Structural and Electronic Properties of Oligo- and Polythiophenes Modified by Substituents

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Abstract

Electronic and structural properties of oligo- and polythiophenes that can be used as building blocks for molecular electronic devices have been studied using periodic density functional theory calculations. We have in particular focused on the effect of substituents on the electronic structure of thiophenes. Whereas singly bonded substituents such as methyl, amino or nitro groups change the electronic properties of thiophene monomers and dimers, they hardly influence the band gap of polythiophene. In contrast, phenyl-substituted polythiophenes as well as vinyl-bridged polythiophene-derivatives exhibit drastically modified band gaps. These effects can not be explained by simple electron removal or addition, as calculations for charged polythiophenes demonstrate.

Keywords

thiophene, substituents, band gaps

Introduction

Since the first report about the electrical conductivity of doped polyacetylene (PA) in 1977 [1] significant efforts have been spent in studying organic polymers as an alternative to common in-

organic semi-conducting materials [2], as they can, e.g., form supramolecular architectures on surfaces [3,4] that can serve as building blocks in molecular electronics or can be used in the future solar energy technology [5]. Although the electrical conductivity of well prepared PA is nearly the same as for copper [6], its technical applications are very rare due to its instability towards air and humidity [7]. Searching more stable compounds, thiophene-based materials turned out to be promising candidates and thus they have gained considerable attention during the past 20 years [6,8].

Like PA, nano-sized polythiophene (PTp) shows a diffuse widespread conjugated π-system [8]. Consequently, removing an electron from the highest occupied polymer orbital or adding an electron to the lowest unoccupied orbital is relatively easy [9]. In a chemist's terminology one might call these processes redox-reactions whereas from a physicist's point of view one more likely will call them n- and p-doping, respectively, to stress the analogy to the doping processes in traditional semi-conducting materials like silicon. By that, neutral polymers which usually show semi-conducting or isolating properties can transform into highly conductive compounds with a metal-like behavior.

The advantages of these *synthetic metals* are obvious. On the one hand they are nearly as conductive as metals but on the other hand they are as light and durable as plastics [10]. Furthermore, especially in the case of PTp the doping processes causing the high conductivity of polymers are highly reversible [9]. This offers the opportunity to switch between conducting and insulating properties very easily and opens a broad field of application in the area of micro- and opto-electronics, e.g., as organic transistors, photo resistances oder polymer light-emitting diodes (LEDs) [11]. In particular, thiophene-based organic solar cells have shown remarkable efficiency [5,8]. Nevertheless they are still relatively cheap in production [12].

For all these applications, the particular electronic structure of polymers is crucial. In particular, a directed manipulation of the bandgap to tailor the electronic properties is very desirable. Considering the significant potential of organic chemistry at synthesizing and manipulating compounds, there is definitely a demand for a better understanding of how the electronic structure of com-

pounds like PTp can be manipulated using these tools. There have been already several studies addressing the electronic structure of thiophenes with electronic structure methods [13-20]. In these computational studies, typically oligothiophenes of varying size have been considered based on density functional theory (DFT), and properties of polythiophenes have been derived using scaling relations [21].

Here, we focus on the modification of the electronic properties of oligo- and polythiophenes by substituents based on periodic DFT calculations. Hence we are able to address oligo- and poly-thiophenes within the same computational method so that no scaling relations have to be invoked. Our aim has particularly been to determine the influence of different substituents on the electronic structure and especially on the bandgap of thiophene-based polymers, as it is known that there is a close relationship between the geometrical structure and physical properties of conductive polymers [22].

As a starting point, we have first considered thiophene monomers and dimers, and then compared their properties to those of infinite chains of thiophene which can also act as a model for macro-cyclic systems, namely cyclothiophenes [23]. As substituents we considered both singly bonded substituents such as methyl, amino or nitro groups as well as phenyl-like substituents. In addition, we have studied vinyl-bridged polythiophene-derivatives. Finally, we have also addressed charged polythiophenes in order to model doped systems and to check whether the modified electronic properties can simply be regarded as effects resulting from band-filling or band-emptying.

Methods

Our calculations are based on the periodic DFT code implemented in the *Vienna Ab initio Simu-lation Package* (VASP) [24,25]. Exchange and correlation effects have been treated in the gener-alized gradient approximation (GGA) using the Perdew-Becke-Ernzerhof (PBE) functional [26] which gives a reliable description of intramolecular properties [27,28]. Dispersion corrections [29] are not necessary since we are not concerned with intramolecular interaction or adsorption of the aromatic molecules [30,31]. The ionic cores have been represented by projector augmented wave

(PAW) potentials [32] as constructed by Kresse and Joubert [33]. The electronic one-particle wave functions have been expanded in a plane-wave basis set up to a cutoff energy of 400 eV which has been checked for convergence.

