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From Short Conjugated Oligomers to Conjugated Polymers. Lessons from Studies on Long Conjugated Oligomers

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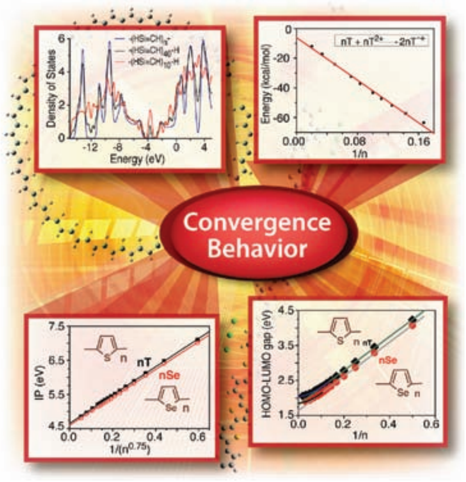
CONSPECTUS

Given their utility in a variety of electronic devices, conjugated oligomers and polymers have attracted considerable research interest in recent years. Because polymeric materials consist of very large molecules with a range of molecular weights (that is, they are polydisperse), predicting their electronic properties is a complicated task. Accordingly, their properties are typically estimated by extrapolation of oligomeric properties to infinite chain lengths. In this Account, we discuss the convergence behavior of various electronic properties of conjugated oligomers, often using thiophene oligomers as a representative example. We have observed some general trends in our studies, which we briefly summarize below for five properties. Most of the calculated values are method dependent: the absolute values can be strongly dependent on the computational level used.

Band Gap. The generally accepted approximation used to estimate polymer band gap, whereby a plot of HOMO−LUMO gap versus $1/n$ (where n is the number of monomer units) is extrapolated to infinite n, fails for long oligomers, because convergence behavior is observed for band gaps. At the B3LYP/6-31G(d) level, it is possible to extrapolate oligomer HOMO−LUMO gaps with a second-order polynomial equation. Alternatively, PBC/B3LYP/6-31G(d) is a very good method to reliably predict the band gap of conjugated polymers.



Reorganization Energy. Values of the internal reorganization energy (λ) do not scale linearly with $1/n$, instead exhibiting an inverse correlation with the square-root of the number of monomer units for $n = 2-12$. For larger n (10−50), a linear relationship is observed between reorganization energy and the reciprocal chain length, and the extrapolation approaches $\lambda \approx 0$ for infinite numbers of oligomer rings.

Ionization Potential. The relationship between the first adiabatic ionization potential IP_{1a} of oligothiophenes and oligoselenophenes and chain length linearly correlates with an empirically obtained value of $1/(n^{0.75})$. The first vertical ionization potential (IP_{1v}) linearly correlates with a similarly empirically obtained value of $1/(n^{0.70})$.

Polaron−Bipolaron Balance. The contribution of a polaron pair to the electronic structure of the short oligothiophene dication is small; for medium-length oligothiophene chains, the contribution from the polaron pair state begins to become significant. For longer (above 20-mer) oligothiophenes, the polaron pair state dominates. A similar picture was observed for multications as well as doped oligomers and polymers. The qualitative polaron−bipolaron picture does not change when a dopant is introduced; however, quantitatively, the bipolaron−polaron pair equilibrium shifts toward the bipolaron state.

Disproportionation Energy. The stability of a single oligothiophene dication versus two cation radical oligothiophene molecules increases with increasing chain length, and there is an excellent correlation between the relative disproportionation energy and the inverse of chain length. A similar trend is observed in the disproportionation energies of oligothiophene polycations as well as doped oligomer and polymers.

We also examine doped oligothiophenes (with explicitly included counterions) and polymers with a repeating polar unit. From our experience, it is clear that different properties converge in different ways, and long oligomers (having about 50 double bonds in the backbone) must often be used to correctly extrapolate polymer properties.

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Introduction

Conjugated oligomers and polymers have attracted considerable interest in recent years due to their applications in photovoltaic cells, light-emitting diodes (LED), field-effect transistors (FET), electrochromic devices, chemical sensors, microelectronic actuators, and so on.[1] Significant experimental and computational efforts have been devoted to studying the electronic properties of conjugated polymers. However, such studies are quite complicated, because polymers do not have well-defined structures, many of them are insoluble and polydisperse, and computational techniques are significantly less developed for infinite polymers than for well-defined molecules. Therefore, it is usual to estimate the electronic properties of polymers by extrapolating oligomer properties to infinite chain lengths.[2] This Account deals with the various aspects of such extrapolation and discusses how different properties converge with increasing oligomer chain length. This Account highlights interesting findings and lessons learned from recent studies of long conjugated oligomers and polymers (mostly using hybrid density functional theory (DFT)). Discussion of experimental results is kept to minimum due to space limitations.

Answering the question of how the electronic and other properties of conjugated systems depend on chain length is crucial to understanding the electronic behavior of known systems and to enabling the rational design of new systems with tailor-made properties. Since, from both experimental and computational points of view, the most-studied conjugated oligomers and polymers are those of thiophene,[1,2] they serve as a representative example; however, the discussion in this Account is general and applies also to other conjugated oligomers and polymers.[3]

Conducting polymers are not infinitely long. Usually, 40−50 repeating heterocyclic rings corresponding to $M_w \approx$ 5000−10 000 g/mol and about 80−100 conjugated double bonds are sufficient to achieve electronic properties indistinguishable from those of very long polymers.[4] The synthesis of well-defined long oligomers[1a] is usually very difficult, tedious, and even impractical, and calculations for such long oligomers were uncommon until recently. In addition, the very poor solubility of such oligomers requires that solubilizing groups be introduced onto them. However, such groups often cause twisting and disturb conjugation, which precludes their use in studies of the dependence of electronic properties on conjugation length.[5] Consequently, only limited experimental data suitable for studying the dependence of different electronic properties on chain length are available for very long oligomers.[4,6,7] We note that some conjugated polymers having very high molecular weights and describing the properties originated from their supramolecular organization would require approaches different from those discussed below.

