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Extrapolating the Excitation Energy of Polythiophene from Thiophene Oligomers

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ABSTRACT Organic semiconductors are used in solar cells and as energy transferring materials. Organic semiconductors can be small molecules, oligomers, or polymers. Polymers are of interest but are difficult to represent computationally. In current computational studies oligomers can be used to extrapolate the behavior of polymers. To do so, many oligomers are generated to extrapolate trends based on oligomer size. In this study a computer program was created to enable the quick and efficient production of oligomers ranging from 1 to 166 monomer units in length. Several methods of fitting were used to predict the excitation energy of the polymer and all three reported the value to be 2.0 eV. The study shows that the computer program was able to create accurate models of thiophene oligomers from preexisting Gaussian files that agree with existing literature and so should be applicable to other materials and to real materials.

INTRODUCTION

Semiconductors are substances that can support electrical conduction and have conductivity that is between that of a conductor and an insulator (Juster 1963). Semiconductors can be separated, into organic and inorganic semiconductors. Organic semiconductors have received interest due to their low cost and flexibility (Brédas, et al. 2004). Organic semiconductors are structures that contain carbon-carbon bonds and have conductivity (Juster 1963). Organic semiconductors can be separated into oligomer and

polymer chains (Coropceanu, et al. 2007). Polymer chains are categorized as an infinite or very large chain length while oligomers are chains of defined length. These materials have found use in photovoltaic devices, such as solar cells (Brédas, et al. 2004; Roseli, et al. 2017).

Computational modeling of organic semiconductors is a heavily studied field (Torras, et al. 2012). One study conducted by the Heully group applied density functional theory (DFT)

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and time dependent density functional theory (TD-DFT) calculations to poly (3-hexylthiophene-2,5-diyl), P3HT. The study applied each method to P3HT to compare them to experimental results to study the effectiveness of each computational method (Farouil, et al. 2018). Another study applied *ab initio* methods in conjunction with an experimental study to learn more about the electronic states of thiophene (Holland, et al. 2014). The computational studies are limited by two parameters, the method and extrapolating the data. There are other computational methods that have been applied to determine polymer behaviors such as periodic boundary conditions (Sai, et al. 2014).

To predict polymer behaviors several methods have been developed (Torrás, et al. 2012; Zade, et al. 2006). In The Torrás group utilized applied several fits to approximate polymer behaviors of three oligothiophenes to study the effectiveness of each approximation method (Torrás, et al. 2012). The second study extrapolated polymer behaviors of polythiophene and polyselenophene through extrapolating behaviors based on oligomer behaviors (Zade, et al. 2006). Both studies extrapolated the band gaps of the studied molecules and compared them to experimental results.

In computational studies the key limitation is cost. Cost in this case is defined as the time it takes to generate each oligomer and the processing power used to run each calculation. While the time render any single oligomer is a relatively short process the creation of a large set of oligomers is a significantly longer process. The other studies utilized oligomers ranging from 1 to 50 monomers in length (Torrás, et al. 2012; Zade, et al. 2006). While the study showed that accurate results can be determined from sets with as few as 30 oligomers, larger data sets should be studied to determine if significantly larger data sets improve accuracy. Processing power, and by extension the time it takes to run the calculation, cannot be improved without access to more computational resources. Since there are

relatively few computational facilities capable of running full *ab initio* calculations on large polymers this study instead attempts to shorten the rendering time of each oligomer. To decrease the time needed to generate oligomers this study created a custom computer program to quickly render oligomers of any size from the optimized monomer and dimer of the needed molecule. Through using a computer program to render each oligomer the chance for error in the job file is limited and the work needed to create each file is decreased.

One commonly studied organic semiconductor is polythiophene due to its versatility in application (Farouil, et al. 2018). The studies explore how the polymer changes when annealed, the effect of combing poly (3-hexylthiophene-2,5-diyl), P3HT, with other semiconductors and how varying computational methods represent thiophene. Thiophene was used as a case study due to the simple structure and the many uses of thiophene (Chung, et al. 1984; Holland, et al. 2014; Li, et al. 2016). In these studies thiophenes electronic structure and uses are explored. Studying thiophenes excitation energy and electronic structure can then be used to determine its applications as an organic semiconductor (Holland, et al. 2014). To do so improved computational representations of thiophene polymers are required.

