Short communication

Atomic scale modeling of interfacial structure of PEDOT/PSS

Ahmed Dkhissi [a,b,*], David Beljonne [a], Roberto Lazzaroni [a]

[a] Centre de Recherche en Electronique et Photonique Moléculaires, Université de Mons-Hainaut, 20 Place du Parc, B-7000 Mons, Belgium
[b] Interdisciplinary Research Institute c/o IEMN, Cite Scientifique, UMR8520, Avenue Poincare BP60069, F-59652 Villeneuve d'ascq Cedex, France

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ABSTRACT

Theoretical calculations are performed in the framework of the interaction between the charged poly(ethylenedioxythiophene) (PEDOT^{2+}) and two p-toluensulfonic acid (TSA^{-1}). The influence of the counterion on the charge distribution in the PEDOT is investigated indicating that a strong influence of the interionic correlation on the stability of PEDOT by TSA. Further several configurations are studied for the interaction between PEDOT and PSS. The calculations indicate that the side assembly is the most stable configuration, however in the presence of the solvent both parallel and side assemblies have similar stability. These results give a new insight about the charge transport conduction in PEDOT/PSS interactions.

1. Introduction

Poly(3,4ethylenedioxythiophene) is one of the best known p-conjugated polymers that has widely used in several industrial applications because cast films are both electronically conductive and optically transparent. These characteristics are required in many applications including electrode material for solid electrolyte capacitors, antistatic coating in photographic films, indium tin oxide (ITO) electrode-replacement material in inorganic electroluminescent lamps, hole conducting material in organic/polymer-based light-emitting diodes (OLEDs/PLEDs), and novel memory devices [1–5]. The solubility problem of PEDOT can be circumvented by poly(styrenesulfonic acid) (PSS), as the charge balancing dopant during polymerization, yielding PEDOT/PSS [6,7]. The conductivity of PEDOT/PSS can be increased by a factor of 100, mainly due to the effect of the solvent [8]. The commercialization of PEDOT/PSS is largely due to its processable nature; therefore; the ability to chemically and electrochemically synthesize fully water-soluble PEDOT derivatives greatly increases its versatility for deposition and application. Very recently, the morphology of PEDOT/PSS layers [9–13] have been addressed. Aasmundtveit et al. [14] reported the structure of thin films of PEDOT/TSA. Later, Froberg and coworkers [15], studied the degree of crystallinity of PEDOT films as a function of the electrochemical polymerization potential in TBAPF6-ACN. And based on their observations they calculated a model for PEDOT/PF6. Contrary to the experimental little known about the structure of doped PEDOT in the presence of the counterions, there are none theoretical calculations giving their molecular arrangement. So our aim here is to determine the interaction between doped PEDOT and their counterions and determine the solid-state packing of charged conjugated chains. This knowledge is of utmost importance in obtaining a material with excellent macroscopic properties.

As PEDOT is typically applied in each application of oxidized PEDOT chains electrostatically associated with a poly(styrene sulfonic acid) (PSS) dopant, our work consist in particular to study the interaction between the charged PEDOT; PEDOT^{2+} and charged PSS; PSS^{2-}. These calculations provide information about the structure of the association of PEDOT with PSS. So, in order to achieve our objectives, i.e., the molecular structure of PEDOT/PSS, we have started with a simple case: concerning PSS, we considered p-toluensulfonic acid (pTSA) as model for PSS and for PEDOT, we considered the oligomer containing eight repeat units, because we demonstrated recently that the octamer is a good model for the polymer [16,17]. After determining the stable structure between charged polymer (bipolaron) and the two pTSA, we studied the effect of the counterions on the charge distribution in the polymer. In the second part, we determined the molecular arrangements of PEDOT/PSS.

