

## *Supporting Information* for

### Towards a Better Understanding of Conjugated Polymer Blends with Non-Spherical Small Molecules: Coupling of Molecular Structure to Polymer Chain Microstructure

Michael Roders,<sup>a</sup> Vincent V. Duong,<sup>a</sup> Alexander L. Ayzner<sup>\*,a</sup>

<sup>a</sup> Department of Chemistry and Biochemistry, UC Santa Cruz, Santa Cruz, CA, USA

\* [aayzner@ucsc.edu](mailto:aayzner@ucsc.edu)

#### **SI. Experimental Methods**

Doped silicon wafers (Silicon Quest International, 0.005  $\Omega \cdot \text{cm}$  resistivity) were cleaned by ultrasonication in acetone followed by isopropyl alcohol and subsequently blown dry under a nitrogen stream. Substrates were then exposed to UV-ozone treatment (Novascan, PSD-UV4) for 30 minutes in order to remove organic contaminants as well as to increase substrate wettability. An aqueous suspension of PEDOT:PSS (Heraeus, Clevious PH 1000) was spin-coated at 5000 rpm for 60 seconds to mimic a common surface found in organic photovoltaic devices. PEDOT:PSS-coated Si slides were then annealed for 30 minutes at 150° C in air to drive off residual moisture. Chloroform solutions of PCBM (Solenne b.v), PDI (Solarmer), Spiro-MeOTAD (Sigma-Aldrich), regioregular P3HT (Reike Metals, MW = 57,000 g/mol, polydispersity = 2.9, 92% regioregularity), regiorandom P3HT (Reike Metals, MW = 57,000 g/mol, polydispersity = 2.9) and poly(isobutylmethacrylate) (Sigma Aldirch, MW = 70,000 g/mol) were prepared by dissolving the solids and stirring overnight at 45° C. All materials were purchased and used as is.

All polymer/small molecule solutions were prepared at a total polymer concentration of 10 mg/mL. The P3HT:Spiro-MeOTAD solution was fixed at 1:1 w/w, while P3HT:PCBM and P3HT:PDI ratios were matched by mole to that of the Spiro-MeOTAD blend solution, resulting in weight ratios of 1:0.74 and 1:0.84, respectively. Blend solutions were filtered with a 0.45  $\mu\text{m}$  PTFE filter (Fisher Brand) prior to thin film deposition. Thin films were spin-coated from chloroform at 1500 RPM for 1 min. Samples were annealed on a hot plate at 150° C for 30 min in a N<sub>2</sub> atmosphere and then transferred to a room-temperature metal surface in the same atmosphere.

For REXS measurements, PEDOT:PSS and polymer/small molecule blend films were deposited in a nearly identical fashion as described above. However, PEDOT:PSS was not annealed to allow for its sacrificial dissolution upon exposure to water. This results in a free-standing film, which can be picked up with a soft X-ray-transparent substrate. A 0.5 cm<sup>2</sup> section of film was cut with a diamond scribe and dipped into a petri dish filled with deionized water at an approximate angle of 45° with respect to the water surface. The thin film was then floated off of the silicon wafer and picked up by a 100 nm-thick silicon nitride membrane supported by a silicon frame (Norcada, 5100XC). Excess water was wicked off with a Kimwipe, and the membranes were then dried under vacuum. Samples were annealed in a N<sub>2</sub> atmosphere at 150° C for thirty minutes followed by cooling on a room-temperature metal surface.

Grazing incidence X-ray diffraction (GIXD) was performed at the Stanford Synchrotron Light Source beamline 11-3 using a 26-pole, 2.0-Tesla ID source operating at 12.7 keV (0.974 Å). The sample-to-detector distance and scattering vector were calibrated using a polycrystalline lanthanum hexaborate sample. Samples were exposed to the incident beam for 180 s. 2D scattering data collected using an area detector and processed in the WxDiff software package. Grazing-incidence small-angle X-ray scattering (GISAXS) was performed at the Advanced Light Source

beamline 7.3.3 using a 10 keV (1.24 Å) beam from a bend magnet source. The sample-to-detector distance (approximately 4 m) was calibrated with a crystalline silver behenate standard. Measurements were performed at multiple positions along the surface of a sample in order to collect statistically representative data. Scattering data was collected by a Pilatus 2M detector and normalized by the incident photon flux. One-dimensional line cuts of intensity as a function of the in-plane scattering vector component  $Q_{xy}$  were taken at  $Q_z = 0.18 \text{ \AA}^{-1}$ . Grazing incidence angles greater than the calculated critical angle for materials comprising the thin films were used for GIXD ( $0.12^\circ$ ) and GISAXS ( $0.15^\circ$ ) in order to probe the bulk of the films. We performed incident angle-dependent GISAXS measurements to ensure that the bulk of the film was probed (not shown).

Transmission resonant elastic X-ray scattering (REXS) measurements were performed at the Advanced Light Source beamline 11.0.1.2 using a 5.0 cm period elliptical polarization undulator (EPU5) source in a high vacuum scattering chamber ( $10^{-7}$  Torr) with a 150 mm sample-to-detector distance calibrated with 300 nm polystyrene spheres. Prior to scattering measurements, near-edge X-ray absorption spectra were collected using a photodiode detector to determine the X-ray energy set used for REXS measurements. 2D REXS images were collected using an in-vacuum CCD for nine positions per sample and reduced to one-dimensional curves by angular averaging in the Nika analysis package written in IGOR by Jan Ilavsky (Advanced Photon Source, Argonne National Lab). Scattering due to the silicon nitride substrate was subtracted from the total scattering.

