QUANTUM MECHANICAL INVESTIGATION OF THE POTENTIAL OF OLIGOTHIOPHENES AND OLIGOSELENOPHENES AS ACTIVE MATERIALS IN ORGANIC PHOTOVOLTAIC CELLS

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To my family

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ABSTRACT

QUANTUM MECHANICAL INVESTIGATION OF THE POTENTIAL OF OLIGOTHIOPHENES AND OLIGOSELENOPHENES AS ACTIVE MATERIALS IN ORGANIC PHOTOVOLTAIC CELLS

The geometrical, optical and electronic properties of dicyanovinyl substituted oligothiophenes and oligoselenophenes are studied by using Density Functional Theory. The geometry of the oligomers are best predicted using B3LYP, and the absorption properties are calculated using Time-Dependent Density Functional Theory (TD-DFT) methods using M06-2X and ω B97XD functionals. It is found that M06-2X and ω B97XD perform best for predicting absorption properties. The electronic properties are investigated by calculating transfer integrals. The conclusion drawn is that oligoselenophenes are more efficient in charge transfer compared to the oligothiophenes.

ÖZET

OLİGOTİYOFEN VE OLİGOSELENOFENLERİN ORGANİK FOTOVOLTAİK PİLLERDE AKTİF MATERYAL OLMA POTANSİYELLERİNİN KUANTUM MEKANİĞİ İLE İNCELENMESİ

Disiyanovinil sübstitüte oligotiyofenlerin ve oligoselenefenlerin geometrik, optik ve elektronik özellikleri Yoğunluk Fonksiyonel Teorisi kullanılarak incelendi. Oligomerlerin geometrik yapısı B3LYP fonksiyoneli ile bulundu. Absorptivite özellikleri Zamana Bağımlı Yoğunluk Fonksiyonel Teorisi kulanılarak hesaplandı ve M06-2X ile ωB97XD fonksiyonellerinin absorpsiyon özellikleri tahmin etmede iyi performans gösterdiği tespit edildi. Elektronik özellikler yük transfer integralleri hesaplanarak incelendi. Oligoselenofenlerin, oligotiyofenlere göre yük transferlerinde daha verimli oldukları sonucuna varıldı.

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LIST OF ACRONYMS/ABBREVIATIONS

AA	Adiabatic Approximation
ADF	Amsterdam Density Functional
BLA	Bond Length Alternation
DFT	Density Functional Theory
Ε	Potential energy
ei	Site energy
ε _i	Eigenvalue
$E_{\rm xc}$	Exchange-correlation Potential
$\Delta \mathbf{E}_{ij}$	Energy difference between i and jstates
G	Gibbs Free Energy
GGA	Generalized Gradient Approximation
Ĥ	Hamiltonian operator
h _i	One-electron hamiltonian
НОМО	Highest Occupied Molecular Orbital
HF	Hartree-Fock
$\mathbf{J}_{\mathbf{ij}}$	Charge transfer integral
K	Exchange Integral
KS	Kohn-Sham
k _{ij}	Electron Transfer Rate
LC	Long-range Corrected
LDA	Local Density Approximation
LUMO	Lowest Unoccupied Molecular Orbital
m	Mass
Ν	Total number of electrons
РСМ	Polarized Continuum Model
$\mathbf{q}_{\mathbf{i}}$	Partial charge on atom i
$\mathbf{q}_{\mathbf{j}}$	Partial charge on atom j
r _{ij}	Distance between atoms i and j
РСВМ	[6,6]-phenyl- C_{61} -butyric acid methyl ester
РСЕ	Power Conversion Efficiency
PW91	Perdew-Wang 1991 Exchange Correlation

S	Overlap Matrix
SCRF	Self-Consistent Reaction Field
TD-DFT	Time-Dependent Density Functional Theory
TW	Terawatts
TZP	Triple Zeta Plus Polarization
VWN	Vosko-Wilk-Nusair Density Approximation
χ	Spin orbital
ΔG_{cs}	Thermodynamic Force of Separation
λ_{ij}	Reorganization Energy
Ψ	Many electron wavefunction

1. INTRODUCTION

Today, the primary energy source to cover the World's consumption needs is carbonbased fossil fuels. However there are many downsides of using fossil fuels as the major energy source: Even though the global demand is increasing every day, fossil fuels are expected to cease in the future. They have serious negative impacts on environment such as causing severe atmospheric pollution through carbon dioxide emission and hence increasing the greenhouse effect. Carbon dioxide emission has negative effects on land and ocean ecosystems as well, since nearly half of the emissions are absorbed by these ecosystems [1]. The environmental costs of consuming fossil fuels have been the subject of many studies, and now we are looking for solutions for altering the current situation in order to provide a sustainable future.

The term "environmental sustainability" refers to systematic conditions where neither on a planetary, nor on a regional level do human activities disturb the natural cycles more than planetary resilience allows, and at the same time do not impoverish the natural capital that has to be shared with future generations [2]. In order to satisfy the conditions of sustainability, researchers now focus on finding alternative and renewable energy sources, and improving the efficiency of energy production through these resources.

Despite the fact that fossil fuels still provide the largest portion of the energy needed, other sources such as nuclear energy, biofuels, hydraulic and geothermal energy, wind and solar energy are also used to satisfy the demand.

The greatest theoretical potential of renewable energy is solar energy, about 89,000 terawatts (TW) [3]. In order to sustain the lifestyle of 6.5 billion people, nearly 13 terawatts of energy is needed. It is expected that we will need an extra 10 TW of clean energy to maintain the current lifestyle [4]. Taking into account the environmental cost, abundance and sustainability, solar energy is the most advantageous among the aforementioned energy sources. Hence developing new methods to harness sunlight is especially important to satisfy the future energy demands of humanity in a clean, carbon-free way.

To provide a widespread primary energy source, solar energy must be harvested, converted and stored in a cost-effective fashion. However cost reduction is not the only requirement for a solar energy system. It also requires advancements in science and technology to enable the harvest-convert-store cycle in a convenient, manufacturable form. Hence the main goal in solar cell technology is to develop the material efficiency while decreasing the production cost and increasing the availability.

Current commercial solar cells are based on inorganic materials such as Si, CdTe and CuIn_{1-x}Ga_xSe₂ [5, 6]. There are also TiO₂ [7], ZnO [8], Nb₂O₅ [9] based dye sensitized solar cells.

Today, 85% of the market share belongs to the single or multi crystalline p-n junction silicon solar cells [10]. In these type of solar cells, silicon crystals are stacked in an alternant fashion: n-type and p-type. n-type and p-type doping of silicon is made in order to enable the charge deposition and capture between the layers, and upon photovoltaic effect, this results with the production of the direct current. The current obtained can be used immediately or may be stored in a battery. However, these silicon-based solar cells require high purity, high fabrication temperatures and the production costs.

Another class of solar cells is CdTe based solar cells. CdTe, being a good absorber in order to obtain high efficiency, is a direct band gap material with a high decomposition temperature. The properties of CdTe based cells make the solar cell unit thermally and chemically stable, and advantageous for low-cost production. With several different deposition techniques, 10% efficiency is obtained [11].

In a dye-sensitized solar cell, a random, disordered network of TiO_2 particles is used to collect the charge carriers. Absorption is made possible through dye molecules: The porous structure of the oxide will increase the surface area available for chemisorption. It is necessary to use a liquid or a conductive polymer so as to keep the interfacial distance at a minimum, which, in the end, enables the penetration to the pore structure of the solid to happen easier, hence charges can be collected and the circuit is completed. The rate of reactions occurring on anode and cathode affect the electrode response: If electrons are transferred faster, cathodic current will be obtained. However, if hole transfer occurs at a higher rate, then an anodic current will be obtained [12].

Even though the power conversion efficiencies of these photovoltaic devices are relatively high, the toxicity and cost-efficiency is unfavorable. Organic semiconductors, however, are advantageous over aforementioned solar cells in terms of ease of fabrication, relatively lower cost, lightweight, diversity and the possibility to fabricate flexible devices [13]. The research to develop photovoltaics began a few decades earlier, however, because of the possibilities of decreasing the costs and facilitating the production, the focus on organic photovoltaic devices increased sharply after 2000s.

In contrast to inorganic material based photovoltaic cells, a wide variety of active material and electrode combinations for constructing new cells is made possible by organic photovoltaics technology, hence there is a greater chance to improve the device performance [14].

There are different device architectures reported in the literature for organic photovoltaic cells: Single layer, bilayer, and bulk-heterojunction structures. Single layer and bilayer devices are examples of earliest studies with very low efficiencies [15-16]. Bulk-heterojunction structures, however, have higher efficiencies compared to the first two. Device structures are shown in Figure 1.1.



Figure 1.1. Device structure for a) Single layer b) Bilayer c) Bulk Heterojunction Organic Photovoltaic Cells.

The basic requirements for the materials used in organic solar cells are low band gaps in order to harvest more sunlight, suitable energy levels to achieve high circuit voltage V_{oc} , suitable exciton separation driven force, relatively high molecular weight to promote crystallinity and good charge mobilities [17].

"Organic semiconductor" is a term that represents the organic materials that can transport charge carriers. A typical organic solar cell consists of an active layer that has a p-type semiconductor as the donor, and an n-type semiconductor as the acceptor. Charge carriers are holes and electrons in p orbitals of the semiconductor, and the charge transport is dependent on the movement of these carriers from one molecule to the other. The energy gap between the highest occupied molecular orbital (HOMO) level with the lowest unoccupied molecular orbital (LUMO) level affects the charge movement rate and efficiency. It is possible to adjust the physical properties of an organic semiconductor material: HOMO/LUMO levels, charge carrier mobility, crystal structure can be arranged by chemical modifications [18]. Combining correct donor and acceptor groups taking into account these requirements will give us the optimized device structure.

The mechanism of the charge transfer in p-n junction cells is well understood and described [19]. However, the situation is different for organic semiconductors. Figure 1.2 illustrates the charge transfer mechanism in donor-acceptor bulk heterojunction solar cells.



Figure 1.2. Fundamental steps of charge transfer occurring in donor-acceptor heterojunction solar cells.

The first step of the mechanism is the formation of an exciton by the donor. In heterojunction solar cells, instead of electrons, excitons are formed (Step 1). These excitons have binding energies varying in between 0.1 eV to 0.5 eV, and they are bound neutral excitonic states. Direct current cannot be obtained because these materials do not form free electrons and holes for charge transport since the binding energy is large. The excitons need to dissociate first: They diffuse into the donor-acceptor interface (Step 2), and if they cannot reach the interface, they recombine. After the diffusion, dissociation occurs to transfer an electron into the acceptor layer (Step 3). Finally, the charge is collected at the external electrodes (Step 4).

Power Conversion Efficiency (PCE) is defined as the measure of incoming light that is converted to electricity. It is possible to maximize the PCE by maximizing three different parameters: Short circuit current density J_{SC}, fill factor FF, and open circuit voltage V_{OC}. Short circuit current density is related to charge carrier density and the charge carrier mobility. Increasing these two parameters, mobility and density, will result in an increase in J_{SC}. Short circuit current density is also maximized by decreasing the electronic excitation energy of the donor, which will result in an increase in the thermodynamic driving force of charge separation (ΔG_{cs}) at the donor-acceptor interface. Open circuit voltage V_{OC} is related to the highest occupied molecular orbital (HOMO) level of the donor and lowest unoccupied molecular orbital LUMO level of the acceptor [20, 21]. Open circuit voltage is also affected by the nano-morphology of the active layer in the polymer fullerene bulk heterojunction solar cells [22]. Voc is maximized by increasing the LUMO energy of the acceptor and decreasing the HOMO energy of the donor. However, since decreasing the HOMO of the donor increases the band gap, maximization of J_{SC} and V_{OC} must be balanced. Fill factor is determined by charge carriers reaching the electrodes [23], and is affected by charge separation, mobility and the morphological properties of the device, such as active layer depth.

