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Twisting of Conjugated Oligomers and Polymers: Case Study of Oligo- and Polythiophene

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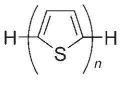
Abstract: Interring twisting (change in the dihedral angle between conjugated rings) of polythiophene was studied theoretically using periodic boundary conditions (PBC) at the B3LYP/6-31G(d) level. We find that the band gap of polymers is strongly dependent on the interring twist angle; yet twisting requires very little energy. A twist of 30° increases the band gap by 0.75 eV in polythiophene, while requiring only 0.41 kcal mol^{-1} per monomer unit. Such a small energetic value is of the order of crystal packing or van der Waals forces. These results are compared with calculations performed on model oligomers. Sexithiophene, its radical cations, and its dication are optimized at 0–180° end-to-end twist angles (which correspond to 0–36° interring dihedral angles) using the B3LYP/6-31G(d) method. The theoretical results suggest that the HOMO–LUMO gap, ionization potential, and charge distribution of oligomers are strongly dependent on twisting, whereas, similar to the case of polythiophene, twisting of neutral oligothiophenes costs very little energy. In the case of the radical cation, the lowest energy transition is shifted to a longer wavelength region on twisting, while the second-lowest energy transition is shifted to a shorter wavelength region. This implies that twisted, doped conducting polymers (modeled here by an oligomer radical cation), in contrast to planar, doped polymers, should be transparent within a certain optical window (in the far-visible region, at ≈1.5 eV). This observation is explained on the basis of changes in the shape and overlap of the frontier molecular orbitals.

Keywords: density functional calculations • oligothiophene • polymers • polythiophene

Introduction

Conducting polymers have attracted considerable attention over past decades in view of their potential applications in electronic and optoelectronic devices.[1,2] Polythiophenes are among the most promising and best studied conducting polymers.[2] Oligothiophenes are important materials in organic electronics, for example in FET (field effect transistors),[3] LED (light-emitting diodes),[4] and photovoltaic cells.[5] The optoelectronic properties of conjugated polymers vary significantly with the band gap.[2] The band gap depends on the degree of extended conjugation, which, in turn, should depend on the level of planarity of the polymer. In more planar systems, orbital overlap is better, which leads to a lowering of the band gap. The significant effects of interring twisting on the different properties of conjugated oligomers/polymers, for example, on emission and absorption spectra[6] and fluorescence quantum yield,[7] have been studied experimentally. The fact that the conjugation length changes on twisting has been applied to the development of polythiophene-based sensors[8] and to thermochromism.[9] Furthermore, the concept of oligothiophene twisting has been utilized to understand photoinduced electron transfer in polyether-bridged sexithiophene; a porphyrin-sexithiophene-fullerene triad that can function as a complexation-gated molecular wire.[10] Interring twisting of the polythiophene chain, which has attracted interest on account of its probable application in biomolecular devices, artificial enzymes, and biosensors, has been demonstrated through supermolecular self-assembly of a negatively charged polythiophene with a positively charged synthetic peptide.[11]

The effects of twisting have only been extensively theoretically studied for bithiophene and terthiophene.[12,13] The



n = 6: Sexithiophene (6T)

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effect of twisting on the electronic properties of longer oligothiophenes and polythiophenes has not yet been systematically studied.[14,15] *In particular, the effects of interring twisting on the band gap and on the relative orbital energies have never been quantitatively determined for conjugated polymers.* Experimentally, the effect of twisting on the band gap is more difficult to evaluate owing to the effect of substitution and, in the case of bulky groups, incomplete polymerization. The gas-phase structure of bithiophene is not planar;[16] however, as the conjugation length increases, oligothiophenes become planar. It is known experimentally that even small substituents (such as two adjacent alkyl chains on the same or neighboring rings; 3,4 or 3,3′-substituents, respectively) cause the oligomer to become nonplanar, although such substitution increases the processability of the material.[17] 3,3′-Substituted bithiophene units give rise to higher redox potentials and optical band gaps than 3,4′-substituted bithiophene units, and it is believed that 3,3′-substituted bithiophene units result in the conformation of adjacent thiophene rings becoming nearly perpendicular.[18]

It is known that aromatic molecules with bonds twisted to small angles still maintain their aromaticity.[19,20] Vogel et al. demonstrated that delocalization in conjugated systems remains intact as long as the angle between adjacent p orbitals does not become exceedingly large.[19] Recently, twisting in oligoacenes was studied. It was found that the electronic features (including the HOMO–LUMO gap) of oligoacenes are not sensitive to geometric distortions induced by twisting; however, twisting costs a very significant amount of energy. For example, for pentacene, a 150° end-to-end twist requires 65 $\mathrm{kcal\,mol^{-1}}$, while the calculated HOMO–LUMO gap is constant at 2.2 eV.[21]

The number of known types of conducting polymers is small, with examples including polythiophene, polypyrrole, etc. In most cases, the synthesis of a new conducting polymer requires the introduction of a twist-inducing substituent onto the oligomer/polymer chain. We believe that it is important to study theoretically the optical and electronic properties of twisted oligothiophenes and polythiophenes with a view to designing tailor-made processable materials.

Herein, we have studied changes in oligothiophene and polythiophene properties, such as relative energies, ionization energies, bond lengths, HOMO–LUMO gaps (in oligothiophenes), band gaps (in polythiophene), and charge distribution upon gradual interring twisting. The neutral molecule and radical cation of sexithiophene (6T) and pentadecathiophene (15T), and the dication of sexithiophene, were studied. Twisting in polythiophene and substituted polythiophenes was studied using periodic boundary conditions (PBC), and the results were compared with those from the study of oligothiophenes.

Theoretical Methods

Thiophene oligomers are denoted by nT, where n represent the number of thiophene rings. Density functional theory (DFT) with the B3LYP hybrid functional[22] and the 6-31G(d) basis set are used throughout the paper. The Gaussian 03 program was used for all computations.[23] The calculations for polymers were performed using PBC as implemented in Gaussian 03.[24] The same theoretical level (B3LYP/6-31G(d)) was used for both oligomer and polymer calculations, which allowed us to compare results for oligomers and polymers. The HOMO–LUMO gaps for oligomers were estimated as the orbital energy difference between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), and were compared to the band gaps of the polymers.[25] It was shown that band gaps predicted for conducting polymers using the hybrid B3LYP functional coupled with PBC were in excellent agreement with experimental values.[26]

We are aware that DFT, in general, and the B3LYP hybrid density functional, in particular, overestimate twisting energies compared to the ab initio MP2 method.[12a] However, a recent report has shown that the discrepancies between the DFT and MP2 studies observed earlier are mainly caused by the use of a small basis set for the MP2 calculations, and B3LYP results are close to the benchmark at CCSD(T)/cc-pVDZ, while increasing the basis set for MP2 calculations also brings the MP2 results close to the benchmark.[13i] We also note that, in contrast to many ab-initio methods (such as MP2, CISD, CCSD, etc.), the B3LYP level always yields real frequencies for benzene regardless of the basis set used.[27] The B3LYP level is currently widely used for studying organic electronic materials because it predicts geometries very reliably and provides good estimates for HOMO–LUMO gaps.[25,26d,28,29] To calculate optical transitions (UV-Vis-NIR spectra), we used the time-dependent density functional theory (TD-DFT)[30] with the 6-31G(d) basis set. Increasing the size of the basis set (up to 6-311++G(2d,p)) for TD-DFT calculations does not change the calculated optical band gap significantly in our cases. At least the first six and ten lowest transitions are calculated for the sexithiophene and 15T radical cations, respectively. The restricted wave function for the sexithiophene dication is unstable, as was shown previously,[31] thus all calculations for the sexithiophene dication were performed also using the spin-unrestricted broken-symmetry DFT calculations (UB3LYP/6-31G(d)). For charge distribution analysis, we used a Mulliken charge distribution calculated at B3LYP/6-31G(d).

