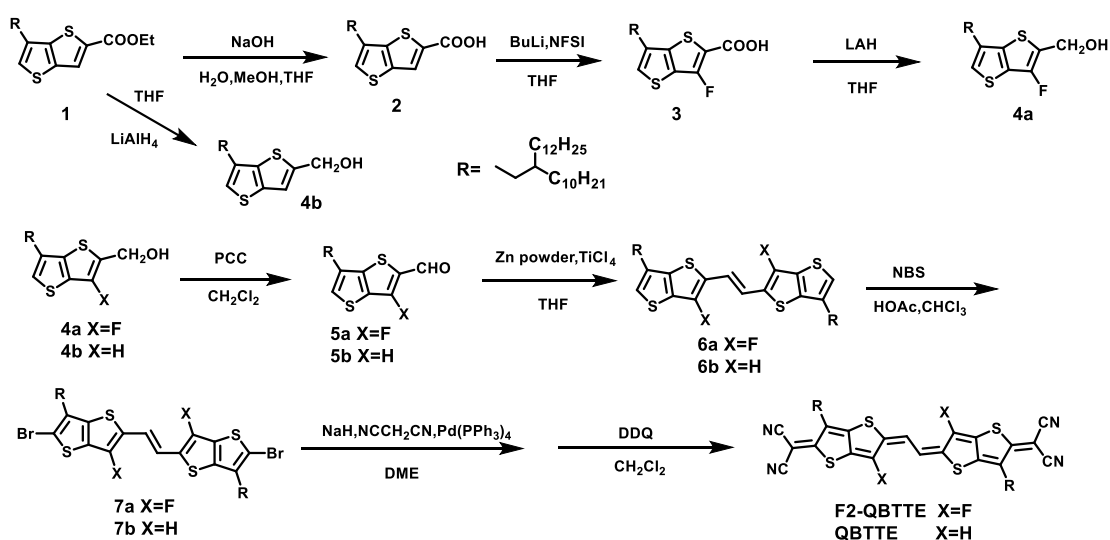


Supporting Information:

Fluorine-Substituted Quinoidal Thiophene with F-H Hydrogen Bond Locked Conformation for High Performance n-Channel Organic Transistor

Deliang Wang, Xiaolan Qiao, Guangcheng Ouyang, Hongzhuo Wu, Hongxiang Li

1. Synthesis and Characterizations



Scheme S1. Synthetic routes of F2-QBTTE and QBTTE

Compound 1

A three neck flask was charged with 3-bromo-4-decyltetradecanylthiophene-2-carbaldehyde (5.43 g, 10.29 mmol), K_2CO_3 (3.42 g, 24.76 mmol) and DMF (30 mL). To this mixture, ethyl mercaptoacetate (1.80 g, 14.94 mmol) was added dropwise. The reaction mixture was stirred for 8 hours at 80 °C under nitrogen and then cooled to room temperature. The reaction mixture was quenched with 30 mL water and extracted with ethyl acetate. The combined extracts were washed with brine and dried over anhydrous MgSO_4 . The solvent was removed by rotary evaporation and the crude product was purified by silica gel column chromatography (eluent: Petroleum ether/ $\text{CH}_2\text{Cl}_2 = 5:1$) to yield compound **1** (5.42 g, 96%). ^1H NMR (300 MHz, CDCl_3) δ 7.97 (s, 1H), 7.16 (s, 1H), 4.38 (q, $J = 7.0$ Hz, 2H), 2.65 (d, $J = 6.9$ Hz, 2H), 1.84 (br, 1H), 1.40 (t, $J = 7.0$ Hz, 3H), 1.24 (br, 40H), 0.88 (t, $J = 6.1$ Hz, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 162.78, 144.83, 138.14, 134.50, 134.46, 126.94, 126.18, 61.34, 37.27, 34.82, 33.65, 32.03, 32.02, 30.05, 29.80, 29.79, 29.76, 29.74, 29.72, 29.47, 29.46, 26.62, 22.80, 14.46, 14.21. MS (MALDI-TOF) m/z : 549.3 ($\text{M}+\text{H}^+$); HRMS (MALDI) m/z : calcd for $\text{C}_{33}\text{H}_{57}\text{O}_2\text{S}_2^{+1}$ 549.3800, found 549.3776.

