

Supporting Information

Effect of thiophene/furan substitutions on organic field effect transistor properties of arylthiadiazole based organic semiconductors

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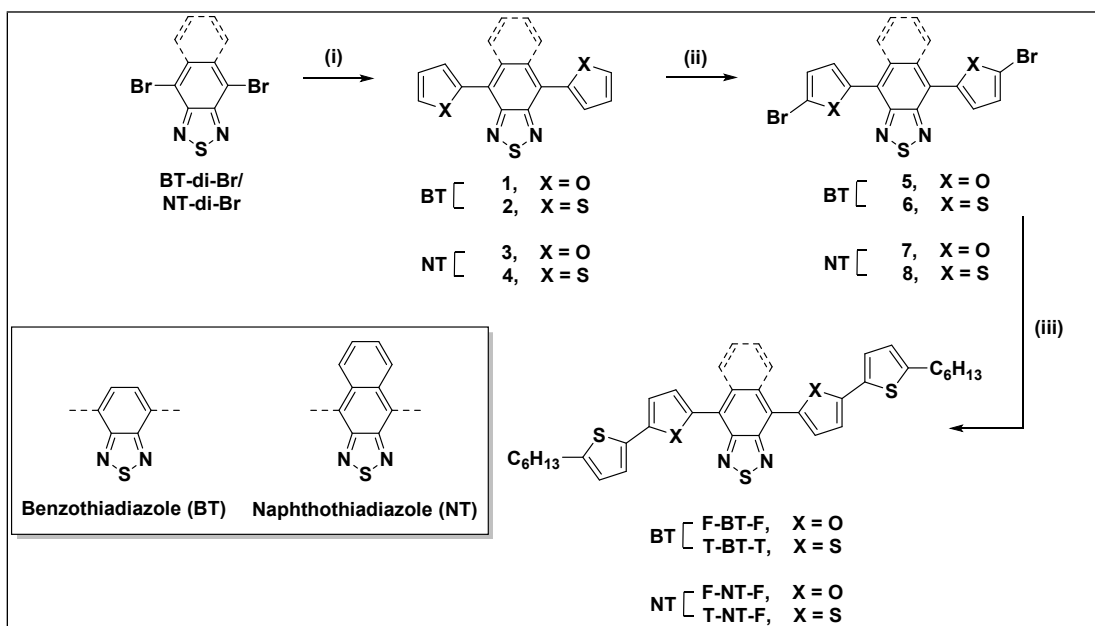
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Material Synthesis and Characterizations:



Scheme S1. Synthesis route to **F-BT-F**, **T-BT-T**, **F-NT-F**, and **T-NT-T**. Reagents and conditions: (i) 2-thiophene boronic acid or 2-furyl boronic acid, Pd(PPh₃)₄, 2M Na₂CO₃, THF, 65 °C, 24 h. (ii) N-bromosuccinimide (NBS) in THF, RT, 12 h. (iii) 5-hexyl-2-thiophene boronic acid pinacol ester, Pd(PPh₃)₄, 2M Na₂CO₃, THF, 65 °C, 24 h.

Synthesis of 1: **BT-di-Br** (500 mg, 1.7 mmol), 2-furylboronic acid (475 mg, 4.3 mmol), Pd(PPh₃)₄ (98 mg, 0.08 mmol), and 2M Na₂CO₃ (30 mL) were added into a 250 mL round-bottom flask. THF (30 mL) was added as a solvent then the mixture was stirred and degassed with N₂ for 5 min. The mixture was stirred at reflux under N₂ for 24 h. After cooling, the mixture was extracted with dichloromethane (80 mL x 2).

The combined organic phase was washed with water (80 mL), brine solution (80 mL), dried over anhydrous Na₂SO₄, filtered and evaporated to dryness. To obtain a product of higher purity, the residue was further purified by silica column chromatography eluting with mixture of dichloromethane and hexane (1:6) to obtain orange solid (76.8%). ¹H NMR (600 MHz, CDCl₃) δ ppm: 8.07 (s, 2H), 7.71 (d, *J* = 2.70 Hz, 2H), 7.61 (s, 2H), 6.65 (t, *J* = 1.32 Hz, 2H); ¹³C NMR (151 MHz, CDCl₃) δ 151.36, 150.17, 142.81, 123.54, 121.83, 112.48, 112.16; HRMS (APCI): calcd. for C₁₄H₈N₂O₂S [M + H]⁺ 269.0385; found 268.9409.

Synthesis of 2: BT-di-Br (500 mg, 1.7 mmol), 2-thiophene boronic acid (543 mg, 4.3 mmol), Pd(PPh₃)₄ (98 mg, 0.08 mmol), and 2M Na₂CO₃ (30 mL) were added into a 250 mL round-bottom flask. THF (30 mL) was added as a solvent then the mixture was stirred and degassed with N₂ for 5 min. The mixture was stirred at reflux under N₂ for 24 h. After cooling, the mixture was extracted with dichloromethane (80 mL x 2). The combined organic phase was washed with water (80 mL), brine solution (80 mL), dried over anhydrous Na₂SO₄, filtered and evaporated to dryness. The residue was further purified by silica column chromatography eluting with mixture of dichloromethane and hexane (1:5) to obtain orange solid (86.8%). ¹H NMR (600 MHz, CDCl₃) δ ppm: 8.12 (d, *J* = 2.88 Hz, 2H), 7.87 (s, 2H), 7.45 (d, *J* = 4.86 Hz, 2H), 7.25 (s, 2H), 7.21 (t, *J* = 4.08 Hz, 2H); ¹³C NMR (151 MHz, CDCl₃) δ 152.68, 139.37, 128.01, 127.53, 126.80, 126.05, 125.81; HRMS (APCI): calcd. for C₁₄H₈N₂S₃ [M + H]⁺ 300.9928; found 300.8940.

