CHEMISTRY
A EUROPEAN JOURNAL

DOI: 10.1002/chem.200701182

Study of Hopping Transport in Long Oligothiophenes and Oligoselenophenes: Dependence of Reorganization Energy on Chain Length

Sanjio S. Zade[a, b] and Michael Bendikov*[a]

Abstract: Internal reorganization energies for self-exchange hole-transfer process were calculated at the B3LYP/6-31G(d) level of theory for a series of oligothiophenes and oligoselenophenes up to the 50-mers. This is the first study of reorganization energy in very long π-conjugated systems. We observed a linear correlation between reorganization energy and the reciprocal chain length for these long π-conjugated heterocyclic oligomers, which can be explained by the changes in bond length that occur between the neutral and cation radical species and by the charge distribution in the cation radicals. In contrast to the saturation behavior observed for the HOMO–LUMO gaps of long π-conjugated heterocyclic oligomers, the reorganization energy does not show saturation behavior for any length of the oligomers in this study, even up to the 50-mers. Interestingly, the reorganization energy approaches zero for infinite numbers of oligomer units (at the B3LYP/6-31G(d) level of theory), that is, for polythiophene and polyselenophene. The absolute values of the reorganization energies of oligoselenophenes, and the changes that occur in those energies with chain length, are similar to those found for oligothiophenes.

Keywords: charge transfer • density functional calculations • oligoselenophenes • oligothiophenes • semiconductors

Introduction

Conjugated oligomers and polymers[1] attract considerable interest due to their applications in light-emitting diodes (LED),[2,3] field-effect transistors (FET),[3,4,5] photovoltaic cells,[6] and so on. Designing better organic electronic materials requires a comprehensive understanding of the electronic structure of conjugated oligomers and polymers and of the factors that affect it. By systematically studying a series of conjugated oligomers, valuable information can be generated not only on the properties of oligomers, but also on those of conducting polymers.[1]

Applications of organic electronic materials in organic FETs (OFETs) are of major current interest.[3,5] Plastic flexible organic-based transistors already meet the requirements for mass applications in microelectronics as pixel drivers for flexible displays, as well as for identification and product-tagging purposes.[7] Currently, the most highly developed organic FETs are based on pentacene.[8] The field-effect mobility in pentacene-based thin-film transistors has improved to equal that of hydrogenated amorphous silicon ($0.5\,cm^2V^{-1}s^{-1}$) and has recently superseded it at up to $3\,cm^2V^{-1}s^{-1}$.[4,8] Higher mobilities of $5\,cm^2V^{-1}s^{-1}$ (achieved by surface modification)[9] and even as high as $35\,cm^2V^{-1}s^{-1}$ (achieved for single crystals)[10] were reported for pentacene. Efforts to improve the mobility of acene by appropriate chemical modification (substitution) are also underway.[11,12] Recently, a mobility of $8\,cm^2V^{-1}s^{-1}$ was achieved with single crystals of rubrene,[13] and OFETs that were fabricated on the surface of free-standing rubrene single crystals[14] were found to have charge-carrier mobilities as high as $15\,cm^2V^{-1}s^{-1}$.

Oligothiophenes were also intensively studied as possible active semiconducting materials for FETs[4,15] Polythiophene and its derivatives were originally shown to have a lower mobility than acenes and oligothiophenes, possibly due to their less ordered solid-state structure.[4,16] This has significantly improved in recent years, with mobilities reaching $0.1\,cm^2V^{-1}s^{-1}$ for regioregular polythiophenes and their derivatives.[17,18] More recently, liquid-crystal polythiophene-

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[a] Dr. S. S. Zade, Dr. M. Bendikov
Department of Organic Chemistry
Weizmann Institute of Science
76100 Rehovot (Israel)
Fax: (+972) 8-934-4142
E-mail: michael.bendikov@weizmann.ac.il

[b] Dr. S. S. Zade
Current address: School of Chemistry
Indian Institute of Science Education and Research
Kolkata (India)

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type polymers showed mobility as high as 0.6 $cm^2 V^{-1} s^{-1}$.[19] Other types of conjugated systems have also exhibited high mobilities in FET devices.[4,20] 2,2′:5′,2″:5″,2‴-Quaterselenophene (4Se)[21] and selenophene-containing oligomers[22,23] have been used as active semiconductors in OFETs. Selenium-containing oligomers have attracted great interest as OFET materials[23] since Takimiya et al.[22] reported higher hole mobilities for selenium-containing compounds compared to the corresponding sulfur analogues.

