

Molecular mechanics study of the influence of the alkyl substituents on the packing of the conjugated PEDOT chains

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Abstract

The solid state packing of neutral chains of the conjugated polymers is studied by theoretical simulations. The conjugated systems considered here are the pol(3,4-ethylenedioxythiophene (PEDOT) and their substituted PEDOT derivatives PEDOT-C10H21. The molecular mechanics calculations indicate that the polymers tend to form stable π stacks and indicate that the alkyl side groups freeze the conjugated segments and allow a good organization of PEDOT-C10H21 chains. This explains the increase of conductivity in these systems compared to un-substituted PEDOT. Finally, the introduction of one defect in region-regularity causes a steric hindrance, resulting in less order and less compact π -stacking.

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1. Introduction

Conjugated polymers are extensively investigated for the development of a variety of organic-based electronic applications [1]. Among the numerous polymers that have been developed and studied over the past decades, poly(3,4-ethylenedioxythiophene), abbreviated as PEDOT, has developed into one of the most successful materials from both a fundamental and practical perspective. Due to its excellent conducting and electro-optical properties, PEDOT are now utilized in several industrial applications (e.g., electrode material for solid electrolyte capacitors, antistatic coating in photographic films, indium tin oxide (ITO) electrode-replacement material in inorganic electroluminescent lamps, and hole conducting material in organic/polymer-based light-emitting diodes (OLEDs/PLEDs) [2–4]. In the recent reviews [2,3], the most significant papers devoted to the study of the PEDOT and PEDOT/PSS are recalled. In

addition to a very high conductivity (ca. 550 S cm^{-1}), PEDOT is highly transparent in thin, oxidized films and is stable in its oxidized state [5–8]. Their solubility problem can be circumvented by poly(styrenesulfonic acid) (PSS), as the charge balancing dopant during polymerization, yielding PEDOT/PSS [9,10]. The conductivity of PEDOT-PSS can be increased by a factor of 100, mainly due to the effect of the solvent [11].

The influence of interactions among chains on the electronic properties in the solid state is a matter of major current interest [12,13]. Inter-chain interactions can have a major impact on the operation of devices, since they determine the charge transport properties. More generally, charge transport in a molecular solid is critically dependent on the intermolecular interactions, and these interactions are dependent on the molecular packing. Therefore, it is important to investigate and control the effects of ordering and structure in conjugated polymers. Different attractive intermolecular forces, such as hydrogen bonding [14], metal coordination, and π -stacking [15], can dominate individually or cooperate to establish the organization and stability of the system [16].

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The conjugated backbones are usually substituted with alkyl chains in order to ensure solubility in common organic solvents. So the best-known substituted PEDOT derivatives are the alkylated PEDOT species as originally developed by Jonas et al. [17]. In this Letter, we have investigated the packing of chains of PEDOT and poly($C_{10}H_{21}$ -substituted EDOT) (hereafter called C10-PEDOT), via molecular mechanics model calculations. These systems are stable and stabilized by electrostatic forces (π -stacking). This study is motivated by the experimental observation indicating that the conductivity of electrochemically -prepared alkylated PEDOT species initially decreases and then increases again by increasing the size of the alkyls groups [18]. Since alkyl substituents are not supposed to affect directly the energies of the π electronic levels, the increase in conductivity is thought to originate from a better solid-state organization of the chains, i.e compact π -stacking should favor interchain hopping. In this study, our aim

is to determine the arrangement of the polymer chains in solid films, and allows to understand the effect of the alkyl chains and their regioregularity on the morphology of the PEDOT. So, we considered neutral (undoped) chains, and our search is to determine the most favorable packing configurations of the following systems: PEDOT dimer and C10-PEDOT dimer.

2. Methodology

The structural properties of the polymer (Octamer) are calculated with ab initio method (HF/6-31G) using the GAUSSIAN 98 program [19]. Based on the saturation of several physico-chemical properties, the octamer is considered as a good model for polymer [20]. The relative position of the conjugated chains PEDOT and C10-PEDOT within the aggregates is optimized with molecular mechanics, while the internal geometry of the sub-units was frozen. In all

