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From Oligomers to Polymer: Convergence in the HOMO–LUMO Gaps of Conjugated Oligomers

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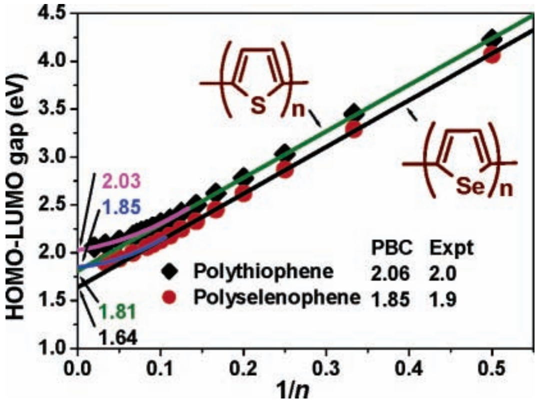
ABSTRACT



Extrapolation of HOMO–LUMO gaps for π-conjugated oligomers at the B3LYP/6-31G(d) level of theory predict accurately (within 0.1–0.2 eV) the band gaps of conjugated polymers only when long (at least 20-mer) π-conjugated oligomers are used for the extrapolation.

Conjugated oligomers and polymers[1] attract considerable interest due to their applications in light-emitting diodes (LED),[2] field effect transistors (FET),[3] photovoltaic cells,[4] etc. Designing better organic electronic materials requires a comprehensive understanding of the electronic structure of conjugated polymers and the factors affecting it. By systematically studying a series of oligomers, valuable information can be generated regarding the properties of conducting polymers,[1a] particularly with respect to band gap and band width, and major experimental and theoretical efforts are directed toward understanding the effect of different factors on the band gap.[1] It is generally accepted[5,6] that, for conjugated oligomers, extrapolating the linear curve 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.[7] Recently, it has been shown, using the Perdew−Wang exchange-correlation functional, that this empirical linear expression does not hold for long

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conjugated oligomers (up to $n = 36$ has been studied).[6] However, since a nonhybrid "pure" density functional (LDA) was used,[6] no direct correlation of the predicted band gap with experimental values was possible (the results need to be scaled by an empirical factor to obtain experimental band gaps).

Here, we studied oligomers of major types of conducting polymers[8] (oligothiophene, -pyrrole, -furan, -paraphenylene, and -3,4-ethylenedioxythiophene (EDOT)) using the hybrid density functional B3LYP level of theory, which should allow a direct comparison to be made with experimental values. We have shown that, using the correct extrapolation procedure, the band gaps of conducting polymers can be predicted[9] to within a couple of tenths of electronvolts of the experimental values with hybrid DFT and moderate basis set. However, it is essential to use long oligomers, at least up to 20-mer, for correct band gap prediction.[10] As expected, when the band gaps of conducting polymers are predicted from the HOMO−LUMO gaps of long oligomers, they match those predicted by periodic boundary conditions (PBC). Using short oligomers (up to $n = 10$, as used in most previous studies) is insufficient for prediction of the band gaps of conducting polymers.

All calculations were carried out using the Gaussian 03 program.[11] The geometries of all oligomers were fully optimized[12] using a hybrid density functional;[13] Becke's three-parameter exchange functional combined with the LYP correlation functional (B3LYP)[14] and with the 6-31G(d) basis set. The calculations for polymers were performed using PBC as implemented in Gaussian 03.[15] We built up a unit cell comprising two monomers anti to each other. The optimizations using PBC were carried out without any symmetry constraints. It was shown that band gaps predicted for conducting polymers using the hybrid B3LYP functional coupled with PBC were in excellent agreement with experimental values.[16] For discussion of applicability of DFT to study band gaps of conjugated polymers, see ref 17. The same theoretical level (B3LYP/6-31G(d)) was used for both oligomer and polymer calculations, which allowed us to evaluate the applicability of studying conjugated polymers by means of extrapolation from oligomer properties.

