Supporting Information

Ternary Organic Solar Cells: Compatibility Controls for Morphology Evolution of Active Layers

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Author contributions. Q. Ai and W. Zhou contributed equally to this work.

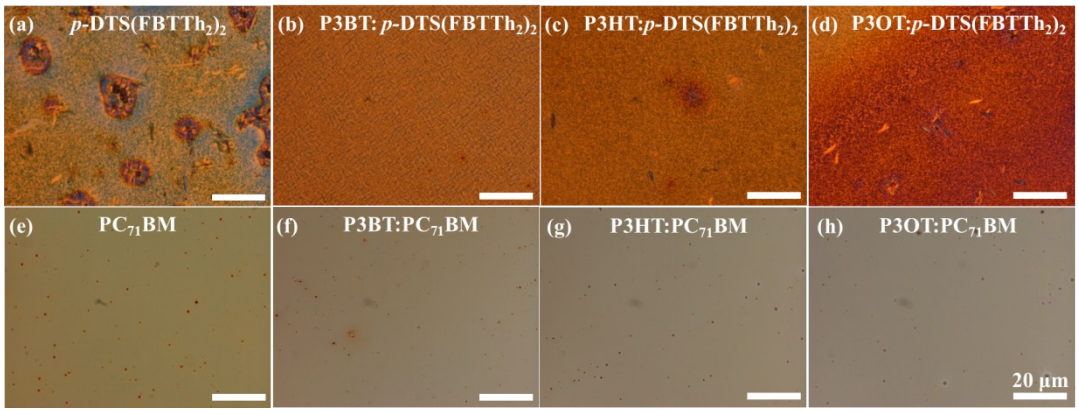

Figure S1. POM images of (a) *p*-DTS(FBTTh$_2$)$_2$, (b) P3BT:*p*-DTS(FBTTh$_2$)$_2$, (c) P3HT:*p*-DTS(FBTTh$_2$)$_2$, (d) P3OT:*p*-DTS(FBTTh$_2$)$_2$, (e) PC$_{71}$BM, (f) P3BT:PC$_{71}$BM, (g) P3HT:PC$_{71}$BM, and (h) P3OT:PC$_{71}$BM, respectively. The scale bar is 20 μm.

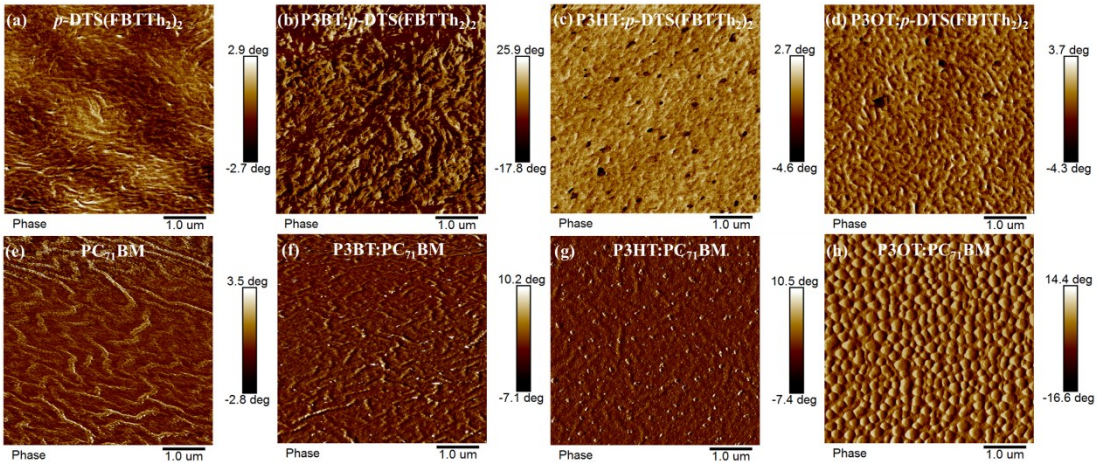

Figure S2. AFM phase images (5 × 5 μm^2) of (a) *p*-DTS(FBTTh$_2$)$_2$, (b) P3BT:*p*-DTS(FBTTh$_2$)$_2$, (c) P3HT:*p*-DTS(FBTTh$_2$)$_2$, (d) P3OT:*p*-DTS(FBTTh$_2$)$_2$, (e) PC$_{71}$BM, (f) P3BT:PC$_{71}$BM, (g) P3HT:PC$_{71}$BM, and (h) P3OT:PC$_{71}$BM, respectively.

