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Electronic structure of conducting polymers: Limitations of oligomer extrapolation approximations and effects of heteroatoms

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Density-functional methods are used to analyze the scaling of discrete oligomeric π-electron conducting molecules towards idealized isolated polymer chains, treated in periodic boundary conditions. The band gaps of a series of conjugated oligomers of incrementally increasing lengths exactly fit a nearly-free-electron molecular-orbital picture and exhibit a smooth deviation from the classical empirical ''1/N'' trend for long oligomers and infinite polymers. The calculations also show a smooth convergence of bond lengths. The full band structures and densities of states of a polyacetylene, polypyrrole, polyfuran, and polythiophene show that band crossing, localized bands, and other effects cannot be accurately determined from simple extrapolation of oligomer electronic structures. Systematic comparisons of the electronic structure variations of the polymers investigated indicate that the electron affinity, rather than the electronegativity of the heteroatom or the bond-length alternation of the conjugated backbone, significantly affects the band gap of the resulting polymer as indicated by the presence of heteroatom states in the partial density of states of the conduction band, requiring revision of previous semiempirical analyses. Consequences for doping processes are also studied, along with a comparison of valence bandwidths, conduction bandwidths, and carrier effective masses as a function of heteroatom.

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I. INTRODUCTION

Semiconducting and conducting conjugated organic polymers have received considerable interest since initial landmark reports of a dramatic increase in conductivity upon halogen doping of polyacetylene by Shirakawa *et al.*, Heeger, and MacDiarmid.[1–4] Since these initial discoveries, which paralleled earlier conductivity enhancements reported for oxidative halogen doping of metallomacrocyclic materials,[5,6] numerous studies, both experimental and theoretical, have been performed both on short chain conjugated oligomers and on the full polymers. Furthermore, applications of conducting polymers now exist in many areas, ranging from conducting fabrics,[7] antistatic coatings for use in photographic films or electronic device fabrication,[8,9] and low-voltage electrochromic windows[10–15] to organic light-emitting diodes,[16–18] photodiodes, and photovoltaic devices.[19,20] In regard to theoretical investigations, some studies have modeled the electronic structure of the full polymers,[21–30] although a great many more have extrapolated results from the expected convergence, with increasing chain length, of the electronic structures of the component oligomers.[31–48]

Density-functional theory (DFT) methods within the local-density approximation (LDA) (DFT-LDA) are well known to compute equilibrium geometries in excellent agreement with experiment for both conjugated organic oligomers and polymers.[49–51] However, Kohn-Sham eigenvalues cannot be formally interpreted as orbital energies for excited states,[52] and calculated band gaps are typically on the order of 40% smaller than the experimental optical-absorption band-gap data for conjugated organic materials.[50] In contrast, calculations using the DFT-LDA methodology to predict band diagrams, bandwidths, and densities of states (DOS), using periodic boundary conditions to model the infinite solid via one repeated unit cell, have yielded accurate results for many types of conventional inorganic semiconductors.[53]

In order to design new materials with improved properties, the challenge is to understand the basic mechanisms involved in conduction and optical processes in conducting polymers, and use this understanding to predict the properties and to direct the design of completely new materials. In this contribution, we investigate the classic conjugated organic polymers polythiophene, polypyrrole, and polyfuran as well as the related polyphosphole and polyselenophene using both a series of discrete oligomers and isolated polymer chains in periodic boundaries, to model an idealized infinite polymer. Although the minimal unit cells used here do not address such issues as defect states or torsional disorder (nor do most computational studies), which may be present to some extent in the actual materials,[54,55] they provide an interesting and informative comparison with experimental data, especially that reported recently for oligofurans.[56] In principle, a larger ''supercell'' could be used with explicitly introduced disorder or torsional effects to further improve the model in future studies. Some previous theoretical studies on conjugated polymers and oligomers have been performed using semiempirical Hamiltonians,[57,58] empirical adjustments to density-functional methods,[32,33] or uncorrelated Hartree-Fock methods.[59–61] Our recent work has compared results from multiple methods on a set of 60 neutral conjugated oligomers.[62] As noted above, other investigations have often preferred the approach of empirically extrapolating polymeric electronic structure from a series of oligomers of vary-

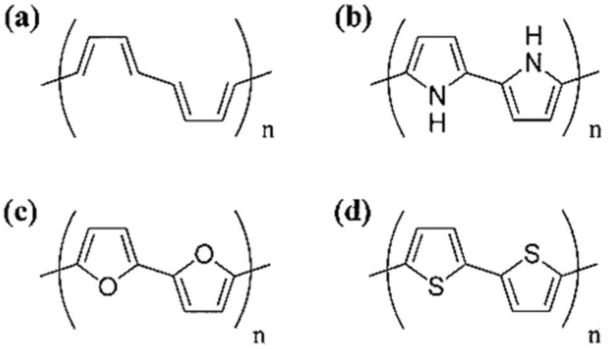

FIG. 1. Structures of (a) *b*-polyacetylene, (b) polypyrrole, (c) polyfuran, and (d) polythiophene.

ing lengths.[32,35,45] While several studies have analyzed the band structures of individual polymers such as polyacetylene,[49,63–65] polyphenylenevinylene,[51,66] or polythiophene[23,67] using density-functional methods, few have attempted a systematic comparison between a large range of analogous polymers and the effects of various substituents on the electronic structures, particular in the widely studied polyheterocycle family.[68,69]

In the present contribution, we consider the systematic scaling of a series of conjugated oligomers and polymers over many lengths, from short oligomers (1–4 unit cells), to long oligomers (8–16 unit cells), to the infinite idealized polymer. The comparative focus includes one isomer of polyacetylene, polypyrrole, polyfuran, polythiophene, polyphosphole, and polyselenophene (Fig. 1). It is shown here that through systematic variation of the conjugated polymer structures, it is possible to deduce explicit trends in electronic structure, such as the effect of the heteroatom in polyheterocyclic systems. The results are shown to be in favorable agreement with experimental data[56,70–76] and show that the band gaps of polyheterocycles are directly proportional to the electron affinity of the heteroatom.

II. COMPUTATIONAL METHODS

The DMol^3 program[53,77] was used for density-functional calculations using the Perdew-Wang exchange-correlation functional[78,79] and a doubled numeric basis set[77,80] with varying local basis cutoffs for each polymer (polyacetylenes, 7.5 a.u.; polyfuran, polypyrrole, polythiophene, polyphosphole, and polyselenophene 9.0 a.u.). No significant changes were detected if a larger local basis cutoff was used. For calculations on oligomers, equilibrium geometries were calculated for each compound, and eigenvalues were extracted from the final geometries for chain lengths having 1–36 monomer units (1/2 to 18 unit cells).

