Tuning charge transport dynamics via clustering of doping in organic semiconductor thin films

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A significant challenge in the rational design of organic thermoelectric materials is to realize simultaneously high electrical conductivity and high induced-voltage in response to a thermal gradient, which is represented by the Seebeck coefficient. Conventional wisdom posits that the polymer alone dictates thermoelectric efficiency. Herein, we show that doping — in particular, clustering of dopants within conjugated polymer films — has a profound and predictable influence on their thermoelectric properties. We correlate Seebeck coefficient and electrical conductivity of iodine-doped poly(3-hexylthiophene) and poly[2,5-bis(2-octyldodecyl)pyrrole-1,4(2H,5H)-dione-3,6-diyl)-alt-(2,2′;5′,2′′;5′′,2′′′-quaterthiophen-5,5′′′-diyl)] films with Kelvin probe force microscopy to highlight the role of the spatial distribution of dopants in determining overall charge transport. We fit the experimental data to a phonon-assisted hopping model and found that the distribution of dopants alters the distribution of the density of states and the Kang-Snyder transport parameter. These results highlight the importance of controlling dopant distribution within conjugated polymer films for thermoelectric and other electronic applications.
Heat dissipation is ubiquitous—most of the energy we use begins and ends as heat, with more than 60 quads being lost to the environment annually in the US alone.1 Thermoelectrics (TEs) are solid-state devices that offer reliable and environmentally friendly scavenging of waste heat into electricity. However, their modest efficiency and relatively high cost have hampered their widespread adoption. The conversion efficiencies of inorganic TEs based on crystalline semiconductors have been steadily improving thanks to our growing knowledge of material selection and nanostructuring, aided by first-principles numerical modeling. Organic thermoelectrics (OTEs), on the other hand, are lightweight, flexible, low-cost, and solution-processable, but progress in raising their conversion efficiency has been sporadic and severely hampered by the complexity of their thin film structure and a lack of systematic guidelines for materials discovery and improvement.

TE devices consist of two types of conducting materials, one with holes, which are positive charge carriers, and the other with electrons, which are negative carriers. When one end of a TE is heated, the charge carriers transport heat away from the hot end and move away from the cold end creating a voltage difference. In reverse, when a voltage is applied, the charge carriers transport heat from the cold end to the hot end. Thus, the transport of charge carriers is central to the function of thermoelectric devices.

TE energy conversion efficiency is closely related to its dimensionless figure-of-merit, $ZT = a^2σ/k$. Much of the improvement in $ZT$ of inorganic TEs has come from reducing their thermal conductivity, $k$, by alloying and nanostructuring. In OTEs, $k$ is inherently low due to lack of long-range periodicity in structure. Therefore further improvements in OTEs must come from the simultaneous increase of the Seebeck coefficient, $α$, which captures the voltage produced per Kelvin of temperature gradient, and electrical conductivity, $σ$. A straightforward method to increase electrical conductivities in these materials is to increase the number of charge carriers via chemical doping through oxidation or reduction. Unfortunately, $α$ and $σ$ are strongly interdependent. Doping can negatively impact the Seebeck coefficient, generally resulting in a tradeoff between $α$ and $σ$. This implies that precise control of the amount of doping is critical for obtaining the maximum power factor, $α^2σ$, and further progress will rely on altering the shape of the $α$ vs. $σ$ curve.

Studies have developed empirical relationships between $α$ and $σ$ that scale as $α ∝ σ$ and $α ∝ σ^α$, but their physical significance and origin are unclear and thus limiting their utility in the design of OTEs. Recently, Kang and Snyder proposed a generalized two-parameter charge transport model for conducting polymers. They fit the variation in Seebeck coefficient as a function of electrical conductivity to their model to obtain a value for a transport parameter, $s$, and found most polymers to follow a shallow $α$ vs. $σ$ trend. The exception was PEDOT:Tsos, which exhibited a sharper curvature, leading Kang and Snyder to conclude that the shape of the $α$ vs. $σ$ curve is unique to the polymer.

In charge transport, conductivity, $σ$, is dictated by the expression: $σ = nμq$, where $n$ is concentration of charge carriers, $q$ is the carrier charge, and $μ$ is the charge carrier mobility. Determining the charge carrier mobility and its dependence on temperature, field, or carrier concentration in conjugated polymers has led to considerable progress in understanding their charge transport. However, this methodology becomes complicated by the difficulty in determining the carrier concentration with certainty and discrepancies in the reported mobilities for a given material. The discrepancies in the reported mobilities arise from differences in device architecture and the measurement technique. Furthermore, measured mobilities are the direct result of a carriers’ drift velocity, $v_d$, at an applied field, $F$, given by the realtion: $v_d = μF$. Thus, mobility measurements cannot be used to determine the energy carried per unit carrier or information about the density of states (DOS) that are model and calculation independent.

