrate was sonicated once with deionized water and

twice with isopropanol (IPA) for 4 minutes each time. After drying the substrate with nitrogen, the substrate was treated with UV-ozone (UV/O₃) for 15 min, and then baked at 90 °C for 30 min at 0.1 Pa in a vacuum oven. OTS treatment was performed by placing the cleaned substrate in OTS vapor for 180 min at 120 °C in a vacuum oven. The OTS-modified substrate was ultrasonically cleaned with n-hexane, chloroform, and IPA for 4 minutes, respectively, and then blown dry with nitrogen. BDD-BT, BDD-FBT, and BDD-2FBT solutions (in chlorobenzene at 5 mg/ml) were prepared. The polymer solution was spin-coated on the cleaned substrate at 2500 rpm for 60 s, then the samples were annealed at 160 °C on a hotplate for 15 min. For After cooling down the samples to room temperature, we have conducted the following test.

For top gate-bottom contact (TG-BC) devices, the substrates undergo the same processing methods as the bottom gate devices and were surface-modified with OTS. BDD-BT, BDD-FBT, and BDD-2FBT dissolved in chlorobenzene at 5 mg/ml solution and polymethylmethacrylate (PMMA) in ethyl acetate at 60 mg/ml solution were prepared. The BDD-BT, BDD-FBT, and BDD-2FBT polymer solution was spin-coated on the processed substrate at 2500 rpm for 60 s, then annealed at 160 °C on a hotplate for 15 min. After cooling down to room temperature, PMMA solution was spin-coated on the polymer layer at 2000 rpm for 60 s. Then baked at 80 °C for 90 min at 0.1 Pa in a vacuum oven. 80 nm aluminum (Al) layer was thermally evaporated onto the PMMA layer to form the gate electrode.

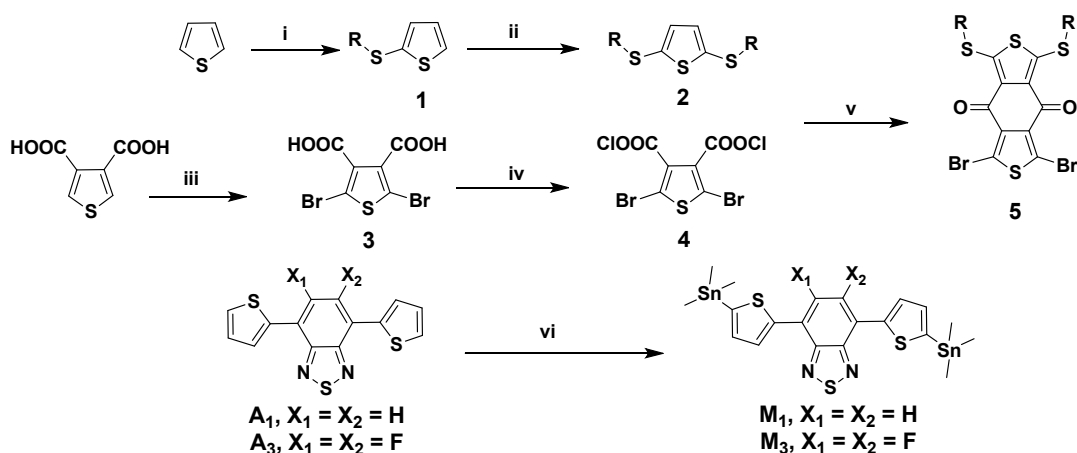
2.1 Device testing

The devices were characterized using Keithley 4200-SCS semiconductor parameter analyzer in the nitrogen environment. The threshold voltage (V_{th}) and field-effect mobility (μ) in the saturation region were determined from

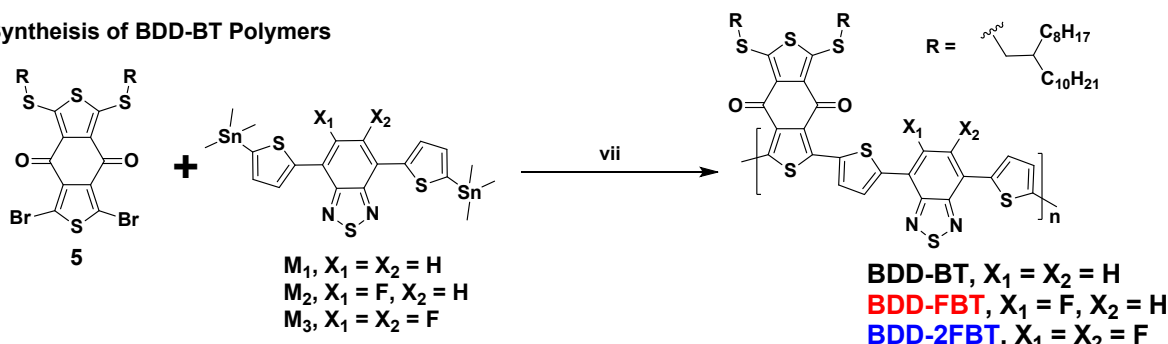
$$I_{DS} = (W / 2L) C_i \mu (V_{GS} - V_{th})^2$$

where I_{DS} is the current density between drain and source, V_{GS} is the voltage between gate and source, W and L are the channel width and length, respectively, and C_i is the capacitance of the insulator.

Synthesis of Monomer



Synthesis of BDD-BT Polymers



Scheme 1, reagents and conditions: (i) THF, sulphur powder, n-BuLi, -78 °C; (ii) THF, sulphur powder, n-BuLi, -78 °C, 50 °C, 2hr, overnight room temperature; (iii) acetic acid, Br₂, 50 °C; (iii) Oxalyl chloride, methylene chloride, ambient temperature; (iv) AlCl₃, methylene chloride, ambient temperature, then reflux for several hours; (v) DCM, AlCl₃, 0 °C; (vi) THF, n-BuLi, -78 °C, 2,2,2,6,6-tetramethylpiperidine (TMP); (vii) chlorobenzene using Pd(PPh₃)₄, 125°C, overnight.

2-((2-octyldodecyl)thio)thiophene (1)

Under N₂, n-butyllithium (2.5 M in hexane, 26.5 mL, 66.5 mmol) was added to a solution of thiophene (5 mL, 126.57 mmol) in dry THF (100 mL) at 0 °C. The mixture had been stirred at the same temperature for 1 h, and sulfur powder (4.45 g, 139.23 mmol) was added in one portion and then the suspension was stirred for another 2h. Subsequently, 9-(bromomethyl)nonadecane (25.2 g, 69.6 mmol) was added dropwise, and then the mixture was

stirred overnight at room temperature. The reaction was quenched through the addition of ice-cooled saturated aqueous NH_4Cl (50 mL). The organic phase was extracted into diethyl ether, washed with water, and dried (MgSO_4). The solvent was evaporated under reduced pressure and the residue was purified through distillation to afford a colorless oil (17.1 g, 68%). ^1H NMR (400 MHz, CDCl_3), δ (ppm): 7.30–7.28 (dd, 1H), 7.08–7.07 (dd, 1H), 6.95–6.93 (m, 1H), 2.80–2.79 (d, $J=2\text{H}$), 1.60–1.54 (m, 1H), 1.47–1.25 (m, 32H), 0.90–0.86 (t, $J=8.6\text{ Hz}$ 6H). ^{13}C NMR (100 MHz, CDCl_3): δ :138.57, 132.54, 43.93, 37.65, 32.80, 31.95, 31.93, 29.92, 29.70, 29.68, 29.65, 29.60, 29.39, 29.37, 26.46, 22.72,14.15.

2,5-bis((2-octyldodecyl)thio)thiophene (2)

In a flame-dried clean 250 mL round bottom flask, n-butyllithium (2.5 M in hexane, 18.9 mmol, 7.56 mL) was added dropwise into the solution of (1) (5.0 g, 12.6 mmol) in dry THF (50 ml) at 0 °C under N_2 for 1 hr. The mixture was stirred at 50 °C for 2 h, then cooled to -78 °C and keep for a few minutes. Subsequently, sulfur powder (0.48 g, 15.0 mmol) was added to the mixture and maintain the same temperature for 1 h, followed by the addition of 9-(bromomethyl)nonadecane (35.0 g, 25.1 mmol) was added and the mixture was stirred at 50 °C for 2 h and then room temperature for overnight. The mixture was extracted by ether, then dried over anhydrous MgSO_4 , and evaporated under reduced pressure, and then the crude product was purified by column chromatography on silica gel (hexane) to obtain **2** as a yellow viscous oil (7.5 g, yield 83%). ^1H NMR (400 MHz, CDCl_3): δ 6.90 (s, 1H), 2.79 (d, $J=8.4\text{ Hz}$, 4H), 1.60-1.55 (m, 2H), 1.39-1.25 (m, 64H), 0.89-0.86 (t, $J=8.8$, 12H). ^{13}C NMR (100 MHz, CDCl_3): δ :138.57, 132.54, 43.93, 37.65, 32.80, 31.95, 31.93, 29.92, 29.70, 29.68, 29.65, 29.60, 29.39, 29.37, 26.46, 22.72,14.15.

