Supporting Information

# Critical Factors Governing Vertical Phase Separation in Polymer-PCBM Blend Films for Organic Solar Cells

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Table S1. Calculations of surface energies for the pure polymer films.

| Material | $\theta_{water}$ | $\theta_{diiodomethane}$ | $\gamma_{polar}$ | $\gamma_{dispersive}$ | $\gamma_{total}$ |
|---|---|---|---|---|---|
| P3HT-RR91 | 108.2 | 63.1 | 26.8 | 0.015 | 27.1 |
| P3HT-RR98 | 107.3 | 62.7 | 26.4 | 0.048 | 26.8 |
| P3HT-RA | 104.9 | 54.8 | 31.6 | 0.013 | 31.6 |
| P3EPT | 74.1 | 31.9 | 43.4 | 4.78 | 48.2 |
| PBDT2FBT-Th | 106.2 | 62.5 | 27.1 | 0.04 | 27.2 |
| PBDT2FBT-O | 106.8 | 61.5 | 27.9 | 0.022 | 28.0 |
| PCBM | 88.1 | ($\theta_{formamide}$= 78) | - | - | 35.4* |

*The surface energy of PCBM film was calculated using Neuman's method (formamide's contact angle)

Contact angle values of the polymers and $PC_{61}BM$ films and the corresponding surface energy calculated using geometric mean approach[1, 2]. The polymers and PCBM solutions dissolved in dichlorobenzene were spin-coated onto the glass substrate. Then, the contact angle of each film was measured using water and diiodomethane. From contact angle data, the surface tension of different polymers can be determined using the Owens and Wendt geometric mean equation which is commonly used to obtain the surface energy with two kinds of liquid.

$$\gamma_1(1+\cos\theta_1) = 2(\gamma_1^d\gamma_2^d)^{1/2} + 2(\gamma_1^p\gamma_2^p)^{1/2}$$

$$\gamma^{total} = \gamma^d + \gamma^p$$

where $\theta_i$ is the droplet contact angle (water or diiodomethane) on the polymer films; $\gamma^{total}$ is the total surface tension; $\gamma^d$ and $\gamma^p$ are the dispersive and polar components of $\gamma^{total}$; $\gamma_i$ is the total surface tension of the i material (i = water or diiodomethane); $\gamma_i^d$ and $\gamma_i^p$ are the dispersive and polar components of $\gamma_i$.

1. D. Owens, R. Wendt *J. Appl. Polym. Sci*. 1969**, 13**, 1741.

2. X. Bulliard, S.-G. Ihn, S. Yun, Y. Kim, D. Choi, J.-Y. Choi, M. Kim, M. Sim, J.-H. Park, W. Choi, K. Cho *Adv. Funct. Mater.* 2010, **20**, 4381.

