1. Introduction

Organic semiconductors (OSCs) are emerging as a powerful technology for practical applications in displays, solar cells, and sensors by virtue of their low density, chemical diversity, mechanical flexibility, biocompatibility, low-temperature processing, and low-cost of manufacturing.\(^{1,2}\) There are generally two classes of OSCs, molecular semiconductors and conjugated polymers. For the latter, polythiophenes and their derivatives represent a state-of-the-art model system due to their ordered, semicrystalline nature, and resultant relatively high charge carrier mobilities. These materials also display good chemical stability as well as ease of synthesis with controllable chemical structure modification.\(^{3,4}\)

Heavy heteroatom substitution of the backbone is an effective strategy to improve molecular packing and charge delocalization in polymer semiconductors. Such a backbone modification also facilitates oxidative doping as a result of reduced ionization potential (IP). Here, the effect of single-atom selenium substitution on doping and charge transport properties of a class of polythiophene copolymers is explored. The room temperature (RT) conductivities of the doped polymers are significantly enhanced by the selenium substitution for both molecular doping and ion exchange doping. The enhanced conduction is rationalized by the better crystallinity of the selenium-containing system, which can be reinforced by a chain-extended ribbon-phase morphology induced by thermal annealing, which is robust toward doping. The resulting increase in the charge delocalization of the doped selenium-containing system is evidenced by temperature-dependent conductivities. In ion exchange doped films the maximum conductivity of \(\approx 700 \text{ S cm}^{-1}\) and a high thermoelectric (TE) power factor (PF) of 46.5 \(\mu\text{W m}^{-1}\text{K}^{-2}\) is achieved for the doped selenophene polymer and signatures of a metal-insulator (M–I) transition are observed that are characteristics for heterogeneous conduction systems. The results show that single-atom selenium substitution is an effective molecular design approach for improving the charge transport and TE properties of conjugated polymers.
including neural electrodes\textsuperscript{[5]} and thermoelectric (TE) converters.\textsuperscript{[2,6]} Due to the electron-rich nature of their conjugated ring, polythiophene-based conjugated polymers usually have a small ionization potential (IP), which facilitates the oxidation of the polymer backbone and the creation of mobile hole polarons.\textsuperscript{[5]} Through rational molecular design and fine-tuning of doping, high electrical conductivities exceeding $10^3$ S cm$^{-1}$ have been achieved in a number of polythiophene systems, such as heavily doped poly(3,4-ethylenedioxythiophene) (PEDOT)\textsuperscript{[9]} and poly(2,5-bis(3-alkylthiophen-2-yl)thieno(3,2-b)thiophene) (PBTTT)\textsuperscript{[9,10]} with charge carrier densities approaching $10^{21}$ cm$^{-3}$. However, doping can introduce extra sources of structural and energetic disorder into the polymer hosts and can lead to trapping of charge carriers in the Coulombic wells created by the dopant counterions, which impairs the charge transport. Recent studies have shown that high carrier concentrations are achievable, for example, through ion exchange doping method,\textsuperscript{[11]} in which it is possible to enter a regime in which charge transport is not limited by ionic trapping, i.e., the potential seen by the mobile carriers is sufficiently smoothened compared with thermal energies.\textsuperscript{[12,13]} To achieve high conductivities in these systems, minimizing structural disorder is crucial.

Substitution of sulfur (S) by selenium (Se) is an established strategy to modify the properties of a semiconducting polymer, resulting in a chemically and structurally similar polymer. The introduction of selenium atoms into the polymer backbone causes a reduction in aromaticity, which leads to a slight increase in the highest occupied molecular orbital (HOMO) energy level and decrease in the lowest unoccupied molecular orbital (LUMO) energy level, thus giving a shrinkage in the optical bandgap.\textsuperscript{[14]} Due to the larger size of the Se atoms intermolecular interactions are increased and polymer aggregation and crystallization are facilitated, which also contributes to raising the HOMO energy level and potentially resulting in less torsional disorder.\textsuperscript{[15]} Theoretical calculations\textsuperscript{[16]} demonstrate that the halogen-induced intermolecular interaction enhances the wavefunction overlap and thus inter- or intrachain charge transfer, which can help to enhance the field-effect transistor (FET) mobility as experimentally reported in a broad range of polymers.\textsuperscript{[14,15,17]} In addition, selenium and tellurium substitution have also been shown to benefit the TE performance of doped polymers. It results in the reduction of the activation energies for electronic transport and thus a higher maximum power factor ($PF_{\text{max}}$) of above 10 $\mu$W m$^{-1}$ K$^{-2}$ compared with the thiophene counterpart poly(3-alkylthiophene) (P3RT).\textsuperscript{[18]} The PF is one of the key parameters for the evaluation of TE performance and defined as $S^2\sigma$, with $S$ and $\sigma$ representing the Seebeck coefficient and electrical conductivity, respectively. Selenium substitution in a high mobility sulfur-based DPP derivative (DPDPSe-12) doped with a strong oxidizing agent FeCl$_3$ exhibited a high $PF_{\text{max}}$ of 364 $\mu$W m$^{-1}$ K$^{-2}$ and a high figure of merit (ZT, delineated as $PF/\kappa$ with $\kappa$ representing the thermal conductivity) of 0.25 at 328 K.\textsuperscript{[19]} Through detailed microstructural and morphological characterization, the authors attributed the origin of the high TE performance of DPDPSe-12 to the strong intermolecular interaction caused by the Se–Se interaction, which enables the dopants to be incorporated into the polymer domains without disturbing the molecular packing, and thus keeps a high mobility of 2.3 cm$^2$ V$^{-1}$ s$^{-1}$ characterized by Hall effect measurements.