Our calculations on oligothiophenes and oligoselenophenes at B3LYP/6-31G(d) reveal that the generally accepted[5] approximation of polymer band gap based on a linear relationship between HOMO−LUMO gap and $1/n$ holds only up to $n \approx 12$ (Figure 1a). However, the linear prediction is not particularly accurate, yielding band gaps of 1.81 and 1.64 eV for polythiophene and polyselenophene, respectively, compared to experimental values of 2.0[18] and 1.9 eV,[19] respectively. This extrapolation method fails to consider asymptotic behavior since saturation occurs at longer conjugation lengths (Figure 1a).[20] 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.[21] The quadratic equations ($n \geq 10$, $R^2 = 0.999$) 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 (2.0[18] and 1.9 eV,[19] respectively) and, as expected, to PBC/B3LYP/6-31G(d) calculated band gaps (2.06 and 1.85 eV for polythiophene and polyselenophene, respectively).

In the case of alkyl-substituted polythiophene, indeed, the convergence in the HOMO−LUMO gaps has been observed

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(7) More precisely, the band gap of a conjugated polymer can be expressed in terms of Kuhn's equation: $\Delta E = h^2(N + 1)/8md^2\,(N + l)^2 + V_0(1 - 1/N)$, where h is Planck's constant, m is 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 π-conjugated system, and V_0 is the constant corresponding to the band gap at infinite length. (a) Kuhn, H. J. *Chem. Phys.* **1949**, *17*, 1198. (b) Taubmann, G. *J. Chem. Educ.* **1992**, *69*, 96. (c) de Melo, J. S.; Silva, L. M.; Arnaut, L. G.; Becker, R. S. *J. Chem. Phys.* **1999**, *111*, 5427.

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(9) For comparison of different theoretical levels used to predict band gaps of conducting polymers, see: Hutchison, G. R.; Ratner, M. A.; Marks, T. J. *J. Phys. Chem. A* **2002**, *106*, 10596.

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(12) The geometries of oligothiophenes, -selenophenes, -pyrroles, and -furans are constrained to C_{2h} and C_{2v} symmetries for even and odd values of n, respectively. The energy difference between the symmetry constrained and non-constrained geometries is always less than 0.12 kcal/mol for oligothiophenes and 0.05 kcal/mol for oligoselenophenes. The optimized geometries of 20T and 30T without symmetry constraints have planar structures which are indistinguishable from symmetry constrained geometries (energy difference is less than 0.01 kcal/mol). The geometries of oligoparaphenylenes and oligoEDOTs are optimized without symmetry constraints (geometries of oligoEDOTs are practically planar). Only in the case of oligopyrroles is the difference between constrained planar and non-constrained geometries significant (1.3 kcal/mol for the 6-mer and 9.2 kcal/mol for the 30-mer).

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(21) Oligothiophenes were constrained to be planar.[12] Oligothiophenes without symmetry constraints (C_1 symmetry) were also studied, and their HOMO−LUMO gaps showed similar behavior; see Supporting Information (Figure S1) for details.

