Charge carrier transport mechanism in doped conjugated polymers

M. Duhandžić and Z. Akšamija
Materials Science and Engineering, University of Utah, 201 Presidents' Circle, 84112 Salt Lake City, UT, USA
e-mail: zlatan.aksamija@utah.edu

ABSTRACT

Carriers in conjugated polymers (CP) are localized over couple of molecular sites within the polymer chain. The inverse participation ratio (IPR) ranges between 1 in the tail to ~8 in the middle of the Gaussian density of states (DOS). Delocalized states deep in the DOS can be accessed through doping, which a priori leads to band-like transport. Conversely, dopant counterions create traps and an exponential tail in the density of states (DOS). However, the effect of doping on carrier delocalization is still not well understood. We capture transport properties of doped CPs by developing a tight-binding Hamiltonian that includes dopant-induced energetic disorder (DID) via Coulomb interactions. We show that carriers at the Fermi level localize with doping. This prohibits the occurrence of band-like transport in CPs. We anticipate our work to contribute to understanding of the underlying transport physics in CPs.

INTRODUCTION

Organic electronic materials are an environmentally friendly and low-cost alternative to inorganic semiconductors. Among them, conjugated polymers (CPs) are a broad family of organic semiconductors, and frequently employed as a platform for electronic devices. [1] Carrier transport in CPs occurs through phonon-assisted hopping between sites that are localized over several mer units. The number of units depends on the conformational disorder of the CP [2] and conjugation breaking. In the tail of the density of states (DOS) carriers are localized and the inverse participation ratio IPR = 1, while the IPR can be as high as ~8 in the middle of DOS. [3]

To increase their conductivity (σ), CPs are usually heavily (comparable to the density sites) doped. The increase in σ is attributed to carriers being more delocalized with doping and the transport changing from a hopping to band-like. Conversely, Coulomb interactions with dopant counterions impact carrier mobility by creating heavy tails in the DOS. However, the impact of dopants on delocalization and how that translates into carrier transport is not fully understood.

Here we show that doping localizes carriers close to the Fermi level and that the transport mechanism remains phonon-assisted hopping even at high doping. We include dopant-induced disorder (DID) via Coulomb interactions in our tight-binding (TB) Hamiltonian. We utilize perturbation theory to calculate the transition rates between states from eigenenergies and eigenfunctions. Then we solve Pauli master equation (PME) for site-occupational probabilities and compute transport properties of doped CPs. Our results stress the important role of DID in delocalization. Nevertheless, the effective IPR remains low (~2) even at high carrier concentrations (n).

MODEL

To capture the impact of doping, we add Coulomb interactions to the Gaussian disorder model according to the Arkhipov model [4] that includes carrier screening [5] of counterions with finite size R_d at a distance R_s from carriers. We set the resulting DOS as onsite energies of the TB Hamiltonian (20x20x20 sites) and the overlaps $t_{nk} = t$ as off diagonal elements. Solving for eigenvalues and eigenfunctions, we obtain the resulting DOS and wavefunctions. We calculate $\mathrm{IPR}_i = 1/\sum_j |V_j|^4$ for state i, where V_j are components of the eigenstate vector ψ_i. In order to understand the impact on the carriers that contribute to transport, we define the effective IPR as $\mathrm{IPR}_{eff} = \frac{1}{Z}\sum_i \mathrm{IPR}_i\, e^{-(E_i-E_F)/k_BT}$, where $Z = \sum_i e^{-(E_i-E_F)/k_BT}$ and E_F is the Fermi level. The transition rates can be calculated using [10]:

$$W_{ij} = \frac{\pi}{\hbar}\sum_q |M_{ij,q}|^2 \delta(E_i - E_j \pm \hbar\omega_q) \quad (1)$$

where $M_{ij,q} = u\langle\psi_i|dH/du|\psi_j\rangle$ is the electron-phonon coupling constant due to phonon mode q and displacement u [6]. In a nutshell, the phonon energy is $E = \hbar\omega\left(N(E) + \frac{1}{2}\right) = \frac{1}{2}m\omega^2 u(r)^2$. The phonon displacement contains two contributions given as the sum of distribution functions of downward and upward hops, $N(E) + 1$ and $N(E)$, respectively. Then in the continuum limit, for downward hops we obtain

$$W_{ij} = \frac{\pi\hbar}{\rho}\left|\left\langle\psi_j\left|\frac{dH}{du}\right|\psi_i\right\rangle\right|^2 \left(N(E_{ij}) + 1\right)\frac{D(E_{ij})}{E_{ij}}, \quad (2)$$

where $D(E_{ij})$ is the vibrational DOS and ρ mass density. Using these rates, we solve PME for the

distribution function and calculate σ and the Seebeck coefficient (α). [5]

RESULTS

The increase of overlap integral t, shifts and skews the DOS to higher energies as shown in Fig. 1a). t delocalizes carriers so that a large enough t leads to completely delocalized carriers and band-like transport. However, with DID the effective IPR is significantly lower as shown in Fig 1b). The effect of doping on delocalization overtakes and $\mathrm{IPR}_{eff} \approx 1$ even at high doping. The IPR at every energy is shown in Fig 1c) and d), for $R_s = 0.3$ nm and d) $R_s = 0.8$ nm, respectively. Below the Fermi level (thin solid lines), carriers are localized, while they remain delocalized deeper in the DOS.

