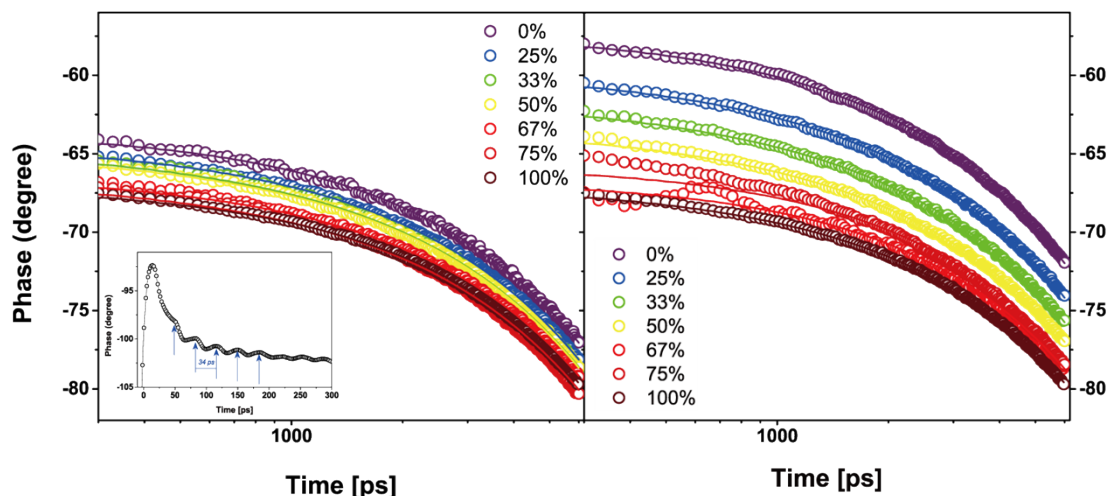


Supporting Information

Thermal Conductivity of Organic Bulk Heterojunction Solar Cell: *Unusual Binary Mixing*

Effect, by Zhi Guo *et al.*

1. TDTR phase signal and fitting

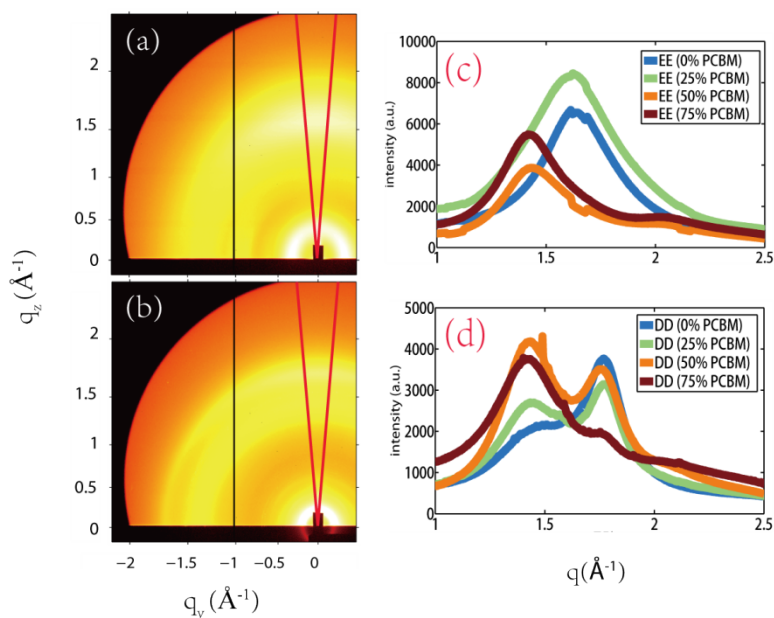


SI-Figure 1. Phase signal obtained from lock-in amplifier used to determine the thermal conductivity of BHJs (PBDTTT-EE and PBDTTT-DD respectively). BHJs composed of different PCBM volume fractions are presented in different colors. Experimental data are indicated as open circles, and the corresponding fits are shown in solid lines. Inset: acoustic echoes used to determine the actual aluminum film thickness (~106 nm).

2. GIWAXS measurements

GIWAXS measurements were conducted at beamline 8-ID-E of the Advanced Photon Source at Argonne National Laboratory, using 7.35 keV energy photons ($1.6868 \text{ \AA}$), with an incident angle at 0.2° . The beam size was $20 \text{ }\mu\text{m}$ (V) x $200 \text{ }\mu\text{m}$ (H). The BHJ films were spin cast on silicon wafer substrates. To extract the π - π stacking distance change as a function of PCBM volumetric fraction, line cuts were performed to obtain the intensity as a function of the wave vector transfer vector q by integration over a small azimuthal angle range ($\pm 5^\circ$ from the out-of-plane direction) where the π - π stacking feature is strongest. Linecuts were computed using the GIXSGUI package¹ (GIXSGUI available for download <http://www.aps.anl.gov/Sectors/Sector8/Operations/GIXSGUI.html>) for Matlab (Mathworks). Example line cuts are shown in SI-figure 2a,b. Two sets of line cuts from the GIWAXS patterns of PBDTTT-EE BHJs and PBDTTT-DD BHJs are shown in SI-figure 2b and 2c, respectively. GIWAXS from the neat PBDTTT-EE film exhibits a single feature at large q , the π - π stacking peak, which shifts to smaller q (larger characteristic length) when PCBM is first added. When the PCBM loading 50% or larger, the scattering from PCBM (peak at $q \approx 1.4 \text{ \AA}^{-1}$) dominates. This possibly implies that PCBM molecules are intercalated into the PBDTTT-EE polymer structure and enlarge the π - π stacking distance, ultimately disrupting the π - π stacking order at even higher PCBM loading ($\geq 50\%$). GIWAXS from the neat PBDTTT-DD thin film exhibits two features at large q , at $q = 1.7 \text{ \AA}^{-1}$ and $q = 1.4 \text{ \AA}^{-1}$. The feature at larger q is the π - π stacking peak, while the origin of the latter is unclear, a similar feature has been observed in a similar polymer system². This latter peak is in superposition with the scattering from the PCBM. In PBDTTT-DD BHJs, the addition of PCBM does not shift the polymer π - π stacking peak significantly, and though the intensity of the peak experiences a significant

decrease only at very low polymer volumetric concentration (~25%), but it is still identifiable. Therefore, we conclude that polymer nano-crystalites always exist in PBDTTT-DD BHJ films.



SI-Figure 2. 2D GIWAXS patterns of PBDTTT-EE neat film (a) and PBDTTT-DD neat film (b). The line cuts were performed along q vector and integrated in a small azimuthal angle (indicated by red lines) as described in the text. (c,d) Overlaid line cuts profiles obtained from both neat polymer films and BHJ films

1. Z. Jiang, X. Li, J. Strzalka, M. Sprung, T. Sun, A. R. Sandy, S. Narayanan, D. R. Lee and J. Wang, *Journal of Synchrotron Radiation* **19** (4), 627-636 (2012).
2. J. T. Rogers, K. Schmidt, M. F. Toney, E. J. Kramer and G. C. Bazan, *Advanced Materials* **23** (20), 2284-2288 (2011).