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REGULAR ARTICLE

Modeling of the solid-state packing of charged chains (PEDOT) in the presence of the counterions (TSA) and the solvent (DEG)

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Abstract Molecular mechanics and ab-initio calculations are performed in the framework of the interaction between the charged poly(ethylenedioxythiophene) (PEDOT), the *p*-toluensulphonic acid (TSA), and the diethylene glycol (DEG). Different possibilities of positioning the counterion along the conjugated polymer are studied. For each possibility (or orientation), the influence of relative position of the counterion on the stability of these charged interfaces is considered. The results indicate that the perpendicular orientation corresponds to the most stable structure of the PEDOT/TSA complex. The influence of the counterion on the charge distribution in the PEDOT is also investigated indicating that a strong influence of the interionic correlation on the stability of PEDOT by TSA. Further the packing of doped chains with their counterions is also determined. In the larger aggregates, the effect of the solvent is considered. These results give a new insight about the molecular arrangements of PEDOT/TSA interactions and allow to understand how charge transport along the stacks can take place.

1 Introduction

Conjugated polymers have been extensively developed into useful materials for a variety of 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], are recalled the most significant papers devoted to the study of the PEDOT and PEDOT/PSS. In addition to a very high conductivity (ca. $550\,\mathrm{S\,cm^{-1}}$), 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 dopand 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]. In contrast to the numerous studies that have been performed to understand the electrical and optical properties of PEDOT, relatively little is known about their molecular structure and their surface and bulk morphology. Very recently, the morphology of PEDOT/PSS layers [12–16] have been addressed.

Aasmundtveit et al. [17] reported the structure of thin films of PEDOT/TSA. Studying the films by grazing-incidence X-ray diffraction using synchrotron radiation, the material was found to be highly anisotropic. The crystalline order is limited and evidence was found for a para-crystalline

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structure. Since very little amorphous scattering was observed, this means that the para-crystalline state accounts for the entire volume of the material. Further, the authors present a structural model in which the experimental peak positions and intensities are fairly reproduced. Later, Froberg et al. [18], 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 counterion and determine the solid state packing of charged conjugated chains. This knowledge is of utmost importance in obtaining a material with excellent macroscopic properties. So, in order to achieve our objectives, i.e., the molecular structure of PEDOT/PSS, we have started with a simple case: PEDOT/TSA. Concerning PEDOT, we considered the oligomer contains eight repeat units, because we demonstrated recently basis on the saturation of several physical properties that the octamer is a good model for the polymer [19,20].

In the present paper, we present the first theoretical calculations devoted to determine the solid state packing of charged PEDOT in the presence of the counterions (TSA). In the first part, we have considered the charged conjugated chain PEDOT^{+1}. The large part of this charge is nearly localized in the middle of the polymer ‘polaronic state’ as been calculated with ab-initio HF and MP2 methods [19–21]. Different orientations of the counterion with respect to the polymer are investigated. For each orientation, we search the most stable structure of charged PEDOT stabilized with *p*-toluensulphonic acid. This is done with Combined Molecular Mechanics to Ab-initio methods. The presence of the counterion affects the charge distribution in the polymer especially the positions for which the large part of charge is localised. The second part is dedicated to the large molecular aggregates because in order to be able to further optimize the materials properties of PEDOT derivatives, the relationship between the morphology of a material and its conductivity is of utmost importance.

2 Methodology

The geometries of the doped polymer and the counterion are calculated with ab-initio HF/6-31G* method using the Gaussain 98 [22]. We selected HF method to calculate the geometric and electronic structures of polymer instead of DFT, because it is very well know that DFT predicts complete charge delocalization over the whole chain [19,21,23,24].

The position relative of the conjugated chains and their conterions is performed with Molecular Mechanics. In all calculations, the Universal Force Field (UFF) [25–27] is used. This force field is available in the Cerius2 package by Molecular Simulations, Inc. In the recent study [28], the authors 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 force fields (PCFF, CFF9 and Compass).

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 [19,22]. The formation of polarons is an essential feature of the conjugated systems, it’s 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 polaron formation cannot be described. To overcome this problem, we have imposed the polaron charge PEDOT^{+1} 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 the interaction bewteen one conjugated chain and one counterion, the optimizations of the molecular structures with molecular mechanics were followed by single point energy calculations at MP2/6-31++G** approach. This bias set is sufficient to predict more accurately the properties of the intermolecular interactions [29,30].

