Electronic Supplementary Information

Ultra-Narrow-Bandgap Thienoisoindigo Polymers: Structure–Property Correlations in Field-Effect Transistors

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Instrumentations: ^{1}H NMR spectra were recorded on a Varian VNRS 400 MHz (Varian USA) spectrophotometer using $CDCl_3$ as solvent and tetramethylsilane (TMS). UV-Vis-NIR spectra were taken on Cary 5000 (Varian USA) spectrometer. Number-average (M_n) and polydispersity indices (PDI) of the polymer products were determined by high temperature gel-permeation chromatography (HT-GPC) with a FUTECS NS-4000 using a series of mono disperse polystyrene standards in 1,2,4-trichlorobenzene (TCB, HPLC grade) at 120 °C. Cyclic voltammetry (CV) measurements were performed on AMETEK VersaSTAT 3 with a three-electrode cell in a nitrogen bubbled 0.1 M tetra-*n*-butylammonium hexafluorophosphate (n-Bu_4NPF_6) solution in acetonitrile at a scan rate of 0.1 V/s at room temperature. Ag/Ag^+ (0.01 M of $AgNO_3$ in acetonitrile) electrode, platinum wire and polymer coated glassy carbon electrode were used as the reference electrode, counter electrode and working electrode, respectively. The Ag/Ag^+ reference electrode was calibrated using a ferrocene/ferrocenium redox couple as an external standard, whose oxidation potential is set at –4.8 eV with respect to zero vacuum level. The HOMO energy levels were obtained from the equation HOMO= –($E_{ox}^{onset} - E_{(ferrocene)}^{onset} + 4.8$) eV. The LUMO levels of polymers were obtained from the equation LUMO= –($E_{red}^{onset} - E_{(ferrocene)}^{onset} + 4.8$) eV.

AFM Characterization: Agilent 5500 scanning probe microscope (SPM) running with a Nanoscope V controller was used to obtain AFM images of polymer films. AFM images were recorded in high-resolution tapping mode under ambient conditions. Premium silicon cantilevers (TESP-V2) were used with a rotated tip to provide more symmetric representation of features over 200 nm.

GIXD Characterization: Grazing incidence X-ray diffraction (GIXD) measurements were conducted at PLS-II 9A U-SAXS beamline of the Pohang Accelerator Laboratory in Korea. The X-rays coming from the in-vacuum undulator (IVU) are monochromated (wavelength λ = 1.10994 Å) using a double crystal monochromator and focused both horizontally and vertically (450 (H)×60 (V) μm^2 in FWHM @ sample position) using K-B type mirrors. The GIXD sample stage is equipped with a 7-axis motorized stage for the fine alignment of sample, and the incidence angle of X-ray beam was set to be 0.120º to 0.135º for TIIG-based polymer films. GIXD patterns were recorded with a 2D CCD detector (Rayonix SX165) and X-ray irradiation time was 6–9 s, dependent on the saturation level of the detector. Diffraction angles were calibrated with a pre-calibrated sucrose (Monoclinic, P21, a = 10.8631 Å, b = 8.7044 Å, c = 7.7624 Å, β = 102.938°), and the sample-to-detector distance was ~231 mm.