While the beneficial effects of Se substitution have been generally well established this strategy also implies significant synthetic challenges and difficulties in controlling solubility, in particular, for polythiophene co-polymers when attempting to replace all S atoms with Se. Here, we explore the effects of single-atom substitution of sulfur for selenium within the repeat unit of a polythiophene co-polymer and compare poly[2,5-bis(3-dodecyliothien-2-yl)thiophene] (C10-PTT) and poly[2,5-bis(3-dodecyliothien-2-yl)selenophene] (C10-PTTSe). We show that despite only every third S atom being substituted the selenium substitution leads to a significant increase in electrical conductivity by up to 100% at certain doping conditions accomplished by improved molecular ordering and crystallinity in C10-PTTSe. Interestingly, such a disorder-mitigating effect can be further amplified by the thermal treatment of the undoped polymer, which allows inducing a highly crystalline ribbon-phase in C10-PTTSe similar to that previously observed in PBTTT. We compare the temperature dependent charge transport properties of the two polymers for both molecular charge transfer doping as well as ion-exchange doping and demonstrate that it is possible to achieve high conductivities of $691 \text{ S cm}^{-1}$ and good PF of 46.5 $\pm$ 2.6 $\mu$W m$^{-1}$ K$^{-2}$ in C10-PTTSe, the latter being almost 50% higher than the $PF_{\text{max}}$ of 34.3 $\pm$ 4.3 $\mu$W m$^{-1}$ K$^{-2}$ obtained by us on ion exchange doped PBTTT prepared under the same conditions.\textsuperscript{[20]}
2. Results and Discussion

2.1. Effect of Single-Atom Chalcogen Substitution on Room Temperature Conductivity Achieved by Sequential Molecular Doping and Ion Exchange Doping

Sequential molecular doping is a technique that involves exposing a predeposited polymer film to a solution- or vacuum-deposited molecular dopant that then diffuses into the film without introducing large perturbations of the polymer morphology, thus benefitting the charge transport. This was applied to films of C10-PTTT and C10-PTTSe. The basic physical and electrochemical properties of the two polymers are summarized in Table S1 (Supporting Information). We first measured the room temperature (RT) conductivity of these two polymer films doped by the molecular doping method involving immersion of the films in solutions of four molecular dopants: 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinoxidimethane (F4-TCNQ, EA (electron affinity) = 5.25 eV),[9] 1,3,4,5,7,8-hexafluorotetrazyanophthaloquinodimethane (F6-TCNNQ, EA = 5.33 eV),[9] Molybdenum tris-[1-trifluoroethanol)-2-trifluoromethylethenyl-1,2-dithiolen] (Mo(tfd-COCF$_3$)$_3$, EA = 5.60 eV),[9] and hexacyano-trimethylene-cyclopropane (CN6-CP, EA = 5.87 eV).[9] The IP of C10-PTTT and C10-PTTSe are 5.09 and 5.13 eV, respectively (Table S1, Supporting Information). Both are lower than the EA of the selected molecular dopants, which should provide a sufficient driving force for doping. The influence of selenium substitution on the doped polymer conductivity was also evaluated at each doping level by the ion exchange doping method using FeCl$_3$ as the molecular dopant and BMP-TFSI as the electrolyte. Figure 1a shows the chemical structures of the two polymers and all the dopants involved in this work. This initial molecular doping study was performed on films that were annealed at 100 °C for 20 min after spin-coating and before the exposure to the doping solution to remove residual solvent from the film.

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Figure 1. a) Chemical structures of the polymers and dopants used in this work. b) Room temperature (RT) conductivities of PTTT and PTTSe doped with molecular dopants and their stability in a nitrogen atmosphere. The molecular doping was implemented by immersing the polymer films on glass substrates in dopant-containing acetonitrile solution overnight, in which case they were maximally doped as was found by optimization studies. Both neat polymer films were annealed at 100 °C for 20 min without any postannealing after doping. c) RT conductivities of PTTT and PTTSe doped by the ion exchange method with increasing doping level. The neat films for ion exchange doping were annealed with thermal treatment B in Section 2.2. Both the concentration of dopant solution and exposure time to the dopant solution are varied to obtain different doping levels. The doping conditions in detail are shown in Table S2 (Supporting Information). The ion exchange doping method was implemented by a two-step spin-coating process with the dopant solution containing the oxidizing agent FeCl$_3$, the ion exchange agent BMP-TFSI and acetonitrile as the solvent. Further details of our ion exchange doping method have been reported in an earlier work.[9] The conductivity was measured with Van der Pauw (VdP) devices in a nitrogen-containing glovebox.
As shown in Figure 1b each dopant can successfully dope both polymers. Among the molecular dopants, CN6-CP, the strongest dopant with the largest EA, gives the highest conductivity of 230 and 385 S cm\(^{-1}\) for PTTT and PTTSe, respectively. The Mo(tfid-COCF\(_3\))\(_3\) doped samples exhibit around half of the CN6-CP conductivity values, while F6-TCNNQ and F4-TCNQ only exhibit conductivities <100 S cm\(^{-1}\). The obtained conductivities of both doped polymers show a positive correlation with the energy difference between the polymer IPs and the dopant EAs (Section S3, Supporting Information). The relatively high conductivity of Mo(tfid-COCF\(_3\))\(_3\) could be also related to its bulky three-dimensional shape and large size, which may reduce the Coulombic binding between the generated charge and dopant counterion by enlarging the mean electron–hole distance.[22] Irrespective of the dopant type, the selenium-containing polymer PTTSe always exhibits higher as-doped conductivities.

