Project Title: Influence of energy landscapes, charge-carrier mobilities, and morphology on the thermoelectric properties of π-conjugated polymer blends

Kenneth R. Graham, University of Kentucky

Conductive polymers are an exciting class of inexpensive materials that can be used in thermoelectric devices to capture wasted thermal energy and convert it into useful electrical energy. Polymer based thermoelectrics have the potential to be low cost and mechanically flexible, thus permitting a range of novel applications that are not suited to the current expensive and mechanically stiff inorganic thermoelectric materials. However, for these polymers to be successfully used in thermoelectric devices at a large scale, their thermoelectric performance metrics must be improved. From a fundamental standpoint, improving the thermoelectric performance demands a better understanding of how to control the electrical conductivity and the energy dependence of charge transport. One means of manipulating both the electrical conductivity and the energy dependence of charge transport is to blend two different polymers together, whereby the energetic and charge transport properties of both polymers could be individually selected to systematically tune the thermoelectric properties of the polymer blend. It is the primary goal of this research to determine how energy offsets between the ionization energies (IEs) of the different polymers, charge-carrier mobility imbalances, and film morphology influence the charge transport behavior and thermoelectric properties of π-conjugated polymer blends.

The first year of the project focused on several different aspects, including probing how energy offsets influence the Seebeck coefficient, electrical conductivity, and power factor in organic-inorganic composites, investigating different molecular dopants for use in the polymer blend systems, and developing a theoretical model to calculate the electrical conductivity, Seebeck coefficient, and power factor in polymer blends. Overall, in year one of this project we have published four manuscripts in peer-reviewed scientific journals, two of which are based primarily on work carried out in our laboratory, and two of which involved us contributing to work carried out primarily by other groups. This report focuses on the two manuscripts that were led by my laboratory as well as the theoretical and experimental work that is still in progress.

Initial work involved organic-inorganic composite materials as a model system to test one of the primary concepts proposed, i.e., by combining different components with appropriately offset energy levels we could enhance the thermoelectric performance of the material. Here, rather than the two components being doped π-conjugated polymers, one component was a π-conjugated polymer
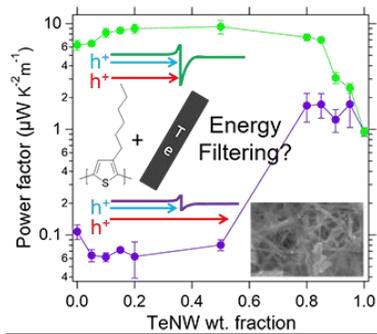

Figure 1. *Experimentally measured power factors and schematics of the two energy filtering landscapes in the P3HT:TeNW composites.*

while the other was an inorganic nanowire. The energetics of the polymer were varied based on the amount of dopant ($FeCl_3$) introduced. At low doping amounts, the IE is similar to that of the tellurium nanowires, with an energy offset of 0.08 eV. At higher doping amounts, the IE is increased to create an energy offset of 0.88 eV with the tellurium nanowires. In the case that energy filtering is occurring, we expected to see an increase in the Seebeck coefficient with the lightly doped system (0.08 eV energy offset) and no increase in the Seebeck coefficient in the highly doped system (0.88 eV energy offset). We found that both composite materials showed an increase in the power factor, as shown in Figure 1; however, neither system showed the characteristic increase in the Seebeck coefficient that is a signature of energy filtering. The data was fit to a simple composite model that accounts for both serial and parallel charge and thermal transport, and this model predicted the increased power factors and fit the experimental data well. Thus, contrary to what most literature reports have suggested, our results imply that energy filtering is not playing a major role in these composite materials. Promisingly, the results show that increased power factors over both pure components (i.e., doped P3HT or TeNWs) are possible in these polymer-nanowire composites.

