

Unraveling the Lithium Bis(trifluoromethanesulfonyl)imide (LiTFSI) Doping Mechanism of Regioregular Poly(3-hexylthiophene): Experimental and Theoretical Study

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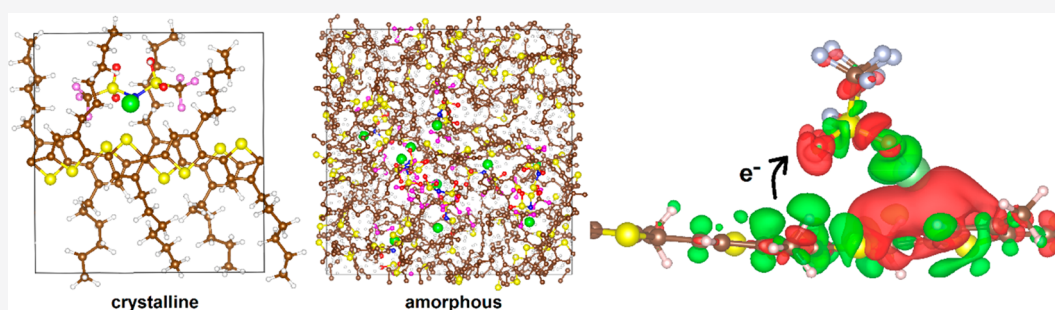
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ABSTRACT: In the present report, we present a combined experimental and theoretical study on the lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) doping mechanism of regioregular poly(3-hexyl thiophene) (P3HT). First, we focus on the effects of LiTFSI doping in both crystalline and amorphous structures of P3HT by performing a complete structural analysis supported by classical molecular dynamics (MD) calculations. Then, we study the effects of LiTFSI doping on electronic properties such as charge transfer and charge transport by performing Raman and impedance spectroscopy, in both cases supported by density of functionals theory (DFT) calculations using periodic boundary conditions. Our structural analysis suggests that the LiTFSI dopant is mainly located in the amorphous region and only a small fraction is located in the crystalline region. In addition, our DFT calculations also suggest that the LiTFSI dopant can effectively act as an electronic acceptor only when it is located in the vicinity of and is accessible to the thiophene rings of P3HT due to the formation of a $\pi\cdots\text{Li}$ chemical bond as an anchoring mechanism, permitting the electronic charge loss of thiophene rings through the sulfonyl groups. A thorough understanding of the LiTFSI doping mechanism of poly(alkyl thiophenes) (P3HT in this particular case) is crucial to elucidating not only the electronic but also the eventual mixed ionic–electronic transport mechanism and its promising properties, particularly as electrodes for lithium ion battery applications.

1. INTRODUCTION

There is growing interest in semiconducting polymers due to their remarkable optoelectronic properties combined with their low-cost solution processability. These properties have attracted the attention of the materials science community with the promise of a wide range of applications.^{1–4} One of the most promising semiconducting polymers is regioregular poly(3-hexylthiophene) (P3HT) due to its crystallization driven by strong intermolecular interactions. This feature defines well-ordered crystalline domains and thus favors efficient charge transport pathways through the polymer structure.⁵ Pursuing an enhancement of the electrical transport of P3HT, the use of molecular dopants such as the typical case of ferric chloride (FeCl_3),^{6,7} 7,7,8,8-tetracyanoquinodimethane (TCNQ) in its different fluorinated derivatives,^{8–10} and bis(trifluoromethanesulfonyl)imide (TFSI) salts has been studied.^{11,12} The particular case of lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) dopant has been of interest

mostly due to its promising mixed electronic–ionic transport properties.^{13,14} Nonetheless, the presence of dopant molecules in relatively high concentration can induce dramatic microstructural changes, such as the appearance of cocrystallized phases,^{9,15} microstructural instabilities, and, in some cases, modifications in the crystallinity of P3HT.^{16–18} However, only a few reports in the literature, and particularly for the TCNQ dopant, discuss the effects on the degree of crystalline or the location of dopants in the crystalline or amorphous polymeric structure. In addition, there are many reports studying the doping mechanism of thiophene oligomers by means of first-

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principles methodology but in most cases by using radical cations (i.e. no explicit dopant) or explicit chlorine (Cl) atoms as the dopant.^{19–22} More recently, theoretical studies on the doping effects of thiophene oligomers with explicit dopants such as TCQN have been reported, revealing very interesting features on the electronic properties.^{23,24} Briefly, this theoretical approach revealed that the configuration of the real dopant molecule gives relevant information on the stability and effectiveness of the doping process, allowing us to understand the experimental results properly.^{23,24} In parallel, there have been first-principles DFT-based calculations studying the charge carrier formation in polythiophene in its periodic form without and with the use of explicit chlorine atoms as doping agents.^{25–27} In the present report, we present a combined experimental and theoretical study on the LiTFSI doping mechanism of regioregular poly(3-hexyl thiophene). First, we focused on the effects of LiTFSI doping in both crystalline and amorphous structures of P3HT by performing a complete structural analysis supported by classical molecular dynamics (MD) calculations. Then, we study the effects of LiTFSI doping on the vibrational and electronic properties such as charge transfer and charge transport by performing Raman and impedance spectroscopy, respectively, in all cases supported by density functional theory (DFT) calculations using periodic boundary conditions.

2. METHODS

2.1. Preparation of the Samples. Regioregular poly(3-hexylthiophene-2,5-diyl) (P3HT) polymer with an average M_w of 50 000–100 000 (CAS: 156074-98-5) and lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) (CAS: 90076-65-6) were provided by Sigma-Aldrich. LiTFSI was previously dried and stored under an argon atmosphere, and LiTFSI-doped P3HT (P3HT-LiTFSI) was prepared by dissolving P3HT and dried LiTFSI with a thiophene/LiTFSI ratio of 10:1 in dry THF with a final concentration of 10 mg/mL. P3HT was also suspended in dry THF with the same concentration (10 mg/mL) to prepare LiTFSI-undoped P3HT as reference. P3HT and P3HT-LiTFSI suspensions were deposited on glass substrates by the spin-coating method after two stages of spinning at 1000 and 2000 rpm for 30 s each, in both cases.

2.2. Characterization of Samples. X-ray diffraction (XRD) was performed using a Rigaku Ultima IV diffractometer with Cu $K\alpha$ radiation, working in Bragg–Brentano configuration, in the $2\theta = 4.00$ – 37.00° range, using steps of 0.02° , with 10 s of integration time per step. The samples were studied by confocal Raman spectroscopy utilizing a WITec Alpha 300-RA with excitation lasers of 532 and 785 nm wavelengths. AC impedance spectroscopy was collected using 100 mV AC voltage amplitude in the 1 Hz–1 MHz frequency range.