3 Results and discussion

3.1 Charged chain (Polaron) in the presence of the counterion

The structure of charged chain/counterion and the influence of the presence of counterion on the charge distribution of polaronic defects have been investigated.

In the beginning of our calculations, we considered the counterion located in the top of the polymer, Fig. 1. And by moving the counterion along the conjugated chain, several local minima are obtained, corresponding to the stable structures (Structure 1–7, in Table 1) of the PEDOT/TSA complex. Further, different orientations of the counterion with respect to the conjugated chain have been considered (perpendicular, lateral and parallel orientations). For each stable

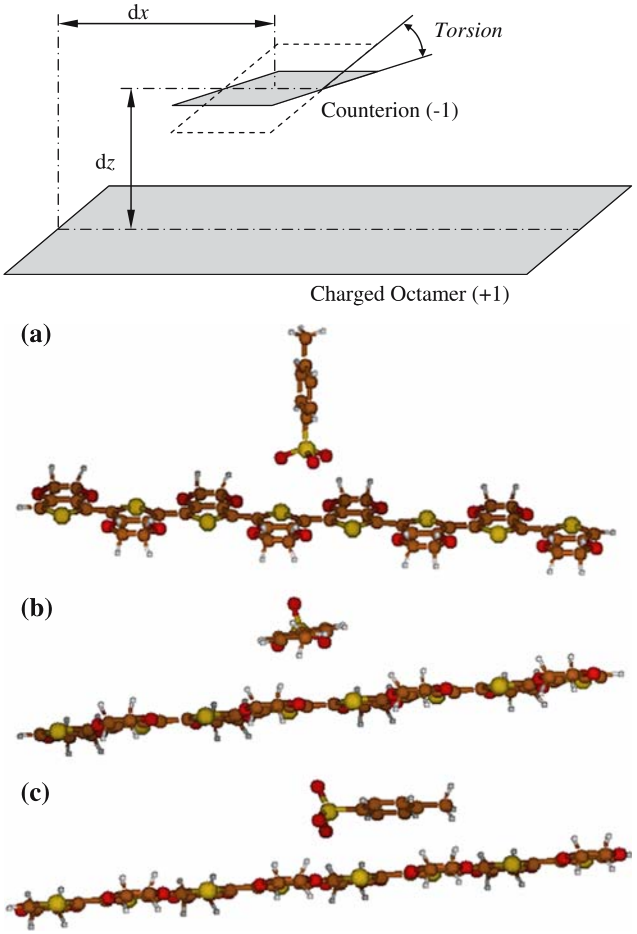


Fig. 1 Position of the counterion with respect to the polymer. **a** Perpendicular situation, **b** lateral situation, **c** parallel situation

Table 1 Selected structural data and variation energy of PEDOT/TSA complex in the case of perpendicular orientation

Stable structures	dz(Å)	dx(Å)	Torsion (°)	ΔE (kcal/mol)[a]
1	3.8	14.5	80.4	0.0
2	3.6	11.9	85.7	4.8
3	3.7	4.0	86.3	10.9
4	3.8	0.0	67.0	20.6
5	3.8	19.8	86.1	4.7
6	3.8	26.3	89.7	10.0
7	4.0	30.2	77.0	21.0

dx: distance along the polymer, dz: distance between the counterions and the polymer, torsion: is the angle between the plans formed by the phenyl of the counterions and the thiophene of the polymer

[a] The structure 1 is the most stable. The structure i is less stable than the structure 1 by ΔEi

structure obtained with MM, we calculated the electronic structure with Ab initio MP2/6-31++G** method. Table 1 summarizes the theoretically predicted selected structural and energetical properties of PEDOT/TSA complex in the perpendicular situation, and Fig. 2 represents the energy variation as function of translational shift (along the polymer) for all orientations. The results indicate that in all orientations of the counterion with respect to the conjugated chain, the most stable structure corresponds to that with the counterions localized in the middle of the EDOT-oligomer. This is also the spatial domain were most of the positive charge carried out by the polymer is located. This stability can be explains by a strong influence of interionic correlation. And one moving away from the center, the stability of the system decreases because the electrostatic interaction becomes increasingly weak (Fig. 2). From the three possible orientations of the counterions (perpendicular, lateral and parallel), the calculations show that the perpendicular position leads to the most stable structure, with an energy stabilization of about 5 and 8 kcal/mol by comparison to the lateral and parallel positions, respectively. The stability in favor of the perpendicular orientation is due the stronger electrostatic attraction between the negative charge shared equally on the three oxygen atoms of TSA and the localized positive charge in PEDOT. In this orientation, the distance between the three oxygen atoms and the center of the polymer is the same, however in the two other orientations only two oxygen atoms are approximately at the same distance.