Two mechanisms were proposed for charge transport in organic materials: hopping- and band-type mechanisms. In π-conjugated organic electronic materials charge motion occurs predominantly by a hopping-type mechanism.[24,25,26] When vibronic coupling becomes comparable to or stronger than electronic coupling, bandlike transport is expected to take place only in perfectly ordered systems at very low temperature.[27] The internal reorganization energy λ due to geometric relaxation is an important parameter for charge transfer in organic electronic materials, since it is one of the major factors controlling the rate of charge hopping and is related to the field-effect carrier mobility μ.[24,26] According to the Marcus expression,[28] the rate of charge transfer (of the hole or electron) depends on two factors: 1) the reorganization energy, and 2) the effective electronic coupling (orbital overlap V) between neighboring molecules [Eq. (1)],

$$k_{\text{transfer}} = \left(\frac{\pi}{\lambda k_B T}\right)^{1/2} \frac{V^2}{\hbar} \exp\left(\frac{-\lambda}{4 k_B T}\right) \tag{1}$$

where T is the temperature, $\hbar$ the Planck constant, and k_B the Boltzmann constant. The drift mobility of hopping charges μ is given by Equation (2),

$$\mu = \frac{e L^2 k_{\text{transfer}}}{k_B T} \tag{2}$$

where e is the electronic charge and L the separation between two regions taking part in charge hopping. So, in order to achieve high charge carrier mobility, reorganization energy should be minimized, and the effective electronic coupling maximized.

The reorganization energy results from modifications to the molecular geometry that occur when an electron is added to or removed from a molecule (inner reorganization), as well as from modifications in the surrounding medium due to polarization effects (outer reorganization). For most practical purposes, organic electronic materials can be considered to be condensed-state systems in which no solvent reorganization occurs. Since most organic electronic materials are of p type, we consider the reorganization energy for hole transfer. The reorganization energy for self-exchange consists of two components λ_+ and λ_0 (see Figure 1). It corresponds to the sum of the geometric relaxation energies on going from the geometry of the neutral state to that of the cation radical (λ_+), and from the geometry of the cation radical state to that of the neutral state (λ_0). The hole-transfer process on the basis of reorganization energy for p-type organic materials can be expressed by Equation (3),[26a]

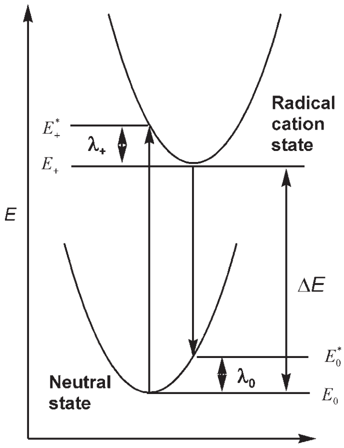


Figure 1. Internal reorganization energy $\lambda_+ + \lambda_0$ for hole transfer and the adiabatic ionization energy ΔE.

$$\lambda = \lambda_0 + \lambda_+ = (E_0^* - E_0) + (E_+^* - E_+) \tag{3}$$

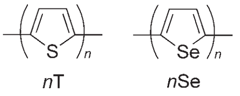
where E_0 and E_+ are the energies of the neutral and radical cation species in their optimized geometries, respectively, and E_0^* and E_+^* are the energies of the neutral and radical-cation species, having the geometries of radical cation and neutral species, respectively (see Figure 1).

Recently, we[29] and others[30] have shown that the generally accepted[31] linear relationship between the HOMO–LUMO gap of π-conjugated oligomers and $1/n$ only holds up to $n \approx 12$ (where n is the number of heterocyclic rings). This extrapolation method fails to consider asymptotic behavior, since saturation occurs at longer conjugation lengths. For higher n values ($n > 12$), second-order polynomials are required to describe the relationship between HOMO–LUMO gap and reciprocal chain length. Recently, it was observed that reorganization energies are inversely linearly correlated with the square root of the number of monomer units n in conjugated oligomers for $n = 2$–12, in contrast to the linear relationship between HOMO–LUMO gap and $1/n$ in short conjugated oligomers.[26a] Despite the importance of reorganization energy for hole transport in organic semiconductor devices, the reorganization energies of π-conjugated oligomers longer than $n = 12$ have never been investigated by the DFT approach.

