

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%). ¹H NMR (300 MHz, CDCl₃): 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). ¹³C NMR (75 MHz, CDCl₃): spectrum could not be obtained completely due to the poor solubility of the compound. ¹⁹F NMR (282 MHz, CDCl₃): δ -138, -152, -160. MS (HR-FAB, m/z) calcd. for C₃₀H₁₉F₁₀NO₂S₂: 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%). ¹H NMR (300 MHz, CDCl₃): 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). ¹³C NMR (75 MHz, CDCl₃): 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 $\text{C}_{38}\text{H}_{35}\text{F}_{10}\text{NO}_2\text{S}_2$: 791.1950 (M^+). Found: 791.1947.

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

Identification code	240955LT_auto
Empirical formula	$\text{C}_{30}\text{H}_{19}\text{F}_{10}\text{NO}_2\text{S}_2$
Formula weight	679.58
Temperature/K	100.00(10)
Crystal system	monoclinic
Space group	$\text{P2}_1/\text{c}$
$a/\text{\AA}$	21.9217(9)
$b/\text{\AA}$	5.26044(18)
$c/\text{\AA}$	23.2688(7)
$\alpha/^\circ$	90
$\beta/^\circ$	94.557(3)
$\gamma/^\circ$	90
Volume/ \AA^3	2674.83(16)
Z	4
$\rho_{\text{calc}}/\text{g/cm}^3$	1.688
μ/mm^{-1}	2.753
$F(000)$	1376.0
Crystal size/ mm^3	$0.28 \times 0.01 \times 0.01$
Radiation	$\text{Cu K}\alpha$ ($\lambda = 1.54184$)
2Θ range for data collection/ $^\circ$	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 [$R_{\text{int}} = 0.0551, R_{\text{sigma}} = 0.0674$]
Data/restraints/parameters	5203/266/474
Goodness-of-fit on F^2	1.024
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0573, wR_2 = 0.1260$
Final R indexes [all data]	$R_1 = 0.1018, wR_2 = 0.1487$
Largest diff. peak/hole / e \AA^{-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 ₂ S 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
ρ _{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 ≤ h ≤ 34, -4 ≤ k ≤ 6, -28 ≤ l ≤ 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**.

