

## Original Research Article

### **Electronic Structure, Charge-transfer and Optical properties of Neutral, Anionic and Cationic Poly(3-hexylthiophene-2,5-diyl) (P3HT) Using DFT and TD-DFT Quantum Mechanical Methods**

#### **Abstract**

Poly(3-hexylthiophene-2,5-diyl) (P3HT) with linear formula  $(C_{10}H_{14}S)_n$  and its derivatives are polymer-based materials with  $\pi$  conjugation framework. It is useful in photoelectric material and can be used as a promising material for applications in solar cells, light-emitting diodes, displays, or other optoelectronic devices. In this work, a theoretical study on Poly(3-hexylthiophene-2,5-diyl) (P3HT) using together quantum methods, density functional theory (DFT) and its derivative time dependent-density functional theory (TD-DFT) as implemented in Gaussian 09 package using B3LYP/6-31++G (d, p) and B3LYP/6-31+G(d) basis sets. Electronic properties, charge transfer properties such as frontier molecular orbitals (FMOs), ionization potential (IP), and electron affinity (EA), and optical properties such as the maximum absorption ( $\lambda_{max}$ ) along with oscillator strengths ( $f$ ) at the excited states in vacuum and solvents were calculated and reported for the neutral, anionic, and cationic forms of the molecule. The energy band gap ( $E_g$ ) of the material was best obtained at the anionic form with a value of 2.073eV using the 6-31+G(d) basis set. This small band gap of the material eases the transporting of electrons from HOMO level to LUMO level when the material absorbs the wavelength light. The NLO properties show that anionic has the highest value of total dipole moment ( $\mu_{tot}$ ) as 5.84116a.u while cationic has the highest value of first order hyperpolarizability ( $\beta_{tot}$ ) as  $(2.623 \times 10^{-30} \text{esu})$  using 6-311++G(d,p) basis. This value is found to be seven times more than that of urea ( $0.3728 \times 10^{-30} \text{esu}$ ) which is commonly used for the comparison of NLO properties. The oscillator strength expresses the probability of absorption of electromagnetic radiation, larger oscillator strength represents larger absorption coefficient. The UV-vis results show that thiophene solvent at excited state  $S_1$  corresponds to the strongest absorption at 370.34nm ( $f = 0.8517$ ) with excitation energy of 3.3479 eV using 6-311++G(d,p) basis set. The theoretical values of the open circuit voltage were found to be 1.685 eV for neutral, 2.729 eV for cationic, and 0.576 eV for anionic. The ir spectra results confirm the stability of the molecule with the most intense frequency of  $3023 \text{cm}^{-1}$  at an intensity of 91.2256km/mol for neutral molecule and the least intense frequency was found to be  $1112.9091 \text{cm}^{-1}$  at an intensity of 158.8877km/mol for the cationic molecule. This work could be applied in the design of more efficient functional photovoltaic organic materials.

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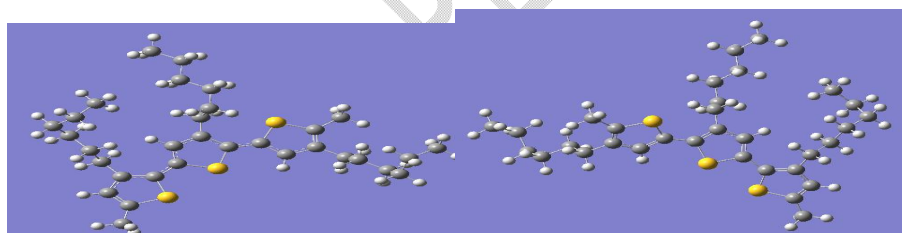
## Introduction

Shortage of energy has become a serious issue around the globe in the 21st century [1]. The urge to look for renewable energy to replace fossil fuel has driven substantial research effort into the energy sector [2]. Many research efforts were made in order to study the properties of other materials to solve the problem of this energy shortage, heterocyclic compounds included. Heterocyclic compounds are commonly distributed in nature and are essential to life in various ways [3]. Since the emergence of organic metals, a large amount of research work has been carried out in order to improve the conductivities of salts and charge transfer complexes (CT) of P3HT derivatives. Organic semiconductors such as small molecules [4] and conjugated polymers [5] are widely used in organic photovoltaic cells [6], dye-sensitized solar cells [7], organic field-effect transistors [8], and organic light-emitting diodes [9]. Poly (3-hexylthiophene-2,5-diyl) (P3HT) with linear formula  $(C_{10}H_{14}S)_n$  is a semiconducting polymer that is widely used in electronic applications. It belongs to a class of semicrystalline polymers referred to as regioregular poly (3-alkyl thiophene)s (P3AT)s. It is of particular interest for applications in quite technology due to its high carrier mobilities, stability, precedent use in devices, and tunable young's modulus [10]. However, interest in P3HT molecules goes beyond the area of conducting materials. To investigate its role as an important building block in supramolecular conductivity, various categories of organic conductors have now been described [11]. These include systems based upon molecular charge-transfer complexes, conjugated polymers, and stacked organometallic species, where the metal atoms play no active role in the conduction. Donor-acceptor type dyads using a Poly(3-hexylthiophene-2,5-diyl) (P3HT) framework have received considerable interest as materials for fluorescence switches, chemical sensors, molecular rectification, photovoltaic, and NLO applications [12]. Quantum mechanical calculation is one of the emerging methods in analyzing the physical and chemical properties of these molecules. Density Functional Theory (DFT) has emerged as a powerful method for the study of electronic properties of polyatomic molecules. The application of DFT to chemical molecular systems has received much attention because of its faster convergence in time than traditional quantum mechanical correlation methods [13]. Interestingly, many experimental and theoretical studies have been carried out in the synthesis and applications of poly(hexylthiophene-2,5-diyl) and its derivatives including Density Functional Theory and Time-Depended Density Functional Theory. For example, [14] carried out the study of electronic properties of P3HT by first principles density functional theory. A major breakthrough of over 10% power conversion efficiencies (PCEs) in both polymer and low molecular weight OPVs has been reported [15]. [16] examined the behavior of poly (3-hexylthiophene-2,5- diyl) between the upper and lower gold electrodes using the Fowler-Nordheim model and reported that the HOMO level of

P3HT was 5.2 eV and LUMO 3.1 eV. [17], investigated the effect of using single wall carbon nanotube (SWCNTs)-based hybrids as the hole transport layer on the performance of organic solar cells based on P3HT: PCBM blend using UV-Vis spectrophotometer. [18], investigated the effect of CuI doping in P3HT: PCBM active layer in inverted OSC for low light application using fluorine tin oxide (FTO)-Coated glass substrates. They reported that, the performance of the device with CuI-doped P3HT: PCMB improved hole collection and reduced charge recombination, leading to increased  $J_{sc}$ , FF and PCE of the device. Theoretical computational method such as geometry optimization is very important for understanding and predicting the pathways of electron and energy transfer processes in photoactive assemblies [13]. As a result, a set of global and local descriptors parameters to measure the reactivity of the molecule have been investigated.