We used sexithiophene as a model compound because the length of its oligomeric chain is sufficient to accept doping[32] and subject it to either spiral or up–down twisting. In spiral twisting, the desired end-to-end dihedral angle (Φ) between the two terminal C_1–C_2 and C_3–C_4 bonds of the oligomer chain is constrained and then scanned in steps of 10° between 0° and 180° (Figure 1). An end-to-end dihedral angle of 180° yields interring dihedral angles (ϕ) of approximately 36°[33] between each ring and its neighbor (Figure 1), thus, ϕ corresponds to the end-to-end dihe-

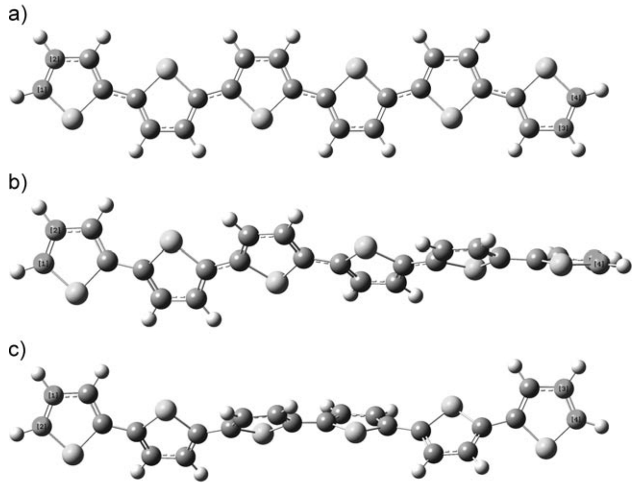


Figure 1. Views of spirally twisted sexithiophene at interring twist angles (ϕ) of a) 0°, b) 18°, and c) 36°, which correspond to total end-to-end dihedral angles (Φ) of 0°, 90°, and 180° between carbon atoms 1, 2, 3, and 4.

dral angle divided by the number of interring bonds, that is, $\phi = \Phi/(n-1)$. With respect to the up–down twisting of 6T, all C_{β}-C_{α}-$C_{\alpha'}$-$C_{\beta'}$ interring angles are constrained. For 15T, all C_{β}-C_{α}-$C_{\alpha'}$-$C_{\beta'}$ interring angles are constrained and so is the end-to-end dihedral angle. For polymer calculations, all C_{β}-C_{α}-$C_{\alpha'}$-$C_{\beta'}$ and S-C_{α}-$C_{\alpha'}$-S′ interring dihedral angles are constrained, as is the end-to-end dihedral angle of the unit cell. The unit cell consists of an appropriate number of monomer units (thiophene rings) to enable a full 360° end-to-end rotation (24, 12, 6, and 4 monomer units for interring twists of approximately 15°, 30°, 60°, and 90°, respectively).[34] Two monomer units in the unit cell were used to represent a planar structure or substituted thiophenes.

Results and Discussion

Twisting energy: Figure 2a shows a plot of the twisting energy ($\Delta E = E_{\phi} - E_0$) as a function of the interring dihedral twist angle (ϕ) for a spiral twist of sexithiophene.[35] Our calculations reveal that the energy required to twist neutral oligothiophene is very small. Twisting to a 36° interring dihedral angle requires only 2.5 kcal mol^{-1}[36] and twisting to a 20° interring angle requires only 0.4 kcal mol^{-1}. These calculations clearly show that oligothiophene chains are very flexible, and even small substituents or solid packing forces can significantly bend or twist them. In the gas phase, bithiophene is considerably bent;[16] however, as the number of thiophene rings in the chain increases, oligomer bending decreases. Quaterthiophene[37a,b] and sexithiophene[37c,d] are planar in the solid state. According to our calculations, sexithiophene in the gas phase has an average interring dihedral angle of about 14° and a planarization energy of only 0.1 kcal mol^{-1}, which is smaller than the crystal packing forces. Decathiophene (10T) has an average interring dihedral angle of only about 13° and its planarization energy is still 0.1 kcal mol^{-1} (which corresponds to 0.01 kcal mol^{-1} per thiophene ring). 20T is already completely planar according to our DFT calculations at B3LYP/6-31G(d).[38] In addition, we extended our study to 15T and increased the end-to-end dihedral angle up to 630°, which corresponds to a 45° interring dihedral angle (which is a realistic number for the experimental systems). The energy change with twisting for 15T (Figure 2a) is very small and is comparable to that observed for sexithiophene.

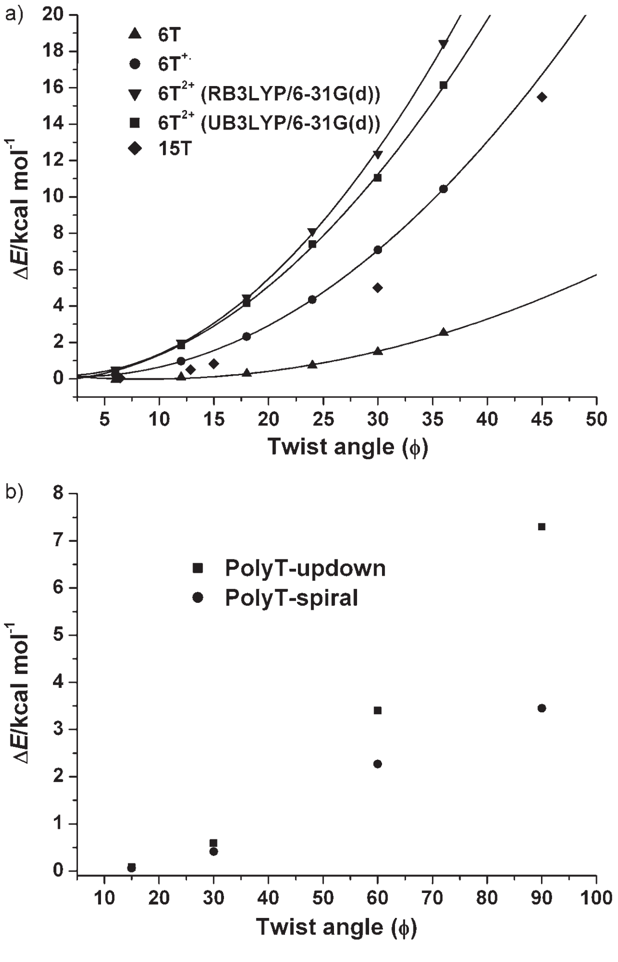


Figure 2. a) Energy changes ($\Delta E = E_{\phi} - E_0$) versus interring twist angle for spirally twisted sexithiophene (6T), its radical cation, and its dication, and for pentadecathiophene (15T). b) Energy changes per thiophene ring versus interring twist angle for polythiophene (twisted up–down and spirally).

We studied the relative energies, band gaps, and geometries of unconstrained and constrained polythiophene by means of a PBC approximation (see Table S2 in the Supporting Information).[39] Figure 2b shows the relative energy (per thiophene ring) against the interring twist angle for polythiophene undergoing up–down and spiral twisting.[35] Similarly to the results for the oligothiophenes mentioned above, twisting of polythiophenes requires relatively small energies, for example, for low interring twist angles (up to 30°), the required energy is within the crystal packing forces (0.41 kcal mol^{-1} per one thiophene unit is required for a 30° spiral interring twist).

Next we proceeded to study the radical cations of oligothiophene. The radical cation was used as a model for doped polythiophene.[32] We first studied the change in the ionization potential (IP) on twisting 6T. The IP changes considerably with twist angle (5.73 eV for 0° and 6.08 eV for 36° in sexithiophene, see Figure S15 in the Supporting Information). The first step in the oxidative doping of the conjugated polymer/oligomer is the formation of a radical cation (polaron), therefore oxidation of twisted oligomers should be more difficult than the oxidation of planar molecules.