All geometrical optimizations were carried out using the conjugated gradient algorithm implemented in VASP. Molecules were geometrically optimized using a sufficiently large unit cell in the supercell approach and one k-point. In contrast, the polymers have been described as one-dimensional infinite chains with a $7 \times 1 \times 1$ k-point sampling to replace the integration over the one-dimensional first Brillouin zone. k-point convergence was carefully checked. When optimizing the polymer structure, both the geometric structure within the unit cell as well as the width of the unit cell were optimized as the latter correlates directly with the intercellular bondlength.

For molecules, calculations concerning the density of states (DOS) were carried out at the Γ point with a Gaussian smearing ($\sigma = 0.01$ eV). For polymers, in contrast, a grid of $29 \times 1 \times 1$ Γ-centered k-points and linear tetrahedron smearing with Blöchl corrections [34] were used. Geometrically optimized structures were taken as a basis for all of these calculations. Polymers of different oxidation states were modeled by changing the number of electrons per unit cell. In order to preserve the electroneutrality of the cell, a compensating background charge is generated by default.

As we are interested in the HOMO-LUMO gap of oligothiophenes and the band gaps of polythiophenes, we have to be concerned with the well-known deficiency of DFT using current-day GGA exchange-correlation functionals to reproduce the correct magnitude of band gaps. The calculated band structure can be improved by including self-energy corrections. However, including such corrections basically just affects the distance between valence and correction band, the shape and k-point dependence of valence and conduction bands remain more or less unchanged [35]. Furthermore, the more costly time-dependent DFT methods also do not yield necessarily better results [21]. Furthermore, hybrid functionals which apparently work well for thiophenes [16] still require a significant computational effort in plane-wave codes such as VASP. As we are mainly interested in trends in the local density of states depending on the choice of the substituent, GGA-DFT calculations should be sufficient to reproduce these trends. However, one has to be aware that

4

all absolute values of HOMO-LUMO and band gaps reported in this work are severely underestimated.

Results

Unsubstituted Oligo- and Polythiophenes

As a first step and as a reference, we determined the properties of unsubstituted oligo- and polythiophenes. All oligomers were modeled using a sufficiently large box in 3 dimensions to avoid intermolecular interaction due to the use of a periodic DFT code. For the unsubstituted monomer (thiophene, Tp), experimental geometric parameters obtained by Bak *et al.* [36] were reproduced quite well. Small deviations from experimental values concerning the dihedral angle were observed modeling the dimer (2,2'-bithiophene, BTp): Calculations predicted a dihedral angle of $17.5°$ with a very flat rotational potential for angles from $0°$ to $30°$ whereas Almenningen *et al.* obtained an angle of about $34°$ using gas-phase electron diffraction [37]. There are known problems using GGA-DFT to compute rotational barriers especially for conjugated systems [38], but there is definitely a planarizing effect of a growing chain length as the trimer (2,5-bis(thiophen-2-yl)thiophene, TTp) was predicted to show a totally flat structure. This should be due to the extended π-system and hence definitely agrees with expectations.

Regarding HOMO-LUMO gaps for the unsubstituted oligomers listed in Tab. 1, the previously mentioned problem of GGA-DFT when it comes to bandgaps is obvious. The calculated values are about $1\,\mathrm{eV}$ smaller than those measured by Diaz *et al.* [39]. Yet, the trend that the width of the HOMO-LUMO gap decreases with increasing size of the oligomer is reproduced by the calculations.

Table 1: Calculated HOMO-LUMO gaps for thiophene oligomers (in eV) compared with experimental values obtained by Diaz *et al.* [39].

	Calculations	Experiment
Monomer (Tp)	4.49	5.37
Dimer (BTp)	2.93	4.12
Trimer (TTp)	2.21	3.52

₁₂₄ The polymer PTp was modeled as an one-dimensional chain which was separated by sufficiently

₁₂₅ large distances from their periodic images perpendicular to the chain in order to avoid any sizable

₁₂₆ interaction between them. As shown in Fig. 1 the unit cell contained two thiophene rings. We also

₁₂₇ modeled a unit cell that contained 4 rings but neither structural nor electronic parameters differed

₁₂₈ from the results for the two-ring-cell.
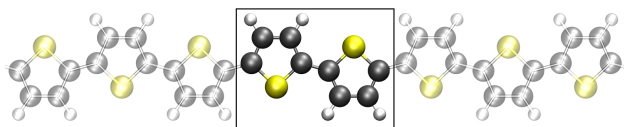
Figure 1: Considered structure of polythiophene (PTp). The frame indicates the unit cell used in the calculations that contained two thiophene rings connected via the respective α-positions.

