Supporting Information for

Observation of a distinct surface molecular orientation in films of a high mobility conjugated polymer

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Full details of synchrotron experiments:

Nearly perfectly linearly polarized photons (P ≈ 1) from an undulator x-ray source with high spectral resolution of E/ΔE ≤ 10 000 were focused into an ultrahigh vacuum chamber with a ~0.4 × 1 mm sampling area. The AEY signal was recorded with a SPECS Phoibos 150 Hemispherical Analyzer set to a kinetic energy of 230 eV, while the TEY signal was recorded via the drain current through the sample. TEM grids were mounted onto the sample holder with conductive carbon tape to ensure electrical connectivity. The electron yield signals were normalized to the incident photon flux using the "stable monitor method",[26] in which the sample signal is compared consecutively to a clean reference sample and the time variations in flux measured via a gold mesh. The normalized spectra were scaled by subtracting a background which scales according to the atomic scattering factors of the material prior to the onset of the first feature setting (that is, the absorption measured at 280 eV) and then normalizing to the value at 320 eV. Transmission spectra were acquired by measuring the transmitted photon flux with an AXUV100 photodiode from International Radiation Detectors, Inc, placed directly behind the sample holder. The measured transmitted x-ray intensity, I, was compared to the incident x-ray intensity, I_0, and converted to optical density via:

$$OD = \ln(I_0/I)$$

The resulting transmission spectra were similarly normalized by subtracting the value at 280 eV and normalizing to the value at 320 eV. Fluorescence yield (FY) NEXAFS spectra were also simultaneously acquired using a multi-channel plate fluorescence yield detector for comparison. Peak fitting was performed using 'Whooska,' a MatLab-based GUI developed by Dr. Benjamin Watts.

Grazing-incidence wide-angle scattering (GIWAXS) measurements were performed at the SAXS/WAXS beamline at the Australian Synchrotron. 14 keV photons were directed onto the sample to produce 2D scattering patterns recorded on an MAR-165 CCD detector. The sample-to-detector distance was calibrated using a silver behenate standard. A grazing angle of 0.10° was used that is close to the critical angle of the polymer films (giving a penetration depth similar to the film thickness) but below the critical angle of the substrate. GIWAXS data were also taken as a function of angle of incidence to check for any changes with differing surface sensitivity. Data acquisition times of 60 s were used with no evidence found for beam damage when comparing data taken at shorter and longer acquisition times. GIWAXS data were analyzed using the software SAXS15ID version 3299. X-ray diffraction data are expressed as a function of the scattering vector, q, that has a magnitude of (4π/λ)sinθ, where θ is half the scattering angle and λ is the wavelength of the incident radiation.

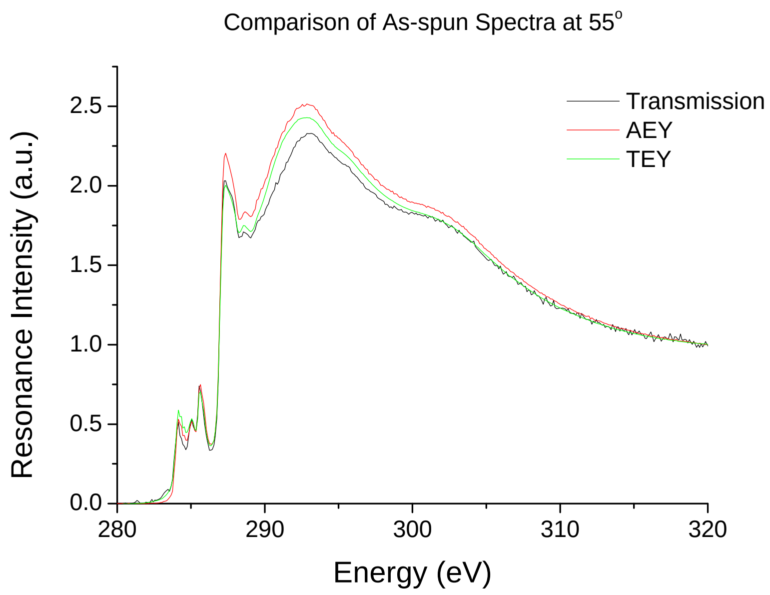


Figure S1. Comparison of the NEXAFS spectrum of the as-spun P(NDI2OD-T2) film acquire using the three different acquisition modes.

