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### **Fluoro-alkyl Substituted Isothianaphthene Bisimides as Stable n-Type Semiconductors**

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### 1. Experimental

#### 1.1 General Experiment

All the reagents and solvents were purchased from Aldrich or TCI and used as received without further purification.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker Avance 300 NMR spectrometer operating at 300 MHz (for  $^1\text{H}$ NMR) / 75 MHz (for  $^{13}\text{C}$ NMR). Thermal gravimetric analysis (TGA) was performed using a TA Instruments analyzer TA2950 at a heating rate of 10 °C/min under nitrogen flow rate of 50 cm<sup>3</sup>/min. Differential scanning calorimetry (DSC) experiments were carried out on a TA Instruments calorimeter DSCQ1000 at a heating or cooling rate of 10 °C /min under nitrogen flow. Thin film morphologies were studied by atomic force microscopy (AFM) using a Seiko Instruments AFM microscope SPA400HV with a SPI 3800 controller. XRD patterns were recorded using a Bruker D8 Advance X-ray diffractometer with a Cu K $\alpha$  irradiation source ( $\lambda = 1.541 \text{ \AA}$ ). UV-Vis absorption spectra measurements were carried out on a Perkin-Elmer Lambda 750 spectrophotometer in dilute chloroform solution or for vacuum deposited thin films. Cyclic voltammetry measurements were conducted using a Gamry Interface 1000 electrochemical workstation in DCM solution containing 0.1 M Bu<sub>4</sub>NPF<sub>6</sub> as an electrolyte at a scan speed of 0.1V/S. A glassy carbon electrode as a working electrode, a Pt wire counter electrode and an Ag wire quasi-reference electrode were used. Ferrocene/ferrocenium redox couple (Fc/Fc<sup>+</sup>) was used as the internal reference for CV measurements. The LUMO energy levels were estimated from the following equation:

$$E_{LUMO} = \left\{ -4.8 - \left( E_{red}^{1/2} - E_{Fc/Fc^+} \right) \right\} [\text{eV}],$$

Where  $E_{red}^{1/2}$  refers to the first reduction potential and  $E_{ox, Fc/Fc^+}$  is the oxidation potential of ferrocene in the given system.

The band gaps were calculated from the edge of the thin film absorptions by the below mentioned equation:

$$E_g = \left( 1240 / \lambda \right) [\text{nm}],$$

and the HOMO energy levels were derived from the following equation:

$$E_{HOMO} = (E_{LUMO} - E_g) [\text{eV}]$$

The energy level and reorganization energy were calculated by DFT method at B3LYP/6-311G(d)<sup>1</sup> level of theory using Gaussian 09 package of software.

### 1.2 OTFT Fabrication and Analysis

Silicon wafers with 300 nm silicon oxide layer were seriatim washed with acetone, deionized water and isopropanol (for 30 min each) in an ultrasonic bath followed by drying in nitrogen flow and then UV treatment for 15 min. The substrate was then dipped in a toluene solution of 0.1 M octadecyltrichlorosilane (OTS) at 65 °C for 2h, washed with toluene to remove the residual OTS and dried under nitrogen.<sup>2</sup> The materials were evaporated at a rate of around  $\sim 0.5 - 1 \text{ \AA/s}$  to form  $\sim 40 - 50 \text{ nm}$  active layers at different substrate temperatures under  $10^{-5} \text{ Pa}$ . In next step, gold with a thickness of 30 nm was deposited on the active layer as source and drain electrodes. The current–voltage ( $I$ – $V$ ) curves of the devices were measured on Agilent B1500A instrument, both in ambient air and in a nitrogen glovebox. The electron mobility ( $\mu_e$ ) was obtained from the saturation regime ( $V_d = 40 \text{ V}$ ) according to the saturation region.