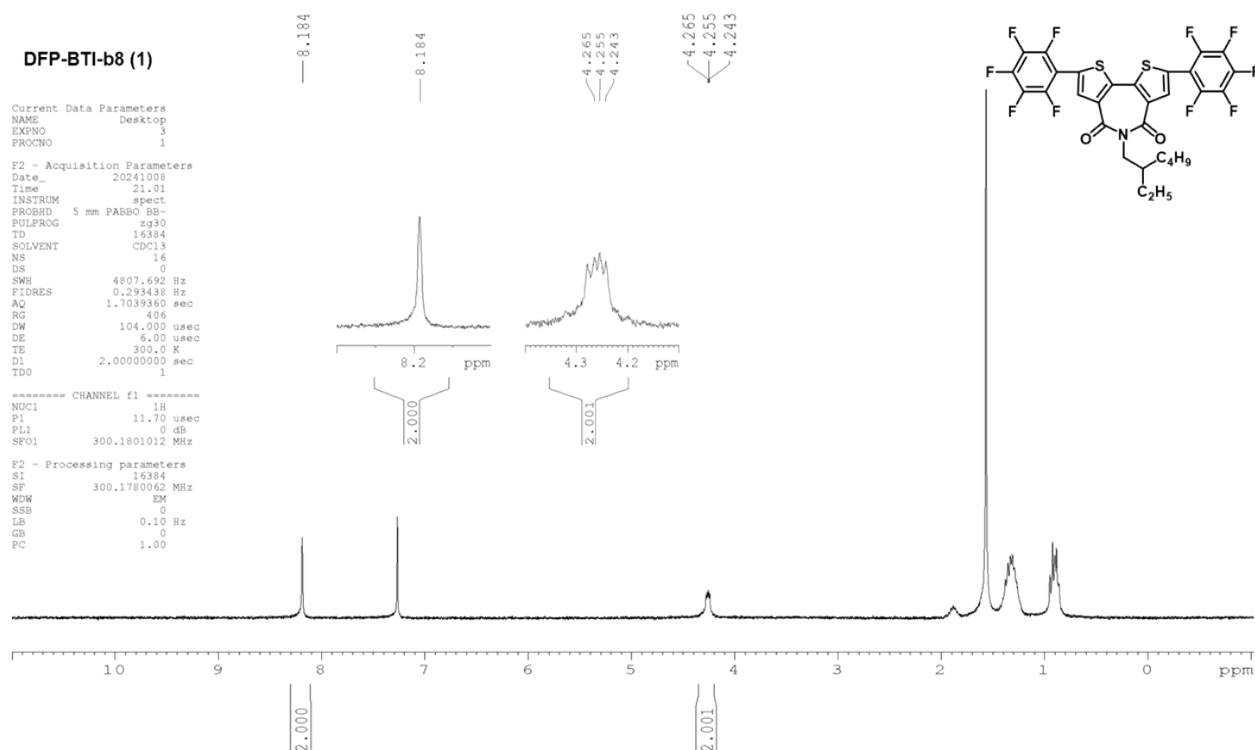


Fig. S1. ^1H NMR spectrum of **DFP-BTI-b8 (1)** in CDCl_3 .