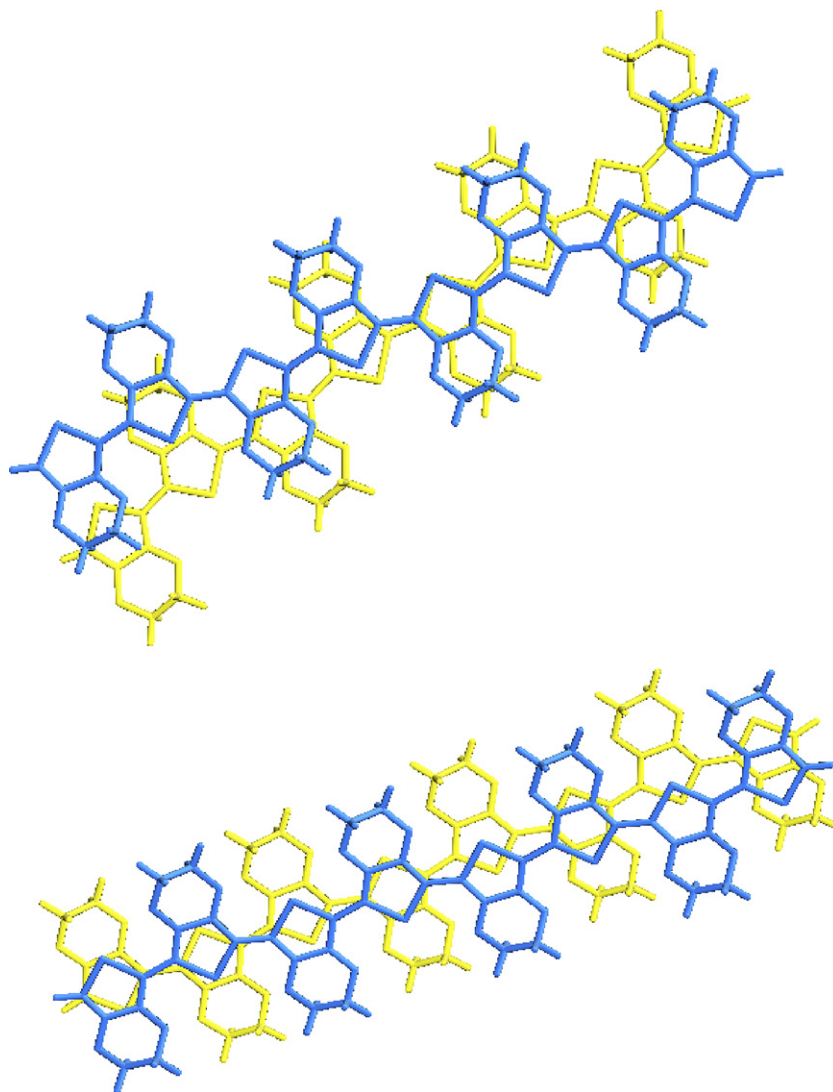


Fig. 1. The two most stable structures for the assembly of two PEDOT molecules. Top: when starting from a superimposed configuration; bottom: when starting from a flipped configuration.

calculations, the universal force field (UFF) [21–23] is used. This force field is available in the CERIUS2 package by Molecular Simulations, Inc. In the recent study, Leclère et al. [24] have compared the predictive abilities of different forces field in reproducing the experimental data or high level ab initio results for conjugated molecules. As expected, the study showed that the UFF seems to predict accurately the properties of the conjugated polymers compared to others forces field (PCFF, CFF9 and Compass).

In the case of the unsubstituted PEDOT, the interaction energy of PEDOT dimer is calculated with B3LYP/6-31++G**. As we have demonstrated recently [25] this basis set is sufficient to predict more accurately the properties of the intermolecular interactions.

3. Results and discussion

In each system, PEDOT dimer and C10-PEDOT dimer, two configurations are studied: the first one when the molecules are initially exactly superimposed (Figs. 1, top, 2, top) and the second configuration when the molecules are flipped relative to each other (Fig. 1 bottom, 2 bottom).

3.1. Packing of PEDOT chains

Fig. 1. shows the two most stable structures for the assembly of two PEDOT polymers. The first initial configuration was with the two molecules exactly superimposed (as this is supposed to maximize the intermolecular π over-