### 1.3 Single Crystal Structure Determination

Single crystals of **BTDI-OCF<sub>3</sub>** were grown by solution method via the slow evaporation of chloroform. 10 mg of BTDI-OCF<sub>3</sub> was dissolved in 2 ml chloroform/methanol (V: V= 4: 1) mixed solvent, then filtrated through 0.25  $\mu\text{m}$  membrane filter to a 2 ml tube. After that, they were placed in a clean room and the solvent was gradually evaporated for several days at room temperature to obtain good quality crystals suitable for the single-crystal X-ray analysis. The single crystals were analyzed on a Rigaku diffractometer at 100 K.

## 2. Materials Synthesis and Characterizations

**Compound BTDI-OCF<sub>3</sub>**: To a suspension of BTDNI (0.55 g, 2 mmol) and K<sub>2</sub>CO<sub>3</sub> (1.1 g, 8 mmol) in 15 mL dry DMF in a 50 mL sealed tube and degassed for 10 min, followed by addition of 1-(bromomethyl)-4-(trifluoromethoxy)benzene (2.03 g, 8 mmol). The mixture was stirred for 12 h at 100°C, cooled down to the room temperature and poured into 50 mL water, extracted with CHCl<sub>3</sub> (30 ml  $\times$  3 times), concentrated the organic phase and purified by column chromatography on silica gel (PE: DCM = 1: 1), and the yellow product was further purified by sublimation (0.55 g, 44%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  8.39 (s, 2H), 7.57 (d,  $J = 8.7 \text{ Hz}$ , 4H), 7.16 (d,  $J = 7.9 \text{ Hz}$ , 4H), 5.33 (s, 4H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  162.57, 159.22, 148.94, 136.11, 135.42, 131.33, 131.06, 130.98, 124.06, 122.22, 121.18, 118.81, 43.47. HRMS (+ESI):  $m/z$  calculated for C<sub>28</sub>H<sub>14</sub>F<sub>2</sub>N<sub>2</sub>O<sub>6</sub>S (M+H)<sup>+</sup> 621.0447; found 621.0554.

**Compound BTDI-CF**: Compound **BTDI-CF** was synthesized by the same method as **BTDI-OCF<sub>3</sub>**, however, the post-treatment was slightly different due to its worse solubility. After the mixture was

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poured into water, it was filtrated followed by drying the solid via vacuum oven and finally purified by sublimation (0.55 g, 36%).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.42 (s, 2H), 4.26 (t,  $J = 7.2$  Hz, 4H), 2.35 – 2.14 (m, 4H), 2.13 – 1.97 (m, 4H). HRMS (+ESI):  $m/z$  calculated for  $\text{C}_{34}\text{H}_{14}\text{F}_{34}\text{N}_2\text{O}_6\text{S}$  ( $\text{M}+\text{H}$ ) $^+$  1193.0131; found 1193.0217.

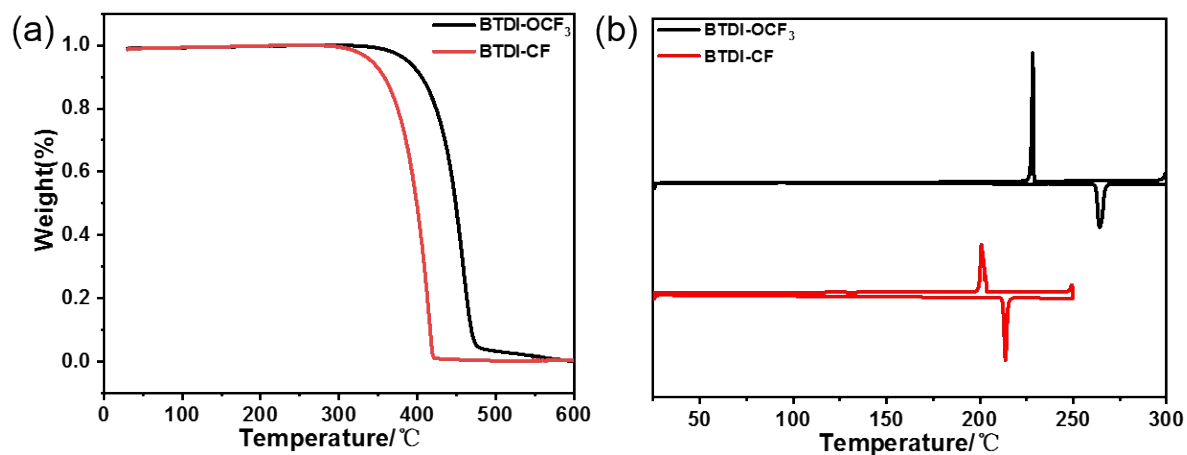


Figure S1. Thermal analysis of two BTDI derivatives: (a) TGA and (b) DSC traces.