Compound 2

A three neck flask was charged with THF (50 mL), methanol (20 mL), water (10 mL), NaOH (5.0 g), compound **1** (5.40 g, 9.84 mmol) and a catalytic amount of tetrabutylammonium iodide (0.50 g, 1.35 mmol). The mixture was refluxed for 4 hours. After cooling down to room

temperature, dilute hydrochloric acid was added to adjust PH to below 7.0. Most of the solvent was evaporated and the residue was extracted with ethyl acetate. The combined extracts were washed with brine and dried over anhydrous MgSO₄. The solvent was removed by rotary evaporation and the crude product was purified by silica gel column chromatography (eluent: Petroleum ether/ EA= 4:1) to yield compound **2** (4.27 g, 83.4%). ¹H NMR (400 MHz, CDCl₃) δ 8.08 (s, 1H), 7.22 (s, 1H), 2.67 (d, *J* = 7.0 Hz, 2H), 1.85 (br, 1H), 1.24 (br, 80H), 0.88 (t, *J* = 6.2 Hz, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 168.36, 146.23, 138.34, 134.65, 133.02, 128.06, 128.02, 37.27, 34.78, 33.62, 32.03, 30.03, 29.76, 29.72, 29.47, 26.62, 22.80, 14.24. MS (ESI) *m/z*: 543.35 (M+Na)⁺.

Compound 3

To a solution of compound **2** (1.58 g, 3.04 mmol) in 15 mL dry THF, n-butyllithium (2.8 mL, 6.72 mmol, 2.4 M in hexane) was added dropwise under nitrogen at -78 °C. After the addition was finished, the resulting mixture was stirred for another one hour and then N-Fluorobenzenesulfonimide (1.16 g, 3.67 mmol) was added. The final mixture was allowed to warm to room temperature and was stirred overnight. The reaction was quenched with 10 mL water and then acidified with dilute HCl to PH<7. The mixture was extracted with ethyl acetate. The combined extracts were washed with brine and dried over anhydrous MgSO₄. The solvent was removed by rotary evaporation and the crude product was purified by silica gel column chromatography (eluent: Petroleum ether/ EA= 6:1) to yield compound **3** (1.32 g, 80.3%). ¹H NMR (400 MHz, CDCl₃) δ 7.24 (s, 1H), 2.63 (d, *J* = 7.1 Hz, 2H), 1.80 (br, 1H), 1.25 (br, 40H), 0.88 (td, *J* = 6.8, 1.3 Hz, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 167.07 (d, *J* = 3.1 Hz), 154.71 (d, *J* = 280.9 Hz), 142.39 (d, *J* = 7.4 Hz), 135.37, 128.61, 127.24 (d, *J* = 22.7 Hz), 111.74 (d, *J* = 9.9 Hz), 37.43, 33.93, 33.60, 32.05, 32.04, 30.02, 29.82, 29.80, 29.78, 29.77, 29.76, 29.73, 29.49, 29.48, 27.01, 26.62, 22.81, 14.24. ¹⁹F NMR (376 MHz, CDCl₃) δ -114.50. MS (MALDI-TOF) *m/z*: 539.2 (M+H)⁺.

Compound 4a

A solution of compound **6** (1.32 g, 2.44 mmol) in tetrahydrofuran (5 mL) was added to a mixture of lithium aluminum hydride (0.21 g, 5.4 mmol) in dry THF (10 mL) under nitrogen at 0 °C. The reaction mixture was stirred overnight at room temperature and was quenched slowly with water (0.2 mL), 15% aqueous NaOH solution (0.4 mL) and water (0.6 mL) successively. The mixture was extracted with ethyl acetate. The combined extracts were washed with brine and dried over anhydrous MgSO₄. The solvent was removed by rotary evaporation and the crude product was purified by silica gel column chromatography (eluent: Petroleum ether/ EA= 5:1) to yield compound **4a** (0.71 g, 55.7%). ¹H NMR (400 MHz, CDCl₃) δ 6.96 (s, 1H), 4.85 – 4.84 (m, 2H), 2.59 (d, *J* = 7.1 Hz, 2H), 1.80 (br, 1H), 1.24 (br, 40H), 0.88 (t, *J* = 6.8 Hz, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 147.31 (d, *J* = 260.3 Hz), 135.43 (d, *J* = 6.4 Hz), 134.68 (d, *J* = 1.3 Hz), 125.18 (d, *J* = 25.5 Hz), 120.94 (d, *J* = 17.4 Hz), 111.81 (d, *J* = 1.4 Hz), 55.93, 37.27, 33.68, 33.53, 32.03, 30.01, 29.80, 29.79, 29.77, 29.76, 29.75, 29.71, 29.47, 29.45, 26.59, 22.79, 14.21. ¹⁹F NMR (376 MHz, CDCl₃) δ -135.19. MS (MALDI-TOF) *m/z*: 507.2 (M-OH)⁺.