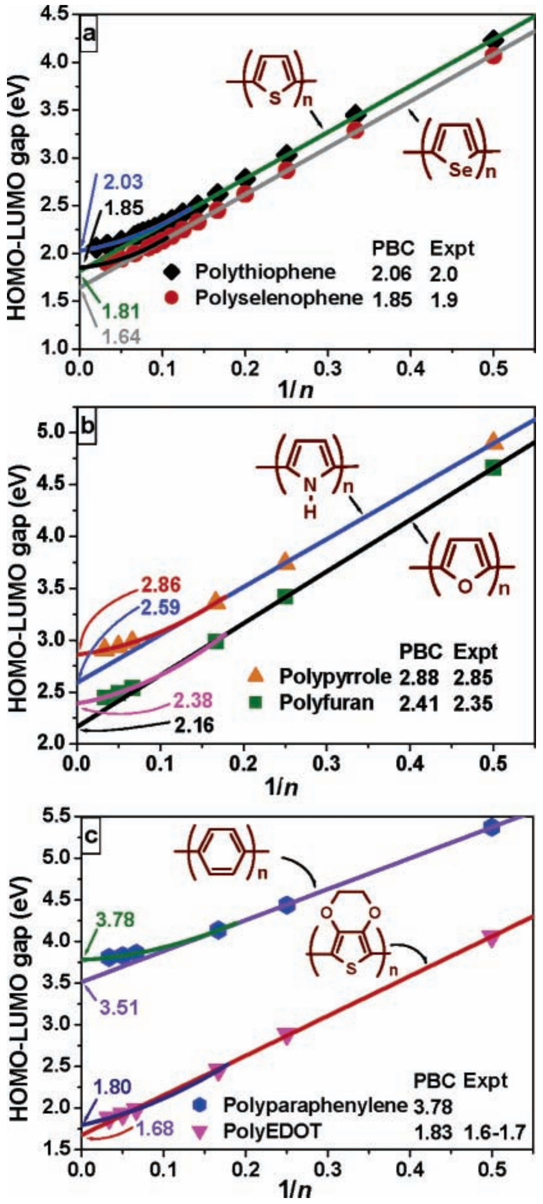

Figure 1. HOMO−LUMO gap versus the reciprocal of the number of oligomer units (at B3LYP/6-31G(d)) for (a) oligothiophene and -selenophene, (b) oligopyrrole and -furan, and (c) oligoparaphenylene and -EDOT. PBC/B3LYP/6-31G(d) calculated band gaps and experimentally determined band gaps are also indicated on the graphs. The linear fits are drawn by considering (a) $n = 2-10$, (b and c) $n = 2, 4, 6$; in all cases $R^2 \geq 0.999$. Nonlinear fits are drawn by considering (a) $n \geq 10$, (b and c) $n \geq 6$ using second-order polynomials and did not merge with linear fits.

experimentally.[22,23] For instance, an excellent example of the convergent behavior of HOMO−LUMO gaps in oligothiophenes is given in ref 22b. Although the authors concluded that the oligothiophenes studied “exhibit no convergent limit for the extended conjugation up to the 96-mer”, the convergent behavior is evident from spectroscopic data: $\lambda_{\max} =$ 524, 526, 527, and 528 nm for the 36-, 48-, 72-, and 96-mer, respectively. In the presence of the substituents, which disturb the planarity of the oligothiophene backbone, the deviation from $1/n$ dependence in HOMO−LUMO gaps starts earlier compared to the fully planar oligothiophenes.[23]

Further, the results for oligopyrroles, -furans, -paraphenylenes, and -EDOTs match very well the results for oligothiophenes and -selenophenes discussed above. Figure 1b summarizes the calculation on oligopyrroles and oligofurans. The $1/n$ ($n = 2$, 4, and 6) linear extrapolation of the HOMO−LUMO gaps estimates band gaps of 2.59 and 2.16 eV for polypyrrole and polyfuran, respectively. However, the modified extrapolation (quadratic equation) of $1/n$ ($n = 6-30$) affords HOMO−LUMO gap values of 2.86 and 2.38 eV for polypyrrole and polyfuran, respectively. These latter values more closely match the PBC calculated values (2.88 and 2.42 eV) and the experimentally evaluated band gaps (2.85 and 2.35 eV) for polypyrrole[24] and polyfuran,[25] respectively. The results for oligoparaphenylenes and -EDOTs are depicted in Figure 1c. In the case of polyparaphenylene (PPP),[26] the modified extrapolated band gap (3.78 eV, for $n = 6-30$) and PBC calculated band gap (3.78 eV) are similar and higher than the underestimated value of the linear extrapolation (3.51 eV, for $n = 2$, 4 and 6). We note that the calculated band gap of polyparaphenylene is strongly dependent on inter-ring dihedral angles. In our PBC calculation, the twisting is ∼36° in PPP and, in 30-mer paraphenylene, average twisting is also ∼36°. The PBC calculation for planar PPP gives a band gap of 3.08 eV, which is 0.7 eV lower than the band gap for the minimal structure. In the case of EDOT oligomers, the difference between the linear and quadratic regressions is smaller than that for the other oligomers studied here. Thus, the experimental band gap (1.6−1.7 eV)[27] is in the range predicted by the linear extrapolation (1.68 eV, for $n = 2$, 4 and 6) and is 0.1−0.2 eV lower than predicted by the quadratic equation (1.8 eV, for $n = 6-30$) and by PBC calculations (1.83 eV). PolyEDOT (PEDOT) is slightly more conjugated than polythiophene (the inter-ring C−C bond lengths in polythiophene and PEDOT are 1.441 and 1.434 Å, respectively, at PBC/B3LYP/6-31G(d)), indicating that saturation of the HOMO−LUMO gap may commence at longer chain lengths.

