Link Foundation Energy Fellowship Final Report
Quantifying Charge Transport in Chemically Doped Semiconducting Polymers

Shawn A. Gregory

Advised by Dr. Shannon K. Yee and Mark D. Losego

Georgia Institute of Technology, Atlanta GA, United States of America

Abstract: This report is for the Link Foundation, which generously provided me a graduate research fellowship. In this report, I outline a segment of the organic electronics and organic thermoelectrics fields, then detail the contributions I have made, and finally conclude with a perspective on these fields. Subsequently, in accordance with the fellowship reporting requirements, I list all articles that I have published or will publish whose funding originated (in part) from the Link Foundation. Lastly, I share some personal notes on how this fellowship impacted my PhD experience and career.

Introduction: Semiconducting polymers are materials that engenders the solution processibility, mechanical compliancy, and biocompatibility of archetypal polymeric materials with the charge transport properties, optical properties, and device physics of archetypal inorganic semiconductors.[1, 2] Oftentimes, pristine semiconducting polymers are electrically insulative with comparatively few mobile charge carriers with low mobilities. The charge carrier density and mobility can be increased via chemical doping, and chemical doping oftentimes involves adding or removing electrons from the pristine polymer via a redox chemical reaction. Ultimately, the resulting optical and electronic properties of chemically doped semiconducting polymers is a convoluted function of multiple parameters, including polymer chemistry, dopant chemistry, and processing techniques. While this convolution enables a nearly infinite number of permutations, each of which can be designed for a specific application, this convolution obfuscates the establishment of charge transport models and fundamental process-structure-property relationships.

Developing charge transport models for chemically doped semiconducting polymers is necessary for their deployment as flexible and cost-effective photovoltaic, electrochromic, and thermoelectric devices. These devices can be used to generate electrical energy and/or control the flow of heat, and therefore these semiconducting polymer devices can augment our existing energy technologies. For example, the propensity for a semiconducting polymer to generate an electric voltage from a thermal gradient is quantified using the thermoelectric power factor (PF), which is a product of the Seebeck coefficient squared and electrical conductivity ($PF = S^2\sigma$). Notably, the Seebeck coefficient and electrical conductivity are both macroscopic charge transport properties that are functions of the microscopic distribution of the charge carriers, as detailed in the Boltzmann transport equations,[3, 4]

$$\sigma = \int_{-\infty}^{+\infty} \sigma_{\text{E}}(E,T)\left(-\frac{df}{dE}\right)dE \tag{1}$$

$$S = \frac{k_{\text{B}}}{e}\frac{1}{\sigma}\int_{-\infty}^{+\infty}\sigma_{\text{E}}(E,T)\left(\frac{E-E_{\text{F}}}{k_{\text{B}}T}\right)\left(-\frac{df}{dE}\right)dE \ . \tag{2}$$

Here, $\sigma_{\text{E}}(E,T)$ is the transport function, and its mathematical form embodies the physical processes responsible for charge transport. The transport function is a function of both the energy levels that the charge carriers occupy (E) and their temperature (T). $\left(-\frac{df}{dE}\right)$ is the first derivative of the Fermi-Dirac distribution with respect to energy, and it ascertains a maximum value at the Fermi energy level, where 50% of the states are filled. The integral is evaluated over all electron energy levels (E). Additionally, the Seebeck coefficient has a prefactor of $\frac{k_{\text{B}}}{e}$, which is Boltzmann's constant divided by the fundamental charge constant, and the Seebeck coefficient is weighted by energetic difference of the carriers with respect to the Fermi energy level (E_{F}). Notably, as the extent of doping and number of charge carriers increases, σ increases, E_{F} increases with respect to a band edge, and S decreases. Because S and σ are anticorrelated, optimizing PF for thermoelectric applications is nontrivial. One means to optimize PF is to better understand the mathematical form of $\sigma_E(E,T)$, the physical processes that govern $\sigma_E(E,T)$, and how $\sigma_{\text{E}}(E,T)$ changes as a function of materials system. To date, several transport models and frameworks exist, but there are several shortcomings such as explaining the carrier- and temperature- dependence of the

transport properties and the $S(\sigma)$ anticorrelation. These shortcomings hinder the rational and quantitative development of polymer semiconductors for thermoelectric applications. Therefore, in my thesis, I developed and compiled experimental methods, which are used to create and substantiate novel charge transport functions and models, which are then used to contextualize the charge transport properties of chemically doped semiconducting polymers.