2,5-Dibromothiophene-3,4-dicarboxylic acid (3)

Br₂ (9.2) was added dropwise to a solution of thiophene-3,4-dicarboxylic acid (5 g, 29.1 mmol) and glacial acetic acid (50 mL) in the 250 ml round-bottomed flask. The mixture was stirred overnight at room temperature (RT). A saturated sodium bisulfate solution (about 750 gm was used) was added until the reddish color became yellowish. The precipitate was filtered and washed with each 100 mL of water and hexane to get an off-white solid and 5.8 g (yield: 61%). The product could use for the next step without any further purification.

2,5-Dibromothiophene-3,4-dicarboxylic acid chloride (4)

Under N₂, to a solution of compound 3 (1 gm, 3.0 mmol) in dry dichloromethane DCM (10 mL) at 0 °C, oxalyl chloride (2.0 mL) with DMF (1 drop) was slowly added. The mixture was stirred 30 min at 0 °C and then stirred at room temperature for overnight. The reaction mixture was evaporated by a rotatory evaporator under reduced pressure and under air protection to remove the solvent and other volatiles and further dried by the vacuum pump. The product was used for the next step without any further purification.

1,3-dibromo-5,7-bis((2-octyldodecyl)thio)benzo[1,2-c:4,5-c']dithiophene-4,8-dione (5):

To a stirred solution of the compound 4 (1.0 g, 2.5 mmol) and 2,5-bis((2-octyldodecyl)thio)thiophene (2) (1.6 g, 2.25 mmol) in dry 1,2-dichloroethane (20 ml), AlCl₃ (2.18 g, 10.0 mmol) was added in small portions at 0 °C. The mixture was allowed to stir at 0 °C for 30 min and then at room temperature for 6 h. The mixture was poured into the ice with 1 M hydrochloric acid (20 ml) and then extracted with DCM. The organic layer was collected then dried over anhydrous MgSO₄ and evaporated under reduced pressure. The crude product was purified by column chromatography on silica gel (hexane: DCM = 4:1) to obtain **5** as a pale yellow solid (0.72 g, 36%).

^1H NMR (400 MHz, CDCl_3) δ 3.06 (d, $J = 6$ Hz, 4H), 1.78-1.81 (m, 2H), 1.66 (m, 1H), 1.31-1.57 (m, 42 H), 1.31-1.51 (m, 22), 0.91-0.94 (m = 12H). ^{13}C NMR (100 MHz, CDCl_3) δ 173.22, 150.88, 134.27, 130.91, 119.64, 133.45, 133.26, 124.64, 120.90, 120.49, 41.46, 34.88, 32.31, 28.75, 25.53, 22.90, 14.08, 10.76. MALDI-TOF Calculated $m/z = 1000.3564$; found $m/z = 1000.3550$. Anal. calculated for $\text{C}_{50}\text{H}_{82}\text{Br}_2\text{O}_2\text{S}_4$, C, 59.86; H, 8.24; O, 3.19; S, 12.78. Found: C, 59.81; H, 8.20.

4,7-bis(5-(trimethylstannyl)thiophen-2-yl)benzo[c][1,2,5]thiadiazole (M1):

Monomer M1 was synthesized from previous reported procedures with 70 % yield.¹

^1H NMR (400 MHz, CDCl_3) δ : 8.17 (d, $J = 3.6$ Hz, 2H), 7.86 (s, 2H), 7.30 (d, $J = 3.6$ Hz, 2H), 0.44 (s, 18H). ^{13}C NMR (100 MHz, CDCl_3) δ : 152.48, 145.07, 140.27, 136.12, 128.40, 125.9, 125.8, -8.22. Anal. calcd for $\text{C}_{20}\text{H}_{22}\text{N}_2\text{S}_3\text{Sn}_2$: C, 38.37; H, 3.86; N, 4.47; S, 15.37. Found: C, 38.10; H, 3.78; N, 4.41.

5,6-difluoro-4,7-bis(5-(trimethylstannyl)thiophen-2-yl)benzo[c][1,2,5]thiadiazole (M3):

Monomer M3 was synthesized from previous reported procedures with 70 % yield.¹

^1H NMR (400 MHz, CDCl_3) δ : 8.31 (d, 2H, $J = 3.6$ Hz), 7.33 (d, 2H, $J = 3.6$ Hz), 0.45 (s, 18H). ^{13}C NMR (100 MHz, CDCl_3) δ : 150.88, 150.67, 148.97, 148.30, 142.59, 137.6, 131.43, 135.42, 111.63, -8.09. Anal. calcd for $\text{C}_{20}\text{H}_{22}\text{F}_2\text{N}_2\text{S}_3\text{Sn}_2$: C, 36.29; H, 3.35; N, 4.23; S, 14.53. Found C, 36.50; H, 3.27; N, 4.21.

General procedure for the synthesis of BDD-BT polymers (BDD-BT, BDD-FBT, and BDD-2FBT).

To a 20 ml clean and dry microwave vial were charged with compound 5 (0.150 mmol), monomer M1-M3 (0.150 mmol), and $\text{Pd}(\text{PPh}_3)_4$ (0.010 g, 0.01 mmol). The reaction was applied in three cycles vacuum and purge N_2 for and then added chlorobenzene (5 mL) followed by

125 °C for overnight. After cooling to room temperature, the reaction mixture was dropwise into a mixture of hydrochloric acid (1N, 10 mL) and methanol (200 mL). The polymer precipitate was by filtered through a thimble and purified with Soxhlet extraction using methanol 24 hr, acetone, hexane, dichloromethane, and chlorobenzene. The chlorobenzene soluble fraction was concentrated and reprecipitated into methanol, filtered, and dried under a vacuum to achieve the desired polymers as a dark purple solid.

BDD-BT: Using compound 5 = 150.4 mg and monomer M1 = 93.9 mg, Yield = 131 mg, 74%; GPC: $M_n = 38.0$ kDa, $\bar{D} = 1.8$; UV-Vis: $\lambda_{\max} = 629$ nm (dilute chlorobenzene solution), $\lambda_{\max} = 628, 684$ nm (solid film).

BDD-FBT: Using compound 5 = 150.4 mg and monomer M2 = 96.6 mg, Yield 121 mg, 67%; GPC: $M_n = 35$ kDa, $\bar{D} = 2.1$; UV-Vis: $\lambda_{\max} = 596$ nm (dilute chlorobenzene solution), $\lambda_{\max} = 612, 671$ nm (solid film).

BDD-2FBT: Using compound 5 = 150.4 mg and monomer M3 = 99.3 mg, Yield 138 mg; 76%; GPC: $M_n = 30$ kDa, $\bar{D} = 2.5$; UV-Vis: $\lambda_{\max} = 608, 662$ nm (dilute chlorobenzene solution), $\lambda_{\max} = 605, 659$ nm (solid film).

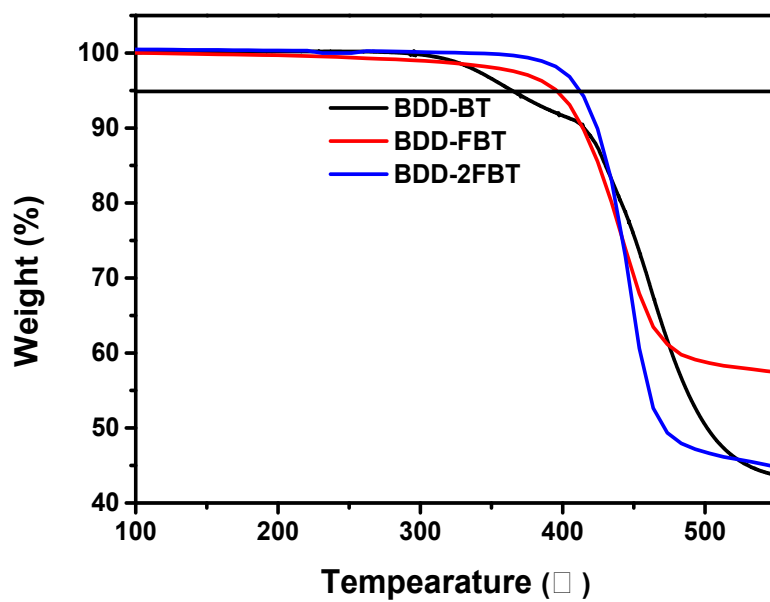


Figure S1. TGA thermograms of copolymers **BDD-DPPOD**, **BDD-DPPEH**, **BDDTH-DPPOD**, and **BDDTH-DPPEH** under nitrogen flow at $10\text{ }^{\circ}\text{C min}^{-1}$.