Figure 3 shows the charge distribution in the positively charged oligomer, without counterion and in the presence of counterion arranged in different orientations. From this Figure, we see that the counterion tend to increase the charge at the center of the molecule and decrease it on the chain ends (pinning effect). We stress that this effect is particularly pronounced for the perpendicular arrangement, for which a large part of the positive charge is located on the central rings. Since the electro-static interactions between the positive charge carried out by the chain and the negative one carried by the counterion are maximized in this situation, it is not again surprising that the perpendicular complex is also the most stable one.

3.2 Packing of charged chains in the presence of the counterions

3.2.1 Packing of two charged chains

For this part of the study, we have considered two conjugated chains with one positive charge per molecule, counterbalanced by one p-toluensulphonic acid.

We have examined the effect of the relative position of the counterions on the stability of the two-chain assemblies. Three situations have been considered: (i) the two counterions are placed one on each side of the assembly; (ii) the assembly is sandwiched between the two counterions; (iii) the chains and the counterions are stacked alternatively. In all

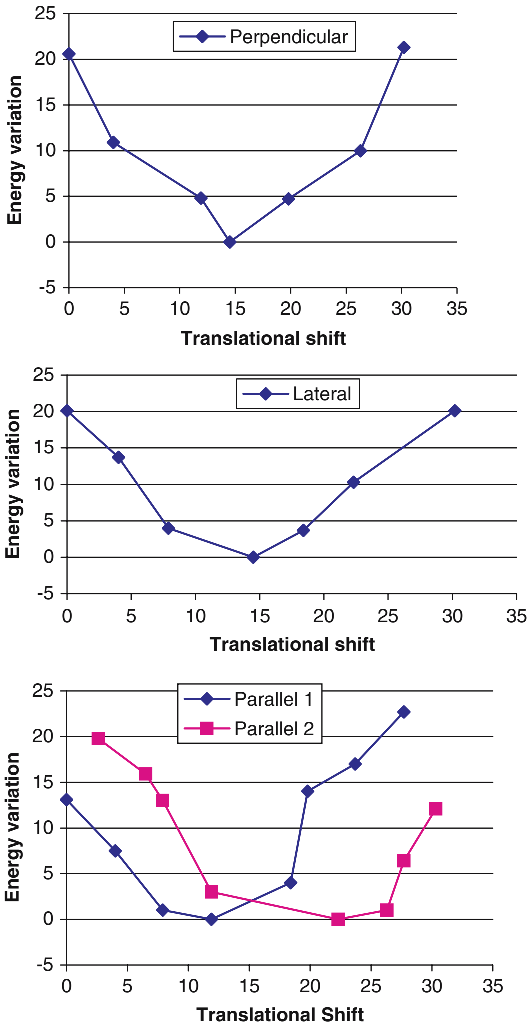


Fig. 2 Relative stability as function of translational shift for optimized structures in different orientations

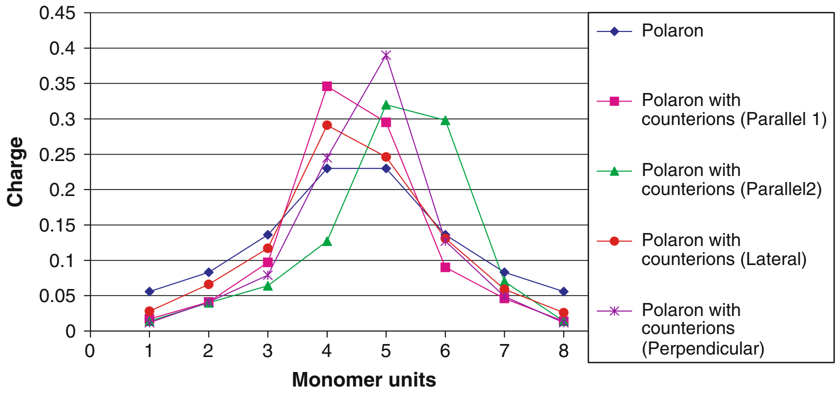
three cases, the counterions are located in front of the center of the chains. Each configuration has been optimized.