EXPERIMENTAL

A thiophene monomer and dimer were first rendered using GaussView 6.0 (Dennington, et al. 2016). The geometry of each molecule was then optimized using Gaussian 16 at the semi-empirical level using PM6 calculations (Frisch, et al. 2016). Computer software was written using GNU Octave 4.2 that used the optimized monomer and dimer to generate oligomers ranging from the 1 to 166 monomer units in length (Eaton, et al. 2016).

The computer program utilizes several steps to be able to create the oligomers. First the program imported the entirety of the monomer Gaussian file. Once imported, the code performed a series

of operations on the Cartesian coordinates to generate new oligomer files. The current code is incapable of performing these operations on symbolic z matrices, matrices that rely on an internal coordinate system which refer to atoms relative to other atoms. The code centered the Cartesian coordinates, a three dimensional coordinate system that represent the location of each atom in the molecule, of the monomer file. To be centered the monomers center of mass was zeroed and then the molecule was rotated so that it laid on the z axis making all of the z coordinates zero. The code then rotated the thiophene monomer so that the sulfur atom pointed up on the x axis.

From the monomer file three new monomer files were created. The code created the new files by removing hydrogens from the monomer based on bonding location. The code used the bond length between the joining carbons of the dimer and the distance from the center of mass to the bonding carbon of the monomer (Figure 1).

The code then used the structure from the monomer to generate each of the oligomers. The oligomers that were generated were made planar to reflect the structure of solid semiconductors. To guarantee that they remained planar the new structures were not optimized after being produced. From the oligomers excited state calculations were performed using Gaussian 16. The calculations were done at the semi-empirical level using ZINDO calculations. Five excited states were calculated for each oligomer but only the

first excited state was used. From the excited state data a linear and a W. Khun line of best fit were created. The W. Khun fit is shown in Equation 1.

$$\nu = \nu_0 \sqrt{1 + 2 \frac{k'}{k_0} \cos \frac{\pi}{n+1}} \quad (1)$$

In the W. Khun fit ν_0 represents the frequency of an isolated oscillator unit, k_0 is the restoring force constant, k' is the coupling force constant and n is the number of repeating monomer units. (Torras, et al. 2012) The isolated oscillator unit as used in this study is defined as the oscillation frequency of a single monomer unit. In other variants of the W. Khun fit n can be represented as N where it represents the number of double bonds, referred to in the cited study as oscillator units. When changing the values of n to N only the numeric value of $\frac{k'}{k_0}$ changes to adjust to the shift from number of double bonds to number of monomer units. These were done to extrapolate the excitation energy at infinite length.

The wavelength given by the excited state data was fitted to a trinomial equation. The additional figure and trinomial were introduced because the wavelengths were found to follow a different trend then the excitation energy when compared to the inverse of the size of the oligomer chain. The wavelength given by the trinomial was then converted to energy using the relationship $E = hv$.

