# Simple Extrapolation Method To Predict the Electronic Structure of Conjugated Polymers from Calculations on Oligomers

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Ⓢ Supporting Information

ABSTRACT: We introduce two simple tight-binding models, which we call fragment frontier orbital extrapolations (FFOE), to extrapolate important electronic properties to the polymer limit using electronic structure calculations on only a few small oligomers. In particular, we demonstrate by comparison to explicit density functional theory calculations that for long oligomers the energies of the highest occupied molecular orbital (HOMO), the lowest unoccupied molecular orbital (LUMO), and of the first electronic excited state are accurately described as a function of number of repeat units by a simple effective Hamiltonian parametrized from electronic structure calculations on monomers, dimers and, optionally, tetramers. For the alternating copolymer materials that currently comprise some of the most efficient polymer organic photovoltaic devices one can use these simple but rigorous models to extrapolate computed properties to the polymer limit based on calculations on a small number of low-molecular-weight oligomers.
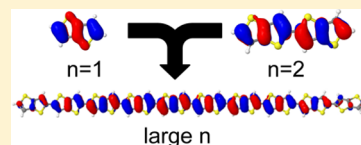
1. INTRODUCTION

Conjugated polymers (CP) have emerged over the last few decades as useful and promising materials[1,2] for a variety of applications: organic light emitting diodes (OLED);[3−8] organic field effect transistors;[9,10] thin film transistors;[11] chemical detectors;[12] and organic photovoltaics (OPV).[13−16] These technologies remain of interest because devices based on CP can be made flexible and wearable[12,17] and because roll to roll processing techniques can reduce the capital expenditures associated with production.[15] Within the past five years, the efficiencies of OPV devices have more than doubled,[18] largely by taking advantage of the fact that the electronic properties of CP can be tuned across broad parameter ranges to optimize electronic energy levels or the overlap of the absorption spectrum with the solar spectrum.[19] As a result of this tunability, dramatic improvements in OPV efficiency have been driven by the development of new materials with specific properties optimized by modifying the polymer backbone.

Although the optimization of materials has been driven extensively by considerations of single-molecule electronic properties, it has been suggested[20,21] that further improvements require attention to other properties, such as morphology and intermolecular interactions. For example, intermolecular interactions can shift the optical absorption spectrum of a material and the alignment or partial crystallization of polymer chains can lead to better charge transport than in disordered polymer films.[7,22] In addition, disorder may exist at boundaries between different materials or between ordered and disordered phases and this may alter exciton splitting and charge recombination probabilities.[23] All of these important processes must play a role in the ultimate charge generation and power conversion efficiencies, so design of materials for real world applications requires considerations beyond single molecule properties. Nevertheless, the search for novel materials likely

will continue to rely as a first step on designing electronic properties intrinsic to a candidate CP that can be used to screen out undesirable candidates prior to synthesis or device fabrication.[24]

The tunability of CP electronic properties that has driven OPV efficiency improvements has been based on the idea of combining multiple fused ring building blocks to tune backbone electronic properties.[13,15,21,25] Because synthesis of any new molecule may take months, one would like to be able to predict the electronic properties of candidate materials prior to attempting the synthesis. Several groups have employed high throughput computational approaches to discover interesting candidate organic molecular materials from electronic structure calculations.[24,26,27] Most of the high-throughput effort has focused, however, on calculating properties of small molecules rather than infinite chains, although polymers have been considered in principle,[26] because predicting electronic structure of a polymer or large oligomer is computationally expensive.

Broadly speaking, there are two approaches taken to predict polymer properties with finite computational resources: by approximating a polymer with a small number, n, of repeat units with periodic boundary conditions (PBC)[28−30] or by computing the properties for oligomers of varying n and extrapolating to the infinite limit with some model.[28,29,31−36] PBC based methods may not be the ideal choice for fused-ring copolymers used in current OPV applications,[7,13−16,21,37] because the angle between rings along the polymer backbone is not always zero; hence, it is not trivial to define a periodic system absent some additional assumptions about helicity. One

could artificially planarize the polymer but this would lead to shifts in predicted orbital and excitation energies due to the resulting overestimates of the intermonomer conjugation. Hence, such an approach might be untrustworthy. Similarly, oligomer extrapolation methods also can be problematic because they generally have been found to require calculations for fairly large n to fit results to a chosen extrapolation model.[28,29,36] If fitting the model takes too large an n, it may not be useful in practice since large enough n might not be readily calculated for complex fused-ring structures. Hence, predictions of electronic structure for CP that use extrapolations that rely on large n or that use PBC based methods may not be feasible for day-to-day prediction or for high throughput screening of hundreds or thousands of candidates.

To overcome these limitations, in this paper we describe two approaches to building a tight-binding-like model that we call fragment frontier orbital extrapolation (FFOE) and use them to extrapolate to the polymer limit based on a finite number of small oligomers. The FFOE methods can be considered, depending on one's theoretical bent, to be in the spirit of Hückel models,[38,39] of tight-binding approaches,[40] or of more recent fragment molecular orbital (FMO) approaches[41–43] for electronic structure. We limit the scope of the models we introduce here to predicting the frontier orbital energies: the highest occupied molecular orbital (HOMO); the lowest unoccupied molecular orbital (LUMO); and the first excited state energy. With this restriction to frontier energies, the model becomes extremely simple and useful for predicting polymer properties.

There have been several important studies and review articles of how to extrapolate energy gaps to the polymer limit for conjugated polymers.[28,29,36,39] It is not our purpose here to recapitulate these authors' discussions, but it is worth noting that all of these papers find that simple extrapolations that go as $1/n$ fail to accurately predict oligomer properties in the large n limit. This is unsurprising, since the $1/n$ behavior for gaps is expected only for nearly free electron models that likely do not represent the physics of π electrons in complicated conjugated polymers. Extrapolation forms from the literature include versions that add a $1/n^2$ term, include a periodic modulation of a potential for nearly free electrons, use simple exponential forms, or use Kuhn-type extrapolations based on interacting single and double bonds treated as coupled oscillators.[28,29,33,36,39] A detailed and important discussion of how the two parameters in a Kuhn-like model relate to energy shifts and the ultimate band gap of a polymer has been given by Wykes et al.[36] They have stated that extrapolations based on a Kuhn model appear to need larger n ($n \geq \sim 10$) than we have found necessary with the alternative FFOE extrapolation presented here.

The literature on oligomer-based extrapolations has focused on excitation energies or HOMO−LUMO gaps.[28,29,31–35] This is useful but extrapolations of the individual molecular orbital energies are themselves of interest because the orbital energetics can determine, for instance, the choice of electrodes for a working device (to the extent that isolated molecule energetics control energetics within a film). The tight binding FFOE described here allows energy levels and gaps to be extrapolated with equal ease. In their review of extrapolation procedures to the polymer limit, Torras et al.[39] have pointed out that ionization potentials seem to be fitted better by a Hückel model approach so one would expect HOMO levels, which approximate ionization potentials, to follow this form.

The first form of FFOE we introduce here is mathematically identical to the Hückel method and we will see that FFOE does do well for modeling HOMO energies as a function of oligomer length.