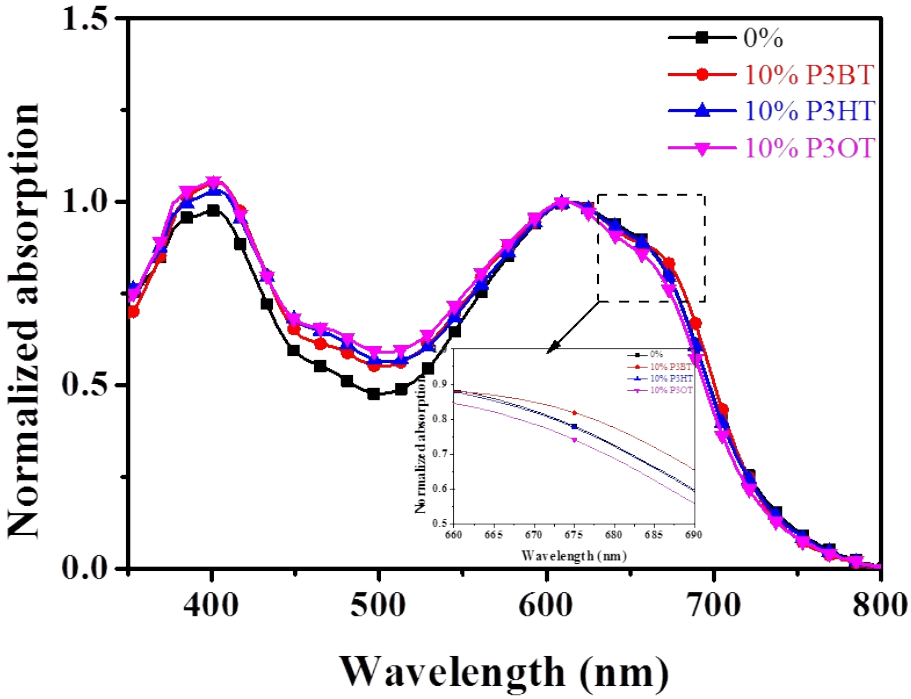

Figure S3. Normalized absorption spectra of the *p*-DTS(FBTTh$_2$)$_2$:PC$_{71}$BM film containing 0 wt%, 10 wt% P3BT, 10 wt% P3HT, and 10 wt% P3OT, respectively.

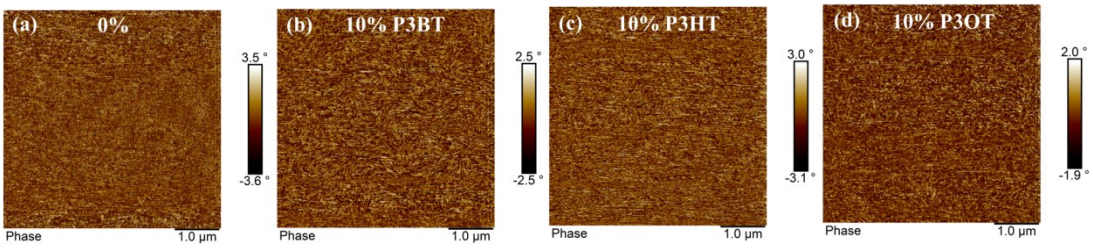

Figure S4. AFM phase images (5 × 5 µm) of *p*-DTS(FBTTh$_2$)$_2$:PC$_{71}$BM film containing (a) 0 wt%, (b) 10 wt% P3BT, (c) 10 wt% P3HT, and (d) 10 wt% P3OT, respectively.