Compound 4b

Compound **4b** was synthesized according to the same procedure as for compound **4a**. Yield: 94.9%. ¹H NMR (300 MHz, CDCl₃) δ 7.17 (s, 1H), 6.93 (s, 1H), 4.87 (d, *J* = 5.6 Hz, 2H), 2.62 (d, *J* = 7.1 Hz, 2H), 1.88 (br, 1H), 1.24 (br, 40H), 0.88 (t, *J* = 6.0 Hz, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 145.40, 140.19, 137.85, 134.34, 122.33, 118.41, 61.07, 37.32, 34.92, 33.66, 32.04, 30.09, 29.78, 29.77, 29.48, 29.47, 26.66, 22.81, 14.23. MS (MALDI-TOF) *m/z*: 507.3 (M+H)⁺; HRMS (MALDI) *m/z*: calcd for C₃₁H₅₅OS₂⁺¹ 507.3694, found 507.3675.

Compound 5a

To a stirred suspension of pyridinium chlorochromate (0.42 g, 1.94 mmol) in dichloromethane (8 mL), compound **4a** (0.65 g, 1.23 mmol) was added. The mixture was stirred overnight and then filtered through funnel filled with silica gel. The gum in the flask was washed with dichloromethane three times. The combined filtrate was evaporated under reduced pressure. The crude product was flash chromatographed on silica. Light petroleum-ethyl acetate (ratio 5:1) eluted compound **5a** (0.52 g, 80%). ¹H NMR (400 MHz, CDCl₃) δ 10.10 (s, 1H), 7.26 (s, 1H), 2.63 (d, *J* = 7.5 Hz, 2H), 1.87 (br, 1H), 1.24 (br, 40H), 0.88 (d, *J* = 8 Hz, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 180.20, 156.51 (d, *J* = 279.4 Hz), 144.60 (d, *J* = 7.5 Hz), 135.79, 129.73, 126.52 (d, *J* = 21.9 Hz), 123.33 (d, *J* = 9.2 Hz), 37.45, 33.90, 33.62, 32.02, 32.00, 29.98, 29.78, 29.77, 29.75, 29.72, 29.68, 29.45, 29.43, 26.63, 22.78, 14.19. ¹⁹F NMR (376 MHz,) δ -123.70. MS (MALDI-TOF) *m/z*: 523.3 (M+H)⁺; HRMS (MALDI) *m/z*: calcd for C₃₁H₅₂FOS₂⁺¹ 523.3438, found 523.3431.

Compound 5b

Compound **5b** was synthesized according to the same procedure as for compound **5a**. Yield: 80%. ¹H NMR (400 MHz, CDCl₃) δ 10.10 (s, 1H), 7.29 (s, 1H), 7.26 (s, 1H), 2.62 (d, *J* = 7.1 Hz, 2H), 1.79 (br, 1H), 1.24 (br, 40H), 0.90 – 0.85 (m, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 183.50, 146.73, 144.84, 138.63, 134.91, 129.65, 129.26, 37.31, 34.72, 33.65, 32.02, 32.01, 30.01, 29.78, 29.77, 29.75, 29.73, 29.70, 29.46, 29.44, 26.64, 22.78, 14.21. MS (MALDI-TOF) *m/z*: 505.3 (M+H)⁺; HRMS (MALDI) *m/z*: calcd for C₃₁H₅₃OS₂⁺¹ 505.3538, found 505.3526.

Compound 6a

To a 50 mL three-neck flask containing zinc powder (1.34 g, 20.72 mmol) and THF (20 mL) was added TiCl₄ (2.24 g, 11.8 mmol) dropwise under a nitrogen stream. The solution was stirred for 2 h at 0 °C and compound **5a** (1.08 g, 2.06 mmol) was added in one portion. The mixture was refluxed for 5 h and then cooled to room temperature. The reaction mixture was quenched with water and extracted with ethyl acetate. Then the organic layer was washed with brine and dried over MgSO₄. After removing the solvent by rotary evaporation, the crude product was purified by silica gel column chromatography (eluent: Petroleum ether) to yield **6a** (0.92 g, 87.7%). ¹H NMR (300 MHz, CDCl₃) δ 6.97 (s, 2H), 6.96 (s, 2H), 2.59 (d, *J* = 6.9 Hz, 4H), 1.80 (br, 2H), 1.25 (br, 80H), 0.87 (m, 12H). ¹³C NMR (101 MHz, CDCl₃) δ 148.58 (d, *J* = 265.7 Hz), 135.37 (d, *J* = 7.1 Hz), 135.19, 127.51 (d, *J* = 24.5 Hz), 123.70, 121.84 (d, *J* = 14.5 Hz), 116.23, 37.45, 34.08, 33.60, 32.04, 30.05, 29.81, 29.79, 29.77, 29.74, 29.48, 26.63, 14.24. ¹⁹F NMR (282 MHz, CDCl₃) δ -133.44. MS (MALDI-TOF) *m/z*: 1013.7 (M-H)⁺; HRMS (MALDI) *m/z*: calcd for

C₆₂H₁₀₃F₂S₄⁺¹ 1013.6905, found 1013.6881.