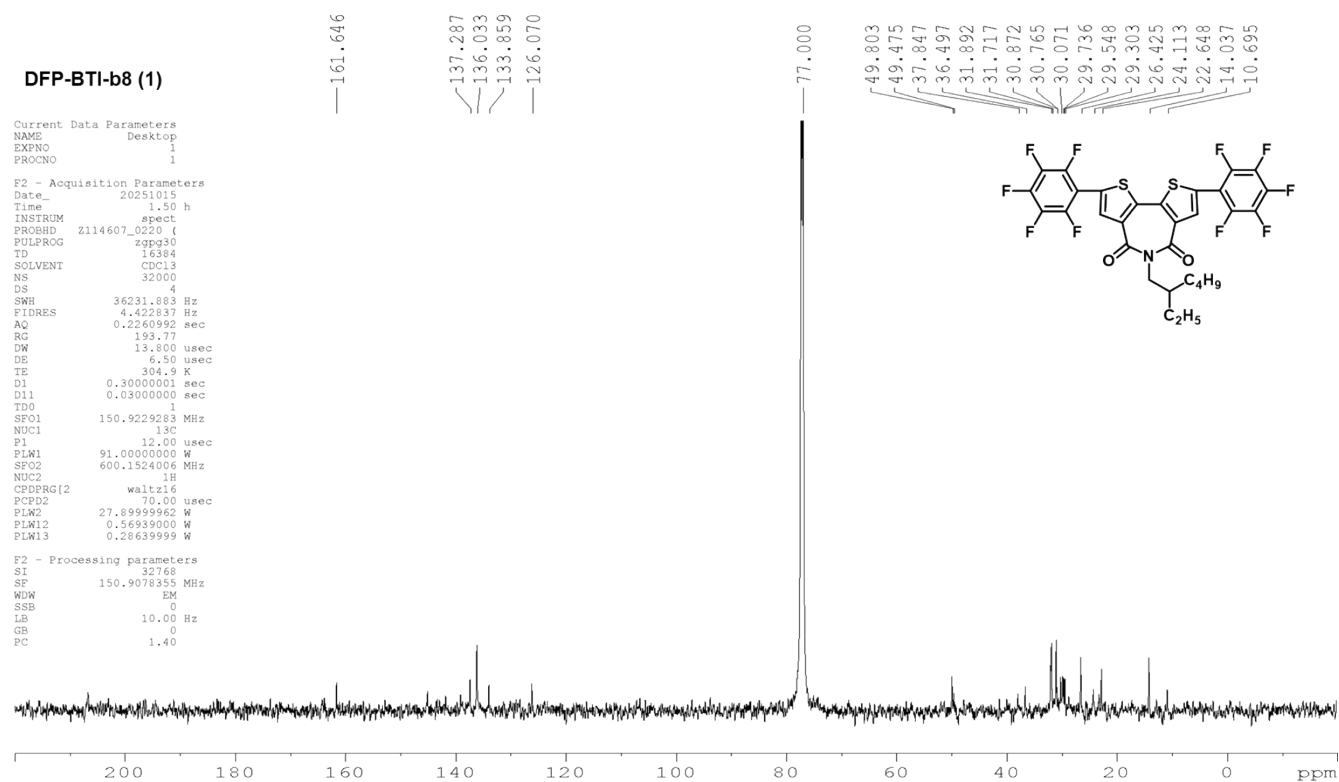


Fig. S2. ¹³C NMR spectrum of **DFP-BTI-b8 (1)** in CDCl₃.

DFP-BTI-b8 (1)

Current Data Parameters
NAME Desktop
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20241008
Time 20.57
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 131072
SOLVENT CDCl3
NS 16
DS 0
SWH 59523.809 Hz
FIDRES 0.454131 Hz
AQ 1.1010048 sec
RG 2050
DW 8.400 usec
DE 6.00 usec
TE 300.0 K
D1 1.50000000 sec
d11 0.03000000 sec
d12 0.00002000 sec
TD0 1

===== CHANNEL f1 =====
NUC1 19F
P1 8.95 usec
PL1 -4.00 dB
SFO1 282.4212754 MHz

===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL12 17.70 dB
PL2 0 dB
SFO2 300.1792007 MHz