We have now studied the internal reorganization energy of the self-exchange hole-transfer process (λ) in oligothiophenes and oligoselenophenes for up to $n = 50$ and found that, for long oligomers, the reorganization energy correlates linearly with the reciprocal of chain length. Moreover, it approaches zero for infinite chain length (i.e., for polymers). We note that effective electronic coupling is another important factor governing charge-carrier mobility, but its evaluation is outside of the current study.

Theoretical Methods

All calculations were carried out with the Gaussian 03 program.[32] The geometries of all oligomers were fully optimized by using a hybrid[33] Becke three-parameter exchange density functional with the LYP correlation functional (B3LYP)[34] and the 6-31G(d) basis set (B3LYP/6-31G(d) method). We note that B3LYP/6-31G(d) is a very accurate method for predicting the band gap of conjugated polymers such as polythiophene and polyselenophenes[29] and that the B3LYP method gives the best results compared to the BHandHLYP and MP2 methods with respect to experiments for reorganization energy[35] of pentacene. The internal reorganization energies λ for the self-exchange hole-transfer process are taken as the sum of the relaxation energies for the cation radical moving from the geometry of the neutral state to that of the cation-radical state (λ_+) and for the neutral oligomer moving from the geometry of the cation radical state to that of the neutral state (λ_0); see Figure 1. Oligothiophenes and oligoselenophenes are denoted by *n*T and *n*Se, respectively, where *n* is the number of heteroaromatic rings. The scf=tight keyword was used in all single-point energy calculations. In addition, to calculate the reorganization energies of long oligothiophenes and oligoselenophenes such as *n*T and *n*Se ($n=20$, 30, and 50) the additional keyword integral(grid=ultrafine) was used.



The geometries of oligothiophenes and oligoselenophenes were constrained to C_{2h} and C_{2v} symmetries for even and odd values of *n*, respectively, since the oligothiophene structures that are relevant to OFET devices have a planar conformation in the solid state. The energy difference between the symmetry-constrained and -unconstrained geometries is always less than 0.12 kcal mol^{-1} for oligothiophenes and less than 0.05 kcal mol^{-1} for oligoselenophenes. The optimized geometries of 20T, 30T, and 50T without symmetry constraints have planar structures which are indistinguishable from the symmetry-constrained geometries (energy difference <0.01 kcal mol^{-1}). While the optimized geometries of symmetry-unconstrained 20Se, 30Se, and 50Se are slightly curved,[36] the energy difference between the symmetry-constrained and symmetry-unconstrained structures is less than 0.03 kcal mol^{-1} (<1.5 meV). Since the energy differences between the planar and nonplanar minimal structures of all oligothiophenes and oligoselenophenes are negligible, small torsional changes in the oligomers do not contribute to the reorganization energies.[37] We are also aware that large spin contamination leads to unreliable estimations of reorganization energies.[38] Fortunately, spin contamination is negligible for all the cation radicals studied in this paper at the B3LYP/6-31G(d) level of theory. The largest S^2 values are found for the 9T cation radical ($S^2=0.77$) and for the 9Se cation radical ($S^2=0.78$). The S^2 values for long cation radicals are even smaller (0.752 for the 50T cation radical). The S^2 values after annihilation of the first spin contaminant are 0.75 for all the cation radicals studied here.

The adiabatic ionization potential (IP_{1a}) was calculated as the energy difference between the optimized structures of the cation radical and neutral molecule, while the vertical ionization potential (IP_{1v}) was calculated as the energy difference between the cation radical having the optimized geometry of the neutral molecule and optimized geometry of the neutral molecule.