For calculations on an isolated, infinite, one-dimensional polymer, one full unit cell was used, starting from the geometry of the central portion of the corresponding oligomer. Full geometry optimization was performed inside a given lattice length and the lattice parameter was then varied to locate both the equilibrium lattice parameter and the lowest-energy structure in that unit cell. To ensure that polymers were isolated from neighboring cells in the directions perpendicular to the polymer chain, cell vectors were set to at least three times the basis radial cutoff point. Note that there is no difference between the functional or basis set used between the oligomer calculations and the periodic unit-cell calculations. Larger supercells were calculated as well, but showed no difference relative to the primitive unit cell.

Band-structure diagrams were calculated along the k vector of the polymer chain for all polymers and plotted relative to the calculated valence-band maxima, for ease of comparison. Densities of states for the polymers were calculated by the tetrahedron method[81] using 64 k points along the chain direction and two points in the two perpendicular directions, and were plotted relative to the valence-band maximum as well. Little improvement was found if a larger number of points were used. Partial DOS for the aromatic heteroatoms were computed for s-, p-, and d-orbital electrons, although only the p electrons are plotted because only these were found to have a significant influence on the chemically important region from $-10\,\mathrm{eV}$ to $+4\,\mathrm{eV}$ relative to the valence-band maximum.

All species studied were in the neutral, undoped forms. While the conductivity of the doped polymers is well known to be significantly higher, it is important to provide a consistent background with the neutral, semiconducting species before addressing the more complex issues relevant to charge-transfer processes and structural distortions characteristic of doped conjugated polymers.

III. RESULTS AND DISCUSSION

We first discuss calculations on isolated oligomers and the scaling of oligomeric properties in the infinite periodic unit-cell polymer models. We then discuss the band structures and density of states of each polymer, studied individually, comparatively, and then as a group.

A. Oligomer electronic structures

Since the exact length distributions and geometries of long-length conducting polymers are usually not well characterized, it is often useful to perform experiments on shorter-length, well-defined oligomers.[70,82] Additionally, this approach circumvents experimental difficulties arising from the poor solubility and processability of many of the full-length polymers, although some physical measurements have been performed on thin-film samples. Since it is possible to synthesize several well-defined lengths of oligomers, previous studies have examined the changes in electronic structure as a function of chain length, typically measured as the number of component rings or number of monomer units in the oligomer.[83,84]

From the calculated energy levels of oligomeric species, previous workers have attempted to extrapolate the derived electronic structures to those of the corresponding polymers. Such an extrapolation for estimating polymer band gaps was generated in the present work by plotting the highest occupied molecular-orbital (HOMO)–lowest unoccupied molecular-orbital (LUMO) energy gap of the corresponding

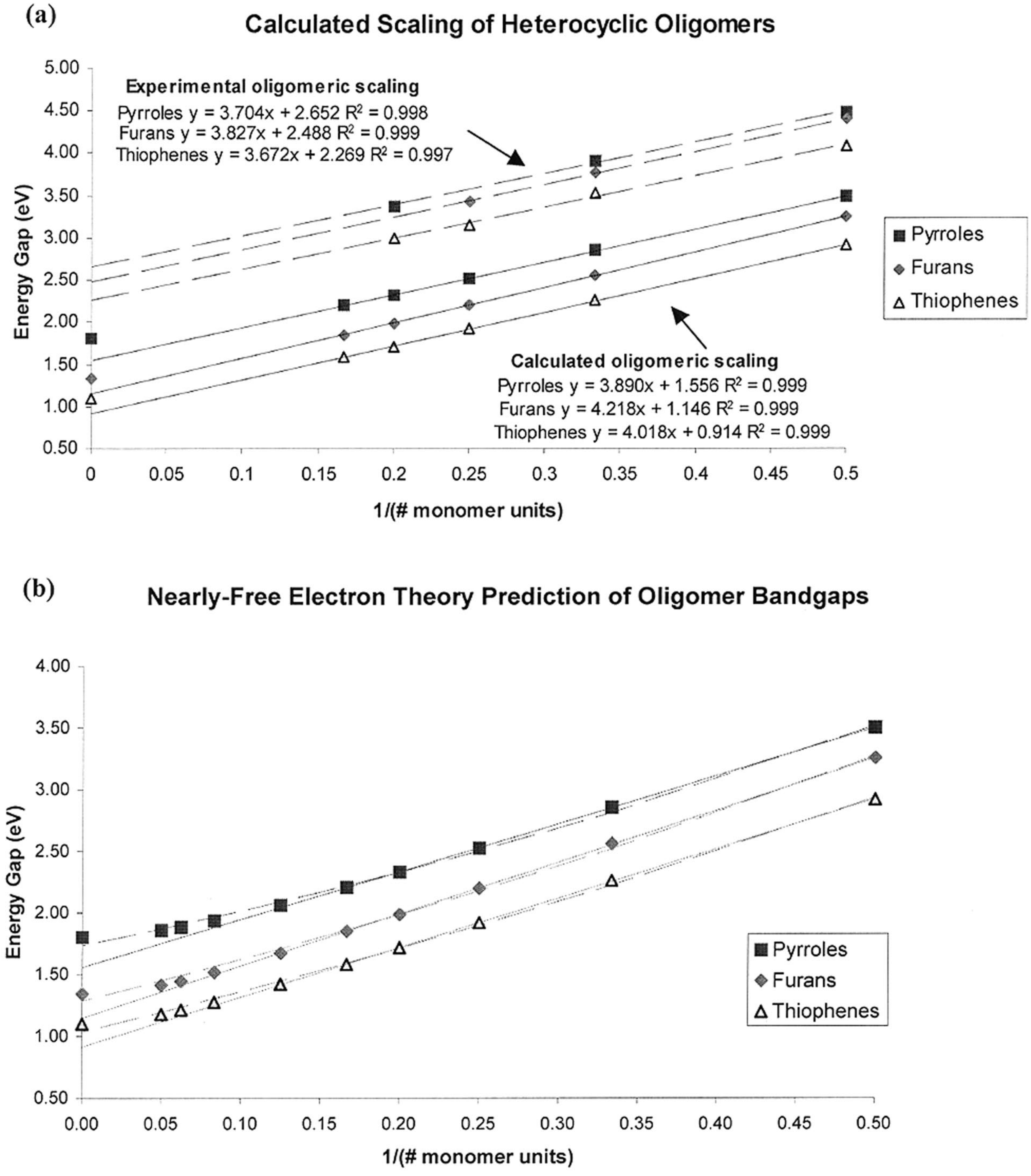

FIG. 2. Comparisons of polymer band gaps derived from extrapolating calculated HOMO-LUMO energy gaps to infinite systems calculated using periodic boundary conditions. (a) Comparison between DFT calculated band gaps and experimental absorption energies. The dashed lines indicate the extrapolation behavior of the experimental absorption energies in acetonitrile and are given by the linear regression relationships indicated Refs. 56, 70. The experimental polymer band gaps are not indicated as these are from thin-film measurements and so are not strictly comparable to the solution-phase oligomer values given here. (b) Comparison between empirical $1/N$ relationship (Eq. 1) and nearly-free electron molecular orbital curves for DFT results for 2-36 monomer units, showing smooth curve of DFT oligomer and polymer band gaps and deviation from $1/N$ relationship at long oligomer lengths.