Synthesis of 3: NT-di-Br (200 mg, 0.58 mmol), 2-furyl boronic acid (143 mg, 1.28 mmol), Pd(PPh₃)₄ (34 mg, 0.03 mmol), and 2M Na₂CO₃ (4.37 mL) were added into a 100 mL round-bottom flask. THF (25 mL) was added as a solvent then the mixture was stirred and degassed with N₂ for 5 min. The mixture was stirred at reflux under N₂ for 24 h. After cooling, the mixture was extracted with dichloromethane (70 mL x 2). The combined organic phase was washed with water (70 mL), brine solution (70 mL), dried over anhydrous Na₂SO₄, filtered and evaporated to dryness. The residue was further purified by silica column chromatography eluting with mixture of dichloromethane and hexane (1:2.5) to obtain purple solid (60.3%). ¹H NMR (600 MHz, CDCl₃) δ ppm: 8.61 (dd, *J* = 7.14 Hz, 2.88 Hz, 2H), 7.81 (2, 2H), 7.48 (dd, *J* = 7.2 Hz, 2.82 Hz, 2H), 7.35 (d, *J* = 2.64 Hz, 2H), 6.77 (s, 2H); ¹³C NMR (151 MHz, CDCl₃) δ 150.71, 149.84, 143.59, 131.75, 127.39, 127.03, 119.24, 114.97, 111.93; HRMS (APCI): calcd. for C₁₈H₁₀N₂O₂S [M + H]⁺ 319.0541; found 319.0620.

Synthesis of 4: NT-di-Br (200 mg, 0.58 mmol), 2-thiophene boronic acid (164 mg, 1.28 mmol), Pd(PPh₃)₄ (34 mg, 0.03 mmol), and 2M Na₂CO₃ (4.37 mL) were added into a 100 mL round-bottom flask. THF (25 mL) was added as a solvent then the mixture was stirred and degassed with N₂ for 5 min. The mixture was stirred at reflux under N₂ for 24 h. After cooling, the mixture was extracted with dichloromethane (70 mL x 2). The combined organic phase was washed with water (70 mL), brine solution (70 mL), dried over anhydrous Na₂SO₄, filtered and evaporated to dryness. The residue was further purified by silica column chromatography eluting with mixture of dichloromethane and hexane (1:2.5) to obtain dark purple solid (80.3%). ¹H NMR (600 MHz, CDCl₃) δ ppm: 8.30 (dd, *J* = 6.9 Hz, 3.0 Hz, 2H), 7.68 (dd, *J* = 6.9 Hz, 3.0 Hz, 2H), 7.47 (dd, *J* = 3.6 Hz, 1.2 Hz, 2H), 7.43 (dd, *J* = 6.9 Hz, 3.0 Hz, 2H), 7.34 (dd, *J* = 5.1 Hz, 3.3 Hz, 2H); ¹³C NMR (151 MHz, CDCl₃) δ 151.73, 136.41, 132.99, 130.45, 127.91, 127.26, 127.00, 126.97, 123.58; HRMS (APCI): calcd. for C₁₈H₁₀N₂S₃ [M + H]⁺ 351.0084; found 351.0134.

Synthesis of 5: 1 (200 mg, 0.75 mmol) was added into a 100 mL round bottom flask. THF (15 mL) was added as solvent. NBS (332 mg, 1.86 mmol) was added to the reaction. The reaction was stirred under N₂ atmosphere for 12 h. After completing, sodium thiosulphate was added to the mixture to remove excess bromine. The reaction was extracted with dichloromethane (50 mL x 2). The combined organic phase was washed with water (50 mL x 3), dried over anhydrous Na₂SO₄, filtered, and evaporated to dryness. To

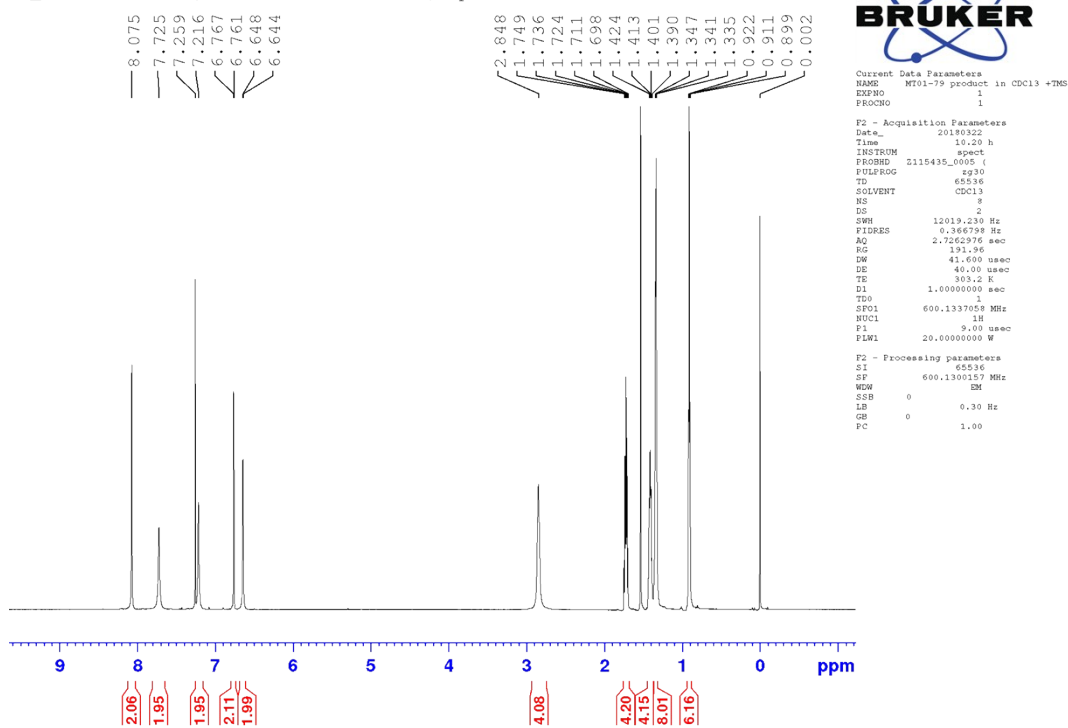
obtain a product with higher purity, the residue was further purified by column chromatography eluting with mixture of dichloromethane and hexane (1:3) to obtain yellow solid (41.1%). ^1H NMR (600 MHz, CDCl_3) δ ppm: 7.92 (s, 2H), 7.57 (s, 2H), 6.47 (s, 2H); ^{13}C NMR (151 MHz, CDCl_3) δ ppm: 152.02, 150.80, 123.37, 123.24, 120.95, 114.80, 114.36; HRMS (APCI): calcd. for $\text{C}_{14}\text{H}_6\text{Br}_2\text{N}_2\text{O}_2\text{S}$ [$\text{M} + \text{H}$] $^+$ 426.8575; found 426.7498.