Results: The crux of my work is the development of the semi-localized transport (SLoT) model (Figure 1).[5] The SLoT model was the result of reading and learning from several pivotal studies[4, 6-8] and learning from several hand-on experiences.[9-12] The SLoT model asserts a transport function that captures both localized (hopping-like, insulator-like) and delocalized (band-like, metal-like) contributions to the observable transport properties. In other words, the SLoT model can hypothetically capture the entire transport spectrum, which has not been rationalized before in a single mathematical and physical model. Specifically, the SLoT model asserts,

$$\sigma_{\mathrm{E}}(E,T) = \begin{cases} 0, & E < E_{\mathrm{t}} \\ \sigma_0 \exp\left(\frac{-W_{\mathrm{H}}(c)}{k_{\mathrm{B}}T}\right)\left(\frac{E-E_t}{k_{\mathrm{B}}T}\right), & E > E_{\mathrm{t}} \end{cases}. \tag{3}$$

Here, σ_0 is a transport function prefactor that is independent of the number of charge carriers and independent of the energy levels they occupy. σ_0 captures energy-independent parameters such as the mobility prefactor and effective mass.[13] $\exp\left(\frac{-W_{\mathrm{H}}(c)}{k_{\mathrm{B}}T}\right)$ is Arrhenius-like activation energy term, commonly

$$\sigma = \sigma_0 \exp\left(-\frac{W_{\mathrm{H}}(c)}{k_{\mathrm{B}}T}\right)\int_0^\infty \left(\frac{E-E_t}{k_{\mathrm{B}}T}\right)\left(-\frac{df}{dE}\right)dE \qquad S = \frac{k_B}{e}\frac{\sigma_0 \exp\left(-\frac{W_{\mathrm{H}}(c)}{k_{\mathrm{B}}T}\right)\int_0^\infty \left(\frac{E-E_t}{k_{\mathrm{B}}T}\right)\left(\frac{E-E_F}{k_{\mathrm{B}}T}\right)\left(-\frac{df}{dE}\right)dE}{\sigma_0 \exp\left(-\frac{W_{\mathrm{H}}(c)}{k_{\mathrm{B}}T}\right)\int_0^\infty \left(\frac{E-E_t}{k_{\mathrm{B}}T}\right)\left(-\frac{df}{dE}\right)dE}$$

