Electronic Supplementary Material (ESI) for Energy & Environmental Science.

Electronic Supplementary Information for

Isolating and Quantifying the Impact of Domain Purity on the Performance of Bulk Heterojunction Solar Cells

Wenchao Huang, Eliot Gann, Naresh Chandrasekaran, Lars Thomsen, Shyamal K. K. Prasad, Justin M. Hodgkiss, Dinesh Kabra, Yi-Bing Cheng, and Christopher R. McNeill**

Derivation of TSI with constant mass fraction.

To solve for the volume fraction of the domains, we use the mass and density of each component of the domains:

$$v_1 = \frac{\frac{m_{11}}{\rho_1} + \frac{m_{21}}{\rho_2}}{\frac{m_{11} + m_{12}}{\rho_1} + \frac{m_{21} + m_{22}}{\rho_2}} \tag{1}$$

$$v_2 = \frac{\frac{m_{12}}{\rho_1} + \frac{m_{22}}{\rho_2}}{\frac{m_{11} + m_{12}}{\rho_1} + \frac{m_{21} + m_{22}}{\rho_2}} \tag{2}$$

where m_{ij} is the mass (or a fraction of total system mass) of material *i* in domain *j*, and ρ_i is the density of material *i*. We can normalize m_{ij} relative to the overall mass of the film by defining the overall fraction of mass of each material (m_1 and m_2 where $m_1 + m_2 = 1$) and the weight precent of component *i* in domain *j* (p_{ij}).

$$m_{11} = m_1 - m_{12} \tag{3}$$

$$m_{22} = m_2 - m_{21} \tag{4}$$

$$\frac{m_{21}}{m_{21} + m_{11}} = P_{21} \tag{5}$$

$$\frac{m_{12}}{m_{12} + m_{22}} = P_{12} \tag{6}$$

The denominator in the preceding two equations is the global mass fraction of the corresponding domain.

Solving these coupled equations for v_1 and v_2 in terms of only relevant or known variables $m_1, P_{12}, P_{21}, \rho_1, and\ \rho_2$ we obtain

$$v_1 = \frac{(m_1 - P_{12})\left(\frac{1}{\rho_1} + P_{21}\left(\frac{1}{\rho_2} - \frac{1}{\rho_1}\right)\right)}{\left(\frac{1-m_1}{\rho_2} + \frac{m_1}{\rho_1}\right)(1 - P_{12} - P_{21})} \tag{7}$$

$$v_2 = \frac{\left(\frac{1-P_{12}}{\rho_2} + \frac{P_{12}}{\rho_1}\right)(1 - m_1 - P_{21})}{\left(\frac{1-m_1}{\rho_2} + \frac{m_1}{\rho_1}\right)(1 - P_{12} - P_{21})} \tag{8}$$

Contrast between two domains (C_{d1d2}) is a function of the differences in refractive indicies in the two domains, n_{d1} and n_{d2}

$$C_{d1d2} = (n_{d1} - n_{d2})^2 \tag{9}$$

Defining the indices of refraction for the pure materials as n_i for material *i*, we can solve for n_{d1} and n_{d2} as the volume average of the components within each domain

$$n_{d1} = n_1 v_{11} + n_2 v_{21} \tag{10}$$

$$n_{d2} = n_2 v_{22} + n_1 v_{12} \tag{11}$$

where $v_{ij}$is defined to be the volume fraction of material *i* in domain *j* (importantly different than the earlier v_i which were volume fractions of the domains), which we can solve for as

$$v_{ij} = \frac{\frac{m_{ij}}{di}}{\frac{m_{1j}}{d_1} + \frac{m_{2j}}{d_2}} \tag{12}$$

Using equations (4-7), (11-13), again solving only in terms of known variables, we obtain:

$$n_{d1} = \frac{\frac{n_1(1 + P_{21})}{\rho_1} + \frac{n_2 P_{21}}{\rho_2}}{\frac{1 - P_{21}}{\rho_1} + \frac{P_{21}}{\rho_2}} \tag{13}$$

$$n_{d2} = \frac{\frac{n_2(1 + P_{12})}{\rho_2} + \frac{n_1 P_{12}}{\rho_1}}{\frac{1 - P_{12}}{\rho_2} + \frac{P_{12}}{\rho_1}} \tag{14}$$

To calculate the relative contrast between the domains, C we can normalize by the contrast when there is no mixing, C_0

$$C_0 = (n_1 - n_2)^2 \tag{15}$$

$$C = \frac{C_{d1d2}}{C_0} = \frac{\frac{(1 - P_{12} - P_{21})^2}{\rho_1^2 \rho_2^2}}{\left(\frac{1 - P_{12}}{\rho_2} + \frac{P_{12}}{\rho_1}\right)^2 \left(\frac{P_{21}}{\rho_2} + \frac{1 - P_{21}}{\rho_1}\right)^2} \tag{16}$$

so only the densities of the components and the degree of mixing matters in the final relative contrast.