To the best of our knowledge, work on anionic and cationic effects on the global chemical index, non-linear optical properties, thermodynamics properties, and IR spectra of poly(3-hexylthiophene-2,5-diyl) have not been reported. In the present work, we investigated the effect of anionic and cationic on the structural properties, molecular geometry, thermodynamic properties, nonlinear optical (NLO) properties, and chemical reactivity such as HOMO-LUMO, energy gap, chemical hardness, chemical potential, and IR spectra of the P3HT molecule. For this purpose, it was also investigated the effects induced on the bond lengths, bond angles, and UV Visible spectrum. Figure 1 shows the ptimized structures of anionic and neutral P3HT. [Aim of present work ???]

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Anionic P3HT

Neutral P3HT

Figure 1. Optimized structures of anionic and neutral P3HT

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## 2.0 Theoretical Background

### 2.1 Density Functional Theory (DFT)

Density Functional Theory (DFT) is a computational method that derives properties of the molecules based on a determination of their electron density. DFT methods have become the most widely-spread ab-initio methods in Computational Material Science (CMS) and Solid-state Physics, due to their high computational efficiency and very good accuracy for the structure of molecules, crystals, surfaces and their interactions. In DFT methods, the energy of the molecule is a functional of the electron density [19]. Density functional theory (DFT) was proposed by Hohenberg and Kohn as a method to determine the electronic structure of a system at ground state with a theory stating that all ground-state properties for many-particle systems are functional of the electron density. In 1965, Kohn and Sham (KS) reformulated the problem in a more familiar form and opened the way to the practical application of DFT [20].

The theorem states that the ground state electron density uniquely determines the electronic wave function and hence all ground state properties of an electronic system.

$$\rho(r) = \psi^2(r) \quad (1)$$

$$E = E_{in} + E_{en} + \frac{1}{2} \int \rho(r) dr \int \frac{\rho(r)}{r_e - r_i} dr + E_{xc} \quad (2)$$

The other theorem says that: the energy of an electron distribution functional reaches a minimum in correspondence to the actual ground-state electron density [21].

But  $\psi' \neq \psi$

$$E(n) = \langle \psi' | H | \psi' \rangle - \langle \psi_0 | H | \psi_0 \rangle \quad (3)$$

### 2.1.1 Time Dependent Density Functional Theory (TD-DFT)

The extension of Density functional theory (DFT) to the time-dependent domain, known as time-dependent density functional theory (TD-DFT) has been originally proposed by Runge and Gross 30 years ago. After ten years, Casida developed an effective linear-response (LR) formalism for TD-DFT (so-called random-phase approximation or Casida's equations) allowing to rapidly and efficiently determine the solution of the TD-DFT equations for molecules [22]. TDDFT is a conservatory of DFT but provides exact and basically suitable methods to evaluate electronic excitation energies of isolated systems and less commonly, solids [23]. TDDFT is a quantum mechanical theory used in physics and chemistry to investigate the properties and dynamics of many-body systems in the presence of time-dependent potentials, such as electric or magnetic fields. TD-DFT has become an extremely popular approach for modelling the energies, structures, and properties of electronically excited states (ES).

The Rung and Gross approach considers a single component system in the presence of time –dependent scalar field where the Hamiltonian is represented in the form [24].

$$H_s(t) = \hat{T} + \hat{V}_s(t) + E \quad (4)$$

Where T is the kinetic energy operator, E is the electron-electron interaction,  $V_{\text{exact}}(t)$  the external potential which defines the system in as well as number of electrons.

## 2.2 Vibrational Frequency

The vibrational frequencies are calculated with the following equations [25]:

$$V_{ij} = \frac{1}{\sqrt{m_i m_j}} \left( \frac{\partial^2 V}{\partial q_i \partial q_j} \right) \quad (5)$$

Where  $V_{ij}$  is the Hessian matrix,  $m_i$  refers to the mass of atom i, and  $\partial_{q_i}$  refers to a displacement of atom i in the x-, y-, or z-direction,

$$VU = \lambda U \quad (6)$$

Where  $U$  is a matrix of eigenvectors and  $\lambda$  is a vector of eigenvalues, and

$$\lambda_k = (2\pi\nu_k)^2 \quad (7)$$

Where  $\lambda_k$  is the  $k$ th eigenvalue and  $\nu_k$  is the  $k$ th vibrational frequency.

The infrared intensities can be computed with the equation [25]

$$\frac{\partial E_{SCF}}{\partial f \partial a} = 2 \sum_i^{d.o} h_{ij}^{fa} + 4 \sum_i^{d.o} \sum_j^{all} U_{ji}^a \quad (8)$$

Where

$$h_{ij}^{fa} = \sum_{\mu\nu}^{AO} C_{\mu}^{i0} C_{\nu}^{j0} \left( \frac{\partial^2 h_{\mu\nu}}{\partial f \partial a} \right) \quad (9)$$

Where ESCF is the self-consistent field energy, f is the electric field,  $a$  is the nuclear coordinate,  $h_{UV}$  is the one-electron atomic orbital integral,  $U_{ji}^a$  is related to the derivative of the molecular orbital coefficient with respect to  $a$  by

$$\frac{\partial C_{\mu}^i}{\partial a} = \sum_m^{all} U_{mi}^a C_{\mu}^{m0} \quad (10)$$

## 2.3 Global Reactivity Descriptors

The global reactivity descriptors are represented by [26,27] follows:

$$\mu = -\chi \quad (11)$$

The absolute electronegativity ( $\chi$ ) is given by the relation;

$$\chi = \frac{IPEA}{2} \quad (12)$$

The global hardness ( $\eta$ ) and global softness ( $S$ ) are defined as;

$$\eta = \frac{IPEA}{2} \quad (13)$$

$$S = \frac{1}{2} \eta \quad (14)$$

The electrophilicity ( $\omega$ ) can be calculated using the chemical potential and the chemical hardness;

$$\omega = \frac{\mu^2}{2} \quad (15)$$

The energy corresponding to HOMO represents the ionization potential and LUMO corresponds to the electron affinity of the molecule. Using Koopmans theorem;

$$\text{Ionization Potential (IP)} = -E_{\text{HOMO}}$$

$$\text{Electron Affinity (EA)} = -E_{\text{LUMO}}$$

#### 2.4 Electron donating Power ( $\omega^-$ ), Electron accepting Power ( $\omega^+$ ) and Net electrophilicity ( $\Delta\omega^\pm$ )