Delocalized, metal-like contributions   Localized, hopping-like contributions
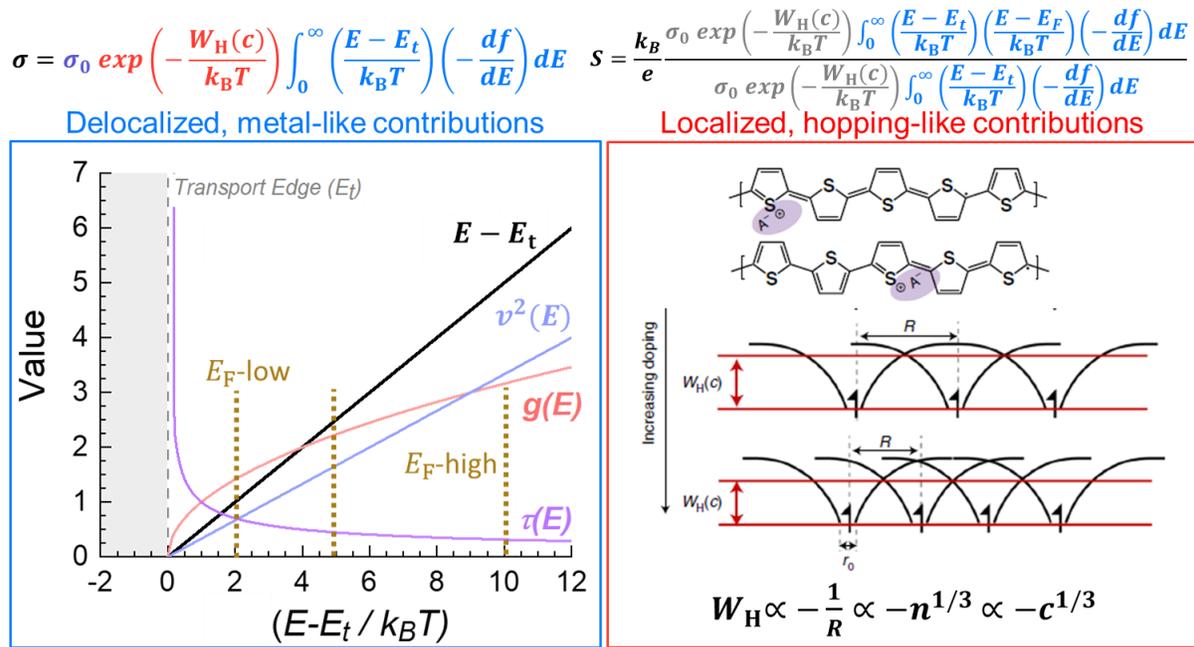

Figure 1: Summarizing the semi-localized transport (SLoT) model. The top row shows Eq. 1 and Eq.2 with the SLoT transport function (Eq. 3) evaluated in the integral expressions. Notably, σ is a function of all three terms, while S is only a function of the energy-dependent integral values. The leftmost blue box shows energy-dependent contributions, commonly found in delocalized and metal-like transport expressions. This plot shows that as the extent of doping increases, E_{F} increases with respect to the transport edge, E_{t}. Furthermore, the velocity squared of the carriers (v^2), the density of states ($g(E)$), and the relaxation time $\tau(E)$, all vary as a function of doping. The product of these three terms is linear with respect to the x-axis, and therefore a linear transport function is used in the integrals. The rightmost red box shows energy-independent and localized contributions to the transport function. Poly(thiophene) chains can be oxidative doped, yielding polaronic charge carriers that are electrostatically attracted to the doping counterion (A⁻). These polaronic charge carriers (represented by single barbed arrows) are localized in potential energy wells with depth W_{H} and separated by some distance R. In the above example, the carrier ratio is 2/10 or 0.2, representing two charge carriers for every ten aromatic ring sites. As the extent of doping increases, the distance between the carriers and the activation barrier decreases. At some carrier density (n) or carrier ratio (c), $W_{\mathrm{H}} \to 0$ and the transport is thought to be delocalized. Figures adapted from Ref. 5.

found in hopping-like transport models.[6, 14, 15] W_H is the localization activation energy and captures the energetic barrier between carrier sites. c is the carrier ratio, or the ratio of occupied sites to total available sites. c can be though as the extent of doping and is linearly proportional to the carrier density (n). $W_H \propto -c^{1/3}$, or as the extent of doping increases, the barrier between sites decreases.[14] Eventually, at some c, $W_H = 0$, and the transport is considered to be delocalized. $\left(\frac{E-E_t}{k_B T}\right)$ is a linear energy-dependent term, commonly found in delocalized transport models.[3, 4, 13, 16, 17] As the extent of doping increases and the energy levels that the charge carriers occupy increases, with respect to the transport edge, E_t (akin to a band edge), the energy-dependent contribution increases. Notably, when Eq. 3 is evaluated in Eq. 1, all three terms contribute to the observable electrical conductivity. In contrast, when Eq. 3 is evaluated in Eq. 2, only the energy-dependent terms are responsible for the observable Seebeck coefficient.

