

Electronic Supplementary Information (ESI)

High face-on ratio isoindigo copolymers with extended nano-fibrillar network in fullerene-based thick (>300 nm) photovoltaics achieving high efficiency 10.7%

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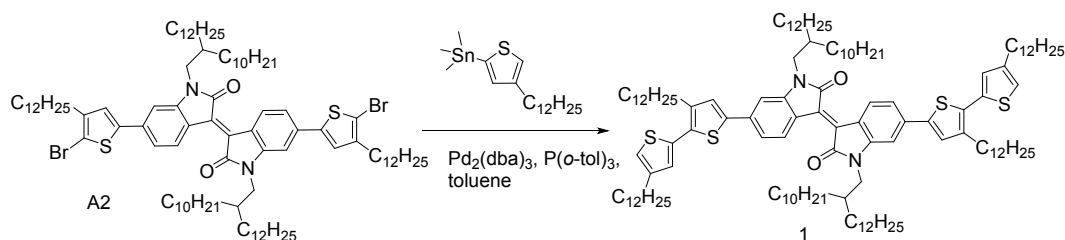
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S1. Synthesis, Characterization of Materials and Instrumentation

S1.1. Synthesis

Compound (4-dodecylthiophen-2-yl) trimethylstannane,¹ (3,3'-difluoro-[2,2'-bithiophene]-5,5'-diyl)bis(trimethylsilane) (D1),² (*E*)-6,6'-dibromo-1,1'-bis(2-decyltetradecyl)-[3,3'-biindolinylidene]-2,2'-dione (A1),³ and (*E*)-6,6'-bis(5-bromo-4-dodecylthiophen-2-yl)-1,1'-bis(2-decyltetradecyl)-[3,3'-biindolinylidene]-2,2'-dione (A2)³ were synthesized according to the literatures. The solvents were dried using standard procedures. All other reagents were used as received from commercial sources, unless specified otherwise.

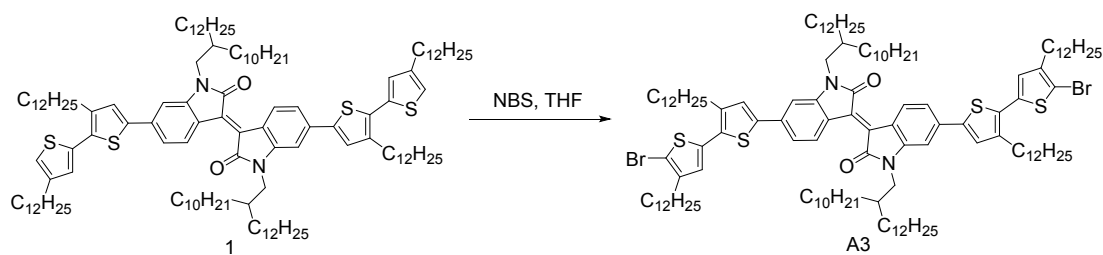
(*E*)-1,1'-Bis(2-decyltetradecyl)-6,6'-bis(3,4'-didodecyl-[2,2'-bithiophen]-5-yl)-[3,3'-biindolinylidene]-2,2'-dione (1)



Monomer A2 (2.65 g, 1.66 mmol), (4-dodecylthiophen-2-yl)trimethylstannane (1.59 g, 3.82 mmol), and tri(*o*-tolyl)phosphine (P(*o*-tol)₃) (405 mg, 1.33 mmol) were dissolved in dried toluene (50 mL). The solution was purged with nitrogen gas for 30 min first, and then tris(dibenzylideneacetone)dipalladium(0) (Pd₂(dba)₃) (152 mg, 0.17 mmol) was added quickly into the reaction mixture under vigorous flushing of nitrogen gas. The reaction mixture was then heated to reflux for 16 h. After cooling down to room temperature, the reaction mixture was concentrated by solvent evaporation under reduced pressure, and the residue was purified via column chromatography with silica gel (hexanes: dichloromethane = 1:5). The product was recrystallized from isopropyl alcohol affording a deep blue solid. Yield: 2.95 g (91.5

%); ^1H NMR (600 MHz, CDCl_3 , δ): 9.15 (d, $J = 8.30$ Hz, 2H; Ar H), 7.25 (dd, $J = 8.30$ Hz, 1.56 Hz, 2H; Ar H; partially overlapping with the solvent peak), 7.23 (s, 2H; Ar H), 7.01 (d, $J = 0.72$ Hz, 2H; Ar H), 6.95 (d, $J = 1.56$ Hz, 2H; Ar H), 6.92 (d, $J = 0.72$ Hz, 2H; Ar H), 3.71 (d, $J = 7.20$ Hz, 4H; CH_2), 2.78 (t, $J = 7.80$ Hz, 4H; CH_2), 2.62 (t, $J = 7.74$ Hz, 4H; CH_2), 1.97-1.86 (m, 2H; CH), 1.71-1.63 (m, 8H; CH_2), 1.50-1.10 (m, 152H; CH_2), 0.89-0.84 (m, 24H; CH_3); ^{13}C NMR (150 MHz, CDCl_3 , δ): 168.72, 145.71, 143.75, 141.18, 140.58, 137.47, 135.57, 132.27, 131.76, 130.14, 127.39, 127.17, 121.07, 120.30, 118.80, 104.62, 44.48, 36.45, 31.98, 31.89, 31.82, 30.66, 30.52, 30.45, 30.03, 29.72, 29.68, 29.64, 29.51, 29.48, 29.46, 29.44, 29.43, 29.37, 29.35, 29.33, 29.30, 26.69, 22.69, 14.13, 14.10, 14.08, 14.06; HRMS (MALDI) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{128}\text{H}_{210}\text{N}_2\text{O}_2\text{S}_4$, 1937.3584; found, 1937.3596. Anal. calcd for $\text{C}_{128}\text{H}_{210}\text{N}_2\text{O}_2\text{S}_4$: C 79.36, H 10.93, N 1.45, S 6.62; found: C 79.26, H 11.21, N 1.42, S 6.56.

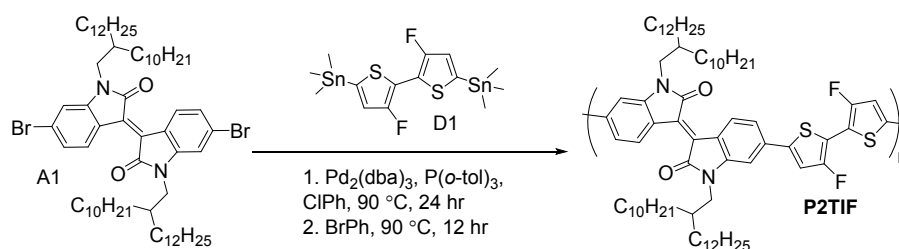
(E)-6,6'-bis(5'-bromo-3,4'-didodecyl-[2,2'-bithiophen]-5-yl)-1,1'-bis(2-decyltetradecyl)-[3,3'-biindolinylidene]-2,2'-dione (A3)



To a solution of compound 1 (2.60 g, 1.34 mmol) in tetrahydrofuran (THF) (50 mL), *N*-bromosuccinimide (NBS) (526 mg, 2.95 mmol) was added separately in 12 portions in 4 hr at room temperature. After the addition of the last portion of NBS, the reaction was stirred for another 20 min, and monitored by thin-layer chromatography. When the reaction finished, the reaction mixture was poured into water. The organic layer was extracted by dichloromethane, dried over MgSO_4 , and evaporated till dryness under reduced pressure. The residue was purified by column chromatography

with silica gel (hexanes: dichloromethane = 1:5) twice, followed by recrystallization from isopropyl alcohol. A dark blue solid of monomer A3 was obtained. Yield: 2.43 g (86.5 %); ¹H NMR (400 MHz, CDCl₃, δ): 9.14 (d, *J* = 8.3 Hz, 2H; Ar H), 7.23 (dd, *J* = 8.44 Hz, 1.64 Hz, 2H; Ar H; partially overlapping with the solvent peak), 7.21 (s, 2H; Ar H), 6.91 (d, *J* = 1.64 Hz, 2H; Ar H), 6.86 (s, 2H, Ar H), 3.68 (d, *J* = 7.00 Hz, 4H; CH₂), 2.73 (t, *J* = 7.68 Hz, 4H; CH₂), 2.57 (t, *J* = 7.84 Hz, 4H; CH₂), 1.92 (m, 2H; CH), 1.70-1.60 (m, 8H; CH₂), 1.50-1.10 (m, 152H; CH₂), 0.90-0.84 (m, 24H; CH₃); ¹³C NMR (100 MHz, CDCl₃, δ): 168.65, 145.72, 142.57, 141.69, 141.08, 137.24, 135.40, 131.81, 131.13, 130.19, 127.10, 126.83, 121.19, 118.85, 109.02, 104.62, 67.96, 44.47, 36.44, 30.02, 31.99, 31.98, 31.95, 31.93, 31.90, 31.88, 31.87, 31.85, 31.81, 30.65, 30.01, 29.79, 29.76, 29.75, 29.72, 29.67, 29.63, 29.61, 29.59, 29.58, 29.53, 29.47, 29.44, 29.37, 29.34, 29.32, 29.28, 29.26, 26.68, 25.61, 22.76, 22.73, 22.72, 22.70, 22.68, 22.65, 14.16, 14.14, 14.13, 14.09, 14.06; HRMS (MALDI) *m/z*: [M+H]⁺ calcd for C₁₂₈H₂₀₈Br₂N₂O₂S₄, 2096.1575; found, 2096.1558. Anal. calcd for C₁₂₈H₂₀₈Br₂N₂O₂S₄: C 73.38, H 10.01, N 1.34, S 6.12; found: C 73.20, H 10.46, N 1.26, S 6.07.