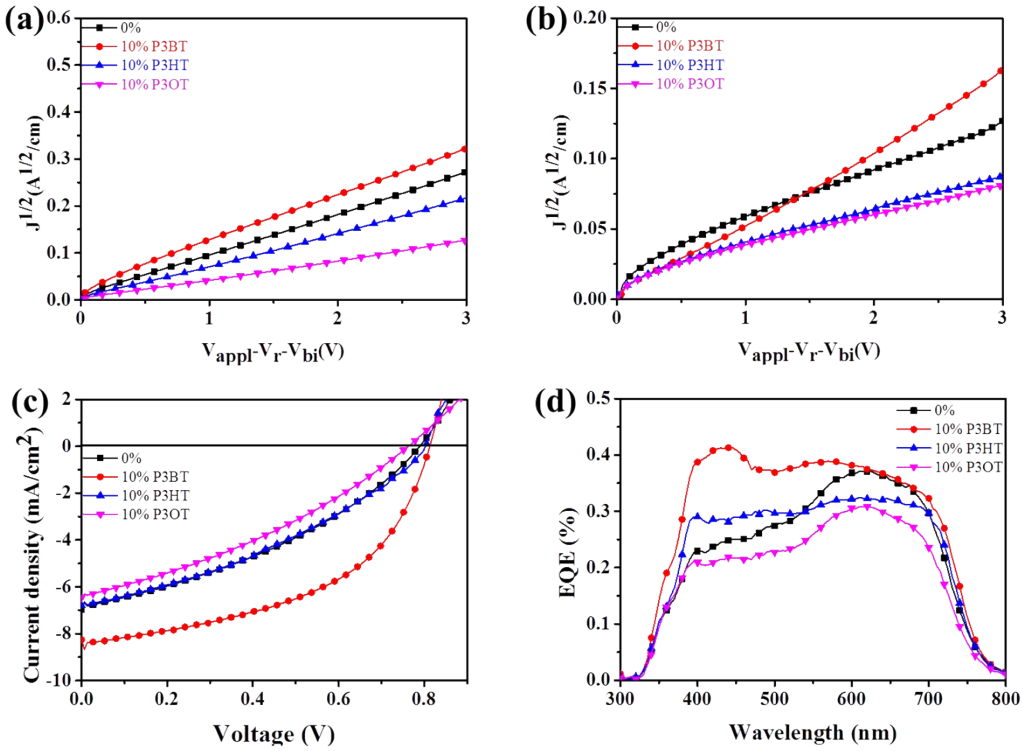

Figure S5. $J^{1/2}$–V characteristics of (a) hole-only and (b) electron-only *p*-DTS(FBTTh$_2$)$_2$:PC$_{71}$BM devices containing 0 wt%, 10 wt% P3BT, 10 wt% P3HT, and 10 wt% P3OT. (c) J–V curve of *p*-DTS(FBTTh$_2$)$_2$:PC$_{71}$BM solar cells containing 0 wt%, 10 wt% P3BT, 10 wt% P3HT, and 10 wt% P3OT. (d) The corresponding EQE measurements.