2. Methodology

The geometries of the doped polymer (PEDOT) and the counterion (pTSA) are calculated with ab initio method using the Gaussain 98 [18]. The position relative of the conjugated chains and their counterions is performed with molecular mechanics. In all calculations, the universal force field (UFF) [19–21] is used. This force field is available in the Cerius2 package by Molecular Simulations, Inc. In

* Corresponding author at: Interdisciplinary Research Institute c/o IEMN, Cite Scientifique, UMR8520, Avenue Poincare BP60069, F-59652 Villeneuve d'ascq Cedex, France.
E-mail address: adkissi@laas.fr (A. Dkhissi).

our recent work [22] dedicated to the modeling of the solid-state packing of charged chains (PEDOT) in the presence of the counterions and the solvent (DEG), we explained why we used this force field.

The description of the distribution of the positive charge on the conjugated chain is very important, because the electrostatic interactions are expected to play the major role in determining the supramolecular arrangement. When running molecular mechanics calculations on a charged PEDOT chain with the possibility of charge relaxation, we obtain that the charge equally spreads on all sites. This is in strong contrast to what is known from the quantum chemical description, in which the charge remains confined in the central part of the molecule, i.e., a polaron is formed [16,23]. The formation of bipolarons is an essential feature of the conjugated systems, it is related to the intimate coupling between the electronic system and the backbone. Because molecular mechanics methods do not explicitly consider electron, the charge confinement related to bipolaron formation cannot be described. To overcome this problem, we have imposed the charge ($PEDOT^{2+}$) distribution and charge of the counterion (TSA^{-1}) coming from Hartree–Fock quantum chemical calculations and we have not allowed this charge distribution to relax during the molecular mechanics simulations.

In the case of PEDOT/PSS complex, we considered PSSH chain containing eight repeat units and on the fourth and sixth phenyl-SO_3H groups, we removed the hydrogen atom and we added a negative charge shared between the oxygen atoms of the group. The geometry of the PEDOT chain was frozen, while the internal geometry of PSS and the relative position of the molecules were optimized with molecular mechanics, using the universal force field. The charge of the complex $PEDOT^{2+}/PSS^{2-}$ was not allowed to relax during the optimization of the assembly.

3. Results and discussion

3.1. Charged chain (bipolaron) in the presence of the counterions

In the doped polymer (oligothiophene dications) without counterions, only singlet state is considered. Thus is due the fact that a DFT study by Gao et al. [24] showed that the closed shell bipolaron is more stable for oligothiophene dications of pentathiophene and smaller ($n < 5$), while the open shell two-polaron structure is the ground state for sexithiophene dications and longer dications. Further, very recently Zade and Bendikov [25] demonstrated that the triplet state is of lesser or equal stability compared to the singlet for every oligothiophene dication up 50 units and provided more evidence for a preference for the polaron pair over the bipolaron electronic state for long oligothiophene dications.

Further in our recent study dedicated to the modeling of the solid-state packing of charged PEDOT chains in the presence of the counterions (TSA) [22], we have studied different possibilities of positioning the counterion along the conjugated polymer. The results indicate that the perpendicular orientation corresponds to the most stable structure of the PEDOT/TSA complex. Therefore, the later orientation is used for study larger aggregates and also for this study of charged $PEDOT^{2+}$ stabilized with two counterions $pTSA^{-1}$.

Two counterions were placed above and below the plane of the conjugated chain and their positions optimized at the molecular mechanics level. The calculations indicate that the most stable complex corresponds to one counterion on top of unit 3 and one below unit 6 (see Fig. 1). These positions correspond to the maxima in the charge density wave associated with a bipolaron in the octamer. The charge distribution of the bipolaron alone and the bipolaron in the presence of the counterions is plotted in Fig. 2. The charge increases for the units that are in front of the counterions and decreases elsewhere. To conclude this part, we found that the presence of the
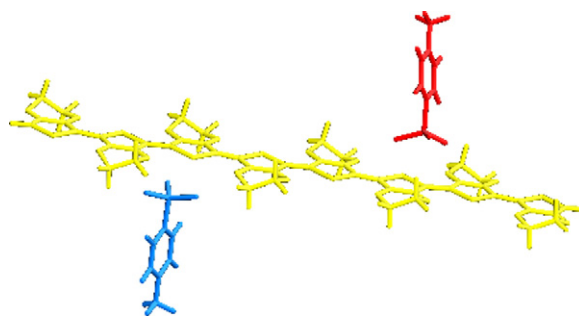

Fig. 1. Most stable structure of the interaction between bipolaron and counterions.

counterions leads to a stabilization of doubly charged species, and results in a pinning effect with concentration of the positive charge on the polymer chain close to the negative charge carried mostly by the oxygen atoms of the PSS chains.