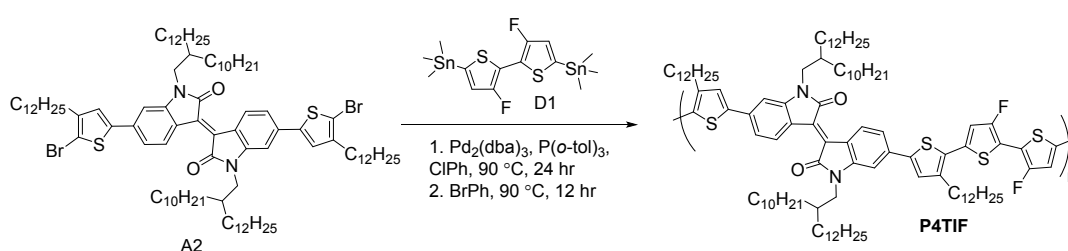
Synthesis of P2TIF



Monomer A1 (322 mg, 0.29 mmol, 1.0 equiv.), monomer D1 (155 mg, 0.29 mmol, 1.0 equiv.) and P(*o*-tol)₃ (72 mg, 0.24 mmol, 0.8 equiv.) were dissolved in 8.6 mL of distilled chlorobenzene. The mixture was degassed by three freeze-pump-thaw cycles. After the mixture was warmed up to room temperature and further purged with nitrogen gas for 10 min, Pd₂(dba)₃ (27 mg, 0.03 mmol, 0.1 equiv.) was added in one

portion under a vigorous flushing of nitrogen gas. The solution was heated at 90 °C for 24 hr under nitrogen, and 1.0 mL bromobenzene was added into the reaction mixture by a syringe for end-capping the copolymer chain. The reaction was carried on for 12 hr further. After cooling to room temperature, the reaction product was precipitated in 200 mL of methanol. The crude copolymer was collected by filtration and washed by Soxhlet extraction with methanol, acetone, hexane, and dichloromethane to remove the impurities including the low-molecular-weight oligomers. Finally, the product was retrieved by Soxhlet extraction with hot CF. The hot CF fraction was concentrated and re-precipitated in 200 mL of methanol. The precipitates was collected and dried in vacuum to afford the title copolymer as a dark blue solid. Yield: 318 mg (95.4 %). GPC (50 °C, CF): $M_n = 156.1$ kDa, $M_w = 211.5$ kDa, PDI = 1.35 (Fig. S1). $^1\text{H NMR}$ (400 MHz, CDCl_3 , δ): 9.47-8.15 (br, 2H; Ar H), 7.71-5.53 (br, 6H; Ar H), 4.26-3.74 (br, 4H; CH_2), 2.50-0.95 (br, 80H; CH, CH_2) 0.95-0.50 (br, 12H, CH₃) (Fig. S4); Anal. calcd for $(\text{C}_{72}\text{H}_{106}\text{F}_2\text{N}_2\text{O}_2\text{S}_2)_n$: C 76.28, H 9.42, N 2.47, S 5.66; found: C 75.80, H 9.36, N 2.37, S 5.49.

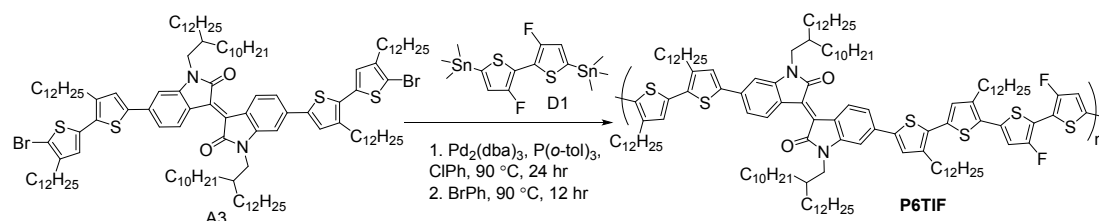
Synthesis of **P4TIF**



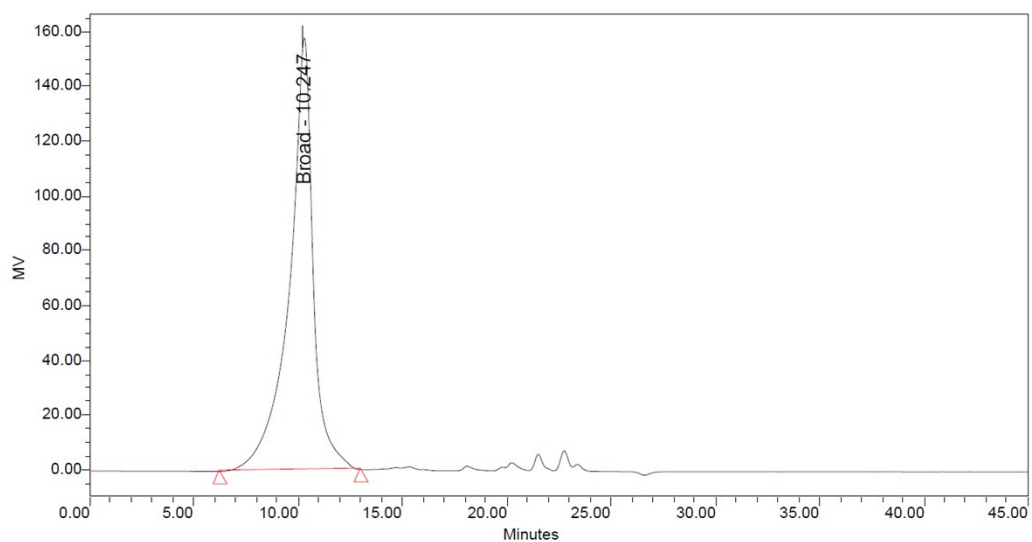
The synthesis and purification of **P4TIF** was following the same procedure as that for **P2TIF**. A mixture of monomer A2 (346 mg, 0.22 mmol, 1.0 equiv.), monomer D1 (115 mg, 0.22 mmol, 1.0 equiv.), $\text{P}(o\text{-tol})_3$ (53 mg, 0.17 mmol, 0.8 equiv.), and $\text{Pd}_2(\text{dba})_3$ (20 mg, 0.02 mmol, 0.1 equiv.) were copolymerized in 4.6 mL of CB to afford **P4TIF** as a dark green solid. Yield: 331 mg (93.2 %). GPC (50 °C, CF): $M_n = 109.6$ kDa, $M_w = 175.9$ kDa, PDI = 1.60 (Fig. S2). $^1\text{H NMR}$ (400 MHz, CDCl_3 , δ):

9.32-8.33 (br, 2H; Ar H), 7.68-5.49 (br, 8H; Ar H), 3.86-3.40 (br, 4H; CH₂), 3.00-2.67 (br, 4H; CH₂), 2.50-1.06 (br, 122H; CH, CH₂), 1.06-0.50 (br, 18H; CH₃) (Fig. S5); Anal. calcd for (C₁₀₄H₁₅₈F₂N₂O₂S₄)_n: C 76.42, H 9.74, N 1.71, S 7.85; found: C 76.21, H 9.92, N 1.65, S 7.70.

