**Supplementary Information**

**Morphological characterization of fullerene and fullerene-free organic photovoltaics by combined real and reciprocal space techniques**

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**Optical constants and scattering contrast functions from transmission NEXAFS experiments**

In the energy range 0.05–30 keV, the scalar complex index of refraction for an isotropic material is given as $n=1-δ+iβ$ where *δ* and *β* are related through a Kramers-Krönig (KK) relation. The imaginary or absorption part of the index of refraction can be measured in a transmission geometry by applying Beer’s law $I=I\_{0}e^{-4πβt/λ}$, where *I* is the transmitted intensity, *I0* the incident intensity, *t* the film thickness and *λ* is the wavelength in vacuum. Assuming an isotropic molecule, the absorption part *β* can be obtained if the film thickness is known. The real part *δ* can then be derived from the imaginary part via the KK relations.1, 2 The scattering contrast between two materials (say, 1 and 2) is proportional to $E^{4}(∆δ(E)^{2}+∆β(E)^{2})$ where $∆δ=δ\_{1}-δ\_{2}$ and $∆β=β\_{1}-β\_{2}$ and can be therefore calculated by measuring the respective absorption spectra of neat films of the materials 1 and 2. Note that for vacuum *δ* = *β* = 0.



**Figure S1:** (a) R-SoXS profiles at high mass-roughness (270 eV) and higher material contrast (284.1 eV) energies; (b) PTB7-Th:PC71BM Material and vacuum contrast functions and the integrated scattering intensity (ISI) at different energies for the “No-additive” and “3% DIO” samples. Contrast functions were calculated from real and imaginary parts of the refractive index. The imaginary part of the refractive index was determined from transmission NEXAFS measurements and the real part was obtained by taking the Kramers-Krönig transform of the imaginary part.



**Figure S2**: Fits (solid lines) to X-ray (Cu Kα) reflectivity3 data (open circles) for (a) PTB7-Th and (b) α-TPB neat films cast from CB solution on thermally grown silicon oxide on Si substrates. Film thicknesses were predetermined from VASE experiments and were held constant for the fitting procedure. Insets show the scattering length densities (SLDs) obtained from the fits as a function of film thickness. Mass densities ($ρ\_{PCE10}=1.20\pm 0.01$ gm/cm3; $ρ\_{α-TPB}=1.22\pm 0.01$ gm/cm3) for the films were calculated using SLDs from fits and NIST SLD calculator.4

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**Figure S3**: (a) R-SoXS profiles at high mass-roughness (270 eV) and higher material contrast (283.7 eV) energies for the sample cast from CB solution; (b) PTB7-Th:α-TPB Material and vacuum contrast functions and the integrated scattering intensity (ISI) at different energies for the “No-additive” and “8% DPE” samples.



**Figure S4**: Sector-averaged scattering profiles in direction perpendicular and parallel to the E‑field of the incident X-ray beam for (a) no-additive and 3% DIO PTB7-Th:PC71BM blend samples; (b) no-additive and 8% DPE PTB7-Th:α-TPB blend samples. Insets show q-dependence of the dichroic ratio of scattered intensities parallel and perpendicular to the X-ray beam. The magnitude of the dichroic ratio is found to be relatively low and nearly identical for all the systems. This implies that the ordering at the donor-acceptor interface has a negligible role in modulating the device performance.

**References**

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