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Supporting Information

Wide Band Gap Pyromellitic Diimides for Photo Stable n-Channel Thin Film Transistors

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Synthesis procedures of PyDI-BOCF$_3$

Pyromellitic dianhydride (1.16 g, 5.32 mmol), zinc acetate (0.25 g, 1.36 mmol) and acetic acid (1.5 ml) were suspended in anhydrous DMF (100 mL) and stirred at room temperature for 30 min. Then 4-(trifluoromethylthio)benzylamine (3.05 g, 15.96 mmol) was added into the above mixture with heating process at 60 ℃ for 30 min. Under the stirring condition, it was further heated to 180 ℃ for 12 h in the inert system. After cooling, the mixture was poured into ice water and the precipitate was collected by filtration. Thereafter, the collected product was washed by water and methanol solution. After drying, it was further purified by using a 5-zone furnace under high vacuum sublimation for twice to obtain the pure crystal compounds (yield: 81 %). ^{1}H NMR (300 MHz, DMSO-d6) δ 8.25 (s, 2H, Ph-H), 7.50 (d, J = 8.7 Hz, 4H, Ph-H), 7.34 (d, J = 7.9 Hz, 4H, Ph-H), 4.86 (s, 4H, CH_2). ^{13}C NMR (101 MHz, CDCl3): δ 165.67, 149.10, 137.25, 134.12, 130.46, 121.32, 118.64, 41.52, 29.71. Elemental annal.calcd for $C_{26}H_{14}F_6N_2O_6$: C, 55.33; H, 2.50; F, 20.20; N, 4.96; O, 17.01;Found C, 54.86; H, 2.30; N, 4.95. The synthesis procedure of PyDI-BSCF$_3$ is similar to PyDI-BOCF$_3$ (Yield:80 %).

Experimental

1H and 13 C NMR spectra of soluble intermediates were recorded on a Bruker DRX NMR spectrometer operating at 300 MHz in Dimethylsulfoxide-d solutions. Cyclic voltammetry was tested on CH Instruments Inc CHI660E. Three-electrode system including glassy carbon as the working electrode, Pt disk as the counter electrode, and non-aqueous Ag/Ag+ as the reference electrode was used in this case. Voltammograms were performed in Dry N,N-Dimethylformamide (DMF) solution versus Ag/Ag+ using tetrabutylammonium hexafluorophosphate (Bu4NPF6) as electrolyte and ferrocene as inner standard at a scan rate of of 100 mV/s. The UV-vis spectra were tested on Shimadzu UV-1750U spectrophotometer. Thermgravimetric analysis (TGA) measurements were performed on Perkin Elmer TGA7 at a heating

rate of 10 °C/min in nitrogen atmosphere. Differential scanning calorimetry (DSC) were analysed by Netzsch calorimeter model Polyma DSC 214 at a heating and cooling rates of 10 °C/min in nitrogen atmosphere. The morphology of the thin-films were obtained by using the tapping mode of MultiMode 8 atomic force microscope (Bruker, German) in the glove box. The XRD patterns were perform on a Bruker D8 advance X-ray diffractometer equipped with a Cu Kα source (λ = 1.541 Å). Density functional theory (DFT) calculations of the molecular geometry and electronic sturecture were optimized for isolated molecules in a gas phase, using B3LYP gradient-corrected functional and the 6-311G(d,p) basis set in Gaussian 09 program. The transfer integral calculations were performed on PW91 functional (GGA:PW91) and the basis set of triple-Z 2 plus polarization functions (TZ2P) in Amsterdam Density Functional (ADF) program.