Acceptor materials used in bulk heterojunction solar cells do not vary much. Fullerene derivatives that are soluble such as [6,6]-phenyl- C_{61} -butyric acid methyl ester (PCBM) are used as the acceptor material generally, since buckminsterfullerene (C_{60}) has a limited solubility [24]. However, there are various organic semiconductors designed to use in bulk heterojunction solar cells. These semiconductors might be small molecule organic solar cells (SMOSC), oligomers with structures consisting of a short chain of a repeating unit, or polymer chains. Polythiophenes [20], oligothiophenes [25], oligoselenophenes [26], soluble acenes, triaryl amines, diketopyrrolopyrroles (DPP) [27] are examples of these various classes of donor materials. The stability issues of small molecules, and the electron trapping properties that might be present in a polymer chain leave the oligomers a more preferable choice for the utilization in the photovoltaic cells as donor groups.

Considering the aforementioned fact that donor materials vary a lot, it is important for researchers to predict the absorption properties, charge transfer efficiencies, crystal structures and packing in order to understand the possible outcomes after the preparation of an heterojunction interface. Understanding and foretelling these properties will increase the efficiency in the syntheses and make it possible to tell whether it is appropriate to synthesize that particular material. In order to achieve this, different methods should be developed and examined to be validated through experimental data.

The content of this thesis focuses on understanding the physical and chemical properties of a certain class of donor oligomers that are used in bulk heterojunction solar cells: Dicyanovinyl-substituted oligothiophenes (DCVnT) shown in Figure 1.3 and dicyanovinyl-substituted oligoselenophenes (DCVnS) shown in Figure 1.4 [25, 26]. The purpose is to develop computational methods to comprehend and predict the efficiency, stability and charge transfer properties of DCVnT and DCVnS.



Figure 1.3. Dicyanovinyl substituted oligothiophene.



Figure 1.4. Dicyanovinyl substituted oligoselenophene.

Here, comprehensive investigations on DCV3T, DCV4T, DCV5T and DCV3S, DCV4S, DCV5S oligomers are reported. Detailed calculations of the optimized structures of the oligomers are carried out with a variety of Density Functional Theory (DFT) methods in order to fully understand the conformations. Time Dependent Density Functional Theory (TD-DFT) is used to observe the absorption properties of these oligomers. Also, to understand the charge transport properties, transfer integrals are calculated using the Amsterdam Density Functional (ADF) softwares.

2. METHODOLOGY

This chapter aims to describe the theoretical background of the Density Functional Theory, basis sets, Polarizable Continuum Model, properties of the functionals used for the calculations, Time-Dependent Density Functional Theory, and Transfer Integrals. Quantum chemical calculations are performed using Gaussian '09 [28] and Amsterdam Density Functional (ADF) [29] software.

2.1. Density Functional Theory

Density Functional Theory is a quantum mechanical method, which allows computing the electronic structure of a system. In quantum mechanics, it is impossible to determine the exact position and the momentum of a particle at the same time. Hence the position is expressed as the probability of finding that particle in a given space. Probability is the square of the wavefunction, and the wavefunction is found by solving Schrödinger's Equation:

$$H\psi = E\psi \tag{2.1}$$

H is the Hamiltonian, and it gives the system energy as an eigenvalue.

$$H = -\sum_{i} \frac{\hbar^{2}}{2m_{e}} \nabla_{i}^{2} - \sum_{i} \frac{\hbar^{2}}{2m_{k}} \nabla_{k}^{2} - \sum_{i} \sum_{k} \frac{e^{2}Z_{k}}{r_{ik}} + \sum_{i < j} \frac{e^{2}}{r_{ij}} + \sum_{k < l} \frac{e^{2}Z_{k}Z_{l}}{r_{kl}}$$
(2.2)

where i, j are electrons, k, l are nuclei, \hbar is the Planck's constant divided by 2π , m_k is the mass of the nucleus, m_e is the mass of the electron, ∇^2 is the Laplacian Operator, Z is atomic number and r_{ab} is the distance between the particles.

In Equation 2.2, there are five different components that contribute to the energy of a system. The first two terms represent the motion of the electrons and nuclei respectively, the third term represents the attraction of the electrons to the nuclei, the fourth term represents the interelectronic repulsions and the final term represents the internuclear

repulsions.

Equation 2.1 has many acceptable eigenfunctions ψ , each associated by a different eigenvalue, which means that it might have an infinite set of solutions. Therefore for each ψ_i , there is an eigenvalue, E_i .

$$H\psi_n = E\psi_n(x), n = 1, 2, 3, ...$$
 (2.3)

However, it is extremely difficult to find the exact solution of the Schrödinger's Equation for many electron systems, as the electron-electron interaction term in the correct Hamiltonian derived for the system is too complex. Hence, in order to find an approximate solution, the wavefunction describing the whole system should be separated to the product of many one-electron systems, i.e. $\chi_1(1), \chi_2(2), \chi_3(3)$... When Hamiltonian consists of one-electron kinetic energy and nuclear attraction terms, we can separate it:

$$H = \sum_{i=1}^{N} h_i \tag{2.4}$$

where N is the number of electrons, and h_i is one-electron Hamiltonian:

$$h_{i} = -\frac{1}{2}\nabla_{i}^{2} - \sum_{k=1}^{M} \frac{Z_{k}}{r_{ik}}$$
(2.5)

where M is the total number of nuclei.

Hence, it must satisfy that

$$h_i \boldsymbol{\psi}_i = \boldsymbol{\varepsilon}_i \boldsymbol{\psi}_i \tag{2.6}$$

which means eigenvalues of one-electron Hamiltonian satisfies the one-electron Schrödinger's equation. Since the Hamiltonian operator defined by Equation 2.4 is separable, its eigenfunctions can also be separated, i.e.

$$\boldsymbol{\psi}_{HP} = \boldsymbol{\psi}_1 \boldsymbol{\psi}_2 \dots \boldsymbol{\psi}_N \tag{2.7}$$

 ψ_{HP} is called a "Hartree Product" wavefunction. Yet, since treating electrons like they are independent from each other ignores some of the interactions in the system,

correction terms should be added after the calculations.

It should be noted that Pauli Exclusion Principle requires the wavefunction to be antisymmetric. However, since expressing ψ as the product of one-electron wavefunctions will violate the Pauli Exclusion Principle, ψ is expressed as a Slater determinant.

$$\psi_{SD} = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_1(x_1) & \chi_2(x_1) & \cdots & \chi_N(x_1) \\ \chi_1(x_2) & \chi_2(x_2) & & \chi_N(x_2) \\ \vdots & \vdots & & \vdots \\ \chi_1(x_N) & \chi_2(x_N) & \cdots & \chi_N(x_N) \end{vmatrix}$$
(2.8)

N being the total number of electrons, and χ is a spin-orbital.

$$E_{HF} = \int \psi_0 H_0 \psi_0 = \sum_{i}^{N} (i |\hat{h}|i) + \frac{1}{2} \sum_{i}^{N} \sum_{j}^{N} (ii|jj) - (ij|ji)$$
(2.9)

$$(i|\hat{h}|i) = \int \chi_i^*(x_1) \left(-\frac{1}{2} \nabla_i^2 - \sum_A^M \frac{Z_A}{r_{iA}} \right) \chi_i(x_1) dx_1$$
(2.10)

$$(ii|jj) = \iint |\chi_i(x_1)|^2 \frac{1}{r_{12}} |\chi_j(x_2)|^2 dx_1 dx_2$$
(2.11)

$$(ij|ji) = \iint \chi_i(x_1) \chi_i^*(x_1) \frac{1}{r_{12}} \chi_j(x_2) \chi_j^*(x_2) dx_1 dx_2$$
(2.12)

Equation 2.10 describes the kinetic energy of an electron and the interaction energy between this electron and the nuclei. Equation 2.11 is known as the Coulomb integral, which gives the total Coulombic repulsion between two electrons. Equation 2.12 is called the exchange integral K. It has no classical counterpart, and arises completely from the Pauli Exclusion Principle [30].

The Hartree-Fock Method described above lacks certain corrections as mentioned earlier, since it describes electrons as they are independent from each other, which, in the end, causes errors in the calculations. The movement of electrons is of course dependent on each other's positions in space, hence errors resulting from treating electrons as separate systems should be corrected. There are methods developed for minimizing these errors, however they are time consuming and expensive. Density Functional Theory, however, is an alternative to these methods.

In Density Functional Theory, the electrons interact with each other, and they also interact with an external potential. Hohenberg-Kohn Existence Theorem states that the employed ground state density is enough to determine the Hamiltonian, and hence the wavefunction. Hohenberg-Kohn's Variational Theorem, on the other hand, states that we can choose different densities providing lower energies. That is, the energy predicted with a density will be greater than the actual energy unless we solve the whole Schrödinger Equation. Since the motivation of Density Functional Theory is to avoid solving the whole equation, we will be insufficient with providing an accurate result.

In 1965, Kohn and Sham [31] noticed that the calculations would be a lot simpler if the Hamiltonian is expressed for a non-interacting system of electrons.

$$E[\rho(\mathbf{r})] = T_{ni}[\rho(\mathbf{r})] + V_{ne}[\rho(\mathbf{r})] + V_{ee}[\rho(\mathbf{r})] + \Delta T[\rho(\mathbf{r})] + \Delta V_{ee}[\rho(\mathbf{r})]$$
(2.13)

Equation 2.13 has the kinetic energy of the non-interacting electrons, the nuclearelectron interaction, electron-electron repulsion and the kinetic energy correction and the non-classical corrections to the electron-electron repulsion energy.

$$E[\rho(\mathbf{r})] = \sum_{i}^{N} \left(\left\langle \chi_{i} \middle| -\frac{1}{2} \nabla_{i}^{2} \middle| \chi_{i} \right\rangle - \left\langle \chi_{i} \middle| \sum_{k}^{nuclei} \frac{Z_{k}}{|\mathbf{r}_{i} - \mathbf{r}_{k}|} \middle| \chi_{i} \right\rangle \right)$$

$$+ \sum_{i}^{N} \left\langle \chi_{i} \middle| \frac{1}{2} \int \frac{\rho(\mathbf{r}')}{|\mathbf{r}_{i} - \mathbf{r}'|} d\mathbf{r}' \middle| \chi_{i} \right\rangle + E_{xc}[\rho(\mathbf{r})]$$

$$(2.14)$$

where N is the number of electrons, and the density function is

$$\rho = \sum_{i=1}^{N} \left\langle \chi_i | \chi_i \right\rangle \tag{2.15}$$

 ΔT and ΔV_{ee} are included in the term E_{xc} , which is the exchange-correlation energy. Exchange-correlation energy includes both the quantum mechanical exchange and correlation, and the correction term for the classical self-interaction energy. It also includes the difference in the kinetic energy between the non-interacting system and the real system.

$$h_i^{KS} \chi_i = \varepsilon_i \chi_i \tag{2.16}$$

and the Kohn-Sham operator is defined as

$$h_i^{KS} = -\frac{1}{2}\nabla_i^2 - \sum_{k}^{nuclei} \frac{Z_k}{|\mathbf{r}_i - \mathbf{r}_k|} + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r}_i - \mathbf{r}'|} d\mathbf{r}' + V_{xc}$$
(2.17)

and the functional derivative is

$$V_{xc} = \frac{\delta E_{xc}}{\delta \rho} \tag{2.18}$$

Since we are minimizing the *E* in Equation 2.13, the orbitals χ should provide the exact density. These orbitals form the Slater-determinant eigenfunction for the Equation 2.17, such that

$$\sum_{i=1}^{N} h_i^{KS} |\chi_1 \chi_2 \cdots \chi_N\rangle = \sum_{i=1}^{N} \varepsilon_i |\chi_1 \chi_2 \cdots \chi_N\rangle$$
(2.19)

hence Kohn-Sham approach is consistent internally.

The exact form of exchange-correlation functional is not known. Hence since the Density Functional Theory was developed, different approximations have been used for E_{xc} . Local Density Approximation is a method in which a real non-homogenous system is divided into infinitesimal volumes, and the electron density in these volumes is taken as constant. However it is not a suitable approximation for rapidly varying electron densities

of different materials, so a gradient of density is needed.

Hybrid functionals add the exact exchange calculated through HF functional to DFT exchange and correlation. Adiabatic connection formula, Equation 2.20 connects the non-interacting system with the real system

$$E_{xc} = \int U_{xc}^{\lambda} d\lambda \tag{2.20}$$

where λ is an interelectronic coupling strength parameter.