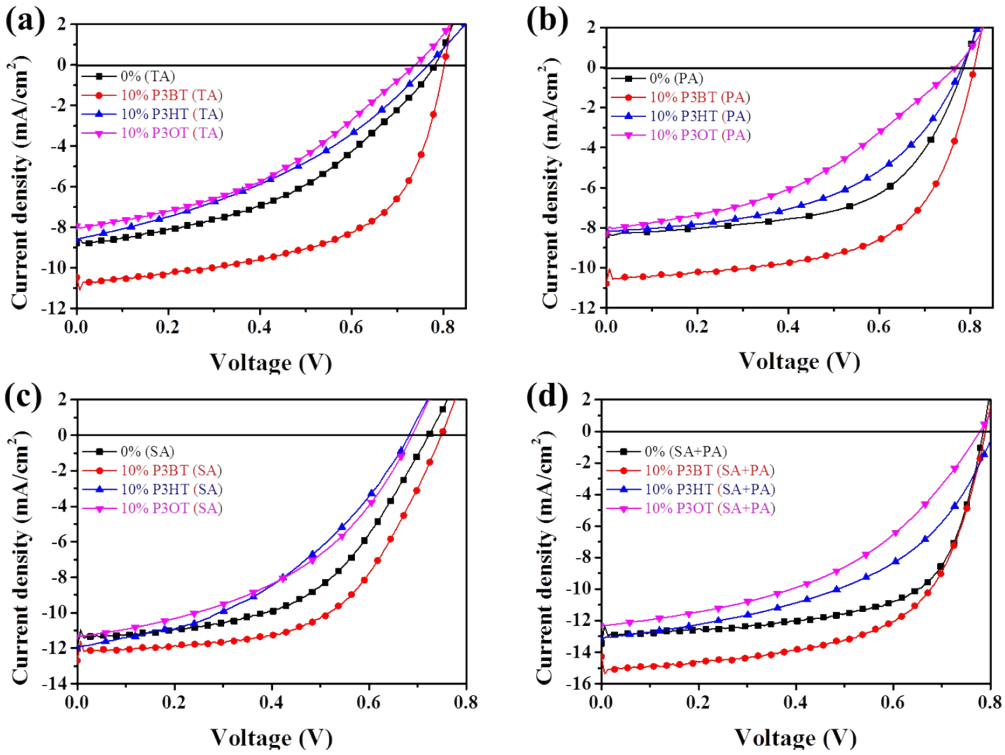

Figure S6. (a) *J-V* curves of *p*-DTS(FBTTh$_2$)$_2$:PC$_{71}$BM solar cells containing 0 wt%, 10 wt% P3BT, 10 wt% P3HT and 10 wt% P3OT under four optimal conditions: (a) Thermal annealing at 70 ^{o}C for 10 min; (b) Post annealing at 100 ^{o}C for 10 min; (c) Solvent annealing 30 min; and (d) Solvent annealing 30 min and post-annealing at 100 ^{o}C for 10 min.

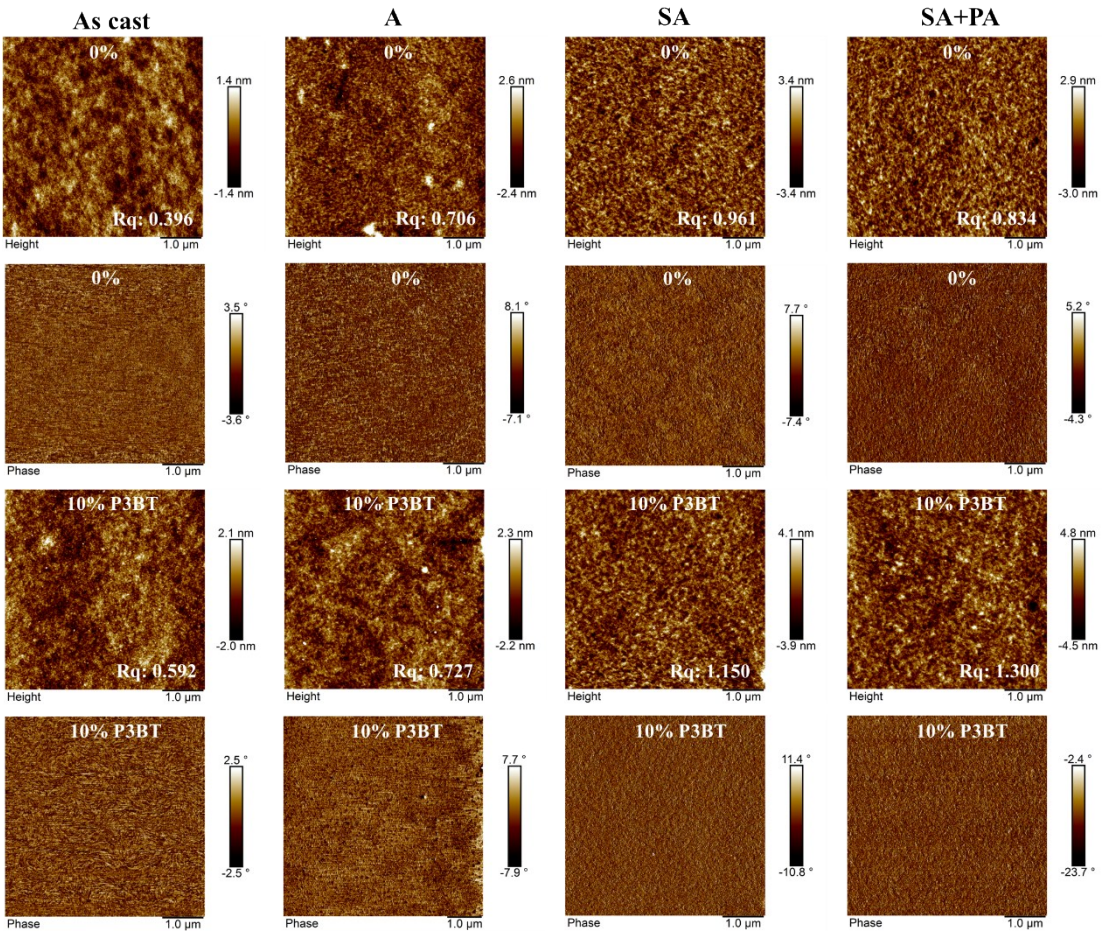

Figure S7. AFM height and phase images (5×5 μm^2) of *p*-DTS(FBTTh$_2$)$_2$:PC$_{71}$BM film containing 0 wt%, 10 wt% P3BT under different annealing conditions.

