Increasing fluorine substituent of thieno[3,4-c]pyrrole-4,6-dione (TPD) terthiophene copolymers progressively narrows the nano-fibrils and enhances the efficiency of fullerene-based polymer photovoltaics

Adane Desta Fenta, a,b,c Song-Fu Liao, a Syuan-Wei Li, a Chun-Fu Lu d and Chin-Ti Chen a

a Institute of Chemistry, Academia Sinica, Taipei 11529, Taiwan, ROC
b Molecular Science and Technology, Taiwan International Graduate Program (TIGP), Taipei, 10617, Taiwan, ROC
c Department of Chemistry, National Tsing Hua University, Hsinchu, 30013, Taiwan, ROC
d Department of Materials Science and Engineering, National Taiwan University, Taipei 10617, Taiwan, ROC

*E-mail: chintchen@gate.sinica.edu.tw

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S1. General Experimental Details

Instrumentation: The \textsuperscript{1}H and \textsuperscript{13}C NMR spectra were taken on a Bruker AV III-400 (400 MHz
and 100 MHz) spectrometer equipped with BBFO probe head, using the residual solvent resonance
of CDCl\textsubscript{3} at ambient temperature. Matrix-assisted laser desorption/ionization high resolution mass
spectrometry (MALDI HRMS) was determined on a Bruker New ultrafleXtreme™ instrument by Mass Spectroscopic Laboratory in-house service of the Institute of Chemistry, Academia Sinica. UV-visible absorption spectra were obtained on a Hewlett Packard 8453 diode-array spectrophotometer. The solution absorption spectra of copolymers were recorded on chloroform solutions, and the film optical absorption spectra were recorded from films cast from 10 mg/mL chloroform solutions. Elemental analysis was carried out on an Elementar Vario EL Cube elemental analyzer at laboratory of the Precision Instrumentation Center, National Taiwan University. Gel permeation chromatography (GPC) analysis of copolymers was performed on Waters 1515 chromatography unit equipped with a Waters 2414 refractive index detector, in which polystyrene was used as a calibration standards and chloroform as the eluent at 50 °C. Thermogravimetric analysis (TGA) measurements were taken on a Perkin Elmer Pyris 1 thermogravimetric analyzer. The samples (weight 2.0 mg) were heated with a rate of 10 °C/min under nitrogen in the temperature up to 900 °C. Differential scanning calorimetry (DSC) was obtained using a Perkin Elmer Pyris 6 DSC analyzer at a heating/cooling rate of 10/-10 °C/min under a nitrogen flow in the temperatures up to 400 °C. Cyclic voltammetry (CV) measurements were performed by using CH Instruments CHI620A electrochemical analyzer in a three-electrode cell in anhydrous acetonitrile solvents solution of tetrabutyl ammonium hexafluorophosphate (TBAPF6) with a scan rate of 100 mV/s at room temperature under nitrogen. The polymer solution (5 mg/ml, chloroform) was drop-cast on a glassy carbon electrode and used as the working electrode. The potential of Ag/Ag⁺ reference electrode was calibrated by using ferrocene/ferrocenium (Fc/Fc⁺) as the redox couple. Then, the energy levels of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) were calculated by employing the following equations:
\[
HOMO (eV) = - (E_{onset}^{\text{ox}} \text{ v.s. } \text{ferrocene} + 4.8),
\]
\[
LUMO (eV) = -(E_{onset}^{\text{red}} \text{ v.s. } \text{ferrocene} + 4.8)
\]

Where \(E_{onset}^{\text{ox}}\) is the onset of oxidation potential and \(E_{onset}^{\text{red}}\) is the onset of reduction potential. Density functional theory (DFT) calculations were carried out using B3LYP/6-31G* (d, p) basis set with Gaussian 09 package. To shorten the computational times, an A-D-A-D dimer model was used. The model has an isobutyl-substituted TPD unit and an ethyl group to replace the dodecyl side-chain of the thiophene ring.

