

Supporting Information

The Impact of the Crystallite Orientation Distribution on Exciton Transport in Donor-Acceptor Conjugated Polymers

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S1. Experimental Details

PII2T-ref and PII2T-Si were synthesized according to procedures described previously. Polymer solid was dissolved in chloroform and stirred while heating at $\sim 55\text{ }^{\circ}\text{C}$ in an N_2 glovebox until dissolution. Solutions were cooled down to room temperature on the hotplate and used soon after to avoid issues associated with solution metastability. Films were deposited onto both pre-cleaned microscope glass and titania films on glass side by side. Titania was deposited by ALD and subsequently annealed in air at $370\text{ }^{\circ}\text{C}$ for one day, resulting in $\sim 40\text{ nm}$ thin films. After spin-coating polymer solutions at 1000 rpm for 30 s, films were thermally annealed at $170\text{ }^{\circ}\text{C}$ for one hour. The films were placed on the hotplate at room temperature and removed from it when the temperature reached $\sim 45\text{ }^{\circ}\text{C}$.

Steady-state PL measurements were performed in air with a Horiba Nanolog fluorometer using front-face detection. Integration times were set to 0.1 s per point, which minimized the light exposure time while providing sufficient signal-to-noise ratios. Generally, care was taken to strictly limit film exposure to ambient lights between measurements. Spectra were first integrated in order to compute the PL quenching ratio.

Grazing-incidence X-ray diffraction measurements were performed at the Stanford Synchrotron Radiation Lightsource (SSRL) at beamline 11-3. Samples were placed in a He atmosphere during X-ray exposure to minimize background scattering and limit beam-induced damage. The incidence angle was set to 0.12 ° , and vertical and horizontal slits were set to 50 and $150\text{ }\mu\text{m}$, respectively. X-ray reflectivity measurements were performed at SSRL beamline 2-1, and no sign of sample damage was seen during any of the measurements.

NEXAFS measurements were collected at the NIST/Dow beamline U7A of the National Synchrotron Light Source (NSLS-I) of Brookhaven National Laboratory. Measurements were

collected at the carbon K-edge in partial electron yield (PEY) mode with a grid bias of -50V in front of the channeltron detector. The energy resolution of the beamline was ± 0.1 eV. The uncertainty of the yield measurement is $\pm 2\%$ of its reported value.

Photoluminescence (PL) decays were recorded after excitation through the glass (quartz) substrate at 660 nm with a train of pulses (~ 150 ps FWHM), and emission was collected at 760 nm with a cooled photon counting photomultiplier tube (Hamamatsu H6279) using time-correlated single-photon counting. The PL decays were analyzed using a non-linear least squares iterative reconvolution procedure, where the finite width of the instrument response function was effectively deconvoluted from the measured data to give an overall temporal response of ~ 20 ps. Data were fit to a sum of two exponentials.

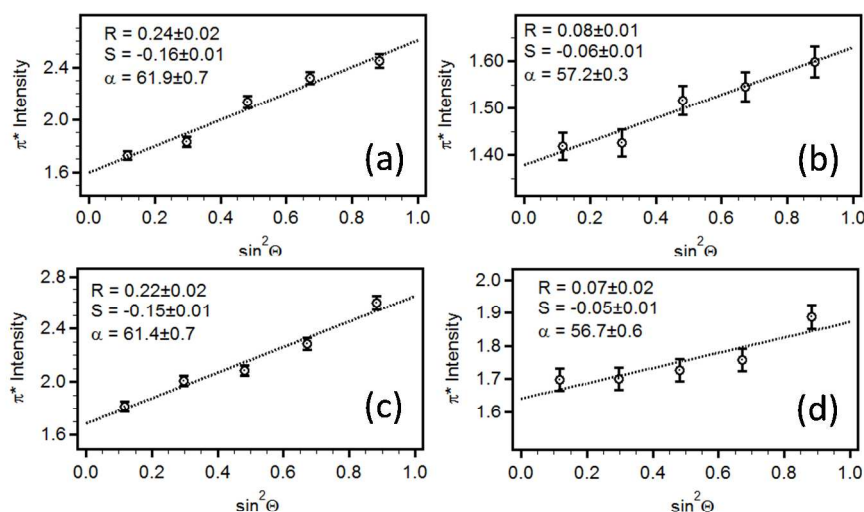


Figure S1. Angular dependence of NEXAFS π^* intensities for PII2T-ref (a, b) and PII2T-Si (c, d).

