SOLVENT AND SUBSTITUENT EFFECTS ON ELECTROCHEMICAL PARAMETERS OF 5-MEMBERED HETERO AROMATIC MONOMERS: DENSITY FUNCTIONAL THEORY STUDY

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I hereby certify that I have read and evaluated this Thesis titled 'Solvent and Substituent Effects on Electrochemical Parameters of 5-membered Hetero Aromatic monomers: Density Function Theory Study' prepared under our guidance by Rehima Sheberu. I recommend that it be submitted as fulfilling the thesis requirement.

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DEDICATION

This thesis manuscript is dedicated to my mother Muntaha Ahmed, to my spouse Ashenafi Jumato and to all my families who encouraged and strengthened me in whole my life.

STATEMENT OF THE AUTHOR

By my signature below, I declare and affirm that this Thesis is my own work and I have followed all ethical and technical principles of scholarship in the preparation, data collection, data analysis and compilation of this thesis. Any scholarly matter that is included in the Thesis recognized through citation.

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BIOGRAPHICAL SKETCH

The author was born in Gurage Zone, Mareko Woreda in Southern Nation and Nationalities Peoples Region on May 26, 1995.She attended her elementary and junior education from 2002-2009 at Koshe Primary School and secondary education at Koshe Secondary & Preparatory School from 2010-2013. After completing preparatory school, she joined Kotebe University College in 2014 and graduated in 2016 from Department of Chemistry with Bachelor of Science Degree in Applied Chemistry. Soon after graduation, the author was recruited by MOE (Ministry of Education) as a Graduate Assistant at Bonga University and joined Haramaya University, College of Natural and Computational Sciences, Department of Chemistry in 2017 to pursue her postgraduate studies in Physical Chemistry.

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ACRONYMS AND ABBREVIATIONS

B3LYP	Becke–Lee–Young–Parr Composite of Exchange Correction Functional
CP	Conjugated Polymer
DFT	Density Functional Theory
E_{gap}	Bandgap energy
E_{HOMO}	Higher Occupied Molecular Orbital energy
E_{LUMO}	Lowest Unoccupied Molecular Orbital energy
IEF-PCM	Integral Equation Formalism with Polarizable Continuum Model
IP	Ionization Potential
IPk	Ionization Potential predicted by Koopman's theorem
IPv	Ionization Potential calculated from the energy differences between the neutral monomer and the radical cations.
MO	Molecular Orbital
PA	Poly acetylene
PANI	Polyaniline
PFu	Poly furan
PPy	Polypyrrole
PTh	Poly thiophene
ζ	Zeta

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ABSTRACT

Pyrroles, thiophenes and furans represent building blocks conjugated poly(heterocycles) which, as organic conductors are potential materials for various applications. Oxidation of β-substituted pyrroles, thiophenes and furans constitutes an important first step in the process of electroplymerization. Key electrochemical parameters such as function coefficient (Fn), atomic charge distribution, ionization potential (IP) and bandgap and salvation energy are most important properties regarding monomers and their radical cations. These properties are studied as a function of electron withdrawing and electron donating substituent of pyrrole, thiophene and furan ring and studied as a function of solvent polarity. Evaluation of electrical, structural and thermodynamic properties the monomers and their corresponding radical cations are studied as an effect on various electrochemical parameters using density functional theory (DFT) and B3LYP methods with 6-31G(d, p) and 6-31++G(d, p) basis set in solution phase using Polarized Continuum Model (PCM) method. The theoretical calculation indicates electron-withdrawing solvents increase the IP while electron-donating groups decrease the value and hence contributing for easer oxidation step. It was also observed that dipole moment, Fn, atomic charge distribution and bandgap follows generally the order pyrroles > furans > thiophenes. Besides, the results showed that charge distribution decrease with polarity of solvent and in the case of electron donating group whereas solvent polarity on Fn have no significant effect. On the other hand, bandgap of monomers are greater than their radical cations indicating the stability of the monomers. Generally, the DFT calculation demonstrates that efficiency of polymerization is affected with the nature of substituent and solvent polarity.

