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### Title

Microstructure and heteroatom dictate the doping mechanism and thermoelectric properties of poly(alkyl-chalcogenophenes)

### Permalink

<https://escholarship.org/uc/item/5vx3s40p>

### Journal

Applied Physics Letters, 118(23)

### ISSN

0003-6951

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### Publication Date

2021-06-07

### DOI

10.1063/5.0052604

### Supplemental Material

<https://escholarship.org/uc/item/5vx3s40p#supplemental>

Peer reviewed

1 **Microstructure and heteroatom dictate doping mechanism and thermoelectric properties**  
2 **of poly(alkyl-chalcogenophenes)**

3  
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27 **Abstract:** Heteroatom substitution is one promising way to favorably alter electronic transport in  
28 conductive polymers to improve their performance in thermoelectric devices. This study reports  
29 the spectroscopic, structural, and thermoelectric properties of poly(3-(3',7'-dimethyloctyl)  
30 chalcogenophenes) (P3RX) doped with 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane  
31 (F4TCNQ), where the doping methodology, the heteroatom (X = Thiophene (T), Selenophene  
32 (Se), Tellurophene (Te)) and the extent of doping are systematically varied. Spectroscopic  
33 measurements reveal that while all P3RX polymers are appreciably doped, the doping  
34 mechanism is inherently different between the polymers. Poly(3-hexylthiophene) (P3HT, used in  
35 this study as a control) and P3RTe doped primarily via integer charge transfer (ICT), whereas  
36 P3RSe and P3RT appear to be doped via charge-transfer complex (CTC) mechanisms. Despite  
37 these differences, all polymers saturate with roughly the same number of F4TCNQ counterions  
38 (1 dopant per 4 to 6 heterocycles), reinforcing the idea that the extent of charge transfer from  
39 polymer to dopant varies significantly on the preferred doping mechanism. Grazing incidence  
40 wide-angle X-ray scattering measurements provide insight into the structural driving forces  
41 behind these different doping mechanisms - P3RT and P3RSe have similar microstructures in  
42 which F4TCNQ intercalates between the  $\pi$ -stacked backbones resulting in CTC doping  
43 (localized charge carriers), while P3HT and P3RTe have microstructures in which F4TCNQ  
44 intercalates in the alkyl-side chain region, giving rise to ICT doping (delocalized charge  
45 carriers). These structural and spectroscopic observations shed light on why P3HT and P3RTe

46 obtain maximum electrical conductivities *ca.* 3 S/cm, while P3RT and P3RSe obtain maximum  
47 electrical conductivities  $<10^{-3}$  S/cm under the same thin film processing conditions. Ultimately,  
48 this work quantifies the effects of heteroatom, microstructural ordering, extent of doping, and  
49 doping mechanism on optical and electronic properties and provides rational guidance for  
50 designing future polymer and dopant chemistries for high performance thermoelectric materials.  
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53         Semiconducting polymers are an attractive class of materials for optical and electronic  
54 devices where processability and mechanical flexibility are desired.<sup>1-3</sup> Integration of these  
55 polymers into thermoelectric devices, used for energy harvesting and/or localized heating and  
56 cooling, has risen in popularity over the last decade.<sup>2,4,5</sup> P3HT (poly(3-hexylthiophene)) is a  
57 promising, well-studied p-type organic semiconducting polymer, but its electrical conductivity ( $\sigma$ )  
58 and Seebeck coefficient ( $S$ ) fall short of conventional inorganic materials, thereby limiting  
59 P3HT's practical use in thermoelectric devices. One avenue for improving electronic  
60 performance is through polymer main chain heteroatom substitution; the heteroatom identity can  
61 fine-tune the molecular packing and the frontier molecular orbital energies, both of which  
62 influence charge transport properties.<sup>6-9</sup> In a previous study, we demonstrated that substituting the  
63 heteroatom in poly(alkyl-chalcogenophenes) from S to Se to Te results in smaller optical band  
64 gaps and increases the susceptibility to FeCl<sub>3</sub> oxidation, *i.e.*, a smaller amount of dopant is  
65 needed.<sup>10,11</sup> This in turn yields an optimal thermoelectric power factor ( $S^2\sigma$ ) of *ca.* 13  $\mu\text{W}/\text{mK}^2$   
66 for poly(alkyl-tellurophenes) that achieve appreciable  $\sigma$  and low  $S$  values (*ca.* 50 S/cm and 30  
67  $\mu\text{V}/\text{K}$ , respectively) that are indicative of high doping levels. This previous work demonstrated  
68 that heteroatom substitution can alter doping susceptibility and thermoelectric performance, but  
69 fundamental insights into the doping-induced charge transfer mechanisms and resulting

70 structure-property relationships for this class of poly(alkyl-chalcogenophenes) remain  
71 unexplored.

