

Supporting Information

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

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KEYWORDS: Bithiophene imide; pentafluorophenyl; solution-processing; organic semiconductors; organic thin-film transistor

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	$\text{P}2_1/\text{c}$
$a/\text{\AA}$	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**.

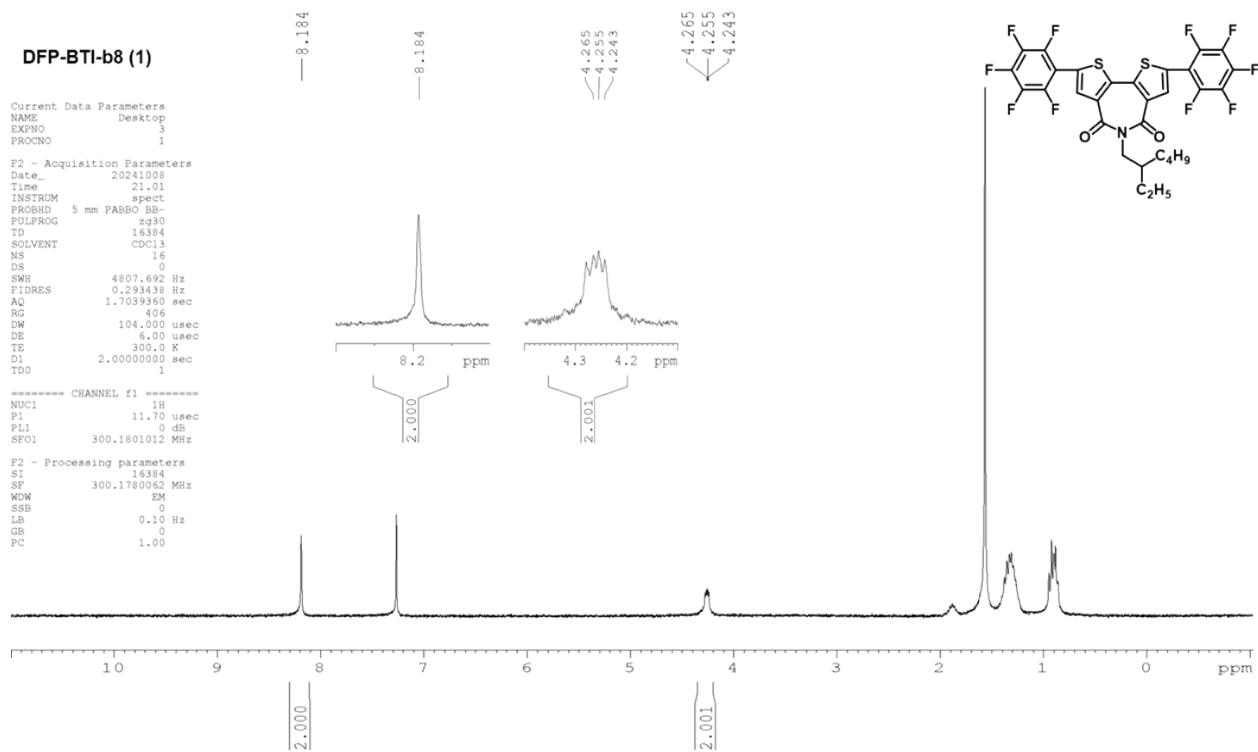


Fig. S1. ¹H NMR spectrum of **DFP-BTI-b8 (1)** in CDCl₃.

