On the validity of the bipolaron model for PEDOT, with and without $AlCl_4^-$ anions

Ben Craig[a], Peter Townsend[b], Chris Kriton-Skylaris[c], Carlos Ponce de Leon[a], Denis Kramer[a, d]

[a] School of Engineering, University of Southampton, University Road, Southampton, SO17 1BJ, UK

[b] Guest, Department of Chemistry and Chemical Biology, Rutgers University, 123 Bevier Rd, Piscataway, NJ 08854, United States

[c] School of Chemistry, University of Southampton, University Road, Southampton, SO17 1BJ, UK

[d] Faculty of Mechanical Engineering, Helmut-Schmidt-University, Holstenhofweg 85, 22043 Hamburg, Germany

Abstract

The conducting polymer poly(3,4-ethylenedioxythiophene) (PEDOT) is one of the most researched materials. The 1980s bipolaron model remains the dominant interpretation of the electronic structure of PEDOT. Recent theoretical studies have provided updated definitions of key concepts such as bipolarons or polaron pairs, but these have not yet become widely known. In this work, we use density functional theory to investigate the electronic structure of PEDOT oligomers, with and without co-located $AlCl_4^-$ anions. By considering the influence of oligomer length, oxidation or anion concentration and spin state, we find no evidence for self-localisation of positive charges in PEDOT as predicted by the bipolaron model at the hybrid functional level. Our results show distortions that exhibit either a single or a double peak in bond length alternations and charge density. Either can occur at any oxidation or anion concentration. We note that other distortion shapes are also possible. Rather than representing bipolarons or polaron pairs in the original model, these are electron distributions driven by a range of factors. Localisation of distortions does occur with anions, and distortions can span an arbitrary number of nearby anions. Conductivity in conducting polymers has been observed to reduce at anion concentrations above 0.5. We show at high anion concentrations, the energy of the localised, non-bonding anionic orbitals approaches that of the system HOMO due to Coulombic repulsion between anions. We hypothesize that with nucleic motion in the macropolymer, these orbitals will interfere with the hopping of charge carriers between sites of similar energy, lowering conductivity.

1. Introduction

Despite having been used in a variety of applications, fundamental understanding of conducting polymers (CPs) is still incomplete and remains a highly active area of research. CPs are semiconducting in their pure form, and only become conductive when an oxidising or reducing species co-locates with the polymer chain via a redox reaction, a process conventionally referred to as doping by analogy with doped inorganic semiconductors. CPs have a carbon backbone consisting of alternating single-double carbon bonds [1, 2]. PEDOT continues to be the subject of particularly intensive research due to its chemical stability and tuneable conductivity [3]. To date, PEDOT has found applications in supercapacitors [4], sensors [5], solar cells, bioelectronics, electrochemical transistors, sensors, electrochromic displays [6], battery electrodes [7] and spintronics [8]. The present work studies the PEDOT/$AlCl_4^-$ system, inspired by the use of PEDOT as a cathode in a battery with $AlCl_3$:EMIm[Cl] electrolyte and an aluminium anode [9]. However, the co-locating of PEDOT with a small symmetrical anion [9] also allows comprehensive analysis of the electronic structure of PEDOT relevant to a wider field and is a useful complement to the more commonly studied, larger and less mobile anions such as polystyrene sulfonate (PSS) or tosylate (Tos) [1].

While many computational studies on PEDOT exist to date [10-14], to the best of our knowledge the present study is the first that concerns the introduction of $AlCl_4^-$ onto PEDOT, except the authors' own prior work [15, 16].

1.1. Structure and electronic properties of PEDOT, and the bipolaron model

In conventional semiconductors, the high coordination number (four and greater) of covalent bonds between atoms to their neighbours provides a rigid structure such that electronic excitations can be viewed as electrons or holes in a lattice. In CPs, each monomer unit is bound to a maximum of two other monomer units by carbon-carbon bonds, making CPs subject to structural distortions caused by the addition or removal of electrons. Much of the early theoretical work on conducting polymers focussed on attempting to fit existing semiconductor theory to these new materials.

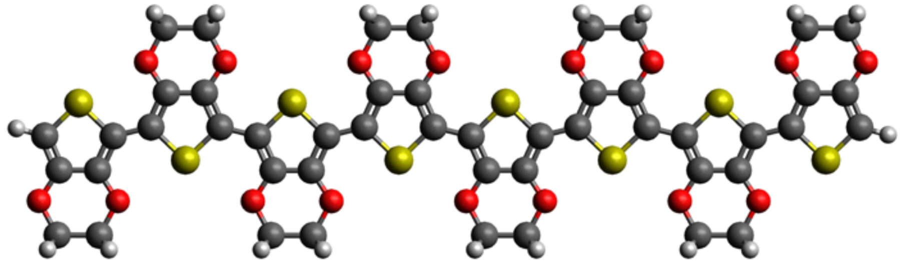
It has been consistently observed and predicted that when counterions are added to conducting polymers, localized charge-carrying distortions occur over a length of a few monomer units [17, 18] as shown in Figure 1. A key feature is that the change in bond lengths observed closely corresponds to the charge density. Electron kinetic energy drives increased distortion length, while the lattice relaxation drives decreased distortion length; the resulting length is a balance of both [14, 19]. The theory of few-monomer distortion lengths is based on the observation that the distortions in conducting polymers are localized around the part of the chain where the anions are located, and their orbitals do not mix enough to form extended energy bands [20]. Instead, they form a series of localized, overlapping states with significant electronic and structural distortions [21].

The bipolaron model in its original form was developed from theoretical and experimental results in the 1980s, shortly after conducting polymers were discovered, in an attempt to explain some of their key characteristics. For example, in inorganic semiconductors, trapped polarons would be expected to build up throughout the lattice as they are oxidised. In contrast, when a conducting polymer is oxidised, the spins build up, before disappearing again, with no spins detected in the fully charged polymer [18, 22, 23] . To explain this, the bipolaron model was devised, which stated that spins first appear as localised singly charged states termed polarons with spin ½, and then as the polymer is further oxidised, the charges co-locate into doubly-charged spinless states termed bipolarons, explaining the disappearance of the spins [18]. Polarons and bipolarons according to the original 1980s bipolaron model are shown in Figure 1.

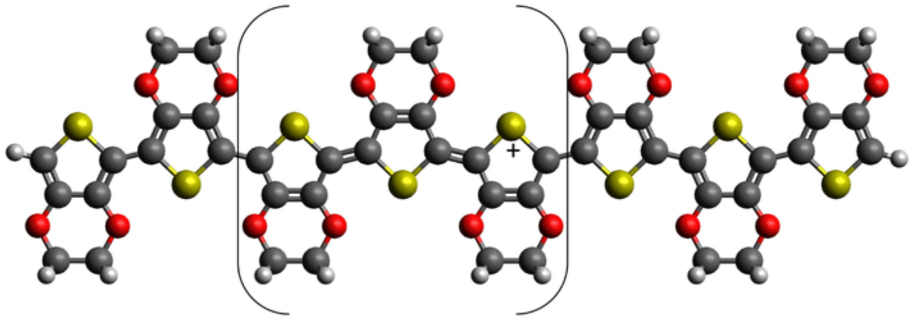
The single-double bond pattern in the conjugated carbon backbone is critical to the characteristics of conducting polymers**.** For the simplest conducting polymer, trans-polyacetylene, the hydrogen atoms are on alternating sides of the carbon atoms. The conjugated carbon backbone has alternating single-double bonds due to a Peierls distortion [24]. No change of energy results from inverting the single-double bond pattern: that is to say, the two possible orientations are degenerate. The presence of a counterion introduces a local region with inverted single-double bond patterns, termed a soliton in the 1980s bipolaron model [25].

Thiophene derivatives including PEDOT have three carbon-carbon bonds in each monomer unit, and so bond inversion is not energetically neutral. A neutral PEDOT monomer unit has a long central bond and a shorter bond either side, described as aromatic structure. The inverted pattern appears in the presence of anions; this is described as quinoid [25, 26] as shown in Figure 1. A polaron is the term given to a localized single-charged distortion, with an accompanying surrounding lattice distortion carrying a distinct charge, analogous to polarons found in inorganic polar insulators and semiconductors [25]. PEDOT and polythiophene are typically treated with anions, becoming oxidised (p-doped), so the polarons are hole polarons [27].

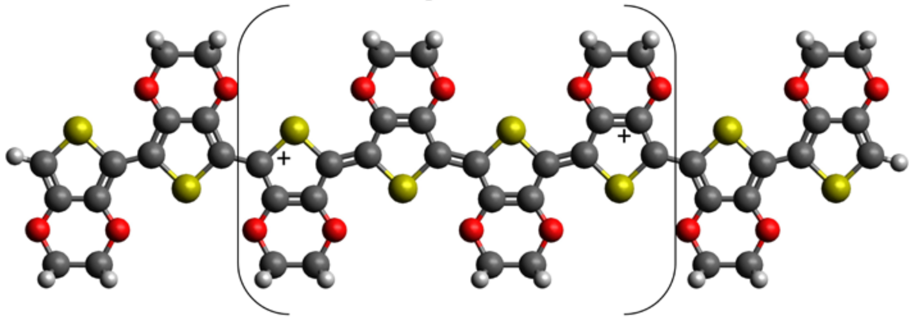
When the polymer is further oxidised, so that it carries two charges per oligomer, the bipolaron model predicts that the charges locate together into a doubly charged excitation termed a bipolaron [28], illustrated in Figure 1. The theoretical driving force is that the energy saved by structural relaxation is greater than the energy penalty from Coulombic repulsion between the two like charges [14]. Further increases in anion concentration lead to multiple bipolaron formation [18]. The 1980s bipolaron model was supported by predictions from early theoretical methods such as one-electron extended Hückel theory. For example, Hückel theory finds that the energy of distortion to form two polarons or one bipolaron is quite similar, but the ionization energy is less for a bipolaron than two polarons [18]. Hückel theory predicted polarons and bipolarons to be around 4 monomer units long in polypyrrole [29]. A semiempirical analysis using the modified neglect of diatomic overlap (MNDO) method showed similar results [30].



Neutral – aromatic structure throughout



Polaron, one electron removed; quinoid structure between brackets



Bipolaron, two electrons removed; quinoid structure between brackets

Figure 1 – 8-PEDOT according to the original 1980s bipolaron model, demonstrating the proposed form of a polaron and bipolaron compared to a neutral oligomer, with accompanying inversions of the single-double carbon-carbon bonds. Yellow atoms are sulphur, red atoms are oxygen, grey are carbon and white are hydrogen. The positive charges are indicated on single carbon atoms with three single bonds, but are distributed over a few monomer units as indicated by the brackets. The bond lengths are not to scale and are illustrative only. Adapted from the review by Heinze et al. [17]

When conducting polymers are in their pure state and unoxidised, they have a bandgap characteristic of semiconductors and the HOMO-LUMO gap is too large to allow much or any conduction. The bipolaron model, set out by Brédas *et al.* [18] and based on an infinite periodic polymer with a band structure, predicts that the removal of an electron from a neutral conducting polymer causes the half-filled energy level to be pushed upwards into the gap. The half-filled level is termed the polaron level. An empty state also appears below the conduction band, termed the bipolaron level. The appearance of these states reduces the bandgap. Removing a further electron causes the newly unoccupied polaron level to be pushed up further still, with a similar decrease in energy of the bipolaron level, further reducing the bandgap [18].

Brédas *et al.* also predicted that the valence band, not including the half-filled level which is described as the polaron band under the bipolaron model, would always be full [18]. It was proposed that the levels appearing in the bandgap corresponded to the π (bonding) and π* (antibonding) states created by the mixing of the anionic states with the existing system [29]. The reduction of the bandgap via the introduction of anions is a key contributor to increased conductivity.

The actual mechanism of conductivity in conducting polymers is a mix of intra- and interchain electron and hole mobility. Conductivity along a PEDOT molecule occurs once there are sufficient numbers of well-distributed anions adsorbed onto it. This causes the quinoid regions to overlap and pass electrons or holes down the conjugated carbon backbone via resonance between many states of nearly identical energy, with many orders of magnitude larger conductivity than the pure polymer [21]. This is possible via rapid swapping of the single-double bonds which allow the charge carriers to travel efficiently [5], and conductivity along the PEDOT molecules is typically very high at moderate anion concentrations. This movement can be thought of as intrachain hopping of charge carriers between nearby sites of similar energy [4].

Hopping or tunnelling of charge carriers between different PEDOT molecules and regions of the polymer is also required for conductivity. PEDOT and other conducting polymers are generally a mix of ordered and disordered regions with some degree of self-ordering due to π-π interactions. In the ordered regions, the conductivity depends on the direction of hopping in the stacked polymer. Various models have been developed or adapted for interchain conductivity [4], including Mott's Variable Range Hopping (VRH) [31] or Sheng's fluctuation induced tunnelling [32]. Further work has suggested that only some regions in the PEDOT achieve polaronic structure and that hopping must also take place between these highly conductive regions [33]. In general, interchain hopping between different molecules or regions has been found to be the limiting factor in conductivity [4].

The bipolaron model predicted that as the concentration of counterions rises, the spinless bipolarons become mobile, and are able to conduct due to the broadening of the bipolaron band, which forms from the bipolaron level as many electrons are removed [17]. At the highest counterion concentrations, the bands can even merge to produce a metal or semimetal [21]. This explanation fits well with the experimentally observed increase in conductivity of conducting polymers at low anion concentrations.

However, experiments on conducting polymers including several thiophene derivatives, albeit not including PEDOT, has shown that conductivity increases up to counterion concentrations of 0.5, then decreases above this [34], for which the bipolaron model offers no explanation [17]. The same behaviour was observed for a hexathiophene and polyphenylene hybrid [35]. Heinze *et al.* suggested that conducting polymers have a maximum of conductivity at 0.5 due to the same mechanism as radical ion salts [17, 36]. This is proposed to be the point at there is a maximum of charge carriers available to hop between sites of similar energy on different chains. Heinze *et al.* proposed that during the wide plateau of conductivity, overlapping redox states are reached successively, keeping the system in a mixed valence state until the last redox sites are emptied and the conductivity drops [17]. Meanwhile, Brédas *et al.* attributed this discrepancy with the bipolaron model to screening of the attraction between counterions and their polarons at high anion concentrations [18]. Others have found that at high anion concentrations, the anions can cluster into regions which inhibit electron hopping between PEDOT regions [37]. Ofer *et al.* suggested that the presence of both charged and uncharged sites would be required for charge carrier hopping. They theorized that the loss of conductivity at high anionic concentrations was due to some kind of localization of charges due to Coulombic repulsion between solvent and charges in the highly charged states [34].