Keywords: Conducting polymers, Density functional theory, Electroplymerization, Furan, Thiophene, pyrrole

1. INTRODUCTION

Electrochemical oxidation of aromatic heterocycles such as pyrrole, furans, thiophenes, indoles, carbazoles and their derivatives are known to be the best monomers, frequently leads to the formation of desirable conductive polymers in terms of high conductivity and processibility for ease manufacture of electrically conducting polymers. These aromatic heterocycles are oxidized to form a conducting electro active polymer (CEP) with the best conductivity, when created from α-α' linkages (Wallace*et al*., 2009), because non-α-α'-coupling linkage have been found experimentally and they are known to cause breaks in the conjugation of the polymer, reducing conductivity and electro activity of the film (Yamamoto,1981). Polymers based on heteroaromatics monomers have received considerable attention due to their potential applications in material sciences such as in microelectronic devices, sensors, rechargeable batteries, super capacitors, electro chromic displays and solar devices (Schilinskya *et al*., 2002; Ando and Ueda, 2002; Jameh-Bozorghi and Beigi, 2011).

Since the initial electron transfer (intermediate radical cation) is usually the rate-determining step in the electroplymerization process, the ease of electro oxidation and hence the ionization potential, stability of the formed radical cation, charge distribution (Mullikan) and aromaticity (expressed by Fn), are among the key parameters, which determine the efficiency of the electroplymerization process (Waltman *et al.,* 1984; Vaschetto and Retamal, 1997; Jameh-Bozorghi and Beigi, 2011). Beside this, their stability partially determines the nature of products formed (Hepburn and Met, 1991). Among these researcher, Jameh-Bozorghi *et al*., (2011), reported electronic and structural properties of all chlorothiophene (shown in Figure 5) and their radical cations using DFT-B3LYP methods. Results show that electroplymerization of β-substitute chlorothiophene can be more favorable ratio with respect to other.

In view of the above information, we have focused on β-substitution, as no electroplymerization is observed for α substitututed pyrroles, for example Waltman *et al*. (1984) showed using theoretical calculations that the ability to distinguish between the α and β-positions decreases as the conjugation increases for pyrrole oligomers, due to the presence of available sites for coupling in the β-positions (Buchałal *et al*., 2016).

In addition to the position of substituent effect, solvent effects also attract considerable attention because most of the chemical processes occur in the solution phase (Funt and Diaz, 1991). The ionization potentials were affected because of the perturbation of the electronic states of the molecules in solvent environment (Taras-Goslinska and Jonsson, 2006). (Figure 1) presents the systems investigated.

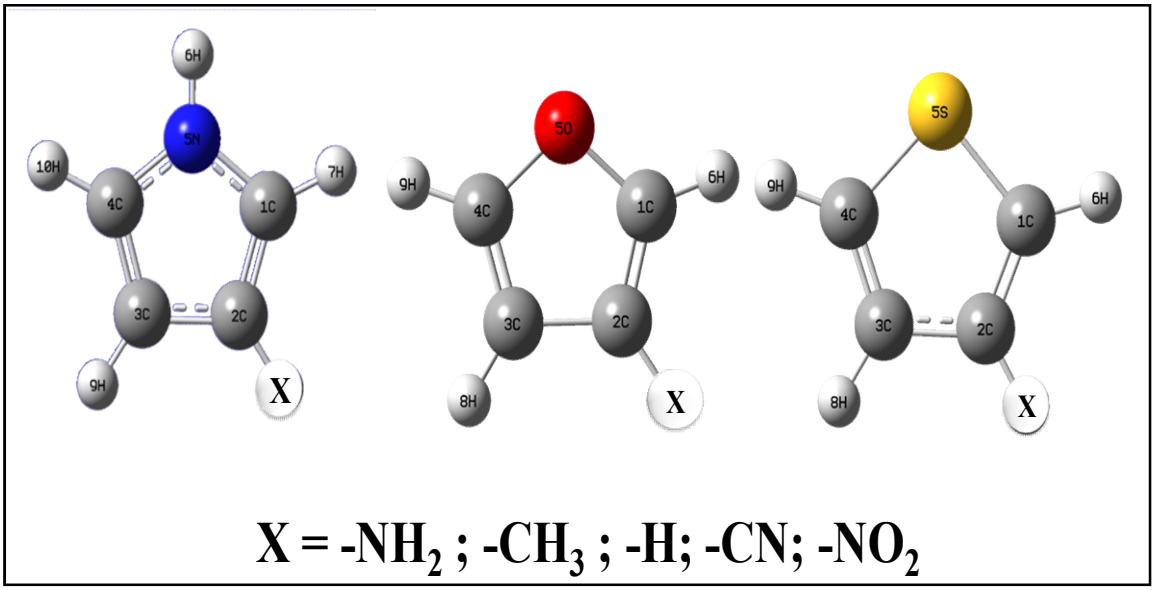


Figure 1. Structures of pyrrole, furan, thiophene and their β-substituted derivative