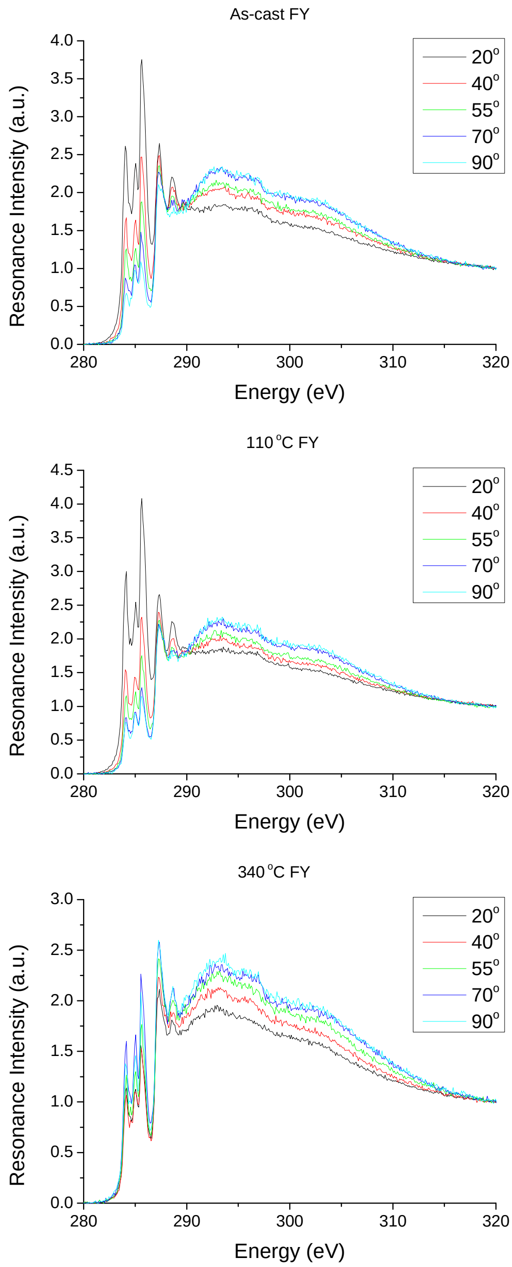


Figure S2. Angle-resolved fluorescence yield (FY) NEXAFS demonstrating similar bulk dichroism to that measured using transmission mode acquisition. Note that the FY spectra are distorted relative to the spectra acquired using the other transition modes making quantitative analysis with FY problematic.