Compound 6b

Compound **6b** was synthesized according to the same procedure as for compound **9a**. Yield: 58.3%. ¹H NMR (400 MHz, CDCl₃) δ 7.15 (s, 2H), 7.06 (s, 2H), 6.94 (s, 2H), 2.63 (d, *J* = 6.9 Hz, 4H), 1.84 (br, 2H), 1.25 (br, 80H), 0.87 (t, *J* = 6.6 Hz, 12H). ¹³C NMR (101 MHz, CDCl₃) δ 143.89, 138.90, 138.89, 134.41, 123.10, 122.14, 119.12, 37.34, 34.92, 33.68, 32.05, 30.09, 29.84, 29.83, 29.81, 29.80, 29.78, 29.77, 29.50, 26.67, 22.82, 14.23. MS (MALDI-TOF) *m/z*: 977.6 (M-H)⁺; HRMS (MALDI) *m/z*: calcd for C₆₂H₁₀₅S₄⁺¹ 977.7099, found 977.7083.

Compound 7a

N-Bromosuccinimide (0.32 g, 1.8 mmol) was added in portions to a solution of compound **6a** (0.87 g, 0.86 mmol) in AcOH (6 mL) and CHCl₃ (6 mL) at room temperature. After the solution was stirred at room temperature for 1.5 h, water (10 mL) and sat. NaHCO₃ (aq) was added to adjust pH to neutral. The aqueous layer was extracted with CH₂Cl₂ and combined organic layer was washed with brine and dried over MgSO₄. After removing the solvent by rotary evaporation, the crude product was purified by silica gel column chromatography (eluent: Petroleum ether) to yield compound **7a** (0.84 g, 83.4%). ¹H NMR (300 MHz, CDCl₃) δ 6.93 (s, 1H), 2.59 (d, *J* = 7.5 Hz, 2H), 1.88 (br, 1H), 1.25 (br, 40H), 0.87 (m, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 147.88 (d, *J* = 266.8 Hz), 134.82, 134.04 (d, *J* = 6.9 Hz), 125.98 (d, *J* = 24.6 Hz), 121.33 (d, *J* = 14.2 Hz), 116.08, 112.53, 37.25, 33.66, 33.53, 32.04, 30.03, 29.82, 29.79, 29.77, 29.73, 29.49, 29.48, 26.59, 22.81, 14.24. ¹⁹F NMR (282 MHz, CDCl₃) δ -133.01. MS (MALDI-TOF) *m/z*: 1171.5 (M-H)⁺; HRMS (MALDI) *m/z*: calcd for C₆₂H₁₀₁Br₂F₂S₄⁺¹ 1169.5115, found 1169.5092.

Compound 7b

Compound **7b** was synthesized according to the same procedure as for compound **10a**. Yield: 91.2%. ¹H NMR (400 MHz, CDCl₃) δ 7.07 (s, 2H), 7.03 (s, 2H), 2.62 (d, *J* = 7.3 Hz, 4H), 1.92 (br, 2H), 1.25 (br, 80H), 0.87 (t, *J* = 5.7 Hz, 12H). ¹³C NMR (101 MHz, CDCl₃) δ 142.98, 137.37, 137.17, 133.97, 121.87, 118.49, 111.32, 37.08, 34.07, 33.60, 31.95, 29.96, 29.74, 29.73, 29.70, 29.68, 29.65, 29.40, 26.93, 26.52, 22.72, 14.14. MS (MALDI-TOF) *m/z*: 1134.5 (M)⁺; HRMS (MALDI) *m/z*: calcd for C₆₂H₁₀₄Br₂S₄⁺¹ 1132.5227, found 1132.5237.

Compound F2-QBTTE

Malononitrile (0.22 g, 3.36 mmol) was added to an ice-water cooled suspension of sodium hydride (0.16 g, 6.7 mmol) in 1,2-dimethoxyethane (15 mL) under a nitrogen stream. The mixture was stirred at room temperature for another 30 min. Then compound **7a** (0.70 g, 0.60 mmol) and tetrakis(triphenylphosphine)palladium (42 mg, 0.036 mmol) were added. The reaction mixture was refluxed for 6 h. The resulting solution was quenched with water carefully and extracted with CH₂Cl₂. After dried over MgSO₄, the solvent was removed by rotary evaporation to afford the product which was used without further purification.