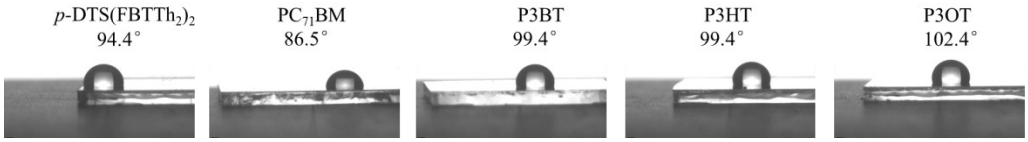

Figure S8. The contact angle measurements with water on the thin film of *p*-DTS(FBTTh$_2$)$_2$, PC$_{71}$BM, P3BT, P3HT and P3OT.

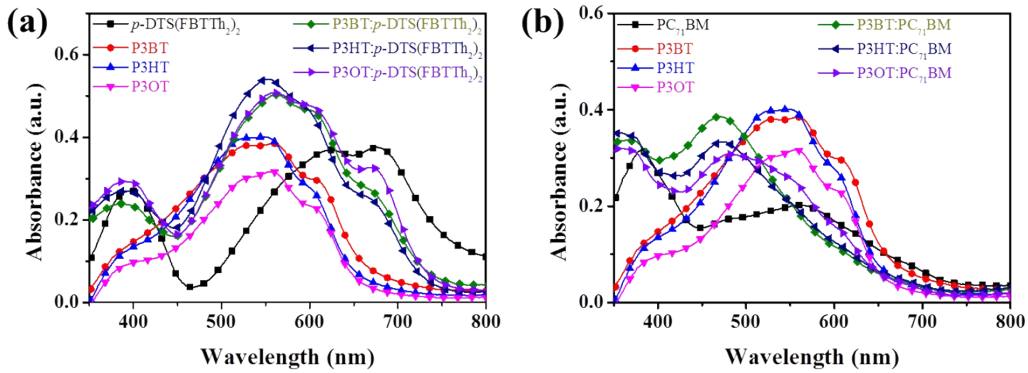

Figure S9. (a) UV–vis absorption spectra of *p*-DTS(FBTTh$_2$)$_2$ and P3ATs:*p*-DTS(FBTTh$_2$)$_2$ (1:1, w/w) blend. (b) UV-vis absorption spectra of PC$_{71}$BM and P3ATs:PC$_{71}$BM (1:1, w/w) blend.

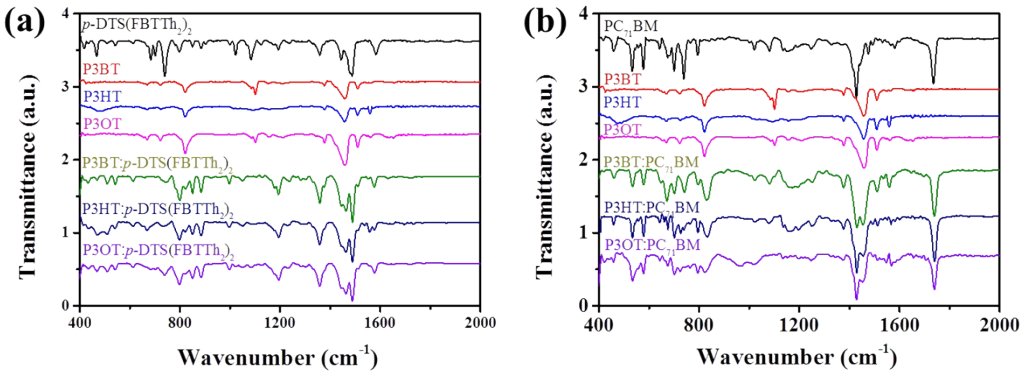

Figure S10. (a) FTIR spectra of *p*-DTS(FBTTh$_2$)$_2$ and P3ATs:*p*-DTS(FBTTh$_2$)$_2$ (1:1, w/w) blend. (b) FTIR spectra of PC$_{71}$BM and P3ATs:PC$_{71}$BM (1:1, w/w) blend.