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

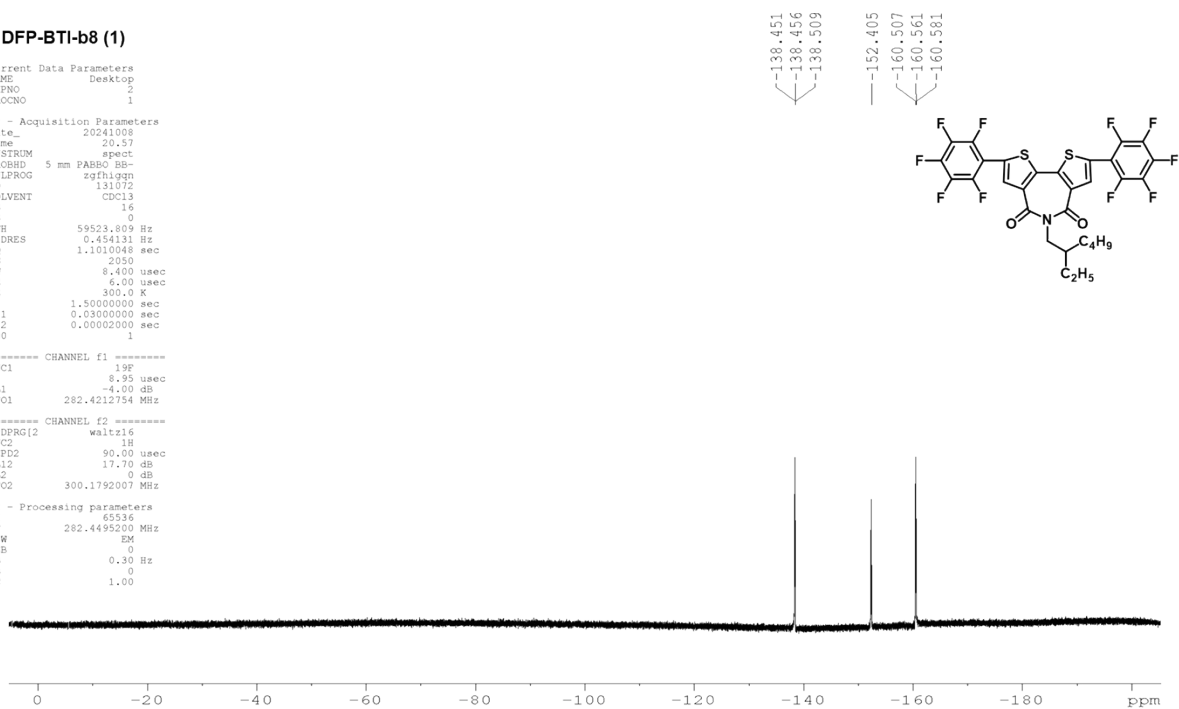


Fig. S3. ^{19}F NMR spectrum of **DFP-BTI-b8 (1)** in CDCl_3 .

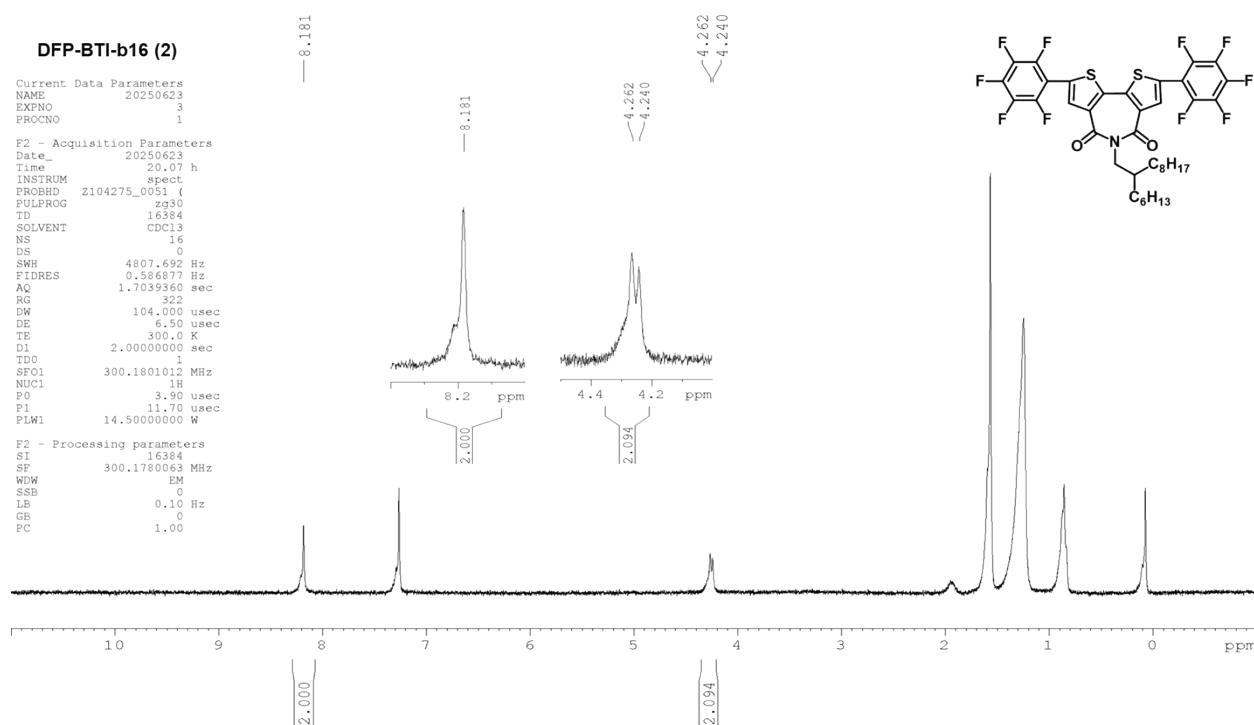


Fig. S4. ¹H NMR spectrum of **DFP-BTI-b16 (2)** in CDCl₃.