oligomers against the reciprocals of the oligomer lengths, given here as the number of monomer units in the oligomer. It can be seen in Fig. 2 that this inverse relationship roughly holds since both the number of electrons and the length of the π system simultaneously increase as additional monomer units are added.[84] This empirical relationship, however, provides an incomplete picture for very long oligomers and the infinite polymer since it does not correctly express the actual asymptotic behavior. Conjugated pseudo-one-dimensional π systems are often modeled by a free-electron model, although here as the size of the "box" increases by adding more monomer units, the number of electrons increases as well. This explains the empirical $1/N$ relationship, but a free-electron model does not recover a finite band gap at infinite length. A more realistic approach is to use a sine-shaped potential along the chain, which recovers the Peierls distortion and finite band gap and gives the relation[84–86]

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

where h is Planck's constant, m is the electron mass, d is the averaged C—C and C═C bond lengths, N is the number of π electrons, l is the effective length of the conjugated π system, and V_0 is a constant corresponding to the band gap at infinite length. This relation fits well for band gaps of short and long oligomers as well as the infinite polymer, as shown in Fig. 2(b).

Previous work suggesting that the origin of the long-length deviation from the aforementioned reciprocal scaling in polyacetylenes simply derives from changes in the bond-length alternation still relies on the same physically unrealistic $1/N$ picture.[41,87] If the results for long polyheterocylic oligomers having up to 18 unit cells (36 monomer units) are examined, it can be seen that the bond-length alternation in these systems converges to the infinite value, as shown in Fig. 3, while the band gaps still decrease smoothly. Beyond a certain oligomer length, the central region of all oligomers exhibits a "converged" region, where the carbon-carbon bond lengths exhibit the same bond alternation and lengths as those of the infinite periodic model. Therefore, it can be suggested that for the polyheterocycles examined here, the empirical $1/N$ relationship may yield a better fit for very short oligomers (2–6 monomer units) because of the slight variations in the carbon-backbone bond lengths, but the correct physical behavior is better expressed in terms of the nearly-free-electron relationship above.

It has also been suggested that the total density of states of the polymers can be extrapolated from calculations on a series of oligomers, as shown in Fig. 4.[32] Furthermore, it has been proposed that features of the band structure can be readily assigned from such extrapolations,[32] however, this is clearly not straightforward in the case of overlapping bands. Thus, such an extrapolation may look qualitatively correct (e.g., by using broadening to produce a density of states as in Fig. 4) but it cannot be as accurate as explicit calculation of the band structure of an extended system, especially since saturation effects will occur at some long chain length as outlined above. For example, extrapolations using the $1/N$ relationship fail due to the incorrect description of the asymptotic behavior, described above. Use of longer oligomers will improve the accuracy of such extrapolations or quasiband calculations,[88] as contributions of the hydrogen end groups diminish and the C—C bond lengths converge towards the polymer (cf. Fig. 3), but this is at the cost of higher computation. Consequently, band-structure calculations present a more accurate electronic structure at lower computational cost than does a quasiband calculation.[88]

B. Polymer electronic structures

1. Effective conjugation lengths

As shown in Fig. 2, the present calculated band gaps of the isolated, infinite-length polymers lie significantly higher in energy than the extrapolated values from oligomers, due to saturation effects as the band gap becomes roughly constant at some large length. Experimentally, oligomers longer than approximately 6 subunits become insoluble; hence it has proven difficult to establish the scaling of experimental band gaps for larger oligomers. On the other hand, the "effective conjugation length," defined here as the point at which the band gap no longer decreases for longer-length oligomeric materials, can be calculated from linear regression analysis on the $1/N$ behavior of the calculated energy gaps of short oligomers for a series of oligomers as shown in Fig. 2(a). From these $T=0$ K calculations, for both polythiophene and polyfuran, we find that the computed effective conjugation length is 21 monomer units, versus 15 monomer units for polypyrrole. This agrees very well with experimental estimates for polythiophene and similar conjugated polymers, 21 monomer units at 10 K and 15 monomer units at room temperature,[71,72] even though the calculation here does not explicitly treat effects such as defects in the conjugated π system, torsional disorder, or intermolecular effects from neighboring polymer chains.

2. Band structures and densities of states

The full band structures and densities of states of the isolated polymer chains of *b*-polyacetylene, polypyrrole, polyfuran, and polythiophene are shown in Figs. 5 and 6, respectively, and a comparison of the calculated lattice constants, band gaps, and bandwidths is summarized in Table I. Qualitatively, the band structures are all quite similar, especially in the size and dispersion of the large carbon π-backbone bands. The heteroatoms contribute more localized, sharp bands in the valence-band region as well as some more localized bands in the conduction-band region in the case of polypyrrole and polythiophene. As indicated by the partial DOS plots in Fig. 6, the highest-lying valence bands are exclusively composed of carbon π density, so that the heteroatoms should contribute little to the exact energy of the valence-band edge. On the other hand, the heteroatom orbitals clearly contribute to the lower edge of the conduction band, indicating that modification of the heteroatom electron density should have a significant effect on the magnitude of the band gap as long as this does not introduce additional torsional disorder.

a. Polyacetylene. While the all-*trans*-isomer of polyacetylene is the most thermodynamically stable form, we confine ourselves here to the explicit carbon backbone of the heterocyclic polymers under investigation, as indicated in Figs. 1 and 7.[76] We designate this as *b*-polyacetylene to denote the backbone of the heterocyclic polymers. This isomer