The as-doped samples were then stored in nitrogen for 48 h to test the sample stability over time as displayed in Figure 1b. There is a clear difference between the organic small molecule and molybdenum thiene complex, with the latter dopant almost maintaining the initial conductivity. The conductivities of CN6-CP doped samples drop significantly, although they still remain the highest after 2 days in nitrogen. The F6-TCNNQ doped samples also reduce in conductivity while F4-TCNQ provides good stability.

In Figure 1c, we illustrate the other doping process that is relevant in this study, ion exchange doping using FeCl\(_3\) as molecular dopant, and BMP-TFSI as an electrolyte. We compared the conductivities of ion exchange doped PTTT and PTTSe at various doping levels. In the low doping region, PTTSe-TFSI\(^-\) and PTTT-TFSI\(^-\) show only subtle differences in the conductivities (see the first three data points in Figure 1c), although interestingly doped PTTT contains more charges at these low doping concentrations as is suggested by the stronger bleaching of the neutral \(\pi-\pi\) absorption around 600 nm peak in PTTT than in PTTSe (Figure S3, Supporting Information). This could be presumably explained by the more crystalline microstructure of PTTSe (Figure 2 and Figure 3f); more ordered/denser molecular packing in PTTSe makes it harder for counterions to become incorporated into the crystalline regions, especially in the light doping regime, as this requires an expansion of the lamellar lattice spacing. Considering that \(\sigma = n\epsilon\mu\) (\(n\) and \(\mu\) denote the charge concentration and carrier mobility, respectively; \(\epsilon\) is the elemental charge), we can deduce that PTTSe-TFSI\(^-\) must possess a higher average \(\mu\) than PTTT-TFSI\(^-\) in the low doping regime as both polymers have similar conductivities in this low-doping regime. At higher doping concentrations, once this possible structural phase transition has occurred, this difference in doping concentrations is no longer present and in both polymers the neutral \(\pi-\pi\) absorption is completely bleached (Figure S3, Supporting Information). In this regime PTTSe-TFSI\(^-\) consistently exhibits higher conductivity values than PTTT-TFSI\(^-\) reflecting higher mobility values. We reach a maximum conductivity of 759 S cm\(^{-1}\) for PTTSe-TFSI\(^-\) at intermediate doping levels. At higher doping levels we observe a plateau in conductivity for PTTSe-TFSI\(^-\), possibly due to the electrochemical degradation of the polymer under strongly oxidizing potentials or the lower maximum doping level PTTSe can achieve, while for PTTT-TFSI\(^-\), the conductivity keeps increasing with the maximum value of 514 S cm\(^{-1}\). We also performed X-ray photoemission spectroscopy (XPS) measurements to determine the carrier density at the saturated doping level for each polymer system doped by the ion exchange method (Section S7, Supporting Information). We observe a slightly higher maximum doping level in doped PTTT (1.00 ± 0.05 ion per monomer) versus PTTSe (0.84 ± 0.07 ions per monomer); these values match the doping level achieved in PBTTT under the same doping conditions.[23] The lower doping level and higher conductivity observed in doped PTTSe indicates that the carrier mobility in this material must be significantly higher than PTTT in the heavy doping regime.

The results reported in this section on molecular doping as well as ion exchange doping show clearly that the selenium single-atom substitution is beneficial in improving the doped polymer conductivity of the studied polythiophene system for both molecularly and ion exchange doped films.

For the ion exchange doping experiments in Figure 1c we used higher temperature annealing conditions for the as-deposited films prior to doping (180 °C and 210 °C annealing for 20 min for PTTT and PTTSe, respectively) as we had found that higher temperature annealing resulted in higher conductivities. The dependence on annealing temperature is discussed in detail in the next section.

2.2. Influence of Thermal Annealing on Thin Film Microstructure and Electrical Properties in Films Doped by Sequential Molecular Doping

Thermal annealing of the as-deposited films is an important way to tune the microstructure and morphology of semicrystalline polymers, thereby reducing the intrinsic disorder and improving the electronic properties.[13,24] Besides, thermal annealing of the films after doping can further improve the conductivity of some molecularly doped semicrystalline polymer systems, such as PBTTT/F4-TCNQ, which could be possibly explained by better structural arrangement induced by thermal annealing that reduces traps created by the dopant and slightly promotes doping efficiency.[13,25] To investigate the effect of postdeposition as well as postdoping thermal annealing on the microstructure and conductivities of PTTT and PTTSe we used molecular doping with F4TCNQ. Despite not yielding the highest conductivities (Figure 1b) doping with F4TCNQ is a well-controlled doping process that results in stable conductivities. We used grazing incidence wide-angle X-ray scattering (GIWAXS) and atomic force microscopy (AFM) to characterize both polymer systems before and after doping.

