

Ab Initio Molecular Dynamics Assessment on the Mixed Ionic–Electronic Transport for Crystalline Poly(3-Hexylthiophene) Using Full Explicit Lithium-Based Dopants and Additives

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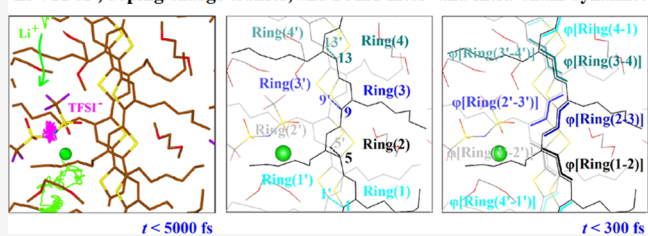
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ABSTRACT: Here, we report ab initio molecular dynamics calculations dealing with mixed ionic–electronic transport in a poly(3-hexylthiophene) crystalline supercell, including the use of full explicit lithium-based dopants and additives. Up to now and to the best of our knowledge, the use of full explicit dopants and additives for both ionic and electronic transport calculations has remained practically unexplored probably due to their high computational cost. The use of fewer artifacts and other common assumptions in our calculations allowed us to reveal some interesting behavior associated with the presence of lithium bis(trifluoromethanesulfonyl) imide (LiTFSI) dopants and dimethoxyethane (DME) additives on the mixed ionic–electronic transport in a wide temperature range. Our ionic and electronic conductivity calculations show a good correlation with the experimental reports of similar mixed ionic–electronic conductors in the very recent literature. For the electronic transport, our transfer integral (J) and reorientation energies (λ) values showed increment respect to typical unexplicit-doped calculations. Furthermore, we also introduce the role of the explicit dopant in the interchain, intrachain, “effective” doping, and charge-transfer complex bonding distances, and their associated static and dynamic disorder effects on electronic transport. These new insights can be extremely helpful to unravel not only the doping mechanism but also, and simultaneously, the mixed ionic–electronic transport mechanism for organic semiconductors. Advancing in the fundamental understanding of mixed ionic–electronic organic conductors is a key to boosting their properties for different applications going from energy storage to bioelectronic devices.

Li+/TFSI-, doping/charge transfer, and P3HT inter- and intra-chain dynamics



1. INTRODUCTION

Organic semiconductors have proven to achieve relatively high carrier mobilities and particularly high hole carrier conductivities mainly due to their capability to form delocalized electronic states.^{1–3} This ability is strongly related to large transfer integrals, small electron–phonon coupling, and the absence of energetic disorders, which are common features of highly ordered systems such as inorganic crystals or organic crystals comprising small molecules.⁴ However, polymers are mostly considered as disordered systems, even considering that, in some cases, they can crystallize into well-ordered crystalline domains up to several hundreds of nanometers such as regio-regular poly(3-hexylthiophene-2,5-diyl), commonly known as P3HT.^{5–7} It is important to mention that the disorder is not only exclusively attributed to the amorphous regions but also to different types of intrinsic disorders of the crystalline domains, which alters the charge carrier localization of electronic states and, hence, the charge-carrier transport.^{8,9} For instance, molecular dynamics (MD) studies on crystalline P3HT dynamic disorders have shown that the introduction of defects in the regioregularity did not influence the location or depth of the charge traps.^{10,11} Other studies using Monte Carlo calculations revealed that both side-chain and backbone

disorders contributed to the broadening of the density of states (DOS) near the valence-band edge and that the backbone disorder played a larger role in increasing charge localization.^{8,12,13} Furthermore, although the addition of dopants into organic semiconductors is a successful way to improve carrier transport, it is also a source of disorders in the system. In the case of organic semiconductors, the dopant ionizes while transferring a hole to the organic semiconductor, forming an electron–hole pair, which is further separated, creating a free hole.^{14,15} In addition, even upon considering the complete ionization of dopant scenario, a considerable fraction of the generated charges remain bonded in the form of charge-transfer complexes and, thus, only a small fraction contributes to the carrier mobility.^{15–18} The most typical P3HT dopants are ferric chloride (FeCl₃),^{19,20} 7,7,8,8-tetracyanoquinodimethane (TCNQ) in all of its fluorinated forms,^{21–23} and

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bis(trifluoromethanesulfonyl)imide (TFSI) salts.^{24,25} There are some reports in the literature studying the doping mechanism of thiophene oligomers using the ab initio methodologies using radical cations or explicit chlorine (Cl) atoms as the dopant.^{26–29} More recently, the doping effects of thiophene oligomers with explicit dopants such as TCQN have been studied, revealing a more realistic picture of the charge-transfer process in chemical doping.^{30,31} Our group has recently reported a joint theoretical and experimental study focusing on the lithium bis(trifluoromethanesulfonyl) imide (LiTFSI) explicit doping mechanism in crystalline and amorphous regions of P3HT.³² However, the model used in the later report comprised an explicit LiTFSI dopant in a single periodic P3HT chain, as an approach to understand the doping mechanism but without evaluating directly neither crystalline nor amorphous regions.³² Nonetheless, there is consensus about treating amorphous regions with a simplified one-dimensional approach, while their crystalline counterparts necessarily require a two-dimensional approach to consider P3HT chain π -stacking into lamellae sheets with quite short (~ 3.8 Å) interlamellar distances.^{33,34} Recently, some particular dopants such as LiTFSI have attracted a lot of attention mostly because of their promising mixed ionic–electronic transport properties in a wide range of applications.^{35–37} Because most electronic-conducting polymers, and particularly P3HT, usually exhibit low ionic mobilities, the addition of ionic conducting polymers (e.g., polyethylene oxide) has been explored to enhance both ionic (lithium-ion in this case) and electronic transport simultaneously.³⁵ More recently, the modification of thiophene oligomers with ethylene oxide groups at the backbone [i.e., 4 T-PEO block oligomers]³⁶ and the modification of P3HT side chains with ethylene oxide groups [i.e., poly(3-methoxyethoxyethoxythiophene) (P3MEET) and poly(3-methoxyethoxyethoxymethyl thiophene) (P3MEEMT)] have been just successfully experimentally synthesized, pursuing an enhancement on both electronic and ionic conductivities.^{37,38} Furthermore, a very recent report on polythiophene side-chain modifications with ethylene oxide groups at different positions has just revealed that the increasing distance of the oxygen atoms in the polythiophene side chain with respect to the backbone [i.e., poly(3-methoxyethoxybutyl)thiophene (P3APPT)] is a key to enhance both electronic and ionic conductivities simultaneously.³⁹ These reports also include ionic mobility calculations without the use of the full explicit dopant using a classical MD approach, showing a good correlation with experimental data.^{37,39} Inspired by these previous outstanding advances, here, we present ab initio MD (AIMD) calculations to shed some light on the mixed ionic–electronic transport mechanism of crystalline P3HT using explicit LiTFSI dopants and dimethoxyethane additives. Using a more realistic model with fewer artifacts in the calculations, we aim at showing a comprehensive analysis of both static and dynamic effects on the mixed ionic–electronic transport for explicit chemically doped conducting polymers.

