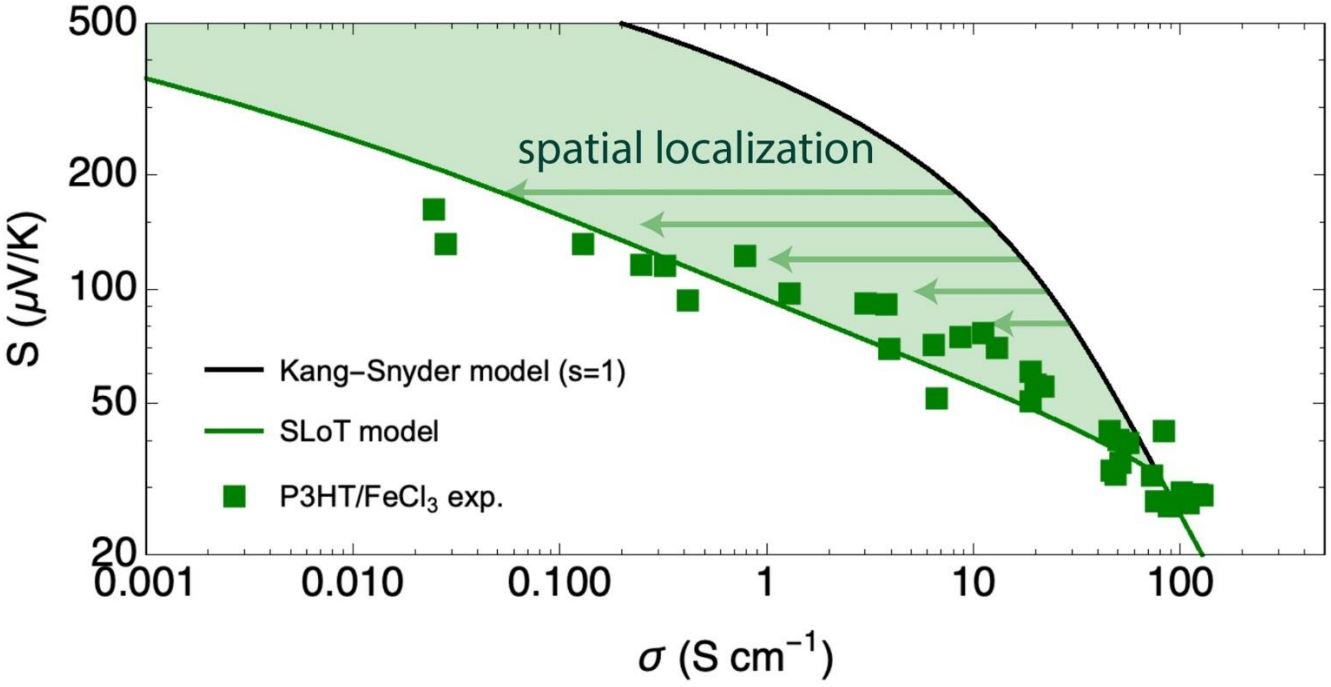
Quantifying charge carrier localization and charge transport properties in chemically doped semiconducting polymers

Shawn Gregory[1], Riley Hanus[1], Amalie Atassi[1], Joshua Rinehart[1], Jamie Wooding[1], Akanksha Menon[2], Mark Losego[1], G.Jeffery Snyder[3], and Shannon Yee[1]

1. Georgia Institute of Technology, Marietta, Georgia, United States
2. E O Lawrence Berkeley National Laboratory, Berkeley, California, United States
3. Northwestern University, Evanston, Illinois, United States

Charge transport in semiconducting polymers ranges from localized (hopping-like) to delocalized (metal-like), and the transport physics can vary significantly as a function of several engineering parameters (*e.g.,* polymer chemistry, dopant chemistry, dopant quantity, and processing.) Despite the increasing ubiquity of semiconducting polymers, there is not a succinct transport model that captures this wide spectrum of transport physics nor its dependency on carrier densities and these engineering parameters. To inform the development of an improved transport model, we collected temperature-dependent thermoelectric measurements on poly(3-hexylthiophene) chemically doped with $FeCl_3$. The extent of doping and carrier densities were quantified using XPS, and we observed that with increasing carrier density, the electrical conductivity increased, the thermal activation energy for electrical conductivity decreased, and the Seebeck coefficient decreased. We then used these measurements to develop the semi-localized transport model (SLoT model). The SLoT model uses a modified Boltzmann transport approach to quantify the effects of several engineering parameters and carrier densities on the observable transport properties. Additionally, the SLoT model predicts how quickly the localization activation energy decreases and how quickly the Fermi energy level increases with increasing carrier density. Furthermore, several literature studies are well modeled using SLoT, including organic field-effect transistor thermoelectrics and chemically doped single-walled carbon nanotubes. This consistency validates the SLoT model and suggests broad utility. Ultimately, for the first time, this SLoT model quantifies both localized and delocalized contributions to charge transport in chemically doped semiconducting polymers, and it enables us to design the next generation of semiconducting polymer electronics more rationally and quantitatively.



S-σ plot showing that a nominal s = 1 Kang-Snyder model cannot explain the P3HT-$FeCl_3$ experimental data. The SLoT model accounts for a localization energy that decreases with increasing carrier concentration.