

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

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Project Overview: Conductive polymers are an exciting class of inexpensive materials that can be used in TE devices to capture wasted thermal energy and convert it into useful electrical energy. Polymer based thermoelectrics (TEs) have the potential to be low cost and mechanically flexible, which will enable a range of applications to which conventional inorganic TEs are not suited. However, for these polymers to be successfully used in TE devices, their TE performance metrics must be improved. This research project was based on obtaining a fundamental understanding of how polymer blends can be used to alter the electrical conductivity and the energy dependence of charge transport. The basis being that the energetic and charge transport properties of both polymers could be individually selected to systematically tune the TE properties of the polymer blend. Specifically, this project focused on 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 TE properties of π -conjugated polymer blends.

Year 1: Briefly, year 1 involved two important discoveries. First, we discovered that power factors in organic-inorganic composites can exceed those of both pure materials, even in the case where energy filtering does not occur. This work also uncovered that doped conjugated polymers can help to facilitate charge transfer between inorganic nanowires. Second, we discovered that the degree of polaron delocalization in conjugated polymers is highly dependent on the dopant molecules added. Here, larger organometallic dopants (e.g., $\text{Mo}(\text{tfd})_3$) were observed to yield more delocalized polarons as compared to the smaller FeCl_3 dopant. Furthermore, the difference between the electron affinity (EA) of the dopant molecule and the ionization energy (IE) of the polymer was observed to correlate strongly with the doping efficiency and electrical conductivity. These results led us to select a large dopant with a high EA, $\text{Mo}(\text{tfd})_3$, for the polymer blend work that was carried out in year 2. Additionally, in year 1 we also began developing the theoretical calculations that were applied to the polymer blends. A more detailed summary of year 1 results can be found in the previous report.

Year 2: Research during this second year focused primarily on the polymer blends. Here, we used a combined theoretical and experimental approach to address the primary questions laid out in the original ACS PRF proposal: namely, how the ionization energy

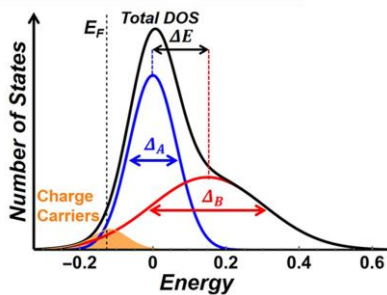


Figure 1. Overview of the polymer blends showing the variation in the width of the DOS of the polymers and the energy offsets between the DOS distributions.

difference and charge carrier mobility difference between conjugated polymers in a polymer blend can be used to manipulate charge transport and the TE performance. Figure 1 highlights these parameters.

From the theoretical side, we adapted 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 then be used to calculate the Seebeck coefficient. These equations involve three primary variables that we analyzed, including the width of the density of states (DOS) of each polymer, energy offsets between the transport states in each polymer, and the charge-carrier localization length, with the charge-carrier localization length and density of states width both having a large impact on the charge carrier mobility. To establish the theoretical model we began with modeling materials with only one polymer. Here, we found that a higher localization length led to higher electrical conductivity and a lower Seebeck coefficient for a given DOS width. We also found that the DOS width, or the amount of disorder in a polymer, had a much larger impact on the electrical conductivity than the Seebeck coefficient. In summary, our modeling of single polymer materials shows that the variable with the largest impact on the TE power factor is the DOS width.

For the blend systems, we calculated how the Fermi energy and the population of the occupied and unoccupied states varied as a function of the energy offsets between the polymers and the widths of their DOS as the blend composition is varied. Figure 2 shows that when the polymer with its DOS centered at a higher energy has a broader DOS, there is little change in the Fermi energy and the charge-carriers occupy states on both polymer A and polymer B. This situation is expected to be beneficial, as both polymers will contribute to charge-carrier transport in the blend. On the other hand, when the DOS of the polymer with its DOS centered at a higher energy has a narrower DOS, the Fermi energy changes more drastically and in general the charge carriers remain on polymer A until very high concentrations of polymer B are reached. These results suggest that for both polymers to contribute to transport in the polymer blends, the polymer with the higher energy DOS