2.3. Computational Methods. Theoretical calculations of XRD patterns were performed by means of Debye scattering theory for P3HT and P3HT-LiTFSI atom cluster models in both their crystalline and amorphous systems.²⁸ Prior to XRD pattern calculations, the crystalline periodic cell models were subjected to a full geometry optimization, and the amorphous cell models were subjected to molecular dynamics (MD) calculations in the NVT ensemble starting from 800 K and ending at 300 K in order to erase any structural polymer history, followed by MD calculations under the NPT ensemble and final geometry optimization at 300 K in all cases using the universal force field in LAMMPS.²⁹ Theoretical calculation of

Raman spectra were calculated by means of density functional theory (DFT)^{30,31} using Gaussian 09,³² selecting the B3LYP^{33–36} xc potential at the 6-31++g (d,p) level of theory for a trimer of 3-methyl thiophene [tri(3MT)] and the same trimer with the addition of a chlorine atom [tri(3MT)-Cl]. The electronic structure properties were studied by means of DFT methodology^{30,31} utilizing the VASP code (Vienna ab initio simulation package)^{37–40} for a periodic poly(3-methylthiophene-2,5-diyl) (P3MT) structure with 6 monomers per unit cell, and to study the doping process, we included the bis(trifluoromethane)sulfonimide lithium salt (LiTFSI) molecule in three different positions with respect to the polymer. An analogous structure of P3MT doped with chlorine (P3MT-Cl) was also simulated in this work as a reference for the typical simulation of the doping process. This model consists of a unit cell with $a = 23.5$ Å, $b = 24.4$ Å, $c = 16.0$ Å, $\alpha = 95^\circ$, $\beta = 88^\circ$, $\gamma = 98^\circ$, having a vacuum space of ~ 15 Å aligned along the b and c axes. Pseudopotentials were applied with a plane-wave basis set utilizing the projector-augmented wave (PAW) method,⁴¹ with the generalized gradient approximation (GGA) as the exchange-correlation functional according to Perdew–Burke–Ernzerhof (PBE).^{42,43} The plane wave cutoff energy of 400 eV was employed, and a regular Monkhorst–Pack grid of $8 \times 1 \times 1$ k points was adopted in order to sample the full (reducible) brillouin zone, allowing the convergence of the stress tensor and total forces down to 1 kbar and 0.01 eV/Å, respectively.

3. RESULTS AND DISCUSSION

3.1. Doping Effect on Crystalline and Amorphous Structure. X-ray diffraction (XRD) patterns for P3HT- and LiTFSI-doped P3HT (P3HT-LiTFSI) films are shown in Figure 1a. A typical diffraction peak for pure P3HT polymer films are observed at $2\theta \approx 5.3$, 10.8, and 16.2° , associated with the (100), (200), and (300) Bragg planes, respectively,

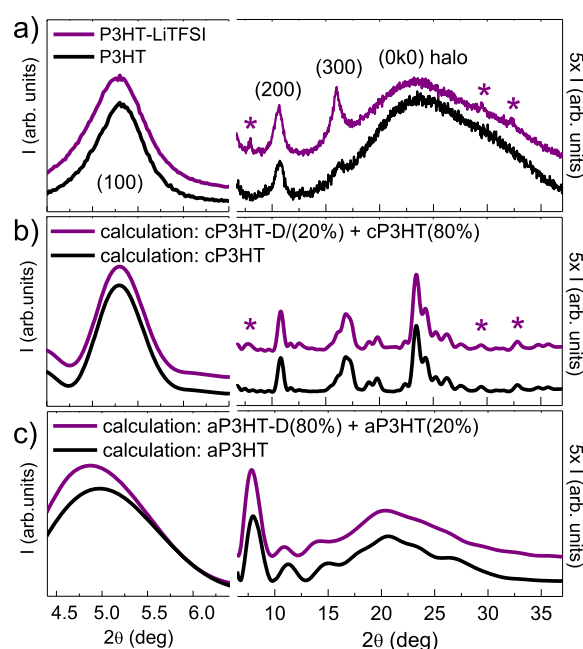


Figure 1. (a) Experimental X-ray diffraction patterns for P3HT and P3HT-LiTFSI. Theoretical calculation of X-ray diffraction patterns for P3HT and P3HT-LiTFSI in their (b) crystalline (cP3HT and cP3HT-D) and (c) amorphous models (aP3HT and aP3HT-D).

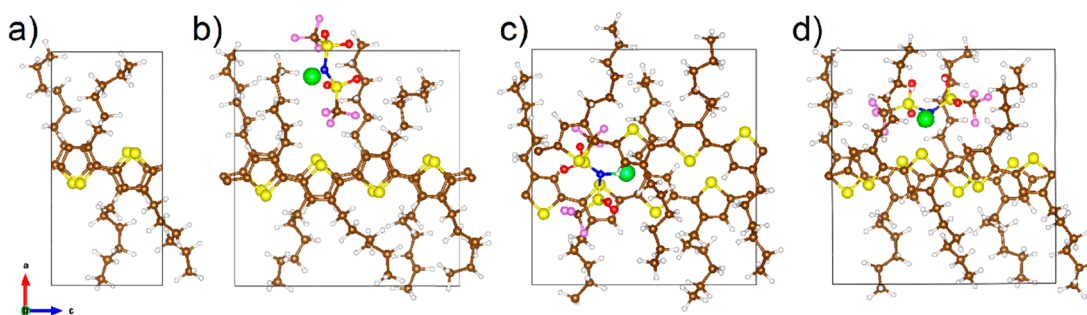


Figure 2. Unit cell for crystalline (a) cP3HT, (b) cP3HT-D/ (LiTFSI dopant parallel to hexyl side chains of P3HT), (c) cP3HT-D// (LiTFSI dopant perpendicular to the thiophene backbone of P3HT), (d) cP3HT-D/// (LiTFSI dopant perpendicular to hexyl side chains and parallel to the thiophene backbone of P3HT) after geometrical optimization. Reference colors for atoms are carbon (brown), sulfur (yellow), hydrogen (white), oxygen (red), nitrogen (blue), fluorine (pink), and lithium (green).

