

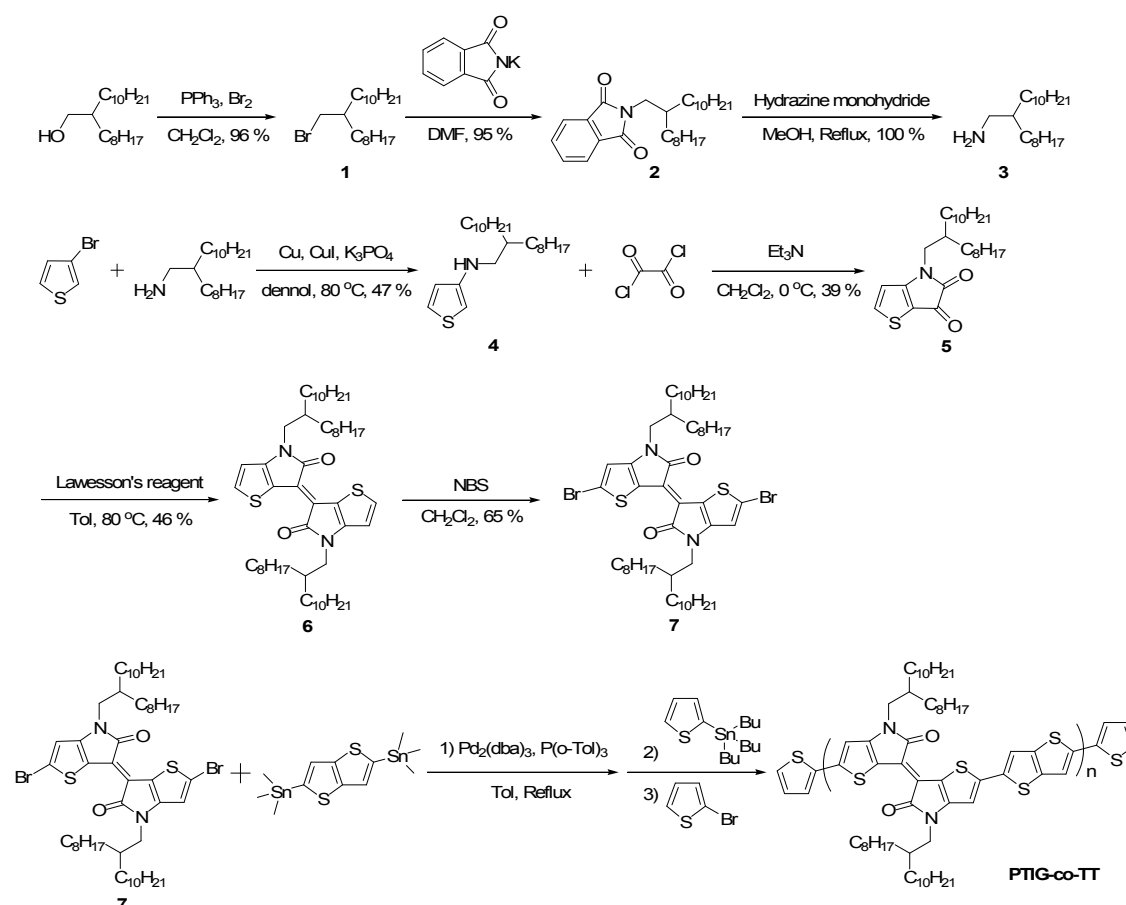
Supporting Information

Thienoisindigo-based copolymer with fused thieno[3,2-*b*]thiophene as donor in transistor application with high performance

Chi-Min Chen,^a Sunil Sharma,^a Yi-Lun Li,^a Jey-Jau Lee^b and Show-An Chen^{*a}

S1. Materials and synthesis

All chemicals and reagents were purchased from commercial suppliers and used without any further purification. The chemical structures and synthetic routes of the monomer and PTIG-co-TT are shown in Scheme S1. Compounds 1-7 were synthesized according to procedures in the literature.^[S1-S3]



Scheme S1 Chemical structures and synthetic routes of monomer and PTIG-co-TT.