**Materials:** All chemicals were purchased from commercial sources (Sigma-Aldrich, Alfa Aesar, Merck, ADS, etc) and were used without further purification, unless specified otherwise. Solvents were dried and purified using standard techniques. All reactions were carried out under an atmosphere of nitrogen.

**S2. Synthesis of Monomer and Copolymers**

**Synthesis of 5-(2-decyltetradecyl)-1,3-bis(3-dodecylthiophen-2-yl)-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione (4)**

A solution of compound 3 (2.00 g, 3.09 mmol) and (3-dodecylthiophen-2-yl)trimethylstannane (2.95 g, 7.10 mmol, 2.3 eq) in 30 mL dry THF was degassed with nitrogen for 40 minutes, and then \(\text{PdCl}_2(\text{PPh}_3)_2\) (0.22 g, 0.31 mmol, 0.1 eq) was added. The reaction mixture was then heated at 70 °C for 24 h. After cooling to room temperature, the solvent was removed by evaporation.
under reduced pressure to afford a yellowish oil, which was later purified by column chromatography over silica gel with DCM/hexane (1:3) as eluent to yield a yellow solid as the product (2.25 g, 73.5% yield). \( ^1\)H NMR (400 MHz, CDCl\(_3\), \( \delta \)): 7.40 (d, \( J = 5.2 \) Hz, 2H), 7.01 (d, \( J = 5.2 \) Hz, 2H), 3.51 (d, \( J = 7.2 \) Hz, 2H), 2.79 (t, \( J = 8.2 \) Hz, 4H), 1.83 (m, 1H), 1.61 (m, 4H), 1.25 (m, 76H), 0.88 (m, 12H). \( ^{13}\)C NMR (100 MHz, CDCl\(_3\), \( \delta \)): 162.10, 145.14, 137.15, 130.54, 130.04, 127.84, 124.68, 37.63, 32.95, 30.45, 29.72, 29.68, 29.55, 29.42, 29.39, 29.24, 28.52, 26.81, 22.60, 14.11; MALDI-HRMS [M+H]\(^+\), for C\(_{62}\)H\(_{103}\)NO\(_2\)S\(_3\): m/z calcd. 989.7151; found: 989.7214. Anal. calcd. for C\(_{62}\)H\(_{103}\)NO\(_2\)S\(_3\) (%): C, 75.17; H, 10.48; N, 1.41; S, 9.71 Found (%): C, 75.06; H, 10.62; N, 1.35.

**Synthesis of 1,3-bis(5-bromo-3-dodecylthiophen-2-yl)-5-(2-decyltetradecyl)-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione (M1)**

N-Bromosuccinimide (0.79 g, 4.45 mmol, 2.1 eq) was added to a solution of 4 (2.1 g, 2.12 mmol, 1 eq) in chloroform/acetic acid (10:1, total amount = 50 mL) at room temperature, purged with nitrogen. The reaction mixture was stirred for 16 h. The reaction mixture was then poured into water, the combined organic layer was extracted with chloroform and dried over MgSO\(_4\). After removal of the solvent by rotary evaporation, the crude product was purified by column chromatography over silica gel with DCM/hexane (1:4) as eluent, affording a yellow solid of monomer M1 (2.14 g, 88% yield). \( ^1\)H NMR (400 MHz, CDCl\(_3\), \( \delta \)): 6.97 (s, 2H), 3.50 (d, \( J = 4.0 \) Hz, 2H), 2.73 (t, \( J = 16 \) Hz, 4H), 1.83 (m, 1H), 1.61 (m, 4H), 1.24 (m, 76H), 0.88 (m, 12H). \( ^{13}\)C NMR (100 MHz, CDCl\(_3\), \( \delta \)): 162.07, 144.93, 135.43, 132.59, 130.77, 126.32, 115.42, 38.57, 31.92,
MALDI-HRMS [M+H]+, for C_{62}H_{101}Br_{2}NO_{2}S_{3}: m/z calcd. 1147.5341; found: 1146.5439. Anal. calcd. for C_{62}H_{101}Br_{2}NO_{2}S_{3} (%): C, 64.84; H, 8.86; N, 1.22; S, 8.37. Found (%): C, 63.86; H, 8.83; N, 1.16.