corresponding to the monoclinic structure with the $P2_1/c$ space group.^{44–47} Another typical diffraction feature of P3HT polymer films is a broad halo at $2\theta \approx 22\text{--}25^\circ$, usually associated with the $(0k0)$ disordered Bragg planes.^{6,46–48} The addition of small amounts of LiTFSI dopant in the P3HT polymer diffraction pattern yielded a slight shift of the $(h00)$ Bragg diffraction peaks toward lower 2θ values, suggesting a slight expansion of the unit cell. A slight increase in the (300) Bragg diffraction peak and the emergence of other lower-intensity sharp diffraction peaks at $2\theta \approx 8.0, 29.5$, and 32.3° were observed with LiTFSI addition, suggesting an apparent slight modification of the crystalline structure. It is important to remark that these XRD peaks do not correlate with those associated with isolated LiTFSI crystalline structure, discarding eventual dopant segregation.⁴⁹ The mean crystallite size using the full width at half-maximum (FWHM) for the (100) Bragg diffraction peak yielded a diameter of ~ 15 nm for both the undoped and for doped cases. However, the location of LiTFSI dopant in the crystalline or amorphous region of the P3HT polymer structure has not been thoroughly discussed in the literature yet. For this reason, we performed a theoretical calculation of the X-ray diffraction pattern by means of Debye methodology for full crystalline P3HT (cP3HT) and full crystalline P3HT-LiTFSI (cP3HT-D) systems using in both cases an ~ 15 nm size crystalline cluster to simulate, as close as possible, the experimentally estimated crystallite dimensions. The unit cell for cP3HT was obtained for the phase I polymorph with monoclinic structure ($P2_1/c$ space group),^{50,51} and the unit cell for cP3HT-D was obtained from the same P3HT unit cell but expanded to a $1 \times 2 \times 1$ supercell and transformed to the $P1$ space group to remove translational symmetry. Then, LiTFSI dopant was added to obtain a thiophene/LiTFSI ratio of 8:1, which is similar to the experimental nominal thiophene/LiTFSI $\approx 10:1$ ratio to consider quasi-full doping on the crystalline structure. Prior to the theoretical calculation of XRD patterns, crystalline models comprising cP3HT and cP3HT-D with different LiTFSI dopant positions were subjected to geometry optimization: the optimized structures are shown in Figure 2. The different dopant positions, including no LiTFSI (pure cP3HT), LiTFSI parallel to the hexyl side chains of P3HT (cP3HT-D/), LiTFSI dopant perpendicular to the thiophene backbone of P3HT (cP3HT-D//), and LiTFSI dopant perpendicular to the hexyl side chains and parallel to the thiophene backbone of P3HT (cP3HT-D///), are shown in Figure 2a–d, respectively. It is important to remark that final energies after geometrical optimization for cP3HT, cP3HT-D/, cP3HT-D//, and

cP3HT-D/// were 65.1, 274.5, 478.6, and 365.9 kcal/mol, respectively, suggesting that the more favorable configuration is cP3HT-D/ among all doped configurations. Regarding the calculated XRD pattern, the undoped case (cP3HT) showed very good matching with the P3HT experimental pattern, particularly for those peaks at $2\theta \approx 5.3, 10.8$, and 16.2° ascribed to the (100) , (200) , and (300) Bragg diffraction peaks, as shown in Figure 1b. However, as expected, the broad halo region at $2\theta > 20^\circ$ was not possible to reproduce properly with the crystalline model.

On the other hand, the calculated XRD patterns for cP3HT with LiTFSI dopant at different positions cP3HT-D/, cP3HT-D//, and cP3HT-D/// are shown in Figure S1. As a general trend, all of these cases showed a slight shift of the peak at $2\theta \approx 5.3^\circ$ and splitting of the peak at $2\theta \approx 10.8^\circ$ (toward 11.1 and 12.3°) and the peak at $2\theta \approx 16.2^\circ$ (toward 15.7 and 16.6°) but also the emergence of a strong diffraction peak at $2\theta \approx 7.8^\circ$ (Figure 1b), in good correlation with the position of the peak but with a lower intensity than that observed experimentally. The peak at $2\theta \approx 7.8^\circ$, associated with the (110) Bragg plane, could enhance its intensity probably because of the presence of the LiTFSI dopant in a position that is partially crossed by the (110) Bragg plane in the unit cell. According to this, the intensification of the (110) Bragg diffraction peak could suggest the presence of part of the LiTFSI dopant in the crystalline structure of the doped P3HT polymer. Nonetheless, the relatively high (110) peak intensity in comparison with the experimental XRD data could also suggest that LiTFSI is not fully doping the P3HT crystalline structure. In order to roughly quantify the effect, the sum of weighted 80% cP3HT and 20% cP3HT-D/ patterns is plotted in Figure 1b, showing acceptable similarity with the experimental pattern. However, the broad halo at $2\theta > 20^\circ$ observed experimentally could not be explained with the crystalline models because it is more probably due to the amorphous region of the samples. For this reason, we also study P3HT- and LiTFSI-doped P3HT amorphous models to have better insight on the microstructure of this semicrystalline polymer. P3HT and P3HT-LiTFSI amorphous models (aP3HT and aP3HT-D, respectively) were obtained for two identical amorphous cells with $3 \times 3 \times 3$ nm³ volume containing 2663 atoms, including in one case pure P3HT (aP3HT) and in the other case P3HT with LiTFSI dopant in a thiophene/LiTFSI ratio of 10:1 considering full doping of the amorphous structure (aP3HT-D).

Both aP3HT and aP3HT-D amorphous systems, after the complete optimization routine described in the Computational

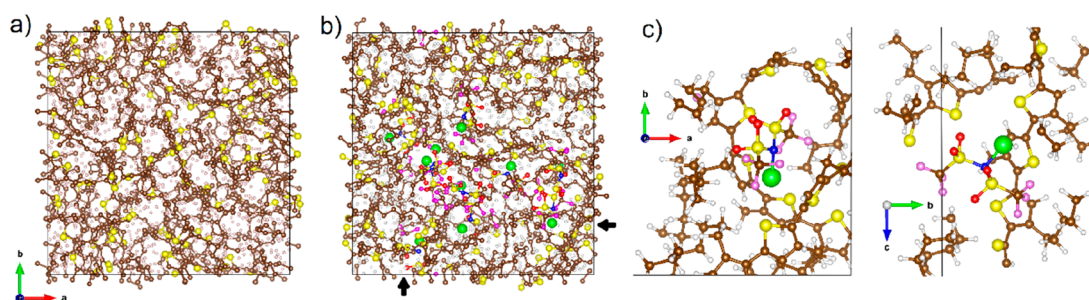


Figure 3. Amorphous cells for (a) aP3HT and (b) aP3HT-D after molecular dynamics and geometrical optimization. (c) Selected LiTFSI dopant regions enlarged for clarity corresponding to those indicated with arrows in panel b. Reference colors for atoms are carbon (brown), sulfur (yellow), hydrogen (white), oxygen (red), nitrogen (blue), fluorine (pink), and lithium (green).