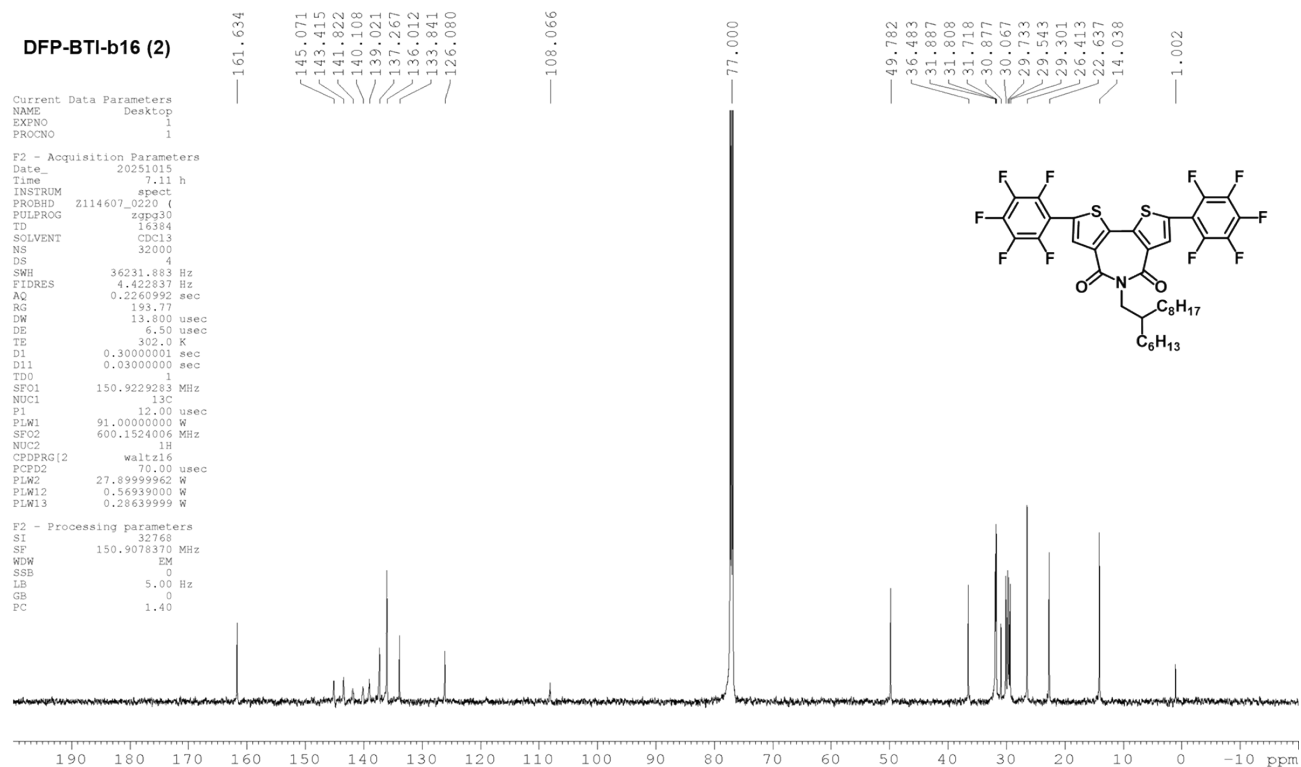


Fig. S5. ^{13}C NMR spectrum of **DFP-BTI-b16 (2)** in CDCl_3 .

