

Using 4D-STEM to Track Structural Changes Due to Electrochemical Doping in Organic Electrochemical Transistors

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Organic electrochemical transistors (OECTs) consist of a conjugated semiconducting polymer active layer patterned with source/drain electrodes in contact with an electrolyte solution. Under an external electrical bias, an electrochemical doping process occurs as ions from the solution are driven into the polymer thus altering the conductivity of the polymer layer. Because the ion uptake occurs throughout the entire volume of the layer, the devices can convert small changes in ion concentration into large changes in electrical current. This makes them ideal candidates for bio-sensing applications¹.

The performance of these devices is heavily dependent on the structure and distribution of the crystalline and amorphous phases in the polymer active layer. Generally, charge transport occurs more readily within the crystalline domains, while ion uptake scales with increased amorphous content. However, the interplay between ion uptake and electron mobility is complex and not easily predicted^{2,3}. In an effort to understand this behavior, we had previously⁴ reported the use of four-dimensional (4D) scanning transmission electron microscopy (STEM) to spatially map the in- and out-of-plane crystalline features in the OECT polymer poly(3{[2-(2-methoxyethoxy) ethoxy]methyl}thiophene-2,5-diyl) (P3MEEMT)^{3,5}.

Here, we expand upon our previous work to measure the structural and morphological changes undergone during electrochemical doping by P3MEEM. To prepare the samples for STEM analysis, gold was evaporated onto the frame of silicon nitride TEM windows using a shadow mask and thermal evaporator. Polymer films were then transferred to the gold-coated windows by water floatation and then annealed at the desired temperature for 20 minutes. To facilitate the electrochemical doping process a thin wire was bonded to the gold frame using conductive carbon paste. The windows were then submerged completely into the electrolyte solution (100 mM KPF₆) and used as the working electrode in a classic 3 electrode cell. The reference electrode was a Ag/AgCl pellet and the counter electrode was a Pt mesh. The films were then oxidized by applying 0.6 V with a potentiostat for 60 seconds. The doping was confirmed visually by the orange to blue color change of the film, as shown in Figure 1. This change is stable for several days during which time the films were analyzed via 4D-STEM.

Figure 2 shows 4D-STEM results collected from P3MEEMT films that were annealed at 175 °C. The diffracted intensity was more strongly peaked after doping, indicating that either the number or quality of the crystals had increased. Real space images were extracted from the 4D-STEM datasets using an annular mask surrounding the pi-pi diffractions peaks ($q \approx 17 \text{ nm}^{-1}$). These images reveal the spatial distribution of the edge-on oriented crystals, and clearly indicate that the injection of KPF₆ ions into the polymer layer causes a significant coarsening of the microstructure. The trend in these alterations with doping and heat treatment temperature will be discussed, as will the determination of dopant ion locations within the layer via spectroscopic methods.

References

1. J. Rivnay, *et al.* Nat Rev Mater **3** (2018) 17086. doi: 10.1038/natrevmats.2017.86
2. A. Giovannitti, *et al.* Proc National Acad Sci **113** (2016) 12017. doi: 10.1073/pnas.1608780113
3. L. Q. Flagg, *et al.* J Am Chem Soc **141** (2019) 4345. doi: 10.1021/jacs.8b12640
4. A. A. Herzing, *et al.* Microsc Microanal **27S1** (2021) 1792. doi: 10.1017/s1431927621006553
5. B. X. Dong, *et al.* Chem Mater **31** (2019) 1418. doi: 10.1021/acs.chemmater.8b05257

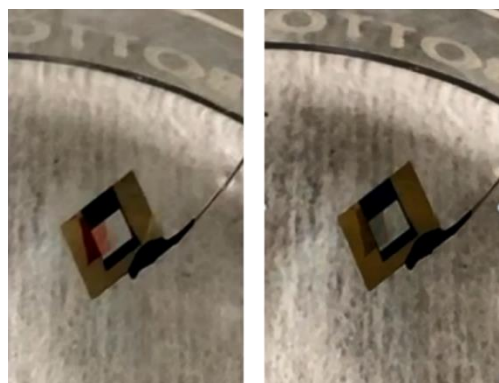


Figure 1 – Images collected during electrochemical doping of a P3MEEMT film with KPF_6 on a silicon nitride window. The undoped film (left) shows a characteristic purple color in transmission which changes to blue after doping (right).

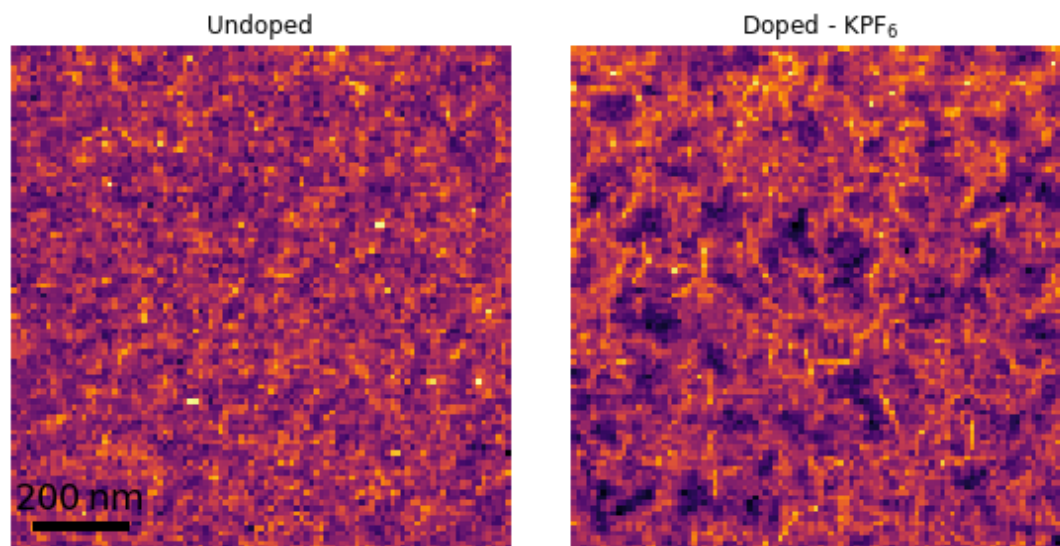


Figure 2 – Morphological effects of KPF_6 doping of P3MEEMT. Virtual images extracted from the 4D-STEM datasets using annular masking of the π - π diffraction peaks ($\approx 17 \text{ nm}^{-1}$) before (left) and after doping (right).