An effective method to overcome these challenges is to measure both the conductivity and the Seebeck coefficient across a broad range of carrier concentrations. The Seebeck coefficient is the voltage response to an applied temperature gradient, given by the equation: $α = \frac{E}{F}$. This methodology takes advantage of the fact that $α$ can be expressed, according to Fritzsche’s general equation, as $α = \left(\frac{F}{F_0}\right)^n \frac{E}{F}$, where $E$ and $α$ as $α = f(E)dE = q(\frac{g(E)}{\mu(E)}f(E)|1 - f(E)|)dE$. In these equations, $E_0$ is the Fermi level and a relative indicator of the level of doping, $g(E)$ is the DOS, and $f(E)$ is the Fermi distribution. This approach is more widely applicable than the simpler Mott formula, $α = -(\frac{E}{T})^2 \frac{\partial}{\partial E} \ln(\sigma(E)|E=E_F)$ and has the advantage of connecting $α$ to the average entropy per carrier. Since these expressions are valid (neglecting correlation effects) across all doping levels regardless of the conduction mechanism or the semiconductor’s crystalline, semi-crystalline, or amorphous nature, they support numerous mechanisms of conduction in disordered semiconductors, including hopping models based on the Miller-Abrahams and Marcus jump rates, that add to our physical explanation of charge transport in conjugated polymers and provide structural design criteria for improving their performance.

Generally, both $α$ and $σ$ depend on the carrier concentration $n = \frac{g(E)f(E)dE}{E_0}$ via the Fermi level but they have opposite trends—increasing $n$ fills more states and boosts $σ$ but also brings the Fermi level closer to them, decreasing $α$. Thus, there is a narrow range of doping that optimizes the thermoelectric power factor, $α^2σ$, which typically occurs when 10–20% of the states are occupied by a charge carrier. The DOS affects the trade-off between $n$, $σ$, and $α$—a sharp DOS separates the $E_F$ from the densely-spaced states, increasing the average energy per carrier ($E − E_F$) and with it $α$, while a broad DOS implies that the Fermi level moves further to fill the scattered states, flattening the $α$ vs. $σ$ curve. Thus, the shape of the DOS has an enormous impact on the scale and the trend of $α$, which is not yet fully understood.

Snyder and Kang’s recent charge transport model also employs these expressions, substituting for the term $g(E)μ(E)$ the empirical fitting transport function $σ_E(E, T) = σ_{E_0}(T) \left(\frac{E-E_F}{E_T}\right)^s$ which successfully fits a diverse array of conjugated polymers and small molecules using a transport coefficient $σ_{E_0}$, comparable to the mobility of the semiconductor, and the transport parameter $s$. Snyder and Kang state that the differences in the $s$ parameter “could be understood as a different ‘type’ of charge transport” and “may result from the percolation of charge carriers from conducting ordered regions through poorly ordered regions”. They speculated that a “search for cases with $s = 1$ could lead to discovery of high-$σ_{E_0}$ polymers”. Characterizing both $α$ and $σ$ across a broad range of doping levels enables a more complete explanation of charge transport that is not possible from measurements of $σ$ or mobility alone. Thus far, however, the factors that determine the transport parameter, $s$, in the Snyder-Kang model are unclear.

Here, we show that the value of the transport parameter is neither unique to a polymer nor is it confined to specific values; it can be tuned by altering the distribution of the dopants. We show that the way the semiconductor has been doped is fundamentally important to its thermoelectric performance across all carrier concentrations. We also show that the spatial distribution of dopants in the conjugated polymer has a profound impact on the shape of the $α$ vs. $σ$ curve and that clustering of dopants in the polymer modifies the shape of the DOS and alters the trend of $α$. 


vs. $\sigma$ curve. We conclude that the heavy-tailed DOS results in a qualitative change of the $\alpha$ vs. $\sigma$ curve. Therefore, for any given polymer, precise control of amount of doping and the distribution of the dopants are critical for obtaining the maximum power factor. Our work thus opens a straightforward pathway to alter the $\alpha$ vs. $\sigma$ curve, and design efficient organic thermoelectric devices or other organic-based electronic devices.

