**Supporting Information**

# Pentafluorophenyl End-Capped Bithiophene Imide (BTI) based n-Type Semiconductors for Organic Thin-Film Transistors.

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## Experimental Section

### 1. Synthesis

#### 1. 1. Synthesis step of DFP-BTI-b8 (1)

Compound **3a** (0.1g, 1eq) was dissolved in toluene under a nitrogen atmosphere. To the solution, trimethyl(perfluorophenyl)stannane (0.195g, 3eq) and bis(triphenylphosphine)palladium(II) dichloride (13 mg, 0.1eq) were added sequentially. Then the reaction was heated to reflux for two days. Upon completion, the mixture was cooled to room temperature, and the solvent was removed under reduced pressure. The crude was purified by column chromatography (hexanes/ethyl acetate = 90:10 vol/vol). The title compound was obtained as a yellow solid. Yield (0.11 g, 82%).$^{1}$H NMR (300 MHz, $CDCl_3$): δ 8.18 (s, 2H), 4.26–4.24 (m, 2H), 1.86–1.83 (m, 1H), 1.36–1.25 (m, 8H), 0.92–0.86 (m, 6H). $^{13}$C NMR (75 MHz, CDCl3): spectrum could not be obtained completely due to the poor solubility of the compound. $^{19}$F NMR (282 MHz, $CDCl_3$): δ -138, -152, -160. MS (HR-FAB, m/z) calcd. for $C_{30}H_{19}F_{10}NO_2S_2$: 679.0698 (M+). Found: 679.0692.

#### 1. 2. Synthesis step of DFP-BTI-b16 (2)

Synthesized according to **DFP-BTI-b8** (**1**) compound procedure using compound **3b** (0.1g, 1eq), trimethyl(perfluorophenyl)stannane (0.160g, 3eq) and bis(triphenylphosphine)palladium(II) dichloride (11 mg, 0.1eq). The title compound was obtained as a yellow solid. Yield (0.1g, 78%).$^{1}$H NMR (300 MHz, $CDCl_3$): δ 8.18 (s, 2H), 4.26-4.24 (d, $J$ = 6 Hz, 2H), 1.94 (m, 1H), 1.24 (m, 24H), 0.85–0.83 (m, 6H). $^{13}$C NMR (75 MHz, $CDCl_3$): δ 161.63, 145.07, 143.41, 141.82, 140.10, 139.02, 137.26, 136.01, 133.84, 126.08, 108.06, 49.78, 36.48, 31.88, 31.80, 31.71, 30.87,

30.06, 29.73, 29.54, 29.30, 26.41, 22.63, 14.03. $^{19}$F NMR (282 MHz, $CDCl_3$): δ -138, -152, -160. MS (HR-FAB, m/z) calcd. for $C_{38}H_{35}F_{10}NO_2S_2$: 791.1950 (M+). Found: 791.1947.

**Table S1.** Summary of crystal structure data for **DFP-BTI-b8 (1).**

| | |
|---|---|
| Identification code | 240955LT_auto |
| Empirical formula | $C_{30}H_{19}F_{10}NO_2S_2$ |
| Formula weight | 679.58 |
| Temperature/K | 100.00(10) |
| Crystal system | monoclinic |
| Space group | $P2_1/c$ |
| a/Å | 21.9217(9) |
| b/Å | 5.26044(18) |
| c/Å | 23.2688(7) |
| α/° | 90 |
| β/° | 94.557(3) |
| γ/° | 90 |
| Volume/Å$^3$ | 2674.83(16) |
| Z | 4 |
| $\rho_{calc}$g/cm$^3$ | 1.688 |
| μ/mm$^{-1}$ | 2.753 |
| F(000) | 1376.0 |
| Crystal size/mm$^3$ | 0.28 × 0.01 × 0.01 |
| Radiation | Cu Kα (λ = 1.54184) |
| 2Θ range for data collection/° | 7.622 to 146.246 |
| Index ranges | $-26 \leq h \leq 27$, $-5 \leq k \leq 6$, $-27 \leq l \leq 28$ |
| Reflections collected | 18812 |
| Independent reflections | 5203 [$R_{int}$ = 0.0551, $R_{sigma}$ = 0.0674] |
| Data/restraints/parameters | 5203/266/474 |
| Goodness-of-fit on $F^2$ | 1.024 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0573, $wR_2$ = 0.1260 |
| Final R indexes [all data] | $R_1$ = 0.1018, $wR_2$ = 0.1487 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.31/-0.52 |

