# Electronic Supplementary Information

## Naphthodithieno [3, 2-b] thiophene-based Copolymer as a Novel Third Component in Ternary Polymer Solar Cells with Simultaneously Enhanced Open Circuit Voltage, Short Circuit Current and Fill Factor

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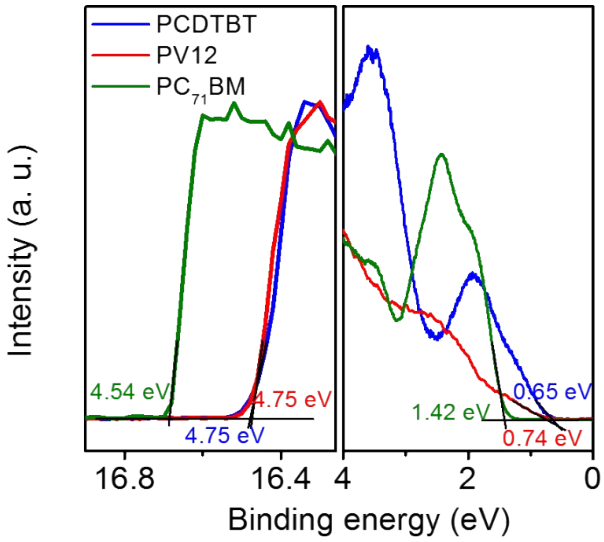
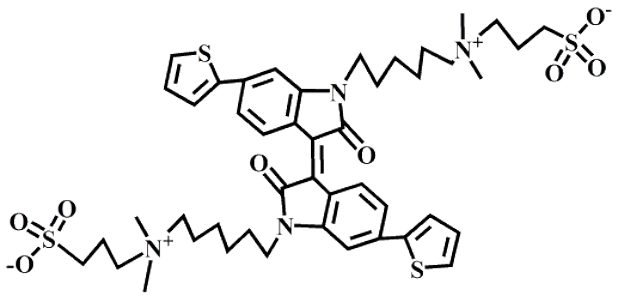



**Fig. S1.** Ultraviolet photoelectron spectra of PCDTBT, PV12 and $PC_{71}BM$ films on ITO in the secondary electron cutoff region (left) and valence band region (right). HOMO versus vacuum level of PCDTBT is 5.40 eV PV12 is 5.49eV and $PC_{71}BM$ is 5.96 eV.

**Equation S1** $E_{HOMO} = E_{LUMO} - E_g^{opt}$

**Table S1.** Energy parameters of PCDTBT, PV12 and $PC_{71}BM$ derived from UPS spectra (Figure S1) and UV-vis absorption spectra (Figure 1).

| | $E_{cut\text{-}off}$(eV) | $E_{onset}$(eV) | HOMO(eV) | LUMO(eV) | Eg(eV) |
|---|---|---|---|---|---|
| PV12 | 16.47 | 0.74 | 5.49 | 3.90 | 1.59 |
| PCDTBT | 16.47 | 0.65 | 5.40 | 3.55 | 1.85 |
| $PC_{71}BM$ | 16.68 | 1.42 | 5.96 | 4.26 | 1.7 |



**Scheme. S1.** The chemical structure of IIDTh-NSB.

**Table S2.** *J*ph–*V*eff curves of all the corresponding solar cells.

| wt % | *J*ph,sc/*J*ph,sat | *J*ph,max/*J*ph,sat |
|---|---|---|
| 0 | 91.7% | 73.5% |
| 10 | 94.4% | 78.6% |
| 15 | 96.6% | 80.5% |
| 20 | 96.5% | 77.5% |
| 30 | 94.6% | 74.1% |
| 100 | 86.5% | 59.0% |

