Supplementary information

A new strategy to engineer polymer bulk heterojunction solar cells with thick active layers via self-assembly of columnar phase

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PCBM Weight Percentage Calculation

The weight fraction of PCBM (Φ) along the perimeter of the PMMA columns was calculated by using the following equation: $\Phi = \dfrac{V_c \rho_c}{V_t \rho_t}$, , where V_c is the volume of cylindrical shell of PCBM along the PMMA columns, ρ_c is the density of PCBM, V_t is the volume of active layer, ρ_t is the concentration of PCBM in the blend. We assume the PCBM aggregation layer along the PMMA columns as a cylindrical shell: $V_c = 2\pi r h \Delta$, where r is the column radius, h is the height of the cylindrical shell, Δr is the interfacial width of PCBM aggregation layer.

**Domain Size Calculation by Scherrer Equation**

The domain size of crystalline phase (e.g., P3HT, PCBM) can be calculated by the Scherrer equation using the full width at half maximum of a corresponding X-ray scattering peak: $d = \dfrac{0.9\lambda}{\beta \cos\theta}$, where d is the size of crystalline domain, λ is the X-ray wavelength, β is the full width at half maximum of a diffraction peak, and θ is the peak position.
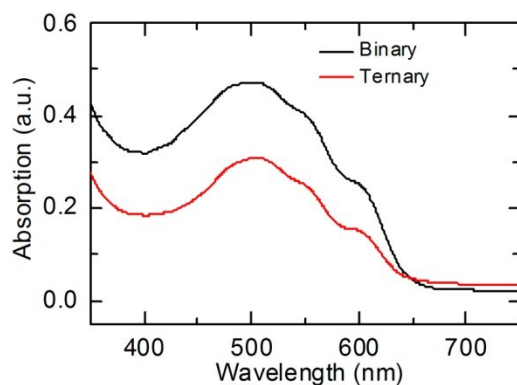
Fig. S1. Ultraviolet-visible light absorption spectra of ~210 nm thick thin film samples after thermal annealing at 150 °C for 1 hr in ~10 mTorr vacuum: P3HT:PMMA:PCBM ternary blend (red line); P3HT:PCBM binary blend (black line). The integrated absorption of the ternary blend in the measurement range is ~60% of that for the binary blend, which is consistent with the geometric volume fraction of photoactive P3HT:PCBM in the ternary blend sample.
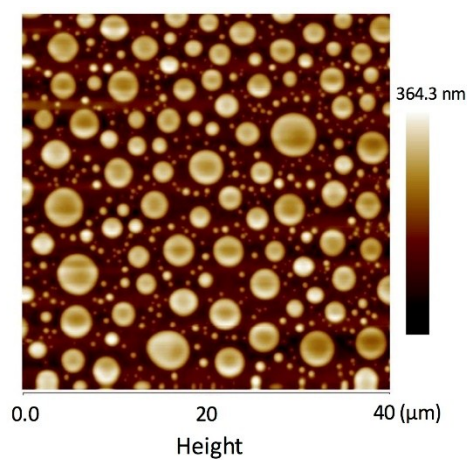
Fig. S2. Topographical AFM image of P3HT:PMMA:PCBM ternary BHJ blend thin film (1:1:1 wt. ratio, spin-cast on the PEDOT:PSS-coated ITO substrate, annealed at 150 °C for 1 hr in ~10 mTorr vacuum) *with top Al contact*. The scan size is 40 μm × 40 μm.
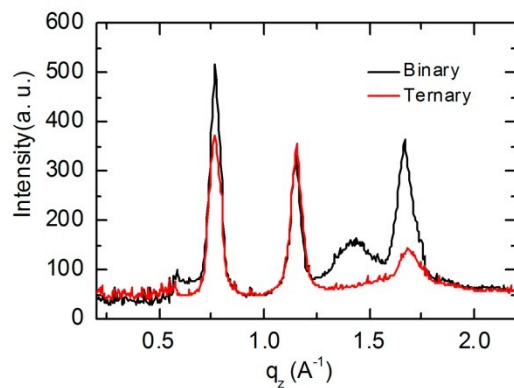
Fig. S3. Linear X-ray scattering intensity profile along the q_z axis obtained from the two-dimensional GIWAXS data measured from the binary P3HT:PCBM and ternary P3HT:PMMA:PCBM blend thin films prepared on Si. The films were annealed at 150 °C for 4 hr in ~10 mTorr vacuum before the measurement.

Fig. S4. Summary of percolating column structure formation for different simulation parameter settings. Three simulations were conducted for each combination of film thickness and ε. Y and N, respectively, denote the cases when percolating column structure is observed and not observed.

Table S1. Ternary blend solar cell photovoltaic parameters at different blend layer thicknesses

Thickness (nm)	V_{OC} (V)	J_{SC} (mA/cm^2)	FF	PCE
560.2 ± 2.55	0.615 ± 0.01	7.7247 ± 1.21	52.4 ± 0.8%	2.488 ± 0.56%
486.4 ± 2.35	0.625 ± 0.005	8.9235 ± 1.40	53.2 ± 1.1%	2.968 ± 0.57%
298.8 ± 1.42	0.625 ± 0.005	9.4326 ± 0.42	53.3 ± 1.3%	3.14 ± 0.25%
283.8 ± 1.14	0.615 ± 0.005	7.1042 ± 0.75	55.3 ± 0.6%	2.41 ± 0.15%
217.2 ± 0.75	0.615 ± 0.009	6.0629 ± 0.19	47.5 ± 1.8%	1.77 ± 0.12%
195.5 ± 0.64	0.615 ± 0.006	5.4106 ± 0.59	47.7 ± 1.9%	1.59 ± 0.14%
155.3 ± 0.51	0.615 ± 0.01	5.3796 ± 0.14	45.3 ± 1.6%	1.51 ± 0.13%

Table S2. Binary blend solar cell photovoltaic parameters at different blend layer thicknesses

Thickness (nm)	V_{OC} (V)	J_{SC} (mA/cm^2)	FF	PCE
320.4 ± 1.78	0.595 ± 0.01	6.0622 ± 0.25	53.6 ± 1.8%	1.934 ± 0.18%
231.8 ± 1.65	0.575 ± 0.02	6.3613 ± 0.74	54.3 ± 3.1%	1.989 ± 0.42%
221.4 ± 1.37	0.585 ± 0.005	6.5416 ± 0.99	54.1 ± 3.3%	2.069 ± 0.15%
167.2 ± 1.16	0.605 ± 0.005	7.0661 ± 0.36	50.1 ± 0.7%	2.1459 ± 0.16%
126.8 ± 0.55	0.605 ± 0.006	7.6671 ± 0.09	51.4 ± 1.4%	2.3860 ± 0.11%
111.8 ± 0.44	0.605 ± 0.005	8.4706 ± 0.24	49.4 ± 2.8%	2.5314 ± 0.08%
98.8 ± 0.31	0.595 ± 0.01	6.4094 ± 0.14	51.9 ± 1.7%	1.9791 ± 0.12%