The most widely used functional, B3LYP [32], has the following form:

$$E_{xc} = E_{xc}^{LSDA} + a_1 (E_x^{HF} - E_c^{LSDA}) + a_2 \Delta E_x^{GC} + a_3 \Delta E_c^{GC}$$
(2.21)

B3LYP is a three-parameter hybrid functional that has Becke'88 exchange Lee-Yang-Parr correlation. The parameters are $a_1=0.2$, $a_2=0.72$, $a_3=0.81$. E_{xc}^{LSDA} is the exchange energy obtained from local spin density approximation, E_x^{GC} and E_c^{GC} are the gradient corrections for exchange and correlation respectively. Other functionals such as BH&HLYP, PBE, MPW1K, X3LYP also use the same method as B3LYP, however, with different coefficients.

Another functional M06-2X, which belongs to the same class of functionals with M06 and M06-L, is Zhao and Truhlar's hybrid meta-exchange correlation functional, which is parametrized only for non-metals. It is used for thermochemical properties, excited state calculations along with other members of its class, and when electronic excitations are considered, it gives accurate results [33].

 ω B97XD is a long-range corrected (LC) hybrid density functional that employs 100% Hartree-Fock exchange for long-range electron-electron interactions, and 22% for short-range exact exchange. Hybrid density functionals such as B3LYP mostly fail when

long-range charge transfer excitations between a donor and an acceptor, and ω B97XD, as well as other LC hybrid functionals eliminate this problem. [34].

CAM-B3LYP is similar to B3LYP, but has improved long-range properties. "CAM" stands for "Coulomb attenuating method". The functional has 0.19 Hartree Fock (HF) and 0.81 Becke '88 exchange in short range, and 0.65 HF and 0.35 Becke '88 at long-range [35]. It is reported to predict the charge transfers better.

2.2. Basis Sets

Basis sets describe the wavefunctions, and are necessary to solve the Schrödinger Equation. Split valence basis sets of Pople et al. are the most common basis sets used. 3-21G, 6-21G, 6-31+G and 6-311G* are the examples. The functions are splitted, i.e. the first number denotes the primitives in the core functions, and the numbers after the hyphen represent the number of primitives used in the valence functions. Two numbers mean valence double- ζ basis, and three numbers mean valence triple- ζ basis. One can add polarization functions, and extend the basis set, describe the system better and have more mathematical flexibility in calculations. Diffuse functions can also be added, where it is not possible for the basis set to provide enough flexibility to include an electron so far away from the core. Diffuse functions are denoted by the + sign. Polarization functions on non-hydrogen atoms are shown by "*", and if two asterisks "**" are present, it means that the polarization functions are also added to the light atoms, hydrogen and helium.

2.3. Polarizable Continuum Model

Polarizable Continuum Model (PCM) is used to describe the electrostatic solutesolvent interactions [36]. DFT methods provide a computationally efficient calculation and modeling for the solvent effects, hence using PCM is a powerful tool for simulating the molecular and spectroscopic properties of solute-solvent systems. PCM method assumes that the solvent has a single specific dielectric constant. The charge distribution of the solute induces a polarization, which, in turn, results in a change of the polarization field of the solvent [37]. The energy required to polarize both the solvent and the solute is the electrostatic contribution to the free energy of solvation.

The Gibbs free energy of solvation is calculated as

$$G = G_{ele} + G_{disp} + G_{rep} + G_{cav}$$
(2.22)

 G_{ele} consists of the electrostatic components, which are related to the Hamiltonian and the solute-solvent electrostatic polarization effects:

$$G_{ele} = \left\langle \psi \middle| H(\psi) - \frac{1}{2} V(\psi) \middle| \psi \right\rangle$$
(2.23)

Hamiltonian is written as

$$H(\boldsymbol{\psi}) = H^0 + V(\boldsymbol{\psi}) \tag{2.24}$$

where H^0 is the Hamiltonian of the isolated molecule. And the energy of the molecule in vacuo is

$$E^{0} = \left\langle \psi^{0} \middle| H^{0} \middle| \psi^{0} \right\rangle \tag{2.25}$$

From Equation 2.22,

$$\Delta G_{ele} = G_{ele} - E^0 \tag{2.26}$$

neglecting the entropic contributions.

 G_{disp} and G_{rep} are the dispersion and repulsion terms, and G_{cav} is the cavitation term, which is the work required to form a cavity in the solution.

2.4. Time Dependent Density Functional Theory

Time Dependent Density Functional Theory, TD-DFT, is a tool for calculating the electronic excited states. The Hamiltonian in Equation 2.1 and Equation 2.2 can be expressed as

$$\hat{H} = \hat{T}(\underline{r}) + \hat{W}(\underline{r}) + \hat{V}_{ext}(\underline{r},t)$$
(2.27)

such that the first term denotes the kinetic energy of the electrons, the second term describes the Coulomb interaction between the electrons, and the third term defining the time-dependent potential that the electrons are under the influence of. The excited state energy depends on the external potential; it is therefore necessary to know the effects of the potential on the system to be able to calculate the excited state properties.

The Hohenberg-Kohn Theorem is applied a variational principle involving the action

$$A = \int_{t_0}^{t_1} \left\langle \psi(t) \middle| i \frac{\partial}{\partial t} - \hat{H} \middle| \psi(t) \right\rangle dt$$
(2.28)

and the wavefunction is determined up to a time-dependent constant:

$$\boldsymbol{\psi}(\mathbf{r}_1,\dots,\mathbf{r}_N,t) = \boldsymbol{\psi}[\boldsymbol{\rho}](t)e^{-i\alpha(t)}$$
(2.29)

The phase factor adds a constant to the action in Equation 2.28:

$$A[\rho] = \int_{t_0}^{t_1} \left\langle \tilde{\psi}[\rho](t) \middle| i \frac{\partial}{\partial t} - \hat{H}(t) \middle| \tilde{\psi}[\rho](t) \right\rangle dt + \alpha(t_1) - \alpha(t_0) = A[\rho] + const.$$
(2.30)

And $A[\rho]$ can be written as

$$A[\rho] = B[\rho] - \int d\mathbf{r} \int_{t_0}^{t_1} dt \, \mathbf{v}(\mathbf{r}, t) \rho(\mathbf{r}, t)$$
(2.31)

where $B[\rho]$ is independent of the external potential. Assume an independent system which

has the property in Equation 2.32:

$$\rho(\mathbf{r},t) = \sum_{i} f_{i} |\psi_{i}(\mathbf{r},t)|^{2}$$
(2.32)

Hence to rewrite $B[\rho]$,

$$B[\rho] = \sum_{i} f_{i} \int_{t_{0}}^{t_{1}} \mathrm{d}t \left\langle \psi_{i}(t) \middle| i \frac{\partial}{\partial t} - \frac{1}{2} \nabla_{i}^{2} \middle| \psi_{i}(t) \right\rangle - \frac{1}{2} \int_{t_{0}}^{t_{1}} \mathrm{d}t \iint \mathrm{d}\mathbf{r}_{1} \,\mathrm{d}\mathbf{r}_{2} \frac{\rho(\mathbf{r}_{1}, t)\rho(\mathbf{r}_{2}, t)}{\left|\mathbf{r}_{1} - \mathbf{r}_{2}\right|} - A_{xc}[\rho] \quad (2.33)$$

where $A_{xc}[\rho]$ is the exchange and correlation action functional. Applying the variational principle to (2.31) with the constraint that

$$\rho(\mathbf{r},t) = \sum_{i} f_{i} |\psi_{i}(\mathbf{r},t)|^{2} = \sum_{i}^{N} |\psi_{i}(\mathbf{r},t)|^{2}$$
(2.34)

we obtain the time-dependent Kohn-Sham Equation in Equation 2.35:

$$\left[-\frac{1}{2}\nabla^{2} + \mathbf{v}_{\text{eff}}(\mathbf{r},t)\right]\psi_{i}(\mathbf{r},t) = i\frac{\partial}{\partial t}\psi_{i}(\mathbf{r},t)$$
(2.35)

$$\mathbf{v}_{\text{eff}}(\mathbf{r},t) = \mathbf{v}_{H}(\mathbf{r},t) + \mathbf{v}_{xc}(\mathbf{r},t) + \mathbf{v}_{ext}(\mathbf{r},t)$$
(2.36)

and the unknown is now the time-dependent exchange potential, and all exchange and correlation effects in TD-DFT are collected in Equation 2.37:

$$\mathbf{v}_{xc}(\mathbf{r},t) = \frac{\delta A_{xc}[\rho]}{\delta \rho(\mathbf{r},t)}$$
(2.37)

In time-dependent density functional theory equations, there is not any approximations made, and the theory is exact. However, since the exchange correlation action functional is not known, approximations should be introduced.

The adiabatic approximation (AA) is shown in Equation 2.38:

$$\mathbf{v}_{xc}[\rho](\mathbf{r},t) = \frac{\delta A_{xc}[\rho]}{\delta \rho(\mathbf{r},t)} \approx \frac{\delta E_{xc}[\rho]}{\delta \rho(\mathbf{r})}\Big|_{\rho=\rho(\mathbf{r},t)}$$
(2.38)

Meaning that, if the electron density is changed, the exchange and correlation potential changes instantaneously.

2.5. Reorganization Energies

Charge transport in organic materials might occur in two different ways: hoppingtype and band-type [38]. In π -conjugated molecules, hopping-type charge transfer is observed. While an electron is moving from one oligomer to the other, internal arrangements occur on the geometry of the oligomer. Since it controls the charge hopping, this internal reorganization is an important parameter when charge transfer properties of organic materials are in question.

Inner reorganization energy is a result of the alterations occurred in the geometry of a molecule when an electron is removed or added. In order to calculate the reorganization energy, one should know how the conformations and energies of the molecule in the cation and anion states change, and also what the energies of the neutral conformation with an electron added or removed are.



Figure 2.1. Internal reorganization energy $\lambda_+ + \lambda_0$ for hole transfer, and the adiabatic ionization energy ΔE .

The λ_+ part of the reorganization energy is calculated as the difference of the energy required to go with the neutral conformation to the cation state, and the energy of the cation. The second λ_0 part of the reorganization energy is calculated as the difference of energy required for cation geometry to have neutral state and the energy of the neutral. The sum of the two components gives the hole transfer reorganization energy. Equation 2.39 is a brief summary of this calculation.

$$\lambda = \lambda_0 + \lambda_+ = (E_0^* - E_0) + (E_+^* - E_+)$$
(2.39)

For the calculation of electron transfer reorganization, similar calculation is done. The λ_{-} part of the reorganization energy is calculated as the difference of the energy required to go to the anion state with the neutral conformation, and the energy of the anion state. The second λ_0 part of the reorganization energy is calculated as the difference of energy required for anion geometry to have neutral state and the energy of the neutral state. The sum of the two components gives the electron transfer reorganization energy. Equation 2.40 is a brief summary, and Figure 2.2 is a graphical illustration of this calculation.

$$\lambda = \lambda_0 + \lambda_2 = (E_0^* - E_0) + (E_2^* - E_2)$$
(2.40)



Figure 2.2. Internal reorganization energy $\lambda_{\perp} + \lambda_0$ for electron transfer, and the adiabatic ionization energy ΔE .

2.6. Transfer Integrals

Crystal structure and packing properties have a great influence on how charge transfers occur in a π -conjugated oligomer. Intramolecular π -conjugation enhances the charge transfer rates, and molecular structure has a great influence on the charge transfer, because it determines the crystal packing, i.e. the way the molecules are ordered in space.

Well-defined crystal structure information enables us to predict the charge transfer rates by using the Amsterdam Density Functional Theory Suite [29]. Charge transfer rates are determined by a parameter called "Transfer Integral". Transfer Integral is simply explained as the parameter defining the possibility of the transfer of a charge between the two chains that are interacting with each other. In order to calculate the Transfer Integral between two molecules, the packing structure of the crystal should be known.

Transfer integrals are calculated between the two monomers of choice, for example, the face-to-face positioned dimers, or the edge-to-face interacting dimers, and so on. The important factor determining the charge transport between the two layers is the overlap of wavefunctions of each monomer. Hence, enhanced overlap, i.e. in dimers with layers parallel to each other with a distance that can electrons hop from one to another will also enhance the charge transfer.

