

Structural and Morphological Characterization of Novel Organic Electrochemical Transistors via Four-dimensional (4D) Scanning Transmission Electron Microscopy

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Conjugated semiconducting polymers are being widely studied for their application in a host of new technologies. For bioelectronic applications, organic electrochemical transistors (OECTs) show great promise for their ability to convert small changes in ion concentration into large changes in electrical current¹. In an OECT, an active polymer layer is patterned with source/drain electrodes on the underside, while the top surface is in contact with an electrolyte solution. When an electrical bias is applied to the solution via a gate electrode, ions from the solution are driven into the polymer by an electrochemical doping process. The result is a change in conductivity of the polymer layer which can be monitored by measuring the current flow between the source and drain.

Much progress has been made in the development of new, optimized materials for these applications. In particular, the introduction of polar side-chain species to the backbone of OECTs has been shown to significantly increase the uptake of ions from the electrolyte². However, there appears to be a complex trade-off between ion uptake and electronic mobility. For example, in some OECTs increased crystallinity has been shown to decrease performance³. There has been speculation that this behavior can be attributed to the preferential swelling of the amorphous region of the film, however this is difficult to measure experimentally. Moving forward, the ability to spatially resolve the crystalline domains of the polymer is essential to understanding the role of crystallinity and nanoscale morphology on the performance of novel OECT materials, and therefore enable the design of better OECT materials and processing conditions.

Scanning transmission electron microscopy (STEM) is ideally suited to simultaneously revealing the morphological and structural characteristics of materials organized at nanometer length scales and below. However, the high-energy electron beam employed in STEM rapidly destroys the crystal structure in many organic materials and can completely vaporize material at elevated doses. The development of high-sensitivity, direct electron detectors offers one way of surmounting this barrier, as the required data can be collected with a far lower electron dose. Four-dimensional (4D)-STEM, where a full two-dimensional electron scattering distribution is rapidly collected at every point in an image scan, offers a route to collecting spatially resolved diffraction data from beam sensitive samples using a much lower dose than required using CCD-based cameras.

In this paper we will discuss the application of 4D-STEM to the characterization of a newly-developed, OECT material^{3,4}, poly(3{[2-(2-methoxyethoxy) ethoxy]methyl}thiophene-2,5-diyl) (P3MEEMT). P3MEEMT contains ethylene glycol-based side chains for enhanced ion uptake and exhibits carrier mobilities comparable to state-of-the-art OECTs. 4D-STEM data was collected using a primary beam energy of 80 keV and a probe current of approximately (10 to 30) pA. A small (10 μm) probe-forming aperture was used resulting in a convergence semi-angle of < 1 mrad in order to ensure any separation of Bragg diffraction discs. A high-speed, direct detection camera with 256 pixel x 256 pixel array was used to collect the electron scattering patterns using a readout time of 1 msec per pixel. Data processing was performed using the FPD Python package^{5,6} along with custom scripts developed for this application.

A cursory inspection of the data shows that most specimen locations do not show any strong coherent scattering, indicating that the specimen is non-crystalline in these locations. However, at some specimen locations strong Bragg diffraction discs are observed at $q=3.3$ nm⁻¹ (Fig. 1a) and the orientation of these discs

varies almost continuously. This reflection corresponds to the sidechain spacing in face-on oriented crystals. Second and third order discs were also observed in most of these patterns, suggesting that the crystal quality in these domains is very high. Some sense of the orientational distribution of the crystals in the film can be visualized by extracting virtual images using a segmented annular mask (Fig. 1b). This reveals crystalline domains on the order of (40 to 50) nm which are elongated in the direction perpendicular to the crystalline planes giving rise to the diffraction discs (Figs. 1c-f). Additionally, a second population of crystals was observed which showed a Bragg disc at $q=17.0 \text{ nm}^{-1}$, corresponding to the (010) π - π stacking in edge-on orientation crystals which are spatially distinct from the face-on crystals (Fig. 2). The quantitative characterization of these morphological features as a function of film processing conditions, dopant concentration, and heat treatment will be presented.