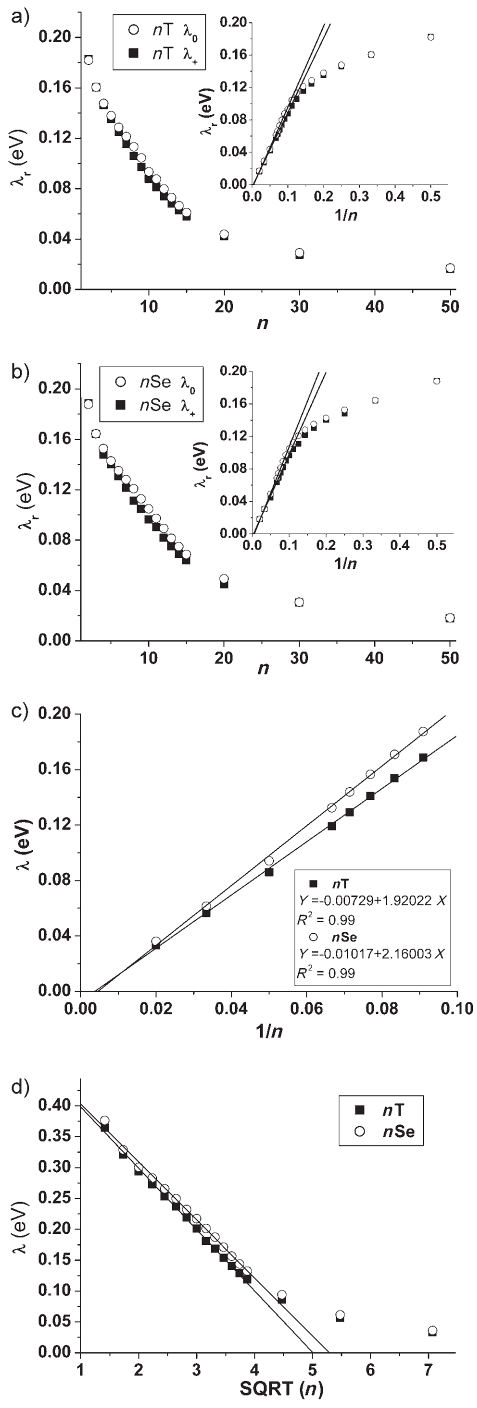


Figure 2. Relaxation energies λ_0 and λ_+ of a) oligothiophenes and b) oligoselenophenes versus chain length ($n=10$–50) and versus reciprocal chain length (insets, lines indicate the linear relation for $n>10$). Reorganization energy $\lambda=\lambda_0+\lambda_+$ versus c) reciprocal chain length (lines indicate the linear relation for $n>10$), and versus d) the square root of *n* at the B3LYP/6-31G(d) level.

Results

We studied the relationship between reorganization energy λ and conjugated chain length for oligothiophenes and oligoselenophenes (Figure 2). The two components of the reorganization energy λ_+ and λ_0 are nearly the same for oligothiophenes and oligoselenophenes (Figure 2a and b, respectively). This is in accordance with previous studies on reorganization energies for biphenyl, triphenylamine, and *N*,*N*′-diphenyl-*N*,*N*′-bis(3-methylphenyl)-1,1′-biphenyl-4,4′-diamine (TPD).[39] For medium-length oligothiophenes and oligoselenophenes, λ_0 is slightly larger than λ_+ (by up to 7 meV for 8T and by up to 10 meV for 8Se), while the two components are equal (within 1 meV) for very long (50-mers) and very short (di- and trimers) oligomers. The reorganization energies of oligothiophenes and oligoselenophenes show similar behaviors, however, the reorganization energies of oligoselenophenes are always slightly higher (between 1.02 to 1.11 times) than those of oligothiophenes (Figure 2c). We note that the calculated reorganization energies of oligofurans and oligopyrroles are somewhat lower than those of oligothiophenes.[26a]

Our calculations of the reorganization energy for oligothiophenes and oligoselenophenes up to the 50-mers show that a linear relationship between the square root of n and λ is maintained only up to $n \approx 15$ (Figure 2d). For larger n ($n = 10$–50), a linear relationship is observed between reorganization energy and reciprocal chain length with $R^2 = 0.99$ (Figure 2c), and no saturation behavior is observed in the $1/n$ correlation (at the B3LYP/6-31G(d) level).[40]

