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# Quantifying Charge Carrier Localization in PBTTT using Thermoelectric and Spectroscopic Techniques

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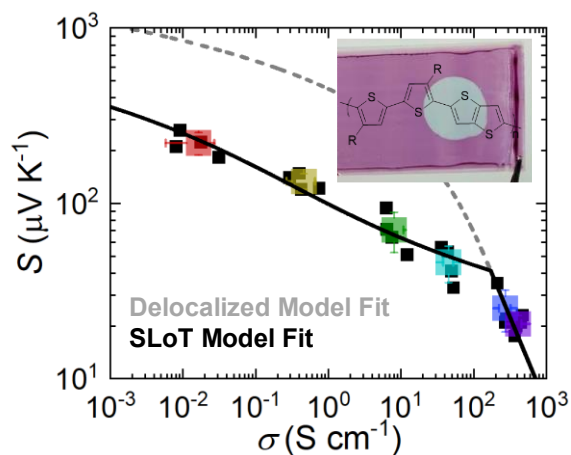
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**Abstract:** Chemically doped poly[2,5-bis(3-alkylthiophen-2-yl)thieno[3,2-b]thiophene] (PBTTT) shows promise for many organic electronic applications, but rationalizing its charge transport properties is challenging because conjugated polymers are inhomogeneous, with convoluted optical and solid-state transport properties. Herein, we use the semi-localized transport (SLoT) model to quantify how the charge transport properties of PBTTT change as a function of iron (III) chloride FeCl<sub>3</sub> doping level. We use the SLoT model to calculate fundamental transport parameters, including the carrier density needed for metal-like electrical conductivities and the position of the Fermi energy level with respect to the transport edge. We then contextualize these parameters with other polymer-dopant systems and previous PBTTT reports. Additionally, we use grazing incident wide-angle x-ray scattering (GIWAXS) and spectroscopic ellipsometry (SE) techniques to better characterize inhomogeneity in PBTTT. Our analyses indicate that PBTTT obtains high electrical conductivities due to its quickly rising reduced Fermi energy level, and this rise is afforded by its locally high carrier densities in highly ordered microdomains. Ultimately, this report sets a benchmark for comparing transport properties across polymer-dopant-processing systems.

**Keywords:** redox doping, charge transport, electrical conductivity, organic electronics, conjugated polymers

**ToC Image:**



33 **Introduction:**

34 Semiconducting polymers are used in a variety of optical and electronic applications because of  
35 their synthetic tunability, mechanical compliancy, and processability.<sup>1</sup> One example is poly[2,5-bis(3-  
36 alkylthiophen-2-yl)thieno[3,2-b]thiophene] (PBTTT), which shows promise in many applications, such as  
37 thermoelectrics<sup>2-4</sup> and transistors.<sup>5, 6</sup> PBTTT is used in these applications because it is a solution processible  
38 conjugated polymer that has remarkably high carrier mobilities ( $\mu$  ranging from  $\sim 0.1$  to  $10 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ ,  
39 measured using multiple techniques)<sup>7-10</sup> and electrical conductivities ( $\sigma$ , ranging from  $10^1$  to  $\gg 10^3 \text{ S cm}^{-1}$ ),<sup>10-19</sup>  
40 depending on the doping and processing conditions (**Figure 1a**). Despite these high performing  
41 transport properties, it is not fully and quantifiably understood how and to what extent side-chain chemistry,  
42 dopants, and other processing conditions affect transport in PBTTT. Quantifying key parameters and  
43 characteristics that lead to these macroscopic transport properties is needed for the rational development of  
44 polymer-dopant-processing systems.

45 Charge transport models contextualize macroscopically measurable transport properties to  
46 microscopic spatial and energetic distributions and can provide insights into rational design. We have  
47 previously demonstrated that a semi-localized transport (SLoT) model can isolate and quantify localized  
48 (hopping-like) and delocalized (metal-like) contributions to the measurable electrical conductivity ( $\sigma$ ) and  
49 Seebeck coefficient ( $S$ ).<sup>20</sup> Central to charge transport models is the assertion of a transport function; for the  
50 SLoT model, the transport function,  $\sigma_E(E, T, c)$ , is given as:

$$\sigma_E(E, T, c) = \begin{cases} 0, & E_t < 0 \\ \sigma_0 \exp\left(\frac{-W_H(c)}{k_B T}\right) \times \left(\frac{E-E_t}{k_B T}\right), & E_t \geq 0, W_H \geq 0 \\ \sigma_0 \times \left(\frac{E-E_t}{k_B T}\right), & E_t \geq 0, W_H < 0 \end{cases} \quad (1)$$

51  
52 This transport function quantifies the contributions of charge carriers at a specific electron energy level ( $E$ ),  
53 temperature ( $T$ ), and carrier ratio ( $c$ , the number of charge carriers per site, which is linearly related to the  
54 carrier density,  $n$ )<sup>20, 21</sup> to the measurable transport properties,  $\sigma$  and  $S$ .<sup>22-24</sup> Eq. 1 states that charge carriers  
55 at some energy level ( $E$ ) less than the transport edge ( $E_t$ , which can be synonymous with a band edge and

56 the reference zero energy level, see illustrations in **Figure 1b**) do not contribute to the transport function  
57 nor to charge transport. In contrast, charge carriers that have some  $E$  greater than  $E_t$  contribute meaningfully  
58 to charge transport and their contribution is weighted by  $\sigma_0 \exp\left(\frac{-W_H(c)}{k_B T}\right) \times \left(\frac{E-E_t}{k_B T}\right)$ .  $\sigma_0$  is independent of  
59 doping level, can ideally be related to the effective mass and energy independent mobility, and laterally  
60 shifts the  $S(\sigma)$  curve.<sup>22</sup> The  $\exp\left(\frac{-W_H(c)}{k_B T}\right)$  term captures the hopping-like contribution to charge transport  
61 due to the spatial and electrostatic localization of charge carriers in an inhomogeneous medium, such as a  
62 semiconducting polymer like PBTTT (see illustrations in **Figure 1b**).<sup>25-28</sup> For example, charge transport is  
63 likely greater along the conjugated backbones and between more ordered  $\pi - \pi$  stacks, rather than between  
64 alkyl side chains and less ordered regions.<sup>29-32</sup>  $W_H(c)$  is the localization energy, and it is calculable from  
65 macroscopic transport measurements; therefore,  $W_H(c)$  represents a bulk ensemble average.  $W_H(c)$   
66 generally decreases as the carrier ratio, or carrier density, increases because the carriers' electrostatic  
67 potential wells increasingly impinge on one another and the barrier for hopping decreases (see illustrations  
68 in **Figure 1b**).<sup>27, 29, 33, 34</sup> Eventually, at some carrier ratio,  $W_H$  may be near negligible ( $\lesssim k_B T$  or zero), but  
69 all polymer-dopant-processing systems do not necessarily obtain these low  $W_H$  values.<sup>34-36</sup> If  $W_H \lesssim 0$ , then  
70 localization is not the dominant physical contribution that explains  $\sigma(T)$ , the SLoT model asserts  
71  $\exp\left(\frac{-W_H(c)}{k_B T}\right) = 1$ , and the transport function is dependent on only  $\sigma_0$  and  $\left(\frac{E-E_t}{k_B T}\right)$ . Lastly,  $\left(\frac{E-E_t}{k_B T}\right)$  captures  
72 the electron energy dependent contribution to the transport function, akin to delocalized and metal-like  
73 transport formalisms.<sup>22-24</sup> As the charge carrier ratio and density increases, the energy levels which charge  
74 carriers occupy ( $E$ ) and the Fermi energy level ( $E_F$ ) increase with respect to the transport edge (see  
75 illustrations in **Figure 1b**).

76 Evaluating the transport function with the Boltzmann transport equation yields expressions that  
77 relate the macroscopic and measurable  $\sigma$  and  $S$  values to these microscopic parameters and distributions  
78 detailed in Eq. 1.<sup>22-24</sup> The electrical conductivity expression is,

$$\sigma = \sigma_0 \exp\left(\frac{-W_H(c)}{k_B T}\right) \times \int_0^\infty \left(\frac{E-E_t}{k_B T}\right) \left(-\frac{df}{dE}\right) dE, \quad (2)$$

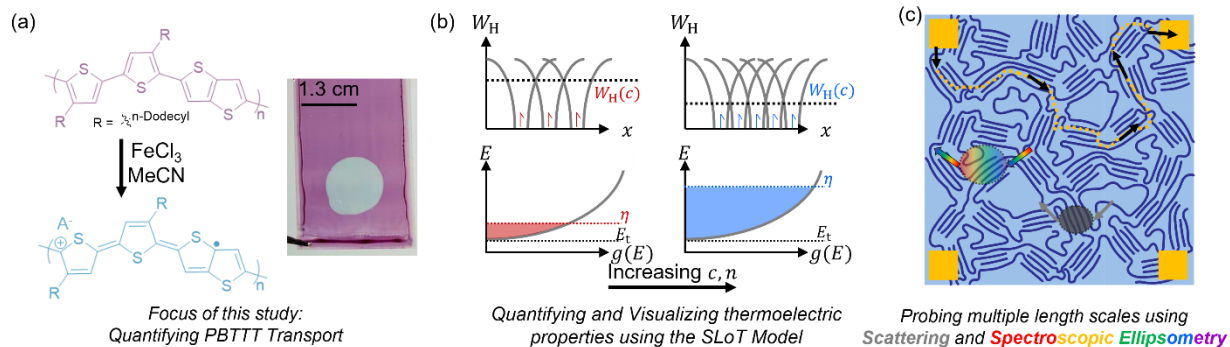
79 and Eq. 2 is a function of the energetic distribution of the charge carriers and their localization. As the  
 80 extent of doping increases, localization decreases and the energy levels that charge carriers occupy  
 81 increases, leading to large increases in  $\sigma$ . The Seebeck coefficient expression is,

$$S = \frac{k_B}{e} \frac{\int_0^\infty \left(\frac{E-E_t}{k_B T}\right) \left(\frac{E-E_t}{k_B T} - \eta\right) \left(-\frac{df}{dE}\right) dE}{\int_0^\infty \left(\frac{E-E_t}{k_B T}\right) \left(-\frac{df}{dE}\right) dE}, \quad (3)$$

82 where  $\eta = \frac{E_F - E_t}{k_B T}$ , is known as the reduced Fermi energy level, and represents the energetic distance between  
 83 the Fermi energy level ( $E_F$ ) and the transport edge (see illustrations in **Figure 1b**). Notably, Eq. 3 is only a  
 84 function of the energetic distribution of the charge carriers and is not a function of  $\sigma_0$  nor  $W_H$ . Therefore,  
 85 there is only one  $\eta$  value and one set of Fermi integral values for Eq. 3 to be true at a fixed and measured  
 86 Seebeck coefficient.<sup>24</sup> Furthermore, by measuring  $\sigma(T)$  and  $S(T)$  and by calculating the Fermi integral  
 87 values,  $W_H$  and  $\sigma_0$  in Eq. 2 are calculable at each doping level. Therefore, all SLoT model parameters are  
 88 calculable from experimental measurements. With the SLoT model, one can isolate the interrelationships  
 89 between macroscopic transport properties, fundamental transport parameters (*e.g.*  $\sigma_0, \eta(c), W_H(c)$ ), and  
 90 other physical observables (*e.g.* interchain distances, doping level, dopant intercalation).

91         Herein, we measure the charge transport properties of a n-dodecyl functionalized PBTTT doped  
 92 with iron(III) chloride ( $\text{FeCl}_3$ ) and use the SLoT model to benchmark its charge transport properties for the  
 93 first time (**Figure 1 a,b**). Furthermore, we contextualize the PBTTT SLoT parameters by comparing with  
 94 other polymer-dopant-processing systems. Lastly, we expand the SLoT model and its physical significance  
 95 by performing grazing incidence wide angle x-ray scattering (GIWAXS) and spectroscopic ellipsometry  
 96 (SE) measurements (**Figure 1c**). With these techniques, we find that the localization energy is independent  
 97 of paracrystalline disorder and that the carrier density in metal-like microdomains are likely higher than  
 98 that of the macroscopic average.