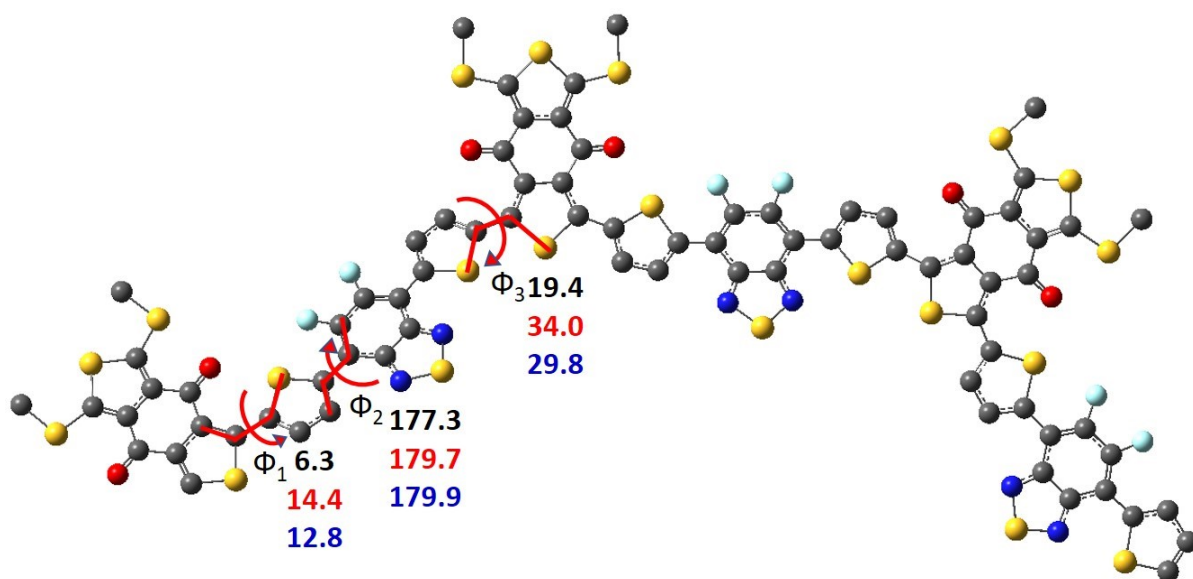


Figure S2. Dihedral angles of the optimized geometries of BDD-BT (black), BDD-FBT (red), and BDD-2FBT (blue) trimers. The dihedral angles between the planes of BDD and thiophene (intra-chain), BT and thiophene, and BDD-thiophene (inter-chain) are defined by Φ_1 , Φ_2 , and Φ_3 , respectively. The BT-moiety as well as its two adjacent thiophene units remain planar in each monomer of the trimeric structure, while the BDD-moiety does not exhibit planarity.

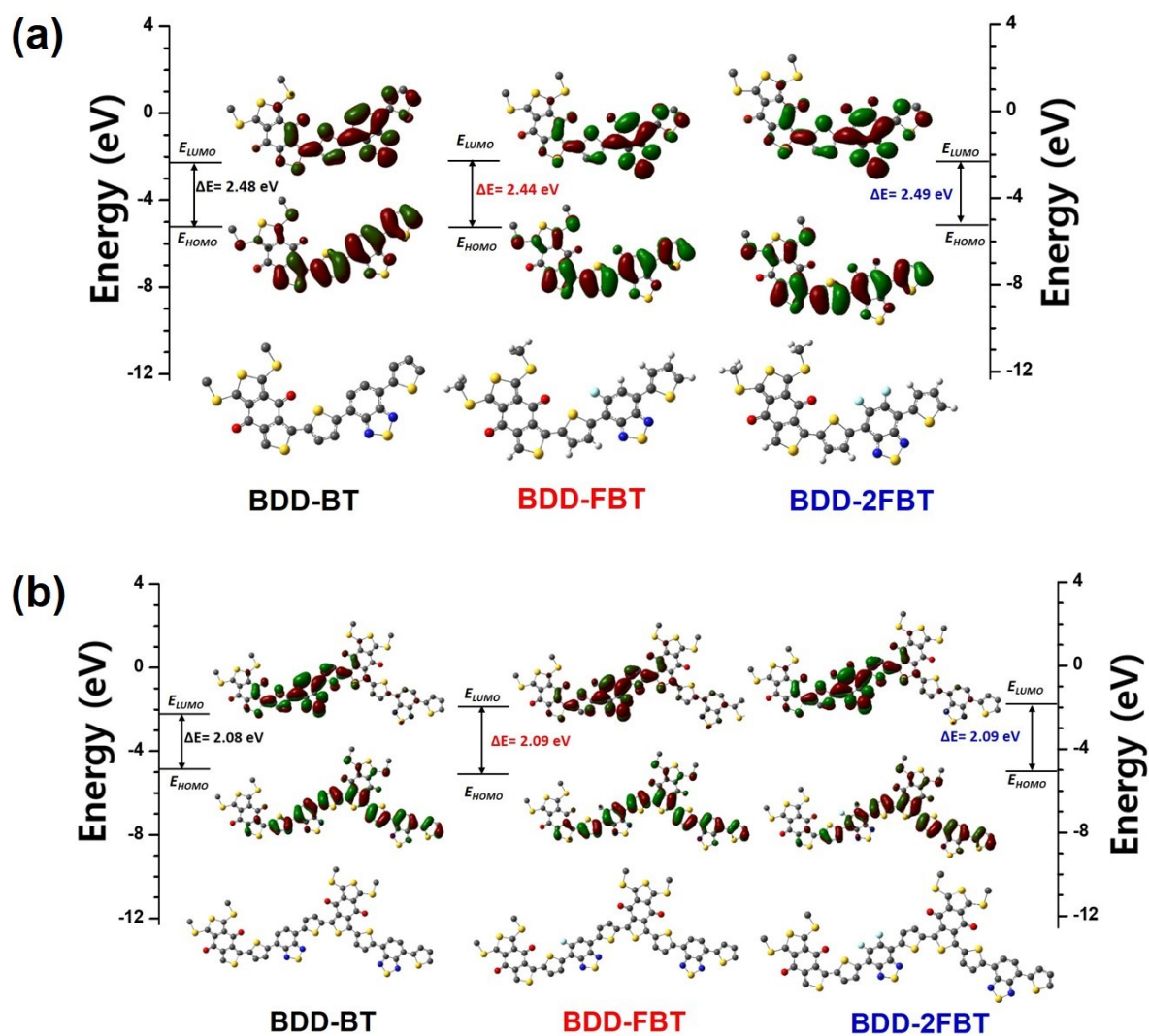


Figure S3. The HOMO-LUMO energy diagram of the (a) monomeric and (b) dimeric units of BDD-BT, BDD-FBT, and BDD-2FBT moieties. The optimized structures as well as the calculated HOMO, LUMO energy levels, and the HOMO-LUMO energy gaps (in the units of eV) are shown in the figure.

