

Introduction: Organic (polymeric) semiconductors (OSCs) are readily processible, leading to numerous advantages over traditional inorganic semiconductors.^[1] These advantages include the ability to be fine-tuned for properties such as solubility, thermal processing, and optoelectronic properties, which allows OSCs to be leveraged for a variety of applications.^[2] Through this molecular design, the charge carrier mobility of OSCs has been improved over the past three decades by seven orders of magnitude.^[2] OSCs have been targeted for use in many future technologies, such as organic thermoelectric devices and organic solar cells, which can be used as alternative, green energy sources.

One challenge in realizing this potential is the inherent structural and electronic disorder in polymers used as OSCs. In analogue to inorganic semiconductors, OSCs can be doped to increase electron or hole conductivity. These dopants take the form of small acceptor/donor molecules, which can be introduced into the polymer matrix a variety of ways. These methods include mixing the polymer and dopant in solution (solution doping), immersing or casting the dopant solution on top of the previously-cast polymer film (sequential doping), and subliming the dopant into the previously-cast polymer film (vapor doping). Although solution doping can be utilized for scale-up procedures such as roll-to-roll processing, solution doping leads to polymer aggregation and eventual precipitation, which leads to poor quality films. This causes a lower conductivity than as sequential and vapor doping, which have better local and long range ordering.^[3]

Despite the progress in doping methods, the dynamics for molecular doping into polymer films are not well known. This is due to the complexity of the charge transfer mechanism of molecular dopants in OSCs. *In consequence, I propose to develop an easy-to-use platform to study the dynamics of OSC doping in situ, which will reveal both fundamental doping mechanisms as well as efficient and effective doping methods.* The Institute for Molecular Engineering (IME) at The University of Chicago is a vibrant place for collaboration, and in conjunction with the Rowan group (synthetic) developing novel polymers for OSCs and the de Pablo group (computational) modelling advanced doping mechanisms, this platform would provide a method for probing the dynamics and optimization of a polymer/dopant pairing. Further understanding on the dynamics of OSC doping will inform further fine-tuning of OSCs and their development for use in novel, alternative-energy sources.

Preliminary Results: In order to develop a platform for studying the dynamics of doping, I have used a model polymer-dopant pairing of Poly(3-hexylthiophene) (P3HT) and 2,3,5,6-Tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F4TCNQ). P3HT has been widely studied as a conductive polymer due to its processability and ability to form an ordered semi-crystalline morphology. The conductivity of doped P3HT has been shown to increase six orders of magnitude from pristine to highly doped states.^[5] Our custom-built chamber allows for measurement of *in situ* conductivity response to doping (Fig. 1), which is crucial for this platform. I have performed

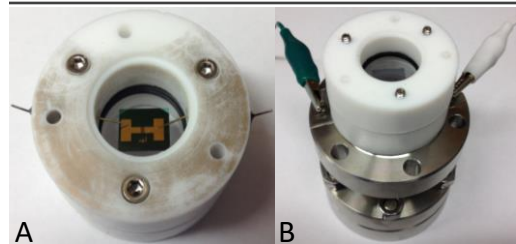


Figure 1: (A) Chamber holds electrode array with tungsten contacts. (B) Chamber sits above subliming dopant, with contacts for *in situ* conductivity measurements.

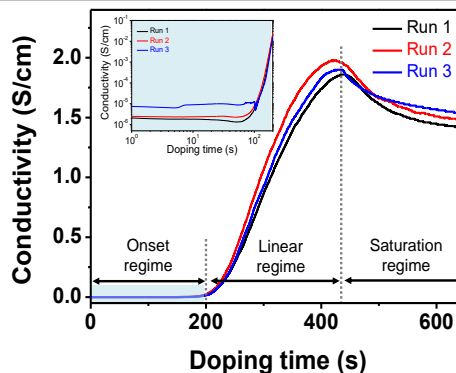


Figure 2: *In situ* conduction data taken on three separate P3HT-F4TCNQ samples. Inset shows log-log plot of onset regime, showing growth from 2E-6 to 2 S/cm over nine minutes of vapor doping. Data collected 14 Sept., 16:00 CST.