2. METHODOLOGY

Our initial crystalline system structure corresponds to a supercell with the $P1$ space group symmetry expanded in the c -axis ($1 \times 1 \times 2$) from the original unit cell with a monoclinic $P2_1/c$ space group, reported for regioregular P3HT.⁴⁰ We have already studied the lowest energy location of the LiTFSI dopant in our crystalline P3HT supercell using classical MD

being in very good correlation with X-ray diffraction studies.³² In the present case, the system comprises two regioregular poly(3-hexylthiophene) P3HT chains with four thiophene rings each, a single molecule of lithium bis(trifluoromethanesulfonyl)imide (LiTFSI), and five molecules of dimethoxyethane (DME), named P3HT-LiTFSI-DME. The inclusion of DME molecules as additives is not only inspired in the modification with ethylene oxide groups of side chains performed recently^{37–39} but also accounts as a theoretical alternative to enhance lithium-ion transport. Our system presents $\text{LiTFSI}/3\text{HT} = 1/8 \sim 0.12$ and $\text{LiTFSI}/\text{EO} = 1/10 \sim 0.10$ ratios, which are very close to those reported as optimal ratios to enhance mixed ionic–electronic transport in the literature.^{35,37,39} Other lower amounts of DME molecules were also tested but did not present relevant ionic conductivity. Classical MD calculations were performed using the universal force field in large-scale atomic/molecular massively parallel simulator (LAMMPS)⁴¹ under an NPT ensemble to optimize the inclusion of DME molecules into the P3HT-LiTFSI-DME supercell. Then, MD calculations were computed under an NVT ensemble at 300, 500, 1000, and 1500 K for a 500 ps total simulation time using a time step of 0.3 fs. Additional MD calculations on a larger $2 \times 4 \times 4$ supercell under NPT and NVT ensembles at 300, 500, 1000, and 1500 K for a 500 ps total simulation time using a time step of 0.3 fs were also computed, as depicted in Figure S1. It is important to remark that our MD calculations under the NPT ensemble for both ($1 \times 1 \times 2$) and ($2 \times 4 \times 4$) supercells showed only a small decrease in density from ~ 1.3 to 1.2 g cm^{-3} with increasing temperature from 300 to 1500 K, as depicted in Figure S2. Based on the fact that larger supercells and longer simulation times are needed to explain the P3HT structural transitions such as the “melting” temperature observed around 500 K, we only focused on the local short-range ionic–electronic features of the crystalline system having in mind that our relatively small supercell is probably artificially stabilized in the higher temperature regime. AIMD calculations were performed on the ($1 \times 1 \times 2$) supercell using the VASP code (Vienna ab initio simulation package),^{42–45} with projector augmented wave (PAW) method,^{46,47} using generalized gradient approximation (GGA) as the exchange–correlation functional according to Perdew–Burke–Ernzerhof (PBE).⁴⁸ The PAW potentials correspond to the following electronic configurations: $3s^2 3p^4$ for S, $2s^2 2p^5$ for F, $2s^2 2p^4$ for O, $2s^2 2p^3$ for N, $2s^2 2p^2$ for C, $2s^1$ for Li, and $1s^1$ for H. The selected plane-wave cutoff energy was 400 eV, being enough to achieve good tolerance in force (0.02 eV/Å) and energies (1×10^{-6} eV). AIMD calculations were performed under an NVT ensemble at 300, 500, 1000, and 1500 K for a 4 ps total simulation time using a time step of 0.1 fs for integrating the equations of motion, being sufficient to describe fine motions such as C–H stretching vibrations. The total energy as a function of the simulation time is depicted in Figure S3. AIMD data were processed using OVITO Pro.⁴⁹ Additional density functional theory (DFT) calculations were performed with the Gaussian09 package to obtain the reorganization energy for LiTFSI dopants in vacuum using the B3LYP hybrid functional and a 6-31G(d,p) basis set.^{50–54}

3. RESULTS AND DISCUSSION

3.1. Ionic Transport. The mean square displacement (MSD) for Li^+ (MSD_{Li^+}) and TFSI^- ($\text{MSD}_{\text{TFSI}^-}$) ions obtained by our MD and AIMD calculations are shown in Figure 1a,b,

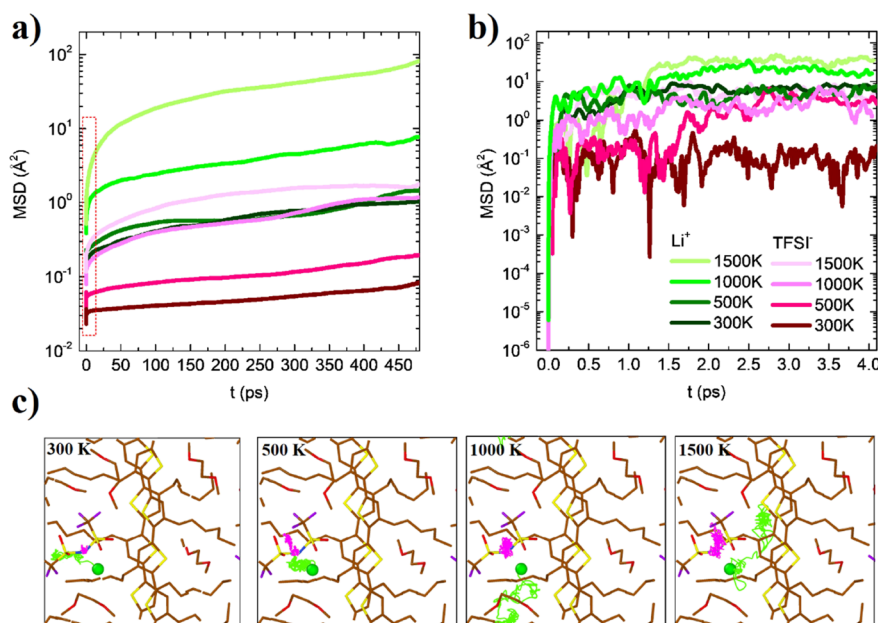


Figure 1. MSD for Li^+ and TFSI^- ions computed using (a) MD and (b) AIMD calculations at 300, 500, 1000, and 1500 K. (c) Lithium-ion (Li^+) (green line) and TFSI^- (pink line) trajectories using AIMD calculations. References for atom colors are carbon (brown), sulfur (yellow), oxygen (red), nitrogen (blue), fluorine (purple), lithium (green), and hydrogen (omitted for clarity).

respectively. We use the MSD values obtained from classic MD calculations to estimate the self-diffusion coefficient of the ionic species as they were computed up to 500 ps simulation time. Hence, the self-diffusion coefficient for Li^+ (D_{Li^+}) and TFSI^- (D_{TFSI^-}) ionic species was calculated from MD calculations using the following equation:

$$D_{\text{Li}^+, \text{TFSI}^-} = \lim_{t \rightarrow \infty} \frac{1}{6t} \text{MSD}_{\text{Li}^+, \text{TFSI}^-} \quad (1)$$

Then, assuming that the ionic diffusion is uncorrelated, the transference number for Li^+ is estimated using the following equation:

$$t_{\text{Li}^+} = \frac{D_{\text{Li}^+}}{D_{\text{Li}^+} + D_{\text{TFSI}^-}} \quad (2)$$

and finally, we estimate the total ionic conductivity using the Nernst–Einstein equation:

$$\sigma_i = \frac{e^2}{Vk_B T} (n_+ z_+^2 D_{\text{Li}^+} + n_- z_-^2 D_{\text{TFSI}^-}) \quad (3)$$

where e is the elementary charge, k_B is the Boltzmann constant, V is the volume, T is the temperature, n_+/n_- are the numbers, z_+/z_- are the charges of cations/anions, respectively.⁵⁵ All the estimated parameters are summarized in Table 1. The Li^+ transference number is ~ 0.9 and almost independent with temperature, and the total ionic conductivity increases from $\sigma_i \sim 1.15 \times 10^{-4}$ to $\sim 16.6 \times 10^{-4} \text{ S cm}^{-1}$ when the temperature increases from 300 to 1500 K.

