

Annual Report: Funding period Sept. 1, 2017 – Sept. 30, 2018.

ACS PRF UR #55521:

Electrochemical Interactions between Conjugated Polymers and Polymerizable Salts,
Janelle Leger, Western Washington University

Goals of the Project:

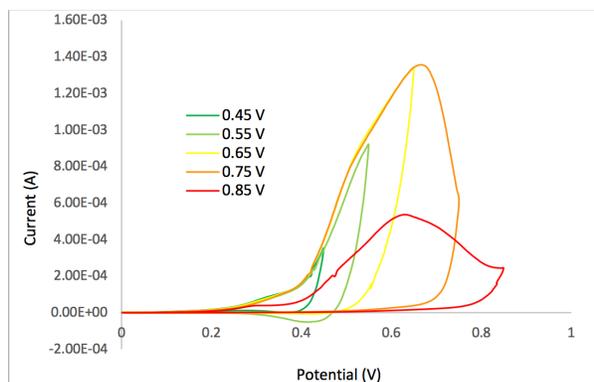
Several emerging organic electronic technologies, known as ‘iontronic’ devices, utilize the unique mixed ionic/electronic conducting character of conjugated polymeric materials. In the majority of iontronic devices, all steps of device operation are reversible; once the bias that assembles the ion profile is removed, the device discharges and the ions redistribute. In our lab, we have developed a process by which a remarkably robust fixed junction can be formed in commercially available conjugated polymers that is not subject to ion relaxation or redistribution. We achieve this by replacing the salt used in traditional iontronic devices with polymerizable ionic liquids (PILs) that can potentially be polymerized via radical initiation. While the effects of including PILs as the source of counterions on device characteristics are well understood, little is understood about the mechanism that leads to these effects. Our working hypothesis is that a covalent bond forms between the PIL and the conjugated polymer, initiated by the formation of a radical during the electrochemical doping process of the conjugated polymer itself. However, no direct evidence for covalent bond formation has been shown. The overarching goal of this work is to elucidate the nature of the electrochemical interactions between these species and the resulting structures formed, determine whether the reaction results in a covalent bond between the PIL and the CP, and determine how the reaction and any resulting structural changes affects the physical properties of the CP. We also plan to explore the design of new PILs with improved properties for a variety of applications.

Research Progress:

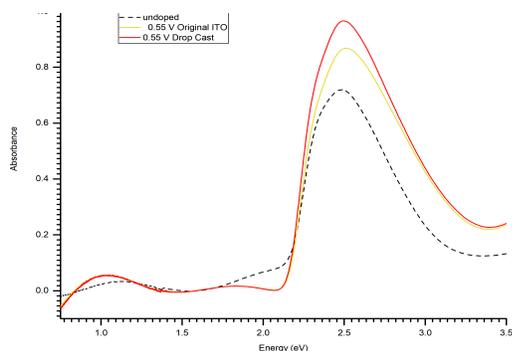
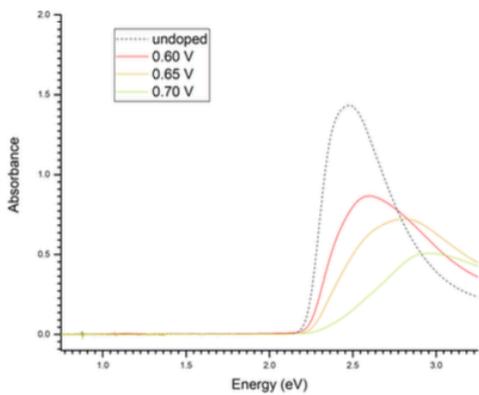
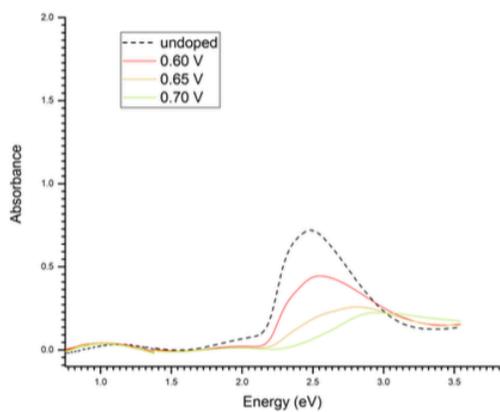
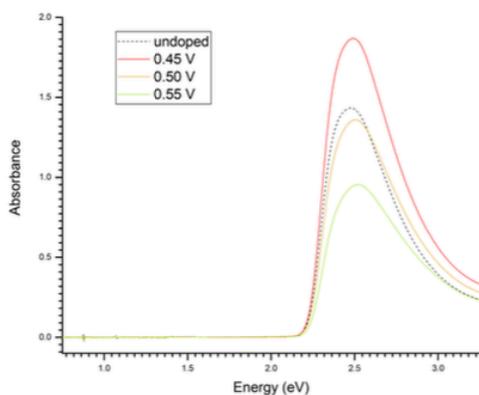
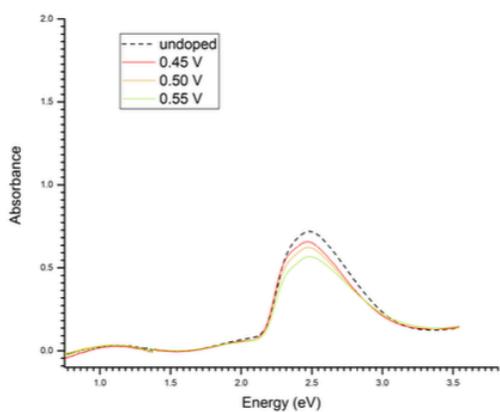
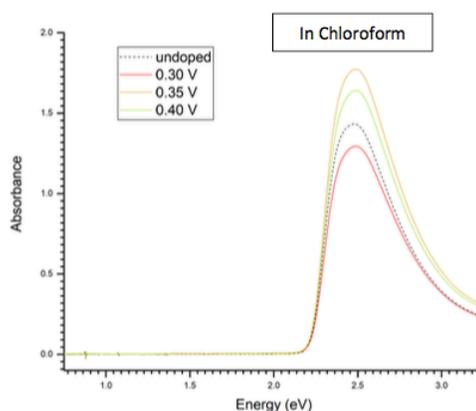
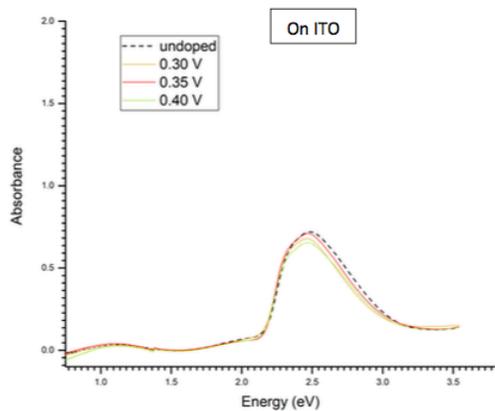
In our last annual report, I described the work we had done to overcome the persistent problem we were having with the purity of our primary synthetic target (ATOAS) and explained the work that would be enabled by finally tackling that problem. Because of that progress, this year we have finally been able to make real progress toward the goals of the grant, as described below:

