

PEDOT, Altered Surfactants, and Lamellar Stability

This summer in the Stupp lab, with a grant generously provided by the URG program and through ISEN, I have conducted experiments aiming towards the ultimate goal of creating alternative solar photovoltaic devices. Utilizing the electrodeposition system to create hybrid inorganic-organic lamellar architectures, I first focused on studying different organic surfactants to incorporate into the system with the aid of the PEDOT coating. With a greater library of surfactant molecules, we hope to understand what characteristics will allow for more consistent depositions. These new surfactants, such as the DPP, the 5T linker, the 3T-DCA, and the PyBA-DCA exhibited expected properties according to our hypothesis of lamellar formation. Secondly, I studied the stability of the lamellar after chemical and annealing treatments in order to improve our techniques concerning device synthesis.

Utilizing the PEDOT:PSS organic substrate preparation, the DPP (**Figure 1**) proved to be relatively easy to deposit. Based upon its role in other papers, I spun coated PEDOT onto ITO substrates prior to the depositions to form a thin layer of this electron blocking organic on the surface. In comparison with the plain ITO substrates, the depositions on PEDOT resulted in a dramatic increase in lamellar density, alignment, and deposition consistency. The scanning electron microscope image in **Figure 2** shows macro scale morphology of the lamellar flakes in which each flake consists of many sheets of layered DPP in complex with the $Zn(OH)_2$. The film from Figure 1 was electrodeposited at -1.0 volts for forty minutes on PEDOT coated substrates. With the advance of the PEDOT processing method, other surfactant targets were explored in order to examine how PEDOT affected other surfactant depositions.

I ran electrodepositions with the 5T linker surfactant (**Figure 1**) on both PEDOT and plain ITO substrates in order to further examine the role of PEDOT. The electrodeposition was run with a 1 mM 5T linker solution in a 64:36 DMSO:H₂O ratio. After half an hour, at -1.0 volts, the 5T linker grew good lamellar films on the PEDOT coated substrates in which the surface was covered by a dense plate-like morphology as shown by **Figure 3**. **Figure 4** exhibits the less dense growth of the plates on the plain ITO surface. Thus the PEDOT was influential in changing the surface chemistry in a manner that favored dense growth. The PyBA-DCA (**Figure 1**) has a second carboxylic acid, as in the 5T surfactants, and may reveal more information about the role of dicarboxylic acid organics. Our hypothesis is that one carboxylic acid with a linker should produce the most uniform and aligned films. At a 3.4 mM concentration, the PyBA-DCA deposited consistently on the PEDOT substrates. The SEM shows a flake like morphology with both smaller and larger flake regions. Although the PyBA-DCA molecule deposited, it did not exhibit uniform density and morphology as seen in **Figure 5**.

The 3T-DCA surfactant (**Figure 1**) was run at 3.4 mM 3T-DCA at -1.0 V on PEDOT. As predicted, the second carboxylic acid contributed to less ideal density characteristics that are visible in the SEM shown in **Figure 6**.

Overall, these studies have highlighted PEDOT's favorable role in the electrodeposition system and have increased the library of surfactants that have been successfully incorporated into the lamellar system. Eventually, we hope to achieve a molecular design of the surfactant, based upon favorable properties of previously studied molecules that will produce ideal lamellar films for photovoltaic use.

The second focus of this summer's work has been to characterize the stability of the lamellar in response to chemical treatments and annealing. PyBA substrates were grown from a single electrodeposition bath of 0.1 wt % PyBA at -1.0 volts on PEDOT to reduce the variability of the films. The substrates were then immersed in the appropriate solvents as diagramed in **Figure 7**. After three hours, none of the substrates showed visible degradation, and upon X-ray analysis, showed no discernible changes. These substrates were then subsequently annealed at 150 degrees Celsius and then soaked again in the same solvents for another three hours. Annealing is crucial step in converting the $\text{Zn}(\text{OH})_2$ to the active ZnO. Due to a malfunction with the X-ray, the substrates could not be analyzed immediately. Instead, the substrates continued to soak for three days. The substrates in the acidic, DMSO, and acetonitrile solvents displayed visible thinning of the white film and had no X-ray peaks that would have indicated the presence of the lamellar. In the other solvents, the lamellar maintained a single peak in the X-ray, which is similar to the graph of an annealed substrate. This information should be helpful in maintaining the lamellar through device synthesis process. In summary, the $\text{Zn}(\text{OH})_2$ lamellar is stable in the solvents, but the ZnO annealed lamellar is only stable in basic H_2O and Ethanol.

More PyBA substrates were grown in order to study the lamellar stability with different annealing conditions. The substrates were individually annealed at 60°, 80°, 100°, 120°, and 150° for three hours each. **Figure 8** shows the X-ray of the 60° film after annealing, and exhibits the characteristic three peaks of the PyBA lamellar. However, the 150° anneal (**Figure 8**) did not maintain the larger order peaks in the X-ray, which indicates degradation in the order of lamellar. With increased temperature, the strength of the peaks decreased, again exhibiting the varying levels of degradation. In order to determine the presence of the ZnO phase in the lamellar, I examined the PyBA films for fluorescence under UV light. All except the 150° anneal showed some fluorescence, but there was a slightly discernible gradient as a function of annealing temperature. There may be a temperature between 120° and 150° or an annealing duration longer than three hours that may be more optimal in converting the $\text{Zn}(\text{OH})_2$ to the ZnO that does not degrade the lamellar to the same degree.