S2. NEXAFS Spectroscopy

As noted in the main text, we found that NEXAFS intensities as a function of incidence angle exhibited sample-to-sample variation. Figure S1 below shows these intensities as a function of angle for two samples for each polymer. As can be seen from the Figure, the tilt

angle varied from near magic angle to $\sim 28^\circ\text{C}$. These results suggest that the presence of a surface may induce a molecular orientation that is different from the bulk.

S3. Exciton Quenching Calculations

We attempted to model the exciton quenching as a function of thickness using the 1-D exciton diffusion equation with perfectly-quenching perfectly-reflecting exciton boundary conditions for titania and glass, respectively. Briefly, the spatial distribution of excitons along the direction of incoming light is given by the diffusion equation as

$$\frac{d^2n}{dx^2} - \frac{n}{D\tau} + \frac{G}{D} = 0$$

where n is the exciton density, D is the diffusion coefficient, τ is the exciton lifetime, and G is the generation rate of excited states, which depends on the spatial coordinate x . The exciton generation rate is proportional to the intensity of the incident light, which we calculated using the transfer matrix formalism using a modified version of the MATLAB code from the McGehee group at Stanford University.

The complex refractive index used in the above calculations was obtained via spectroscopic ellipsometry. Absorption values for the films at a range of wavelengths were collected and fit to a model within the J. A. Woolam CompleteEASE software that included each layer of the sample. Based on the absorption values, the thickness of the film and refractive index were determined.

The boundary value problem was solved using a built-in MATLAB routine. To connect with experiment, the exciton density was integrated over the film thickness, making it proportional to the measured PL intensity. We find that this model is unable to describe our data satisfactorily, resulting in an unacceptably large spread in extracted exciton diffusion values. This is shown in Figure S2 for both PII2T-ref and PII2T-Si. The discrepancy between the data and the model could arise from a number of factors, such as the simplistic boundary conditions used in the model, the assumption of zero quenching by the glass substrate, and vertical inhomogeneity in film microstructure at different thicknesses, the latter being difficult to isolate using bulk-averaged X-ray diffraction.

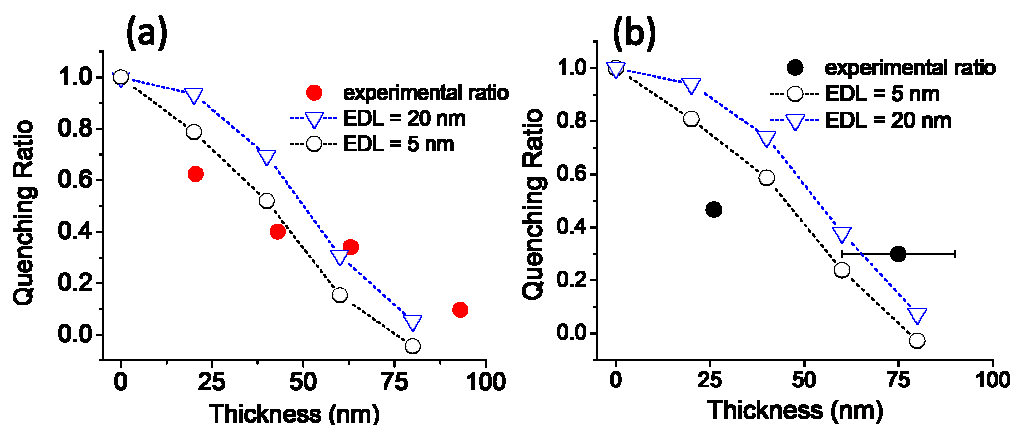


Figure S2. Exciton diffusion calculations superimposed on the experimental quenching ratios of a) PII2T-ref and b) PII2T-Si. The fits to the data are far from satisfactory. The highest thickness data point for PII2T-Si is not shown on this scale.