Synthesis of P6TIF



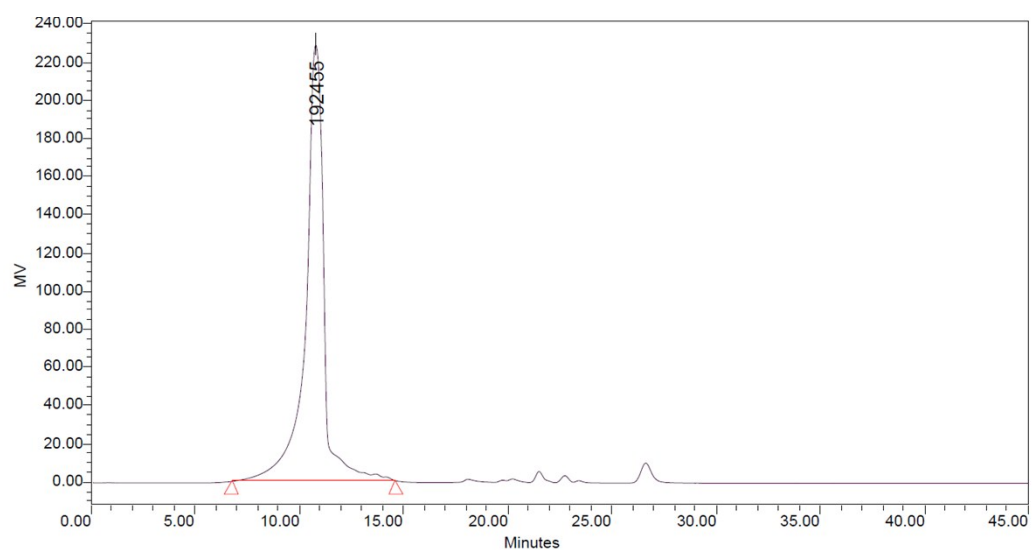
P6TIF was synthesized by following the same procedure as that for **P2TIH** and **P4TIF**. A mixture of monomer A3 (325 mg, 0.16 mmol, 1.0 equiv.) and monomer D1 (82 mg, 0.16 mmol, 1.0 equiv.), P(*o*-tol)₃ (38 mg, 0.12 mmol, 0.8 equiv.), and Pd₂(dba)₃ (14 mg, 0.016 mmol, 0.1 equiv.) were copolymerized in 4.1 mL of CB to give **P6TIF** as a dark green solid. Yield: 282 mg (85.2 %). GPC (50 °C, CF): $M_n = 113.2$ kDa, $M_w = 176.2$ kDa, PDI = 1.56 (Fig. S3). ¹H NMR (400 MHz, CDCl₃, δ): 9.36-8.63 (br, 2H; Ar H), 7.70-5.46 (br, 10H; Ar H), 3.96-3.39 (br, 4H; CH₂), 3.11-2.43 (br, 8H; CH₂), 2.22-1.78 (br, 2H; CH), 1.78-1.66 (br, 8H; CH₂), 1.50-1.01 (br, 152H; CH₂), 1.01-0.53 (br, 24H, CH₃) (Fig. S6); Anal. calcd for (C₁₃₆H₂₁₀F₂N₂O₂S₆)_n: C 76.49, H 9.91, N 1.31, S 9.01; found: C 76.36, H 10.11, N 1.27, S 8.94.



GPC Results

Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw	Mz+1/Mw
1	10.247	10.247	10.247	156113	211502		244306	263011	1.155099	1.243537

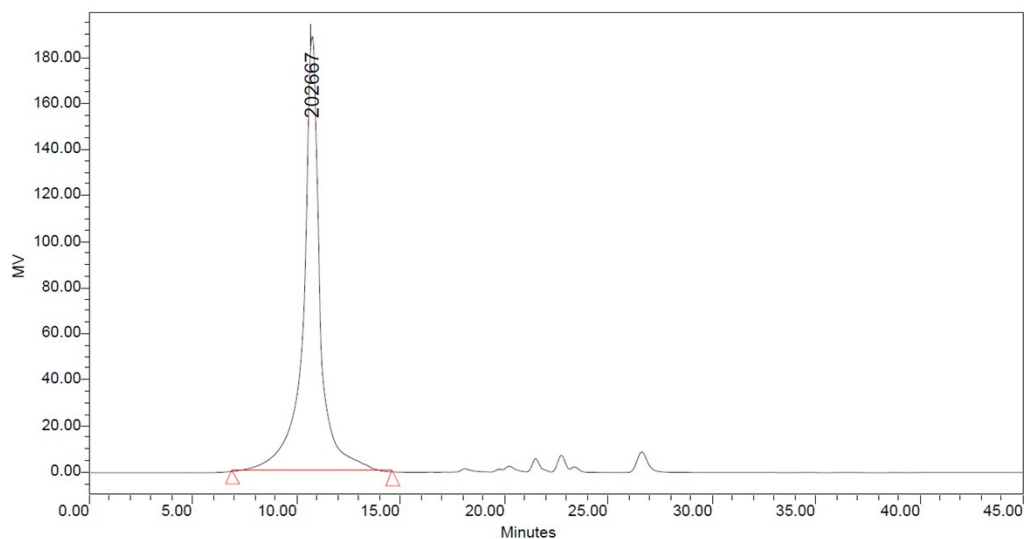
Fig. S1. GPC result of **P2TIF**.



GPC Results

Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw
1	10.743	10.743	10.743	109616	175875	192455	206617	226895	1.174795

Fig. S2. GPC result of **P4TIF**.



GPC Results

Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw
1	10.706	10.706	10.706	113153	176182	202667	209096	229593	1.186817

Fig. S3. GPC result of P6TIF.

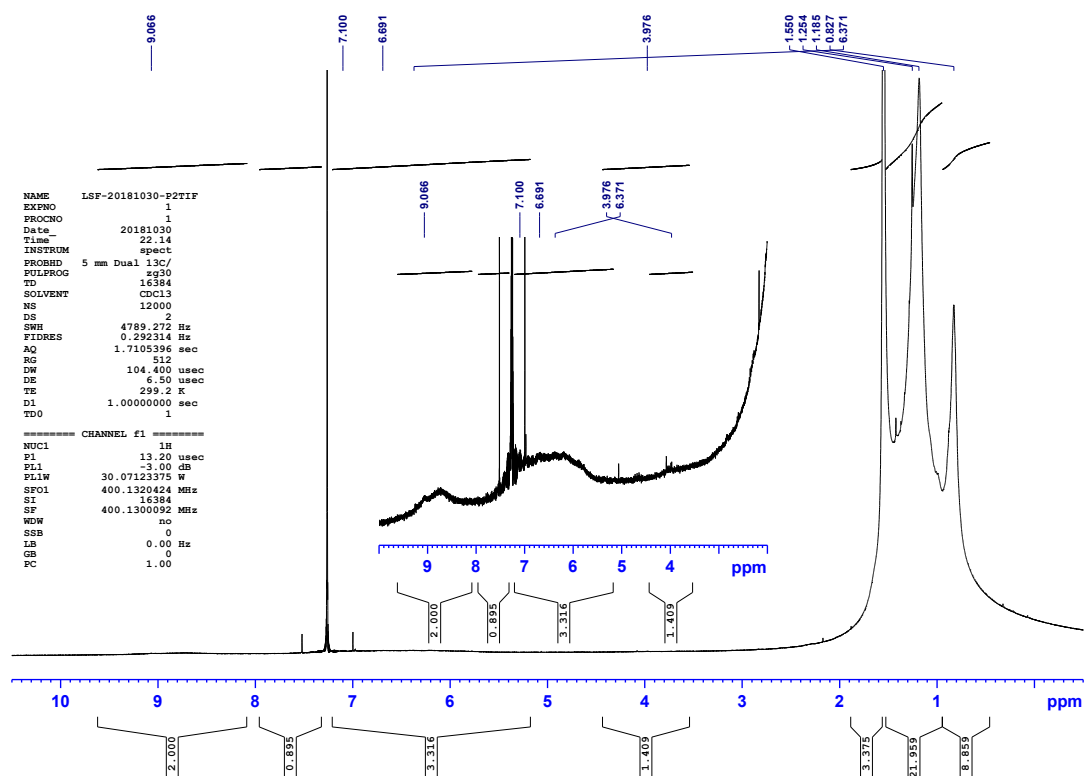


Fig. S4. ¹H NMR of P2TIF.

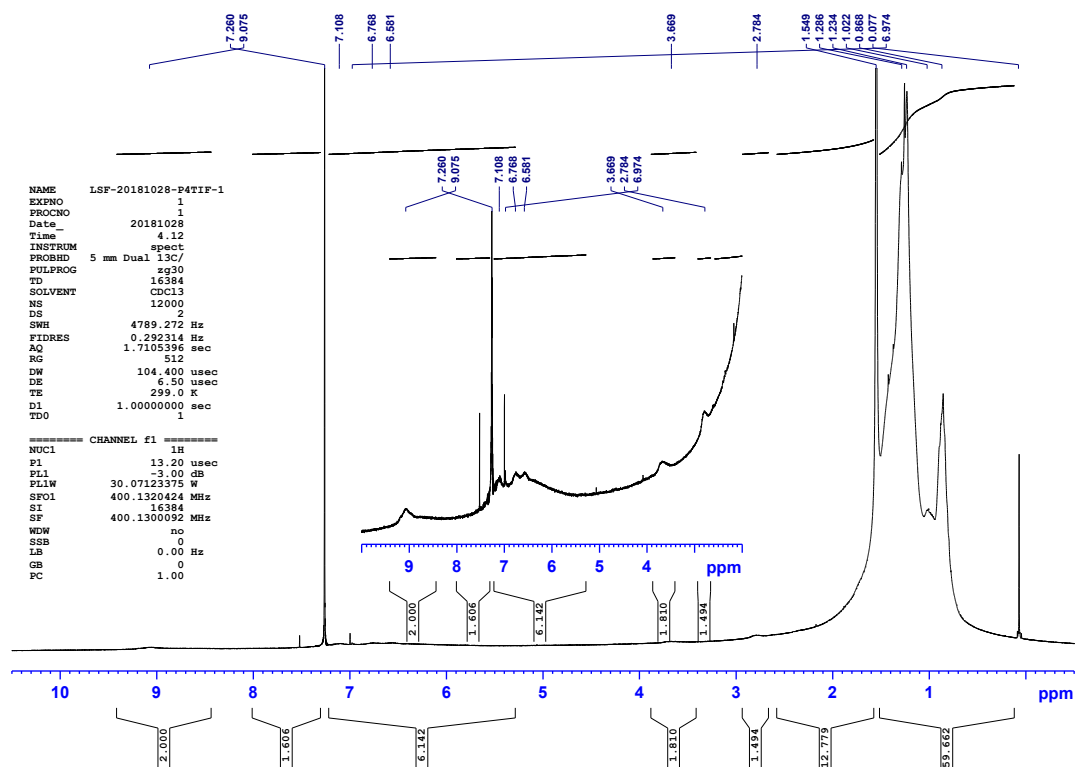


Fig. S5. ¹H NMR of P4TIF.