Mostly substituent effect is studied using the above parameter independently in order to determine the efficiency of the electroplymerization process in vacuum. However, there is no organized work for this material to determine efficiency of the electro polymerization either computationally or experimentally. Therefore, in this work, we evaluate the efficiency of electroplymerization process and characteristics of monomers (conductivity and solubility) are related to the stability of their radical cations which is closely dependent on solvent polarities and nature of substituents (NO_2, CN, CH_3 and NH_2) on thiophene, pyrrole and furan ring (Wallace *et al*., 2009) in organized way using density functional theory DFT/B3LYP method. Such study is significant to provide data for controlled and optimized design of electroplymerization process.

Objective of the Study

General Objective

- To study the solvent and substituent effects on electrochemical parameters of thiophene, furan, pyrrole and their radical cations, using density functional theory (DFT).

Specific Objectives

- To optimize geometries of thiophenes, furans, pyrroles and their radical cations using different common types of solvent (cyclohexane, dichloromethane, acetonitrile and water).
- To determine an electronic and thermodynamic properties of thiophene, furan, pyrrole and their radical cations with different substituent group in common types of solvent (cyclohexane, dichloromethane, acetonitrile and water)using DFT.
- To compare the results (bond length and ionization potential) of this study with that of literature reported ones.
- To identify best condition, which can be used in conducting polymer materials preparation and for maximizing efficiency of electroplymerization.

2. LITERATURE REVIEW

2.1. Basic Concepts of Electroplymerization Conjugated Polymers

Polymers are large molecules, produced by the union of many monomers (10^2-10^6) or smaller repeating units. Electrically conducting organic polymers consisting of chains with alternating single and double bonds (conjugated polymers). They are very important materials, because of their wide range of applications in batteries, corrosion protections, biosensors, coating material for metals, photo resists, photovoltaic devices, optical switches, sensors, electro chromic and electroluminescent devices (Otero and Nalwa, 1997; Skotheim *et al*., 1998; Kassim *et al*., 2002; Hutchison *et al*., 2003; Ullah *et al*.,2014). Some of the conventional representatives of conjugated organic polymers include Polythiophene, Polypyrrole, Polyaniline, polyacetylene, and polyfuran (Lange *et al*., 2008; Balint *et al*., 2014). These conjugated polymers are easily obtained upon oxidation of their corresponding monomer.

In the polymerization procedure, the first step is the formation of a positively charged species, which is a radical cation of the monomer. Then this radical cation reacts with another monomeric radical cation to form a dimmer. In the second step, the dimmer loses one electron to form a radical cation of the dimmer, which either reacts with a monomeric radical cation to form a trimmer, or reacts, with another dimmeric radical cation to form a tetramer (McCullough, 1998).

During electroplymerization different mechanism are proposed like radical–radical and radical–neutral coupling. The more commonly accepted mechanism involves the coupling of two radicals again these radicals which consist of more than one unit to form the dihydrodimer in for example ,the dihydrodimer intermediate formed in the radical–radical coupling of two pyrrole cations (Lacroix *et al*., 2001; Yurtsever, 2001). The radical–radical coupling of electroplymerization of aromatic five-membered heterocycles (Figure2).