Table S1: Single Crystal parameters of PyDI-$BOCF_3$ and PyDI-$BSCF_3$

	PyDI-$BOCF_3$		PyDI-$BSCF_3$	
Space group	P -1		P -1	
Unit cell dimensions	a = 4.6859 Å (5)	α =86.980°(7)	a = 4.7270 Å (6)	α =85.692° (6)
	b = 6.1771 Å (6)	β = 89.653°(8)	b = 6.3735 Å (4)	β = 87.707° (9)
	c = 19.2053 Å (15)	γ = 88.699°(9)	c = 19.4848 Å (16)	γ = 86.270° (7)
Cell Volume	554.98 $Å^3$ (9)		583.77 $Å^3$ (10)	

Table S2: The observed distances of all short contacts in PyDI-$BOCF_3$ and PyDI-$BSCF_3$ crystals

Material	Bond distance	t_1	t_2	t_3	t_4
PyDI-$BOCF_3$	*Centroid Distance* (Å)	4.686	7.668	6.177	7.838
	C-O (Å)	3.128 3.128	3.212 3.212	3.207 3.207 3.200 3.200	-
	O-H (Å)	-	2.629 2.629 2.413 2.413	-	-
	C-C (Å)	3.383 3.383 3.282	-	-	-
PyDI-$BSCF_3$	*Centroid Distance* (Å)	4.727	7.684	6.374	8.178
	C-O (Å)	3.210 3.210	3.220 3.220	3.173 3.173	-
	O-H (Å)	-	2.616 2.616 2.383 2.383	-	-
	C-C (Å)	3.388 3.388 3.368	-	-	-

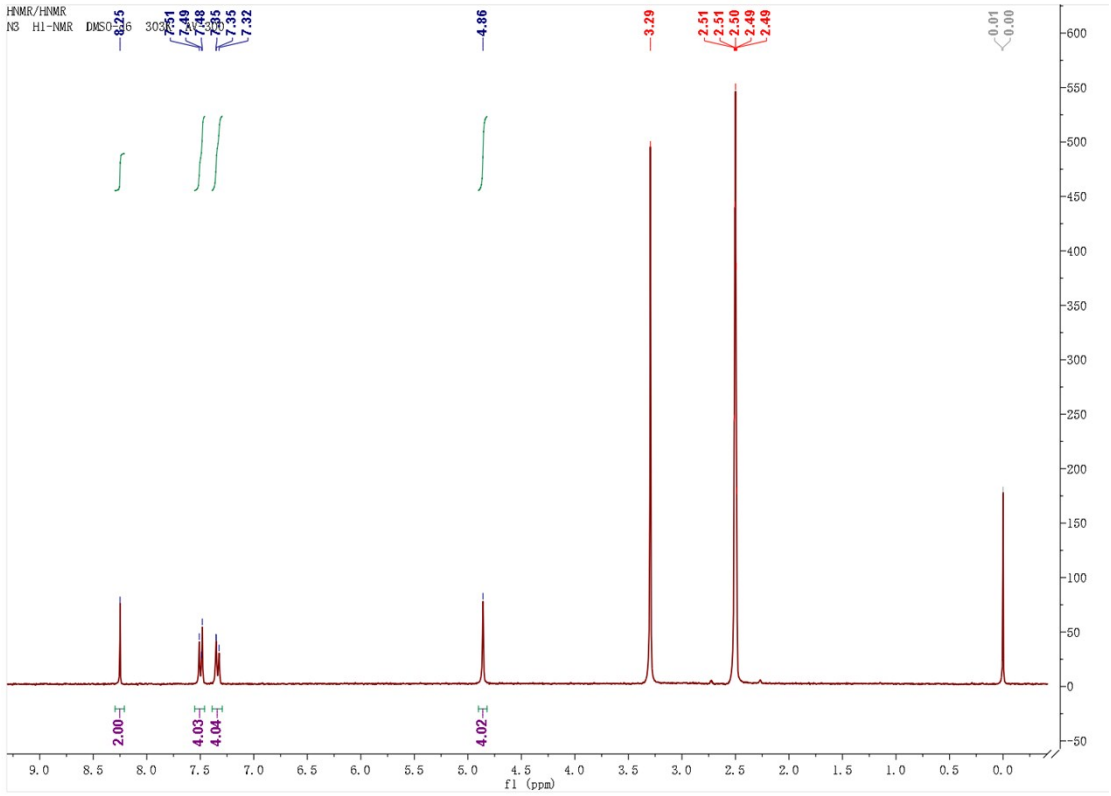

Figure S1: ^{1}H NMR Spectrum of PyDI-BOCF_3.