Particularly, our σ_i values obtained below 500 K are in good correlation with those $\sim 10^{-4} \text{ S cm}^{-1}$ values observed experimentally at 300–400 K for LiTFSI-doped P3MEEMT and P3APPT mixed ionic–electronic conductors.^{37,39} However, it is important to remark that our calculations neither consider the ionic conductivity contribution of fully amorphous regions, and due to the relatively small size of the system, nor consider other possible structural transitions

Table 1. Most Relevant Parameters for the Ionic Transport Obtained from MD Calculations at Different Temperatures^a

T (K)	300	500	1000	1500
D_{Li^+} ($10^{-6} \text{ cm}^2/\text{s}$)	0.034	0.058	0.26	2.60
D_{TFSI^-} ($10^{-6} \text{ cm}^2/\text{s}$)	0.003	0.006	0.036	0.053
t_{Li^+}	0.927	0.886	0.875	0.979
σ_i (10^{-4} S/cm)	1.15	1.20	2.74	16.6

^aThese values were obtained from MD calculations based on the larger $2 \times 4 \times 2$ crystalline supercell (Figure S1), but results are similar when using the small crystalline supercell (Figure 1c).

such as the “melting” of P3HT starting at $\sim 500 \text{ K}$, as observed for larger systems in the literature.⁵⁶ Interestingly, our MD calculations below 1000 K have almost reached the diffusion regime at relatively short simulation times (Figure 1a) and have shown a good correlation with our AIMD calculations (Figure 1b). Thus, both Li^+ and TFSI^- ionic species MSDs and their corresponding trajectories obtained from AIMD calculations (Figure 1c) were used to have more insight into the ionic–electronic interactions of our system computed at relatively short simulation times but with first principles accuracy.

Li^+ showed quite a low mobility at 300 K, and only a slight increase was observed at 500 K, where the LiTFSI ionic pair dissociation is more evident. Nonetheless, it is interesting to note that the TFSI^- anion exhibits very low mobility at 300 K in comparison with that observed at 500 K, in agreement with the slightly larger transference number observed in our MD calculations at longest simulation times (see Table 1), but also envisaging that the TFSI^- anion will probably behave as a “better” doping agent at 300 K. At 1000 K, the Li^+ mobility increase mediated by its interactions with DME molecules is clearly evidenced, yielding trajectories globally parallel with respect to the P3HT chain backbone. At 1500 K, the Li^+ trajectories deviate from globally parallel toward perpendicular

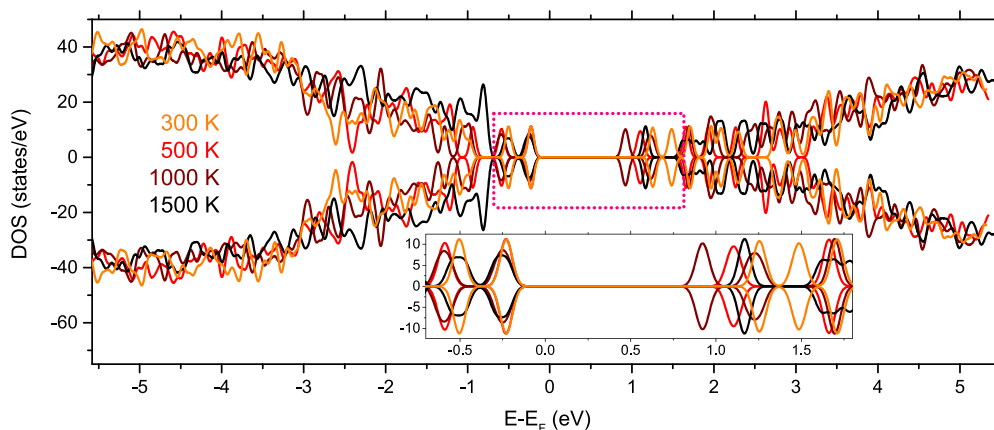


Figure 2. DOS as a function of energy for the stabilized structures at different temperatures ($T = 300$ – 1500 K). The inset shows the DOS near the Fermi level to identify the HOMO(−1), HOMO, LUMO, and LUMO(+1) states.

respect to the P3HT chain backbone until getting partially “stacked” in-between P3HT chain backbones. The formation of the lithium-to-thiophene bond was already envisaged for a simplified system comprising the LiTFSI dopant and a single P3HT chain favoring dopant fixation, while electronic doping through the sulfonic groups takes place, particularly for the P3HT amorphous region.³² It is quite interesting to note that the Li^+ trajectories are globally parallel with respect to P3HT chain backbones for $T \leq 1000$ K and deviate to globally perpendicular respect to the P3HT chain backbone for $T > 1000$ K. This is mainly due to the prevalence in the competition between the relatively high affinity of lithium ions for DME molecules (until 1000 K) and for the thiophene rings via $\text{Li}^+ \cdots \pi$ interactions (particularly evidenced at 1500 K), as depicted in Figure 1c.

3.2. Electronic Transport. The AIMD calculation total energy for the system at 300, 500, 1000, and 1500 K showed an expected increment on the thermal fluctuations with increasing temperature, as depicted in Figure S3. The DOS calculated for the stabilized structures obtained at the longest AIMD simulation times reached in this report ($t \sim 4000$ fs) is depicted in Figure 2. From the DOS analysis, many useful parameters can be obtained to evaluate electronic transport. For instance, the semiconductor gap energy (E_{gap}) can be simply obtained using the following equation:

$$E_{\text{gap}} = E_{\text{LUMO}} - E_{\text{HOMO}} \quad (4)$$

The DOS shows an expected p -type semiconductor behavior with the typical feature of the bipolaron configuration (i.e., lack of unpaired electrons because of the complete balance of spins), as also observed theoretically for periodic systems with a relatively high level of doping using explicit chlorine atoms with dopant:thiophene ratios of 1:4 and 1:8.^{57,58} The DOS also allows for the estimation of the hole (h^+) and electron (e^-) carrier concentration, which can be expressed using the following equations:

$$[h^+] = N_V e^{(E_V - E_F)/k_B T} \quad (\text{for } h^+) \quad (5)$$

$$[e^-] = N_C e^{(E_F - E_C)/k_B T} \quad (\text{for } e^-) \quad (6)$$

with E_F being the Fermi energy, E_V being the top valence-band energy, E_C being the bottom conduction band energy, N_V and N_C being the effective DOS of the valence and conduction bands, respectively. The estimated carrier's concentration

increases from $[h^+] \sim 10^{19}$ to $10^{22}/\text{cm}^3$ and from $[e^-] \sim 10^1$ to $10^{18}/\text{cm}^3$ when the temperature increases from 300 to 1500 K, respectively, corroborating that the electronic transport is expected to be mostly due to hole carriers. Our estimated hole carrier concentrations are in good agreement with those reported for P3HT in the literature.⁵⁹