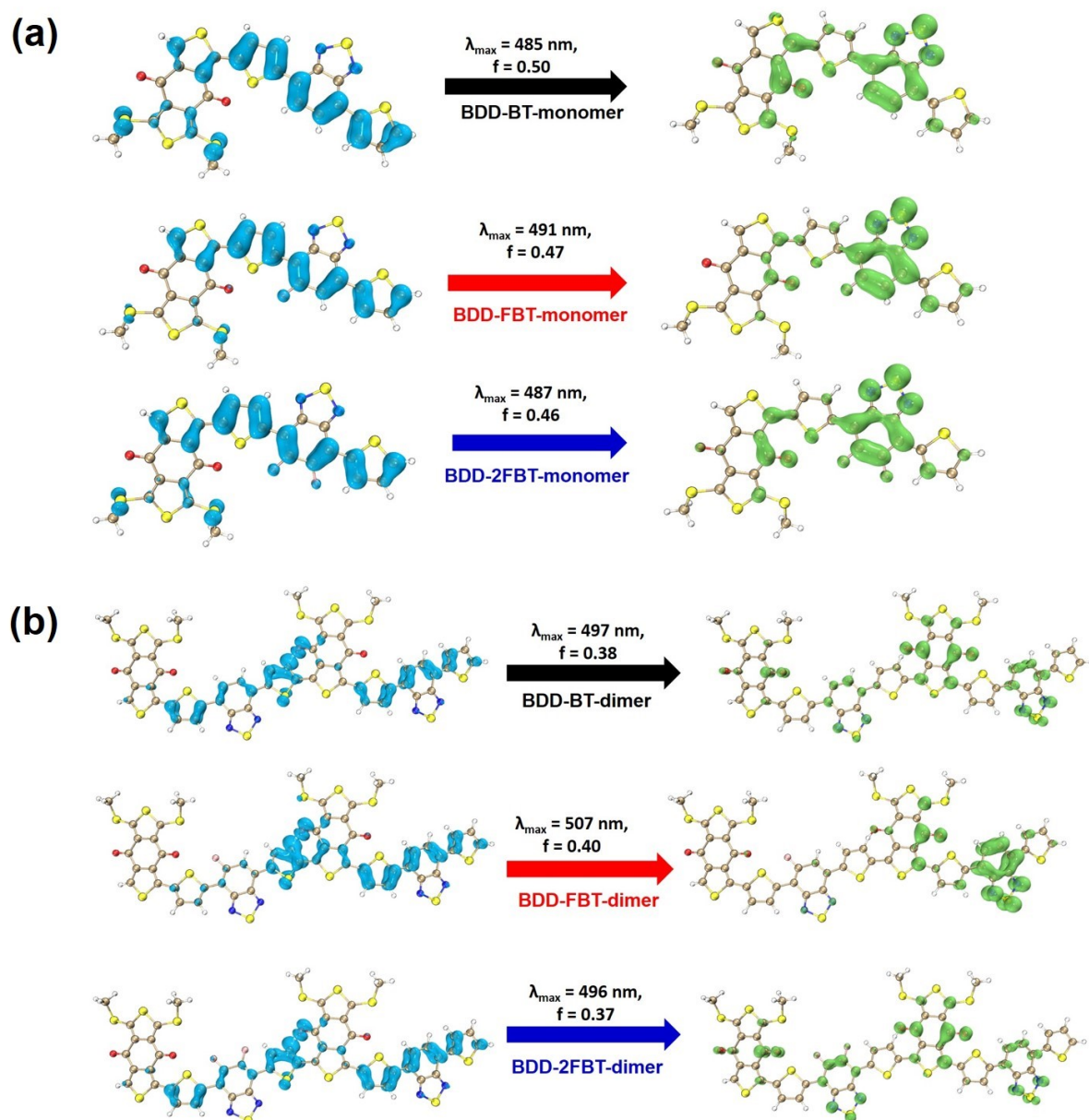


Figure S4. Natural transition orbitals (NTO) correspond to the characteristic UV-Vis absorption in the (a) monomeric and (b) dimeric BDD-BT, BDD-FBT, and BDD-2FBT systems. For each NTO, the hole and electron orbitals are given in left and right, respectively. The transition wavelength (λ_{\max}) and oscillator strength (f) for each transition is denoted.

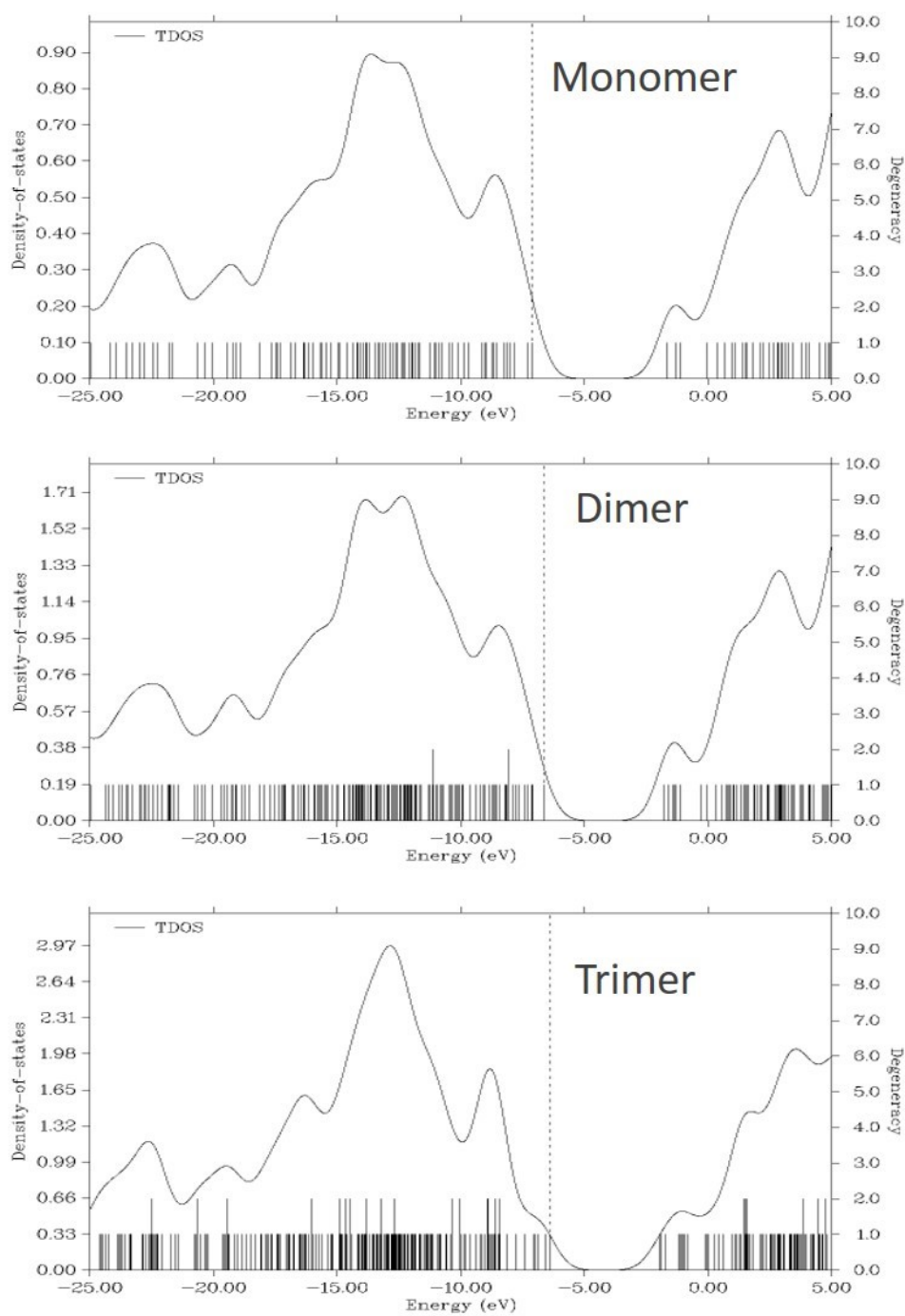


Figure S5. The density of states (DOS) is plotted against the orbital energies (eV) of the monomer (upper panel), dimer (middle panel), and trimer (lower panel) of BDD-2FBT moiety.

The vertical dashed line represents the HOMO energy level. The increased density of states of the trimer near the HOMO and LUMO energy levels of BDD-2FBT is indicative of the formation of a band structure.

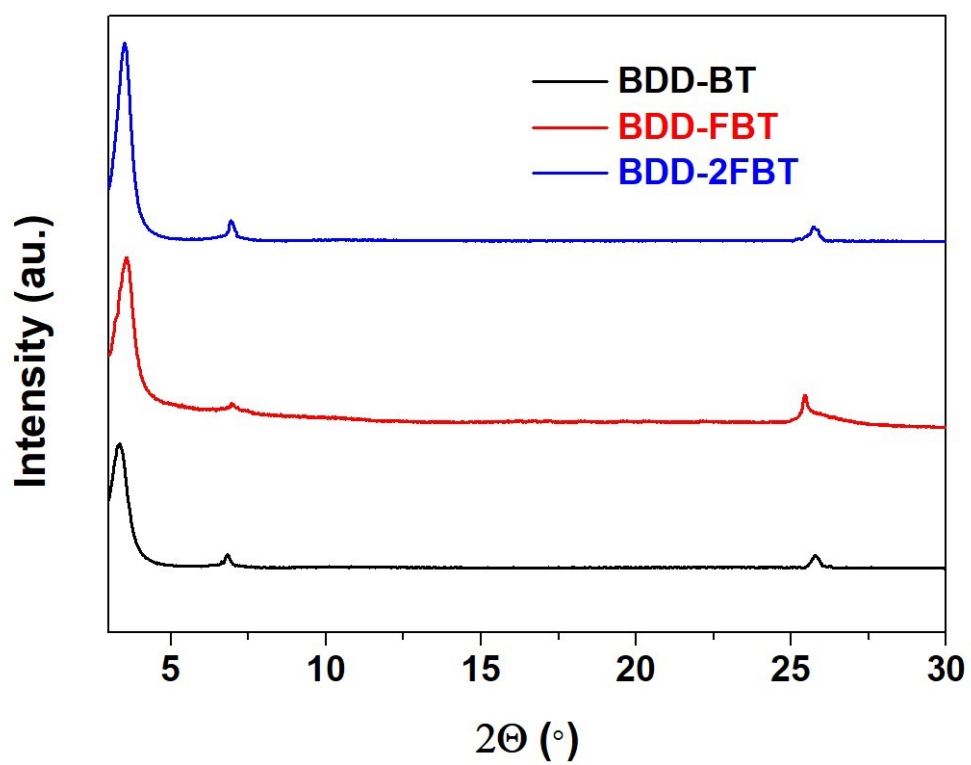


Figure S6. X-ray diffraction profiles of the BDD-BT-based polymer films spin coated on glass surfaces and annealed at 160 °C.