99



100 **Figure 1:** Visual summarizing the key facets of this study. (a) Neutral PBTTT-C12 (purple) is sequentially doped with FeCl<sub>3</sub> at  
 101 various concentrations to control the extent of oxidation and resulting thermoelectric properties. Oxidatively doped PBTTT (blue)  
 102 contains polaronic charge carriers (likely a combination of polarons and bipolarons) and distinctly different electronic and optical  
 103 properties (see inset for a digital photograph of neutral PBTTT with a doped circular region). (b) The SLoT model is used to  
 104 contextualize the thermoelectric properties of PBTTT at various doping levels. At low FeCl<sub>3</sub> concentrations and low extents of  
 105 oxidation, PBTTT is lightly doped, the density of states,  $g(E)$ , is lightly filled with mobile charge carriers, has a low reduced Fermi  
 106 energy level,  $\eta$ , and the charge carriers are spatially localized with high hopping activation energies,  $W_H$  (see leftmost figures in  
 107 red). In contrast, at high FeCl<sub>3</sub> concentrations and high extents of oxidation, PBTTT is heavily doped, the density of states is heavily  
 108 filled with mobile charge carriers, has a high reduced Fermi energy level, and the charge carriers can be thought as spatially  
 109 delocalized with little-to-no hopping activation energies. (c) Cartoon illustrating different measurement techniques and their  
 110 interaction area and conditions. Thermoelectric measurements, represented by gold square contact pads and dashed gold percolated  
 111 transport pathway, are indicative of the appropriately weighted bulk ensemble average charge transport in all inhomogeneous  
 112 microdomains along a closed circuit and percolated pathway. In contrast, scattering and spectroscopic measurements can glean  
 113 insight on microstructure and transport properties in specific microscopic domains that do not require a closed circuit and percolated  
 114 pathway but may require other physical conditions to be met (e.g., periodic ordering for Bragg diffraction).  
 115  
 116

117 **Methods:**

118  
119 PBTTT-C12 was prepared via a Migita-Kosugi-Stille (Stille) polymerization, as outlined in **Note**  
120 **S1**. The repeat unit structure was confirmed with  $^1\text{H-NMR}$ , as shown in **Figure S1**, and is consistent with  
121 previous reports.<sup>37</sup> The molecular weight and dispersity ( $M_n = 102$  kg/mol,  $D = 1.8$ , seen in **Figure S2**) of  
122 this polymer were estimated by gel permeation chromatography (GPC) in 1,2,4- trichlorobenzene (TCB) at  
123 140 °C relative to narrow polystyrene standards. Electrochemical measurements show that the onset of  
124 electrochemical oxidation, and the redox estimated ionization potential value dictating it, is comparable to  
125 previous reports (**Figure S3**).<sup>37</sup>

126 PBTTT-C12 thin films (*ca.* 100 nm thick) were prepared by wire bar coating from chlorobenzene  
127 onto glass substrates and then thermally annealed at 180 °C for 20 minutes, unless otherwise stated. Films  
128 were sequentially doped by dropping a  $\text{FeCl}_3$  -acetonitrile solution onto the film and allowing the film to  
129 oxidize. After oxidation, films were rinsed with excess acetonitrile to remove excess dopant and doping  
130 byproducts and then vacuum dried to remove solvent. **Figure 1a** shows the chemical structures and a  
131 representative digital photograph that shows pristine PBTTT with a subsection doped with and 50 mM  
132  $\text{FeCl}_3$ . Cursorily, we note that doping alters the optical absorbance of the film, which will be detailed in  
133 subsequent sections. In general, sets of films were doped and then immediately measured to mitigate  
134 ambient environment and temporal effects. Additional procedural details and pristine PBTTT  
135 characterizations are in **Note S1**.

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## 138 **Results and Discussion**

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### 140 **SLoT Modeling of PBTtT**

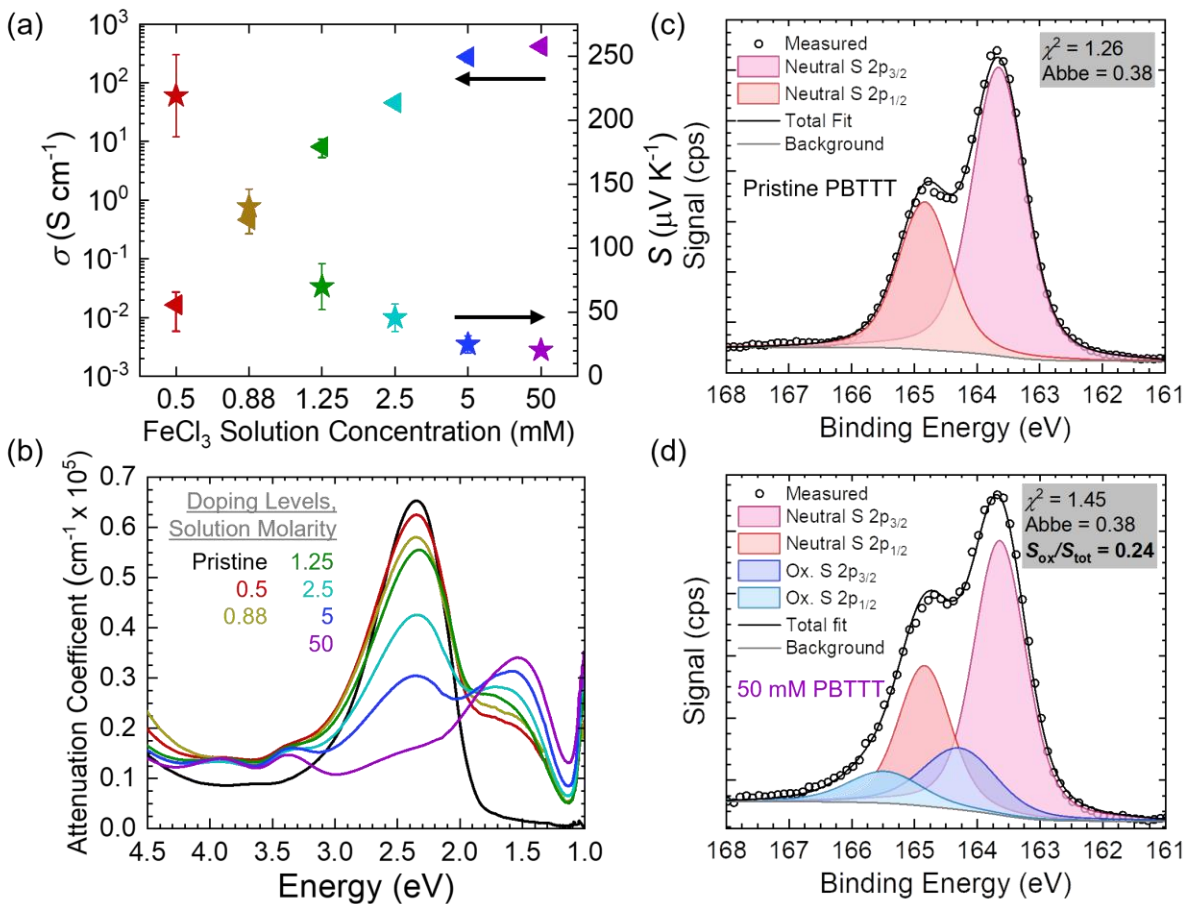
141 **Figure 2a** shows  $\sigma$  and  $S$  for PBTtT-C12 as a function of the sequential doping  $\text{FeCl}_3$  solution  
142 concentration. The  $\text{FeCl}_3$  solution concentration was systematically swept from 0.5 to 50 mM to access a  
143 wide range of extents of oxidation and thermoelectric transport properties. At 0.5 mM  $\text{FeCl}_3$  the PBTtT  
144 films show low  $\sigma$  ( $\sim 0.01 \text{ S cm}^{-1}$ ) and high  $S$  ( $\sim +200 \mu\text{V K}^{-1}$ ), indicating that these films are p-type and  
145 lightly doped. With increasing  $\text{FeCl}_3$  concentration,  $\sigma$  increases and  $S$  decreases, which is consistent with  
146 the expected  $S - \sigma$  anticorrelation and indicates higher carrier densities.<sup>20</sup> At 50 mM, PBTtT films show  
147 a high  $\sigma$  ( $420 \pm 45 \text{ S cm}^{-1}$ ) and low  $S$  ( $20 \pm 2.3 \mu\text{V K}^{-1}$ ), consistent with several other PBTtT reports.<sup>10, 13,</sup>  
148 <sup>14, 17</sup> We note that higher  $\sigma$  and lower  $S$  values have been reported in highly oriented thin films<sup>11, 12, 18</sup> that  
149 can be attributed to a more ordered microstructure (improved inter-chain transport) and to a broadened  
150 electronic structure with better orbital overlap.<sup>38, 39</sup>

151 To quantify the effects of  $\text{FeCl}_3$  doping concentration on the electronic structure and extent of  
152 doping, ultraviolet-visible-near infrared (UV-Vis-NIR) and X-ray photoelectron spectroscopic (XPS)  
153 measurements were performed. **Figure 2b** shows the UV-Vis-NIR spectra for PBTtT films at each  $\text{FeCl}_3$   
154 solution concentration. As the  $\text{FeCl}_3$  concentration increases, the pristine  $\pi - \pi^*$  optical transition at 2.4  
155 eV bleaches and polaronic absorbances at 1.5 eV emerges and increases, consistent with previous reports<sup>13</sup>  
156 and our measured thermoelectric trends. Additionally, in the range of 3 to 4 eV, two peaks emerge and  
157 increase in intensity with increasing doping level. These peaks are attributed to  $\text{FeCl}_4^-$  counterions, which  
158 are Coulombically associated with positive polaronic charge carriers.<sup>15</sup> In **Figures S5, S6** we deconvolute  
159 these peaks and use known extinction coefficients<sup>15, 40</sup> to calculate the molar ratio of  $\text{FeCl}_4^-$  counterions to  
160 BTTT repeat units and then the charge carrier volumetric density.<sup>15</sup> At 50 mM  $\text{FeCl}_3$ , we calculate a molar  
161 ratio of  $0.80 \pm 0.08$  charge carriers per BTTT monomer. This molar ratio is equivalent to a charge carrier  
162 ratio of 0.4 (assuming two charge carriers per PBTtT monomer),<sup>14</sup> and a carrier density of  $7.6 \times 10^{20}$   
163 carriers  $\text{cm}^{-3}$  (see **PBTtT-SLoT.xlsx** supporting information for calculations).<sup>14</sup> The value of  $0.80 \pm 0.08$   
164 charge carriers per BTTT monomer when doped with 50 mM  $\text{FeCl}_3$  and measured using optical  
165 spectroscopies is consistent and within error of the XPS measurements and analysis (**Figure 2c,d, Figure**  
166 **S7**), and the presence of  $\text{FeCl}_x$  counterions in the films are confirmed using survey and elemental spectra  
167 (**Figure S8, Table S1**). These XPS measurements show that oxidizing PBTtT with 50 mM  $\text{FeCl}_3$  results  
168 in an increased signal at higher binding energies with respect to the pristine and neutral S-2p<sub>3/2</sub> signal. Using  
169 previously established deconvolution procedures,<sup>20, 29, 35, 41-43</sup> we calculate that this oxidized sulfur signal is  
170 approximately 24% of the total signal in the S-2p spectra ( $S/S_{\text{ox}} \sim 0.24$ , **Figure 2d**). Therefore, the XPS  
171 deconvolution indicates that approximately 1 out of every 4 sulfurs in PBTtT are oxidized, or a molar ratio  
172 of 0.96 charge carriers per BTTT monomer. Additionally, this maximum carrier density of  $7.6 \times 10^{20}$



173 carriers  $\text{cm}^{-3}$  is approximately  $2\times$  greater than those in PBTTT-F4TCNQ studies,<sup>7, 10, 40</sup> and a PBTTT-TFSI  
174 OECT study,<sup>14</sup> and BTTT copolymer doped with F4TCNQ (ranged from  $3\text{-}5 \times 10^{20}$ ),<sup>21</sup> but this carrier  
175 density is consistent with several PBTTT- $\text{FeCl}_3$  studies (ranging from  $5.8 \times 10^{20}$  carriers  $\text{cm}^{-3}$  to  $9 \times 10^{20}$   
176 carriers  $\text{cm}^{-3}$ ).<sup>12, 15, 44</sup> While some of the differences in the calculated carrier densities could be attributed to  
177 measurement methods and assumptions (e.g., UV-Vis-NIR, XPS, AC Hall), this spread in carrier densities  
178 is also likely a function of processing conditions (e.g., dopant chemistry and reduction potential) and the  
179 resulting microstructure (*vide infra*).