Crystallographic data (excluding structure factors) for the structure(s) reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. **CCDC 2499871.**

**Table S2.** Summary of crystal structure data for **DFP-BTI-b16 (2).**

| | |
|---|---|
| Identification code | 2508004lt_auto |
| Empirical formula | $C_{38}H_{35}F_{10}NO_2S_2$ |
| Formula weight | 791.79 |
| Temperature/K | 100.00(15) |
| Crystal system | monoclinic |
| Space group | $P2_1/c$ |
| a/Å | 28.1941(13) |
| b/Å | 5.2713(3) |
| c/Å | 24.0617(11) |
| α/° | 90 |
| β/° | 102.298(5) |
| γ/° | 90 |
| Volume/Å$^3$ | 3494.0(3) |
| Z | 4 |
| $\rho_{calc}$g/cm$^3$ | 1.505 |
| μ/mm$^{-1}$ | 2.191 |
| F(000) | 1632.0 |
| Crystal size/mm$^3$ | 0.32 × 0.03 × 0.01 |
| Radiation | Cu Kα (λ = 1.54184) |
| 2Θ range for data collection/° | 6.418 to 146.482 |
| Index ranges | $-33 \leq h \leq 34$, $-4 \leq k \leq 6$, $-28 \leq l \leq 29$ |
| Reflections collected | 24992 |
| Independent reflections | 6766 [$R_{int}$ = 0.0558, $R_{sigma}$ = 0.0403] |
| Data/restraints/parameters | 6766/442/616 |
| Goodness-of-fit on $F^2$ | 1.060 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0768, $wR_2$ = 0.2262 |
| Final R indexes [all data] | $R_1$ = 0.1047, $wR_2$ = 0.2492 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.70/-0.39 |

Crystallographic data (excluding structure factors) for the structure(s) reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. **CCDC 2499872.**