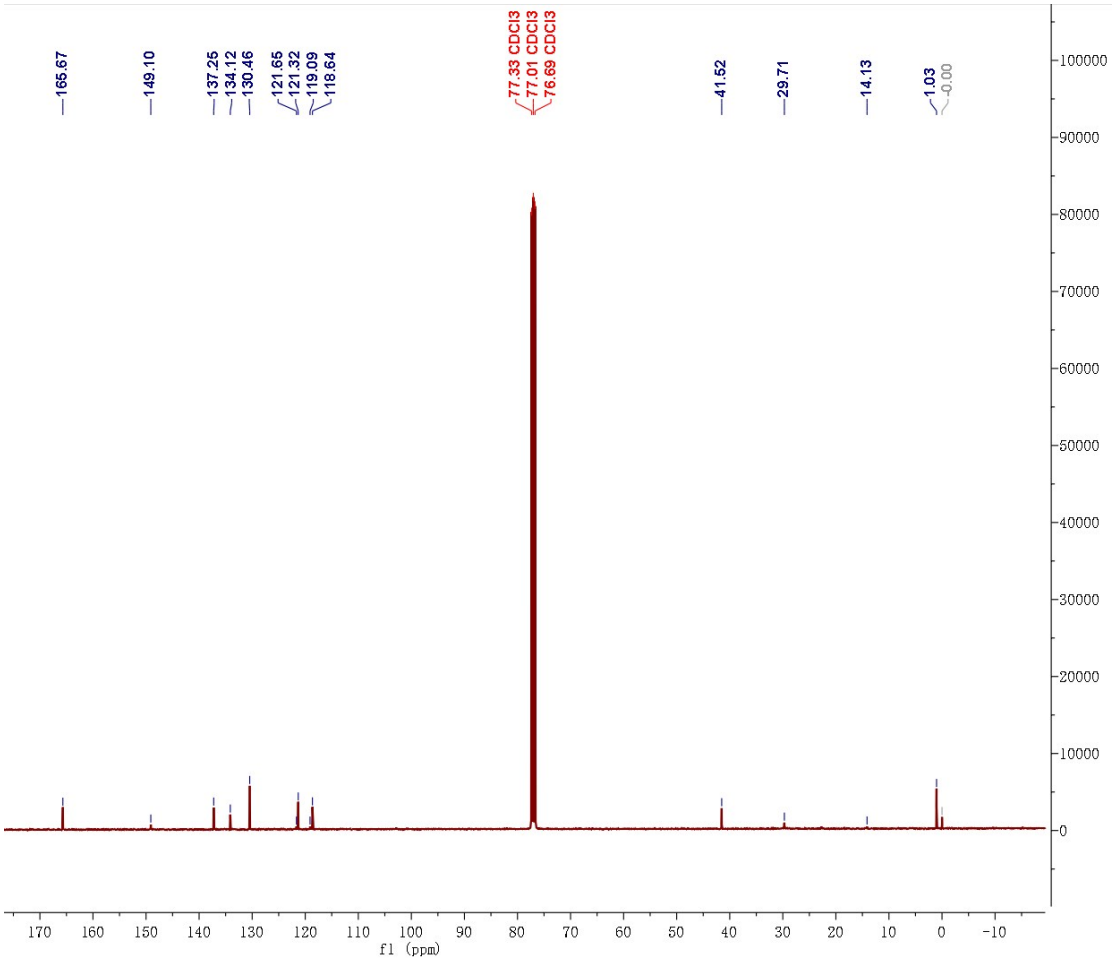

Figure S2: ^{13}C NMR Spectrum of PyDI-BOCF_3.