DFP-BTI-b16 (2)

Current Data Parameters
NAME 20250623
EXPNO 4
PROCNO 1

F2 - Acquisition Parameters
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Time 20.13 h
INSTRUM spect
PROBHD Z104275.0051 ()
PULPROG zgpg30
TD 131072
SOLVENT CDCl3
NS 16
DS 0
SWH 59523.809 Hz
FIDRES 0.908261 Hz
AQ 1.1010048 sec
RG 2050
DW 8.400 usec
DE 6.50 usec
TE 300.0 K
D1 1.50000000 sec
D11 0.03000000 sec
D12 0.00002000 sec
TD0 1
SFO1 282.4212757 MHz
NUC1 19F
P1 8.95 usec
PLW1 26.39999962 W
SFO2 300.1792007 MHz
NUC2 1H
CPDPRG2 waltz16
PCPD2 90.00 usec
PLW2 14.50000000 W
PLW12 0.24505000 W

F2 - Processing parameters
SI 65536
SF 282.4495203 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

-138.438
-138.455
-138.509
-152.319
-152.394
-152.469
-160.474
-160.492
-160.544
-160.565
-160.618

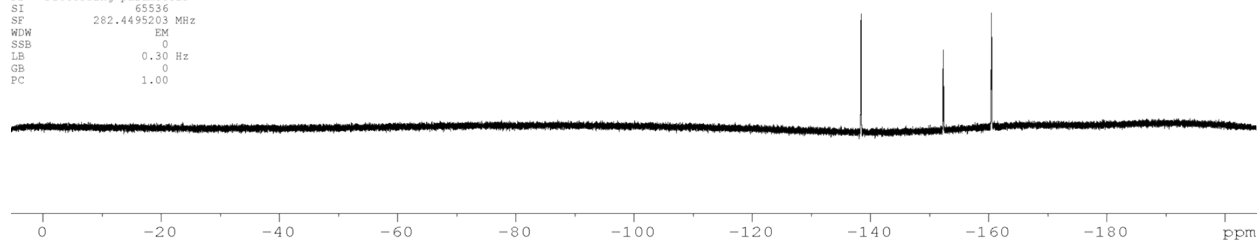
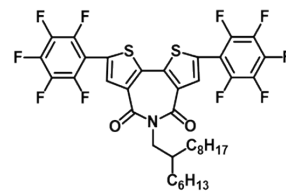


Fig. S6. ^{19}F NMR spectrum of **DFP-BTI-b16 (2)** in CDCl_3 .

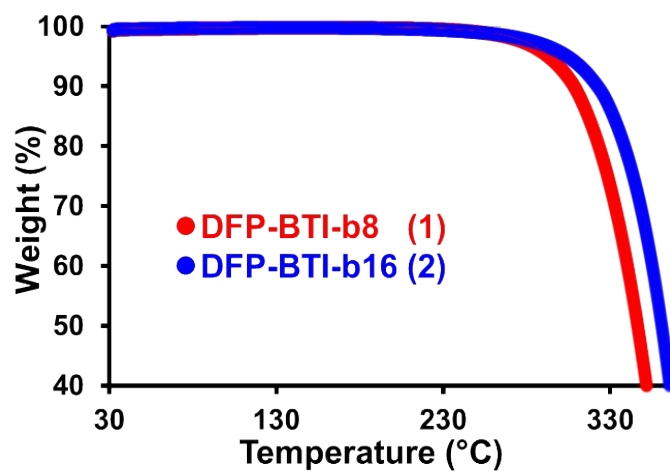


Fig. S7. TGA thermogram of compounds (1-2).

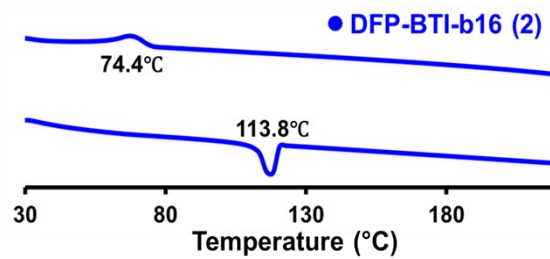
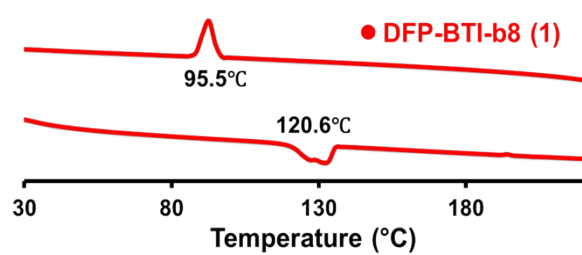


Fig. S8. DSC thermogram of compounds (1-2).