2,3-dichloro-5,6-dicyano-1,4-benzoquinone (0.14 g, 0.61 mmol) in CH₂Cl₂ (5 mL) was added dropwise to the solution of crude product above in CH₂Cl₂ (15 mL). After stirring for 30 min, the reaction mixture was filtrated. Hexane (10 mL) was added to the filtrate to precipitate crude product after removing the most of solvent by rotary evaporation. The crude product was purified

by silica gel column chromatography (eluent: Petroleum ether/CH₂Cl₂=3:1) to yield **F2-QBTTE** (0.15 g, 22.6%). ¹H NMR (400 MHz, CDCl₃) δ 6.95 (s, 2H), 2.78 (d, *J* = 7.8 Hz, 4H), 1.88 (br, 2H), 1.25 (br, 80H), 0.87 (t, *J* = 6.2 Hz, 12H). ¹³C NMR (101 MHz, CDCl₃) δ 170.42, 152.40, 152.33, 137.99, 133.52, 133.45, 125.78, 119.75, 114.50, 113.14, 38.31, 33.30, 33.04, 32.02, 32.00, 30.06, 29.78, 29.75, 29.73, 29.72, 29.69, 29.45, 29.43, 26.21, 22.78, 22.77, 14.20. ¹⁹F NMR (376 MHz, CDCl₃) δ -119.54. MS (MALDI-TOF) *m/z*: 1139.7 (M+H)⁺; HRMS (MALDI) *m/z*: calcd for C₆₈H₁₀₁F₂N₄S₄⁺ 1139.6872, found 1139.6827. Anal. Calcd for C₆₈H₁₀₀F₂N₄S₄: C, 73.99; H, 9.31; N, 5.08; Found: C, 73.99; H, 9.28; N, 5.00.

Compound QBTTE

Compound **QBTTE** was synthesized according to the same procedure as for compound **F2-QBTTE**. Yield: 63.5%. ¹H NMR (400 MHz, CDCl₃) δ 7.02 (s, 2H), 7.00 (s, 2H), 2.83 (d, *J* = 7.3 Hz, 4H), 1.91 (br, 2H), 1.25 (br, 80H), 0.87 (t, *J* = 6.3 Hz, 12H). ¹³C NMR (101 MHz, CDCl₃) δ 170.82, 158.38, 151.70, 145.27, 131.97, 126.18, 125.24, 124.06, 123.50, 115.90, 114.90, 113.55, 67.65, 38.17, 33.96, 33.02, 31.94, 31.62, 29.99, 29.71, 29.67, 29.66, 29.62, 29.38, 29.37, 26.20, 22.71, 14.14. MS (MALDI-TOF) *m/z*: 1103.6 (M+H)⁺; HRMS (MALDI) *m/z*: calcd for C₆₈H₁₀₃N₄S₄⁺ 1103.7066, found 1103.7047. Anal. Calcd for C₆₈H₁₀₂N₄S₄: C, 71.66; H, 8.84; N, 4.92; Found: C, 71.77; H, 8.82; N, 4.72.