We find it useful to define rather than ρ_1 and ρ_2 the relative difference bewteen the densities ρ_r as

$$\rho_r = 1 - \frac{\rho_1}{\rho_2} \tag{17}$$

Putting this all together, we can now solve for TSI in terms of relevant variables.

$$TSI \propto \frac{(1 + \rho_r)^2 \, (m_1 - P_{12}) \, (1 - m_1 - P_{21})}{(1 + m_1 \rho_r)^2 \, (1 + \rho_r P_{12}) \, (1 + \rho_r (1 - P_{21}))} \tag{18}$$

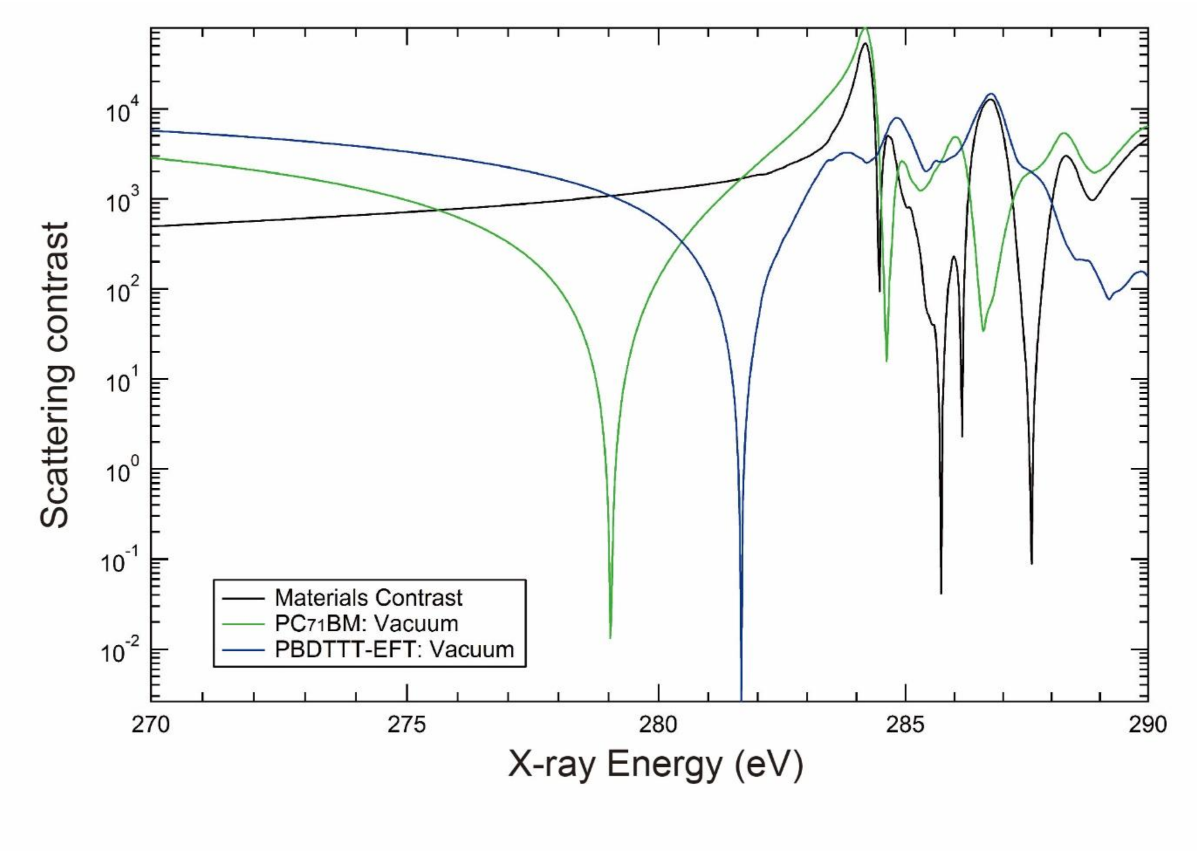