**Synthesis of PHT**

![Reaction Scheme](image)

In a 10 mL two-necked round bottom flask monomer M1 (200.0 mg, 0.17 mmol), monomer M2 (71.01 mg, 0.17 mmol), and P(o-tol)_3 (21.20 mg, 0.069 mmol) were dissolved into 5.5 mL dry chlorobenzene under nitrogen. The mixture was then degassed by three freeze-pump-thaw cycles, and further purged with nitrogen for 15 minutes at room temperature. Then, under intense flushing of nitrogen, Pd_2(dba)_3 (7.97 mg, 0.0087 mmol) was added in one portion. The flask was put into an oil bath and heated at 100 °C for 24 h under nitrogen. With the aid of a syringe, 0.5 ml of bromobenzene was then added to the reaction mixture as an end-capping for the copolymer chains and the reaction was allowed to progress for another 12 h. After cooling to room temperature, the polymer mixture was precipitated in 150 mL methanol, filtrated over a Soxhlet thimble. The crude polymer was subjected to Soxhlet extraction sequentially using methanol (6 h), acetone (8 h), hexane (12 h) and dichloromethane (12 h) to remove oligomers and catalyst residue. Finally, the desired copolymer was extracted with chloroform, re-precipitated in 150 ml methanol, filtered out and dried in vacuum to afford the polymer PHT as a purple solid (176 mg, 94.3 %). GPC (CF, 50 °C): $M_n = 48.7$ kDa, $M_w = 81.7$ kDa, and PDI = 1.67. $^1$H NMR (400 MHz, CDCl_3, δ): 7.18 (s, 2H), 7.10 (s, 2H), 3.55 (br, 2H), 2.82 (m, 4H), 1.89 (br, 1H), 1.70 (br, 4H), 1.25 (m, 76H), 0.87 (m, 76H).
Anal. calcd. for \((\text{C}_{66}\text{H}_{101}\text{NO}_2\text{S}_4)_n\) (%): C, 74.03; H, 9.70; N, 1.31; S, 11.98. Found (%): C, 73.52; H, 10.14; N, 1.24.

**Synthesis of PFT**

The synthetic procedure and purification method for PFT is similar to those of PHT as stated above. Hence, here monomer M1 (200.0 mg, 0.17 mmol), monomer M3 (77.62 mg, 0.17 mmol), P(\(\text{O-tol}\))\(_3\) (21.20 mg, 0.069 mmol), Pd\(_2\)(dba)\(_3\) (7.97 mg, 0.0087 mmol), and 5.8 ml chlorobenzene were engaged in the reaction. After final extraction of crude copolymer by using chloroform in the Soxhlet extraction, PFT was obtained as a dark purple solid (180 mg, 93.7 %). GPC (CF, 50 °C): \(M_n = 46.8 \text{kDa}, M_w = 84.2 \text{kDa}, \text{and PDI} = 1.80\). \(^1\)H NMR (400 MHz, CDCl\(_3\), \(\delta\)): 7.20 (s, 2H), 3.54 (br, 2H), 2.82 (br, 4H), 1.86 (br, 1H), 1.69 (br, 4H), 1.24 (br, 76H), 0.86 (br, 12H). Anal. calcd. for \((\text{C}_{66}\text{H}_{101}\text{F}_2\text{NO}_2\text{S}_4)_n\) (%): C, 71.62; H, 9.20; N, 1.27; S, 11.59. Found (%): C, 71.43; H, 9.65; N, 1.19.