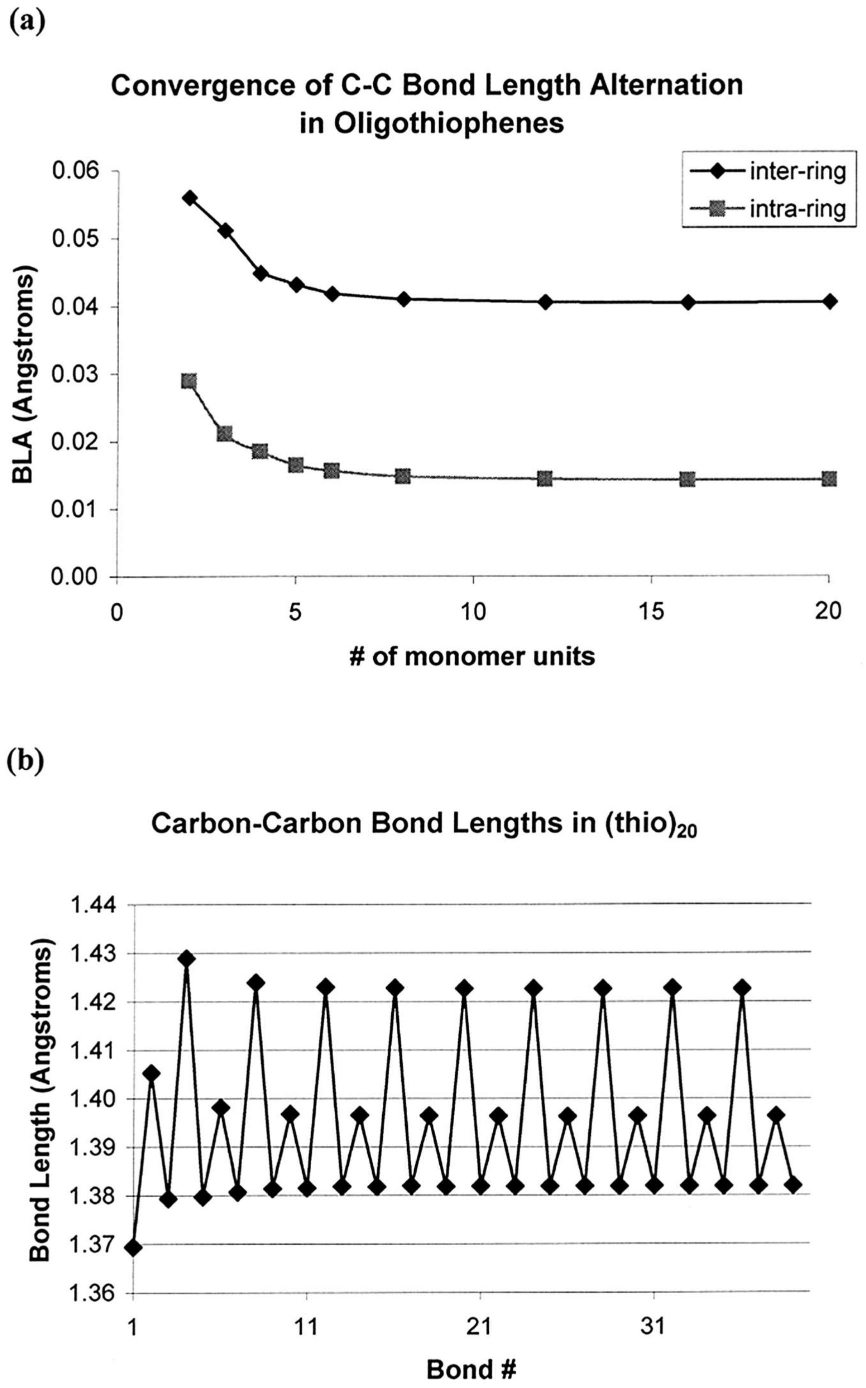

FIG. 3. Comparisons of C–C bond lengths in oligothiophenes, showing (a) fast convergence of bond length alternation for both intra-ring bonds and interring bonds as a function of number of the number of monomer units and (b) converged central region in a 20-mer oligothiophene, with bond lengths and bond alternation at the infinite values.

resembles a *cis*-polyacetylene chain with twice the normal unit-cell length and a center of inversion between the two components (cf. Fig. 7). The calculated lattice constant for the *b*-polyacetylene isomer in Fig. 7(c) is approximately double that calculated for *cis*-polyacetylene (8.86 Å vs 4.41 Å), while the calculated band gap decreases (0.51 eV vs 0.80 eV). The latter is not surprising considering that an all-*trans*-polyacetylene isomer is calculated to have a lower band gap still (0.10 eV). Furthermore, *b*-polyacetylene has both a smaller conduction bandwidth (3.55 eV vs 6.51 eV for *cis*-polyacetylene and 5.11 eV for *trans*-polyacetylene) and a smaller valence bandwidth (3.48 eV vs 4.79 eV for *cis*-polyacetylene). These changes in the electronic structure of this *b*-polyacetylene isomer are probably due to a lower symmetry than either the all-*cis*-polyacetylene or all-*trans*-polyacetylene forms as well as the doubling of the unit-cell