## **III. As-Cast GIXD**

Figure S1 shows GIXD images of as-cast neat polymer films spin-coated from chloroform solutions. The regioregular P3HT (reP3HT) film (Fig. S1a) shows expected diffraction peaks due to lamellae ( $h00$ ) and backbone  $\pi$ -stacking ( $0k0$ ). reP3HT crystallites are oriented predominantly edge-on, though the distribution is quite broad. The absence of Bragg peaks in regiorandom P3HT (raP3HT) and poly(isobutylmethacrylate) (Figs S1b and S1c, respectively) show that both polymers are amorphous.

Figure S2 shows GIXD images of as-cast (a) and thermally annealed (b) reP3HT:PDI blends spin-cast from chlorobenzene, which has a slower evaporation rate than chloroform, allowing more time for the components to lower their free energies before the film morphology becomes locked in. The annealed blend image shows that PDI forms unoriented crystallites in reP3HT when cast from chlorobenzene, which is on contrast to the same blend cast from chloroform. The latter showed no evidence for PDI crystallization.

Figure S3 shows the as-cast reP3HT crystallite orientation distribution functions in neat films and in blends as a function of small molecule. Though quantitatively this data differs from thermally annealed ODFs, qualitatively the trends are still preserved. The only qualitative difference is in Spiro-MeOTAD blends, which appear to contain reP3HT crystallites that are less oriented edge-on relative to neat reP3HT.

### **SIII. As-Cast GISAXS**

Figure S4 shows 1D GISAXS curves for as-cast blends in both reP3HT and raP3HT matrices. All curves appear relatively featureless, indicating that the small molecules are well-

dispersed in polymer matrices. This is consistent with the rapid evaporation kinetics of chloroform, which suppress small molecule clustering on the 10s of nanometers length scale.

#### **SIV. REXS of reP3HT:PCBM Blend**

The REXS curve of a thermally annealed reP3HT:PCBM blend collected above the absorption threshold at 284.4 eV is shown in Figure S5 over a Q range that has been extended to higher values relative to Figure 6c of the main text. The extended REXS curve makes the similarity with the corresponding (off-resonant) GISAXS curve (Figure 5a of the main text) clear, as both curves exhibit a well-defined plateau region. We interpret this as a signature of a relatively well-defined length scale of blend phase separation.

#### **SV. Near-Edge X-Ray Absorption Spectra**

Near-edge X-ray absorption spectra collected at the carbon K-edge are shown in Figure S6. We have magnified the region in the immediate vicinity of the absorption onset; absorption in this region for organic semiconductors is primarily due to C 1s  $\rightarrow$   $\pi^*$  transitions. Since all the molecules in this study contain unoccupied  $\pi^*$  orbitals, transitions due to different species overlap fairly strongly. Once above the absorption threshold, we did not find significant qualitative changes in REXS curves as a function of photon energy.

FIG. S1. GIXD patterns for thin films of neat as-cast polymer films: a) regioregular P3HT, b) regiorandom P3HT, and c) poly(isobutylmethacrylate). The semicrystalline nature of rrP3HT is illustrated by three orders of Bragg reflections along the  $Q_z$  direction corresponding lamellar packing in the  $(h00)$  crystallographic direction and a reflection at  $Q \sim 1.6 \text{ \AA}^{-1}$  corresponding to inter-chain  $\pi$ -stacking in the  $(010)$  plane. The other two polymers are amorphous.

FIG. S2. GIXD patterns for (a) as-cast and (b) annealed blends of rrP3HT and PDI spin-coated from chlorobenzene (boiling point = 130 °C). In contrast to films spin-coated from chloroform (boiling point  $\sim 60 \text{ °C}$ ), the amorphous PDI phase evolves into isotropic crystallites upon thermally annealing, indicated by the presence of several isotropic Bragg reflections.

FIG. S3. Orientation distribution functions of the rrP3HT lamellar  $(100)$  Bragg reflections as a function of the polar angle in as-cast thin films of neat rrP3HT films as well as in blends with small molecules at the same monomer/small molecule mole ratio. The polar angle =  $0^\circ$  for the surface normal.

FIG. S4. GISAXS curves for (a) rrP3HT and (b) raP3HT blends of small molecules. All curves are featureless corresponding to films with no phase segregation on the order of 10 – 100 nm.

FIG. S5. REXS curve collected at 284.4 eV for a blend film of reP3HT and PCBM showing a distinct shoulder at approximately  $Q \sim 0.01 \text{ \AA}^{-1}$ . This is in good agreement with results from GISAXS measurements. An extended  $Q$ -range is collected by stitching together measurements from the same sample and two sample-to-detector distances (50 and 150 mm).

FIG. S6. Near-edge X-ray absorption spectra at the C K-edge. The shown spectral region primarily corresponds to  $C 1s \rightarrow \pi^*$  transitions.

FIG. S7. 3D models of (a) Spiro-MeOTAD and (b) PDI. Two perspectives are shown for each molecule. Structures were built using the Avogadro Software Package. Structural optimization was done using the included UFF force field.

TABLE 1. Molecular parameters calculated using Biovia's Discovery Studio.

Molecule	Solvent-Excluded Volume ( $\text{\AA}^3$ )	Surface Area ( $\text{\AA}^2$ )
PCBM	735	541
PDI	1418	1306
Spiro-MeOTAD	1463	1217