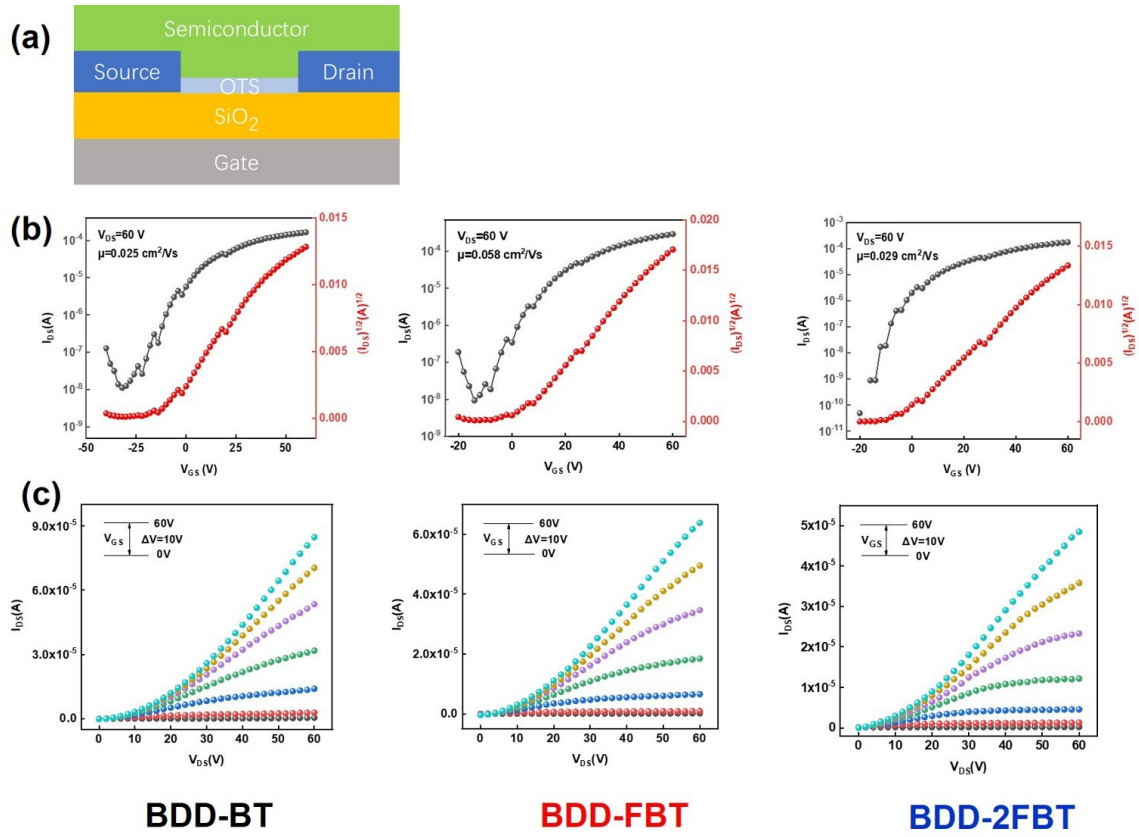


Figure S7. Transfer and output characteristics of the best OTFT devices with bottom-gate bottom-contact (BG-BC) geometry using BDD-BT, BDD-FBT, and BDD-2FBT (b) Transfer characteristics and (c) output characteristics of BDD-BT, BDD-FBT, and BDD-2FBT.

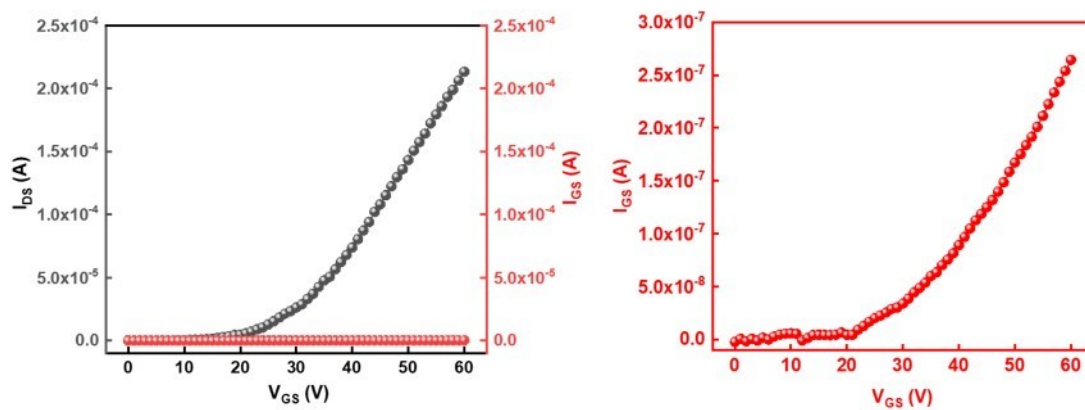


Figure S8 leakage current of the BDD-2FBT-based device and compared the leakage current with the transfer curve.

Table S1. The HOMO-LUMO gap (eV) for monomer, dimer, and trimer of BDD-BT and its fluorine substituted forms.

Polymers	Monomer (eV)	Dimer	Trimer
BDD-BT	2.48	2.08	1.86
BDD-FBT	2.44	2.09	1.99
BDD-2FBT	2.49	2.09	2.02

Table S2. The absorption maxima (λ_{max}) corresponds to the characteristic UV-Vis absorption calculated from the TD-DFT method for monomer, dimer, and trimer of BDD-BT and its fluorine substituted forms.

Polymers	Monomer (nm)	Dimer	Trimer
BDD-BT	485-368 nm	600-470 nm	616-571 nm
BDD-FBT	491-436 nm	597-466 nm	603-499 nm
BDD-2FBT	486-438 nm	608-465 nm	609-510 nm

Table S3. Parameters of field-effect transistor devices based on copolymers BDD-BT, BDD-FBT, and BDD-2FBT.

Material	Method ^a	Mobility (cm ² v ⁻¹ s ⁻¹) ^b		V _{Th} (V)		On/Off Ratio
		N-	P-	N-	P-	
BDD-BT	As cast	7.3 x10 ⁻³	1.57 x10 ⁻⁵	20.12	70.23	10 ²
	80 °C	1.43x10 ⁻²	5.57 x10 ⁻⁵	15.51	6.99	10 ²
	120 °C	2.53x10 ⁻²	2.40 x10 ⁻⁵	21.10	21.95	10 ³
	160 °C	2.40x10⁻²	3.06 x10⁻⁵	3.85	39.77	10⁴
	200 °C	1.8 x10 ⁻²	-	14.65	-	10 ⁵
BDD-FBT	As cast	2.39 x10 ⁻³	3.05x10 ⁻⁵	10.23	-17.23	10 ³
	80 °C	6.27 x10 ⁻³	0.1x10 ⁻³	16.46	-12.86	10 ³
	120 °C	1.20 x10 ⁻²	0.13x10 ⁻³	11.7	-20.1	10 ³
	160 °C	2.66 x10⁻²	-	18.09	-	10⁴
	200 °C	1.72 x10 ⁻²	-	15.84	-	10 ⁵
BDD-2FBT	As cast	1.26 x10 ⁻³	-	5.24	-	10 ⁵
	80 °C	2.60 x10 ⁻²	-	10.70	-	10 ⁷
	120 °C	5.78 x10 ⁻²	-	15.17	-	10 ⁷
	160 °C	8.38 x10⁻²	-	9.91	-	10⁶
	200 °C	5.20 x10 ⁻²	-	10.89	-	10 ⁶

^aMethodology used in the film fabrication, as-cast or annealed at 120 or 160 or 180 or 200 °C for 15 min. ^bDetermined from the following equation in the saturation region; $I_{DS} = (W / 2L) C_i \mu (V_{GS} - V_{th})^2$

