Four-Dimensional Scanning Transmission Electron Microscopy Identification of Molecular Ordering in Organic Semiconducting Polymers

Gabriel Calderon Ortiz[1], Menglin Zhu[1], Letian Dou[2] and Jinwoo Hwang[3]

[1]The Ohio State University, United States, [2]Purdue University, United States, [3]Materials Science and Engineering, The Ohio State University, United States

A wide variety of materials has been studied in order to fabricate affordable and flexible electronic devices such as solar cells, and transistors. Among these, organic semiconducting polymers have several desirable qualities such as low cost, easy processing, and structural flexibility. The main challenge so far is the relatively low efficiency of these devices compared to inorganic materials. A thorough characterization of these polymers is required to establish structure-property relationships that could lead to improved performance [1]. However, challenges arise because the molecular ordering in polymer-based films is much more subtle and illusive as compared to the ordering in small molecule-based systems that tend to crystallize easily. As a result, the nanoscale details of the ordering in polymer-based systems still remain largely unknown. In this work, we demonstrate a novel characterization based on four-dimensional scanning transmission electron microscopy (4D-STEM) that enables the identification and quantification of nanoscale ordered domains in organic semiconducting polymers [2]. 4D-STEM acquires multiple diffraction patterns as function of position as shown in Figures 1a and 1b. Our characterization combines high spatial resolution (~1nm) and high dynamic range in signal detection, which allows for quantitative determination of ordering parameters such as type, size, and volume fraction of the ordered domains with unprecedented precision.

We studied Poly(3-hexylthiophene-2,5-diyl) (P3HT) and P3HT: Phenyl-C61-butyric acid methyl ester (PCBM) (P3HT: PCBM). These polymers have been used as a standard organic photovoltaic material, but their structural ordering is complex and hence not fully understood. We first calculated the intensity variance (Figure 1c) among thousands of diffraction patterns, which was found to be correlated to the expected alkyl and π-π stackings of P3HT. With the addition of the new generation pixelated detector, real space reconstruction of the nanoscale ordered regions can be achieved at different scattering vectors (k), which provides further information of the type of ordering and orientation of the polymer. Two-dimensional histograms were constructed showing the average number of the ordered domains as a function of their size and scattering vector, shown in Figure 1d. The histogram shows a very detailed size distribution of the ordered domains and how they are related to the type of the ordering (which is represented by the k value). The new detailed information on molecular ordering can be directly compared to theoretical models and simulations, as presented in Figure 1e, in which is shown that simulated models of each type of ordered domain reveled in the 2D histogram can be identified, as indicated in Figure 1d by the red marker [3].

