A Theoretical Study of P3HT/Carbon Nanotubes Nanocomposites

Lorenzo Cutaia, Andrea Minoia, Simon Desbief, Florian Boon, Jérôme Cornil, Roberto Lazzaroni
Laboratory for Chemistry of Novel Materials, University of Mons

I. INTRODUCTION

Organic photovoltaic devices (OPVs) using conjugated polymers or molecules, are interesting for their potential of obtaining cheap and easy methods to produce energy from light. In OPVs the electron is dissociated at the interface between a donor and an acceptor molecule (see Fig. 1).

The most common used molecules in OPVs are the poly(3-hexylthiophene) (P3HT) as donor and the [6,6]-phenyl-C$_{61}$-butyric acid methyl ester (PCBM) as acceptor (see Fig. 2). However, the charge transport in OPVs is low and the use of carbon nanotubes (who have high electric conductivity) as a conductive material to bring charges to electrodes are proposed (see Fig. 2).

In this work, we investigate the supramolecular organization at the interface between different type of CNT and P3HT by theoretical calculations based on molecular mechanics (MM) and molecular dynamics (MD) approaches. We also quantify the interaction energy for different system P3HT-CNT.

II. METHODOLOGY

The P3HT chain’s lengths are from ten to thirty monomer units. The diameters of the armchair CNT are 1.36 and 5.42 nm. We performed the geometry optimizations of our P3HT at MM level using the OPLS-AA force field. OPLS-AA is chosen because it correctly reproduces the \( \pi-\pi \) and CH-\( \pi \) interactions [2]. The interaction energy between the polymer and the nanotube is the energy difference between the total system (nanotube + polymer) and the energy of the two separate components in the same geometric configuration:

\[
E_{\text{interaction}} = E_{\text{total \ (P3HT-CNT)}} - (E_{\text{CNT}} + E_{\text{polymer}})
\]

III. RESULTS

1. Our calculations show that the interaction energy per monomer unit (\( E_{\text{int}} \)) is independent of the chain length. \( E_{\text{int}} \) is mainly due to \( \pi-\pi \) interactions between the P3HT conjugated backbone & the CNT \( \pi \) system, and CH-\( \pi \) interactions between the P3HT side chains and the CNT \( \pi \) system.

2. The CNT wrapping is also observed [3]. This wrapping decrease when the CNT diameter increase.

3. The \( E_{\text{int}} \) of the covalently grafted P3HT gives similar \( E_{\text{int}} \) compared one chain in interaction (\( \approx 14 \) kcal/mol) monomer unit). The pyrene unit at the end of the P3HT chain stabilizes the latter \( \approx 20 \) kcal/mol.

4. Recent AFM measurements show that P3HT chains are parallel to the CNT axis [1] (see Fig. 4, up-left).

In order to understand this conformation, MD between one CNT and ten P3HT chains (one fibril) on a graphene was performed (only five chains are represented on the Fig.4, up-right and bottom). In the presence of the substrate, the polymer chains tend to interact with the surface, thereby leading to the final structure shown in Fig. 4.

The driving forces of this movement are:

- \( \pi-\pi \) interactions between the thiophene units and the \( \pi \)-system of the tube, and between thiophene units from other chains.
- CH-\( \pi \) interactions from the hexyl side groups between the chains and the CNT, and between the chains and the graphite.

IV. CONCLUSIONS

1. Interactions between P3HT chains and CNT are mainly of type \( \pi-\pi \) and CH-\( \pi \).
2. CNT wrapping has been highlighted.
3. Pyrene unit stabilize the chain because of more \( \pi-\pi \) interactions.
4. P3HT chains in fibrils are lying parallel to the CNT axis.

V. PERSPECTIVES

- Study low band gap polymers.
- Modelize larger system using other program and method like coarse grained.

REFERENCES


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