Poly((E)-4,4'-bis(2-octyldodecyl)-[6,6'-bithieno[3,2-*b*]pyrrolylidene]-5,5'(4H,4'H)-dione-co-thieno[3,2-*b*]thiophene (PTIG-co-TT).

In a reactor, the mixture of (E)-2,2'-dibromo-4,4'-bis(2-octyldodecyl)-[6,6'-bithieno[3,2-*b*]pyrrolylidene]-5,5'(4H,4'H)-dione (200 mg, 0.20 mmol) (7), 2,5-bis(trimethylstannyl)-thieno[3,2-*b*]thiophene (93.8 mg, 0.20 mmol), tris(dibenzylideneacetone)dipalladium(0) (6.45 mg, 7.04 μ mol) and tri(*o*-tolyl)phosphine (10.36 mg, 34.04 μ mol) was dissolved in 8 ml of anhydrous toluene under a nitrogen-filled glove-box. The reaction mixture was heated at 110 °C to polymerize for 72 h, and then 2-tributylstannylthiophene (150 mg, 0.40 mmol) and 2-bromothiophene (130 mg, 0.80 mmol) as end-capping agent were added sequentially to react for 24 h more for termination of the polymerization, respectively. After cooling to room temperature, the reaction solution was poured into methanol and the precipitated polymer was obtained after filtration. The collected polymer was further purified by Soxhlet extraction with methanol, hexanes, and chloroform for removal of impurities and oligomers. The chloroform fraction was concentrated and then reprecipitated in hexane, and the reprecipitated polymer was collected by filtration. The resulting polymer was dried under vacuum to obtain PTIG-co-TT as dark green solid (130 mg, 66.45 %). ^1H NMR (500 MHz, CDCl_3): δ 7.27-7.21 (b, 2H), 7.01-6.99 (dd, 2H), 3.74-3.71 (b, 4H), 1.85-1.80 (b, 2H), 1.80-1.00 (b, 64H), 1.00-0.64 (b, 12H).

S2. General instrumentation

The ^1H NMR spectra were carried out on Br \ddot{u} Ker AM-500 spectrometer in CDCl_3

with tetramethylsilane (TMS) as an initial standard. The molecular weight and polydispersity index (PDI) of copolymer were measured by gel permeation chromatography (GPC) analysis with Waters 2481 UV detector and Waters 2410 RI detector using HPLC grade THF as the eluent at a flow rate of 1.0 mL min⁻¹ at 40 °C and calibrated against polystyrene (PS) standards (Fig. S1). Thermal gravity analyses (TGA) of copolymer was performed using a TA Instrument SDT-Q600 analyzer at a heating rate of 10 °C min⁻¹ under a nitrogen flow (100 mL min⁻¹), as shown in Fig. S2. UV-Vis-NIR absorption spectra were taken on the polymer solution with 5 × 10⁻⁵ M (based on repeat unit) in 1,2,4-trichlorobenzene (TCB) and the thin film cast onto quartz glass by using a Perkin-Elmer Lambda 19 spectrophotometer. The thickness of the active layer films were measured by a Tencor P-10 Surface Profiler.

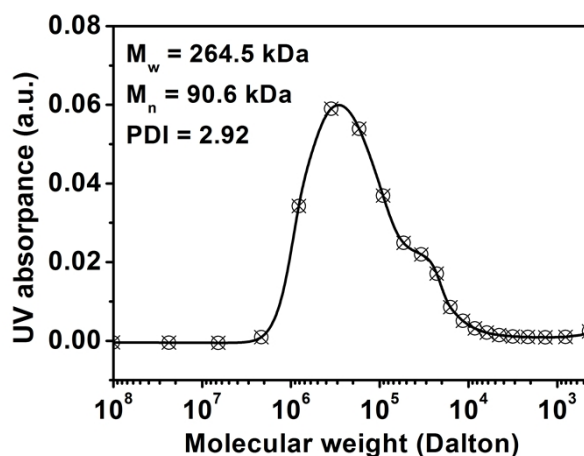


Fig. S1 Gel permeation chromatography trace of PTIG-co-TT.