S4. Grazing-Incidence X-ray Diffraction (GIXD)

To ensure that the dominant textural motifs were preserved for different thickness and on different substrates, in Figure S3 we show GIXD images of PII2T-ref and PII2T-Si thin films on both glass and titania substrates. It is clear that both polymers preserve their crystallographic texture; that is, PII2T-ref remains edge-on oriented and PII2T-Si shows dual texture with a

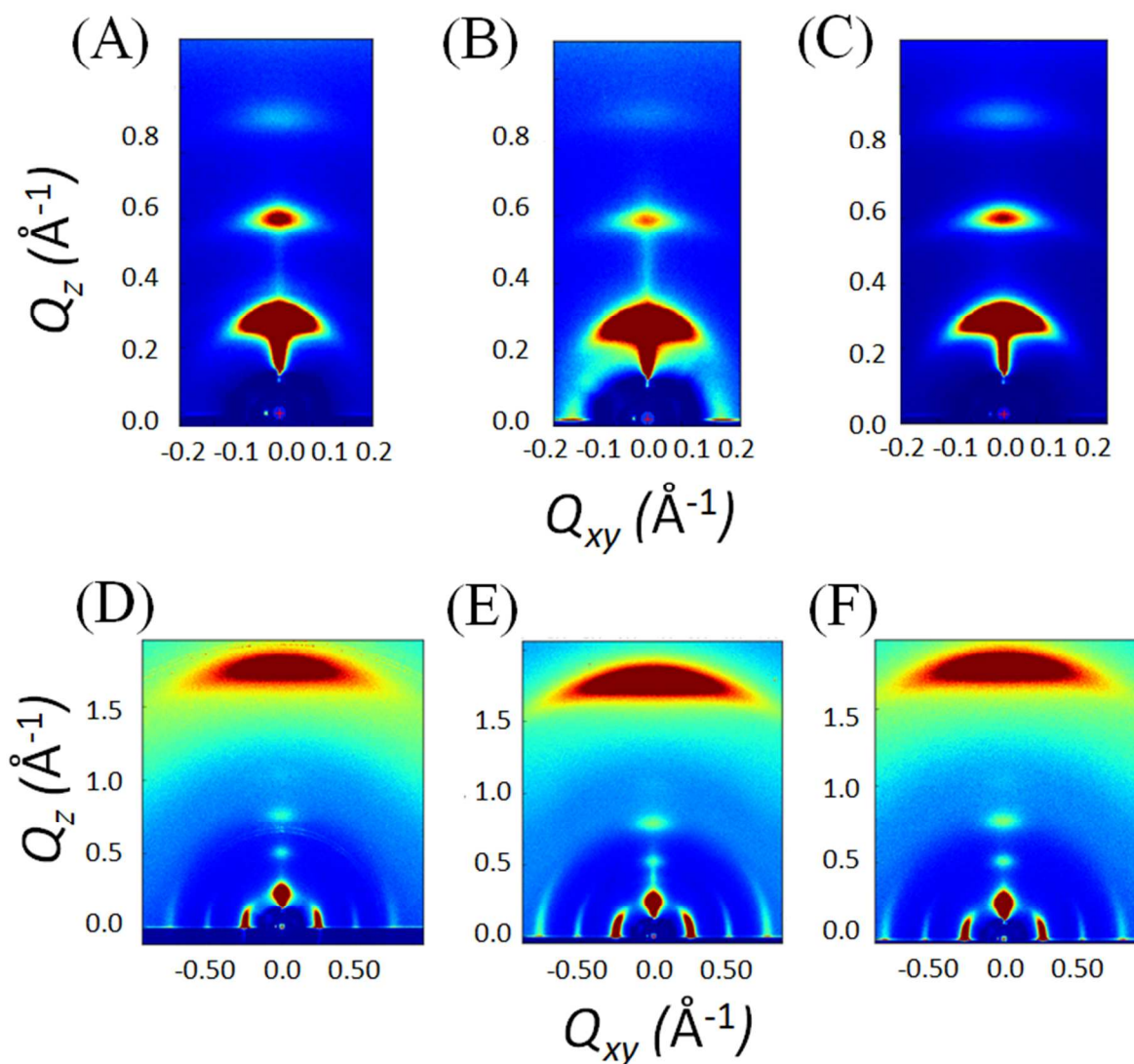


Figure S3. GIXD patterns of PiI2T-ref and PiI2T-Si on glass and titania. A) PiI2T-ref ~ 60 nm on glass; B) PiI2T-ref ~ 100 nm on glass; C) PiI2T-ref ~ 100 nm on titania; D) PiI2T-Si ~ 65 nm on glass; E) PiI2T-Si ~ 100 nm on glass; F) PiI2T-Si ~ 65 nm on titania.

dominant face-on motif independent of the substrate or thickness. We note that for the lowest thicknesses, PiI2T-ref is actually more edge-on than higher thicknesses, since thicker films show some deviation from perfect edge-on orientation, as discussed in the main text. At such small

thicknesses, PiI2T-ref shows a clear (200) lamellar Bragg reflection, but the (100) reflection is absent.