72 Chemical doping involves oxidizing or reducing the polymer main chain, thus altering  
73 the density and filling of electronic states. Additionally, dopant geometry,<sup>12</sup> dopant intercalation  
74 in the polymer microstructure,<sup>13,14</sup> and the alignment of polymer and dopant frontier molecular  
75 orbital energies<sup>15,16</sup> must also be considered when engineering a polymer/dopant system.<sup>17</sup> While  
76 FeCl<sub>3</sub> is commonly used for oxidative doping, its relatively small molecular size (~3-6 Å) can  
77 make it challenging to track the dopant position and interactions with the semiconducting  
78 polymer.<sup>15</sup> On the other hand, the molecular oxidant F4TCNQ (2,3,5,6-tetrafluoro-  
79 tetracyanoquinodimethane) is suitable for quantifying doping mechanisms and establishing  
80 structure-doping relationships as its larger molecular size causes a greater disruption to the  
81 polymer's microstructure. Additionally, F4TCNQ has been shown to be an effective dopant for  
82 enhancing thermoelectric performance in a variety of ways,<sup>18</sup> including charge transfer  
83 complexation (CTC),<sup>13</sup> integer charge transfer (ICT),<sup>19-21</sup> and/or double doping<sup>22</sup> depending on  
84 the polymer microstructure, energy levels, and processing conditions. CTC involves the  
85 formation of new local hybridized molecular orbitals with a partial, non-integer charge transfer  
86 from the polymer to the dopant.<sup>13</sup> In contrast, ICT involves the transfer of an integer of charge  
87 (*e.g.* 1*e* or 2*e* transfer)<sup>13</sup> and leads to more electrically conductive materials as the polaronic  
88 carriers are not localized in a hybridized orbital between the polymer and dopant.<sup>19</sup> By  
89 engineering F4TCNQ to dope P3HT primarily through the ICT pathway and intercalate among  
90 the hexyl side chains, solution doping studies have reported electrical conductivities of 1-10  
91 S/cm,<sup>23-25</sup> vapor doped conductivity of 1-100 S/cm,<sup>26</sup> and high-temperature rubbing-induced  
92 conductivities of >100 S/cm.<sup>18</sup> Unlike P3HT, its branched side chain analog P3EHT (poly(3-(2'-

93 ethyl)hexylthiophene)), is doped by F4TCNQ through a CTC pathway with dopant molecules  
94 intercalating between the  $\pi$ -stacks, which leads to a low electrical conductivity of  $10^{-3}$  S/cm.<sup>13</sup>  
95 Despite having the same conjugated backbone as P3HT, this P3EHT study demonstrated that  
96 microstructural ordering significantly influences the doping mechanism and resulting optical and  
97 electronic properties.

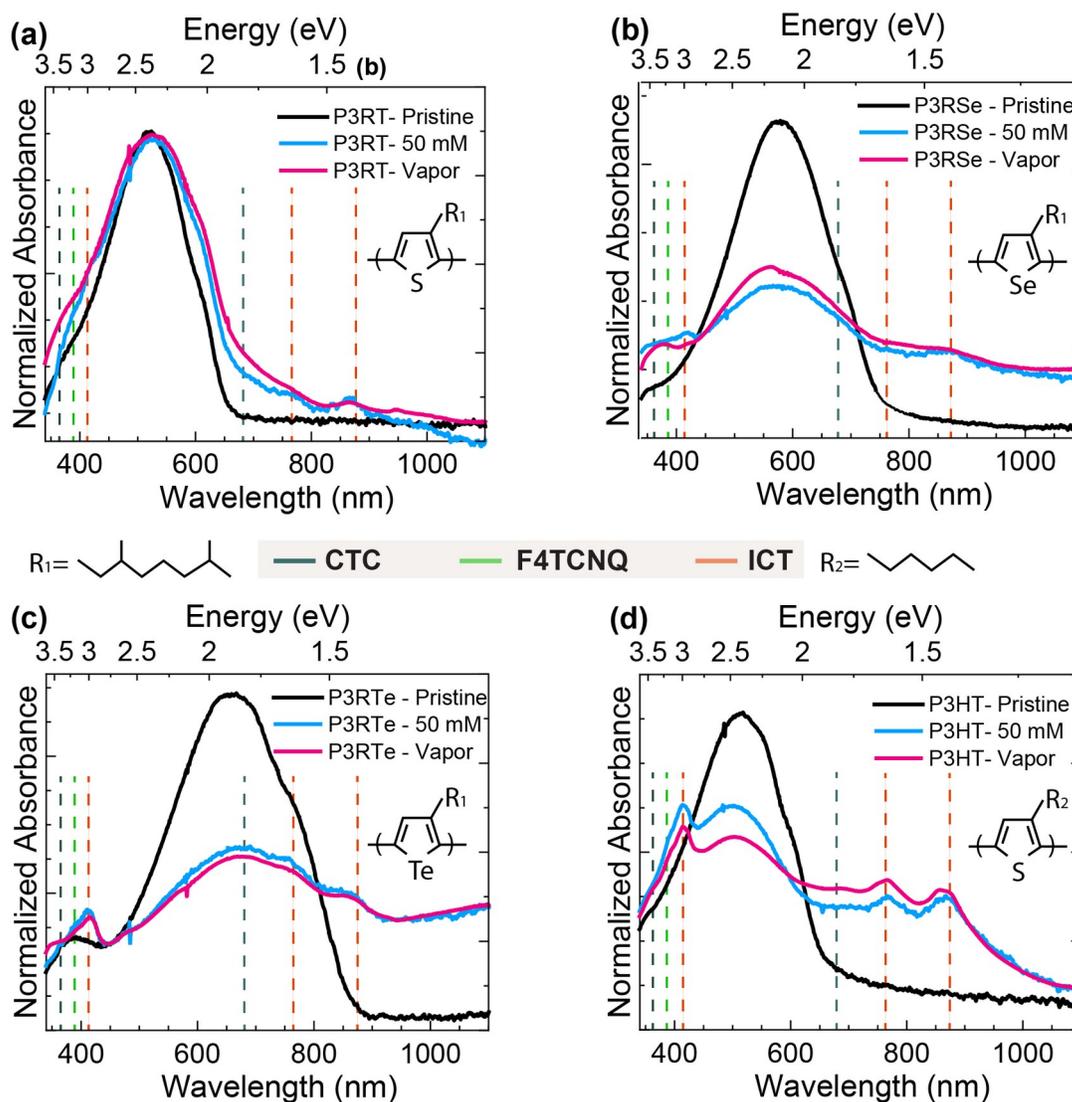
98         Herein, we investigate the effects of heteroatom substitution, doping method, and dopant  
99 concentration on the resulting thermoelectric and charge transport properties of a series of  
100 poly(3-(3',7'-dimethyloctyl) chalcogenophenes), where the chalcogen is either S, Se, or Te  
101 (P3RT, P3RSe, P3RTe, respectively). Through optical, infrared and photoelectron  
102 spectroscopies, we find that F4TCNQ dopes P3RT primarily via CTC, P3RSe via both CTC and  
103 ICT, and P3RTe primarily via ICT. Experiments with P3HT are also performed and confirm that  
104 the doping and processing procedures are comparable to prior literature reports. Grazing  
105 incidence wide-angle x-ray scattering (GIWAXS) sheds light on the underlying cause for these  
106 different doping mechanisms. P3RT and P3RSe have similar structural ordering where F4TCNQ  
107 intercalates between the  $\pi$ -stacks, leading to primarily localized, CTC based doping. In contrast,  
108 P3RTe and P3HT have similar microstructural ordering with F4TCNQ primarily intercalating  
109 into the lamellar side chain region, resulting in more delocalized, ICT based doping.  
110 Thermoelectric measurements reveal the performance impacts of the different doping  
111 mechanisms; CTC dominated P3RT and P3RSe have low carrier mobilities and electrical  
112 conductivities ( $\sigma < 10^{-2}$  S/cm), whereas ICT dominated P3RTe and P3HT have considerably  
113 higher carrier mobilities and electrical conductivities ( $\sigma \approx 3$  S/cm) upon doping with F4TCNQ  
114 via both solution and vapor doping methods.