Simple tight-binding approximation: [39]

$$H = \sum_{m} \epsilon_m a_m^+ a_m + \sum_{m \neq n} t_{mn} a_m^+ a_n$$
(2.41)

 a_m and a_m^+ are creation and annihilation operators. ϵ_m is the site energy of the electron at molecular site m, t_{mn} is the transfer integral.

The charge carrier mobility in a hopping-type donor material is approximated by Equation 2.42:

$$k_{ij} = t_{ij}^2 \sqrt{\frac{\pi}{\hbar^2 k_B T \lambda_{ij}}} \exp\left(-\frac{(\Delta E_{ij} - \lambda_{ij})^2}{4\lambda_{ij} k_B T}\right)$$
(2.42)

where k_{ij} is the Electron Transfer Rate, λ_{ij} is the Reorganization Energy, ΔE_{ij} is the Energy difference between the initial and final states.

Equation 2.43 describes the orbital energies of a dimer:

$$\mathbf{HC} - E\mathbf{SC} = \mathbf{0} \tag{2.43}$$

Where H and S are

$$\mathbf{H} = \begin{pmatrix} e_1 & J_{12} \\ J_{12} & e_2 \end{pmatrix}$$
 The Hamiltonian (2.44)

$$\mathbf{S} = \begin{pmatrix} 1 & S_{12} \\ S_{12} & 1 \end{pmatrix}$$
 Overlap Matrix (2.45)

and e_i and J_{ij} are

$$e_i = \left\langle \psi_i \middle| \hat{H} \middle| \psi_i \right\rangle \tag{2.46}$$

$$J_{ij} = \left\langle \boldsymbol{\psi}_i \middle| \hat{H} \middle| \boldsymbol{\psi}_j \right\rangle \tag{2.47}$$

The elements e_i and J_{ij} are related to ϵ_i and t_{ij} . However, they need to be converted into orthonormalized basis. Hence,

$$\mathbf{H}^{eff} = \begin{pmatrix} e_1^{eff} & J_{12}^{eff} \\ J_{12}^{eff} & e_2^{eff} \end{pmatrix}$$
(2.48)

and $e_{l(2)}^{e\!f\!f}$ can be calculated as follows:

$$e_{1(2)}^{eff} = \frac{1}{2} \frac{(e_1 + e_2) - 2J_{12}S_{12} \pm (e_1 - e_2)\sqrt{1 - S_{12}^2}}{1 - S_{12}^2}$$
(2.49)

$$J_{12}^{eff} = \frac{J_{12} - \frac{1}{2}(e_1 + e_2)S_{12}}{1 - S_{12}^2}$$
(2.50)

Now, e_i^{eff} and J_{ij}^{eff} are the same as ϵ_i and t_{ij} .

Hence Equation 2.43 becomes

$$\mathbf{H}^{eff}\mathbf{C} = E\mathbf{C} \tag{2.44}$$

The absolute value of the energy difference is then

$$\Delta E_{12} = \sqrt{(e_1^{eff} - e_2^{eff})^2 + (2J_{12}^{eff})^2}$$
(2.45)

Transfer Integral calculations are performed using Amsterdam Density Functional (ADF) software [29], using Perdew-Wang 1991 (PW91) exchange correlation as gradient correction, and Vosko-Wilk-Nusair (VWN) [40] as local density approximation with TZP basis set. TZP is a core double zeta, valence triple zeta, polarized basis set and extends the valence space.

3. RESULTS

3.1. Geometrical Features

The very first step to be taken in order to understand the basic features of dicyanovinyl-substituted oligothiophenes and dicyanovinyl-substituted oligoselenophenes is to figure out the orientations of the thiophene or selenophene rings, and the position of dicyanovinyl groups. A rigorous assessment is required in that matter, since the geometrical features of these oligomers are needed to specify the crystal structure and packing. Depending on the molecular topology, packing properties change, and hence charge transfer rates change. Enhanced overlap between the molecules improves charge mobility between the layers, and since charge movement along a circuit is dependent on the mobility, the power conversion efficiency, as a result, is also dependent on the geometric orientations of the thiophene or selenophene rings with respect to dicyanovinyl end-groups.

3.1.1. Conformations

In order to establish a basis for the efforts to understand the geometrical features, it is important to note that thiophene and selenophene groups in a three, four or five membered oligomer structure will need to arrange themselves in a way which ensures the oligomer backbone to have a stable structure. The arrangement in space can be in lots of different ways. When the oligomer with three thiophene rings attached together is taken into consideration, it can be seen that thiophene groups can be combined in many ways to form the backbone. They can be attached all of them looking in the same direction as shown in Figure 3.1, or they can change positions, and may have an alternant fashion as shown in Figure 3.2.



Figure 3.1. Three membered oligothiophene, thiophene rings looking in the same direction.



Figure 3.2. Three membered oligothiophene: thiophene rings in an alternant fashion.

As Figure 3.1 and Figure 3.2 show, the combination of three thiophene groups leads to different structures, which, consequently, will result in different packing structures and trends. Hence it is necessary to understand the conformation of the backbone, and also how the dicyanovinyl end groups are positioned with respect to the backbone conformation.

Table 3.1 and Table 3.2 list the possible three and four membered chains with thiophene in the backbone, with dicyanovinyl end groups and their energies relative to each other. The names of the oligomers are given according to the positions of the thiophene groups looking in the same direction or the opposite direction. If the first sulfur in the thiophene ring is looking up, it is named "Up", and the sulfur in the consecutive thiophene ring is named according to the first, i.e. if it is pointing downwards, it is named "Down". The positions of dicyanovinyl end-groups are specified according to the direction the sulfur of the first and last thiophene ring. To exemplify, if dicyanovinyl end-group is looking towards the same direction as the sulfur in the thiophene ring to which it is added, it is called to be in *cis-* position, and if otherwise, it is called to be in *trans-* position. An example is shown in Figure 3.3.



Figure 3.3. An example for the naming of the oligomers: Up-Up-Down-trans-cis. (UUDTC).

The first two thiophene groups are pointing upwards, so to be named as "Up-Up", and the third is pointing downwards, to be named as "Down". The backbone is named "Up-Up-Down". The first dicyanovinyl group on the left is positioned *trans*- according to the following thiophene ring's sulfur, i.e. dicyanovinyl group is looking in the opposite direction as the sulfur of the thiophene ring it is added, and the second dicyanovinyl group on the right is positioned *cis*- according to the preceding thiophene ring's sulfur. The oligomer's name is specified as Up-Up-Down-trans-cis (UUDTC).

Below in Table 3.1 and Table 3.2, Electronic Energies (HF) and Gibbs Free Energies of the optimized various combinations for the three and four membered thiophene backbones are listed.

Table 3.1. Conformations of three membered thiophene chains. Optimized with B3LYP/6-31+G*.

NAME	STRUCTURE	HF (Hartree)	REL. HF (kcal/mol)	REL. GIBBS (kcal/mol)
UUUCC	A A A	-2180.432919	2.30	2.70

UUUTT	YAAK	-2180.432703	2.43	2.87
UUUCT	Lager (-2180.433081	2.20	2.31
UUDCC	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	-2180.435693	0.56	0.93
UUDTT	1444	-2180.433711	1.80	2.00
UUDCT	Laga-	-2180.434301	1.43	1.75
UUDTC	Yadah	-2180.434855	1.08	1.34
UDUCC		-2180.436584	0.00	0.00
UDUTT	YAAA	-2180.434757	1.15	0.02
UDUCT	1242-	-2180.435799	0.49	0.38

Table 3.1. Conformations of three membered thiophene chains. Optimized with B3LYP/6-31+G* (cont.).

NAME	STRUCTURE	HF (Hartree)	REL. HF (kcal/mol)	REL. GIBBS (kcal/mol)
UUUUCC	F F	-	-	-
UUUUTT	Y A A A	-2732.253182	3.35	3.96
UUUUCT	Y A A A	-2732.253504	3.15	3.55
UUUDCC	FAA+	-	-	-
UUUDTT	1444	-2732.25423	2.70	3.09
UUUDCT	FAAA	-	-	-
UUUDTC	Yappy	-2732.255365	1.98	2.36
UDUUCC	LARDE	-	-	_

Table 3.2. Conformations of four membered thiophene chains.

Optimized with B3LYP/6-31+G*.

UDUUTT	YAAAA	-2732.255479	1.91	2.18
UDUUCT	-1000	-		
UDUUTC	12442	-	_	_
UUDDCC	XXXXX	-	-	-
UUDDTT	YAAAA	-2732.254407	2.59	2.50
UUDDCT	Lagott,	-2732.255103	2.15	1.82
UDDUCC	-tottot	-2732.257424	0.69	1.11
UDDUTT	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	-2732.25529	2.03	2.33
UDDUCT	10000	-	-	-
UDUDCC	-10000	-2732.258527	0.00	0.00

Table 3.2. Conformations of four membered thiophene chains. Optimized with B3LYP/6-31+G* (cont.).

UDUDTT	YAAAA	-2732.256458	1.30	1.31
UDUDCT	よなななよ	-2732.257372	0.72	2.13

Table 3.2. Conformations of four membered thiophene chains. Optimized with B3LYP/6-31+G* (cont.).

The data summarized in Table 3.1 and Table 3.2 draw us to the conclusion that the thiophene chain is in its most stable conformation when sulfur atoms of the consecutive thiophene rings point in the opposite directions, and the dicyanovinyl endgroups occupy the cis- positions depending on the direction of the sulfur atom of the thiophene group to which they are attached. Hence, the Up-Down-Up and Up-Down-Up-Down combinations for three and four membered thiophene backbones, with *cis-* positioned dicyanovinyl end-groups have the preferred structure.

With the insight obtained from the energy differences between the conformations, the preferred structure for five-membered ring is also chosen as "Up-Down-Up-Down-Up-trans-cis". The conclusion we draw from computing the energies of the different combinations of thiophene oligomers is also supported by Salzner's work in 2011, in which the extended thiophene chains were investigated [41]. Similarly to what is shown here, in Salzner's work, six membered and eight membered thiophene chains without dicyanovinyl groups that are optimized with a wide variety of methodologies including B3LYP/6-311G* have an alternant structure in positioning the thiophene rings, that is, Up-Down-Up-Down sequence is kept, with slight differences in the dihedral angles including the bridges connecting the two rings. Hence, in agreement with Salzner's results [41], and the crystal structure of the four-membered thiophene ring [25], we conclude that the alternant combination of thiophene rings depict the correct conformations of three, four and five membered rings in question. Figure 3.4 lists all the structures chosen to run the computations with.

From now on, the preferred structures of three, four and five membered thiophene chains in Figure 3.4 are going to be named as DCV3T, DCV4T, and DCV5T respectively, DCV implying the dicyanovinyl group, and 3T, 4T and 5T denoting the three, four and five thiophene rings forming the backbone. Similarly, oligoselenophene analogues are named as DCV3S, DCV4S and DCV5S.



Figure 3.4. Structures of three, four and five membered oligothiophene chains.

3.1.2. Bond Length Comparison

To find out the best density functional method that can locate the structure of DCV3T, DCV4T and DCV5T and their selenophene analogues, benchmark studies are carried out for DCV4T and DCV4S since the crystal structures for these two structures exist in the literature [25, 26]. Optimizations are done with the B3LYP, M06-2X, ω B97XD and CAM-B3LYP levels of theory, using 6-31+G** basis set.

Table 3.3 below lists the bond lengths obtained by computations together with the bond lengths obtained through the crystal structure data of DCV4T [25]. The numbering

system is shown in Figure 3.5.



Figure 3.5. Numbering system used in DCV4T.

Table 3.3. DFT calculated bond lengths of DCV4T, with values from the crystal structure
(Å) [25].