3.2. Structure of PEDOT/PSS

This part deals with the interaction between PEDOT and PSS. As a model system, we considered the presence of a positive bipolaron on an EDOT octamer, interacting with a zig-zag planar syndiotactic PSSH chain containing eight repeat units. On the fourth and sixth phenyl-SO_3H groups, we removed the hydrogen atom and we added a negative charge shared between the oxygen atoms of the group. The relative position of the molecules were optimized with molecular mechanics, using the universal force field.

Several different positions of the PSS chain with respect to the PEDOT segment have been considered. Here we report only the three most stable structures (Fig. 3), corresponding to situations where the PSS chain lies above and roughly parallel to the PEDOT chain (a), above and roughly perpendicular to the PEDOT chain (b), and along the PEDOT chain (c). The blue circles indicate the negatively charged sulfonate groups.

As the internal geometry of PSS can relax during the optimization, the initial zig-zag planarity of the PSS backbone is expectedly lost, due to the steric hindrance between the side groups. More interesting, a large change in the PSS structure occurs as a result of the electrostatic repulsion between the charged phenyl-SO_3 groups. In the neutral compound, the distance between these two groups is about 5.2 Å. For the charged system, this distances strongly increases to 14.7, 12.2 and 12.2 Å in structures (3a), (3b) and (3c) respectively. This change can also be responsible for the loss of planarity of PSS. Energetically, structure (3c) is the most stable complex, and the relative energies between structure (3c) and structures (3a) and (3b) are around 20 and 52 kcal/mol, respectively. This difference mostly comes from the electrostatic interactions. In structure (3b), only one charged sulfonate group is close to the positively charged PEDOT chain, thereby reducing the attractive
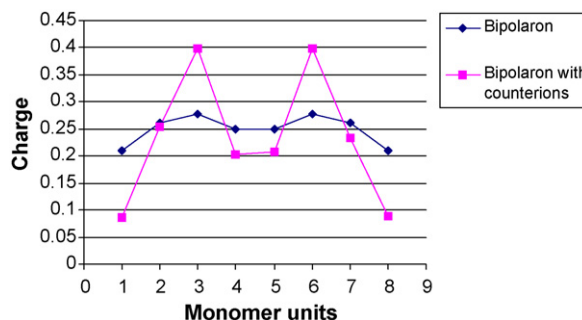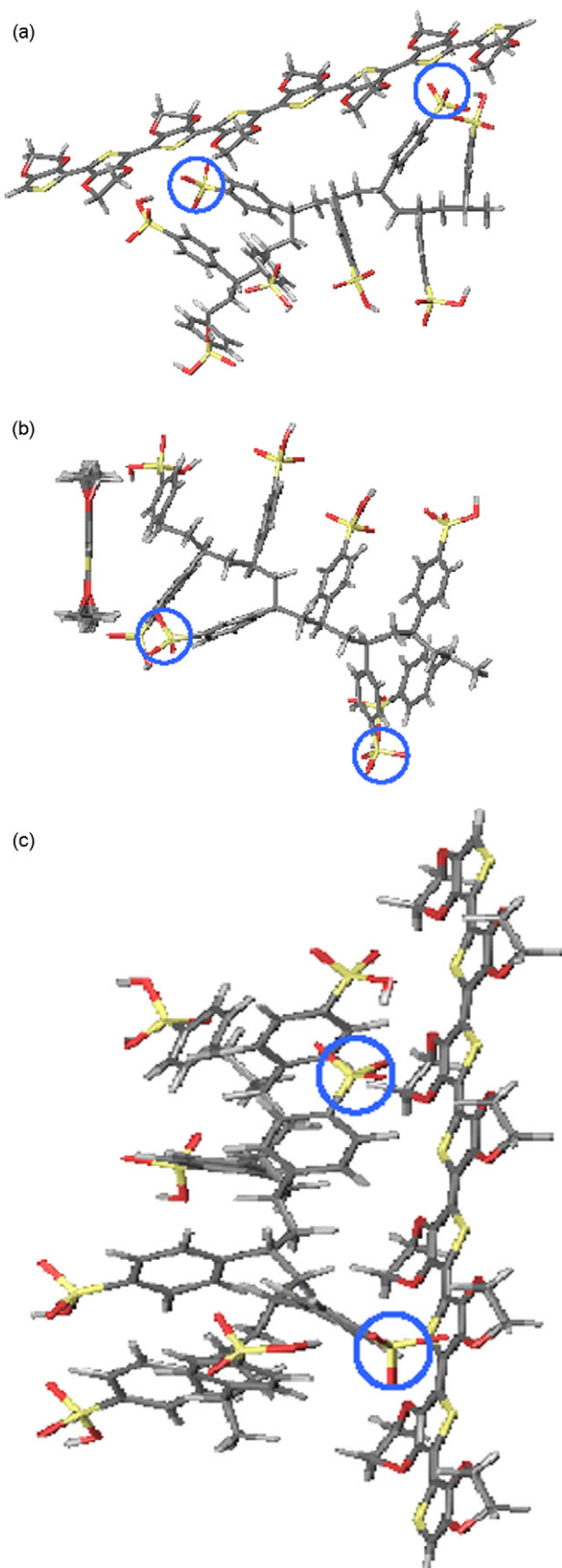