115 Thin films (*ca.* 300 nm) of each polymer were spin coated from toluene solutions. These  
116 films were either solution-doped with varying F4TCNQ molarities in acetonitrile or vapor-doped  
117 by subliming F4TCNQ for 60-minutes. Detailed experimental procedures and polymer  
118 characterization can be found in **Note S1**, and in our prior study.<sup>10</sup>

119 UV-Visible-Near Infrared (UV-Vis-NIR) spectroscopy is used to provide cursory  
120 evidence for the extent of doping and the mechanism as a function of dopant concentration and  
121 heteroatom. **Figure 1** plots the UV-Vis-NIR spectra for polymer thin films on glass substrates in  
122 their pristine, solution doped (50 mM), and vapor doped forms. In each panel of **Figure 1**, black  
123 lines show the pristine spectra, and the pink and blue lines represent the vapor and 50 mM  
124 solution doped films, respectively. An in-depth analysis of the UV-Vis-NIR spectra shown in  
125 **Figure 1** is provided in the supporting information (**Note S2**).

126 **Figure 1** provides qualitative insight into the extent of doping; as the intensity of the  
127 pristine polymer  $\pi$ - $\pi^*$  peak between 500-700 nm decreases, the extent of doping increases. For  
128 both the solution and vapor doped scenarios, P3RT is least susceptible to F4TCNQ doping  
129 (**Figure 1a**) and P3RSe demonstrates a stronger degree of doping (*i.e.*, greater  $\pi$ - $\pi^*$  bleaching,  
130 **Figure 1b**). P3RTe (**Figure 1c**) shows the highest degree of F4TCNQ doping, and the optical  
131 features at 410 nm, 760 nm and 875 nm are indicative of ICT being the predominant doping  
132 mechanism at play.<sup>19,27-29</sup> While P3RSe also demonstrates these ICT features, peaks at 364 nm  
133 and 685 nm suggest the presence of CTC doping as well (**Figure 1b**).<sup>19,27-29</sup> In contrast, P3RT  
134 demonstrates predominantly CTC doping peaks (**Figure 1a**). To facilitate direct comparisons  
135 with prior literature, measurements were also made on P3HT films (**Figure 1d**), which  
136 demonstrate strong ICT features at 410 nm, 760 nm and 875 nm and a fair degree of F4TCNQ

137 doping susceptibility, like P3RSe. Note that in all three P3RX films and P3HT films, there is  
 138 little variation in the optical spectra of solution doped and vapor doped films, which suggests that  
 139 the extent of doping is comparable with both methods.



**Figure 1:** Normalized UV-Vis-NIR spectra of the pristine polymers, and the F4TCNQ solution doped (50 mM) and vapor doped films, (a) poly(3-(3',7'-dimethyloctyl)thiophene) (P3RT), (b) poly(3-(3',7'-dimethyloctyl)selenophene) (P3RSe), (c) poly(3-(3',7'-dimethyloctyl)telurophene) (P3RTe), and (d) poly(3-hexylthiophene) (P3HT). The dashed lines in each panel show the peak locations of CTC (teal lines *ca.* 364, 685 nm), residual F4TCNQ dopant (green lines *ca.* 390 nm) and ICT (orange lines *ca.* 410, 760, 875 nm).