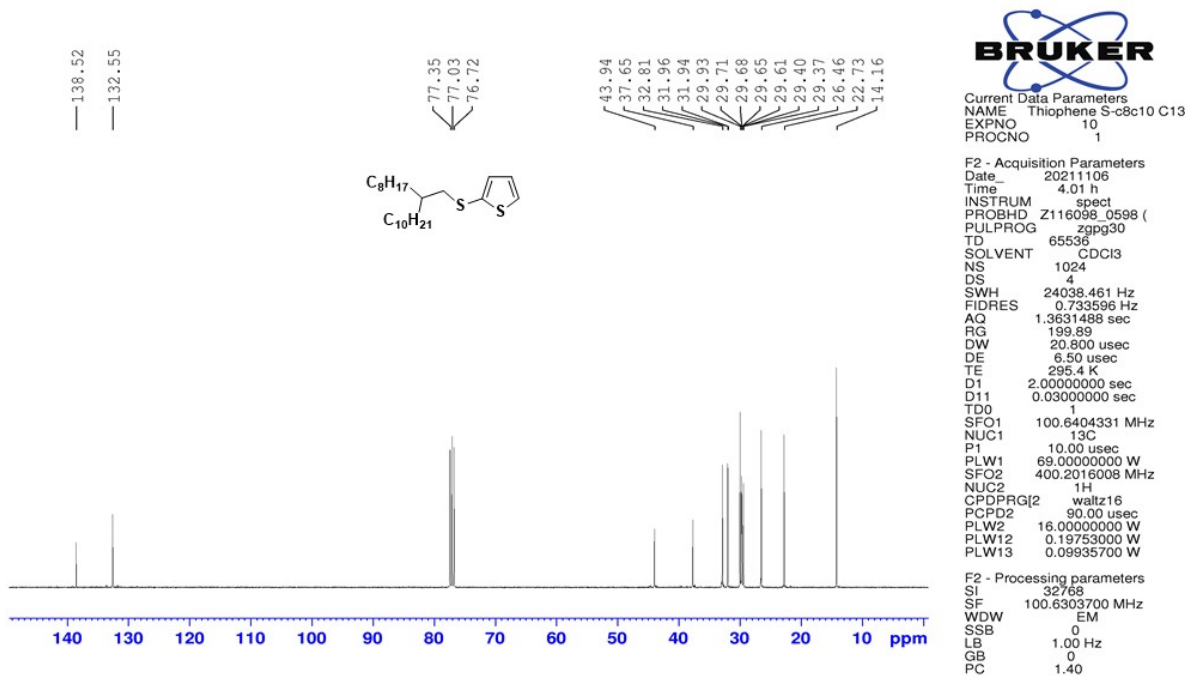
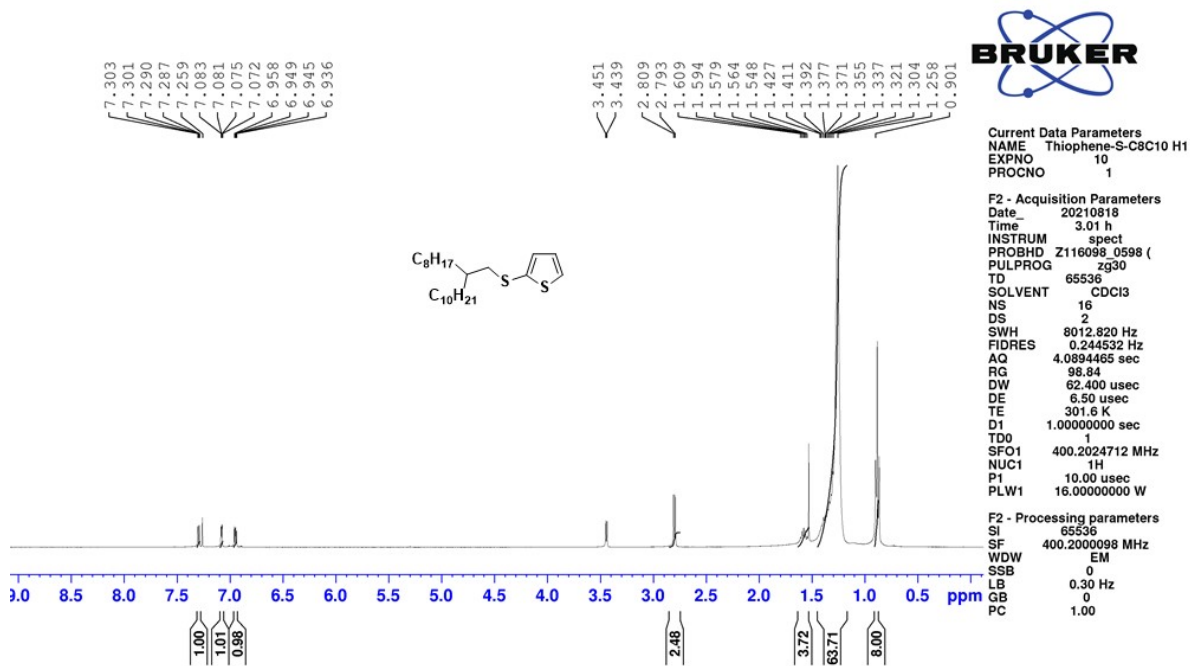
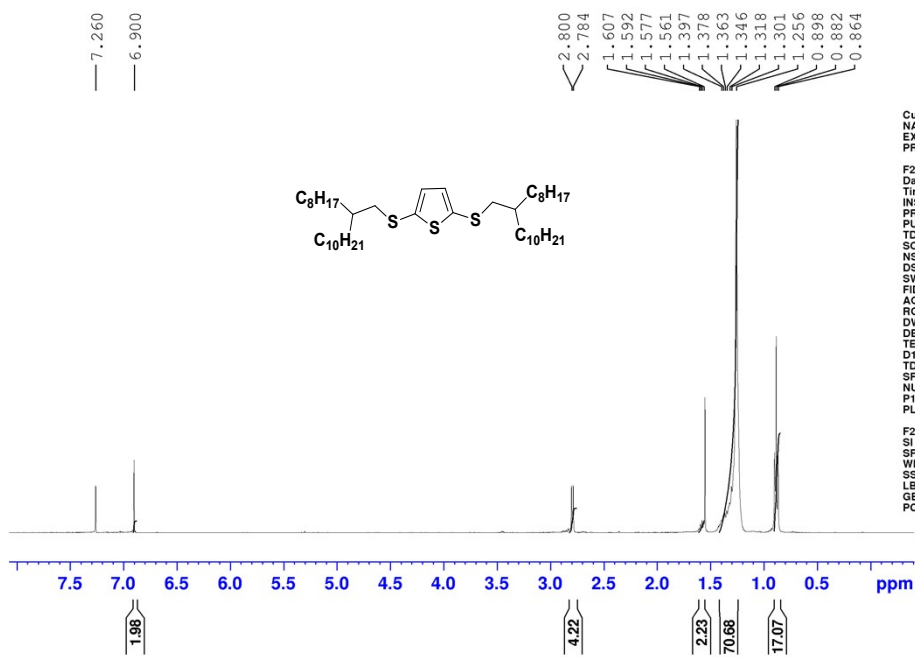


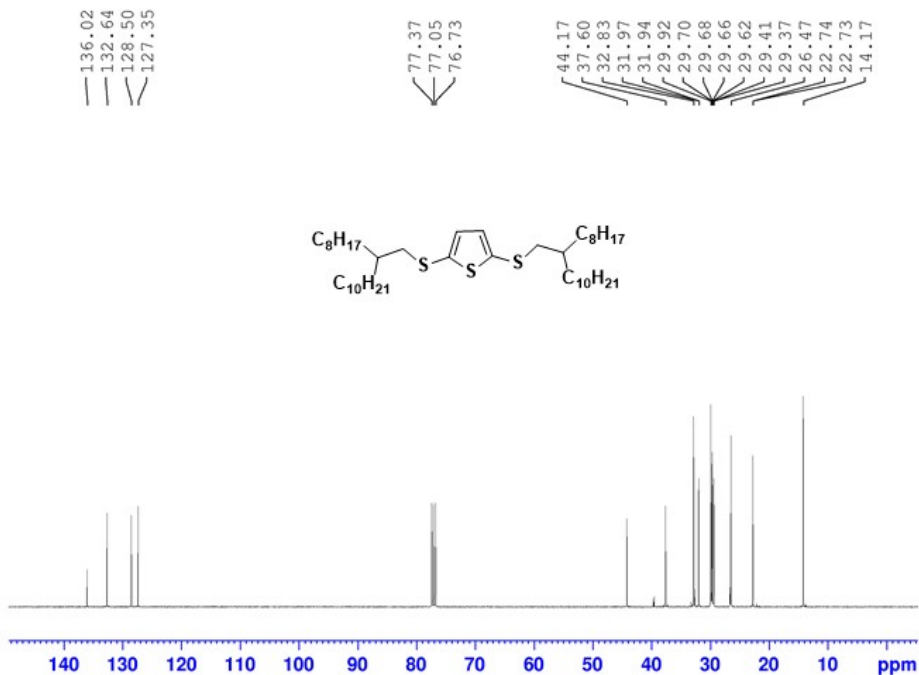
Figure S9. ¹H and ¹³C Spectra of compound 1.