Twisting a radical cation requires more energy than twisting the corresponding neutral oligomer (10.4 kcal mol^{-1} compared to 2.5 kcal mol^{-1}, respectively, for a 36° interring angle in sexithiophene, Figure 2a). Indeed, all oligothiophene radical cations studied ($n = 1$ to 20) are planar. This is because the delocalization of the positive charge in radical cations is best achieved in a planar conformation. Therefore, neutral molecules that are not planar, owing to the steric effects of substituents, become more planar upon oxidation/doping. It is known that only a very small geometrical change is required to move from the geometry of the neutral oligo- or polythiophene molecule to that of its radical cation (and, consequently, the change in reorganization energy is also very small).[40] However, our calculation predicts that this will not be the case for twisted oligothiophenes and also not, apparently, for twisted polythiophenes, since the effects of twisting on the energies of neutral oligothiophene, its radical cation, and its dication are very different. Because the geometric change experienced by neutral molecules on becoming radical cations is predicted to be large for twisted molecules, reorganization energies for substituted oligo- and polythiophenes should be relatively large, which is expected to prevent the use of oligo- and polythiophenes with bulky substituents in FET applications.

The ionization potential for the formation of a dication from neutral sexithiophene (double ionization) is 16.14 eV, and the change in IP associated with a 36° interring twist angle is 0.70 eV, which is higher than that for the radical cation (0.35 eV). The dication requires more energy to twist (16.1 $\mathrm{kcal\,mol^{-1}}$ for a 36° spiral twist, Figure 2a) than is required to similarly twist a radical cation (10.4 $\mathrm{kcal\,mol^{-1}}$). Dications optimized at the spin-unrestricted UB3LYP/6-31G(d) level require slightly less energy for twisting compared to dications optimized at the spin-restricted RB3LYP/6-31G(d) level. This suggests that if these calculations for oligomers are applied to polythiophenes, the twisted polythiophenes will favor the formation of the polaron pair over the bipolaron compared to planar polythiophenes.

Bond-length alternation (BLA) and charge distribution: Bond-length alternation (BLA) is the important criterion for comparing the geometries and extents of conjugation in different oligothiophene conformations.[41] Figure 3a shows the C–C bond length alternation in sexithiophene for 0° and 36° twist angles. Comparing the BLA for twist angles of 0° and 36° in neutral sexithiophene, there is no significant change in the C–C bond length within the ring; however, interring C–C bond lengths change noticeably (the average interring C–C bond lengths difference is 0.007 Å).[42] Figure 3b indicates that twisting of polythiophene also causes the interring bond length (bond number 4) to increase considerably, while the two terminal ring bonds shorten slightly and the middle bond elongates slightly. These results indi-

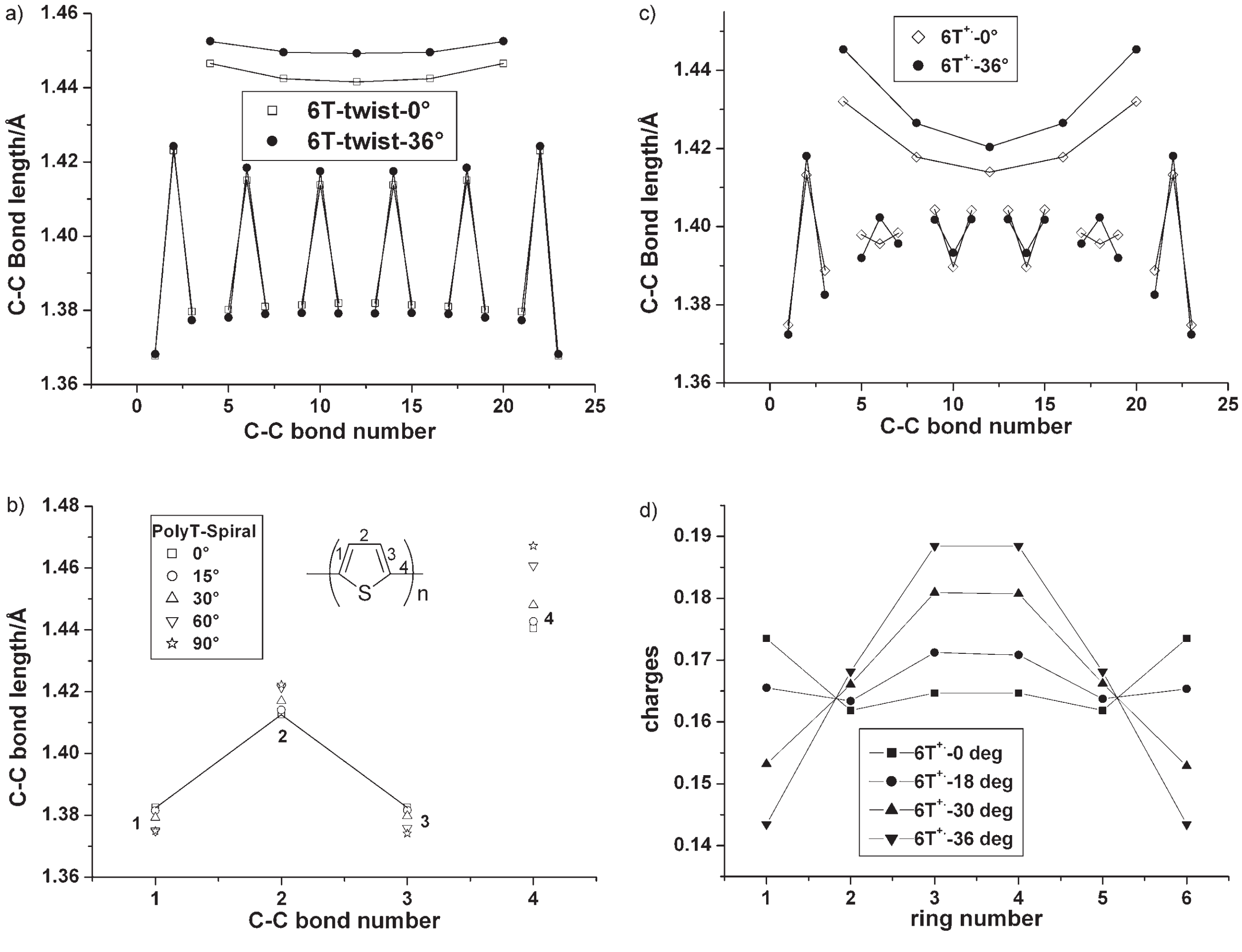
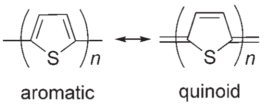


Figure 3. a) Bond-length alternation for 0° and 36° interring twist angles in spirally twisted sexithiophene (6T). The x axis represents the C–C bond number starting from one end of the conjugated chain. The repeating sets of three linked points represent intraring C–C bonds, while every fourth point on the x axis corresponds to an interring C–C bond (see the labeled thiophene unit inset in Figure 3b). The points are linked solely as a visual aid. b) Bond-length alternation plotted against bond number for spirally twisted polythiophene. c) Bond-length alternation for 0° and 36° interring twist angles for the spirally twisted sexithiophene radical cation. d) Charge distribution across the rings of the sexithiophene radical cation for various twist angles.

cate that the aromatic character of the thiophene unit in oligo- and polythiophene increases with twisting (Scheme 1).[43,44]



Scheme 1.

Figure 3c shows the BLA pattern of the sexithiophene radical cation for interring twist angles of 0° and 36°. Similarly to what occurs in neutral molecules, the bond lengths within the rings generally do not change significantly, whereas a considerable change is observed in the interring C–C bond length on twisting. The interring C–C bond length in the radical cation is shorter than that in the neutral molecule (average interring C–C bond lengths are 1.451 Å for 6T and 1.433 Å for $6T^{+\bullet}$ at a 36° twist angle). One more interesting point in the BLA pattern of the radical cation is that, at a 0° twist angle, 6T is comprised of four quinoid rings (indicated by the V-shaped patterns in the data shown in Figure 3c) and two aromatic rings (indicated by the Λ-shaped patterns) at a 0° twist angle, whereas, at a 36° twist angle, two rings are quinoid and four are aromatic (Scheme 1).[44] Thus, similarly to the situation with neutral 6T, twisting makes the oligothiophene radical cation more aromatic and less quinoid, which corresponds to a decrease in the degree of conjugation. In agreement with this finding, the localization of charge on the middle of the sexithiophene radical cation chain increases with increasing twist angle (Figure 3d).