For the undoped polymers, we varied the annealing temperatures from 100 °C to 300 °C to optimize the conductivities. Two representative annealing temperatures for each polymer were selected here to illustrate the effect of thermal annealing. 100 °C postdeposition annealing was used as a reference condition at which the residual solvent within the film is largely removed. Postdeposition annealing temperatures of 180 °C and 210 °C for PTTT and PTTSe, respectively, were selected based on the conditions that give the highest conductivities for PTTT/F4-TCNQ and PTTSe/F4-TCNQ. After doping, the postannealing condition was fixed as 80 °C, which is similar to that for PBTTT.[13]
Figure 2a shows the measured electrical conductivities of PTTT/F4-TCNQ and PTTSe/F4-TCNQ films prepared with different annealing treatments. The annealing of neat PTTT and PTTSe at 180 °C and 210 °C, respectively, before doping (treatment B in Figure 2a), increases $\sigma$ by nearly 100% compared to treatment A (100 °C postdeposition annealing to remove the solvent). Note that the annealing temperatures that produce the optimum conductivity values are different for the two polymers. For PTTT, postannealing at 80 °C after doping causes $\sigma$ to drop almost back to the conductivity value for treatment A whereas the conductivity of doped PTTSe after postdoping annealing (treatment C) doubles with respect to films without postdoping annealing (treatment B).

The high-temperature annealing of neat PTTT and PTTSe significantly enhances the electrical performance of both doped films, which could be explained by better crystallinity as observed by UV–Vis (Figure 2b–e), AFM (Figure 3a–d) as well as GIWAXS characterization (Figure 3e–h). In general, PTTSe shows more ordered molecular packing than PTTT, as evidenced by the change of the ratio of two neutral absorption peaks ($I_B/I_A$) in the undoped films. Spano et al. suggested such a ratio for a conjugated polymer represents the strength of the intermolecular coupling and increases with decreasing disorder in the system, reflecting improved charge delocalization and higher charge mobility. The spin-coated PTTSe film baked at 100 °C has a slightly higher $I_B/I_A$ ratio than PTTT (Figure 2b–e). The high T annealing raises the $I_B/I_A$ ratios of both PTTT and PTTSe, which indicates more ordered structures forming in both systems (Figure 2d,e). Notably, the effect of thermal annealing on the $I_B/I_A$ ratio is intensified in PTTSe,
Figure 3. a–d) Atomic force microscopy (AFM) images and e–h) 2D Grazing incidence wide-angle X-ray scattering (GIWAXS) images for neat PTTT and PTTSe with treatment A and B (see Figure 2 for the details of process conditions). The films were prepared on glass substrates for AFM characterization and on bare silicon substrates to reduce the background signal for GIWAXS characterization.
which possibly rationalizes the large improvement in conductivity with high T annealing. The high T thermal annealing also leads to a distinct redshift of the $\pi$-$\pi^*$ absorption peak by $\approx 5$ nm for PTTSe (Figure 2d,e). Such a redshift manifests the bandgap reduction (Table S1, Supporting Information) induced by selenium substitution, which is further reduced by the high T thermal annealing. This suggests an even lower IP of the high-T annealed PTTSe film, as previously reported in a few other studies on the chalcogen-substituted polythiophenes.[27] The even lower IP of PTTSe after the high T annealing could also contribute to a more significant difference in the electrical conductivity of doped PTTT and PTTSe obtained under treatment B (Figure 2a).

The more ordered molecular packing in PTTSe is further verified by the morphology characterization by AFM. The 100 °C annealed PTTT and PTTSe films showed disorder surface morphologies (Figure 3a,c), while both high-T annealed polymer films exhibited ordered surface morphologies (Figure 3b,d), which do not change much after doping and postdoping annealing (Figure S4d,h, Supporting Information). Intriguingly, PTTSe annealed at 210 °C exhibits a ribbon-like structure with a ribbon width of $\approx 80$ nm (Figure 3d), which is similar to the crystalline, ribbon phase observed in PBT TT films annealed at 250 °C.[24] In PTTT films annealed at 180 °C there is also an indication of ribbon-like features in the surface topography, but the phase is less well formed than in PTTSe (Figure 3b).

The better crystallinity induced by the thermal annealing, especially for PTTSe, is also testified by the microstructural evolution of both systems characterized by GIWAXS measurements (Figures 3e–h). We focus here on the neat films, but corresponding GIWAXS data for the doped samples is provided in Section S6 (Supporting Information). All the samples exhibit edge-on orientation with respect to the substrate, as evidenced by the lamellar diffraction along the out-of-plane direction. From the comparison of Figure 3e vs. 3f and Figure 3g,h, we observe the reduced polar angle spread for the high-T annealed PTTT and PTTSe samples, which indicate that the thermal annealing can effectively promote edge-on packing orientation. Even without thermal annealing at high T, the polar angle spread of the lamellar diffractions of the as-coated PTTSe film is narrower than PTTT (Figure 3e vs. Figure 3g), suggesting that the PTTSe film is intrinsically more edge-on. After the high-T annealing, the dominant lamellar stacking peaks for both polymer films become slightly stronger and shift to lower q values (Figure 3f,h; Figure S7a,c, Supporting Information), indicating a larger (100) spacing compared to the as-coated films. As with the trend of lamellar diffraction, the high-T thermal annealing treatment leads to narrower $\pi$-$\pi^*$ diffraction peaks for both PTTT and PTTSe films (Figure S7b,d, Supporting Information), which signifies improved molecular packing along the $\pi$-$\pi$ direction. Such an improvement in the $\pi$-$\pi$ packing is more significantly maintained in the ion exchange doped PTTSe than ion exchange doped PTTT (Figures S6 and S7, Supporting Information), consistent with the observed higher electrical conductivity of doped PTTSe shown in Figure 1c. In addition, the high-T thermal annealing also introduces well-defined mixed-index diffractions in the 2D GIWAXS images (Figure 3f,h), which suggests an emergence of long-range molecular order along the three principal crystallographic axes.[28] Such mixed index diffractions are again more distinct in high-T annealed PTTSe.