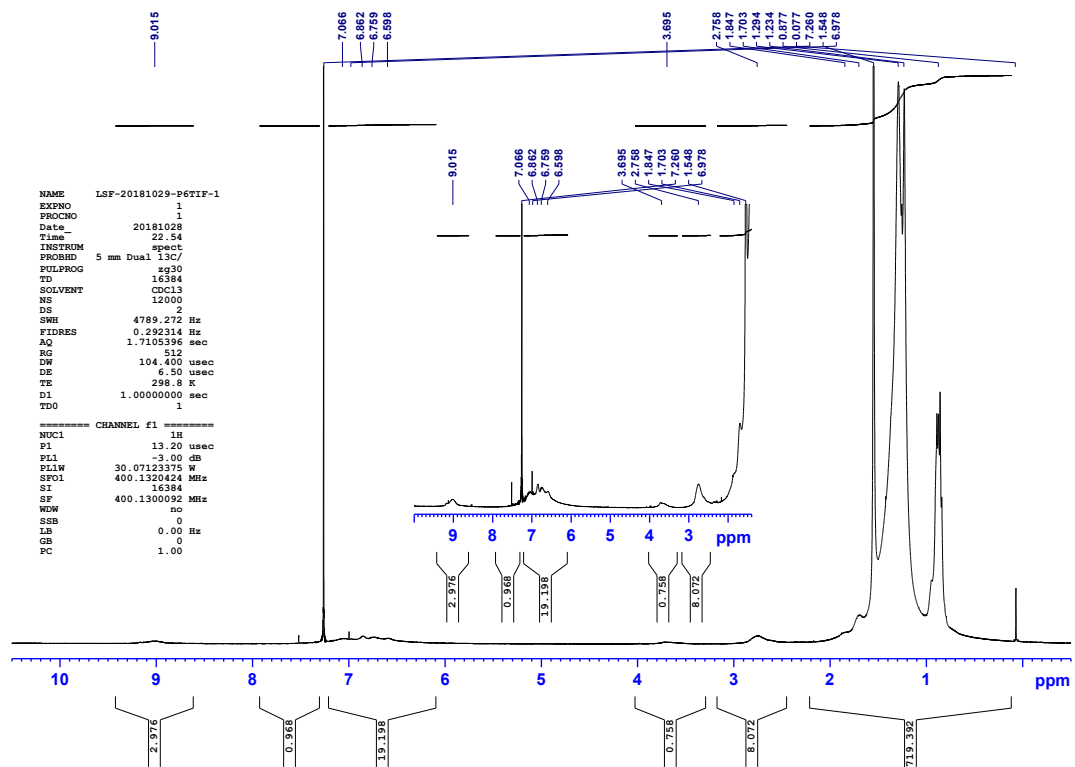


Fig. S6. ¹H NMR of P6TIF.

S1.2. Characterization of Materials and Instrumentation

^1H and ^{13}C NMR spectra were recorded on Bruker Avance 400 MHz and Bruker Avance III HD 600 MHz spectrometer equipped with Dual z-gradient probe and BBFO probe head, respectively. Matrix-assisted laser desorption/ionization high resolution mass spectroscopy (MALDI HRMS) were obtained by a Bruker New ultrafleXtreme™ spectrometer in Mass Spectroscopic Laboratory in-house service of the Institute of Chemistry, Academia Sinica. Elemental analysis (EA) was performed by using an Elementar Vario EL Cube (for NCSH) elemental analyzer, which is equipped in the Elemental Analyses Laboratory of the Precision Instrumentation Center, College of Science, National Taiwan University. The synthesized copolymers molecular weights and their distribution were measured by gel permeation chromatography (GPC) using a Waters 1515 chromatography unit interfaced to a Waters 2414 refractive index detector with CF as the eluent at 50 °C and calibrated by polystyrene standards.

Thermogravimetric analysis (TGA) was performed using a Perkin Elmer Pyris 1 TGA instrument. The thermal stabilities of the samples under a nitrogen atmosphere were determined according to their weight losses (5 wt.%) while heating up from 50 °C to 900 °C at a heating rate of 10 °C min⁻¹ (Fig. S7a). Differential scanning calorimetry (DSC) was performed using a Perkin Elmer Pyris 6 DSC analyzer system operated at a same heating/ cooling rate of 10 °C min⁻¹, respectively. For **P2TIF**, the sample was scanned from 30 to 400 °C; for **P4TIF** and **P6TIF**, it was scanned from 30 to 350 °C, and then they were all cooled down back to 30 °C to complete one heating-cooling cycle (Fig. S7b).

UV-visible absorption spectra were measured using a Hewlett Packard 8453 diode-array spectrophotometer for both solution and thin film samples. For the measurement of solution samples, *PnTIF* copolymers were dissolved in diluted CF solutions at

different temperatures (Fig S8a-c). For solid thin film samples, *PnTIF* copolymers were spin-coated on cleaned quartz substrates at a spin rate of 400 rpm for 20 sec in CF/DCB (1/1, v/v) solutions with a concentration of 3.0 mg mL⁻¹ without heating. Right after the spin-coating, the thin film sample was covered by a Petri dish and kept in a N_{2(g)}-filled glove box for 16 hr.

The experimental HOMO and LUMO energy levels of *PnTIF* copolymers were deduced from monitoring the onsets of oxidation and reduction potentials of cyclic voltammograms (Fig. S9). Cyclic voltammetry (CV) measurements were conducted using a CH Instruments CHI620A electrochemical analyzer operated at a scanning rate of 100 mV s⁻¹, and employing tetrabutylammonium hexafluorophosphate (TBAPF₆) dissolved in anhydrous acetonitrile (0.1 M) as the supporting electrolyte. The copolymer solution (2.0 mg mL⁻¹ in CF) was drop-cast on the top of glassy carbon electrode which was used as the working electrode. A Pt wire was used as the auxiliary electrode. The potentials were measured against an Ag/Ag⁺ (0.01 M AgNO₃ in acetonitrile) reference electrode, using ferrocene (Fc) as the calibration of redox potential. The CV measurements were processed by monitoring the onsets of oxidation and reduction potentials of materials in thin film state. Fc/Fc⁺ onset redox potential in our CV measurement was +0.027 V relative to Ag/Ag⁺ (Fig. S9). The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) were estimated by the following equation:

$$HOMO (eV) = -(E^{ox} + 4.8) \quad , \quad LUMO (eV) = -(E^{red} + 4.8)$$

Where E^{ox} is the onset oxidation potential versus Fc/Fc⁺; E^{red} is the onset reduction potential versus Fc/Fc⁺. The frontier molecular orbitals and the torsion (dihedral) angles of *PnTIF* copolymers were simulated by DFT calculation using Gaussian 09 with the hybrid functional B3LYP and 6-31G (d, p) basis set. To shorten the

calculation time, an A-D type model with single repeating unit of *PnTIF* was used. The model has an isobutyl-substituted isoindigo unit and an oligothiophene segment composed by two monofluoro-substituted thiophenes (for **P2TIF**) in addition to two and four ethyl-substituted thiophenes for **P4TIF** and **P6TIF**, respectively (Fig. S10).