Atom	U ¹¹	U ²²	U ³³	U ¹²	U ¹³	U ²³
C1	0.021	0.021	0.021	0.000	0.000	0.000
C2	0.021	0.021	0.021	0.000	0.000	0.000
C3	0.021	0.021	0.021	0.000	0.000	0.000
C4	0.021	0.021	0.021	0.000	0.000	0.000
C5	0.021	0.021	0.021	0.000	0.000	0.000
C6	0.021	0.021	0.021	0.000	0.000	0.000
C7	0.021	0.021	0.021	0.000	0.000	0.000
C8	0.021	0.021	0.021	0.000	0.000	0.000
C9	0.021	0.021	0.021	0.000	0.000	0.000
C10	0.021	0.021	0.021	0.000	0.000	0.000
C11	0.021	0.021	0.021	0.000	0.000	0.000
C12	0.021	0.021	0.021	0.000	0.000	0.000
C13	0.021	0.021	0.021	0.000	0.000	0.000
C14	0.021	0.021	0.021	0.000	0.000	0.000
C15	0.021	0.021	0.021	0.000	0.000	0.000
C16	0.021	0.021	0.021	0.000	0.000	0.000
C17	0.021	0.021	0.021	0.000	0.000	0.000
C18	0.021	0.021	0.021	0.000	0.000	0.000
C19	0.021	0.021	0.021	0.000	0.000	0.000
C20	0.021	0.021	0.021	0.000	0.000	0.000
C21	0.021	0.021	0.021	0.000	0.000	0.000
C22	0.021	0.021	0.021	0.000	0.000	0.000
C23	0.021	0.021	0.021	0.000	0.000	0.000
C24	0.021	0.021	0.021	0.000	0.000	0.000
C25	0.021	0.021	0.021	0.000	0.000	0.000
C26	0.021	0.021	0.021	0.000	0.000	0.000
C27	0.021	0.021	0.021	0.000	0.000	0.000
C28	0.021	0.021	0.021	0.000	0.000	0.000
C29	0.021	0.021	0.021	0.000	0.000	0.000
C30	0.021	0.021	0.021	0.000	0.000	0.000
C31	0.021	0.021	0.021	0.000	0.000	0.000
C32	0.021	0.021	0.021	0.000	0.000	0.000
C33	0.021	0.021	0.021	0.000	0.000	0.000
C34	0.021	0.021	0.021	0.000	0.000	0.000
C35	0.021	0.021	0.021	0.000	0.000	0.000
C36	0.021	0.021	0.021	0.000	0.000	0.000
C37	0.021	0.021	0.021	0.000	0.000	0.000
C38	0.021	0.021	0.021	0.000	0.000	0.000
C39	0.021	0.021	0.021	0.000	0.000	0.000
C40	0.021	0.021	0.021	0.000	0.000	0.000
C41	0.021	0.021	0.021	0.000	0.000	0.000
C42	0.021	0.021	0.021	0.000	0.000	0.000
C43	0.021	0.021	0.021	0.000	0.000	0.000
C44	0.021	0.021	0.021	0.000	0.000	0.000
C45	0.021	0.021	0.021	0.000	0.000	0.000
F1	0.021	0.021	0.021	0.000	0.000	0.000
F2	0.021	0.021	0.021	0.000	0.000	0.000
F3	0.021	0.021	0.021	0.000	0.000	0.000