Together, these results from AFM, UV–Vis, and GIWAXS characterization provide solid evidence for a more ordered morphology and molecular packing resulting from the thermal annealing and the selenium substitution, which rationalizes the observed variation in the electrical conductivity of PTTT/F4-TCNQ and PTTSe/F4-TCNQ obtained under treatment A and treatment B shown in Figure 2a.

For treatment C in Figure 2a, the postannealing after 80 °C causes a decrease in $\sigma$ and possibly a de-doping of PTTT/F4-TCNQ with the dopant diffusing out, as previously reported in the de-doping study of F4-TCNQ doped PBTTT.[13] By contrast, PTTSe/F4-TCNQ prepared under the same condition shows an improved conductivity up to 123 S cm$^{-1}$, which potentially results from a stronger charge transfer interaction between the polymer and F4-TCNQ as suggested by the enhanced bleaching of neutral peak and the stronger polaron-induced absorption peaks above 700 nm. We also tried lower annealing temperatures for PTTT but did not find any temperatures that could give rise to the postdoping annealing induced enhancement in $\sigma$ observed for doped PTTSe in the current work and doped PBTTT in previous work.[13,25] This suggests a higher thermal stability of the molecular dopant in PTTSe than in PTTT.

### 2.3. Comparison of the Temperature Dependence of the Conductivity in F4-TCNQ Doped PTTT and PTTSe

To better understand the effect of single-atom selenium substitution on the charge transport physics of films subjected to sequential molecular doping, we measured the temperature dependence of conductivity for F4-TCNQ doped PTTT and PTTSe using one of the most widely studied-doping methods: Sequential doping with F4-TCNQ does not produce the highest conductivities (see Section 2.1), but it has been widely studied for other thiophene polymers, such as PBTTT and P3HT, and allows therefore useful comparisons. The measured conductivities of both F4-TCNQ doped PTTT and PTTSe show a thermally activated behavior with temperature coefficients of conductivity being positive (Figure 4a). The ratio of the conductivity at the highest measured temperature of 270 K to that at the lowest measured temperature of 20 K, $\sigma$ (270 K)/$\sigma$ (20 K) for PTTSe/F4-TCNQ of 91 is much smaller than the value of 369 for PTTT/F4-TCNQ. Such weaker temperature dependence for PTTSe/F4-TCNQ suggests a lower degree of energetic disorder encountered by charge carriers and is consistent with the more ordered microstructure of PTTSe compared to PTTT discussed above.

For an in-depth analysis of $\sigma(T)$, we applied the Zabrodskii plot analysis, where the logarithmic derivative of $\sigma(T)$, $W = \ln(\sigma)/\ln(T)$, versus $T$ is plotted on a log-log scale, and the slope $k$ of such a plot represents the transport regime: $k < 0$, insulating regime; $k = 0$, critical regime of Metal–Insulator (M–I) transition; $k > 0$, metallic regime.[29] The two doped systems show a distinct difference in the Zabrodskii plot: PTTT/F4-TCNQ has a negative slope of $-0.35$ for the whole measured temperature range (Figure 4b) while PTTSe/F4-TCNQ exhibits a change of the slope value from $-0.45$ to $-0.32$ around 55–65 K (Figure 4c). $\sigma(T)$ is further analyzed by the Mott variable-range...
hopping (Mott–VRH) model,[30–32] in which \( \sigma(T) \) takes the form \( \sigma_0 \exp\left[-\left(\frac{T_0}{T}\right)^{1/\gamma}\right] \), where \( \sigma_0 \) is the characteristic conductivity; \( T_0 \) is the characteristic temperature that is related to the activation energy \( E_0 = k_B T_0 \) with \( k_B \) denoting the Boltzmann constant; \( \gamma = 1/(d + 1) \) is determined by the dimensionality \( d \) of charge transport in the Mott–VRH regime with \( \gamma = 1 \) representing nearest-neighbor hopping.[30] The \( \gamma \) value equals the slope \( k \) in the Zabrodskii plot. The \( \gamma \) values around 1/3 for both systems indicate a two-dimensional (2D) VRH charge transport mechanism for PTTT/F4-TCNQ across the whole temperature range and for PTTSe/F4-TCNQ in the high T region, which may be consistent with the 2D, edge-on lamellar microstructure of both polymers. The slightly smaller \( \gamma \) for PTTSe/F4-TCNQ probably implies that the doped selenium-substituted system is a bit closer to the critical regime of the M–I transition,[31,33] potentially reflecting stronger interchain interactions that largely determines the charge transport in organic polymer systems.[34] Moreover, PTTSe/F4-TCNQ shows a crossover from 2D VRH (\( \gamma = 1/3 \)) to Efros–Shklovskii variable-range-hopping (ES-VRH) (\( \gamma = 1/2 \)) behavior around 55–65 K. The ES-VRH mechanism describes the electrical conduction of localized charges in disordered conductors at a low temperature with a Coulomb gap at the Fermi level due to the strong Coulomb interaction between the charge carriers.[35] It is noteworthy that a few other models with different physical origins, such as intercluster hopping between metallic clusters[36] or tunneling