Fig. 2. Charge distribution of charged PEDOT (bipolaron).

Fig. 3. The most stable structures of the PEDOT/PSS complex. PSS chain lies above and roughly parallel to the PEDOT chain (a), above and roughly perpendicular to the PEDOT chain (b), and along the PEDOT chain (c).

contribution to the electrostatic energy. In structures (3a) and (3c), both charged sulfonate groups interact with the PEDOT chain, the distance being 5.2 Å for both groups in 3c, vs. 5.2 and 6.0 Å for the groups in 3a. This slight difference may explain the slight energetic difference in favor of 3c.

These results show the type of conformation that is likely for PSS chains interacting with charged PEDOT segments. In the solid, assemblies with PSS and PEDOT chains lying alongside thus appear quite reasonable.

The influence of a high boiling solvent on the geometric organization of PEDOT/PSS is explored in this section; we chose diethyl glycol (DEG) as the solvent molecule since this has been shown experimentally to lead to the most significant increase in conductivity. The goal here is to simulate the effect of the solvent on the arrangement of the conjugated chains in the early stage of film formation; we conjecture that the presence of the solvent might lead to an improved ordering of the PEDOT chains in the suspension, which is then reflected in the film morphology and leads to increased electric conductivity. The solvent is introduced implicitly by introducing the dielectric constant of DEG (ε = 31.82) (all Coulombic interactions are hence screened).

The calculations are done for the three stable structures (Fig. 3). Energetically, the structures (3a) and (3c) are the most stable configurations. Their relative stability is similar and slightly (2 kcal/mol) in favor of structure (3a). The distance between the two negative charges beared by the fourth and sixth phenyl-SO_3 groups is lowered to around 7.5 and 8.2 Å for perpendicular and along side configurations, respectively (with respect to 14.7 and 12.2 Å for ε = 1).

4. Conclusion

The molecular modeling study of $PEDOT^{2+}/2(TSA^{-1})$ interactions is done with molecular mechanics coupled to ab initio calculations. We have employed this method to investigate the relative position of TSA with respect PEDOT for the stability of the PEDOT/TSA complex. The most stable configuration correspond to that where the electrostatic interactions between the positive charge carried out by the chain and the negative one carried by the counterion and are maximized. While in the case of the interaction between PEDOT and PSS, several configurations are studied, and we found that the side assembly is the most stable configuration. While in the presence of the solvent, the parallel and side assemblies have similar stability. Considering larger aggregates and based on results obtained in this work, the structure of PEDOT/PSS can be viewed as "channels" of stacked conjugated chains, along which charge transport should be easy, separated by channels populated by the counterions molecules.

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