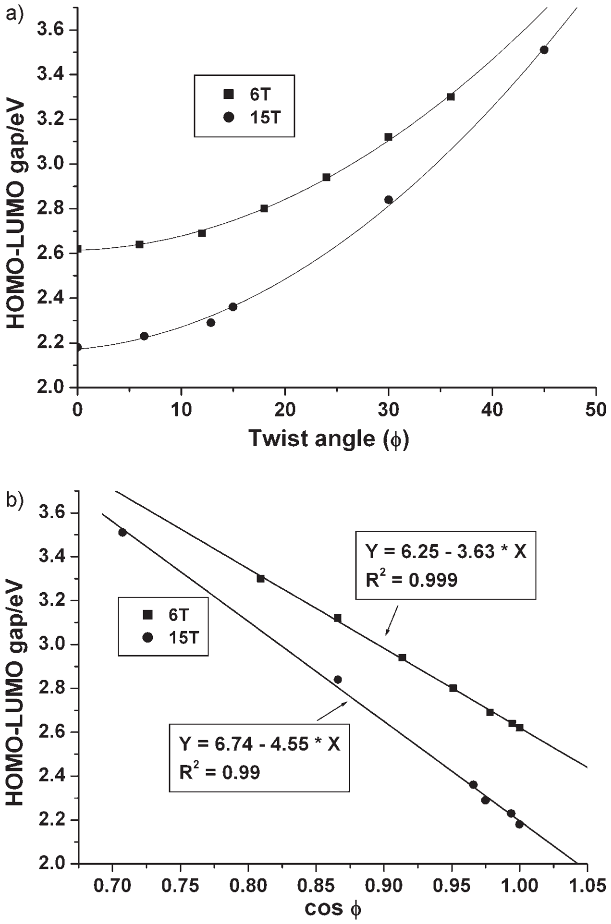


Figure 4. a) HOMO–LUMO gap versus interring twist angle for sexithiophene (6T) and pentadecathiophene (15T). b) Relationship between the HOMO–LUMO gap and the cosine of the interring twist angle for 6T and 15T.

HOMO–LUMO gaps in oligothiophenes: The band gap in polymers and the HOMO–LUMO gap in oligomers depend on the extent of conjugation along the chain. Planar oligothiophenes are expected to display a smaller HOMO–LUMO gap than their twisted counterparts owing to a better orbital overlap in the planar configuration. It is important to understand to what extent the bending influences oligothiophene properties such as the HOMO–LUMO gaps. Figure 4a shows a plot of the HOMO–LUMO gap in 6T as a function of the interring twist angle. In contrast to the energetic change on twisting, the change in the HOMO–LUMO gap is very significant; 0.68 eV for a 0° to 36° interring dihedral angle twist in 6T (while the energy change for this twist is less than 2.5 $kcal\,mol^{-1}$). Thus, in neutral oligothiophene, even a small change in the interring dihedral angle causes a momentous change in the HOMO–LUMO gap and, consequently, in the electronic properties of the oligomers. Because very little energy is required to achieve such twisting, even small substituents, such as two methyl groups, can cause very significant changes to the HOMO–LUMO gap in oligothiophenes.[45,46] Indeed, a change in the λ_{max} of polythiophene is observed under twisting.[8] These observations are in contrast to those found for the acenes, where the energies increase dramatically with increased twisting, while orbital energies and HOMO–LUMO gaps remain practically unchanged.[21] Similarly to sexithiophene, the increase in the HOMO–LUMO gap of 15T with twist angle is very significant. Expectedly, the differences between the HOMO–LUMO gaps of 6T and 15T reduce with increasing twist angle.

The HOMO–LUMO gap relates linearly to the cosine of the interring twist angle (Figure 4b), as expected when orbital energies are proportional to the degree of orbital overlap (which is, in turn, proportional to the cosine of the angle between the orbitals).[12a,47] As $\cos 0 = 1$, at an interring twist angle of zero (i.e. in a planar system), there is maximum overlap of molecular orbitals.

The large change in the HOMO–LUMO gap can be explained on the basis of the effect of twisting on the frontier molecular orbitals of sexithiophene (Figure 5). Twisting chiefly affects the interring bond in oligothiophene while the thiophene rings remain practically intact (which is in contrast to oligoacenes and other conjugated systems where twisting affects all bonds equally). The LUMO has bonding

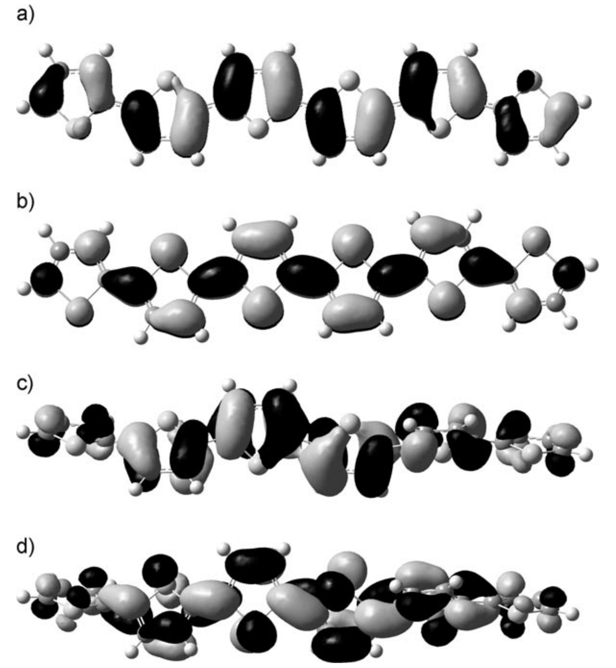


Figure 5. The HOMO (a and c) and LUMO (b and d) of sexithiophene at 0° and 36° interring twist angles, respectively.

interactions located on the interring bonds, therefore, twisting disturbs the interring bonding interactions and the LUMO is destabilized. The reverse situation exists for the HOMO, which has antibonding interactions located on interring bonds. Thus, the HOMO is stabilized under twisting as the antibonding interactions are removed, and interactions even become bonding for large interring twists (Figure 5).

Band gaps in polythiophenes: Similarly to the results for oligothiophenes, in polythiophene the band gap changes significantly with twist angle (the change is 0.75 eV for spirally twisting to a 30° interring dihedral angle, Figure 6 a), while the energy changes by only 0.41 kcal mol^{-1} (Figure 2 b) per one thiophene unit. The band gap for 90° spiral twisting is 4.91 eV, which is even higher than the calculated HOMO–LUMO gap of bithiophene (4.23 eV). Also, the band structures of polythiophene change significantly with interring twist angle (Figure 6 b). The bandwidths of the valence band and of the conduction band are not equal, decreasing significantly with increasing twist angle.[48] Thus, up–down twisting of the planar structure by 30° causes the valence bandwidth to decrease from 4.20 to 3.47 eV (a decrease of 0.73 eV) and causes the conduction bandwidth to decrease from 3.74 to 2.62 eV (a decrease of 1.12 eV). As expected, 90° twisting completely destroys the conjugation, and both valence and conduction bandwidths are close to zero. The PBC calculated band gap for planar polythiophene (2.06 eV; Figure 6 a) is consistent with the experimental value (2.0 eV)[49] and with the value extrapolated (at B3LYP/6-31G(d)) from the oligothiophene HOMO–LUMO gap (2.03 eV).[26d]