The electron donating ( $\omega^-$ ) and electron accepting ( $\omega^+$ ) powers are defined as [27]

$$\omega^- = \frac{(3I+A)^2}{16(I-A)} \quad (16)$$

and

$$\omega^+ = \frac{(I+3A)^2}{16(I-A)} \quad (17)$$

where  $I$  and  $A$  are the ionization potential and electron affinity respectively. It follows that a larger  $\omega^+$  value corresponds to a better

capability of accepting charge, whereas a smaller value of  $\omega^-$  value of a system makes it a better electron donor. In order to compare  $\omega^+$  with  $\omega^-$ , we use the following net electrophilicity as proposed by [27].

$$\Delta\omega^\pm = \omega^+ - (-\omega^-) = \omega^+ + \omega^- \quad (18)$$

that is, the electron accepting power relative to the electron donating power.

## 2.5 Open-Circuit Voltage (VOC)

The maximum open-circuit voltage ( $V_{OC}$ ), is a crucial photovoltaic parameter that can be obtained theoretically by the difference between the highest occupied molecular orbital (HOMO) of the donor and the lowest unoccupied molecular orbital (LUMO) of the electron acceptor. The theoretical value of  $V_{OC}$  has been calculated from the expression [28]

$$V_{OC} = E_{HOMO}^{Donor} - E_{LUMO}^{Acceptor} - 0.3 \quad (19)$$

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## 2.5 Non-Linear Optical (NLO) Properties

To have a clearer picture for the study of the non-linear optical properties (NLO) of poly(3-hexylthiophene-2,5-diyl) (P3HT) and its substituted molecules; the dipole moment ( $\mu$ ), polarizability ( $\alpha$ ), anisotropic polarizability ( $\Delta\alpha$ ), and hyperpolarizability ( $\beta$  and  $\gamma$ ) were computed at DFT/B3LYP with two basis sets.

For molecular systems, dipole moment can be obtained from [13,29];

$$\mu_{tot} = [\mu_x + \mu_y + \mu_z]^2 \quad (20)$$

Where  $\mu_x$ ,  $\mu_y$ , and  $\mu_z$  are the components of dipole moment in x, y and z coordinates

Electric dipole polarizability is given by [30];

$$\alpha = \frac{\partial^2 E}{\partial F_a \partial F_b} \quad (21)$$

where a and b are coordinates of x, y, and z.

The mean polarizability is calculated using [31];

$$\langle \alpha \rangle = \frac{1}{2} (a_{xx} + a_{yy} + a_{zz}) \quad (22)$$

Where  $a_x$ ,  $a_y$ , and  $a_z$  quantities are known as principal values of polarizability tensor.

The anisotropic polarizability is given by [32];

$$\Delta\alpha = 2^{-1/2} [(a_{xx} - a_{yy})^2 + (a_{yy} - a_{zz})^2 + (a_{zz} - a_{xx})^2 + 6(a_{xz} + a_{xy} + a_{yz})]^1/2 \quad (23)$$

The first hyperpolarizability is defined as [29];

$$\beta = [(\beta_{xxx} + \beta_{yyy} + \beta_{zzz})^2 + (\beta_{yyy} + \beta_{yzz} + \beta_{yxx})^2 + (\beta_{zzz} + \beta_{xzz} + \beta_{zyy})^2]^1/2 \quad (24)$$

The second order hyperpolarizability is given by [30];

$$\gamma = \frac{1}{5} [\gamma_{xxxx} + \gamma_{yyyy} + \gamma_{zzzz} + 2(\gamma_{xxyy} + \gamma_{xxzz} + \gamma_{yyzz})] \quad (25)$$

### 3. COMPUTATIONAL METHODS

All computations were performed using the G09 suite of programs [33]. The molecular structures and geometries of P3HT were completely optimized using ab-initio quantum mechanical calculations at the DFT levels of theory without using any symmetry constraints using (6-31++G (d, p) and 3-21G (d,)) basis sets. The parameters were allowed to fully relax and each of the calculations converged to an optimized geometry corresponding to a true energy minimum. Geometry optimization is a name given to the procedure that attempts to find the configuration of minimum energy of the molecule. The procedure calculated the wave function and the energy at the starting geometry and then proceeded to search a new geometry of a lower energy. This was repeated until the lowest energy geometry was obtained. Stability check was performed on the molecule to confirm its stability status prior to geometry optimization. The optimized geometries were then used to set up further calculations to compute the HOMO, SOMO, and LUMO values as well as global chemical index parameters. At the same levels of the theory, dipole moment, electric dipole polarizability, mean polarizability, anisotropic polarizability, hyperpolarizability were also computed using the same optimized geometries. The nonlinear optical properties of the molecule such as dipole moment, isotropic polarizability, anisotropic polarizability and total first and second order hyperpolarizability were also computed by using similar procedure. The IR frequencies were calculated by obtaining the Hessian matrix and the force constants for all the normal modes of the molecule. No imaginary frequencies were seen thus confirming the stability of the molecule. The analysis of the spectra was done using IRPal 2.0 version software [34]. The excited states of the molecules were determined using time-dependent density functional theory (TD-DFT) [35] utilizing B3LYP functional with (6-31++G (d, p) and 3-21G (d,)) basis sets from ground state optimized geometry in vacuum and in some solvents (Chloroform, Acetone, Methanol, Toluene, and Thiophene).