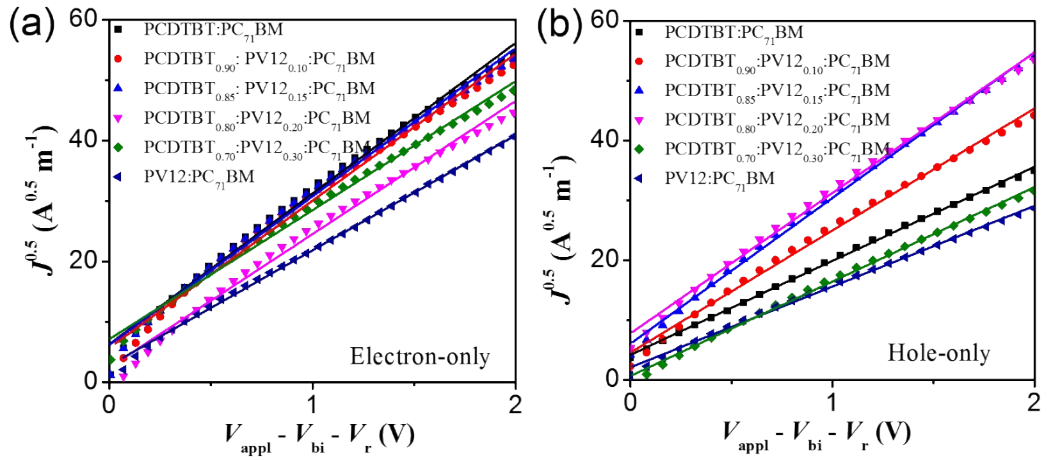



**Fig. S2.** The $J^{0.5}$ versus $V_{appl}$-$V_{bi}$-$V_r$ plots for (a) electron-only Al/LiF/active layer/LiF/Al and (b) hole-only ITO/PEDOT:PSS/active layers/$MoO_3$/Ag devices with different PV12 doping ratios in donors.

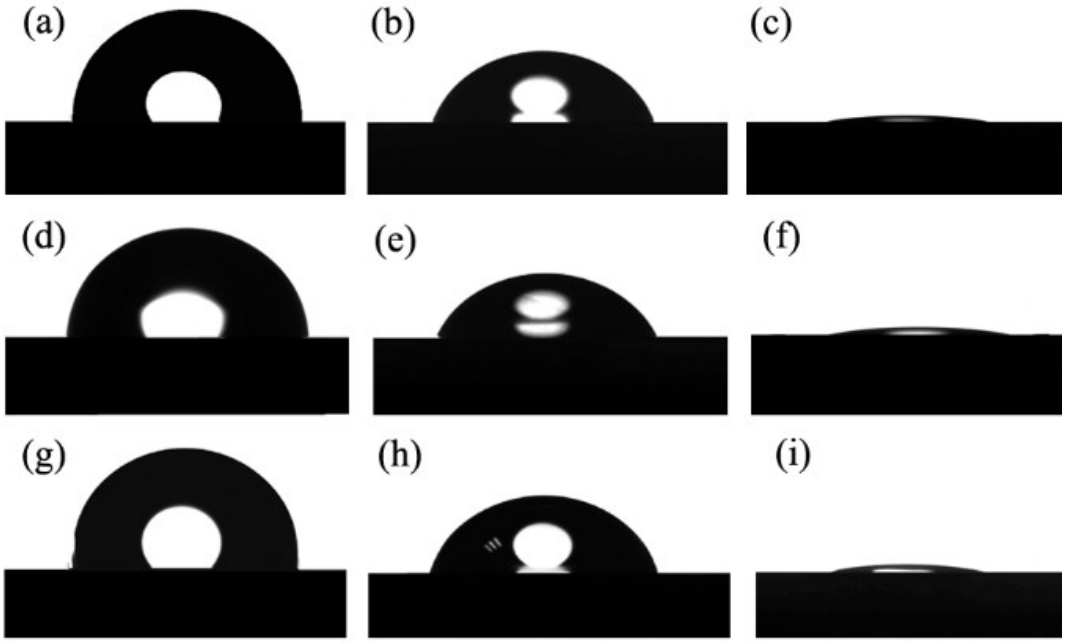



**Fig. S3.** Contact angle measurements. Photos of water droplets on the surfaces of (a) PCDTBT film; (d) $PC_{71}BM$ film; (g) PV12 film. Photos of ethylene glycol droplets on the surfaces of (b) PCDTBT film; (c) $PC_{71}BM$ film; (d) PV12 film. Photos of Hexadecane liquid droplets of (c) PCDTBT film; (i) $PC_{71}BM$ film; (f) PV12 film.