2. DFT MO Calculations

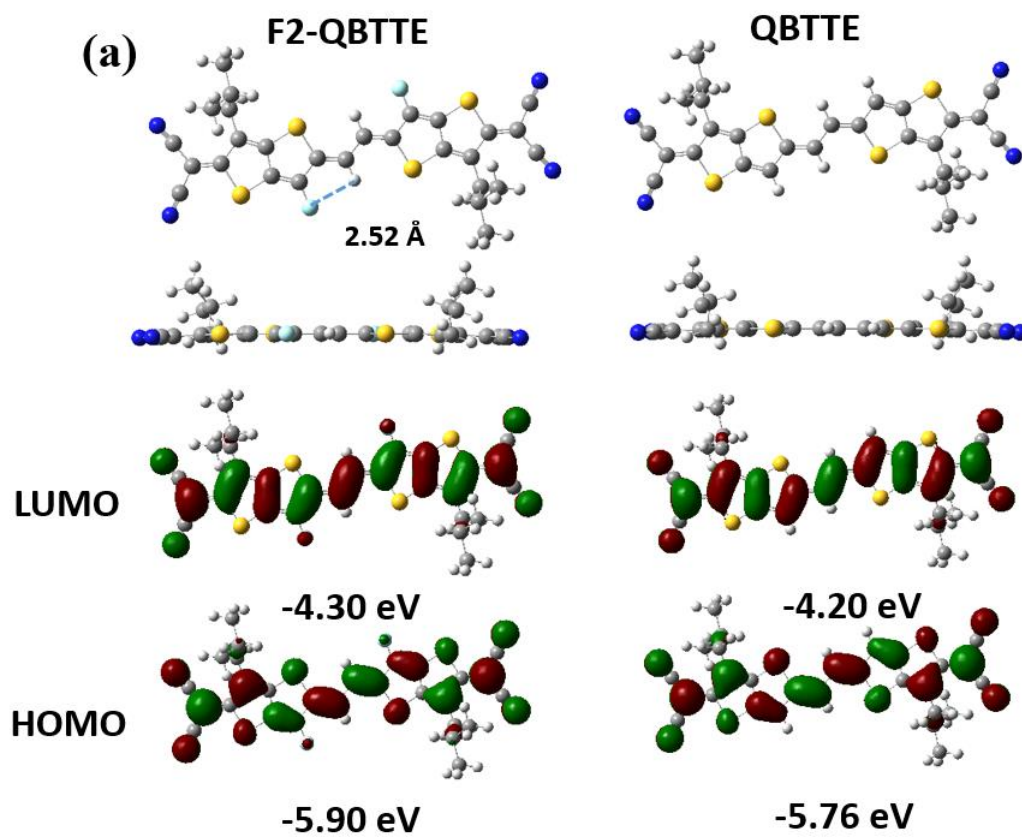


Figure S1. Molecular geometry and frontier molecular orbitals of **F2-QBTTE** and **QBTTE** at the DFT-B3LYP/6-31G(d,p) level.

3. TGA and DSC Analysis

TGA and DSC was measured on a TAQ500 instruments under a dry N2 flow at a heating rate of 10 °C/min