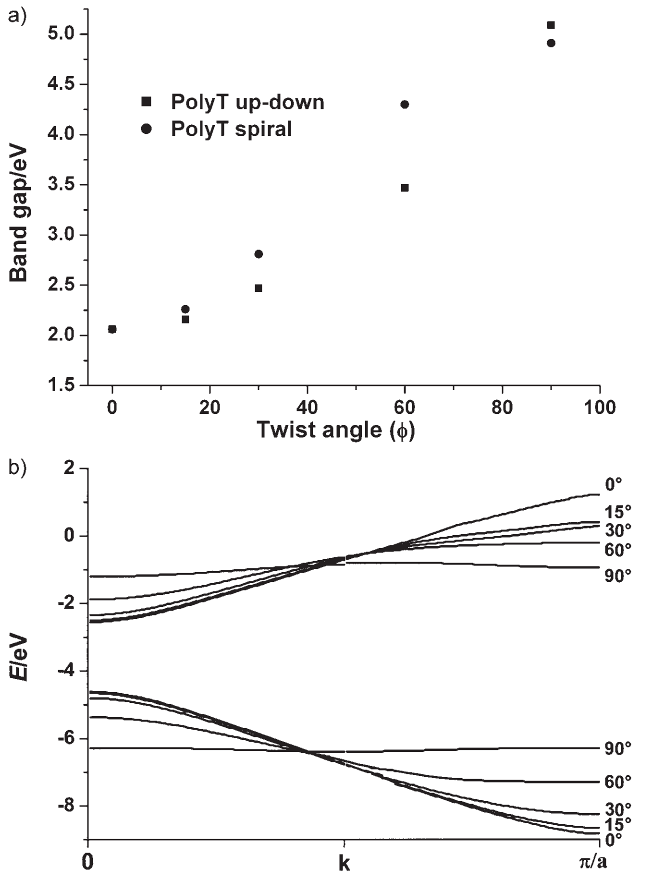
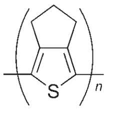


Figure 6. a) Band gap versus twist angle for polythiophene (twisted up–down and spirally). b) Band structures of polythiophene for the valence band (highest occupied crystal orbital, HOCO) and conduction band (lowest unoccupied crystal orbital, LUCO) at different interring twist angles (twisted in up–down conformation).

At the PBC/B3LYP/6-31G(d) level, poly(3-methylthiophene) has a calculated band gap of 2.00 eV (c.f. an experimental value of 1.9 eV[50]) and is planar. If the methyl groups in poly(3-methylthiophene) are placed in a head-to-head arrangement, the polymer is still planar and has a calculated band gap of 2.03 eV and it is 0.6 kcal mol^{-1} per thiophene unit higher in energy than the polymer with methyl groups in head-to-tail arrangement. Thus, one alkyl substitution in a regioregular arrangement does not alter the planarity or band gap of the polythiophene backbone.[51] However, at the PBC/B3LYP/6-31G(d) level, even a very minor additional steric hindrance leads to nonplanar structures and larger band gaps.[52] Indeed, the optimized structure of poly(3-ethylthiophene) is already nonplanar and the thiophene rings are twisted by 20°, which leads to a calculated band gap of 2.18 eV for ethyl substituents in a head-to-tail arrangement. If such a polymer is constrained to be planar, then the calculated band gap is 1.94 eV and it is by only 0.2 kcal mol^{-1} per thiophene unit higher in energy than the minimal conformation. The twisting is even larger (32°) for a head-to-head arrangement of the ethyl groups in poly(3-ethylthiophene), which leads to a calculated band gap of 2.43 eV, while such a polymer has an energy relative to the head-to-tail polymer of 0.8 kcal mol^{-1} per thiophene unit.[53,54] Because all polythiophenes adopt *anti* conformations of thiophene rings and on the basis of the above-mentioned results for poly(3-methylthiophene) and poly(3-ethylthiophene), we conclude that the significant differences observed experimentally between regioregular and regiorandom polythiophenes are attributable to differences in solid-state packing and interchain interactions are and not attributable to a significantly different backbone structure. This is also supported by our observations that band gaps for different arrangements of poly(3-methylthiophene) and poly(3-ethylthiophene) are different, while experimental band gaps for different poly(3-alkylthiophenes) are similar ($\approx$2 eV)[2g,51] and also similar to the band gap of polythiophene.

In the case of 3,4-dimethyl substitution, the molecule becomes more twisted, with the interring dihedral angle increasing to 67.8°. Consequently, a large change in the band gap is observed (calculated band gap is 3.50 eV, corresponding to a change of $\approx$1.4 eV), which is in excellent agreement with the data shown in Figure 6a.[55] It has been suggested that cyclopentene substitution onto polythiophene will reduce steric hindrance.[56] Indeed, the calculated structure of polymer **1** shows a completely planar backbone and the calculated band gap is 2.0 eV. Polymer **1** is also known experimentally and has similar properties to those of polythiophene.[56] Furthermore, we performed calculations for a polythiophene in which each second thiophene unit has two *n*-butyl groups at the β positions (polymer **2c**). Corresponding oligomers (up to 19-mer) and cyclic oligomers have been studied experimentally by Bäuerle et al.[57] Interestingly, the band gap obtained through extrapolation from experimental studies (2.85 eV)[57a] is in good agreement with the calculated values (the band gap for **2c** is 2.74 eV and it has an interring twist angle of 46°), which shows that 3,4-dialkyl substitution causes significant twisting of the polythiophene backbone.[58] A comparison of the results of replacing *n*-butyl substituents in polymer **2** with methyl or ethyl substituents reveals that even changing a methyl group to an ethyl group causes an observable band gap increase owing to steric interactions. Thus, the band gap and the twist angle for methyl-substituted polymer **2a** are 2.61 eV and 40°, while the same values for ethyl-substituted polymer **2b** are 2.71 eV and 45°, respectively. These examples show that great caution should be taken when experimentally studied polythiophenes with large substituents are theoretically modeled using polythiophene with small substituents.[59]



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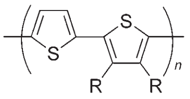

2a R=Me, **2b** R=Et, **2c** R=*n*Bu

Orbital energy gaps in oligothiophene radical cations: In radical cations, there are two possible types of electronic transition: from the SOMO(α) to the LUMO(α) and from the HOMO(β) to the SOMO(β). Figure 7a shows the dependence of the energies of these orbitals on the twist angle for the sexithiophene radical cation. The energy of the HOMO(β) reduces and that of the LUMO(α) increases with increasing twist angle; however, these changes are smaller than the significant decreases in energy observed for the SOMOs with increasing twist angle. Consequently, SOMO(α)→LUMO(α) and HOMO(β)→SOMO(β) bands are hypsochromically and bathochromically shifted, respectively. Examination of the molecular orbitals yields an explanation for the changes in orbital energies, which is analogous to that given in the case of neutral molecules. The twisting mostly affects the interring bonds in the oligothiophene radical cation (Figure 8). The LUMO(α) has bonding interactions located on these bonds, therefore, twisting disturbs the bonding interactions and the LUMO(α) is destabilized. SOMO (α and β) in the radical cation are equivalent in shape to the HOMO of neutral 6T and are similarly stabilized on twisting. HOMO(β) has both bonding and antibonding interactions on the interring C−C bond, and the net result is the stabilization of HOMO(β) to a small extent. Figure 7b shows SOMO(α)→LUMO(α) and HOMO(β)→SOMO(β) gaps for the sexithiophene radical cation. The difference between the two gaps increases as the twist angle increases. The orbital energy gap in the radical cation is linearly related to the cosine of the twist angle (Figure 7b insert), which is similar to what occurs in neutral molecules. In contrast to neutral molecules, where the small energy change that occurs as twisting progresses is accompanied by a large change in the HOMO–LUMO gap (Figure 4), in radical cations, twisting-induced energy changes and orbital energy changes are of having similar magnitudes. Thus, twisting the radical cation to 36° requires 10.4 kcal mol^{-1} (Figure 2a) and changes the SOMO(α)→LUMO(α) gap by 0.46 eV (which corresponds to 10.6 kcal mol^{-1}, Figure 7b).

Vertical electronic excitation energies for the sexithiophene radical cation were determined by means of time-dependent density functional theory (TD-DFT) at the B3LYP/6-31G(d) level with the optimized geometries discussed above over a 0–36° interring twist angle (Figure 7c). The calculations predicted two immense bands for all the radical cations.[60] The TD-DFT results follow a generally similar trend to that obtained from the orbital energy gaps shown in Figure 7b, with both α and β transitions predicted to be at slightly lower energies at the TD-B3LYP/6-31G(d) level. The intensity of the high-energy transition (α transition, Figure 7d) decreases with increasing twist angle (accompanied by a blue shift in energy). Exactly the reverse trend is observed for the low-energy transition (β transition). Thus, at high twisting angles, both transitions should have a similar intensity (Figure 7d).