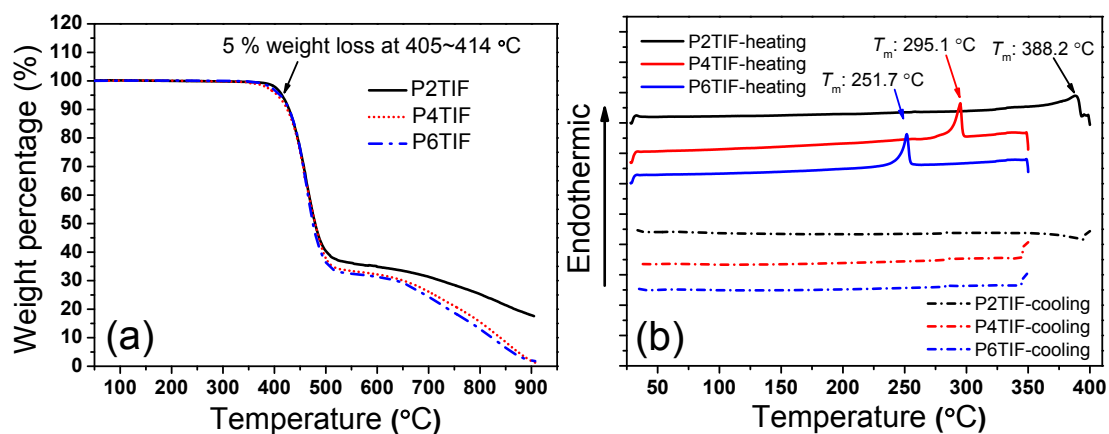


Fig. S7. (a) TGA thermograms and; (b) DSC thermography of *PnTIF* copolymers.

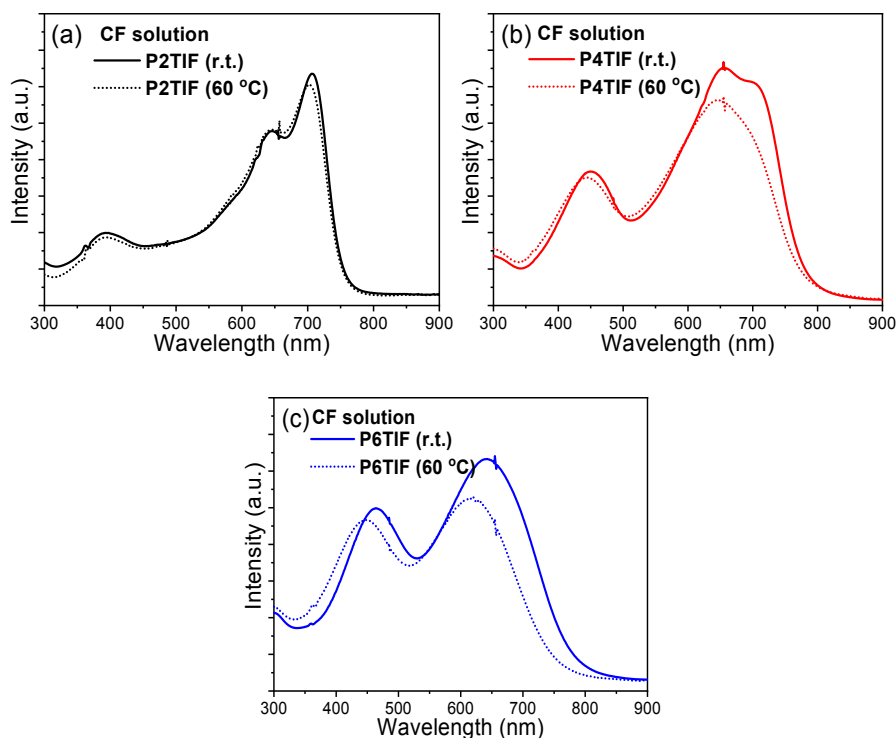


Fig. S8. Solution UV-visible absorption spectra of **P2TIF** (a), **P4TIF** (b), and **P6TIF** (c).

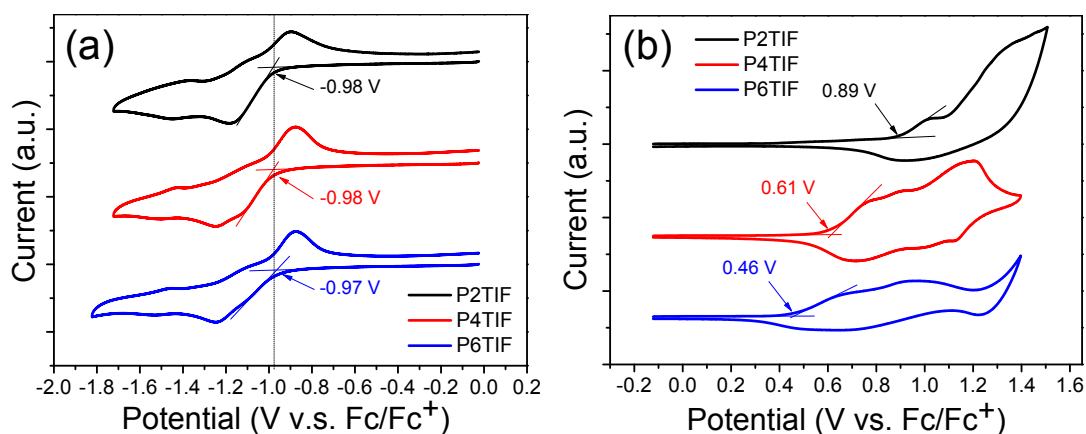


Fig. S9. Cyclic voltammetry measurement of *PnTIF* copolymer films cast on glassy carbon electrode in CH_3CN solution with 0.1 mol L^{-1} TBAPF_6 electrolyte: (a) reduction; (b) oxidation.

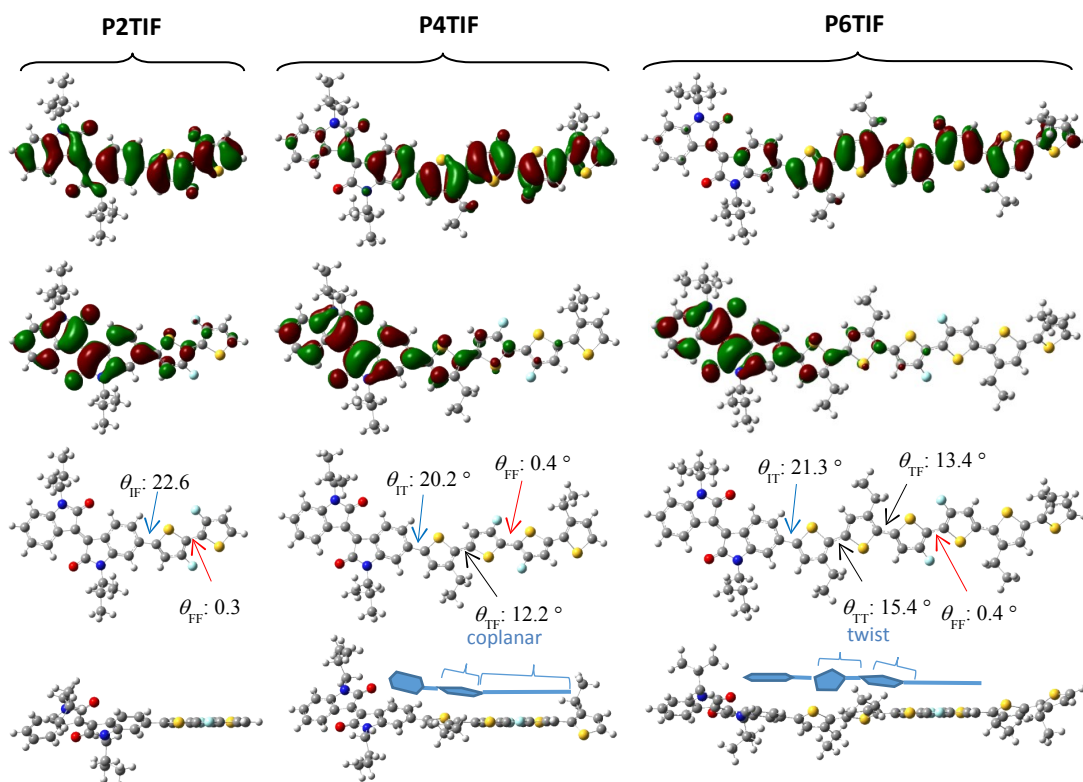


Fig. S10. Electron density distribution of HOMOs (top three figures) and LUMOs (second top three figures), dihedral angles (second bottom three figures), and optimized molecular structures (bottom three figures) of A-D monomer model of *PnTIF* polymers.

S2. Photovoltaic Device Fabrication and Characterization

S2.1. Polymer Solar Cells Device Fabrication

At first, electron accepting material PC₆₁BM was used together with *PnTIF* in the optimization of active layer fabrication, and various halogenated processing solvents, such as CF, CB, DCB, and CF/DCB mixed solvent systems were chosen. The best *PnTIF*:PC₆₁BM blending ratio was found to be 1:1.5 (w/w) for all three copolymers and the mixed solvent of CF/DCB (1/1, v/v) was tested to be the best processing solvent. After adjusting the concentration of *PnTIF*:PC₆₁BM solution to find the optimal thickness of active layer, PC₆₁BM was replaced by PC₇₁BM as the electron accepting material for comparison. Finally, for a purpose of further optimization, solvent additives, such as 1,8-diodooctane (DIO), 1-chloronaphthalene (CN), or diphenyl ether (DPE) were included in the fabrication process. Among them, DPE was tested to be the best solvent additive. For the device fabrication reported herein, all the *PnTIF*:PCBM active layers can be deposited on the substrates at room temperature without heating. The details for the device fabrication and characterization are shown in below.