Synthesis of 6: 2 (100 mg, 0.33 mmol) was added into a 50 mL round bottom flask. THF (10 mL) was added as a solvent. NBS (147 mg, 0.83 mmol) was added to the reaction. The reaction was stirred under N_2 atmosphere for 12 h. After completing, excess bromine was removed by sodium thiosulphate then the reaction was extracted with dichloromethane (70 mL x 2). The combined organic phase was washed with water (70 mL x 2), dried over anhydrous Na_2SO_4 , filtered, and evaporated to dryness. To obtain a product with higher purity, the residue was further purified by column chromatography eluting with mixture of dichloromethane and hexane (1:5) to obtain orange solid (63.6%). ^1H NMR (600 MHz, CDCl_3) δ ppm: 7.92 (d, $J = 3.84$, 2H), 7.71 (s, 2H), 7.08 (d, $J = 3.84$, 2H); ^{13}C NMR (151 MHz, CDCl_3) δ ppm: 152.30, 140.65, 130.81, 127.37, 125.43, 125.12, 114.80; HRMS (APCI): calcd. for $\text{C}_{14}\text{H}_6\text{Br}_2\text{N}_2\text{S}_3$ [$\text{M} + \text{H}$] $^+$ 458.8039; found 458.6950.

Synthesis of 7: 3 (111 mg, 0.35 mmol) was added into a 100 mL round bottom flask. THF (15 mL) was added as solvent. NBS (155 mg, 0.87 mmol) was added to the reaction. The reaction was stirred under N_2 atmosphere for 12 h. After completing, sodium thiosulphate was added to remove excess bromine then the reaction was extracted with dichloromethane (50 mL x 2). The combined organic phase was washed with water (50 mL x 3), dried over anhydrous Na_2SO_4 , filtered, and evaporated to dryness. The residue was further purified by column chromatography eluting with mixture of dichloromethane and hexane (1:4) to obtain purple solid (46.9%). ^1H NMR (600 MHz, CDCl_3) δ ppm: 8.52 (dd, $J = 6.90$ Hz, 2.76 Hz, 2H), 7.45 (dd, $J = 7.14$ Hz, 2.82 Hz, 2H), 7.26 (d, $J = 3.12$ Hz, 2H), 6.61 (d, $J = 3.12$ Hz, 2H); ^{13}C NMR (151 MHz, CDCl_3) δ ppm: 151.70, 150.30, 131.55, 127.49, 127.13, 123.60, 117.69, 113.83, 108.73; HRMS (APCI): calcd. for $\text{C}_{18}\text{H}_8\text{Br}_2\text{N}_2\text{O}_2\text{S}$ [$\text{M} + \text{H}$] $^+$ 476.8751; found 476.7491.

Synthesis of 8: 4 (163 mg, 0.46 mmol) was added into a 50 mL round bottom flask. THF (10 mL) was added as a solvent. NBS (207 mg, 1.16 mmol) was added to the reaction. The reaction was stirred under N_2 atmosphere for 12 h. After completing, sodium thiosulphate was added to remove excess bromine and the reaction was extracted with dichloromethane (50 mL x 2). The combined organic phase was washed with water (50 mL x 2), dried over anhydrous Na_2SO_4 , filtered, and evaporated to dryness. To obtain a product with higher purity, the residue was further purified by column chromatography eluting with mixture of dichloromethane and hexane (1:4) to obtain dark pink solid (56.2%). ^1H NMR (600 MHz, CDCl_3) δ ppm: 8.31 (dd, $J = 10.14$ Hz, 3.78 Hz, 2H), 7.46 (dd, $J = 10.14$ Hz, 4.02 Hz, 2H), 7.28 (d, $J = 3.72$ Hz, 2H), 7.22 (d, $J = 3.84$ Hz, 2H); ^{13}C NMR (151 MHz, CDCl_3) δ ppm: 151.37, 137.88, 132.86, 130.80, 130.19, 127.40, 126.72, 122.81, 115.07; HRMS (APCI): calcd. for $\text{C}_{18}\text{H}_8\text{Br}_2\text{N}_2\text{S}_3$ [$\text{M} + \text{H}$] $^+$ 508.2640; found 508.8442.