Figure 4. Temperature dependence of conductivity for maximally doped PTTT and PTTSe with F4-TCNQ. a) The electrical conductivity versus \( T \). b,c) The Zabrodskii plots for PTTT/F4-TCNQ and PTTSe/F4-TCNQ, respectively. d–f) The variable-range hopping (VRH) hopping analyses for PTTT/F4-TCNQ and PTTSe/F4-TCNQ. The temperature range for the measurement is from 20 to 270 K, which is determined by the temperature limit of the cryostat we used for this experiment.
induced by temperature-dependent voltage fluctuation-noise,[37] can also lead to such a temperature dependence with $\gamma = 1/2$. However, the observed crossover temperature shows a good agreement with the calculated theoretical crossover temperature ($T_{\text{cross}}$) of 55 K by assuming the crossover from ES-VRH to 2D VRH with the equation $T_{\text{cross}} = 11.4T_{\text{ES}}^{3/2}/T_{\text{2D}}^{1}(38)$ (see Figure 4e,f for the characteristic temperature values for $T_{\text{ES}}$ and $T_{\text{2D}}$). Thus, we attribute the $\sigma(T)$ behavior of PTTSe/F4-TCNQ with $\gamma = 0.45$ at low temperatures to the ES-VRH mechanism. Similar cross-over phenomena has also been observed in F4-TCNQ doped PBT TT and electrochemically doped PBT TT as well as P3HT.[25,31,33,39] Such a similar common temperature dependence in those highly doped polythiophene polymers suggest that also in PTTSe/F4-TCNQ it may be possible to realize 2D coherent charge transport, which has been reported in PBT TT/ F4-TCNQ doped via the sequential doping method.[25]

2.4. Investigation of the Temperature-Dependence of Conductivity and Seebeck Coefficient in Optimally Ion Exchange Doped PTTSe

Finally, we discuss the charge transport physics of PTTSe under optimal processing and doping conditions. For this we combined optimum annealing conditions and microstructure (treatment B in Section 2.2) with the ion exchange doping method that produced the highest conductivity at RT. In these films the PTTSe is present in its ribbon phase. For the ion exchange doping[9] we compared iron chloride (FeCl$_3$, $E_A = -5.89$ eV) and phosphomolybdic acid (PMA, $E_A = -5.42$ eV) as the oxidizing agents to provide a strong driving force for doping. The temperature-dependent electrical conductivities and Seebeck coefficients were measured and analyzed to elucidate the charge transport mechanism.

Figure 5a shows the $T$ dependence of the electrical conductivity for four samples with different dopant times and oxidants. The RT conductivity ($\sigma_{RT}$) values are indicated in the legend of the plot. For all samples the conductivity was found to decrease monotonically with decreasing temperature, but the temperature dependence is significantly weaker than for the samples doped by F4TCNQ molecular doping in Section 2.3. At 25 K, the films retained about 35–45% of their RT conductivity values. More in-depth insight into the temperature dependence is again obtained from a Zabrodskii plot analysis (Figure 5b). Overall, the PTTSe-FeCl$_3$-TFSI$^-$ samples exhibit a weaker temperature dependence of $\sigma$ than the PTTSe-PMA-TFSI$^-$ system. The latter exhibits the largest negative slope $k$ value of $-0.37$ at low $T < 200$ K (Figure 5b), indicating the most strongly insulating VRH behavior.[32] This is surprising as this PTTSe-PMA-TFSI$^-$ sample (Sample D) has the second highest $\sigma_{RT}$ of 614 S cm$^{-1}$ comparable to that of the most conductive

![Figure 5. a) Temperature dependence of conductivity, b) the corresponding Zabrodskii plot analysis, and c) temperature dependence of thermopower for heavily doped PTTSe via the ion exchange method. We doped our samples with two oxidizing agents (PMA and FeCl$_3$), and the exchange agent is BMP-TFSI (See Figure 1a for the chemical structures). The measurement for the Seebeck coefficient is valid only above 100 K due to the limit of the setup. The detailed description for each sample is shown as below. Sample A: PTTSe-FeCl$_3$-TFSI$^-$-6s with $\sigma(300 \text{ K}) = 132$ S cm$^{-1}$; Sample B: PTTSe-FeCl$_3$-TFSI$^-$-60s with $\sigma(300 \text{ K}) = 692$ S cm$^{-1}$; Sample C: PTTSe-FeCl$_3$-TFSI$^-$-300s with $\sigma(300 \text{ K}) = 240$ S cm$^{-1}$; Sample D: PTTSe-PMA-TFSI$^-$-60s with $\sigma(300 \text{ K}) = 614$ S cm$^{-1}$.