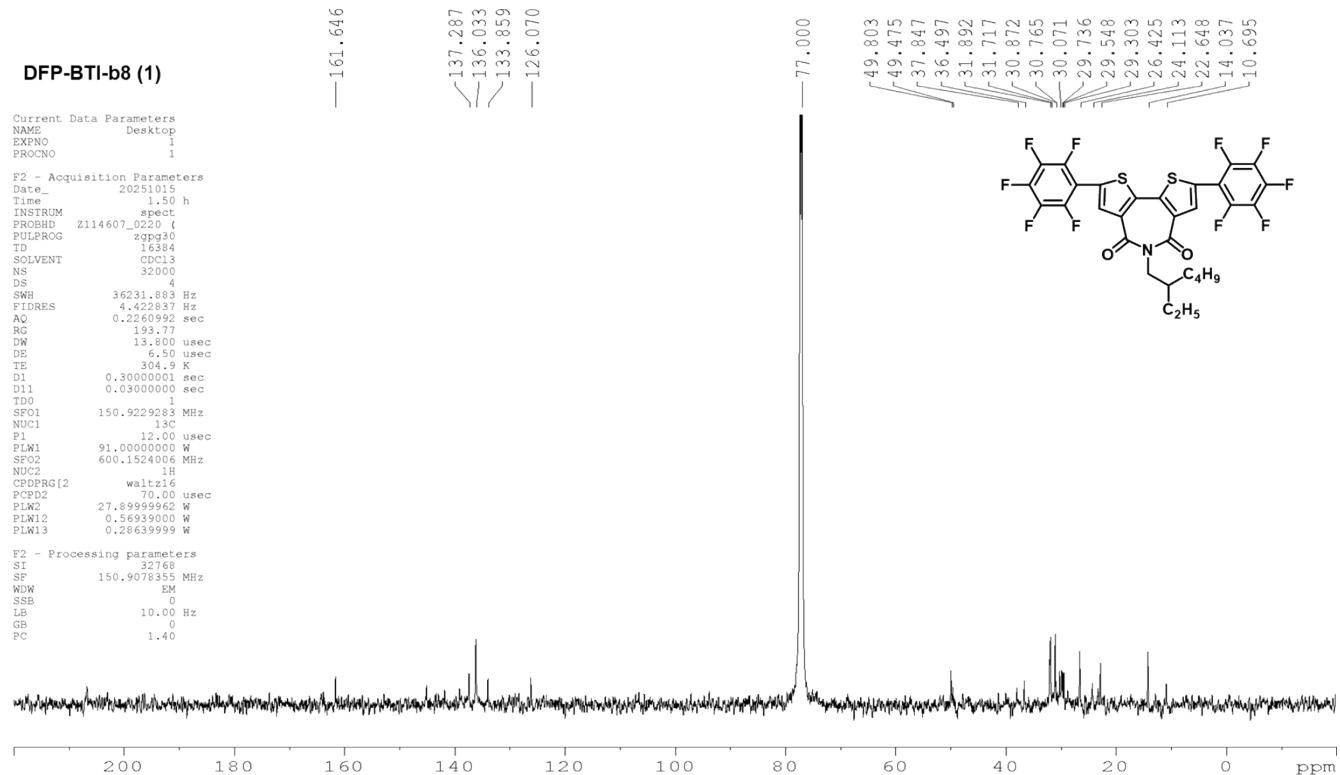


Fig. S2. ^{13}C NMR spectrum of **DFP-BTI-b8 (1)** in CDCl_3 .

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 zgpr3d9f
TD 65536
SOLVENT CDCl3
NS 16
DS 0
SWH 59523.809 Hz
FIDRES 0.454131 Hz
AQ 1.101048 sec
RG 2050
DW 80.0 usec
DE 6.00 usec
TE 300.0 K
D1 1.5000000 sec
d11 0.0300000 sec
d12 0.00002000 sec
TDO 1

===== CHANNEL f1 =====
NUC1 19F
P1 8.95 usec
PL1 -4.00 dB
SF01 282.4212754 MHz

===== CHANNEL f2 =====
CPDPRG[2 waltz16
NUC2 19F
PCPD2 90.00 usec
PL12 17.70 dB
PL2 0 dB
SF02 300.1792007 MHz

F2 - Processing parameters
SI 65536
SF 282.4495200 MHz
WDW ²2M
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

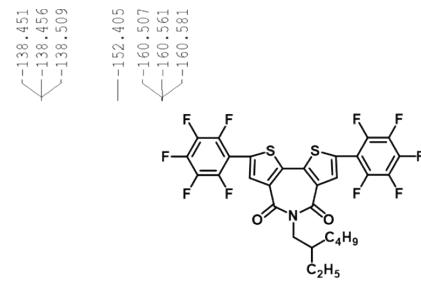


Fig. S3. ^{19}F NMR spectrum of **DFP-BTI-b8 (1)** in CDCl_3 .