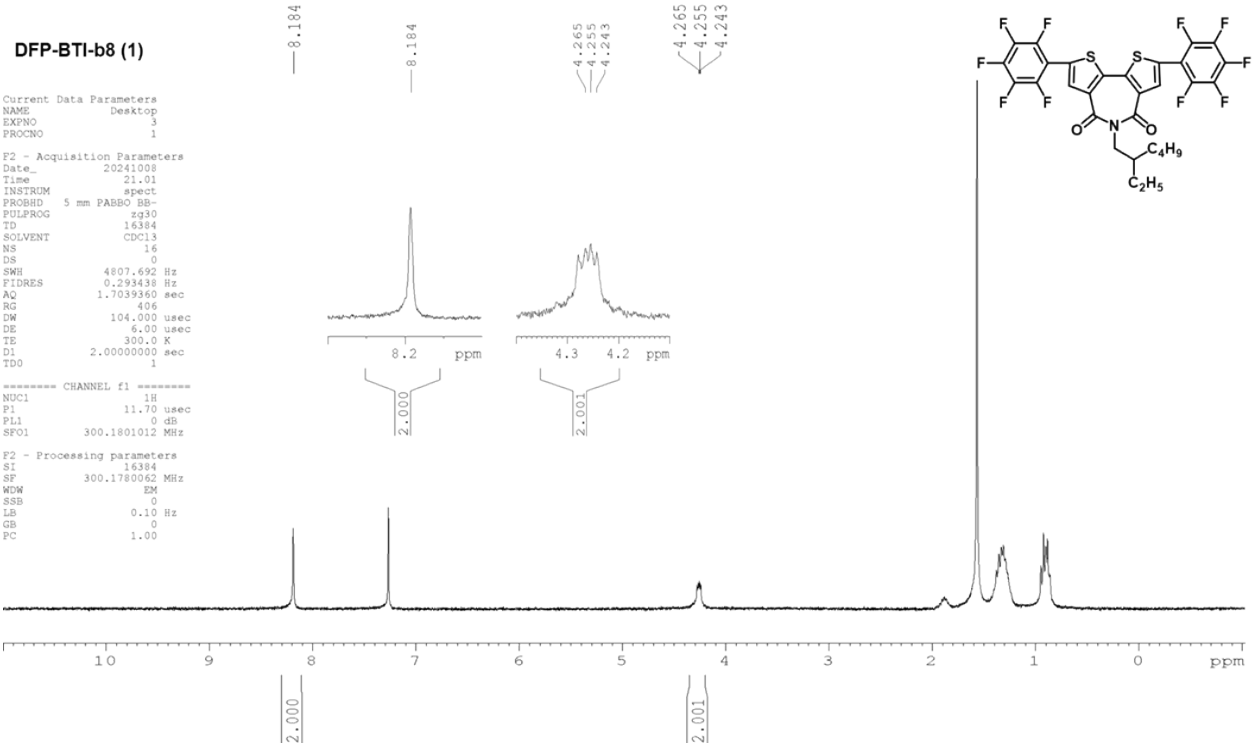



**Fig. S1.** $^1$H NMR spectrum of **DFP-BTI-b8** (**1**) in $CDCl_3$.

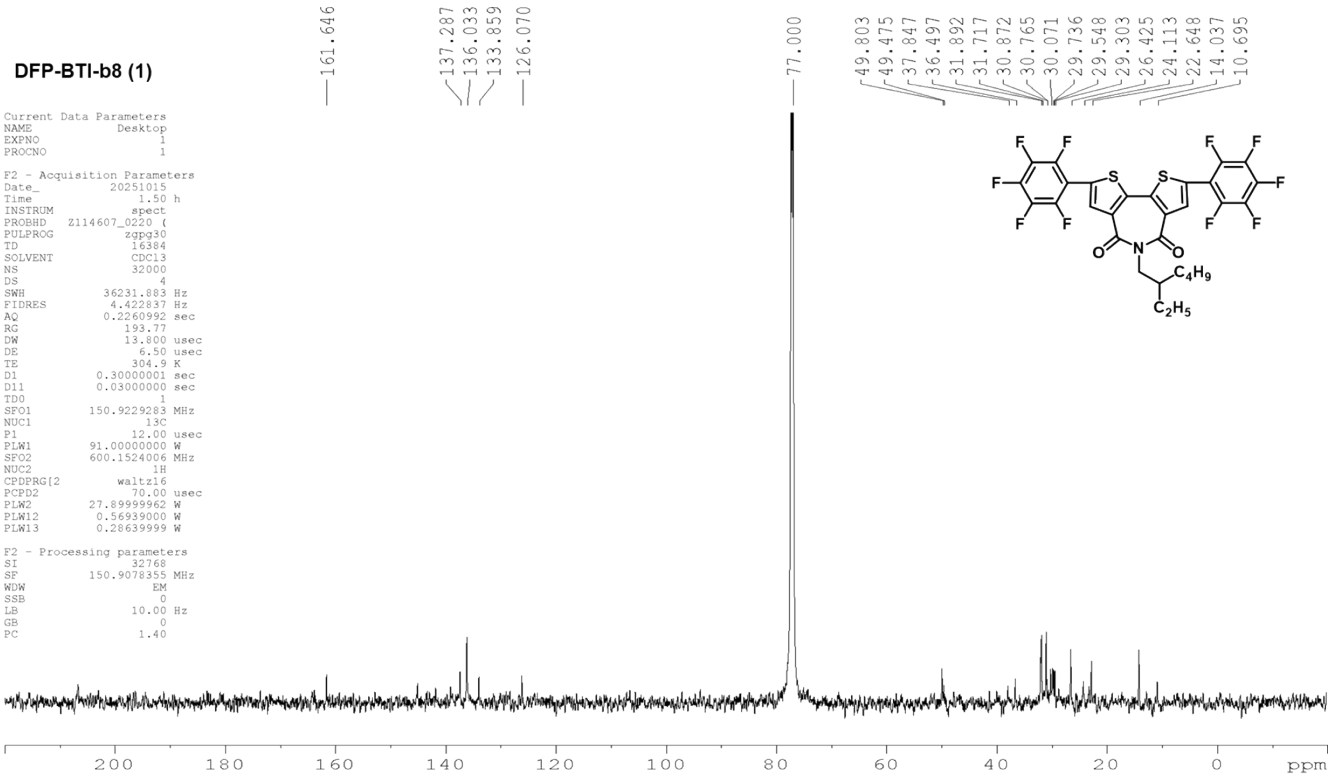



**Fig. S2.** $^{13}$C NMR spectrum of **DFP-BTI-b8** (**1**) in $CDCl_3$.