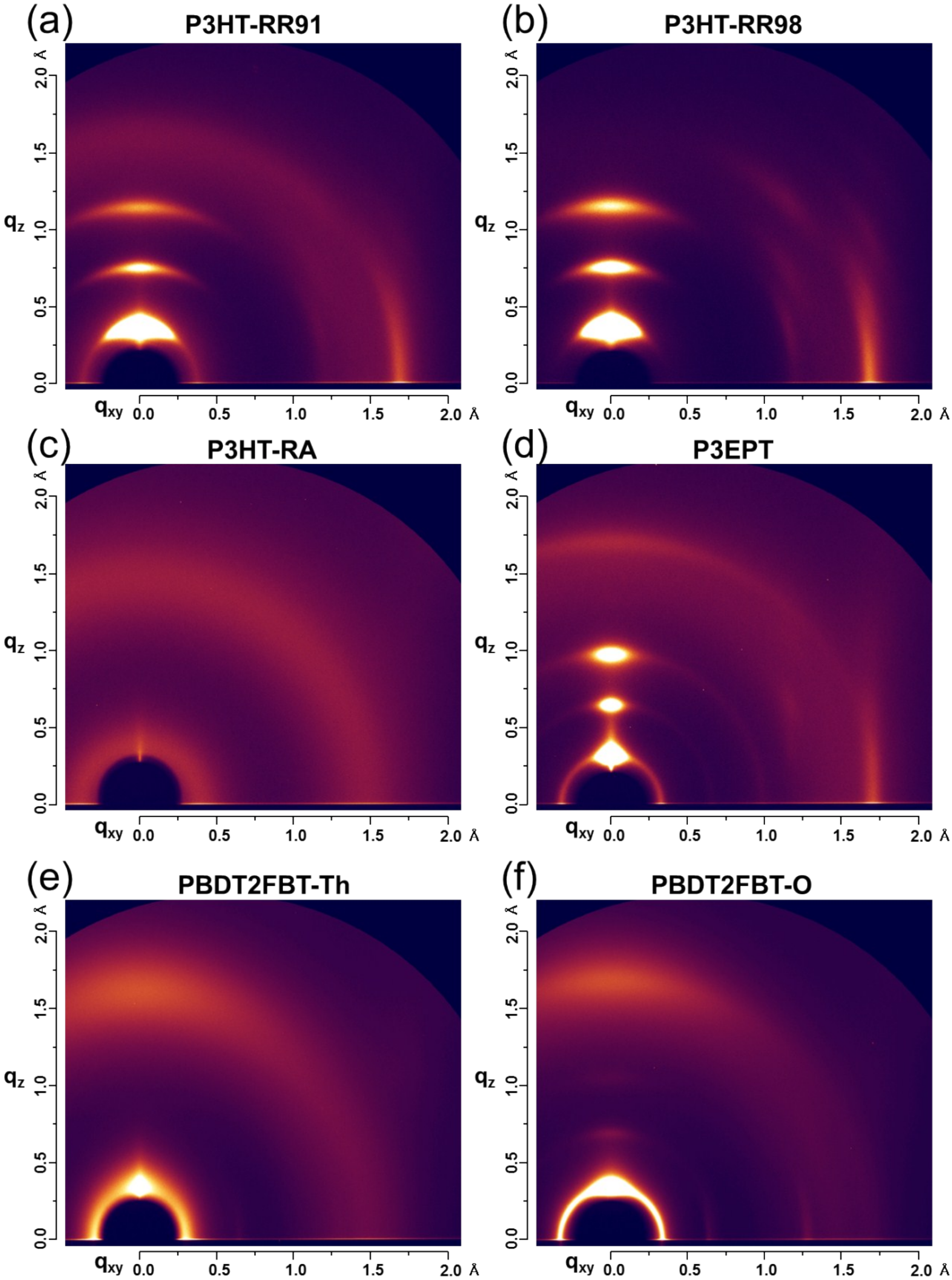


**Figure S1**. 2D image of Grazing incidence X-ray diffraction for pure (a) P3HT-RR91 film, (b) P3HT-RR98 film, (c) P3HT-RA film, (d) P3EPT film, (e) PBDT2FBT-Th film, and (f) PBDT2FBT-O film.

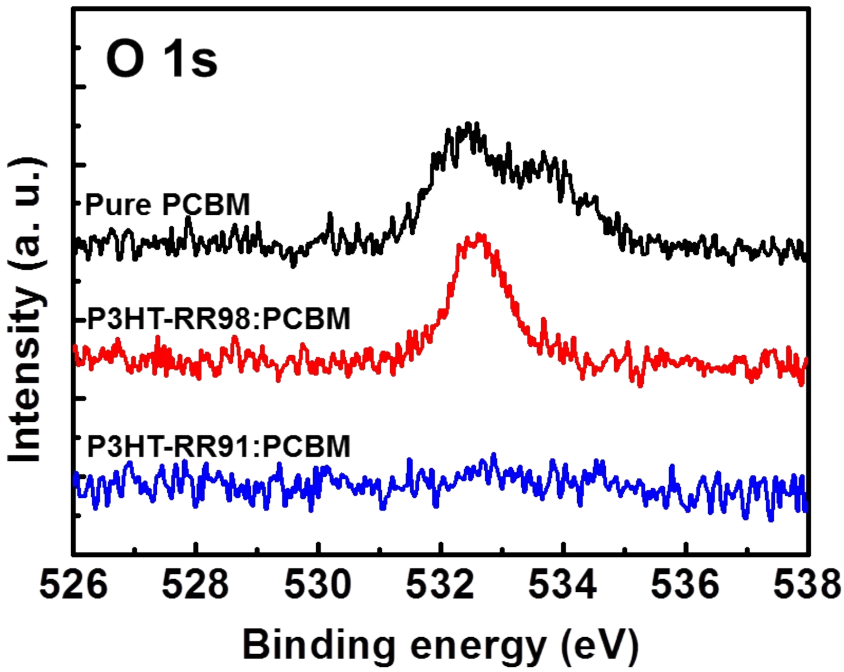


**Figure S2**. X-ray photoemission spectra of the 1s core levels of oxygen for pure PCBM, P3HT-RR98:PCBM blend film, and P3HT-RR91:PCBM blend film.

