

## Determining Nanoscale Molecular Ordering in Semiconducting Polymers

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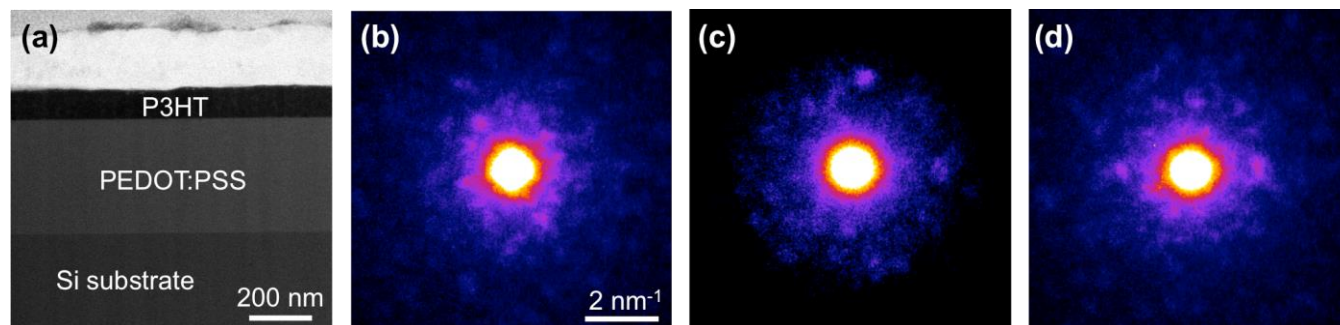
Organic semiconductors have opened tremendous new opportunities in novel electronics and energy generation with their unmatched advantages including structural flexibility and inexpensive processing methods. Enhancing the materials' performance and stability is necessary to fully utilize their properties, and this requires establishing the detailed relationship between processing, structure, and properties of the material. In particular, the nanoscale molecular ordering in their structure critically affects their electric, photovoltaic, and mechanical properties [*e.g.* 1], and therefore understanding the details of the molecular ordering and how it relates to the properties is critically required. However, the characterization of ordering has been difficult since it is typically buried inside a disordered matrix, and the signal from such small and elusive ordering is usually very weak. Moreover, radiation damage has largely prevented the detailed investigation of the ordering using electron microscopy (EM) techniques.

We present a new EM technique that can determine the detailed structure of molecular ordering in organic semiconductors. Our technique is based on electron nanodiffraction using a highly coherent electron probe that captures the diffraction signal directly from the local ordering, and determines the type, size, connection, and distribution of the ordering far beyond the limits of any conventional methods. High-brightness electron source enables high signal-to-noise ratio even with a very short exposure time (100 msec) and low beam current, which also greatly suppress radiation damages. Combined with *in situ* conditions (*e.g.* cryo and annealing), we study the structure and dynamics of molecular ordering, which is critical for understanding the detailed structure-property relationship that has been unobtainable using other methods, including the commonly used grazing incident X-ray diffraction. The ordering needs to be determined in a statistically robust manner, and therefore we acquire at least a few hundred nanodiffraction patterns from one sample, and analyze the data using fluctuation microscopy [2] and angular correlation analyses [3] to reveal the details of the ordering.