Bond	Atom1	Atom2	B3LYP	ωB97XD	M06-2X	CAM-B3LYP	Crystal [25]
1	S3	C9	1.753	1.735	1.735	1.737	1.727
2	S3	C12	1.756	1.738	1.737	1.739	1.735
3	S4	C13	1.749	1.729	1.730	1.731	1.732
4	S4	C16	1.759	1.742	1.741	1.744	1.745
5	S2	C8	1.753	1.735	1.735	1.737	1.734
6	S2	C5	1.756	1.737	1.737	1.739	1.736
7	S1	C1	1.749	1.729	1.730	1.731	1.730
8	S1	C4	1.759	1.742	1.741	1.744	1.739
9	C15	H15	1.085	1.084	1.085	1.084	0.951
10	C15	C16	1.395	1.384	1.385	1.383	1.389
11	C15	C14	1.402	1.406	1.407	1.405	1.400
12	C8	C9	1.443	1.454	1.451	1.451	1.450
13	C8	C7	1.386	1.374	1.376	1.373	1.381
14	C1	C5	1.441	1.452	1.449	1.449	1.447
15	C1	C2	1.393	1.381	1.382	1.380	1.385
16	C5	C6	1.386	1.374	1.376	1.373	1.377
17	C3	H3	1.085	1.084	1.085	1.084	0.950
18	C3	C2	1.402	1.407	1.407	1.405	1.402
19	C3	C4	1.395	1.384	1.385	1.383	1.390
20	C9	C10	1.386	1.374	1.376	1.373	1.384
21	C13	C12	1.441	1.452	1.449	1.449	1.448
22	C13	C14	1.393	1.381	1.382	1.380	1.387
23	C7	H7	1.084	1.084	1.084	1.083	0.951
24	C7	C6	1.411	1.417	1.416	1.415	1.411

25	C12	C11	1.386	1.374	1.376	1.373	1.379
26	C2	H2	1.084	1.083	1.084	1.083	0.951
27	C4	C21	1.424	1.432	1.432	1.429	1.432
28	C11	H11	1.084	1.084	1.084	1.084	0.950
29	C11	C10	1.411	1.417	1.416	1.415	1.411
30	C16	C17	1.424	1.432	1.432	1.430	1.426
31	C21	H21	1.088	1.087	1.088	1.087	0.950
32	C21	C22	1.375	1.362	1.361	1.361	1.366
33	C10	H10	1.084	1.083	1.084	1.083	0.950
34	C17	H17	1.088	1.087	1.084	1.087	0.949
35	C17	C18	1.375	1.361	1.088	1.361	1.361
36	C14	H14	1.084	1.083	1.084	1.083	0.950
37	C6	H6	1.084	1.084	1.084	1.084	0.951
38	C18	C20	1.429	1.432	1.434	1.431	1.435
39	C18	C19	1.431	1.434	1.435	1.433	1.440
40	C22	C24	1.431	1.434	1.435	1.433	1.443
41	C22	C23	1.429	1.431	1.434	1.431	1.436
42	C20	N4	1.165	1.160	1.158	1.158	1.149
43	C19	N3	1.165	1.160	1.158	1.157	1.151
44	C24	N2	1.165	1.160	1.158	1.157	1.151
45	C23	N1	1.165	1.160	1.158	1.158	1.146

Table 3.3. DFT calculated bond lengths of DCV4T, with values from the crystal structure (Å) [25] (cont.).

Table 3.4 below lists the bond lengths obtained at various levels of theory, in comparison with the values from the crystal structure of DCV4S [26]. The numbering system is shown in Figure 3.5.

Table 3.4. DFT calculated bond lengths of DCV4S, with values from the crystal structure (Å) [26].

Bond	Atom1	Atom2	B3LYP	ωB97XD	M06-2X	CAM-B3LYP	Crystal
1	Se3	C9	1.889	1.864	1.866	1.868	1.875
2	Se3	C12	1.893	1.865	1.868	1.871	1.880
3	Se4	C13	1.886	1.858	1.862	1.863	1.874
4	Se4	C16	1.899	1.876	1.876	1.878	1.892
5	Se2	C8	1.889	1.864	1.866	1.868	1.886
6	Se2	C5	1.893	1.865	1.868	1.871	1.875
7	Se1	C1	1.886	1.858	1.862	1.863	1.880

v	+5, with va		ystar structt
С	ont.).		
)-		
	1.876	1.878	1.883
	1.085	1.085	0.951
	1.383	1.381	1.370
	1.407	1.406	1.402
	1.443	1.443	1.445

Table 3.4. DFT calculated bond lengths of DCV4S, with values from the crystal structure (Å) [26] (c

$\begin{array}{ c c c c c c c c c c c c c c c c c c c$								
$\begin{array}{ c c c c c c c c c c c c c c c c c c c$	8	Se1	C4	1.899	1.876	1.876	1.878	1.883
$\begin{array}{ c c c c c c c c c c c c c c c c c c c$	9	C15	H15	1.086	1.085	1.085	1.085	0.951
$\begin{array}{ c c c c c c c c c c c c c c c c c c c$	10	C15	C16	1.393	1.382	1.383	1.381	1.370
$\begin{array}{ c c c c c c c c c c c c c c c c c c c$	11	C15	C14	1.403	1.408	1.407	1.406	1.402
$\begin{array}{ c c c c c c c c c c c c c c c c c c c$	12	C8	C9	1.433	1.448	1.443	1.443	1.445
$\begin{array}{ c c c c c c c c c c c c c c c c c c c$	13	C8	C7	1.384	1.371	1.374	1.370	1.372
$\begin{array}{ c c c c c c c c c c c c c c c c c c c$	14	C1	C5	1.432	1.447	1.442	1.442	1.439
$\begin{array}{ c c c c c c c c c c c c c c c c c c c$	15	C1	C2	1.391	1.378	1.380	1.377	1.379
$\begin{array}{ c c c c c c c c c c c c c c c c c c c$	16	C5	C6	1.384	1.371	1.374	1.370	1.370
$\begin{array}{ c c c c c c c c c c c c c c c c c c c$	17	C3	H3	1.086	1.085	1.085	1.085	0.951
$\begin{array}{ c c c c c c c c c c c c c c c c c c c$	18	C3	C2	1.403	1.408	1.407	1.406	1.410
$\begin{array}{ c c c c c c c c c c c c c c c c c c c$	19	C3	C4	1.393	1.382	1.383	1.381	1.381
$\begin{array}{ c c c c c c c c c c c c c c c c c c c$	20	C9	C10	1.384	1.371	1.374	1.370	1.367
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	21	C13	C12	1.432	1.447	1.442	1.442	1.439
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	22	C13	C14	1.391	1.378	1.380	1.377	1.376
$\begin{array}{ c c c c c c c c c c c c c c c c c c c$	23	C7	H7	1.085	1.085	1.085	1.084	0.95
$\begin{array}{ c c c c c c c c c c c c c c c c c c c$	24	C7	C6	1.411	1.419	1.417	1.417	1.407
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	25	C12	C11	1.384	1.371	1.374	1.370	1.366
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	26	C2	H2	1.085	1.084	1.085	1.084	0.95
$\begin{array}{ c c c c c c c c c c c c c c c c c c c$	27	C4	C21	1.420	1.429	1.429	1.426	1.425
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	28	C11	H11	1.086	1.085	1.086	1.085	0.951
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	29	C11	C10	1.411	1.419	1.417	1.417	1.405
$\begin{array}{ c c c c c c c c c c c c c c c c c c c$	30	C16	C17	1.420	1.429	1.429	1.426	1.414
$\begin{array}{ c c c c c c c c c c c c c c c c c c c$	31	C21	H21	1.088	1.088	1.089	1.087	0.95
33 C10 H10 1.085 1.085 1.085 1.084 0.95 34 C17 H17 1.088 1.088 1.089 1.087 0.949 35 C17 C18 1.376 1.362 1.362 1.361 1.357 36 C14 H14 1.085 1.084 1.085 1.084 0.95 37 C6 H6 1.086 1.085 1.086 1.085 0.95 38 C18 C20 1.428 1.430 1.433 1.429 1.439 39 C18 C19 1.430 1.432 1.434 1.431 1.437 40 C22 C24 1.430 1.432 1.434 1.431 1.434 41 C22 C23 1.428 1.430 1.432 1.429 1.427 42 C20 N4 1.166 1.160 1.158 1.152 43 C19 N3 1.165 1.160 <td>32</td> <td>C21</td> <td>C22</td> <td>1.376</td> <td>1.362</td> <td>1.362</td> <td>1.361</td> <td>1.363</td>	32	C21	C22	1.376	1.362	1.362	1.361	1.363
34 C17 H17 1.088 1.088 1.089 1.087 0.949 35 C17 C18 1.376 1.362 1.362 1.361 1.357 36 C14 H14 1.085 1.084 1.085 1.084 0.95 37 C6 H6 1.086 1.085 1.086 1.085 0.95 38 C18 C20 1.428 1.430 1.433 1.429 1.439 39 C18 C19 1.430 1.432 1.434 1.431 1.434 41 C22 C23 1.428 1.430 1.432 1.429 1.427 42 C20 N4 1.166 1.160 1.159 1.158 1.152 43 C19 N3 1.165 1.160 1.158 1.157 1.151 44 C24 N2 1.165 1.160 1.158 1.157 1.151 45 C23 N1 1.166 <td>33</td> <td>C10</td> <td>H10</td> <td>1.085</td> <td>1.085</td> <td>1.085</td> <td>1.084</td> <td>0.95</td>	33	C10	H10	1.085	1.085	1.085	1.084	0.95
35C17C181.3761.3621.3621.3611.35736C14H141.0851.0841.0851.0840.9537C6H61.0861.0851.0861.0850.9538C18C201.4281.4301.4331.4291.43939C18C191.4301.4321.4341.4311.43740C22C241.4301.4321.4341.4311.43441C22C231.4281.4301.4321.4291.42742C20N41.1661.1601.1591.1581.15243C19N31.1651.1601.1581.1571.15145C23N11.1661.1601.1591.1581.141	34	C17	H17	1.088	1.088	1.089	1.087	0.949
36C14H141.0851.0841.0851.0840.9537C6H61.0861.0851.0861.0850.9538C18C201.4281.4301.4331.4291.43939C18C191.4301.4321.4341.4311.43740C22C241.4301.4321.4341.4311.43441C22C231.4281.4301.4321.4291.42742C20N41.1661.1601.1591.1581.15243C19N31.1651.1601.1581.1571.15145C23N11.1661.1601.1591.1581.141	35	C17	C18	1.376	1.362	1.362	1.361	1.357
37 C6 H6 1.086 1.085 1.086 1.085 0.95 38 C18 C20 1.428 1.430 1.433 1.429 1.439 39 C18 C19 1.430 1.432 1.434 1.431 1.437 40 C22 C24 1.430 1.432 1.434 1.431 1.434 41 C22 C23 1.428 1.430 1.432 1.429 1.427 42 C20 N4 1.166 1.160 1.159 1.158 1.152 43 C19 N3 1.165 1.160 1.158 1.158 1.146 44 C24 N2 1.165 1.160 1.158 1.157 1.151 45 C23 N1 1.166 1.160 1.159 1.158 1.141	36	C14	H14	1.085	1.084	1.085	1.084	0.95
38 C18 C20 1.428 1.430 1.433 1.429 1.439 39 C18 C19 1.430 1.432 1.434 1.431 1.437 40 C22 C24 1.430 1.432 1.434 1.431 1.437 41 C22 C23 1.428 1.430 1.432 1.434 41 C22 C23 1.428 1.430 1.432 1.429 1.427 42 C20 N4 1.166 1.160 1.159 1.158 1.152 43 C19 N3 1.165 1.160 1.158 1.158 1.146 44 C24 N2 1.165 1.160 1.158 1.157 1.151 45 C23 N1 1.166 1.160 1.159 1.158 1.141	37	C6	H6	1.086	1.085	1.086	1.085	0.95
39 C18 C19 1.430 1.432 1.434 1.431 1.437 40 C22 C24 1.430 1.432 1.434 1.431 1.437 41 C22 C23 1.428 1.430 1.432 1.434 1.431 1.434 41 C22 C23 1.428 1.430 1.432 1.429 1.427 42 C20 N4 1.166 1.160 1.159 1.158 1.152 43 C19 N3 1.165 1.160 1.158 1.158 1.146 44 C24 N2 1.165 1.160 1.158 1.157 1.151 45 C23 N1 1.166 1.160 1.159 1.158 1.141	38	C18	C20	1.428	1.430	1.433	1.429	1.439
40 C22 C24 1.430 1.432 1.434 1.431 1.434 41 C22 C23 1.428 1.430 1.432 1.429 1.427 42 C20 N4 1.166 1.160 1.159 1.158 1.152 43 C19 N3 1.165 1.160 1.158 1.158 1.146 44 C24 N2 1.165 1.160 1.158 1.157 1.151 45 C23 N1 1.166 1.160 1.159 1.158 1.141	39	C18	C19	1.430	1.432	1.434	1.431	1.437
41 C22 C23 1.428 1.430 1.432 1.429 1.427 42 C20 N4 1.166 1.160 1.159 1.158 1.152 43 C19 N3 1.165 1.160 1.158 1.158 1.146 44 C24 N2 1.165 1.160 1.158 1.157 1.151 45 C23 N1 1.166 1.160 1.159 1.158 1.141	40	C22	C24	1.430	1.432	1.434	1.431	1.434
42 C20 N4 1.166 1.160 1.159 1.158 1.152 43 C19 N3 1.165 1.160 1.158 1.158 1.146 44 C24 N2 1.165 1.160 1.158 1.157 1.151 45 C23 N1 1.166 1.160 1.159 1.158 1.141	41	C22	C23	1.428	1.430	1.432	1.429	1.427
43 C19 N3 1.165 1.160 1.158 1.158 1.146 44 C24 N2 1.165 1.160 1.158 1.157 1.151 45 C23 N1 1.166 1.160 1.159 1.158 1.141	42	C20	N4	1.166	1.160	1.159	1.158	1.152
44 C24 N2 1.165 1.160 1.158 1.157 1.151 45 C23 N1 1.166 1.160 1.159 1.158 1.141	43	C19	N3	1.165	1.160	1.158	1.158	1.146
45 C23 N1 1.166 1.160 1.159 1.158 1.141	44	C24	N2	1.165	1.160	1.158	1.157	1.151
	45	C23	N1	1.166	1.160	1.159	1.158	1.141