Importantly, the extrapolation approaches $\lambda \approx 0$ for infinite numbers of oligomer rings (i.e., polythiophene or polyselenophene with one unit of charge) assuming that the B3LYP/6-31G(d) level of theory correctly predicts polaron delocalization (see discussion below). Linear extrapolation of reorganization energies versus $1/n$ predicts reorganization energies of very close to zero, of -0.007 and -0.010 eV for polythiophene and polyselenophene, respectively (for infinite n). Quadratic extrapolation of reorganization energies versus $1/n$ results in a fit of similar quality ($R^2 = 0.999$, see Supporting Information), and the predicted reorganization energies for infinite n are even closer to zero (0.0008 eV and 0.0009 eV for polythiophene and polyselenophene, respectively). Thus, our calculations suggest that the ideal polymer, which is well defined, ideally ordered,[41] has a long conjugated chain, is planar, and carries one unit of charge, may serve as a very good FET material.[42] This is because, according to our extrapolations from oligothiophene and oligoselenophene, such polymers should have low reorganization energies, and field-effect mobility is known to increase with diminishing reorganization energy.[24,26,43,44] Interestingly, the free-carrier mobility of the mobile states in the ordered regions of regioregular polythiophene film is estimated to be much higher than that in amorphous polythiophene (1–4 cm^2 V^{-1} s^{-1}, based on experimental data fitted to a mobility edge model).[45] Also, it was recently shown that the chain conformation determines the charge-transport properties of conjugated polymers to a large extent, and that the mobility of a single stretched polymer chain should increase by few orders of magnitude compared to multiple strongly coiled polymer chains.[46] The recently discovered high mobility in liquid-crystal polythiophene-type polymers is attributed to their crystallinity.[19,47]

The reorganization energy for cyclic oligothiophenes in an *anti* conformation has been studied previously by us, although correlation with $1/n$ was not explored.[48] The absolute values of λ are significantly higher for cyclic oligothiophene than for linear oligothiophenes; however, as expected, the reorganization energy approaches zero for infinite n.[48,49] For details, see the Supporting Information.

Discussion

To explain why the extrapolation of the reorganization energy approaches $\lambda \approx 0$ for an infinite number of thiophene units, we studied bond-length changes on reorganization from a neutral to a cation-radical geometry (Figure 3) and charge distribution in cation radicals (Figure 4) for oligothiophenes.[50] As the number of oligomer units increases, the total number of geometric parameters which are changed on moving from the neutral molecule to a cation-radical geometry and vice versa increases, but each change in a geometric parameter becomes smaller, since one unit of charge in the cation radical is well delocalized over the backbone.

Geometric changes on moving from the neutral molecule to the cation radical for oligothiophenes are shown in Figure 3 as the bond-length alternation (BLA) pattern.

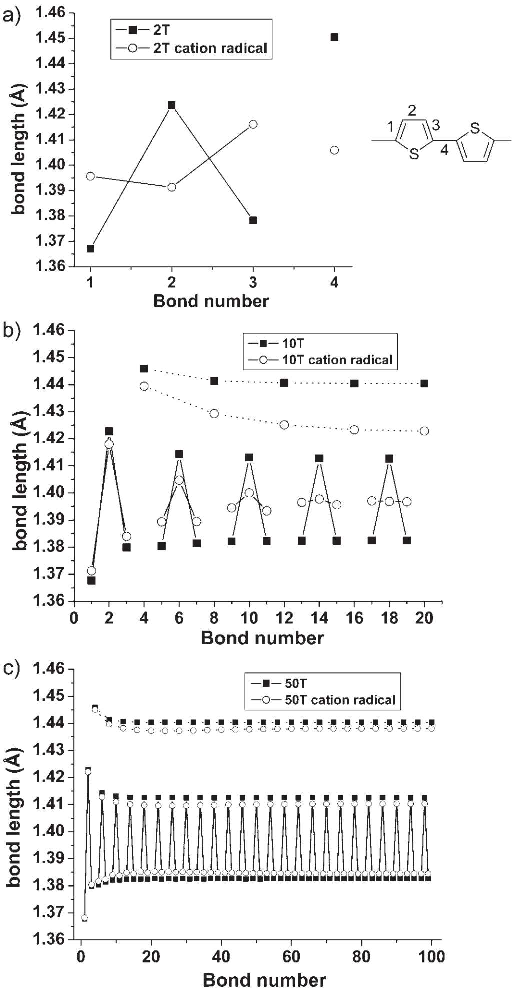


Figure 3. Bond-length alternation in a) 2T and 2T$^{\cdot+}$, b) 10T and 10T$^{\cdot+}$, and c) 50T and 50T$^{\cdot+}$ at the B3LYP/6-31G(d) level. The x axis is the C–C bond number starting from one end of the conjugated chain. The repeating sets of three linked points represent intra-ring C–C bonds, while every fourth point on the x axis corresponds to an inter-ring C–C bond. The points are linked solely as a visual aid. Only half of the molecule is represented in the figures, as the second half is the mirror image of the first.