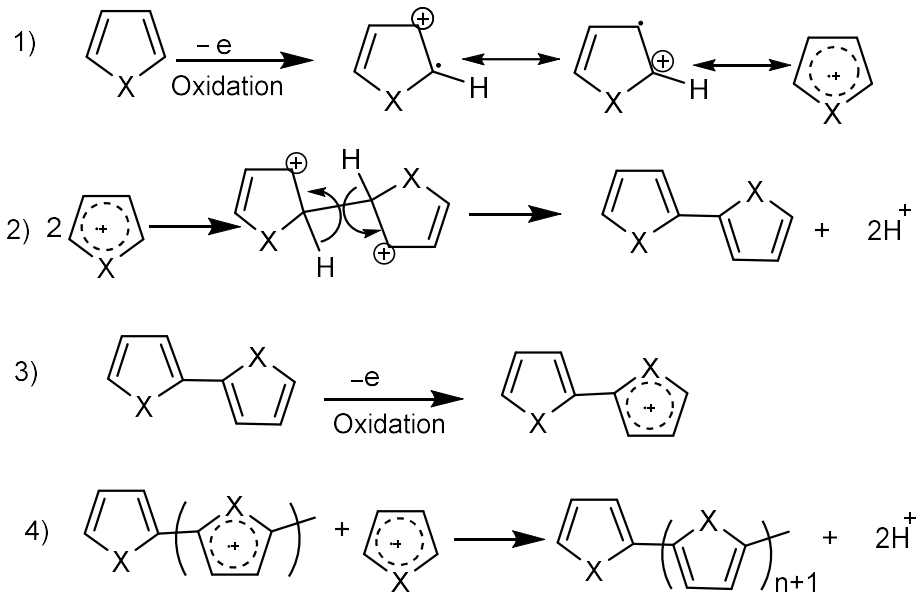


Figure 2. General schematic for electroplymerization of aromatic five-membered heterocycles: X = NH, S or O (Taye *et al*., 2007)

When mono-substituted aromatic five-membered heterocycles are polymerized in three different couplings are possible: head-to-head (HH), head-to-tail (HT), or tail-to-tail (TT) (McCullough, 1998; Andersson *et al*., 1999). Polymerization of substituted aromatic five-membered heterocycles is usually achieved in the cases that a substituent is present at 3-position (β-position).The synthesis of 98% head-to-tail (HT) poly(3-alkylthiophene) have shown great improvement in conjugation length and electronic properties(McClain *et al*., 1995). Such synthesis can be performed as an asymmetric chemical activation of 2- and 5-positions on the thiophene ring, which results in HT (head-to-tail)coupling. Among the substituted aromatic five-membered heterocycles, the highest electron mobility, highest conductivity, and narrowest bandgap is found in the perfect HT linked isomers (Figure 3).

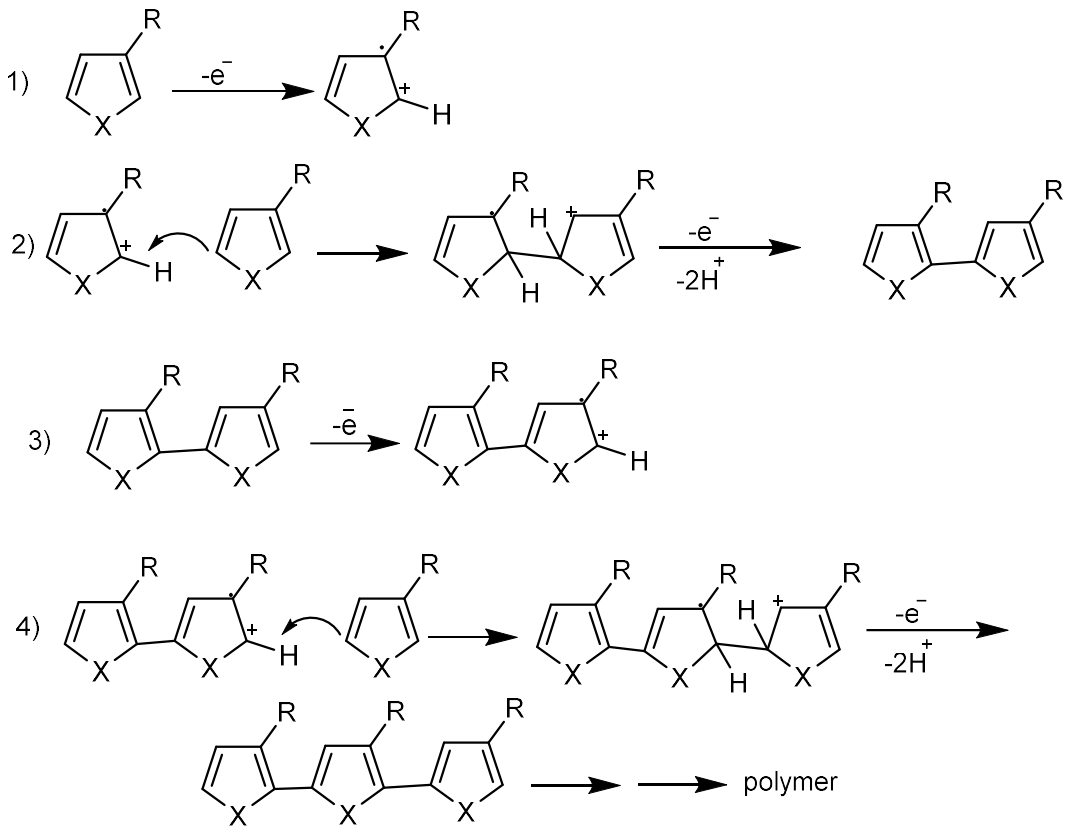


Figure 3. Electroplymerization of mono- substituted aromatic five-membered heterocycles:

X = NH, S or O and R= substituent (Winokur *et al*.,2007).