Notes on Computational Methodology

Finding the appropriate computational level to obtain a reliable description of long conjugated systems is a very challenging task. Obviously, they are forbiddingly large for high level *ab initio* methods, which can describe reliably the electronic properties in gas phase of experimentally unknown systems. Since the aim is to study the dependence of electronic properties on lengths for long conjugation systems, high level ab initio methods cannot be used even to calibrate other computational methods, such as those based on different density functionals.

Calculations for infinitely long polymer chains can be performed using periodic boundary conditions (PBC) with one-dimensional periodicity. Until recently, commercially available programs for PBC calculations were available only for pure density functionals. However, pure density functionals cannot quantitatively describe the electronic properties of conjugated systems, such as band gaps, and empirical corrections need to be used. Recently, a hybrid DFT with PBC method was introduced,[8] and it performs well for different properties of conjugated polymers, such as geometries and band gaps. While PBC is a very good method, many interesting polymer properties (reorganization energy, ionization potential, etc.) cannot be studied by PBC due to the presence of uncompensated charge on the polymer backbone. In this case, it is necessary to carry out the computational study on long oligomers, to introduce explicitly charge compensation (introducing dopant ions into the calculations which usually significantly increases unit cell length), or to compensate for the charge empirically (using, e.g., outside charge potential).

We note that most of the calculated values are method dependent (the absolute values can be strongly dependent on the computational level used). For example, restricted open-shell Hartree−Fock (HF) based methods strongly favor charge localization, while pure DFT strongly favors charge delocalization.[9,10] However, most qualitative descriptions should be practically independent of the level used. At relatively low and economical computational levels, such as DFT, trends can be established with respect to the relationship between different properties and conjugated chain length. Other methods to estimate electron delocalization in conjugated molecules also exist; for example, Lüthi et al. recently suggested the NBO based scheme for the evaluation of electron delocalization in

π-conjugated systems.[11] We also note that, in DFT, the basis set convergence is relatively fast and that using a small basis set, such as 6-31G(d), generally gives a good trade-off between reliability and computational speed.

Obviously, calculating isolated oligomers or even "ideal" infinitely long polymers chains in gas phase as a model for bulk polymers which are usually polydisperse and disordered has many disadvantages. It is clear that the reasonable results obtained at the B3LYP/6-31G(d) level of theory are a consequence of the cancellation of different errors.[12] Hybrid DFT methods, such as B3LYP, predict many of the electronic properties correctly; however, such excellent agreement between experimental and calculated values can be considered "the right answer for the wrong reason." Indeed, calculations are performed in the gas phase without taking into account solid state effects and other effects that impact estimation of the different properties of conjugated oligomers and polymers. This leads to error cancellation due to deficiencies of the computational level and due to incorrect comparisons between the computational and experimental environment. A recent review addressed in detail the factors responsible for precise prediction of band gaps and comparisons between experimental and computational results.[13] The most discrepancies between experimental and calculated data originate from omitting of important factors which determine the optical properties of π-conjugated polymers, such as conformational effects, substitution effects, and both solvent and solid-state effects as well as inappropriate extrapolation procedures and the use of inadequate theoretical frameworks.[13]

In summary, it is very difficult to describe precisely calculated properties, such as the band gap, of conjugated polymers. In most cases, it is currently unfeasible to obtain "the right answer for the right reason." For convenience and systematic reasons, it is common to compare the polymer band gap obtained via the extrapolation of the HOMO−LUMO gaps in oligomers with the optical band gap obtained from the onset of the UV−vis-NIR spectra or from the onset of oxidation and reduction peaks in cyclic voltammetry measurements.[1b,2] Such comparisons will be used in this Account.

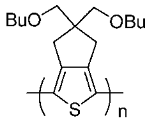
Band Gap Convergence

It was generally accepted that, for conjugated oligomers, extrapolating the linear fit of the HOMO−LUMO gap against the reciprocal of the number of monomer units (1/*n*) affords a prediction of the band gap for the corresponding polymer.[14] A more precise dependence of the band gap of a conjugated polymer on the length of the conjugated backbone is given by Kuhn's equation (eq 1):

$$\Delta E = \frac{h^2}{8md^2}\,\frac{(N+1)}{(N+l)^2} + V_0\left(1 - \frac{1}{N}\right) \qquad (1)$$

where m is electron mass, d is the mean of the C−C and C=C bond lengths, N is the number of π electrons, l is the effective length of the π conjugated system, and V_0 is the constant corresponding to the band gap at infinite length.[15]

The effective conjugation length of oligothiophenes is about 10−20 repeating units,[1,16] which is somewhat similar for other conjugated heterocyclic oligomers. A study of the absorption spectra of **1** ($n \leq 96$)[4] indicated that λ_{max} red-shifted up to the 96-mer; however, convergent behavior is evident from the spectroscopic data, as very small changes occur in λ_{max} values: λ_{max} = 524, 526, 527, and 528 nm for the 36-, 48-, 72-, and 96-mer, respectively. For quinoid oligothiophenes (terminated by dicyanomethylene groups), interesting ground state change from closed shell to biradical was observed;[17] however, oligothiophenes substituted via single bond have always closed shell singlet ground state.