Methods section, ended with a stabilized $1.1\text{--}1.2\text{ g}\cdot\text{cm}^{-3}$ density at 300 K yielding to the optimized structures for aP3HT and aP3HT-D shown in Figure 3a,b, respectively. The calculated XRD pattern for aP3HT showed peaks at $2\theta \approx 5.0, 8.2, 11.2, 15.0^\circ$ and two broad peaks at $2\theta \approx 21$ and 27° , as shown in Figure 1c, in good agreement with experiments and explaining with particularly good accuracy the typical halo observed experimentally at $2\theta > 20^\circ$. In the case of aP3HT-D, the calculated XRD pattern showed a slight shift of all peaks toward lower 2θ values with respect to pure P3HT, also in good correlation with experimental data. In addition, the broad peak at $2\theta \approx 27^\circ$ decreases its intensity when doped, converging to a broad single halo at $2\theta \approx 21^\circ$, as shown in Figure 1c, in good correlation with that observed experimentally for the LiTFSI-doped P3HT case. A close-up view of selected LiTFSI dopant regions of aP3HT-D is shown in Figure 3c, evidencing relatively good homogeneity and the LiTFSI dopant proximity to thiophene groups of P3HT. Thus, we suggest that the addition of LiTFSI dopant could induce the partial loss of short-range coherence between P3HT thiophene-to-thiophene distances, with those related to the (0k0) halo but mainly associated with the amorphous region. On the basis of these results, we suggest that the LiTFSI dopant could be located in both crystalline and amorphous regions of the P3HT polymer, at least for the typical solution preparation methodology in a typical thiophene/LiTFSI 10:1 dopant concentration, such as the one used in this manuscript.

3.2. Doping Effect on Vibrational Properties: Raman Signature. We use a Raman spectroscopy technique to study the LiTFSI doping process on P3HT polymer as evidenced by the subtle modifications of some structural features of P3HT when the doping process takes place. Raman spectra of P3HT and P3HT-LiTFSI samples using two different excitation wavelengths, 785 nm for off-resonance and 532 nm for resonance conditions, are shown in Figure 4a,b, respectively. Although Raman spectra collected under off-resonance conditions showed no significant modifications with the doping process (Figure 4a), Raman spectra collected under resonance conditions showed some differences for P3HT and P3HT-LiTFSI samples (Figure 4b). The enhancement of the relative intensities of some vibrational modes for the resonance conditions is well known. Briefly, the similarity of the excitation energy with the energy needed to promote the molecule to vibrational excited states yields an enhancement of the Raman intensity of those modes mainly due to the activation of the A-term of polarizability. However, it is important to remark that the resonance conditions alter almost equally the Raman signature of both P3HT and P3HT-LiTFSI

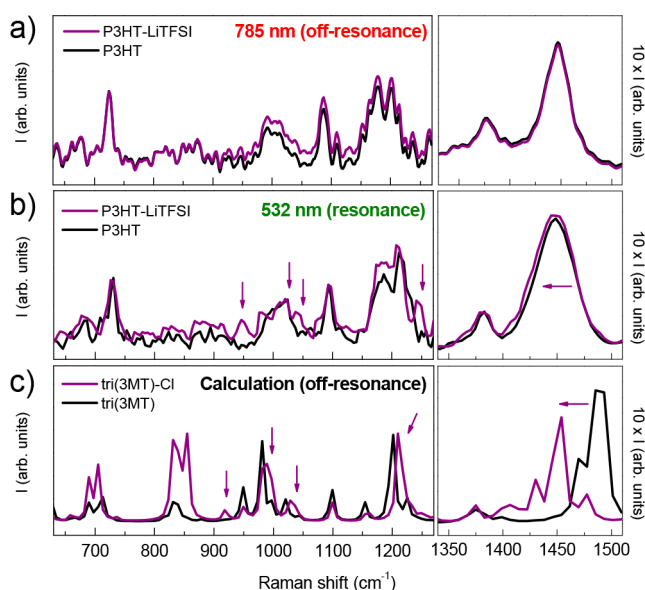


Figure 4. Experimental Raman spectra for P3HT and P3HT-LiTFSI collected under (a) off-resonance (using an 785 nm laser) and (b) resonance (using a 532 nm laser) conditions. (c) Theoretical off-resonance calculation of Raman spectra for undoped [tri(3MT)] and doped [tri(3MT)-Cl] models (Figure S1).

because the absorption energies for both cases are not drastically modified from the typical absorption region of 470–620 nm with a broad maximum from ~ 500 to 560 nm for both the undoped and LiTFSI-doped P3HT.⁵²

The major differences in the resonance Raman spectra with respect to off-resonance Raman spectra for undoped P3HT are a slight enhancement of the relative intensity of some vibrational modes (e.g., the thiophene C–C stretching mode at $\sim 1450\text{ cm}^{-1}$ and thiophene C–H bending modes at ~ 1210 and 1095 cm^{-1}) and other subtle modifications below 1000 cm^{-1} . However, the main modifications in the resonance Raman spectra with respect to off-resonance conditions are observed when the doping process takes place. The typical modification of the Raman spectra for doped P3HT, which has been widely studied in the literature, is mainly focused on the shift of the P3HT C–C stretching mode at 1450 cm^{-1} toward lower wavenumbers when doped, mainly due to the formation of charge carriers in the thiophene rings.^{53,54} However, we also observed subtle modifications in other regions of the Raman spectra (i.e., $900\text{--}1100\text{ cm}^{-1}$), especially for resonance conditions, as shown in Figure 4b. Looking for better knowledge on the doping process and for an explanation of