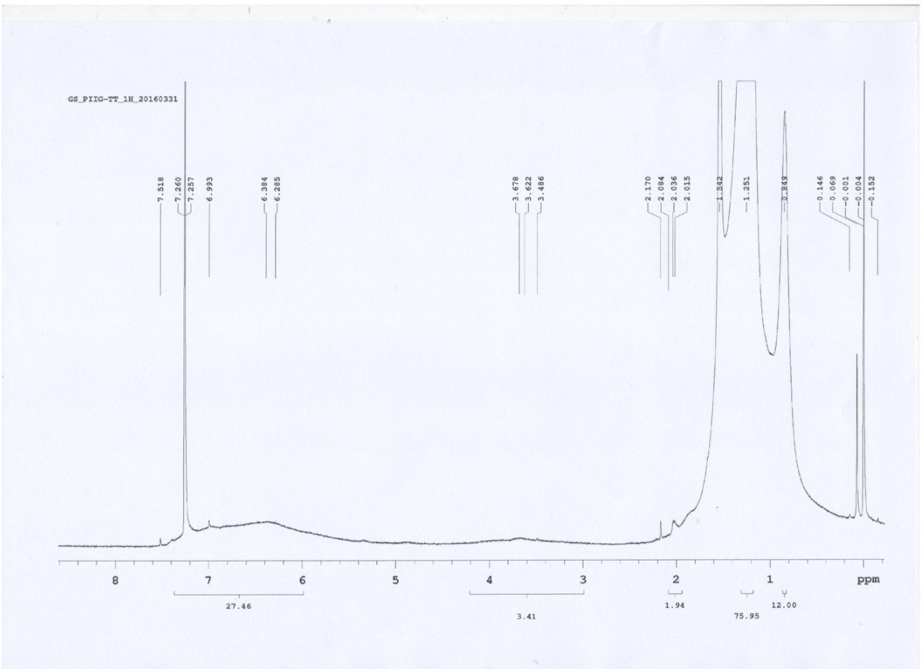

Figure S1. ^{1}H NMR result of **PTIIG-TT**.

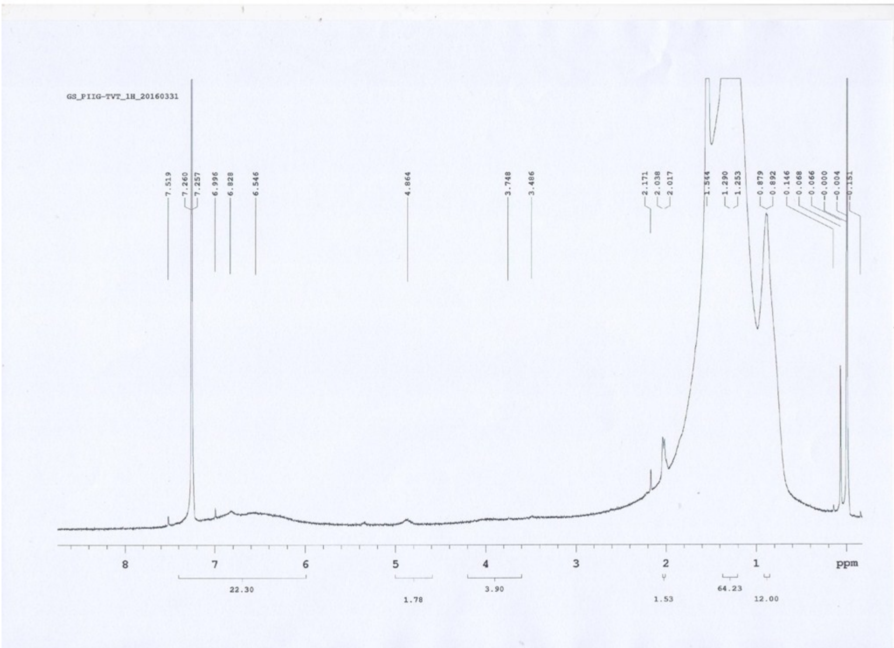

Figure S2. ^{1}H NMR result of **PTIIG-TVT**.

2016-08-11 오후 5:09 Chromatogram D:\ DATA\ Desktop\ DATA\ 2015-08-20\ 2015-08-20 오후 2_27_57 - PTIIG-TT.PRM Page 1 of 2

Clarity GPC Report

DataApex

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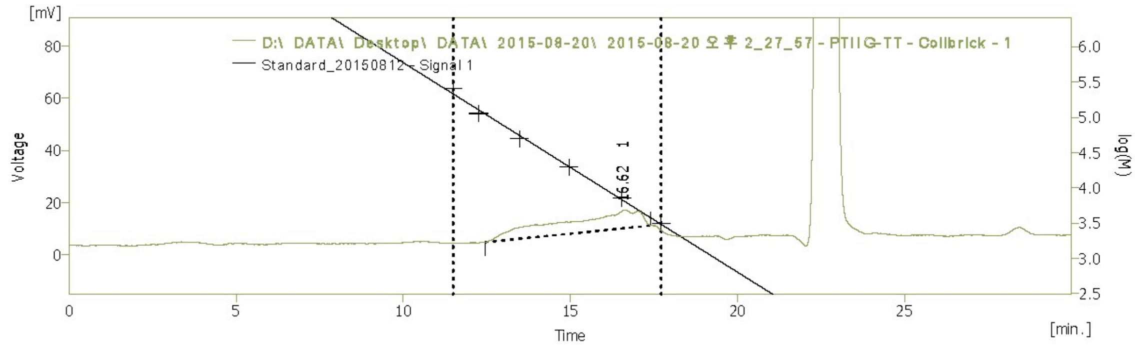