Results
Doping P3HT and PDPP4T with iodine vapor. Measuring the $\sigma$ and $\alpha$ over a wide range of values requires a large range of doping densities for a particular semiconductor. Chemical\textsuperscript{27,28,36,37} or electrochemical oxidation\textsuperscript{31} have been used to prepare organic semiconductors at many different doping densities for such characterization, but this requires the preparation of many different samples and the assumption that each sample has a nearly identical morphology. Modulation doping using field-effect transistors\textsuperscript{34,35} has been used to measure the $\sigma$ and $\alpha$ at many different, finely controlled doping densities, but the dipole distribution within the dielectric layer can influence the DOS by shifting shallow energy states to a deeper level\textsuperscript{22,36} and thus impacts the $\alpha$ vs. $\sigma$ trend in a way that traditional, chemically doped thermoelectric devices would not be affected. Recently, modulation doping using electrochemical field-effect transistors has also been used to control the doping density of thermoelectric materials\textsuperscript{37,38}. The manner in which ion infiltration into the conjugated polymer during and after gating the electrochemical field-effect transistor impacts the shape of the DOS currently remains unclear. The methodology we report herein uses spontaneous de-doping of chemically doped conjugated polymers as a rapid and convenient way to capture $\alpha$ vs. $\sigma$ across four orders of magnitude of $\sigma$, using an individual sample, and without gating across a dielectric or electrolytic layer.

Doping organic semiconductors with iodine vapor\textsuperscript{39-45} is a well-established strategy to increase the p-type carrier (hole) concentration, resulting in an increased $\sigma$ and decreased $\alpha$. Samples doped in this manner can spontaneously de-dope over time, resulting in a gradual decrease in $\sigma$ and increase in $\alpha$ from their values in the initial doped state. We exploited this de-doping process and measured $\alpha$ as a function of $\sigma$ over a five-orders of magnitude $\sigma$ window. Our method thus captures the trend of $\alpha$ and $\sigma$ using a single sample and without modulation doping.

We used this method to measure the $\alpha$ vs. $\sigma$ relationship over a wide range of $\sigma$ in poly(3-hexylthiophene) (P3HT) and poly[2,5-bis(2-octyldodecyl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione-3,6-diy]-alt-(2,2'5,2'-5',2'-quaterthieniophene-5,5''-diyl)] (PDPP4T), two widely-studied semiconducting conjugated polymers. By exposing the films to iodine vapor, the polymer films acquire a strongly spatially heterogeneous and reversible chemical oxidation (de-doping) (Fig. 1) that changes both conductivity and Seebeck coefficient over a time scale of ~4-24 h.

Doping by iodine vapor was performed by exposing the polymer films to iodine vapor (Methods section) for 2 h at either 25 °C or 75 °C. We then measured, in situ, $\alpha$ and $\sigma$ as the films underwent spontaneous de-doping. In each sample, $\alpha$ increased and $\sigma$ decreased over time as the film de-doped (Fig. 2), as is expected for organic semiconductors with decreasing carrier concentration. Both $\alpha$ and $\sigma$ depend on the free carrier concentration, but this concentration is difficult to determine because of the spontaneous de-doping process and the absence of electron paramagnetic resonance signal from bipolaron carriers. Plotting the Seebeck coefficient vs. the conductivity measured at each time interval on the log-log scale illustrates the comparison of the charge transport properties of these samples while avoiding the need to measure carrier concentration (Fig. 3). The shape of the $\alpha$ vs. $\sigma$ curve for P3HT is similar for the sample doped at 25 °C and at 75 °C, and both curves appear to be consistently flat with a low Seebeck coefficient. In contrast, the shape of the $\alpha$ vs. $\sigma$ curve for PDPP4T changed with the doping temperature. Next, to isolate the effect of doping temperature from possible annealing effects, we sequentially annealed PDPP4T at 75 °C and then doped the sample at 25 °C. The $\alpha$ vs. $\sigma$ trend for the annealed sample was similar to the un-annealed polymer that was doped at 25 °C (Supplementary Fig. 1), indicating that thermal annealing at 75 °C alone may not be cause of the modified $\alpha$ vs. $\sigma$ trend. We additionally found that repeatedly doping the same sample of PDPP4T at 25 °C, de-doping it, and re-doping it recovered the same $\alpha$ vs. $\sigma$ trend (Supplementary Fig. 2). To verify the unusual dependence of doping temperature on the thermoelectric properties of PDPP4T, we repeated the doping and measurement at temperatures of 25 °C and 75 °C using PDPP4T synthesized in-house, and observed similar behavior (Supplementary Fig. 3).