these other subtle modifications, we calculated Raman spectra by means of DFT calculations (Figure 4c) using a trimer of 3-methyl thiophene [tri(3MT)], and to simulate a one-electron doping process, we added a chlorine atom [tri(3MT)-Cl], as shown in Figure S2a. This relatively small system was chosen to study the short-range effect of the doping process only for Raman calculation purposes to balance the high computational cost. It also important to remark that the doping process in this system is based on a thiophene/Cl ratio of 3:1, which is clearly heavier than that expected for the experimental case with a nominal thiophene/LiTFSI ratio of $\sim 10:1$. However, even beyond the limitations of our model, we observed not only the clear shift of the C–C stretching mode at 1450 cm^{-1} toward lower wavenumbers due to charge carrier formation but also other interesting features in the $\sim 900\text{--}1100\text{ cm}^{-1}$ region, in good agreement with the experimental Raman spectra of P3HT-LiTFSI samples. Specifically, our theoretical Raman calculations shown in Figure 4c showed that the doping process leads to a Raman shift from ~ 1480 to 1450 cm^{-1} for the thiophene C–C backbone stretching mode, no drastic shift from $\sim 1375\text{ cm}^{-1}$ for the thiophene C–C ring stretching mode, a shift from 1200 to 1210 cm^{-1} for the thiophene C–H bending mode of the doped ring, no drastic shifts from 1155 and 1098 cm^{-1} for the thiophene C–H bending mode of undoped rings, a shift from 1020 to 1032 cm^{-1} for the methyl C–C–H bending mode, a shift from 981 to 989 cm^{-1} for the thiophene C–C–C bending mode of the doped ring, no drastic shift from 950 cm^{-1} for the thiophene C–C–C bending mode of undoped rings, an increment of 920 cm^{-1} for the thiophene C–C–C cooperative bending mode, and increments of $830\text{--}850$ and $690\text{--}710\text{ cm}^{-1}$ for the thiophene C–S stretching modes. Most of these features are in good agreement with the experimental Raman spectra of both P3HT and P3HT-LiTFSI samples, suggesting that the doping process took place.

3.3. Doping Effect on Electronic Properties: Charge Transfer. For this purpose, we studied the LiTFSI doping mechanism in P3HT by means of DFT calculations using periodic boundary conditions as a short-range approach to doping a single polymer chain, without considering long-range structural features such as crystallinity and amorphousness. In this model, the system used for calculations is based in a P1 space group cell containing a single poly(3-methyl thiophene) chain (P3MT) with different LiTFSI dopant positions, as shown in Figure 5. In this model, we are assuming a thiophene/LiTFSI ratio of 6:1, which is close to a nominal thiophene/LiTFSI ratio of $\sim 10:1$, to balance the computational cost of using the complete LiTFSI dopant molecule. It is important to remark that an identical model but using a chlorine (Cl) atom as a dopant instead of a LiTFSI molecule was also calculated (named P3MT-Cl) as a reference to a typical one-electron doping process with a small atom such as chlorine. The structure of P3MT-Cl after optimization is shown in Figure S2b, and both the backbone and thiophene ring carbon-to-carbon bond alternation lengths are shown in Figure S3a. The major electronic charge loss is located at the thiophene carbon atom C10, near the chlorine dopant, but it also showed a certain localization at thiophene carbon atoms C3, C7, C11, C15, C19, and C23 (all carbon atoms were assigned, as can be seen in Figure 5), and those bonded to the alkyl substituent, as shown in Figure S3b. In addition, the major magnetic moment is mainly located at thiophene carbon atom C9, in the same thiophene ring where the charge is

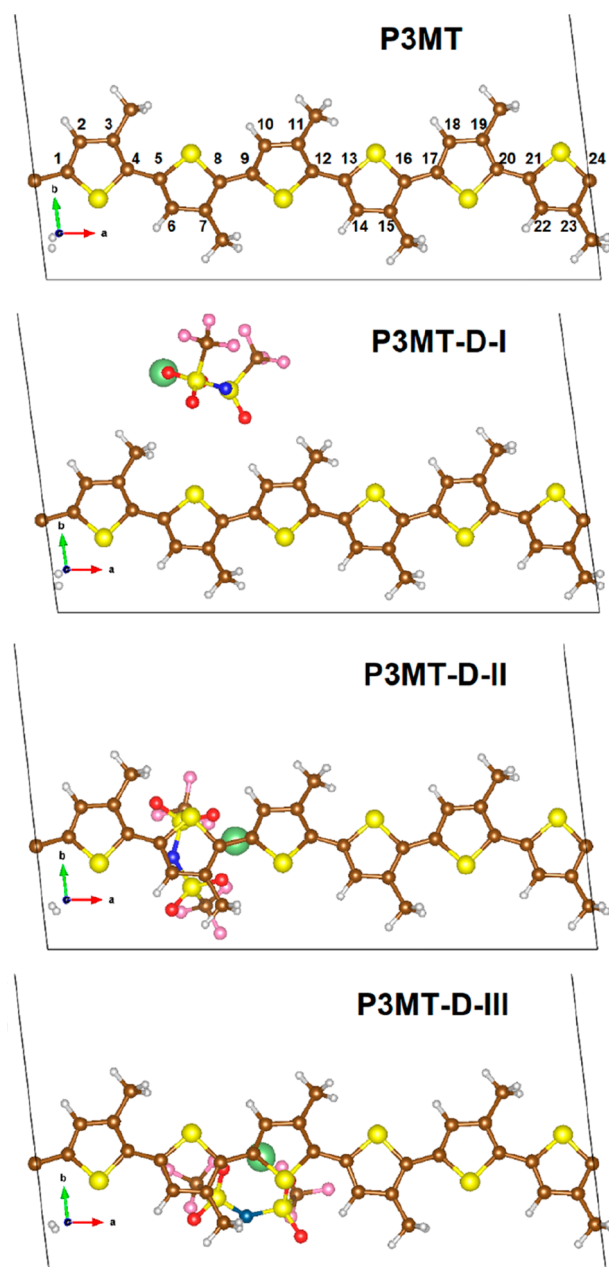


Figure 5. Poly(3-methyl thiophene) periodic models after geometrical optimization for an undoped case (P3MT), LiTFSI doped on the side chain (P3MT-D-I), LiTFSI doped on the top perpendicular to the chain (P3MT-D-II), and LiTFSI doped on the top parallel to chain (P3MT-D-III) positions. Reference colors for atoms are carbon (brown), sulfur (yellow), hydrogen (white), oxygen (red), nitrogen (blue), fluorine (pink), and lithium (green).