₁₂₉ Our calculations predict PTp to form a totally planar structure like it was already calculated for

₁₃₀ the trimer. This confirms the already mentioned planarizing effect of a growing chain length also

₁₃₁ found in DFT calculations for other large oligomers [27,31]. It also agrees with results of Azumi *et*

₁₃₂ *al.* [40] who found a planar structure for the crystaline penta- and heptamer via X-ray diffraction.

₁₃₃ The calculated bondlengths are the same as in the middle ring of TTp and fit quite well to the

₁₃₄ experimental values for the heptamer [40]. This definitely justifies our ansatz to approach the

₁₃₅ polymer via smaller molecules.

₁₃₆ Regarding the electronic structure of PTp (see Fig. 2a), we obtained a bandgap of 1.2 eV. Again,

₁₃₇ the tendency of DFT to underestimate bandgaps is obvious as the calculated value is about 60% of

₁₃₈ the experimental value of 2.0 eV [41]. One might ask whether modeling linear polymers as a planar

₁₃₉ chain of infinite length could be an additional source of error in comparison with experimental

₁₄₀ values which were obtained for large, but finite and most likely twisted polymers. But as there are

₁₄₁ known saturation effects for electronic properties in PTp when it comes to chains consisting of

₁₄₂ 10–12 rings [42,43], this should not be no source of additional errors.

₁₄₃ In principle, there is a second possibility to build up a polymer from thiophene monomers. Instead

₁₄₄ of connecting the individual rings via their respective α-positions (2,5-connection) they can be

₁₄₅ coupled in an alternating 2,5/3,4-connection. We also modeled such an α, β-PTp system, the cor-

₁₄₆ responding structure is illustrated in the inset of Fig. 2b. Note that modeling a polymer consisting
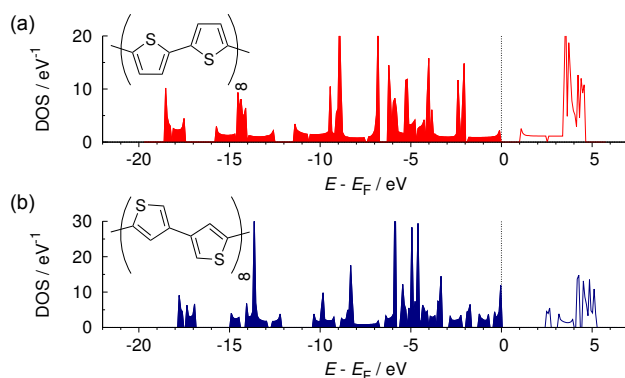
**Figure 2:** Structure and density of states for (a) PTp and (b) α,β-PTp.

of exclusively 3,4-connected thiophene monomers with a two-ring-unit cell is not possible because

of sterical hindrance. Fig. 2 compares the density of states for PTp and α,β-PTp. Obviously, there

is a considerable difference in the band gap of both isomers. As already mentioned, for PTp we ob-

tained a value of 1.2 eV whereas for α,β-PTp the calculated band gap of 2.5 eV is twice as large.

This difference is most probably due to a less effective conjugation between the single ring-systems

in α,β-PTp compared to PTp. As shown in Fig. 3, for PTp the highest occupied crystal orbital

(HOCO) as well as the lowest unoccupied crystal orbital (LUCO) are delocalized over the whole

polymer chain whereas for α,β-PTp the corresponding orbitals look rather localized. Especially

in the area of the 2,5-bonds there is nearly no electron density which suggests that this compound

consists of basically conjugatively isolated dimeric units. This explanation is supported by the

DOS-plots in Fig. 2. On the one hand, for PTp there are several broad populated areas which in-

dicate a relatively widespread conjugation over the polymer. But on the other hand, for α,β-PTp

some small sharp areas of occupied states are visible, especially close to the Fermi-edge. This im-

plies flat energy bands in this area and is indicative of a relatively weak interaction between the

unit cells [44]. In constrast, the DOS plot of PTp shows rather broad energy bands and thus a rel-

atively strong intercellular interaction. The large band gap of α,β-PTp is not very favorable for

most technical applications, hence we focused on PTp-derivatives in the following.