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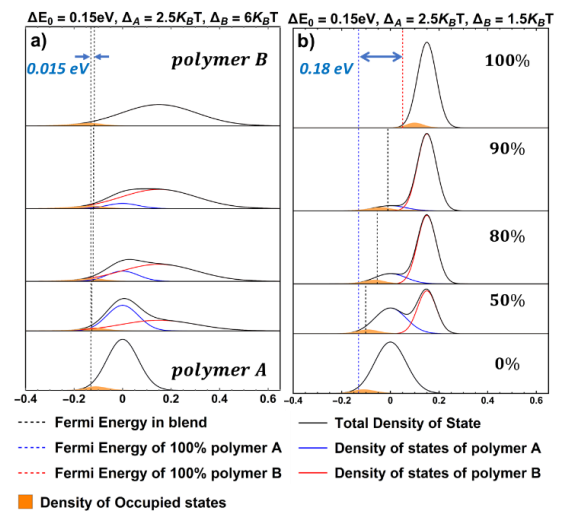


Figure 2. DOS of two polymer blends with varying compositions. In (a) the polymer with its DOS centered at higher energies has a broader DOS than the polymer with its DOS centered at lower energies and in (b) the polymer with the higher energy DOS has a narrower DOS. In both cases the DOS distributions of the polymers display a 0.15 eV energy offset.

should have a broader energy DOS. Figure 3 takes the calculations a step further and analyzes how the Seebeck coefficient, electrical conductivity, and power factor vary as the mobility ratio between polymer A and B varies as a function of polymer composition for two different DOS widths of polymer B. The heat map in Figure 3a illustrates that when polymer B has a narrow DOS the Seebeck coefficient in the blend can be increased over both pure polymers. However, the electrical conductivity is much lower in the blends than for pure polymer B, and thus the power factor of pure polymer B exceeds the power factors in the blends. On the other hand, when polymer B has a broad DOS, the power factor in the blend can exceed both pure polymers. Furthermore, polymer B should have a charge-carrier mobility that is approximately an order of magnitude higher than that of polymer A in order to observe a power factor improvement in the blends. To summarize, our theoretical results indicate that polymer blend TEs will benefit from blending a more disordered polymer with a more ordered polymer, with the disordered polymer having a higher mobility and a DOS that is centered at higher energies.

The experimental results depicted in Figure 4 for a series of polymer blends show that indeed polymer blends can lead to higher power factors than can be achieved in either of the two polymers. Here, the polymer blend that shows improved performance over the two pure polymers is RR-P3HT with PDPP-4T.

This polymer combination satisfies two of the required parameters, the mobility of PDPP-4T is approximately an order of magnitude greater than that of P3HT and PDPP-4T has a higher IE. Furthermore, the other polymer blends, which theory predicts should not show improvements in power factor, indeed do not show power factor improvements for the blends. Notably, multiple other parameters influence charge transport in polymer blends, but our work provides a significant step for understanding how the electronic properties of the individual polymers influence the TE properties of the polymer blends.

During the course of this work we observed an unexpected result in that certain polymers can show a change in the sign of their Seebeck coefficient upon heavy doping with FeCl_3 . This observation has led us to probe the electronic structure of these polymers and interestingly we observe that the transport gap narrows and is eventually eliminated upon heavy doping. The switch in sign of the Seebeck coefficient and elimination of the transport gap has significant fundamental implications for understanding charge transport in doped conjugated polymers and is the subject of a manuscript that we are currently finishing.