On twisting the 15T radical cation, the energy of the SOMO(β) decreases slightly faster than that of the HOMO(β) (Figure 9a). The LUMO(α) shows a steep increase in energy, whereas the SOMO(α) shows a steep decrease in energy. Consequently, on twisting, the energy gap

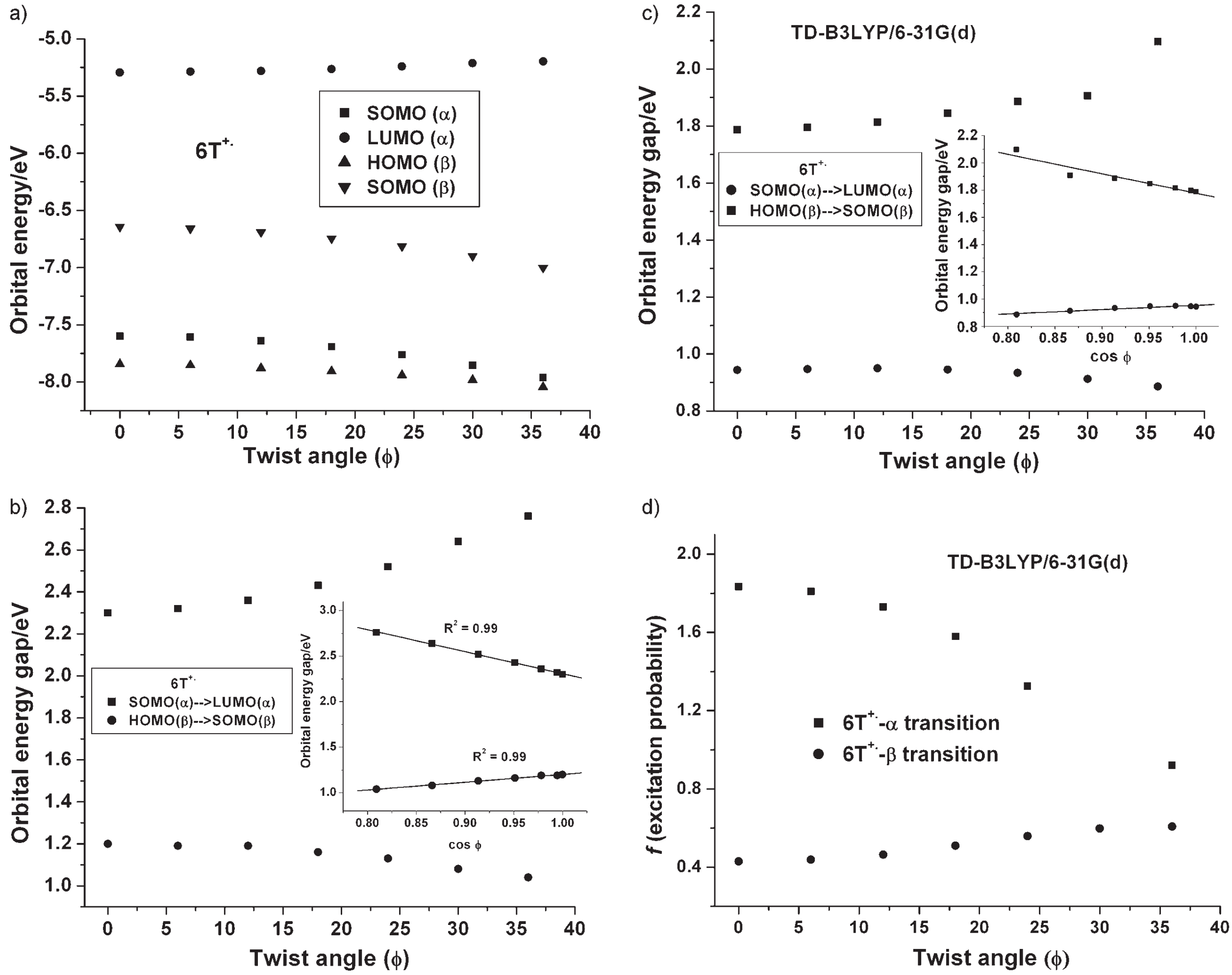

Figure 7. a) Dependence of the SOMO(α), LUMO(α), HOMO(β), and SOMO(β) energies of the sexithiophene (6T) radical cation on the twist angle. b) Dependence of the orbital energy gaps (SOMO(α)→LUMO(α), HOMO(β)→SOMO(β)) of the sexithiophene radical cation ($6T^{+\cdot}$) on the twist angle, and the relationship between the orbital energy gaps in twisted $6T^{+\cdot}$ with the cosine of the interring twist angle (inset graph). c) Dependence (at the TD-B3LYP/6-31G(d) level) of the orbital energy gaps (SOMO(α)→LUMO(α), HOMO(β)→SOMO(β)) of the sexithiophene radical cation on the twist angle, and the relationship between the orbital energy gaps in twisted $6T^{+\cdot}$ (at the TD-B3LYP/6-31G(d) level) with the cosine of the interring twist angle (inset graph). d) Dependence of excitation probability (*f*) for α and β transitions in sexithiophene radical cation on the twist angle (at the TD-B3LYP/6-31G(d) level).

for the high-energy transition of SOMO(α)→LUMO(α) is significantly increased, whereas the energy gap for the low-energy transition HOMO(β)→SOMO(β) reduces slightly (Figure 9b). TD-B3LYP/6-31G(d) calculations revealed similar observations for the 15T radical cation. SOMO(α)→LUMO(α) and HOMO(β)→SOMO(β) gaps in the 15T radical cation are also hypsochromically and bathochromically shifted, respectively (Figure 9b). However, in contrast to the 6T radical cation, the intensity of both the bands decreases with increasing twist angle.

Orbital energy gap in sexithiophene dication: Figure 10 shows the change in the HOMO and LUMO energies with the twist angle for the 6T dication (α and β sets of orbitals are degenerate). Both orbital energies decrease similarly with increasing twist angle. Consequently, there is no significant change in the orbital energy gap of the dication as the twist angle changes. The HOMO–LUMO gap changes by only 0.05 eV for a 36° twist. Thus, as twisting increases, while the change in energy increases significantly from the neutral oligothiophene to its radical cation and then to its dication (Figure 2a), the change in the frontier orbital energy gap on twisting diminishes: from 0.7 eV for neutral sexithiophene (Figure 4a) to less than 0.1 eV for the dication twisted by 36° (Figure 10). Unlike the case of neutral sexithiophene and its radical cation, for which the change in the shape of the frontier orbitals with twisting is relatively small, the sexithiophene dication undergoes a significant change in the shape of its frontier orbitals on twisting (Figure 11). On twisting, the orbitals become localized to one end of the chain (the α and β orbitals are mirror images of one another, having the same shape and energy).