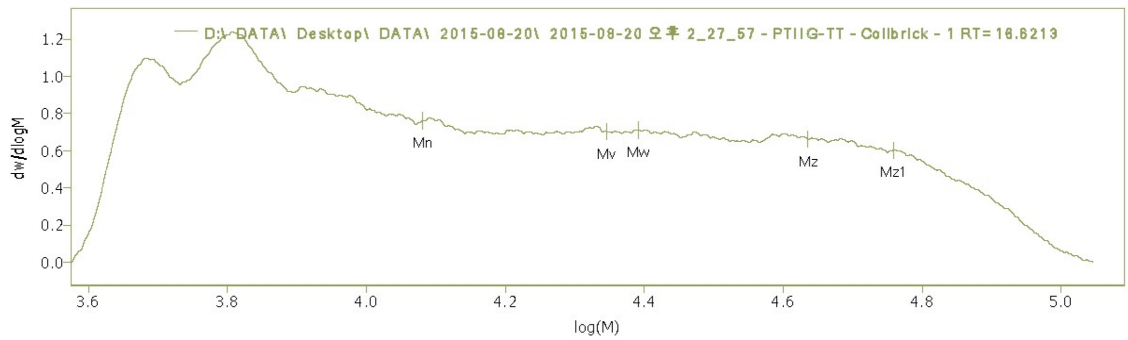

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Correlation Factor: 0.9976854

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	12.45	17.40	1.0000	6411	12054	24609	43215	57363	22150	2.0415

Figure S3. GPC result of **PTIIG-TT**

Clarity GPC Report

DataApex

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Chromatogram Info:

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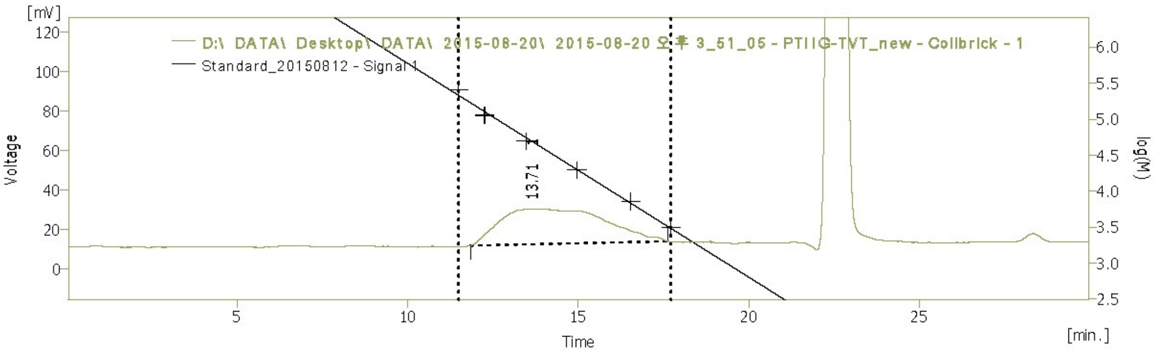

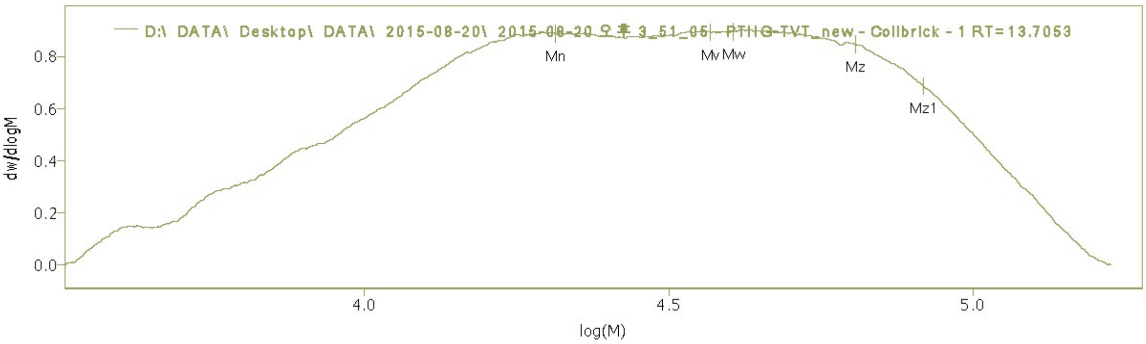

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*Equation: Y = - 0.29716*X + 8.74608*