In Kang and Snyder’s model, a flatter and more gradual curve is indicative of a transport parameter of $s = 3$, while a curve maintaining a greater $\alpha$ until a sudden, sharp drop-off at high $\sigma$ is consistent with $s = 1$ We applied the Kang and Snyder model to our experimental data and surprisingly did not achieve the best fit using either $s = 1$ or $s = 3$ (Supplementary Fig. 4). We instead focused our attention to the effect of doping on the $\alpha$ vs. $\sigma$ trend, since doping results in coulombic potentials distributed throughout the polymer and these potentials alter the DOS and therefore the $\alpha$ vs. $\sigma$ trend. Most studies assume that doped semiconductor films are homogenous\textsuperscript{46}. We reasoned there is an alternate possibility: the dopants in the films may be heterogeneously distributed in the thin films as nanoscopic clusters similar to the nanoscopic charged regions in a contact electrified sample\textsuperscript{47}. Dopant clusters have been observed in inorganic semiconductors\textsuperscript{48} but are not commonly invoked in organic semiconductors as they are often doped in solution\textsuperscript{49}. We then hypothesized that doping temperature alters the clustering of the dopants and thus the shape of the DOS, which in turn alters the relationship between the Seebeck coefficient and electrical conductivity. To test this hypothesis, we probed the clustering and spatial heterogeneity of dopants in the conjugated polymer films using KPFM. We characterized the polymer films using photoluminescence spectroscopy (Supplementary Fig. 5) for doping and X-ray scattering to identify any structural changes upon doping. We also computed the effect of the dopant-induced distribution of the DOS on the $\alpha$ vs. $\sigma$ curve (Supplementary Fig. 6).

X-ray scattering studies. The wide angle X-ray Scattering (WAXS) patterns for pristine and unannealed P3HT showed two signature peaks at $q$ values of 0.37 Å$^{-1}$ ($d_{100} = 16.98$ Å), and 1.65 Å$^{-1}$ ($d_{020} = 3.81$ Å) (Supplementary Fig. 7) and is consistent with literature values. Annealing the pristine films at 75 °C results in slight peak shifts with peaks appearing at $q = 0.38$ Å$^{-1}$ ($d_{100} = 16.53$ Å) and 1.67 Å$^{-1}$ ($d_{020} = 3.76$ Å). For unannealed pristine PDPP4T, we observed two signature peaks at $q$-values of 0.30 Å$^{-1}$ ($d_{100} = 20.94$ Å), and 1.66 Å$^{-1}$ ($d_{020} = 3.79$ Å). For films annealed at 75 °C, the peaks appear at $q$ values of 0.30 Å$^{-1}$ ($d_{100} = 20.94$ Å), and 1.67 Å$^{-1}$ ($d_{020} = 3.76$ Å). Both polymers had broad peak around $q = 1.25$ Å$^{-1}$ attributed to the amorphous phase. We did not observe additional peaks in thermally annealed samples.

The WAXS pattern of a P3HT film doped at 25 °C was identical to the pattern of a pristine P3HT film (Supplementary Fig. 8a) indicating that the dopants may reside in the amorphous regions\textsuperscript{50,51}. The WAXS pattern of the de-doped film was also identical to the pattern of a pristine film. The WAXS pattern of P3HT films doped at 75 °C shows peaks at $q = 0.35$ Å$^{-1}$ ($d_{100} = 17.95$ Å) and 1.73 Å$^{-1}$ ($d_{020} = 3.63$ Å) indicating that the
The presence of dense regions in the polymer doped at 25 °C and 75 °C. In the SPC maps, we observed the SPC than the surrounding sections. Photoluminescence microscopy studies showed that chemically oxidized P3HT films with similar cross-sectional areas on the order of 1 µm², indicating the wide distribution of SPC and regions of densely doped states with distributions. P3HT iodine-doped states within the polymer, but are unstable and gradually de-dope in the absence of iodine vapor.

Kelvin probe force microscopy and photoluminescence microscopy studies. We tracked the SPC distribution of P3HT doped at 25 °C over time as the sample spontaneously de-doped to determine the effect of de-doping on the dopant distribution homogeneity (Fig. 5a). The SPC distributions recorded at each time were fit to a Gaussian distribution (Fig. 5b) so that the dopant homogeneity can be described in terms of the mean (Fig. 5c) and width of this distribution (Fig. 5d). The width of the SPC distribution decreases over time, indicating that the dopant distribution becomes more homogeneous as the sample de-dopes and the concentration of dopant counterions in the film decreases. The mean of the Gaussian fit of the SPC distribution becomes more positive over time, consistent with the increase in $E_F$ of P3HT upon de-doping.