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### 4. RESULTS AND DISCUSSION

#### 4.1 Optimized Bond Lengths (Å) of poly(3-hexylthiophene-2,5-diyl) (P3HT) Molecule for neutral, anionic, and cationic

The distance between the nuclei of two atoms covalently bonded together named as bond length whereas bond angle is the angle between two adjacent bonds of an atom in a molecule [27]. The optimized values of bond lengths and bond angles of the studied molecule were calculated and reported in Tables 1 and 2 at DFT/B3LYP level using 3-21G(d) and 6-311++G (d, p) basis sets in neutral, anionic, and cationic. From Table 1, there are small variations in bonds lengths of P3HT when optimized in anionic and cationic compared with that in neutral. The result shows that the lowest value obtained was 1.0827 Å R (4,5) in

cationic. However, when compared the results of P3HT molecule in neutral and anionic, the bond lengths are a bit lower than in neutral and cationic forms. It is worth noting that, the smaller the bond length, the higher the bond energy and stronger the bond will be [36]. Accordingly, this shows that the bond energy of P3HT in cationic is slightly stronger than in neutral and anionic forms. Hence, large amount of energy is required to break these bonds. However, the longest bond length which doubles as the weakest is 1.7701 Å (C<sub>21</sub>-S<sub>23</sub>). This is found in anionic molecule. It requires smaller amount of energy to break the bonds. The structural geometry of the studied molecule that consists of bond lengths and bond angles are found to be in good agreement with those from previous work reported by [37,38].

**Table 1. Selected bond lengths (Å) of the optimized structure of P3HT molecule the neutral, anionic, and cationic molecule**

Bond length	Neutral	Anionic	Cationic	Neutral	Anionic	Cationic	Previous work [35,36]
	<b>3-21G(d)</b>			<b>6-311++G (d, p)</b>			
R(1,2)	1.754	1.7701	1.7222	1.7542	1.7575	1.7221	1.70
R(1,3)	1.7482	1.7658	1.7686	1.7483	1.7538	1.7686	
R(2,4)	1.3706	1.3861	1.4431	1.3706	1.376	1.4431	1.43
R(2,6)	1.4996	1.4946	1.4815	1.4998	1.5018	1.4815	
R(3,5)	1.3626	1.3782	1.3931	1.3626	1.3674	1.3931	1.37
R(3,7)	1.4979	1.4929	1.4800	1.4983	1.5004	1.4800	1.42
R(4,5)	1.0857	1.0866	1.0827	1.0845	1.0866	1.0827	
R(5,9)	1.0939	1.0945	1.0979	1.0939	1.0959	1.0980	
R(6,10)	1.0955	1.108	1.0893	1.0953	1.1006	1.0893	
R(6,11)	1.0917	1.0934	1.095	1.0953	1.0951	1.095	
R(6,12)	1.0946	1.1056	1.0964	1.0944	1.0993	1.0964	
R(7,13)	1.0946	1.0958	1.0965	1.0945	1.097	1.0965	
R(7,14)	1.0946	1.0958	1.0965	1.0945	1.097	1.0965	

#### 4.2 Optimized bond angle (°) of poly(3-hexylthiophene-2,5-diyl) (P3HT) molecule for neutral, anionic, and cationic.

The optimized bond angles of P3HT molecule in neutral, anionic, and cationic forms are listed in Table 2. The bond angle is the average angle between the orbitals of the central atom containing the bonding electron pairs in the molecule [39]. It is expressed in degrees. The bond angle throws more light on the distribution of orbital's around a central atom in a molecule. The bond angles also contribute to the shape of a molecule. From Table 2, there is a slight increase in the bond angles of the studied molecule in neutral and anionic when compared to cationic. From the results obtained, the values obtained in neutral and anionic are a bit higher than the one obtained in cationic. This indicates that, in terms of bond angles, P3HT molecule has

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greater stability in neutral and anionic than in cationic. The bond angles were found to have an average value of  $110^\circ$  in neutral, anionic as well as cationic. The structural geometry of the titled molecule that consists of bond lengths and bond angles are found to be in good agreement with those from previous work reported by [40]

**Table 2. Selected bond angles ( $^\circ$ ) of the optimized structure of P3HT molecule in the gas phase and in different solvents**

Bond length	Neutral	Anionic	Cationic	Neutral	Anionic	Cationic	Previous work [40]
	<b>3-21G(d)</b>			<b>6-311++G (d, p)</b>			
A (2,1,3)	92.4398	92.1881	91.3787	92.4426	92.5301	91.3815	
A (1,2,4)	110.7346	110.274	111.9248	110.7087	110.673	111.9221	
A (1,2,6)	119.5339	119.4881	121.4864	119.5614	119.8534	121.4926	
A (4,2,6)	129.7199	129.2237	126.5722	129.7222	129.3944	126.5672	
A (1,3,5)	109.7536	109.3478	110.8397	109.7741	109.6247	110.8361	
A (1,3,7)	121.4481	120.9921	120.8342	121.445	121.7466	120.8368	
A (5,3,7)	128.7954	128.6271	128.3249	128.7783	128.6206	128.326	129.00
A (2,6,11)	111.9626	112.5354	112.5927	111.8166	111.9442	112.5936	113.00
A (2,6,12)	110.8115	110.8893	110.5018	110.5603	110.6712	110.5112	
A (10,6,11)	107.2157	106.5283	108.3085	107.4199	107.3053	108.3109	
A (10,6,12)	107.378	107.0605	106.5245	107.5957	107.531	106.5191	
A (11,6,12)	107.3385	106.8315	109.0086	107.5138	107.173	109.015	109.00
A (3,7,13)	112.0727	112.322	110.8435	111.9088	112.0313	110.835	

### 4.3 Frontier Molecular Orbital Energies

Table 3, gives the total energy, values of Highest Occupied Molecular Orbital (HOMO), Lowest Unoccupied Molecular Orbital (LUMO), Singly-Occupied Molecular Orbital (SOMO), and Energy gap ( $E_{\text{gap}}$ ) in electron volt (eV) of the studied molecule in neutral, anionic, and cationic forms calculated at the DFT/B3LYP level using 3-21G(d) and 6-31++G (d, p) basis sets. The values of HOMO, LUMO and their energy gap reflect the chemical activity of the molecule. The values of the SOMO are only associated with the ionic forms of the molecule. Molecules with lower HOMO-LUMO gap value tend to have higher stability [20]. Both HOMO and LUMO are the main orbital taking part in chemical reaction. It is clear from Table 3 that the HOMO-LUMO energy gap for anionic is lower in 6-31G basis set with value of about 2.125eV, but for 6-311++G(d,p) basis set, the value is a bit higher of about 3.02 eV. This is followed by cationic molecule with value of 3.050 eV, using 6-31G(d) basis set and neutral with value of 3.882 eV, by 6-311++G(d,p) basis set. The results show that, P3HT has the best band gap energy in anionic form as 2.125 eV than in cationic and neutral. Conjugation allows free movement of electrons within the molecule. The more conjugation (and therefore free movement of electrons) there is in a molecule, the less of an energy gap will exist between the Highest Occupied Molecular Orbital (HOMO) and the Lowest Unoccupied