Fig. S1 Calculation of R-SoXS scattering functions

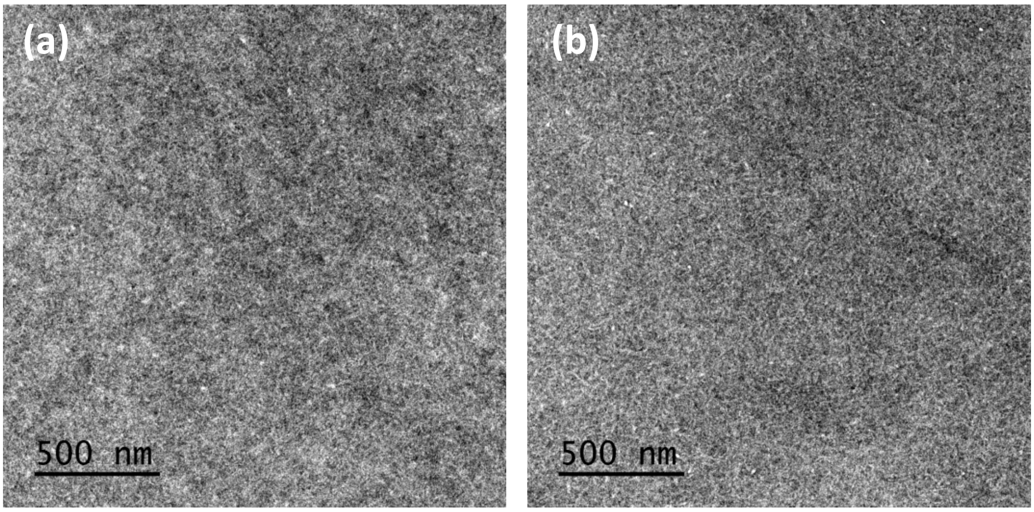


Fig. S2 Bright-field TEM images of PBDTTT-EFT:$PC_{71}BM$ films prepared with (a) AST just after spin-coating and (b) after 24 hours revealing no significant difference in the visual morphology.

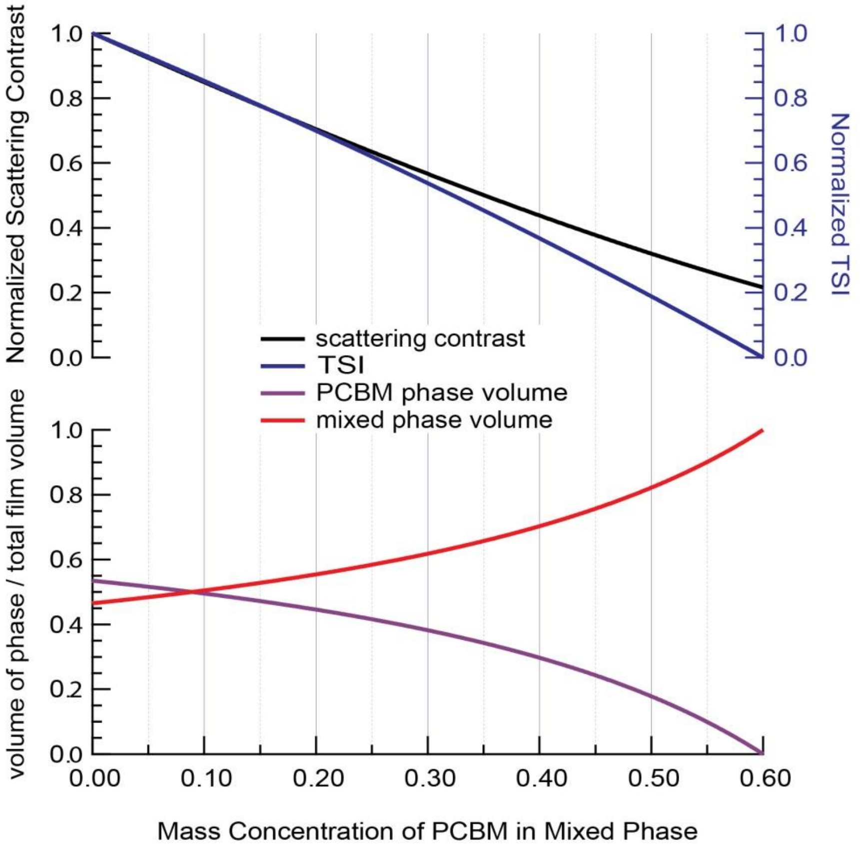
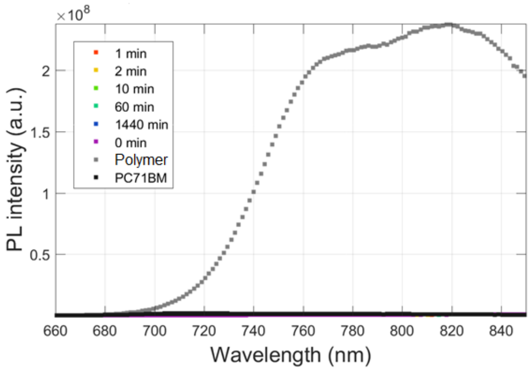


Fig. S3 Plot of equation 2 from the main manuscript.