B3P86 functional with empirically selected 30% of HF exchange (B3P86−30%) has been suggested previously for band gap estimations of conjugated polymers, based on extrapolation of HOMO−LUMO gaps of short (up to $n =$ 6) conjugated oligomers, while B3LYP functional showed poorer performance in these studies.[5a,17] Our results suggest

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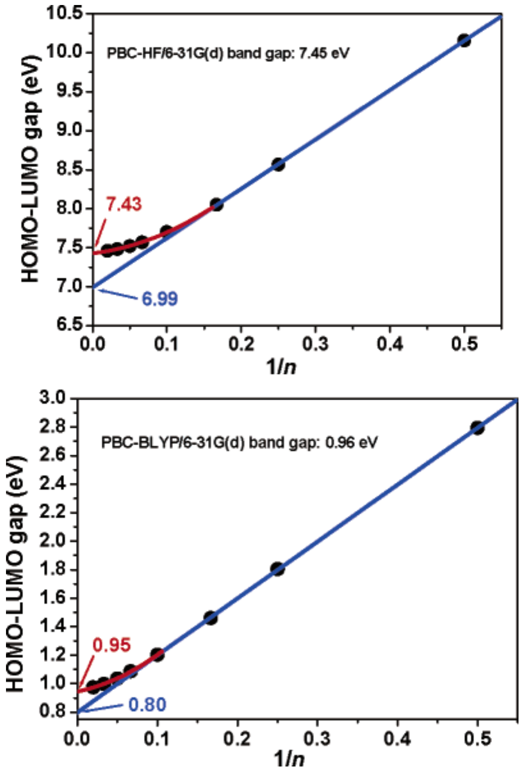

Figure 2. HOMO−LUMO gap versus inverse of chain length (1/*n*) for oligothiophene optimized at (a) HF/6-31G(d) and (b) BLYP/6-31G(d). PBC calculated band gaps are also indicated on the graphs. The linear fits are drawn by considering $n = 2, 4, 6$; in all cases $R^2 \geq 0.999$. Nonlinear fits are drawn by considering (a) $n \geq 6$, (b) $n \geq 10$ using second-order polynomials and did not merge with linear fits.

that B3LYP/6-31G(d) level (using long oligomer extrapolation approach or combined with PBC) shows excellent performance for evaluation of band gaps of conjugated polymers.

The equations for linear fits shown in Figure 1 provide further information about the effective conjugation length. These linear equations are as follows: oligothiophenes, $Y = 1.82 + 4.84X$; oligoselenophenes, $Y = 1.65 + 4.86X$; oligopyrroles, $Y = 2.59 + 4.62X$; oligofurans, $Y = 2.16 + 5.02X$; oligoparaphenylenes: $Y = 3.51 + 3.72X$; oligoEDOTs, $Y = 1.68 + 4.77X$, where X is the reciprocal of chain length and Y is the HOMO−LUMO gap. The slopes of these equations are directly proportional to the effective conjugation. The lowest number for oligoparaphenylenes means there is less conjugation along the chain, whereas the highest number for oligofurans represents the highest degree of conjugation.

Calculations for oligothiophenes (up to $n = 50$) performed at HF/6-31G(d) and at "pure" density functional BLYP/6-31G(d) levels show similar convergence behavior of the HOMO−LUMO gaps, although calculated band gaps are very far away from experimental values (Figure 2). Actually, convergence of HOMO−LUMO gaps is observed even for earlier *n* values at HF/6-31G(d) than at B3LYP/6-31G(d).[28]

In summary, the 1/*n* extrapolation of HOMO−LUMO gaps of conjugated oligomers fails to predict correct band gaps for conjugated polymers. This study suggests that the application of DFT at the B3LYP/6-31G(d) level to the extrapolation of 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 for predicting reliably (within a couple of tenths of electronvolts) the band gap of conjugated polymers.[10] These two methods produce values that very closely match each other[29] and the experimental values.

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Supporting Information Available: Energies and Cartesian coordinates for the optimized geometries of all the oligomers studied here and unit cells for PBC calculations; a few representative figures of optimized geometries of oligomers and unit cells of polymers. This material is available free of charge via the Internet at http://pubs.acs.org.

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(28) After this work had been submitted for publication, calculations on long (up to $n = 40$) oligothiophenes and oligopyrroles at B3P86-30%/CEP-31G* level had been published. Salzner, U.; Karalti, O.; Durdagi, S. *J. Mol. Model.* **2006**, *12*, 687. Convergence of HOMO−LUMO gaps can also be observed at this level (see Figure 1 in ref 28).

(29) We have also discovered several cases (which belong to yet experimentally unknown types of conjugated polymers) where PBC results do not match values obtained from oligomer extrapolation. The details will be reported in a future publication.