Organic thermoelectric (TE) generators have the potential for low grade waste heat recovery and energy harvesting. These devices can be fabricated via printing processes that are low cost from materials that are lightweight and flexible, for applications ranging from self-powered sensors to wearable electronics. Polymers have an inherently low thermal conductivity, which makes them attractive TE materials and in the past decade, significant progress has been made with high performing p-type materials based on PEDOT:PSS and its derivatives. The primary challenge for n-type organic materials is achieving a sufficiently high electrical conductivity ($\sigma$) via methods of doping that will not decrease the Seebeck coefficient ($S$). This is because the band-like transport framework describes these material properties as inherently coupled and opposing. Polymers are unique because their morphology can play a role in decoupling or simultaneously improving $S$ and $\sigma$, and charge transport is better described by hopping conduction. Metallo-organic polymers are a suitable class of materials to understand how thermal vibrations couple to electrons in these disordered systems and lead to transport. In this work, we report the synthesis, characterization and thermoelectric properties of poly(nickel-ethenetetrathiolate) or Ni-ETT and poly(nickel-tetrathiooxalate) or Ni-TTO that are intrinsically electrically conducting and n-type. These polymers form as infusible black powders and are dispersed in a poly(vinylidene fluoride) matrix to fabricate films. By performing controlled syntheses and modifying the reaction conditions (counterion and oxidation states), we investigate the extent to which $S$ and $\sigma$ can be enhanced simultaneously. By optimizing the film fabrication, we can reduce energy-independent scattering mechanisms (electron-phonon scattering, interface scattering, or impurity scattering), which in turn enhance $\sigma$ while $S$ remains unchanged. We also report the effects of annealing as a viable technique to improve the Seebeck coefficient of these n-type polymers. The temperature dependent properties for these polymers show thermally-activated behavior that is consistent with hopping transport, where both $\sigma$ and $S$ increase with temperature.

Fig. 1: Thermally-activated charge transport in semiconducting polymers result in a simultaneous increase in $\sigma$ and $S$ with temperature