180



181

182 **Figure 2:** Quantifying nominal thermoelectric properties, optical properties, and extent of doping for PBTTT-C12 doped with  
 183 FeCl<sub>3</sub>. (a) Electrical conductivity and Seebeck coefficient as a function of FeCl<sub>3</sub> solution concentration. Error bars represent the  
 184 sample-to-sample standard deviation. (b) UV-Vis-NIR attenuation coefficient as a function of photon energy. (c) Pristine PBTTT-  
 185 C12 XPS measurement and deconvolution. (d) 50 mM FeCl<sub>3</sub> doped PBTTT-C12 XPS measurement and deconvolution. The low  
 186  $\chi^2$  values, Abbe criterion, and residual signal (see **Figure S6**) provide a high level of confidence in these deconvolutions.  
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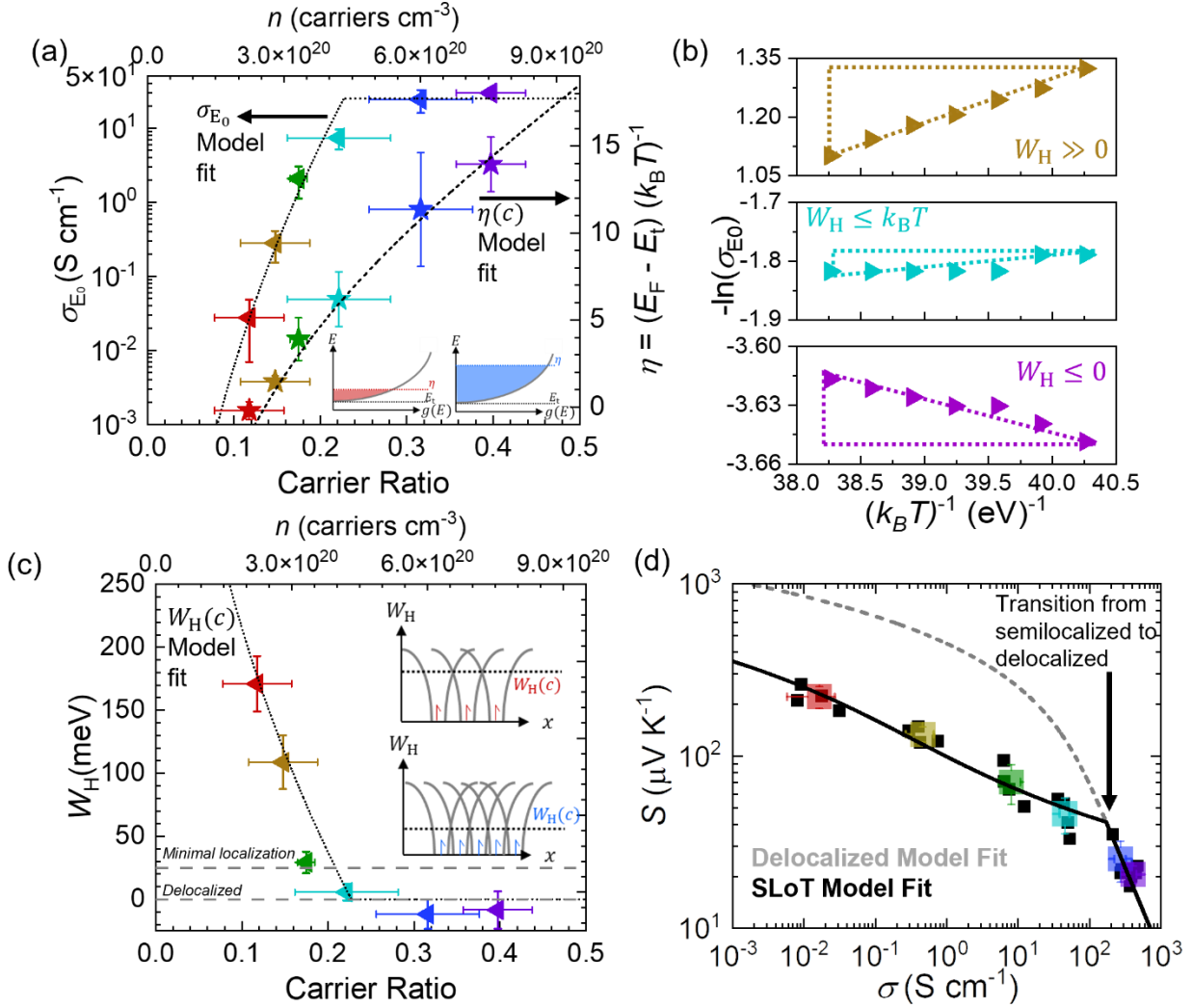
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With these carrier ratios and thermoelectric measurements, we apply the SLoT model to gain deeper insights. **Figure 3a** shows  $\sigma_{E_0}$  and  $\eta$  as a function of  $c$ , as calculated using the thermoelectric and spectroscopic measurements from **Figure 2** and Eq. 1-3.  $\sigma_{E_0}$  is the transport function prefactor and can be calculated by dividing the measurable electrical conductivity by the calculated electrical integral (see the look-up table in **PBTTT-SLoT.xlsx**). **Figure 3a** shows that as  $c$  increases,  $\sigma_{E_0}$  exponentially increases and then plateaus near 25 S cm<sup>-1</sup>. **Figure 3a** also shows that as  $c$  increases,  $\eta$  increases, and this is interpreted as charge carriers occupying increasingly higher electronic states with respect to the transport edge. Note that when  $\eta > 0$ ,  $\eta \sim \int_0^\infty \left( \frac{E-E_t}{k_B T} \right) \left( -\frac{df}{dE} \right) dE$ , so  $\eta$  alone linearly increases  $\sigma$ . Lastly, we note that  $\eta$  increasing to a maximum of 14 (equivalent of  $E_F$  shifting by ~0.36 eV with respect to  $E_t$  at 300 K) is consistent with the ~0.3 eV shift intensity-weighted binding energies from XPS (**Note S3, Figure S7**);<sup>42</sup>,<sup>43</sup> this indicates that a linear-energy dependent transport function (Eq. 1) reasonably describes the electronic structure with these chemistries and processing conditions, and that the shifts in  $\eta$  may be used to contextualize the electronic structure.

To quantify the extent of localization, the electrical conductivity and Seebeck coefficient were measured as a function of temperature. At each temperature,  $\sigma_{E_0}$  was calculated from dividing the measured electrical conductivity by the Fermi integral value, and then  $W_H$  was calculated from the Arrhenius plot of  $-\ln(\sigma_{E_0})$  vs.  $\frac{1}{k_B T}$  (**Figure 3b**). **Figure 3b** shows representative Arrhenius plots at low (0.88 mM), medium (2.5 mM) and high (50 mM) doping levels. **Figures 3b,c** show that the slope and calculated  $W_H$  values start high (greater than 100 meV), decrease to the order of 25 meV ( $k_B T$  at 300 K), and continue to decrease to negative slopes (metal-like and thermally deactivated electrical conductivities).<sup>20, 45</sup> These metal-like  $W_H$  values calculated at high doping (5 and 50 mM) consistent with other reports on PBTTT.<sup>17</sup> Note that although  $W_H$  can be calculated to be less than zero from temperature dependent measurements,  $W_H$  is always modeled in Eq. 1 to be greater than or equal to zero because  $W_H$  captures the systematic decrease in  $\sigma$  due to localization effects.<sup>20, 25</sup> For each film and at each doping level,  $\sigma_0$  is calculated from temperature dependent measurements, and **Figure S9** shows that  $\sigma_0$  values are *ca.* 25 S cm<sup>-1</sup>, on average, and do not have a statistically significant linear dependence on  $\eta$ . This is consistent with the plateauing of  $\sigma_{E_0}(c)$ .

Lastly, the  $S(\sigma)$  anticorrelation is evaluated. **Figure 3d** plots the  $S, \sigma$  coordinates for each film and doping level averages. The solid black curve is calculated using the SLoT model (Eq. 1-3), using the experimental thermoelectric and carrier ratio measurements and their  $\eta(c), W_H(c)$ , and  $\sigma_0$  regression parameters. This SLoT model curve has no freely adjustable values and accurately captures the experimental data. Additionally, the dashed grey curve represents the delocalized  $S(\sigma)$  anticorrelation (*i.e.*

220 Kang-Snyder  $s = 1$ ) which assumes that  $\sigma_{E_0} = \sigma_0$  at all doping levels and that  $\sigma_{E_0}$  (and ergo  $W_H$ ) does not  
221 change as a function of doping level.<sup>23</sup> Notably, the SLoT model and delocalized models become colinear  
222 when  $W_H \lesssim k_B T$ , and captures the data points that have little to no thermal activation at high doping levels.  
223 We note that the SLoT fit is calculated with no freely adjustable parameters in **Figure 3d**, and this fit is  
224 remarkably consistent with the SLoT fits previously predicted using previous literature data sets and an  
225 adjustable  $W_H(c)$  relationship (**Figure S10**).<sup>14, 17, 20</sup> This consistency further affirms the use of the SLoT  
226 model to predict transport parameters from  $S(\sigma)$  data when temperature and/or carrier dependent data is  
227 not available.  
228



229  
 230 **Figure 3:** SLoT modeling of PBTTT-C12 sequentially doped with FeCl<sub>3</sub>. (a) SLoT model transport function prefactor and reduced  
 231 Fermi energy as a function of carrier ratio and density. Inset illustrates the interpretation of increasing  $\eta$  values, akin to Figure 1.  
 232 (b) Representative Arrhenius plots, where the slopes are equal to  $W_H$ . Note that in this narrow temperature range (288 K – 303 K),  
 233 the electrical conductivity (and ergo  $\sigma_{E_0}$ ) oftentimes has a statistically significant temperature dependence while the Seebeck  
 234 coefficient does not (ergo  $\eta$  does not observably vary). (c) Localization energy as a function of carrier ratio. Inset illustrates that  
 235 localization decreases as carriers begin to spatially impinge, akin to Figure 1. Note that the carrier densities reported herein assume  
 236 the carriers have a +1e and do not transport as a pair (i.e., bipolaron); if all charges were bipolaronic in nature, then the  $n$  values in  
 237 (a,c) would be halved of what is presently shown. (d)  $S(\sigma)$  curve showing doping level average properties (colored squares, error  
 238 bars represent sample to sample standard deviation), individual films properties (black squares), delocalized transport model (grey  
 239 dashed line) and the SLoT model fit with no freely adjustable variables (black line). See Note S3 and PBTTT-SLoT.xlsx for  
 240 additional details.  
 241

## 242 **Developing microstructural-charge transport relationships**

243 The SLoT model becomes more useful when coupled with additional characterization techniques.

244 At minimum, the SLoT model requires temperature dependent thermoelectric and carrier density  
245 measurements, but these measurements do not quantify how the atomic structure and/or microstructure  
246 affect the resulting observables. Therefore, we now examine how GIWAXS furthers the utility of the SLoT  
247 model for this PBTTT-FeCl<sub>3</sub> system.