The calculations indicate that the first situation (i) is the most stable configuration. Despite the fact that the sulfonate groups are quite far (about 8 Å) from the conjugated backbone in the structure of Fig. 4, which decreases the electrostatic attraction, the two positively charged chains remain close to each other (about 5.1 Å). The same intermolecular distance is found in the second assembly. Obviously, the chain separation is significantly larger in the third situation. These results suggest that doped PEDOT chains can assemble into stable π stacks, with the counterions located alongside. Charge transport along the stacks could then take place easily. Alternating stacks appear to be less stable and they are clearly less likely to lead to effective charge transport. Note that the overlapping EDOT units are 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.

3.2.2 Packing of larger charged chains

In the last paragraph, we have reported the calculations on assemblies of two chains of PEDOT (especially the charged PEDOT dimer in the presence of the counterions). The influence of the relative position of the counterions on the stability of the dimer has been examined. Here our aim is to extend our calculations to larger aggregates, in order to understand how charge transport along the stacks can take place, and propose, among different aggregates investigated, in which one transport is expected to be easier. The strategy used in this part is the same as that used in the dimer, i.e., we considered EDOT octamers with one positive charge per molecule, counterbalanced by one toluene sulfonate counterion. The relative positions of the molecules in the aggregates were optimized with molecular mechanics, with the geometries of the sub-units kept frozen. The charge distribution of each system is coming from Hartree-Fock quantum chemical calculation and it is not allowed to relax during the molecular mechanics calculations. In this part of the study, we have considered only systems based on the most stable situation obtained in the case of the dimer, i.e., the counterions are placed on each side of each assembly.

Fig. 3 Charge distribution of polaron without and in the presence of the counterion



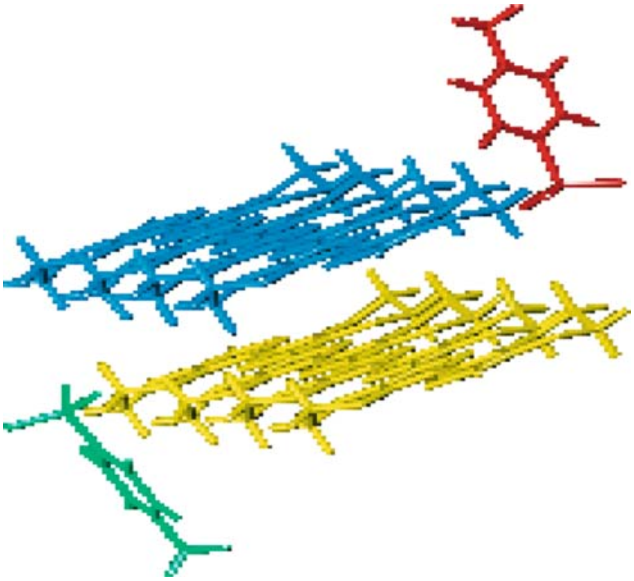


Fig. 4 The most stable structure for the assembly of two charged PEDOT molecules with two counterions