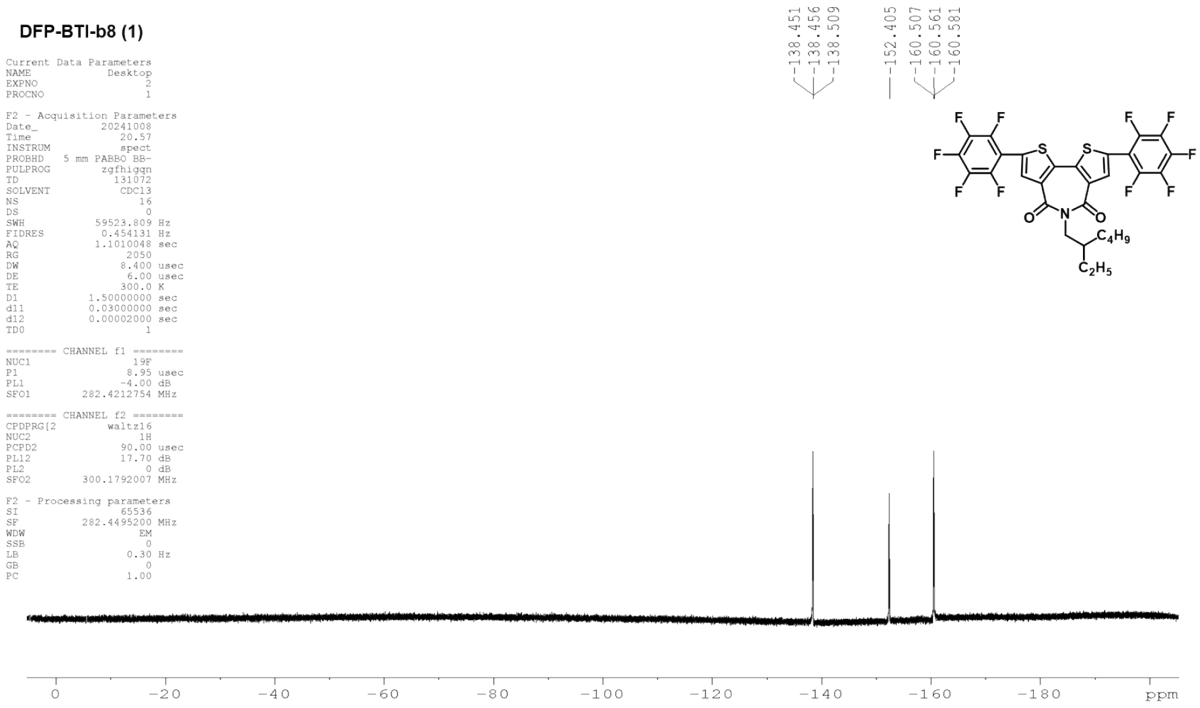



**Fig. S3.** $^{19}F$ NMR spectrum of **DFP-BTI-b8** (**1**) in $CDCl_3$.

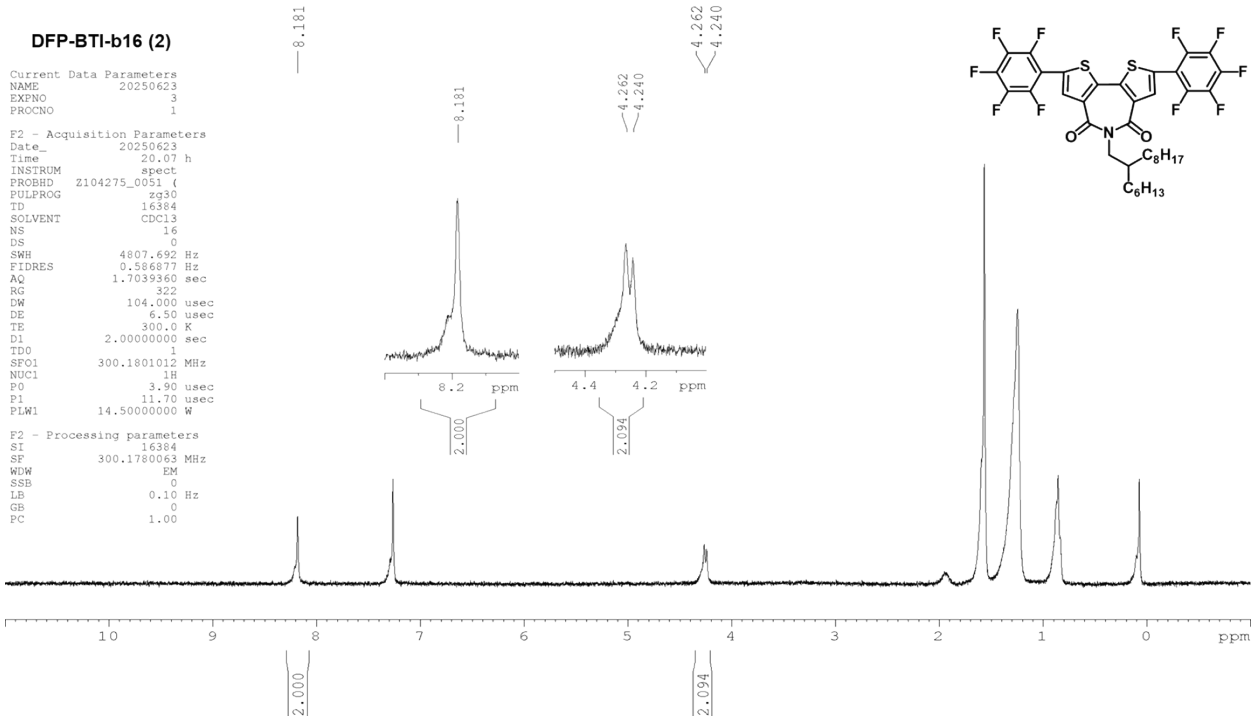



**Fig. S4.** $^{1}$H NMR spectrum of **DFP-BTI-b16** (**2**) in $CDCl_3$.