Adv. Electron. Mater. 2022, 2200053
PTTSe-FeCl₃-TFSI⁻ sample (Sample A) with a $\sigma_{RT}$ of 692 S cm⁻¹. For PTTSe-FeCl₃-TFSI⁻ samples, the values of the slope $k$ change from negative to positive at low $T$ with increasing exposure time/doping levels, suggesting the emergence of a $M\to I$ transition.[40] Surprisingly again, it is not the highest conductivity (PTTSe-FeCl₃-TFSI⁻-60s) sample that exhibits the most metallic behavior, but the PTTSe-FeCl₃-TFSI⁻-300s sample (Sample C), which only exhibits a $\sigma_{RT}$ of 240 S cm⁻¹.

Such a nonmonotonic dependence of the temperature dependence revealed by the Zabrodskii analysis on $\sigma_{RT}$ has previously been observed in other conducting polymers such as camphor sulfonic acid doped polyaniline.[41] It has been interpreted as a signature of heterogeneous metallic conductors in which anisotropic metallic grains are separated by disordered grain boundaries. In these the conductivity reflects not just the charge transport in the metallic grains, but can also become limited by transport through the grain boundaries. Such a nonmonotonic behavior is not expected for a homogeneous, disordered system, that undergoes an Anderson-type $M\to I$ transition. It is interesting to note that we did not observe such nonmonotonic behavior in our transport studies on PBTTT-FeCl₃-TFSI⁻ doped via the same method.[41,42] It is not clear at present whether this is a coincidence due to the limited number of samples measured or to differences in microstructure between the two polymers. However, it is also possible that in the case of PTTSe-FeCl₃-TFSI⁻ we obtained a polymer system where the localization length ($L_{loc}$) in the disorder region is comparable with or smaller than the crystalline coherence length; and such a polymer system can be better described with a random network model proposed by Prigodin and Efetov,[43] which portrays a physical network of crystalline regions with metallic chain bundles weakly connected by “spaghetti-like” disordered chains. In this heterogeneous model, most of the conducting charge carriers in the isolated ordered crystalline region are three-dimensional (3D) delocalized while the disordered regions determine the energy barriers that charge carriers need to overcome to allow conduction between ordered regions via hopping or phonon-assisted delocalization,[41,42] or even tunneling.[44] As the coupling between the ordered regions strengthens via increasing the polaron delocalization in crystalline regions or the density or strength of interconnections/disorders regions, the in-chain $L_{loc}$ becomes larger than the average distance between the ordered domains and the charge carriers can diffuse macroscopically, forming the percolation paths through the disordered regions. In this case, the $M\to I$ transition occurs with the logarithmic derivative of the conductivity showing a positive temperature coefficient at low $T$. If the film morphology facilitates the phonon-assisted delocalization, it is possible for the charge carriers in an intrinsically insulating sample with a negative $k$ value at low $T$ to percolate at RT (Figure 5d), making the $M\to I$ transition no longer monotonically $\sigma_{RT}$/doping level-dependent. Such a phonon-assisted percolation theory can rationally explain the obtained nonmonotonic evolution of $\sigma(T)$ versus $\sigma_{RT}$. As for different charge transport properties between PTTSe-FeCl₃-TFSI⁻-60s sample and PTTSe-PMA-TFSI⁻-60s sample with similarly high conductivities around 600–700 S cm⁻¹ (Figure 5a,b), we speculate the intrinsic insulating behavior for the PTTSe-PMA-TFSI⁻ could originate from a perturbation of the crystalline structure and the associated impairment of the charge delocalization, which could be possibly caused by the different ion exchange doping mechanisms caused by different oxidizing agents.

The heterogeneous nature of transport is also evident in the temperature dependence of the Seebeck coefficient. Despite the nonmetallic temperature dependence of the conductivity of all but one of the samples we measured a nearly linear temperature dependence of the Seebeck coefficient for all the investigated samples except the PTTSe-FeCl₃-TFSI⁻-6s sample with the lowest conductivity/doping level. The Seebeck coefficient of the PTTSe-FeCl₃-TFSI⁻-6s sample exhibits an approximate $T^{1/2}$ dependence (Figure 5d). The $T^{1/2}$ dependence of $S(T)$ and the negative slope of Zabrodskii plot at low $T$ for the PTTSe-PMA-TFSI⁻-6s sample are concordant with the description of a TE behavior from the VRH hopping theory.[32] The linear dependence of $S(T)$ and the positive slope of Zabrodskii plot at low $T$ for the PTTSe-PMA-TFSI⁻-300s sample consistently support its intrinsic metallicity. By contrast, the “metallic” nature for the PTTSe-FeCl₃-TFSI⁻-60s sample and PTTSe-PMA-TFSI⁻-60s sample deduced from their linear $S(T)$ contrasts with the intrinsic insulating behavior deduced from their temperature dependences of $\sigma$. This “decoupling” of $S$ and $\sigma$ has been commonly observed in conducting polymers and has been also interpreted as a signature of heterogeneous transport: In a heterogeneous system the Seebeck coefficient can be described by a simplified equation, $S_{total} = f_c S_c + f_{nonc} S_{nonc}$, where $S_c$ and $S_{nonc}$ represent the Seebeck coefficients for the crystalline region and the disordered region, respectively; $f_c$ and $f_{nonc}$ are characteristic factors to evaluate the contribution from each region, which depends on the geometries of heat and electrical conduction paths.[45] Likewise, the overall conductivity can be determined by a formula, $\sigma_{total} = f_c \sigma_c + f_{nonc} \sigma_{nonc}$, with $f_c$ and $f_{nonc}$ representing temperature-independent geometrical weighting factors. In our PTTSe system, we are in a regime in which $S$ is dominated by the crystalline regions, i.e., the narrow grain boundaries do not contribute measurably to the TE voltage, while large grain boundary resistances limits $\sigma_{total}$.