248 **Figure 4a-d** show representative two-dimensional diffractograms for pristine, 0.88 mM, 2.5 mM,  
249 and 50 mM doped films. These diffractograms show a high extent of ordering for a conjugated polymer  
250 system, with lamellar (*h*00) peaks up to a (400) reflection, consistent with previous reports on PBTTT.<sup>8, 15</sup>  
251 Furthermore, these diffractograms show that the crystallite lamellar stacking direction is predominantly  
252 along the out-of-plane direction (*q<sub>z</sub>* axis), the (003) intra-chain spacing is predominantly along the nearly-  
253 in-plane (*q<sub>xy</sub>*) axis. Additionally, there is a distribution of (110) interchain  $\pi - \pi$  stacks, with a bimodal  
254 predominance near the two poles at all doping conditions. These orientations indicate that these PBTTT  
255 films are preferentially ordered edge-on with respect to the substrate; however, we note this extent of edge-  
256 on is qualitatively weaker than that reported in other studies, and may be because these films are thicker  
257 (hundreds of nanometers) compared to those commonly used in other studies (tens to hundred of  
258 nanometer).<sup>15</sup>

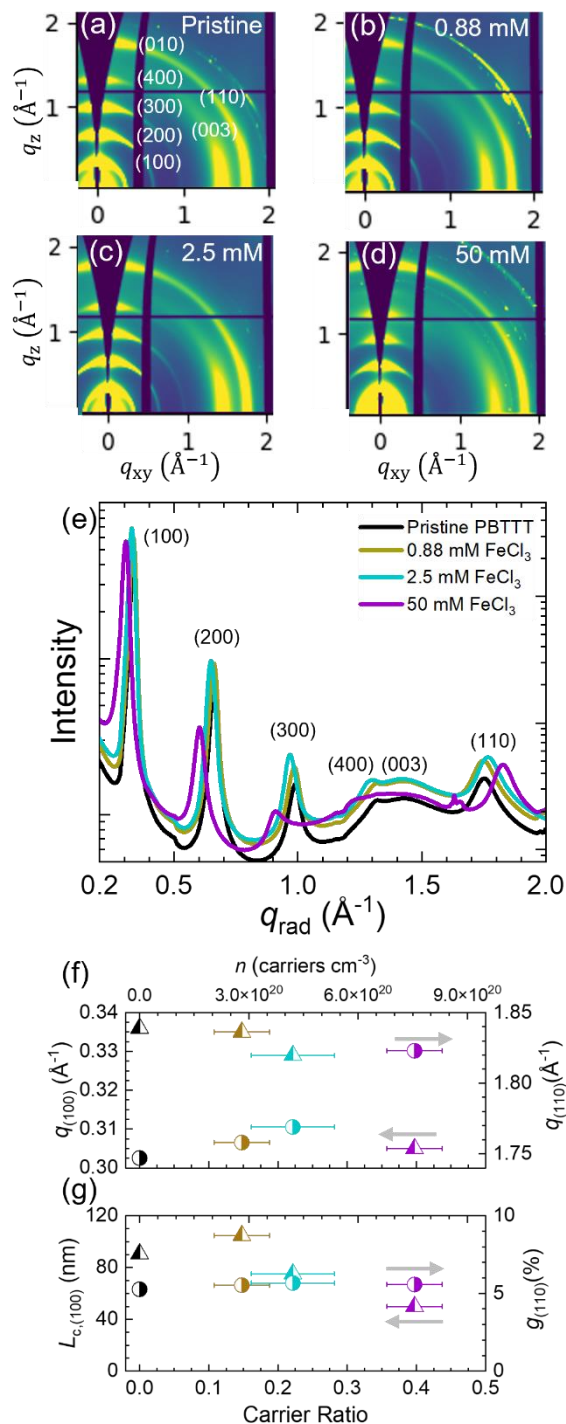
259 To gain deeper insight on these diffractograms, we analyzed radially integrated profiles (**Figure**  
260 **4e**). These profiles show that as the extent of doping increases, the lamellar peaks shifts to small *q* values,  
261 indicating an expansion in real space from 18.7 Å to 20.6 Å, as shown in **Figure 4f**. Concomitantly, the  
262  $\pi - \pi$  stacks contract in real space from 3.58 to 3.45 Å, which suggests dopant intercalation in the side  
263 chain region, consistent with previous reports.<sup>10, 15</sup> The PBTTT-C12 reported here has smaller lamellar  
264 spacings compared to PBTTT-C14 (20 Å pristine, 26 Å FeCl<sub>3</sub> doped),<sup>15</sup> as expected, but has notably tighter  
265  $\pi - \pi$  stacks compared to previous PBTTT-C<sub>x</sub> reports (~3.7 Å pristine, ~3.55 Å doped).<sup>15, 17</sup> These tighter  
266  $\pi - \pi$  stacks may be afforded by the smaller side chains and likely improves charge transport within  
267 crystalline domains. Furthermore, the quality of the crystalline domain can be evaluated using the

268 paracrystallinity ( $g$ ) and the coherence length ( $L_c$ ).<sup>46-48</sup> Detailed notes on the interpretation and calculations  
269 of  $g$  and  $L_c$  are found in the supporting information (**Note S4, Figures S11-12, Table S2**), and here we  
270 highlight two key findings. First, **Figure 4g** shows that  $g = 5.5\%$ , on average, for this PBTTT-C12/FeCl<sub>3</sub>  
271 system in the (110) direction. This is a remarkably low level of paracrystalline disorder for a conjugated  
272 polymer (generally  $\sim 7\text{--}20\%$ ).<sup>49</sup> Therefore, we believe that the ordered domains are exceptionally well  
273 ordered and tightly packed, but this amount of order does not provide insight on percolation pathways  
274 between spatially separated domains. Second, we note that the amount of paracrystallinity (*i.e.* structural  
275 disorder) in the (110) direction varies slightly ( $\sim 10\%$ ) as a function of doping level; but, the coherence  
276 length (*i.e.* crystallite size) in the (100) direction significantly decreases ( $-44\%$ ) with increasing doping  
277 level (**Figure 4g**). This indicates that FeCl<sub>3</sub> doping substantially decreases the quality of the ordering of the  
278 electrically insulating alkyl region, but doping does not as substantially affect the quality of the ordering of  
279 the electrically conductive  $\pi - \pi$  stacking direction.

280         The fact that  $g$  is independent of doping level is quite notable because previous reports have linked  
281 (110) paracrystallinity to the broadening of the density of electronic states and the creation of trap and/or  
282 localized electronic states; these trap states have energetic breadths and field-effect thermal activation  
283 energies on the order of *ca.* 100 meV in the pristine polymer.<sup>28, 46-50</sup> Similarly, in the dilute carrier limit  
284 ( $c \sim 0.1$ ), the localization energy ( $W_H$ ) is within a factor of  $2\times$  as predicted using paracrystallinity models.  
285 Although  $g$  remains effectively constant with respect to doping level, we observe that  $W_H$  decreases  
286 significantly with increasing doping level. We hypothesize that this apparent discrepancy between  $g$  and  
287  $W_H$  at higher doping levels is because the reduced Fermi energy levels (and transport properties) probed  
288 are not at the same energy levels where there is energetic disorder due to paracrystallinity. This hypothesis  
289 is reinforced by the fact that when PBTTT is “doped” using a field effect method (*i.e.* controlling the applied  
290 biases), PBTTT oftentimes obtains Seebeck coefficients on the order  $700\text{--}1000 \mu\text{V K}^{-1}$ ,<sup>51</sup> which is akin to  
291 an  $\eta$  of  $-7$  ( $\sim 0.2$  eV below  $E_t$  and  $\sim 0.55$  eV below 50 mM FeCl<sub>3</sub> doped PBTTT herein). Therefore, this  
292 study suggests that the (110) paracrystallinity and structural disorder is not a significant contributing factor

293 to  $W_H$  at these degenerate doping levels, and we hypothesize the physical mechanisms that limit  $W_H$  in  
294 chemically doped semiconducting polymers are likely the electrostatic attraction of polaronic charge  
295 carriers to counteranions, polarization of the local bond order, and the spatial percolation of charge carriers  
296 on larger length scales ( $> \sim 10$  nm).<sup>20, 25, 27</sup>  
297





299 **Figure 4:** PBTtT-FeCl<sub>3</sub> GIWAXS measurements and analysis. Representative diffractograms for (a) Pristine, (b)  
 300 0.88 mM FeCl<sub>3</sub> doped, (c) 2.5 mM FeCl<sub>3</sub> doped, and (d) 50 mM doped PBTtT films. Pristine diffractogram shows  
 302 annotated indices. (e) Radially integrated linecuts. (f) Lamellar (100) and  $\pi - \pi$   $q$  values. (g) Coherence length and  
 303 paracrystallinity. Note that in (f) and (g), the top and bottom x-axes are the same for both plots and that the arrows  
 304 correspond to the y-axis for each data series. Explicitly, the triangle data points correspond to the left y-axes while the  
 305 circles correspond to the right y-axes.  
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307 **Quantifying localization and charge transport using spectroscopic ellipsometry**

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The SLoT model uses macroscopic thermoelectric measurements to define transport parameters that represent an appropriately weighted average of the microscopic ensemble. Though SLoT allows us to model the macroscopic average, conjugated polymers are known to be inhomogeneous. Explicitly, the macroscopic  $\sigma$  is a single value, but it is known that there are regions within the polymer that have larger  $\sigma$  values that are likely electrically insulated (to some extent) by regions with smaller  $\sigma$  values.<sup>30, 52, 53</sup> This inhomogeneity has been used to improve charge transport and thermoelectric performance; for example, Ma *et al.* recently demonstrated that higher thermoelectric power factors are obtained by preferentially doping the ordered regions.<sup>53</sup> Although  $W_H$  is a useful tool to capture the macroscopic effects of localization, and GIWAXS is a useful tool to quantify the quality and spacing or molecular packing within crystalline domains, these approaches do not provide information on how the ordered domains are distributed and/or percolated throughout the film and their microscopic transport properties. Measurement techniques, such as atomic force microscopy,<sup>52</sup> scanning kelvin probe microscopy,<sup>54</sup> atom probe tomography,<sup>55</sup> and transmission electron microscopy,<sup>56</sup> can have sufficient spatial resolution to quantify inhomogeneous spatial distributions, but these techniques do not necessarily provide information on the microscopic transport properties. In contrast, there are reports that use thermal<sup>57, 58</sup> and dielectric properties<sup>59-62</sup> to contextualize the effects of percolation and effective medium inhomogeneity on the resulting  $\sigma(n, T)$  and  $S(n, T)$  properties.<sup>63</sup> Ultimately, we posit that spectroscopic ellipsometry measurements are useful for characterizing inhomogeneous materials with microscopic regions of varying transport properties.