**Synthesis of P1F3HT, P1F1HT and P3F1HT**

The synthesis of the random copolymers (P1F3HT, P1F1HT and P3F1HT) were carried out by using a similar procedure as that of PFT and PHT copolymers mentioned above. But now for
**P1F3HT**, monomer M1 (200.0 mg, 0.17 mmol), monomer M2 (53.52 mg, 0.13 mmol), and monomer M3 (19.41 mg, 0.044 mmol); for **P1F1HT**, monomer M1 (200.0 mg, 0.17 mmol), monomer M2 (35.61 mg, 0.087 mmol) and monomer M3 (38.81 mg, 0.13 mmol); for **P3F1HT**, monomer M1 (200.0 mg, 0.17 mmol), monomer M2 (17.84 mg, 0.044 mmol), and monomer M3 (58.22 mg, 0.13 mmol) were used accordingly. The final products were obtained as a dark purple solid.

**P1F3HT**: $M_n = 37.9$ kDa, $M_w = 75.0$ kDa, and $D = 1.98$; yield (166 mg, 88.2%). Anal. calcd. (%): C, 73.41; H, 9.57; N, 1.30; S, 11.88. Found (%): C, 73.39; H, 10.10; N, 1.22.

**P1F1HT**: $M_n = 38.1$ kDa, $M_w = 70.9$ kDa, and $D = 1.86$; yield (172 mg, 90.7%). Anal. calcd. (%): C, 72.81; H, 9.44; N, 1.29; S, 11.78. Found (%): C, 72.76; H, 9.94; N, 1.23.

**P3F1HT**: $M_n = 38.7$ kDa, $M_w = 68.12$ kDa, and $D = 1.76$; yield (170 mg, 88.9%). Anal. calcd. (%): C, 72.21; H, 9.32; N, 1.28; S, 11.68. Found (%): C, 72.13; H, 9.86; N, 1.21.

![Figure S1. GPC chromatogram of PFT copolymer.](image)
**Figure S2.** GPC chromatogram of P1F1HT copolymer.

**Figure S3.** GPC chromatogram of PHT copolymer.
Figure S4 (a) TGA thermograms of the copolymers. (b) DSC thermograms of PFT, P1F1HT, and PHT.

Figure S5. Cyclic voltammograms of the copolymer thin films cast on glassy carbon electrode: (a) oxidation, (b) reduction.
Figure S6. DFT-computed electron density distribution of HOMOs and LUMOs for PHT, PFT, P1F1HT (fluorine substituted thiophene residing between two TPD moieties) and P1H1FT (fluorine substituted thiophene residing next to TPD moiety) dimers, and the corresponding chemical structures.
Figure S7. Low energy photo-electron spectroscopy (AC-2) results of PHT, P1F1HT, and PFT copolymers.

Figure S8. Temperature dependence UV-visible absorption spectra of PFT (a), P1T1HF (b), and PHT (c) in chlorobenzene at room temperature (r.t) to 130 °C, 100 °C and 80 °C, respectively. Figure (d) illustrates the color changing of the copolymer chlorobenzene solutions, PHT, P1T1HF, PFT (from left to right in each picture), from room temperature (picture at far left) to 130 °C (picture at far right).

Table S1. Absorption wavelengths of the copolymers in chloroform solution and thin film state

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$\lambda_{\text{soln}}^\text{max}$ (nm)</th>
<th>$\lambda_{\text{film}}^\text{max}$ (nm)</th>
<th>$\lambda_0-2$ (nm)</th>
<th>$\lambda_0-1$ (nm)</th>
<th>$\lambda_0-0$ (nm)</th>
<th>$E_g^{\text{opt}}$ (eV)$^a$</th>
<th>$E_{\text{HOMO}}$, $E_{\text{LUMO}}$ (eV)$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PHT</td>
<td>503</td>
<td>582</td>
<td>~503</td>
<td>~575</td>
<td>~627</td>
<td>1.76</td>
<td>-4.87, -2.64</td>
</tr>
<tr>
<td>P1F3HT</td>
<td>575</td>
<td>578</td>
<td>~503</td>
<td>575</td>
<td>~623</td>
<td>1.79</td>
<td>-2.23</td>
</tr>
</tbody>
</table>