MT01-79 product in CDCl3 +TMS
 CP_PROTON8 CDCl3 {C:\VISTEC NMR Data\VP} vpmt 5



F-BT-F_CNMR
 CP_C13CPD32_DE12 CDCl3 {C:\VISTEC NMR Data\VP} vpmt 10

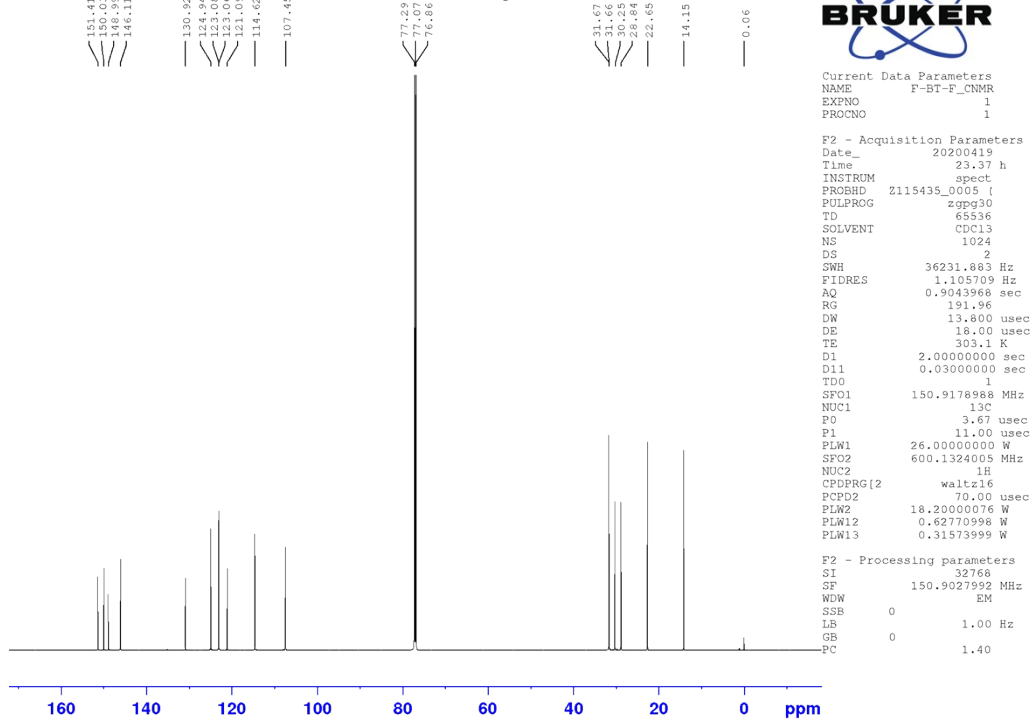
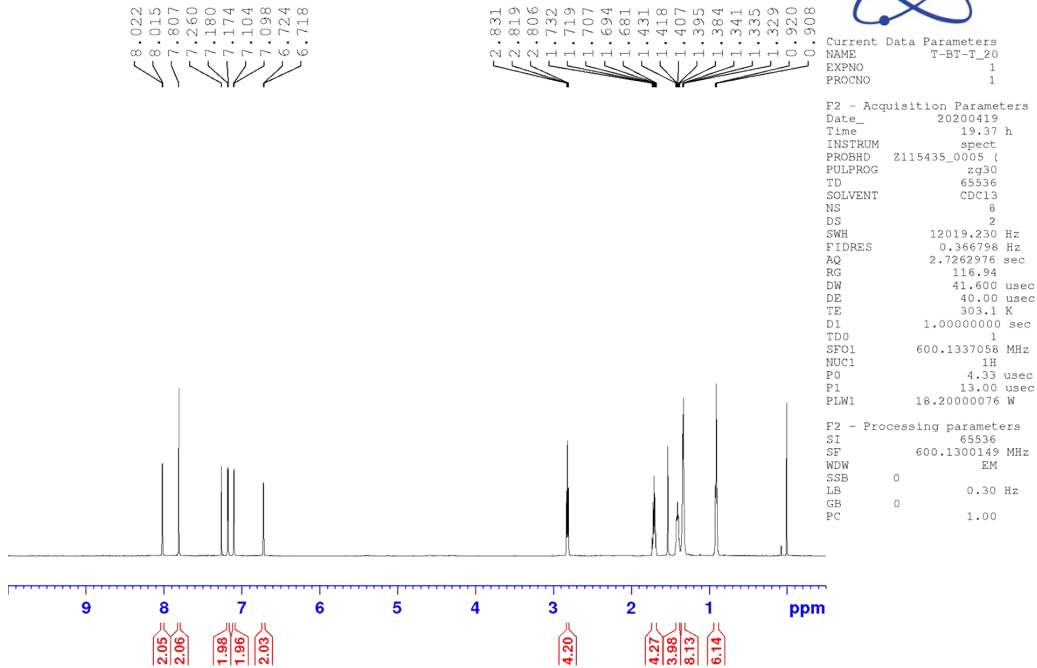


Fig. S1 ¹H-NMR and ¹³C-NMR of F-BT-F.