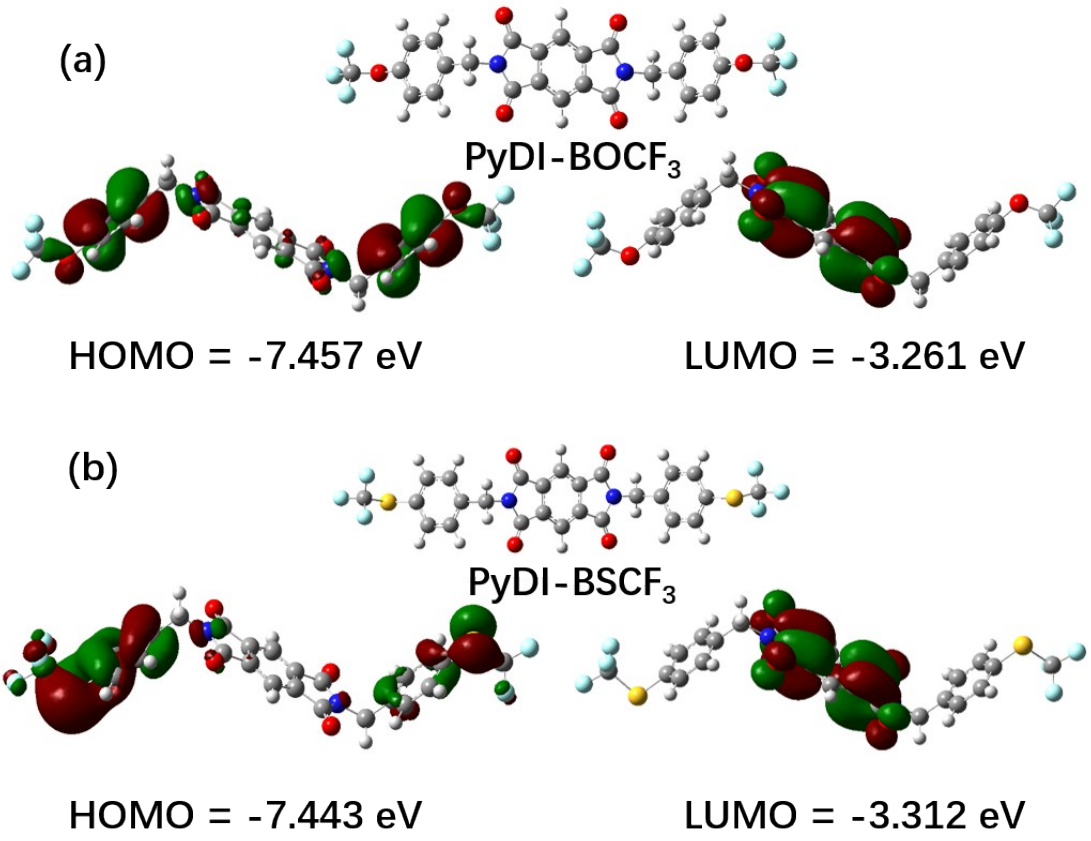

Figure S3: The molecular orbital surfaces of HOMO and LUMO of PyDI-$BOCF_3$ and PyDI-$BSCF_3$, calculated at the DFT B3LYP/6-31G.