An initial goal of this project was to identify suitable polymer-dopant systems for probing the influence of energy landscapes and charge-carrier mobilities on the thermoelectric properties of π-conjugated polymer blends. The desire to have varying energy offsets between the transport states of the polymers in the blend meant that we had to identify dopants that were capable of doping polymers with varying transport energies. Here, we use the IE as a measurement of the energy of the transport states. To identify appropriate dopant molecules we selected a series of dopants and conjugated polymers, as highlighted in Figure 2a. The dopants were applied to this series of conjugated polymers and we found that the electrical conductivity of the doped polymer film is determined by two major factors: 1) the difference in energy between the dopant electron affinity (EA) and polymer IE, and 2) the size of the dopant molecule. The electrical conductivity at a given dopant concentration increases as the difference between the polymer IE and dopant EA increases, which agrees with previous findings and expectations. We also find that the electrical conductivity at lower doping concentrations is approximately an order of magnitude greater with $Mo(tfd)_3$ than with $FeCl_3$ (See Figure 2c). This trend, which cannot solely be attributed to doping efficiency, appears to be due to the presence of more delocalized polarons when $Mo(tfd)_3$ is added. Absorbance and Raman scattering data, see Figure 2d, support the presence of more delocalized polarons. Here, the $C_\alpha=C_\beta$ stretching mode at *ca.* 1440 cm^{-1} only broadens upon addition of $FeCl_3$, likely the result of increased disorder, but shifts to lower wavenumbers upon addition of $Mo(tfd)_3$, which is attributed to formation of a delocalized polaron. We currently suspect that the more delocalized polaron upon $Mo(tfd)_3$ doping is the result of the

large size of Mo(tfd)$_3$ and thus a reduced coulomb attraction to the charged polaron. Overall, this work has shed important light on dopant size effects and has guided the selection of Mo(tfd)$_3$ for future experiments.
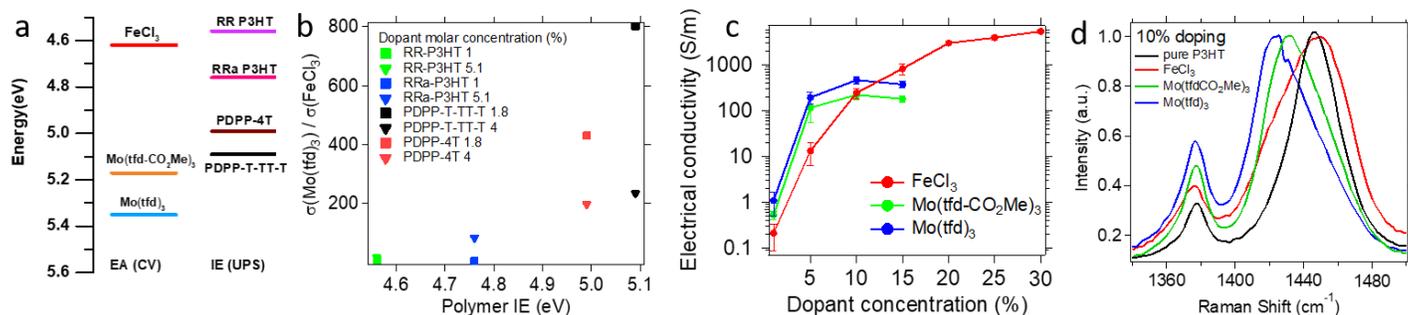
Figure 2. *EAs and IEs of dopants and polymers investigated, respectively (a), electrical conductivity ratio for polymers doped with Mo(tfd)$_3$ vs. FeCl$_3$ at 1-2% and 4-5% (b), electrical conductivity for P3HT with varying dopants as a function of dopant concentration (c), and Raman scattering spectra of P3HT with varying dopants at 10% dopant concentration.*
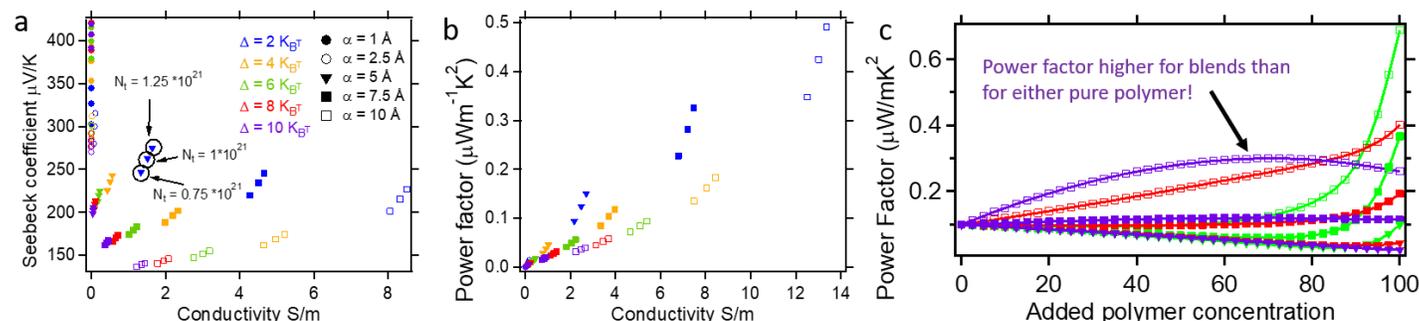
Figure 3. *Calculated Seebeck coefficients (a) and power factors (b) as a function of electrical conductivity for pure polymers with varying width of the density of states, Δ, and localization length, α, (b). Calculated power factors for polymer blends as a function of blend composition (c).*