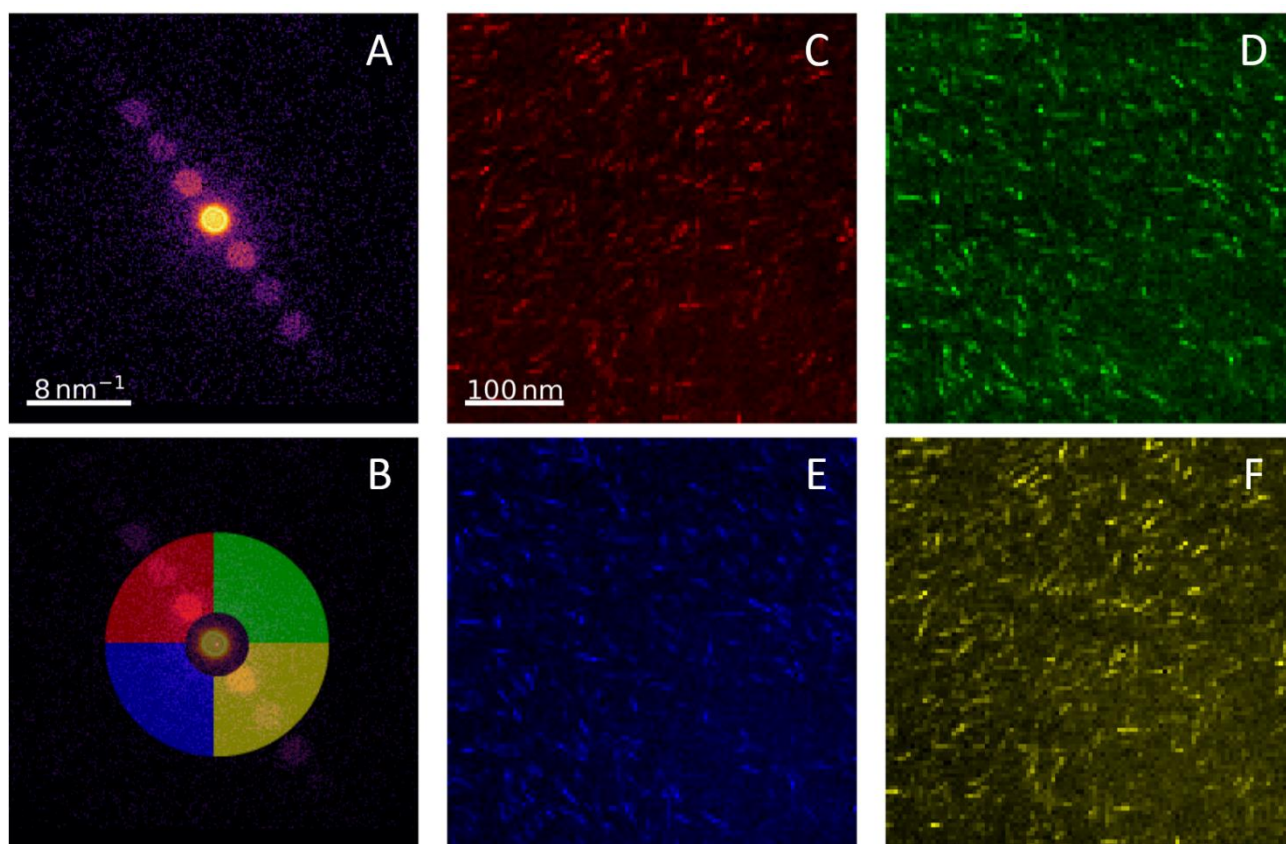


Figure 1. 4D-STEM analysis of P3MEEMT film. Individual diffraction pattern extracted from a single scan location (A). Same pattern shown with overlaid bright-field and segmented annular masks (B) for extraction of virtual images. Virtual images extracted using the corresponding colored section of the segmented annular mask (C-F).

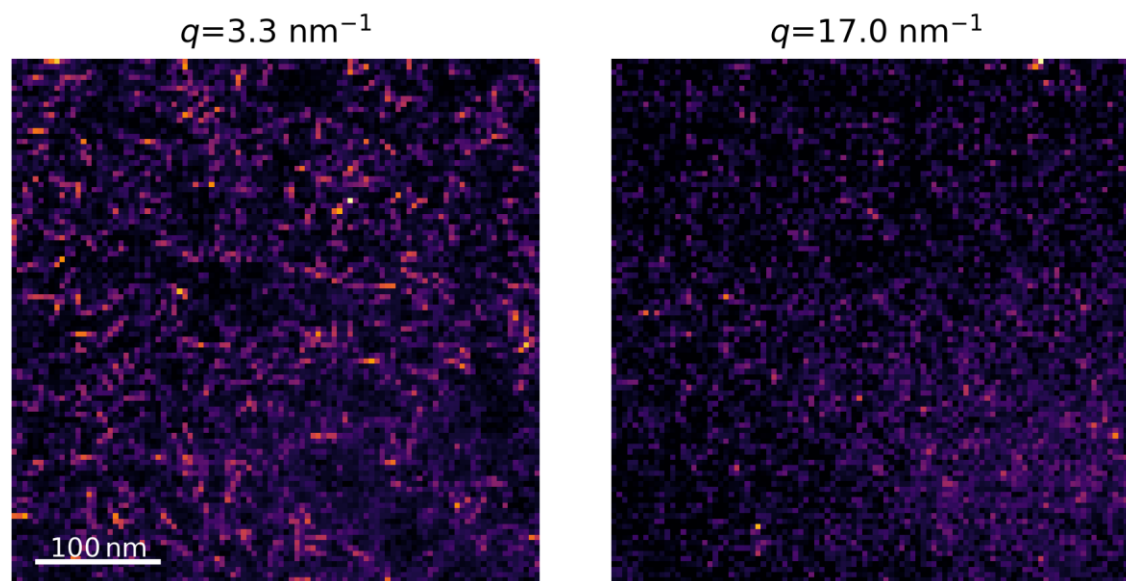


Figure 2. Virtual images extracted from the 4D-STEM dataset using annular masking of the diffraction patterns. Images show the distribution of face-on (left) and edge-on (right) oriented crystals.

References

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