Considering that our crystalline model includes the presence of an explicit large dopant inducing high disorders and that we will focus on the above-room temperature regime, a charge partial localization scenario is reasonable to consider the use of the semiclassical Marcus theory to model the electronic transport.⁶⁰ Here, the hopping probability for each carrier per unit time is defined as the charge-transfer rate (k_{CT}), which can be expressed as follows:

$$k_{CT} = \frac{2\pi}{\hbar} J^2 \sqrt{\frac{1}{4\lambda\pi k_B T}} e^{[-(\Delta G^0 + \lambda)^2 / 4\lambda k_B T]} \quad (7)$$

with k_B being the Boltzmann constant, T being the temperature, J being the transfer integral associated with the energy splitting of the electronic level because of segment interaction, λ being the reorientation energy, and ΔG^0 being the difference in the Gibbs free energy of the system before and after the charge-transfer process. The later terms typically follow $\Delta G^0 < \lambda$, and thus, ΔG^0 is commonly neglected.^{61–64} The transfer integral (J) can be obtained from the DOS analysis using the following Koopman's theorem

$$2J_{h^+} = E_{\text{HOMO}} - E_{\text{HOMO}-1} \quad (\text{for } h^+) \quad (8)$$

$$2J_{e^-} = E_{\text{LUMO}+1} - E_{\text{LUMO}} \quad (\text{for } e^-) \quad (9)$$

for hole (h^+) and electron (e^-) carriers, respectively.⁶⁵ The transfer integral values obtained for our explicitly LiTFSI-doped P3HT-stabilized crystalline systems shown in Table 2 are similar to those reported for one-hole and one-electron-charged thiophene oligomers⁶³ and periodic systems.⁶⁵ According to our calculations, both J_{h^+} and J_{e^-} showed comparable values between each other, and no clear trend was observed with further increasing temperature. However, focusing on the predominant hole carriers, J_{h^+} exhibits an increase from 0.14 to 0.19 eV when the temperature increases from 300 to 500 K, but then progressively decreases to 0.12 eV at 1500 K, as depicted in Table 2. It is well known that even a slight mismatch (<1 Å) between thiophene rings comprising adjacent segments can drastically modify the transfer integral

Table 2. Most Relevant Parameters Obtained from Electronic Transport Calculations Using the Semiclassical Marcus Theory Approach at Different Temperatures^a

<i>T</i> (K)	300	500	1000	1500
<i>E</i> _{gap} (eV)	1.49	1.33	1.16	1.42
[<i>h</i> ⁺] (10 ²⁰ /eV cm ³)	0.07	2.66	29.1	80.9
[<i>e</i> [−]] (10 ²⁰ /eV cm ³)	~0	~0	0.006	0.021
2 <i>J</i> _{<i>h</i>+} (eV)	0.28	0.38	0.35	0.25
2 <i>J</i> _{<i>e</i>−} (eV)	0.23	0.56	0.30	0.47
<i>μ</i> _{<i>h</i>+} (10 ^{−3} cm ² /V s)	23.5	1084	6464	4863
<i>μ</i> _{<i>e</i>−} (10 ^{−3} cm ² /V s)	~0	0.084	22.3	297
<i>σ</i> (S/cm)	0.028	46.2	3014	6303

^aMobilities were estimated using that the reorganization energies calculated for isolated components in the vacuum, including the LiTFSI dopant contribution and those calculated for P3HT by Oliveira and Lavarda.⁶⁶

values associated with holes and electrons.⁶³ In our case, large thermal fluctuations observed at 1500 K are probably the predominant factor affecting the mismatch between thiophene rings, but we will discuss this further along with the manuscript. The reorientation energy (*λ*) associated with the charge transfer between two charge localization sites is defined as the energy difference associated with the deformation of the intramolecular coordinates (inner-sphere, *λ*_{in}) and the surrounding media (outer-sphere, *λ*_{out}). Considering that the outer-sphere contribution is non-negligible but rather small in crystalline systems,⁶⁰ we will just focus on the inner-sphere contribution. Hence, considering that the charge-transfer process in the explicitly doped case is mediated by the redox process between P3HT and LiTFSI, we estimated the *λ*_{in} parameter as follows:

$$\lambda_{in,h+} = E_{P3HT+}(0) - E_{P3HT+}(+) + E_{LiTFSI-}(0) - E_{LiTFSI-}(-) \text{ (for } h^{+}) \quad (10)$$

$$\lambda_{in,e-} = E_{P3HT-}(0) - E_{P3HT-}(-) + E_{LiTFSI+}(0) - E_{LiTFSI+}(+) \text{ (for } e^{-}) \quad (11)$$

where *E*_{P3HT+/(−)}(0) and *E*_{P3HT+/(−)}(+/(−)) are the energy for one-hole/electron-charged P3HT in its neutral optimized geometry

and one-hole/electron charged geometry, respectively.⁶³ The analogous definition applies for the LiTFSI dopant, where *E*_{LiTFSI−/(+)}(0) and *E*_{LiTFSI−/(+)}(−/(+)) are the energy for one-electron/hole-charged P3HT in its neutral optimized geometry and one-electron/hole-charged geometry, respectively.⁶³ For simplicity, for the P3HT contribution, we use the inner-sphere reorientation energy values *λ*_{in,*h*+}(P3HT) = 0.9 eV and *λ*_{in,*e*−}(P3HT) = 1.1 eV, calculated by Oliveira and Lavarda⁶⁶ and, for the LiTFSI dopant, we use our calculated inner-sphere reorientation energy values at the same level of theory in the gas phase. Thus, the resulting total inner-sphere reorientation energy values are *λ*_{in,*h*+}(P3HT-LiTFSI) = 1.0 eV and *λ*_{in,*e*−}(P3HT-LiTFSI) = 2.7 eV, evidencing that the LiTFSI dopant strongly contributes to the total reorganization energy.

Then, each carrier's mobility (*μ*) considering uncorrelated hopping processes can be obtained via the Einstein relation given as follows:

$$\mu = \frac{ea^2}{k_B T} k_{CT} \quad (12)$$

with *e* being the elementary charge and *a* being the hopping transport length defined by our fixed localization periodic distance ~1.6 nm, in agreement with those typical values observed in the literature.⁶⁷ Finally, the total conductivity (*σ*) considering the contribution of both carriers can be obtained using the following equation:

$$\sigma = e([h^{+}]\mu_{h+} + [e^{-}]\mu_{e-}) \quad (13)$$

with *μ*_{*h*+} and *μ*_{*e*−} being the hole and electron carrier's mobility, respectively. These values are depicted in Table 2, and as it is observed, they drastically increase from 10^{−2} toward 10³ S cm^{−1} when the temperature increases from 300 to 1000 K, while keep increasing but with a slower rate above 1000 K. Our electronic conductivity calculated at room temperature is well above those reported experimentally using the LiTFSI dopant in P3HT-PEO,³⁵ P3MEET, P3MEEMT,³⁷ and P3APPT systems.³⁹ However, in the later experimental reports, the electronic conductivities slightly increase or remain constant from *T* ~ 300 to 400 K,^{35,39} while our calculations indicate a three-order magnitude increase from *T* ~ 300 to 500 K. Here, it is important to remark that our calculations are strictly valid for a full crystalline system, and the experimental conductivities