Molecular Orbital (LUMO). Thus the smaller the band gap, the much better is the result. Therefore, the electron transfer from HOMO to LUMO of the molecule in anionic is relatively harder than that in cationic and neutral. This shows that P3HT molecule is having higher stability in anionic than in cationic and neutral. However, P3HT has larger energy gap in neutral (3.882 eV) than in anionic and cationic, thus, the electron jumps from the HOMO to the LUMO energy orbital more easily in neutral than in ions. The HOMO-LUMO/SOMO gap of P3HT obtained in both vacuum and charged molecules are almost close to 3.10 eV and 2.20 eV reported by [41,42]. The total energy calculation shows that the neutral molecule is most stable having the lowest energy value of  $-867.678429941$  a.u. with 6-311++G (d, p) basis set. The Calculated values of ionization potential (IP), electron affinity, electron donating Power ( $\omega^-$ ), electron accepting Power ( $\omega^+$ ) and Net electrophilicity ( $\Delta\omega^+$ ) of neutral and ionic Poly(hexylthiophene-2,5-diyl) are presented in Table 4. Ionization potential (IP) and electron affinity (EA) are important parameters for optoelectronic applications of conjugated organic materials and are called charge transfer properties of the molecule. A smaller IP value facilitates the hole injection from HOMO, whereas a larger EA value will ease the electron injection into the empty LUMO of the semiconducting materials which may be good for the electron transport and behaves as n-type semiconducting materials. Since a smaller value of  $\omega^-$  makes it a better electron donor, it can be observed the ionic form of the molecule is lowest with a value of 2.053 eV using 6-311++G(d,p) basis set. Thus the ionic molecule will be a better electron donor compared to the neutral form of the molecule. Similarly a larger value of  $\omega^+$  corresponds to a better capability of the molecule to accept charge. Based on this, the neutral molecule has the largest value of  $\omega^+$  as 6.468 eV using 6-311++G(d,p) basis set. This makes it a better charge acceptor.

**Table 3: Calculated Total Energy, HOMO, LUMO and Energy gap of Poly(hexylthiophene-2,5-diyl)**

Molecule	Basis Sets	Total Energy (a.u)	$E_{\text{HOMO/SOMO}}$ (eV)	$E_{\text{LUMO}}$ (eV)	$E_{\text{gap}}$ (eV)	Previous work (eV) [42,43]
Neutral	3-2G(d)	-867.652024657	-5.008	-1.125	3.883	2.20
	6-311++G (d, p)	-867.678429941	-5.2109	-2.1488	3.062	
Anionic	3-2G(d)	-867.622896352	0.9012	2.9742	2.073	3.10
	6-311++G (d, p)	-867.551493384	0.6894	3.7132	3.024	
Cationic	3-2G(d)	-867.403538100	-8.3417	-5.2913	3.050	
	6-311++G (d, p)	-867.403777116	-6.4549	-3.3796	3.075	

**Comment [MF17]:** Approximated to 4 digit for whole paper.

**Comment [MF18]:** Split the computed value for 3-21 and 6-31 basis on new table.

**Comment [MF19]:** Why the high difference between band gap values.

**Comment [MF20]:** According the values of previous study, your present work doesn't agreement with experimental values. You can check an other basis set.

**Comment [MF21]:** Why the high difference between band gap values.

**Comment [MF22]:** Why the high difference between band gap values.

**Table4: Calculated Ionization potential (IP) , Electron affinity , Electron donating Power( $\omega^-$ ), Electron accepting Power ( $\omega^+$ ) and Net electrophilicity( $\Delta\omega^\pm$ ) of neutral and ionic Poly(hexylthiophene-2,5-diyl)**

Molecule	IP (eV)		EA (eV)		$\omega^-$ (eV)		$\omega^+$ (eV)		$\Delta\omega^\pm$ (eV)	
	6-31G(d)	6-311++G(d,p)	6-31G(d)	6-311++G(d,p)	6-31G(d)	6-311++G(d,p)	6-31G(d)	6-311++G(d,p)	6-31G(d)	6-311++G(d,p)
Neutral	5.008	5.2109	1.125	2.149	4.198	6.468	1.138	2.774	5.336	9.242
Ionic	6.762	7.474	-0.793	-3.44	3.143	2.053	0.157	0.0464	3.300	2.099

#### 4.4 Global Chemical Reactivity Parameters (GCRP)

The Global Chemical Reactivity Descriptors parameters of molecules such as hardness ( $\eta$ ), softness ( $J$ ), chemical potential ( $\mu$ ), electronegativity ( $\chi$ ) and electrophilicity index ( $\omega$ ) in neutral, anionic and cationic forms are calculated and reported in Table 5. Chemical hardness is proportional to the HOMO-LUMO energy gap. An increase in the chemical hardness makes the molecule more stable and less reactive. As seen in Table 5, P3HT molecule in the cationic with slightly higher value of chemical hardness of 1.3eV is considered to be harder and more stable. This is followed by neutral and anionic with values as 1.2 eV and 0.9 eV respectively. This indicates that P3HT molecule in cationic is more stable. Electronegativity and chemical potential are important parameters in the quantum chemical reaction. The higher the value of electronegativity, the greater the ability of the atoms or molecules to attract electrons, whereas the greater the value of chemical potential, the more the reactivity and less stable the molecule [44]. P3HT molecule in the cationic has a higher electronegativity than in the neutral and anionic as. The molecule also has the greatest value of chemical potential in cationic. Consequently, this molecule is more reactive and less stable in cationic form. The electrophilicity index value is used for the determination of chemical reactivity of molecules. The result indicates that the electrophilicity index with value

as 25.7179 eV was highest in the cationic form. This affirms the stability of the molecule in cationic than in the neutral and anionic forms.