T-BT-T_20
 CP_PROTON8 CDC13 {C:\VISTEC NMR Data\VP} vpmt 7



T-BT-T_CNMR
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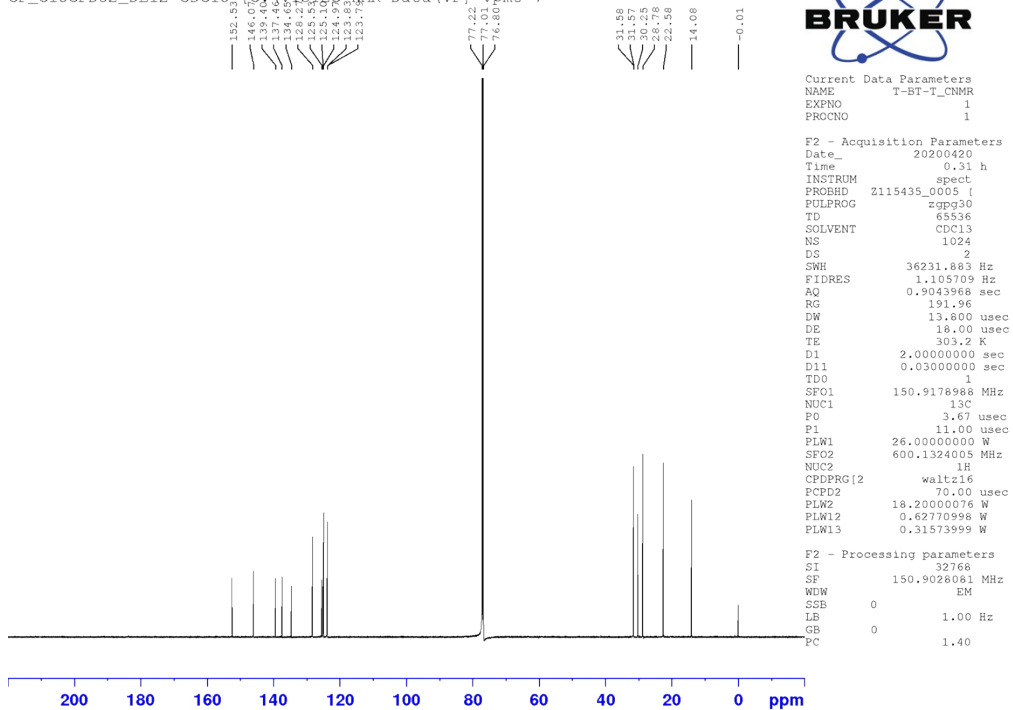
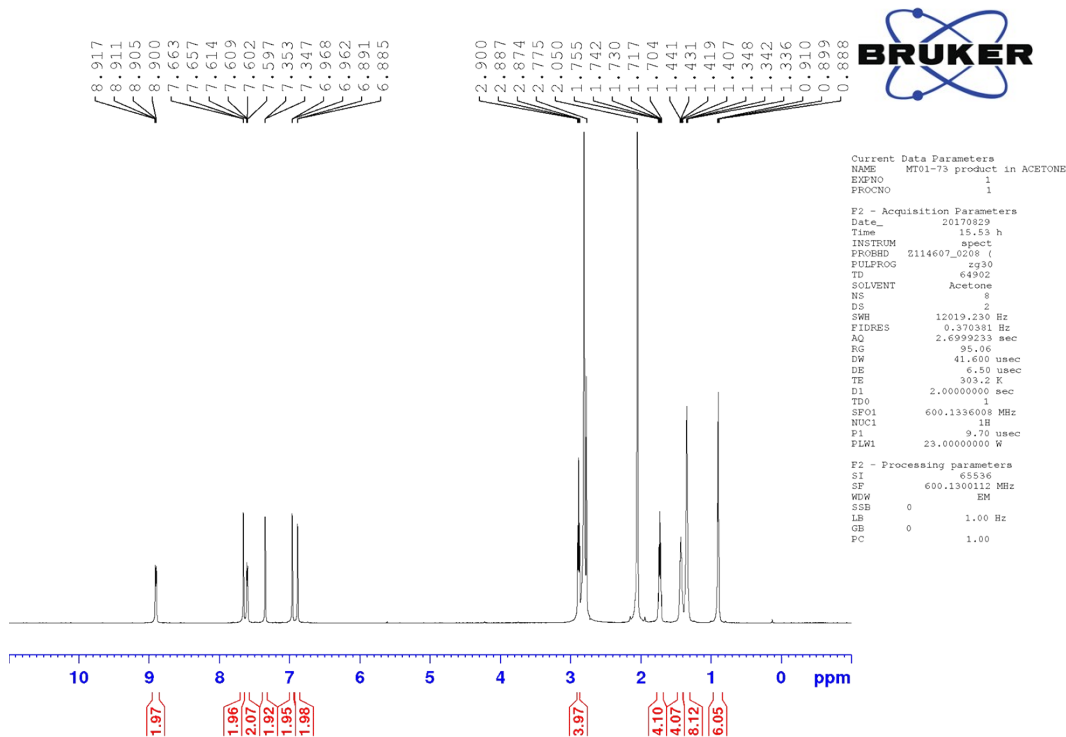


Fig. S2 ¹H-NMR and ¹³C-NMR of T-BT-T.