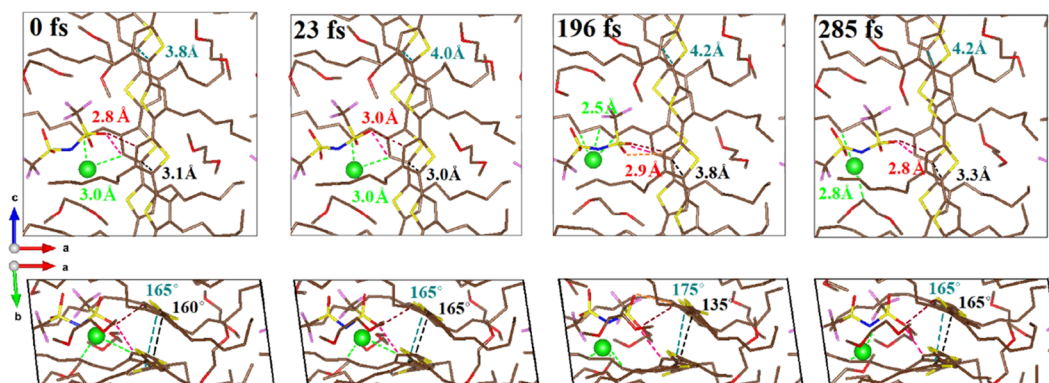


Figure 3. Selected frames to monitor the evolution with simulation times (*t* < 300 fs, *T* = 500 K) for selected nearest P3HT and P3HT' chain doping distances {*d*[C_{6,7}---O_{6,7}(TFSI[−])]} (represented with dashed red lines), selected nearest lithium-to-carbon atom distances {*d*[C_#(P3HT)---Li⁺]} (represented with dashed green lines), selected P3HT-to-P3HT' backbone interchain distance {*d*[C_#---C_#]} (*#* = *#*' = 5 and *#* = *#*' = 16 represented with dashed black and light blue lines, respectively) and selected torsion angles between adjacent thiophene rings of the P3HT chain {*φ* [Ring(*i* − *i* + 1)]} for *i* = 1 (values depicted in black) and *i* = 3 (values depicted in dark cyan).

are expected to be lower because of the contribution of less electronic-conducting amorphous regions. Furthermore, these calculations were obtained for the AIMD “stabilized” regime ($t \sim 4000$ fs) and, to this point in the manuscript, only represent a simplified “static” picture of a much more complex scenario that we will be discussed further in the following sections.

3.3. Electronic Transport Static and Dynamic Disorders. It is well known that the energy disorder and electrostatic effects yield to a broadening of the DOS for organic semiconductors [particularly the highest occupied molecular orbital (HOMO) level] but also for the explicit dopant (particularly the LUMO level), thus playing an important role in the hole carrier’s transport.^{18,68,69} Furthermore, it has been also recently shown that there is even a larger contribution to the total conformational disorder because of dynamic effects, which has the potential to hinder charge transport.^{4,69,70} For instance, machine-learning studies have recently shown that the HOMO energy dynamic and total disorder can be well-described with a Gaussian distribution, while the static disorder is often slightly asymmetric.⁷⁰ However, the dynamic disorder associated with other parameters relevant to the electronic transport in explicitly doped conducting polymers remained unexplored yet. Thus, in order to evaluate some dynamic effects on the charge transport, selected frames to monitor the evolution with simulation times ($t < 300$ fs, $T = 500$ K) are shown in Figure 3. At the first inspection, these selected frames evidence that the distance from the oxygen atoms of the LiTFSI sulfonic groups to the nearest carbon atoms of the thiophene ring for a given P3HT chain (that we will define later as the “doping” distances) varies slightly in the 2.8–3.0 Å range. It can be also evidenced that the lithium-ion dissociation and further location near the hexyl side chains and DME molecules vicinities only slightly modifies the TFSI[−] “doping” position. There is also a notorious difference in the P3HT-to-P3HT’ interchain distances, not only at different simulation times but also if measured near the dopant or far from it. Furthermore, the torsion angles between adjacent thiophene rings of a given P3HT chain also show deviations from the typical antiparallel conformation not only at different simulation times but also considering different positions with respect to the dopant location.

Thus, in the following lines, we will focus on discussing these dynamic features and their effect on the charge carrier transport.

3.3.1. Doping and Charge-Transfer Complex Dynamics. First, we will focus our attention on the “doping” distance dynamics, which can also be referred to as the charge-transfer complex dynamics. The typical chemical doping mechanism in organic semiconductors consists of the ionization of the dopant with the donation of a hole to the host, and then, the electron–hole pair is further separated creating a free hole.^{15–18} Particularly, the charge carrier formation in P3HT via the chemical doping mechanism with the LiTFSI dopant is quite interesting, involving its simultaneous fixation through lithium-to-thiophene bonding, while the doping process itself is mostly through the sulfonic groups located at “bonding distances” from thiophene rings, at least for a single P3HT chain in vacuum, as predicted recently by our research group.³² In the latter case, the vacuum space allows for the formation of a lithium-to-thiophene $\text{Li}^+ \cdots \pi$ bond in a typical out-of-plane fashion and can be useful to understand the doping process mainly in solution or at the amorphous region of the P3HT

polymeric structure.³² However, the doping mechanism in crystalline P3HT is quite different as the proximity of parallel polymer backbones do not favor the formation of the lithium-to-thiophene $\text{Li}^+ \cdots \pi$ bond in an out-of-plane fashion, but instead, a $\text{Li}^+ \cdots \pi$ bond in an in-plane fashion is formed with a particular thiophene carbon atom (named C6’), as depicted in Figure 4a,b. The particular P3HT chain, which allows for the

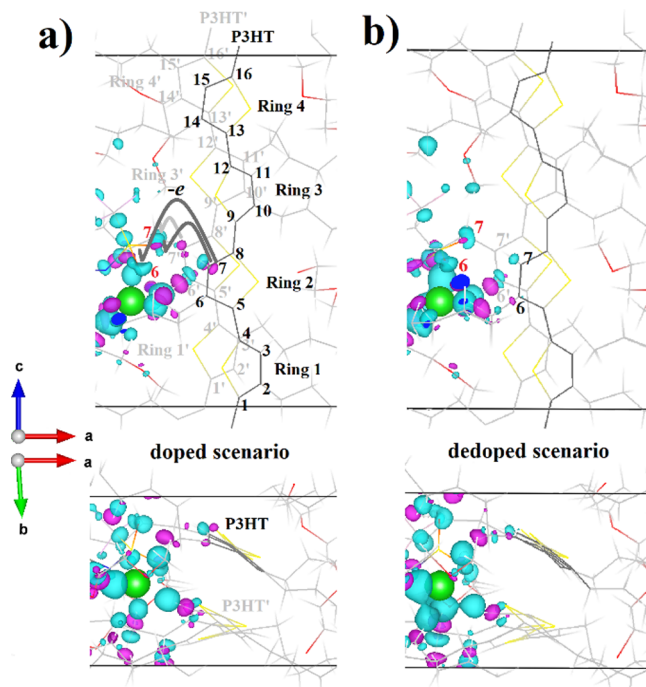


Figure 4. Differential electronic density gain (cyan) and loss (magenta) for (a) $t = 0$ and (b) 23 fs at $T = 500$ K. The doping zone is marked with a curved arrow for clarity, showing the TFSI[−] bidentate sulfonate doping of the P3HT-chain (involving C7---O6 and C7---O7 atoms) and the TFSI[−] monodentate sulfonate doping of the P3HT'-chain (involving C7'---O7 atoms). Note the persistence of the Li^+ and P3HT'-chain bonding (particularly with the C6' atom but also interacting with its corresponding hexyl moiety) for both simulation times. The labeling of P3HT atoms, rings, and chains is also presented.

formation of this lithium-to-thiophene bond will be named P3HT' from now on, as labeled in Figure 4a. Then, the sulfonic group whose oxygen atoms are located at “bonding” distances from the thiophene rings of both chains (named O6 and O7) allows for the electronic charge transfer from thiophene rings of both P3HT and P3HT' chains (particularly with those carbon atoms named C7 and C7'), as depicted in Figure 4a. To learn more about the doping process, we define the doping distance parameter as the distance between the nearest carbon atoms (from P3HT and P3HT' chains) and the oxygen atoms (from the sulfonic doping group). The doping distance for the selected P3HT and P3HT' carbon atom (C7 and C6') and the nearest LiTFSI oxygen atom (O6 and O7) $\{d[\text{C}_{6,7} \cdots \text{O}_{6,7}]\}$ dependence with the simulation time is plotted in Figure 5a. It is interesting to note that the LiTFSI interaction with both chains is quite different and can be considered as monodentate-like for the P3HT' chain (C6'---O6 distance oscillates between 2.4–3.4 Å, but C6'---O7 distance is larger than 4.5 Å) and bidentate-like for the P3HT chain (both C7---O6 and C7---O7 distances oscillate between 2.4–3.4 Å).