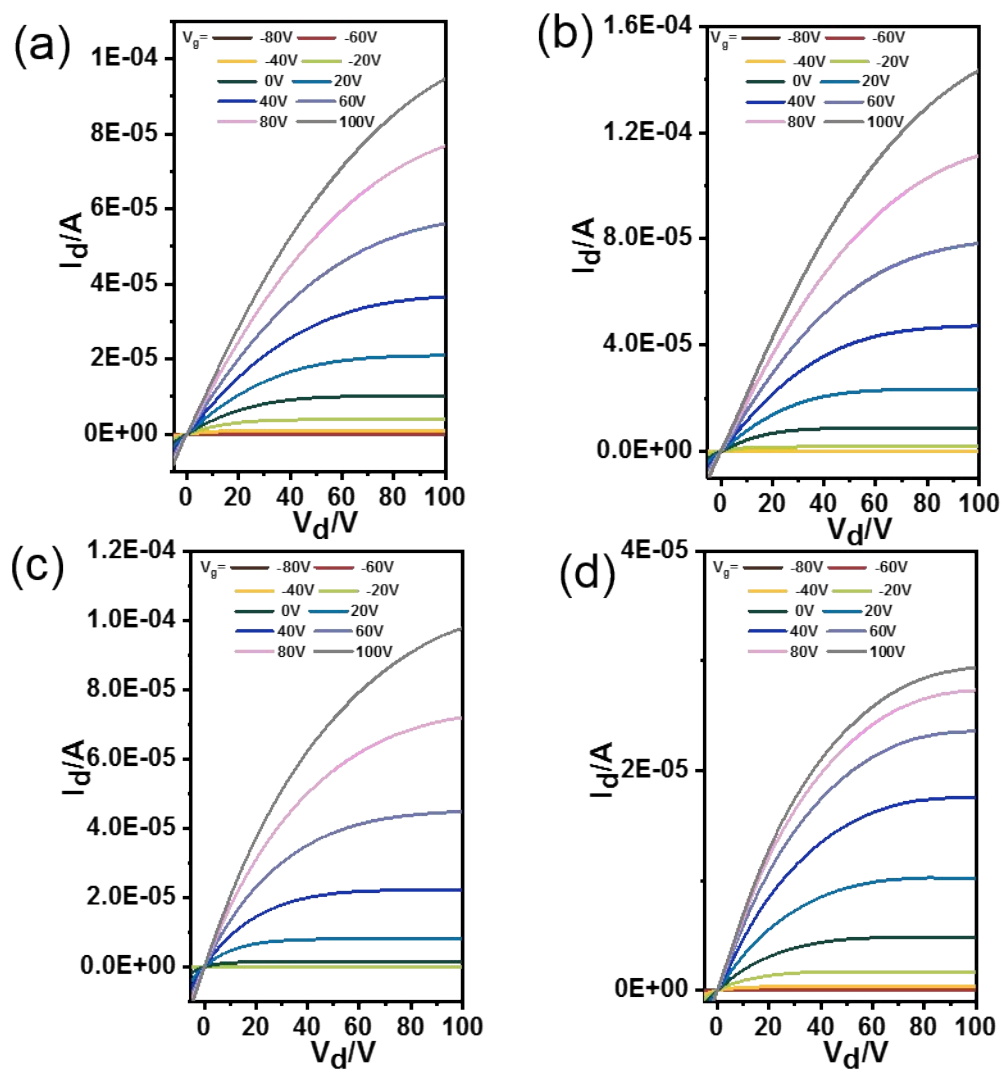


Figure S2. Output curves of **BTDI-CF** with substrate temperature of (a) RT (b) 50°C (c) 80°C as tested in glovebox and (d) tested in air at different gate voltage.