$^a$ Optical band gap

$^b$ DFT calculated HOMO and LUMO levels
<table>
<thead>
<tr>
<th></th>
<th>576</th>
<th>575</th>
<th>~503</th>
<th>576</th>
<th>~617</th>
<th>~542</th>
<th>575</th>
<th>619</th>
<th>1.80</th>
<th>-4.95, -2.67</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1F1HT</td>
<td>576</td>
<td>573</td>
<td>~503</td>
<td>576</td>
<td>~619</td>
<td>~539</td>
<td>573</td>
<td>617</td>
<td>1.81</td>
<td>-</td>
</tr>
<tr>
<td>P3F1HT</td>
<td>576</td>
<td>567</td>
<td>~503</td>
<td>576</td>
<td>623</td>
<td>~535</td>
<td>567</td>
<td>614</td>
<td>1.83</td>
<td>-5.10, -2.71</td>
</tr>
<tr>
<td>PFT</td>
<td>576</td>
<td>575</td>
<td>~503</td>
<td>576</td>
<td>619</td>
<td>~542</td>
<td>575</td>
<td>619</td>
<td>1.80</td>
<td>-4.95, -2.67</td>
</tr>
</tbody>
</table>

*Optical energy gap from UV-visible absorption spectroscopy ($E_{\text{opt}}^g$). HOMO and LUMO energy levels ($E_{\text{HOMO}}$ and $E_{\text{LUMO}}$) and energy gap ($E_{\text{DFT}}^g$) obtained from DFT calculation.

### S3. Solar Cell Device Fabrication and Measurement

The copolymer solar cells were fabricated as an inverted structure of ITO/ZnO/copolymers:PC_{61}BM/MoO_{3}/Ag. The indium doped tin oxide (ITO) coated glass substrates were cleaned sequentially by ultra-sonication in detergent, deionized water, acetone, and isopropyl alcohol each for 15 minutes. The substrates were then dried with pressurized nitrogen and baked at 100 °C before being exposed to a UV−ozone plasma for 15 min. A sol-gel-derived ZnO, zinc acetate dihydrate (0.5 g) dissolved in a mixed solvent of monoethanolamine (0.14 mL) and 2-methoxyethanol (5 mL), interfacial layer was prepared by spin-coating the above mentioned solution at 4000 rpm onto the pre-cleaned ITO substrate followed by a thermal treatment at 200°C for 1 h. Subsequently, the ZnO-coated ITO substrates were transferred into a nitrogen-filled glove box. Then the blended solution, copolymer: PC_{61}BM (1:2, wt/wt) dissolved in chloroform containing 2 vol. % of diphenyl ether (DPE) as the processing solvent additive, was stirred at 60 °C for 2 h, spin-coated at 1200 rpm for 30 s to form the active layer. Finally, under base pressure of ~10^{-6} Torr, a 8 nm of MoO_{3} film and a 100 nm of Ag were deposited sequentially on top of active layer to complete the inverted device structure. The active areas of devices are 4.00 mm², which was defined by the metal mask for MoO_{3} and Ag.

The current density-voltage ($J−V$) characteristics of PSCs were measured using a Keithley 2400 Source Measure Unit under 100 mW cm⁻² simulated 1.5 Global (AM 1.5 G) solar simulator (Newport 91160A 300 W). The light intensity was calibrated by a standard Si solar cell (SRC-
2020, Enli Technology Co., Ltd). Nation Renewable Energy Laboratory (NREL)-certified monocrystalline Si photodiode (PVM 172; area= 3.981 cm\(^2\)) was used to calibrate the light intensity. External quantum efficiency (EQE) measurements were carried out under the ambient condition with the as-fabricated PSCs by illuminating incident light from a Xe lamp (300 W) passing through a monochromator (Jobin Yvon Horiba TRIAX 190) focused on the active area of the cell. In addition, the film thickness of the active layers was determined by a Veeco Dektak-150 surface profilometer.