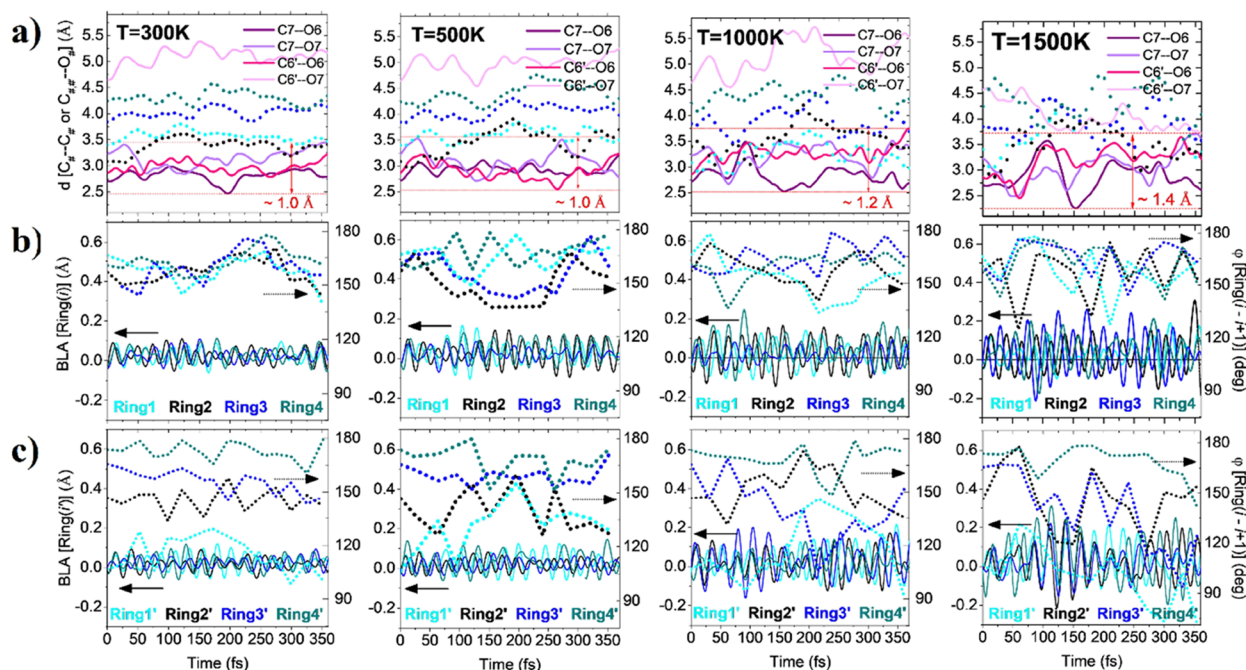


Figure 5. (a) Doping distances between the selected carbon atoms from P3HT (or P3HT') and oxygen atoms from LiTFSI [$d(C_{6,7} \cdots O_{6,7})$] (solid lines) and selected interchain P3HT to P3HT' backbone distances [$d(C_{\#} \cdots C_{\#})$ for $\# = 5$ (black), 9 (blue), 13 (dark cyan), and 1 (cyan)] represented with dotted lines versus simulation time ($t < 350$ fs) at different temperatures ($T = 300$ – 1500 K). (b) Bond length alternation for P3HT thiophene rings {BLA[Ring(1)] (cyan), BLA[Ring(2)] (black), BLA[Ring(3)] (blue), and BLA[Ring(4)] (dark cyan)} represented with solid lines and torsion angles between adjacent rings for the P3HT chain [ϕ [Ring(1-2)] (black), ϕ [Ring(2-3)] (blue), ϕ [Ring(3-4)] (dark cyan), and ϕ [Ring(4-1)] (cyan)] represented with dotted lines versus simulation time ($t < 350$ fs) at different temperatures ($T = 300$ – 1500 K). (c) Bond length alternation for P3HT different thiophene rings {BLA[Ring(1')] (cyan), BLA[Ring(2')] (black), BLA[Ring(3')] (blue), and BLA[Ring(4')] (dark cyan)} represented with solid lines and torsion angles of adjacent rings for the P3HT' chain [ϕ [Ring(1'-2')] (black), ϕ [Ring(2'-3')] (blue), ϕ [Ring(3'-4')] (dark cyan), and ϕ [Ring(4'-1')] (cyan)] represented with dotted lines versus simulation time ($t < 350$ fs) at different temperatures ($T = 300$ – 1500 K).

However, even at temperatures below 500 K, the doping distances oscillate in a quite broad (~ 1.0 Å) range and oscillate even with a larger amplitude for temperatures above 500 K, as depicted in Figure 5a. Thus, it is important to evaluate what are the “effective” doping distances in which the dopant can still be effectively acting as an electronic acceptor. Additional differential electronic density mapping, where the dopant slightly separates from the polymer backbone (e.g., at selected 23 fs simulation time) is depicted in Figure 4b. This suggests that these doping distances above 3.0 Å are less effective in terms of doping but, at the same time, are also favorable to the dissociation of the charge-transfer complex. To quantify these doping dynamic effects, we calculate the global doping distance considering LiTFSI dopant monodentate (with P3HT' chain) and bidentate (with P3HT chain) bonding and its corresponding standard deviation (shown in parenthesis) assuming a normal distribution yielding 2.99(0.10), 3.01(0.10), 3.10(0.12), and 3.13(0.21) Å for $T = 300$, 500, 1000, and 1500 K, respectively. The distribution of the global “doping” distances for each temperature is shown in Figure S4, where it is important to note that they exhibit a quite asymmetric feature, particularly at 1500 K, but not considered for our rough estimation of the doping dynamic disorder. Our results suggest that when the temperature increases above 1000 K, the global doping distance is less effective and the doping dynamic disorder also increases. Nonetheless, the presence of these short de-doping periods and a small “doping” dynamic disorder can be also favorable for electronic transport as it also represents a momentary charge-transfer complex separation

favoring the free charge carrier mobility along the polymer chains.^{15–18} However, we will discuss this further in terms of the time-scale of the electron–phonon coupling dynamic processes in the final part of this manuscript.