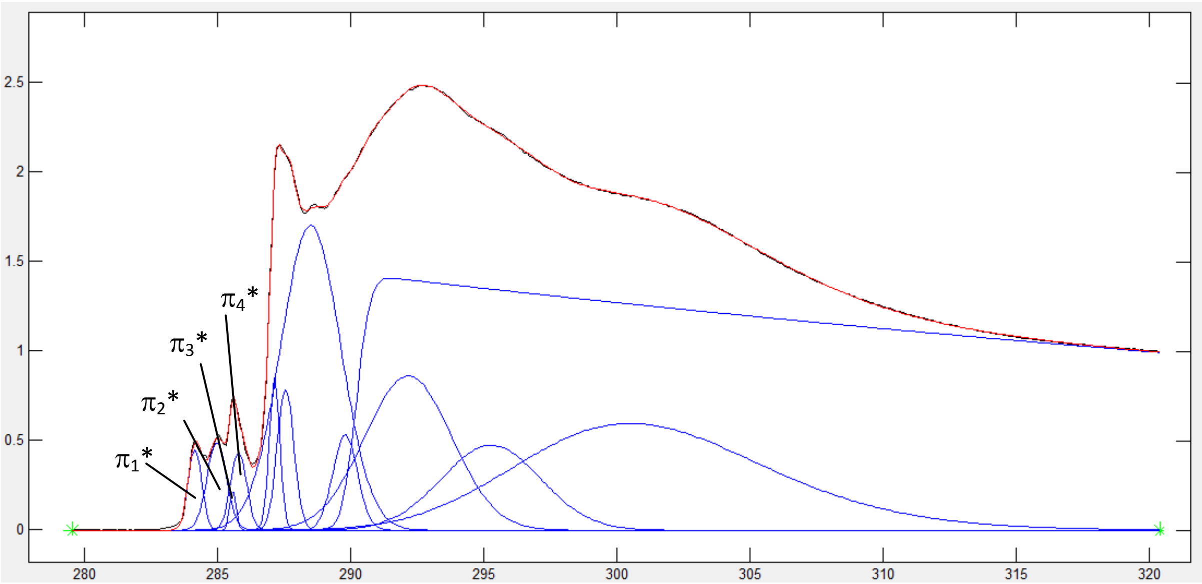


Figure S3. Example of NEXAFS peak fitting using the MatLab-based GUI 'Whooska' developed by Dr. Benjamin Watts. The NEXAFS spectrum is fitted to a sum of Gaussian peaks and a step-edge corresponding to ionization of the 1s state. The first four peaks used for determining the area of the π* manifold are identified.

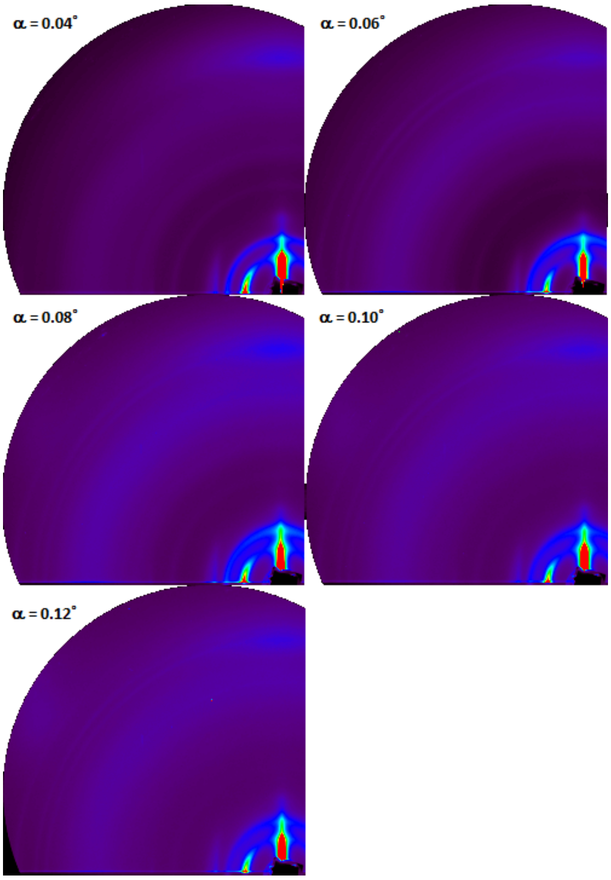


Figure S4. GIWAXS spectra of the as-cast film as a function of angle of x-ray angle of incidence. Note that the concentric rings that are more prominent in the images taken at lower angles are due to scattering from a kapton window used in the experiment.

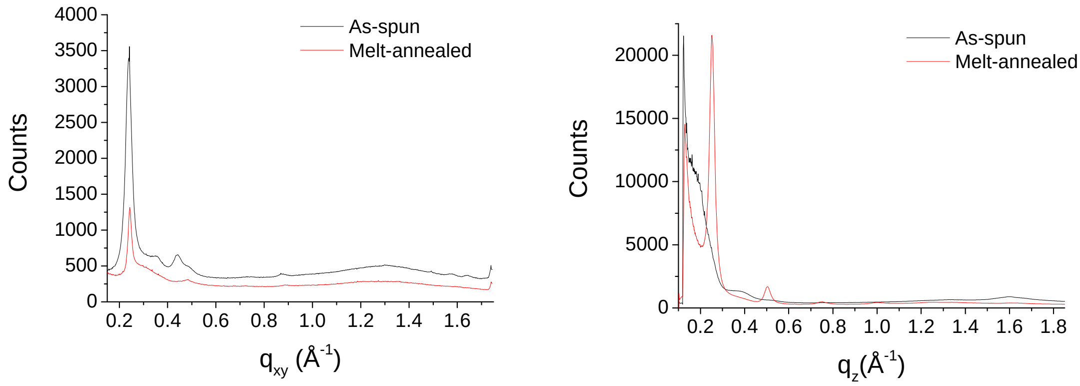


Figure S5. GIWAXS projections along q_{xy}, left, and q_z, right, for the as-spun and melt-annealed films.