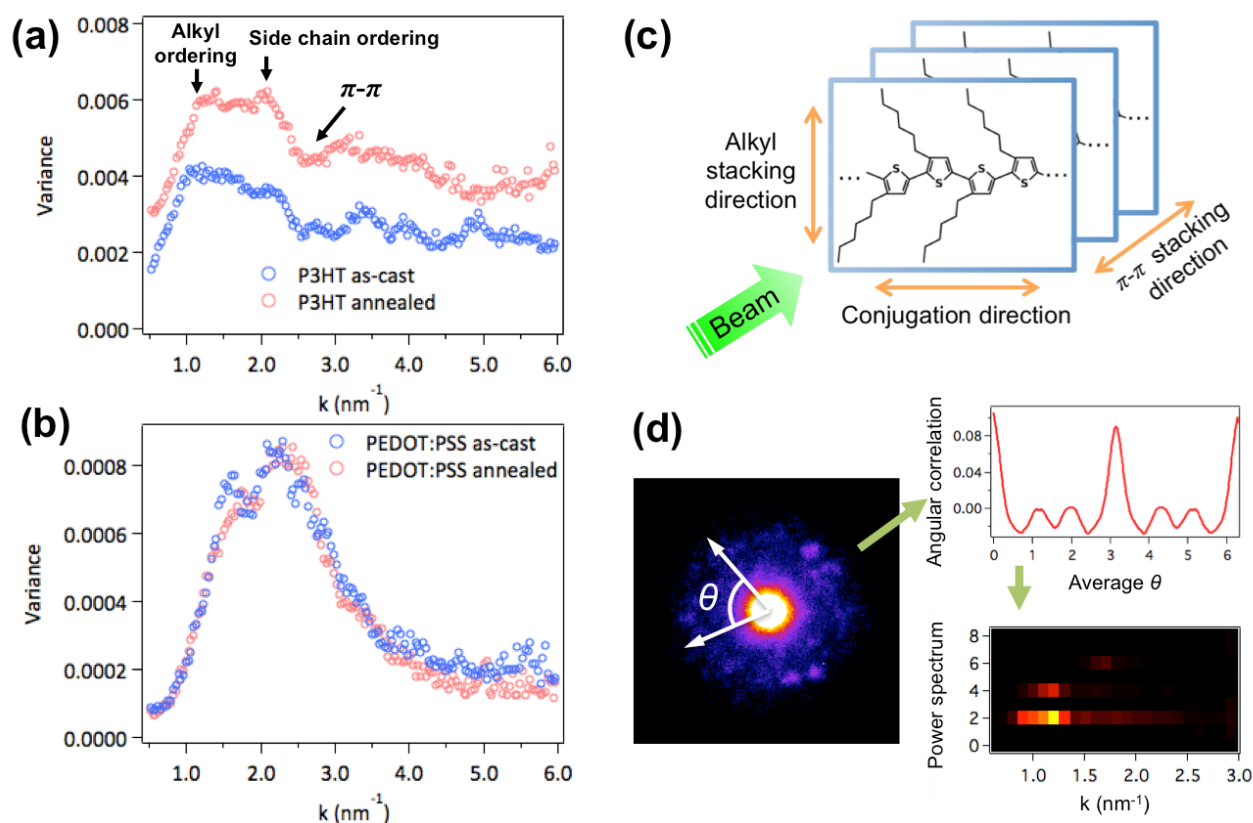
We investigated spin-coated P3HT and PEDOT:PSS polymer semiconductors (Fig. 1a). Using a 2 nm-sized probe, the diffraction patterns were taken from ~ 500 different areas of each layer. The patterns (Fig. 1b-d) are different from each other, indicating structural heterogeneity at the nanoscale. Statistically robust information on the scattering vector magnitude ( $k$ ) and the rotational symmetry of the diffraction speckles can reveal the details of the ordering, which we obtain using fluctuation microscopy and angular correlation analyses, respectively. Fig. 2a and 2b shows the intensity variance among the diffraction patterns, which represents the degree of the ordering, as a function of  $k$  that relates to the "intermolecular" spacing inside the ordering. The peak at  $\sim 1.2 \text{ nm}^{-1}$  (the expected distance of alkyl stacking) is high, while the peak at  $\sim 2.5 \text{ nm}^{-1}$  ( $\pi$ - $\pi$  ordering), is relatively low, indicating the orientation of the ordering with respect to the beam (Fig. 2c). The peak at  $\sim 2 \text{ nm}^{-1}$  may be related to the side chain ordering, which had been difficult to observe previously. *In situ* annealing at  $130^\circ\text{C}$  increased the degree of ordering in P3HT (Fig. 2a), but the PEDOT:PSS structure was not changed by the annealing (Fig. 2b), as it typically requires higher temperature ( $\sim 250^\circ\text{C}$ ) for the change. Angular correlation analysis revealed that the ordering mostly has 2-fold symmetry (Fig. 2d), consistent with the expected molecular stacking morphology. Our new approach therefore provides a powerful new tool to establish important structure-property relationships in a broad range of functional organic materials.

## References

- [1] Y. Olivier et al., *Advanced Materials*, 26, 2119 (2014).  
 [2] J. Hwang et al., *Phys. Rev. Lett.* 108, 195505 (2012).  
 [3] J. M. Gibson, M. M. J. Treacy, T. Sun, and N. J. Zaluzec, *Phys. Rev. Lett.* 105, 125504 (2010).



**Figure 1.** (a) Cross sectional view of the sample containing P3HT and PEDOT:PSS polymer layers. (b to d) Examples of electron nanodiffraction patterns acquired using 2 nm probe from the P3HT layer. Speckles in the patterns contain detailed information about the structure of the local molecular ordering.



**Figure 2.** Fluctuation microscopy variance data showing the details of the molecular ordering in (a) P3HT and (b) PEDOT:PSS. Annealing enhances the degree of ordering in P3HT. (c) Molecular stacking model of P3HT. The detailed type and orientation of the ordering change the peak position and amplitude in variance plot. (d) Angular correlation analysis procedure. Each diffraction pattern is unwrapped and the averaged angular correlation as a function of the azimuthal angle,  $\theta$ , is calculated. Power spectrum of the correlation may further provide quantitative symmetry information.