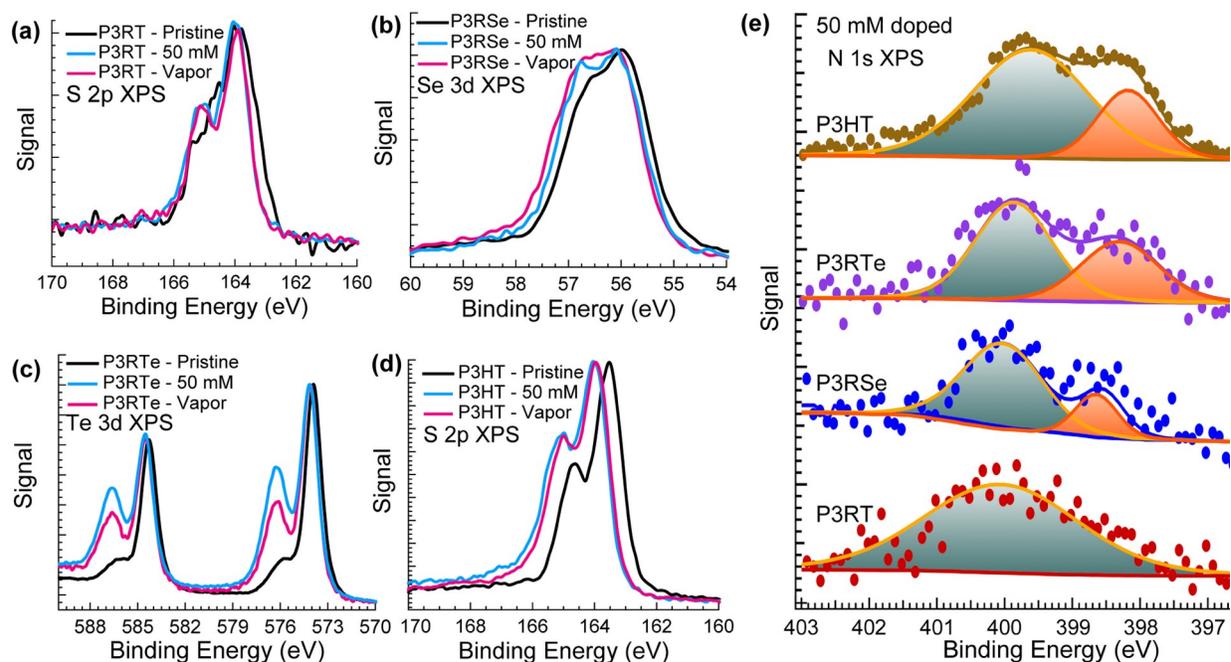
140  
 141 To corroborate these optical trends, attenuated total reflection Fourier-transform infrared  
 142 spectroscopy (ATR-FTIR) was performed on these films. ATR-FTIR measurements can provide  
 143 insights into the extent of doping (*via* polaronic absorbance in the mid-IR), degree of charge

144 carrier delocalization (broad optical absorbance ranging from *ca.* 1500 cm<sup>-1</sup> to over 5000 cm<sup>-1</sup>)  
145 and the doping mechanism (*via* changes in the C  $\equiv$  N stretching mode absorbance near 2200 cm<sup>-1</sup>).  
146 For the sake of brevity, full discussion on this technique is provided in **Note S3**. These  
147 measurements reveal that P3RTe and P3HT demonstrate strong peak intensities at 2194 cm<sup>-1</sup>  
148 correlated with ICT, while P3RT has peak intensities between 2200-2015 cm<sup>-1</sup> linked to CTC  
149 features, and P3RSe has intensities associated with both ICT and CTC absorption features.  
150 Overall, these ATR-FTIR results are consistent with the doping mechanisms elucidated by UV-  
151 Vis-NIR.

152         These optical and infrared spectroscopic measurements provide qualitative insight into  
153 the charge transfer mechanism but fail to quantify the extent of doping in the P3RX films and the  
154 relative contribution of each doping mechanism at play. To this end, X-ray photoelectron  
155 spectroscopy (XPS) surface profiling was used. **Figure 2a-d** shows the heteroatom spectra (S-2p,  
156 Se-3d, Te-3d) for the pristine polymer films, 50 mM solution doped films, and vapor doped  
157 films; additional XPS spectra are in **Note S4**. To provide insight into the dopant-polymer  
158 interactions, deconvoluted N-1s spectra for 50 mM doped films are shown in **Figure 2e**.

159         Upon doping there is a clear shift to higher binding energies, which is indicative of a loss  
160 in electron density with the introduction of dopant in **Figure 2a-d**. XPS heteroatom spectra  
161 confirm that vapor doping and 50 mM solution doping yield similar results based upon their  
162 analogous shifts in binding energy. In-depth discussion of heteroatom peak positions and their  
163 deconvolutions can be found in **Note S4**. In order to quantify the extent of doping, the atomic  
164 abundance for F and N with respect to the heteroatom (S, Se, Te) was used. We examine here the  
165 solution doped films due to the better stability of the dopant molecule under vacuum, leading to

166 less background noise. We find that the dopant to heterocycle ratio for 50 mM doped P3RT is 19  
167  $\pm 3$  %, P3RSe is  $19 \pm 2$  %, P3RTe is  $23 \pm 8$  %, and P3HT is  $18 \pm 4$  % (**Note S4**). These results  
168 suggest that each P3RX polymer has roughly equal amounts of F4TCNQ present at the film's  
169 surface (*ca.* 1 dopant per 5 rings), which is consistent with previous P3HT-F4TCNQ reports.<sup>30,31</sup>  
170 Inspection of the N-1s spectra shown in **Figure 2e** provides additional insight as Watts *et al.*  
171 studied ICT and CTC in P3HT doped with F4TCNQ and assigned the N<sup>-1</sup> peak at 398.2 eV to  
172 ITC and the N<sup>0</sup> peak at 400 eV to CTC.<sup>19</sup> The motivation behind these assigned differences in  
173 binding energy arises from the electron density differences in F4TCNQ for these two doping  
174 mechanisms. ICT involves a full electron transfer to the F4TCNQ molecule, resulting in a higher  
175 electron density and thus a shift to lower binding energies, whereas CTC appears at higher  
176 binding energies.