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Using the Perdew−Wang exchange-correlation, it was computationally shown that the empirically obtained linear 1/*n* expression does not hold for long conjugated oligomers (which have been studied up to $n = 36$).[18] However, since a nonhybrid "pure" density functional (LDA) was used,[18] it is not possible to directly correlate the predicted band gap with experimental values (the results need to be scaled by an empirical factor to obtain experimental band gaps). Other deviations from 1/*n* extrapolation were observed especially if extrapolation begins from monomers.[19] The extrapolation of HOMO−LUMO gaps for π-conjugated oligomers using the hybrid B3LYP functional and the 6-31G(d) basis set predicts the band gaps of conjugated polymers (polythiophenes, polyselenophene, polypyrrole, polyfuran, and poly-*p*-phenylene) quite accurately (to within 0.1−0.2 eV) when long (at least 20-mer) π-conjugated oligomers are used for the extrapolation.[12] However, the excellent agreement between the calculated (at B3LYP/6-31G(d)) and experimental band gap values is partially due to the cancellation of several errors from the theoretical level used, as described above, and from comparison of gas-phase calculations with experimental measurements performed in the solid state.[12] The generally accepted approximation of polymer band gap based on a linear relationship between HOMO−LUMO gap and 1/*n* holds only up

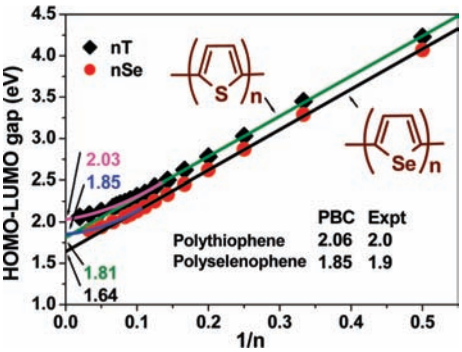

FIGURE 1. HOMO−LUMO gap versus the reciprocal of the number of oligomer units (at B3LYP/6-31G(d)) for oligothiophene and oligoselenophene.[12]

to $n = 12$ (Figure 1). The linear extrapolation method fails to consider asymptotic behavior since saturation occurs at longer conjugation lengths. Indeed, for higher n values ($n > 12$), second-order polynomials are required to describe the relationship between the HOMO−LUMO gap and the reciprocal of chain length. The quadratic equations (for $n \geq 10$) afford estimated band gaps of 2.03 and 1.85 eV for polythiophene and polyselenophene, respectively, which are very close to the corresponding experimental values of 2.0 and 1.9 eV, respectively, and, as expected, to band gaps calculated using PBC at B3LYP/6-31G(d) (2.06 and 1.85 eV for polythiophene and polyselenophene, respectively) (Figure 1). These results suggest that the B3LYP/6-31G(d) level (using the long oligomer extrapolation approach or in combination with PBC) performs exceptionally well in evaluating the band gaps of conjugated polymers.[12] Slightly poorer agreement between calculated and experimental values is obtained when the polymer unit cell is polar as, for example, in donor−acceptor polymers (B3LYP/6-31G(d), where the calculated values are about 0.4 eV higher than the experimental values).[10]

Similar convergence behavior was also observed at the HF,[12] pure DFT BLYP,[12] and hybrid DFT B3P86-30%/CEP-31G*[20] levels. It is known that deviation from $1/n$ dependence in HOMO−LUMO gaps starts earlier when substituents that disturb the planarity of the oligothiophene backbone are present than it does for fully planar oligothiophenes.[21]

Reorganization Energy

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).[22,23] In order to achieve a high charge carrier mobility (which is a crucial parameter in FET devices), reorganization energy should be minimized and the effective electronic coupling should be maximized.[22,23]

Generally, the internal reorganization energies of each oligomer family decrease as the oligomer length increases, due to the greater positive charge delocalization in longer oligomers. In the case of a self-localized polaron, this trend will eventually level off, as the reorganization energy beyond the localization length of the polaron will remain constant.[23] The computed localization length of the polaron is strongly dependent on the theoretical method used, and, in DFT, it strongly depends on the amount of HF exchange, with pure DFT methods predicting delocalization, while inclusion of HF exchange leads to localization (see discussion above).[9] If an oligomer is longer than the localization length, then the regions outside the polaron will not change geometry and hence will not contribute to λ.[23] At B3LYP/6-31G(d), this behavior is indeed observed for a series of *all-trans*-oligoenes of increasing length.[23] The internal reorganization energies computed for oligothiophenes, oligopyrroles, and oligofurans do not exhibit the self-localized polaron effects mentioned above for the lengths studied (2−12 monomer units). Furthermore, the internal reorganization energies do not scale linearly with $1/n$, instead exhibiting an inverse correlation with the square root of the number of monomer units.[23] If long oligomers (up to the 50-mer) are considered, the reorganization energies for oligothiophenes and oligoselenophenes show that a linear relationship between the square root of n and λ is maintained only up to $n \approx 15$ (Figure 2a).[24] For larger n ($n = 11-50$), a linear relationship is observed between reorganization energy and the reciprocal chain length, with $R^2 = 0.99$ (Figure 2b), and no saturation behavior is observed in the $1/n$ correlation (at the B3LYP/6-31G(d) level).[24] This linear correlation is explained on the basis of bond length changes that take place as the oligomer geometry moves from that of a neutral molecule to that of a cation radical and on the basis of the charge distribution in cation radicals. Importantly, the extrapolation approaches $\lambda \approx 0$ for infinite numbers of monomer 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.[24]

The reorganization energies for cyclic oligothiophenes are significantly higher than those for linear oligothiophenes; however, as expected, the reorganization energy approaches zero for infinite n.[25] Plotting reorganization energy versus $1/n$ does not result in a linear correlation for up to $n = 30$ for cyclic oligothiophenes. This is probably due to significant strain energies in cyclic oligothiophenes up to $n = 20$, so that oligomers