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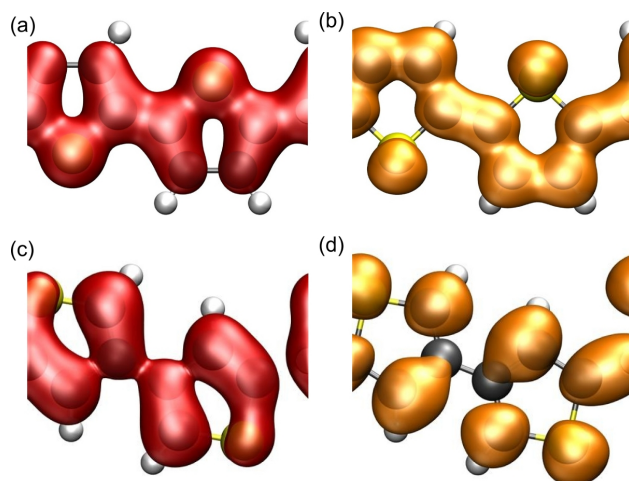
Figure 3: Electronic density isosurfaces ($\rho(r) = 0.01\,e/^3$) of the highest occupied crystal orbital (HOCO, red) and the lowest unoccupied crystal orbital (LUCO, orange) for PTp (a, b) and α, β-PTp (c, d).

Influence of substituents

The main goal of this study is to determine how substituents affect the electronic properties of oligothiophenes and whether the underlying effects can be transfered to the respective polymers. First, we have taken into account *classical* substituents, namely methyl (CH_3), amino (NH_2) and nitro groups (NO_2) and the chlorine atom (Cl). We have chosen these substituents because they exemplify the basic electronic effects on the electronic charge distribution of conjugated systems known from organic chemistry. The considered substitution patterns for singly bonded substituents are illustrated in Fig. 4. Furthermore, we have considered an annulated phenyl-ring as a kind of special-substituent to see how an explicitly extended π-system influences the respective systems.
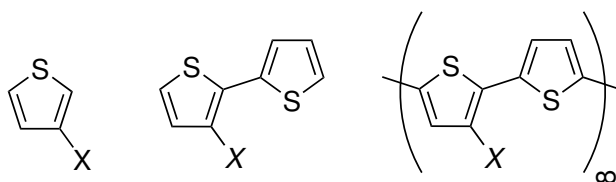
Figure 4: Illustration of the substitution patterns for singly bonded substituents of oligo- and poly-thiophenes considered in this study.

Structural effects concerning bond lengths in the monomers and dimers compared to the unsubstituted Tp and BTp turned out to be negligibly small. Nevertheless, the dihedral angle between

the two aromatic ring-systems in the substituted dimers differs from BTp. Except for the chlorine-substituted dimer (ClBTp), all BTp derivatives show dihedral angles of about 22° to 24°. ClBTp itself is predicted to appear in a totally flat structure, probably caused by the intramolecular dipole-dipole interaction. The already mentioned planarizing effect of a growing chain length again becomes observable as the dihedral angles of the substituted polymers are about 12° for NO_2PTp and NH_2PTp, and the methyl- and chlorine-substituted polymers, like PTp, turn out to be both completely flat.

The substituents lead to recognizable effects in the electronic structure of the oligothiophenes. As shown in Tab. 2, except for the methyl-substituted dimer all substituted molecules reveal a lowered HOMO-LUMO gap. The nitro group definitely causes the largest effect among the considered substituents, lowering the gap by about 1.3 eV for the monomer and by about 0.7 eV for the dimer, respectively, which we tentatively assign to the strong negative mesomeric effect of the nitro group. The influence of all other considered substituents on the electronic structure is rather minor. Regarding the chlorine-substituted bithiophene, one should take its planar structure into account. Hence, the gap-lowering effect can not solely be accredited to the direct electronic influence of chlorine. In addition, the sterical effect has to be considered as flat structures generally tend to form more stable conjugated systems and therefore smaller HOMO-LUMO gaps.

Table 2: Calculated HOMO-LUMO gaps E_g (in eV) for substituted oligothiophenes compared to the unsubstituted ones.