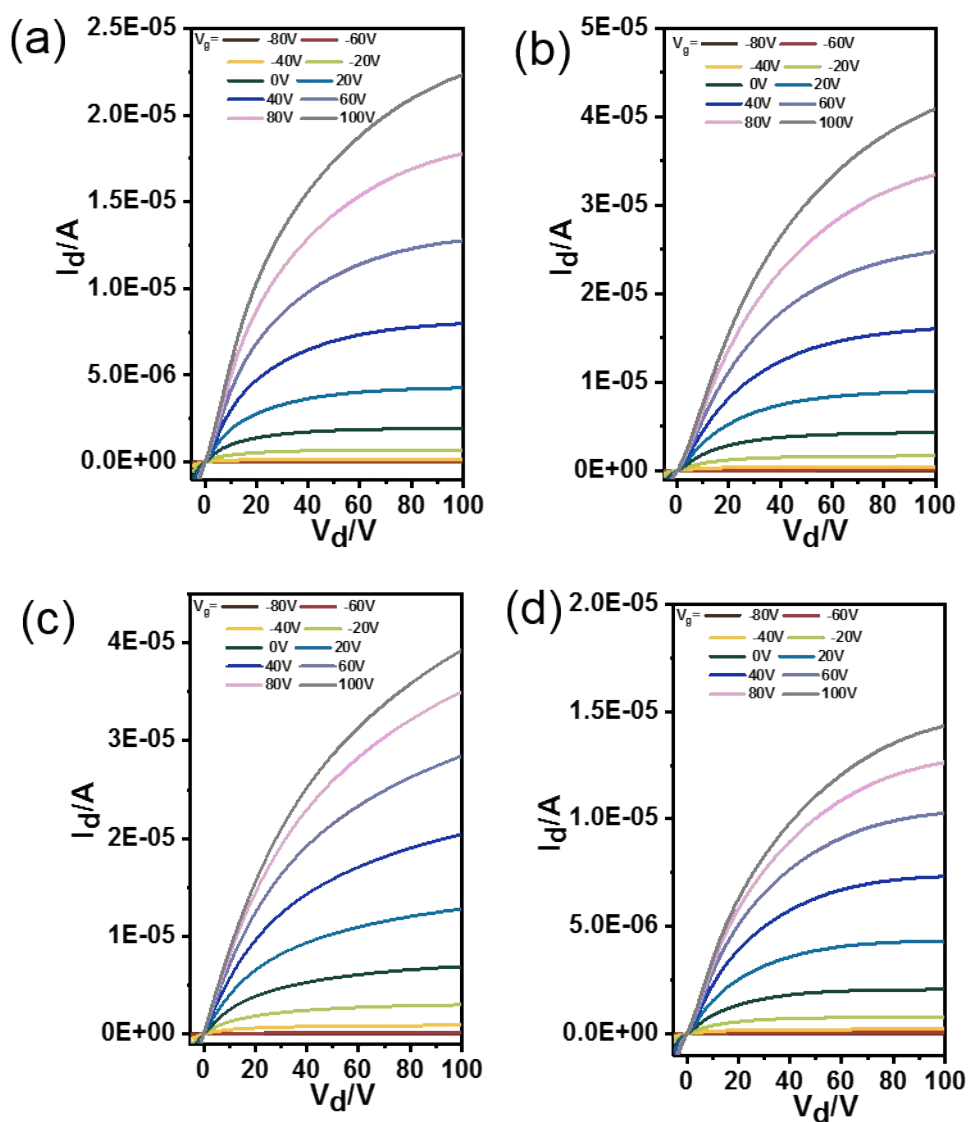


Figure S3. Output curves of **BTDI-OCF<sub>3</sub>** with substrate temperature of (a) RT (b) 60°C (c) 90°C as tested in glovebox and (d) tested in air at different gate voltage.