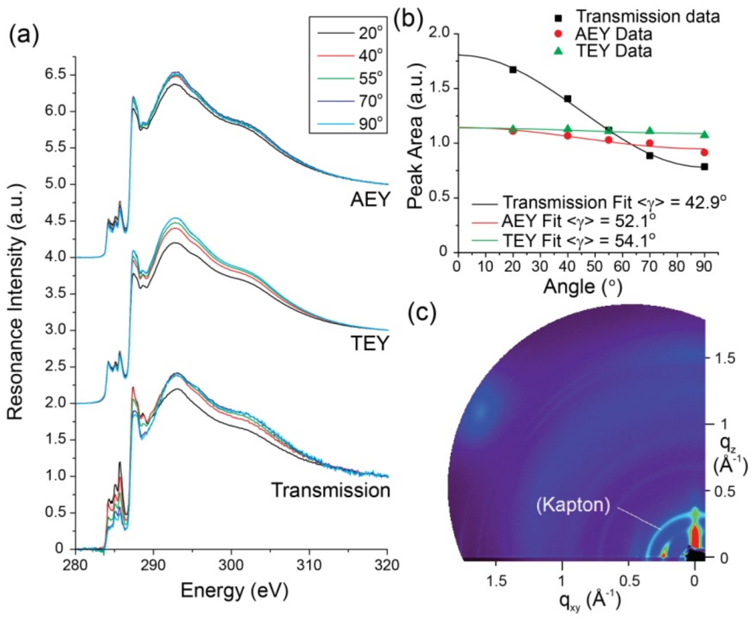


Figure S6. (a) Angle-resolved AEY, TEY and transmission NEXAFS spectra of the 110˚C-annealed P(NDI2OD-T2) film. (b) Plot of the area of the π* manifold vs angle (points) with solid lines showing fits to the data. (c) 2D GIWAXS scattering pattern of the same film.

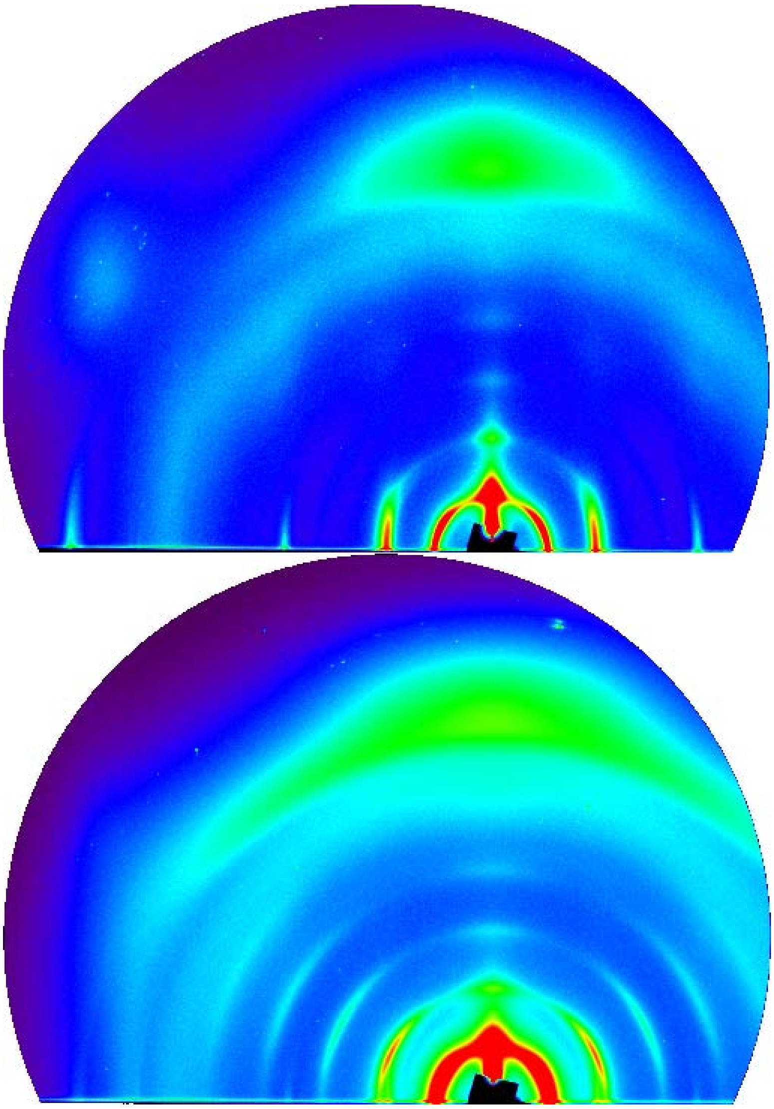
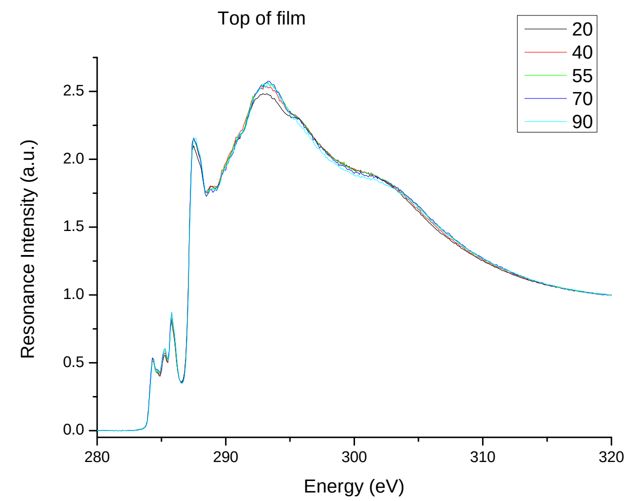