My research over the course of the summer has been a positive experience in the Stupp lab and I greatly appreciate the opportunity work on such an interesting project. The techniques and general research acumen will undoubtedly help me on my future career in science.

Appendix –

Figure 1. Chemdraw of DPP-C3CA (top left), 5T linker (top right), PyBA-DCA (bottom left), and 3T-DCA (bottom right)

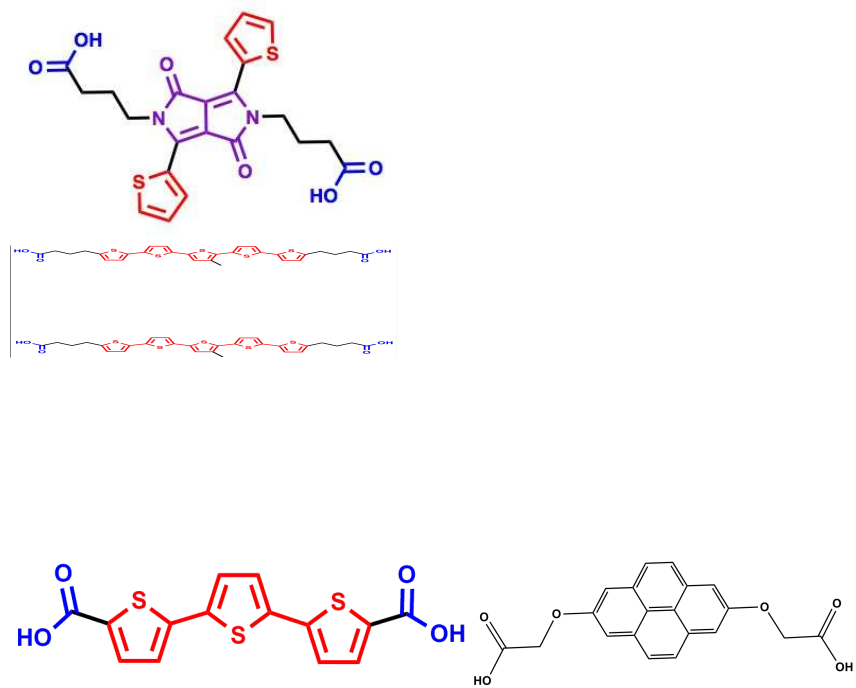


Figure 2. DPP-C3CA on PEDOT

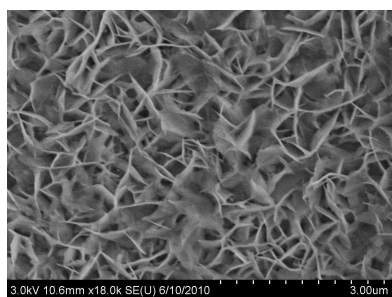


Figure 3. 5T linker on PEDOT

Figure 4. 5T linker on ITO

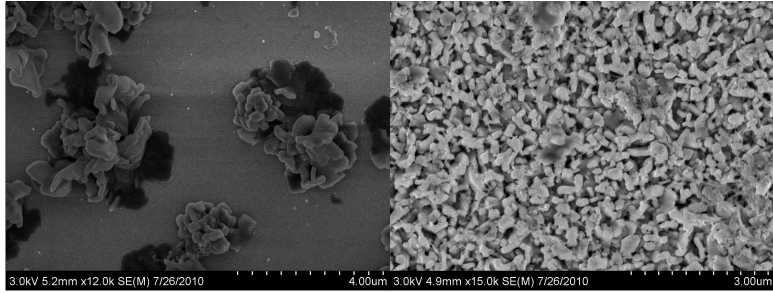


Figure 5. PyBA-DCA on PEDOT

Figure 6. 3T-DCA on PEDOT (right)

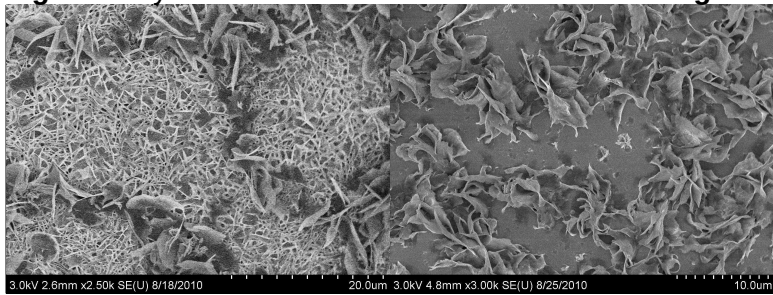
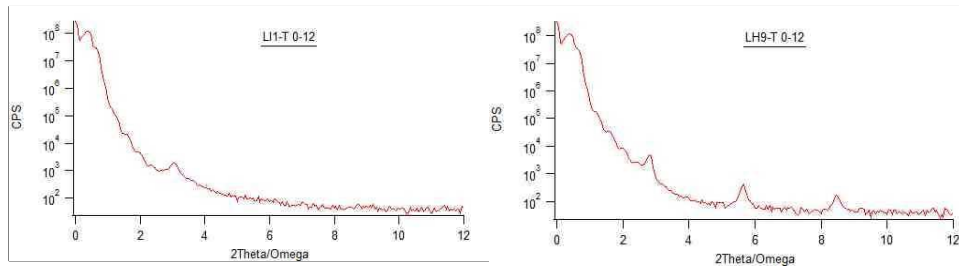


Figure 7. Diagram of Lamellar Stability Experiment

Figure 8. X-ray Scan



of 60°C annealed lamellar (left) vs. 150°C annealed lamellar (right)