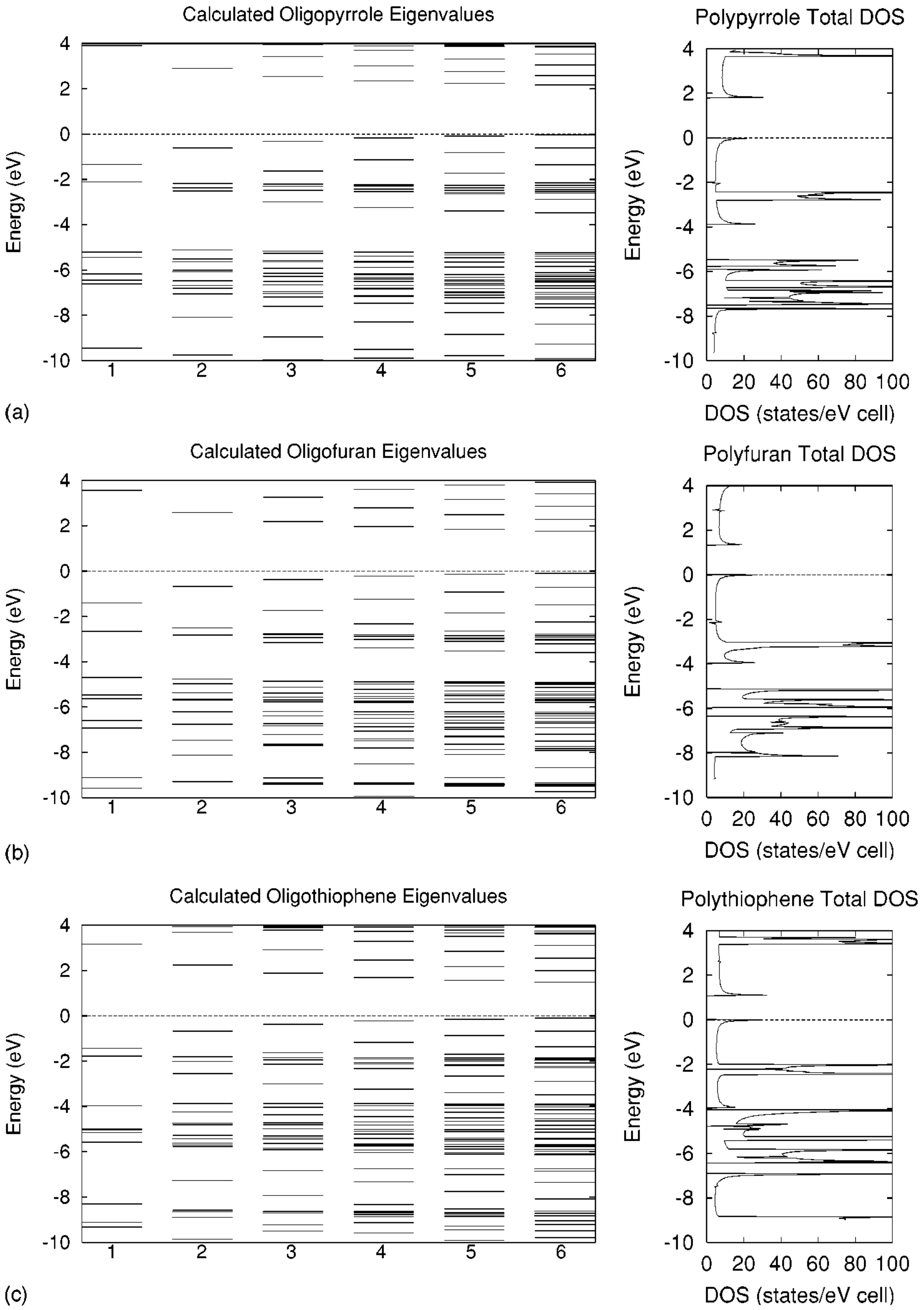

FIG. 4. Calculated density of states scaling from oligomers (for one to six monomer units) to the infinite polymer structures of: (a) polypyrrole, (b) polyfuran, and (c) polythiophene.

size, since in this structure the bands will be "folded" into the reduced Brillioun zone. All of these calculated band gaps are unphysically small and are apparent only for the polyacetylenes[87,89]—other systems do not appear to be affected (see below).

As in the case of *cis*polyacetylene, *b*-polyacetylene does not have a degenerate ground state lying between the geometry indicated in Fig. 7 and the quinoidlike form indicated in Fig. 8(b). These two forms correspond to the aromatic and quinoid forms in the heterocyclic polymers, Figs. 8(c) and 8(d), and the greater stability of the aromatic form holds in *cis*-polyacetylene, *b*-polyacetylene, and the heterocyclic polymers mentioned here. This stability, however, can be reversed by substitutent effects,[21] although it has been shown that the most stable form will be that with the largest band gap.[21]

b. Polypyrrole. While polypyrrole currently has many applications,[70] it has a significantly larger band gap and lower conductivity than polythiophene. On the other hand, polypyrrole shows the largest carbon π valence bandwidth of the five polyheterocycles considered here, and a dispersion of the carbon valence band similar to that of the other poly-

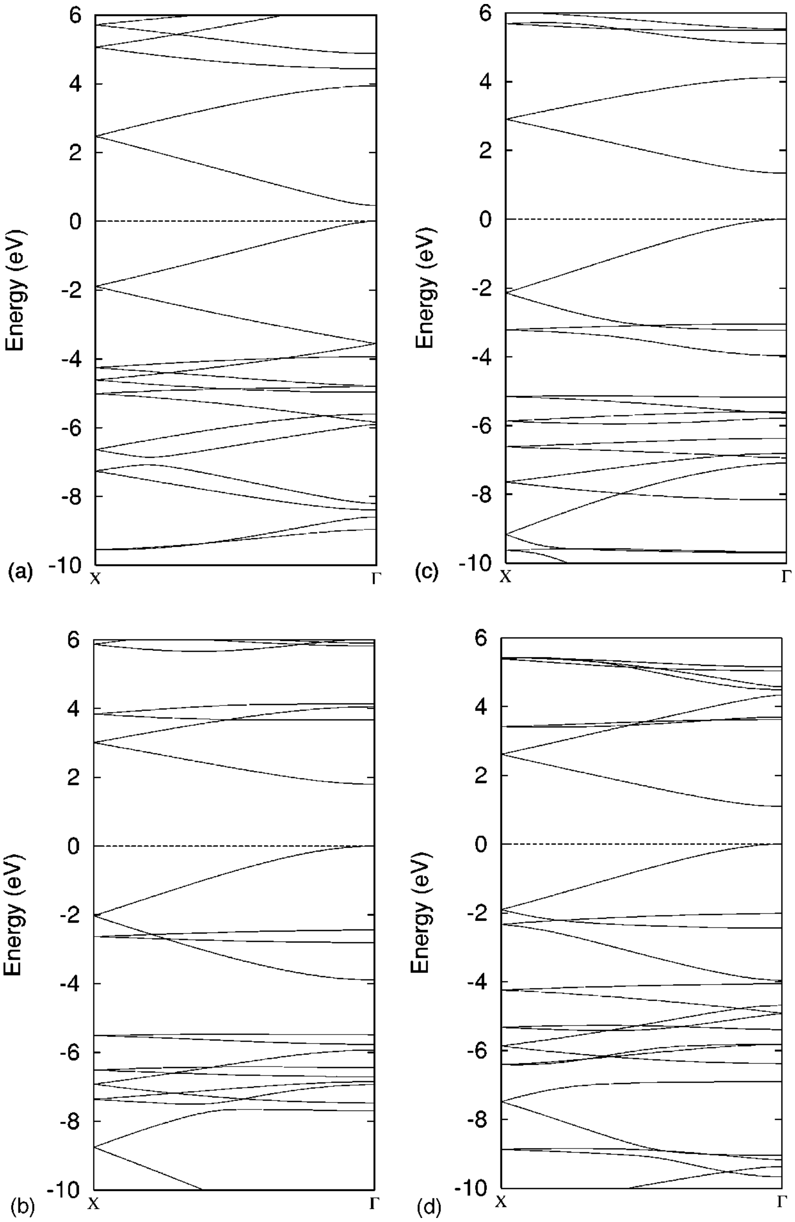

FIG. 5. Calculated band structures of: (a) *b*-polyacetylene, (b) polypyrrole, (c) polyfuran, and (d) polythiophene, plotted relative to the calculated valence band maxima.

mers. The effective mass of holes in the valence band, however, is higher than any of the polyheterocycles studied here and the effective mass of electrons in the conduction band is similarly higher than any polyheterocycle studied here, as found in Table I.