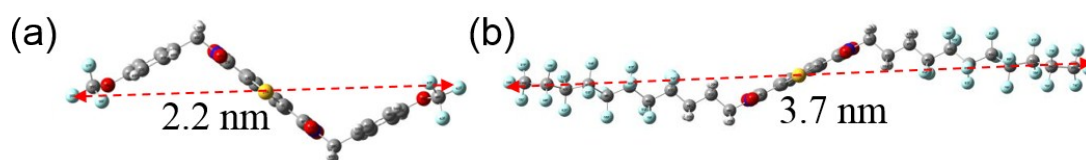


Figure S4. Molecular lengths of (a) **BTDI-OCF<sub>3</sub>** and (b) **BTDI-CF**.

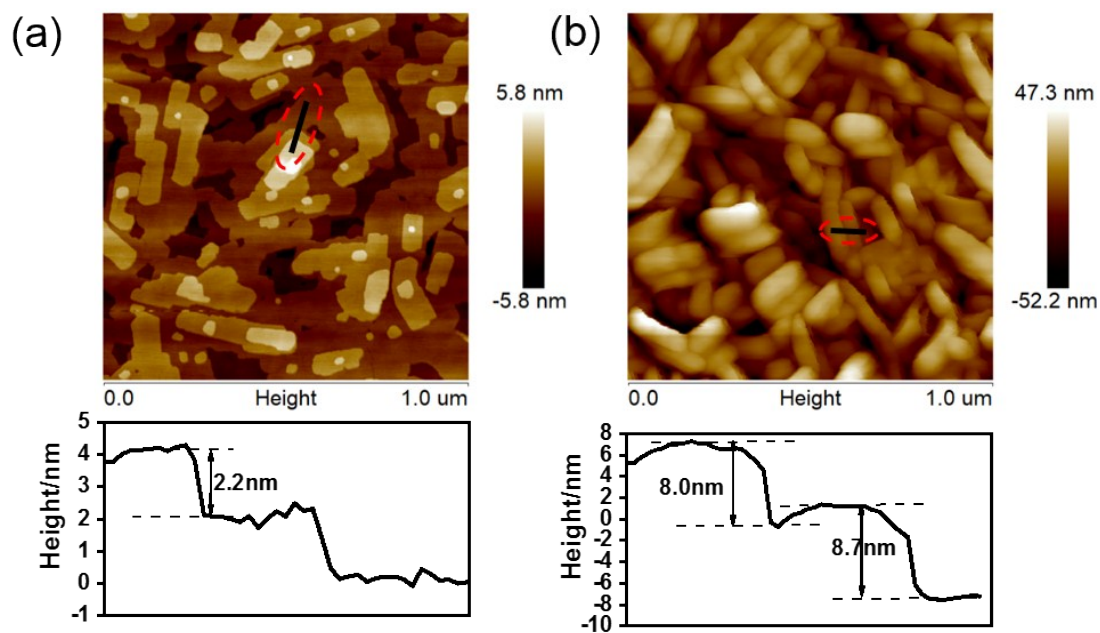


Figure S5. The step-height of (a) **BTDI-OCF<sub>3</sub>** and (b) **BTDI-CF**.

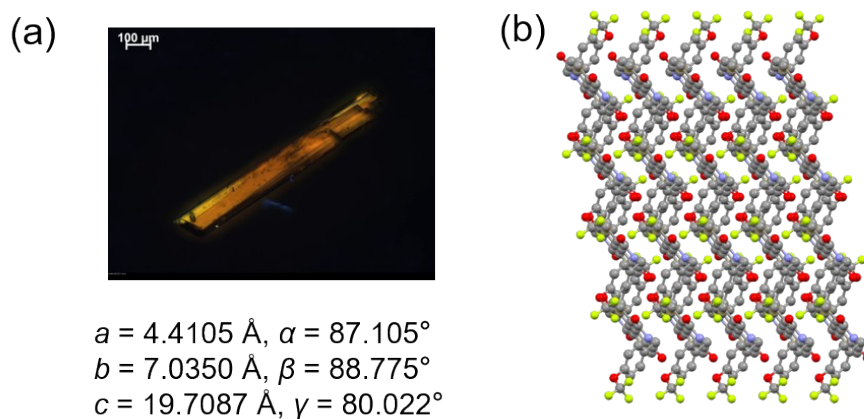


Figure S6. (a) The POM image of single crystal for **BTDI-OCF<sub>3</sub>**. (b) Molecular packing style of **BTDI-OCF<sub>3</sub>** along the b-axis.