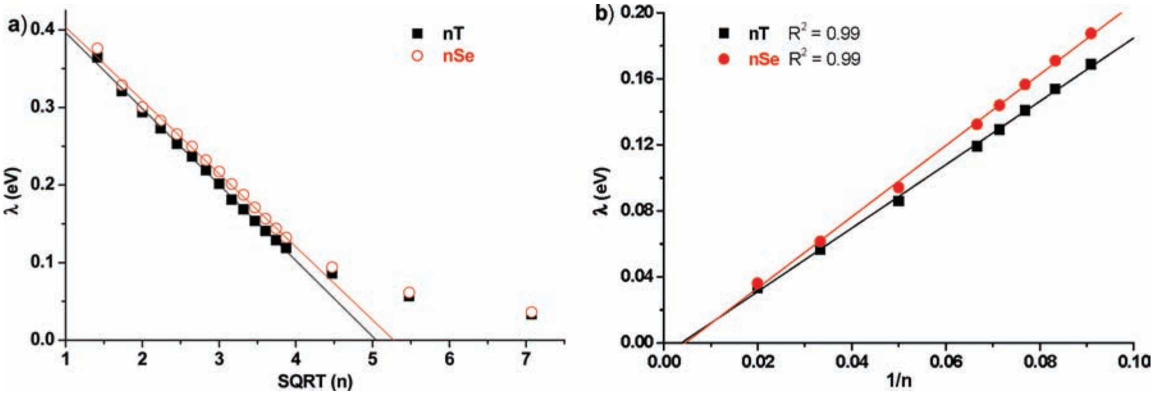

FIGURE 2. Reorganization energy λ for oligothiophenes (*n*T) and oligoselenophenes (*n*Se) versus (a) the square root of *n* (lines indicate the linear relation for $n \leq 15$) and (b) reciprocal chain length at the B3LYP/6-31G(d) level.[24]

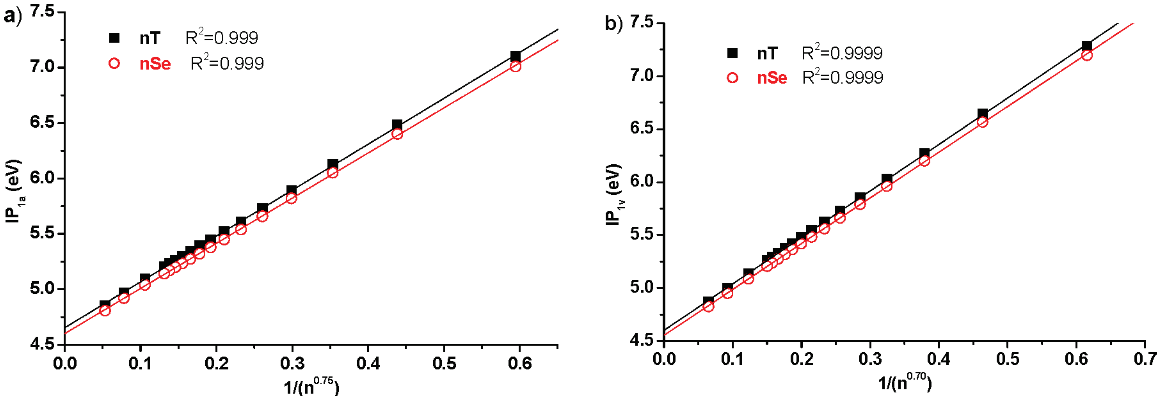

FIGURE 3. (a) Adiabatic ionization potentials (IP_{1a}) versus $1/n^{0.75}$ and (b) vertical ionization potentials (IP_{1v}) versus $1/n^{0.70}$ for oligothiophenes and oligoselenophenes, where *n* is the number of monomer units.[24]

larger than 20-mers might exhibit a linear correlation for reorganization energy versus $1/n$.[25]

Ionization Potential

The dependence of the first adiabatic ionization potential (IP_{1a}) and first vertical ionization potential (IP_{1v}) on chain length for oligothiophenes and oligoselenophenes is shown in Figure 3.[24] We note that the difference between the adiabatic and vertical ionization potential is the internal reorganization energy, discussed above. Interestingly, the relationship between IP_{1a} or IP_{1v} and chain length is not similar to that between the reorganization energy or the HOMO–LUMO gap and chain length. Instead, the IP_{1a} and IP_{1v} of oligothiophenes and oligoselenophenes linearly correlate with an empirically obtained $1/(n^{0.75})$ (Figure 3a) and $1/(n^{0.70})$ (Figure 3b), respectively.

Polaron–Bipolaron Balance

Cationic Species. Whether the charge carriers are spinless bipolarons (i.e., dications whose excess charge is concentrated over a limited section of the chain) or spin-carrying polaron pairs (i.e., pairs of cation radicals located on different sections of the chain) is one of the most basic questions which has still to be answered, despite considerable experimental and theoretical efforts, to understand the conductivity and electronic properties of doped conjugated polymers.[26–32]

A DFT study by Gao et al., showed that the closed-shell bipolaron structure was more stable for oligothiophene dications ($n\mathrm{T}^{2+}$) of $n \leq 5$, whereas the open-shell polaron pair structure was the ground state for longer oligothiophene dications of $n \geq 8$.[28] Geskin and Brédas calculated spin restricted singlets of up to 10T at the HF and MP2 levels of theory and calculated triplet states using restricted open-shell HF and MP2 with 3-21G*.[29] They concluded that, in oligothiophene dications up to $8\mathrm{T}^{2+}$ or $10\mathrm{T}^{2+}$, the bipolaron would be a strongly localized species. The MP2 optimized singlet structure for $8\mathrm{T}^{2+}$ clearly corresponds to two separate polarons squeezed at the chain ends, thus resembling the HF or BHandHLYP optimized triplet structures. The polaron pair character is more pronounced for the longer oligomers, with the charge per ring increasing toward the chain ends. Closed-shell HF and DFT calculations predict the formation of a single defect, namely, a bipolaron.[29]