Impact on Student and PI Development: This funding has supported the Graham group's work on charge transport, doping, and TE properties of organic semiconductors. The funding has resulted in 5 published papers in peer-reviewed journals, with 1 more manuscript in progress with submission expected this fall. The project has resulted in 9 posters and talks being presented at national meetings, including multiple Materials Research Society Meetings, an American Chemical Society Meeting, and an American Physical Society Meeting. Out of these 9 presentations, 5 were given by graduate students and 4 were given by the PI. The talks have had a large impact on both the graduate students and PI, with both parties learning from the meetings, promoting the group's scientific advances, and networking to advance career development. One of the graduate students who initially worked on this project graduated with a PhD in May, 2018 and is currently working as a post-doctoral researcher with Prof. Susan Odom at the University of Kentucky. Another graduate student who worked extensively on this project is expected to graduate with a PhD in Spring 2019, and is planning to pursue a post-doctoral position in a related area. Four additional graduate students were also partially supported on this project, with their work involving smaller contributions such as helping with material characterization and photoelectron spectroscopy measurements. In general, this grant has enabled the PI to stay connected with the organic electronics community through expanding into a new area, organic TEs, which has grown into a core focal area for the group. The data and discoveries made through this grant have enabled the PI and Prof. Chad Risko from the University of Kentucky to submit a collaborative grant to the National Science Foundation entitled "Disentangling Relationships among Dopant Structure, Dopant and Polymer Energetics, Thin-Film Morphology, and the Electrical Properties of Doped Conducting Polymer Films", which was funded and began on Sept. 1, 2019. This federally funded grant builds upon this ACS PRF grant and will enable the Graham group to continue to make meaningful contributions in the area of doped organic semiconductors and polymer TEs.

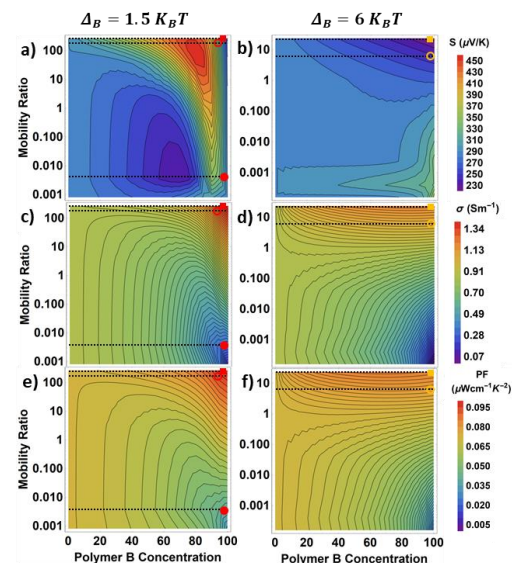


Figure 3. Calculated (a,b) Seebeck coefficient, (c,d) electrical conductivity, and (e,f) power factor for polymer blends.

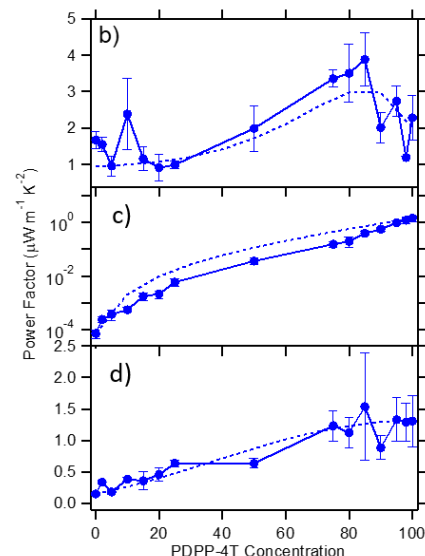
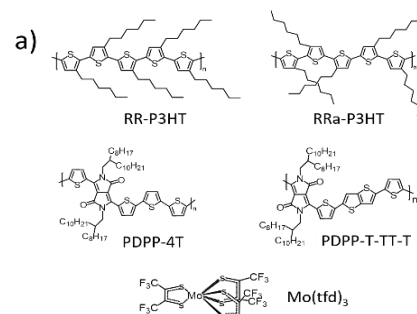


Figure 4. Polymer and dopant structures (a) and experimentally measured power factors of polymer blends with PDPP-4T:RR-P3HT (b), PDPP-4T:RRa:P3HT (c) and PDPP-4T:PDPP-T-TT-T (d)