We validated the SLoT model (Eq. 3) using by measuring the thermoelectric properties as a function of temperature and carrier ratios (using X-ray photoelectron spectroscopy[18-20]). Through this validation, we can measure or calculate (through simple linear extrapolations or interpolations) more fundamental transport parameters that provide deeper insight on charge transport in chemically doped semiconducting polymer systems. For example, we can now quantify the carrier ratio (or density) needed for delocalized and metal-like transport (c_d,n_d) as well as the carrier ratio (or density) needed for the Fermi energy level to be greater than the transport edge and degenerately doped (c_d,n_d). Furthermore, we can

Table 1: Compiled notes and parameters for literature studies analyzed with the SLoT model. $S(\sigma)$, $\eta(c)$, $W_H(c)$ refers to whether the literature studies provided sufficient data to analyze the S-σ curve, the $\eta(c)$, and/or $W_H(c)$ relationship. Studies that have Y (yes) for all three categories have sufficient data to apply the SLoT model without freely adjustable parameters. Rows are shaded blue and white corresponding to the number of "Yes" answers which determines the confidence of the model. W_H^{max} and W_H^{slope} are the maximum localization energy and the rate which localization decays with increasing c, respectivelyc_d, n_d refers to the carrier ratio or density (x10^{20}) needed to achieve $W_H = 0$ and converge with the Kang-Snyder $s = 1$ model. c_t refers to the carrier ratio needed to achieve $\eta = 0$ or equivalently $E_F = E_t$. At $c > c_t$ the SLoT model indicates that the Fermi level has entered the band. Adapted from Ref. 5, and see Ref. 5 for additional information.

Polymer	Dopant	$S(\sigma)$	$\eta(c)$	$W_H(c)$	σ_0 [S/cm]	W_H^{max} [meV]	W_H^{slope} [meV]	c_d [-], n_d [cm^{-3}]	c_t [-]
P3HT	FeCl$_3$	Y	Y	Y	9	288	443	0.27, 9.9	0.04
P3HT	NOPF$_6$	Y	Y	Y	0.5	325	410	0.5, 18	0.06
PBTTT	TFSI$^-$	Y	Y	N	22	240	640	0.052, 0.91	0.007
PA	FeCl$_3$ & More	Y	Y	Y	10	265	775	0.039, 9.1	9.4 x 10^{-4}
PEDOT	Fe(OTs)$_3$	Y	Y	N	75	700	1200	0.20, 8.4	0.22
CNT	OA	Y	N	N	250	300	1100	0.02, 2.5	0.01
N2200	FET	N	Y	Y	2	150	220	0.32, 1.9	0.09

quantify how the electronic structure fills with increased doping level, how localization decays (via W_H slope and maximum intercept values) and model the hypothetical maximum electrical conductivity. In our previous report, we succinctly tabulated these transport parameters for several organic systems (see Table 1).

Impact and Perspective: The SLoT model was published in 2021,[5] so its full impact has not been realized; therefore, the potential impact shared here is more speculative and from an inherently personal perspective. As stated in its original publication, the SLoT model and its parameters will be the quantitative language needed and used for developing more advanced polymer, dopant, and processing systems. If you open any undergraduate solid-state physics or electronic materials textbook,[21] you will find tables of fundamental transport parameters, such as the effective density of states at the band edge, effective masses, and mobilities as a function of carrier density and temperature for a variety of inorganic semiconductors and dopants. This kind of quantitative language enabled the rational development of inorganic semiconductors, including silicon. Unfortunately, these quantitative descriptors were not ubiquitously documented nor experimentally accessible for chemically doped semiconducting polymers before the SLoT model. The SLoT model enables these more fundamental transport parameters to be quantified for semiconducting polymers because the SLoT model accounts for and isolated localized and delocalized contributions to the observable transport properties. I recognize that all models are wrong, but some are useful; I believe that SLoT will be useful because it bridges both localized and delocalized (archetypal organic and inorganic) transport formalisms. Hopefully, the SLoT model will accelerate the development of polymer semiconductors.