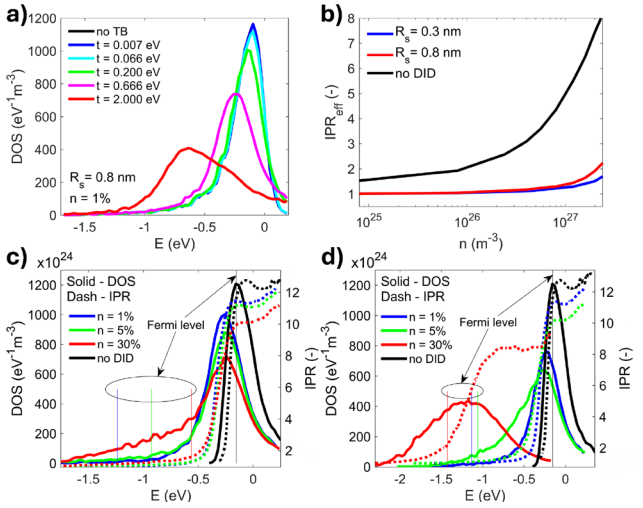

Fig. **1**. a) effect of overlap integral t on the DOS. Increasing t the DOS shifts and skews to higher energies. b) effective IPR with and without DID that shows carriers close to the Fermi level localize significantly with doping. DOS (left axis) and IPR (right axis) at different doping concentrations for c) $R_s = 0.3$ nm and d) $R_s = 0.8$ nm. The IPR at the Fermi level (thin solid lines) does not exceed 2 even at $n = 30\%$ in both cases.

An IPR_{eff} close to 1 indicates that the leading transport mechanism is carrier hopping between localized sites, even at high carrier concentrations. We test this hypothesis by comparing σ and α from the tight-binding (TB) to the same quantities simulated using phonon-assisted hopping (VRH) model (shown in Fig. 2 for a) $R_s = 0.3$ nm and b) $R_s = 0.8$ nm). $\sigma(n)$ and $\alpha(n)$ are essentially similar from both models. Qualitatively, in the TB model the Fermi level crossed the peak of the DOS at a lower n compared to the VRH, which is characterized by the change in sign of $\alpha(n)$ and a negative slope of $\sigma(n)$.

Although transition rates increase roughly as t^2, there is a trade-off between higher rates and the DOS being "too skewed", when the conductivity starts dropping with doping at $n < 50\%$. As a consequence, higher overlap does not necessarily increase conductivity (at every n) as shown in Fig. 3a) (left axis). At the point of conductivity drop, the Seebeck coefficient (α) changes sign, meaning that the Fermi level has crossed the peak of the DOS (right axis in Fig. 3a)), which confirms the previous statement. Both quantities are combined into the commonly plotted $\alpha(\sigma)$ curve shown in Fig. 3b). Qualitatively, the curve for realistic values of t (≈ 0.7 eV) is similar to the ones from simpler hopping models in which carriers are treated as completely localized. This is an important result that we anticipate will further advance the understanding of transport of doped organic semiconductors.

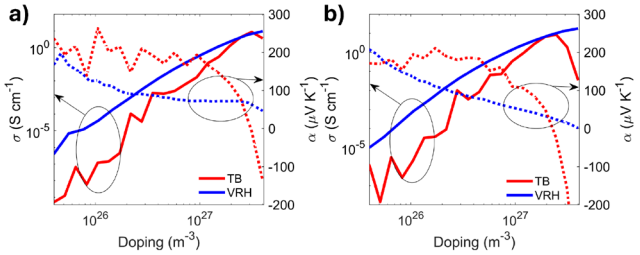

Fig. **2**. Compare of σ (left axis) and α (right axis) as a function of n simulated using the hopping (VRH) and our current (TB) model for a) $R_s = 0.3$ nm and b) $R_s = 0.8$ nm. Results indicate that hopping captures the underlying carrier transport physics in CPs.

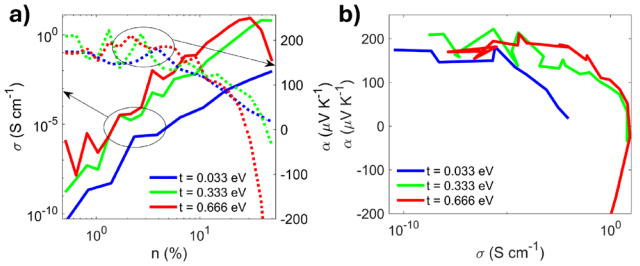

Fig. **3**. a) σ (left axis) and α (right axis) as a function of n that are combined in b) as $\alpha(\sigma)$. The switch in sign of α indicates that the Fermi level has crossed the peak of the DOS.

CONCLUSION

We utilize the TB Hamiltonian to simulate transport in doped CPs. We find that carriers localize with doping due to carrier-counterion Coulomb interactions and DID. Our results stress the importance of DID in carrier delocalization and we anticipate our work to be useful for further advancements in this field.

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