These geometric changes are very significant for 2T (Figure 3a). However, they become smaller for 10T (Figure 3b) and very small for long oligomers such as 50T. Importantly, for medium length (10T) and long oligomers (50T), the geometric changes occurring between the neutral molecule and its cation radical are roughly constant for all C–C bonds (Figure 3b and c). Total change in lengths of all C–C bond ($\Sigma(|\Delta x|)$, where Δx is a change in bond length) on moving from the neutral oligomer to its cation radical remain constant for $n \geq 9$ and are roughly equal to 0.45±0.01 Å per molecule for all oligomers (0.45 Å per molecule for 9T and 10T, 0.46 Å per molecule for 20T and 0.45 Å per molecule for 50T). However, the $\Sigma(|\Delta x|)$ value increases gradually up to $n=9$ (0.24 Å per molecule for 2T, 0.40 Å per molecule for 6T). Since the number of C–C bonds increases linearly with n, while the total geometric changes stay constant for $n \geq 9$, the change in a particular C–C bond length decreases with $1/n$.

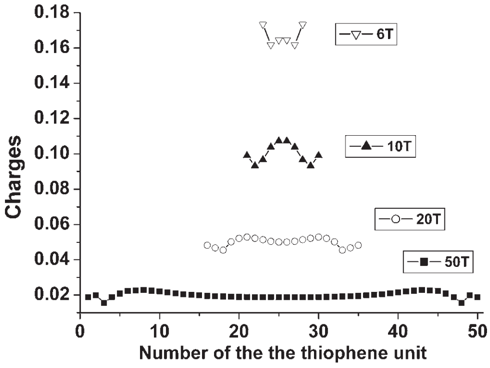


Figure 4. Mulliken charge distribution for $6T^{\cdot+}$, $10T^{\cdot+}$, $20T^{\cdot+}$, and $50T^{\cdot+}$ at the B3LYP/6-31G(d) level.

The charge distribution at the B3LYP/6-31G(d) level in oligothiophene cation radicals is shown in Figure 4. There is some charge localization (although relatively small) for the 6T and 10T[51] cation radicals, while for longer oligomer cation radicals, such as those of 20T and 50T, the charge is practically completely delocalized over the oligomer backbone.[42] Thus, for the cation radicals of long oligomers we can assume that each ring carries $1/n$ units of charge. We note that the charge distribution pattern in oligothiophene cation radicals is significantly dependent on the amount of Hartree–Fock (HF) exchange used. Localization of charges is proportional to the amount of HF exchange; the charge distribution is highly localized at the HF level and practically completely delocalized at pure DFT levels.[52] We believe that if the charges in cation radicals are localized (due to solid-state effects or deficiencies of theoretical methods) then reorganization energy might approach a finite (although very small) value even for infinite chains.[53] While presently it is unclear which theoretical method reproduces charge-distribution patterns correctly,[54] we note that the B3LYP functional employed here gives the best results when compared to experiment for the reorganization energy of pentacene.[35]

Based on Figures 3 and 4, we can understand the linear relationship found between reorganization energy and reciprocal chain length (Figure 2). First, we consider changes in oligomer bond lengths on going from a neutral to a cation-radical geometry (Figure 3). From Equation (3), we see that $\lambda \sim \Delta E$, where $\Delta E = E_0^* - E_0$ or $\Delta E = E_+^* - E_+$. Now, let us assume a harmonic oscillator approximation for energy changes as a function of bond length change, so we get Equation (4),

$$\lambda \sim \sum (|\Delta x|)^2 \qquad (4)$$

and define $N_{C-C} = 4n-1$, where N_{C-C} is the total number of C–C bonds and n is the number of oligomer rings. All Δx are practically equal for long oligomers (Figure 3), so Equations (5) and (6) hold.

$$\sum (|\Delta x|) = N_{C-C} |\Delta x| \qquad (5)$$

$$\sum (|\Delta x|)^2 = N_{C-C} (|\Delta x|)^2 \qquad (6)$$

From Equations (4) and (6) we can write $\lambda \sim N_{C-C}(\Delta x)^2$. From Equation (5) we obtain Equation (7).

$$\Delta x = \sum (|\Delta x|)/N_{C-C} \qquad (7)$$

Thus, $\lambda \sim N_{C-C}(\Sigma(|\Delta x|)/N_{C-C})^2$ and consequently $\lambda \sim \Sigma(|\Delta x|)^2/N_{C-C}$. Remembering that $\Sigma(\Delta x)$ is constant for long oligomers (see Figure 3 and discussion above) and is independent of N_{C-C} or n, and since $N_{C-C} \sim n$, we obtain $\lambda \sim 1/n$; that is, the reorganization energy is inversely proportional to oligomer length for long oligomers (oligothiophenes).