Figure S7. GIWAXS patterns of the zone-cast film taken for the two cases where the in-plane momentum transfer is parallel (top) and perpendicular (bottom) to the zone-casting direction.



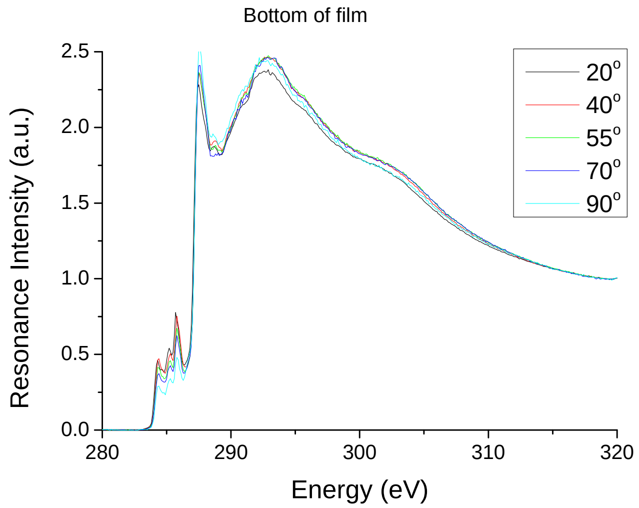


Figure S8. Angle-resolved AEY NEXAFS spectra of the top and bottom of an P(NDI2OD-T2) film prepared on OTS-treated silicon.

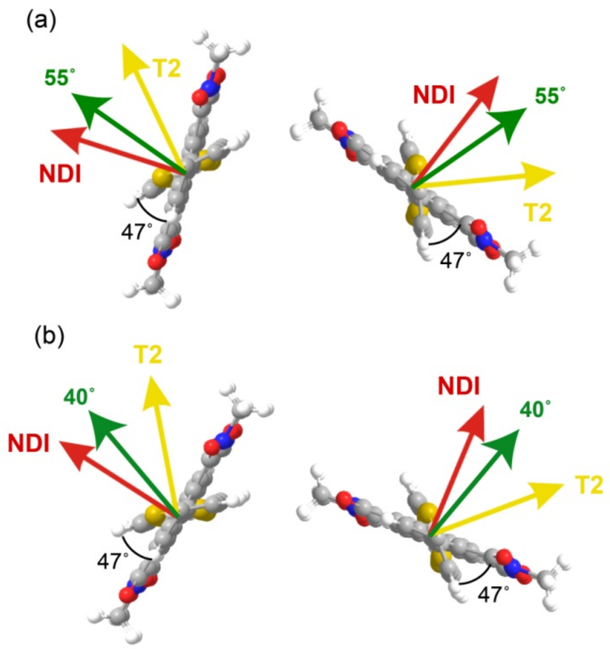


Figure S9. Schematic diagram showing two different molecular configurations corresponding to the tilt angles of the overall TDM (green) of 55˚, (a), and 40˚, (b).