The calculated LDA band gap compares well with experimental thin-film measurements,[73] as well as previous oligomer and polymeric electronic structure calculations.[61,90,91] Both experimental measurements and hybrid functional calculations give band gaps of approximately 2.8–2.9 eV, implying the LDA band gap calculated here is a factor-of-0.63 too small, as shown in Table I. Extrapolated time-dependent DFT (TDDFT) calculations give slightly larger band gaps, but still underestimate the experimental thin-film values.[61,91]

c. Polyfuran. Experimentally, it has proven difficult to consistently convert furan into a well-defined polymeric material.[56,74,92,93] However, it has a lower calculated band gap than polypyrrole and a larger conduction bandwidth as well as similarly broad band dispersion, which would imply that the material might potentially be *n* doped and have higher *n*-type conductivity than polypyrrole. The ionization potential and electron affinity for doping should lie between those of polypyrrole and polythiophene. Similarly, the effective masses of holes and electrons in the valence and conduction bands lie between those of polypyrrole and polyfuran. The calculated band gap in Table I also compares well with experimental thin-film measurements,[74] and hybrid density-functional calculations,[90] showing that the LDA band gap is a factor-of-0.57 too small, compared with experiment. As with the polypyrrole system, extrapolated time-dependent

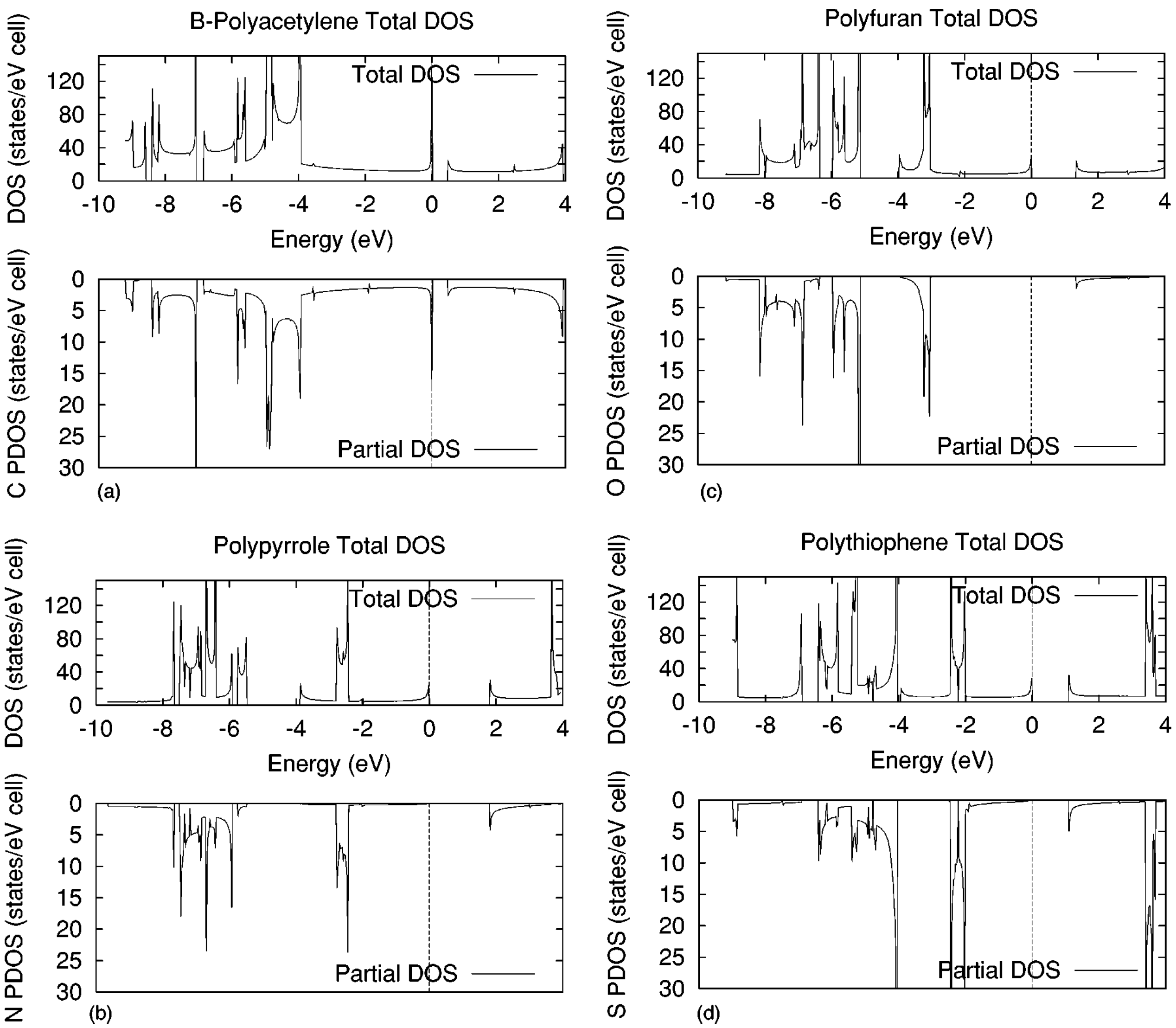

FIG. 6. Calculated total and partial (p-orbital) densities of states (DOS) for (a) b-polyacetylene, (b) polypyrrole, (c) polyfuran, and (d) polythiophene. Plots of the partial density of states are shown with the y axis inverted to enhance comparison.

DFT calculations give slightly larger band gaps, but still underestimate the experimental thin-film values.[61,91]

d. Polythiophene. Polythiophene exhibits both the smallest band gap and the broadest conduction band of the three aromatic conjugated polymers examined. Recent studies have treated polythiophene at the high-level GW approximation[94,95] and compared isolated chains to the bulk polymer.[23,96] As expected, these studies find a significantly increased band gap using the GW approximation relative to that calculated by the LDA, since it is well known that the LDA consistently underestimates band gaps.[50,52] Compared with experimental thin-film measurements,[75,76] the LDA band gap is a factor-of-0.55 too small. Finally, the differences in Kohn-Sham band gaps between the case of an isolated chain, as treated here, and crystalline environments are found to be small,[23] which implies that such effects may be small for conducting polymers in general. Again, as with polyfurans and polypyrroles, recent extrapolated TDDFT calculations give slightly larger band gaps, but still underestimate the experimental thin-film values.[61,91]

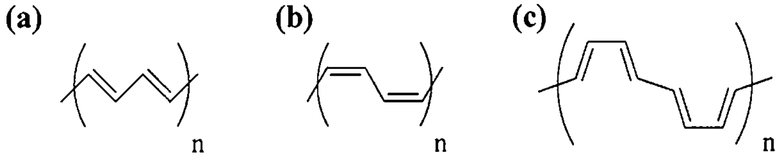

FIG. 7. Structures of (a) all *trans*-polyacetylene, (b) all *cis*-polyacetylene, and (c) the carbon backbone of polythiophene, polypyrrole, and polyfuran (b-polyacetylene).