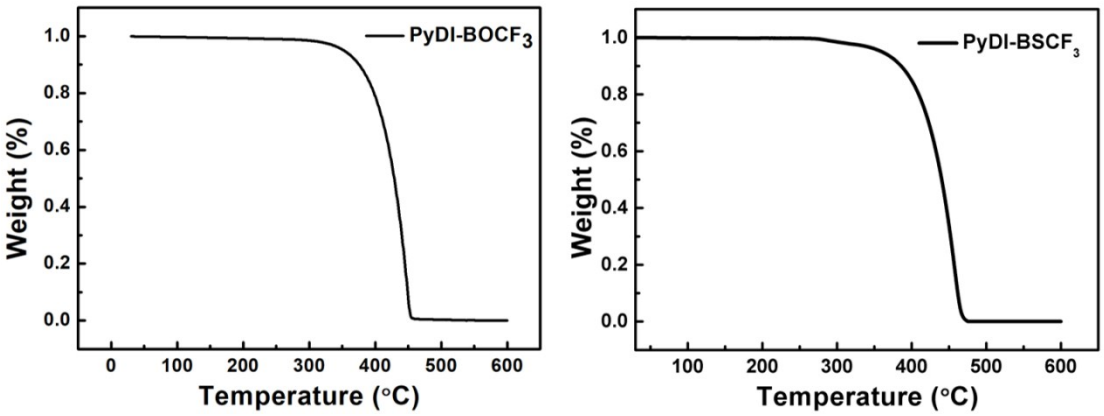

Figure S4: TGA analysis of PyDI-$BOCF_3$ and PyDI-$BSCF_3$

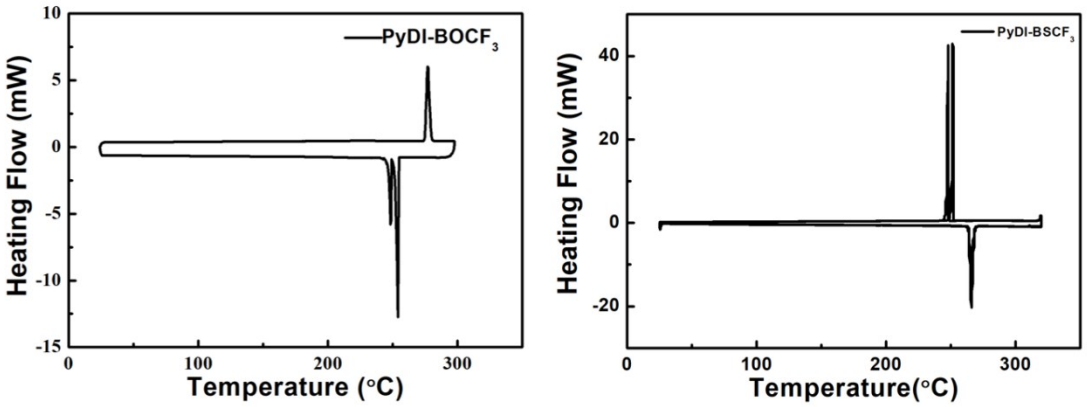

Figure S5: DSC analysis of PyDI-$BOCF_3$ and PyDI-$BSCF_3$