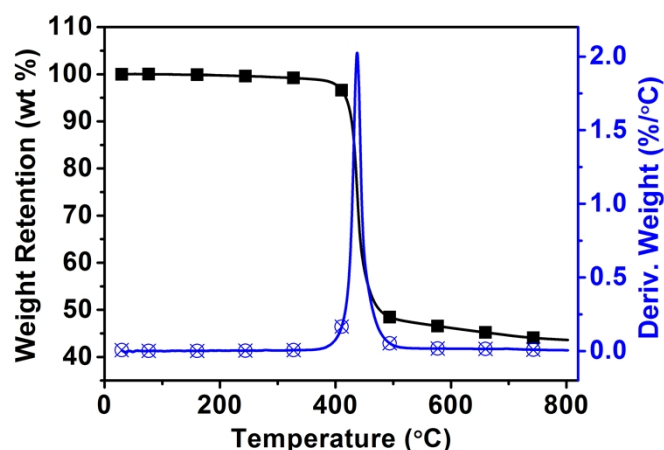


Fig. S2 Thermogravimetric analysis plot of PTIG-co-TT. Scan rate = 10 °C/min from 10 to 800 °C. (5% loss, 418 °C).

S3. Ultraviolet photoelectron spectroscopy (UPS) measurement

The PTIG-co-TT samples for UPS analysis were spin-coated on ITO glasses in a nitrogen-filled glove box and annealed at 200 °C under vacuum for 30 min, and then moved into a desiccator. The whole assembly was taken out from a glove box, and the UPS samples were then transferred quickly (in less than 10 s in air) to the sample loading chamber. Such transferring process would minimize a possible influence by an exposure to air. The UPS spectra were obtained by a VG Multilab 2000 instrument equipped with the high-performance Alpha110 hemispherical electron energy analyzer and were carried out using the He I ($h\nu = 21.22$ eV) source. During UPS measurements, a sample bias of -2.0 V was applied in order to observe the secondary electron cutoff.

The HOMO energy level (E_{HOMO}) of PTIG-co-TT was determined by the following equation, $E_{\text{HOMO}} = h\nu - (E_{\text{cutoff}} - E_{\text{onset}})$, where $h\nu$ is incident photon energy

(21.22 eV) of He I, the high binding energy cutoff (E_{cutoff}) and HOMO region (E_{onset}) are the turning points shown in Fig. S3.

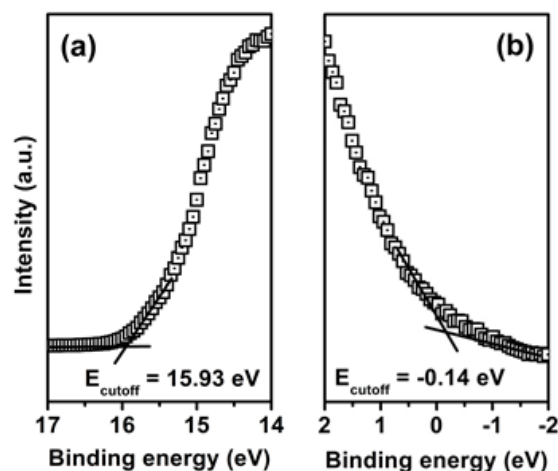


Fig. S3 UPS spectra at (a) high binding energy region and (b) low binding energy region of PTIG-co-TT spin-cast on ITO glasses as substrates.

S4. Polymer thin-film transistor (PTFT) fabrication and performance measurement

PTFTs were fabricated by using bottom-gate bottom-contact (BG/BC) configuration on a highly n-doped silicon wafer with thermally grown 300 nm thick of SiO_2 dielectric as substrate. The gold source and drain electrodes with channel lengths (L) of 10-20 μm and channel widths (W) of 5,000-10,000 μm were utilized and photolithographically patterned by the National Nano Device Laboratories (NDL). Before the deposition of polymer semiconductors, the SiO_2 surface was modified with n-octadecyltrimethoxysilane (OTS) self-assembled monolayer (SAM) to reduce electron trapping as previous reported.^[S4] In a glove box with nitrogen, PTIG-co-TT dissolved in TCB (8 mg mL^{-1}) was spin-coated on OTS-treated substrate, followed by drying under vacuum (below 10^{-1} Torr) for 48 h to remove residual