The research in this area is limited partly because of a generally accepted view that anion concentrations normally reach a maximum of about 0.4 in electrochemically synthesized conducting polymer films [17, 38, 39]. Higher levels are achievable, but special electrolytes are required to reach concentrations above 0.5 [34]. No studies could be found that examined PEDOT conductivity specifically as a function of calculated anion concentrations above 0.5, but several show a trend for conductivity to drop as the concentration of anions available for adsorption increases past a certain point [40-43].

What all these mechanisms have in common is that they rely on charge carriers hopping between different sites of similar energy. In this work, we find that at high anion concentrations of 0.66 on single PEDOT molecules, the Coulombic repulsion between the anions pushes up the energy of their highly localised orbitals so that they are close in energy to the HOMO of the overall system, which is normally a delocalised orbital extending over the conjugated carbon backbone. We suggest that combined with movements of the polymer at temperatures above 0 K, these highly localised orbitals might be pushed up in energy sufficiently that they begin to interfere with the hopping mechanism between different sites of similar energies, affecting both intra- and interchain conductivity.

1.2. Progress from density functional theory

Since the 1980s when the original bipolaron model was developed, density functional theory (DFT), particularly hybrid DFT incorporating a proportion of Hartree-Fock exact exchange energy, has become standard for modelling conducting polymer systems due to its ability to handle electron correlation effects while remaining efficient for reasonably large systems [16]. Investigations via DFT have provided significantly different insights into the electronic structure of conducting polymers and have led to revised explanations of experimental observations.

A key limitation of one-electron theories is that they omit electron-electron repulsion [14]. One-electron methods assume degeneracy of the spin orbitals even for spin-asymmetric configurations with a partially occupied level, treating the half-filled band as fully occupied. The spin degeneracy assumption distorts the results between odd and even oxidation levels, as the independence of spin-up (α) and spin-down (β) orbitals is an important part of the energy minimization process for any open-shell system. Consequently, Hückel theory predicts that two new spin-degenerate levels are created in the gap for each oxidation step of the PEDOT; a lower singly occupied state and upper unoccupied state for a polaron, and two empty states for a bipolaron [44]. In contrast, *ab initio* methods do not predict spin degeneracy for polarons, and only one state appears in the gap [6]. Meanwhile, semiempirical methods need parameterising carefully from appropriate *ab initio* methods [14].

Hybrid DFT calculations generally do not support the existence of the type of spinless bipolaron predicted by the one-electron or semiempirical approaches where charges co-locate by energetic preference of structural relaxation [6, 45]. A review of DFT studies indicates that bipolarons do not exist in long oligomers without counterions [14]. Only oligomers shorter than eight units long [14], and oligomers with one dopant per six or fewer thiophene rings [46] exhibit bipolaron-like behaviour [10], and then only because there is not enough room for the distortions to separate into polarons. Also, spectroscopic experiments on oligothiophenes have demonstrated that the sub-gap transitions previously attributed to bipolarons were actually two separated polarons in long oligothiophenes [47]. Findings such as this led to the invention of the term polaron pair, which consists of two polarons for which it is not energetically favourable to co-locate, so they tend to move apart along the chain if there is space to do so. In this conception, bipolarons are closed-shell singlet states and therefore spinless, while two polarons on the same chain can be singlet or triplet biradicals [48].

The presence of counterions also serves to pin charge carriers in a particular location, which can give rise to apparent bipolaronic behaviour [25]. Modelling of thiophene chains of various lengths up to 25 monomer units has indicated that polarons tend to spread out but do interact still in the middle of the chain, observed via bond length changes compared to neutral oligomers, implying an interaction spread over a much larger part of the chain. These results have also been interpreted to support the concept of polaron pairs rather than bipolarons, referring to the triplet state reported for oligomers longer than ten monomer units with +2 oxidation state which shows two peaks in bond length alternations [49].

In contrast to previous explanations of the build-up and disappearance of spins, more recent DFT work has proposed that the tendency for spins to build up during oxidation and then reduce or disappear once oxidation is complete is caused by the removal of multiple single electrons from fully occupied valence states across different chains in the polymer, and then the subsequent removal of the singly occupied electrons, leaving the original HOMO-1 as the new, fully occupied HOMO [6]. This explanation is much simpler than the bipolaron model.

To account for the developments from modern theoretical methods, it has become convention to refer to the original 1980s bipolaron model as the ‘traditional model’ or its predictions as those of the ‘traditional methods’. Since 2019, some authors have adapted the terms from the original bipolaron model to fit modern understanding [6, 50]. Perhaps the clearest elucidation of the updated terms polaron, bipolaron and polaron pair is provided by Sahalianov *et al.*, with a polaron referring to a doublet with +1 charge, a polaron pair to a triplet with +2 charge, and a bipolaron to a singlet with +2 charge [50]. In this approach, states with more than two charges are referred to as polaron(ic) or bipolaron(ic) for odd and even charged states respectively, and the distortion shape is longer a characteristic of a polaron, bipolaron or polaron pair [6, 50]. An important feature is that the terms are no longer linked to distortion characteristics, unlike other less recent theoretical work [10, 48, 49]. Sahalianov *et al.* adds that a bipolaron is a distortion shared between two nearby anions, and a polaron pair two anions that are far enough apart to produce two separate distortions, but with no structural preference for co-location of charges [50]. Ambiguity remains over how to describe what happens when more than two anions are near enough to share a single distortion.

This change in definition means that a bipolaron or a polaron pair is no longer associated to a distortion shape or to an energetic preference for co-location or separation of two charges, leaving very little of the original meaning. We believe this adaptation of the original language is confusing and presents a barrier to accessing modern theoretical understanding for experimentalists and those new to the field. This is evidenced by the fact that many researchers are still using the bipolaron model in its original 1980s form based on pre-DFT methods [17, 21, 27, 39, 51-58] as also pointed out elsewhere [6, 50]. The picture from modern theoretical methods is not confusing when explained from first principles, as we reinforce throughout this work based on our own results. For clarity and because others still base their understanding on it, we refer in this work to the bipolaron model in its original 1980s form. We describe our own results, and those from other modern theoretical studies, using first-principles descriptions. We propose that this approach, which disproves and then abandons the terminology of the original bipolaron model, is simpler and more accessible.

2. Results and discussion

In this section we present and discuss the results of hybrid DFT calculations of the electronic ground states and low-lying excited states of neutral and oxidised PEDOT oligomers of various lengths, with and without $AlCl_4^-$ anions. For each system, the geometry was relaxed after the spin or oxidation state has been applied and after any anions have been introduced. We discuss charge densities, bond lengths, energy levels and molecular orbitals of the DFT calculations. The method is discussed in detail in the Methodology section.

2.1. Electronic structure of neutral and oxidised PEDOT oligomers without anions

Partial charge analysis is used to provide insights into the nature of the charge carrying distortions in the PEDOT oligomers without anions, using the Merz-Kollman electrostatic potential (ESP) method [59]. The partial charge summed over the monomeric units of 4-PEDOT, 8-PEDOT, 16-PEDOT and 20-PEDOT is shown in Figure 2, where a positive charge means a lower electron density on that monomer unit.

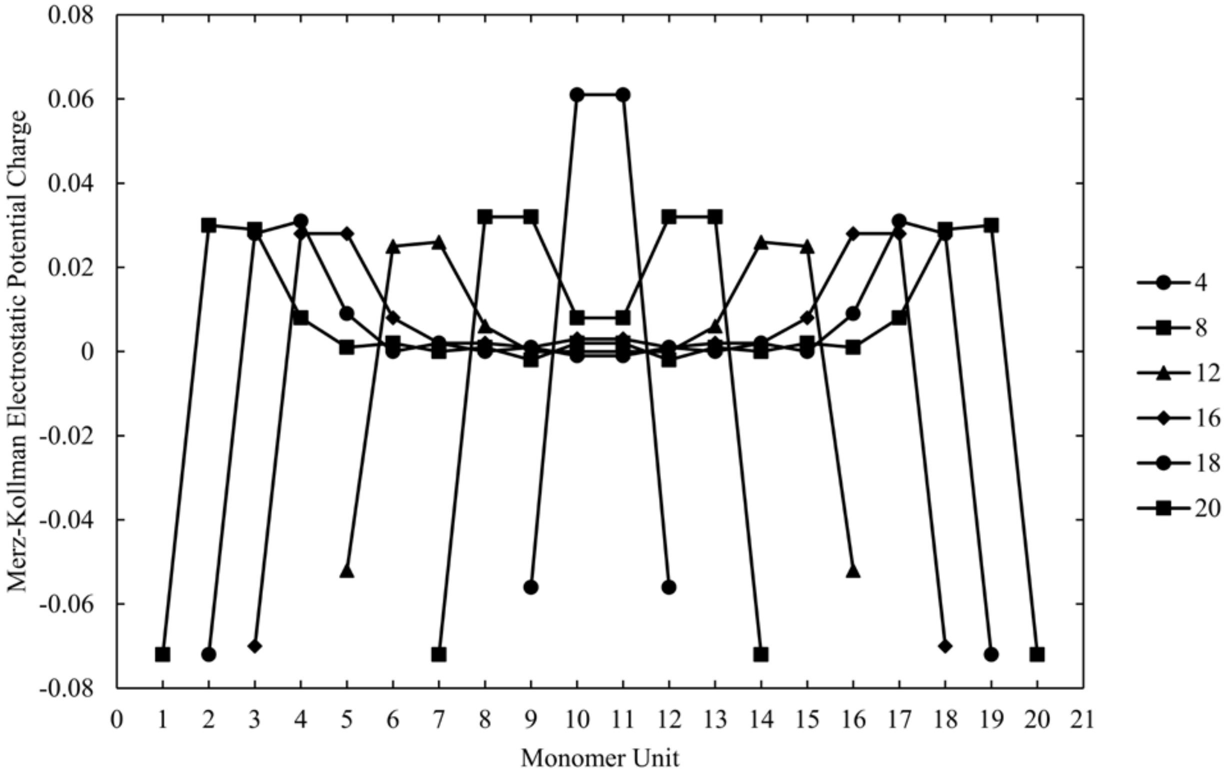


Figure 2 - Merz-Kollman ESP atomic charges summed over each monomer unit for 4-, 8-, 12-, 16-, 18- and 20-PEDOT. Each curve shows a high concentration of negative charge on the terminal units, with a more extended region of positive charge inside of these. These end effects are around 4 monomer units long, with a neutrally charged midsection appearing on oligomers longer than 8-PEDOT. For the 4- and 8- PEDOT, there is not room for a neutrally charged midsection.

There is a clear tendency for electrons to gather at the ends of the chains, with a small region of positive charge over the adjacent monomer units. The longer oligomers (> 12) show the overall end effect spans four monomer units at each end with an almost neutral middle section. Chains shorter than 12 units are dominated by two overlapping end effects. This correlates with the observed change in optical properties from short to long thiophene chains, which has led others to describe an oligomer with less than 9 rings as ‘short’ and longer than 12 rings as ‘long’ [49].

Providing the oxidation state is not too high, the electrons tend to spill out at the ends of the system. If this were a metal, it would be termed the Smoluchowski effect [60]. The small positively charged rebound effect on the second and third monomer units from the end may be analogous to a Friedel oscillation [61]. This charge profile is not just seen for PEDOT but also for polyacetylene (see

Supplementary Material, Figure 12) and we propose that this is a general feature of conducting polymers. We would expect little additional difference to the role of the end effects when extending the oligomer beyond 20-PEDOT, because this trend has already been observed for polythiophene oligomers with similar methods [62].

To understand the effect of oxidising the polymer, an 8-PEDOT oligomer was modelled at oxidation states from 0 to +8, in the lowest two multiplicity states for each configuration. It was found that oxidation states 0, +2 and +4 had singlet ground states, while +1 and +3 had doublet ground states. The energy of the lowest lying excited configurations (triplets, quartets) was at least 0.4 eV above the ground state, indicating a strong preference for singlets/doublets for 8-PEDOT at these oxidation states. The exception was 8-PEDOT +2 where the triplet state was only 0.19 eV above the singlet ground state. The partial charges, summed over each monomer unit, are shown in Figure 3 for oxidation states up to +4. A key observation is that the whole oligomer carries the charge: there is no distinct region on the oligomers that carries a single charge, which immediately raises questions about the definition of a polaron, which under the bipolaron model is a localised charge carrier with a distinct charge. However it is also noted that this is an effect of using B3LYP [12].