**Calculation of Surface Energy:** The surface energies of different films were calculated based on the results of the contact angle measurement and equation from the "three-liquid procedure" developed by van Oss et al. was used. Water and ethylene glycol were selected as the polar pair, whereas the hexadecane was used in terms of the apolar

liquid. Surface energy parameters are shown in Table S3.

$$\gamma_{LV1}(1+\cos\theta_1) = 2(\sqrt{\gamma_s^{LW}\gamma_{lv1}^{LW}} + \sqrt{\gamma_s^{+}\gamma_{lv1}^{-}} + \sqrt{\gamma_s^{-}\gamma_{lv1}^{+}})$$

$$\gamma_{LV2}(1+\cos\theta_2) = 2(\sqrt{\gamma_s^{LW}\gamma_{lv2}^{LW}} + \sqrt{\gamma_s^{+}\gamma_{lv2}^{-}} + \sqrt{\gamma_s^{-}\gamma_{lv2}^{+}})$$

$$\gamma_{LV3}(1+\cos\theta_3) = 2(\sqrt{\gamma_s^{LW}\gamma_{lv3}^{LW}} + \sqrt{\gamma_s^{+}\gamma_{lv3}^{-}} + \sqrt{\gamma_s^{-}\gamma_{lv3}^{+}})$$

$$\gamma = \gamma^{LW} + \gamma^{AB}$$

$$\gamma_i^{AB} = 2\sqrt{\gamma_i^{+}\gamma_i^{-}}$$

Here, γ is the surface energy, $\gamma^{LW}$ refers to the Lifshitz-van der Waals interaction and $\gamma^{AB}$ refers to the acid-base interaction. $\gamma^{+}$ and $\gamma^{-}$ stand for the Lewis acid and base parameters of surface energy.

**Table S3.** Surface Energy Parameters (in mN/m) of Testing Liquids.

| | $\gamma$ | $\gamma^{LW}$ | $\gamma^{AB}$ | $\gamma^{+}$ | $\gamma^{-}$ |
|---|---|---|---|---|---|
| Water | 72.8 | 21.8 | 51 | 25.5 | 25.5 |
| Ethylene Glycol | 48 | 29 | 19 | 1.92 | 47 |
| Hexadecane | 27.5 | 27.5 | 0 | 0 | 0 |

**Table S4.** Advancing contact angles of three probing liquids on various surfaces at initial state and calculated surface energies (mN $m^{-1}$).

| | | **PCDTBT** | **$PC_{71}BM$** | **PV12** |
|---|---|---|---|---|
| **Contact angle (deg)** | Water | 99.3 | 84.5 | 103.7 |
| | Ethylene Glycol | 69.5 | 55.6 | 71.3 |
| | Hexadecane | 9.5 | 9.2 | 11.2 |
| **Calculated surface energy component (mN $m^{-1}$)** | $\gamma$ | 27.83 | 31.19 | 27.27 |
| | $\gamma^{LW}$ | 27.12 | 27.11 | 26.98 |
| | $\gamma^{AB}$ | 0.72 | 4.07 | 0.29 |
| | $\gamma^{+}$ | 0.24 | 0.92 | 0.23 |
| | $\gamma^{-}$ | 0.54 | 4.52 | 0.09 |

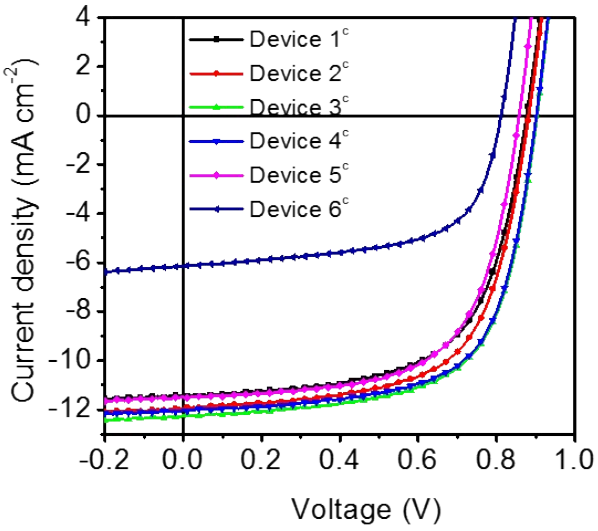



**Fig. S4.** *J-V* curves of all solar cells with cathodic interface layer under AM 1.5G illumination at intensity of 100 mW/cm$^2$.