Correlation Factor: 0.9976854

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	11.85	17.63	1.0000	47148	20585	40357	64016	82923	37037	1.9605

Figure S4. GPC result of **PTIIG-TVT**

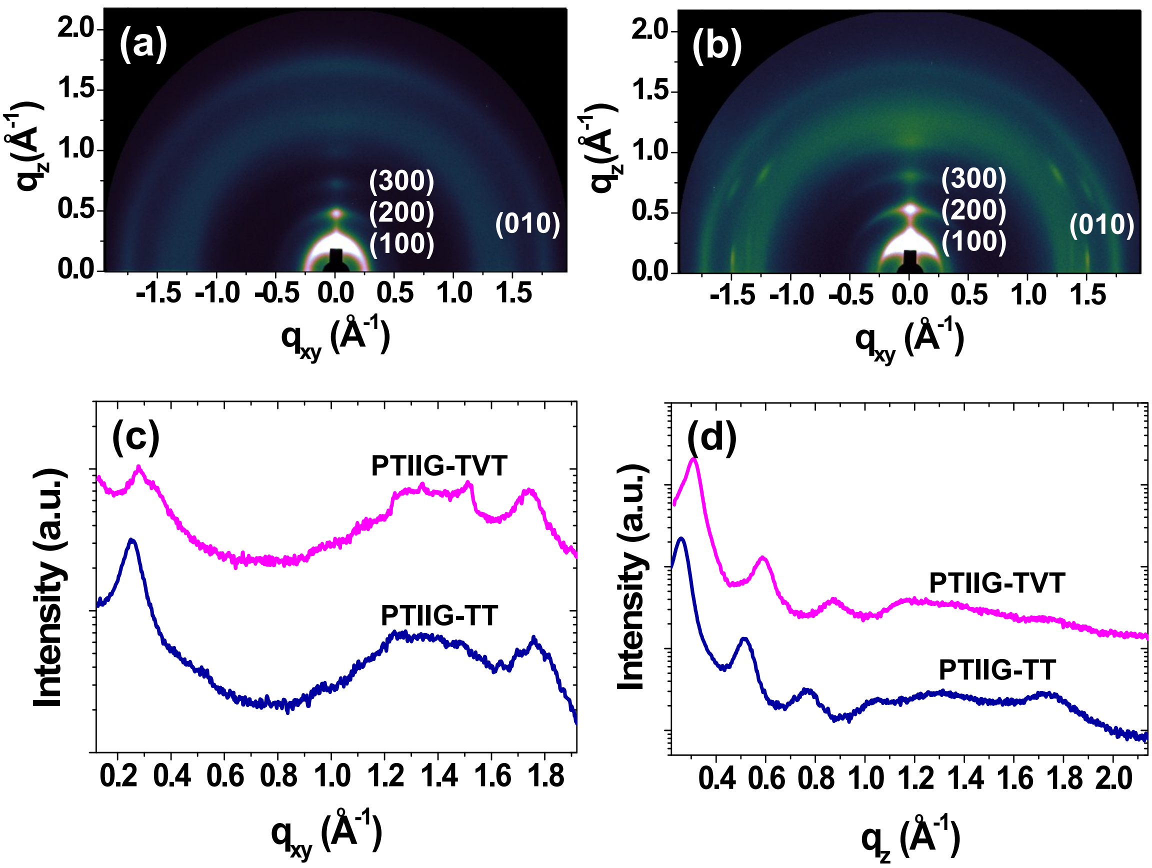

Figure S5 GIXD images of solution-sheared TIIG-based polymer films: (a) **PTIIG-TT** and (b) **PTIIG-TVT**. The corresponding GIXD diffractogram profiles: (c) in-plane and (d) out-of-plane GIXD patterns.