Substituent	Monomer	Dimer
H	4.49	2.93
CH_3	4.44	2.97
Cl	4.22	2.87
NH_2	4.46	2.75
NO_2	3.21	2.22

In Fig. 5, the resulting DOS of the substituted polymers is compared with the DOS of the unsubstituted PTp. Interestingly enough, although there are some changes in the band structure, there is only a minor effect of the substituents on the band gap. The band gap of 1.19 eV for the unsubstituted polythiophene is changed to 1.19 eV (CH_3PTp), 1.22 eV (ClPTp), 1.14 eV (NH_2PTp), and

9

1.27 eV (NO$_2$PTp), respectively.The nitro group, which caused the largest reduction in the HOMO-LUMO gap for the monomer and dimer, now even leads to an increase of the band gap.
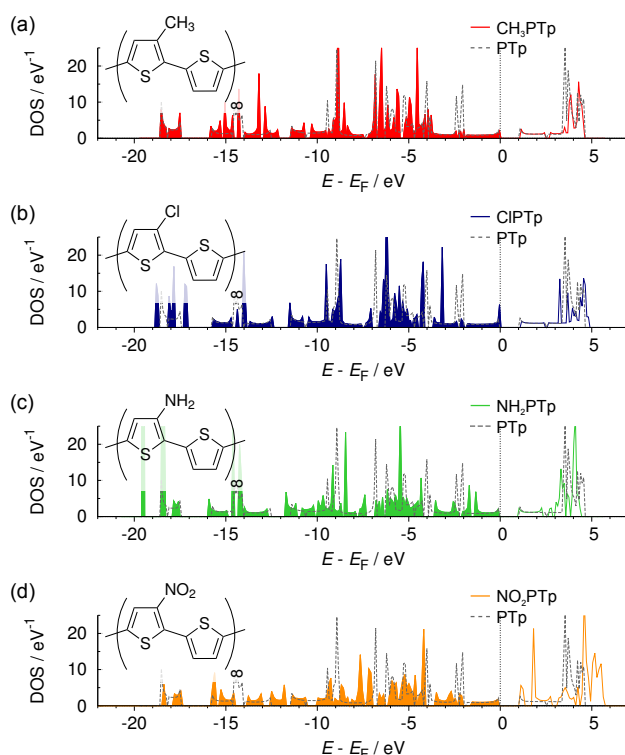
Figure 5: Density of states of substituted polymers: (a) CH$_3$PTp, (b) ClPTp, (c) NH$_2$PTp and (d) NO$_2$PTp. As a comparison, in each panel the DOS of the unsubstituted PTp is indicated by the dashed lines.

Hence the influence of the substituents on the electronic structure is significantly reduced upon the transition from oligo- to polymer. This agrees with results obtained by Salzner who reported similarly small effects of hydroxyl- and cyano-substituents [15]. These groups lower the bandgap of polymers by about only 0.1 eV whereas they reduce the HOMO-LUMO gap of monomers by more than 1 eV.

One might assume that the small changes in the band gaps are a consequence of the fact that the substituents hardly affect the HOCO and LUCO. But this assumption can be rejected regarding Fig. 6. There, the electronic density isosurfaces of the HOCO and the LUCO for the substituted polymers are shown which should be compared to the corresponding plot of unsubstituted polymer in Fig. 3. In particular the nitro and amino groups lead to significant changes in both the HOCO and the LUCO. It is more reasonable to assume a similar energetic shift of both orbitals resulting

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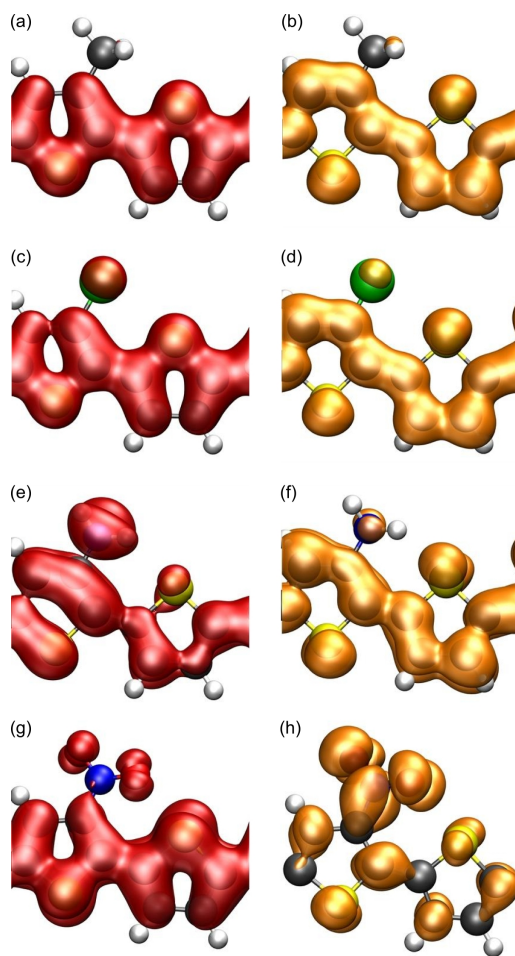
Figure 6: Electronic density isosurfaces ($\rho(r) = 0.01\,e/$) of the HOCO (red) and LUCO (orange) for (a), (b) CH$_3$PTp; (c), (d) ClPTp; (e), (f) NH$_2$PTp; (g), (h) NO$_2$PTp.

