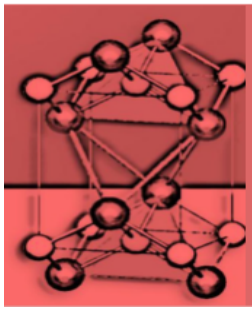

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Studies of doped systems of poly(3-hexylthiophene) (P3HT)

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Here, we present a combined experimental and theoretical study on the lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) doping mechanism of regioregular poly(3-hexylthiophene) (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 $\pi \cdots \mathrm{Li}$ chemical bond as an anchoring mechanism, permitting the electronic charge loss of thiophene rings through the sulfonyl groups.

We also made 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 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 LiTFSI dopant 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. We also introduce the role of the explicit dopant in the interchain, interchain "effective" doping, and charge-transfer complex bonding distances, and their associated static and dynamic disorder effects on the electronic transport. 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.