### Table S2. Effect of active layer thickness on performance of PHT and PFT based devices.

<table>
<thead>
<tr>
<th>Devices</th>
<th>Thickness (nm)</th>
<th>(V_{OC}) (V)</th>
<th>(J_{SC}) (mA cm(^{-2}))</th>
<th>FF (%)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PHT:PC(_{61})BM</td>
<td>340</td>
<td>0.78</td>
<td>13.18</td>
<td>63.42</td>
<td>6.52</td>
</tr>
<tr>
<td>PHT:PC(_{61})BM</td>
<td>300</td>
<td>0.79</td>
<td>13.15</td>
<td>66.80</td>
<td>6.94</td>
</tr>
<tr>
<td>PHT:PC(_{61})BM</td>
<td>260</td>
<td>0.80</td>
<td>12.81</td>
<td>67.54</td>
<td>6.92</td>
</tr>
<tr>
<td>PHT:PC(_{61})BM</td>
<td>220</td>
<td>0.80</td>
<td>12.32</td>
<td>68.92</td>
<td>6.79</td>
</tr>
<tr>
<td>PHT:PC(_{61})BM</td>
<td>180</td>
<td>0.80</td>
<td>11.32</td>
<td>71.06</td>
<td>6.43</td>
</tr>
<tr>
<td>PHT:PC(_{61})BM</td>
<td>350</td>
<td>0.93</td>
<td>16.51</td>
<td>58.13</td>
<td>8.92</td>
</tr>
<tr>
<td>PFT:PC(_{61})BM</td>
<td>300</td>
<td>0.94</td>
<td>15.85</td>
<td>64.07</td>
<td>9.54</td>
</tr>
<tr>
<td>PFT:PC(_{61})BM</td>
<td>250</td>
<td>0.94</td>
<td>15.10</td>
<td>66.23</td>
<td>9.40</td>
</tr>
<tr>
<td>PFT:PC(_{61})BM</td>
<td>200</td>
<td>0.95</td>
<td>14.07</td>
<td>68.36</td>
<td>9.15</td>
</tr>
<tr>
<td>PFT:PC(_{61})BM</td>
<td>150</td>
<td>0.95</td>
<td>12.25</td>
<td>72.47</td>
<td>8.43</td>
</tr>
</tbody>
</table>

*All devices were fabricated with 2% DPE as the processing solvent additive.*

### S4. SCLC measurements

The hole mobility profiles of all devices were determined by using a method called space-charge limited current (SCLC). The hole-only devices were fabricated in the structure of glass/ITO/PEDOT:PSS/active layer/Au. Where, glass/ITO substrates were cleaned following the same procedure of those in PSCs fabrication. Subsequently, a PEDOT:PSS (Al 4083) solution (filtered through a 0.45 μm PVDF filter) was spin-coated on top of ITO substrates at 4000 rpm for 30 s, and then annealed at 150 °C for 10 min. Solutions of copolymer:PC\(_{61}\)BM (1:2, w/w) with or without 2% DPE (v/v) processing solvent additive in chloroform (same blending ratio as the
optimized OPV devices and in suitable concentrations to form the thin films with approximately similar thickness) were prepared and spin coated-coated in nitrogen-filled glove box. Like those thin films (active layers) of PSCs, the thin film samples prepared for SCLC measurements were not subjected to any thermal treatment. The thickness of SCLC thin films (with 2% DPE) were determined to be about 140, 140, 140, 145, and 150 nm, for PHT:PC$_{61}$BM, P1F3HT:PC$_{61}$BM, P1F1HT:PC$_{61}$BM, P3F1HT:PC$_{61}$BM, and PFT:PC$_{61}$BM, respectively. In the end, Au layer was thermally evaporated at low pressures of about $10^{-6}$ Torr. A Keithley 2400 source meter was employed to obtain the dark $J–V$ characteristics of the devices under ambient conditions. The mobility data was then extracted by fitting the $J–V$ curves in the space-charge limited region with the modified Mott-Gurney equation given below.