3.3.2. P3HT Interchain and Intrachain Dynamics. Then, the P3HT-to-P3HT' interchain distance for selected atoms [$d(C_{\#} \cdots C_{\#})$] is defined in Figure S5a, and their corresponding plots as a function of simulation time are shown in Figure 5a. It is easy to note a notorious sensibility of this parameter with the location of the dopant, where $d(C_{\#} \cdots C_{\#})$ near the LiTFSI dopant is ~ 3.2 – 3.5 Å, and far from the dopant is ~ 4.0 – 4.5 Å, considering $T = 300$ K as an example. These notorious differences introduce an exclusive feature to consider when modeling organic semiconductors with explicit dopants, which is directly related to the interchain-transfer integral. According to the literature, J_{h+} values could be altered from ~ 0.18 to ~ 0.05 eV when the interchain distance increases from ~ 3.3 to 4.3 Å.⁶⁵ Thus, without considering dynamic effects and only because of the presence of the dopant, the interchain transfer integral “static” disorder can be roughly estimated to be in the ~ 0.1 – 0.2 eV range for room temperature but further increases with increasing temperatures. Then, to consider the global “dynamic” oscillations for each temperature, we calculate the mean interchain distances and its corresponding standard deviation (shown in parenthesis), assuming a normal distribution yielding 3.83(0.07), 3.88(0.12), 3.76(0.16), and 3.71(0.26) Å for $T = 300$, 500, 1000, and 1500 K, respectively. Hence, this suggests that the interchain transfer integral “dynamic” disorder is small at room temperature and exhibits a

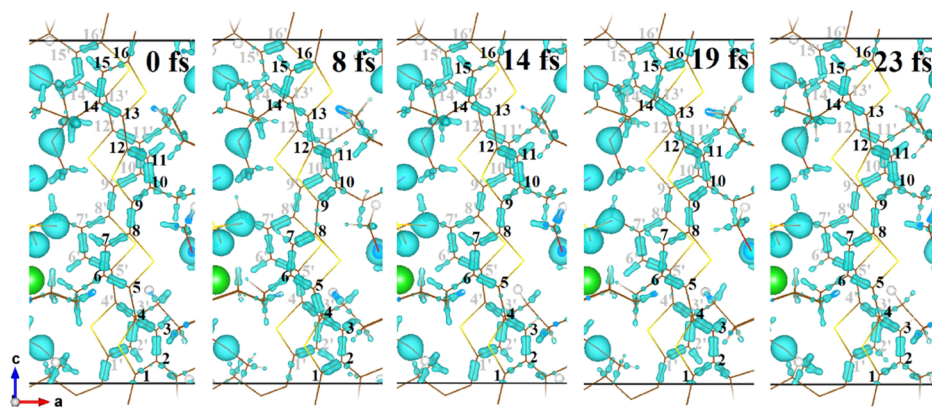


Figure 6. Selected frames selected to monitor the electronic density mapping evolution with simulation times ($t < 25$ fs, $T = 500$ K).

notorious increase with increasing temperatures, but always below the ~ 40 meV range, according to the reference values reported by Lan and Huang⁶⁵. The distribution of the $d(\text{C}\#-\text{C}\#)$ distances, distinguishing the different selected chain positions, is shown in Figure S6, showing that the dynamic disorder is also sensible to this parameter or, in other words, to the proximity to the dopant. The torsion angles between adjacent thiophene rings for P3HT $\{\varphi[\text{Ring}(i-i+1)]\}$ and P3HT' $\{\varphi[\text{Ring}(i'-i'+1)]\}$ chains are shown in Figure 5b,c, respectively. The φ values observed in these graphs correspond to dihedral angles between consecutive thiophene rings, as defined in Figure S5b.

In the case of the P3HT chain, and particularly at temperatures below 500 K, it is interesting to note that the torsion angles follows a relatively well-defined oscillation between $\varphi \sim 170$ and 150° with an associated period of ~ 300 fs, which can be associated to the “slow” phonon mode (~ 0.014 eV or ~ 110 cm^{-1}) assigned to the torsion of thiophene–thiophene in the P3HT chain.^{71,72} However, above 500 K, the φ values oscillate randomly and with larger amplitudes, yielding to the complete loss of the “slow” phonon mode of the P3HT chain, as depicted in Figure 5b. Furthermore, it can be observed that there is a higher degree of torsion in the P3HT' chain in comparison with the P3HT chain for all temperatures. This is probably due to the predominant proximity effects of the LiTFSI dopant with the P3HT' chain rather than with the P3HT chain. It can be noted that φ values for the P3HT' chain are more or less constant and time-independent, with the particularity of being $\varphi \sim 170^\circ$ for the thiophene rings far from the LiTFSI dopant, for example, $\varphi[\text{Ring}(3'-4')]$, and $\varphi \sim 120^\circ$ for the thiophene rings in the proximities of the LiTFSI dopant, for example, $\varphi[\text{Ring}(4'-1')]$ and $\varphi[\text{Ring}(1'-2')]$, as depicted in Figure 5c. This suggests that the presence of the LiTFSI dopant could strongly affect the electronic transport of the particular chain where it is bonded. It is also clear that the disorder of these torsion angles also introduces other exclusive features to consider when modeling organic semiconductors with explicit dopants, particularly concerning the intrachain transfer integral values. According to the literature, J_{h+} values could be altered from ~ 0.75 to ~ 0.42 eV when the intrachain torsion angles decrease from ~ 170 to 120° , considering energy values reported in the literature.⁶⁵ Thus, in our case, the intrachain transfer integral static disorder can be small for the P3HT chain but quite large for the P3HT' chain (~ 0.3 – 0.4 eV) at room temperature and, in both cases, increases even further

with increasing temperatures. Furthermore, if we now consider the dynamic oscillations of these values, the intrachain transfer integral dynamic disorder trend is the opposite, probably in relation to the larger flexibility to the rotation of P3HT compared to P3HT'. However, here, it is important to note that these dynamic effects consist of well-defined (e.g., phonons) and random dynamic oscillations. Hence, in order to roughly quantify this effect, the torsion angles in the “slow” phonon mode for the P3HT chain oscillate between ~ 170 and 150° and, hence, the corresponding dynamic disorder of these phonons is ~ 0.1 eV, while the random oscillations are in the order of a few meV at 300 K, according to the reference values reported by Lan and Huang⁶⁵. However, P3HT' chain oscillation is purely due to random effects and exhibits a much larger disorder mostly because of the static disorder, as discussed above. It is also important to mention that, for all cases, the random dynamic disorder drastically increases with increasing temperatures.

Bond length alternation for thiophene rings comprising P3HT $\{\text{BLA}[\text{Ring}(i)]\}$ and P3HT' $\{\text{BLA}[\text{Ring}(i')]\}$ chains as a function of the simulation time is shown in Figure 5b,c, respectively. The positive and negative BLA values observed in these graphs are associated with mostly aromatic and quinoid configurations of thiophene rings, respectively, as defined in Figure S7. The oscillations between aromatic and quinoid configurations are well-defined and evidenced for each thiophene ring comprising both P3HT and P3HT' chains. It is important to remark that, regardless of the chain or the thiophene ring, BLAs oscillate within a period of approximately 22–24 fs, which can be associated with the “fast” phonon mode (~ 0.18 eV or ~ 1450 cm^{-1}) assigned to the thiophene C–C stretching in the P3HT chain.