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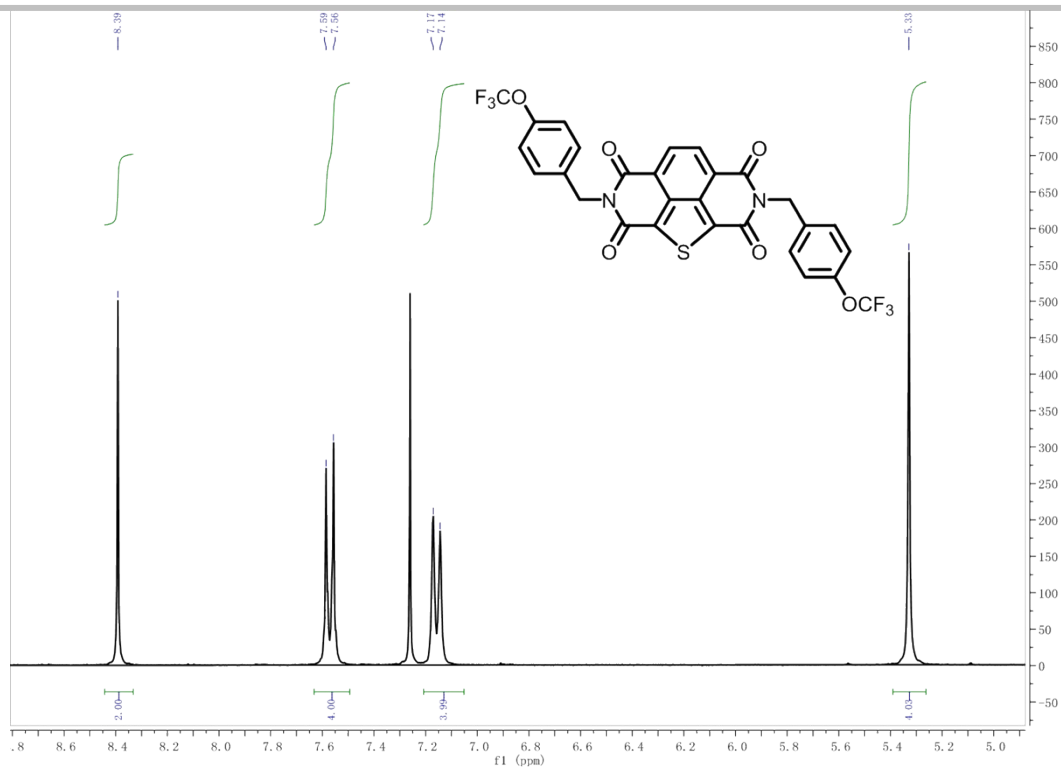


Figure S7. <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>, 300 Hz) of **BTDI-OCF<sub>3</sub>**.