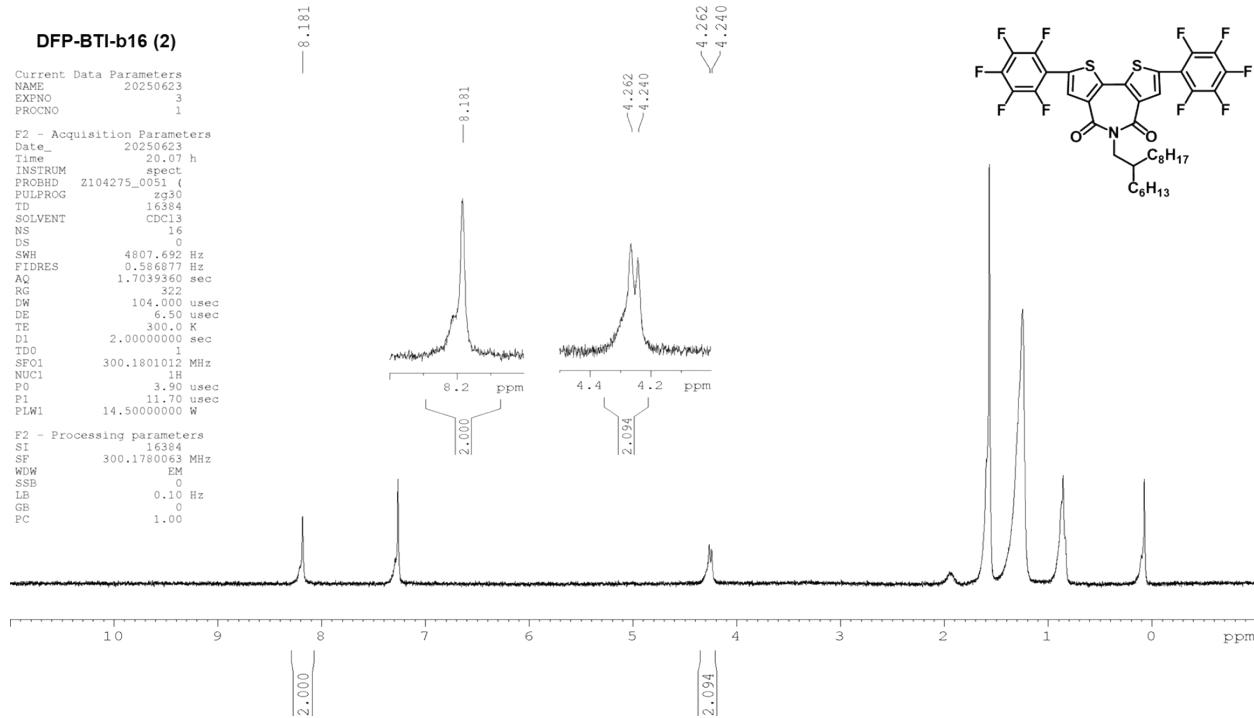


Fig. S4. ^1H NMR spectrum of **DFP-BTI-b16 (2)** in CDCl_3 .

DFP-BTI-b16 (2)

Current Data Parameters
NAME Desktop
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters

Date 20251015
Time 7.11 h
INSTRUM spect
PROBHD Z114607_0220
PULPROG zpg3d
TD 16384
SOLVENT CDCl3
NS 32000
DS 4
SWH 36231.383 Hz
ETDRES 4.444444 Hz
AQ 0.2260992 sec
RG 193.77
DW 13.800 usec
DE 6.50 usec
TE 300.0 K
D1 0.30000001 sec
D11 0.03000000 sec
TD0 1
SF01 150.9229283 MHz
NUC1 13C
P1 12.000 usec
PLW1 91.00000000 W
SF02 600.1524006 MHz
NUC2 1H
CPDPRG[2] waltz16
PCP[2] 0.000 usec
PLW2 27.89999962 W
PLW12 0.56939000 W
PLW13 0.28639999 W