A similar conclusion can be obtained on the basis of charge distribution in cation radicals of long oligomers (Figure 4). Since $\lambda \sim \Delta E$ and $\Delta E \sim \Sigma q_1 q_2$, we assume Equation (8),

$$\lambda \sim \sum q_1 q_2 \qquad (8)$$

where q_1 and q_2 are the charges on neighboring atoms. Taking into account that the charge is equally delocalized over the oligomer backbone for long oligomers (Figure 4), and as first approximation making the rough assumption that the charge is equally distributed between all carbon atoms in the rings, we can write $\Sigma q_1 q_2 = Nq^2$.[55] Each carbon atom carries roughly $1/N$ units of charge (where N is the number of carbon atoms), that is, $q = 1/N$, so we can rewrite Equation (8) as $\lambda \sim N(1/N)^2$ and since $N \sim n$ we again obtain $\lambda \sim 1/n$ for long oligomers.

On the basis of Equation (1) we estimated the contribution of reorganization energy $(1/\lambda)^{1/2}\exp(-\lambda/4k_0T)$ to the rate of charge transfer for oligothiophenes (Figure 5). Since the orbital overlap (bandwidth) V only decreases slightly

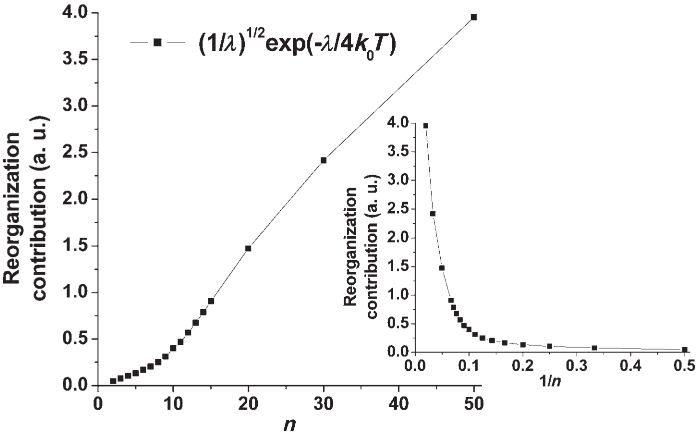


Figure 5. Contribution of reorganization energy $(1/\lambda)^{1/2}\exp(-\lambda/4k_0T)$ to the rate of charge transfer for oligothiophenes versus chain length ($n=2$–50) and versus the reciprocal of chain length (inset).

with increasing oligomer length,[26a] the exponential nature of the contribution of the internal reorganization energy dominates. The rate of charge transfer clearly increases with increasing oligomer length. Interestingly, two independent regions can be observed in Figure 5: a linear region for $n=$ 2–10, and another, even steeper region for $n=10$–50.

Dependence of ionization potentials of oligothiophenes and oligoselenophenes on chain length: The difference between the first vertical (IP_{1v}) and adiabatic (IP_{1a}) ionization potentials is equal to λ_+ (Figure 1). Since the two components of the reorganization energy (λ_+ and λ_0) are nearly the same for oligothiophenes and oligoselenophenes (Figure 2a and b), the difference between IP_{1v} and IP_{1a} almost equal to half the reorganization energy for hole transport. The dependence of the IP_{1a} and IP_{1v} on chain length for oligothiophenes and oligoselenophenes is shown in Figure 6. Interestingly, the relationship between IP_{1a} and IP_{1v} and chain length is not similar to that between the reorganization energy and n (there is a linear correlation between reorganization energy and the square root of n for small n values and with the reciprocal of n for large n values). Nor is it similar to the relationship between the HOMO–LUMO gap and n (there is a linear correlation between the HOMO–LUMO gap and $1/n$ for small n values which converges to a constant value for large n);[29] see Supporting Information for details. Instead, IP_{1a} of oligothiophenes and oligoselenophenes linearly correlates with an empirically obtained $1/n^{0.75}$ (Figure 6b), while IP_{1v} of oligothiophenes and oligoselenophenes linearly correlates with a similarly empirically obtained $1/n^{0.70}$ (Figure 6c). Since the calculated reorganization energy for polythiophene is zero (Figure 2c), both IP_{1a} and IP_{1v} of polythiophene obtained by extrapolating the $1/n^{0.75}$ and $1/n^{0.70}$ lines for oligomers, respectively, are practically the same (4.65 and 4.60 eV, respectively). These values match reasonably well with the experimentally reported value of IP_{1a} for polythiophene (5.0 eV).[56] The predicted ionization potentials (both IP_{1a} and IP_{1v}) for polyselenophene are very similar to those of polythiophene (4.60 and 4.56 eV, respectively).