In summary, our new analysis provides detailed information on type, size, volume fraction, spatial and orientation distribution of the molecular ordering at the nanoscale. By providing such level of detail our technique can potentially help establish better structure-property relationships and improve the overall understanding of P3HT, P3HT:PCBM, and similar beam sensitive systems that have medium range order.
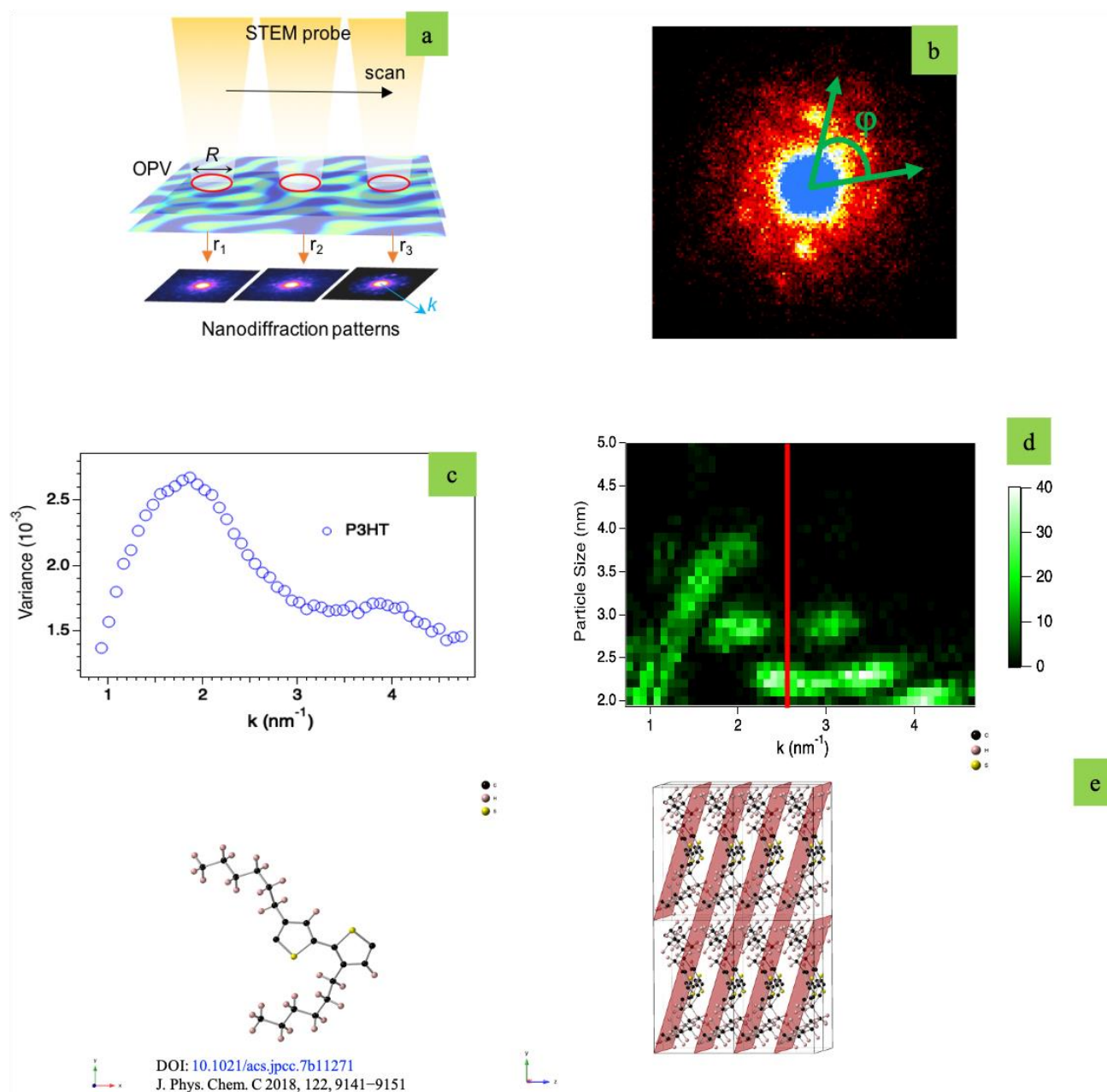
Figure 1. Figure 1: (a) 4D-STEM diffraction pattern acquisition over the polymer matrix. Different nano-diffraction patterns indicate heterogeneity of the sample. (b) Single diffraction pattern from P3HT thin film. (c) Intensity variance of P3HT after in-situ annealing at 130ºC for 1 hr. (d) Two dimensional histogram showing aglomeration of particle sizes at different k space, which provides higher level of detail compared to figure 1c. (e) P3HT model from literature was used to simulate the different ordered domains and identify them in the 2D histogram, as indicated with the red marker on figure 1d.

References
[1] Olivier, Y., Niedzialek, D., Lemaur, V., Pisula, W., Mullen, K., Koldemir, U., … Beljonne, D. (2014). 25th Anniversary Article: High-Mobility Hole and Electron Transport Conjugated Polymers: How

Structure Defines Function. *Advanced Materials VO - 26*, (14), 2119. https://doi.org/10.1002/adma.201305809

[2] Im, S., Chen, Z., Johnson, J., Zhao, P., Hee Yoo, G., Soo Park, E., Wang, Y., Muller, D., Hwang, J. (2018). Direct determination of structural heterogeneity in metallic glasses using four-dimensional scanning transmission electron microscopy, *Ultramicroscopy* (195) 189-193, https://doi.org/10.1016/j.ultramic.2018.09.005.

[3] Andriy Zhugayevych, Olga Mazaleva, Artem Naumov, and Sergei Tretiak (2018). Lowest- Energy Crystalline Polymorphs of P3HT. *The Journal of Physical Chemistry C* 2018 *122* (16), 9141-9151