Electronic Supplementary Information

Use of a Commercially Available Nucleating Agent to Control the Morphological Development of Solution-Processed Small Molecule Bulk Heterojunction Organic Solar Cells

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Figure S1. 2D GIWAXS images of 70:30 DPP(TBFu)₂:PC₇₁BM BHJ films without (a) and with (b) 1.4 wt. % DMDBS after isothermal anneal at 80 °C for 47 mins.

Normalized peak area data in Figure 3 in the main text was calculated using the DPP(TBFu)₂ (100) peak at $q_z = 0.43$ Å⁻¹.



Figure S2. 2D GIWAXS images of 60:40 p-DTS(FBTTh₂)₂:PC₇₁BM BHJ films cast with 1.5 vol% DIO, without (a) and with (b) 1.0 wt. % DMDBS.

The crystalline correlation length (CCL) of p-DTS(FBTTh₂)₂ was calculated using the p-DTS(FBTTh₂)₂ (001) peak at $q_z = 0.28$ Å⁻¹ and Scherrer's equation:

$$CCL = \frac{2\pi}{FWHM}$$

The full width at half maximum (FWHM) was determined by integrating the (001) peak intensity from $chi = 20^{\circ}$ to $chi = 160^{\circ}$ and then fitting with a Pseudo-Voigt function.

For both DPP(TBFu)₂:PC₇₁BM and p-DTS(FBTTh₂)₂:PC₇₁BM BHJ blends it appears that DMDBS does not change the crystal structure or crystalline texture of the donor molecule crystallites as evidenced by Figures S1 and S2.

When using a flat area detector and a grazing incidence geometry some amount of reciprocal space is not probed resulting in a missing wedge centered around $chi = 90^{\circ}$ (directly out of plane, not shown in Figure S1 or S2).¹ However, for the DPP(TBFu)₂ (100) reflection and the p-DTS(FBTTh₂)₂ (001) reflection this missing area is less than 3°, meaning we are probing all crystallites except those oriented within 3° parallel to the substrate and thus this missing wedge likely does not significantly affect our analysis.



Figure S3. Atomic force microscopy topography images of $60:40 \text{ p-DTS}(\text{FBTTh}_2)_2:\text{PC}_{71}\text{BM}$ BHJ films cast with 1.5 vol% DIO, without (a) and with (b) 1.0 wt. % DMDBS. Images are 10 µm x 10 µm.

Atomic force microscopy images of p-DTS(FBTTh₂)₂:PC₇₁BM BHJ films cast with 1.5 vol% DIO show smaller features and a reduction in surface roughness when using DMDBS, consistent with observations made with TEM and GIWAXS in the main text.

Experimental

Photovoltaic device fabrication and testing: PC₇₁BM was purchased from nano-c, DMDBS was obtained from Milliken Chemical and p-DTS(FBTTh₂)₂ was purchased from 1-Material. These materials were used as received. DPP(TBFu)₂ was synthesized as previously reported and all DPP(TBFu)₂:PC₇₁BM BHJ characterization was performed on spin-cast films from solutions identical to those previously reported for use in solar cell fabrication.² In the current work, however, DPP(TBFu)₂:PC₇₁BM BHJ films were spun cast from 60 °C solutions due to DMDBS's limited solubility in chloroform. p-DTS(FBTTh₂)₂:PC₇₁BM BHJ OPV devices were fabricated using parameters described elsewhere.³ DMDBS was incorporated directly into BHJ solutions from a DMDBS/chloroform or DMDBS/chlorobenzene stock solution for devices processed with DMDBS. All DMDBS weight percentages are expressed with respect to the total combined mass of donor and acceptor solids in solution. BHJ OPV devices were fabricated on UV-O₃ treated ITO substrates coated with approximately 45 nm of PEDOT:PSS (Clevios P VP Al 4083). DPP(TBFu)₂:PC₇₁BM or p-DTS(FBTTh₂)₂:PC₇₁BM solutions were spin cast on to PEDOT:PSS coated ITO substrates to produce an active layer approximately 90 or 100 nm thick, respectively, as measured with an Ambios XP-100 stylus profilometer. For p-DTS(FBTTh₂)₂:PC₇₁BM devices approximately 5 nm Ca was thermally evaporated on top of the active layer, followed by 100 nm of Al. For DPP(TBFu)₂:PC₇₁BM devices 100 nm of Al was evaporated directly on top of the BHJ active layer. Device characteristics were measured under illumination by a simulated 100 mW cm⁻² AM1.5G light source using a 300 W Xe arc lamp with an AM 1.5 global filter using an aperture to define a device area of 0.045 cm². Solar-simulator irradiance was calibrated using a standard silicon photovoltaic cell with a protective KG1 filter calibrated by the National Renewable Energy Laboratory. For isothermal anneal data in Figure 2, devices were annealed, then quenched to room temperature and tested, annealed, then quenched to room temperature, etc. The time on the x-axis is therefore the cumulative annealing time. The data presented in Figure 2 is the average of 12 different devices of each processing condition (with and without DMDBS) made on different days from different solutions displayed with error bars denoting the first standard deviation of data from these devices.

GIWAXS: All GIWAXS samples were fabricated by spin-casting solutions identical to those used for BHJ OPV devices fabrication onto silicon substrates previously coated with PEDOT:PSS to mimic a solar cell architecture. Silicon substrates were used to reduce background scattering from the substrate. All GIWAXS measurements were performed at Stanford Synchrotron Radiation Lightsource beamline 11-3 using a photon energy of 12.7 keV with a sample to detector distance of 400 mm. A custom built heating stage was utilized as described elsewhere for in-situ thermal annealing experiments.⁴ Experiments were performed under a helium environment to minimize background scattering and sample damage from the x-ray beam. An incident angle of 0.12° (above the critical angle of the BHJ blend, but below the critical angle of the substrate to ensure probing of the BHJ blend and not the substrate) was used in all cases. Images were collected with a MAR-345 2D image plate and processed with the software package WxDiff, provided by Dr. Stefan Mannsfeld. GIWAXS images were normalized for exposure time during data processing. We estimate our absolute temperature values have an error of \pm 3 °C. This is largely the result of temperature fluctuations as a function of position on the film as well as over time.

Transmission electron microscopy: Samples for TEM were prepared by floating prepared films in deionized water and collected on C-Flat holey carbon-coated support grids. Images were taken on an FEI Titan 300 kV field emission gun transmission electron microscope. Care was taken to minimize electron exposure. Images were taken with a 20 micron objective aperture and contrast was enhanced by inducing a relatively small amount of defocus, such that the relevant features should not be distorted by the contrast transfer function.

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