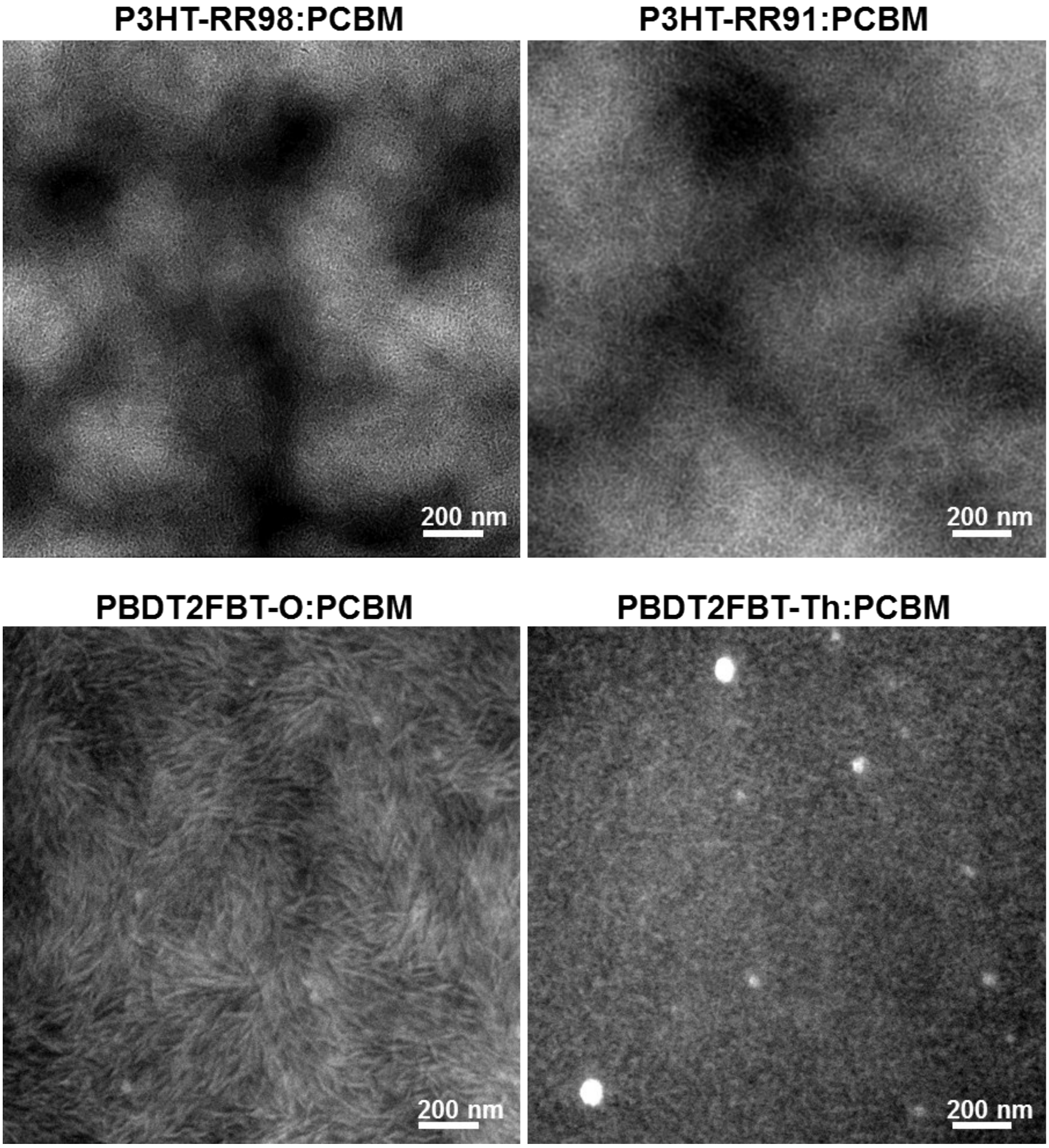


**Figure S3**. Bright-field TEM images of the active layers, P3HT-RR98:PCBM, P3HT-RR91:PCBM, PBDT2FBT-O:PCBM, and PBDT2FBT-Th:PCBM.