MT01-73 product in ACETONE



F-NT-F_CNMR_acetoneD6
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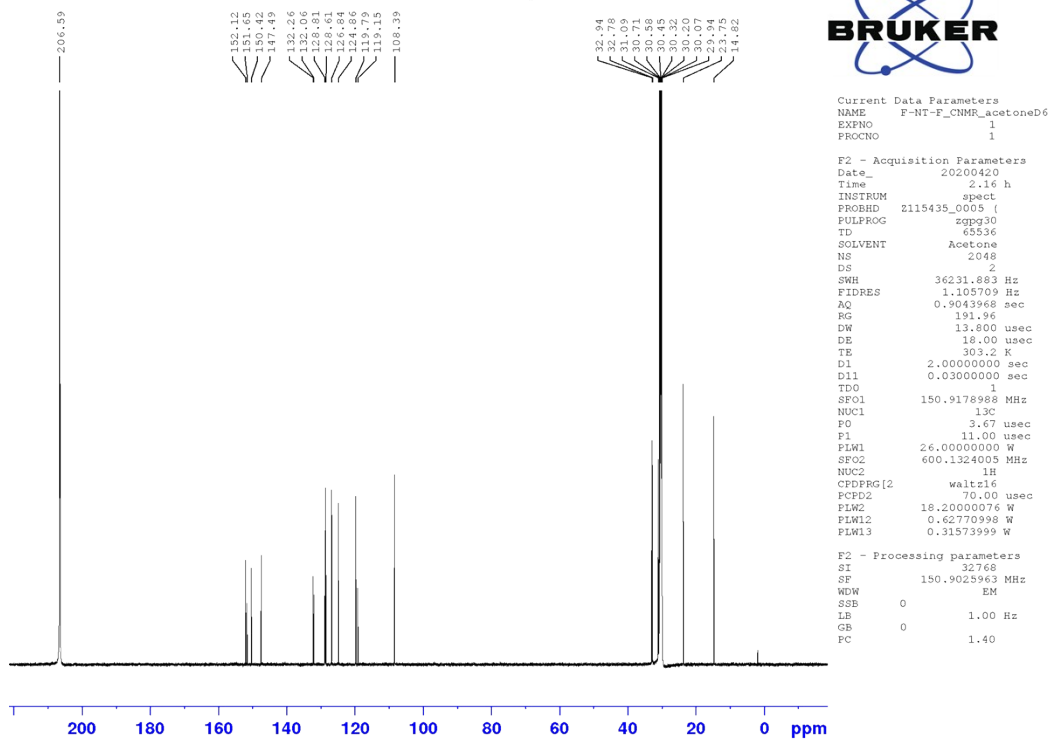
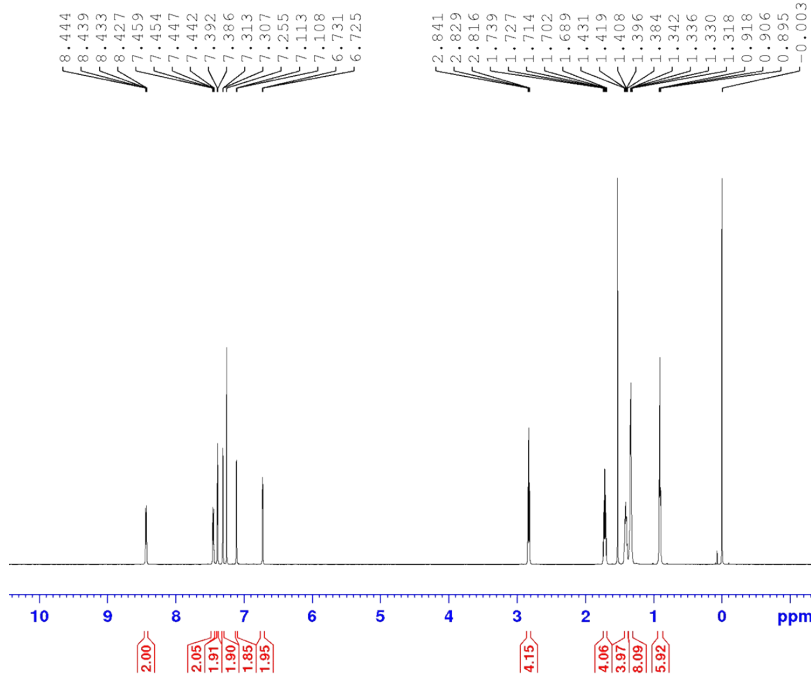


Fig. S3 ¹H-NMR and ¹³C-NMR of F-NT-F.

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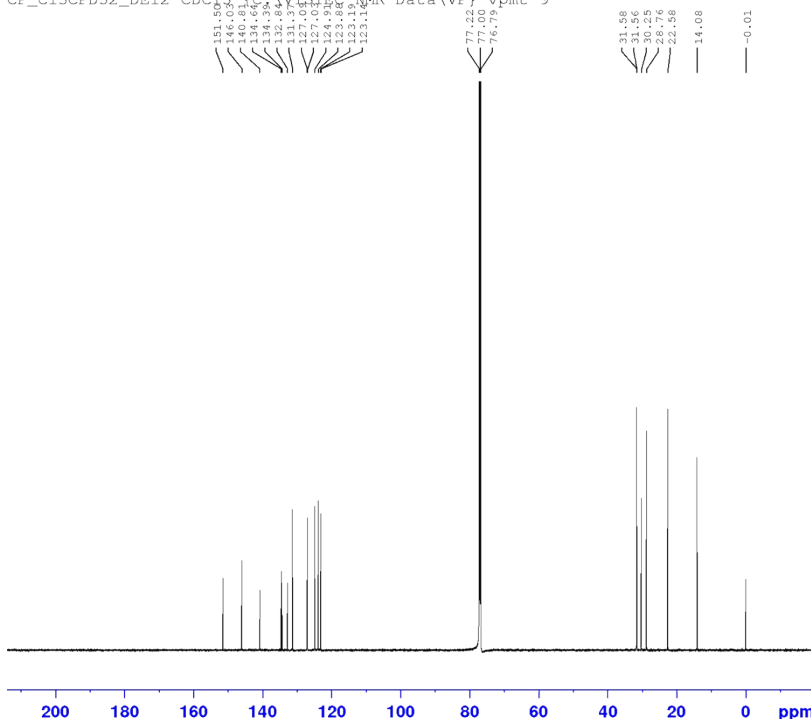


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 PROCNO 1

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 TD 65536
 SOLVENT CDC13
 NS 8
 DS 2
 SWH 12019.230 Hz
 FIDRES 0.366798 Hz
 AQ 2.7262976 sec
 RG 170.86
 DW 41.600 usec
 DE 40.00 usec
 TE 303.2 K
 D1 1.00000000 sec
 TDO 1
 SFO1 600.1337058 MHz
 NUC1 1H
 P0 4.33 usec
 F1 13.00 usec
 PLW1 18.20000076 W

F2 - Processing parameters
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 SF 600.1300179 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00

T-NT-T_CNMR
 CP_C13CPD32_DE12 CDC13 {C:\VISTEC NMR Data\VP} vpmt 9



Current Data Parameters
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 PROCNO 1

F2 - Acquisition Parameters
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 PULPROG zgpg30
 TD 65536
 SOLVENT CDC13
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 DS 2
 SWH 36231.883 Hz
 FIDRES 1.105709 Hz
 AQ 0.9043968 sec
 RG 191.96
 DW 13.800 usec
 DE 18.00 usec
 TE 303.1 K
 D1 2.00000000 sec
 D11 0.03000000 sec
 TDO 1
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 NUC1 13C
 P0 3.67 usec
 F1 11.00 usec
 PLW1 26.00000000 W
 SFO2 600.1324005 MHz
 NUC2 1H
 CPDPRG[2] waltz16
 PCPD2 70.00 usec
 PLW2 18.20000076 W
 PLW12 0.62770998 W
 PLW13 0.31573999 W

F2 - Processing parameters
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 SSB 0
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Fig. S4 ¹H-NMR and ¹³C-NMR of T-NT-T.