**Table 5: Global chemical indices of the optimized poly(hexylthiophene-2,5-diyl)**

Molecule	$\eta$ (eV)	S(eV)	$\chi$ (eV)	$\mu$ (eV)	$\omega$ (eV)
<b>6-311+G(d)</b>					
Neutral	1.2	0.83	1.18	-1.18	0.58
Anionic	0.9	1.1	1.81	-1.81	1.82
Cationic	1.3	0.7692	-7.9783	7.9783	24.4820
<b>6-311++ G (d, p)</b>					
Neutral	1.1	0.91	1.28	-1.28	0.744
Anionic	0.1882	0.0941	1.3822	-1.3822	5.0757
Cationic	1.25	0.8	-8.0184	8.0184	25.7179

#### 4.4 UV-Visible Spectrum

UV-VIS spectrum is due to the interaction of electromagnetic radiation in the UV-Visible region with molecules, ions, or complexes. It forms the basis analysis of different substances such as inorganic, organic and bio-molecules. On the other hand, how the absorption of a new material matches with the solar spectrum is an important factor for the application as a photovoltaic material and a good photovoltaic material should have broad and strong visible absorption characteristics [42]. For this study, the UV-Visible spectrum was calculated from the optimized geometry of the studied molecule using TD-DFT with 6-311+G(d) and 6-311++G(d,p) basis sets. The absorption spectrum was presented as oscillator strength against excitation energy as shown in Fig 1(a) to (d). Gauss View5.0 was used to plot the spectra. The results obtained show that the studied molecule has maximum excitation energy of 362.83nm and oscillator strength of 0.8891 at 6-31+G(d) basis set. While for 6-311++G(d,p) basis set, the maximum excitation energy was 370.34 nm and the oscillator strength was 0.8517. These indicates that P3HT is a good photovoltaic material due to its strong absorption character. The excitation energy and oscillator strength are listed in with solvents: Acetone, Chloroform, Methanol, Thiophene and Toluene. The results obtained show that due to the solvent effect, there was an increase in the excitation energy and oscillator strength.

Comment [MF23]: Should unity basis set.

Comment [MF24]: It wave length, you mean wave length of absorption,

Comment [MF25]: Unity the font types

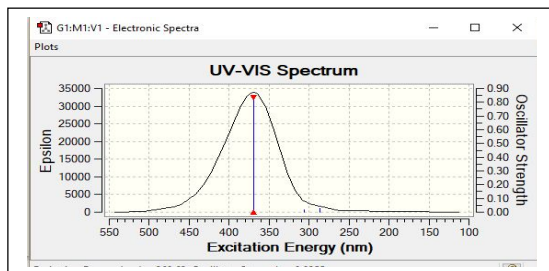
Comment [MF26]: How solvent effect on wavelength, can describe it chemically or physically.

The excitation energies were in the range of 280.56-362.83nm for 6-31+G(d) basis set, and 285.61-370.34nm for 6-311++G(d,p) basis set. The results further show that thiophene solvent at excited state  $S_1$  corresponds to the strongest absorption at 370.34nm ( $f = 0.8517$ ) with excitation energy of 3.3479 eV using 6-311++G(d,p) basis set. Figure 2 shows the spectra of P3HT at different solvents and basis sets.

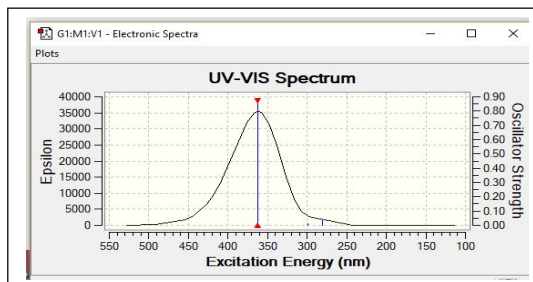
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**Table 6: Wavelength  $\lambda$ (nm), Excitation energy (eV) and Oscillator strength of poly(3-hexylthiophene-2,5-diy)**

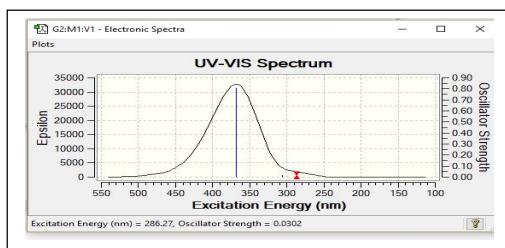
Vacuum/Solvent	Transition state	6-31+G(d)			6-311++G (d, P)		
		Wavelength $\lambda$ (nm)	Excitation energy (eV)	Oscillator strength (f)	Wavelength $\lambda$ (nm)	Excitation energy (eV)	Oscillator strength (f)
Vacuum	$S_0 \rightarrow S_1$	360.72	3.4372	0.7168	361.39	3.4308	0.7152
	$S_0 \rightarrow S_2$	305.57	4.0575	0.0163	305.79	4.0546	0.0160
	$S_0 \rightarrow S_3$	282.82	4.3839	0.0213	284.17	4.3630	0.0011
Chloroform	$S_0 \rightarrow S_1$	362.17	3.4303	0.8552	369.63	3.3543	0.8355
	$S_0 \rightarrow S_2$	299.27	4.1400	0.0116	305.98	4.0520	0.0184
	$S_0 \rightarrow S_3$	280.75	4.4113	0.0350	286.03	4.3347	0.0299
Acetone	$S_0 \rightarrow S_1$	361.44	3.4303	0.8552	368.84	3.3615	0.8160
	$S_0 \rightarrow S_2$	299.48	4.1400	0.0116	305.99	4.0520	0.0171
	$S_0 \rightarrow S_3$	281.06	4.4113	0.0350	286.31	4.3304	0.0303
Methanol	$S_0 \rightarrow S_1$	361.05	3.4340	0.8552	368.44	3.3651	0.8091
	$S_0 \rightarrow S_2$	299.50	4.1397	0.0114	305.97	4.0521	0.0169
	$S_0 \rightarrow S_3$	281.02	4.4119	0.0348	286.27	4.3310	0.0302
Toluene	$S_0 \rightarrow S_1$	362.34	3.4218	0.8839	369.86	3.3522	0.8464
	$S_0 \rightarrow S_2$	299.06	4.1458	0.0133	305.95	4.0524	0.0195
	$S_0 \rightarrow S_3$	280.31	4.4232	0.0340	285.61	4.3410	0.0290
Thiophene	$S_0 \rightarrow S_1$	362.83	3.4172	0.8891	370.34	3.3479	0.8517
	$S_0 \rightarrow S_2$	299.13	4.1448	0.0133	305.99	4.0519	0.0196
	$S_0 \rightarrow S_3$	280.56	4.4192	0.0346	285.86	4.3373	0.0295



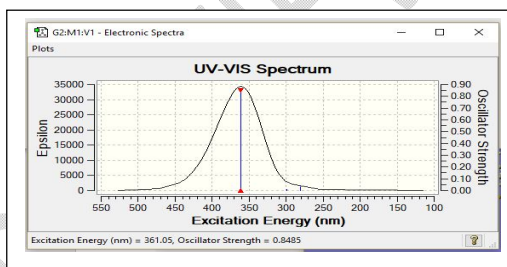
Chloroform 6-31++G(d,p)