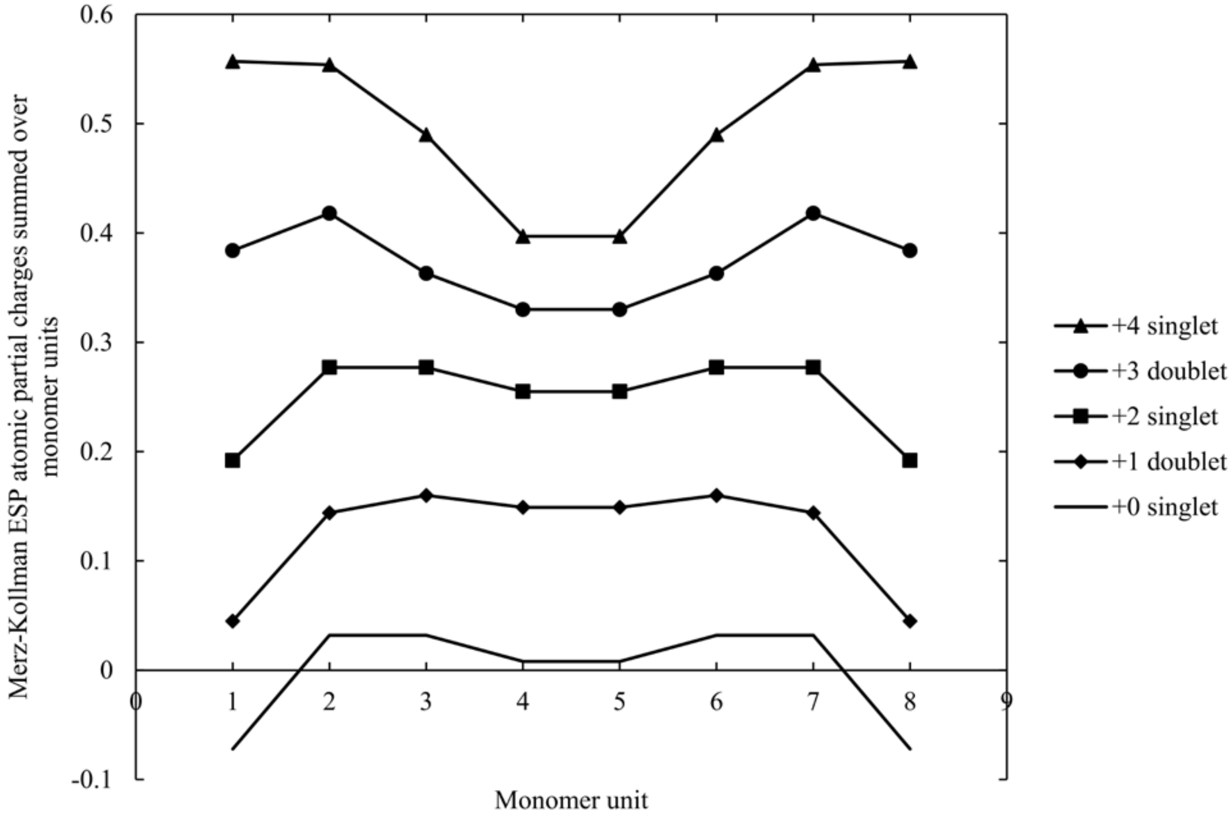


Figure 3 - Merz-Kollman ESP charges summed over each monomer unit for 8-PEDOT oligomers in different oxidation states. As the oxidation state increases from 0 to +2, the higher multiplicity state demonstrates a clear separation of charge effects with the lower multiplicity state showing more of a central plateau. For +3 and above, the positive charge is pushed increasingly to the ends for both spin states. For the oxidised PEDOT, the charge density is distributed over the entire oligomer and never reaches zero, suggesting that the effects seen are peaks in a distribution of positive charge, rather than being distinct charge carriers of integer value localised on an otherwise neutral oligomer.

From 0 to +3 oxidation state in Figure 3, the ends of the chain remain lower in charge as previously observed, demonstrating that for moderate oxidation states the electrons still tend to gather at the ends. At higher oxidation states of +3 and above, the highly positively charged oligomers tend to attract the electrons to the centre instead. It should be noted that it is uncommon for conducting polymer systems to carry more than 1 charge per 3 monomer units in practice [17].

Bond length analysis was used to quantify the structure of the distortions. Figures 4 and 5 show the bond lengths, as well as the atomic partial charges summed over the monomer units, for 8-PEDOT and 16-PEDOT respectively with 1 and 2 electrons removed. The carbon-carbon bonds between monomer units are omitted for the carbon-carbon bond length plots. This allows regions of aromatic and quinoid structure to be identified with aromatic structure having longer central bonds (upwards arrow shape) and the quinoid having shorter central bonds (downwards arrow shape). For comparison, neutral ground state PEDOT oligomers of all lengths have aromatic structure throughout.

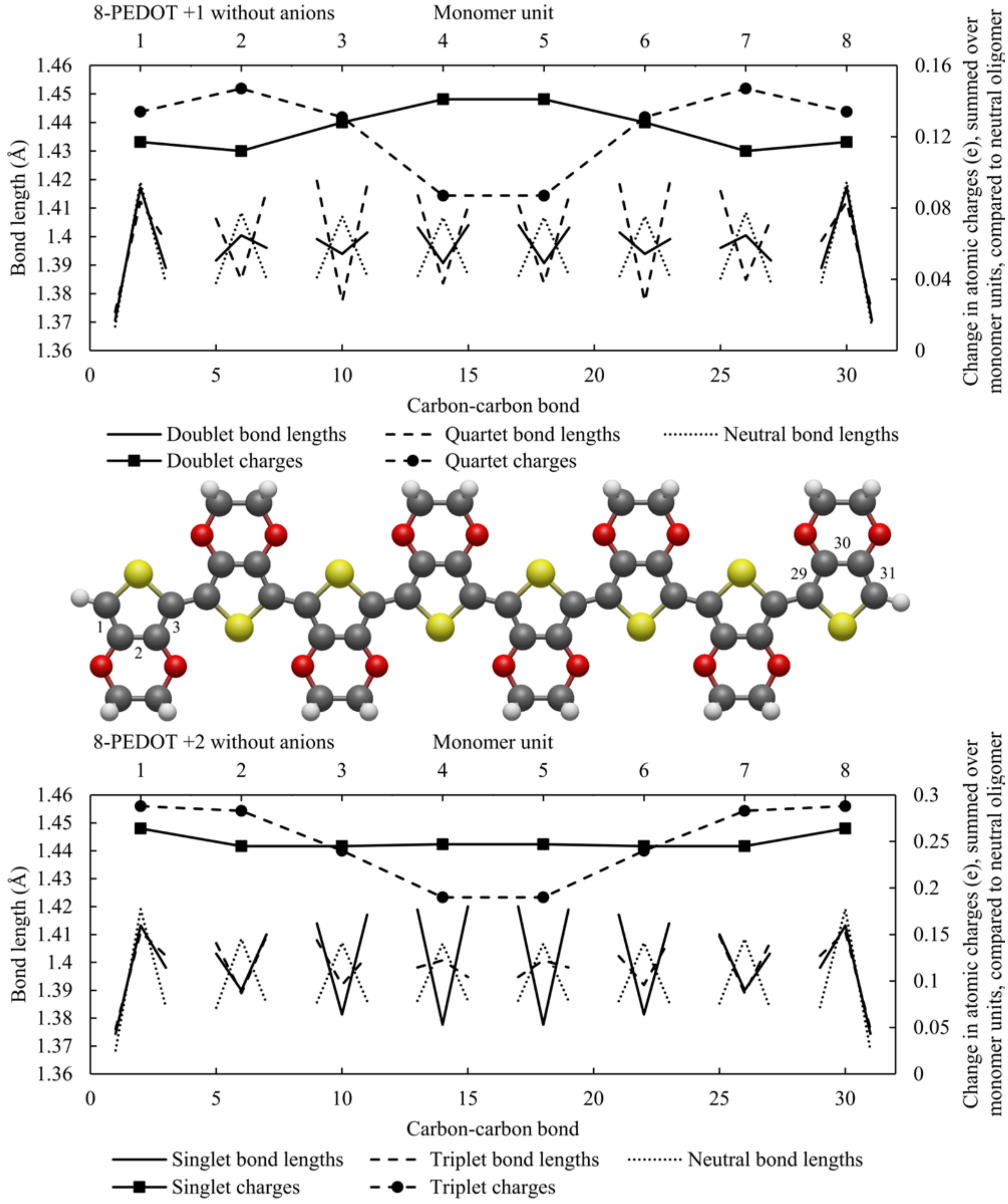


Figure 4 – The changes in atomic partial charges calculated from the ESP summed over monomer units compared to the neutral oligomer, and bond lengths of the carbon-carbon bonds negating those between monomer units in order to highlight the aromatic vs. quinoid structure. The bond lengths of the neutral oligomer are shown for reference. Aromatic regions are indicated by inverted V-shape, quinoid regions by V-shape. Shown for 8-PEDOT +1 doublet and quartet, and 8-PEDOT +2 singlet and triplet. For 8-PEDOT +1, the doublet is the ground state with the quartet 1.4 eV higher in energy, and for 8-PEDOT +2, the singlet is the ground state with the triplet 0.19 eV higher in energy.

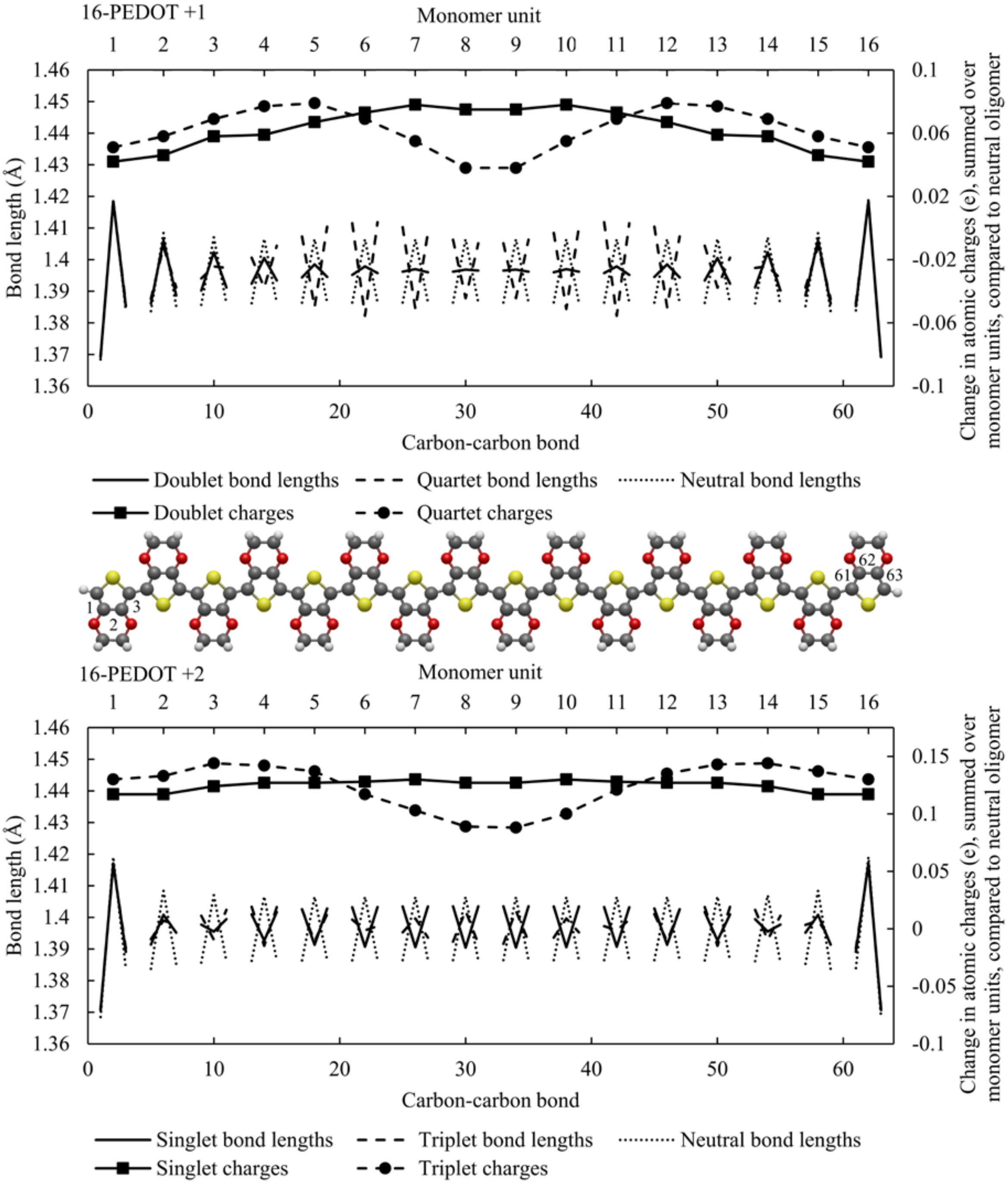


Figure 5 – The changes in atomic partial charges calculated from the ESP summed over monomer units compared to the neutral oligomer, and bond lengths of the carbon-carbon bonds negating those between monomer units in order to highlight the aromatic vs. quinoid structure. The bond lengths of the neutral oligomer are shown for reference. Aromatic regions are indicated by inverted V-shape, quinoid by V-shape. Shown for 16- PEDOT +1 doublet and quartet, and 16-PEDOT +2 singlet and triplet. For 16-PEDOT +1, the doublet is the ground state with the quartet state 1.08 eV higher in energy, while for 16-PEDOT +2, the triplet is the ground state with the singlet state 0.11 eV higher in energy.

For 8-PEDOT +1 doublet, there is a single quinoid region in the middle of the chain, four monomer units long, with the central two monomer units having the most pronounced region of bond length alternation. This corresponds to a well-distributed plateau of positive charge. We call this a single peak distortion. It should be noted that the delocalization of a single peak distortion over the entire chain is particular to the use of hybrid functionals such as B3LYP. The use of range-separated hybrid functionals with short-range Hartree-Fock exchange like wB97XD, on the other hand, has been shown to produce localized distortions that are converged with respect to oligomer length [12], which is expected as pure Hartree-Fock tends to over-localize electrons. A similar investigation using wB97XD to investigate the bond length alternations on a 9-PEDOT +1 without anions shows that although the distortion is much more localized than for B3LYP, it is not completely localized compared to the neutral case: there is still some reduction of bond lengths right out to the end units [63]. A discussion of the relative merits of B3LYP and wB97XD when modelling conducting polymers can be found in [16]. Regardless of functional, the ground state for a singly-charged 8-PEDOT without anions is found to have a single peak distortion regardless of the distortion length. For 8-PEDOT +1 quartet, there are two peaks in bond length alternation and charge distribution, extending over six monomer units, but they do not split into two separate regions of quinoid structure. We term this a double peak distortion, noting that the quartet state is 1.4 eV higher in energy than the ground state and so is highly energetically unfavourable.