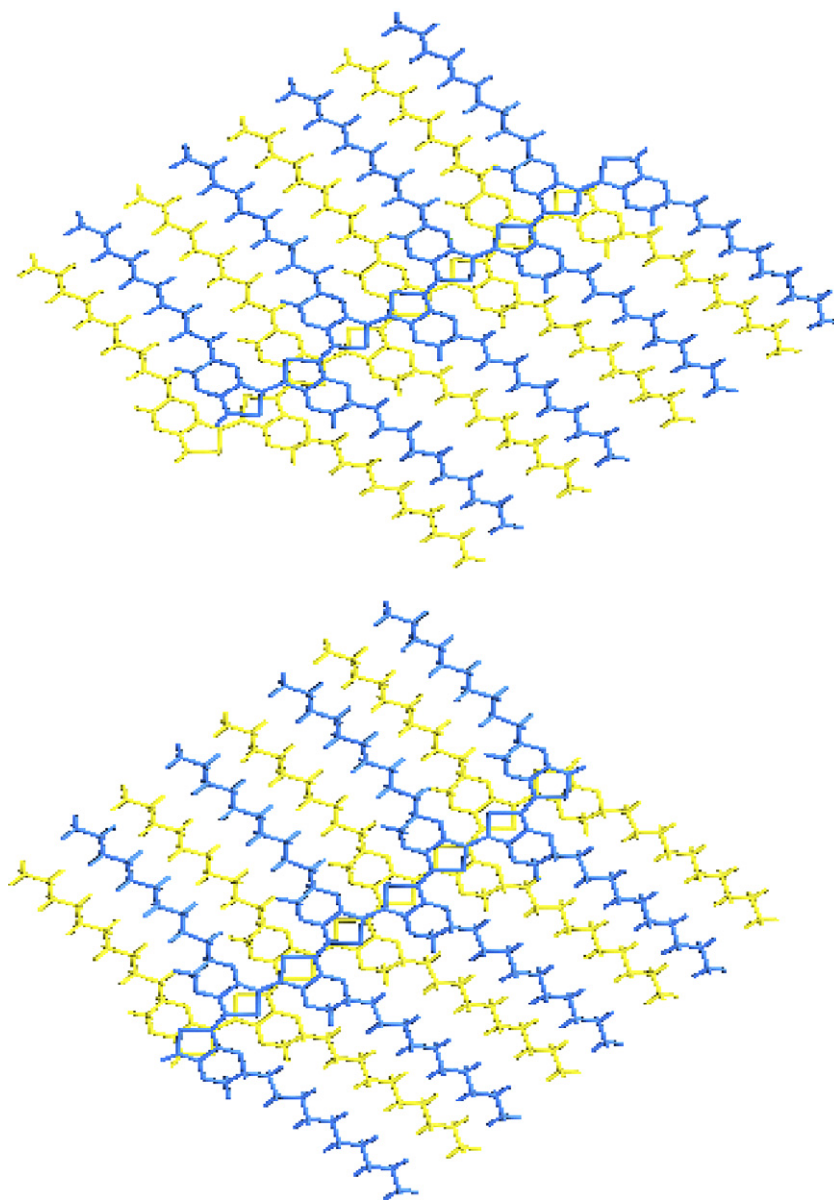


Fig. 2. The two most stable structures for the assembly of two C10-PEDOT molecules. Top: when starting from a superimposed configuration; bottom: when starting from a flipped configuration.

lap). Fig. 1, top clearly shows that the molecules tend to rotate slightly with respect to each other, probably as a result of the repulsion between the sulfur atoms and between the methylene groups. Nevertheless, the intermolecular distance remains rather small (around 3.9 Å), which still allows for a significant π overlap. In the second initial structure, the molecules are flipped relative to each other, so that the overlapping EDOT units are now pointing in opposite directions. This arrangement clearly decreases the intermolecular steric hindrance between the methylene groups while still allowing for π overlap between the thiophene rings. In this case, we indeed find (Fig. 1, bottom) that the two molecules remain better aligned (the lateral drift is very small: the angle between the two molecular axes is only 3°, instead of 13° in the previous case). The reduction of steric hindrance is also probably responsible for the slightly reduced intermolecular distance: the shortest C–C intermolecular contacts are around 3.5 Å in this case. This predicted distance is in good agreement with the intermolecular distance previously determined at MP2/aug-cc-pVDZ level of theory for benzene dimer [26]. The calculations based on the molecular mechanics indicate that this assembly is at least as stable as that of Fig. 1, top: probably the increased π – π interactions compensate for the loss of van der Waals contacts between the ethylene-dioxy units (since they are pointing away from each other in Fig. 1, bottom). Based on the order (compact π -stacking) of the two configurations, we expected that the charge transport along the stacks is better in the second configuration compared to the first.

The binding energies, i.e., the difference in total energy between: (i) the two separate molecules and (ii) the assem-

bly, are calculated with B3LYP/6-31++G** based on the geometries obtained with molecular mechanics. The binding energy can be estimated to be around 17.6 kcal/mol for the first configuration and about 20.4 kcal/mol for the second structure. These values are consistent with what are usually found in π – π interactions between aromatic molecules [27].

3.2. Packing of C10-PEDOT chains

The same strategy has been applied for the assemblies of two C10-PEDOT molecules. One initial configuration is with the two molecules superimposed. The other initial configuration we considered is with the molecules flipped. In both cases, the alkyl chains are fully zig-zag planar. This is the most probable conformation, as determined experimentally in alkyl-substituted polythiophenes by Winokur et al. [28]

The optimized structures are displayed in Fig. 2. In both cases, the molecules arranged in such a way that the alkyl groups of one chain lie in between two alkyl groups of the other chain. For the initially -superimposed assembly, this implies a relative drift of the molecules by about one monomer unit along the chain axis (Fig. 2, top). In the flipped configuration, almost no geometric modifications occur upon optimization, since the alkyl groups are already in a favorable position. In those two assemblies, the steric hindrance between the alkyl groups is minimized, which therefore keeps the two conjugated backbones close to each other (the shortest intermolecular contacts along the PEDOT chains are around 3.7 Å). It is noteworthy that the assembly of Fig. 2, bottom is more stable than its