TABLE I. Comparison of calculated lattice constants, band gaps, valence-band maxima, bandwidths, and effective masses of the various heterocyclic polymers. Values in parentheses for band gaps are the calculated band gaps divided by 0.60, a common procedure (Ref. 50) to facilitate comparison with experimental values.

Polymer	Lattice constant (Å)	Band gap (eV)	Carbon valence bandwidth (eV) and effective mass	Carbon conduction bandwidth (eV) and effective mass
Polypyrrole	7.12	1.80 (3.00)[a]	3.89 ($0.205m_e$)	2.25 ($0.244m_e$)
Polyfuran	6.88	1.34 (2.23)[b]	3.23 ($0.148m_e$)	2.79 ($0.187m_e$)
Polythiophene	7.71[c]	1.10 (1.83)[d]	2.44 ($0.137m_e$)	3.23 ($0.152m_e$)
Polyphosphole	8.07	1.46 (2.43)	1.49 ($0.186m_e$)	2.93 ($0.218m_e$)
Polyselenophene	8.02	0.89 (1.48)	2.06 ($0.110m_e$)	3.55 ($0.116m_e$)

[a] Experimental thin-film value 2.85 eV (Ref. 73).
[b] Experimental thin-film value 2.35 eV (Ref. 74).
[c] Experimental value 7.75 Å (Ref. 108).
[d] Experimental thin-film value 2.0 eV (Refs. 75 and 76).

e. Polyphosphole. Phosphole is not an aromatic heterocycle, due to the larger size of phosphorus relative to nitrogen, and the phosphorus atom is known to be pyramidal in the lowest-energy state.[97–100] In this study, to directly compare with the other aromatic heterocycles, we have taken the planar aromatic conformation of polyphosphole.[90] The band gap calculated here is larger than that recently predicted for the nonaromatic phosphole by TDDFT,[91] but these are not directly comparable since the transitions involve different sets of orbitals. However, the band gap is approximately 0.60 times the size recently predicted for the planar aromatic eight-ring oligophosphole,[90] in line with the typical underestimation of LDA band gaps. In this work, all polyheterocycles considered should have transitions between the same orbital configurations, leaving the contribution of the heteroatom as the only variable.

The band structure of polyphosphole exhibits high effective masses for both holes and electrons, and while it shows a fairly large conduction bandwidth (2.93 eV), the valence bandwidth is rather small (1.49 eV), as summarized in Table I. This result suggests that polyphosphole probably has limited use as a conductive material relative to the other polyheterocycles.

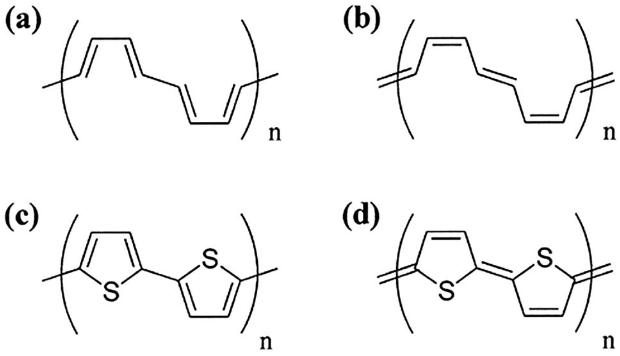

FIG. 8. Aromatic and quinoid bonding patterns of *b*-polyacetylene and polythiophene: (a) "aromatic" form of *b*-polyacetylene, (b) "quinoid" form of *b*-polyacetylene, (c) aromatic form of polythiophene, and (d) quinoid form of polythiophene.

f. Polyselenophene. While not as widely studied as polyfuran or polythiophene, polyselenophene has been synthesized and studied experimentally.[101–106] The present results indicate that while polyselenophene has a smaller carbon valence band than polythiophene, it also has the lowest effective mass for holes in the valence band, which would indicate that mobility of holes should be excellent along the polymer chain. Similarly, the effective mass of electrons in the conduction band is also the smallest of any of the polyheterocycles studied here, and the conduction bandwidth is extremely large (3.55 eV), indicating that polyselenophenes should be excellent n-type conductors. The calculated band gap is a factor-of-0.81 times smaller than polythiophene, which is consistent with previous work involving extrapolations from calculated band gaps of oligomers (0.93 times smaller).[32]

3. Analysis and discussion

In comparing the electronic structures of the three heterocyclic polymers presented here to that of the explicit carbon backbone of b-polyacetylene, it can be seen that while b-polyacetylene has the most broadly dispersed conduction band and smallest band gap, both the band gap and bandwidth are highly sensitive to the influence of the heteroatom. As noted above, the partial DOS data (cf. Fig. 6) reveal that the heteroatoms do not contribute to the composition of the valence-band edge, but do contribute significantly to the composition of the bottom of the conduction band. The bandwidths of the heterocyclic polymers are strongly correlated with the atomic electron affinity of the heteroatoms. Nitrogen does not readily accept an electron, oxygen has an electron affinity of 1.46 eV, and sulfur, 2.08 eV.[107] This heteroatom effect shows that earlier work, implying that heteroatom effects can be predicted as the basis of *electronegativity*,[68] would assign an incorrect band-gap ordering: polyfuran would be predicted to have the *largest* band gap, then polypyrrole and polythiophene, as shown in Figs. 9(a) and 9(b), employing the widely used Pauling scale of electronegativity.