For 8-PEDOT +2, the singlet state (ground state) has a more exaggerated single peak distortion than the 8-PEDOT +1 doublet, with a greater difference between short and long bonds and extending over six monomer units. The longer length of the distortion compresses the aromatic region at each end. For the 8-PEDOT +2 triplet, an area of aromatic structure between the two quinoid regions has appeared, demonstrating a tendency for the double peaks to split into two at higher oxidation states. The whole double peak distortion is six monomer units in length including the aromatic region in the middle. The energy of the 8-PEDOT +2 triplet is 0.19 eV higher than the singlet, which is still much higher than *kT* at room temperature which is 0.026 eV. Comparing again to previous work using wB97XD on 9-PEDOT +2, the wB97XD result also shows a distortion of larger amplitude compared to 9-PEDOT +1 but is much more localised on the a few monomer units in the centre of the oligomer. However, as for 9-PEDOT+1, there is again a reduction in bond lengths all the way to the end units, correlating with our findings of the distortion affecting the entire oligomer, with the end units having a strong tendency to remain sharply aromatic. As for +1, this suggests that even wB97XD shows some degree of delocalisation over the entire oligomer length in PEDOT. As more charges are added to the oligomer, the area of distortion steadily spreads out and the end effects are compressed, until by +4 even the end units are significantly affected, fitting with our observation that electrons tend to gather at the ends of the oligomers and higher oxidation states tend to result in longer distortions and compressed end effects. Indeed the authors of that study suggest that the spreading out of distortions over the oligomer length as anion concentration increases is the reason that PEDOT, when synthesised, can only achieve an anion concentration of 33% [63].

The 16-PEDOT +1 doublet, which is the ground state, has no actual bond inversion, instead showing a widely delocalized region of less aromatic structure over at least eight monomer units with a peak over the central four bonds. There is no distinct region that carries the positive charge. This suggests that one positive charge on a 16-PEDOT oligomer is not sufficient to introduce a quinoid region. 16-PEDOT +1 quartet, which is 1.08 eV higher in energy than the ground state, has two unseparated peaks of quinoid structure over ten monomer units, like 8-PEDOT +1 quartet.

In the case of 16-PEDOT +2, the triplet state has become the ground state with the singlet state 0.11 eV higher in energy. It has a distinctly separated double peak distortion, with a clear aromatic region between them as for 8-PEDOT +2 triplet. It extends over twelve monomer units. This shows that the double peak distortion becomes increasingly energetically favourable over the single peak distortion with increasing oligomer length and increasing oxidation state. Our results correlate with the findings of van Haare *et al.*, who found two separate distortions on longer 12-polythiophene oligomers and only one on 6- and 8-polythiophene oligomers, and who termed this a polaron pair [47].

For both 8-PEDOT and 16-PEDOT, the tendency of the electrons to gather at the ends of the oligomers causes the end units to have aromatic structure. In 8-PEDOT, this is seen over two monomer units at each end for the +1 doublet and over one monomer unit at each end for the +2 singlet, while for 16-PEDOT the aromatic structure extends over four monomer units for the +1 doublet and two monomer units for the +2 singlet. The higher multiplicity states appear to promote greater spreading out of the double peak distortions, with a reduced aromatic region at each end for the quartet *vs.* doublet or triplet *vs.* singlet. In summary, the lengths of the aromatic regions at the ends increase with oligomer length, decrease as a function of the oxidation state, and are also affected by the spin state, with the distortion taking up the rest of the oligomer length. We note that other authors have found that with long enough oligomers of polythiophene, 25 monomer units in this case, a single positive charge on polythiophene modelled using wB97XD can achieve a converged length where it can be repositioned unsymmetrically on the oligomer with negligible change in energy. However, this effect disappears for +2 resulting instead in a sharply separated double peak effect as the ground state [12].

These results have interesting implications for the bipolaron model. The bipolaron model predicts that for singly charged oligomers, a localized polaron carrying a distinct positive charge should form, which would be shown by a region of positive charge and quinoid structure on the PEDOT three to four monomer units in length, even on a long oligomer. As another electron is removed, this distortion should either become more pronounced as two charges co-locate, termed a bipolaron, or separate into two distinct distortions, each carrying a single charge, termed a polaron pair [17]. However, this work shows that the ground state and lowest-lying excited states demonstrate single and double peak characteristics for both +1 and +2 systems. This is in line with other DFT calculations showing that singly and doubly charged oligomers have similar geometries [6]. Furthermore, none of these distortions carry a distinct charge; the charge distribution has peaks, which correspond well to the areas of maximum bond length alternation, but ultimately the positive charge is distributed over the whole oligomer. This can be observed in Figure 5 for 16 PEDOT +2, where the triplet case shows two clear regions of quinoid structure bond lengths with an aromatic region in the middle, with the charge density graph following the same pattern. Finally, our results show that there are clear aromatic regions at each end of the oligomer. These act to constrain the distortions, which otherwise try to spread out, rather than having a fixed length. Rather than being localised and distinct polarons, polaron pairs or bipolarons, we argue that the different distortion types are simply different distributions of electrons over the entire oligomer length driven by a range of factors.

We found the same ordering of the ground and lowest-lying states as Zozoulenko *et al.* [6] for 12-PEDOT, who also studied PEDOT oligomers without counterions with hybrid DFT. However, having examined bond lengths and charge density, and finding no evidence of distortions carrying distinct integer charges, we choose to move away from the terms bipolaron and polaron pair. Table 1 states the ground states of different oxidation states of different oligomer lengths of PEDOT. It is seen that the triplet state becomes preferable only for +2 oxidation states and never for +4 until the oligomer length reaches 18 monomer units. The quartet state is never the ground state. Given that we have shown that the double peak distortion is similar between triplets and quartets in Figures 4 and 5, we propose there is nothing unique about even numbered oxidation states, but rather suggest that having three unpaired electrons (a quartet) never becomes energetically favourable at the oligomer lengths and oxidation states investigated.

It should be noted, as has been elsewhere [6] that in some cases the ground state and lowest lying configurations are close enough to suggest that both would occur regularly at room temperature, though in most cases they are separated by considerably more than *kT* at room temperature. The exact DFT error for this system is not known, and distortion characteristics have been shown to be quite dependent on DFT approach [14]. However, the appearance of a clear double-peak distortion for 16-PEDOT +2 in Figure 5, and also for 12-PEDOT +2 in Figure 7, appears to match experimental observations on 12-polythiophene +2 and lends support to our results [47].

Table 1 - Multiplicity of ground states for different PEDOT oligomer lengths and oxidation states

OXIDATION LEVEL	**6 PEDOT (THIS WORK)**	**8 PEDOT (THIS WORK)**	**12 PEDOT ([6], THIS WORK)**	**16 PEDOT (THIS WORK)**	**18 PEDOT [6]**
+1	Doublet	Doublet	Doublet	Doublet	Doublet
+2	Singlet	Singlet	Triplet	Triplet	Triplet
+3	Doublet	Doublet	Doublet	Doublet	Doublet
+4	Singlet	Singlet	Singlet	Singlet	Triplet

Figure 6 shows the energy levels of 6-PEDOT and 12-PEDOT with the ground states as stated in Table 1. The bipolaron model holds that when PEDOT is oxidised, a half-filled polaron band is created above the valence band and an empty bipolaron band below the conduction band. Oxidising to +2 then moves the polaron and bipolaron bands further away from the valence and conduction bands respectively [44]. It has also been proposed that the states appearing in the gap are the bonding and antibonding states created by the anions [18]. However, what is observed in Figure 6, as elsewhere in theoretical research [6], is that when one electron is removed, a single energy level appears in the gap even in the absence of anions, which is the newly unoccupied β orbital that would be degenerate with the HOMO if it was occupied. When two electrons are removed, the energy level that was previously the HOMO moves up into the gap, and for the triplet 12-PEDOT +2, the two unoccupied states corresponding to the HOMO and HOMO-1 are pushed up into the gap. The pushing up of the unoccupied β orbitals can be explained as follows. When the α and β orbitals both contain an electron, they are spatially identical. When only the α orbital is occupied, the energy of all surrounding levels is increased, with the greatest effect on the equivalent β orbital as it has the greatest overlap. We argue that this is a more intuitive and complete explanation of the energy level structure than describing the states appearing in the gap as polaronic or bipolaronic, a choice others have made to integrate the language of the original bipolaron model with updated electronic structures gained from DFT [50].

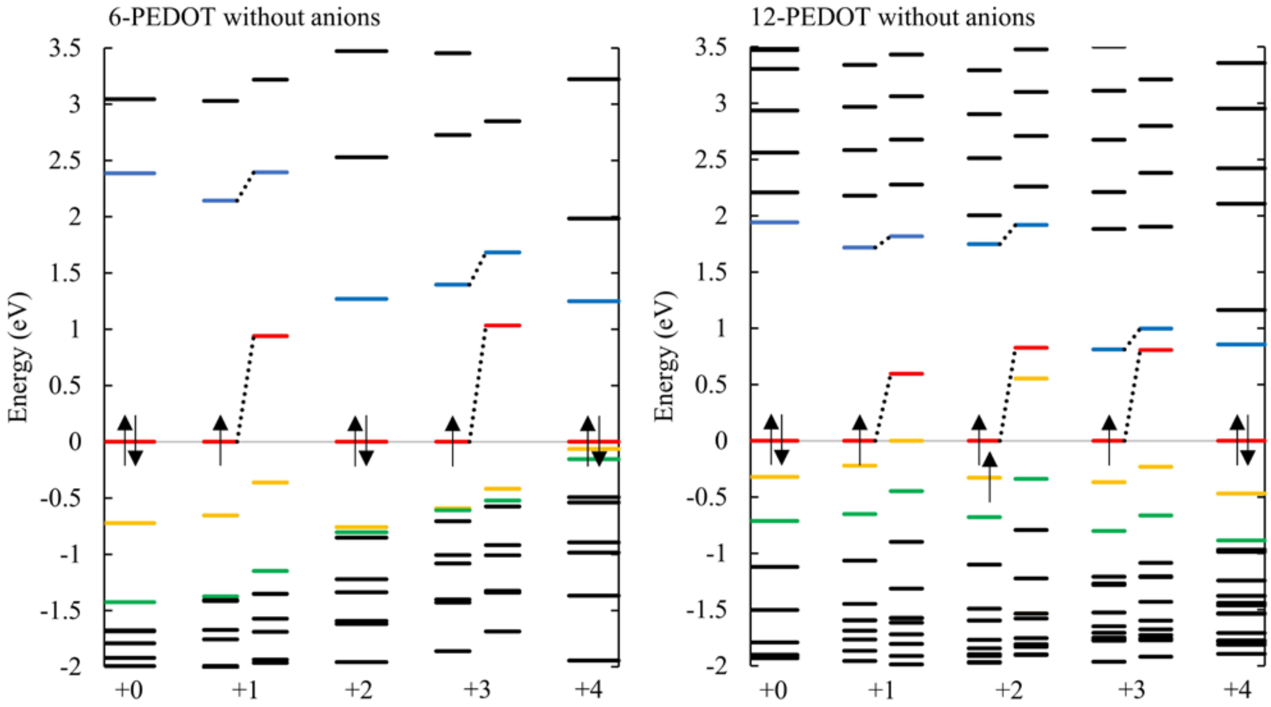


Figure 6 - energy levels for 6-PEDOT and 12-PEDOT, without counterions, at different oxidation states. For filled valence shells the HOMO is indicated with both up and down spin electron arrows, while for partially filled valence shells (including the triplet) only the partially filled α levels are indicated. It is shown that for odd charges, with doublet ground state, a single unoccupied layer appears in the gap, which is the unoccupied β orbital of the HOMO. For 12-PEDOT, the patterns are similar, but the HOMO-LUMO gap reduces faster for longer chain lengths. For the +2 state, which has triplet ground state, two unoccupied levels appear in the gap; these are the unoccupied β orbitals of the two singly occupied orbitals. The HOMOs are normalized to 0 eV. Without this normalization, the overall energy level scale reduces as electrons are removed.

Summarising for PEDOT without counterions, we have found that for the range of oligomer lengths studied, the size of a distortion is not fixed but depends on oxidation and spin state and the oligomer length. Both single and double peak distortions are possible for any oxidation state, albeit with a significant energy difference in some cases. This means that in our findings, the appearance of a double peak distortion cannot be associated with the term polaron pair as it can still appear for singly charged systems. The oligomers always end with an aromatic region of length varying from one to four monomer units, with length also dependent on oxidation and spin state and oligomer length. The HOMO-LUMO gap reduces with increasing oxidation state, but the unoccupied levels that appear in the gap are the unoccupied β orbitals of the highest occupied levels, with two levels appearing in the gap for triplet ground states.

2.2. Electronic structure of PEDOT oligomers with $AlCl_4^-$ anions

When $AlCl_4^-$ anions are introduced to the system, they locate in stable energy wells over the sulfur atoms and between the two oxygen atoms, out of the plane of the PEDOT oligomer, and are able to site either side of the plane of the fused rings. Previous work has shown that this position is generally stable providing only one anion is incorporated per PEDOT chain, though if several anions are positioned on adjacent PEDOT chains, they may spread out during DFT structural relaxation or *ab initio* molecular dynamics to adjacent sites [15]. This result stands in clear contrast to the original bipolaron model which predicts that there is an energetic preference for co-location of charges.

To examine the effects of different numbers of anions on the chain, a 6-PEDOT and 12-PEDOT system were considered with a number of anions varying from zero to four, which could be placed anywhere except the end monomer units. Low energy configurations were chosen from the full range of possible configurations for 6-PEDOT and a large random sample of configurations for 12-PEDOT. The actual configurations used can be seen in Supplementary Material, Figure 13.

Figure 7 shows the effect of introducing one or two anions to 12-PEDOT in terms of bond lengths and electron distribution. The configurations chosen are the lowest energy anion configurations from a large sample. The 12-PEDOT oligomers without counterions, which have doublet ground state for +1 and triplet for +2, show the same trends as seen in Figures 4 and 5, with the distortions spreading out symmetrically across the chain, confined between well-defined aromatic regions at either end caused by electron localisation there. In contrast, when a single anion is introduced on monomer unit 6 (12-PEDOT +1), the bond length alternations localise over just the three monomer units nearest the anion. This demonstrates how the anion effectively pins the distortions in place. For the +2 system with counterions, 12-PEDOT was set up with anions on monomer units 5 and 8. The charge profile and bond length alternations show a distortion six monomer units long, showing that where two anions are near together, a single distortion can occur spanning both.