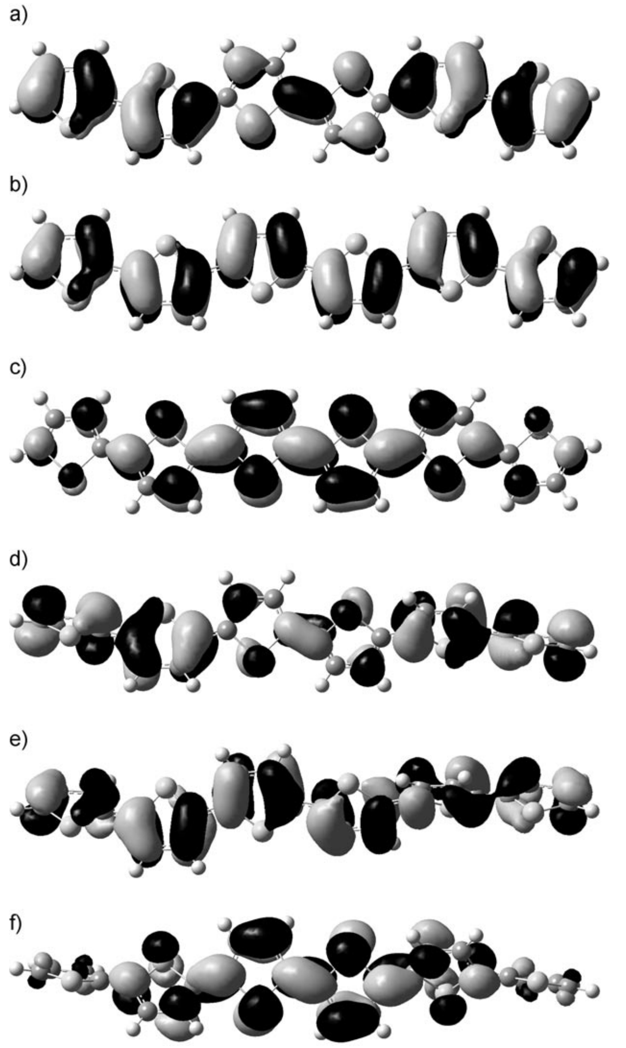

Figure 8. HOMO (a and d), SOMO (b and e), and LUMO (c and e) of the sexithiophene radical cation at 0° and 36° interring twist angles, respectively.

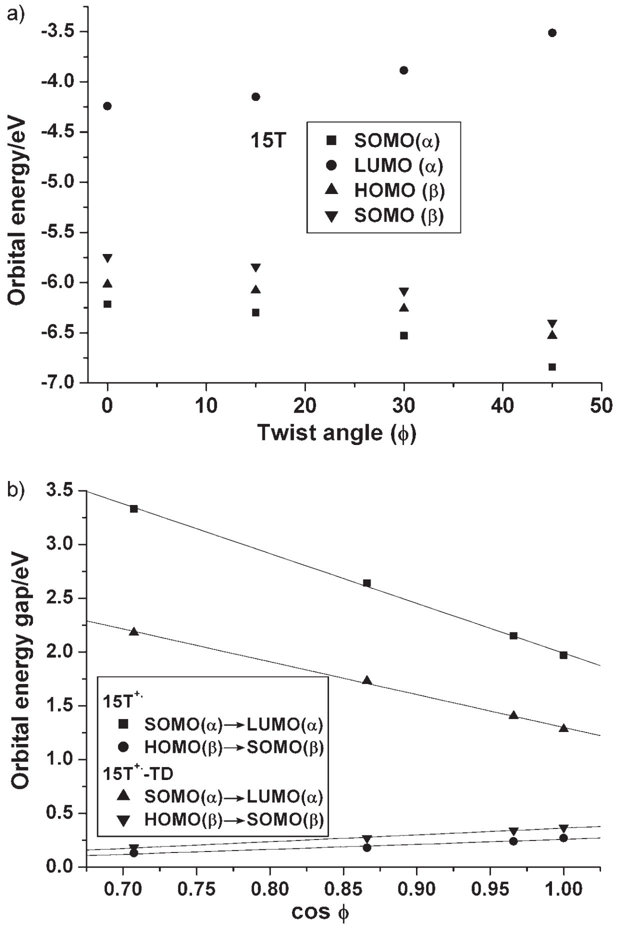

Figure 9. a) Frontier orbital energies versus twist angle for pentadecathiophene (15T). b) SOMO(α)→LUMO(α) and HOMO(β)→SOMO(β) gaps versus the cosine of the twist angle for the radical cation of 15T and the related TD-B3LYP/6-31G(d) calculation.

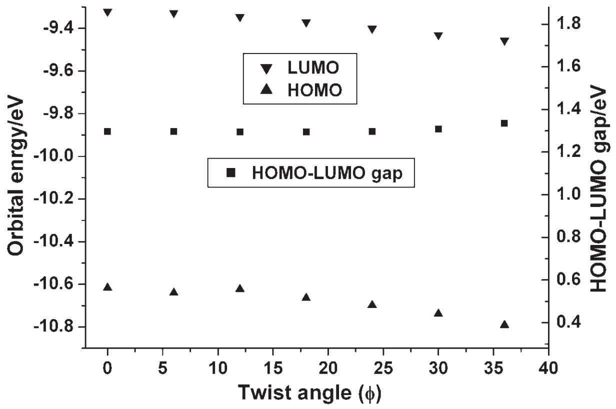

Figure 10. HOMO and LUMO energies (left *y* axis) and HOMO–LUMO gap (right *y* axis) versus twist angle in the sexithiophene dication (at the UB3LYP/6-31G(d) level).

Transparent optical window for twisted polythiophenes: Currently, there is interest in the field of transparent conducting polymers from both an experimental and theoretical perspective.[61,62] As mentioned above, with increasing twist angle, the long-wavelength absorption band (HOMO(β)→SOMO(β) transition) in radical cations is shifted to a longer wavelength (red shift), whereas the shorter wavelength absorption band (SOMO(α)→LUMO(α) transition) is shifted to a shorter wavelength (blue shift) (Figure 12a). Therefore, the difference (or optical window) between these two bands increases with increased twisting. In the case of a polymer, this is expected to lead to the creation of a transparent optical window in which the polymer does not absorb (Figure 12b). In the 15T radical cation (which models polythiophene with a low amount of doping), an increase in the size of the transparent window in the Vis-NIR region is also observed as compared to the 6T radical cation.[63] The window should be in the region of ≈1.0 eV (very roughly, based on the data in Figure 7c and Figure 9b) or ≈1.5 eV (based on spectroelectrohemical data[32a,64] for polythiophene), and will also depend on the nature of the substituents on polythiophene and on the doping level. This concept can be used to

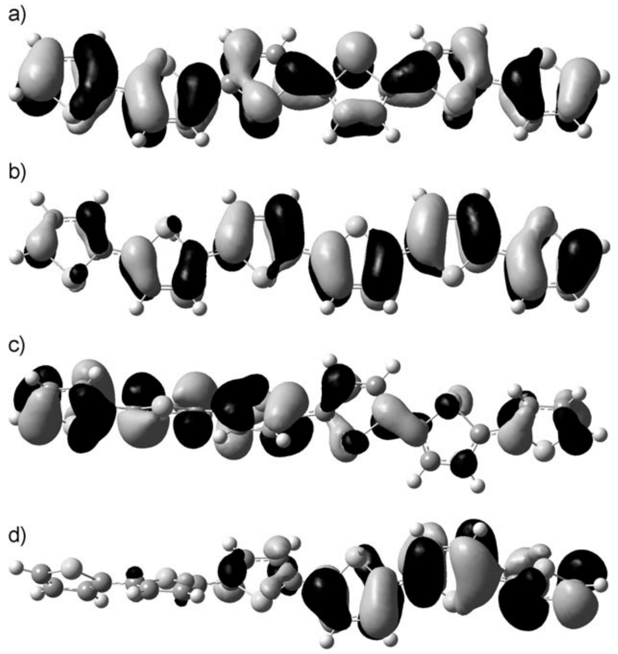

Figure 11. HOMO (a and c) and LUMO (b and d) of the sexithiophene dication at 0° and 36° interring twist angles, respectively. (Only the α orbitals are shown; β orbitals are mirror images of the α orbitals, having the same shape and energy).