Here, we explore the use of spectroscopic ellipsometry (SE) to quantify the complex dielectric function in PBTTT, model the dielectric-like and metal-like contributions to the observable optical properties, and relate these contributions to the measurable thermoelectric properties and SLoT parameters. The complex dielectric function is expressed as,

$$\epsilon(\omega) = \epsilon_1(\omega) + i \epsilon_2(\omega), \quad (4)$$

332 where  $\epsilon_1(\omega)$  is the real component, and  $\epsilon_2(\omega)$  is the imaginary component.<sup>64</sup> The complex dielectric  
333 function can link measurable optical properties, such as reflectivity, to the calculable material parameters,  
334 such as carrier densities. Additionally,  $\epsilon_1(\omega)$  and  $\epsilon_2(\omega)$  capture various physical processes such as charge  
335 polarization, interband optical transitions, and Drude-like charge transport.<sup>64, 65</sup>

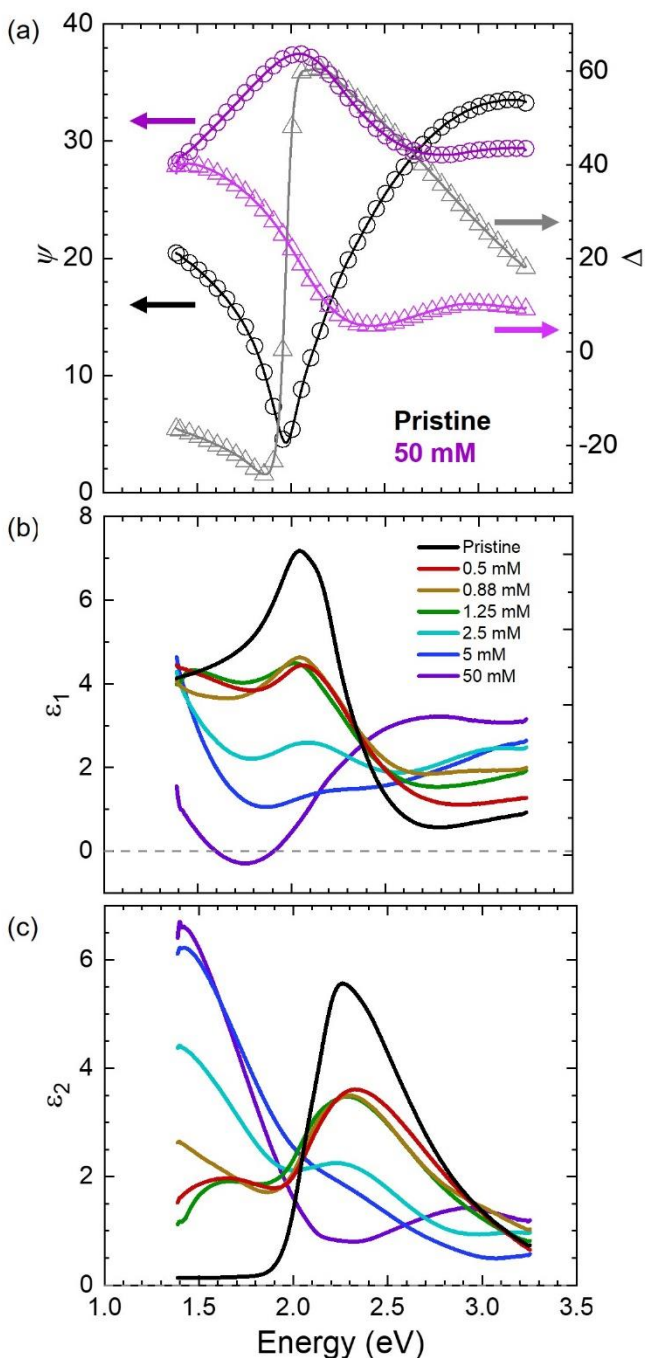
336 SE measures the change in the ratio of the polarized light intensities ( $\tan(\psi)$ ) and phases ( $\Delta$ ) upon  
337 reflection,<sup>64, 66, 67</sup> and these changes in  $\psi$  and  $\Delta$  are related to  $\epsilon_1(\omega)$  and  $\epsilon_2(\omega)$  through an optical model.  
338 **Figure 5a** shows representative  $\psi$  and  $\Delta$  values for pristine PBTTT and 50 mM FeCl<sub>3</sub> doped PBTTT with  
339 comparable thicknesses, and **Figure S13** shows  $\psi$  and  $\Delta$  at each doping level. Clearly, the measurable  $\psi$   
340 and  $\Delta$  change due to doping, consistent with the prior characterizations, and this suggests that  $\epsilon_1(\omega)$  and  
341  $\epsilon_2(\omega)$  also change. To quantify  $\epsilon_1(\omega)$  and  $\epsilon_2(\omega)$  in the PBTTT film, an empirical optical model was  
342 developed to fit the changes in  $\psi$  and  $\Delta$  and extract the film's dielectric function (**Note S5** details the optical  
343 model). **Figure 5a** shows the B-Spline fits from the optical model agree well with the measured values,  
344 indicating that the  $\epsilon_1(\omega)$  and  $\epsilon_2(\omega)$  values calculated with the optical model for the PBTTT films are  
345 consistent with the experimental measurements.

346 **Figure 5b-c** plots the calculated  $\epsilon_1(\omega)$  and  $\epsilon_2(\omega)$  as a function of doping level and photon energy.  
347  $\epsilon_1$  is associated with the ideal polarization of the film without losses, and  $\epsilon_2$  is associated with lossy  
348 processes such as heat generation, interband absorption, and free charge carrier absorption.<sup>64, 65</sup> The values  
349 for  $\epsilon_1(\omega)$  and  $\epsilon_2(\omega)$  (and their corresponding complex index of refraction values,  $\tilde{n}$  and  $\tilde{k}$ , **Figure S14**)  
350 are reasonable and consistent with previous measurements on doped and pristine conjugated polymer  
351 films.<sup>66-68</sup> These consistencies give us a high level of confidence in the  $\epsilon_1(\omega)$  and  $\epsilon_2(\omega)$  calculations.

352 Most notable is that  $\epsilon_1$  in the 50 mM PBTTT shows regimes where  $\epsilon_1 \approx 0$  (**Figure 5b**). Typically,  
353 metals have negative  $\epsilon_1$  values due to free carrier attenuation at frequencies less than the plasma frequency  
354 and a positive  $\epsilon_1$  at frequencies greater than the plasma frequency due to polarization.<sup>64</sup> In contrast, Lorentz-  
355 like oscillators (*e.g.* band gap transitions) typically exhibit  $\epsilon_1 > 0$ . Because 50 mM doped PBTTT exhibits  
356 both positive and negative  $\epsilon_1$  values, it is likely that a combination of free-electron and optical transitions

357 are present, consistent with the UV-Vis-NIR measurements and thermoelectric measurements. This is  
358 qualitatively represented by the cartoon illustration in **Figure 1c**, where the spectroscopic ellipsometry is  
359 probing and measuring transitions in multiple spatial regimes. Furthermore, previous reports have also  
360 observed similar  $\epsilon_1$  behavior with PEDOT:PSS and PEDOT:Tos as a function of processing conditions and  
361 doping level (where  $\epsilon_1$  changes sign multiple times),<sup>69-72</sup> but these studies did not systematically vary the  
362 doping level from the pristine state to a fully doped state. Lastly, the optical transitions and  $\epsilon_2$  values in  
363 **Figure 5** are in good agreement between and the transmission attenuation in **Figure 2**. Both analyses show  
364 that absorption shifts to the infrared region and the visible region is increasingly bleached with increasing  
365 doping level.

366



368  
 369 **Figure 5:** PBTTT-FeCl<sub>3</sub> spectroscopic ellipsometry measurements, B-spline fits, and complex dielectric function  
 370 calculations. (a) Representative  $\psi$  and  $\Delta$  measurements for pristine and 50 mM FeCl<sub>3</sub> doped PBTTT films with  
 371 comparable thickness (~180 nm) on glass substrates. One out of every five measured data points are shown for clarity,  
 372 and line represent the B-spline fitting, calculated using known substrate properties, known film thickness, and assumed  
 373 Kramers-Kronig consistency. (b) Real component ( $\epsilon_1$ ) of the complex dielectric function. (c) Imaginary component  
 374 ( $\epsilon_2$ ) of the complex dielectric function.  
 375

376 We now turn to deconvoluting  $\epsilon(\omega)$  to better quantify the physical phenomena responsible for the  
 377 optical transitions. By deconvoluting  $\epsilon(\omega)$ , we obtain fundamental transport properties such as the carrier  
 378 density. Here, we deconvolute  $\epsilon(\omega)$  using the simplest peak deconvolution models that account for  
 379 polaronic transitions, free charge carriers, and  $\pi - \pi^*$  transitions; however, we note that more complicated  
 380 models exist that account for specific microgeometries (*e.g.*, core-shell, slabs, *etc.*), in- and out-of-plane  
 381 contributions (*i.e.*, ordinary, and extraordinary), and grating.<sup>65, 73, 74</sup>

382 Overall,  $\epsilon(\omega)$  has the functional form of,

$$\epsilon(\omega) \approx \epsilon_{\infty} - \left[ \frac{\sigma}{\epsilon_0 \left( \frac{\omega^2 m^* \mu}{e} + i\omega \right)} \right] - \left[ \sum \frac{A_l}{(\omega^2 - \omega_l^2) + i\omega\gamma_l} \right]. \quad (2)$$

383  $\epsilon_{\infty}$  is the dielectric constant at approaching infinitely high frequencies,  $\epsilon_0$  is the permittivity of free space,  
 384  $\omega$  is the angular frequency,  $A_l$  is the  $l$ -th Lorentzian absorption amplitude,  $\omega_l$  is the resonant frequency of  
 385 the  $l$ -th absorber, and  $\gamma_l$  is the absorption broadening. The first bracketed term accounts for Drude-like free  
 386 carrier contribution, and the second bracketed term accounts for sum of  $l$ -number of oscillator transitions,  
 387 such as  $\pi - \pi^*$  optical, polaronic, and vibrational transitions.<sup>73, 74</sup> The second bracketed term is written in  
 388 the form of a Lorentzian oscillator, but depending on the exact mechanism, the broadening of the Lorentz  
 389 line shape may be more appropriately modeled using a single Gaussian, multiple Gaussians, Tauc-Lorentz,  
 390 or Voigt distributions, to name a few.<sup>74</sup> By deconvoluting  $\epsilon_1$  and  $\epsilon_2$  at each doping level, the contribution  
 391 of each oscillator and free-electron contribution can be systematically quantified.

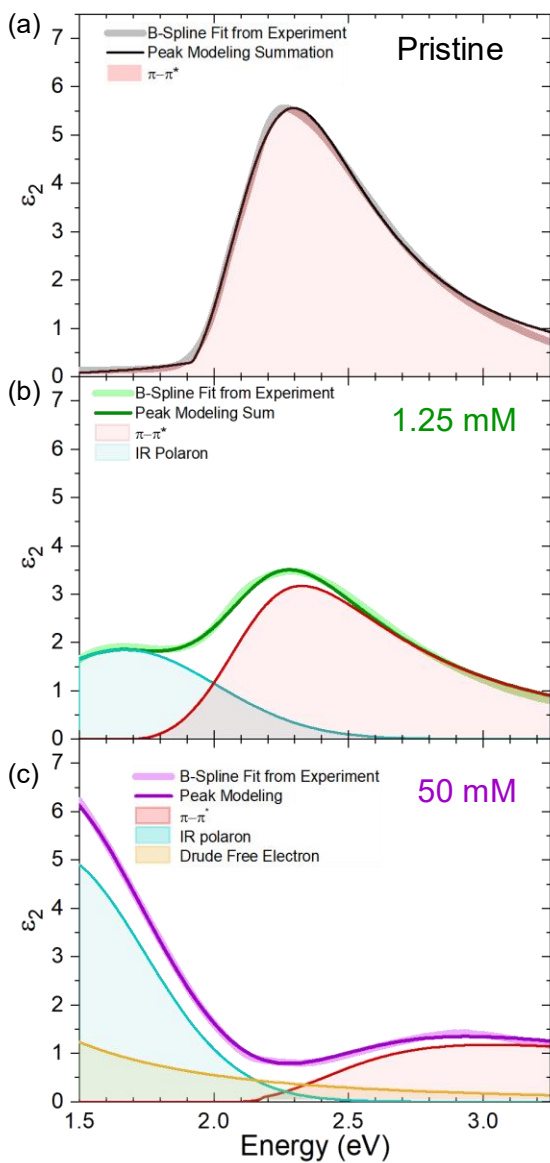
392 **Figure 6** shows a representative set of spectroscopic ellipsometry deconvolutions, which isolate  
 393 the physical contributions to the dielectric loss function. **Figure 6a** shows the deconvolution for pristine  
 394 PBTTT. The B-spline fit is well modeled using a single Cody-Lorentz peak, which captures the optical  
 395 band gap, the  $\pi - \pi^*$  transition. While Lorentzian peaks are symmetrical about the harmonic frequency,  
 396 Cody-Lorentzian peaks are asymmetric about the harmonic frequency and account for more transitions  
 397 above the harmonic frequency and a steeper cut-off for transitions below the harmonic frequency.<sup>75</sup>  
 398 Although multiple peaks could be used to deconvolute the  $\pi - \pi^*$  transition,<sup>76</sup> this becomes increasingly