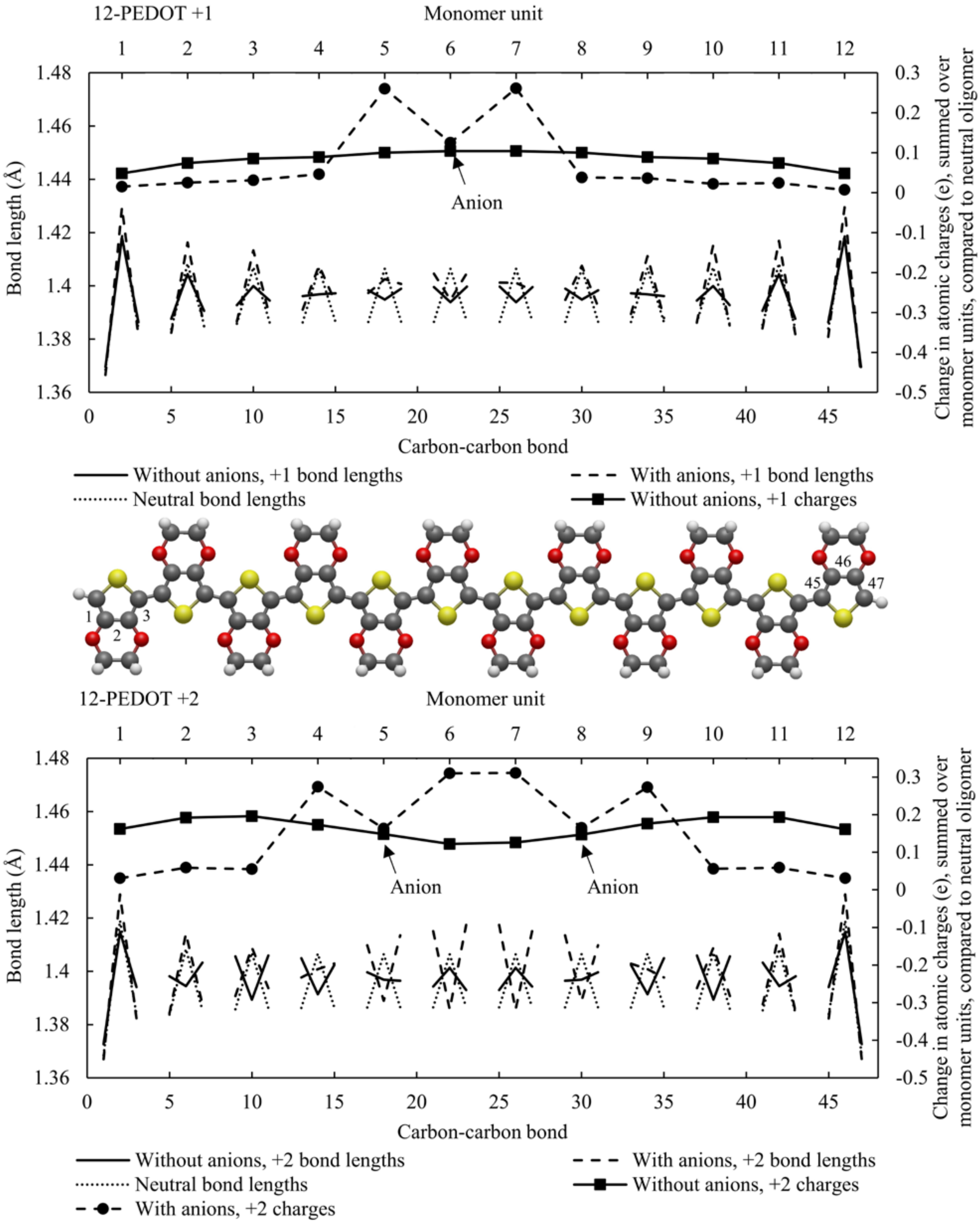


Figure 7 – Upper panel: changes in charge density compared to the neutral oligomer, and bond lengths for 12-PEDOT, both without counterions at +1 oxidation state, and with a single anion on monomer unit 6. The bond lengths of the neutral oligomer are shown for reference. The end three units remain sharply aromatic in both cases as previously observed, indicating a continued tendency for negative charge to collect at the ends of the chain. The 12-PEDOT without counterions, which has a doublet ground state, demonstrates a single area of

quinoid structure as observed for singlets/doublets in Figures 4 and 5, while the system with anions, which also has a doublet ground state, causes the bond length alternation (and area of positive charge) to locate on a smaller region only three monomer units long, demonstrating how anions pin the distortions in place. Lower panel: 12-PEDOT +2 without counterions shows the triplet (ground) state, and with anions, the singlet (ground) state with two anions on monomer units 5 and 8. The end units remain sharply aromatic in both cases as previously observed, indicating a continued tendency for negative charge to collect at the ends of the chain. The 12-PEDOT without counterions, which has a triplet ground state, demonstrates two separate distortions and charge peaks as observed in Figures 4 and 5, while the system with anions, which has singlet ground state, forces the excitation to locate on the four monomer units closest to the anions, with a peak of positive charge in this region.

As observed for the system without anions, there are two general forms of distortion that appear in the PEDOT systems studied in this work: a single or double peak distortion. We find that both can occur for PEDOT systems with anions as well. Figure 7 shows that for 12-PEDOT with anions, a single peak distortion occurs for one and two anions, noting that the charge density exhibits a dip on the monomer unit where the anion is located, with no accompanying change in the bond lengths. This is explained by DFT incorrectly calculating the anions to have less than -1e charge. This single peak distortion observed is a similar result to that presented by Sahalianov *et al.* who found that two counterions a relatively short distance apart would cause a single peak distortion, which they referred to as a bipolaron, whereas two anions further apart could induce a double peak distortion, which they termed a polaron pair [50]. However, Figure 8 shows that for 6- and 16-PEDOT, when 4 anions are placed on adjacent monomer units on the oligomer to examine the effects of a high anion concentration on a localised part of a longer oligomer, a strong double peak distortion occurs. Similar to PEDOT without anions, this implies that higher oxidation states are more associated with double peak distortions. In the case of 16-PEDOT with 4 anions in Figure 8, the pinning of the distortion around the anions is seen as the distortion only extends over eight monomer units compared to the twelve units spanned by the double-peak distortion for the 16-PEDOT +2 triplet without counterions in Figure 5.

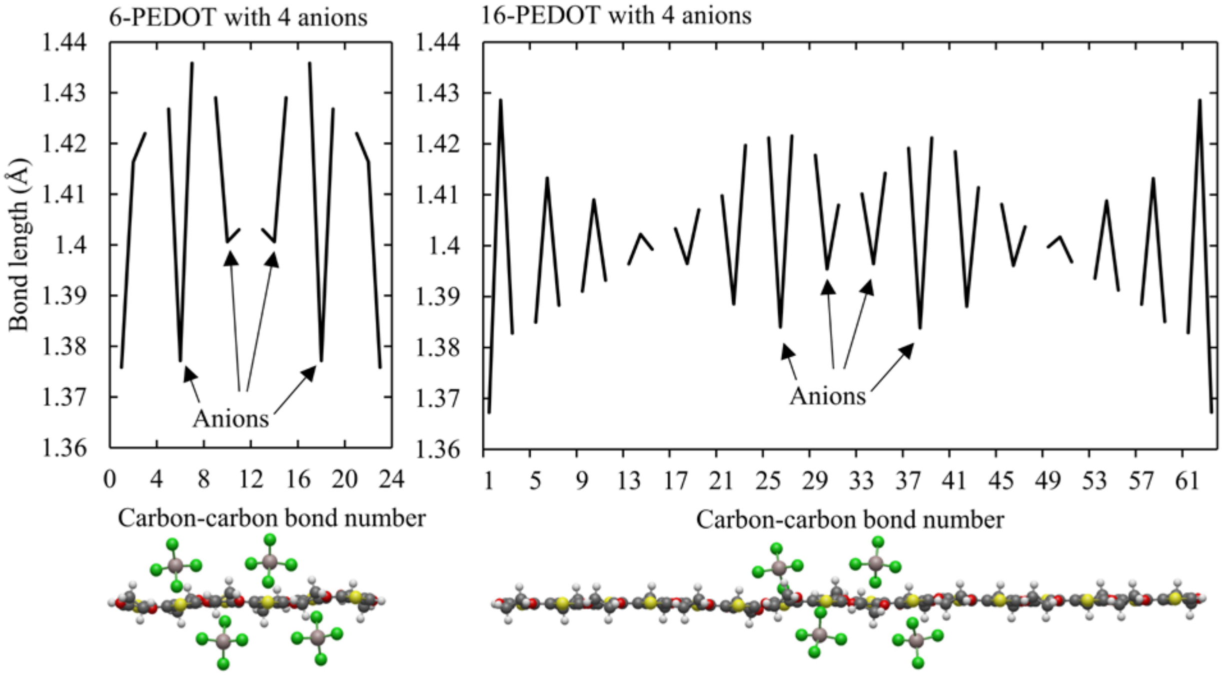


Figure 8 – Left panel: bond lengths for 6-PEDOT with four anions on alternating sides of the central four monomer units, with the anion locations shown on the PEDOT oligomer below. A pronounced double peak region of quinoid structure is seen. Right panel: bond lengths for 16-PEDOT with four anions on alternating sides of the central four monomer units, with the anion locations shown on the PEDOT oligomer below. A pronounced double peak region of quinoid structure is also seen, though it is localised towards the middle of the oligomer due to the location of the anions.

Figure 9 plots the energy levels for these systems for an energy range around the HOMO-LUMO gap. The HOMO-LUMO gap gets progressively smaller as anions are added.

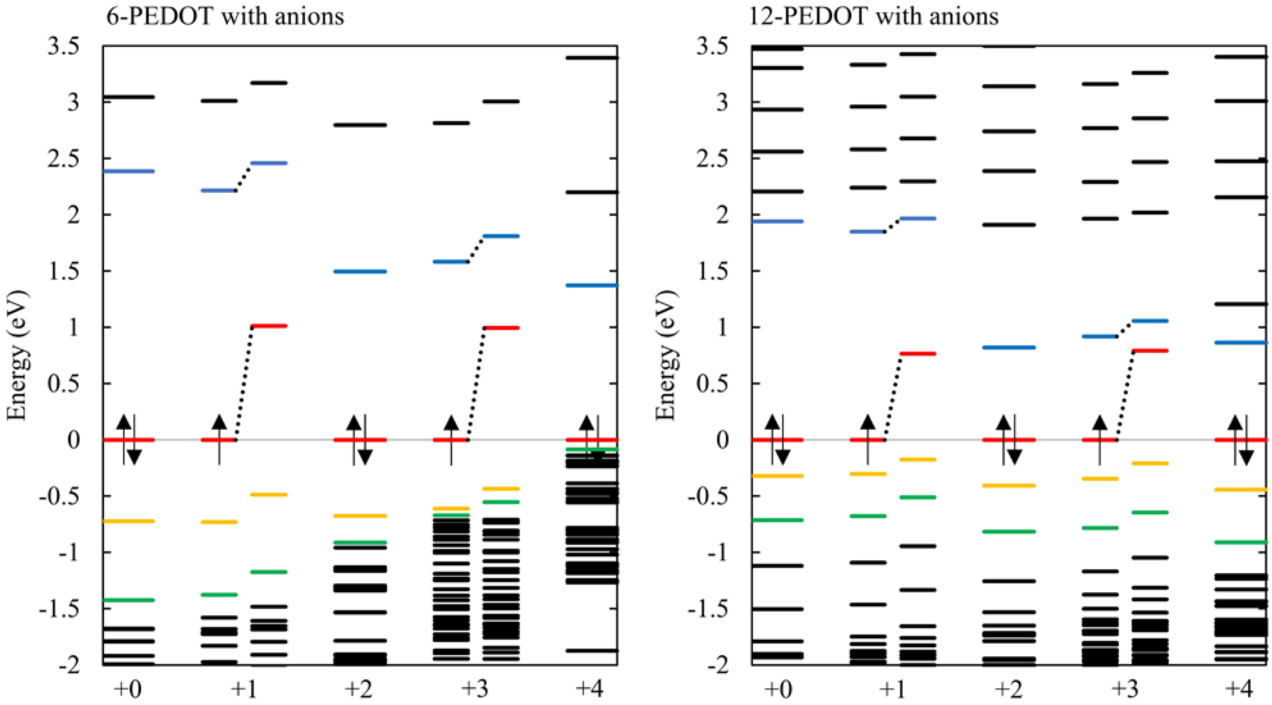


Figure 9 – energy levels for 6- and 12-PEDOT with different numbers of anions. For filled valence shells the HOMO is indicated with both up and down spin electron arrows, while for partially filled valence shells only the partially filled α HOMO are indicated. At high doping levels for 6-PEDOT there is a close grouping of energy levels below the HOMO because the non-bonding orbitals of the anions have been introduced. These are heavily localised on the chlorine atoms of the anions (see Figure 10) and so can bunch closely as they do not interact with each other. Otherwise, the plots with anions are qualitatively similar to those without counterions (Figure 6) with a general decrease in bandgap as electrons are progressively removed from the PEDOT oligomer. For 12-PEDOT compared to 6-PEDOT, the close clusters of energy levels occurs further down the energy scale because for 12-PEDOT, the overall anion concentration is lower and the anions are more spread out. The triplet ground state seen in Figure 6 for 12-PEDOT disappears for 12-PEDOT with two anions, which has singlet and doublet ground states throughout. The configurations are shown in Supplementary Material Figure 13. The HOMOs are normalized to 0 eV as for Figure 6.

The energy level diagrams corresponding to the PEDOT without and with anions in Figures 6 and 9 respectively are very similar in character, showing that the oxidation level of the PEDOT rather than the position or presence of anions is the dominant influence on the energy level structure. However, a key difference is observed at high anion concentrations in Figure 9, where an anion concentration of 0.66 is reached for 6-PEDOT +4. In this case, many energy levels cluster closely under the HOMO. This is caused by Coulombic repulsion between the anions, which causes their orbitals to rise in energy. This result can also be seen in [50] although it is not discussed. These orbitals are highly localized on the chlorine atoms of the anions, as shown in the HOMO to HOMO-2 of 6-PEDOT with four anions in Figure 10. Due to their high localisation, the anionic chlorine orbitals are able to have very similar energies to each other, hence the close stacking of their energy levels in Figure 9. This effect occurs further down the energy scale for 12-PEDOT with anions, because the overall anion concentration is only 0.33 instead of 0.66. This reduces the Coulombic repulsion between the anions and lowers the energy of their orbitals.