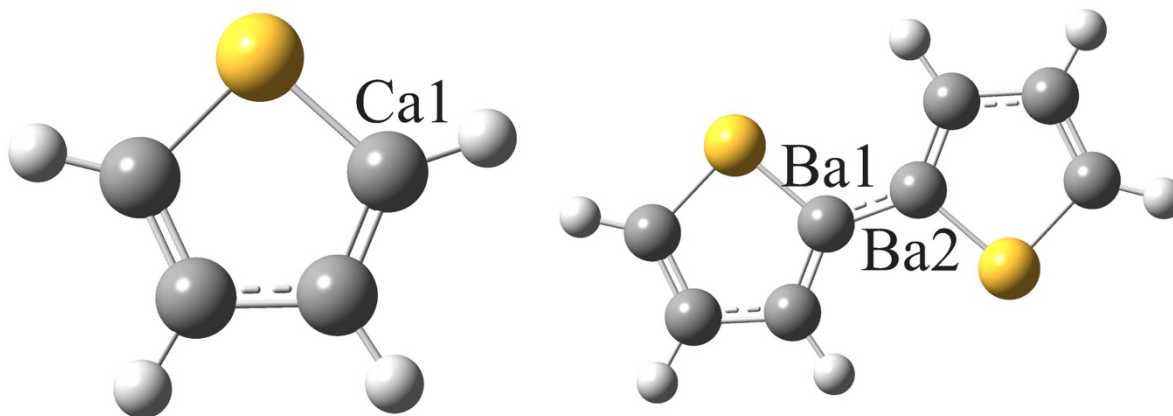


Figure 1. The data from the monomer that was used was the distance from Ca1 to the center of mass. The bonding distance was determined from the dimer (Ba1-Ba2).

RESULTS AND DISCUSSION

The transition dipole moments were compared to the size of the oligomer chains. The transition dipole moment serves as a representation of electric dipole moment for the transition between the electronic ground state and the lowest energy singlet excited state. Transition dipole moments were converted from atomic units to debye (Figure 2).

The line of best fit shows that as the oligomer increases in size the transition dipole moments

approach a linear relationship. The range of 106-166 monomer units in length to show that at larger oligomer sizes the dipole moments approach a linear relationship. The linear relationship shows that as the chain length increases the dipole moment will also increase. As the oligomers approached infinite size the transitional dipole moment approaches an infinite amount. The excitation data was also compared to oligomer size (Figure 3).

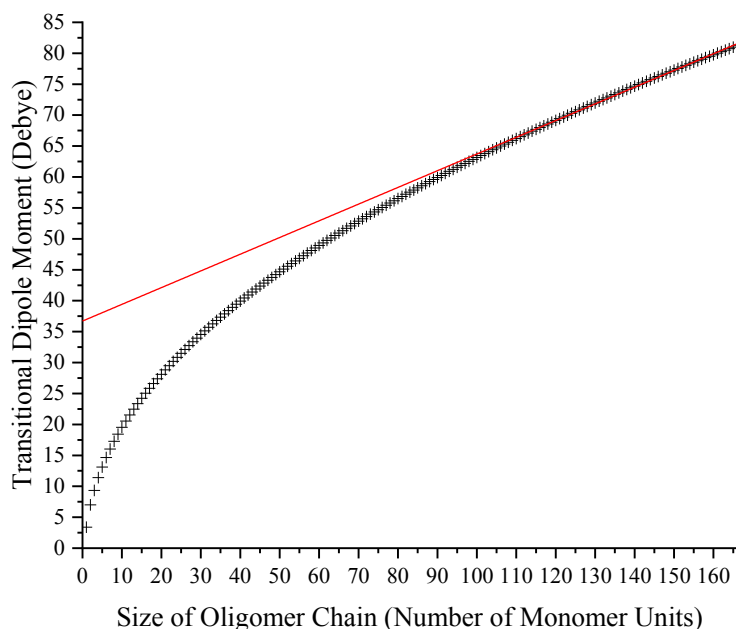


Figure 2. The dipole moments of oligomers ranging from 1 to 166 monomer units in length were collected for the first excited state. The dipole moments are in debye while the size of the chain was based on the amount of monomers composing the chain. A linear fit was applied to data points 106-166 monomer units in length. The line of best fit was determined to be $y = \left(0.270 \pm 0.001 \frac{\text{debye}}{\text{monomer unit}} \right) \cdot n + 36.7 \pm 0.2 \text{ debye}$ and it had an R^2 value of 0.99901.