F2 - Processing parameters

SI 32768

SF 150.9078370 MHz

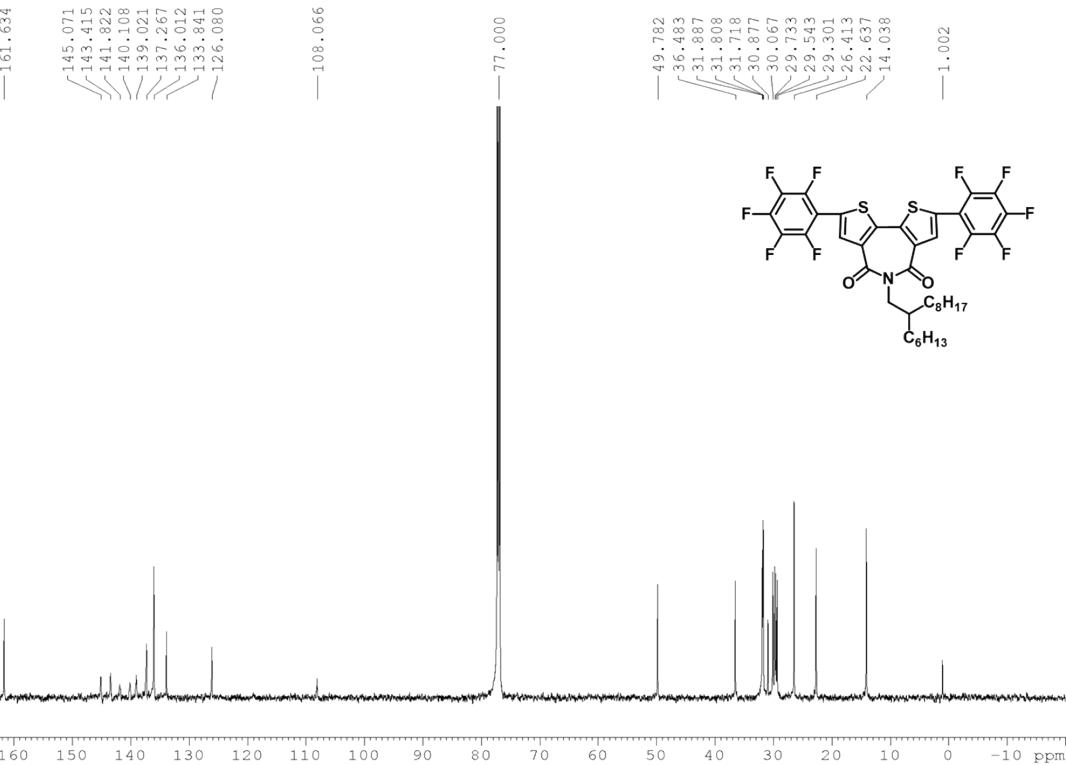
WDW 0

SSB 0

LB 5.00 Hz

GB 1.40

PC 1.40



DFP-BTI-b16 (2)

Current Data Parameters
 NAME 20250623
 EXPT 4
 PRGCNO 1
 F2 - Acquisition Parameters
 Date_ 20250623
 Time 13:13 h
 INSTRUM spect
 PROBID Z104275_0051 (
 PULPROG zgfhigq
 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 6.000 usec
 TB 300.0 K
 D1 1.5000000 sec
 D11 0.03000000 sec
 D12 0.00002000 sec
 TD0 1
 SF01 282.4212757 MHz
 NUC1 1H
 P1 8.95 usec
 PLM1 26.39999962 W
 SF02 300.1792007 MHz
 NUC2 1H
 CDPPLRG[2 waltz16
 PCD2 90 usec
 PLM2 14.5000000 W
 PLM12 0.24505000 W
 PLM2

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

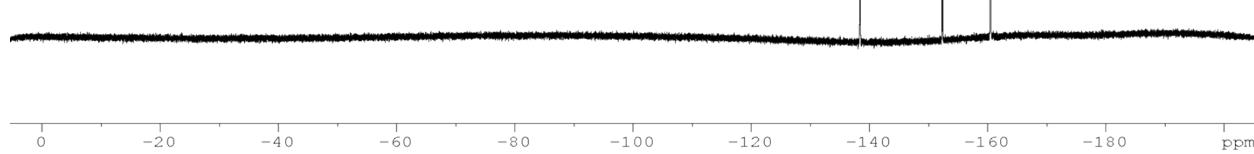
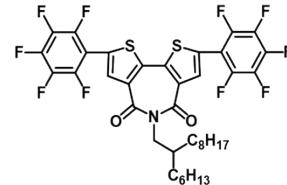
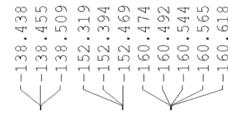


Fig. S6. ^{19}F NMR spectrum of DFP-BTI-b16 (2) in CDCl_3 .