For 6-PEDOT with four anions, the HOMO-1 and HOMO-2 orbitals have dominant anionic character with a small amount of PEDOT character. The mixing of orbitals is due to a DFT error caused by the self-interaction error corrections. In redox systems including conducting polymers, the charge transfer is well known to be very close to 1, whereas DFT calculations predict 0.8-0.9. Therefore, it is reasonable to conclude that the HOMO-1 and HOMO-2 are pure anionic orbitals.

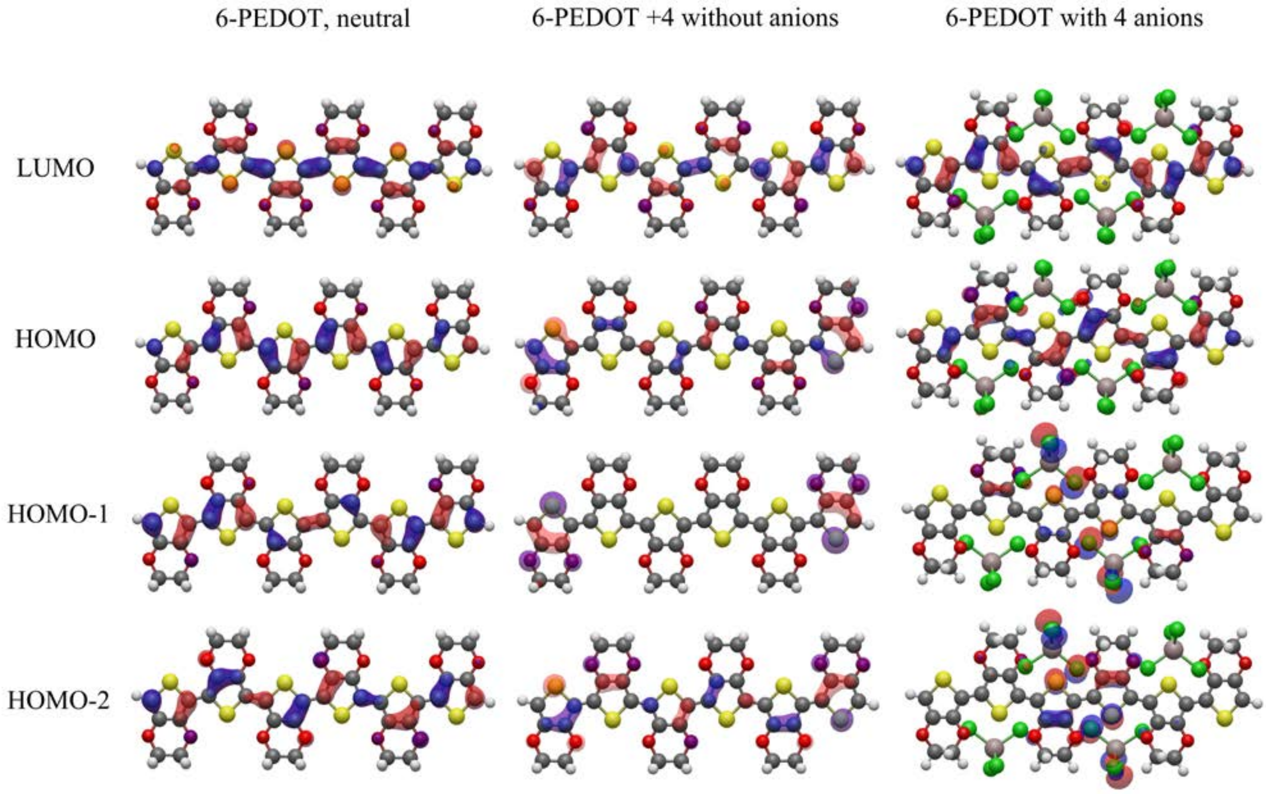


Figure 10 - molecular orbitals, at isovalue 0.03, for neutral 6-PEDOT without counterions, 6-PEDOT with +4 oxidation state without counterions, and 6-PEDOT with four anions. The molecular orbitals show that the HOMO-1 and HOMO-2 for the four anion case are highly localized on the chlorine atoms of the anions. These highly localized anionic orbitals mix with each other much less than the delocalized orbitals in the system without counterions and therefore are able to bunch more closely in energy than the orbitals in PEDOT without counterions. The HOMO-1 and HOMO-2 of the 6-PEDOT with four anions shows predominantly anionic orbitals with a contribution from the PEDOT orbitals: this is due to a DFT error, and the orbitals should be purely anionic.

As discussed in the introduction, conductivity begins to decrease at high anion concentrations, after reaching a peak when about half the redox sites are occupied. Figure 10 shows that at anion concentrations of 0.66, localised anionic orbitals take the place of the HOMO-1 and HOMO-2, where at lower anionic concentrations these energy levels were PEDOT orbitals delocalised along the conjugated carbon backbone. The new localised anionic states are too far below the HOMO to interfere with conductivity at room temperature without nucleic motion – the HOMO-1 is around 0.1 eV below the HOMO (Figure 9). However, we hypothesize that in a macropolymer with thermal nucleic motion, the natural variation in interatomic distances would cause these localised states to be regularly pushed up to a similar or greater energy than the HOMO, where the occupied and unoccupied redox sites that charge carriers hop between are located. This would interfere with the hopping process, lowering conductivity, and would affect both intra- and interchain conductivity. To the best of our knowledge, this is a novel addition to the theory of conducting polymer conductivity.

In order to understand the nature of the states introduced by co-located anions, the anion was studied in isolation. $AlCl_4^-$ has a wide energy gap between its bonding and antibonding states (9.2 eV). When co-located with the PEDOT, the antibonding states sit at high energy, well above the HOMO of the overall system, and the range shown in Figure 8, while the bonding states sit at low energy, well below the range shown. When the anion is considered in isolation, there are 8 p-derived non-bonding states on the $AlCl_4^-$ anion from HOMO to HOMO-7. The bonding, non-bonding and antibonding states are shown in Figure 10. All of the non-bonding states are chlorine p-orbitals of similar character to the anionic HOMO. It is clear from comparing Figure 10 and 11 that the anionic orbitals appearing in the HOMO-1 and HOMO-2 for 6-PEDOT with four anions are non-bonding. None of the anionic orbitals contribute to unoccupied energy levels appearing in the gap as the number of anions increases, in contrast to the predictions of the bipolaron model [29].

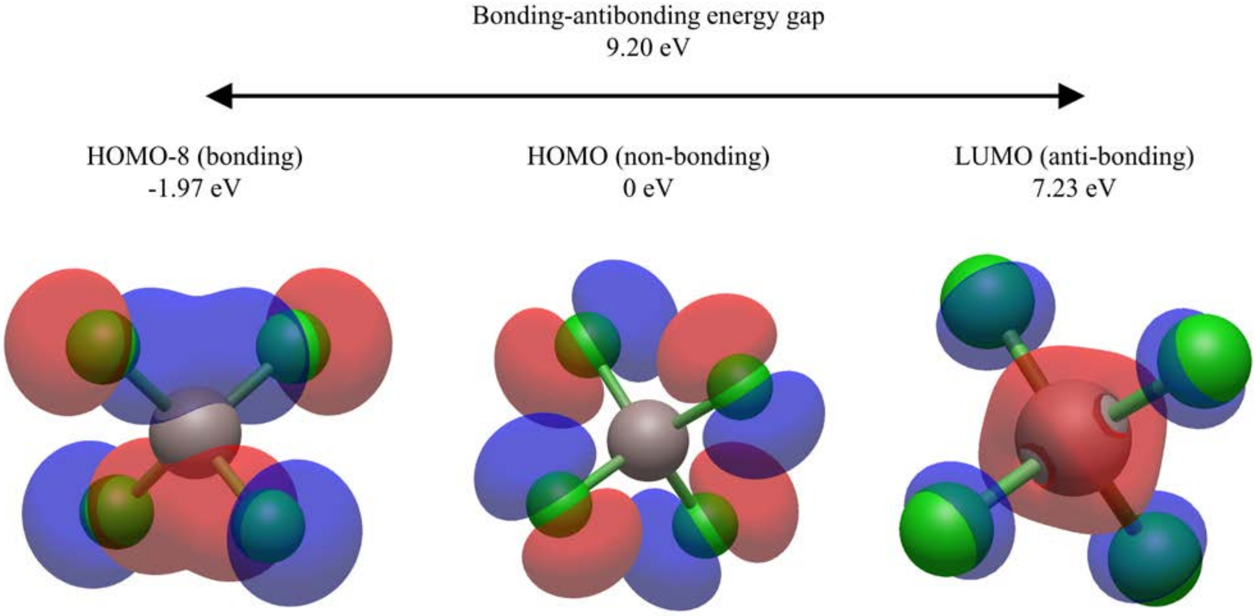


Figure 11 – molecular orbitals at isovalue 0.03 for the HOMO-8 (bonding), HOMO (non-bonding) and LUMO (antibonding) of $AlCl_4^-$ with energy levels shown normalised to the HOMO of the isolated anion. The non-bonding orbitals are all equal mixtures of the chlorine p-orbitals of similar character to the HOMO, explaining why they sit very closely in energy in the case of 6-PEDOT with four anions in Figure 8.

3. Conclusions

Our results and analysis add further evidence to move forwards from the original bipolaron model as developed from pre-DFT methods. There is no tendency found for charges to co-locate due to structural relaxation as suggested by the bipolaron model. Without counterions, the charges tend to significantly delocalise between aromatic regions at each end of the oligomer in PEDOT, as previously observed when using B3LYP, and noting that range-separated hybrid functionals tend to predict much more localised distortions [12]. Consequently, in our results, no distortion in PEDOT without anions carries a localised integer charge. In PEDOT with anions, the distortions are more localised around the anions, and when multiple anions are located near each other, a single longer distortion can appear across them. It is known from this and from previous work [15] that the initial anion locations are almost always stable, but that the anions do have Coulombic repulsion between them and will repel each other if concentration levels are too high. The lowest energy configurations have anions well distributed along the oligomer and not too close to the ends. In future work, we will explore the thermodynamics of these different anion configurations more fully.

Two distinct distortion characteristics are seen for PEDOT both with and without counterions, identified by a single and a double peak in quinoid structure, as measured by carbon-carbon bond length inversions. We note that other numbers of distortion peaks, and different distortion shapes, are possible on longer chains with different anion configurations, with the bond length alternations correlated to the charge density in the PEDOT. The original bipolaron model is based on similar descriptions of distortions and uses the terms polarons, bipolarons or polaron pairs. However, the distortions observed in this work are not reliably associated with +1 or +2, or odd or even oxidation states as predicted by any version of the bipolaron model. Rather, we have shown that between the ground and lowest-lying multiplicity states for PEDOT without counterions, both distortion characteristics can appear for +1 and +2 oxidation states, with the double peak distortion associated with triplet and quartet states. For PEDOT with anions, higher local anion concentrations are associated with double peak distortions appearing as the ground state. The double peak distortion may be similar to the distortion type observed experimentally for longer polythiophene oligomers without counterions with +2 oxidation state [47]. We find no reason to link distortion shapes to the terms polarons, bipolarons or polarons pairs. Instead, the distortions shapes are dependent on many aspects including oxidation state and configuration of anions, oligomer length, anion type and functional. This aligns well with recent research that has stopped directly linking the terms polaron, bipolaron and polaron pair to distortion shapes [6, 50].

These findings add to the existing body of modern theoretical research disproving the original bipolaron model, often now referred to as the ‘traditional models’ in conducting polymer research. Some have chosen to adapt the terminology of the bipolaron model to reflect the modern understanding [6, 50]. Considering how many researchers still refer to the original bipolaron model, we argue that continuing to use the terms at all is confusing, and that it is better to use first-principles language to avoid giving the impression that the original bipolaron model is still valid.

A more intuitive explanation is possible, which describes both ours and others’ DFT research. For any given oligomer, the spin state varies between doublet and singlet depending on the presence of an odd or even number of anions respectively, with an accompanying variation between a spin-asymmetric and spin-symmetric electronic structure. As the polymer is initially oxidised, the counterions are introduced throughout the polymer, leading to the appearance of spins as one electron is removed from the HOMO in many localized parts of the polymer. As more counterions are introduced, the half-empty HOMO is emptied and the previous HOMO-1 becomes the new HOMO, so the spins disappear. The anions have significant Coulombic repulsion between them that prevents them from co-locating, but the holes created by the anions remain delocalised enough for the overall system to relax to a fully occupied HOMO rather than creating many localised half-empty states on the same oligomer if the anions are not too far apart – that is, if the distortions caused by anions overlap. Overall, we believe this is a more intuitive explanation to offer to experimentalists or those new to the field who do not have time to understand the full evolution of the bipolaron model as seen through the eyes of the modern conducting polymer theorist.

While each anion introduces one bonding and one antibonding state, these are far below and above the HOMO-LUMO gap respectively. The apparent new state appearing in the HOMO-LUMO gap is the newly unoccupied half or whole delocalised PEDOT energy level which has been pushed up by the occupied levels below it into the gap, with the non-bonding anionic orbitals clustering below the HOMO.

At the highest anion concentration modelled of 0.66, the non-bonding orbitals of the anions are promoted to an energy level approaching that of the system HOMO, driven by Coulombic repulsion between the anions. We hypothesize that in the macropolymer, these highly localised states would be regularly promoted to the energy of the sites responsible for charge carrier hopping as a result of nucleic motion, interfering with both intra- and interchain conductivity. In our hypothesis, this contributes to the loss of conductivity found in conducting polymers at anion concentrations above 0.5.

4. Methodology

DFT simulations were carried out on single chains of PEDOT in a vacuum, both without anions and also with different numbers and arrangements of anions. These simulations were analysed for energy levels, charge distribution, molecular orbitals and bond lengths. Initial PEDOT geometries were constructed via creation of a single monomer unit, relaxation, and repeated addition and relaxation of additional monomer units.

The lengths of the oligomers were chosen based on the estimate that PEDOT consists of molecules 5-20 monomer units in length [6, 17, 64, 65].