Current and future iterations of the SLoT model will be able to address more challenging transport phenomena. Some examples include the electronic contribution to thermal conductivity, the inversion of the Seebeck coefficient, and between quantifying "narrow" electronic structures. Furthermore, the SLoT model operates under an appropriately weighted homogenous material approximation. Explicitly, the electrical conductivity and Seebeck coefficient and the SLoT parameters are single values used to represent the inhomogeneous ensemble. This approximation is not ideal, because every microdomain can contribute differently to the macroscopic observable. Multi-scale modeling and measurement techniques (*e.g.* atomic force microscopy with electrical conductivity mapping) will be able to better quantify individual spatial domains' contributions to the observable transport properties.

References

1.   Reynolds, J. R.; Thompson, B. C.; Skotheim, T. A., *Handbook of Conducting Polymers*. 1998.
2.   Russ, B.; Glaudell, A.; Urban, J. J.; Chabinyc, M. L.; Segalman, R. A., Organic Thermoelectric Materials for Energy Harvesting and Temperature Control. *Nature Reviews Materials* **2016,** *1* (10), 16050.
3.   May, A. F.; Snyder, G. J., Introduction to Modeling Thermoelectric Transport at High Temperatures. In *Materials, Preparation, and Characterization in Thermoelectrics*, CRC Press: 2017.
4.   Kang, S. D.; Snyder, G. J., Charge-Transport Model for Conducting Polymers. *Nature Materials* **2017,** *16* (2), 252-257.
5.   Gregory, S. A.; Hanus, R.; Atassi, A.; Rinehart, J. M.; Wooding, J. P.; Menon, A. K.; Losego, M. D.; Snyder, G. J.; Yee, S. K., Quantifying Charge Carrier Localization in Chemically Doped Semiconducting Polymers. *Nature Materials* **2021**.
6.   Xuan, Y.; Liu, X.; Desbief, S.; Leclère, P.; Fahlman, M.; Lazzaroni, R.; Berggren, M.; Cornil, J.; Emin, D.; Crispin, X., Thermoelectric Properties of Conducting Polymers: The Case of Poly(3-Hexylthiophene). *Physical Review B* **2010,** *82* (11), 115454.
7.   Thomas, E. M.; Popere, B. C.; Fang, H.; Chabinyc, M. L.; Segalman, R. A., Role of Disorder Induced by Doping on the Thermoelectric Properties of Semiconducting Polymers. *Chemistry of Materials* **2018,** *30* (9), 2965-2972.
8.   Glaudell, A. M.; Cochran, J. E.; Patel, S. N.; Chabinyc, M. L., Impact of the Doping Method on Conductivity and Thermopower in Semiconducting Polythiophenes. *Advanced Energy Materials* **2015,** *5* (4).
9.   Gregory, S. A.; Ponder, J. F.; Pittelli, S. L.; Losego, M. D.; Reynolds, J. R.; Yee, S. K., Thermoelectric and Charge Transport Properties of Solution-Processable and Chemically Doped Dioxythienothiophene Copolymers. *ACS Applied Polymer Materials* **2021**.
10.   Pittelli, S. L.; Gregory, S. A.; Ponder, J. F.; Yee, S. K.; Reynolds, J. R., Inducing Planarity in Redox-Active Conjugated Polymers with Solubilizing 3,6-Dialkoxy-Thieno[3,2-B]Thiophenes (Dotts) for Redox and Solid-State Conductivity Applications. *Journal of Materials Chemistry C* **2020,** *8* (22), 7463-7475.
11.   Un, H.-I.; Gregory, S. A.; Mohapatra, S. K.; Xiong, M.; Longhi, E.; Lu, Y.; Rigin, S.; Jhulki, S.; Yang, C.-Y.; Timofeeva, T. V.; Wang, J.-Y.; Yee, S. K.; Barlow, S.; Marder, S. R.; Pei, J., Understanding the Effects of Molecular Dopant on N-Type Organic Thermoelectric Properties. *Advanced Energy Materials* **2019,** *9* (24), 1900817.
12.   Gregory, S. A.; Menon, A. K.; Ye, S.; Seferos, D. S.; Reynolds, J. R.; Yee, S. K., Effect of Heteroatom and Doping on the Thermoelectric Properties of Poly(3-Alkylchalcogenophenes). *Advanced Energy Materials* **2018,** *8* (34).
13.   Zevalkink, A.; Smiadak, D. M.; Blackburn, J. L.; Ferguson, A. J.; Chabinyc, M. L.; Delaire, O.; Wang, J.; Kovnir, K.; Martin, J.; Schelhas, L. T.; Sparks, T. D.; Kang, S. D.; Dylla, M. T.; Snyder, G. J.; Ortiz, B. R.; Toberer, E. S., A Practical Field Guide to Thermoelectrics: Fundamentals, Synthesis, and Characterization. *Applied Physics Reviews* **2018,** *5* (2), 021303.
14.   Mott, N. F.; Davis, E. A., *Electronic Processes in Non-Crystalline Materials*. Oxford University Press: 2012.
15.   Kim, E. G.; Coropceanu, V.; Gruhn, N. E.; Sanchez-Carrera, R. S.; Snoeberger, R.; Matzger, A. J.; Bredas, J. L., Charge Transport Parameters of the Pentathienoacene Crystal. *J Am Chem Soc* **2007,** *129* (43), 13072-81.
16.   Snyder, G. J.; Pereyra, A.; Gurunathan, R., Effective Mass from Seebeck Coefficient. *Advanced Functional Materials* **2022**.
17.   Snyder, G. J.; Snyder, A. H.; Wood, M.; Gurunathan, R.; Snyder, B. H.; Niu, C., Weighted Mobility. *Adv Mater* **2020,** *32* (25), e2001537.
18.   Harris, J. K.; Neelamraju, B.; Ratcliff, E. L., Intersystem Subpopulation Charge Transfer and Conformational Relaxation Preceding in Situ Conductivity in Electrochemically Doped Poly(3-Hexylthiophene) Electrodes. *Chemistry of Materials* **2019,** *31* (17), 6870-6879.