We examine the effect of the orientation of the counterions with respect to the conjugated segment in the case where the counterions are placed on each side of the assembly of four PEDOT chains. Two situations have been considered: (a) the counterions are perpendicular to the plane of the polymer chain; (b) the counterions are lateral to the polymer, i.e., the long axis of the toluene sulfonate molecules is parallel to the plane of the PEDOT chain. Each configuration has been optimized; the most stable structures are presented in Fig. 5. Energetically, the two structures have basically the same stability: we find only a slight difference of 5 kcal/mol in favor of structure (5a). The stabilization originates from two contributions: electrostatic (coulomb interactions between the charge distributions on PEDOT and the counterions) and van der Waals (intermolecular interactions-VDW). The electrostatic interactions are the same for the two structures (the distance between the sulfur atoms of the polymer and the counterion is around 5.4 Å in both structures. The small energy difference therefore comes form differences in VDW interactions, consistent with the difference observed between the intermolecular distances between the PEDOT molecules. In structure (5a), all intermolecular distances are 5.2 Å, compared to different intermolecular distances obtained for structure (5b): 5.6 Å for the extremity of the assembly and 5.0 Å for the center of the assembly. Globally, the VDW contacts between the PEDOT molecules are therefore slightly more favorable in structure (5a) than in (5b). The structure of assembly (5b) also suggests that there is a relationship between the position of the counterions alongside the PEDOT chains and the intermolecular distance between the stacked PEDOT chains: when the counterion is close to a pair of PEDOT (here, chains 1, 2 and 3, 4), those chains tend to slightly drift away from each other (5.6 vs. 5.2 Å). In contrast, when no counterion perturbs the intermolecular contact (chain 2, 3), the chains are closer (5.0 Å).

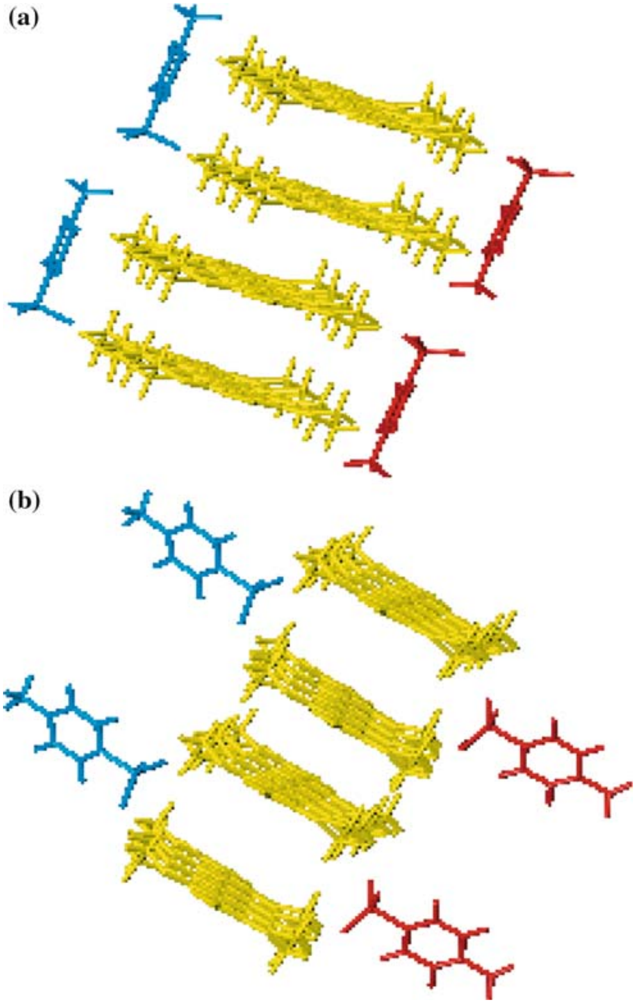


Fig. 5 The most stable structure for the assembly of four charged PEDOT molecules with four counterions. **a** The counterions are perpendicular to the plane of the polymer chain, **b** the counterions are lateral to the polymer

This work can be extended for large molecular aggregates, and based on the results obtained above, we considered only the situation where the counterions are on each side of the polymer (the counterions are perpendicular to the plane of the polymer chain). In this situation, two structures are considered: (a) eight chains are superimposed along two axes (named 4*2), and (b) eight chains are superimposed along one axis (named 8*1). The most stable structures found for these assemblies are reported in Fig. 6. Structure (6b) is more stable than (6a) by about 46 kcal/mol. The major contribution to the stabilization energy comes from the electrostatic contributions. In both structures, the intermolecular distance between the conjugated segments is around 5.2 Å.