**Table S5.** Key photovoltaic parameters of solar cells with different PV12 doping ratios in donors.

| Device[c] | PCE [%] | | $J_{SC}$ | $V_{OC}$ | FF |
|---|---|---|---|---|---|
| | Max. | Aver. | [mA cm$^{-2}$] | [V] | [%] |
| 1 | 6.29 | 6.10 | 11.46 | 0.875 | 62.7 |
| 2 | 6.85 | 6.62 | 11.95 | 0.885 | 65.0 |
| 3 | 7.25 | 7.17 | 12.20 | 0.905 | 65.8 |
| 4 | 7.06 | 6.95 | 11.88 | 0.900 | 66.0 |
| 5 | 6.26 | 6.15 | 11.50 | 0.855 | 64.0 |
| 6 | 3.10 | 3.02 | 6.15 | 0.810 | 62.2 |

[c] Device structure: [ITO/PEDOT:PSS/active layer/ MeOH treatment /Al]. For active layer PCDTBT$_{1-x}$:PV12$_x$:PC$_{71}$BM, Device 1: X=0; Device 2: X=0.1; Device 3: X=0.15; Device 4: X=0.20; Device 5: X=0.30; Device 6: X=1.

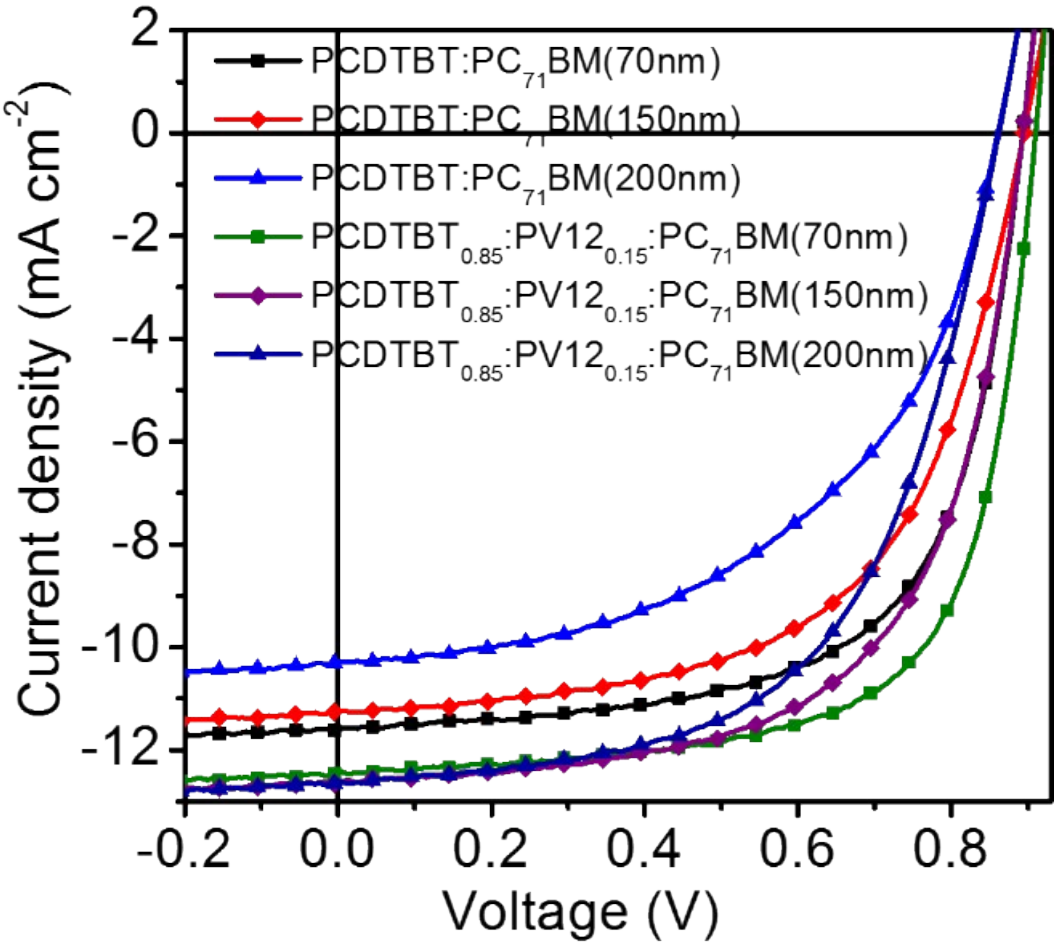



**Fig. S5.** *J-V* curves of all solar cells with device configuration of ITO/PEDOT:PSS (35 nm)/Active layer (x nm)/ IIDTh-NSB (8 nm)/Al (100 nm) under AM 1.5G illumination at intensity of 100 mW/cm$^2$. (Device structure: [ITO/PEDOT:PSS/active layer/ IIDTh-NSB (8 nm) /Al].)