in nearly unaltered values for the respective bandgaps. This has already been discussed [45] and seems to work quite well for π-donating/accepting substituents. Thus one arrives at the conclusion that although the singly bonded substituents have some effect on the electronic structure of both oligomers and polymers, they hardly affect the band gap of the corresponding polymers.

Until now we focused our investigation on classic substituents which are all basically singly bonded to the aromatic ring-system of the thiophene-backbone. In order to extend our study, we considered a phenyl ring as a substituent thus obtaining benzo[c]thiophen (PhTp), 1-(thiophen-3-yl)-benzo[c]thiophen (PhBTp) and the corresponding polymer (PhPTp, see inset of Fig. 7 for an illustration). Since this π-extending substituent differs significantly from those previously re-

garded as it is bonded to two different carbon-atoms of the thiophene-backbone, we discuss it here separately.

Our calculations yielded a dihedral angle of about 34° for PhBTp and 21° for the corresponding polymer, respectively. Note that this is about twice the dihedral angle of NH_2PTp and NO_2PTp due to the sterical demand of the annulated phenyl ring. Still, the previously observed planarizing effect upon growing chain lengths also holds for this system. The HOMO-LUMO gap for PhTp is predicted to be 2.71 eV which is far below the other substituted monomers discussed so far. This is reasonable because the annulated phenyl ring extends the conjugated π-system quite considerably. For the dimer, the calculated HOMO-LUMO gap is further reduced to 2.19 eV which is rather close to the corresponding nitro-substituted analog. However, in contrast to the polymers with single-bonded substituents, the PhPTp polymer exhibits a band gap of 0.7 eV that is also significantly reduced with respect to the unsubstituted polymer PTp, as Fig. 7 shows. Apparently, the larger π-system of the phenyl-substituted polythiophene affects the electronic structure of polythiophene to a larger extend and leads to a smaller band gap. Hence, annulated systems might be promising candidates for the manipulation the bandgap of polythiophene. Note that Hong *et al.* found an increased band gap for an annulated cyclobutene ring [46]. This suggests that it is possible to both increase and decrease the bandgap with the choice of a suitable annulated substituent.
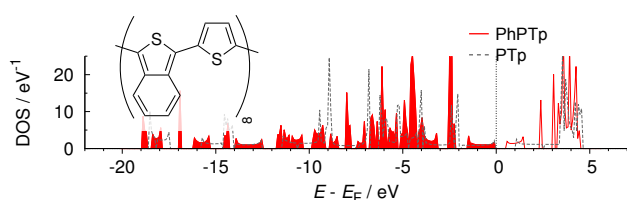

Figure 7: Calculated DOS of PhPTp compared to PTp. The inset illustrates the structure of Ph-PTp.

Vinyl-bridged Polythiophene-Derivatives

In the discussion about the singly bonded substituents we mentioned that the sterical repulsion between the substituents also influences the geometric and electronic structure of the polythiophenes. In order to minimize this sterical repulsion between the substituents, we considered polymers in

which the thiophene rings in the backbone of the polymers are separated by a vinyl bridge (see Fig. 8a). This results in entirely flat structures, independent of the respective substituent. Thus, geometrical effects such as deviations in the dihedral angle of the polymer should not influence the band structure.
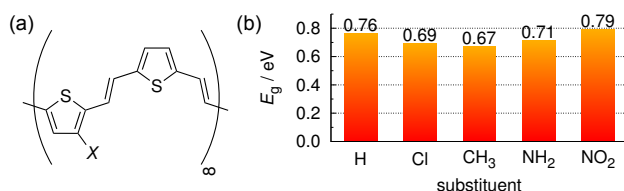
Figure 8: Considered vinyl-bridged polythiophene-derivatives. (a) Structural formula, (b) bandgaps E_g of the corresponding polymers.