We have started carrying out the electrochemical analysis of MEH-PPV using ATOAS as the ion source, starting with basic cyclic voltammetry. This reaction (specifically, the electrochemical oxidation) is known to be irreversible, in contrast to the case when a traditional (inorganic) salt is used as the source of counter-ions. Here, we have started to look at the dependence on sweep rate and maximum voltage. We have discovered an interesting and unexpected trend, where the reversibility of the reaction appears to depend on the maximum voltage in an unexpected way. Specifically, the scans that are taken to relatively small or large voltages appear completely irreversible, whereas the scans at moderate voltage (0.45-0.65 V) show a small reverse current indicating partial reversibility (see figure, below right). We are currently exploring this phenomenon more deeply.

Alongside the electrochemical characterization, we use CV to generate doped samples for optical characterization using UV-Vis absorption spectroscopy. It is known that when electrochemically oxidizing MEH-PPV, two mid-bandgap peaks appear and grow in intensity in the absorption spectrum on ITO glass. We set out to determine whether doping using ATOAS produced the same effect, essentially looking for evidence to clarify the hypothesis that we are “locking in” the doping to our soluble product by employing ATOAS. The upper figure on



page 2 shows the optical absorbance spectra from MEH-PPV films doped to varying levels on ITO glass (left column) and subsequently dissolved in chloroform (right column). Surprisingly, we observed a complete lack of mid-gap states in the dissolved material. To explore this further, we went on to take the dissolved material and recast it onto ITO glass. We observe that the resulting optical absorption spectra are nearly identical to those of the original doped films on ITO (lower figure on page 2), suggesting that the loss of mid-gap states in solution is likely a solvent interaction effect. It indicates as well that the doped material is robust to the process of dissolving and recasting, which is promising for future device applications.



Overall

outcomes:

During this funding period we have been able to make significant progress toward the original goals of the proposal due to the fact that we recently overcame a significant roadblock to our research. While we have not yet published our results, there have been important outcomes in terms of student preparation. Two undergraduate students and one M.S. student were given the opportunity to carry out part time research during the 2017/18 academic year, and one undergraduate student carried out full time research during Summer 2018 as well. This funding is particularly important for the undergraduates, as it allows them the opportunity to carry out independent research prior to applying for graduate programs.

Plans for the next funding period:

Our goals are still in line with those of the original proposal. Specifically, these plans include completing a full electrochemical characterization of MEH-PPV with ATOAAS, optical and electronic characterization of the doped product, synthesis of PTOAPS, and synthesis of novel PILs.