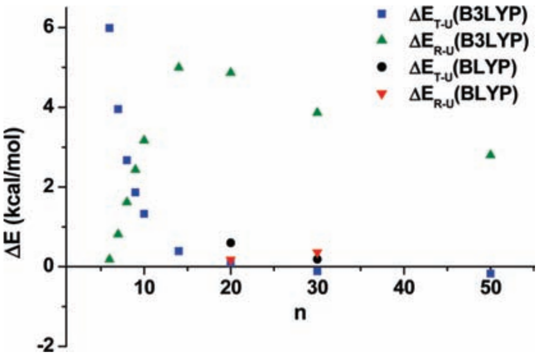

FIGURE 4. Relative energies of the optimized triplet (T) states minus those of the corresponding optimized spin-unrestricted (U) singlet states (i.e., $E_{(T-U)}$), and the optimized spin-restricted (R) minus optimized spin-unrestricted (U) singlet states structures (i.e., $E_{(R-U)}$) in oligothiophene dications as a function of chain length at the B3LYP/6-31G(d) and BLYP/6-31G(d) levels of theory. Based on data from ref 30.

In a more recent paper, a series of oligothiophene dications in singlet and triplet states ($n\mathrm{T}^{2+}$, $n = 6-50$) was studied at the B3LYP/6-31G(d) level and, in some cases, also at the BLYP/6-31G(d) level, while short oligomers were also calculated at CASSCF.[30] The energy difference $E_{(\mathrm{RB3LYP})} - E_{(\mathrm{UB3LYP})}$, which relates to bipolaron instability, increases with increasing oligomer length to $14\mathrm{T}^{2+}$ and then stays constant up to $50\mathrm{T}^{2+}$ (Figure 4). The contribution of the polaron pair configuration to the structure of the ground state becomes more important as oligomer length increases. At the BLYP/6-31G(d) level, which does not include HF exchange, $E_{(\mathrm{RBLYP})} - E_{(\mathrm{UBLYP})}$ values are significantly smaller than those at the B3LYP/6-31G(d) level, so that the contribution of the polaron pair configuration is smaller. However, for sufficiently large oligothiophene dications, the polaron pair state is clearly the ground state even at BLYP/6-31G(d) (Figure 4). CASSCF predicts even more charge separation than the hybrid DFT method B3LYP.

The different electronic states of oligothiophene polycations, such as tri-, tetra-, hexa-, and octacations ($n\mathrm{T}^{3+}$, $n\mathrm{T}^{4+}$, $n\mathrm{T}^{6+}$, and $n\mathrm{T}^{8+}$) up to the 50-mer were studied at the B3LYP/6-31G(d) level.[31] In general, in sufficiently long oligothiophene polycations, the singlet, triplet, and, for very long oligomers, even higher spin states are nearly degenerate. For $10\mathrm{T}^{4+}$, the singlet is clearly the ground state, with the triplet and quintet spin states having significantly higher energies of 6.7 and 23.1 kcal/mol, respectively. However, for the longer tetracations, $30\mathrm{T}^{4+}$ and $50\mathrm{T}^{4+}$, all three spin states (unrestricted singlet, unrestricted triplet, and quartet) become degenerate. The charge distribution graph of the $50\mathrm{T}^{8+}$ spin-unrestricted singlet state and nonet state clearly show eight charge-bearing regions, which correspond to eight polaron regions (Figure 5).[31]

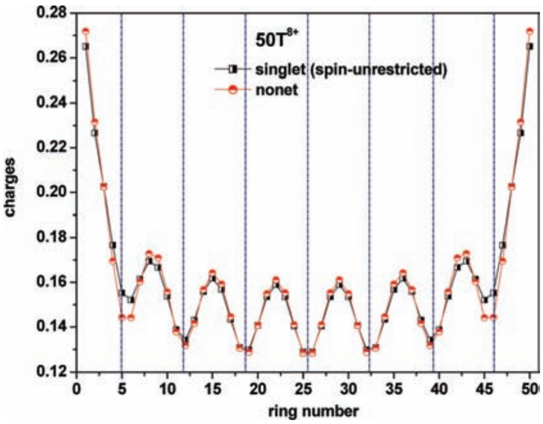

FIGURE 5. Mulliken charge distribution at the B3LYP/6-31G(d) level for $50\mathrm{T}^{8+}$ (dash-dotted vertical lines separate a unit charge).[31]

According to the Su–Schrieffer–Heeger (SSH) model, the effective length of a soliton (either a singly charged species without spin or a neutral species with spin 1/2) in a π-system (polyacetylene) is about 14 carbon atoms.[27] The minimal conjugated length required for a polaron in polythiophene is about five thiophene rings according to B3LYP/6-31G(d) calculations.[31] These results are in good agreement with experimental studies, which indicate that the doping level at which the highest conductivity is obtained is about 20% in polythiophene, which corresponds to one positive charge per five thiophene rings.[4,26,33]

Disproportionation Energy for Charged Conjugated Oligomers. The stability of the oligothiophene dication versus two cation radicals was evaluated using an isodesmic reaction, as shown in eq 2, in which UB3LYP/6-31G(d) singlet energies were used.[30] For short oligothiophenes, such as 6T, the dication is less stable than two cation radicals by at least 63.5 kcal/mol. However, the stability of a dication versus two cation radicals increases with chain length. Correlating the energy of eq 2 with the inverse of the number of thiophene units (Figure 6) in the oligothiophene chain gives a linear plot with $R^2 = 0.99$. Similarly to dication behavior, the stability of the polycations versus a cation radical and dication or two other polycations carrying smaller charges increases with increasing chain length.[31] Extrapolation to infinite oligomer lengths leads to a disproportionation energy of practically zero.