In the calculations on oxidised PEDOT without counterions, the neutral relaxed geometry for each oligomer length was used as the starting geometry for all oxidised configurations, with deliberate asymmetries randomly introduced to check for symmetry pinning that might otherwise freeze the geometry in an unstable configuration. The appropriate number of electrons were then removed from the system and spin state applied, and relaxation carried out to establish the relaxed geometry of the oxidised molecules. In all cases, the oxidised molecules relaxed to have symmetrical bond lengths, angles and charge distributions either side of the central carbon-carbon bond. The work on PEDOT oligomers without anions used Gaussian 09 [66]. These calculations were carried out to B3LYP 6-31+G* [67-69] with Grimme's D3 dispersion corrections with Becke-Johnson damping [70].

Configurations with anions were assembled by finding a starting position for anions relative to sulfur atoms for which the DFT calculation reliably converged. We have shown in a previous work using *ab initio* molecular dynamics that this approach finds minima suitably close in energy to global minima [15]. The work on PEDOT oligomers with anions was completed using NWChem 6.8 [71], with B3LYP 6-31G* with D3 dispersion corrections for the geometry relaxations. We found that including diffuse functions in the basis set did not significantly change the results. Gaussian 09 [66] was subsequently used for the Merz-Kollman electrostatic potential (ESP) charge analysis of the relaxed structures, which was conducted using a custom point density of 5 points per unit area on 5 spherical layers [72].

Supplementary Material

In Section 2.1, the tendency for electrons to gather at the ends of oligomers of conducting polymers was discussed, and polyacetylene was mentioned as a further example of this phenomenon. It is shown below as hexatriene, showing the tendency for electrons to gather at the ends.

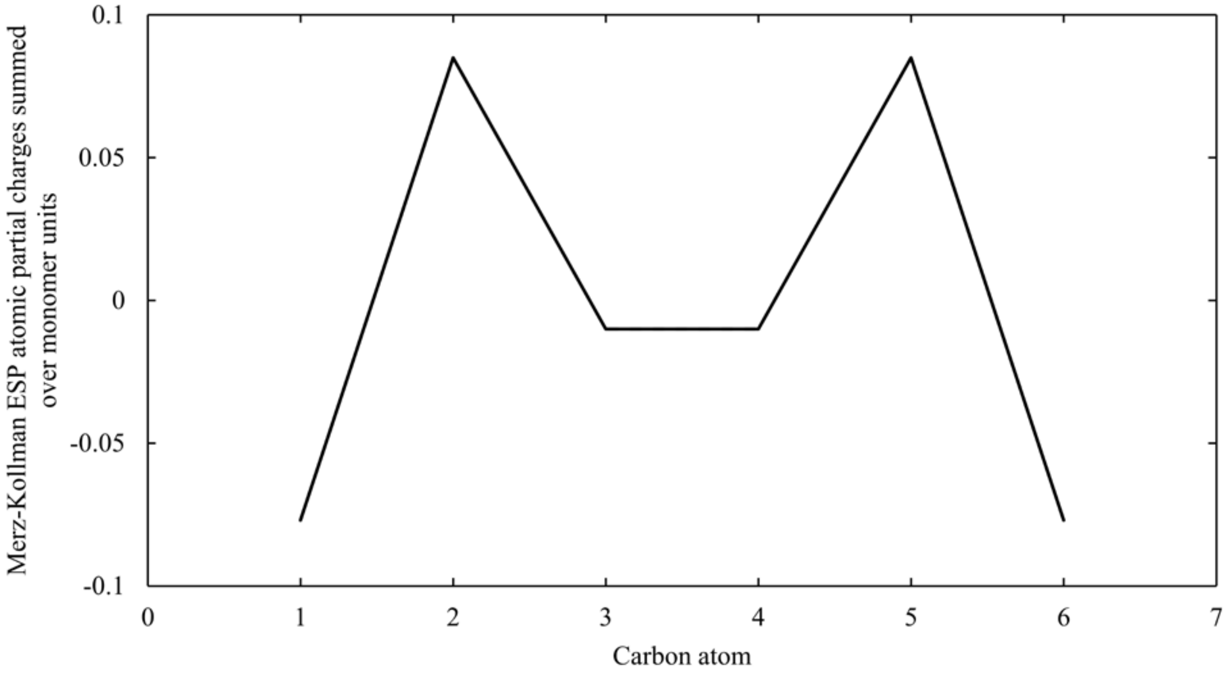
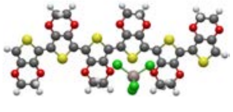
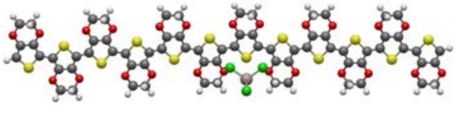
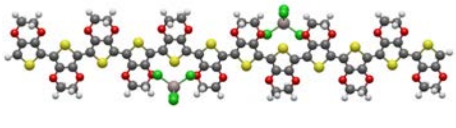
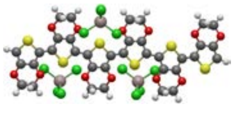
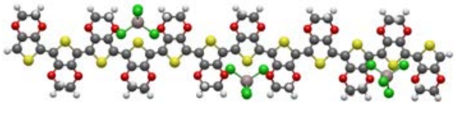


Figure 12 – Merz-Kollman electrostatic potential (ESP) charges summed over each carbon atom and their connected hydrogen atoms, for an oligomer of hexatriene. The tendency of electrons to gather at the ends, with a small positive rebound effect on adjacent carbon atoms, is seen as for the summed monomer units of PEDOT in Figure 2.

The energy level structure in Figure 9 was based on 6- and 12-PEDOT with anions. The following table shows where the anions are located on the oligomers. These are the lowest energy states found for that number of anions from either a complete sample for 6-PEDOT or large random sample for 12-PEDOT.

Number of anions	**6-PEDOT**	**12-PEDOT**
1		
2		
3		

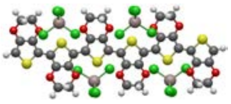
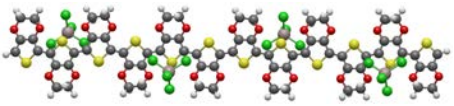
4		

Figure 13 – the relaxed configurations of the PEDOT oligomers with anions for which the energy levels are presented in Figure 9. Anions are placed either above or below the oligomer, which can be observed via overlaps in the molecular drawings.

Acknowledgements

The authors acknowledge support from the International Consortium of Nanotechnologies (ICON) funded by Lloyd's Register Foundation [G0086], a charitable foundation which helps to protect life and property by supporting engineering-related education, public engagement and the application of research, and from the Engineering and Physical Sciences Research Council, through the Centre for Doctoral Training in Energy Storage and its Applications at the University of Southampton [EP/L016818/1]. We are grateful to the UK Materials and Molecular Modelling Hub for computational resources, which is partially funded by EPSRC (EP/T022213/1, EP/W032260/1 and EP/P020194/1), and for the use of the IRIDIS High Performance Computing Facility, and associated support services at the University of Southampton.

Conflict of Interest Statement

The authors have no conflicts to disclose.

Author Contributions Statement

Ben Craig: Conceptualization (lead), Writing/Original Draft Preparation (lead), Writing/Review and Editing (equal). **Peter Townsend**: Writing/Review and Editing (equal). **Denis Kramer**: Writing/Review and Editing (equal), Supervision (equal). **Chris-Kriton Skylaris** and **Carlos Ponce de Leon**: Supervision (equal).

Data availability

The data that support the findings of this study are available from the corresponding author upon reasonable request.

References

[1] W. Shi, T. Zhao, J. Xi, D. Wang, and Z. Shuai, "Unravelling Doping Effects on PEDOT at the Molecular Level: From Geometry to Thermoelectric Transport Properties," *J Am Chem Soc,* vol. 137, no. 40, pp. 12929-38, Oct 14 2015, doi: 10.1021/jacs.5b06584.

[2] E.-G. Kim and J.-L. Brédas, "Electronic Evolution of Poly(3,4-ethylenedioxythiophene) (PEDOT): From the Isolated Chain to the Pristine and Heavily Doped Crystals," *J Am Chem Soc,* vol. 130, 2008 2008.

[3] M. N. Gueye *et al.*, "Structure and Dopant Engineering in PEDOT Thin Films: Practical Tools for a Dramatic Conductivity Enhancement," *J. Chem. Mater.,* vol. 28, no. 10, pp. 3462-3468, 2016, doi: 10.1021/acs.chemmater.6b01035.

[4] M. N. Gueye, A. Carella, J. Faure-Vincent, R. Demadrille, and J.-P. Simonato, "Progress in understanding structure and transport properties of PEDOT-based materials: A critical review," *Progress in Materials Science,* vol. 108, 2020, doi: 10.1016/j.pmatsci.2019.100616.

[5] T. H. Le, Y. Kim, and H. Yoon, "Electrical and Electrochemical Properties of Conducting Polymers," *Polymers (Basel),* vol. 9, no. 4, Apr 23 2017, doi: 10.3390/polym9040150.

[6] I. Zozoulenko, A. Singh, S. K. Singh, V. Gueskine, X. Crispin, and M. Berggren, "Polarons, Bipolarons, And Absorption Spectroscopy of PEDOT," *ACS Applied Polymer Materials,* vol. 1, no. 1, pp. 83-94, 2018, doi: 10.1021/acsapm.8b00061.

[7] N. S. Hudak, "Chloroaluminate-Doped Conducting Polymers as Positive Electrodes in Rechargeable Aluminum Batteries," *The Journal of Physical Chemistry C,* vol. 118, no. 10, pp. 5203-5215, 2014, doi: 10.1021/jp500593d.

[8] K. Ando, S. Watanabe, S. Mooser, E. Saitoh, and H. Sirringhaus, "Solution-processed organic spin-charge converter," *Nat Mater,* vol. 12, no. 7, pp. 622-7, Jul 2013, doi: 10.1038/nmat3634.

[9] T. Schoetz, B. Craig, C. Ponce de Leon, A. Bund, M. Ueda, and C. T. J. Low, "Aluminium-poly(3,4-ethylenedioxythiophene) rechargeable battery with ionic liquid electrolyte," *Journal of Energy Storage,* vol. 28, pp. 101176-101185, 2020, doi: 10.1016/j.est.2019.101176.

[10] N. Zamoshchik, U. Salzner, and M. Bendikov, "Nature of Charge Carriers in Long Doped Oligothiophenes: The Effect of Counterions," *J Phys Chem C,* vol. 112, pp. 8408-8418, 2008, doi: 10.1021/jp7111582.

[11] U. Salzner, "Modelling photoelectron spectra of conjugated oligomers with time dependent density functional theory," *J Phys Chem A,* vol. 114, pp. 10997-11007, 2010, doi: 10.1021/jp105588n.

[12] U. Salzner and A. Aydin, "Improved Prediction of Properties of pi-Conjugated Oligomers with Range-Separated Hybrid Density Functionals," *J Chem Theory Comput,* vol. 7, no. 8, pp. 2568-83, Aug 9 2011, doi: 10.1021/ct2003447.

[13] M. Modarresi, J. F. Franco-Gonzalez, and I. Zozoulenko, "Morphology and ion diffusion in PEDOT:Tos. A coarse grained molecular dynamics simulation," *Phys Chem Chem Phys,* vol. 20, no. 25, pp. 17188-17198, Jun 27 2018, doi: 10.1039/c8cp02902d.

[14] U. Salzner, "Electronic structure of conducting organic polymers: insights from time-dependent density functional theory," *Comput Mol Sci,* vol. 4, pp. 601-622, 2014, doi: 10.1002/wcms.1194.

[15] B. Craig, C.-K. Skylaris, C. P. de Leon, and D. Kramer, "Ab initio molecular dynamics study of AlCl4− adsorption on PEDOT conducting polymer chains," *Energy Reports,* vol. 7, pp. 111-119, 2021, doi: 10.1016/j.egyr.2021.02.035.

[16] B. Craig, C.-K. Skylaris, T. Schoetz, and C. Ponce de Leon, "A computational chemistry approach to modelling conducting polymers in ionic liquids for next generation batteries," *Energy Reports,* 2020, doi: 10.1016/j.egyr.2020.03.025.

[17] J. Heinze, B. Frontana-Uribe, and S. Ludwigs, "Electrochemistry of Conducting Polymers - Persistent Models and New Concepts," *Chem Rev,* vol. 110, pp. 4724-4771, 2010, doi: 10.1021/cr900226k.

[18] J. Brédas and G. Street, "Polarons, Bipolarons, and Solitons in Conducting Polymers," *Acc Chem Res,* vol. 18, pp. 309-315, 1985, doi: 10.1021/ar00118a005.

[19] A. J. Fisher, W. Hayes, and D. S. Wallace, "Polarons and solitons," *J. Phys.: Condens. Matter,* vol. 1, pp. 5567-5593, 1989, doi: 10.1088/0953-8984/1/33/001.

[20] S. Fletcher, "Contribution to the theory of conducting-polymer electrodes in electrolyte solutions," *J Chem Soc Faraday Trans,* vol. 89, no. 2, 1993.

[21] O. Bubnova *et al.*, "Semi-metallic polymers," *Nat Mater,* vol. 13, no. 2, pp. 190-4, Feb 2014, doi: 10.1038/nmat3824.

[22] A. Zykwinska, W. Domagala, A. Czardybon, B. Pilawa, and M. Lapkowski, "In situ EPR spectroelectrochemical studies of paramagnetic centres in poly(3,4-ethylenedioxythiophene) (PEDOT) and poly(3,4-butylenedioxythiophene) (PBuDOT) films," *Chemical Physics,* vol. 292, no. 1, pp. 31-45, 2003, doi: 10.1016/s0301-0104(03)00253-2.

[23] S. Chakrabarti, B. Das, P. Banerji, D. Banerjee, and R. Bhattacharya, "Bipolaron saturation in polypyrrole," *Phys Rev B,* vol. 60, no. 11, 1999.

[24] C. Castiglioni, G. Zerbi, and M. Gussoni, "Peierls distortion in trans polyacetylene: Evidence from infrared intensities," *Solid State Communications,* vol. 56, no. 10, pp. 863-866, 1985/12/01/ 1985, doi: https://doi.org/10.1016/0038-1098(85)90421-1.