3.1.3 Bond Length Alternation

In order to see the effect of the conjugation on the bonds forming the backbone, Bond Length Alternation (BLA) parameter for molecules is calculated. Bond Length Alternation parameter is defined as the difference between the average length of the single bonds in the backbone and the average length of the double bonds of the backbone. In order for a bond to be included in the calculation, it should contribute to the conjugation along the chain. For the BLA calculations, results of the B3LYP, M06-2X, ω B97XD and CAM-B3LYP optimizations (6-31+G**) are used (Table 3.3 and Table 3.4). The BLA parameter of the optimized structures and BLA parameters from of the crystal structures [25, 26] are compared. Table 3.5 summarizes the results for both DCV4T and DCV4S oligomers' BLA results with four different optimization methods.

DCV4T										
Method/6-31+G**	B3LYP	ωB97XD	M06-2X	CAM-B3LYP	Exp. [25]					
Average of Single Bonds	1.422	1.430	1.429	1.428	1.425					
Average of Double Bonds	1.387	1.375	1.349	1.374	1.380					
BLA	0.035	0.055	0.080	0.054	0.045					
		DCV4S								
Method/6-31+G**	B3LYP	ωB97XD	M06-2X	CAM-B3LYP	Exp. [26]					
Average of Single Bonds	1.418	1.428	1.426	1.425	1.421					
Average of Double Bonds	1.386	1.373	1.375	1.372	1.370					
BLA	0.033	0.055	0.051	0.053	0.051					

Table 3.5. Bond Length Alternation parameters of DCV4T and DCV4S.

Data shown in Table 3.5 shows that for DCV4T, BLA calculated with B3LYP, ω B97XD and CAM-B3LYP are very close to that of crystal; i.e. there is only ~0.010 Å difference. However, DCV4S has different results when compared to DCV4T. ω B97XD, M06-2X and CAM-B3LYP predicted almost the same BLA values with that of crystal, all having long-range corrections. Among these three, ω B97XD and CAM-B3LYP are range-separated functionals. An appropriate parametrization in a functional with appropriate short-range HF exchange and a satisfactory short range enhances the performance.

Still, these results alone are not helpful to decide which DFT functional is best to predict the geometries of the oligomers, since bond length is not the only parameter defining the geometry.

3.1.4. Dihedral Angles

To find out which optimization method is the best to choose to predict the geometries of thiophene and selenophene oligomers, the dihedral angles have also been checked. In order to do so, dihedral angles between the sulfurs of the thiophene rings and the dihedral angles between the nitrogen atoms of the end-groups are compared. Computations are done with four different methods: B3LYP, M06-2X, ω B97XD and CAM-B3LYP by using 6-31+G** as the basis set. Figure 3.6 depicts the dihedral angles in DCV4T, and Table 3.6 provides the numerical values of the dihedral angles of DCV4T.

Dihedrals are measured from the sulfur atom of the first thiophene ring to the sulfur atom of the second thiophene ring; i.e. for A-B rings. When dihedral angles of the optimized structures are compared to that of the crystal structure, it can be concluded that B3LYP/6-31+G** is the best method for predicting the conformation of DCV4T.



Figure 3.6. Dihedral Angles of DCV4T.

	B3LYP	ωB97XD	M06-2X	CAM-B3LYP	Experimental [25]
A-B	-175.46°	-160.57°	-167.58°	-162.44°	176.8°
B-C	164.33°	-151.72°	-160.41°	157.17°	176.7°
C-D	-175.44°	155.72°	-167.60°	168.13°	178.7°
N4-A	-0.06°	-0.13°	0.10°	-0.11°	6.4°
D-N1	-0.06°	0.07°	0.11°	0.08°	7.8°

Table 3.6. Dihedral Angles (in degrees) of DCV4T (B3LYP/6-31+G**).

Figure 3.6 also shows the dihedral angles of DCV4S, and Table 3.7 lists the dihedral angle values. Similar to DCV4T, the crystal structure of DCV4S is also best predicted by using the B3LYP/6-31+G** level of theory. DCV4S structure predicted using B3LYP/6-31+G** is more flat compared to the B3LYP/6-31+G** predicted structure of DCV4T, such that there is almost 5° of difference between the A-B and C-D dihedral angles of DCV4T and DCV4S, and more than 15° of difference between the B-C dihedral angles of the two oligomers.

Table 3.7. Dihedral Angles (in degrees) of DCV4S (B3LYP/6-31+G**).

	B3LYP	ωB97XD	M06-2X	CAM-B3LYP	Experimental [26]
A-B	179.92°	-151.36°	-168.94°	-164.67°	178.7°
B-C	-179.93°	146.18°	168.20°	161.88°	175.5°
C-D	179.92°	-151.36°	-168.94°	-164.67°	178.4°
N4-A	0.01°	0.06°	0.03°	0.03°	9.3°
D-N1	0.01°	0.06°	0.03°	0.03°	6.2°

3.2. Optical Properties

In this part, we aim to explain the optical properties of DCVnT and DCVnS oligomers. Other than Hartree-Fock methods, electron-correlated Hartree-Fock methods, semiempirical Hartree-Fock methods; Density Functional Theory is also used to understand the optical properties, such that the experimentally observable properties can be related to the theoretical calculations. Excited state properties, ionization potentials, electron affinities and orbital information can be obtained through applying DFT methods to the oligomer/polymer systems.

3.2.1. TD-DFT Calculations of Excited States

DFT is a widely used method, which has its upsides and downsides in application to the oligomer systems. It provides accuracy and an efficient and fast way to understand the excited state properties. However it also has a self-interaction error, which can be defined as an electron interacting with itself.

Time Dependent Density Functional Theory, is the extension of Density Functional Theory, and the problems caused by self-interaction persists in TD-DFT. Choosing the correct functional is important in order to alter the effects of self-interaction. Here, results of the TD-DFT calculations done by methods that are applied to the model systems by using different functionals in order to specify the functional that can best predict the optical properties of the oligomers in question are reported. A variety of different functionals belonging to different families are used. Gas Phase and solvent (Dichloromethane) TD-DFT results are reported. Solvent calculations are performed in order to understand the solvent effect on the optical properties, because the solvent affects the distribution of the density.

Table 3.8, Table 3.9, Table 3.10, Table 3.11, Table 3.12 and Table 3.13 summarize the gas phase and solvent TD-DFT calculations with different levels of theory. Calculations are performed on the B3LYP/6-31+G** gas phase optimized structure for gas phase TD-DFT, and B3LYP/6-31+G** solvent optimized structure for TD-DFT in solvent, using dichloromethane as the solvent

Table 3.8. $S_0 \rightarrow S_1$ transition energies of DCV3T in vacuum and in dichloromethane calculated at various levels of theory. Basis set: 6-31+G**.

DCV3T								
TD-DFT		Gas Phas	e	Dic	hlorometh	ane		
METHOD/6-31+G**	λ	НОМО	LUMO	λ (nm)	HOMO	LUMO		
EXP. [25]				495	-5.66	-3.54		
B1B95	514	-6.54	-3.68	558.02	-6.2	-3.41		
B1LYP	523.1	-6.37	-3.66	568.56	-6.01	-3.36		
B3P86	530.2	-7.02	-4.55	576.23	-6.69	-4.28		

B972	527.3	-6.38	-3.85	572.85	-6.05	-3.58
B98	528.8	-6.41	-3.85	574.66	-6.07	-3.57
BHandH	472.9	-7.15	-3.1	510.9	-6.8	-2.83
BHandHLYP	477.3	-7.15	-3.09	515.99	-6.79	-2.81
BMK	484.3	-6.99	-3.4	524.79	-6.64	-3.13
HSEH1PBE	531.7	-6.25	-4.17	577.51	-5.91	-3.9
M06-2X	468.5	-7.4	-3.21	506.67	-7.06	-2.96
mPW1LYP	524.0	-6.4	-3.69	569.43	-6.03	-3.39
mPW1PBE	517.4	-6.59	-3.86	561.63	-6.26	-3.59
mPW3PBE	530.4	-6.48	-4.01	576.24	-6.14	-3.73
PBE1PBE	517.0	-6.58	-3.85	561.22	-6.25	-3.58
PBEh1PBE	517.3	-6.58	-3.85	561.6	-6.25	-3.58
ωB97XD	462.0	-8.01	-2.39	498.56	-7.67	-2.13

Table 3.8. $S_0 \rightarrow S_1$ transition energies of DCV3T in vacuum and in dichloromethane calculated at various levels of theory. Basis set: 6-31+G** (cont.).

Table 3.9. $S_0 \rightarrow S_1$ transition energies of DCV4T in vacuum and in dichloromethane calculated at various levels of theory. Basis set: 6-31+G**.