$$n\mathrm{T} + n\mathrm{T}^{2+} \rightarrow 2n\mathrm{T}^{\bullet +} \tag{2}$$

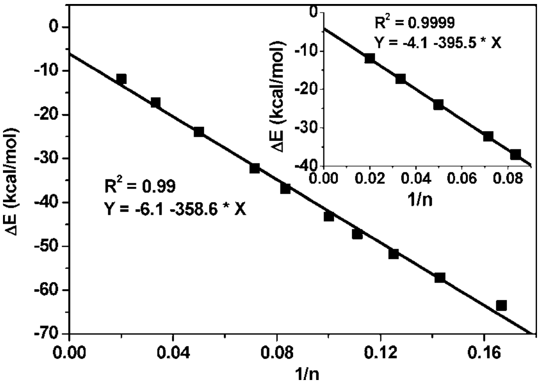

FIGURE 6. Disproportionation energies versus the inverse of oligothiophene chain length according to eq 2. Upper inset shows the graph for the highest five *n* values ($n \geq 12$).[30]

Doped Oligothiophenes with Explicitly Included Counterions. The results described in the previous sections were obtained for bare cations in the gas phase. Such a model for polaron–bipolaron equilibrium may significantly differ from experimental studies, which are performed in solution or in films and include dopant counterions. To describe doped conjugated polymers correctly, it is important to include counterions explicitly; however, such studies are rare.[34] In the case of oligothiophenes, this was achieved by studying oligothiophene dications doped with Cl_3^- ions that are not covalently bound to the oligomer backbone at the B3LYP/6-31G(d) level.[35] Compared to bare dications, in doped oligothiophenes, the charges on oligomer backbone are more localized around the position of counterions. The contribution of the polaron-pair state increases with conjugated chain length and becomes the dominant state in the presence of dopant for systems of sufficient length (20T and longer).[35] The chain length at which bipolarons become unstable is larger in the presence of counterions than in bare oligothiophene dications[30] and polycations.[31]

Similar DFT studies using PBC approximation were performed on explicitly doped polythiophenes with unit cells of different lengths (up to 20 thiophene rings) carrying two counterions (Cl_3^-).[36] The presence of the dopant has a major influence on the electronic structure of polythiophene, while the position of the dopant is flexible over the polythiophene chain at any dopant concentration.[36] For heavily doped polymers (modeled using short unit cells), substantial differences were observed between the polymers and the corresponding oligomers. However, calculations of lightly doped polymers (modeled using long unit cells) can be safely replaced with calculations of the corresponding oligomers. Extrapolating polymer properties from oligomers is more complicated alternatives that lack obvious advantages while modeling doped conjugated systems using positively or negatively charged backbones without balancing counterions might be unnecessary simplification in many cases.[36]

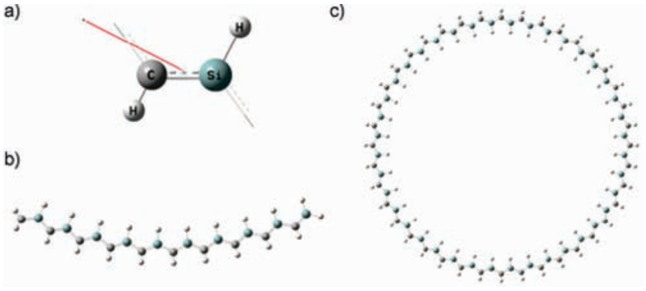

FIGURE 7. (a) Unit cell of polysilaacetylene $-(HSi{=}CH)_n-$ (red narrow line indicates the translational vector of the unit cell), (b) $H-(HSi{=}CH)_{10}-H$, and (c) cyclic $-(HSi{=}CH)_{40}-$.[37]

Polymers with a Polar Repeating Unit[37]

When the repeating unit of a polymer is polar, some discrepancies are observed between oligomer extrapolation and PBC calculations, and therefore, basing the electronic properties of the polymer on oligomer extrapolation should proceed with additional care.[37] However, most of the conclusions discussed above should remain unchanged.

In view of the significant efforts invested in recent years in discovering new types of conjugated polymers, a theoretical study of different polyacetylene analogues of type $-(X{=}Y)_n-$ was undertaken.[37] Here, we will discuss mostly the results obtained for polysilaacetylene ($-(HSi{=}CH)_n-$) (Figure 7a). We note however that $-(HSi{=}CH)_n-$ polymer is unknown and even short oligomers (except for the monomer) are not known experimentally.[38]

A small band gap is expected for $-(HSi{=}CH)_n-$ based on the UV spectra ($\lambda_{max} = 258$ nm, 4.81 eV)[38] and calculated HOMO–LUMO gap (5.18 eV) of $H_2Si{=}CH_2$, which has smaller HOMO–LUMO gap than ethylene (7.76 eV, calculated). Accordingly, calculating the band gap of polymer $-(HSi{=}CH)_n-$ using PBC/B3LYP/6-31G(d) yields a value of 2.71 eV. On the other hand, extrapolation of the HOMO–LUMO gaps for a series of linear oligomers $H-(HSi{=}CH)_n-H$ ($n = 3-10$) (Figure 7b for $n=10$) leads to a negative band gap of −0.74 eV (Figure 8a). If longer oligomers ($n = 20$, 40) are used for the extrapolation, asymptotic behavior is observed,[12] and the band gap converges to zero (Figure 8a). Thus, for polysilaacetylene $-(HSi{=}CH)_n-$, the band gap extrapolated from linear oligomers contradicts the PBC calculated band gap. We note that the PBC-based band gap for polyacetylene (1.20 eV, PBC/B3LYP/6-31G(d)) is consistent with the value obtained from extrapolation based on the HOMO–LUMO gaps of a series of oligoenes (1.09 eV).[37]