399 cumbersome when deconvoluting the doped films as there are more free variables. Using the peak  
400 deconvolution settings from the pristine PBTTT, we then turn to quantifying the polaronic oscillator  
401 contribution. **Figure 6b** shows the deconvolution for 1.25 mM FeCl<sub>3</sub> doped PBTTT. At 1.25 mM,  $\sigma$ ,  $n$ , and  
402  $\mu$  values are likely too low to significantly contribute to the dielectric function in the UV-Vis-NIR region,  
403 but there is a polaronic peak near 1.5 eV, akin to **Figure 2**. This peak is well modeled using a simple  
404 Gaussian peak, like previous reports.<sup>76</sup> Lastly, **Figure 6c** shows 50 mM FeCl<sub>3</sub> doped PBTTT. Using the  
405 incremental change in the dielectric function at each doping level (**Figure 6**), we can begin to isolate the  
406 free electron contribution to  $\epsilon_2$ . Notably, **Figure S15** shows that the 50 mM dielectric function cannot be  
407 as well modeled using a polaronic and  $\pi - \pi^*$  oscillators alone; therefore, we conclude that the Drude free  
408 electron contribution is likely necessary. Additionally, this Drude-like contribution is needed to explain the  
409 slopes and curvatures in the mid-infrared (MIR) as shown in **Figure S6**. We note that the Drude contribution  
410 in the MIR is convoluted with polaronic absorbances (likely a combination of polaron and bipolaron  
411 contributions), and therefore this Drude contribution may be responsible for asymmetric peaks that  
412 decreases with increasing energy. Future spectroscopic ellipsometry measurements deeper in the mid-  
413 infrared and on additional highly electrically conductive polymers will increase the certainty of the Drude  
414 contribution in spatially inhomogeneous polymers.

415 This Drude contribution at 50 mM is modeled by using  $n = 6 \times 10^{21}$  carriers cm<sup>-3</sup> and  $\sigma = 2,200$  S  
416 cm<sup>-1</sup> (**Figure 6c**). Although this Drude contribution is consistent with spectroscopic ellipsometry data, it is  
417 seemingly inconsistent with the thermoelectric transport data which shows  $n = 7.6 \times 10^{20}$  carriers cm<sup>-3</sup>  
418 and  $\sigma = 420$  S cm<sup>-1</sup> (**Figures 2,3**). Interestingly however, we note that this ellipsometry carrier density is  
419 comparable to the carrier density recently reported using an AC Hall technique.<sup>44</sup> We believe that these  
420 substantial differences in transport properties is likely because the ellipsometry measurements are probing  
421 optical oscillators which are on smaller length scales compared to the macroscopic thermoelectric transport  
422 (**Figure 1c**). It is likely that the carrier densities and electrical conductivities calculated using the Drude  
423 component from ellipsometry deconvolutions are a more accurate representation for the electrically

424 conductive domains (likely crystalline regions of the  $\pi - \pi$  stacks) whereas the carrier densities and  
425 electrical conductivities in **Figure 2,3** are better thought as bulk averages, which are systematically lowered  
426 by less ordered domains and insulating side chains. We note that PBTTT is ~50% insulating side chain by  
427 molecular weight, and we recently demonstrated that removing the side chains in dioxythiophene  
428 copolymers increases the measure  $\sigma$  by  $\sim 10\times$  and  $n$  by  $\sim 2\times$ .<sup>29, 77</sup> Furthermore, the Drude electrical  
429 conductivity modeled using ellipsometry is consistent with several reports that show  $\sigma$  in PBTTT is  $>10^3$   
430  $\text{S cm}^{-1}$  when highly ordered.<sup>12, 18, 19</sup> This ellipsometry analysis suggests that highly electrically conductive  
431 PBTTT on the macroscale is afforded by a percolated series of highly ordered and Drude-like domains, and  
432 less electrically conductive PBTTT on the macroscale is due to highly ordered Drude-like domains being  
433 electrically isolated from one another. This percolation picture is akin with previous ellipsometry-charge  
434 transport reports that compared the differences in  $\epsilon$  and  $\sigma$  as a function of evaporated Au film thickness,<sup>61</sup>  
435 atomic layer deposited Pt/Ru/Pd film thickness,<sup>62</sup> and the percolation of Ag nanoparticles in a strained  
436 elastomer.<sup>60</sup> Ultimately, this analysis shows that spectroscopic ellipsometry could be useful for  
437 complimenting structural and thermoelectric measurements and provides a more holistic picture for charge  
438 transport.  
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441  
 442 **Figure 6:** Representative spectroscopic ellipsometry deconvolutions as a function for PBTTT-FeCl<sub>3</sub> doping level. (a)  
 443 Pristine PBTTT, modeled using only a Cody-Lorenz oscillator for the  $\pi - \pi^*$  band gap transition. (b) PBTTT doped  
 444 with 1.25 mM FeCl<sub>3</sub>, modeled using a compared  $\pi - \pi^*$  band gap transition and a Gaussian polaronic absorption. (c)  
 445 PBTTT doped with 50 mM FeCl<sub>3</sub>, modeled using a comparable  $\pi - \pi^*$  optical transition and polaronic absorption as  
 446 well as a Drude free electron contribution. Additional deconvolution notes and methodologies are found in Note S5.  
 447  
 448

449 **Conclusion:**

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451           The charge transport properties of chemically doped semiconducting polymers are difficult to  
452 holistically understand because spatial inhomogeneity leads to charge transport properties that vary  
453 significantly as functions of doping level and spatial coordinate. In this PBTTT-FeCl<sub>3</sub> study, we used the  
454 SLoT model to quantify fundamental transport parameters, such as  $\sigma_0$ ,  $W_H(c)$ , and  $\eta(c)$ , which can be used  
455 to robustly compare and design polymer-dopant-processing systems. Using GIWAXS measurements, we  
456 conjecture that PBTTT's highly conductive transport parameters are likely because of the smaller  $\pi - \pi$   
457 stacking distances that decrease with increasing doping level and have low levels of paracrystalline  
458 disorder. Using spectroscopic ellipsometry measurements and deconvolution, we quantify how the complex  
459 dielectric function varies with doping and model the Drude contribution to optical properties. We find that  
460 these Drude carrier densities and electrical conductivities are larger compared to the SLoT parameters, and  
461 we hypothesize that this could be because only the most electrically conductive and metal-like domains  
462 will have Drude like optical signatures, while the SLoT parameters weighted by the electrically insulating  
463 domains and are more indicative of macroscopic averages.

464           Moving forward, this study serves two primary purposes. First, we contextualized the SLoT  
465 transport parameters for PBTTT-FeCl<sub>3</sub> against other PBTTT studies and semiconducting polymer systems.  
466 This benchmark can be used moving forward to better quantify, understand, and compare other polymer-  
467 dopant-processing systems. Second, we showed how advanced scattering and spectroscopic measurements  
468 can be used in conjunction with SLoT to better understand transport properties. With additional SLoT,  
469 GIWAXS, and SE measurements, we can better quantify to what extent microstructure and inhomogeneity  
470 affect the resulting transport properties.

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474 **Supporting Information**

475 Additional characterization procedures and measurements (PDF). SLoT measurements, calculations, and  
476 look-up table (XLSX).

477

478 **Author Contributions**

479 S.A.G. led optical and thermoelectric measurements, along with analysis of the results and preparing the  
480 manuscript. A.A. prepared thin films, collected and analyzed XPS data. J.F.P. prepared and characterized  
481 the PBTTT used in this study. G.F. collected and helped analyze GIWAXS data. G.M.S helped with  
482 GIWAXS data analysis and interpretation. M.D.L provided insight on and access to spectroscopic  
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486

487 All authors participated in the preparation of this manuscript and agree on its final form.

488

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513 **Conflicts of Interest**  
514 There are no conflicts to declare.

515 **References**

- 516
- 517 1. Reynolds, J. R.; Thompson, B. C.; Skotheim, T. A., *Handbook of Conducting Polymers*. Marcel  
518 Dekker: 1998.
- 519 2. Kroon, R.; Mengistie, D. A.; Kiefer, D.; Hynynen, J.; Ryan, J. D.; Yu, L.; Muller, C., Thermoelectric  
520 plastics: from design to synthesis, processing and structure-property relationships. *Chem Soc Rev* **2016**,  
521 *45* (22), 6147-6164.
- 522 3. Bubnova, O.; Crispin, X., Towards polymer-based organic thermoelectric generators. *Energy &*  
523 *Environmental Science* **2012**, *5* (11), 9345–9362.
- 524 4. Russ, B.; Glauddell, A.; Urban, J. J.; Chabiny, M. L.; Segalman, R. A., Organic thermoelectric  
525 materials for energy harvesting and temperature control. *Nature Reviews Materials* **2016**, *1* (10), 16050.
- 526 5. Siringhaus, H., 25th Anniversary Article: Organic Field-Effect Transistors: The Path Beyond  
527 Amorphous Silicon. *Advanced Materials* **2014**, *26* (9), 1319-1335.
- 528 6. Bubnova, O.; Berggren, M.; Crispin, X., Tuning the Thermoelectric Properties of Conducting  
529 Polymers in an Electrochemical Transistor. *Journal of the American Chemical Society* **2012**, *134* (40),  
530 16456-16459.
- 531 7. Kang, K.; Watanabe, S.; Broch, K.; Sepe, A.; Brown, A.; Nasrallah, I.; Nikolka, M.; Fei, Z.; Heeney,  
532 M.; Matsumoto, D.; Marumoto, K.; Tanaka, H.; Kuroda, S.; Siringhaus, H., 2D coherent charge transport  
533 in highly ordered conducting polymers doped by solid state diffusion. *Nat Mater* **2016**, *15* (8), 896-902.
- 534 8. Chabiny, M. L.; Toney, M. F.; Kline, R. J.; McCulloch, I.; Heeney, M., X-ray Scattering Study of  
535 Thin Films of Poly(2,5-bis(3-alkylthiophen-2-yl)thieno[3,2-b]thiophene). *JACS* **2007**, *129*, 3226-3237.
- 536 9. McCulloch, I.; Heeney, M.; Bailey, C.; Genevicius, K.; MacDonald, I.; Shkunov, M.; Sparrowe, D.;  
537 Tienry, S.; Wagner, R.; Zhang, W.; Chabiny, M. L.; Kline, R. J.; McGehee, M. D.; Toney, M. F., Liquid-  
538 crystalline semiconducting polymers with high charge-carrier mobility. *Nature Materials* **2006**, *51*, 326-  
539 333.
- 540 10. Kang, K.; Schott, S.; Venkateshvaran, D.; Broch, K.; Schweicher, G.; Harkin, D.; Jellett, C.;  
541 Nielsen, C. B.; McCulloch, I.; Siringhaus, H., Investigation of the thermoelectric response in conducting  
542 polymers doped by solid-state diffusion. *Materials Today Physics* **2019**, *8*, 112-122.
- 543 11. Vijayakumar, V.; Durand, P.; Zeng, H.; Untilova, V.; Herrmann, L.; Algayer, P.; Leclerc, N.;  
544 Brinkmann, M., Influence of dopant size and doping method on the structure and thermoelectric  
545 properties of PBTTC films doped with F6TCNNQ and F4TCNQ. *J. Mater. Chem. C* **2020**, *8*, 16470-16482.
- 546 12. Vijayakumar, V.; Zhong, Y.; Untilova, V.; Bahri, M.; Herrmann, L.; Biniek, L.; Leclerc, N.;  
547 Brinkmann, M., Bringing Conducting Polymers to High Order: Toward Conductivities beyond 105 S cm<sup>-1</sup>  
548 and Thermoelectric Power Factors of 2 mW m<sup>-1</sup> K<sup>-2</sup>. *Advanced Energy Materials* **2019**, *9* (24), 1900266.
- 549 13. Thomas, E. M.; Peterson, K. A.; Balzer, A. H.; Rawlings, D.; Stingelin, N.; Segalman, R. A.;  
550 Chabiny, M. L., Effects of Counter-Ion Size on Delocalization of Carriers and Stability of Doped  
551 Semiconducting Polymers. *Adv. Electron. Mater.* **2020**, *6* (12), 2000595.
- 552 14. Thomas, E. M.; Popere, B. C.; Fang, H.; Chabiny, M. L.; Segalman, R. A., Role of Disorder Induced  
553 by Doping on the Thermoelectric Properties of Semiconducting Polymers. *Chemistry of Materials* **2018**,  
554 *30* (9), 2965-2972.
- 555 15. Jacobs, I. E.; Lin, Y.; Huang, Y.; Ren, X.; Simatos, D.; Chen, C.; Tjhe, D.; Statz, M.; Lai, L.; Finn,  
556 P. A.; Neal, W. G.; D'Avino, G.; Lemaure, V.; Fratini, S.; Beljonne, D.; Strzalka, J.; Nielsen, C. B.; Barlow,  
557 S.; Marder, S. R.; McCulloch, I.; Siringhaus, H., High-Efficiency Ion-Exchange Doping of Conducting  
558 Polymers. *Adv Mater* **2021**, e2102988.
- 559 16. Patel, S. N.; Glauddell, A. M.; Peterson, K. A.; Thomas, E. M.; O'Hara, K. A.; Lim, E.; Chabiny, M.  
560 L., Morphology controls the thermoelectric power factor of a doped semiconducting polymer. *Science*  
561 *Advances* **2017**, *3* (6), e1700434.