To fabricate the photovoltaic devices, patterned ITO glass substrates were ultrasonic- cleaned for 10 min with detergent, de-ionized water, acetone, and isopropanol sequentially, and were following baked on the hot plate at 110 °C for 10 min. A further clean of surface of the substrates were treated under UV-ozone at room temperature for 15 min. The effective area of each solar cell device is 0.04 cm². The inverted devices were fabricated with a configuration of ITO/ZnO/PEIE/copolymer:PCBM/MoO₃/Ag. The ZnO electron transporting layer⁴ was prepared by spin-coating (4000 rpm for 1 min) a ZnO precursor solution (1.0 g zinc acetate dihydrate dissolved in 0.28 mL of monoethanolamine and 10 mL of 2-

methoxyethanol mixed solvent). After thermal annealing of the ZnO layer at 200 °C for 1 hour and naturally cooling down to room temperature, a thin layer of ethoxylated polyethylenimine (PEIE, 35-40 wt. % in H₂O, average $M_w \sim 70000$, purchased from Aldrich company) was spin-coated on the top of the ZnO layer from a further diluted solution (0.4 wt. % in 2-methoxyethanol) at 5000 rpm for 1 min and followed by thermal annealing at 150 °C for 10 min. The fullerene derivatives [6,6]-phenyl-C₆₁-butyric acid methyl ester (PC₆₁BM) or [6,6]-phenyl-C₇₁-butyric acid methyl ester (PC₇₁BM) was used as the n-type materials blended with the p-type *PnTIF* copolymers to form the active layers of the photovoltaic devices. The thickness of active layers was adjusted by changing the concentration of *PnTIF*:PCBM solutions keeping the same spin-coating and drying condition during the film formation. To obtain the optimized photovoltaic devices, *PnTIF*:PCBM solutions in different concentrations were prepared. All *PnTIF* copolymers and PCBM were mixed with a blend ratio of 1:1.5 (w/w) and dissolved in a CF/DCB (1/1, v/v) mixed solvent system. For the optimized **P2TIF**:PC₆₁BM photovoltaic device, 4.0 mg **P2TIF**, 6.0 mg PC₆₁BM, 0.49 mL solvent CF, and 0.02 mL solvent additive diphenyl ether (DPE) if required, were mixed and heated at 60 °C for 30 min. After naturally cooling down to room temperature, 0.49 mL DCB was poured into the solution and the solution was further heated at 60 °C for another 30 min. After cooling down to room temperature, the **P2TIF**:PC₆₁BM solution with a total concentration of 10.0 mg mL⁻¹ (containing 98% CF/DCB mixed solvent and 2% DPE additive) was prepared. All the copolymer:PCBM solutions with or without solvent additive DPE were prepared following the same procedure, except for the concentration, 14.0 mg mL⁻¹ and 18.0 mg mL⁻¹ for **P4TIF**:PC₆₁BM and **P6TIF**:PC₇₁BM without DPE solvent additive, respectively. All the prepared *PnTIF*:PCBM solutions were filtered through a 0.45 μm polyvinylidene difluoride (PVDF) filter, and then subjected to spin-coating

onto the PEIE layer at room temperature using the same spin-coating rate of 350 rpm for 20 sec. After spin-coating, the active layer (liquid film) was slowly dried under a cover of Petri dish. The covered *PnTIF*:PCBM samples were kept in a N_{2(g)}-filled glove-box at room temperature for 16 hr. For those sample containing DPE, 24 hr or more was usually required. Subsequently, 8.0 nm of MoO₃ and 100 nm of Ag were thermally deposited onto the *PnTIF*:PCBM active layer in a pressure of $\sim 10^{-6}$ Torr. Finally, the devices were encapsulated using UV-curing epoxy (Nagase) and a cover glass.

S2.2. Polymer Solar Cell (PSC) Device Characterization

The thickness of the active layers was determined by a Dektak 150 surface profiler. The current density–voltage (*J–V*) characteristics of PSCs were measured under ambient conditions using a Keithley 2400 source meter and illuminated under AM 1.5 G from a solar simulator (Newport 91160A 300 W). The light intensity was calibrated using a Si photodiode (PVM 172; area= 3.981 cm²) from Nation Renewable Energy Laboratory. For the incident photon-to-electron conversion efficiency (IPCE) measurement, a light source with an intensity of 300 W was used as the white light bias. A monochromator (Jobin Yvon Horiba TRIAX 190) was chopped at 300 Hz and used to select the wavelengths from 370 to 850 nm. The photocurrent of the PSCs was measured through the lock-in amplifier (Signal Recovery 7265), which was referenced to the chopper frequency.

S3. Morphology Observations

S3.1. Transmission Electron Microscopy (TEM)

The bright field TEM images were collected by a JEOL JEM-1400 TEM operating at 120 kV. The samples for TEM were spin-coated on poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS, AI 4083)-coated ITO substrates using copolymer:PCBM blend solutions prepared identically (350 rpm spin rate last for 20 sec) to those for PSC fabrication. Thin film samples were obtained by immersing the whole ITO substrate in water for 30 min. The peel-off thin film was supported on a copper grid then dried in vacuum for 16 hr before TEM measurement. Considering sufficient transmittance of electron beam in taking TEM image covering a large area (Fig. S11), except for **P2TIF**:PCBM solutions, the solution concentration of all *PnTIF*:PCBM solutions were reduced to half of those in the preparing optimal PSCs. On the other hand, in preparing the *PnTIF* copolymer neat film samples for TEM images (Fig. 4 in text), the concentration of all copolymer solutions was 3 mg mL⁻¹.

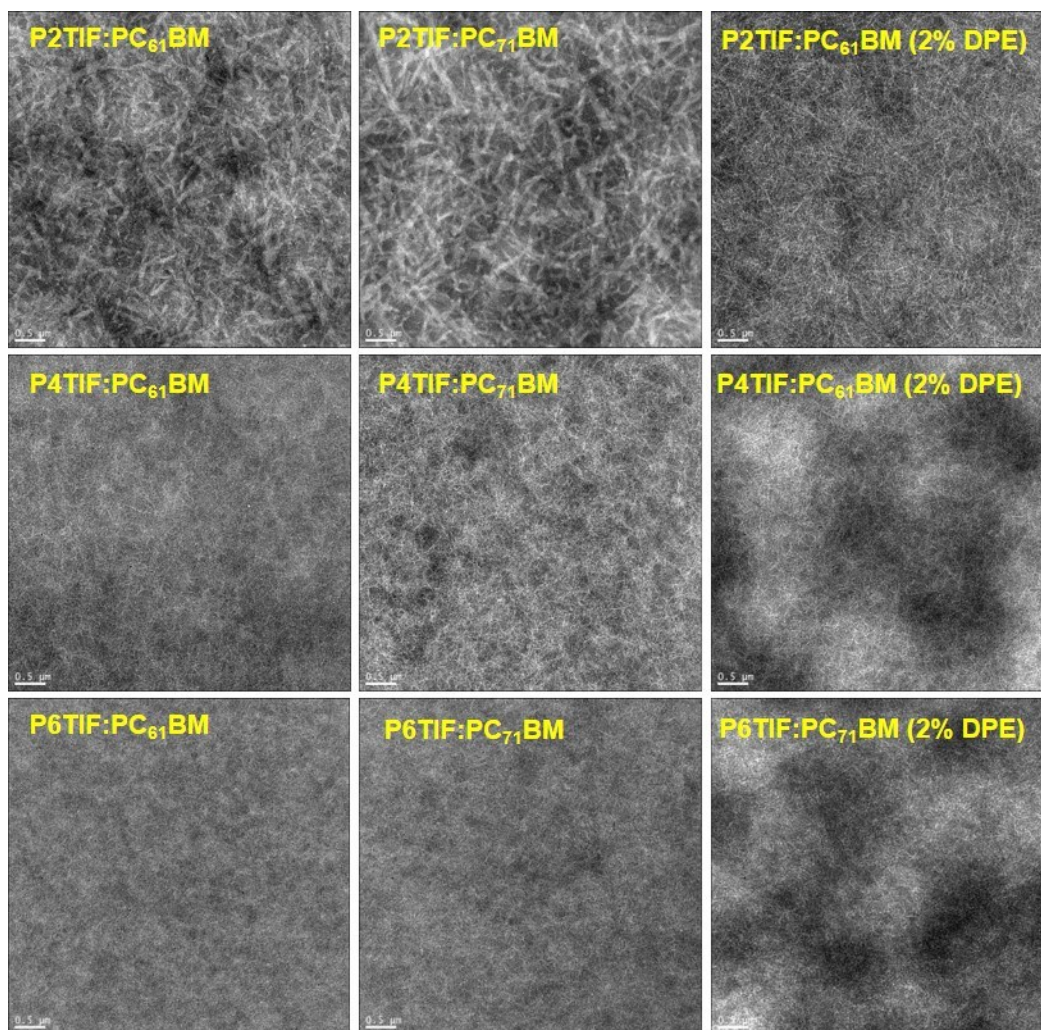


Fig. S11. TEM images of $PnTIF:PCBM$ blend films. The scale bar is $0.5 \mu\text{m}$ ($\times 10000$).