A key conclusion of this paper is that one does not need to go to large n to predict energy levels or gaps that shift by as much as ∼2 eV in going from the monomer to the polymer limit: A shift of ∼1 eV going from the monomer to the dimer implies the ∼2 eV shift for the infinite chain. This ability to get close to the polymer limit with just monomer and dimer calculations may be very useful for materials design because many papers on novel materials include the calculation of electronic properties (HOMO, LUMO, excitation energy) for monomers or dimers to understand the polymer properties.[13–15,21,24,27,34,37,44–47] Hence FFOE allows estimation of polymer properties with no additional computations than typically already are being performed, potentially aiding in materials discovery efforts.

In the rest of this paper we introduce two variations of FFOE and show that both variants provide a simple and inexpensive way to predict CP frontier orbital energetics without having to compute very large or periodic systems. One variant uses calculations with $n = 1$ and $n = 2$ for the extrapolation and the other also incorporates computed electronic structure for $n = 4$ to refine the prediction. We then demonstrate the usefulness of FFOE by comparison to explicit density functional theory calculations on both homopolymers and copolymers, with special attention to a subtlety associated with choosing an appropriate repeat unit for polythiophene. We also compare how well the aforementioned Kuhn-type extrapolation for energy gaps performs in comparison to both FFOE models. We conclude with a discussion of the method, the results, and possible extensions.

2. FFOE TIGHT BINDING MODEL

In this section we describe two simple models that relate the frontier orbital energies and excited state energies of composite conjugated molecules to the frontier energies of the individual monomers comprising the combined system. These models rely on three physically reasonable assumptions, and we show in this paper that these allow accurate extrapolation to the polymer limit.

Our three assumptions are as follows. First, we posit that for any length oligomer a given type of frontier molecular orbital (e.g., the HOMO or the LUMO) is composed solely of a linear combination of that type of orbital from each monomer unit, reminiscent of FMO approaches to electronic structure.[41,42] It is worth noting that when such a tight binding-like approach was applied to understand the density of states of polymer films of a polythiophene,[42] interchain interactions induced mixing among additional monomer orbitals so that the assumption made here that one can use only the frontier orbitals breaks down. Second, we assume that the coupling between monomer orbitals is only between nearest neighbors. If these two approximations are valid, we would expect that the HOMO orbital of a dimer would be the difference between two monomer HOMOs (an antibonding orbital) and that the dimer LUMO orbital would be the sum of two monomer LUMOs (a bonding orbital). This expectation can be seen in Figure 1 to hold for a benzodithiophene monomer and dimer. Third, we take the frontier energy levels of the monomer and of the computed oligomers to be those for a hydrogen-terminated species.
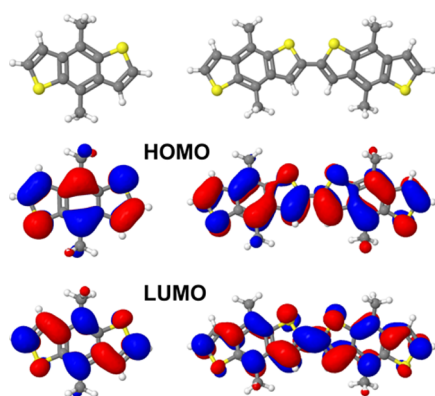
Figure 1. Top: Locally optimized structures for hydrogen-terminated dimethyl-benzodithiophene for the monomer (at left) and dimer (at right); middle: Kohn−Sham HOMO contours with a contour value chosen to encompass 80% of the electron density; bottom: Kohn−Sham LUMO contours with a contour value chosen to encompass 80% of the electron density. The density functional theory calculations were performed as described in section 3.

(a) Monomer   (b) Oligomer   (c) Correlation diagram
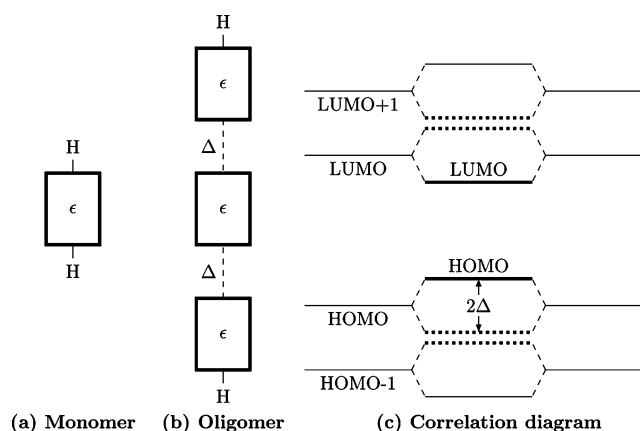
Figure 2. Pictorial schematics of the intermonomer coupling incorporated into the model. Panel a: Representation of the H-terminated monomer and the energy information that enters the single-state Hückel model. Panel b: Schematic representation of coupling between monomer electronic states for a linear trimer. Panel c: Correlation diagram for energetics of dimer orbitals built from monomer molecular orbitals.

The third assumption deserves some examination. One might imagine that a more chemically astute approach would use monomer units with the singly occupied orbitals of a diradical monomer (akin to a dangling σ orbital), since the unpaired electrons on neighboring monomers are what interact and form the bond connecting the monomers. For systems of interest for organic electronic applications, we may ignore this possibility because the electrons in either a carbon−hydrogen or a carbon−carbon σ bond have energies far lower than those expected for the delocalized frontier (π) orbitals. Thus, the states with the unpaired electrons that participate in forming a C−C bond between monomers lie far below the HOMO or LUMO levels of interest to us and are not relevant to the frontier orbitals. A side benefit of our choice is that it is far easier to calculate the electronic structure of hydrogen-terminated neutral molecules than it is for diradicals, making the resulting theory much more convenient for computational modeling. One might wonder whether one would want to methyl terminate rather than hydrogen terminate, thus having a C−C bond for the monomer unit; we do not expect this to be as useful for the polymer limit because a methyl group does have a nonzero Hammett sigma parameter[48] so using methyl termination would likely shift monomer energies more than hydrogen termination relative to the σ bond between two aromatic carbons that occurs in an oligomer.

2.1. Uniform Coupling Model. The simplest model we will consider for monomer−monomer coupling takes all monomer orbitals to have a site energy ϵ (Figure 2a), with a single coupling energy, Δ, between nearest-neighbor monomers. This model is depicted pictorially for linear polymers in Figure 2b. The site energy and coupling energy are different for the different states (HOMO, LUMO, or first excitation energy). In principle, these couplings can be computed from knowledge of the overlap between orbitals on neighboring monomers[7] but because the main goal of this paper is to introduce the use of a simple analytical form to extrapolate to the polymer limit we treat the monomer and coupling energies as parameters to be determined from calculations on small oligomers. We define the notation HOMO(n) and LUMO(n) to denote the HOMO and LUMO orbitals, respectively, for an n-mer, and similarly for HOMO−1(n), LUMO+1(n), etc.

This assumption of uniform site energy and uniform coupling yields a simple and well-known analytical expression for energies as a function of oligomer length but the formulas apply only for homopolymers. For the sorts of donor−acceptor alternating copolymers that give low band gaps and are of interest in OPV,[7,13,15,21,22,24,25,47] we will show that choosing the donor−acceptor pair to be the monomer produces an accurate extrapolation. We attempted to construct a version of this model that takes the individual donors and acceptors to be monomer units with different properties, but we were unable to find formulation based only on frontier energies of the mononers that could reliably predict the energetics of a donor−acceptor pair. Hence, we restrict ourselves here to a view of alternating copolymers as homopolymers with a larger repeat unit.