Modified Gaussian phonon-assisted hopping model. We calculated $\alpha$ and $\sigma$ by numerically solving the Pauli master equation (PME) that describes phonon-assisted carrier hopping between localized sites (see Methods for simulation details) whose energies were sampled from the carrier DOS. We obtained $\alpha$ and $\sigma$ at various carrier densities by varying the Fermi level $E_F$ further and closer to the center of the energy distribution, analogous to doping. Previous studies have used a Gaussian distribution to describe the DOS, where the width of the DOS accounts for the degree of energetic disorder in the structure of excitation. However, we find that in such a model, varying the energetic disorder simply...
shifts the $\alpha$ vs. $\sigma$ on the log-log curve with minimal difference in its shape (Fig. 6b) and cannot fully account for the significant difference in the slope of the $\alpha$ vs. $\sigma$ plots between the P3HT and PDPP4T plots. It has been shown that long-range coulombic interaction between the ionized dopant molecules and the localized carriers further increases energetic disorder and broadens the deep tail of the DOS\cite{Snyder2019}. The physical distribution of dopant molecules within the sample and the size of the dopant clusters both further intensifies the impact on the DOS. We calculate the DOS resulting from doping concentration $N_d$ in clusters having size $C_n$ according to Eq. 2 in the Methods section, and find that doping and clustering result in a heavy-tailed distribution with a Gaussian core and a wide quasi-exponential tail (Fig. 6a). To particularly examine the effect of the exponential tail, we compare the $\alpha$ vs. $\sigma$ plot for a Gaussian and a purely exponential DOS in Fig. 6b. The exponential DOS results in a much flatter $\alpha$ vs. $\sigma$ curve, which can be understood from the Mott formula\cite{Mott1940}: 

$$\alpha \propto \frac{d\ln[g(E)]}{dE} + g(E) \frac{d[\mu(E)]}{dn}$$  

(1)

When the $\mu(E)$ is only weakly dependent on carrier concentration, the second term in Eq. (1) is small and an exponential DOS $g(E) \propto \exp(-E/\Gamma_E)$ leads to a nearly constant $\alpha$ independent of doping or $\sigma$ but inversely proportional to the energetic disorder $\Gamma_E$ that dictates the width of the DOS.

More realistically, Fig. 6c compares the effect of a Gaussian DOS distribution vs. a heavy-tailed DOS distribution computed with several values of $N_d$ and $C_n$. We compare our simulated results to Snyder and Kang’s charge transport model\cite{Snyder2000} and find that a Gaussian distribution results in significantly lower transport parameter $s \leq 1.5$ compared to the exponential case which has $s \geq 1.5$, and this difference increases further with increasing energetic disorder. However, at high energetic disorder in the presence of a heavy tail the curve cannot be fit by transport parameter values of $s = 1$ or $s = 3$ (Fig. 6c and Supplementary Fig. 6), indicating the limitations of a band model in predicting transport in highly disordered systems (Supplementary Note 2). Comparing our hopping model simulations to experimental data from Fig. 3, we find that PDPP4T doped at 75 °C is most closely fit with $\alpha$ vs. $\sigma$ computed from a purely Gaussian distribution.

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**Fig. 2** Conductivity and Seebeck coefficient of polymers measured during de-doping. Conductivity (black markers, left axes) and Seebeck coefficient (blue markers, right axes) for a poly(3-hexylthiophene) (P3HT) doped at 25 °C (circles), b P3HT doped at 75 °C (squares), c poly(2,5-bis(2-octyldecyl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione-3,6-diyl)-alt-(2,2′;5′;2′′;5′′;2′′′-quaterthiophen-5,5′′′-diyl)] (PDPP4T) doped at 25 °C (up triangles), and d PDPP4T doped at 75 °C (down triangles). One of every five data points collected is plotted along a dashed line as a visual guide.

**Fig. 3** Seebeck coefficient vs. conductivity plot. A log-log plot of Seebeck coefficient vs. conductivity for poly(3-hexylthiophene) (P3HT) doped at 25 °C (black circles), P3HT doped at 75 °C (red squares), poly(2,5-bis(2-octyldecyl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione-3,6-diyl)-alt-(2,2′;5′;2′′;5′′;2′′′-quaterthiophen-5,5′′′-diyl)] (PDPP4T) doped at 25 °C (blue up triangles), and PDPP4T doped at 75 °C (purple down triangles). One of every five data points collected is plotted along with a dashed line as a visual guide.
with a width of $10 \, k_B T$, whereas PDPP4T doped at 25 °C and P3HT is best fit with a dopant-induced heavy-tailed DOS that gives us the required change in slope (Fig. 6d).

To further elucidate the relationship of the shape of the $\alpha$ vs. $\sigma$ curve to the shape of the DOS, we compare schematically the curve to the shape of the DOS via the Mott formula in Eq. 1. Focusing on the first term which is typically dominant, a larger slope in the logarithm of the DOS $g(E)$ implies a larger Seebeck coefficient; this can be observed in the red region “1” in Fig. 7a, b. As the Fermi level approaches the middle of the DOS (region “4”), represented by $E = 0$ in our calculations, the slope approaches zero as does the Seebeck coefficient (Fig. 7c). We find that this part of the curve is always fit by $s \leq 0.5$ (Supplementary Fig. 6) as the center of the DOS is symmetric inside the Fermi window ($-\frac{\mu}{k_B T}$) irrespective of the presence of a heavy tail. Thus we conclude that it is this ‘change in shape’ of the DOS that instigates the change in slope in the $\alpha$ vs. $\sigma$ plot.