Table S1 Crystallographic parameters calculated from GIXD profiles.

Annealing Temperature	Crystallographic parameters		PTIIG-TT	PTIIG-TVT
As-cast	(100)	q (Å^{-1})	0.2843	0.3101
		d-spacing (Å)	22.10	20.26
		FWHM (Å^{-1})	0.0655	0.0760
		Coherence length (Å)	86.4	74.4
	π-π stacking	q (Å^{-1})	1.7442	1.7483
		d-spacing (Å)	3.60	3.59
Annealing at 300 °C	(100)	q (Å^{-1})	0.2933	0.3022
		d-spacing (Å)	21.42	20.79
		FWHM (Å^{-1})	0.0317	0.0268
		Coherence length (Å)	178.4	211.1
	π-π stacking	q (Å^{-1})	1.7423	1.7590
		d-spacing (Å)	3.61	3.57

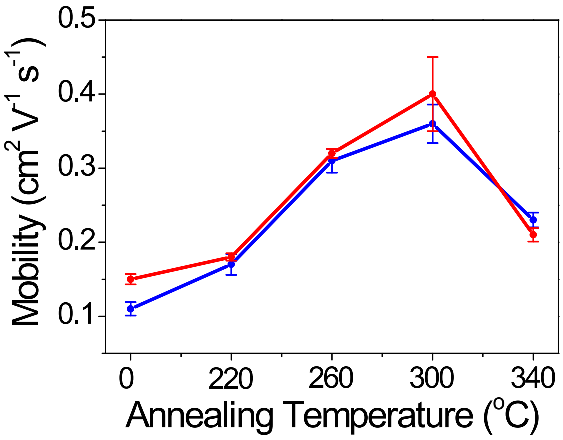

Figure S6 Average hole mobility distributions of solution-sheared TIIG-based polymer films based on various annealing temperatures.

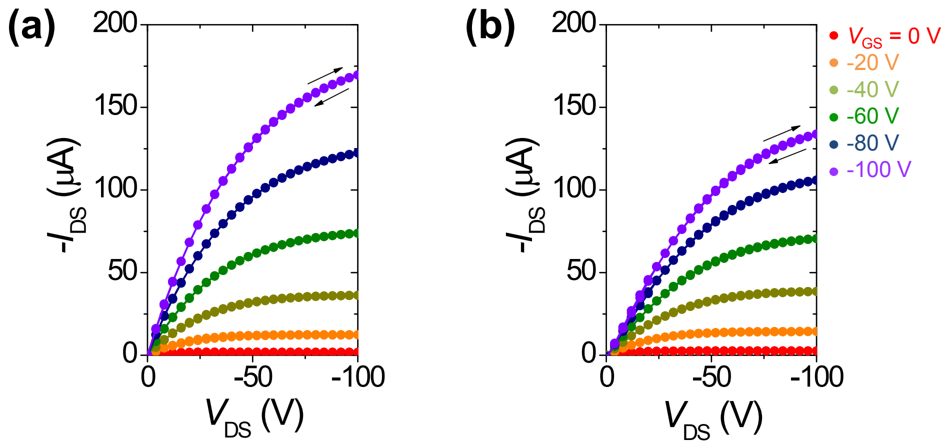

Figure S7 Output characteristics of PTIIG-based polymer films fabricated by solution-shearing method: (a) **PTIIG-TT** and (b) **PTIIG-TVT**.