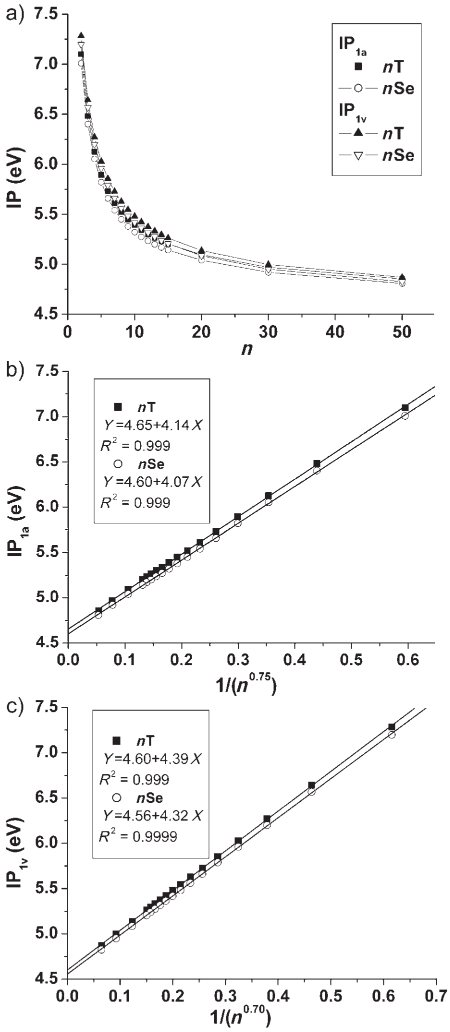


Figure 6. a) Adiabatic and vertical ionization potentials (IP_{1a} and IP_{1v}) of oligothiophene and oligoselenophene versus chain length n. b) Adiabatic ionization potentials (IP_{1a}) of oligothiophene and oligoselenophene versus $1/n^{0.75}$, and c) the vertical ionization potentials (IP_{1v}) of oligothiophene and oligoselenophene versus $1/n^{0.70}$.

Conclusion

We have found that the $1/n$ extrapolation of reorganization energies reaches $\lambda \approx 0$ (at B3LYP/6-31G(d)) for conjugated polymers such as polythiophene and polyselenophene, that is, the ideal polymer, which is well-defined, ideally ordered, has a long conjugated length, is planar, and carries one unit of charge, may serve as a very good FET material. A linear relationship between the internal reorganization energy for a self-exchange hole transfer process λ and the square root of chain length holds only for short conjugated oligomers, such as oligothiophenes and oligoselenophenes, and for longer oligomers ($n>10$) this relationship breaks down. Instead, a linear relationship is observed between reorganization energy and the reciprocal chain length for long π-conjugated oligomers. This linear correlation is explained on the basis of bond-length changes that take place as the oligomer moves from a neutral geometry to being a cation-radical species and on the basis of the charge distribution in cation radicals. In contrast to the saturation behavior that was observed in the correlation between $1/n$ and HOMO–LUMO gaps for long π-conjugated heterocyclic oligomers, no such saturation was observed in the relationship between $1/n$ and reorganization energies. The reorganization energies of oligoselenophenes have been studied for the first time and were found to be very similar (very slightly higher) to those of oligothiophenes, and they show an identical trend with changing oligomer length. We believe that our findings will be important for design of the new materials for OFETs.

Acknowledgements

We thank the Israel Science Foundation and the Helen and Martin Kimmel Center for Molecular Design for financial support. M.B. is the incumbent of the Recanati career development chair, a member ad personam of the Lise Meitner-Minerva Center for Computational Quantum Chemistry, and acknowledges support from DuPont Young Professor Award.

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Received: July 30, 2007
Revised: March 23, 2008