S3.2. Atomic Force Microscopy (AFM)

The surface morphology of pure copolymer (Fig. 4 in text) and $PnTIF:PCBM$ blend thin films (Fig. S12) were examined by tapping mode of atomic force microscopy (OMV-NTSC, Bruker). The analyte copolymer neat films or copolymer:PCBM blend films were prepared by spin-coating on the ITO/ZnO/PEIE multi-layer modified substrates from a CF/DCB (1/1, v/v) mixed solution. The copolymer concentrations and spin-coating conditions were identical to those of the optimal active layers of PSCs (see Section S2.1).

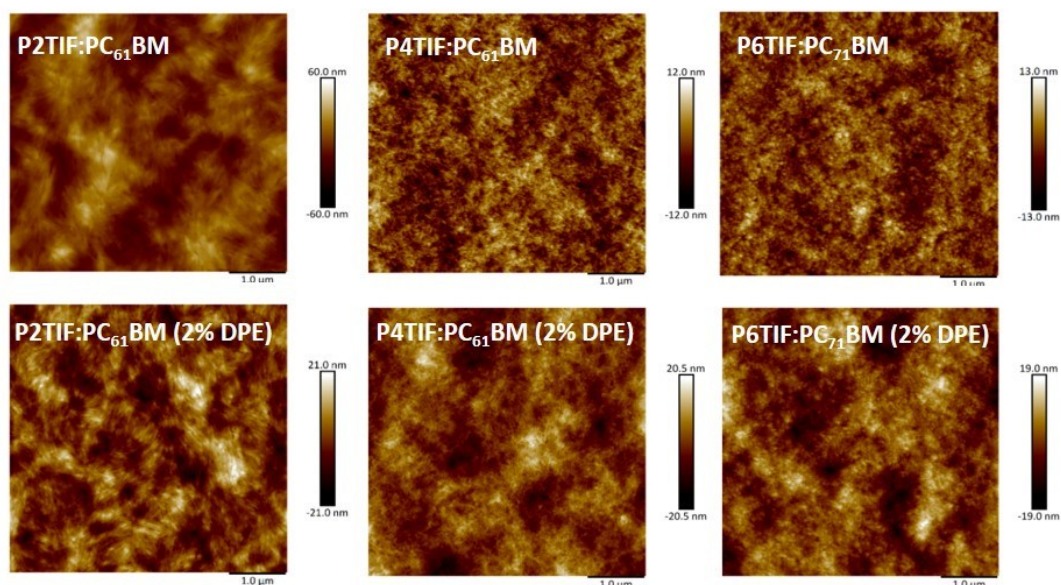


Fig. S12. AFM topography images of $P_nTIF:PCBM$ blend films. The scale bars are $1.0\ \mu\text{m}$. The root-mean-square (RMS) roughness values are 11.5, 2.86, and 2.75 nm for **P2TIF:PC₆₁BM**, **P4TIF:PC₆₁BM**, and **P6TIF:PC₇₁BM** blend films, respectively. For those blend films containing 2% DPE, the RMS roughness values are 5.68, 5.09, and 5.04 nm for **P2TIF:PC₆₁BM**, **P4TIF:PC₆₁BM**, and **P6TIF:PC₇₁BM**, respectively.

S4. Crystallinity and Crystallite Orientation

S4.1. Two-Dimension Grazing Incidence Wide-Angle X-ray Scattering (2D-GIWAXS)

Two-dimension grazing incidence wide-angle X-ray scattering (2-D GIWAXS) measurements were performed at the beamline 13A1 at National Synchrotron Radiation Research Center (NSRRC), Taiwan, R.O.C. For experiments about the active layer of PSCs were carried out at a X-ray photon energy of 12.043 keV and wavelength (λ) of 1.02962 Å. The sample-to-detector distance is 234.29 mm (Fig. 5 in text and Fig. S13 in ESI[†]); for experiments about the TFTs were carried out at a X-ray photon energy of 12.119 keV and wavelength (λ) of 1.02321 Å. The sample-to-detector distance is 238.78 mm (Fig. 6 in text). The sample-to-detector distance was calibrated by a silver behenate standard. The GIWAXS patterns were collected with

an exposure time of 1 sec on a CCD-detector (Mar165 CCD). The analyte copolymer neat films or copolymer:PCBM blend films were spin-coated on the ITO/ZnO/PEIE multi-layer modified substrates from the CF/DCB (1/1, v/v) mixed solution and the spin-coating conditions are identical to those of the optimized active layers of PSCs (see Section S2.1). For comparison, in some cases, a further investigation was conducted by using 2% DPE additive mixed to the sample solutions before spin-coating. For the study of TFTs, the pristine *PnTIF* copolymer films were spin-coated on octadecylsilane modified silicon wafer substrates and following thermal annealed according to the same condition of their optimal TFT device fabrications. (see section S5.2). The GIWAXS characteristics were consolidated in Table 4 in text.

S4.1.1 Calculation of Orientation Percentage and Crystallite Correlation Length

The percentage of the edge-on and face-on orientation of the copolymer crystallite of neat copolymer or PCBM blend films can be estimated by calculating the integral intensity of the (100) diffraction peak through the azimuthal angle scan (Figure 4f and 4g in text). The azimuthal angle in the range of $\chi = 0\sim 35^\circ$ (out-of-plane) is related to the edge-on orientation; in the range of $\chi = 45\sim 90^\circ$ (in-plane) is related to the face-on orientation.

The crystallite correlation length (*CCL*) was determined by the Scherrer equation:⁵

$$CCL = \frac{2\pi}{FWHM}$$

Taking the prominent (100) diffraction peak in out-of-plane GIWAXS profiles (Fig. 5d, Fig. 6d in text and Fig. S13d of ESI[†]), the $CCL_{(100)}$ of each thin film sample was estimated by fitting the diffraction peak with a Gaussian function.

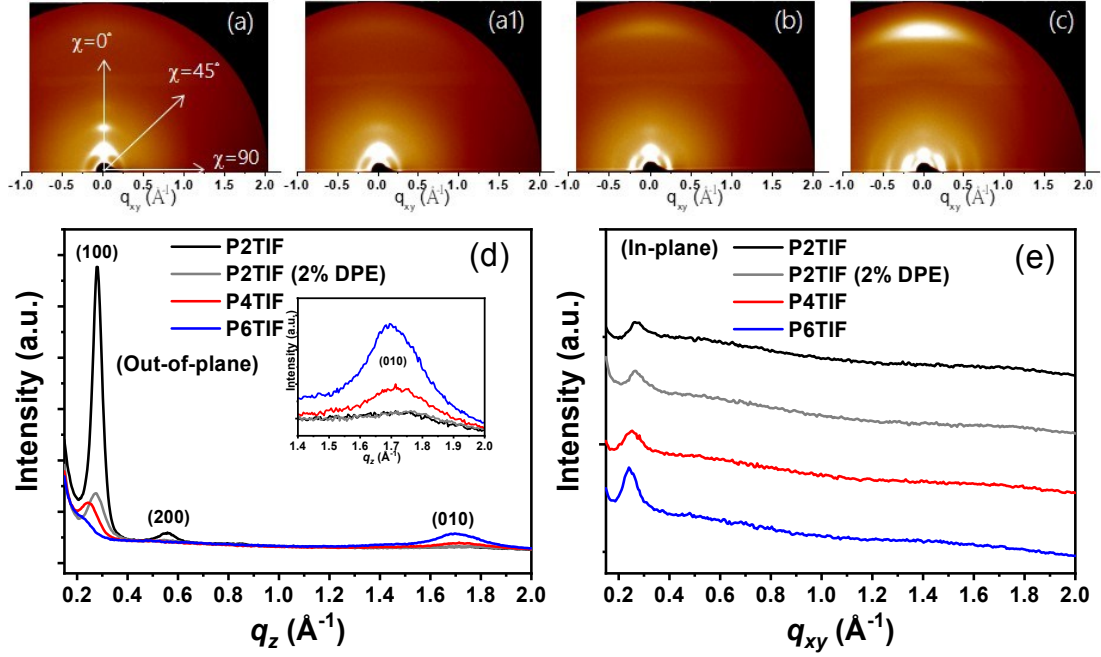


Fig. S13. 2D-GIWAXS patterns of pristine *PnTIF* polymer films: (a) **P2TIF**; (a1) **P2TIF** (with 2% DPE); (b) **P4TIF**; (c) **P6TIF**; the 2D-GIWAXS profiles of (d) out-of-plane integration ($\chi=0\sim45^\circ$) and (e) in-plane integration ($\chi=45\sim90^\circ$).