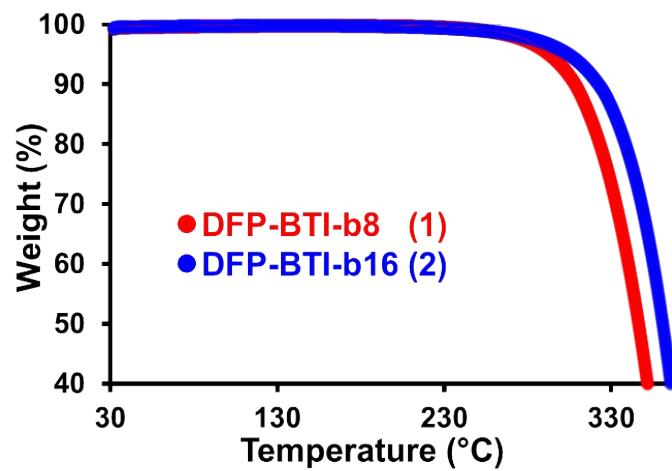


Fig. S7. TGA thermogram of compounds (1-2).

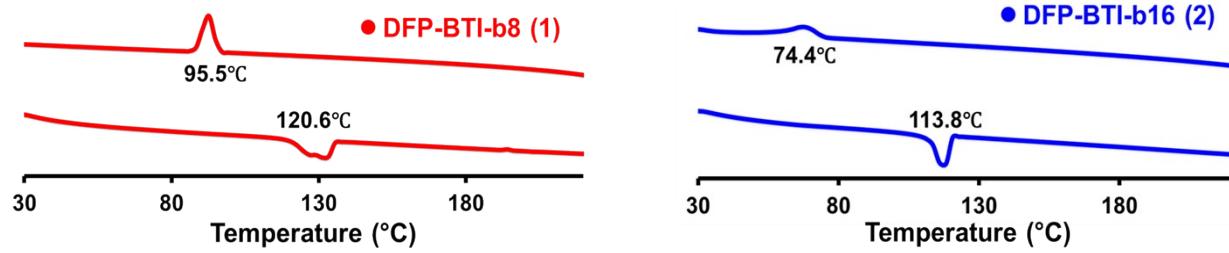
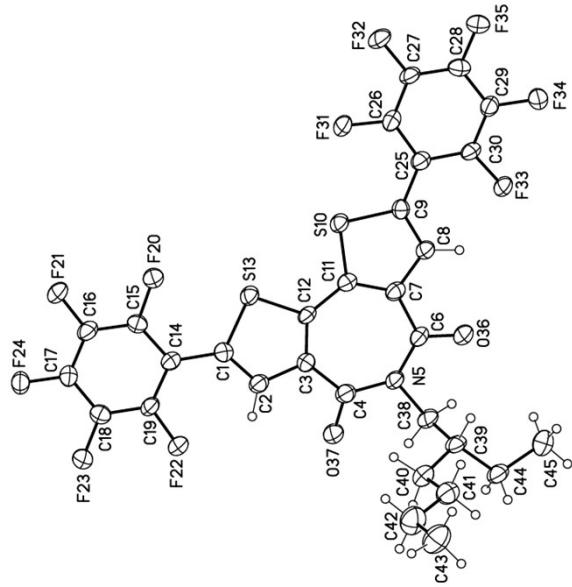


Fig. S8. DSC thermogram of compounds (1-2).

(a)



(b)

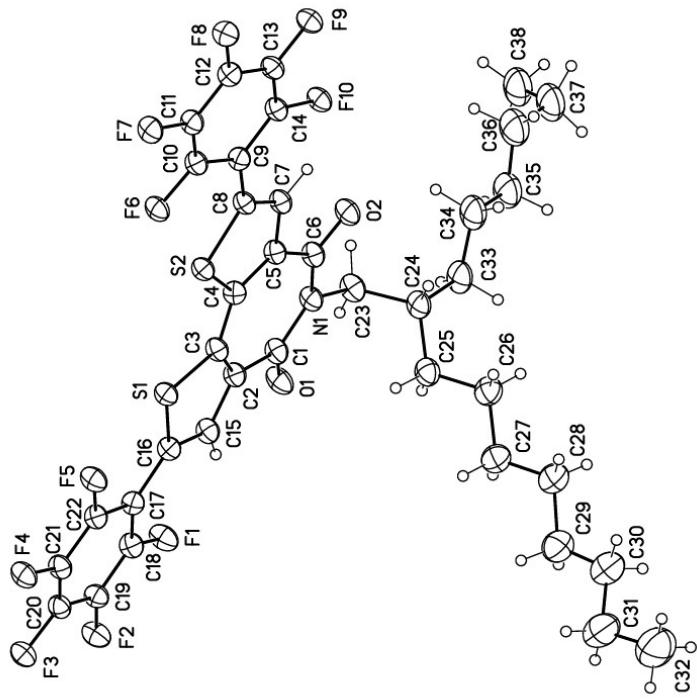


Fig. S9. Perspective ORTEP drawing of the molecular structures of (a) DFP-BTI-b8 (1) and (b) DFP-BTI-b16 (2).