We are currently working on calculating how the energy offset between the polymers and charge-carrier mobility differences impact the expected Seebeck coefficient, electrical conductivity, and power factor. Here, we are using a series of previously published equations based on the generalized Einstein equation and the Abraham-Miller jump rate equations to calculate the energy dependent mobility, which can the be used to calculate the Seebeck coefficient. With these equations we have modeled how the width of the density of states, energy offsets, and carrier localization influence the charge-carrier mobility, electrical conductivity, Seebeck coefficient, and power factor. For a single polymer, we find that a narrow density of states and high localization length leads to the highest power factors. As shown in Figure 3a and b, the highest performing polymer has the narrowest density of states distribution (Δ=2kT) and greatest localization length (10 Å). Furthermore, the modeling shows that certain combinations of polymers should allow for increased Seebeck coefficients and power factors in blends of different conjugated polymers, as shown in Figure 3c. According to our calculations, the power factors of the blends can surpass the power factors of the pure polymers when the two polymers have an IE difference of 0.3 eV and the polymer with the higher IE has a wider density of states distribution and a larger localization length. As the localization length corresponds with the charge-carrier mobility, the higher IE polymer should have a higher charge-carrier mobility. We have identified polymers with a range of IEs and charge-carrier mobilities, including those listed in Figure 2a, and carried out preliminary experiments on blends of these polymers with varying blend compositions. At present, we have identified one system that does show an increased power factor in the blend relative to either of the pure components; however, we are at the early stages of this experimental work and are not yet able to make sound conclusions. Continuing with experimentally probing electrical conductivity, Seebeck coefficients, and morphology in the polymer blends will comprise the majority of this next year's research, combined with comparisons to theoretical predictions.

The research carried out as a part of this funded project has greatly impacted my career development. This funding has supported my group's work on organic semiconductors, allowing us to publish papers in peer-reviewed journals and present multiple talks and posters at scientific meetings (Liang, oral presentation, Materials Research Society Fall 2018 Meeting; Graham, oral presentation, Materials Research Society Spring 2018 Meeting; Abtahi, poster presentation, Materials Research Society 2018 Spring Meeting). This connection to the organic electronics community is important for my continued career development, and the new focus on organic thermoelectrics that this grant has allowed me to pursue is one of my group's core focal areas. The students have benefitted through their publications and travel to scientific conferences. I am currently working on a collaborative grant with Dr. Chad Risko at UK that we plan to submit to the National Science Foundation this Fall to fund related work in this area beyond the end of this ACS PRF grant. The results and publications that we have accumulated thus far, and the future results and publications we will add over the next year, will put my group in a strong position for applying for federal funding in this research area.