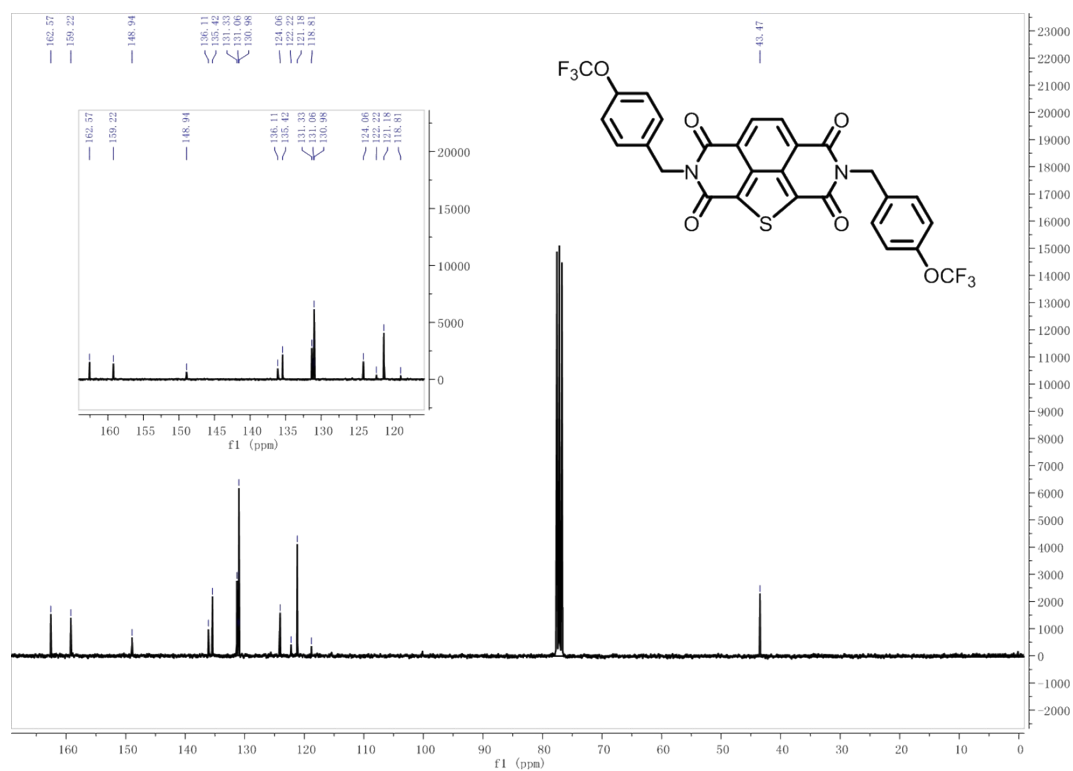


Figure S8. <sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>, 300 Hz) of **BTDI-OCF<sub>3</sub>**.



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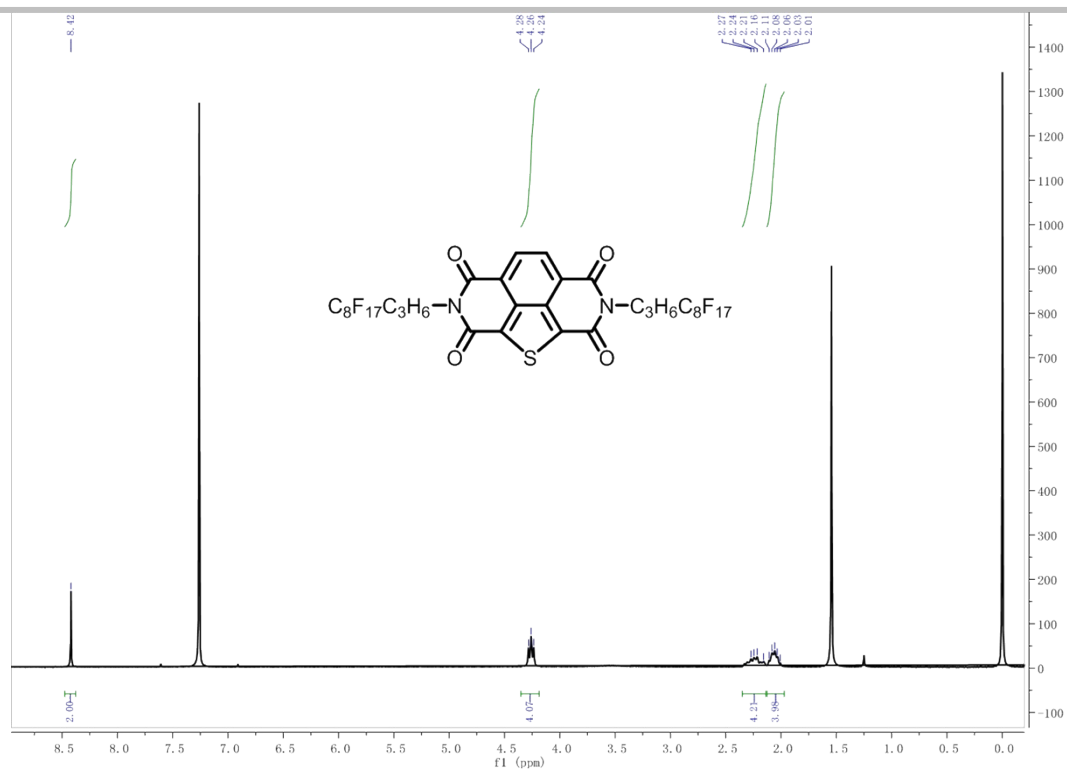