**Figure 2:** XPS analysis for select P3RX films. Heteroatom scans for each polymer (a) S-2p spectra in P3RT, (b) Se-3d spectra in P3RSe, (c) Te-3d spectra in P3RTe, and (d) S-2p spectra in P3HT, all demonstrate a blue shift upon doping. (e) Deconvoluted N-1s spectra of 50 mM doped polymers reveal the relative intensities of  $N^0$  species (teal fitted peak centered at  $\sim 399.5$  eV) versus the  $N^{-1}$  peak (orange fitted peak centered at  $\sim 398$  eV). The strong presence of  $N^{-1}$  in both P3RTe and P3HT further corroborates that ICT is the dominant doping mechanism for these two polymers, as opposed to P3RT and P3RSe which show reduced or no intensity.

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Deconvolution of the N-1s spectra reveals the presence of both the  $N^0$  and  $N^{-1}$  peaks in all

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systems except P3RT, which demonstrates just a broad  $N^0$  peak at  $\sim 399.5$  eV. From the fitting of

180

these N-1s spectra, peak area ratios were calculated to determine the relative percentage of ICT

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doping occurring in P3RSe, P3RTe and P3HT, which all show  $N^{-1}$  features.<sup>32</sup> P3RSe

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demonstrates a relatively low  $N^{-1}$  percentage of  $\sim 18\%$ , further supporting the UV-VIS and FTIR

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measurements that ICT is not the dominant mode of charge transfer, but it is present to some

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extent. On the other hand, P3RTe and P3HT both demonstrate strong  $N^{-1}$  peak percentages of

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$\sim 35\%$ , suggesting that ICT is a major charge transfer mechanism at play.

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Spectroscopic measurements show that the extent of doping and the mechanism vary

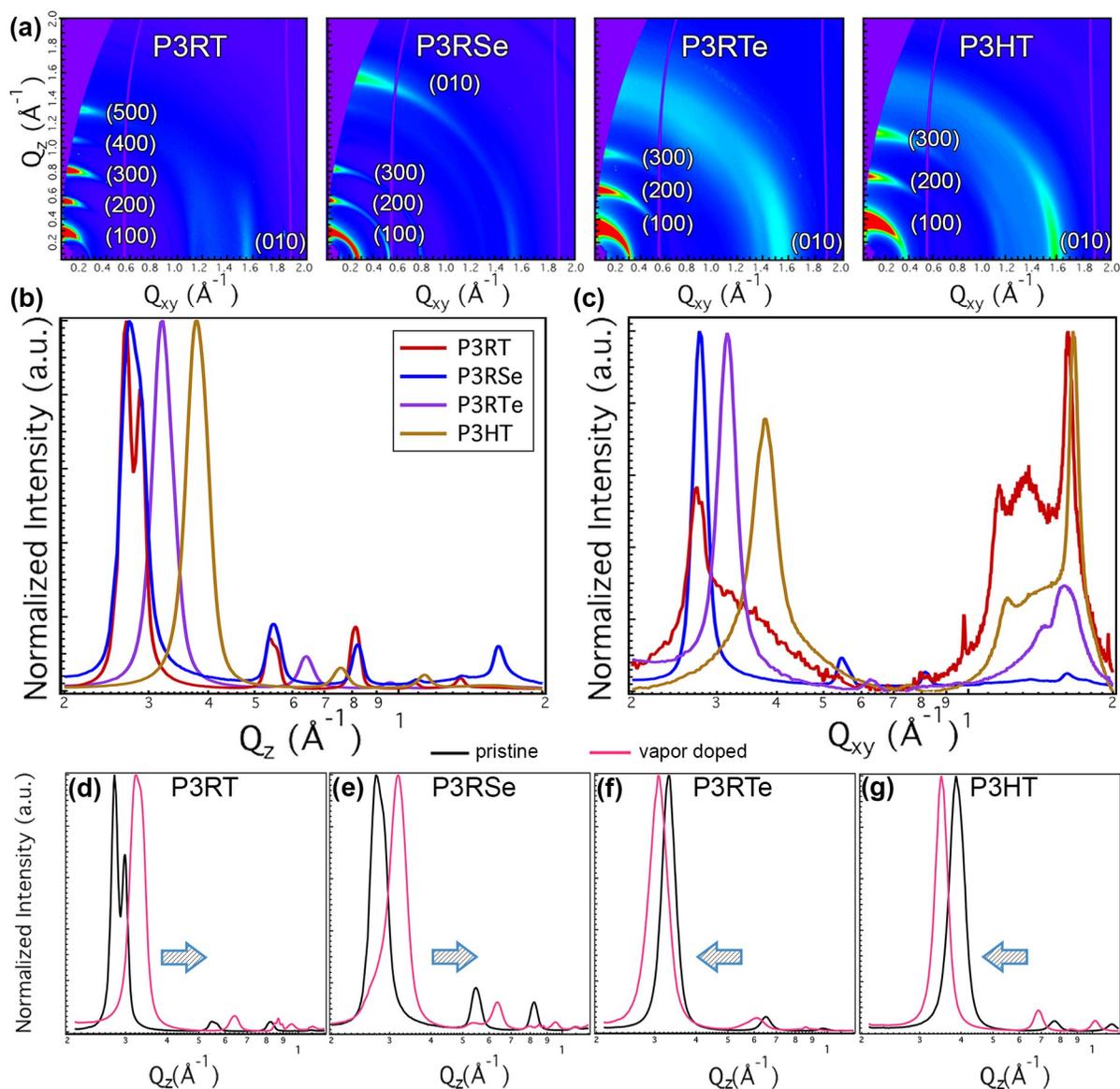
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significantly within the P3RX family, but these measurements alone do not explain why P3RT