For the model of monomer−monomer coupling illustrated in Figure 2b, the Hamiltonian matrix that describes nearest-neighbor coupling between monomer units is a tridiagonal Toeplitz matrix,[49]

$$H(\epsilon, \Delta) = \begin{bmatrix} \epsilon & \Delta & 0 & \cdots\cdots\cdots \\ \Delta & \epsilon & \Delta & 0 & \cdots\cdots \\ 0 & \Delta & \epsilon & \Delta & 0 & \cdots\cdots \\ \cdots\cdots\cdots\cdots\cdots \\ \cdots\cdots & 0 & \Delta & \epsilon & \Delta \\ \cdots\cdots\cdots & 0 & \Delta & \epsilon \end{bmatrix} \quad (1)$$

where ϵ is the isolated monomer energy level of interest for the monomer and Δ is the intermonomer coupling energy associated with that energy level. For an n-mer, standard Fourier techniques give the well-known result that the eigenvalues of eq 1 are[49]

$$\epsilon_j(n) = \epsilon + 2\Delta \cos\left(\frac{\pi j}{n+1}\right), \quad (1 \leq j \leq n) \quad (2)$$

where j is the index of the eigenvalue.

Taking the intermonomer coupling to be a positive number, the HOMO(n) energy level ($j = 1$) is

$$\epsilon_{\mathrm{HOMO}}(n) = \epsilon + 2\Delta\cos\left(\frac{\pi}{n+1}\right) \tag{3}$$

and the LUMO(n) level (or first excited state energy) ($j = n$) is

$$\epsilon_{\mathrm{LUMO/1st}}(n) = \epsilon + 2\Delta\,\cos\left(\frac{\pi n}{n+1}\right) = \epsilon - 2\Delta$$

$$\cos\left(\frac{\pi}{n+1}\right) \tag{4}$$

The tight binding forms above also bear some similarity to Kuhn-type extrapolations that also have appeared in the literature.[28,29,39] These take the form $E_1\sqrt{1 + D_k\cos[\pi/(n+1)]}$, which can be cast into the same cosine dependence shown above when D_k is much less than one. With FFOE, for a dimer the energies in eqs 3 and 4 reduce, respectively, to the usual $\epsilon + \Delta$ and $\epsilon - \Delta$, and in the polymer limit, $n \to \infty$, to $\epsilon + 2\Delta$ and $\epsilon - 2\Delta$. It is worth noting that if there were no mixing expected between HOMO−1(2) and lower-lying orbitals, one could also estimate the intermonomer coupling using the classic energy level splitting between HOMO−1 and HOMO levels for a pair sites, $\Delta = (E_{\mathrm{HOMO}(2)} - E_{\mathrm{HOMO}-1(2)})/2$. By using the shift only of HOMO(1) to HOMO(2), we avoid errors that might be caused by this mixing. In addition to the LUMO energy, in the rest of this paper, we call the first excited state energy either "1st" or "optical LUMO", which we define to be the HOMO energy plus a first excitation energy computed from an appropriate excited-state electronic structure method. The optical LUMO is an approximate energy of an electron in the lowest excited state of the oligomer, under the approximation that the excitation can be considered to involve only a single excitation of an electron out of the HOMO. It serves here as a useful way to show how the energy gap evolves with n on the same plot as the HOMO and LUMO energies.

It is important to keep in mind that in the polymer limit the above formulas should only apply when the HOMO(n) and LUMO(n) levels asymptotically approach different values, which is required for the validity of our assumption that the HOMO of the polymer is just a combination of monomer HOMOs, and that the polymer LUMO consists of monomer LUMOs, Hence, we do not expect the simple formulas given above to apply for a metallic or semimetallic polymer in which the HOMO−LUMO gap becomes small for large n. Similarly, this model explicitly neglects the possibility that more than one monomer state will contribute to the analogous oligomer state. For example, the HOMO−1(1) orbital, is assumed to not contribute to the *two* highest occupied states of the dimer, HOMO(2) and HOMO−1(2), which are taken to have only HOMO(1) contributions. This is illustrated in the correlation diagram of Figure 2c that builds dimer molecular orbitals out of monomer "atomic" orbitals.

The approximation that there is no mixing among different orbitals must break down when the spacing between monomer energy levels is similar to the intermonomer coupling: the dotted molecular orbital energy levels in Figure 2c show that the bonding combination of the HOMO monomer orbitals and the antibonding combination of HOMO−1(1) orbitals (Figure 1) could in principle produce energy levels close enough together that the HOMO−1(2) and HOMO−2(2) states should be treated as mixtures of both the HOMO(1) and HOMO−1(1) orbitals; similar considerations also apply for unoccupied orbitals above the LUMO, again shown as dotted

lines in Figure 2c. In contrast, the HOMO(n) and LUMO(n) molecular orbitals are displaced away from molecular orbitals that could contaminate them with admixtures of other orbitals so we expect that the highest-energy eigenstate of the model will be an accurate representation of HOMO(n) and the lowest-energy eigenstate of this model will be an accurate representation of the LUMO(n) and of the dimer first excited state energy.

In summary, to use the single coupling FFOE to extrapolate to the polymer limit, the algorithm would be to use DFT to compute energies for a monomer and a dimer; take the difference to determine Δ; the polymer limit is $\epsilon \pm 2\Delta$. One can check the efficacy of the approach by using eqs 3 and 4 and comparing the predictions to explicit calculation on as large an n-mer as one can compute with DFT.

There are a few interesting consequences of the model predicted by eqs 3 and 4. The formulas show that Δ can be determined solely from calculations of the monomer and dimer energies: Δ is just the absolute value of the difference between the $n = 1$ and 2 energies. This approach of using energy shifts in going from an isolated molecule to a pair of molecules to determine coupling energies has found success for estimating intermolecular coupling energies for tight-binding models in molecular crystals[7,50,51] and in other organic molecular films,[52] and we will demonstrate below that the approach also works for intramolecular coupling along a polymer backbone.

2.2. Ends-and-Middle Model. The model described in the previous section requires only one parameter, Δ, to describe the length dependence of oligomer energetics. This simplicity comes at the cost of neglecting the possibility of end effects, which may need to be taken into account if one is to extrapolate to the infinite-chain limit from relatively small oligomers. Why might we need to treat the ends differently? Given the distinct environments of a monomer unit somewhere in the middle of an oligomer chain (neighbors on both sides) and of a monomer unit at one end of the chain (only one neighbor), it is likely that the twist angle between monomers in the middle will not be the same as that between a terminal monomer and its lone neighbor. Different inter-ring angles would lead to different overlaps between monomer π orbitals so the intermonomer coupling would not be the same for the two cases. Here we extend the model to incorporate this finite-size effect.