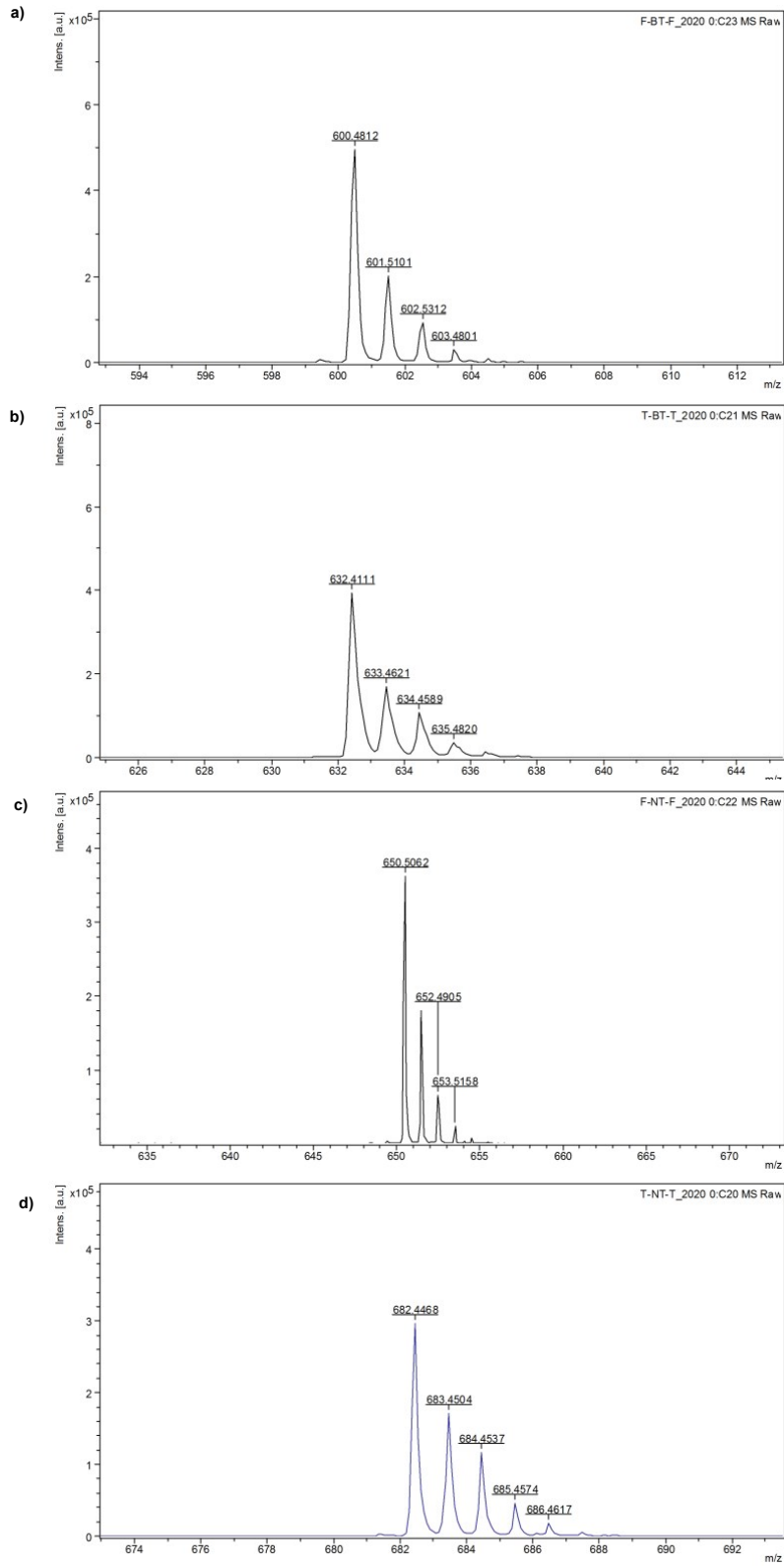


Fig. S5 Mass spectra of a) F-BT-F, b) T-BT-T, c) F-NT-F, and d) T-NT-T.