The transition between mostly quinoid to mostly aromatic configurations in a given P3HT chain takes ~ 10 – 12 fs, and the oscillations of consecutive thiophene rings are out of phase by ~ 3 – 5 fs. These BLA oscillation periods are practically independent of the temperature, but their amplitude increases with increasing temperature. The low amplitudes of BLA oscillations at 300 K are in agreement with a less-localized scenario, and the increment of these amplitudes with temperature can be related to the increment in the localization of the system. It is also important to note that although the “fast” phonon is a process that involves an apparent shorter time scale than most disorder effects discussed above, it could be nonetheless affected by the doping dynamic disorder which

is characterized by doping–dedoping oscillations within a ~ 20 –40 fs.

3.3.3. P3HT Electron–Phonon Coupling Dynamics. To deepen the analysis of the electron–phonon coupling, we calculate the electronic density mapping evolution with simulation times within the range of the fast phonon mode ($t < 25$ fs, $T = 500$ K) for both P3HT and P3HT' chains, as depicted in Figure 6. For instance, it can be clearly observed that the electronic density of the C4–C5 bond is negligible at $t = 0$ fs (single bonding) and enhances at $t = 8$ fs (double bonding), while that associated with the C8–C9 bond is enhanced at $t = 0$ fs (double bonding) and vanishes at $t = 8$ fs (single bonding), and similar features can be evidenced for C12–C13 and C15–C16 bonds. A similar feature can be also observed for the P3HT' chain, and in both cases, this feature is also in strong agreement with the BLA oscillations observed for each ring at $t < 25$ fs and strongly supports the electron–phonon scenario. To add more quantitative value to the discussion, we also plot the thiophene carbon atom ($C_{\#}$) net charge and the carbon-to-carbon ($C_{\#}-C_{\#+1}$) overlap population for both P3HT and P3HT' chains, as shown in Figure 7a,b. From the carbon atom net charges analysis, the

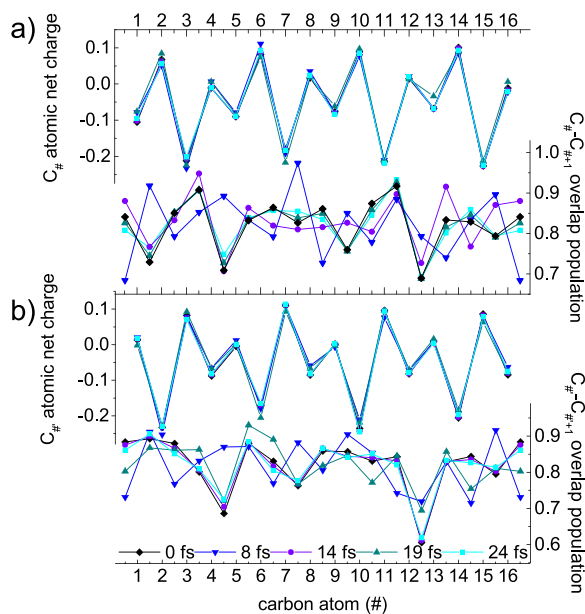


Figure 7. Carbon atomic net charge and bond overlap population corresponding to (a) P3HT- and (b) P3HT'-chains at selected simulation times ($t < 30$ fs, $T = 500$ K). References for carbon atom indexes are shown in Figure 4.

more salient feature is that the hexyl-substituted thiophene carbon atoms (i.e., $\# = 2, 6, 10, 14$ and $\# = 3, 7, 11, 15$) are slightly positive ($\sim +0.1e$) and the thiophene adjacent carbon atoms (i.e., $\# = 3, 7, 11, 15$ and $\# = 2, 6, 10, 14$) are slightly negative ($\sim -0.2e$), remaining practically unchanged in both cases for the whole simulation time, as shown in Figure 7a,b. Here, it is important to remark that these positive and negative atomic net charge values estimated using the Bader approach could be more usefully interpreted as electronic-depleted and electronic-rich carbon atoms, respectively. Hence, the salient feature is that although the charge is partially delocalized in the doped P3HT and P3HT' chains, at least for the <25 fs simulation times, there is a slight preference for those carbon atoms comprising the thiophene rings and directly bonded to

the hexyl substituent to be electronic-depleted, as already observed for our P3HT single-chain approach.³² However, to gain more insight into the electronic charge coupling to the “fast” phonon mode, we also calculate the electronic overlap population for the polymer backbone atom pairs ($C_{\#}-C_{\#+1}$) at selected simulation times.

For both P3HT and P3HT' chains, the overlap population in the P3HT chain suggests the progressive variation of the carbon-to-carbon bonding order in the $t = 0$ –23 fs simulation time, as can be easily correlated with the electronic density mapping discussed above. Finally, to discuss the possible effect of the static and dynamic disorder on the electron–phonon coupling, particularly that involving the “fast” phonon mode, it is important to estimate the maximum charge-transfer rates under resonance conditions.⁷⁰ The maximum hopping rates obtained by evaluating the Marcus prefactor can be used to estimate the residence times ($\tau = 1/k_{\text{ct-prefactor}}$), yielding $\tau = 3.1, 2.2, 3.6,$ and 8.7 fs for 300, 500, 1000, and 1500 K, respectively. Thus, at least considering this semiclassical approach, the charge-transfer residence times are apparently lower than those associated with the “fast” phonon mode (~ 23 fs) and the “doping” dynamic disorder (~ 20 –40 fs), and clearly faster than other sources of the dynamic disorder discussed above. Hence, these charge-transfer processes are faster enough to assure the charge carrier transport but the “fast” phonon dynamics are comparable to those observed for the “doping” dynamic disorder, and thus, the charge carriers are effectively subjected to high disorders, which is expected to hinder the electronic transport, particularly with increasing temperatures.

4. CONCLUSIONS

Herein, we present AIMD calculations shedding some light on the mixed ionic–electronic transport mechanism for P3HT using the explicit LiTFSI dopant and the DME additive. Our lithium ionic conductivities were in excellent agreement with those reported experimentally ($\sim 10^{-4}$ S cm^{-1}) close above room temperature for similar systems, exhibiting an expected increase with temperature. Our electronic conductivities also revealed relatively high values ($\sim 10^{-2}$ – 10^{-3} S cm^{-1}) at room temperature compared with those reported experimentally but also expected considering that our system is fully crystalline. We also conclude that the inclusion of the explicit dopant in our calculations yielded to slightly higher transfer integral (J) values (~ 0.12 – 0.29 eV), but reorientation energies (λ) showed a notorious increase (up to ~ 1.0 eV for hole carriers) compared to those reported for unexplicit doped systems. Furthermore, we also introduce the role of the explicit dopant in the “effective” doping distances and the P3HT inter- and intrachain distance, together with their associated static and dynamic disorder effects. Finally, we analyze the P3HT electron–phonon coupling dynamics discussed in terms of the whole disorder parameters introduced by the presence of the explicit dopant.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.macromol.1c02009>.

Optimization structures after MD calculations performed on the $2 \times 4 \times 4$ supercell under the NPT ensemble. Density versus simulation time calculated using MD calculations under the NPT ensemble. Energy

(eV) versus simulation time calculated using AIMD calculations for the NVT ensemble. Dynamic disorder for the global “doping” distances considering LiTFSI dopant monodentate (with P3HT’ chain) and bidentate (with P3HT chain) bonding. Dynamic disorder for the global and for selected interchain P3HT to P3HT’ backbone distances. Nomenclature of selected interchain P3HT to P3HT’ backbone distances and selected torsion angles between adjacent rings for P3HT and P3HT’ chains. Nomenclature of the bond length alternation (BLA) for P3HT and P3HT’ chains (PDF)

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Notes

The authors declare no competing financial interest.

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