19.   Shallcross, R. C.; Stubhan, T.; Ratcliff, E. L.; Kahn, A.; Brabec, C. J.; Armstrong, N. R., Quantifying the Extent of Contact Doping at the Interface between High Work Function Electrical Contacts and Poly(3-Hexylthiophene) (P3ht). *The Journal of Physical Chemistry Letters* **2015,** *6* (8), 1303-1309.
20.   Ratcliff, E. L.; Jenkins, J. L.; Nebesny, K.; Armstrong, N. R., Electrodeposited, "Textured" Poly(3-Hexyl-Thiophene) (E-P3ht) Films for Photovoltaic Applications. *Chemistry of Materials* **2008,** *20* (18), 5796-5806.
21.   Kasap, S. O., *Principles of Electronic Materials and Devices*. 2005.

Published Articles that Acknowledged the Link Foundation:

9. Khaled Al-Kurdi, Shawn A. Gregory*, James F. Ponder Jr., Amalie Atassi, Joshua Rinehart, Austin Jones, John R. Reynolds, Seth R. Marder, Shannon K. Yee, "**Effects of Iron(III) Dopants on the Charge-Transport Properties of Polythiophene and Poly(dialkoxythiophene) Derivatives**" *Under Revision with ACS Applied Materials and Interfaces*

8. James F. Ponder Jr., Shawn A. Gregory*, Amalie Atassi, Akanksha K. Menon, Augustus Lang, Lisa R. Savagian, John R. Reynolds, and Shannon K. Yee "**Significant Enhancement of the Electrical Conductivity of Conjugated Polymers by Post-Processing Side Chain Removal**" *Accepted, J. Am. Chem. Soc.* (2021).