[25] A. J. Heeger, S. Kivelson, J. R. Schrieffer, and W. P. Su, "Solitons in conducting polymers," *Reviews of Modern Physics,* vol. 60, no. 3, pp. 781-850, 1988, doi: 10.1103/RevModPhys.60.781.

[26] A. Heeger, "Charge Storage in Conducting Polymers: Solitons, Polarons and Bipolarons," *Polymer Journal,* vol. 17, no. 1, pp. 201-208, 1985, doi: 10.1295/polymj.17.201.

[27] W. A. Muñoz, S. K. Singh, J. F. Franco-Gonzalez, M. Linares, X. Crispin, and I. V. Zozoulenko, "Insulator to semimetallic transition in conducting polymers," *Physical Review B,* vol. 94, no. 20, 2016, doi: 10.1103/PhysRevB.94.205202.

[28] Y. Furukawa, "Electronic Absorption and Vibrational Spectroscopies of Conjugated Conducting Polymers," *J Phys Chem,* vol. 100, pp. 15644-15653, 1996, doi: 10.1021/jp960608n.

[29] J. L. Brédas, J. C. Scott, K. Yakushi, and G. B. Street, "Polarons and bipolarons in polypyrrole: Evolution of the band structure and optical spectrum upon doping," *Physical Review B,* vol. 30, no. 2, pp. 1023-1025, 1984, doi: 10.1103/PhysRevB.30.1023.

[30] S. Stafstrom and J. L. Bredas, "Evolution of the electronic structure of polyacetylene and polythiophene as a function of doping level and lattice conformation," *Phys Rev B Condens Matter,* vol. 38, no. 6, pp. 4180-4191, Aug 15 1988, doi: 10.1103/physrevb.38.4180.

[31] N. F. Mott, "Conduction in non-crystalline materials," *The Philosophical Magazine: A Journal of Theoretical Experimental and Applied Physics,* vol. 19, no. 160, pp. 835-852, 1969/04/01 1969, doi: 10.1080/14786436908216338.

[32] P. Sheng, "Fluctuation-induced tunneling conduction in disordered materials," *Physical Review B,* vol. 21, no. 6, pp. 2180-2195, 1980, doi: 10.1103/PhysRevB.21.2180.

[33] L. Zuppiroli, M. N. Bussac, S. Paschen, O. Chauvet, and L. Forro, "Hopping in disordered conducting polymers," *Phys Rev B Condens Matter,* vol. 50, no. 8, pp. 5196-5203, Aug 15 1994, doi: 10.1103/physrevb.50.5196.

[34] D. Ofer, R. Crooks, and M. Wrighton, "Potential Dependence of the Conductivity of Highly Oxidized Polythiophenes, Polypyrroles, and Polyaniline: Finite Windows of High Conductivity," *J Am Chem Soc,* vol. 112, pp. 7869-7879, 1990.

[35] H. John, R. Bauer, P. Espindola, P. Sonar, J. Heinze, and K. Mullen, "3D-hybrid networks with controllable electrical conductivity from the electrochemical deposition of terthiophene-functionalized polyphenylene dendrimers," *Angew Chem Int Ed Engl,* vol. 44, no. 16, pp. 2447-51, Apr 15 2005, doi: 10.1002/anie.200462378.

[36] J. Torrance, "The Difference between Metallic and Insulating Salts of Tetracyanoquinodimethane (TCNQ): How to Design an Organic Metal," *Acc Chem Res,* vol. 12, no. 3, 1977.

[37] T. Stöcker, A. Köhler, and R. Moos, "Why does the electrical conductivity in PEDOT:PSS decrease with PSS content? A study combining thermoelectric measurements with impedance spectroscopy," *Journal of Polymer Science Part B: Polymer Physics,* vol. 50, no. 14, pp. 976-983, 2012, doi: 10.1002/polb.23089.

[38] O. Bubnova *et al.*, "Optimization of the thermoelectric figure of merit in the conducting polymer poly(3,4-ethylenedioxythiophene)," *Nat Mater,* vol. 10, no. 6, pp. 429-33, Jun 2011, doi: 10.1038/nmat3012.

[39] Q. Wei, M. Mukaida, K. Kirihara, Y. Naitoh, and T. Ishida, "Photoinduced Dedoping of Conducting Polymers: An Approach to Precise Control of the Carrier Concentration and Understanding Transport Properties," *ACS Appl Mater Interfaces,* vol. 8, no. 3, pp. 2054-60, Jan 27 2016, doi: 10.1021/acsami.5b10453.

[40] Q. Li, Q. Zhou, L. Wen, and W. Liu, "Enhanced thermoelectric performances of flexible PEDOT:PSS film by synergistically tuning the ordering structure and oxidation state," *Journal of Materiomics,* vol. 6, no. 1, pp. 119-127, 2020, doi: 10.1016/j.jmat.2020.01.001.

[41] Z. Yu, Y. Xia, D. Du, and J. Ouyang, "PEDOT:PSS Films with Metallic Conductivity through a Treatment with Common Organic Solutions of Organic Salts and Their Application as a Transparent Electrode of Polymer Solar Cells," *ACS Applied Materials & Interfaces,* vol. 8, no. 18, pp. 11629-11638, 2016, doi: 10.1021/acsami.6b00317.

[42] X. Li *et al.*, "Effects of Cationic Species in Salts on the Electrical Conductivity of Doped PEDOT:PSS Films," *ACS Applied Polymer Materials,* vol. 3, no. 1, pp. 98-103, 2020, doi: 10.1021/acsapm.0c01084.

[43] G. Cao, S. Cai, Y. Chen, D. Zhou, H. Zhang, and Y. Tian, "Facile synthesis of highly conductive and dispersible PEDOT particles," *Polymer,* vol. 252, 2022, doi: 10.1016/j.polymer.2022.124952.

[44] J. Cornil, D. Beljonne, and J. L. Brédas, "Nature of optical transitions in conjugated oligomers. I. Theoretical characterization of neutral and doped oligo(phenylenevinylene)s," *The Journal of Chemical Physics,* vol. 103, no. 2, pp. 834-841, 1995, doi: 10.1063/1.470116.

[45] G. Heimel, "The Optical Signature of Charges in Conjugated Polymers," *ACS Cent Sci,* vol. 2, no. 5, pp. 309-15, May 25 2016, doi: 10.1021/acscentsci.6b00073.

[46] N. Zamoshchik and M. Bendikov, "Doped Conductive Polymers: Modeling of Polythiophene with Explicitly Used Counterions," *Advanced Functional Materials,* vol. 18, no. 21, pp. 3377-3385, 2008, doi: 10.1002/adfm.200800639.

[47] J. A. E. H. van Haare, E. E. Havinga, J. L. J. van Dongen, R. A. J. Janssen, J. Cornil, and J. L. Brédas, "Redox States of Long Oligothiophenes: Two Polarons on a Single Chain," *Chemistry – A European Journal,* vol. 4, no. 8, pp. 1509-1522, 1998, doi: 10.1002/(sici)1521-3765(19980807)4:8<1509::Aid-chem1509>3.0.Co;2-#.

[48] T. P. Kaloni, P. K. Giesbrecht, G. Schreckenbach, and M. S. Freund, "Polythiophene: From Fundamental Perspectives to Applications," *Chemistry of Materials,* vol. 29, no. 24, pp. 10248-10283, 2017, doi: 10.1021/acs.chemmater.7b03035.

[49] U. Salzner, "Investigation of Charge Carriers in Doped Thiophene Oligomers through Theoretical Modeling of their UV/Vis Spectra," *J. Phys. Chem. A,* vol. 112, pp. 5458-5466, 2008, doi: 10.1021/jp800606m.

[50] I. Sahalianov, J. Hynynen, S. Barlow, S. R. Marder, C. Muller, and I. Zozoulenko, "UV-to-IR Absorption of Molecularly p-Doped Polythiophenes with Alkyl and Oligoether Side Chains: Experiment and Interpretation Based on Density Functional Theory," *J Phys Chem B,* vol. 124, no. 49, pp. 11280-11293, Dec 10 2020, doi: 10.1021/acs.jpcb.0c08757.

[51] N. Massonnet *et al.*, "Improvement of the Seebeck coefficient of PEDOT:PSS by chemical reduction combined with a novel method for its transfer using free-standing thin films," *J. Mater. Chem. C,* vol. 2, no. 7, pp. 1278-1283, 2014, doi: 10.1039/c3tc31674b.

[52] C. Enengl *et al.*, "Doping-Induced Absorption Bands in P3HT: Polarons and Bipolarons," *Chemphyschem,* vol. 17, no. 23, pp. 3836-3844, Dec 5 2016, doi: 10.1002/cphc.201600961.

[53] M. G. Voss, D. T. Scholes, J. R. Challa, and B. J. Schwartz, "Ultrafast transient absorption spectroscopy of doped P3HT films: distinguishing free and trapped polarons," *Faraday Discussions,* vol. 216, pp. 339-362, 2019, doi: 10.1039/c8fd00210j.

[54] J. Yamamoto and Y. Furukawa, "Electronic and vibrational spectra of positive polarons and bipolarons in regioregular poly(3-hexylthiophene) doped with ferric chloride," *J Phys Chem B,* vol. 119, no. 13, pp. 4788-94, Apr 2 2015, doi: 10.1021/jp512654b.

[55] S. S. Kalagi and P. S. Patil, "Secondary electrochemical doping level effects on polaron and bipolaron bands evolution and interband transition energy from absorbance spectra of PEDOT: PSS thin films," *Synthetic Metals,* vol. 220, pp. 661-666, 2016/10/01/ 2016, doi: https://doi.org/10.1016/j.synthmet.2016.08.009.

[56] J. Hwang *et al.*, "In situ measurements of the optical absorption of dioxythiophene-based conjugated polymers," *Physical Review B,* vol. 83, no. 19, 2011, doi: 10.1103/PhysRevB.83.195121.

[57] C. M. Amb, A. L. Dyer, and J. R. Reynolds, "Navigating the Color Palette of Solution-Processable Electrochromic Polymers," *Chemistry of Materials,* vol. 23, no. 3, pp. 397-415, 2010, doi: 10.1021/cm1021245.

[58] S. Rudd *et al.*, "Charge transport and structure in semimetallic polymers," *J Polym Sci B Polym Phys,* vol. 56, no. 1, pp. 97-104, Jan 1 2018, doi: 10.1002/polb.24530.

[59] E. Sigfridsson and U. Ryde, "Comparison of methods for deriving atomic charges from the electrostatic potential and moments," *Journal of Computational Chemistry,* vol. 19, no. 4, pp. 377-395, 1998, doi: 10.1002/(SICI)1096-987X(199803)19:4<377::AID-JCC1>3.0.CO;2-P.

[60] R. Smoluchowski, "Anisotropy of the Electronic Work Function of Metals," *Physical Review,* vol. 60, no. 9, pp. 661-674, 1941, doi: 10.1103/PhysRev.60.661.

[61] D. Vieira, H. J. P. Freire, V. L. Campo, and K. Capelle, "Friedel oscillations in one-dimensional metals: From Luttinger's theorem to the Luttinger liquid," *Journal of Magnetism and Magnetic Materials,* vol. 320, no. 14, pp. e418-e420, 2008, doi: 10.1016/j.jmmm.2008.02.077.

[62] G. R. Hutchison, Y.-J. Zhao, B. Delley, A. J. Freeman, M. A. Ratner, and T. J. Marks, "Electronic structure of conducting polymers: Limitations of oligomer extrapolation approximations and effects of heteroatoms," *Physical Review B,* vol. 68, no. 3, 2003, doi: 10.1103/PhysRevB.68.035204.

[63] D. Kim and I. Zozoulenko, "Why Is Pristine PEDOT Oxidized to 33%? A Density Functional Theory Study of Oxidative Polymerization Mechanism," *The Journal of Physical Chemistry B,* vol. 123, no. 24, pp. 5160-5167, 2019, doi: 10.1021/acs.jpcb.9b01745.

[64] T. Takano, H. Masunaga, A. Fujiwara, H. Okuzaki, and T. Sasaki, "PEDOT Nanocrystal in Highly Conductive PEDOT:PSS Polymer Films," *Macromolecules,* vol. 45, no. 9, pp. 3859-3865, 2012, doi: 10.1021/ma300120g.

[65] D. Kim, J. F. Franco-Gonzalez, and I. Zozoulenko, "How Long are Polymer Chains in Poly(3,4-ethylenedioxythiophene):Tosylate Films? An Insight from Molecular Dynamics Simulations," *J Phys Chem B,* vol. 125, no. 36, pp. 10324-10334, Sep 16 2021, doi: 10.1021/acs.jpcb.1c04079.

[66] *Gaussian 09, Revision C.01*. (2010). Wallingford CT.

[67] J. Perdew, M. Ernzerhof, and K. Burke, "Rationale for mixing exact exchange with density functional approximations," *J Chem Phys,* vol. 105, pp. 9982-9985, 1996, doi: 10.1063/1.472933.

[68] A. D. Becke, "Density-functional thermochemistry. III. The role of exact exchange," *The Journal of Chemical Physics,* vol. 98, no. 7, pp. 5648-5652, 1993, doi: 10.1063/1.464913.

[69] V. A. Rassolov, J. A. Pople, M. A. Ratner, and T. L. Windus, "6-31G* basis set for atoms K through Zn," *The Journal of Chemical Physics,* vol. 109, no. 4, pp. 1223-1229, 1998, doi: 10.1063/1.476673.

[70] S. Grimme, A. Hansen, J. G. Brandenburg, and C. Bannwarth, "Dispersion-Corrected Mean-Field Electronic Structure Methods," *Chem Rev,* vol. 116, no. 9, pp. 5105-54, May 11 2016, doi: 10.1021/acs.chemrev.5b00533.

[71] E. Apra *et al.*, "NWChem: Past, present, and future," *J Chem Phys,* vol. 152, no. 18, p. 184102, May 14 2020, doi: 10.1063/5.0004997.

[72] U. C. Singh and P. A. Kollman, "An approach to computing electrostatic charges for molecules," *Journal of Computational Chemistry,* vol. 5, no. 2, pp. 129-145, 1984, doi: https://doi.org/10.1002/jcc.540050204.