188 and P3RSe have significant CTC populations while P3RTe dopes primarily through ICT.  
189 Previous studies have shown that propensity for CTC or ICT doping is dependent on the method  
190 of intercalation of F4TCNQ into the polymer crystallite; specifically, CTC doping occurs as  
191 F4TCNQ resides between the crystallites'  $\pi$ -stacks and forms localized, hybridized polymer-  
192 F4TNCQ molecular orbitals.<sup>13</sup> Therefore, to probe the structural morphology of these polymers  
193 and understand the impacts of doping with F4TCNQ, grazing incidence wide angle X-ray  
194 scattering (GIWAXS) was performed on the pristine polymers and their F4TCNQ vapor-doped  
195 analogs. Vapor doped films were chosen because it has been demonstrated that this maintains  
196 higher degrees of structural ordering compared to solution doped films, and we observe  
197 comparable spectroscopic properties with both types of doping.<sup>26,30</sup>

198 A brief discussion of the pristine GIWAXS scattering shown in **Figure 3a-c** can be found  
199 in **Note S5**. Upon doping with F4TCNQ in the vapor phase, a clear change in the scattering  
200 pattern occurs for all the polymers (**Figure 3d-f**). Both P3RT and P3RSe demonstrate a  
201 contraction in lamellar lattice spacing (h00 peaks shift to higher Q), whereas P3HT and P3RTe  
202 show an expansion of the lamellar lattice (h00 peaks shift to lower Q). Focus was placed on the  
203 (100) peaks due to its strong scattering intensity. Furthermore, several studies have shown that  
204 changes in the lamellar lattice spacing can be indicative of the doping mechanism. Stanfield *et al.*  
205 demonstrated that a poor doping solvent leads to a contraction of P3HT lamellar lattice spacing,  
206 suggesting that F4TCNQ molecules coordinate within the  $\pi$ - $\pi$  stacking region along the polymer  
207 backbone leading to CTC doping.<sup>33</sup> Thomas *et al.* observed a similar effect in P3HT vs. P3EHT,  
208 where the branched alkyl sidechains in P3EHT create steric hindrance that inhibits F4TCNQ  
209 intercalation into the polymer side chains and promotes F4TCNQ intercalation between the  $\pi$ -

210 stacks, and this was accompanied by a slight decrease of the alkyl stacking distance.<sup>13</sup> Therefore,  
211 we postulate that P3RT and P3RSe are doped via a CTC mechanism, evidenced by the  
212 contraction in alkyl stacking distance (shift in the alkyl stacking peak to higher Q) from 22.6 nm  
213 to 19.7 nm for P3RT, and 22.4 nm to 21.5 nm for P3RSe. This suggests the dopant inserts co-  
214 facially between polymer backbones. Interestingly, while P3RTe has the same branched side  
215 chain as its thio- and seleno- counterparts, it shows a lamellar lattice expansion similar to P3HT,  
216 from 18.9 nm to 20.4 nm. This suggests that F4TCNQ intercalates in P3RTe's lamellar side  
217 chains and allows for ICT doping. There are many factors, such as crystallite size, differences in  
218 electronic interactions, etc., that could be causing these observed differences. However, we  
219 hypothesize that P3RTe's unique behavior could, in part, be due to differences in the P3RX  
220 polymers' degree of backbone rotational freedom. Ye *et al.* performed an in-depth study on the  
221 forces at work to drive crystallization in these polymers and found that as the substituted  
222 heteroatom becomes larger, there is less rotational freedom.<sup>34</sup> Thus, as the heteroatom becomes  
223 larger and the polymer backbone becomes more conformationally-locked in a planar  
224 configuration, the chains can come closer to one another to enable better molecular overlap  
225 which ultimately translates to higher mobility. The lower degree of backbone rotational freedom  
226 in P3RTe may hinder F4TCNQ intercalation between the  $\pi$ -stacks and as a result, the dopant  
227 molecules intercalate into the alkyl side chains and participate in ITC doping. In contrast, higher  
228 degrees of backbone rotational freedom in P3RSe and P3RT (while still having a sterically  
229 hindered branched alkyl side chain) translates to F4TCNQ molecules intercalating between  $\pi$ -  
230 stacks and participating in CTC doping, which is consistent with the spectroscopic results  
231 presented herein.