Current Data Parameters
 NAME Thiophene S-C8C10 two side H1
 EXPNO 10
 PROCNO 1

F2 - Acquisition Parameters
 Date 20211103
 Time 22.21 h
 INSTRUM spect
 PROBHD Z116098_0598 ()
 PULPROG zg30
 TD 65536
 SOLVENT CDCl3
 NS 16
 DS 2
 SWH 8012.820 Hz
 FIDRES 0.244532 Hz
 AQ 4.0894465 sec
 RG 128.25
 DW 82.400 usec
 DE 6.50 usec
 TE 294.7 K
 D1 1.00000000 sec
 TD0
 SFO1 400.2024712 MHz
 NUC1 1H
 P1 10.00 usec
 PLW1 16.00000000 W

F2 - Processing parameters
 SI 65536
 SF 400.2000095 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00



Current Data Parameters
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 EXPNO 10
 PROCNO 1

F2 - Acquisition Parameters
 Date 20211106
 Time 6.33 h
 INSTRUM spect
 PROBHD Z116098_0598 ()
 PULPROG zgpg30
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 SOLVENT CDCl3
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 DS 4
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 FIDRES 0.733596 Hz
 AQ 1.3631488 sec
 RG 199.89
 DW 20.800 usec
 DE 6.50 usec
 TE 295.2 K
 D1 2.00000000 sec
 D11 0.03000000 sec
 TD0 1
 SFO1 100.6404331 MHz
 NUC1 13C
 P1 10.00 usec
 PLW1 69.00000000 W
 SFO2 400.2016008 MHz
 NUC2 1H
 CPDPRG[2] waltz16
 PCPD2 90.00 usec
 PLW2 16.00000000 W
 PLW12 0.19753000 W
 PLW13 0.09935700 W

F2 - Processing parameters
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 SF 100.6303700 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40

Figure S10. ¹H and ¹³C Spectra of compound 2.

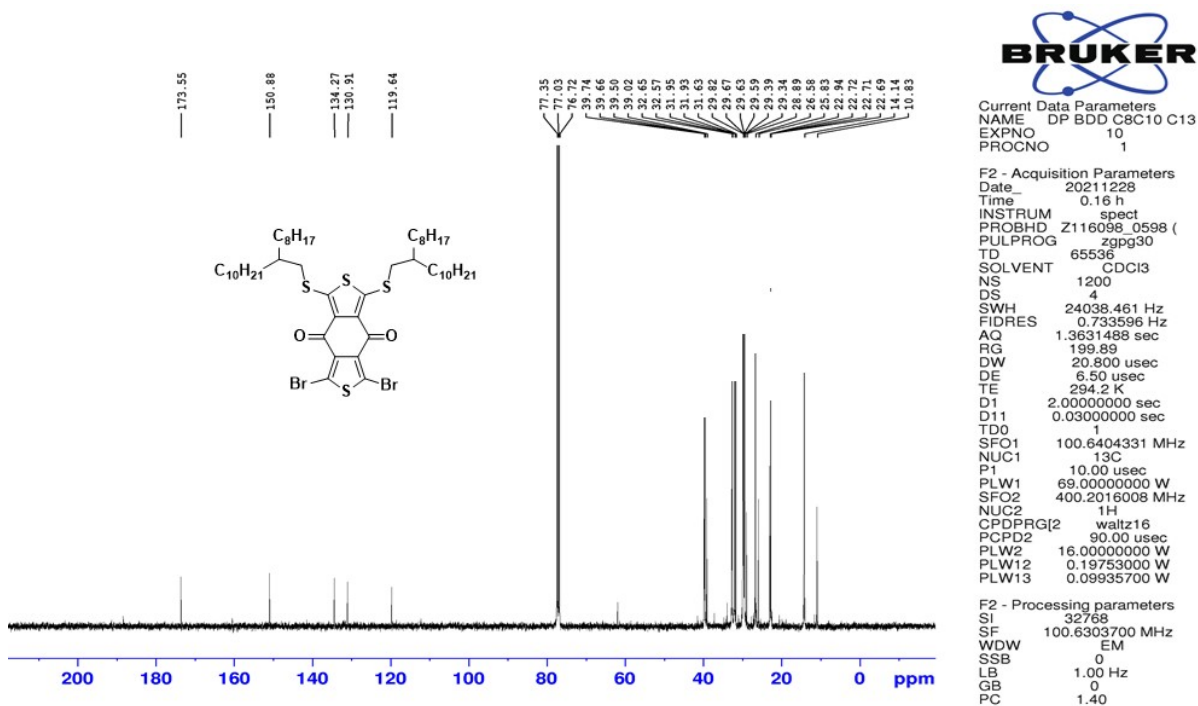
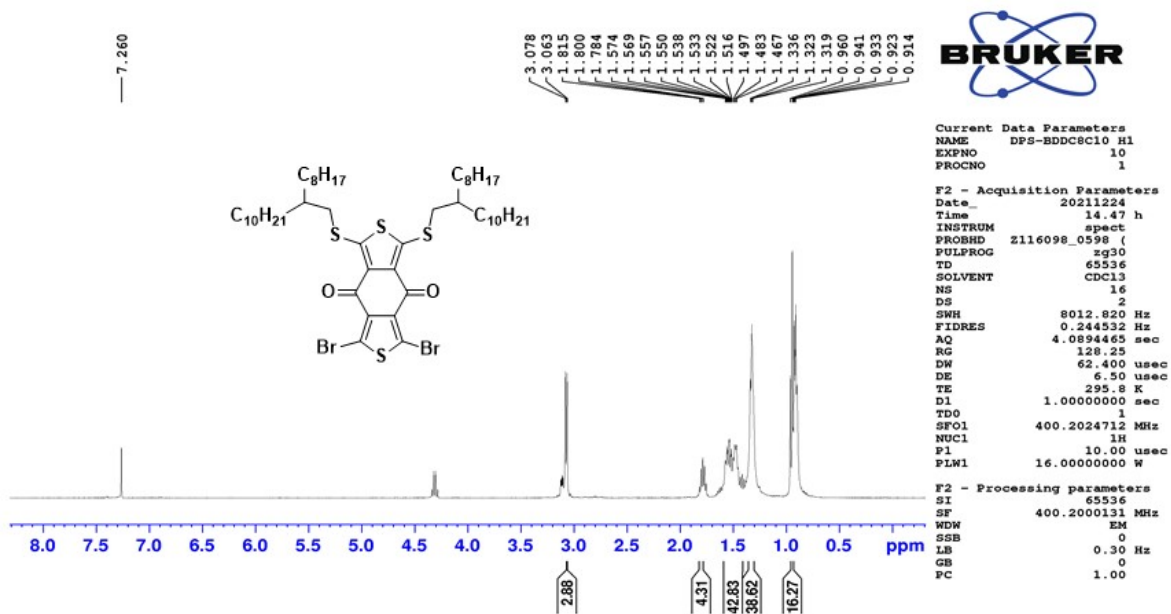


Figure S11. ^1H and ^{13}C Spectra of compound 5.