To include different coupling for the ends, we replace the single coupling energy, Δ, with a coupling, Δ_e, between a terminal, or "end", monomer and its neighbor, and a coupling, Δ_m, between two nonterminal, or "middle", monomers. For dimers and trimers, the only coupling is either between two end monomers ($n = 2$) or between a single monomer in the middle and each of two end monomers ($n = 3$), so eqs 3 and 4 apply for $n = 2, 3$ with Δ replaced by Δ_e. For longer oligomers, both of the coupling coefficients appear. For example, for $n = 4$ the Hamiltonian matrix becomes

$$H(\epsilon, \Delta_e, \Delta_m) = \begin{bmatrix} \epsilon & \Delta_e & 0 & 0 \\ \Delta_e & \epsilon & \Delta_m & 0 \\ 0 & \Delta_m & \epsilon & \Delta_e \\ 0 & 0 & \Delta_e & \epsilon \end{bmatrix} \tag{5}$$

and for $n = 5$ it is

$$H(\epsilon, \Delta_e, \Delta_m) = \begin{bmatrix} \epsilon & \Delta_e & 0 & 0 & 0 \\ \Delta_e & \epsilon & \Delta_m & 0 & 0 \\ 0 & \Delta_m & \epsilon & \Delta_m & 0 \\ 0 & 0 & \Delta_m & \epsilon & \Delta_e \\ 0 & 0 & 0 & \Delta_e & \epsilon \end{bmatrix} \tag{6}$$

The "end" coupling, Δ_e, can be determined from monomer and dimer calculations (or by fitting eqs 3 and 4 to results from $n = 1$, 2, and 3 if desired. To determine Δ_m, one also needs the $n = 4$ HOMO and LUMO/first energies

$$\epsilon_{\text{HOMO}}(4) = \epsilon + \frac{1}{2}\left(\Delta_m + \sqrt{\Delta_m^2 + 4\Delta_e^2}\right) \tag{7}$$

$$\epsilon_{\text{LUMO/1st}}(4) = \epsilon - \frac{1}{2}\left(\Delta_m + \sqrt{\Delta_m^2 + 4\Delta_e^2}\right) \tag{8}$$

The parameter Δ_m for each type of state is determined by inserting the appropriate values for ϵ, (from $n = 1$ case), Δ_e (from $n = 1$ and 2), and the explicitly calculated tetramer energy into either eq 7 or eq 8 and solving numerically for Δ_m with any standard root-finding method.

With some straightforward approximations, one can avoid the need to search for roots of the above equations. In the Appendix, we show that by treating the different coupling value at the ends as a perturbation on an otherwise uniform chain, to first order in $\Gamma = \Delta_e - \Delta_m$ the energy levels are modified from the single-coupling model to obey eqs 11 and 12 in the Appendix. These formulas allow Δ_m to be found from the $n = 4$ energy by simple algebra rather than resorting to a root search. Because a root search is numerically trivial, we will not use them for that purpose in the calculations described below but we do note that the perturbative formulas predict that as n becomes infinite the ends-and-middles energies approach the single-coupling-coefficient forms, with the value of the coupling that survives in the limit being Δ_m: $\lim_{n\to\infty} \epsilon(n) = \epsilon \pm 2\Delta_m$, as one would expect.

We will show in the next Section that the single-coupling FFOE model provides satisfactory agreement with explicit calculations and that the ends-and-middle FFOE model improves the extrapolation. The results show that there is little apparent need for additional parameters, such as next-nearest-neighbor coupling elements or couplings associated with larger n, to describe the length dependence of energetics in CP chains.

3. COMPUTATIONAL METHODS

All of the calculations were performed with the Gaussian 09 electronic structure program using density functional theory (DFT) and time-dependent DFT (TDDFT) for excited state energies[53] and the B3LYP hybrid exchange-correlation functional and a 6-31g(d) Pople-type basis set were used. We saw similar convergence properties as a function of n for other basis sets but those results are not reported here. Reported HOMO and LUMO orbital energies are those of the Kohn−Sham molecular orbitals.

Most of the plots of the length dependence of energy levels in this paper are versus number of repeat units, n. Plots of chain length dependence versus $1/n$ are common in the literature, however, so we also have plotted the results this way in Figures S1−8 of the Supporting Information. We used a derivative-free secant method to determine Δ_m from eqs 7 and 8. The FFOE

parameters (ϵ, Δ_e, and Δ_m) extracted for all of the structures shown in Figure 3 are given in Table 1 and all of the computed oligomer energies, $\epsilon(n)$, are tabulated in the Supporting Information.
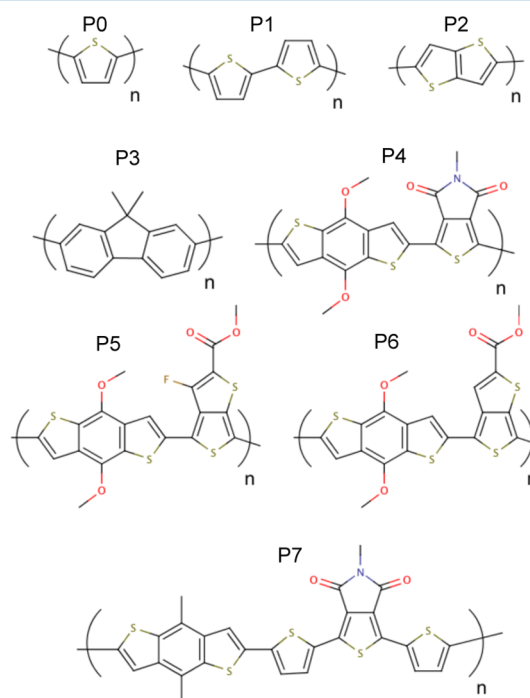

Figure 3. Polymers examined in this work.

4. RESULTS

In this section we demonstrate the accuracy of the FFOE extrapolations for the polymer structures shown in Figure 3. We show results for both homopolymers and low-bandgap push−pull copolymers that have been used recently in OPV applications[15,37,54] and all extracted model parameters are given in Table 1. We found that for polythiophene care must be taken when choosing the size of the repeat unit (P0 or P1). The wrong choice leads to incorrect extrapolated excited-state energies, and we discuss the reasons for this and the proper choice in a separate sub-section.

4.1. Nonthiophene Polymers. Figures 4 and 5 show the frontier orbital energies and the two FFOE models for polymers P2−P7. For all of these systems, the uniform coupling model does fairly well, giving reasonably accurate large-n values more than 1 eV away from the values for $n = 1$ and 2. The ends-and-middles model appears somewhat more accurate such that if one can afford computations at the $n = 4$ level this would be recommended. An interesting trend seen in Table 1 is that the intermonomer coupling appears to be smaller the larger the monomer unit. Hence, larger monomer units lead to smaller shifts going from the $n = 1$ to the polymer limit than smaller monomer units. This feature can be understood from the facts that Δ is proportional to the overlap of orbitals between two monomers and that orbitals must be normalized: A longer monomer has a larger orbital spread along it, so the overlap between orbitals on different monomers will necessarily be smaller just because the requirement that two electrons occupy an orbital means that the normalization will reduce the magnitude of the overlap for larger monomer units.