S5. Hole Mobility Measurements

S5.1. Space-Charge Limited Current (SCLC)

The hole-only devices were fabricated with a configuration of ITO/PEDOT:PSS (35 nm)/ *PnTIF*/Au (100 nm) and ITO/PEDOT:PSS (35 nm)/*PnTIF*:PCBM/Au (100 nm) for *PnTIF* copolymer neat films and *PnTIF*:PCBM blend films, respectively. The hole selecting layer was prepared from PEDOT:PSS (AI 4083) solution which was filtered through a 0.45 μm PVDF filter, spin-coated on ITO substrates at 4000 rpm for 30 s, and then annealed at 150 $^\circ\text{C}$ for 10 min. For preparing *PnTIF* copolymer neat films or *PnTIF*:PCBM blend films (1:1.5, w/w), the materials were dissolved in a CF/DCB mixed solvent (1/1, v/v) in suitable concentrations in order to form the thin films with similar thickness and without changing the spin-coating conditions used for the optimal PSCs. For **P2TIF**, the neat or blend films were prepared from the solutions added 2% DPE resembling to the optimal PSC. The thickness of copolymer

neat film are 115 nm, 125 nm, and 110 nm for **P2TIF**, **P4TIF**, and **P6TIF**, respectively. The thickness of the blend thin film are 145 nm, 145 nm, and 150 nm for **P2TIF:PC₆₁BM**, **P4TIF:PC₆₁BM**, and **P6TIF:PC₇₁BM**, respectively. Finally, Au was vacuum-thermal deposited on the active layers under a pressure of $\sim 10^{-6}$ Torr. The hole mobility was determined by using space-charge limited current (SCLC) method. The dark J - V characteristics of the hole-only devices were measured under ambient conditions using a Keithley 2400 source meter (Fig. S14). The mobility information was extracted by fitting the modified Mott-Gurney equation to the measured dark J - V curves in SCLC region:⁶

$$J = \frac{9}{8} \varepsilon_0 \varepsilon_r \mu \frac{V^2}{L^3} \exp\left(0.89\beta \frac{\sqrt{V}}{\sqrt{L}}\right)$$

Where J is the current density, ε_0 is the permittivity of free space (8.85×10^{-12} C V⁻¹ s⁻¹), ε_r is the relative permittivity constant of the active layer (generally assumed to be 3), μ is the hole mobility, V is the applied voltage, L is the thickness of active layer, and β is the field activation factor. The SCLC hole mobility ($\mu_{h,SCLC}$) data were summarized in Table S1.

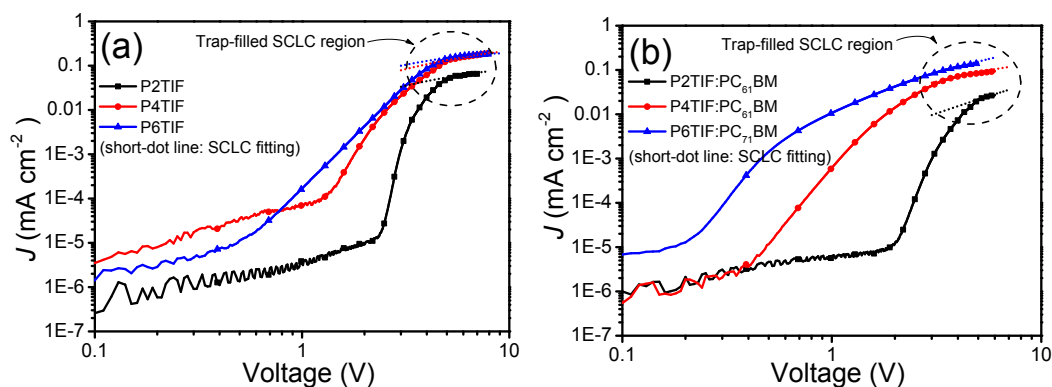


Fig. S14. The dark J - V curves and the fitting lines in SCLC region of (a) pure copolymer thin films; (b) copolymer:PCBM blended thin films.

S5.2. Thin Film Transistors (TFT)

The hole mobility of the *PnTIF* copolymers were further investigated by the thin

film transistor of each copolymer with the bottom-gate top-contact geometry. The highly doped n-type silicon with 300 nm thermally grown oxide was first modified by a single layer of octadecylsilane after cleaning. The copolymers were deposited on the substrates from the CF/DCB mixed solution (1:1, v/v) with a concentration of 1.5 mg mL⁻¹ by spin-coating at 400 rpm for 260 sec, then 800 rpm for 20 sec before thermal annealing (TA) in vacuum for 1 hour. The **P6TIF** thin film were subsequently thermal annealed at 210 °C in vacuum for 1 hour while the annealing process for **P2TIF** and **P4TIF** copolymers was performed at 240 °C to have optimal performance. Au source/drain electrodes of 100 nm thickness were then thermally evaporated on the top of copolymer films through shadow masks. A precision source/measurement unit (Keysight, B2912A) and a probe station were used to measure the electrical properties of the *PnTIF* TFTs under ambient environment (Fig. S15). The mobility (μ) was extracted from the saturation region and calculated by the formula:

$$\mu_{sat} = \frac{\left(\frac{d\sqrt{I_{SD}}}{dV_{SG}}\right)^2}{\frac{1}{2}C_i \frac{W}{L}}$$

where I_{SD} is the source-drain current; V_{SG} is the source-gate voltage; W and L are the channel width (100 μ m) and length (1 mm) and C_i is the dielectric constant of SiO₂ (10⁻⁴ F m⁻²). The TFT performances were also summarized in Table S1.

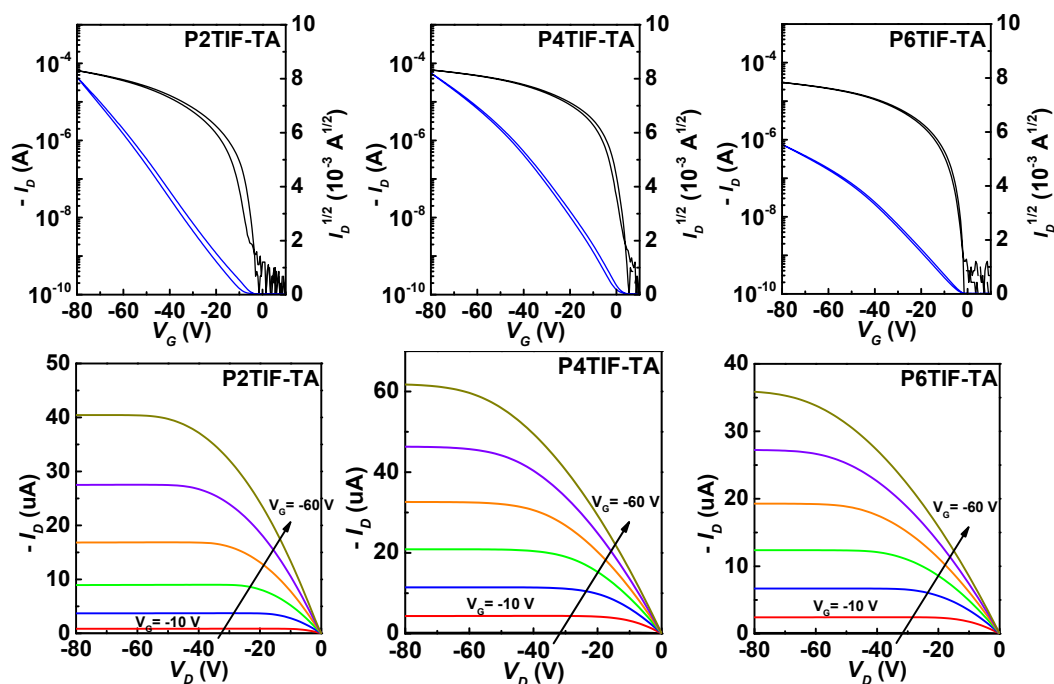


Fig. S15. Transfer (up) and out-put characteristics (down) of *PnTIF* transistors at $V_{DS} = -20$ V ($L = 100$ μm and $W = 1.0$ mm) after thermal annealing (TA) under vacuum.

Table S1. Hole mobilities and the performance of TFT devices.

a) Copolymer neat films were fabricated as hole-only and TFT devices; b) The hole-

Devices ^{a)}	$\mu_{h,SCLC}$ [$\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$]	$\mu_{h,TFT}$ [$\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$]	On/Off	V_T [V]	Devices ^{c)}	$\mu_{h,s}$ [$\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$]
P2TIF ^{b)}	1.18×10^{-4b}	2.5×10^{-1}	$>10^5$	-8.0	P2TIF:PC₆₁BM (2% DPE)	2.24×10^{-5}
P4TIF	3.14×10^{-4}	4.0×10^{-1}	$>10^5$	-4.8	P4TIF:PC₆₁BM	3.08×10^{-4}
P6TIF	4.15×10^{-4}	1.8×10^{-1}	$>10^5$	-0.6	P6TIF:PC₇₁BM	3.56×10^{-4}

only device of neat **P2TIF** for SCLC was fabricated including 2% DPE solvent additive; c) *PnTIF*:PCBM blend films were only fabricated as hole-only devices for SCLC measurements

S6. References

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