mainly located, in relation to the presence of an unpaired electron, as shown in Figure S3b. Finally, the differential electronic charge density and spin density plots evidenced the presence of charge and spin for P3HT when doped with chlorine, as shown in Figure S4. On the basis of all of these calculations, we propose the possible structure schematizing the chlorine (Cl) doping mechanism of the P3MT polymer shown in Figure S4. For the LiTFSI-doped P3MT system, three different dopant positions were chosen: on the alkyl side (P3MT-D-I), on the top perpendicular (P3MT-D-II) to and on the top parallel to the polymer backbone (P3MT-D-III), as shown in Figure 5. We utilized these three different

configurations in our density of functional theory (DFT) calculations to simulate (in a simplified system due to computational cost) not only the most stable location of the LiTFSI dopant in the crystalline region but also two other configurations that were less stable in the crystalline region but very likely to be present in the amorphous region. Indeed, in our molecular dynamics (MD) calculations of the LiTFSI dopant in the amorphous form of P3HT, we evidence the presence of similar LiTFSI locations to those tested in the following simplified system using the DFT approach. The interaction energies between the P3MT and LiTFSI dopants were calculated as follows

$$E_{\text{int}} = E_{\text{P-D}} - (E_{\text{P}} + E_{\text{D}})$$

with $E_{\text{P-D}}$ being the total energy of LiTFSI-doped P3MT, E_{P} being the total energy of P3MT, and E_{D} being the total energy of the LiTFSI dopant systems. The calculated interaction energy (E_{int}) values were -0.05 , -0.60 , and -0.56 eV for P3MT-D-I, P3MT-D-II, and P3MT-D-III structures, respectively.

One important result is that all E_{int} calculated values were negative, which means a favorable interaction between the polymer and dopant. These values also indicate that the most favorable interactions occur for P3MT-D-II and P3MT-D-III configurations. Ring and backbone C–C bond alternation lengths are presented in Figure 6a. P3MT-D-I did not present drastic changes in their ring and backbone C–C bonds in comparison to the undoped system. Nonetheless, the backbone C–C bond lengths between rings 1 and 2 and between rings 2 and 3 for both P3MT-D-II and P3MT-D-III structures are quite different compared to those of undoped P3MT.

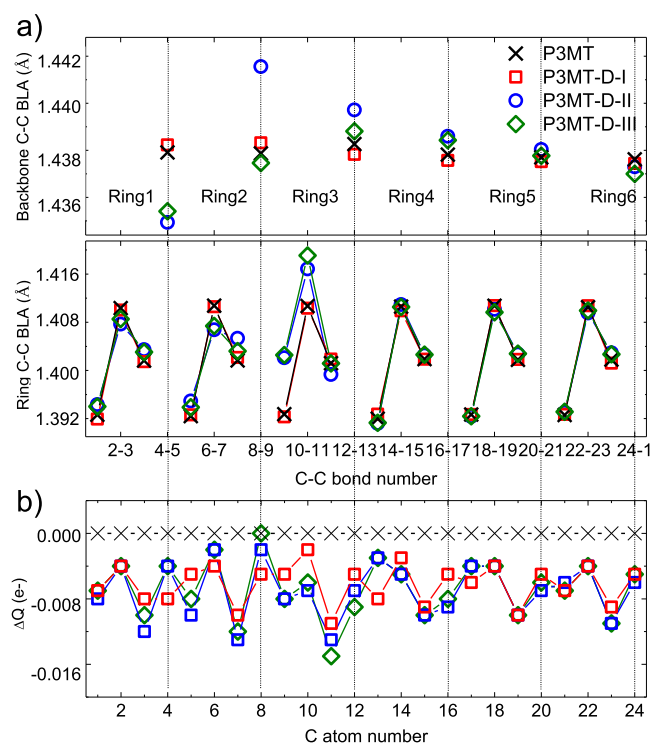


Figure 6. (a) Ring and backbone C–C bond length alternation and (b) charge difference ΔQ_i for P3MT, P3MT-D-I, P3MT-D-II, and P3MT-D-III systems, expressed as a loss of electron density with respect to the isolated P3MT system.

In particular, the backbone C–C bond length between thiophene rings 1 and 2 drastically decreases and the backbone C–C bond length between thiophene rings 2 and 3 drastically increases, suggesting an increase and decrease in the C–C bond order, respectively. The thiophene rings' C–C bond lengths presented drastic modifications in comparison to the undoped P3MT system, especially for C–C bonds comprising rings 2 and 3 of the P3MT-D-II and P3MT-D-III structures, as can be clearly seen in Figure 6a. The electronic charge difference, calculated for each carbon atom is

$$\Delta Q_i = Q_{i,\text{P3MT-D}} - Q_{i,\text{P3MT}}$$

where $Q_{i,\text{P3MT-D}}$ is the charge on atom i in P3MT-D-I, P3MT-D-II-, and P3MT-D-III-doped polymer systems and $Q_{i,\text{P3MT}}$ is the charge of the undoped P3MT polymer, shown in Figure 6b. According to these results, we show a net loss of electronic charge from all carbon atoms of the P3MT polymer chain when doped in any of the three LiTFSI positions, with relatively high delocalization. However, the electronic charge loss tends to be more localized at the C11, C7, and C3 atoms, as shown in Figure 6b, denoting a certain stabilization of P3MT positive charges at those carbon atoms bonded to the alkyl group. Surprisingly, no magnetism was observed in any system, suggesting that the unpaired electron is probably delocalized or is part of a chemical bond, as we will discuss in the following lines. Differential electronic density plots for P3MT-D-I, P3MT-D-II, and P3MT-D-III are shown in Figure 7, with the loss and gain of electron density displayed in green and red, respectively.

The differential electronic density was calculated with the following expression

$$\Delta\rho(\vec{r})_{\text{int}} = \rho(\vec{r})_{\text{P3MT-D}} - (\rho(\vec{r})_{\text{P3MT}} + \rho(\vec{r})_{\text{D}})$$

where $\rho(\vec{r})_{\text{P3MT-D}}$ is the electronic density for the P3MT-D-I-, P3MT-D-II-, and P3MT-D-III-doped polymer systems, $\rho(\vec{r})_{\text{P3MT}}$ is the electronic density of the undoped P3MT polymer, and $\rho(\vec{r})_{\text{D}}$ is the electronic density of isolated LiTFSI dopant. The electronic interaction between the P3MT polymer chain and dopant can be clearly evidenced, particularly for P3MT-D-II and P3MT-D-III systems, while it is only slight in the case of the P3MT-D-I system. For P3MT-D-II and P3MT-D-III systems, the lithium atom is strongly anchored in thiophene ring 3, possibly via the formation of a typical $\pi\cdots\text{Li}$ bond perpendicular to the thiophene ring.^{55,56}

This could suggest that the unpaired electron formed by the one-electron doping in the P3MT polymer structure is part of the $\pi\cdots\text{Li}$ bond, leading to a nonmagnetic solution in the system. In this scenario, our calculations also suggest that the loss of electron density from thiophene rings is mainly due to electronic interactions with the electronic acceptor sulfonyl groups of LiTFSI. On the basis of the discussion above, we propose three possible resonance structures for LiTFSI-doped P3MT structures in order to schematize the doping mechanism process, as shown in Figure 8.