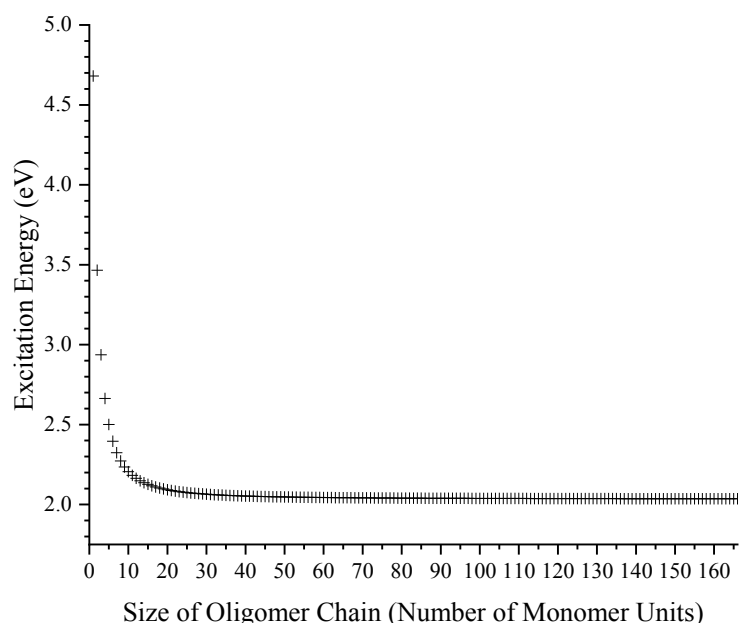


Figure 3. The excitation energy (eV) was compared to the size of the oligomer chain. As the chain length increased in size the excitation energy was seen to approach a minimum value.

The excitation energy was compared to the inverse size of the oligomer (Figure 4). A line of best fit was added to approximate the excitation energy at infinite polymer size. The inverse of the size of the oligomer chain was compared to the excitation energy so that the excitation energy of the polymer could be predicted based on the lines of best fit. A linear fit was applied as a rough estimate of the excitation energy while a W. Khun fit was applied because it has been found in other studies to better fit the behaviors of this specific graph (Torrás, et al. 2012).

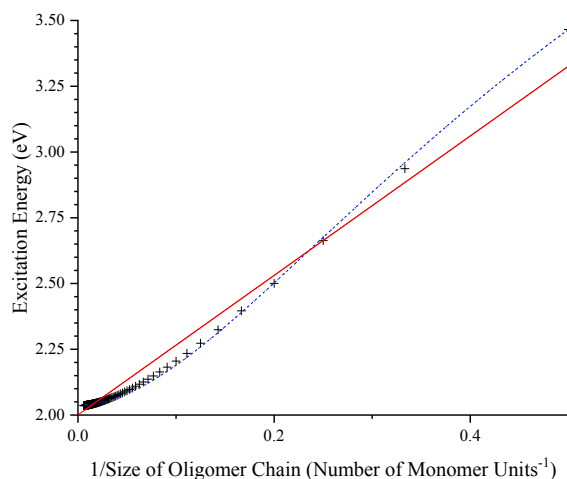


Figure 4. The excitation energy was also compared the inverse size of the oligomer. As shown the results a linear behavior between 0.1 and 0.5 1/Size of the oligomer chain units. A linear fit (red solid line) and W. Khun fit (blue dotted line) were applied to extrapolate the excitation energy of the oligomers at infinite length. The linear fit predicted that at infinite length the excitation energy would be 2.001 ± 0.002 eV. The W. Khun fit found that the excitation energy would be 2.04 ± 0.06 eV. The linear fit had a R^2 value of 0.97306 while the W. Khun fit had a R^2 value of 0.99861.

The W. Khun fit was created using equation 1. The fit was applied to oligomers ranging from 2 to 166 monomer units in size. The monomer was not used in the calculation due to how it impacted the quality of the fit.

The variables k' and k_0 were treated as one variable, k , and was found to be -0.3952 ± 0.0003 and v_0 was determined to be 4.4533 ± 0.0006 . The fit was the extrapolated to infinite length by imposing a limit. It was assumed that as n

approached infinity the values of $1/n$ would become zero. The parameters v_0 and k were determined using Origin.

Additionally the wavelength of excitation was compared to the inverse size of the oligomer chain. The polynomial fit was able to be applied to the wavelength because the polynomial fit was not applicable to Figure 4. The polynomial fit was applied to Figure 5 to serve as an additional method of checking the quality of the computational model.