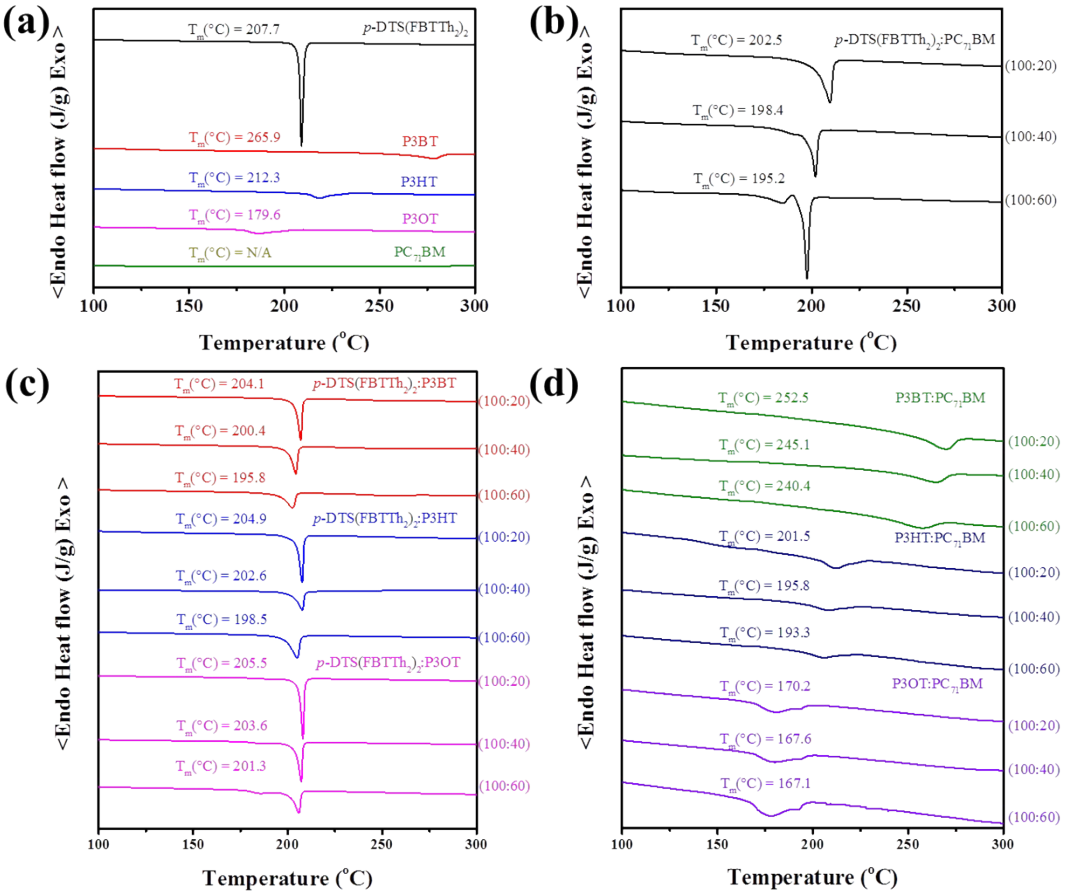

Figure S11. DSC heating curves of (a) *p*-DTS(FBTTh$_2$)$_2$, P3BT, P3HT, P3OT, and PC$_{71}$BM; (b) *p*-DTS(FBTTh$_2$)$_2$:PC$_{71}$BM blends; (c) *p*-DTS(FBTTh$_2$)$_2$:P3ATs blends; and (d) PC$_{71}$BM:P3ATs blends with different weight ratio.