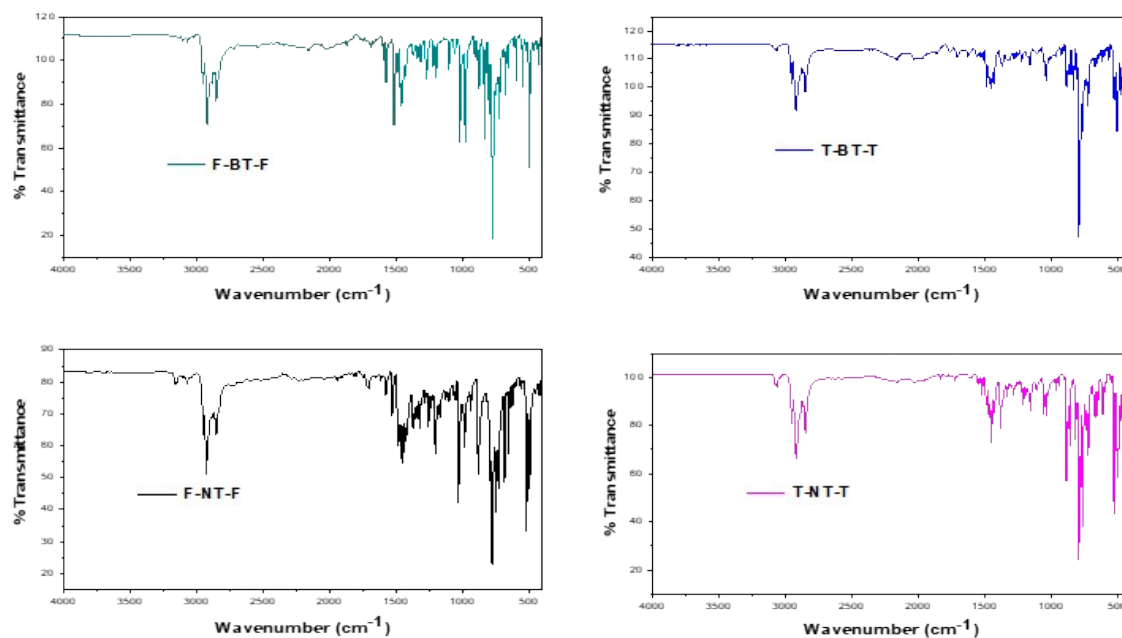


Fig. S6 FTIR graphs for all small molecules.

Table S1 Crystallographic data for F-NT-F and T-NT-T.

Parameters	F-NT-F	T-NT-T
Formula	C ₃₈ H ₃₈ N ₂ O ₂ S ₃	C ₃₈ H ₃₈ N ₂ S ₅
Formula Weight	650.88	683.00
Crystal System	monoclinic	triclinic
Space group	P2 ₁ /n	P-1
a [Å]	7.9181(8)	5.7829(6)
b [Å]	25.263(2)	17.925(2)
c [Å]	16.5549(17)	18.386(2)
α [°]	90	67.293(4)
β [°]	92.076(3)	82.493(4)
γ [°]	90	84.393(4)
V [Å ³]	3309.4(5)	1740.7(3)
Z	4	2
D(calc) [g/cm ³]	1.306	1.303
μ [mm ⁻¹]	0.261	0.363
F (000)	1376	720
Crystal Size [mm ³]	0.15 x 0.36 x 0.48	0.04 x 0.12 x 0.46
Temperature [K]	298	298
Radiation [Å]	0.71073	0.71073
θ range [°]	2.5 to 28.3	2.3 to 25.4
Total no. of reflections	72401	51986
Uniq. Data	8215	6414
R _{int}	0.075	0.088
Parameters	409	409
R	0.0443	0.0452
wR2	0.1134	0.1021
Goodness to fit	1.02	1.04
CCDC deposition number	1972793	1971452

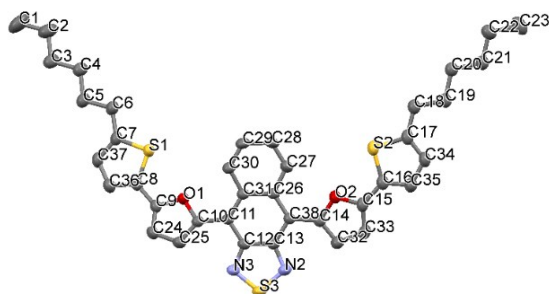


Fig. S7 Asymmetric Unit for F-NT-F.

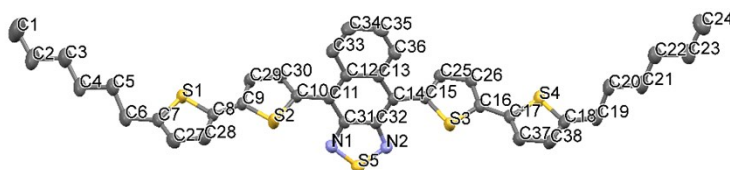


Fig. S8 Asymmetric Unit for T-NT-T.

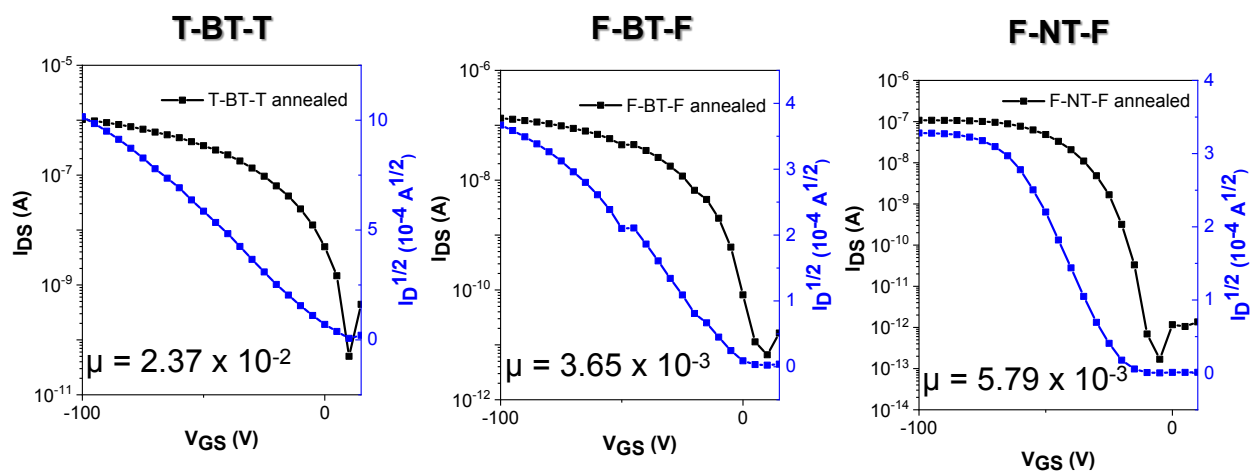


Fig. S9 Transfer curve of T-BT-T, F-BT-F, and F-NT-F annealed (100 °C 1 hr) devices.