Additionally, Figure S4 shows GIXD patterns from a thin PiI2T-ref films below and above the critical angle for total external reflection. Below the critical angle, only the top ~ 5 nm

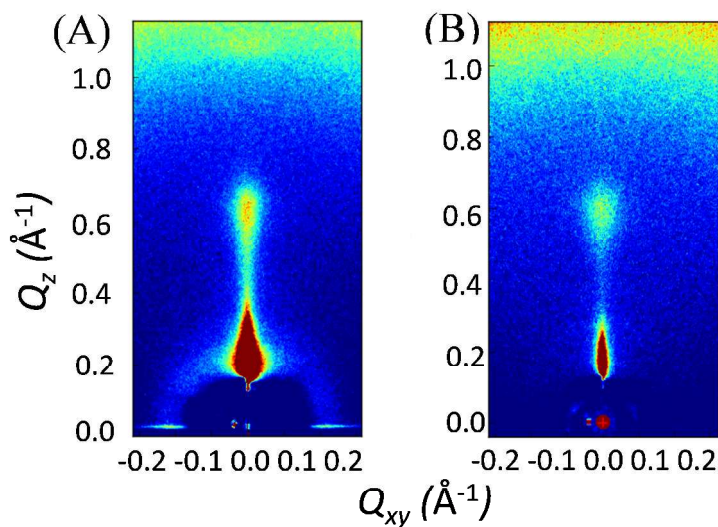


Figure S4. GIXD pattern of ~ 20 nm PiI2T-ref film on glass at two incidence angles: A) above the critical angle; B) below the critical angle. The faint low-Q arc in A) is an artifact from the glass substrate. This arc is absent in B) since only the top ~ 5 nm is probed below the critical angle.

of the film is sampled, whereas above the critical angle, the GIXD pattern is due to the entire film bulk. As is clear from the images, the scattering pattern is essentially unchanged, showing that crystallite orientation at the top surface and the film bulk is similar.

S5. Time-Resolved Fluorescence (TRPL)

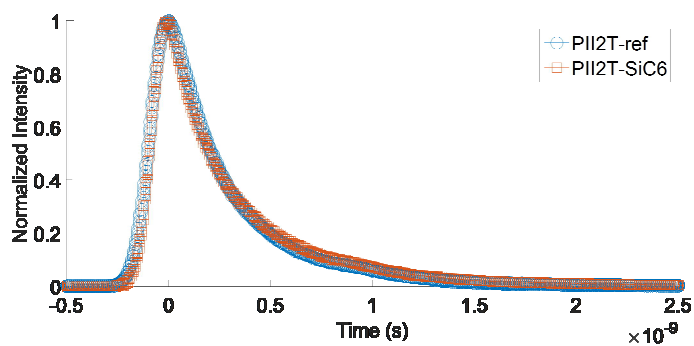


Figure S5. Time-resolved fluorescence curves for the two polymer films collected via time-correlated single-photon counting.

Figure S5 shows the TRPL curves for both polymers on glass. It is clear the PL dynamics are very similar for both films. The PL lifetimes are provided in the main text.