solvent, and obtained the as-spun PTFT with a 50 nm thick layer of the polymer film. For annealed PTFTs, the devices were further annealed at 100, 200 or 300 °C under vacuum for 30 min before cooling down to room temperature. The device performance of PTFTs was measured in nitrogen-filled glove box using a Keithley 4200 SCS semiconductor parameter analyzer. The hole carrier mobility (μ_h) in the saturation regime is calculated according to the equation: $I_{DS} = (W/2L) C_i \mu_h (V_{GS} - V_{th})^2$, where I_{DS} is the drain current, W/L is the channel width/length, C_i is the capacitance per unit area of the gate dielectric, and V_{GS} and V_{th} are the gate voltage and threshold voltage, respectively. V_{th} of the device was retrieved from extrapolation of the linear fitting of the square root of I_{DS} versus V_{GS} curve in the saturation regime to $I_{DS} = 0$. Fig. S4 shows the transfer characteristic and output characteristic curves for PTIG-co-TT-based TFTs with $L = 20 \mu\text{m}$, $W = 10,000 \mu\text{m}$ and dielectric thickness of 200 nm after thermal annealing at 200 °C. And the horizontal range of I_{DS} about 0.01 A above V_{GS} of -70 V in the transfer characteristic curve is due to the upper limit of detection of analyzer.

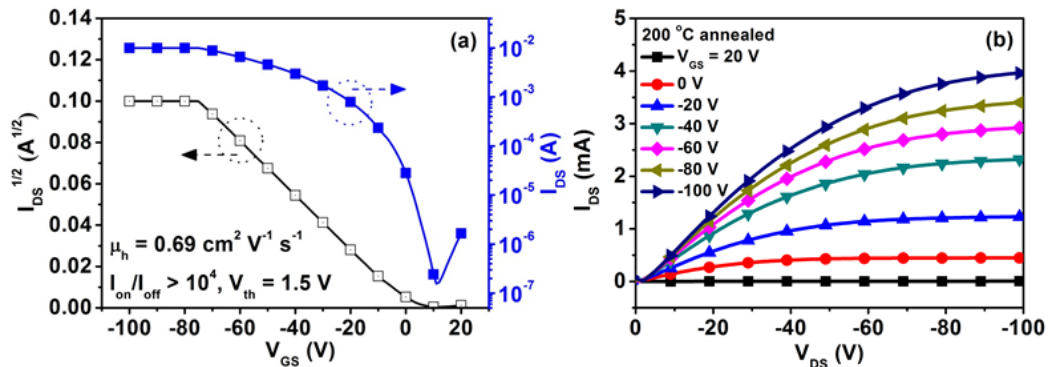


Fig. S4 (a) Transfer characteristic at fixed V_{DS} of -100 V and (b) output characteristic for PTIG-co-TT TFTs based on the annealed film at 200 °C (device geometry with $L = 20 \mu\text{m}$ and $W = 10,000 \mu\text{m}$ and dielectric thickness of 200 nm).

S5. Grazing-incidence X-ray diffraction (GI-XRD) measurements

The crystalline structure of PTIG-co-TT films was characterized by GI-XRD conducted on beam-line 17A1 of the National Synchrotron Radiation Research Center (NSRRC), with the wavelength 1.333 Å. All samples were spun on OTS-treated Si/SiO₂ substrates with the same fabricating conditions of PTFT for mimicking devices. In order to increase the effective X-ray penetrating depth, the angle between the incident beam and the film surface was fixed at 0.15°. The 2D diffraction patterns of PTIG-co-TT films before and after heat treatment (Fig. S5) was collected by a Mar345 Imaging Plate Area Detector, Fuji Bas 2500 IP, Bicron detector.