We obtained a respectable TE PF of 46.5 $\mu$W m⁻¹ K⁻² for the PTTSe-FeCl₃-TFSI⁻-60s sample. To provide a reference we compare this value to our previous experiments on PBTTT-FeCl₃-TFSI⁻ processed and doped under very similar conditions. In PBTTT, we obtained only a PF of 20.7 $\mu$W m⁻¹ K⁻² for similar conductivity values of 600–700 S cm⁻¹. Even under optimum conditions that maximized the PF (for conductivities around 200 S cm⁻¹) the PF of PBTTT-FeCl₃-TFSI⁻ was only 34.3 $\mu$W m⁻¹ K⁻².[20] For a given conductivity value PTTSe exhibits a somewhat higher Seebeck coefficient than PBTTT. This makes PTTSe a promising polymer for TE studies. We tentatively attribute its comparatively good performance to the high degree of 3D structural order that is present in the ribbon-phase of PTTSe and is evident from the pronounced indexed diffractions observed in the GIWAXS (Figure 3h). This is likely to facilitate a high charge carrier mobility that would mean that to reach a given conductivity lower doping levels are needed resulting in a comparatively higher Seebeck coefficient. A more in-depth study of the charge transport physics of PTTSe including of the detailed mechanism that leads to the apparent decoupling between $S$ and $\sigma$ is currently underway.
3. Conclusion

This work addresses the effect of backbone modification with single selenium substitution on polymer doping and electrical as well as TE properties. The majority of the literature describes replacing all of the chalcogen atoms for a polymer repeat unit, which brings both advantages and disadvantages with respect to charge transport, processability, and synthetic utility. We show that the advantages of chalcogen substitution for doping and TE applications can be achieved already without replacing all of the sulfur atoms, which allows tuning solubility and helps avoiding toxic, unreliable chemistry. In PTTSe, we have discovered the existence of a highly ordered, chain-extended ribbon-phase similar to that observed previously in PBTTT. In this ribbon phase, we have observed superior electrical conductivities and charge transport properties. Heavily doped PTTSe samples doped by the ion exchange method display signatures of a M–I transition in a heterogeneous conduction system and exhibit respectable TE PFs of 46.5 μW m⁻¹ K⁻² that are somewhat higher than those found in our previous experiments on PBTTT processed and doped under comparable conditions.

4. Experimental Section

Polymer Synthesis: C10-PTT and C10-PTTSe were prepared by Stille polycondensation as described in Section S1 (Supporting Information).

Sample Preparation: The C10-PTT and C10-PTTSe films were spin-coated from 10 mg mL⁻¹ chloroform solution at 1500 rpm for 120 s in a nitrogen glovebox to form 50 and 60 nm films, respectively. Both films were annealed at the desired temperatures and then slowly cooled down to RT. For the sequential doping with the molecular dopants, the substrates were immersed in dopant-dispersed acetonitrile, which is well-known to be orthogonal to thiophene polymers, for over 2 h to ensure full penetration of dopants into the polymer film. For the ion exchange doping, a drop of electrolyte:dopant solution (~150 μL doping solution per cm² substrate area) at a fixed molar ratio of 1:100 was left on top of the precoated polymer films for a varied exposure period, and then spun off the excess solution at a high speed of 8000 rpm. Meanwhile, the samples were rinsed with 1 mL acetonitrile to remove the extra electrolyte and dopant from the surface. The samples used for UV–Vis, GIWAXS, and conductivity measurements were prepared on spectroscopic glass substrates. The substrates were cleaned by sonication in deionized water, acetone, and 2-propanol with an oxygen atmosphere. The temperature-dependent conductivity and thermopower measurements were performed with a multifunctional device designed in a Cryogen Free Measurement System (CFMS) 9T from Cryogenic Ltd (UK) or a closed-loop LakeShore Cryotronics CRX-4K Helium system equipped with source-meter units Keithley 2612B and Keithley 6430.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

Financial support from the European Research Council for a Synergy grant SC2 (no. 610115) and from the Engineering and Physical Sciences Research Council (EP/R031894/1) is gratefully acknowledged. C.C. thanks the China Scholarship Council for financial support. H.S. acknowledges support from a Royal Society Research Professorship (RP/R1/201082). I.E.J. acknowledges funding through a Royal Society Newton International Fellowship. Y.L. acknowledges funding through a European Commission for a Marie-Sklodowska-Curie fellowship. M.S. thanks the EPSRC for studentship. The authors acknowledge use of the Cambridge XPS System, part of Sir Henry Royce Institute – Cambridge Equipment, EPSRC grant EP/P024947/1.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

chalcogen substitution, doping, organic electronics, polythiophene, thermoelectrics

received: January 13, 2022
revised: March 8, 2022
published online:

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