DCV4T									
TD-DFT		Gas Phase	e	D	Dichloromethane				
METHOD/6-31+G**	λ(nm)	НОМО	LUMO	λ (nm)	HOMO	LUMO			
EXP. [25]				518	-5.49	-3.45			
B1B95	548.11	-6.27	-3.53	606.41	-5.93	-3.31			
B1LYP	560.21	-6.1	-3.51	621.17	-5.73	-3.26			
B3P86	571.4	-6.76	-4.4	633.16	-6.41	-4.17			
B972	567.37	-6.12	-3.7	628.46	-5.77	-3.48			
B98	568.5	-6.15	-3.7	630.05	-5.79	-3.47			
BHandH	495.06	-6.86	-2.95	544.35	-6.49	-2.73			
BHandHLYP	499.86	-6.86	-2.95	550.2	-6.48	-2.71			
BMK	509.8	-6.71	-3.25	562.38	-6.35	-3.03			
HSEH1PBE	577.87	-5.99	-4.03	639.69	-5.64	-3.8			
M06-2X	488.31	-7.12	-3.07	536.36	-6.77	-2.87			
mPW1LYP	561.32	-6.13	-3.54	622.35	-5.75	-3.29			
mPW1PBE	553.77	-6.32	-3.71	612.78	-5.98	-3.49			
mPW3PBE	571.62	-6.22	-3.86	633.2	-5.87	-3.63			
PBE1PBE	553.33	-6.32	-3.7	612.29	-5.97	-3.48			
PBEh1PBE	553.62	-6.31	-3.7	612.69	-5.97	-3.48			
ωB97XD	477.36	-7.73	-2.24	522.39	-7.37	-2.04			

DCV5T								
TD-DFT		Gas Phase			Dichloromethane			
METHOD/6-31+G**	λ(nm)	НОМО	LUMO	λ (nm)	HOMO	LUMO		
EXP. [25]				530	-5.3	-3.43		
B1B95	582.37	-6.05	-3.43	641.8	-5.73	-3.24		
B1LYP	597.8	-5.87	-3.41	661.03	-5.53	-3.18		
B3P86	613.11	-6.54	-4.3	678.53	-6.22	-4.1		
B972	669.02	-5.84	-3.82	672.25	-5.58	-3.4		
B98	608.69	-5.92	-3.61	673.38	-5.6	-3.39		
BHandH	518.06	-6.62	-2.85	564.53	-6.29	-2.66		
BHandHLYP	523.37	-6.62	-2.85	570.96	-6.27	-2.64		
BMK	535.45	-6.47	-3.15	586.41	-6.14	-2.96		
HSEH1PBE	684.86	-5.72	-4.14	692.7	-5.45	-3.72		
M06-2X	508.41	-6.89	-2.98	552.93	-6.58	-2.8		
mPW1LYP	599.15	-5.9	-3.44	662.46	-5.55	-3.21		
mPW1PBE	590.51	-6.1	-3.61	651.43	-5.78	-3.41		
mPW3PBE	613.39	-6	-3.76	678.56	-5.68	-3.56		
PBE1PBE	590	-6.09	-3.61	650.84	-5.78	-3.41		
PBEh1PBE	590.29	-6.09	-3.6	651.25	-5.77	-3.41		
ωB97XD	493.78	-7.49	-2.15	534.2	-7.17	-1.97		

Table 3.10. $S_0 \rightarrow S_1$ transition energies of DCV5T in vacuum and in dichloromethane calculated at various levels of theory. Basis set: 6-31+G**.

Table 3.11. $S_0 \rightarrow S_1$ transition energies of DCV3S in vacuum and in dichloromethane calculated at various levels of theory. Basis set: 6-31+G**.

DCV3S							
TD-DFT		Gas Phase	e	Dichloromethane			
METHOD/6-31+G**	λ(nm)	НОМО	LUMO	λ (nm)	HOMO	LUMO	
EXP. [26]				521	-6.02	-4.00	
B1B95	538.87	-6.48	-3.75	586.84	-6.15	-3.48	
B1LYP	547.8	-6.31	-3.72	597.29	-5.95	-3.43	
B3P86	554.63	-6.97	-4.61	604.62	-6.64	-4.34	
B972	551.78	-6.33	-3.91	601.31	-5.99	-3.64	
B98	553.64	-6.36	-3.92	603.5	-6.02	-3.64	
BHandH	497.81	-7.09	-3.2	539.69	-6.74	-2.93	
BHandHLYP	502.17	-7.09	-3.19	544.74	-6.73	-2.91	
BMK	508.94	-6.93	-3.49	553.27	-6.58	-3.21	
HSEH1PBE	555.85	-6.2	-4.24	605.6	-5.86	-3.96	
M06-2X	491.82	-7.35	-3.32	533.4	-7.01	-3.07	
mPW1LYP	548.84	-6.34	-3.76	598.32	-5.97	-3.45	

mPW1PBE	542.08	-6.53	-3.93	590.27	-6.2	-3.66
mPW3PBE	554.9	-6.43	-4.07	604.74	-6.09	-3.8
PBE1PBE	541.56	-6.53	-3.92	589.72	-6.19	-3.65
PBEh1PBE	-	-	-	589.97	-6.19	-3.65
ωB97XD	486.55	-7.94	-2.49	526.68	-7.59	-2.23

Table 3.11. $S_0 \rightarrow S_1$ transition energies of DCV3S in vacuum and in dichloromethane calculated at various levels of theory. Basis set: 6-31+G** (cont.).

Table 3.12. $S_0 \rightarrow S_1$ transition energies of DCV4S in vacuum and in dichloromethane calculated at various levels of theory. Basis set: 6-31+G**.

DCV4S							
TD-DFT		Gas Phase			Dichloromethane		
METHOD/6-31+G**	λ(nm)	λ (nm) HOMO		λ(nm)	HOMO	LUMO	
EXP. [26]				547	-5.81	-3.96	
B1B95	585.42	-6.2	-3.63	632.13	-5.88	-3.35	
B1LYP	597.53	-6.03	-3.6	647.03	-5.67	-3.3	
B3P86	607.86	-6.69	-4.49	659.02	-6.37	-4.21	
B972	604.05	-6.05	-3.8	654.3	-5.72	-3.51	
B98	605.75	-6.08	-3.8	656.35	-5.75	-3.51	
BHandH	532.45	-6.78	-3.09	568.84	-6.45	-2.8	
BHandHLYP	537.28	-6.78	-3.08	574.4	-6.43	-2.77	
BMK	546.68	-6.63	-3.37	587.13	-6.29	-3.09	
HSEH1PBE	613.79	-5.92	-4.12	665.21	-5.60	-3.83	
M06-2X	523.08	-7.06	-3.21	557.99	-6.74	-2.94	
mPW1LYP	590.88	-6.25	-3.81	648.44	-5.7	-3.33	
mPW1PBE	591.26	-6.26	-3.82	638.62	-5.93	-3.53	
mPW3PBE	641.22	-5.76	-3.95	659.26	-5.82	-3.67	
PBE1PBE	607.59	-6.06	-3.8	637.93	-5.92	-3.52	
PBEh1PBE	-	-	-	638.17	-5.92	-3.52	
ωB97XD	513.06	-7.64	-2.38	545.48	-7.31	-2.1	

DCV5S							
TD-DFT		Gas Phase	e	D	Dichloromethane		
METHOD/6-31+G**	λ(nm)	НОМО	LUMO	λ (nm)	HOMO	LUMO	
EXP. [26]				565	-5.6	-3.84	
B1B95	705.58	-5.92	-3.81	673.75	-5.68	-3.29	
B1LYP	720.91	-5.75	-3.78	693.32	-5.48	-3.23	
B3P86	-	-	-	710.66	-6.18	-4.14	
B972	726.52	-5.78	-3.96	704.44	-5.53	-3.45	
B98	728.64	-5.81	-3.97	706.24	-5.55	-3.44	
BHandH	648.74	-6.45	-3.34	594.72	-6.24	-2.74	
BHandHLYP	657.12	-6.45	-3.33	600.87	-6.22	-2.71	
BMK	660.5	-6.32	-3.58	617.34	-6.09	-3.02	
HSEH1PBE	740.7	-5.67	-4.27	724.5	-5.41	-3.76	
M06-2X	632.84	-6.73	-3.45	579.54	-6.54	-2.89	
mPW1LYP	722.8	-5.78	-3.81	695.05	-5.5	-3.26	
mPW1PBE	711.68	-5.98	-3.99	683.62	-5.74	-3.47	
mPW3PBE	730.49	-5.89	-4.11	710.96	-5.63	-3.6	
PBE1PBE	710.81	-5.97	-3.98	682.79	-5.73	-3.46	
PBEh1PBE	711.03	-5.97	-3.97	682.98	-5.72	-3.45	
ωB97XD	617.14	-7.29	-2.63	561.79	-7.11	-2.04	

Table 3.13. $S_0 \rightarrow S_1$ transition energies of DCV5S in vacuum and in dichloromethane calculated at various levels of theory. Basis set: 6-31+G**.

Investigation of the data listed in Table 3.8, Table 3.9, Table 3.10, Table 3.11, Table 3.12 and Table 3.13 leads to the conclusion that M06-2X/6-31+G** and ω B97XD/6-31+G** are the two methods which predict the maximum absorption peaks of dicyanovinyl oligothiophenes and dicyanovinyl oligoselenophenes best. Key to understand why these two functionals work better at predicting the optical properties is hidden in the long-range corrections and large Hartree-Fock exchange. ω B97XD includes 100% long-range exchange and 22% short-range exchange, with correlations and dispersion corrections. Self-interaction problem is eliminated in ω B97XD functional by the 100% HF exchange for long range, which, as a result, predicts the excited state better. M06-2X, with its 54% HF exchange, again predicts the excited state properties well compared to the experimental results.

Figure 3.7 and Figure 3.8 show the M06-2X and ω B97XD calculated absorption spectra of DCVnT and DCVnS oligomers respectively.

A red shift is observed for both classes of oligomers, i.e. the maximum absorption increases as the wavelength increases. This is in consistency with the experimental results [25, 26] such that the molar absorptivity increases as a shift to longer wavelengths. Figure 3.9 summarizes the experimental data, which is in consistency with the calculations.



Figure 3.7. Absorption spectra of DCVnT in dichloromethane. (M06-2X and ω B97XD).



Figure 3.8. Absorption spectra of DCVnS in dichloromethane (M06-2X and ωB97XD).





 Electronic absorption (a) and emission spectra (b) of the DCVnT-series 1–5 in dichloromethane [22].

2) UV-vis absorption and emission spectraof a) DCV3S-DCV5S measured indichloromethane. B) DCV4S and DCV5S inthin films [23].



2)

3.2.2. Oxidation-Reduction Potentials

The oxidation and reduction energies of DCVnT and DCVnS oligomers are important, since these oligomeric donor materials are mostly coupled with [6,6]-phenyl-C₆₁-butyric acid methyl ester (PCBM) and its analogues as the acceptor material [24]. The energy levels of the donor materials should be reasonably in accordance with the acceptor in order to be used in the heterojunction interface. Table 3.14 and Table 3.15 show the energies required for oxidation and reduction. Calculations are done on the B3LYP/6-31+G** optimized structures of the oligomers, using ω B97XD/6-31+G** and M06-2X/6-31+G** to obtain energies of cationic, anionic and neutral states. Oxidation and reduction potentials are calculated by electronic energies and free energies with two different methodologies, and the results show a trend of decrease in the oxidation potential, and an increase on the reduction potential for both DCVnT and DCVnS oligomers as the oligomer gets longer.

It should be noted that comparing the calculated oxidation and reduction energies with experimental findings should be done with caution, since the measurements depend highly on experimental conditions and the physical condition of the material, i.e. results may vary if the measurement is done in solution or in thin film form of the material [42].

		ωB97XD/6-31+G**//				M06-2X/6-31+G**//				
	B3LYP/6-31+G**			B3LYP/6-31+G**						
	Н	ĺF	Gibb	Gibbs Free		HF Gib		os Free EX		. [25]
	Eox	Ered	Eox	Ered	Eox	Ered	Eox	Ered	Eox	Ered
DCV3T	7.63	-	7.57	-2.79	7.76	-2.79	7.71	-2.87	1.06	-1.25
DCV4T	7.29	-	7.24	-2.66	7.40	-2.67	7.31	-2.81	0.84	-1.41
DCV5T	7.04		6.98		7.14	-2.58	7.09	-2.70	0.64	-1.37

Table 3.14. Oxidation potentials of DCVnT (in eV).

	ωB97XD/6-31+G**// B3LYP/6-31+G**			N	M06-2X/6-31+G**// B3LYP/6-31+G**					
	H	IF	Gibbs Free		H	HF Gibt			EXP. [26]	
	Eox	Ered	Eox	Ered	Eox	Ered	Eox	Ered	Eox	Ered
DCV3S	7.52	-	7.47	-2.91	7.69	-2.91	7.64	-3.00	0.99	-1.17
DCV4S	7.17	-	7.13	-2.79	7.32	-2.84	7.29	-2.90	0.81	-1.25
DCV5S	6.93	-	6.87	-2.77	7.06	-2.75	7.05	-2.86	0.57	-1.38

Table 3.15. Oxidation potentials of DCVnS (in eV).

3.2.3. Frontier Orbitals

It is essential to find out the HOMO and LUMO energy levels of the donor materials DCVnT and DCVnS in order to understand the charge transfer dynamics. In a bulk heterojunction cell, the donor is coupled with an acceptor material, and the electron transfer between the HOMO of the donor and the LUMO of the acceptor is required to obtain the current. The electronic configuration, oscillator strength and the nature of the transition occurring in a donor material should be known –most systems prefer transition occurring between the frontier orbitals, in other words, HOMO \rightarrow LUMO transitions are observed in most conjugated systems.