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

Where $\varepsilon_0$ is the permittivity of vacuum, $\varepsilon_r$ is the relative permittivity constant of the active layer, $\mu$ is mobility of charge carriers, $V$ is the applied voltage, $\beta$ is the field activation factor, and $L$ is the thickness of active layer.

Figure S9. Representative dark $J–V$ characteristics of a hole-only device fabricated for copolymer: PC$_{61}$BM with 2% DPE processing solvent additive.

S5. Morphological characterization
**2D-GIWAXS:** Grazing incidence wide-angle X-ray scattering (GIWAXS) samples were prepared on 1.8 cm × 2.8 cm (same size as those of PSCs) glass/ITO/ZnO substrates. Both copolymer neat film (10 mg/mL) or PC61BM-blended copolymer thin films (at optimized device conditions) were spin-coated on top of ZnO and stored in a nitrogen-filled glove box to remove any residual solvents before measurement. Afterwards, GIWAXS thin film measurements were performed at the National Synchrotron Radiation Research Center (NSRRC) at Hsinchu, Taiwan, using beamline BL13A1 in a helium filled chamber with photon energy of 12.06 KeV and wavelength of $\lambda = 1.02393 \text{ Å}$. 2-Dimensional patterns (signals) were gathered with an exposure time of 3 seconds on a CCD-detector (MAR345CCD), where the sample to detector distance was set to 232.57 mm and the incident angle was adjusted to be 0.1°.

**AFM:** Tapping mode of atomic force microscopy (Brucker OMV-NTSC) was used to examine the surface morphology of both copolymer neat films and PC61BM-blended thin films. Sample solutions were spin-coated on top of 1.8 cm × 2.8 cm (same size as those of PSCs) glass/ITO/ZnO substrates at conditions identical to those of the optimal PSCs. The measurements were performed in ambient condition with a vibration isolation system. Height and phase images were recorded simultaneously.

**TEM:** For transmission electron microscopy (TEM) measurements, samples were prepared by spin-coating of PC61BM-mixed copolymer solution on top of poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS)-coated ITO glass substrates at 2400 rpm for 30 s. Afterwards, films were stored in nitrogen-filled glove box for 16 h to remove any residual solvents before measurements. Then the substrates were immersed in deionized water and the peeled-off films were subsequently transferred to a copper grid followed by vacuum drying for 16 h before TEM imaging. The bright-field TEM images were acquired by FEI Tecnai G2 TF20 Super-TWIN
microscope, operating at 120 KV at the Institute of Cellular and Organismic Biology, Academia Sinica.

**Figure S10.** 2D GIWAXS patterns of PC_{61}BM-blended copolymer thin films without 2% DPE processing solvent additive: (a) PHT, (b) P1F1HT, (c) PFT. The GIWAXS profiles of (d) out-of-plane direction (integration area $\chi = 0-45^0$) and (e) in-plane direction (integration area $\chi = 45-90^0$). Figure (f) is the azimuthal angle scans of lamellar (100) diffraction.

**Figure S11.** AFM height images of PC_{61}BM-blended copolymer thin films (without 2% DPE): (a) PHT: PC_{61}BM (b) P1F3HT:PC_{61}BM, (c) P1F1HT:PC_{61}BM, (d) P3F1HT:PC_{61}BM and (e) PFT:PC_{61}BM.
Figure S12. TEM images of PC_{61}BM-blended copolymer thin films of P1F3HT and P3F1HT with (bottom row) and without (top row) 2% DPE processing solvent additive. (all scale bars are 100 nm, × 15,000)

Figure S13. TEM images of PC_{61}BM-blended copolymer thin films with (bottom row) and without (top row) 2% DPE processing solvent additive. (all scale bars are 200 nm, × 10,000).