The calculation of interaction parameters (χ)

Measurement of the melting point temperature (T_m) depression for blends was used to determine the Flory-Huggins interaction parameter (χ) of organic materials in the melting state. The larger the melting point depression, the smaller the value of χ, and the greater the intermolecular interaction.[2] Equation 3 reflects the melting point depression of organic materials in the presence of a miscible diluent, as derived by Nishi and Wang:[3]

$$\frac{1}{T_m} - \frac{1}{T_m^0} = -\frac{R\ v_2}{\Delta H_f v_1}\left[\frac{In\,\Phi_2}{m_2} + \left(\frac{1}{m_2} - \frac{1}{m_1}\right) \times (1 - \Phi_2) + \chi(1 - \Phi_2)^2\right] \quad (3)$$

where, the subscript 1 identified with the weaker crystalline material and 2 with the stronger crystalline material, respectively; T_m and T_m^0 are the melting points of the mixture and the pure stronger crystalline material; R is the ideal gas constant, ΔH_f is the heat of fusion of stronger crystalline material; v is the molar volumes, m is the degree of polymerization; and Φ is the volume fraction.

For *p*-DTS(FBTTh$_2$)$_2$:PC$_{71}$BM blends, the subscript 1 identified with the amorphous small molecule PC$_{71}$BM and 2 with the crystalline small molecule *p*-DTS(FBTTh$_2$)$_2$, both m_1 and m_2 are 1; eq 3 therefore reduces to

$$\frac{1}{T_m} - \frac{1}{T_m^0} = -\frac{R\ v_2}{\Delta H_f v_1}[In\ \Phi_2 + \chi(1 - \Phi_2)^2] \quad (4)$$

For P3ATs:*p*-DTS(FBTTh$_2$)$_2$ blends, the subscript 1 identified with the semicrystalline polymer P3ATs and 2 with the crystalline small molecule *p*-DTS(FBTTh$_2$)$_2$, m_1 is very large compared to 1 and m_2 is 1; eq 3 therefore reduces to

$$\frac{1}{T_m} - \frac{1}{T_m^0} = -\frac{R\ v_2}{\Delta H_f v_1}[In\ \Phi_2 + (1 - \Phi_2) + \chi(1 - \Phi_2)^2] \quad (5)$$

For P3ATs:PC$_{71}$BM blends, the subscript 1 identified with the amorphous PC$_{71}$BM and 2 with the semicrystalline polymer P3ATs, m_1 is 1 and m_2 is very large compared to 1; eq 3 therefore reduces to

$$\frac{1}{T_m} - \frac{1}{T_m^0} = -\frac{R\ v_2}{\Delta H_f v_1}[-(1 - \Phi_2) + \chi(1 - \Phi_2)^2] \quad (6)$$

By neglecting the effect of entropy and Φ_2, χ can have the following form

$$\chi = \frac{Bv_1}{RT} \quad (7)$$

where B is the interaction energy density characteristic of the organic material pair. Substituting eq 7 into eq 4, eq 5, and eq 6 yields

$$\frac{1}{\Phi_1}\left(\frac{1}{T_m} - \frac{1}{T_m^0} + \frac{R\ v_2}{\Delta H_f v_1} \times In\ \Phi_2\right) = -\frac{Bv_2\ \Phi_1}{\Delta H_f T_m} \quad (8)$$

$$-\frac{1}{\Phi_1}\left[\frac{1}{T_m}-\frac{1}{T_m^0}+\frac{R\ v_2}{\Delta H_f v_1}\times\left(\Phi_1+In\,\Phi_2\right)\right]=\frac{R\ v_2}{\Delta H_f v_1}+\frac{Bv_2\,\Phi_1}{\Delta H_f T_m} \tag{9}$$

$$\frac{1}{\Phi_1}\left(\frac{1}{T_m}-\frac{1}{T_m^0}\right)=\frac{R\ v_2}{\Delta H_f v_1}-\frac{Bv_2\,\Phi_1}{\Delta H_f T_m} \tag{10}$$

From eq 8, eq 9, and eq 10 yields three linear relationship between $(1/T_m-1/T_m^0+Rv_2\ln\Phi_2/\Delta H_f v_1)/\Phi_1$ and Φ_1/T_m, $-[1/T_m-1/T_m^0+Rv_2(\Phi_1+\ln\Phi_2)/\Delta H_f v_1]/\Phi_1$ and Φ_1/T_m, $(1/T_m-1/T_m^0)/\Phi_1$ and Φ_1/T_m; respectively. χ can be extracted by the slope *b* of the linear fit straight line. Due to the temperature of the active layer heating and spin coating is 90 °C， so the final calculated χ value is the interaction parameter of blends at 90 °C.