3.4. Doping Effect on Electrical Properties: Charge Transport. Theoretical calculations of the density of states (DOS) for P3MT, P3MT-D-I, P3MT-D-II, and P3MT-D-III structures are shown in Figure 9. Semiconductor behavior is evidenced for all structures, with a slightly reduction of the electronic band gap from ~ 1.2 to 1.0 eV when the polymer is doped with LiTFSI and did not differ from ~ 1.0 eV for both P3MT-D-II and P3MT-D-III structures. In all cases, the

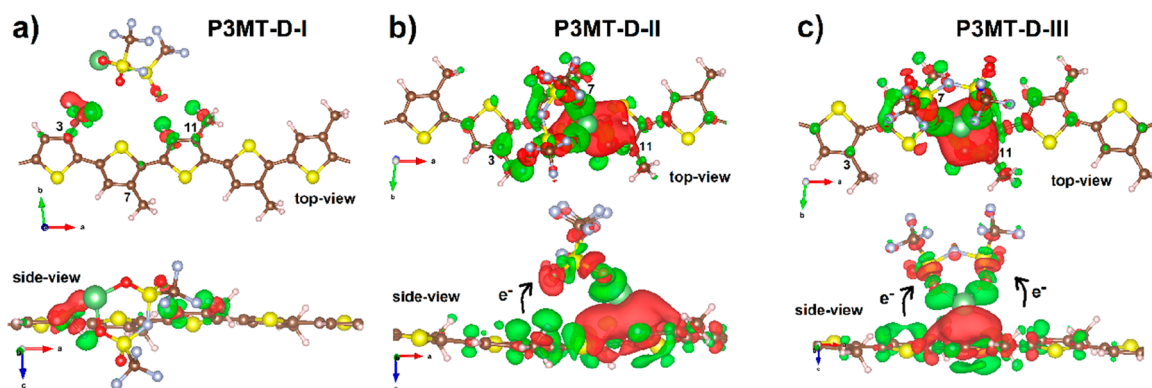


Figure 7. Differential charge density plots for P3MT-D-I, P3MT-D-II, and P3MT-D-III, with the loss and gain of electron density displayed in transparent green and red, respectively. Reference colors for atoms are carbon (brown), sulfur (yellow), hydrogen (white), oxygen (red), nitrogen (blue), fluorine (pink), and lithium (green).

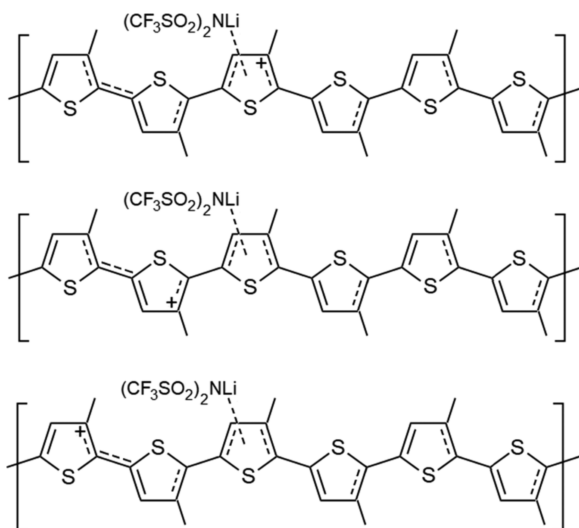


Figure 8. Three possible resonance structures schematizing the LiTFSI doping mechanism of the P3MT polymer.

contribution to the valence and conduction bands near the Fermi level is mainly associated with carbon and sulfur elements of thiophene rings, as shown in the partial density of

states for P3MT, P3MT-D-I, P3MT-D-II, and P3MT-D-III structures (Figure S5).

Experimentally, the semiconducting behavior and charge transport mechanism were studied by means of the impedance spectroscopy technique. The total impedance response (Z) is represented by the following equation

$$Z = Z' - jZ''$$

with Z' as the real part and Z'' as the imaginary part of total impedance. The impedance modulus ($|Z|$) and phase (φ) versus frequency for P3HT and LiTFSI-doped P3HT samples are shown in Figure 10a,b, respectively. Nyquist plots represented as imaginary ($-Z''$) versus real impedance (Z') for all samples are presented in Figure 10c. Impedance data were fitted with a circuit model based on the series combination of two contributions, each of which is formed by the parallel combination of a resistor (R) and a constant phase element (CPE) as a nonideal capacitor, as shown in the Figure 10c inset.

The impedance associated with the CPE element can be described by the following equation

$$\frac{1}{Z_{\text{CPE}}} = Q_0(j\omega)^\alpha$$

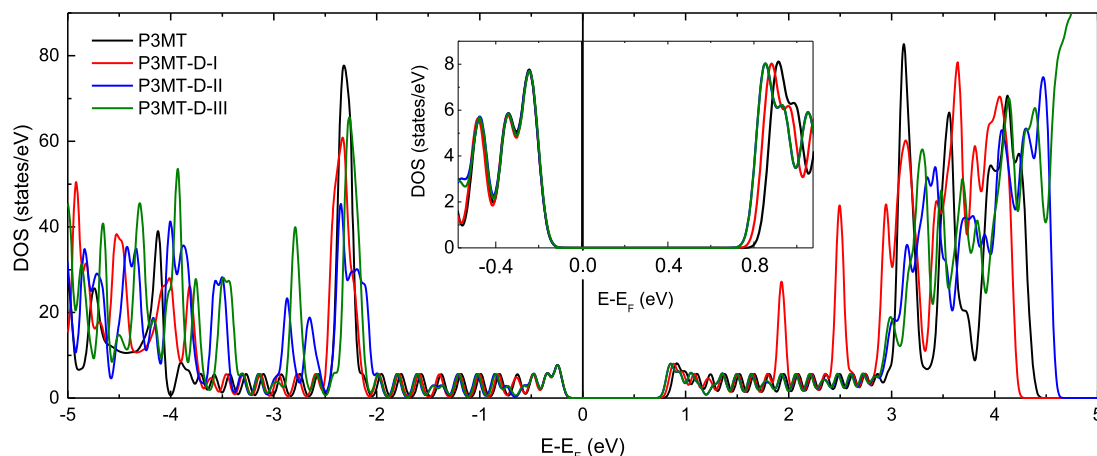


Figure 9. Density of states (DOS) for P3MT, P3MT-D-I, P3MT-D-II, and P3MT-D-III. DOSs in the Fermi zone for all structures are shown in the inset.