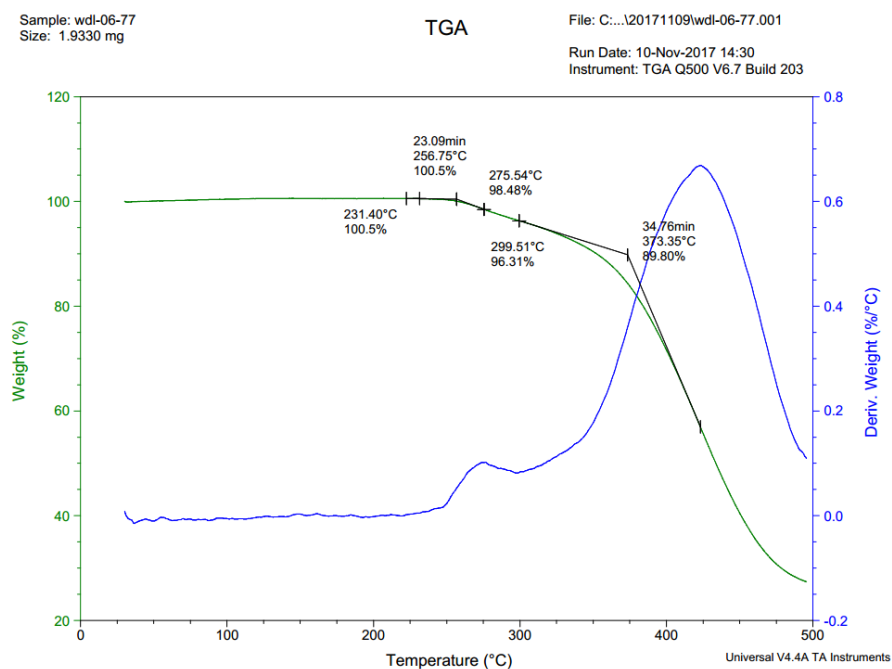


Figure S2. Thermal gravity analysis (TGA) of F2-QBTTE

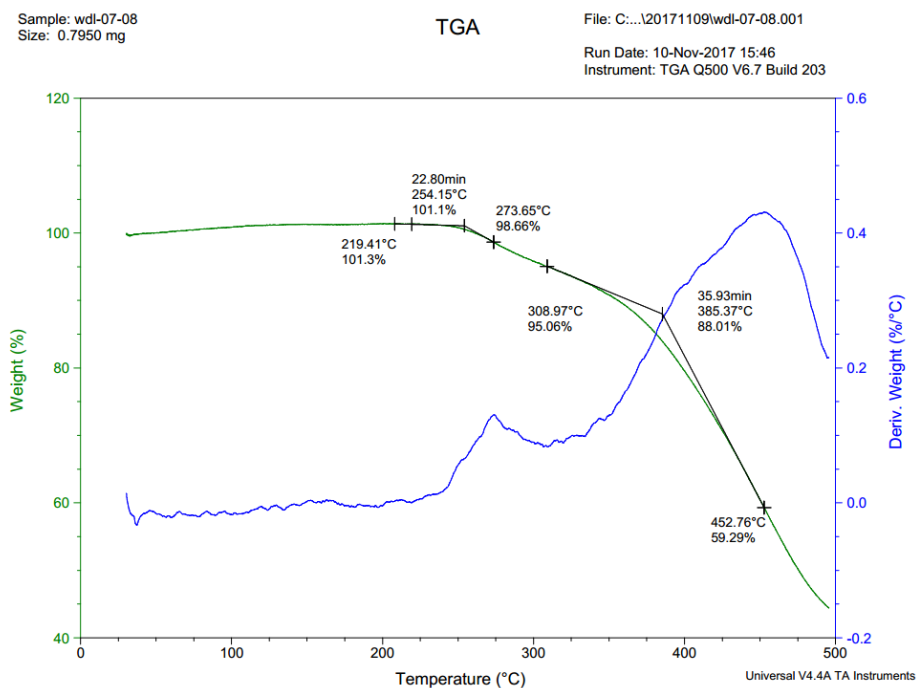


Figure S3. Thermal gravity analysis (TGA) of QBTTE

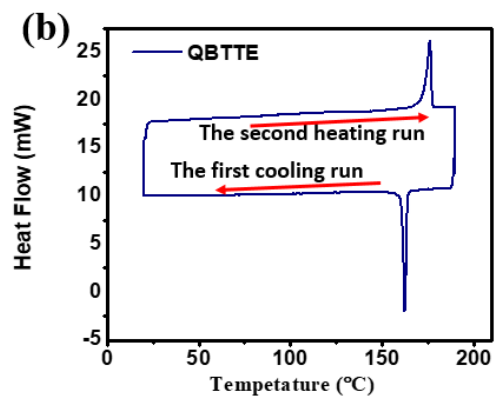
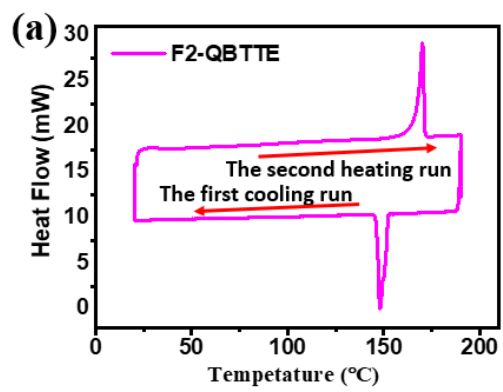