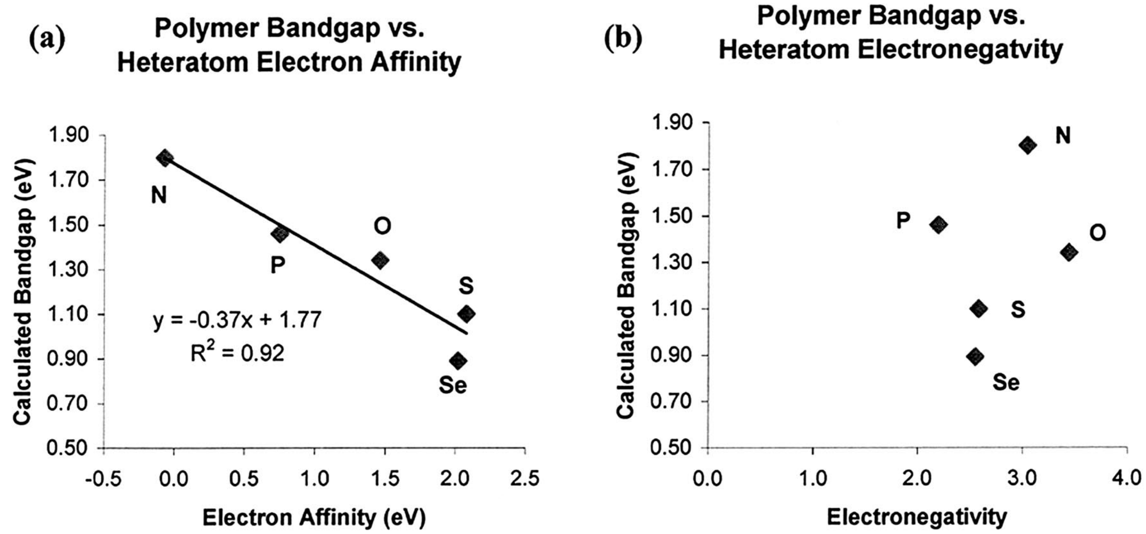

FIG. 9. Correlation of the calculated band gaps of the polyheterocycles with the (a) atomic electron affinity and (b) electronegativity (Pauling scale) of the heteroatoms nitrogen, phosphorous, oxygen, selenium, and sulfur. The indicated line is a linear regression with the formula and fit given. Note that the atomic electronegativities show no correlation with calculated band gaps.

Changing the carbon-carbon bond lengths in the π backbone of a conjugated polymer will readily change the band gap, for example, a polyacetylene with equal carbon-carbon lengths has no band gap and is intrinsically a metal. Previous work suggested on the basis of semiempirical calculations that bond-length alternation effects can explain the band gaps in polyheterocycles.[68] On the basis of the present density-functional calculations, however, we see that the aromatic polymers have quite similar carbon-carbon bond lengths, as illustrated in Table II. The outliers are polyfuran, with somewhat larger intraring bond-length alternation due to the small size of the oxygen atom, and polyphosphole. This bond-length alternation model, however, predicts again that polyfuran and oligofurans should have greater gaps than polypyrrole, which is clearly not found here or in experimental measurements.[56,70] Similarly, since polyphosphole has a smaller bond-length alternation than the rest of the systems studied here, this would argue that it should have a significantly smaller band gap than polyfuran, polythiophene, or polyselenophene, which is not the case. Thus, bond-length alternation does not appear to be a reliable predictor of band gaps in polyheterocycles, in contrast to the correlations with heteroatom electron affinity, discussed above.

TABLE II. Comparison of the carbon-carbon bond-length alternation (BLA) for intraring and interring bonds between the polyheterocycles studied here.

Polymer	Intraring BLA (Å)	Interring BLA (Å)
Polypyrrole	0.0167	0.0370
Polyfuran	0.0338	0.0370
Polythiophene	0.0139	0.0375
Polyphosphole	0.0022	0.0240
Polyselenophene	0.0183	0.0369

Calculations on polyphosphole and polyselenophene band gaps indicate that the band-gap–electron affinity correlation observed for the nitrogen-, oxygen-, and sulfur-based polyheterocycles is a pervasive effect, as indicated in Fig. 9. However, the trend does not appear to be completely general, for example, polyselenophene is predicted to have a smaller band gap than polythiophene, although selenium has a slightly lower electron affinity than sulfur. On the other hand, selenium has a significantly lower elemental ionization potential than sulfur (9.75 eV vs 10.36 eV),[107] so that other heteroatom electronic effects, such as atomic ionization potential, may play a role in the case of larger heteroatoms.

Other polyheterocycle properties, such as bandwidth and effective carrier mass, also appear to have periodic behavior similar to that noted for band gaps. Referring to Table I, the effective masses in the conduction bands have exactly the same ordering as the electron affinities: decreasing from polypyrrole to polyphospole to polyfuran, polythiophene, and polyselenophene. With the exception of polyphosphole, the valence bandwidths and valence-band effective masses both decrease from polypyrrole to polyfuran to polythiophene and polyselenophene. Again, these properties fit better with trends in electron affinity than with those in electronegativity—oxygen has the highest electronegativity of the elements considered here, but the properties of furans fall distinctly between those of thiophenes and pyrroles.

IV. CONCLUSIONS

While a great deal of research has been performed on the electronic structures of conducting conjugated polymer oligomeric fragments, in large part due to their well-defined lengths and architectures, it is clear from the present results that extrapolation from the electronic structures of oligomers cannot accurately model the full band structures of the corresponding polymers. In particular, such extrapolation does not readily provide information on the shapes and dispersions of the bands, reveal overlapping bands, or take saturation effects into account. Explicit electronic structure calculations on the ideal, infinite polymers reveal saturation effects at large chain lengths that are best expressed in terms of the full nearly-free-electron model. Surprisingly, the "effective conjugation length" reached at longer chain lengths agrees well with experimental estimates of conjugation lengths—even though the model used here only treats an isolated chain and does not attempt to include effects such as defects, torsional disorder, or interchain interactions.

Additionally, while the electronic structures of polyacetylenes would seem to be useful comparative benchmarks for the widely studied polyheterocycles such as polythiophene, polypyrrole, and polyfuran, the common *cis*-isomers and *trans*-isomers of polyacetylene do not accurately model the electronic structures as well as does the b-polyacetylene isomer [Fig. 7(c)], which includes the lower symmetry and larger unit cell involved in these heterocyclic polymers.

Finally, while it is well known that varying the heteroatom significantly changes the band gap of conjugated polyheterocycles, it has not been obvious whether these effects arise from geometric distortion of the carbon backbone (bond-length alternation) or from electronic contributions of the p orbitals of the heteroatom (electronegativity). From the partial density of states projected onto the heteroatoms in the present study, it is clear that the character of the valence band is largely due to the carbon backbone, but a significant portion of the lower edge of the conduction band derives character from the heteroatom. Thus, the electron affinity of the heteroatom, and neither bond-length alternation nor electronegativity as expressed in previous work, directly influence the polymer band gaps as a whole. Heteroatom electron affinity is therefore crucial in determining polymer optical properties as well as p- or n-doping characteristics of the polymers.

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