Table 1. Extrapolation Parameters for Oligomers P0−P7, Extracted as Described in the Text from the $n = 1$, 2, and 4 Values of the Computed Electronic Properties[a]

polymer label	energy type	ϵ	Δ_e	Δ_m	1 coupling limit ($\epsilon \pm 2\Delta_e$)	2 coupling limit ($\epsilon \pm 2\Delta_m$)
P0	HOMO	−6.335	0.859	0.834	−4.617	−4.667
	LUMO	−0.207	1.039	1.096	−2.285	−2.400
	optical LUMO	−0.408	1.038	1.084	−2.484	−2.576
	exc. energy	5.926	1.896	1.917	2.134	2.092
P1	HOMO	−5.476	0.513	0.404	−4.450	−4.669
	LUMO	−1.246	0.684	0.619	−2.614	−2.483
	optical LUMO	−1.446	0.675	0.725	−2.796	−2.897
	exc. energy	4.030	1.187	1.133	1.656	1.763
P2	HOMO	−5.853	0.565	0.580	−4.723	−4.693
	LUMO	−0.724	0.883	0.893	−2.490	−2.510
	optical LUMO	−0.972	0.835	0.926	−2.642	−2.825
	exc. energy	4.882	1.401	1.507	2.080	1.869
P3	HOMO	−5.732	0.399	0.339	−4.934	−5.054
	LUMO	−0.743	0.464	0.420	−1.671	−1.582
	optical LUMO	−1.111	0.467	0.477	−2.045	−2.065
	exc. energy	4.621	0.865	0.818	2.891	2.984
P4	HOMO	−5.406	0.126	0.101	−5.154	−5.205
	LUMO	−2.294	0.404	0.305	−3.102	−2.903
	optical LUMO	−2.649	0.341	0.327	−3.331	−3.304
	exc. energy	2.757	0.467	0.428	1.823	1.900
P5	HOMO	−5.260	0.227	0.171	−4.806	−4.918
	LUMO	−2.257	0.331	0.325	−2.919	−2.906
	optical LUMO	−2.582	0.271	0.354	−3.124	−3.291
	exc. energy	2.677	0.498	0.529	1.682	1.619
P6	HOMO	−5.173	0.274	0.167	−4.625	−4.839
	LUMO	−2.181	0.321	0.300	−2.823	−2.780
	optical LUMO	−2.463	0.284	0.344	−3.031	−3.151
	exc. energy	2.711	0.559	0.518	1.593	1.675
P7	HOMO	−5.187	0.126	0.077	−4.935	−5.034
	LUMO	−2.450	0.256	0.202	−2.962	−2.853
	optical LUMO	−2.704	0.310	0.248	−3.324	−3.200
	exc. energy	2.483	0.436	0.325	1.611	1.832

[a]All values are in electronvolts (eV).

The FFOE approach appears to perform about equally well both for homopolymers and push−pull copolymers, provided the repeat unit for the copolymer system is chosen to be the push−pull pair that comprises a repeat unit for what is effectively then a homopolymer. This is an important aspect of the simplified FFOE model. As we pointed out earlier, the simple theory presented in the previous section applies only to frontier orbitals of homopolymers, so for copolymers an appropriate uniform repeat unit must be chosen.

4.2. Polythiophenes. The appropriate choice of monomer unit also is important for homopolymers. In particular, the upper panel of Figure 6 shows that using a single thiophene unit (P0) to model poly thiophene gets the excited states (LUMO and optical LUMO) wrong by several tenths of an eV. If, instead, one takes the monomer unit to be two thiophenes (P1) one obtains much more accurate predictions for excited state energies in the large-n limit.

The need to use P1 instead of P0 for polythiophene may not be unexpected. It is well-known that for polythiophene the excited states are largely quinoidal in character,[30,37,55] with double bonds that run along the backbone including along the carbon−carbon bonds connecting thiophene units. With P0, however, the $n = 1$ unit has terminal C−H bonds and the C−H portion cannot support a double bond. Hence, the $n = 1$ P0 case cannot represent the energy of the quinoidal excited state

accurately. Using P1 allows at least some quinoidal character since $n = 1$ for P1 has an interthiophene C−C bond. This allows the successful extrapolation of excited state energies for poly thiophene shown in the bottom panel of Figure 6. The usefulness of our proposed extrapolation method for polythiophenes also can be seen by comparison to results from a previous paper on oligomer-based extrapolations to the polymer limit:[32] There, the n dependence of the HOMO−LUMO gap for polythiophene and polyselenophene was plotted taking the repeat unit to be a single five-membered ring (cf. P0). If we take their dimer to be our $n = 1$, and similarly their tetramer to be our $n = 2$, the single-coupling FFOE accurately predicts the ∼2 eV shift from their dimer to the polymer limit reported in their calculations for thiophene and selenophene.

Given the presumed importance of supporting a quinoidal state for predicting excited state energetics, why does fused dithiophene, P2, not require a bis-dithiophene monomer unit for accurate extrapolation of excited states? The results suggest that the fused dithiophene moiety is able to support the quinoid form of the excited state well enough that a single unit suffices. Hence, we conclude that the excited state energy of the hydrogen-terminated dithiophene monomer is not appreciably affected by the lack of carbon−carbon bonds on its edges. Apparently, delocalization between two thiophene entities,
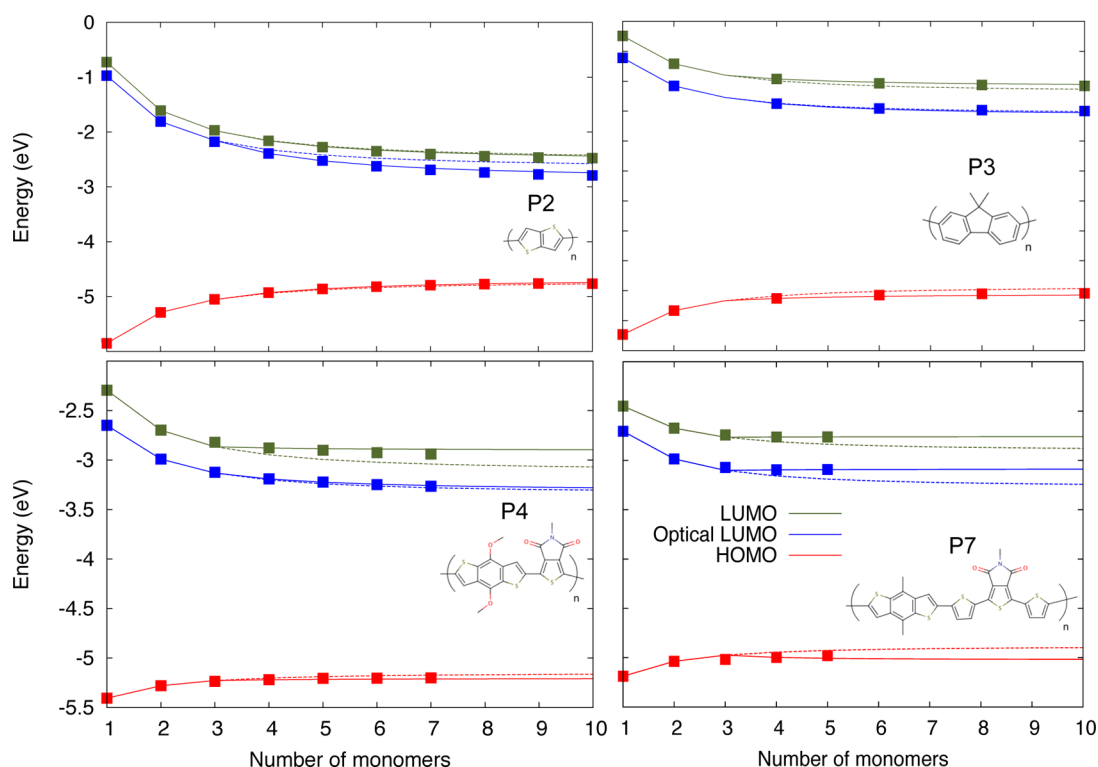
Figure 4. Comparison of computed oligomer energies for various *n* (points) to extrapolations from uniform coupling model (dashed curves) and ends-and-middles model (solid curves) for the indicated homopolymers (top) and push−pull copolymers (bottom). The energy levels (in order of bottom to top in each panel) are HOMO (red), optical LUMO (blue), and LUMO (green).
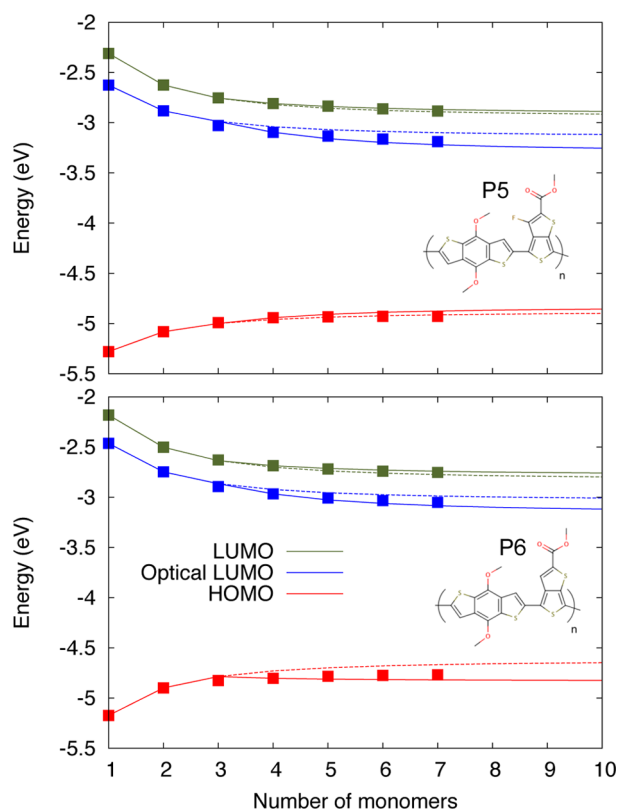