- 562 17. Hisaaki Tanaka, K. K., Naoya Takekoshi, Hiroaki Mada, Hiroshi Ito, Yukihiro Shimoi, Hiromichi Ohta,  
563 Taishi Takenobu, Thermoelectric properties of a semicrystalline polymer doped beyond the insulator-to-  
564 metal transition by electrolyte gating. *Science Advances* **2020**, *6*, 1-8.
- 565 18. Durand, P.; Zeng, H.; Biskup, T.; Vijayakumar, V.; Untilova, V.; Kiefer, C.; Heinrich, B.; Herrmann,  
566 L.; Brinkmann, M.; Leclerc, N., Single Ether-Based Side Chains in Conjugated Polymers: Toward Power  
567 Factors of 2.9 mW m<sup>-1</sup> K<sup>-2</sup>. *Advanced Energy Materials* **2021**, *2103049*, 1-11.
- 568 19. Huang, Y.; Lukito Tjhe, D. H.; Jacobs, I. E.; Jiao, X.; He, Q.; Statz, M.; Ren, X.; Huang, X.;  
569 McCulloch, I.; Heeney, M.; McNeill, C.; Sirringhaus, H., Design of experiment optimization of aligned  
570 polymer thermoelectrics doped by ion-exchange. *Applied Physics Letters* **2021**, *119* (11), 1-8.
- 571 20. Gregory, S. A.; Hanus, R.; Atassi, A.; Rinehart, J. M.; Wooding, J. P.; Menon, A. K.; Losego, M.  
572 D.; Snyder, G. J.; Yee, S. K., Quantifying charge carrier localization in chemically doped semiconducting  
573 polymers. *Nature Materials* **2021**, *20*, 1414–1421.
- 574 21. Gregory, S. A.; Ponder, J. F.; Pittelli, S. L.; Losego, M. D.; Reynolds, J. R.; Yee, S. K., Thermoelectric  
575 and Charge Transport Properties of Solution-Processable and Chemically Doped Dioxithienothiophene  
576 Copolymers. *ACS Applied Polymer Materials* **2021**, *3* (5), 2316–2324.
- 577 22. Zevalkink, A.; Smiadak, D. M.; Blackburn, J. L.; Ferguson, A. J.; Chabinyk, M. L.; Delaire, O.;  
578 Wang, J.; Kovnir, K.; Martin, J.; Schelhas, L. T.; Sparks, T. D.; Kang, S. D.; Dylla, M. T.; Snyder, G. J.; Ortiz,  
579 B. R.; Toberer, E. S., A practical field guide to thermoelectrics: Fundamentals, synthesis, and  
580 characterization. *Applied Physics Reviews* **2018**, *5* (2), 021303.
- 581 23. Kang, S. D.; Snyder, G. J., Charge-transport model for conducting polymers. *Nature Materials*  
582 **2017**, *16* (2), 252-257.
- 583 24. May, A. F.; Snyder, G. J., Introduction to modeling thermoelectric transport at high temperatures.  
584 In *Materials, Preparation, and Characterization in Thermoelectrics*, CRC Press: 2017.
- 585 25. Mott, N. F.; Davis, E. A., *Electronic processes in non-crystalline materials*. Oxford University Press:  
586 2012.
- 587 26. Mott, N. F., The mobility edge since 1967. *J. Phys. C: Solid State Phys.* **1987**, *20*, 3075-3101.
- 588 27. Xuan, Y.; Liu, X.; Desbief, S.; Leclère, P.; Fahlman, M.; Lazzaroni, R.; Berggren, M.; Cornil, J.;  
589 Emin, D.; Crispin, X., Thermoelectric properties of conducting polymers: The case of poly(3-  
590 hexylthiophene). *Physical Review B* **2010**, *82* (11), 115454.
- 591 28. Noriega, R.; Rivnay, J.; Vandewal, K.; Koch, F. P.; Stingelin, N.; Smith, P.; Toney, M. F.; Salleo,  
592 A., A general relationship between disorder, aggregation and charge transport in conjugated polymers.  
593 *Nat Mater* **2013**, *12* (11), 1038-44.
- 594 29. Ponder, J. F., Jr.; Gregory, S. A.; Atassi, A.; Menon, A. K.; Lang, A. W.; Savagian, L. R.; Reynolds,  
595 J. R.; Yee, S. K., Significant Enhancement of the Electrical Conductivity of Conjugated Polymers by Post-  
596 Processing Side Chain Removal. *J Am Chem Soc* **2022**, *144* (3), 1351–1360.
- 597 30. Lim, E.; Glauddell, A. M.; Miller, R.; Chabinyk, M. L., The Role of Ordering on the Thermoelectric  
598 Properties of Blends of Regioregular and Regiorandom Poly(3-hexylthiophene). *Advanced Electronic*  
599 *Materials* **2019**, *5* (11), 1-11.
- 600 31. Fontana, M. T.; Stanfield, D. A.; Scholes, D. T.; Winchell, K. J.; Tolbert, S. H.; Schwartz, B. J.,  
601 Evaporation vs Solution Sequential Doping of Conjugated Polymers: F4TCNQ Doping of Micrometer-Thick  
602 P3HT Films for Thermoelectrics. *The Journal of Physical Chemistry C* **2019**, *123* (37), 22711-22724.
- 603 32. Sezen-Edmonds, M.; Glauddell, A. M.; Chang, W. B.; Segalman, R. A.; Chabinyk, M. L.; Loo, Y.-L.,  
604 Postdeposition Processing Influences the Relative Contributions of Electronic and Ionic Seebeck Effects in  
605 the Thermoelectric Response of Conducting Polymers. *The Journal of Physical Chemistry C* **2021**, *125* (22),  
606 12289-12296.
- 607 33. Un, H.-I.; Gregory, S. A.; Mohapatra, S. K.; Xiong, M.; Longhi, E.; Lu, Y.; Rigin, S.; Jhulki, S.; Yang,  
608 C.-Y.; Timofeeva, T. V.; Wang, J.-Y.; Yee, S. K.; Barlow, S.; Marder, S. R.; Pei, J., Understanding the Effects

609 of Molecular Dopant on n-Type Organic Thermoelectric Properties. *Advanced Energy Materials* **2019**, *9*  
610 (24), 1900817.

611 34. Gregory, S. A.; Menon, A. K.; Ye, S.; Seferos, D. S.; Reynolds, J. R.; Yee, S. K., Effect of Heteroatom  
612 and Doping on the Thermoelectric Properties of Poly(3-alkylchalcogenophenes). *Advanced Energy*  
613 *Materials* **2018**, *8* (34), 1-8.

614 35. Gordon, M. P.; Gregory, S. A.; Wooding, J. P.; Ye, S.; Su, G. M.; Seferos, D. S.; Losego, M. D.;  
615 Urban, J. J.; Yee, S. K.; Menon, A. K., Microstructure and heteroatom dictate the doping mechanism and  
616 thermoelectric properties of poly(alkyl-chalcogenophenes). *Applied Physics Letters* **2021**, *118* (23), 1-8.

617 36. Al Kurdi, K.; Gregory, S. A.; Jhulki, S.; Conte, M.; Barlow, S.; Yee, S. K.; Marder, S. R., Electron  
618 transport in a sequentially doped naphthalene diimide polymer. *Materials Advances* **2020**, *1* (6), 1829-  
619 1834.

620 37. Vijayakumar, V.; Zaborova, E.; Biniek, L.; Zeng, H.; Herrmann, L.; Carvalho, A.; Boyron, O.;  
621 Leclerc, N.; Brinkmann, M., Effect of Alkyl Side Chain Length on Doping Kinetics, Thermopower, and Charge  
622 Transport Properties in Highly Oriented F4TCNQ-Doped PBTBT Films. *ACS Appl Mater Interfaces* **2019**, *11*  
623 (5), 4942-4953.

624 38. Zeier, W. G.; Zevalkink, A.; Gibbs, Z. M.; Hautier, G.; Kanatzidis, M. G.; Snyder, G. J., Thinking  
625 Like a Chemist: Intuition in Thermoelectric Materials. *Angew Chem Int Ed Engl* **2016**, *55* (24), 6826-41.

626 39. Kim, E. G.; Coropceanu, V.; Gruhn, N. E.; Sanchez-Carrera, R. S.; Snoeberger, R.; Matzger, A. J.;  
627 Bredas, J. L., Charge transport parameters of the pentathienoacene crystal. *J Am Chem Soc* **2007**, *129* (43),  
628 13072-81.

629 40. Ma, T.; Dong, B. X.; Grocke, G. L.; Strzalka, J.; Patel, S. N., Leveraging Sequential Doping of  
630 Semiconducting Polymers to Enable Functionally Graded Materials for Organic Thermoelectrics.  
631 *Macromolecules* **2020**, *53* (8), 2882-2892.

632 41. Al Kurdi, K.; Gregory, S. A.; Gordon, M. P.; Ponder, J. F., Jr.; Atassi, A.; Rinehart, J. M.; Jones, A.  
633 L.; Urban, J. J.; Reynolds, J. R.; Barlow, S.; Marder, S. R.; Yee, S. K., Iron(III) Dopant Counterions Affect  
634 the Charge-Transport Properties of Poly(Thiophene) and Poly(Dialkoxythiophene) Derivatives. *ACS Appl*  
635 *Mater Interfaces* **2022**, *14* (25), 29039-29051.

636 42. Harris, J. K.; Neelamraju, B.; Ratcliff, E. L., Intersystem Subpopulation Charge Transfer and  
637 Conformational Relaxation Preceding in Situ Conductivity in Electrochemically Doped Poly(3-  
638 hexylthiophene) Electrodes. *Chemistry of Materials* **2019**, *31* (17), 6870-6879.

639 43. Shallcross, R. C.; Stubhan, T.; Ratcliff, E. L.; Kahn, A.; Brabec, C. J.; Armstrong, N. R., Quantifying  
640 the Extent of Contact Doping at the Interface between High Work Function Electrical Contacts and Poly(3-  
641 hexylthiophene) (P3HT). *The Journal of Physical Chemistry Letters* **2015**, *6* (8), 1303-1309.