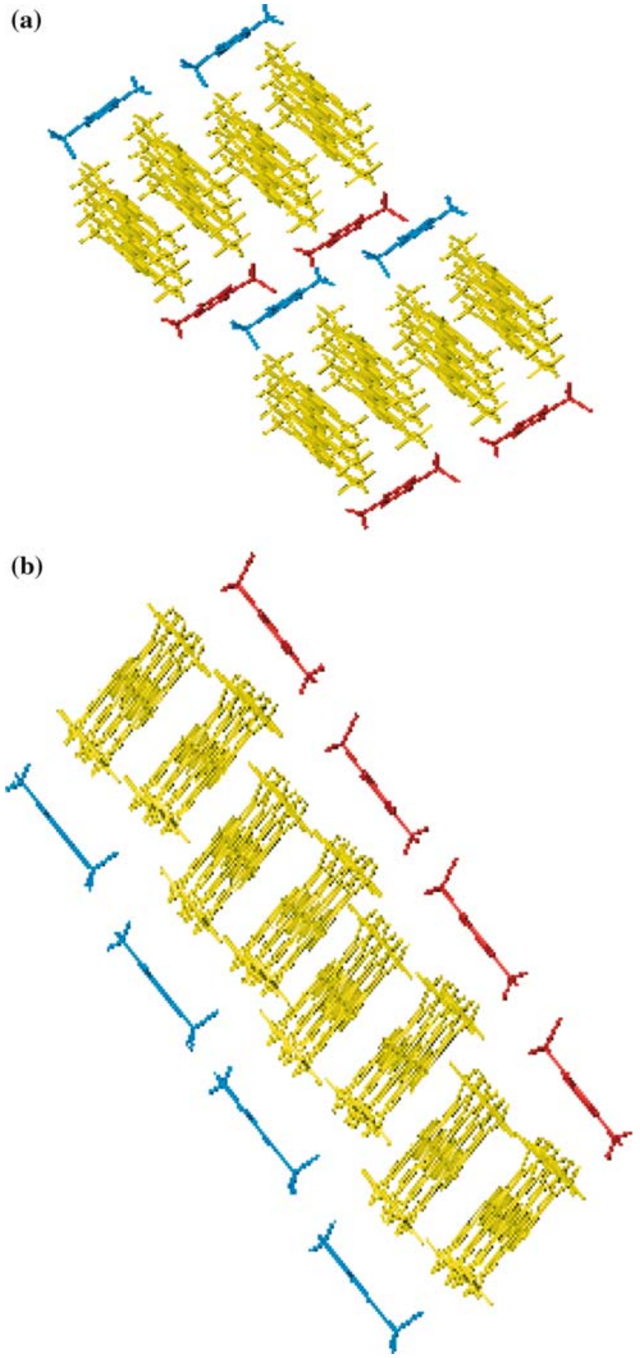


Fig. 6 The two most stable structures of the two different Side assemblies: **a** 4*2 and **b** 8*1. The axis of the PEDOT chains points approximately perpendicular to the view