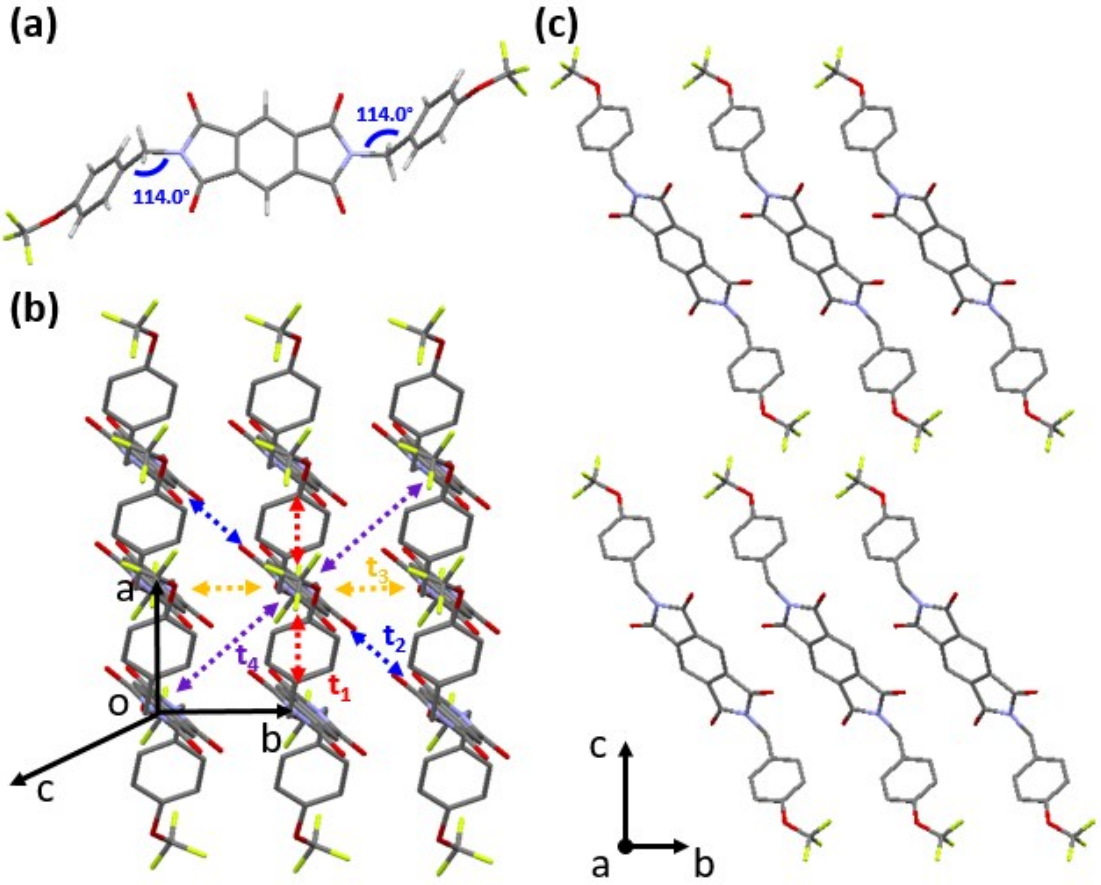

Figure S6: (a) Molecular structure and (b,c) molecular packing of PyDI-BOCF3 (unit cell: a = 4.49, b = 6.18, c = 19.21; α = 87.0°, β = 89.7°, γ=88.7°).