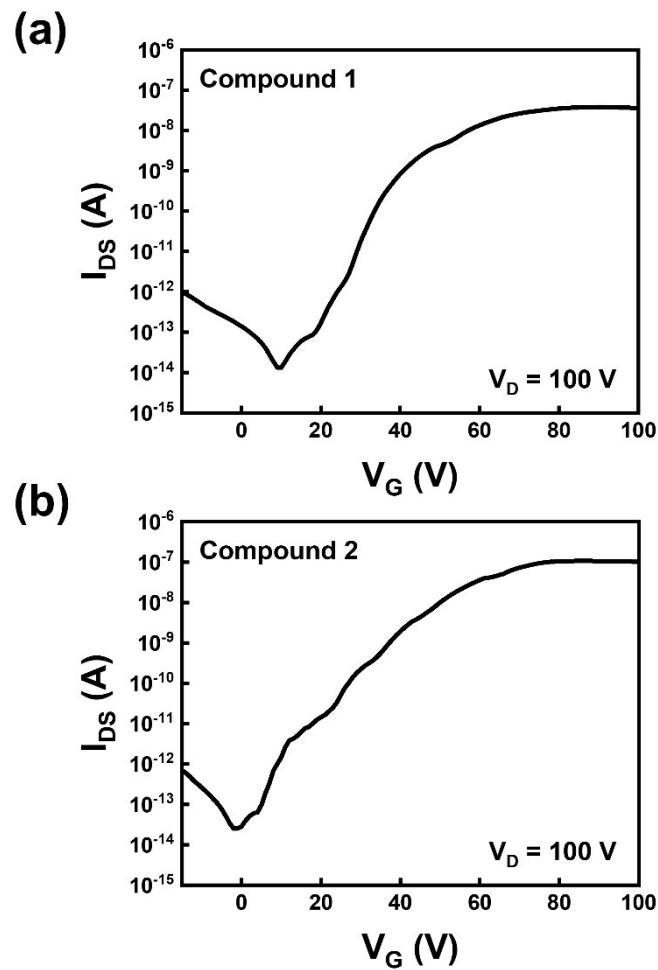


Fig. S10. Representative transfer curves of the OTFT devices using thin-films of (a) compound **1** and (b) compound **2** fabricated via spin-coating.

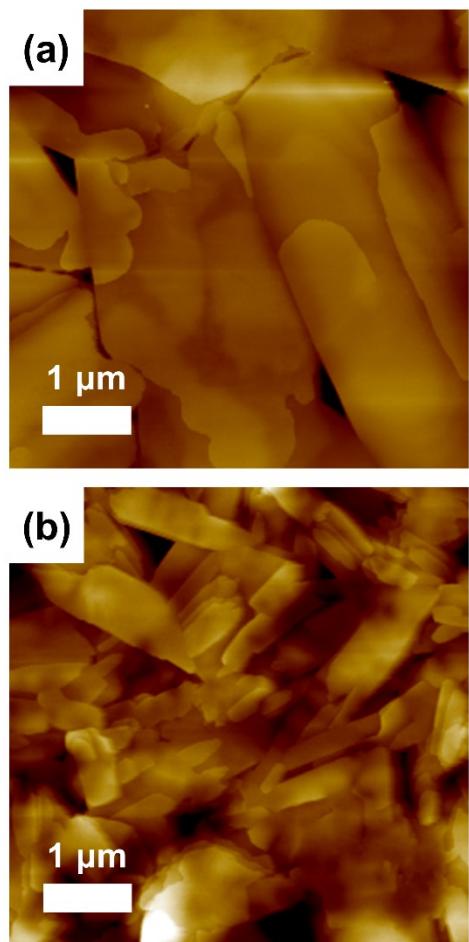


Fig. S11. Surface topographic images of thin-films of (a) compound **1** and (b) compound **2** fabricated via spin-coating obtained by atomic force spectroscopy (AFM).