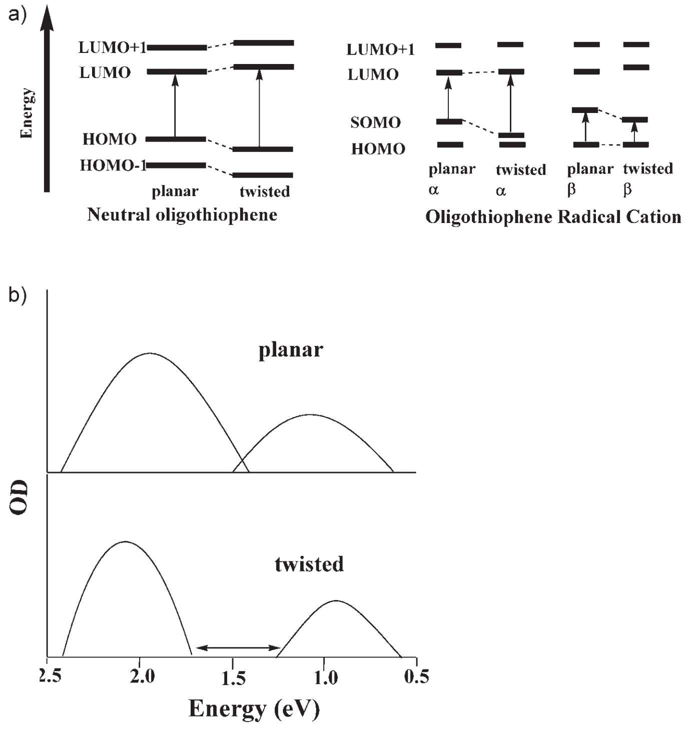

Figure 12. a) Schematic representation of changes in the energies of the frontier orbitals on twisting of neutral oligothiophene and its radical cation. b) Schematic representation of optical density (OD) versus absorption energy, showing the change in the optical transition on twisting of oligo- or polythiophene.

design oligomers/polymers that are appropriately substituted, and thereby appropriately twisted, so as to open up a transparent optical window in the telecommunication wavelength[65] or they can be used in optoelectronic devices and sensors.[8]

Conclusion

We have shown computationally that many substituted oligo- and polythiophenes are not planar, and therefore the effect of twisting on their electronic structures should be considered. We have found that twisting of the polythiophene backbone, which costs very little energy, significantly increases the band gap. For example, twisting by 30° requires only 0.41 kcal mol^{-1} per monomer unit in polythiophene (which is much smaller than the crystal packing or van der Waals forces) while resulting in a band gap increase of 0.75 eV. These results clearly show that polythiophene chains are very flexible and it is predicted that even solid packing forces or small substituents can significantly bend or twist them. For example, it is predicted that poly(3,4-dimethylthiophene) is significantly twisted (calculated band gap is 3.50 eV), poly(3-ethylthiophene) is twisted (calculated band gap is 2.18 eV for a head-to-tail arrangement and 2.43 eV for a head-to-head arrangement), whereas poly(3-methylthiophene) and polycyclopenta[c]thiophene are completely planar (calculated band gaps are 2.00 and 2.03 eV, respectively). Similarly, twisting of the neutral oligothiophene backbone costs very little energy (2.5 kcal mol^{-1} for a 36° twist); however, it does result in a significant increase in the band gap (by as much as 0.68 eV for a 36° twist). Thus, twisting of polythiophenes appears to be one of the major criteria governing their band gaps and should be considered when designing conducting polymers.

We have found that the effects of twisting on neutral oligothiophene are very different from those of twisting its radical cation and dication. Thus, oxidation of twisted neutral oligothiophene (i.e. oligothiophene with bulky substituents, or, presumably, of polythiophene) leads to significant structural reorganizations in the resulting radical cation or dication. This is in contrast to the case for unsubstituted oligo- or polythiophene, where the neutral molecule and radical cation have similar geometries and thus show very low reorganization energies.[40] For radical cations (polarons), and especially for dications (polaron pairs or bipolarons), significant energy is required for backbone twisting, and produces only a minor change in the frontier orbital gap. The electronic effect of twisting on oligothiophenes is also very different from the electronic effect of twisting on oligoacenes. The aromaticity of the thiophene rings in oligo- and polythiophenes is slightly increased by twisting.

Our calculations suggest that twisting of the polythiophene backbone should open up a transparent optical window in the Vis-NIR region, and so provide guidance in the design of new optoelectronic materials[25b,61] and sensors[8] based on polythiophene. We also believe that the majority of the conclusions in this paper will be applicable to other types of conducting polymers, such as polypyrroles.

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[33] On the basis of the experimental results (ref. [17]), we believe 36° to be a realistic number.

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[35] The twist energy was also calculated for up–down twisting of 6T and polythiophene; however, we prefer to rely on a discussion of spiral twisting because, in the case of the oligomer, up–down twisting leads to compensatory curvature of the chain. This leads to a lower relative energy and a smaller band gap in the case of up–down twisting. Nevertheless, we believe that this observation arises not purely as an effect of twisting, but is chiefly attributable to the effect of compensatory curvature. In the case of twisting caused by substituents, chains should not be curved, so we believe spiral twisting represents a better model for the estimation of twisting effects.

[36] When discussing the twisting energy (ΔE), it is important to note that the data reported are on a per oligothiophene molecule basis for oligomers (rendered simply kcal mol^{-1}), while being reported on a per thiophene unit (ring) basis for polymers (i.e. kcal mol^{-1} per thiophene unit (ring)).

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[42] In contrast to a lengthening of the C–C interring bond, a shortening in the oligomer length was observed with increasing twist, about 0.1 Å for 36°. This is caused by the slight curvature of the backbone of the molecule.

[43] We have also carried out PBC calculations on polypyrrole and polyselenophene. Twisting introduces similar changes in their properties (S. S. Zade, M. Bendikov, unpublished results).

[44] For a detailed explanation of aromatic versus quinoid structures in oligo- and polythiophene, see ref. [41].

[45] The fact that significant twisting results in a very small energy increase (of only a few kcal mol^{-1}), whereas orbital energies change significantly ($\approx$1 eV), indicates that in the unsubstituted oligothiophene, there is probably significant steric repulsion which forces the molecule out of planarity. The balance between π systems, which prefer a planar conformation, and steric repulsion is very delicate. This results in the molecules being slightly nonplanar in the gas phase and planar in the solid state (owing to crystal packing forces) and enables small substituents to disturb the conformation of the molecule.

[46] Small cyclic oligothiophenes also show large HOMO–LUMO gaps and they are significantly twisted, while large cyclic oligothiophenes are much less twisted and have smaller HOMO–LUMO gaps, see: S. S. Zade, M. Bendikov, *J. Org. Chem.* **2006**, *71*, 2972–2981.

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[52] We note that the minimal steric hindrance at which deviation from planarity occurs should be strongly dependant on the theoretical method used.

[53] In a head-to-head polymer constrained to be planar, the calculated band gap is similar to a planar head-to-tail polymer (1.97 eV).

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[58] The large difference in the planarity and band gap between polymer **2a** and isomeric poly(3-methyl)thiophene results from the conformation of methyl groups in **2a**. The in-plane hydrogen atom of the methyl group of **2a** is located *anti* to the thiophene ring to minimize steric repulsion of the two methyl groups in the 3,4-positions of thiophene ring. This in-plane hydrogen is affected by steric repulsion from sulfur atom of the adjacent ring thus leading to a deviation from planarity in **2a**.

[59] A large difference between the band gap of poly(3,4-ethylenedithiathiophene) (PEDTT) and poly(3,4-ethylenedioxythiophene) (PEDOT) has been observed and has been explained based on the importance of conformational effects on the band gap of polythiophenes. a) A. Cravino, H. Neugebauer, A. Petr, P. J. Skabara, H. J. Spencer, J. J. W. McDouall, L. Dunsch, N. S. Sariciftci, *J. Phys. Chem. B* **2006**, *110*, 2662–2667; b) M. Turbiez, P. Frère, M. Allain, N. Gallego-Planas, J. Roncali, *Macromolecules* **2005**, *38*, 6806–8612; c) H. J. Spencer, P. J. Skabara, M. Giles, I. McCulloch, S. J. Coles, M. B. Hursthouse, *J. Mater. Chem.* **2005**, *15*, 4783–4792; d) S. Y. Hong, *Synth. Met.* **2003**, *135–136*, 439–441; e) C. Wang, J. L. Schindler, C. R. Kannewurf, M. G. Kanatzidis, *Chem. Mater.* **1996**, *8*, 58–68.

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