642 44. Jacobs, I. E.; D'Avino, G.; Lemaire, V.; Lin, Y.; Huang, Y.; Chen, C.; Harrelson, T. F.; Wood, W.;  
643 Spalek, L. J.; Mustafa, T.; O'Keefe, C. A.; Ren, X.; Simatos, D.; Tjhe, D.; Statz, M.; Strzalka, J. W.; Lee, J.  
644 K.; McCulloch, I.; Fratini, S.; Beljonne, D.; Siringhaus, H., Structural and Dynamic Disorder, Not Ionic  
645 Trapping, Controls Charge Transport in Highly Doped Conducting Polymers. *J Am Chem Soc* **2022**, *144* (7),  
646 3005-3019.

647 45. Ashcroft, N.; Mermin, D., *Solid State Physics*. Cengage Learning: 1976.

648 46. Rivnay, J.; Mannsfeld, S. C.; Miller, C. E.; Salleo, A.; Toney, M. F., Quantitative determination of  
649 organic semiconductor microstructure from the molecular to device scale. *Chem Rev* **2012**, *112* (10), 5488-  
650 519.

651 47. Rivnay, J.; Noriega, R.; Kline, R. J.; Salleo, A.; Toney, M. F., Quantitative analysis of lattice disorder  
652 and crystallite size in organic semiconductor thin films. *Physical Review B* **2011**, *84* (4), 1-20.

653 48. Rivnay, J.; Noriega, R.; Northrup, J. E.; Kline, R. J.; Toney, M. F.; Salleo, A., Structural origin of  
654 gap states in semicrystalline polymers and the implications for charge transport. *Physical Review B* **2011**,  
655 *83* (12), 1-4.

- 656 49. Peng, Z.; Ye, L.; Ade, H., Understanding, quantifying, and controlling the molecular ordering of  
657 semiconducting polymers: from novices to experts and amorphous to perfect crystals. *Mater Horiz* **2021**,  
658 *9*, 577-606.
- 659 50. Abutaha, A.; Kumar, P.; Yildirim, E.; Shi, W.; Yang, S. W.; Wu, G.; Hippalgaonkar, K., Correlating  
660 charge and thermoelectric transport to paracrystallinity in conducting polymers. *Nat Commun* **2020**, *11*  
661 (1), 1737.
- 662 51. de Boor, J.; Muller, E., Data analysis for Seebeck coefficient measurements. *Rev Sci Instrum* **2013**,  
663 *84* (6), 065102.
- 664 52. Maddali, H.; House, K. L.; Emge, T. J.; O'Carroll, D. M., Identification of the local electrical  
665 properties of crystalline and amorphous domains in electrochemically doped conjugated polymer thin  
666 films. *RSC Advances* **2020**, *10* (36), 21454-21463.
- 667 53. Ma, T.; Dong, B. X.; Onorato, J. W.; Niklas, J.; Poluektov, O.; Luscombe, C. K.; Patel, S. N.,  
668 Correlating conductivity and Seebeck coefficient to doping within crystalline and amorphous domains in  
669 poly(3-(methoxyethoxyethoxy)thiophene). *Journal of Polymer Science* **2021**, *59* (22), 2797-2808.
- 670 54. Boyle, C. J.; Upadhyaya, M.; Wang, P.; Renna, L. A.; Lu-Diaz, M.; Pyo Jeong, S.; Hight-Huf, N.;  
671 Korugic-Karasz, L.; Barnes, M. D.; Aksamija, Z.; Venkataraman, D., Tuning charge transport dynamics via  
672 clustering of doping in organic semiconductor thin films. *Nat Commun* **2019**, *10* (1), 2827.
- 673 55. Yu, Y.; Zhou, C.; Zhang, S.; Zhu, M.; Wuttig, M.; Scheu, C.; Raabe, D.; Snyder, G. J.; Gault, B.;  
674 Cojocar-Miréidin, O., Revealing nano-chemistry at lattice defects in thermoelectric materials using atom  
675 probe tomography. *Materials Today* **2020**, *32*, 260-274.
- 676 56. Ponder Jr, J. F.; Chen, H.; Luci, A. M. T.; Moro, S.; Turano, M.; Hobson, A. L.; Collier, G. S.;  
677 Perdigão, L. M. A.; Moser, M.; Zhang, W.; Costantini, G.; Reynolds, J. R.; McCulloch, I., Low-Defect, High  
678 Molecular Weight Indacenodithiophene (IDT) Polymers Via a C–H Activation: Evaluation of a Simpler and  
679 Greener Approach to Organic Electronic Materials. *ACS Materials Letters* **2021**, *3* (10), 1503-1512.
- 680 57. Slade, T. J.; Grovogui, J. A.; Kuo, J. J.; Anand, S.; Bailey, T. P.; Wood, M.; Uher, C.; Snyder, G. J.;  
681 Dravid, V. P.; Kanatzidis, M. G., Understanding the thermally activated charge transport in NaPbmSbQm+2  
682 (Q = S, Se, Te) thermoelectrics: weak dielectric screening leads to grain boundary dominated charge carrier  
683 scattering. *Energy & Environmental Science* **2020**, *13* (5), 1509-1518.
- 684 58. Kuo, J. J.; Kang, S. D.; Imasato, K.; Tamaki, H.; Ohno, S.; Kanno, T.; Snyder, G. J., Grain boundary  
685 dominated charge transport in Mg<sub>3</sub>Sb<sub>2</sub>-based compounds. *Energy & Environmental Science* **2018**, *11* (2),  
686 429-434.
- 687 59. Peterseim, T.; Dressel, M.; Dietrich, M.; Polity, A., Optical properties of VO<sub>2</sub> films at the phase  
688 transition: Influence of substrate and electronic correlations. *Journal of Applied Physics* **2016**, *120* (7), 1-  
689 6.
- 690 60. Gaiser, P.; Binz, J.; Gompf, B.; Berrier, A.; Dressel, M., Tuning the dielectric properties of metallic-  
691 nanoparticle/elastomer composites by strain. *Nanoscale* **2015**, *7* (10), 4566-71.
- 692 61. Hövel, M.; Gompf, B.; Dressel, M., Dielectric properties of ultrathin metal films around the  
693 percolation threshold. *Physical Review B* **2010**, *81* (3), 1-8.
- 694 62. Leick, N.; Weber, J. W.; Mackus, A. J. M.; Weber, M. J.; van de Sanden, M. C. M.; Kessels, W. M.  
695 M., In situ spectroscopic ellipsometry during atomic layer deposition of Pt, Ru and Pd. *Journal of Physics*  
696 *D: Applied Physics* **2016**, *49* (11), 1-12.
- 697 63. Hanus, R.; Gregory, S. A.; Adams, M. J.; Graham, S.; Yee, S. K., Quantifying the Effects of  
698 Inhomogeneity and Doping on the Electronic Contribution to Thermal Conductivity in Semiconducting  
699 Polymers. *Advanced Electronic Materials* **2022**, *8*, 1-8.
- 700 64. Mildred Dresselhaus; Gene Dresselhaus; Stephen Cronin; Antonio Gomes; Filho, S., *Solid State*  
701 *Properties: From Bulk to Nano*. Springer: 2018.
- 702 65. Kasap, S. O., *Principles of Electronic Materials and Devices*. McGraw-Hill Education: 2005.



- 703 66. Cobet, C.; Oppelt, K.; Hingerl, K.; Neugebauer, H.; Knör, G.; Sariciftci, N. S.; Gasiorowski, J.,  
704 Ellipsometric Spectroelectrochemistry: An in Situ Insight in the Doping of Conjugated Polymers. *The*  
705 *Journal of Physical Chemistry C* **2018**, *122* (42), 24309-24320.
- 706 67. Gasiorowski, J.; Hingerl, K.; Menon, R.; Plach, T.; Neugebauer, H.; Wiesauer, K.; Yumusak, C.;  
707 Sariciftci, N. S., Dielectric Function of Undoped and Doped Poly[2-methoxy-5-(3',7'-dimethyloctyloxy)-1,4-  
708 phenylene-vinylene] by Ellipsometry in a Wide Spectral Range. *J Phys Chem C Nanomater Interfaces* **2013**,  
709 *117* (42), 22010-22016.
- 710 68. Vezie, M. S.; Few, S.; Meager, I.; Pieridou, G.; Dorling, B.; Ashraf, R. S.; Goni, A. R.; Bronstein,  
711 H.; McCulloch, I.; Hayes, S. C.; Campoy-Quiles, M.; Nelson, J., Exploring the origin of high optical  
712 absorption in conjugated polymers. *Nat Mater* **2016**, *15* (7), 746-53.
- 713 69. Bednarski, H.; Hajduk, B.; Jurusik, J.; Jarzabek, B.; Domański, M.; Łaba, K.; Wanic, A.; Łapkowski,  
714 M., The Influence of PEDOT to PSS Ratio on the Optical Properties of PEDOT:PSS Thin Solid Films - Insight  
715 from Spectroscopic Ellipsometry. *Acta Physica Polonica A* **2016**, *130* (5), 1242-1244.
- 716 70. Schubert, M.; Bundesmann, C.; Jakopic, G.; Maresch, H.; Arwin, H.; Persson, N. C.; Zhang, F.;  
717 Inganäs, O., Infrared ellipsometry characterization of conducting thin organic films. *Thin Solid Films* **2004**,  
718 *455-456*, 295-300.
- 719 71. Chen, S.; Kang, E. S. H.; Shiran Chaharsoughi, M.; Stanishev, V.; Kuhne, P.; Sun, H.; Wang, C.;  
720 Fahlman, M.; Fabiano, S.; Darakchieva, V.; Jonsson, M. P., Conductive polymer nanoantennas for dynamic  
721 organic plasmonics. *Nat Nanotechnol* **2020**, *15* (1), 35-40.
- 722 72. Girtan, M.; Mallet, R.; Socol, M.; Stanculescu, A., On the Physical Properties PEDOT:PSS Thin  
723 Films. *Materials Today Communications* **2020**, *22*, 1-8.
- 724 73. Chen, S.; Kühne, P.; Stanishev, V.; Knight, S.; Brooke, R.; Petsagkourakis, I.; Crispin, X.; Schubert,  
725 M.; Darakchieva, V.; Jonsson, M. P., On the anomalous optical conductivity dispersion of electrically  
726 conducting polymers: ultra-wide spectral range ellipsometry combined with a Drude–Lorentz model.  
727 *Journal of Materials Chemistry C* **2019**, *7* (15), 4350-4362.
- 728 74. Woollam, J. A. Ellipsometry Resources. <https://www.jawoollam.com/resources> (accessed 2023-  
729 02-01).
- 730 75. Price, J.; Hung, P. Y.; Rhoad, T.; Foran, B.; Diebold, A. C., Spectroscopic ellipsometry  
731 characterization of HfxSiyOz films using the Cody–Lorentz parameterized model. *Applied Physics Letters*  
732 **2004**, *85* (10), 1701-1703.
- 733 76. Moulé, A. J.; Gonel, G.; Murrey, T. L.; Ghosh, R.; Saska, J.; Shevchenko, N. E.; Denti, I.; Ferguson,  
734 A. S.; Talbot, R. M.; Yacoub, N. L.; Mascal, M.; Salleo, A.; Spano, F. C., Quantifying Polaron Mole Fractions  
735 and Interpreting Spectral Changes in Molecularly Doped Conjugated Polymers. *Advanced Electronic*  
736 *Materials* **2021**, *2100888*, 1-9.
- 737 77. Ponder, J. F., Jr.; Gregory, S. A.; Atassi, A.; Advincula, A. A.; Rinehart, J. M.; Freychet, G.; Su, G.  
738 M.; Yee, S. K.; Reynolds, J. R., Metal-like Charge Transport in PEDOT(OH) Films by Post-processing Side  
739 Chain Removal from a Soluble Precursor Polymer. *Angew Chem Int Ed Engl* **2023**, *62* (1), e202211600.

740