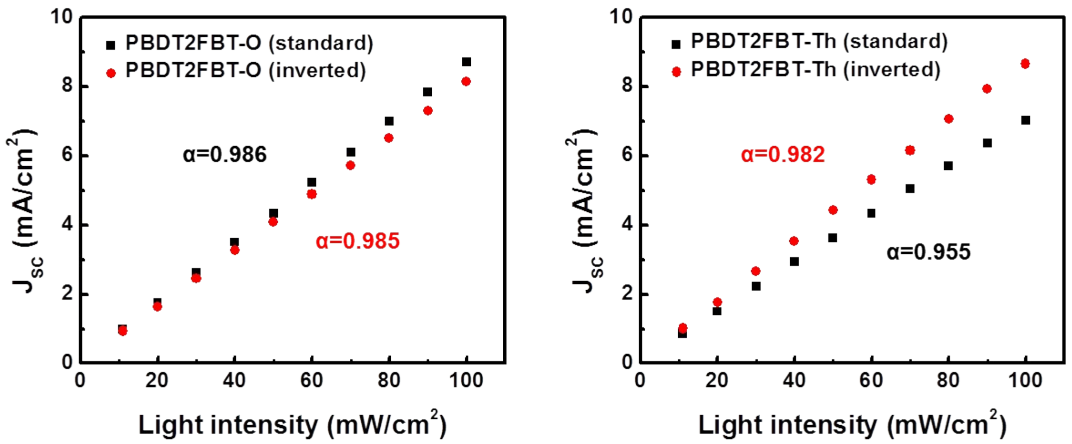


**Figure S4**. Jsc vs. Light intensity of PBDT2FBT-O:PCBM and PBDT2FBT-Th:PCBM based devices processed with and without CN in standard and inverted architectures.

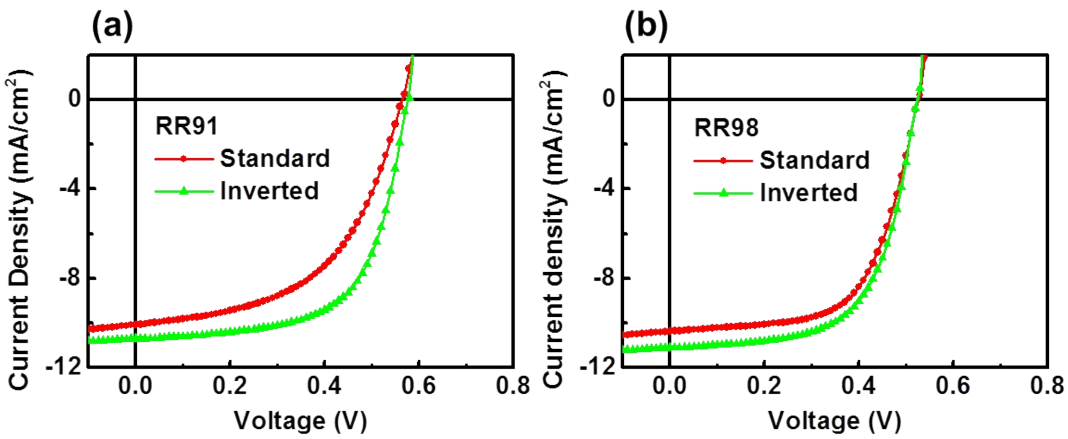


**Figure S5**. Current density–voltage characteristics of P3HT-RR91:PCBM and P3HT-RR98:PCBM based devices processed with and without DIO in standard and inverted architectures.

**Table S2**. Photovoltaic properties of polymers (averaged values from 8 devices of each type under the illumination condition of AM 1.5G, 100 mW $cm^{-2}$)

| Material | Architecture | $\eta$ [%] | $J_{sc}$ [$mA/cm^2$] | $V_{oc}$ [V] | FF |
|---|---|---|---|---|---|
| P3HT-RR91 | standard | 2.98 | 10.1 | 0.570 | 0.518 |
| | inverted | 3.89 | 10.7 | 0.580 | 0.626 |
| P3HT-RR98 | standard | 3.38 | 10.4 | 0.530 | 0.614 |
| | inverted | 3.62 | 11.1 | 0.520 | 0.626 |