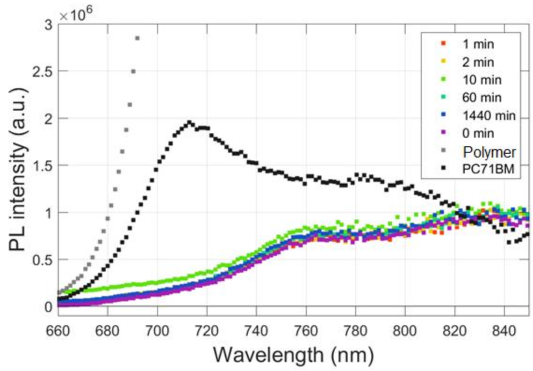


Fig. S4. Photoluminescence spectra of PBDTTT-EFT/$PC_{71}BM$ blends referenced to the photoluminescence spectra of neat polymer and fullerene films. A wavelength of 625 nm was used for photoexcitation.

Table S1. Calculated PL Quenching efficiencies

Delay time	PL Quenching Efficiency (%)
1 minute	93.4
2 minutes	99.4
10 minutes	99.2
1 hour	99.3
24 hours	99.3
No AST	99.4

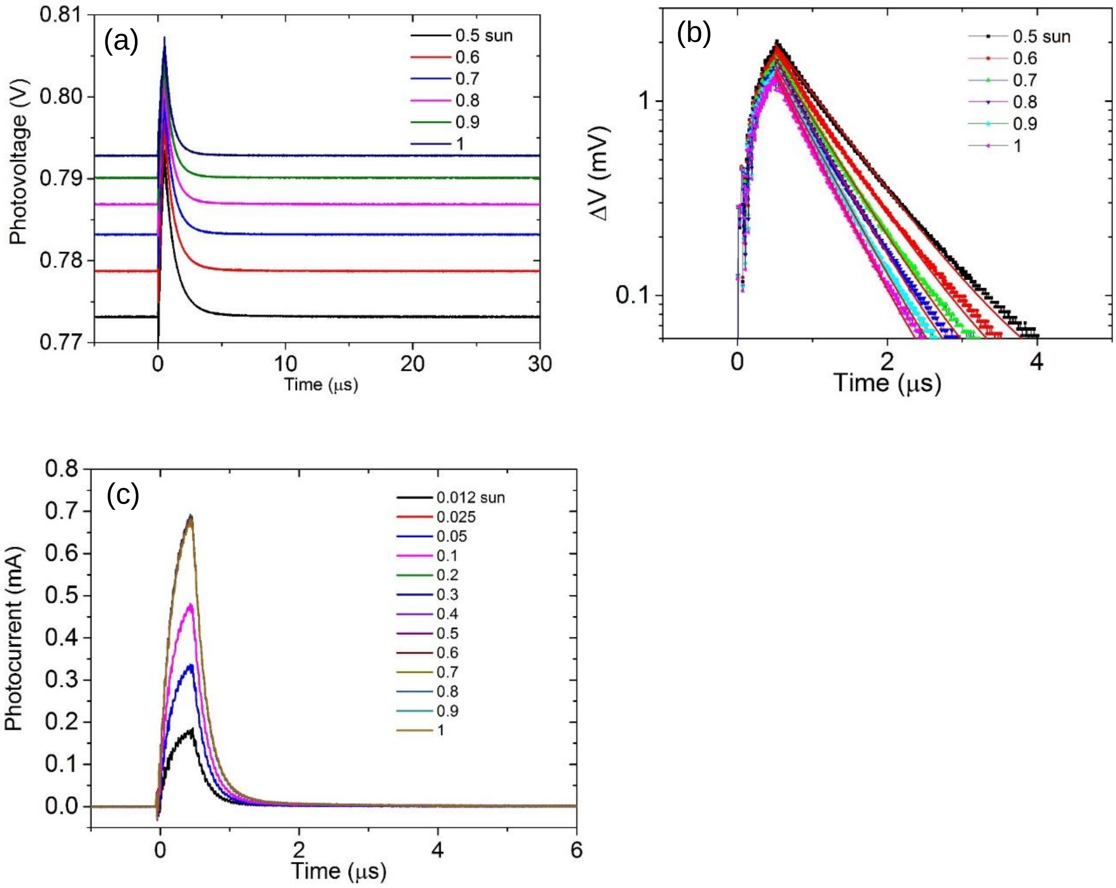


Fig. S5 (a) Raw data of transient photovoltage measurements at different background intensities. (b) Plot showing *ΔV* as the function of time with the monoexponential fits. (c) Transient photocurrent curves obtained by using 50 Ω termination in the oscilloscope.