**Figure 3:** (a) GIWAXS of pristine polymers of P3RT, P3RSe, P3RTe and P3HT, (b) nearly out-of-plane line cuts, and (c) in-plane line cuts. The strong (h00) peaks visible in (b) along with the pronounced (010) peaks in (c) reveals preferential edge-on orientation for all the polymers except P3RSe which shows both edge-on and face-on alignment. Out-of-plane line cuts are shown for (d) P3RT, (e) P3RSe, (f) P3RTe, and (g) P3HT both before and after vapor doping with F4TCNQ. Both P3RT and P3RSe show (h00) peaks shift to higher  $Q$  after doping, indicative of a contraction of the lamellar spacing. P3RTe and P3HT show the lamellar stacking peak shift to lower  $Q$ , indicating an expansion in lamellar spacing and suggestive of F4TCNQ dopant intercalating into the alkyl side chains leading to ITC doping.

233 The electrical conductivity and Seebeck coefficient are a measure of the macroscopic  
234 average charge carrier density, charge carrier mobility and how these properties vary as a  
235 function of polymer chemistry and extent of doping. The P3RX family has appreciable  
236 thermoelectric properties when doped with FeCl<sub>3</sub>,<sup>10</sup> and spectroscopic data suggests that  
237 F4TCNQ dopes all P3RX polymers and P3HT, albeit through various mechanisms. Here, these  
238 thermoelectric measurements are used to quantitatively understand to what extent ICT vs. CTC  
239 doping mechanisms affect the resulting charge transport.

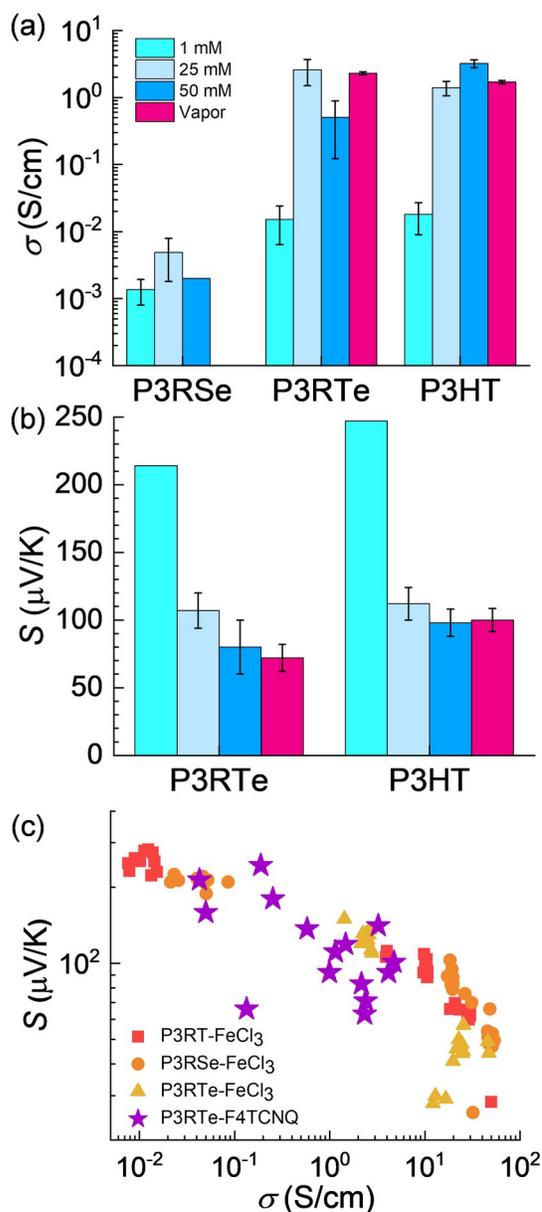
240 **Figure 4a** plots the electrical conductivity ( $\sigma$ ) for both the solution and vapor doped  
241 films. Although P3RT has an appreciable number of F4TCNQ dopant counterions (**Figure 2**),  
242 the number of charge carriers with sufficient mobilities is limited due to its CTC doping  
243 mechanism,<sup>13,19</sup> leading to a very low electrical conductivity ( $\sigma < 10^{-4}$  S/cm). Similarly, P3RSe  
244 shows low electrical conductivities of  $< 5 \times 10^{-3}$  S/cm, likely due to the dopant being incorporated  
245 between the  $\pi$ -stacks (**Figure 3**) resulting in a significant CTC population (**Figure 2**) with  
246 heavily localized charge carriers. The latter is supported by temperature dependent conductivity  
247 measurements, which show a large activation energy (150-200 meV), in comparison to other  
248 highly doped semiconducting polymers ( $< 100$  meV), (**Note S6**). In contrast to P3RT and P3RSe,  
249 P3RTe shows appreciable electrical conductivity at all doping concentrations in this study, with a  
250 maximum of  $2.6 \pm 1.1$  S/cm at 25 mM F4TCNQ and with vapor doping. This is three orders of  
251 magnitude higher than P3RSe at the same doping molarity and XPS counterion concentration  
252 (**Figure 2**), owing to P3RTe being doped primarily via ITC. At a higher solution molarities of 50  
253 mM, the electrical conductivity of P3RTe decreases, likely due to over doping, which has been  
254 reported in several polymer dopant systems.<sup>10,12,35,36</sup> The maximum P3RTe electrical conductivity

255 is roughly equal to the maximum P3HT electrical conductivity of  $3.2 \pm 0.4$  S/cm. Lastly, we note  
256 that the solution doped and vapor doped maximum electrical conductivities for P3HT and P3RTe  
257 are comparable to one another and are similar to the electrical conductivity of P3HT doped with  
258 F4TCNQ reported in previous literature.<sup>25,30</sup>

259 Now we turn to analyze the Seebeck coefficient in **Figure 4b**. The Seebeck coefficient ( $S$ )  
260 is directly related to the asymmetry of the carrier distribution about the Fermi energy. Thus,  $S$   
261 usually decreases as a result of reduced asymmetry as carrier concentration increases. Doped  
262 P3RT and P3RSe films were too insulating for repeatable Seebeck coefficients to be reported,  
263 while both P3RTe and P3HT show observable Seebeck coefficients. As expected, the Seebeck  
264 coefficient decreases as the doping concentration increases for both P3RTe and P3HT; further  
265 discussion can be found in **Note S6**. This trend agrees with the measured increasing electrical  
266 conductivity and increasing charge carrier concentration, as well as previous literature reports.