7. Brandon D. Piercy, Jamie P. Wooding, Shawn A. Gregory, Mark D. Losego, "Pulsed Heating Atomic Layer Deposition for Epitaxial Growth Of Zinc Oxide Thin Films on C-Plane Sapphire" *Dalton Transactions*, (2021)

6. Kristina Malinowski, Shawn A. Gregory, Yi Li, Oliver Hvidsten, Alexandria Jungreis, Mark D. Losego, " *In situ* electrical conductivity of poly(aniline) vapor phase infiltrated and doped with $TiCl_4 + H_2O$" *J. Vacuum Science and Technology A*, (2021)

5. Pooja J. Ayare, Shawn A. Gregory, Ryan Key, Andrew E. Short, Jake G. Tillou, James D. Sitter, Typher Yom, Dustin Goodlett, Dong-Chan Lee, Faisal Alamgir, Mark D. Losego, Aaron Vannucci, "Immobilization of Molecular Catalysts on Solid Supports via Atomic Layer Deposition for Chemical Synthesis in Green Solvents" *RSC. Green Chemistry*, (2021).

4. Shawn A. Gregory, Riley Hanus, Amalie Atassi, Jamie P. Wooding, Akanksha Menon, Mark D. Losego, G. Jeffery Snyder, Shannon K. Yee "**Quantifying Charge Carrier Localization in Chemically Doped Semiconducting Polymers**"*, Nature Materials*, **20**, 1414-1421, (2021).

3. Madeleine Gordon, Shawn A. Gregory*, Jamie P. Wooding, Shuyang Ye, Dwight Seferos, Mark D. Losego, Jeffery Urban, and Shannon Yee, Akanksha K. Menon, "**Effects of F4TCNQ doping on the structural and electronic properties of poly(alkyl-chalcogenophenes)**" *Applied Physics Letters*, **118,** 233301, (2021) *Featured Article*

2. Shawn A. Gregory, James F. Ponder, Sandra L. Pitelli, Mark D. Losego, John R. Reynolds, Shannon K. Yee, "**Charge Transport and Thermoelectric Properties of a Dioxythienothiophene copolymers**" *ACS Applied Polymer Materials,* **3**,5, 2316-2324, (2021)

1. Shawn A. Gregory, Yi Li, Timothy D. Monroe, Junjian Li, Shannon K. Yee, Mark D. Losego, "**Vapor Phase Infiltration Doping of the Semiconducting Polymer Poly(aniline): Mechanisms, Reaction Kinetics, and Electrical and Optical Properties**", *ACS Applied Polymer Materials,* **3**, 720-729, (2021)

Anticipated Articles that will Acknowledge the Link Foundation:

6. Inherently Conductive PEDOT(OH) Films by Post-Processing Side Chain Removal from a Soluble Precursor Polymer
5. Electrical Conductivity Enhancement of Oligoether-Functionalized Dioxythiophene Copolymers Through Comonomer Selection
4. Achieving metal-like charge transport in chemically doped semiconducting polymers with cleavable side chains
3. Electrical Conductivity Enhancement of Oligoether-Functionalized ethylenedioxythiophene polymers
2. Thermoelectric and Charge Transport Properties of Poly[2,5-bis(3-tetradecylthiophen-2-yl)thieno[3,2-b]thiophene].
1. Thermoelectric and Charge Transport Properties of PDPP2T-TT-OD.

Impact of the Fellowship:

I am extremely grateful for the Link Foundation Energy Fellowship. This fellowship has provided me intellectual freedom to pursuit the ideas and work that I find to be most intellectually stimulating while also having the potential to accelerate the field of polymer semiconductors. Because of this freedom and opportunity, I will always have an interest in polymer semiconductors and will want to contribute to this field in the future.