Although, the presence of a heavy tail leads to a constant $\alpha$ and a flatter $\alpha$ vs. $\sigma$ curve advantageous for thermoelectrics, the Coulomb interaction causing the heavy tail also increases the energetic disorder, which has an adverse effect on $\alpha$ (see comparison of a 3 $k_B T$ Gaussian and heavy-tailed DOS in Fig. 7c). Hence, a narrower DOS and a smaller transport parameter $s$ is more advantageous for thermoelectric applications. This impact of an energetically disordered, heavy-tailed DOS on the thermoelectric properties is consistent with that recently reported by Kemerink and co-workers. While Kemerink and co-workers assumed a homogenous distribution of the dopants and use this to capture the experimentally determined $\alpha$ vs. $\sigma$ curve, we find that the spatial heterogeneity of dopants is necessary to describe the impact of doping on the shape of the DOS.

**Discussion**

Our studies establish that the shape of the $\alpha$ vs. $\sigma$ curve depends on the clustering of the dopants in the conjugated polymer. The dopant distribution affects the carrier DOS, with dopant clustering dramatically increasing the energetic disorder, which in turn affects the charge transport properties. We associate flattened $\alpha$ vs. $\sigma$ trends with heterogeneous spatial distributions of dopants throughout the sample using surface potential contrast (SPC) mapping by Kelvin probe force microscopy (KPFM), which
Fig. 6 Simulated dopant-induced Seebeck and conductivity trends. a The effect of doping and clustering on the density of states (DOS) distribution with intrinsic Gaussian width of $3 \, k_B T$. The charge carriers interact coulombically with the ionized dopants creating additional deep trap states, resulting in a heavy-tailed DOS. Log-log plot of Seebeck coefficient vs. conductivity showing the change in slope due to: b Gaussian and exponential DOS, c Doping and clustering induced heavy-tailed DOS. The doping-induced distribution is computed with dopant concentration $N_d = 10\%$ and cluster concentration $C_s = 1$, and the clustering induced distribution with $N_d = 3\%$ and $C_s = 3$. We have fit our simulated results (symbols) to Snyder and Kang’s charge transport model (gray lines) and the corresponding transport parameter ‘s’ values are shown. d Comparison of our model to experimental data from Fig. 3. ($N_d = 4\%$ and $C_s = 1$ for pink dashed line, $N_d = 0.9\%$ and $C_s = 9$ for red dot-dashed line, $\gamma = 0.01$ and $\sum_i = 0.0025$ for all three cases).

Fig. 7 Impact of density of states distribution on Seebeck coefficient vs. conductivity curve. Schematic showing the filling up of the a Gaussian and b heavy-tailed density of states DOS with increasing doping, by varying the Fermi level $E_F$ further and closer to the center of the energy distribution and c the corresponding effect on the log-log plot of Seebeck coefficient vs. conductivity.
suggests that a heterogeneous distribution of coulombic potentials from doping broadens the DOS and thus depresses the Seebeck coefficient. We then calculated the doping-induced DOS and simulated carrier transport using a modified Gaussian disorder model and the Pauli Master equation to explain how the shape of the DOS impacts the $\sigma$ and $\alpha$ trend. Based on these studies, we show that the spatial distribution of dopants in the conjugated polymer has a profound impact on the shape of the $\alpha$ vs. $\sigma$ curve and that clustering of dopants in the polymer modifies the shape of the DOS and alters the trend of $\alpha$ vs. $\sigma$ curve.

We found that PDPP4T exhibited two very distinct shapes of the $\alpha$ vs. $\sigma$ curve, depending only on the temperature at which doping was performed. KPFM measurements uncovered that room-temperature doping resulted in dopant inhomogeneity and clustering. We simulated the effect of clustering in a phonon-assisted hopping model of charge transport and found that it caused a dramatic change in the electronic density of states (DOS) which resulted in a heavy tail, while homogeneous doping maintained a DOS consistent with the Gaussian disorder model. We conclude that the heavy-tailed DOS results in a qualitative change of the $\alpha$ vs. $\sigma$ curve.

Our studies suggest that tuning the energetic disorder by controlling the dopant counterion distribution within the doped film of the organic semiconductor can lead to substantial improvements in the thermoelectric performance of organic semiconductors. The conventional wisdom is that semiconductors will be necessary to improve the existing and future electronic applications. We show that the spatial distribution of dopants in the conjugated polymer has a profound impact on the carrier concentrations. We simulated the effect of clustering in a phonon-assisted hopping model of charge transport and found that it caused a dramatic change in the electronic density of states (DOS) which resulted in a heavy tail, while homogeneous doping maintained a DOS consistent with the Gaussian disorder model. We conclude that the heavy-tailed DOS results in a qualitative change of the $\alpha$ vs. $\sigma$ curve.