As Fig. 8b demonstrates, the inclusion of a vinyl bridge also reduces the bandgaps significantly from $1.2\,\mathrm{eV}$ for PTp to about $0.7\,\mathrm{eV}$ for the vinyl-bridged polymers. Apparently, the vinyl bridges reduce the aromaticity of the polymers, leading to reduced band gaps as the band gap of conjugated polymers depends (among other factors) on the degree of a quinoid or aromatic character of the backbone [20].

The trends among the substituents are similar as for the substituted polythiophenes. Again, the nitro-substituted polymer reveals the largest bandgap among the polymers. Note that the band gap of the vinyl-bridged polymer with an annulated phenyl-ring is even further decreased to $0.25\,\mathrm{eV}$. Obviously, the effects of adding π-extending substituents and including vinyl bridges are roughly additive and can be combined in order to tailor the band gap.
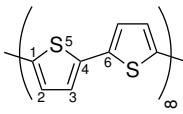
Influence of doping on the electronic structure

The electrical conductivity of a large class of polymers, in particular of polythiophene, can be highly increased when they are doped. The doping process itself corresponds basically to a manipulation of the number of valence electrons of the polymers, often in an electrochemical environment induced by adding counter ions. In order to model these doped compounds we varied the number of valence electrons per unit cell. Counter ions were not explicitly considered but modeled through a homogeneous charge background. Because polythiophene is known to be a good conductor in the

[260] *p*-doped state [47], we limited our study to oxidized states. Note that the exact nature of the charge

[261] carriers in doped polythiophenes is still debated, i.e., it is discussed whether the conductivity is

[262] caused by bipolarons or polaron pairs [18,19]. Since our unit cell only contains two aromatic rings,

[263] we can not address polarons which are supposed to extend over five thiophene rings [18]. Still, our

[264] results might be helpful to understand trends in the band gap engineering. Furthermore, note that

[265] it has been shown that changing the oxidation state through electrochemical potential control can

[266] have a decisive influence on the conductivity of molecular junctions [48].

[267] Tab. 3 lists calculated bond lengths for PTp in different oxidized states. When the polymer is neu-

[268] tral, a unit cell consisting of two thiophene-rings contains 48 valence electrons. Obviously there

[269] are some bonds that lengthen and some bonds that contract when PTp is oxidized. A closer inspec-

[270] tion reveals that the formerly short bonds lengthen *et vice versa*. All in all this results in a change

[271] into a quinoid-like structure that becomes more distinct the more the polymer is oxidized. This

[272] quasi-shift of the double-bond goes along with a loss of aromaticity and thus should be energeti-

[273] cally unfavorable at first glance. Of course the aromatic structure is more stable in the ground state,

[274] which is confirmed computationally [49], but the quinoid-like structure has a smaller ionization

[275] potential and a bigger electron affinity and thus the structural change caused by oxidation can be

[276] explained with the overall higher affinity of the quinoid-like structure towards charges [13].

Table 3: Calculated bond lengths for PTp (in Å) as a function of the charge state per unit cell in units of the elementary charge $|e|$.

	Charge State / Unit Cell					
	2.0	1.0	0.8	0.5	0.3	0.0
C^1-C^2	1.45	1.43	1.42	1.41	1.40	1.39
C^2-C^3	1.37	1.38	1.38	1.39	1.39	1.41
C^4-C^6	1.42	1.41	1.42	1.42	1.42	1.44
C^1-S	1.75	1.73	1.74	1.74	1.74	1.74

[277] Concerning substituted polymers we have limited our investigation in this case to NO_2PTp and

[278] NH_2PTp as these two substituents are considered to have mesomeric effects which are of special

[279] importance when it comes to (de)stabilization of excess charges. Regarding these polymers, the

effects of doping are basically the same. Both reveal a tendency to form a quinoid-like structure in the oxidized state. However, as a consequence of the broken symmetry that comes along with the addition of a substituent, these quinoid-like structures are distorted to a certain extent. Fig. 9 illustrates the color-encoded change of the respective bond lengths in oxidized polymers.
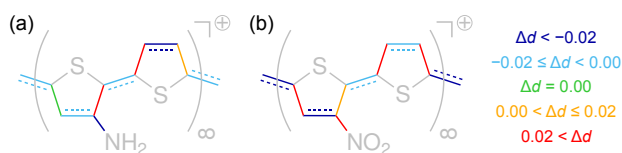

Figure 9: Color-encoded change of bond lengths in (a) NH_2PTp and (b) NO_2PTp for positively charged polymers with the number of electrons per unit cell lowered by one.