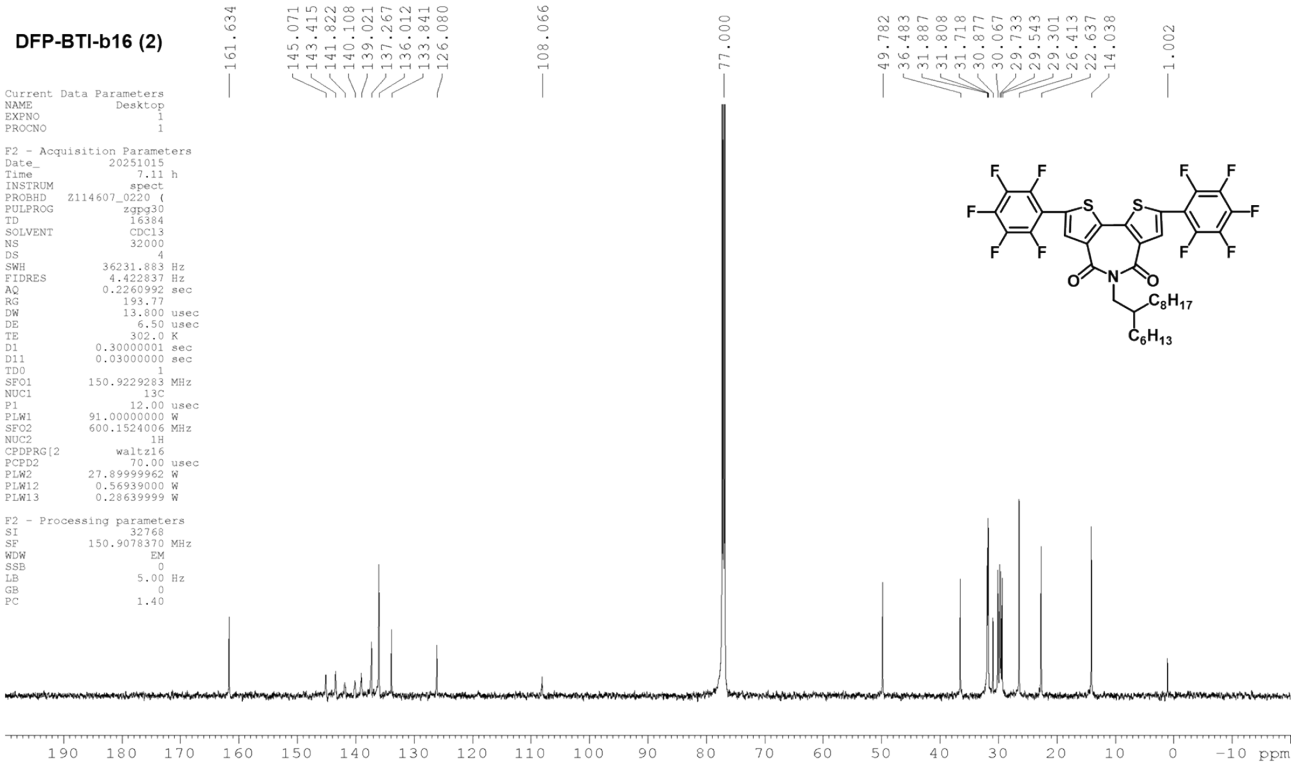



**Fig. S5.** $^{13}$C NMR spectrum of **DFP-BTI-b16** (**2**) in $CDCl_3$.

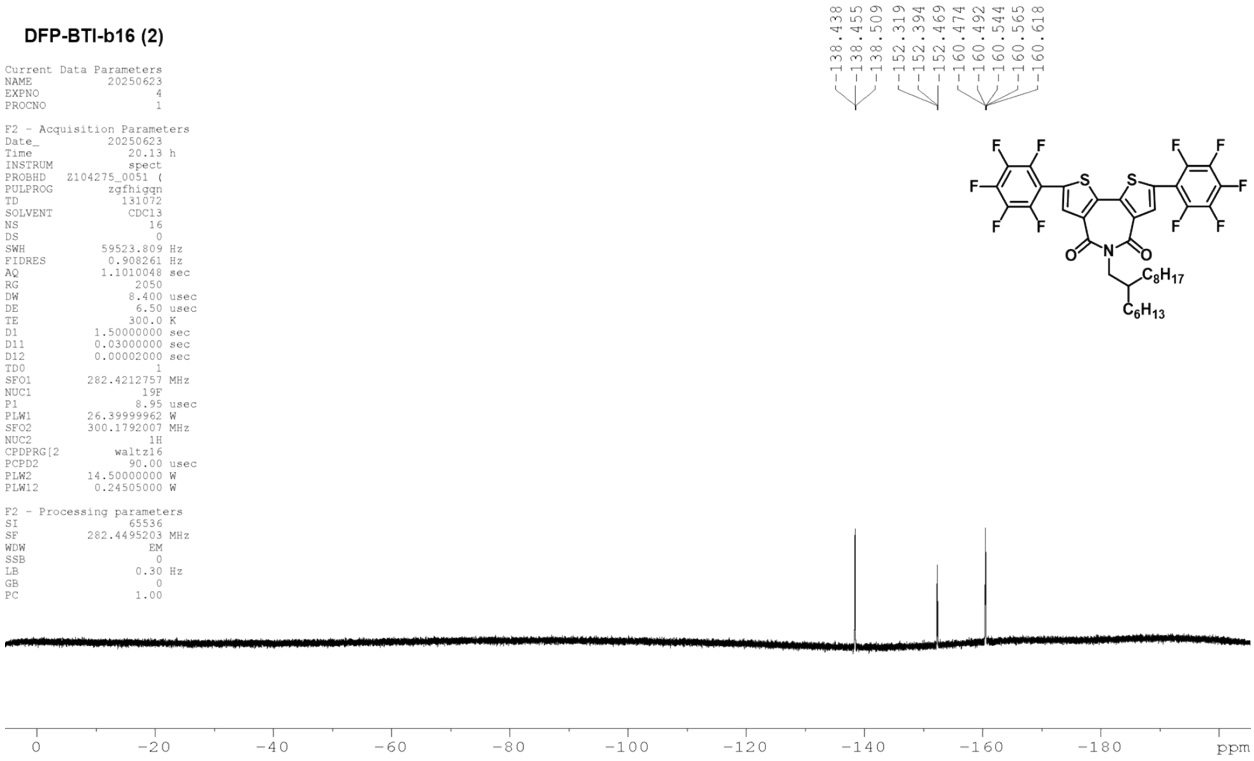



**Fig. S6.** $^{19}$F NMR spectrum of **DFP-BTI-b16** (**2**) in $CDCl_3$.