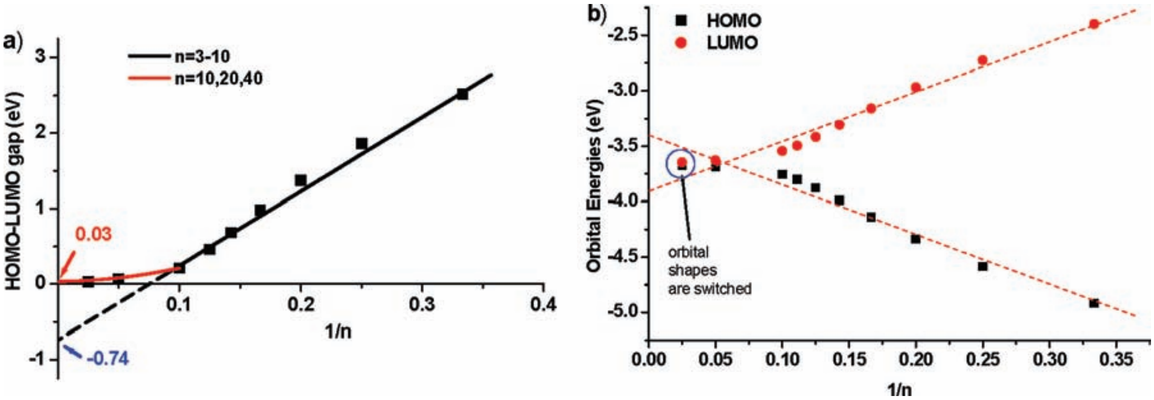

FIGURE 8. (a) HOMO−LUMO gap and (b) frontier orbital energy extrapolation for polysilaacetylene ($-(HSi{=}CH)_n-$) as a function of $1/n$ ($n = 3-40$) at the B3LYP/6-31G(d) level of theory based on $H-(HSi{=}CH)_n-H$ oligomers.[37]

From a geometry and charge distribution perspective, the repeating unit in the middle of long oligomers, $H-(HSi{=}CH)_n-H$, resembles the unit cell of a polymer, while the terminal parts of long oligomers are significantly different. Due to the polar nature of the molecule, there are orbitals localized on the terminals of the oligomers. These orbitals resemble surface states known from solid state physics and do not describe the bulk properties of the polymer. The presence of those states leads to the observed disagreement between the PBC result and the result extrapolated from linear oligomers. Indeed, the HOMO and LUMO of $H-(HSi{=}CH)_n-H$ are located at different ends of the oligomer, and consequently, in this case, oligomer extrapolation should not be used to obtain the electronic properties of the polymer (such as band gap). Rather, the band gap should be extrapolated from the oligomer data on the basis of the orbital located in the center of the oligomers and not from HOMO and LUMO. Under these conditions, extrapolation from oligomer data will lead to results similar to those obtained from PBC. However, since it is unclear which orbital should be used, such an approach is impractical. Another approach is therefore to use the extrapolation of cyclic oligomers (Figure 7c), which lack chain end effect[25,39] due to absence of terminal groups. Extrapolation from cyclic oligomers yields a band gap similar to the PBC calculated band gap (2.72 eV for an extrapolation from $n = 40$, 61, and 70 compared to 2.71 eV obtained using PBC) and very different from the band gap obtained by extrapolation from linear oligomers.[37]

The restricted wave function is unstable for $H-(HSi{=}CH)_9-H$ and higher oligomers.[37] For $n = 9$, 10, and 20, both α and β HOMOs are concentrated at the terminal carbon side, while both α and β LUMOs are concentrated at the terminal silicon side. However, in $n = 40$, the HOMO and LUMO switch their shapes[40] (Figure 8b); that is, in the HOMO, the electron density is concentrated at the terminal silicon side, while in the LUMO it is concentrated at the terminal carbon side. So the $1/n$ trend in the HOMO and LUMO energies clearly does not hold and is even meaningless for long oligomers of this type.[37]

Additional evidence for a similarity between the results from a cyclic model, long oligomers, and the results of PBC calculations as well as for a dissimilarity between the results from short oligomers and PBC-based results in $-(HSi{=}CH)_n-$ comes from the computed density of states (DOS) (Figure 9). From Figure 9a, it is clear that the 20-mer is still unable to describe the electronic structure of the polymer properly, while the 40-mer is sufficient for this purpose if the surface states in the middle of the band gap around −3.5 eV are not considered. The DOS of $-(HSi{=}CH)_n-$ is very similar to the DOS of cyclic $-(HSi{=}CH)_{61}-$ (Figure 9b) which does not have surface states in the middle of the gap.[37]

The results obtained through extrapolation from short oligomers should be inaccurate for other polymers of the family $-(X{=}Y)_n-$. The higher the dipole moment of the oligomers, the greater the difference between the results obtained from oligomer extrapolation compared with those from the PBC method and a fairly linear relationship is observed (Figure 10). In conclusion, care should be taken when using extrapolation to calculate band gaps and other properties when the polymer has a polar unit cell. The problem in such cases is the very strong chain end effect that arises from the use of oligomers.[37]

Summary and Outlook

This Account reviewed the convergence behaviors of different electronic properties of conjugated oligomers that are used to predict the properties of conjugated polymers such as band gap, reorganization energy, ionization potential, and so on. In many cases, it is necessary to study long oligomers (having