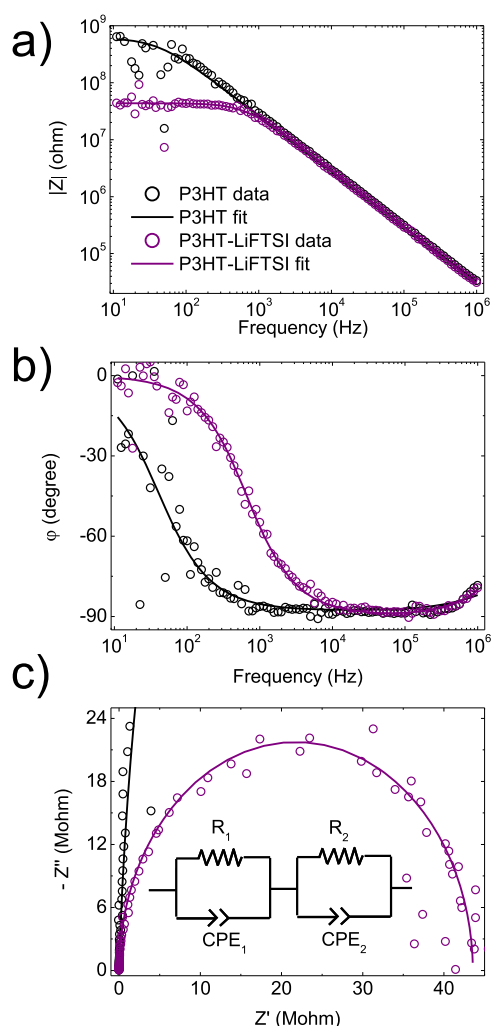


Figure 10. (a) Impedance modulus ($|Z|$), (b) phase (φ) versus frequency, and (c) Nyquist plots ($-Z''$ vs Z') for P3HT and P3HT-LiTFSI. (Inset) Circuit model used to fit impedance data.

where α is an exponential factor, ω is the frequency, and Q_0 is the numerical value of admittance at $\omega = 1 \text{ rad s}^{-1}$. A divergence in both the impedance modulus ($|Z|$) and phase (φ) for P3HT and P3HT-LiTFSI films is observed for frequencies below $\sim 10^4 \text{ Hz}$, suggesting a large decrease in the impedance response for the contribution of lower frequencies associated with the R_1 - CPE_1 parallel combination. A drastic decrease in the semicircle arc of the Nyquist plot for P3HT-LiTFSI with respect to P3HT is also evidenced and is mainly associated with a decrease in the resistance of the low-frequency contribution (R_2) changing from $R_2 \approx 10^9$ to $10^8 \Omega$ when doping. Considering our films' geometry and electrical contacts in the impedance measurements, the conductivity (σ) associated with this major contribution showed an increase from $\sigma \approx 10^{-7}$ to $10^{-6} \text{ S cm}^{-1}$, in good agreement with those observed in the literature.¹³ The first conclusion regarding the electrical transport of the P3HT-LiTFSI sample is that the drastic decrease in the resistance shows the successful doping process. Second, the R_2 - CPE_2 process seems to be governing the overall electric conductivity for both P3HT and P3HT-LiTFSI samples. It is also important to remark that our first-principles calculations suggested that lithium is probably anchored to the thiophene ring via π -Li bonding, and thus a negligible contribution to charge carrier transport is expected

for lithium ion species, also in agreement with the literature.¹³ One possible explanation of the existence of these two contributions could be interpreted by proposing that the R_1 - CPE_1 contribution is associated with an ordered region (possibly crystalline region) and the R_2 - CPE_2 contribution is associated with a disordered region (possibly amorphous region) which showed a major decrease in the resistance, as similarly evidenced when using a TCQN dopant.¹⁵ In our case, this assumption is supported by the fact that our structural analysis, discussed previously, suggested that the LiTFSI dopant is mainly located in the amorphous region and only a small fraction is located in the crystalline region. In addition, our DFT calculations also suggest that the LiTFSI dopant can effectively act as an electronic acceptor only when it is located in the vicinity of and is accessible to the thiophene rings of P3HT. In this sense, the more probable scenario is LiTFSI to be doped more efficiently in the amorphous region mainly because of its particular geometry and the formation of a π -Li chemical bond as an anchoring mechanism, permitting the electronic charge loss of thiophene rings through the sulfonyl groups.

CONCLUSIONS

Our combined experimental and theoretical study on the LiTFSI doping mechanism of regioregular poly(3-hexyl thiophene) suggests that the LiTFSI dopant is not fully doping the P3HT crystalline structure but is mostly located in the amorphous regions of the P3HT polymer, at least for the typical solution preparation methodology in a typical thiophene/LiTFSI 10:1 dopant concentration. In addition, our Raman spectroscopy calculations revealed not only the clear shift of the C-C stretching mode at 1450 cm^{-1} toward lower wavenumbers due to charge carrier formation but other interesting features in the lower-frequencies region, in good agreement with the experimental Raman spectra of P3HT-LiTFSI samples. Finally, our DFT calculations also suggest that the LiTFSI dopant can effectively act as an electronic acceptor only when it is located in the vicinity of and is accessible to the thiophene rings of P3HT. The LiTFSI dopant mechanism mainly obeys its particular geometry by the formation of a π -Li chemical bond as an anchoring mechanism, permitting the electronic charge loss of thiophene rings through the sulfonyl groups. Furthermore, the low dissociation of the LiTFSI ionic pair and the formation of the π -Li chemical bond seem to be blocking the lithium ion transport, making the system a quasi purely electronic conductor.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jpcc.0c00407>.

Calculated XRD patterns for cP3HT with LiTFSI dopant at different positions cP3HT-D/, cP3HT-D//, and cP3HT-D///; a trimer of 3-methyl thiophene [tri(3MT)] with the addition of chlorine atom [tri(3MT)-Cl] models for DFT calculations of Raman spectra; structure of the P3MT-Cl model after optimization and both backbone and thiophene ring carbon-to-carbon bond alternation lengths; differential electronic charge density, spin density plots, and possible structure schematizing the chlorine doping mechanism of the P3MT polymer; and partial density of states for

each element of P3MT, P3MT-D-I, P3MT-D-II, and P3MT-D-III (PDF)

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Notes

The authors declare no competing financial interest.

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