Charge transfers occurring between the donor material HOMO and LUMO levels are of question in this section. Table 3.16 and Table 3.17 list the electron transfers observed in DCVnT and DCVnS, the oscillator strengths and contributions calculated with M06-2X and ω B97XD functionals, using the B3LYP/6-31+G** optimized structures. The reason of choosing ω B97XD and M06-2X, as explained in Section 3.2.1, is that the long-range Hartree-Fock corrections present in these functionals eliminate the error caused by self-interaction. From Table 3.16 and Table 3.17, it is seen that the transitions that have the largest contribution occur from HOMO to LUMO. For both oligothiophene and oligoselenophene classes, the contribution of HOMO-1 to LUMO+1 display the opposite behavior.

	DCVnT								
	TD-DFT (Dichloromethane)								
METHOD/6-31+G** Energy (nm) Os. St. Nature									
	M06-2X	506.67	1.9155	HOMO-1→LUMO+1	4.59				
3T				HOMO →LUMO	93.94				
\mathbf{N}	ωB97XD	498.56	1.9356	HOMO-1→LUMO+1	8.05				
DC				HOMO →LUMO	88.56				
	M06-2X	536.36	2.4135	HOMO-1→LUMO+1	7.18				
Г				HOMO →LUMO	90.14				
V4 ⁻	ωB97XD	522.39	2.4708	HOMO-1→LUMO+1	12.00				
C				HOMO →LUMO	82.26				
I				HOMO →LUMO+2	2.37				
	M06-2X	552.93	2.8068	HOMO-1 →LUMO+1	10.25				
				HOMO →LUMO	84.87				
SΤ				HOMO →LUMO+1	2.60				
No.	ωB97XD	534.2	2.898	HOMO-2 →LUMO+2	2.66				
DC				HOMO-1 →LUMO+1	16.09				
				HOMO →LUMO	74.21				
				HOMO \rightarrow LUMO+2	4.64				

Table 3.16. $S_0 \rightarrow S_1$ transitions in Dichloromethane for DCVnT.

Table 3.17. $S_0 \rightarrow S_1$ transitions in Dichloromethane for DCVnS.

	DCVnS								
	TD-DFT (Dichloromethane)								
	METHOD/6-31+G**	Energy (nm)	Os. St.	Nature	% Cont.				
\sim	M06-2X	533.4	1.9073	HOMO-1 →LUMO+1	3.87				
V3				HOMO →LUMO	94.50				
ğ	ωB97XD	526.68	1.912	HOMO-1 →LUMO+1	6.93				
Ι				HOMO →LUMO	89.38				
	M06-2X	557.99	2.3738	HOMO-1 →LUMO+1	6.36				
4S				HOMO →LUMO	91.01				
Ň	ωB97XD	545.48	2.4058	HOMO-1 →LUMO+1	10.74				
DO				HOMO →LUMO	83.50				
				HOMO →LUMO+2	2.21				
	M06-2X	579.54	2.7884	HOMO-1 →LUMO+1	9.05				
				HOMO →LUMO	86.46				
5S				HOMO →LUMO+2	2.22				
N N	ωB97XD	561.79	2.8456	HOMO-2 →LUMO+2	2.29				
DC				HOMO-1 →LUMO+1	14.35				
				HOMO →LUMO	76.38				
				HOMO \rightarrow LUMO+2	4.23				

Table 3.18 and Table 3.19 depict the wavefunctions of the DFT/M06-2X calculated molecular orbitals for DCVnT and DCVnS. Localization is not observed when the chain length is increased to 5T/5S. Both HOMO and LUMO orbitals are delocalized. The HOMO and LUMO orbitals of all DCVnT and DCVnS oligomers are similar to each other.

		DCVnT
	M06	-2X/6-31+G**//B3LYP/6-31+G**
V3T	ОМОН	
DCA	TUMO	
74T	ОМОН	
DCV	DMU	
VST	ОМОН	
DC	OMUL	

Table 3.18. Wavefunctions of the DFT/M06-2X calculated molecular orbitals for DCVnT.



Table 3.19. Wavefunctions of the DFT/M06-2X calculated molecular orbitals for DCVnS.

3.3. Charge Transport Properties

The alterations in geometry when a charge transfer occurs, and the electron transfers occurring between the layers of a crystal packing model are under investigation in this section.

3.3.1. Reorganization Energies

Here, for the six DCVnT and DCVnS oligomers, both hole and electron transfer reorganization energies are calculated.

Table 3.20. Reorganization energies of DCVnT and DCVnS (B3LYP/6-31+G**// B3LYP/6-31+G**). Calculated using HF energies.

MOLECULE	λ (Hole)	λ (Electron)
DCV3T	176	275
DCV4T	201	257
DCV5T	196	218
DCV3S	188	278
DCV4S	193	253
DCV5S	196	227

Equation 2.42 in Section 2.6 states that

$$k_{ij} = t_{ij}^2 \sqrt{\frac{\pi}{\hbar^2 k_B T \lambda_{ij}}} \exp\left(-\frac{(\Delta E_{ij} - \lambda_{ij})^2}{4\lambda_{ij} k_B T}\right)$$
(2.42)

where k_{ij} is the electron transfer rate, λ_{ij} is the reorganization energy, and ΔE_{ij} is the energy difference between the initial and final states. The increase in the reorganization energy decreases the electron transfer rate k_{ij} as it can be understood through the equation.

The results in Table 3.20 state that the reorganization energy increases for the hole reorganization, and decreases for the electron reorganization as the oligomer length increases. In other words, the geometric relaxations occurring between the anionic state and the neutral state of oligothiophenes and oligoselenophenes decrease as the oligomer length increases, which is an indication of the oligomer to prefer going through electron reorganization rather than hole reorganization. However, the hole reorganization also cannot be neglected as it has significant values compared to the electron reorganization, and that, can also be interpreted as the thiophene and selenophene oligomers are electron and hole transfer materials.

3.3.2. Transfer Integrals

In this section, the transfer integrals between different dimers are reported. The overlap between the orbitals of the two monomer increases the transfer integral, and hence the possibility of charge transfer between the two layers. This information can be made useful to determine whether the donor structure is able to donate electrons and carry these electrons along the interface.

The unit cells of the DCV4T and DCV4S are the same, depicted in Figure 3.11. Crystal structure data are from Bäuerle's works [25, 26]. DCV4T and DCV4S do not exhibit a herringbone structure in the crystal. As seen on Figure 3.11.b, the intermolecular distances are quite close, measured 3.514 Å in DCV4T [25], meaning that the oligomers exhibit a good π - π stacking and compact packing. DCV4S, however, exhibits less compact packing and π - π stacking, as the distance measured between the layers is 3.563 Å [26].



Figure 3.10. DCV4T and DC4S unit cells viewed along **a**) a axis **b**) b axis **c**) c axis [25].



Figure 3.11. Monomers of DCV4T and DCV4S chosen in the packing structure for the calculation of transfer integrals.

	D	CV4T	DCV4S		
Dimer	t (Hole)	t (Electron)	t (Hole)	t (Electron)	
1_2	-62.787	34.383	-88.097	48.498	
1_3	-3.461	12.149	-2.900	9.426	
1_5	-2.775	0.881	-2.524	0.908	
2_3	12.822	-39.438	12.962	-42.264	
2_4	-0.137	0.553	-0.117	0.643	
2_5	4.083	6.938	3.414	6.991	
4_5	-62.787	34.383	-88.097	48.498	
4_6	0.000	0.000	0.000	0.000	
5_8	-8.311	-25.092	-10.740	-15.964	

Table 3.21. Transfer Integrals (in meV) of DCV4T and DCV4S.

Considering the fact that DCV4S oligomers are placed more far away than DCV4T oligomers in the crystal, one might think that since π - π stacking is not good enough in DCV4S as it is in DCV4T. However, this is not the case, as it is seen in Table 3.21. The electron transfer integrals of DCV4S are larger than that of DCV4T, which draws us to the conclusion that a more efficient charge transfer occurs between the parallel layers of DCV4S crystal. The dimer 1_2 (and 4_5) in DCV4S has its two monomers as closest as possible that is observed in the crystal, with t_{electron} 48.498 meV compared to the same dimer of DCV4T, with t_{electron} 34.383 meV. Monomers in dimer 1_3 are placed parallel to each other, however with a shift of the dimer in the lower layer to the side, such that the orbital overlap is decreased in this case, and hence the transfer integrals decrease in both thiophene and selenophene oligomers. The dimer 4_6 is placed on the two distant corners of the unit cell, hence the orbital overlap that may cause a transfer between these layers is almost zero, and the transfer integrals are 0 for both hole and electrons.

Oligoselenophenes are reportedly 30% more power conversion efficiency than the oligoselenophenes [26]. The electron transfer integral between the dimer 1_2 proves that the charge transfer is more efficient in DCV4S than DCV4T.

4. CONCLUSIONS

Geometrical properties of dicyanovinyl substituted oligothiophenes and oligoselenophenes are studied. Both thiophene and selenophene oligomers have an alternant fashion in positioning the thiophene and oligoselenophene rings, i.e. if the first ring is directed upwards, the second is directed downwards and so on. Dicyanovinyl groups, on the other hand, take the *cis*- position to the sulfur or selenium atom of the ring to which they are attached. Quantum mechanical calculations performed at B3LYP level of theory, using 6-31+G** basis set to predict the geometry of DCVnT and DCVnS oligomers yield good results in predicting the bond lengths and the dihedral angles. Bond Length Alternation (BLA), which we can simply define as the difference between the average values of the single and double bonds, is predicted by B3LYP, ω B97XD, M06-2X and CAM-B3LYP functionals with 6-31+G** basis set. The results varied between DCV4T and DCV4S, such that for DCV4T, B3LYP, ω B97XD and CAM-B3LYP predicted the closest BLA values to the crystal BLA, whereas for DCV4S, M06-2X and CAM-B3LYP predicted the closest BLA values to the crystal BLA.

The excited state properties of oligothiophenes and oligoselenophenes are investigated using a variety of different functionals using 6-31+G** basis set. ω B97XD and M06-2X are the two functionals that perform well for predicting the absorption properties. Both functionals have large Hartree-Fock (HF) contributions in long range, the former with 100% HF exchange and the latter with 54% HF exchange.

Oxidation potentials are calculated with ω B97XD and M06-2X together with 6-31+G** basis set, using the B3LYP/6-31+G** optimized structures. The results show that the oxidation potentials of both DCVnT and DCVnS oligomers decrease, and the reduction potentials increase with increasing chain length. TD-DFT calculations performed in dichloromethane with ω B97XD and M06-2X using 6-31+G** as the basis set show the nature of the charge transfers. Charge transfers occurring from HOMO to LUMO have the largest contribution. However, the contribution of HOMO to LUMO transfer decreases as the chain length increases. The wavefunctions of the thiophene and selenophene oligomers are also depicted, which show that there is not any localization present in the HOMO or LUMO orbitals of DCVnT and DCVnS.

Calculation of reorganization energies draws us to the conclusion that the DCVnT and DCVnS oligomers are ambipolar materials. The reorganization energy decreases for the electron reorganization as the chain length increases.

Transfer Integrals, which increase with the orbital overlap and π - π stacking are also calculated using Amsterdam Denstiy Functional software. The crystal structures of four membered thiophene and selenophene oligomers are used in the calculations. The calculations performed with the two closest parallel monomers chosen in the packing structure show that DCV4S has a larger transfer integral than DCV4T, that is, the charge transfers in selenophene oligomers are better than thiophene oligomers, which is also confirmed by the experimental results [26].

5. SUGGESTIONS FOR FUTURE WORK

The properties of thiophene and selenophene oligomers can be investigated by changing the dicyanovinyl endgroups into other electron withdrawing groups in order to observe the end-group effect on optical and charge transfer properties. Similarly, the effects of adding sidechains to the backbone can be investigated. The backbone can be elongated in order to discover the effects of conjugation length on the optical and electronic properties.

The changes in optical properties, excited state properties and charge transfer properties can also be studied by changing the heavy sulfur/selenium atom on the backbone to the tellurium atom.

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