Figure 5. Comparison of computed oligomer energies for various *n* (points) to extrapolations from uniform coupling model (dashed curves) and ends-and-middles model (solid curves) for the indicated push−pull copolymers. The color scheme is the same as in Figure 4.
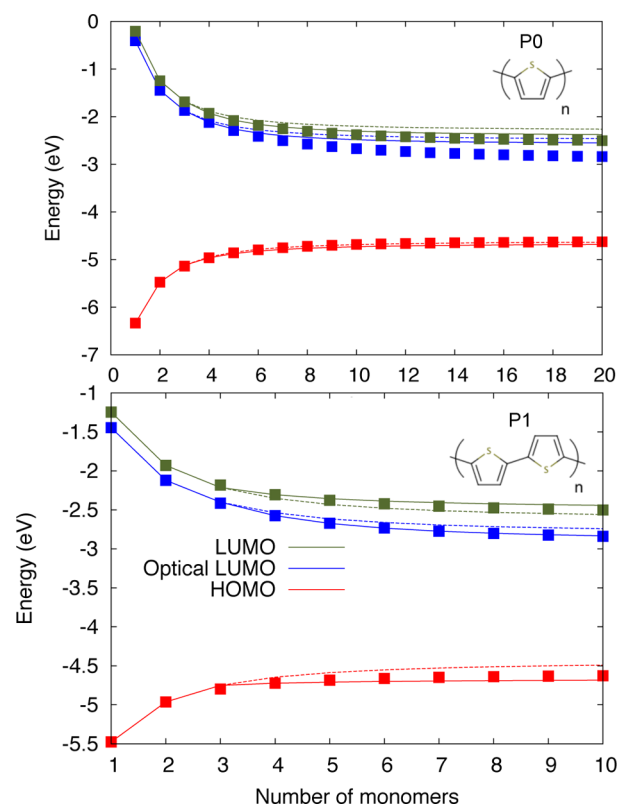
Figure 6. Extrapolation to large *n* for polythiophene with two different choices of monomer unit: a single thiophene (at top) and bis-thiophene (at bottom). The notation is the same as in Figure 4.

fused or not, is all that is needed for reasonably accurate excited state frontier energies of thiophene-based polymers, at least at the DFT level.

4.3. Comparison of FFOE Model to Hückel- and Kuhn-Type Fits. One of the common fitting forms used for oligomer-based extrapolation of energy gaps is the Kuhn form[29,33,36,39] mentioned in the Introduction, which can be put into the form[36] $E(N) = E_1\sqrt{1 + D_k \cos \pi/(N+1)}$. The cosine dependence of this form is strikingly similar to the single-coupling FFOE, or Hückel, model form, either eq 3 or eq 4, but the square root in the Kuhn function means that the shape will differ as a function of n. In this sub-Section, we examine how well such a Kuhn-style form works for energy gaps as compared to the FFOE extrapolations, but we do not report results for fits to energy levels themselves.[56]

In fitting the Kuhn form Wykes et al.[36] take N to be the largest number of double bonds along the shortest conjugated pathway in the oligomer. Hence, for example, $N = 2n$ for a poly thiophene oligomer with the n monomer units if the unit is taken to be just a single thiophene. This is consistent with how the Kuhn model was derived so a fit of the Kuhn model requires the multiplicative factor for the number of double bonds along the shortest conjugated path, n_d, to be determined for each monomer unit, giving $N = n_d n$. The values of n_d chosen for each repeat unit for polymers P1–P7 are given in Table 2.

Table 2. Root-Mean-Squared Error for the Computed Energy Gap for (a) the Two Parameter Kuhn Formula; (b) a Two Parameter Hückel Fit; (c) the Uniform Coupling; and (d) Ends-and-Middle FFOE Models[a]

polymer	n_d	Kuhn	Hückel fit	uniform coupling	ends-and-middle
P1	4	0.058	0.007	0.033	0.038
P2	3	0.098	0.052	0.152	0.022
P3	4	0.056	0.018	0.054	0.004
P4	6	0.034	0.008	0.028	0.011
P5	6	0.049	0.005	0.019	0.019
P6	6	0.039	0.009	0.027	0.013
P7	10	0.017	0.023	0.073	0.026
Avg.		0.050	0.017	0.055	0.019

[a]All quantities are in units of eV. n_d is the number of double bonds in the shortest conjugated path through the monomer needed for the Kuhn fit, as described in the text.

To compare the accuracies of the different models we performed least-squares fits of first excitation energy to the Kuhn form, a (two parameter) Hückel form, eq 4, and the two FFOE extrapolations to first excitation energy for P1–P7 (leaving out P0 because that repeat unit was shown in the previous sub-Section to be inappropriate for excited state energies). We remind the reader that the FFOE extrapolations are not fits to all of the computed energies because the extrapolations are fully determined by the calculated $n = 1,2$, and 4 values. To quantify the quality of the two fits and the two FFOE extrapolations introduced in this paper, we computed the root mean squared error, $\sqrt{1/N_{max} \sum_{n=1}^{N_{max}} (E_n - E_{model}(n))^2}$, for each model as reported in Table 2. For poly fluorene, P3, our computed data set does not include most odd numbered oligomers, hence the summation is only over the data points shown in Figure 4, with appropriate normalization. The results in Table 2 show that for the polymers considered here the Kuhn fits to the energy gap

generally perform about as well as the single-coupling FFOE model, but are not as good as either a (two fitting parameter) Hückel form, $\epsilon \pm 2\Delta \cos[\pi/(n+1)]$, or the ends-and-middle FFOE model.