**Methods**

**Materials.** P3HT ($M_w = 90$ kDa, 96% HT regioregularity) was purchased from Rieke Metals and PDPP4T ($M_w = 171,138$ Da, $D = 2.45$) was purchased from Ossila. Chloroform and iodine were purchased from commercial vendors and used as received.

**Film preparation.** Solutions of 5 mg/mL P3HT or 8 mg/mL PDPP4T in chloroform were stirred for no less than 4 h before drop-casting. 0.23 mL of the polymer solution was drop cast onto a pre-cleaned, handcut, 1.1 cm x 2.2 cm glass cover slip that was preheated to 45°C on a hot plate, and this was immediately covered with a watch glass to impede the escape of chloroform vapors and slow the rate of evaporation during drop-casting. After 10 min, the sample heating element was turned off, and the sample was let stand under ambient conditions for no less than 24 h to evaporate the chloroform further. P3HT films were ~4 µm thick and PDPP4T films were ~9 µm.

**Doping with iodine vapor.** 50 ± 5 mg iodine crystals were loaded into a 1 mL glass vial, and this vial was loaded into a 20 glass mL vial. For samples doped at 25°C, the 20 mL vial was first capped and let stand for no less than 12 h to allow solid-vapor equilibration of the iodine via the vials. For samples doped at 75°C, the 20 mL vial was first capped and let stand in a 75°C oven for 10 min to allow solid-vapor equilibration of the iodine via the vials while the polymer film was simultaneously heated to 75°C for 10 min. In each case, the iodine vapor was carried out by placing the polymer film into the 20 mL vial (which contained iodine vapor and the 1 mL vial of 50 ± 5 mg iodine), capping the vial, and heating to the specified temperature for 2 h.

**Characterization of thermoelectric properties.** Samples were transferred from their iodine doping chamber to a custom-built (reported elsewhere and briefly summarized herein) thermoelectric characterization apparatus in a timely fashion so that they began de-doping immediately and rapidly in the absence of iodine vapor. The sample was placed on an insulating glass slide bridging one heated copper block and one unheated copper block to establish a temperature gradient. A PTFE block containing four platinum wire electrodes in a linear arrangement and two type thermocouples was clamped onto the sample. The thermocouples and probe wires were separated by a distance of 1.4 cm. This entire apparatus was enclosed within an electrically grounded metal box. A LabView program was used to interface with a digital dual input thermometer for the k-type thermocouples, a Keithley 2182A nanovoltmeter, and a Keithley 2440 S A source meter to repeat measurements of the temperature gradient $\Delta T$, voltage gradient $\Delta V$, and $I$-$V$ characteristics respectively across the sample sequentially and repeatedly every 10 min for P3HT and every 2 min for PDPP4T. A $\Delta T$ of ~20°C with an average temperature of ~50°C was applied to P3HT, and a temperature gradient of ~10°C with an average temperature of ~45°C was applied to PDPP4T. $\Delta V$ was taken to be the ratio of 1000 voltage measurements with the Keithley 2182A nanovoltmeter clamped to the sense probes, and $\sigma$ was taken to be $\Delta V/\Delta T$. Only measurements for which the standard deviation of the 1000 voltage measurements is less than 1% of their mean are used to calculate $\sigma$, while the remaining measurements were discarded, to ensure only reliable estimates of $\sigma$ are considered. The conductance was determined from the slope of $I$-$V$ curve obtained by the Keithley 2440 S A using a four-probe measurement.

**Simulation details.** Our charge transport model is based on electron hopping between localized sites and the hopping rate between sites $(i,j)$ is calculated from the Miller-Abrahams rate equation:

$$W_{ij} = \nu_c \exp(-2\gamma R_{ij}) N(\Delta E_{ij}) \left[1 + \frac{1}{2}\right],$$

where $\nu_c = 5 \times 10^{12}$ s$^{-1}$ is the attempt to escape frequency, $\gamma = 1$ is the overlap factor ($\gamma_i = \gamma_j = \gamma$ are the site-specific contributions obtained from a Gaussian distribution of width $\sigma_i = 0.25$) and $R_{ij}$ is the distance between the sites. The Boltzmann-Dirac distribution function is given by $\exp(-\epsilon_j/\kappa B)$ where $\kappa B$ is the potential energy of the Coulomb field, $\epsilon_j$ is the energy of the site $j$, and $\kappa = 10^8$ V m$^{-1}$ is the externally applied electric field. These are the values used throughout the simulation unless stated otherwise. We simulate a $35 \times 25$ lattice of sites with an average distance between adjacent sites $a = 0.38$ nm, and consider up to the third-nearest neighbor, which implies a maximum hopping distance of $\sqrt{3} a$.