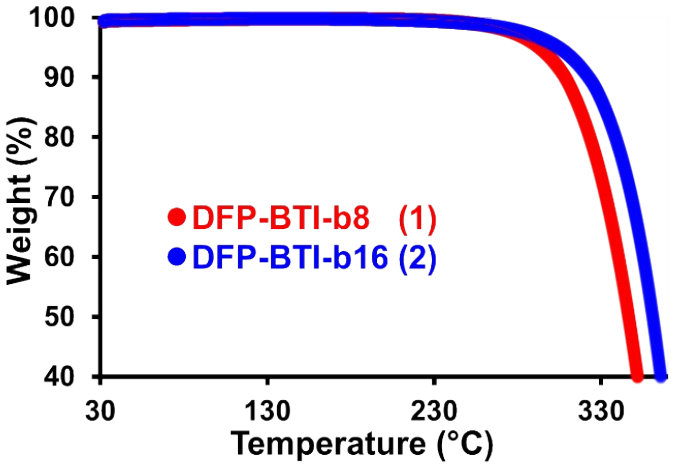



**Fig. S7.** TGA thermogram of compounds (**1-2**).

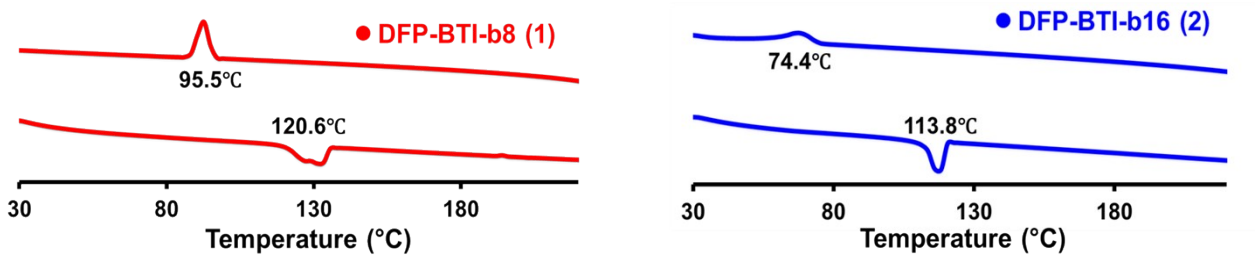
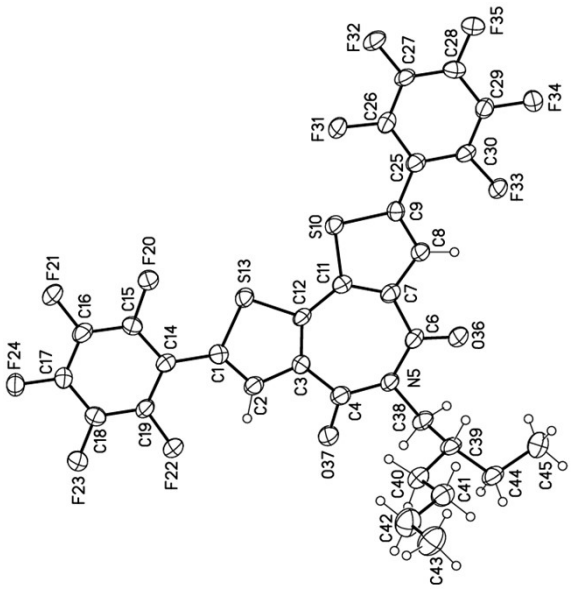