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

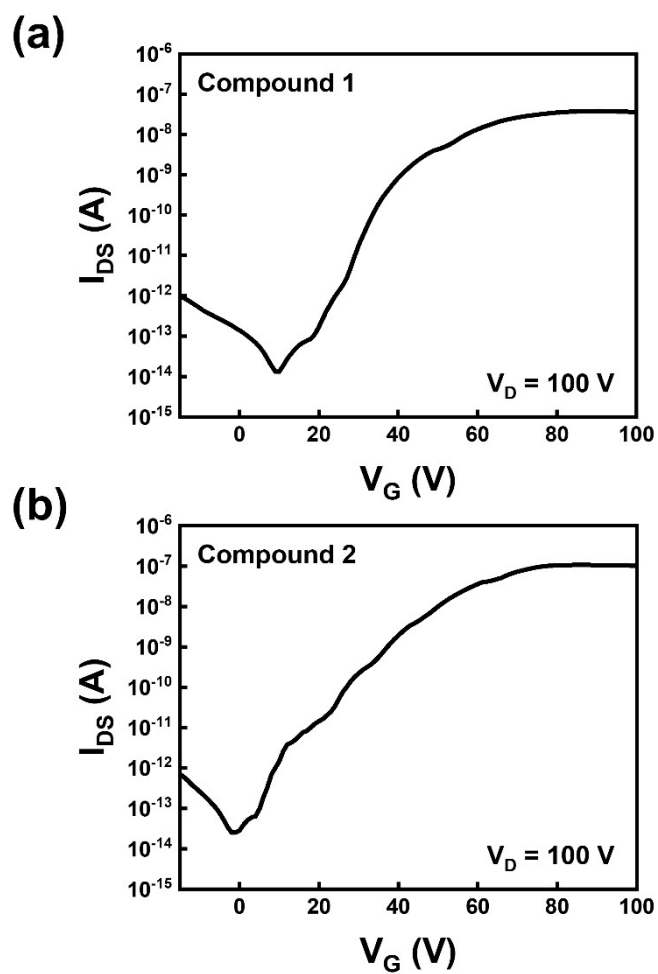


Fig. S10. Representative transfer curves of the OTFT devices using thin-films of (a) compound **1** and (b) compound **2** fabricated via spin-coating.

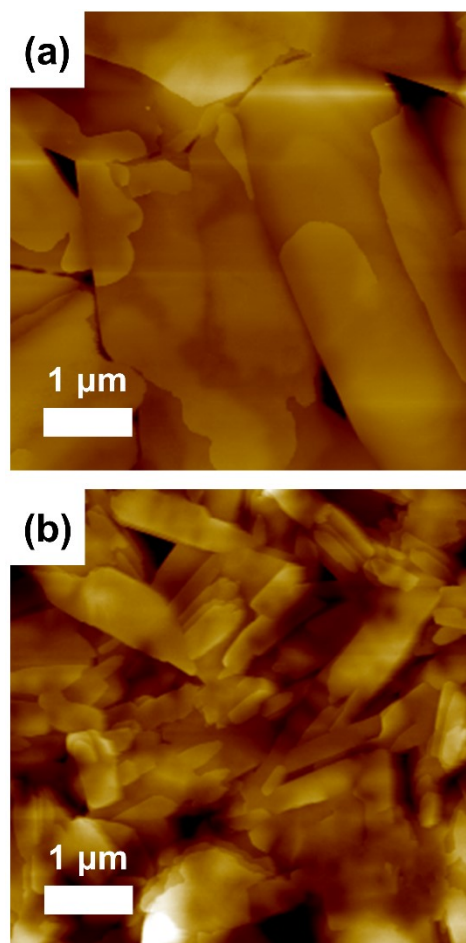


Fig. S11. Surface topographic images of thin-films of (a) compound **1** and (b) compound **2** fabricated via spin-coating obtained by atomic force spectroscopy (AFM).