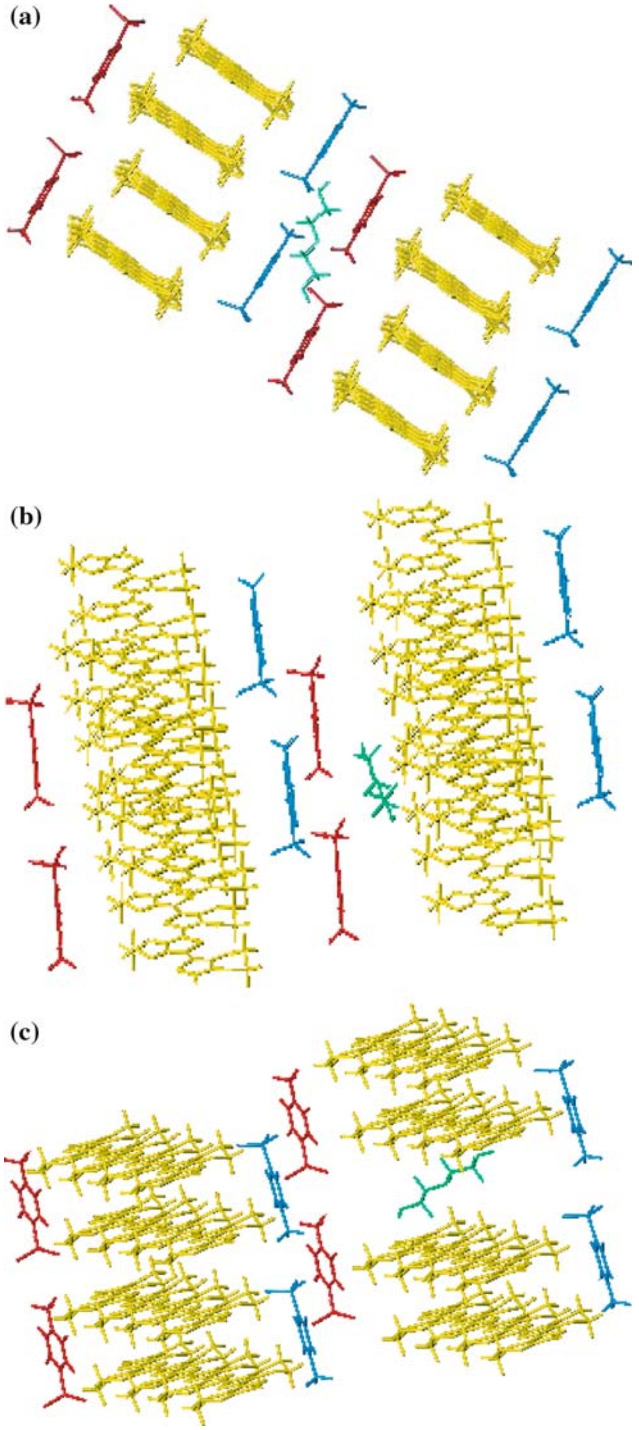


Fig. 7 The three most stable structures for the Side assemblies. **a** DEG molecule is situated between the counterions, **b** DEG molecule is situated between the counterions and conjugated chains, and **c** DEG molecule is situated between the conjugated chains

Note also that the distance between the sulfur atoms of the neighbor counterions (opposite orientations) in the case of the structure (a) is around 7.4 Å. For each structure, this distance between the counterions with same colors (i.e., the same orientations) is around 10.1 Å. Note that the structure (4*2) is in good agreement with the structural model (experimental data) reported by Aasmundtveit et al. [17] and Froberg et al. [18]. Indeed thin films doped with tosylate ions were studied by grazing-incidence X-ray diffraction, and a structural model is proposed. The dopand ions form distinct planes, which alternate with stacks of polymer chains.

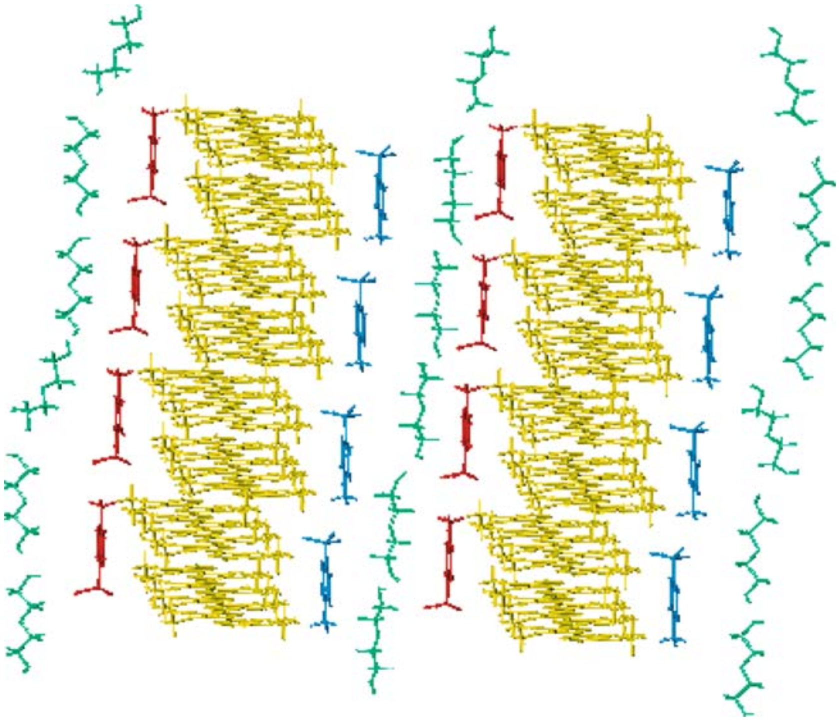


Fig. 8 8*2 assembly embedded in a 'bath' of DEG molecules

The theoretical results suggest that assemblies of stacked charged PEDOT chains, such as Side 8*1, are stable. Considering larger aggregates and based on such type of assembly, the structure of PEDOT/toluene sulfonate (as a model for PEDOT/PSS) can be viewed as "channels" of stacked conjugated chains, along which transport should be easy, separated by channels populated by the counterions molecules.