initial conductivity measurements on P3HT/F4TCNQ polymer-dopant pairing spun coat onto an interdigitated electrode array (IDA) we designed in the Pritzker Nanofabrication Facility at UChicago. These samples were vapor doped in our chamber for over nine minutes while *in situ* conductivity measurements were made. Dopant mass, surface area, and doping temperature were held constant between measurements. These measurements showed a profile that increased six decades in close agreement with multiple literature values.^[1,4,5] These measurements were shown to be consistent over multiple runs (Fig. 2). My measurements also showed three doping regimes: an onset regime, a linear regime, and a saturation regime. These three regimes, which has not been previously reported in literature, will be individually probed for evidence on the dynamics of molecular dopants during the doping process. I have also conducted Grazing-Incidence Wide-Angle X-ray Scattering (GIWAXS) on pristine P3HT and P3HT doped with F4TCNQ at the 8-ID-E beamline in the Advanced Photon Source (APS) at Argonne. This technique showed us detailed information about the crystallinity of the film and how the dopant disrupts this structure. These measurements indicate that, for P3HT, the polymer backbone spacing is reduced and sidechain spacing increased by the presence of molecular dopant.

Research Plan: With the platform for measuring conductivity *in situ* complete, I plan to use this platform in conjunction with complementary characterization techniques to study novel polymer-dopant systems. These polymer-dopant systems will be provided by our collaboration with the Rowan groups within the Institute for Molecular Engineering at UChicago. This project also allows me to be trained further at the Pritzker Nanofabrication Facility to produce the interdigitated electrode arrays necessary to measure polymer-dopant properties *in situ*.

I will employ a complementary group of characterization techniques to probe these systems. UV-Vis-NIR spectroscopy in conjunction with FTIR spectroscopy will be used to identify charged species in films at all three doping regimes, allowing us to measure the concentration of charge carriers in the polymer films. Raman spectroscopy and microscopy will be used to measure and map the distribution of charge carriers in our systems in different doping regimes. Conductive Atomic Force Microscopy will allow us to map conductivity on the surface of our systems. These techniques will occur at the Materials Research Center at UChicago, an NSF MRSEC facility.

Our relationship and proximity with Argonne Nation Laboratory allows us to utilize advanced techniques to characterize the polymer-dopant system. Synchrotron (high energy) X-rays are required for this project to probe the small length scales of our polymer films. As previously detailed, GIWAXS obtains measurements of the local crystallinity of the polymer film. Beamline 8-ID-E at the APS also has expertise in X-ray Photoelectron Correlation Spectroscopy, which allows for *in situ* measurement of the slow dynamics of the doping system. Resonant Soft X-ray Scattering at beamline 29-ID-D obtains morphology over large length scales (10-1000 nm).

Conclusions and Broader Impacts: The data I will obtain from *in situ* measurements and characterizations will give us a more complete picture of how molecular dopants infiltrate and modulate conductive polymers throughout the entire doping process. Through our collaborations with the Rowan and de Pablo groups in the Institute for Molecular Engineering at UChicago, we will be able to use our platform with novel polymer-dopant systems, aiding in the discovery of systems with high conductivities. This, in turn, will allow for the improvement of organic semiconductor devices, furthering the development of OSCs for use in critical (opto)electronic applications such as thermoelectrics and organic photovoltaics. Receiving the NSF GRFP will allow me to realize these goals and to present at public outreach events about the need for alternative energy sources and how my research brings these technologies closer to realization.

1. *Adv. Mater.* 2017, 1703063 2. *MRS Commun.* 2015, 5 (3), 383-395 3. *J. Mater. Chem. C.* 2016, 4, 3454-3466 4. *Macromolecules.* 2017, 50 (20), 8140-8148 5. *Phys. Rev. B.* 2015, 91, 085205