Figure 7 shows plots versus n and $1/n$ of the fits and extrapolations for the energy gaps of polymers P3, P4 and P5, with these three polymers chosen for plotting because they span a range of the relative performances for the Kuhn, Hückel fit and FFOE models. Similar plots for the other polymers are given in figures S9–S16 in the SI. The x axis in the plots is the number of monomers but the value of N that enters the Kuhn fit is $N = n_d n$. Examination of Figure 7 suggests that Hückel-like models do a better job of going through the data at both smaller and larger n than do Kuhn-type extrapolations, which do not capture the shape of the gap versus n for $n \leq 3$. The apparent inability of the Kuhn shape to simultaneously capture changes at small and large n may account for the observation[36] that Kuhn-like extrapolations require fairly large values of n ($n \geq \sim 10$). Such large values were not solely used here because our focus was on extrapolation based on calculations for small n; however, it seems fair to point out that the results in Table 2 likely are not representative of the best possible accuracy of Kuhn-like extrapolation methods.

5. DISCUSSION

In this paper we have shown that the chain length dependence of frontier orbital energies for conjugated polymers can be predicted accurately using either of two simple tight-binding-like models that we call FFOE. The mathematics and chemistry associated with nearest neighbor monomer–monomer coupling are trivial and have appeared in many guises and applications,[7,41,50,51] so the point of this paper is to point out the practical capability that FFOE gives to approximate large-n or infinite chain energetics using only calculations (or, one presumes, experimental measurements) for $n = 1$ and 2 (and optionally, $n = 4$), with the simple form for the infinite n limit, $\lim_{n\to\infty}\epsilon(n) = \epsilon \pm 2\Delta$. What is probably of most practical importance for making use of an FFOE approach is our finding that even though there can be large shifts in the frontier orbital energies and energy gaps ($\sim > 2$ eV) going from the monomer to the polymer limit, one can get a good idea of what the energetics will be just by computing the shift in going from $n = 1$ to 2. The conclusion that this approach works even for complex copolymers of current interest for organic electronics means that one can get estimates of polymer properties from relatively inexpensive calculations, which may be of use in streamlining materials discovery efforts. We also demonstrated that overall the ends-and-middle version of the FFOE appears to provide better fidelity to our simulation results than fits of alternative functional forms, which suggests that for the types of fused-ring polymer systems considered here the simple tight-binding approach succeeds at capturing the relevant physics for the frontier orbital energies. The fact that reasonable extrapolation to the polymer limit is possible based on small systems allows exploration of the frontier energies of polymers and larger oligomers for far less computational expense than is possible with other extrapolation methods that rely on fitting functional forms with larger values of n.[28,32,36,39] In addition, the ability to extrapolate to the polymer limit with reasonable accuracy from just monomer and dimer results means that the many papers that have computed monomer and dimer electronic structures[13–15,21,27,34,37,44–47] can be revisited if
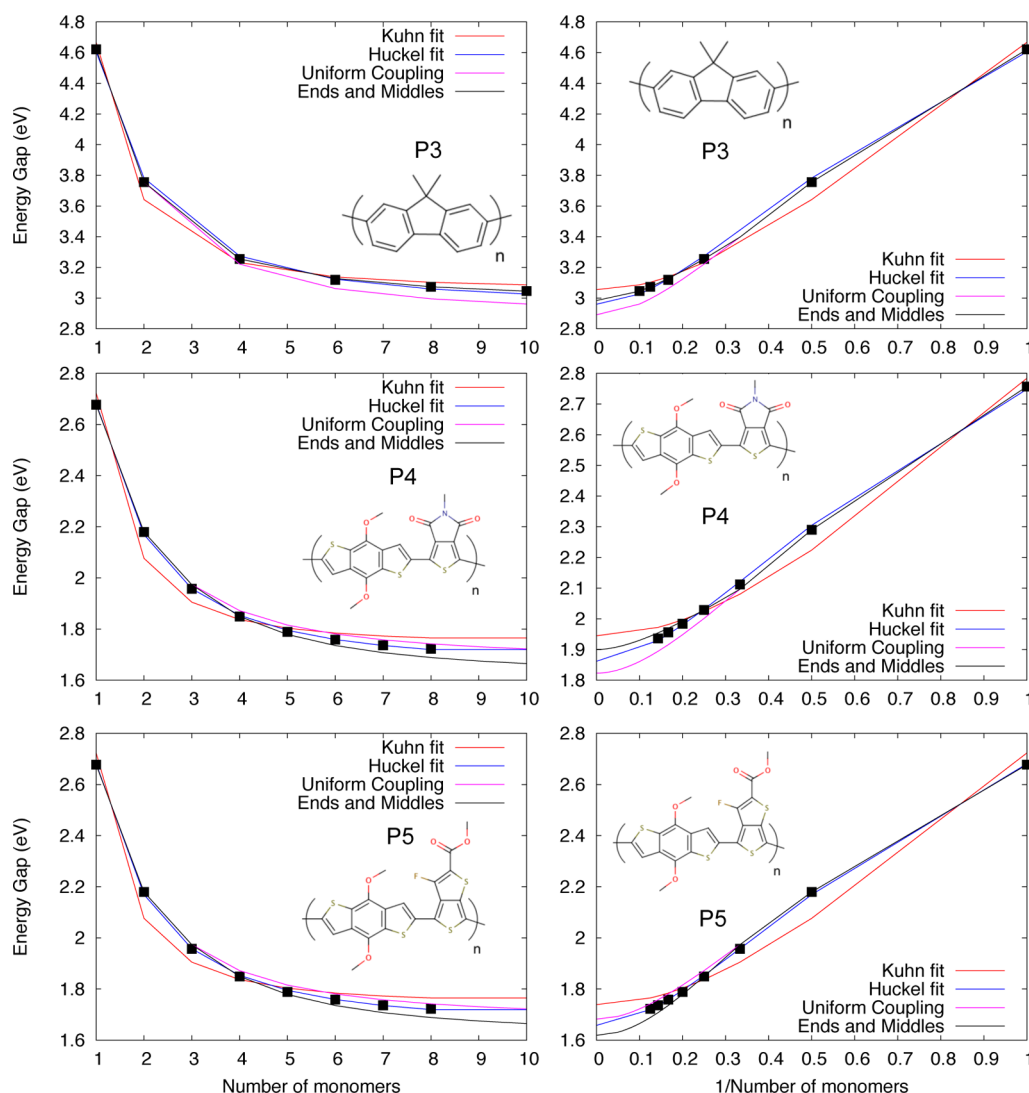
Figure 7. Kuhn (red curve) and Hückel (blue curve) fits to the computed energy gaps (squares) for P3 (top panels), P4 (middle panels), and P5 (bottom panels) as a function of the number of monomer units, n, (at left) and $1/n$ (at right). The uniform coupling FFOE (violet curve) and ends-and-middles (black curve) are also plotted. As described in the text, while the plot is versus the number of monomers, the value of N that enters the Kuhn fit is actually the number of double bonds along the conjugated backbone for the Kuhn type fits, $N = n_d n$.

desired so that approximate polymer-limit energetics can be obtained without the need to redo any calculations.