We numerically solve the Pauli master equation to compute the time-averaged occupational probabilities of the sites using a non-linear iterative solver, and the initial site occupation probability is given by the Fermi-Dirac distribution. In steady-state, for downward hops with the emission of a phonon, $\Delta E_{ij} = E_i - E_j - e\Phi_{ij}$ where, $E_i$ and $E_j$ are the energies of the sites and $\Phi_{ij}$ is the external applied electric field. The Seebeck coefficient is calculated as $S = \frac{e}{k_B T} \left( \frac{\nu_i}{\nu_j} \right)$ where, $\nu_i$ is the average transport energy, and calculated from $\nu_i = \frac{\sum_i \omega_i \exp(-\epsilon_i/\kappa B)}{\sum_i \exp(-\epsilon_i/\kappa B)}$.

Arkhipov et al. have shown that Coulomb interaction between ionized dopants results in a heavy-tailed DOS given by $g(E) = \frac{4\pi^2 N_s^2 g_s(\epsilon)}{\rho_T} \int_0^E dE' \exp\left(-\frac{\epsilon - E'}{k_B T}\right) g_s(E - E')$ where, $N_i$ and $N_s$ are the intrinsic and dopant concentration respectively, $E_i$ is the potential energy of the Coulomb interaction and $g_s$ is the intrinsic Gaussian DOS centered at 0 energy and given by $g_s(E) = \frac{\pi e^2}{3\rho_T} \left( \frac{E}{k_B T} \right)^{-3/2} \exp\left(-\frac{E^2}{3k_B T}\right)$.

However, they do not consider the impact of dopants clustering. In the presence of dopants clustering, the probability density $\pi_c$ of the minimum distance at which a dopant cluster is present can be modeled by a Poisson distribution $\pi_c(E) = \frac{4\pi^2 N_c^2 \rho_T}{3\rho_0^3} E^2$ where, $N_c$ is the cluster density. The potential energy of the Coulomb interaction between the localized charge carrier and dopant cluster is now $E_i = -C_s \sqrt{N_c} e^2$ where, $C_s$ is the number of dopants in each cluster. Combining these equations to obtain the energy distribution of localized states over the intrinsic energy $E_i$, we get

$$g(E) = \frac{4\pi^2 N_c^2 C_s^2}{(4\pi e^2)^3} \int_{0}^{E_i} dE_c \exp\left(-\frac{4\pi^2 N_c^2 C_s^2 e^6}{3(4\pi e^2)^3 e^{6} E_c^3}\right) g_s(E - E_i)$$

where, $N_c = \frac{N_s}{N_i}$. We use the rejection sampling technique to generate an energy distribution from the calculated DOS and then randomly assign an energy to each site from the distribution. Details about solving the non-linear PME has been described in Supplementary Note 1 and further details of our model has been reported in an earlier work.

**X-ray Scattering, KPFM, and PL instrumentation and characterization.** The microstructural characterization of the polymer films was conducted in a SAXSLAB Ganesha 300XL X-ray scattering instrument equipped with a Xenocs GeniX.
3D CuKα source (λ = 0.15418 nm) and a Dectris Pilatus 30 K photon-counting detector. Ultra-high vacuum (<2×10⁻⁵ mbar) was applied to reduce background scattering. X-ray AXS measurements were obtained in transmission mode, and the sample-detector distance was ~100 mm.

KPFM experiments were conducted on a Digital Instruments Bioscope Atomic Force Microscopy (AFM), with AppNano ANSCM-PA Pt/Ir-coated Si cantilever. The probe possesses a resonance frequency of around 254 kHz. A mixed AC and DC voltage electrical excitation signal was applied between the probe, lifted by the AFM, and the sample-detector distance was ~100 nm. The AFM image was captured using a Princeton Instrument Acton Photomax 512 EMCCD camera, which was cooled down thermoelectrically to ~70 °C. The images were captured at an exposure time of 0.2 s.

Data availability

All the data presented in the paper and supporting information is available from the authors upon request. The computer codes used in this work are available from the authors upon request. All the data presented in the figures in the manuscript can be downloaded as a ZIP file from URL: https://doi.org/10.7275/7lkz-k161.

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Author contributions

D.V. and Z.A. conceived the idea. D.V. and C.J.B. designed and implemented the experimental setup for conductivity and Seebeck coefficient characterization. Z.A. and M.U. implemented the phonon-assisted hopping charge transport simulation code. M.U. performed the phonon-assisted hopping charge transport simulations and DOS calculations. M.D.B., P.W., and N.H.-H. measured the KPFM and PL microscopy. L.A.R. updated the code for fitting to the empirical charge transport model. S.P.J. and M.L.-D. performed X-ray scattering analysis the polymer films. L.K.-K. described how structural disorder in polymers is expected to impact the thermolectric charge transport.

Additional information

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