**Fig. S8.** DSC thermogram of compounds (**1-2**).

**(a)**




**(b)**

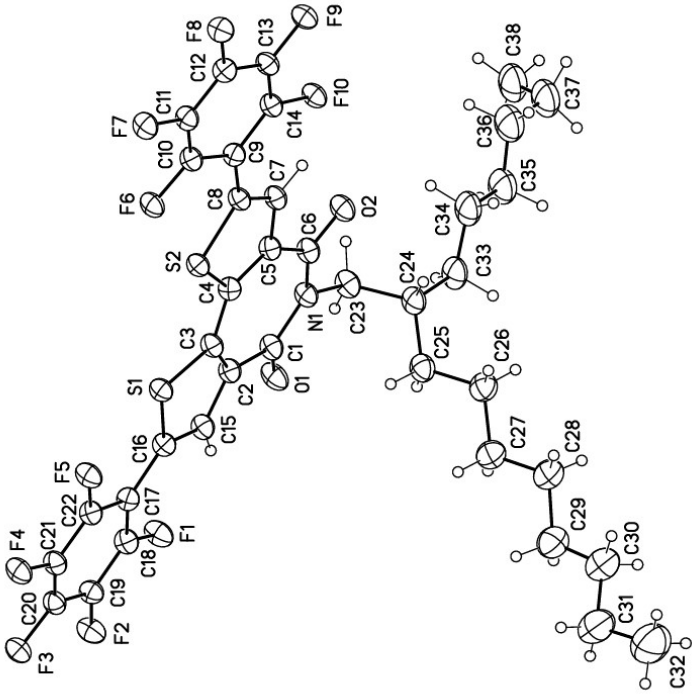



**Fig. S9.** Perspective ORTEP drawing of the molecular structures of (a) **DFP-BTI-b8 (1)** and (b) **DFP-BTI-b16 (2).**