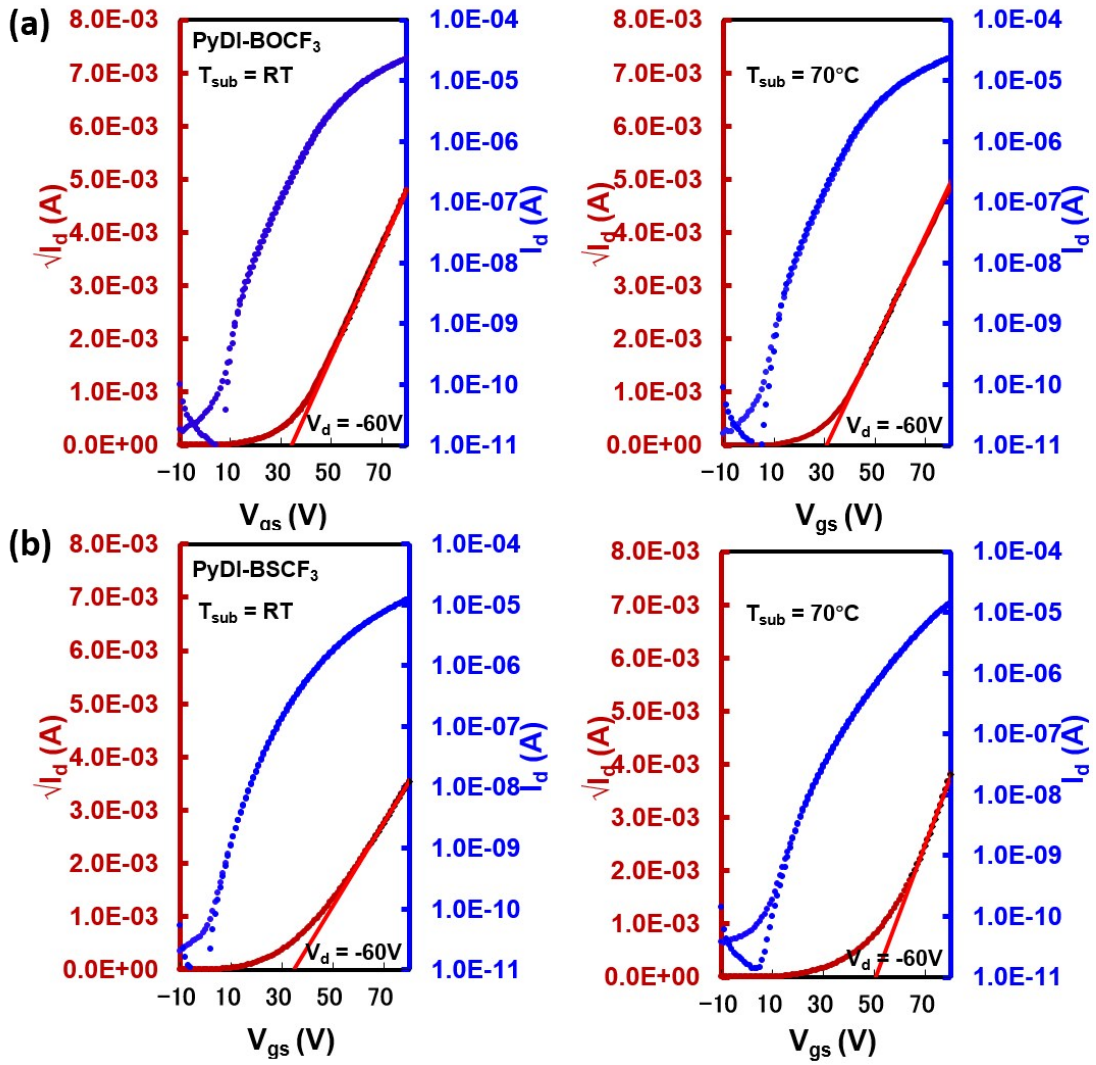

Figure S7: The hysteresis of the transfer curves for PyDI-BSCF$_3$ (a) and PyDI-BOCF$_3$ (b) based OTFTs deposited at temperature of rt and 70 ˚C on the OTS-treated Si/SiO$_2$ substrate.