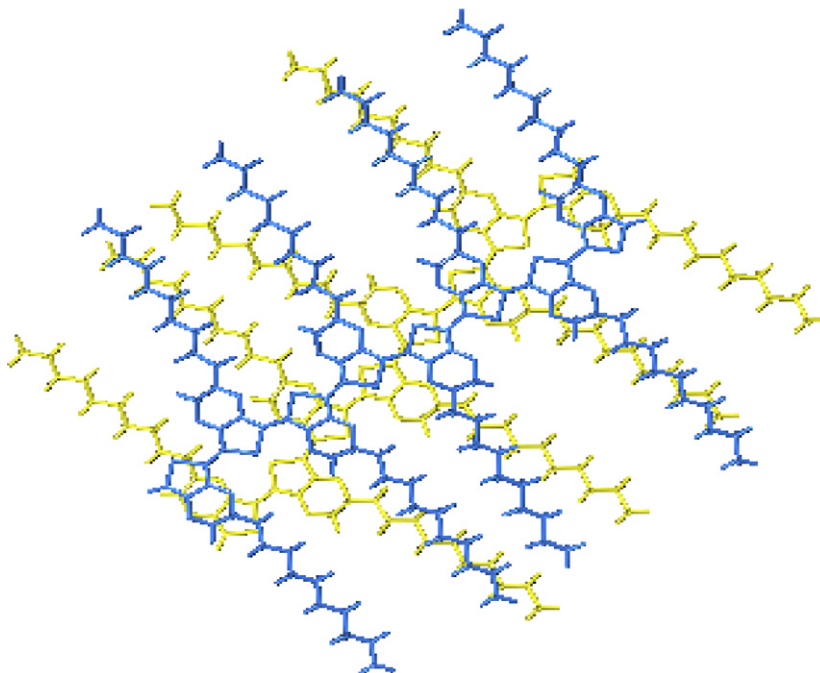


Fig. 3. Most stable structure for the assembly of two C10-PEDOT chains with one defect in regioregularity.

counterpart of Fig. 2, top; this is simply because the overlap between the EDOT units is optimal in the former while π – π interactions are absent for two terminal units in the first configuration, due to the longitudinal drift. More important, there is no lateral drift of the conjugated chains in C10-PEDOT assemblies, in contrast to the case of PEDOT chains. This is probably due to the presence of the long alkyl groups, the packing of which tends to maintain the conjugated backbones perfectly stacked. This is expected to improve the long-range organization of the C10-PEDOT chains, which in turn should improve the inter-chain transport properties. It is therefore reasonable to propose that the increased conductivity observed in doped C10-PEDOT originates from a better solid-state organization induced by the packing of the alkyl side groups.

3.3. Loss of regioregularity

In the above point, we considered the C10-PEDOT chains as perfectly regioregular, i.e., all units are substituted on the same position with alkyl groups. Here we briefly examine how partial loss of regioregularity affects the packing of two chains. For this purpose, we have moved one alkyl group on each chain to the ‘wrong’ methylene site (Fig. 3). The most stable structure is presented in Fig. 3. Clearly the packing in this case is much less compact and regular than in the previous case (see Fig. 2). It appears that the regular, alternating arrangement of the alkyl groups on neighboring chains is seriously disturbed due to the steric hindrance between the alkyl groups. As a consequence, the alignment of the PEDOT backbones, which allows for optimum π overlap, is disrupted (the angle between the axes of the two chains is around 15°). These results suggest that the loss of regioregularity would significantly decrease the effectiveness of charge transport in stacks of PEDOT chains.

The regioregularity (and the high degree of order that it imparts to conjugated materials) is a central parameter for obtaining good electronic properties and has been remarkably demonstrated in alkyl-substituted polythiophenes: the mobility in regioregular compounds is increased by orders of magnitude relative to their non regular counterparts. They have been successfully used in FET’s by Sirringhaus et al. [29].

4. Conclusions

We have described the calculations of the packing of PEDOT and C10-PEDOT. The molecular mechanics calculations indicate that the conjugated segments tend to form stable π -stacks and the alkyls groups play an important role of the organization of the conjugated segments. Our results clearly show that π – π interaction in the packing

of C10-PEDOT is more important than in the packing of PEDOT (Figs. 1 and 2). So the charge transport along the stacks should be better in the substituted PEDOT since this property depends on the supramolecular organization of the polymer chains in the solid state. These calculations confirm the experimental findings [18]. Further we demonstrated that the regioregularity is a central parameter to control the organization of the conjugated PEDOT, and a slight defect (loss of regioregularity) affects considerably the order of the packing allowing to minimize the π – π interaction between the thiophene units which are responsible for charge transport.

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