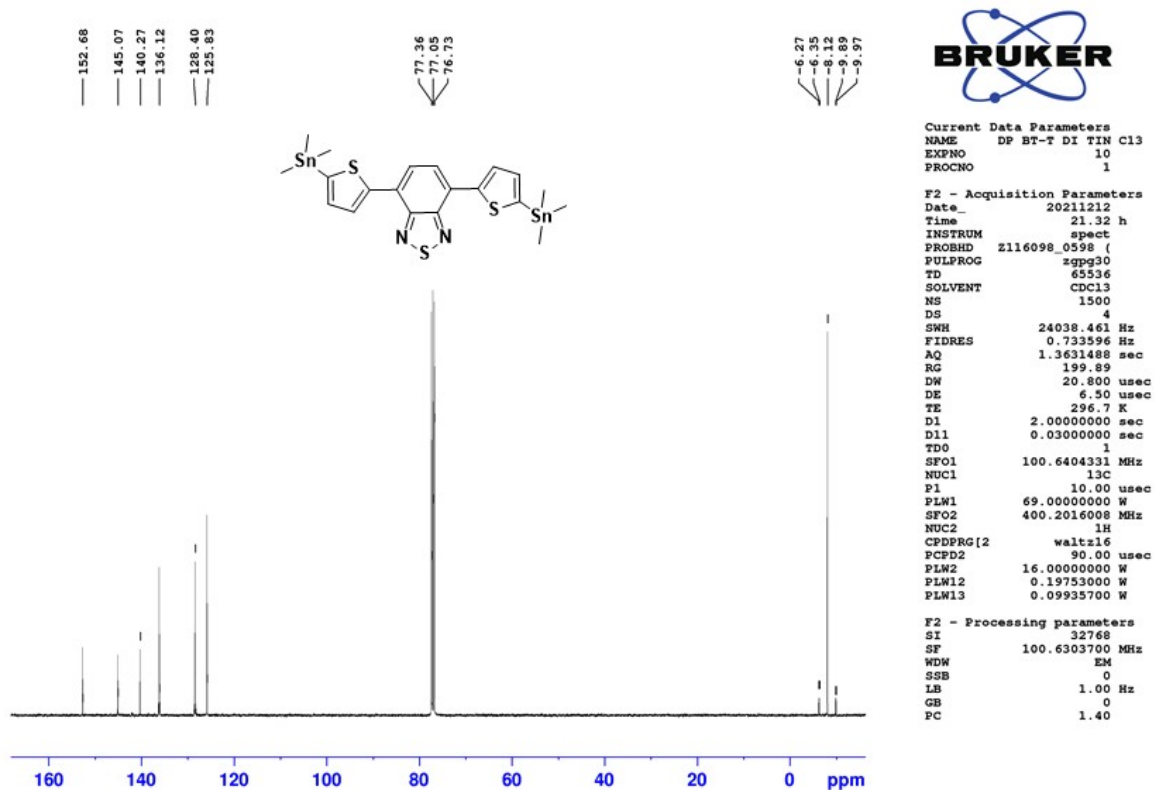
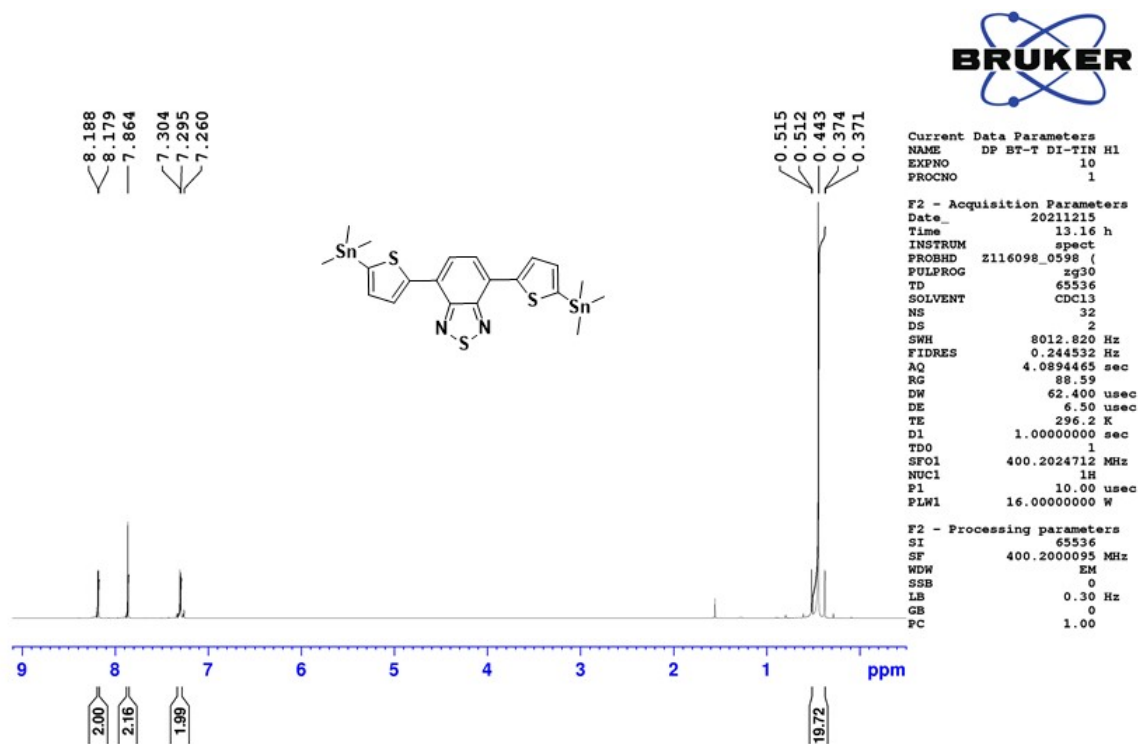
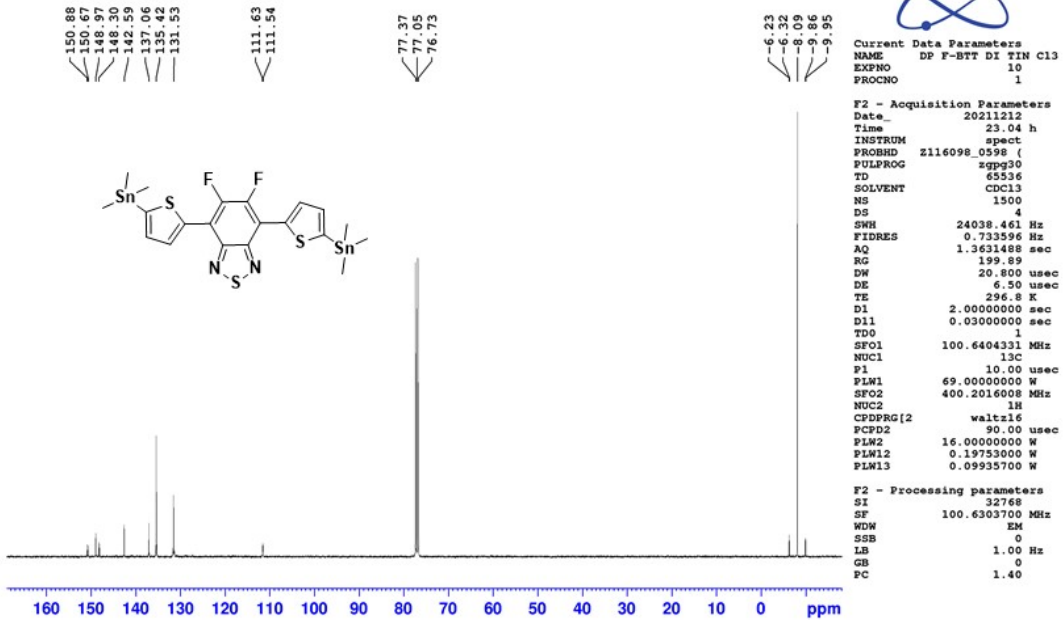
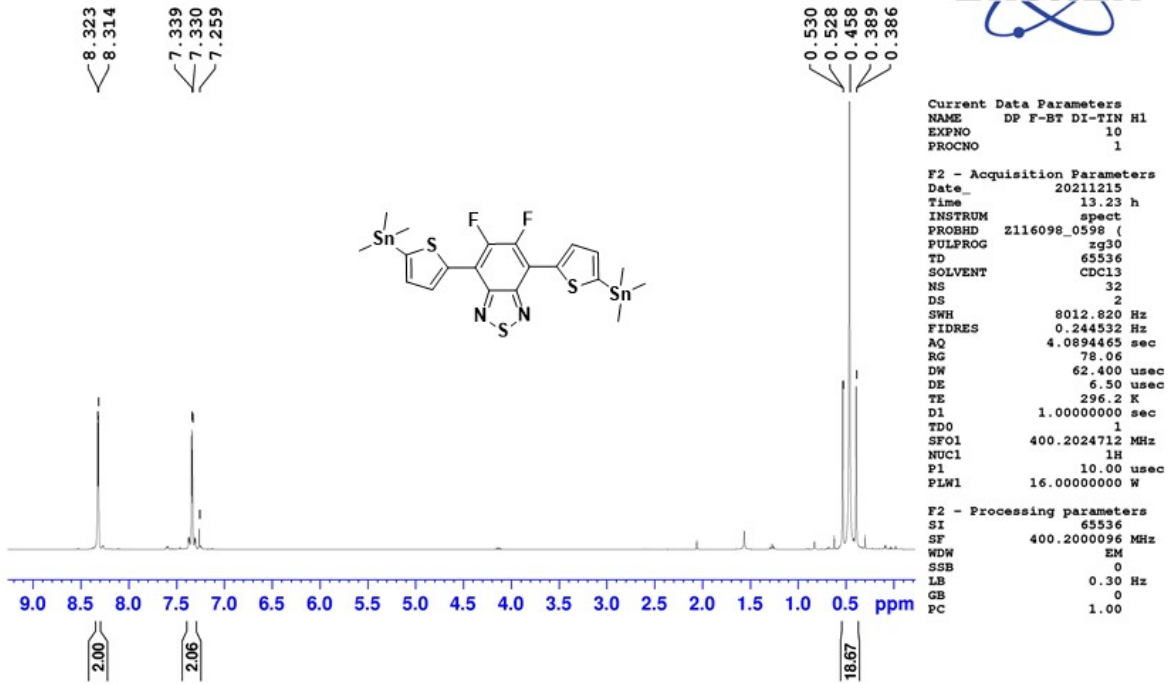


Figure S12. ^1H and ^{13}C Spectra of Monomer M1.



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Figure S13. ^1H and ^{13}C Spectra of Monomer M3.

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