3.3 Solvent effect

The influence of a high boiling solvent on the geometric organization of PEDOT-PSS is explored in this section; we chose DEG (diethylene glycol) as the solvent molecule since this has been shown experimentally to lead to the most significant increase in conductivity [31]. 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. Two strategies have been used to model the presence of DEG: (i) the solvent is introduced implicitly by introducing the dielectric constant of DEG ($\varepsilon = 31.82$) (all Coulombic interactions are hence screened) and (ii) by introducing explicitly the solvent taking into account one or several DEG molecules.

The calculations were performed starting from the side assemblies: 4*2 and 8*1 (see Fig. 6). Energetically, the two structures were found to have similar stability (5 kcal/mol in favor of the side 4*2 configuration). It is worth stressing that the intermolecular distance between the conjugated segments is strongly decreased in comparison to the situation where the dielectric constant was set to 1 (for vacuum): it goes from 4.5 Å at $\varepsilon = 31.82$ to 5.2 Å at $\varepsilon = 1$.

In a next step, one DEG molecule was introduced in the assembly and three possible molecular arrangements were considered: (a) the DEG molecule is located between the counterions; (b) the DEG molecule sandwiched between the counterions and the conjugated chains, and finally (c) the DEG molecule intercalated between the conjugated chains.

The relative positions of the molecules in the aggregates were optimized with molecular mechanics, using the Universal Force Field, while keeping the geometries of the sub-units frozen (in a similar way as done previously). The charge distribution of each system is coming from Hartree-Fock quantum chemical calculation and it is not allowed to relax during the molecular mechanics calculations. Each configuration has been optimized; the most stable structures are presented in Fig. 7. Energetically, the structure (a) is found to be the most stable configuration. The structures (b) and (c) are less stable by around 25 and 70 kcal/mol, respectively. The intermolecular distances between the conjugated segments are around 5.2 Å, expect the distance of 9.2 Å in the case of structure (7c) where one DEG molecule is intercalated. In assemblies (b) and (c), the intermolecular distances between the counterions are on the order of 7 Å, while the corresponding distance obviously increases when one DEG molecule is interacalted (and found to be about 11.7 Å). Therefore, the repulsive interactions between the negative charges localized on the counter-ions are partly reduced, which leads to the highest stability computed for assembly (a). The results obtained above are very interesting and deserve further study. Along this line, we have considered the case where a large number of DEG molecules are introduced along the counterions in the 8*2 side assembly. The most stable structure obtained for such a configuration is displayed in Fig. 8. The intermolecular distances between the conjugated segments vary between 5.2 and 5.4 Å. In the middle of the assembly, the distances between the counterions oscillate between 11.3 and 11.7 Å. In conclusion of this part, we believe that the assembly described in Fig. 8 is representative of the molecular arrangements of PEDOT chains in the presence of the counter-ions (here toluenesulfonic acid molecules as a model for PSS) and a high boiling solvent (here DEG).

4 Conclusions

The molecular modeling study of PEDOT/TSA interactions is done with molecular mechanics coupled to ab-initio calculations. We have employed this method to investigate the influence of the orientation of TSA with respect PEDOT for the stability of the PEDOT/TSA complex. Firstly in the case of Polaron, we found that the perpendicular orientation is the most stable configuration, this is due to the electrostatic interactions between the positive charge carried out by the chain and the negative one carried by the counterion and are maximized in this situation. The packing formed with several chains and their counterions are studied. The results obtained in this work are very interesting and allow to expect that the molecular structure of PEDOT/TSA is formed as the conjugated chains stacks to form a perfect packing and the counterions are placed on each side, as been obtained experimentally [17,18]. Further the assembly described in Fig. 8 is representative of the molecular arrangements of PEDOT chains in the presence of the counterions and a high boiling solvent. So, the view that emerges from the calculations concerning the solid-state organization of PEDOT-PSS involves the existence of a one-dimensional conjugated core (along which charge transport is expected to occur very efficiently) surrounded by an isolating coat (made of PSS). It is likely that the macroscopic electric conduction properties will be limited by hopping of the charge carriers between the conjugated chains of PEDOT.

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