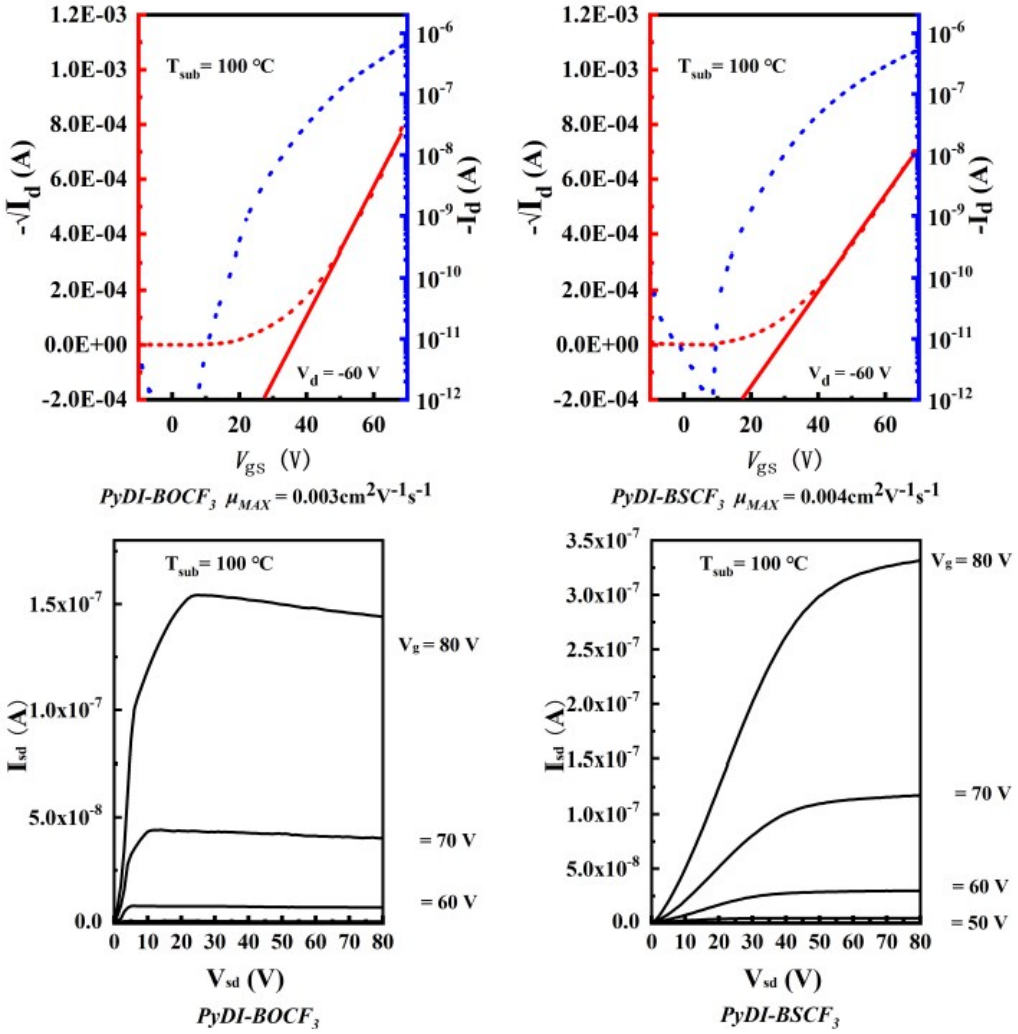

Figure S8: The hysteresis of the transfer curves for PyDI-$BSCF_3$ (a) and PyDI-$BOCF_3$ (b) based OTFTs deposited at temperature of 100 ˚C on the OTS-treated Si/SiO_2 substrate.

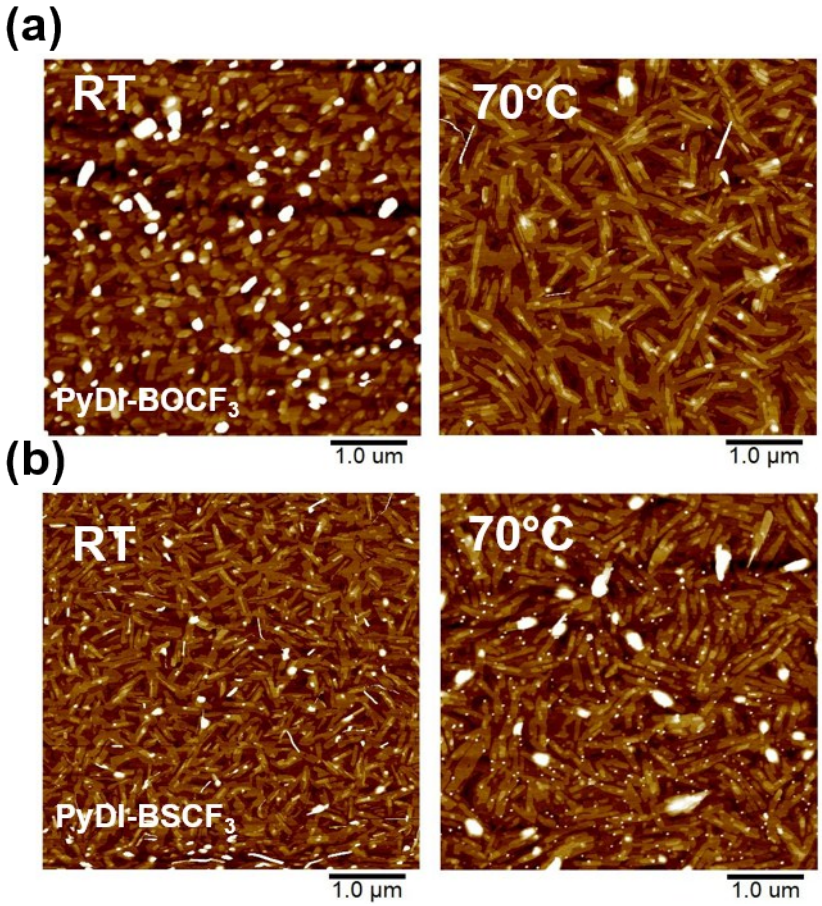

Figure S9: The taping mode AFM images (5 µm) of PyDI-$BOCF_3$ (b) and PyDI-$BSCF_3$ (c) thin films deposited at RT and 70°C