It has been pointed out that different conformational and structural isomers of a material can have quite different electronic properties.[57] This computational study showed, for dimers, that different conformations can have HOMO, LUMO and excitation energies that vary by several tenths of an electronvolt. We found that conformational disorder (e.g., flipping an acceptor around a bond) made little difference in extrapolated energies for polymers such as P2−P4, but that P5−P7 showed extrapolated energy gaps that were far more sensitive to the orientation pattern chosen. Our calculations used the minimum energy conformation for the monomer and repeated this along the chain, but for the materials with asymmetric acceptors (P5 and P6) or a backbone that may have significant curvature (P7), there appears to be more sensitivity to conformation. One could imagine going beyond the single-conformation study we have done here by sampling different conformations of monomers and dimers to compute different ϵ and Δ values as a function of conformation. One could then extrapolate using these uniform parameters to arrive at ranges

of values for the polymer limit. More interestingly, one could construct matrices of the form described in section 2 with nonuniform energies and couplings and numerically solve for frontier energies with these random matrices to arrive at reasonable distributions of polymer properties in the face of conformational and isomeric disorder. Such an effort would largely entail careful sampling and weighting of the possible conformations, with the FFOE providing a relatively inexpensive matrix problem to be solved for each conformation. Such an effort is beyond the scope of this paper, but it is an intriguing possibility for beginning to understand the role played by disorder in the copolymer backbones even before the materials are cast into the solid state.

It is worth emphasizing that the FFOE method we presented is not a first-principles electronic structure method. Rather, it is a model-based way to extrapolate from other electronic structure calculations. As such, the accuracy of the results can be no better than the choice of monomer unit and accuracy of the underlying electronic structure method used for the parametrization. Hence, as we have shown for polythiophene, one must have enough chemical or physical intuition about the

electronic structure of the system to choose the monomer unit appropriately. In addition, if a particular method suffers from over- or under-delocalization that results in error in estimating Δ, then the extrapolation would be suspect.[29,36] It would be interesting to study how ϵ and Δ depend on the exchange-correlation functional and basis set in DFT and TDDFT calculations for FFOE, similar to what has been done for Kuhn models[36] although such a study is beyond the scope of this paper.

In addition to these general considerations, the results in Table 1 show an interesting pattern in the Δ values. Systematically, for all structures considered here, the energy shift, Δ, for the HOMO is always smaller than Δ for the LUMO or the optical LUMO. This implies that for all of these structures, polymerization closes the gap more through stabilization of the excited ($\sim$LUMO) state than from destabilization of the HOMO. One can rationalize this by noting that the excited orbitals tend to have quinoidal character,[30,36,37,55] as is seen in Figure 1. This would imply that the excited state orbitals will extend along the bonds connecting the monomers, as can be seen for the LUMO of benzodithiophene in Figure 1, leading to greater intermonomer orbital overlap and hence a larger Δ for the excited quinoidal-character orbitals.

Finally, another aspect of the tight-binding based FFOE approach is that by construction it can be parametrized from any electronic structure method. Hence, one can consider doing calculations with a higher level method than DFT. One could envision performing extrapolations by using a high-level method for the monomer (e.g., Møller−Plesset perturbation theory, configuration interaction, or coupled cluster approaches[58]) to establish ϵ, and then applying a less expensive method such as DFT to find Δ. Whether this or some other mixed-accuracy approach would work, and what choice of

functional/basis set would give the best DFT estimate for Δ is an interesting question[36,39] that mertits further study.

APPENDIX: PERTURBATION THEORY FOR THE ENDS-AND-MIDDLES MODEL

For the general $n \times n$ two-coupling Hamiltonian (cf. eqs 5 and 6) we are unaware of a closed-form solution analogous to that for the single-coupling case; however, a perturbative solution is straightforward. We expect that the energies become independent of the ends as n approaches infinity, so we expect the large-n limit to approach the uniform coupling result (eqs 3 and 4) with Δ replaced by Δ_m. Hence, we treat the difference between the coupling at the end and the coupling in the middle of the chain as a perturbation. Defining $\Gamma = \Delta_e - \Delta_m$, we can write $H(\epsilon, \Delta_e, \Delta_m) = H(\epsilon, \Delta_m, \Delta_m) + \Delta H(\Gamma)$, where for the $n \times n$ case, $\Delta H(\Gamma)_{i,j} = (\delta_{1,2} + \delta_{2,1} + \delta_{n,n-1} + \delta_{n-1,n}) \times \Gamma$. For example, when $n = 5$

$$\Delta H(\Gamma) = \begin{bmatrix} 0 & \Gamma & 0 & 0 & 0 \\ \Gamma & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & \Gamma \\ 0 & 0 & 0 & \Gamma & 0 \end{bmatrix} \tag{9}$$

Denote the unperturbed eigenstates of $H(\epsilon, \Delta_m, \Delta_m)$ for an n-mer as $|j\rangle_n$

$$|j\rangle_n = \sqrt{\frac{2}{n+1}} \sin\left(\frac{\pi j \alpha}{n+1}\right) |\alpha\rangle_n, \quad (1 \le j, \alpha \le n) \tag{10}$$

where $|j\rangle_n$ is eigenstate number j for an oligomer of length n, and $|\alpha\rangle_n$ is the localized basis set element located at monomer position, α in the n-mer. Then to first order in $\Delta H(\Gamma)$, the HOMO energy is approximately

$$\epsilon_{HOMO}(n) \simeq \epsilon + 2\Delta_m \cos\left(\frac{\pi}{n+1}\right) + \left(\frac{4\Gamma}{n+1}\right)\left[\sin\left(\frac{\pi}{n+1}\right)\sin\left(\frac{2\pi}{n+1}\right) + \sin\left(\frac{n\pi}{n+1}\right)\sin\left(\frac{(n-1)\pi}{n+1}\right)\right]$$

$$= \epsilon + 2\Delta_m \cos\left(\frac{\pi}{n+1}\right) + \left(\frac{8\Gamma}{n+1}\right)\sin\left(\frac{\pi}{n+1}\right)\sin\left(\frac{2\pi}{n+1}\right), \quad n \ge 4 \tag{11}$$

and the LUMO/first excited state level is

$$\epsilon_{LUMO/1st}(n) \simeq \epsilon - 2\Delta_m \cos\left(\frac{\pi}{n+1}\right)$$

$$+ \left(\frac{4\Gamma}{n+1}\right)\left[\sin\left(\frac{n\pi}{n+1}\right)\sin\left(\frac{2n\pi}{n+1}\right) + \sin\left(\frac{n^2\pi}{n+1}\right)\sin\left(\frac{(n-1)n\pi}{n+1}\right)\right]$$

$$= \epsilon - 2\Delta_m \cos\left(\frac{\pi}{n+1}\right) - \left(\frac{8\Gamma}{n+1}\right)\sin\left(\frac{\pi}{n+1}\right)\sin\left(\frac{2\pi}{n+1}\right), \quad n \ge 4. \tag{12}$$

In the limit of large n, the terms proportional to Γ vanish as $1/(n+1)^3$, so the dual coupling case approaches the same form as the single coupling case at large n.

ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.6b02138.

Computed energy levels for each oligomer and showing plots of energies vs $1/n$ for oligomers P0−P7. (PDF)

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Notes

The authors declare no competing financial interest.

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(56) One can, in principle, attempt to fit the Kuhn-type form to the energy levels but we have found that this form is not as flexible as, say, a Hückel-like form. It is always possible to fit energy levels that starts negative and become less negative as N increases (e.g., the HOMO) but we have found that fitting data that starts negative and becomes more negative with N (e.g., the LUMO) is not always possible. The square root form constrains the magnitude of the parameter D_k to be greater than -1 and this constraint can lead to extremely poor fits for the polymers considered here.

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