Table S1. Summary of the hole and electron mobility, μ_h and μ_e and their ratio R_μ (= μ_e/μ_h) of *p*-DTS(FBTTh$_2$)$_2$:PC$_{71}$BM device containing 0 wt%, 10 wt% P3BT, 10 wt% P3HT, and 10 wt% P3OT.

Additive content (wt %)	μ_h (cm^2/V·s)	μ_e (cm^2/V·s)	μ_h/μ_e
0%	2.24×10^{-4}	3.40×10^{-5}	6.59
10% P3BT	2.83×10^{-4}	8.89×10^{-5}	3.18
10% P3HT	1.68×10^{-4}	1.72×10^{-5}	9.77
10% P3OT	5.58×10^{-5}	1.45×10^{-5}	3.85

Table S2. Summary of the photovoltaic parameters of *p*-DTS(FBTTh$_2$)$_2$:PC$_{71}$BM solar cells containing different weight ratios of P3BT, P3HT, and P3OT under AM 1.5G solar illumination.

Additive content (wt)	J_{sc} (mA/cm^2)	V_{oc} (V)	FF (%)	PCE (%)
0%	6.97	0.786	35.7	2.0
5% P3BT	7.66	0.806	44.2	2.7
10% P3BT	8.25	0.812	50.9	3.4
20% P3BT	5.86	0.811	39.2	1.9
5% P3HT	6.87	0.796	37.8	2.1
10% P3HT	6.80	0.797	35.4	1.9
20% P3HT	5.92	0.794	36.5	1.7
5% P3OT	5.85	0.798	36.9	1.7
10% P3OT	5.67	0.765	31.5	1.4
20% P3OT	4.97	0.737	36.4	1.3

Table S3. Surface energy, wetting coefficients, and predicted location of P3BT, P3HT and P3OT within the *p*-DTS(FBTTh$_2$)$_2$:PC$_{71}$BM matrices.

Materials	Surface energy (mN m^{-1})	Wetting coefficient (ω_C)	Predicated location of P3ATs in the blends
p-DTS(FBTTh$_2$)$_2$	26.46		
PC$_{71}$BM	31.39		
P3BT	23.43	2.24	in *p*-DTS(FBTTh$_2$)$_2$
P3HT	23.43	2.24	in *p*-DTS(FBTTh$_2$)$_2$
P3OT	21.56	3.02	in *p*-DTS(FBTTh$_2$)$_2$

The calculation of wetting coefficient (ω_C)

The wetting coefficient of material C (ω_C) in blends of materials A and B can be calculated by Young's equation as follows:[1]

$$\omega_C = \frac{\gamma_{C-B} - \gamma_{C-A}}{\gamma_{A-B}} \quad (1)$$

where γ_{X-Y} is the interfacial surface energy between X and Y. The interfacial surface energy can be calculated by Neumann's equation as follows:

$$\gamma_{X-Y} = \gamma_X + \gamma_Y - 2(\gamma_X \times \gamma_Y)^{0.5} e^{[-\beta(\gamma_X + \gamma_Y)^2]}$$

where $\beta = 0.000115$ m^4 mJ^{-2}. If $\omega_C > 1$, the material C will be located in the domain A; If $\omega_C < -1$, C will be located in the domain B; If $-1 < \omega_C < 1$, C will be located in the interface between A and B.

Table S4. The related parameters of *p*-DTS(FBTT$_2$)$_2$, PC$_{71}$BM, P3BT, P3HT, and P3OT for calculated Flory-Huggins interaction parameter.

Materials	Melting point (°C)	Enthalpy (J/g)	Density (g/cm^3)	Molar volume (cm^3/mol)
p-DTS(FBTT$_2$)$_2$	207.7	69.05	1.15	1059
PC$_{71}$BM	/	/	1.3	793
P3BT	265.9	27.95	1.1	125
P3HT	212.3	23.35	1.1	151
P3OT	179.6	21.74	1.1	176

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2. Ghasemi, M.; Ye, L.; Zhang, Q.; Yan, L.; Kim, J. H.; Awartani, O.; You, W.; Gadisa, A.; Ade, H., Panchromatic Sequentially Cast Ternary Polymer Solar Cells. *Adv. Mater.* **2017**, 29, 1604603.

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