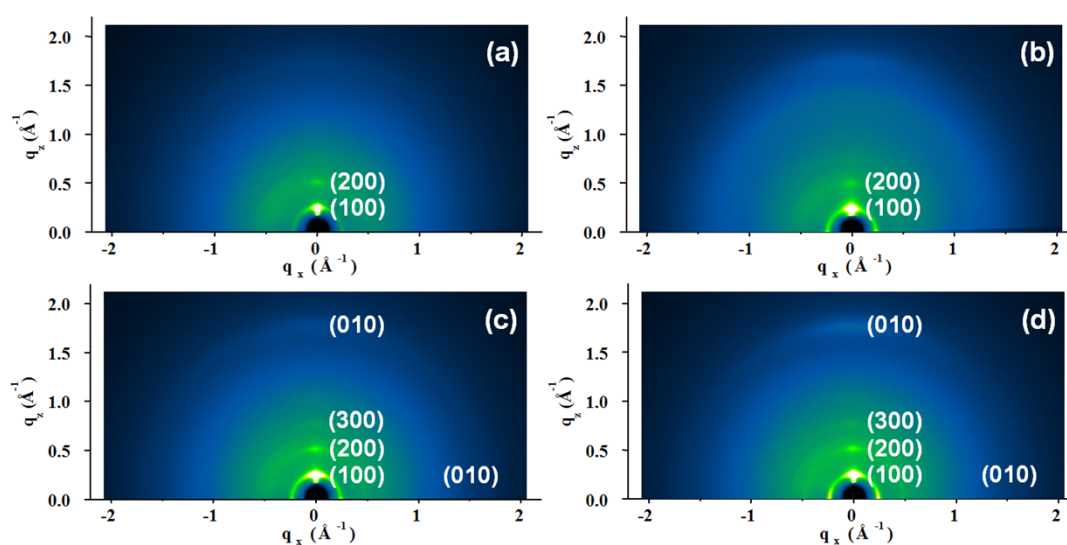


Fig. S5 2D GI-XRD patterns of PTIG-co-TT with (a) as-spun film and annealed film at (b) 100, (c) 200 and (d) 300 °C on OTS-treated Si/SiO₂ substrates.

S6. Scanning probe microscopy (SPM) measurement

The PTIG-co-TT samples for AFM analysis were prepared in accordance with the TFT process on cleaned Si/SiO₂ substrates and were performed by Digital

Instrument Nanoscope V and were measured under ambient atmosphere. Rectangular Au tips (Multi75GB, Budget Sensors) with an estimated force constant of 3 N m^{-1} and resonance frequency of 75 kHz were used in tapping mode for height image. As shown in Fig. S6, the AFM images of PTIG-co-TT films annealed at 100 and 300 °C have similar morphology as the film at 200 °C with a reticular structure consisting of intertwined nanofibrils.

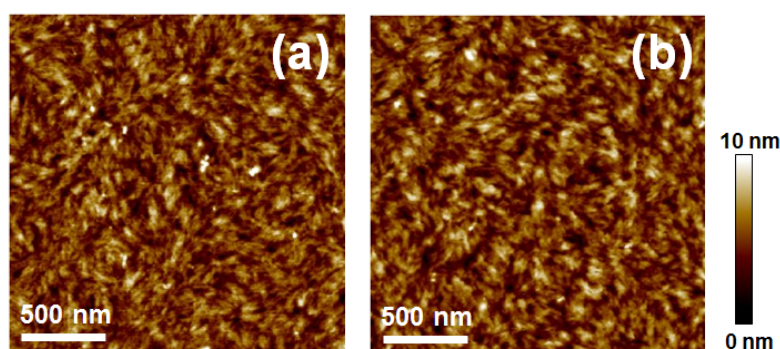


Fig. S6 AFM tomography images of PTIG-co-TT on OTS-treated Si/SiO₂ substrates with annealed film at (a) 100 and (b) 300 °C.

References

- [S1] S. Wang, W. Hong, S. Ren, J. Li, M. Wang, X. Gao and H. Li, *J. Polym. Sci., Part A: Polym. Chem.*, 2012, **50**, 4272.
- [S2] S. Amemori, K. Kokado and K. Sada, *Angew. Chem. Int. Ed.*, 2013, **52**, 4174.
- [S3] S. Ashraf, A. J. Kronemeijer, D. I. James, H. Sirringhaus and I. McCulloch, *Chem. Commun.*, 2012, **48**, 3939.
- [S4] Y. Ito, A. A. Virkar, S. Mannsfeld, J. H. Oh, M. Toney, J. Locklin and Z. Bao, *J. Am. Chem. Soc.*, 2009, **131**, 9396.