Note that in the case of the amino-substituted polymer there is a contraction of the carbon-substituent bond by about 0.05 Å. In contrast, the corresponding bond length in NO_2PTp increases by about 0.03 Å. This might be due to mesomeric effects. The nitro group is known to destabilize positive excess charges whereas the amino group usually stabilizes them via its +M-effect of organic chemistry, i.e., via its capacity to increase the electron density of the rest of the molecule. Hence, on the one hand, the NH_2-group might shift electron density into the formerly aromatic electron-lacking ring system. On the other hand, it might be energetically favorable for an electron-lacking system to quit the conjugation to the nitro group and therefore to lengthen the respective bond. This could be a reason for the observed distortions of the polymer structure.

Regarding the density of states of the oxidized polymers plotted in Fig. 10, it is obvious that positively charging the polymers leads to a partially occupied valence band whereas the band structure is hardly changed compared to the neutral polymers. This indicates that charging the polymers basically corresponds to a shift of the Fermi energy without significant changes in the band structure and leads to a metallic behavior. The substituted polymers, in contrast, still exhibit band gaps, cf. Fig 6. This means that the modification of the electronic structure upon substitution can not be explained by simple electron removal or addition.

The resulting metallic state of the considered polymers seems to be at variance with the well-known fact that for π-conjugated organic polymers electrical conductivity can not be understood with the mobility of unpaired electrons [49]. In fact, one-dimensional metals tend to distort sponta-

15
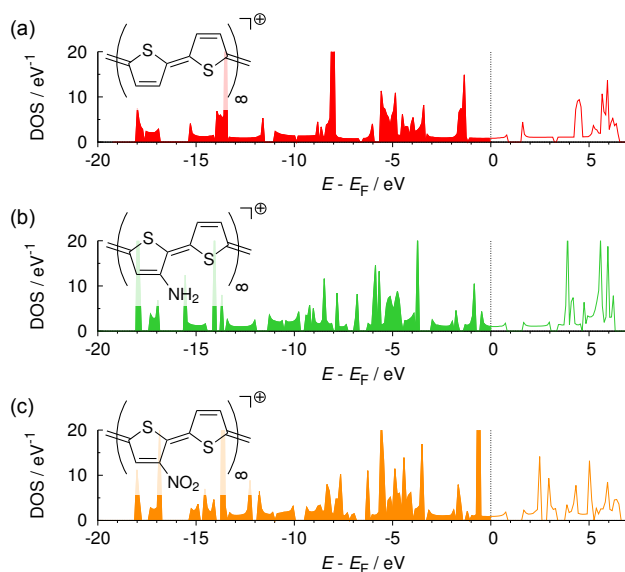
Figure 10: Density of states for positively charge polymers corresponding to a charge of $1|e|$ per unit cell: (a) PTp, (b) NH_2PTp and (c) NO_2PTp.

neously such that the spacing between adjacent unit cells becomes modulated [50]. In the case of polymers, conduction is associated with the formation of polarons or bipolarons. Quite often this leads to the formation of modulated quinoid-like structures [18,19] which extend over about five thiophene rings. In fact, as illustrated in Fig. 9, we also find indications of a quinoid-like modification upon oxidizing the polymers. Yet, since our unit cell only contains at most two thiophene rings, such polarons which would probably lead to the existence of a band gap can not be formed in our periodic DFT calculations. In order to address, larger unit cells are required. Such more time-consuming calculations are planned for the future.

Conclusions

The structural and electronic properties of oligo- and polythiophenes and their modifications through substituents have been studied by periodic density functional theory calculations. Whereas the considered oligothiophenes still exhibit non-vanishing dihedral angles, the corresponding polythiophenes turn out to be basically planar. Among the considered singly bonded substituents, methyl, amino or nitro groups or a chlorine atom, in particular the nitro group leads to a significant modification of the HOMO-LUMO gap of thiophene monomers and dimers. In contrast, the

16

corresponding polythiophenes exhibit a hardly modified band gap compared to the unsubstituted polythiophene.

Phenyl-substituted polythiophenes as well as vinyl-bridged polythiophene-derivatives, on the other hand, have drastically modified band gaps. In addition, positively charged polythiophenes were considered as a model for doped polythiophenes. All considered charged polythiophenes became metallic which shows that the modified band gaps can not be explained by simple electron removal or addition. However, the unit cell in the periodic DFT calculations was still to small to allow for the formation of polarons.

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