Chloroform 6-31+G(d)



Methanol 6-31++G(d,p)



Methanol 6-31+G(d)

Comment [MF28]: Use Microsoft office or an other types of program to draw the UV-Visible spectrum

#### 4.5 Non-Linear Optical Properties

Non-linear optical (NLO) effect arises from the interactions of electromagnetic fields in various media to produce new fields altered in phase, frequency, amplitude and other propagation characteristics from the incident fields [45]. Also, dipole moment in a molecule is an important electronic property which results from non-uniform distribution of charges on the various atoms in the molecule [46]. It is worth noting that, the molecule with higher dipole moment tends to be a polar material. Our investigation considered the effects of ionic on the non-linear optical properties of P3HT. This is necessary for fully understanding of the nonlinear optical response of the molecule. Table 7 shows the non-linear optical properties of P3HT in anionic, cationic and neutral forms. It can be observed from the table that there is an increase in values of total dipole moments ( $\mu_{tot}$ ), anisotropy of polarizability ( $\Delta\alpha$ ), first-

order hyperpolarizability ( $\beta_{tot}$ ), second order hyperpolarizability ( $\gamma_{tot}$ ), and the mean polarizability ( $\alpha$ ) due to the effects of the ionic. From the results obtained, anionic has the highest values of dipole moment with a value of 5.84116 Debye. The increase in the dipole moments of P3HT in anionic affirms that the molecule may behave as polar material in ionic. Our findings reveal that P3HT molecule in the cationic has slightly higher value of mean polarizability when compared with the results obtained in anionic and neutral. However, the results obtained for total anisotropic polarizability show that P3HT in neutral has slightly higher value as  $3.87 \times 10^{-24}$  when compared with the results obtained in anionic and cationic. Also, from the results in Table 7, P3HT molecule in cationic has slightly higher value of first-order hyperpolarizability ( $2.623 \times 10^{-30}$  esu) followed by cationic and neutral with values as ( $1.439 \times 10^{-30}$  esu) and ( $9.48 \times 10^{-31}$  esu) respectively. The value obtained for the first order hyperpolarizability in cationic ( $2.623 \times 10^{-30}$  esu) is seven times more than that of the urea molecule ( $0.3728 \times 10^{-30}$  es), which commonly used for the comparison of NLO properties, which makes the molecule a good material for photovoltaic applications.

**Table 7. Non-linear optical properties (in electrostatic unit, esu) and dipole moment in (Debye) of the optimized P3HT Molecule in the gas phase and different solvents**

Molecule	$\mu_{tot}$	$\langle \alpha \rangle$	$\langle \Delta \alpha \rangle$	$\beta_{tot}$	$\gamma_{tot}$
<b>6-31+G(d)</b>					
Neutral	0.69374	$-3.37 \times 10^{-23}$	$3.77 \times 10^{-24}$	$9.38 \times 10^{-31}$	$-2.475 \times 10^{-17}$
Anionic	5.81114	$-4.091 \times 10^{-23}$	$1.704 \times 10^{-24}$	$1.139 \times 10^{-30}$	$-8.199 \times 10^{-20}$
Cationic	4.58540	$-2.641 \times 10^{-23}$	$1.169 \times 10^{-24}$	$2.523 \times 10^{-30}$	$-8.675 \times 10^{-20}$
<b>6-311++G(d,p)</b>					
Neutral	0.69378	$-3.47 \times 10^{-23}$	$3.87 \times 10^{-24}$	$9.48 \times 10^{-31}$	$-2.485 \times 10^{-17}$
Anionic	5.84116	$-4.061 \times 10^{-23}$	$1.804 \times 10^{-24}$	$1.439 \times 10^{-30}$	$-8.599 \times 10^{-20}$
Cationic	4.71540	$-2.731 \times 10^{-23}$	$1.169 \times 10^{-24}$	$2.623 \times 10^{-30}$	$-8.475 \times 10^{-20}$

#### 4.5 Infrared Spectrum

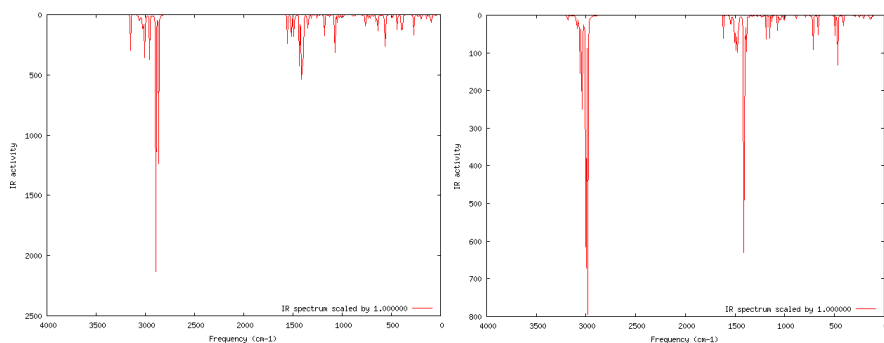
Infrared spectroscopy is the study of how molecules absorb infrared radiation and thus convert it to heat. Thus, an IR spectrum is the study of the interaction of infrared light with matter. When a molecule absorbs infrared radiation, its chemical bond vibrates and may either be stretched, contracted, or bend [19]. molecule has no imaginary frequency in both

