Bridging Molecular and Periodic Models: A Theoretical Study of the Spectroscopic Properties of pristine and doped P3HT

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Poly(3-hexylthiophene), P3HT, thanks to its an electronic structure with delocalized π-electrons along its backbone, can achieve high electrical conductivity through chemical doping processes [1-2]. Its major applications in the doped state include organic thermoelectric materials, sensing, and organic optoelectronics [3-4]. The doping-induced conductivity increase is promoted by the injection of charge carriers, namely polarons, into the polymeric chains. Understanding the peculiar physics of P3HT – as well as of other conducting polymers – relies on the study of the geometrical and electronic properties of polarons as well as their vibrational dynamics, which in turn requires correctly identifying a suitable structural model of the real P3HT material. Starting from politiophene (PT), the unsubstituted parent polymer of P3HT, as reference system, we examine the relationship between finite-size oligomers and the corresponding infinite polymer treated as a one-dimensional (1D) crystal under periodic boundary conditions. Density functional theory (DFT) calculations are performed to examine the convergence of structural parameters and vibrational features (IR and Raman) as the oligomer length increases, critically assessing the results against the limiting case of the 1D infinite model. Once the suitable finite-size molecular model is identified, it is then functionalized with lateral hexyl chains. In particular we demonstrate that an oligomer with eight thiophenes in the backbone and side alkyl chains (3HT8) constitutes the minimal size oligothiophene able to properly mimic the spectroscopic response of the real P3HT polymer, finding a sound balance between accuracy and computational efforts. Finally, we perform Molecular Dynamics (MD) simulations of the 3HT8 model interacting with the e-acceptor dopant F_4TCNQ to accurately reproduce the chemical doping process of P3HT. Upon doping, two possible charge states can form within the P3HT macromolecular chains, namely polarons (or ICTs) and molecular charge transfer complexes (CTCs), depending on whether the charge transfer from the organic semiconductor to the dopant molecule is net or partial, respectively [5-6]. It is fundamental to study the conditions under which polarons and CTCs form, since only polarons effectively promote the conductivity increase of pristine P3HT. Our simulations suggest that P3HT aggregation in solution, combined with the relative position between dopant and polymeric chains, drives the formation of ICTs and CTCs. We also show that Vibrational Spectroscopy, in particular IR, is a powerful characterization technique for the detection of the two charge transfer complexes in conducting polymers.

References

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