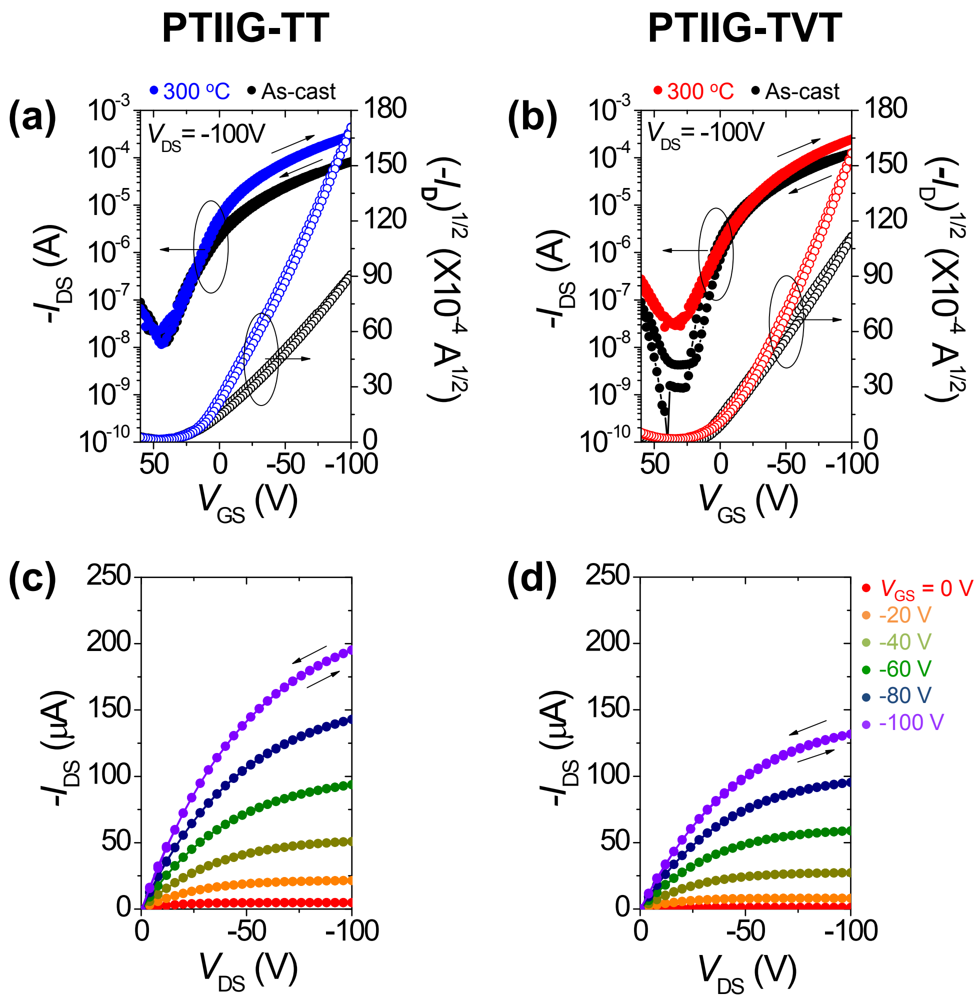

Figure S8 Current-voltage (*I-V*) characteristics of OFET devices of PTIIG-based polymer films fabricated by drop-casting method, with Au electrodes: (a, c) **PTIIG-TT** and (b, d) **PTIIG-TVT**.

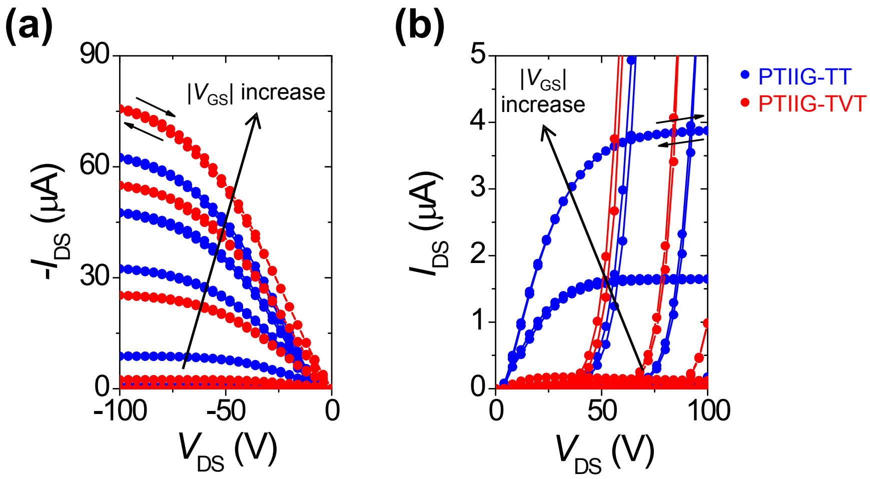

Figure S9 Output characteristics of OFETs with Al electrodes based on solution-sheared TIIG-based polymer films annealed at 300 °C: (a) hole-enhancement operation, V_{DS} = -100 V and (b) electron-enhancement operation, V_{DS} = +100 V.