Figure S4. DSC thermograms of F2-QBTTE and QBTTE

4. HNMR spectra of F2-QBTTE and QBTTE.

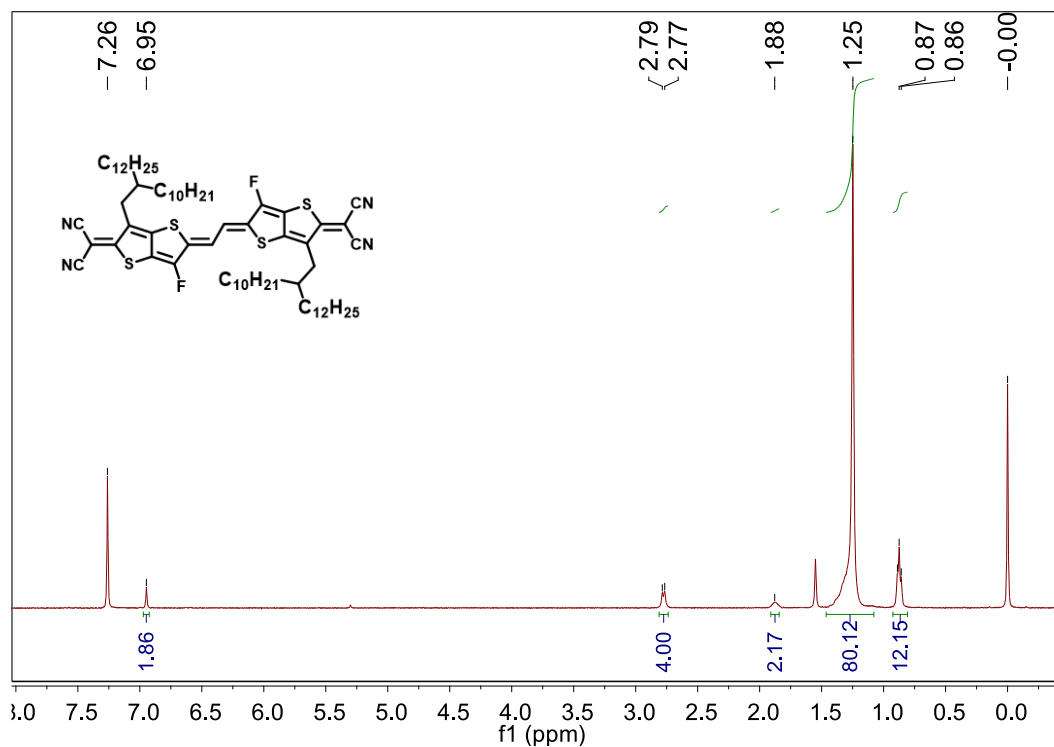


Figure S5. HNMR spectra of F2-QBTTE.

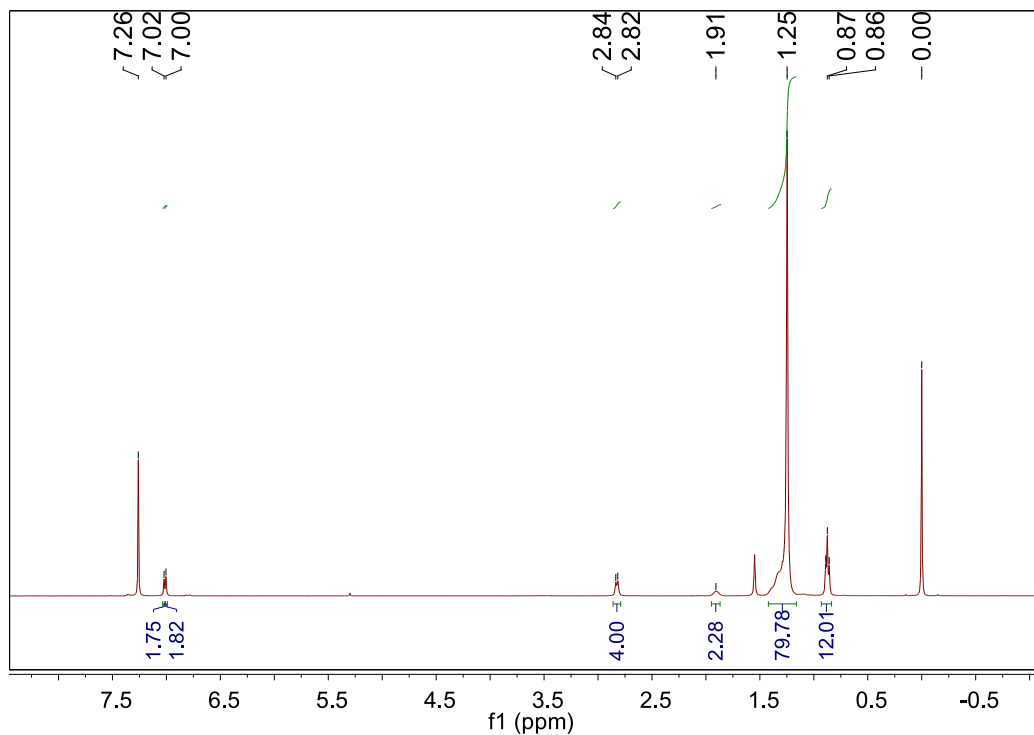


Figure S6. HNMR spectra of QBTTE.

Table S1. F2-QBTTE and QBTTE-based FETs annealed at varied temperatures.

	$T_{\text{anneal}} (\text{°C})$	$\mu_e (\text{cm}^2\text{V}^{-1}\text{s}^{-1})$	$V_{\text{th}} (\text{V})$	$I_{\text{on}}/I_{\text{off}}$
F2-QBTTE	As deposited	0.05 (0.04±0.008)	-0.3	10^4 - 10^5
	80	0.16 (0.12±0.04)	2.1	10^5 - 10^6
	100	0.4 (0.31±0.05)	0.2	10^4 - 10^5
	120	0.27 (0.21±0.05)	1.1	10^4 - 10^5
QBTTE	As deposited	1.6×10^{-3} ($7.0 \times 10^{-4} \pm 4.4 \times 10^{-4}$)	4.2	10^3 - 10^4
	80	0.013 (0.01±0.003)	1.3	10^4 - 10^5
	100	0.021 (0.017±0.003)	3.4	10^4 - 10^5
	120	0.021 (0.016±0.004)	10.9	10^4 - 10^5