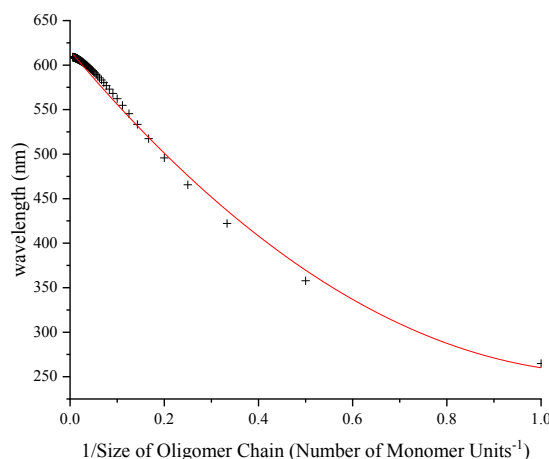


Figure 5. The wavelength was compared to the inverse size of the oligomer. A polynomial fit was applied to the data. The line of best with was determined to be $\lambda = 616.2 \pm 0.4 \text{ nm} - \left(630 \pm 8 \frac{\text{nm}}{\text{monomer unit}} \right) \cdot x + \left(274 \pm 9 \frac{\text{nm}^2}{\text{monomer unit}^2} \right) \cdot x^2$. The R^2 value was determined to be 0.9916.

Based on the polynomial fit the excitation energy was determined using the relationship between energy and wavelength, $E = h\nu$. From the fit the excitation energy was then determined to be 2.012 ± 0.001 eV.

The experimental values from the linear and W. Khun fit were compared to other studies (Torrás, et al. 2012). Other studies found that the linear fit would predict excitation energy of 1.88 eV while their Khun fit predicted a value of 2.05 eV. The linear fit data failed the two tailed Student t -test at 95% statistically while the W. Khun fit was statistically no different from the other study at 95% confidence. A χ^2 test was applied to the W. Khun fit and passed at 95% confidence. The polynomial fit passed the Student t -test at 95%

confidence. A χ^2 test was applied to the polynomial fit and passed at 95% confidence. The linear fit produced a statistically different value due to the inclusion of so many points as the other study demonstrated a linear representation of the excitation energy does not work when more than the first twelve oligomers are included. A χ^2 test was applied to the linear fit and failed at 95% confidence. The theoretical values were also compared to experimental results. The Zade group found that polythiophene had a band gap of 2.0 eV (Zade, et al. 2006). The experimental band gap value was found to be statistically no different from the three fit values at 95% confidence.

CONCLUSION

The predicted excitation energy for the thiophene polymer was predicted to be 2.04 ± 0.06 eV based on a W. Khun fit while it was predicted to be 2.001 ± 0.002 eV based on a linear fit. The polynomial fit found that the excitation energy of the polymer was 2.012 ± 0.001 eV. The W. Khun fit was found to be statistically no different from literature and experimental values while the linear value was found to differ. The W. Khun fit and the polynomial fit both passed the χ^2 test while the linear fit failed the χ^2 test at 95% confidence. This indicates that the W. Khun fit and the polynomial fit are both representative of

the data while the linear fit is not an useable fit for the data. To expand upon these results the W. Khun fit and the polynomial fit should both be applied to other oligomer models to determine if the fits only worked when applied to polythiophene and polythiophene derivatives.

Since the excitation values were shown to be statistically no different from literature values the current computer program is capable of generating oligomers. Additionally to further test the program other computational methods should be applied such as density functional theory or Hartree-Fock. The application of DFT and *ab initio* models while computationally more expensive than semi empirical methods, due to the increase in job time and processing power required, would be valuable in testing the limitations of the code. This would help test if the code produces computational models that can be studied with other calculation methods or if it only works with the semi empirical method.

Additionally other organic semiconductors will need to be tested to determine if the code is accurate for other models. Some other molecules that should be tested are non-symmetric molecules such as Poly(9,9-dioctylfluorene-alt-benzothiadiazole), P3HT, and polyfluorene. Through further improvement of the code more types of oligomers can be created.

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