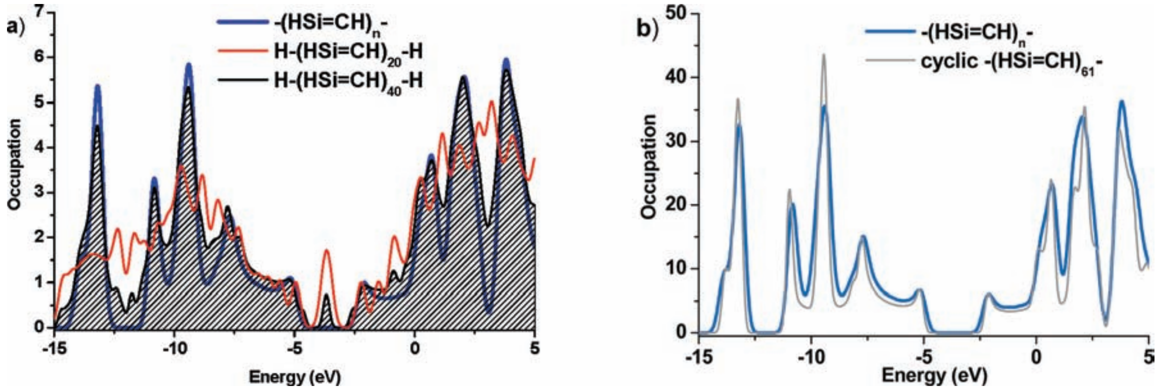

FIGURE 9. Density of states of (a) polymer $-(HSi{=}CH)_n-$ and oligomers $H-(HSi{=}CH)_{20}-H$ and $H-(HSi{=}CH)_{40}-H$; (b) polymer $-(HSi{=}CH)_n-$ and cyclic $-(HSi{=}CH)_{61}-$. For ease of comparison, the *Y* axis was normalized.[37]

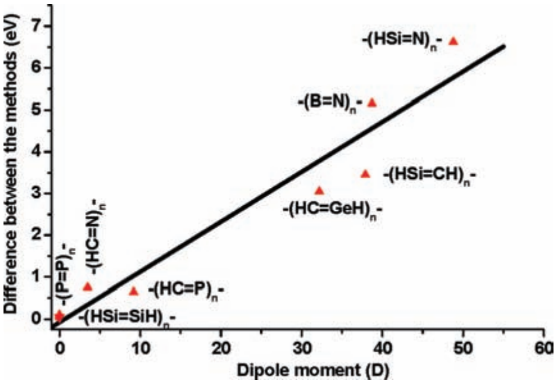

FIGURE 10. Difference between the band gaps obtained from PBC and oligomer extrapolation (from trimer, hexamer, and decamer) as a function of the dipole moment of the decamers (at B3LYP/6-31G(d)).[37]

more than 50 double bonds in the backbone) to predict the properties of conjugated polymers reliably. As expected, very long oligomers have calculated geometries and band gaps similar to those obtained for polymers using periodic boundary conditions based methods. However, extrapolation based only on short oligomers is unreliable in many cases, as the dependence of electronic properties on chain length changes with increasing length.

Here, we summarized some general trends keeping in mind that most of the calculated values are method dependent (the absolute values can be strongly dependent on the computational level used): (i) The generally accepted approximation used to estimate polymer band gap, whereby a plot of HOMO−LUMO gap versus $1/n$ (n = number of monomer unit) is extrapolated to infinite n, fails for long oligomers, because convergence behavior is observed for band gaps. At the B3LYP/6-31G(d) level, it is possible to extrapolate oligomer HOMO−LUMO gaps using a second-order polynomial equation or, alternatively, the application of PBC/B3LYP/6-31G(d) is a very good method to reliably predict the band gap of conjugated polymers. (ii) The internal reorganization energies do not scale linearly with $1/n$, instead exhibiting an inverse correlation with the square root of the number of monomer units for $n = 2-12$. For larger n ($n = 10-50$), a linear relationship is observed between reorganization energy and the reciprocal chain length and the extrapolation approaches $\lambda \approx 0$ for infinite numbers of oligomer rings. (iii) The relationship between the IP_{1a} of oligothiophenes and oligoselenophenes and chain length linearly correlates with an empirically obtained value of $1/(n^{0.75})$, while IP_{1v} linearly correlates with a similarly empirically obtained value of $1/(n^{0.70})$. (iv) The contribution of a polaron pair to the electronic structure of the short oligothiophene dication is small; for medium-length oligothiophene chains, the contribution from the polaron pair state begins to become significant. For longer (above 20-mer) oligothiophenes, the polaron pair state dominates. A similar picture was observed for multications as well as doped (contained counterions) oligomers and polymers. The qualitative polaron−bipolaron picture does not change when a dopant is introduced; however, quantitatively, the bipolaron−polaron pair equilibrium shifts toward the bipolaron state. (v) The stability of a single oligothiophene dication versus two cation radical oligothiophene molecules increases with increasing chain length, and there is an excellent correlation between the relative disproportionation energy and the inverse of chain length. A similar trend is observed in the disproportionation energies of oligothiophene polycations as well as doped oligomer and polymers.

For oligomers with a polar monomer unit (of type $-(X{=}Y)_n-$), frontier orbitals (HOMO, LUMO, HOMO − 1, LUMO + 1, etc.) are located on the chain ends and correspond to surface states, so the electronic structure of the polymer and the band gap cannot be obtained through extrapolation of oligomer data, but can be obtained using cyclic oligomers or methods based on periodic boundary conditions.

For heavily doped polymers, substantial differences are observed between the polymers and the corresponding oligomers. However, the electronic structure of lightly doped polymers can be safely obtained from calculations based on the corresponding oligomers. Extrapolating polymer properties from oligomers is more complicated alternatives that lack obvious advantages while modeling doped conjugated systems using positively or negatively charged backbones without balancing counterions might be unnecessary simplification in many cases.

We note that various electronic properties may diverge from the trends presented in this Account if the oligomer and polymer structures deviate significantly from planarity due to bulky substituents, if they have a quinoid ground state, or if strong interchain interactions are present. For example, according to computational studies, polyisothianaphthene (PINT) has a quinoid ground state[14] and its oligomers are not planar,[10] and consequently, the general trends mentioned above may not apply to its oligomers.

Both inter- and intrachain interactions are important in attaining desired conductivity and electronic properties. From a computational point of view, the next challenge would be to describe the bulk properties of polymers having inter-chain interactions. This is a very difficult task for computational techniques, however, recent progress in density functional theory, which now includes functionals that describe the dispersion correction,[41] may make the calculation of bulk three dimensional polymer structures feasible.

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FOOTNOTES

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