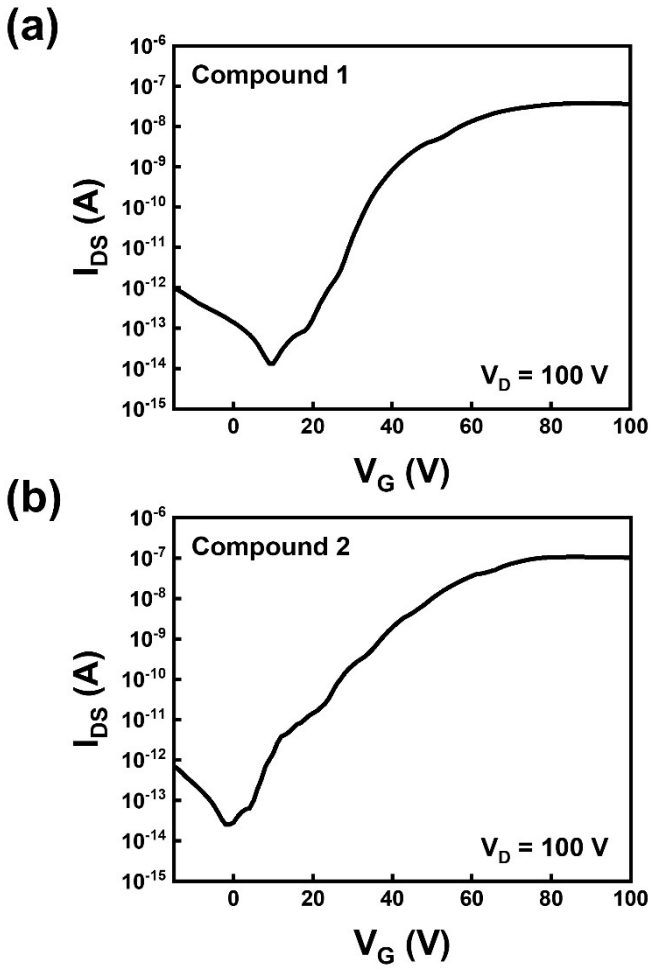



**Fig. S10.** Representative transfer curves of the OTFT devices using thin-films of (a) compound **1** and (b) compound **2** fabricated via spin-coating.

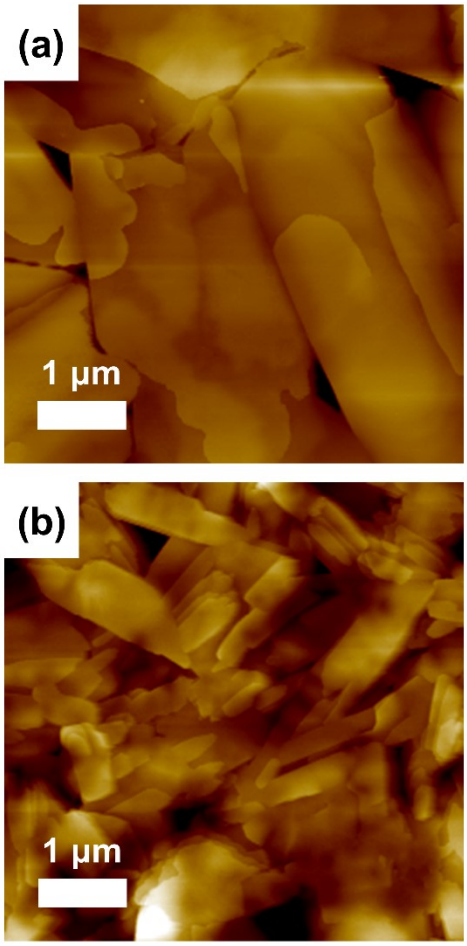



**Fig. S11.** Surface topographic images of thin-films of (a) compound **1** and (b) compound **2** fabricated via spin-coating obtained by atomic force spectroscopy (AFM).