Figure S9.  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ , 300 Hz) of **BTDI-CF**.

Table S1. The performance of BTDI-CF based OTFTs stored in air.

Duration/day	Store Condition	Test Condition	$\mu_e/\text{cm}^2\text{V}^{-1}\text{s}^{-1}$	$I_{\text{on}}/I_{\text{off}}$	$V_{\text{th}}/\text{V}$
Initial	Air	Air	<sup>a</sup> $9.83 \times 10^{-3}$ <sup>b</sup> $(1.16 \times 10^{-2})$	$10^5$	-50
<b>1</b>	Air	Air	$4.39 \times 10^{-3}$ $(4.65 \times 10^{-3})$	$10^5$	21
<b>3</b>	Air	Air	$1.95 \times 10^{-3}$ $(2.18 \times 10^{-3})$	$10^5$	23
<b>5</b>	Air	Air	$1.80 \times 10^{-3}$ $(1.92 \times 10^{-3})$	$10^5$	30
<b>10</b>	Air	Air	$1.32 \times 10^{-3}$ $(1.41 \times 10^{-3})$	$10^5$	33
<b>20</b>	Air	Air	$9.14 \times 10^{-3}$ $(9.76 \times 10^{-3})$	$10^5$	37
<b>30</b>	Air	Air	$9.48 \times 10^{-3}$ $(9.96 \times 10^{-3})$	$10^5$	38

<sup>a</sup> average mobility. <sup>b</sup> highest mobility.

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Table S2. The performance of BTDI-OCF<sub>3</sub> based OTFTs stored in air.

Time/day	store condition	Test condition	$\mu_e / \text{cm}^2\text{V}^{-1}\text{s}^{-1}$	$I_{\text{on}}/I_{\text{off}}$	$V_{\text{th}} / \text{V}$
Initial	Air	Air	<sup>a</sup> $4.40 \times 10^{-3}$ <sup>b</sup> $(4.58 \times 10^{-3})$	$10^4$	-40
1	Air	Air	$2.85 \times 10^{-3}$ $(3.00 \times 10^{-3})$	$10^4$	-25
3	Air	Air	$2.09 \times 10^{-3}$ $(2.22 \times 10^{-3})$	$10^4$	-10
5	Air	Air	$1.82 \times 10^{-3}$ $(2.05 \times 10^{-3})$	$10^4$	-6
10	Air	Air	$1.60 \times 10^{-3}$ $(1.68 \times 10^{-3})$	$10^4$	-4
20	Air	Air	$1.19 \times 10^{-3}$ $(1.26 \times 10^{-3})$	$10^4$	4
30	Air	Air	$1.17 \times 10^{-3}$ $(1.21 \times 10^{-3})$	$10^4$	10

<sup>a</sup> average mobility. <sup>b</sup> highest mobility.

## References

1. T. Lu and F. Chen, Multiwfn: A multifunctional wavefunction analyzer, *J. Comput. Chem.*, 2012, **33**, 580-592.
2. H. Meng, F. Sun, M. B. Goldfinger, G. D. Jaycox, Z. Li, W. J. Marshall and G. S. Blackman, High-Performance, Stable Organic Thin-Film Field-Effect Transistors Based on Bis-5'-alkylthiophen-2'-yl-2,6-anthracene Semiconductors, *J. Am. Chem. Soc.*, 2005, **127**, 2406-2407.