267 Lastly, we examine the  $S$ - $\sigma$  plot for the P3RX polymers doped with  $\text{FeCl}_3$  and F4TCNQ  
268 (**Figure 4c**). The curvature, slope, and nominal values on the  $S$ - $\sigma$  plot are indicative of  
269 fundamental transport phenomena, so analyzing these curves enables rational polymer and  
270 dopant design for optimal thermoelectric performance.<sup>37</sup> Although the values in **Figure 4c** do not  
271 lead to record-high thermoelectric power factors (maximum of *ca.*  $3.8 \mu\text{W}/\text{mK}^2$  for the P3RTe-  
272 F4TCNQ films), it is notable that all P3RX- $\text{FeCl}_3$  and P3RTe-F4TCNQ datasets lie on the same  
273 curve. According to the Kang-Snyder model, a generalized transport model developed for  
274 polymers, materials that lie on the same curve have a similar set of governing transport physics  
275 (*e.g.* mobilities, energy dependence, electronic structures).<sup>37</sup> Based on this framework, we find  
276 that the heteroatom, dopant concentration, and chemistry are all parameters that shift transport

277 properties along the same  $S$ - $\sigma$  curve, but do not laterally or vertically shift the  $S$ - $\sigma$  curve (as long  
278 as the polymers are doped via ICT mechanisms). Therefore, we hypothesize that in addition to  
279 using poly(tellurophenes) for their advantageous ordering and doping susceptibility, employing  
280 additional orienting methods such as drawing,<sup>38</sup> or rubbing,<sup>18,39</sup> which have been shown to  
281 laterally shift the  $S$ - $\sigma$  curve, will likely lead to enhanced thermoelectric performance beyond  
282 what is reported in this work.



**Figure 4:** Thermoelectric properties as a function of heteroatom and doping. (a) Electrical conductivity, (b) Seebeck coefficient, (c) Jonker curve comparing this study (P3RTe-F4TCNQ) with our previously reported P3RX-FeCl<sub>3</sub> dataset. Error bars, when present, represent the sample-to-sample standard deviation.

283

284 In this work, we demonstrated that varying the heteroatom (S, Se, Te) alters the polymer

285 microstructure, doping mechanism, and charge transport properties. Moving from S to Se to Te,

286 the susceptibility to F4TCNQ doping increases. Optical and photoelectron spectroscopies

287 suggest that all P3RX polymers have a comparable number of F4TCNQ counterions, but P3RT  
288 is not heavily oxidized and is doped dominantly via CTC mechanisms, P3RSe is more oxidized  
289 and is likely doped through both CTC and ICT, and that P3RTe is heavily oxidized and primarily  
290 doped through ICT. GIWAXS measurements suggest that P3RT and P3RSe are prone to CTC  
291 doping because of their microstructural ordering, resulting in dopant intercalation between  $\pi$ -  
292 stacks. In contrast, P3RTe is similar to P3HT (ICT) because of its planar packing that enables  
293 dopant intercalation into the lamellar side chains. Lastly, we note that P3RTe/F4TCNQ has  
294 similar transport properties to P3RX/FeCl<sub>3</sub>, suggesting that more sophisticated processing  
295 techniques (*e.g.* rubbing, drawing) may be needed to laterally shift the  $S$ - $\sigma$  curve for the P3RX  
296 family. The observations herein quantify how polymer and dopant synthetic engineering  
297 (heteroatom, side chain, microstructure, dopant chemistry) affect charge transport and provides  
298 guidance for future improvement of semiconducting polymers.

299

300 **Supporting Information Contents:**

301

302 **Funding:** MPG and JPW gratefully acknowledge support from the National Science Foundation

303 Graduate Research Fellowship. SAG appreciates the partial support from the Office of Naval

304 Research (award number N00014-19-1-2162), the Department of Education Graduate Assistance

305 in Areas of National Need (GAANN) program at the Georgia Institute of Technology (Award

306 #P200A180075), the Link Energy Foundation, and the Science and Technology of Material

307 Interfaces (STAMI) group at the Georgia Institute of Technology. SY and DSS are grateful for

308 support from the NSERC of Canada and the University of Toronto Connaught Foundation for a

309 McLean Award.

310 This work was performed in part at the Molecular Foundry and the Advanced Light Source

311 (beamline 7.3.3), Lawrence Berkeley National Laboratory, and was supported by the Department

312 of Energy, Office of Science, Office of Basic Energy Sciences, Scientific User Facilities Division

313 of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231. Part of this work

314 was also performed at the Georgia Tech Institute for Electronics and Nanotechnology, a member

315 of the National Nanotechnology Coordinated Infrastructure, which is supported by the National

316 Science Foundation (Grant ECCS-1542174).

317

318 **Data Availability Statement:** The data that supports the findings of this study are available

319 within the article and its supplementary material.

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