ions and neutral. This shows that the molecule was stable. The spectrum was plotted as IR against frequency in Figure 3(a) and (b). In a neutral, the most intense frequency was found to be  $3023\text{cm}^{-1}$  at an intensity of  $91.2256\text{km/mol}$ , at this frequency there is a medium =C-H stretch, strong (broad) dimer OH, and small Ar-H stretch mode of vibrations were observed. The second most intense frequency was found to be  $3018\text{cm}^{-1}$  at an intensity of  $75.7146\text{km/mol}$ . At this frequency there is a medium =CH stretch, strong(broad) dimer OH and small Ar-H stretch mode of vibrations were observed. IR PAL 2.0 was used to interpret these frequencies [43]. In the medium, the most intense frequency for anionic was found to be  $2980.5244\text{cm}^{-1}$  at an intensity of  $1497.1328\text{km/mol}$ . At this frequency, medium =CH stretch, strong (broad) dimer OH, strong (broad)dimer OH, and Ar-H stretch were observed. The second most intense frequency was  $3088\text{cm}^{-1}$  at an intensity of  $958.2909\text{km/mol}$ . At this frequency, strong (broad) dimer OH, strong (broad) dimer OH, and small Ar-H stretch were observed. For the cationic,the most intense frequency was found to be  $1112.9091\text{cm}^{-1}$  at an intensity of  $158.8877\text{km/mol}$ . At this frequency, there was a strong = C-F stretch, strong C-O stretch, medium stretch, small C=S thiocarbonyl, wagg P-H phosphine oxide, strong P=O phosphate and as well as strong C-O stretch mode of vibrations were observed. The second most intense frequency was found to be  $1112.9030\text{cm}^{-1}$  at an intensity of  $157.7526\text{km/mol}$ . At this frequency, there was a strong = C-F stretch, strong C-O stretch, medium stretch, small C=S thiocarbonyl, wagg P-H phosphine oxide, strong P=O phosphate and as well as strong C-O stretch mode of vibrations were observed.

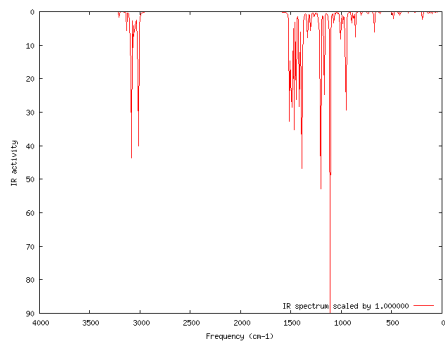
**Comment [MF29]:** Check the values of vibration frequencies for all bonds

**Comment [MF30]:** The structure doesn't contain P???

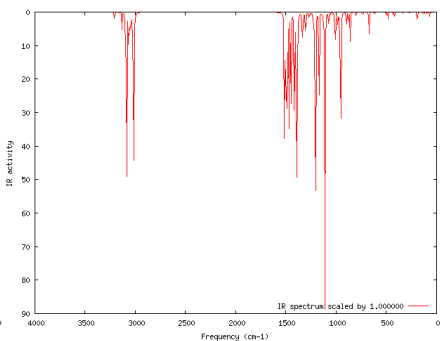
**Comment [MF31]:** The structure doesn't contain P???



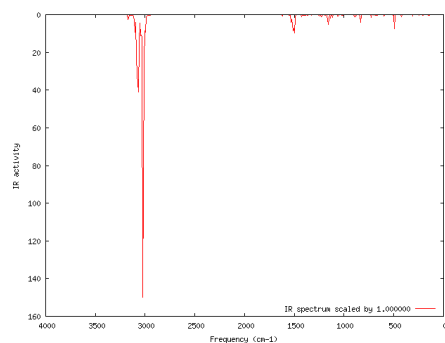
Anionic +



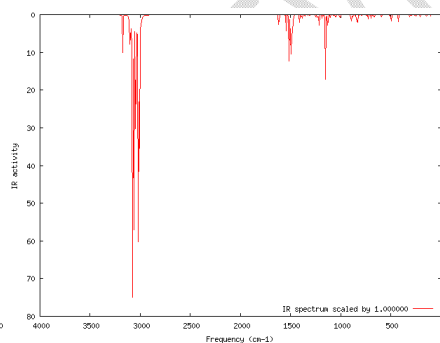
Anionic ++



Cationic +



Cationic ++



Neutral +

Neutral ++

Figure 3 IR Spectrum of P3HT (a) Vacuum (b) Medium

#### 4.6 Open-circuit Voltage ( $V_{OC}$ )

The open-circuit voltage of an organic solar cell is related to the difference between the HOMO of the donor and the LUMO of the electron acceptor, considering the energy loss during photo charge generation [44]. The theoretical values of  $V_{OC}$  have been calculated using equation (16), the values obtained were: 1.685 eV for neutral, 2.729 eV for cationic, and 0.576 eV for anionic. These values are sufficient for possible efficient electron injection; therefore, the studied molecule can be used for organic solar cell application.

**Comment [MF32]:** Same note about the UV-Visible, use some program to draw the spectrum

**Comment [MF33]:** I pointed the correct unit for  $V_{OC}$

**Comment [MF34]:** [Theoretical study on dye-sensitized solar cells using graphene quantum dot and curcumin, phthalocyanine dyes - IOPscience](#)  
You can read this article to take a look about the process of injection process in organic solar cell

#### 5. CONCLUSION

We presented a detailed theoretical characterization of the most stable neutral, anionic and cationic P3HT. This allows knowledge of its relative stability, structural and thermochemical and spectroscopic properties to be expanded. This is certainly an important step for the determination of their composition and the possible reactions leading to their formation in both laboratory and industrial environments, reactions that occur either in the gas phase, on small aggregates or on medium surfaces. The optimized parameters (bond length and bond angle) were calculated at DFT/B3LYP/6-311+G(d), the results obtained show that the lowest average value of bond length in vacuum and medium are 1.08311Å and 1.0830Å while the lowest value of the bond angle ranges from 105.429-105.815<sup>0</sup> in vacuum and 105.449-105.923<sup>0</sup> in medium. The HOMO, LUMO, and energy gap were obtained as -5.2109 eV, -2.1488 eV, and 3.06 eV in vacuum. While in medium they were obtained as 1.0897 eV, 4.1021 eV, and 3.01 eV. The chemical potential, electronegativity, hardness, softness and electrophilicity of the studied molecule were calculated and reported. The results indicate high stability and low reactivity of the molecule in chemical reaction and also indicate that the studied molecule is a good electrophile. The result of the IR spectrum shows that the studied molecule was stable in both the neutral and ions since no imaginary frequency was observed. It was also observed that the most intense frequency was found to be 3023cm<sup>-1</sup> at an intensity of 91.2256km/mol in neutral. In the medium, the most intense frequency for anionic was found to be 2980.5244cm<sup>-1</sup> at an intensity of 1497.1328km/mol. At this frequency, medium =CH stretch, strong (broad) dimer OH, strong (broad)dimer OH, and Ar-H stretch were observed. The theoretical values of the open circuit voltage were found to be 1.685 eV for neutral, 2.729 eV for cationic, and 0.576 eV for anionic. Thus, these values are sufficient for possible electron injection, thus making poly (3-hexylthiophene -2,5- diyl) as a useful material for solar cells applications.

**Comment [MF35]:** Re-write this part and use only the best result that need to present.

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**Comment [MF36]:** Unity the style of references

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