When one electron is removed from neutral monomer formation of an intermediate radical cations having only one charge (Figure 4), is the first step in electro polymerization of conducting polymers. The energy difference involved in the process is proportional to the ionization potential (and numerically equal to the ionization energy for one electron transfer reaction). This was predicted to be energetically more favored than the neutral monomer. The reason is that the radical cations are considerably greater than that for the neutral monomer (Beigi, 2012).

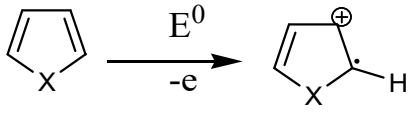


Figure 4. Electro oxidation of five-member heterocycles: X = NH, S and O (Taye *et al*., 2007)

2.2. Computational Chemistry

Computational chemistry is an outgrowth of theoretical chemistry, which has sought to device and implements quantitative algorithms for organizing massive amounts of data from the laboratory and for predicting the course and extent of chemical phenomena in situations that are difficult or even impossible to observe directly in the laboratory (Foresman and Frisch, 1993; Cramer, 2004). In addition to these Computational chemistry has become a useful way to investigate materials that are too difficult to find or too expensive to purchase. It also helps chemists make predictions before running the actual experiments so that they can be better prepared for observing (Young, 2004).

The term theoretical chemistry may be defined as the mathematical description of chemistry, use of computational techniques is becoming increasingly common throughout all the various fields of research in chemistry (Davison, 2000). It uses computers to generate information such as properties of molecules or simulated experimental results. Very few aspects of chemistry can be computed exactly, but almost every aspect of chemistry has been described in a qualitative or approximate quantitative computational scheme. In quantum chemistry calculations different software are available, like Gaussian, GAMESS, DMOL and others. Among these Gaussian is the most widely used application software. Quantum Chemistry calculations are composed of different approximations and theories, among them density functional theory is discussed in this study which are available in Gaussian09W software.

2.2.1. Density Functional Theory

Density functional theory is a quantum mechanical method used in physics and chemistry to investigate the electronic structure of many-electron systems, in particular, molecules based up on a strategy of modeling electron correlation via general functional of the electron density and calculate the physical properties of atoms, molecules and solids (Orio *et al*., 2009). It is one of the suitable approaches to study short, medium, and long π-conjugated system without spin contamination (Ullah *et al*., 2013; Kamran *et al*., 2015).The predecessor to density functional theory was the Thomas-Fermi model, developed by Thomas and Fermi in 1927. Thomas and Fermi, in 1927, used fermions statistical mechanics to derive the kinetic energy for the system is given as:

$$T[\rho(r)] = \frac{3}{10}(3\Pi^2)^{2/3}\int \rho^{5/3}(r)dr \quad (1)$$

They calculated the energy of an atom by representing its kinetic energy as a functional of the electron density, combining this with the classical expressions for the nuclear-electron and electron-electron interactions, which can both also be represented in terms of the electron density (Jensen, 2004; McQuarrie, 2005).

Density functional theory formalism has the same starting point as the wave function based methods, that is the Born-Oppenheimer approximation where the nuclei of the treated molecules are seen as fixed, coupled with an external potential (V_{ext}) where the electrons are moving. The Hamiltonian written as:

$$\hat{H} = \hat{F} + \hat{V}_{ext} \quad (2)$$

Where, F is the sum of the kinetic energy of the electrons and the electron-electron Coulomb interaction. In the DFT approach, the key variable is the particle density, and for this Hamiltonian, the ground state gives rise to a ground state electronic density $\rho_0(r)$defined as:

$$\rho_0(r) = \langle \Psi_0 | \hat{\rho} | \Psi_0 \rangle = \int \prod_{i=2}^{N} dr_i \mid \Psi_0(r_1, r_2, r_3, K, r_N) \mid^2 \quad (3)$$

The Hamiltonian depends only on the positions and atomic numbers of the nuclei and the total number of electrons. The dependence on total number of electrons immediately suggests that a useful physical observable would be the electron density ρ(r).

Density functional theory (DFT) takes another approach. The system interaction of electrons are approximated by using a function to describe the electron density (a functional) rather than individual wave functions for each of the electrons (Hehre, 2003). That is, DFT relies on the total electron density, with the electron "placed" in non-interacting Kohn–Sham (KS) orbital (Baerends and Gritsenko, 1997).The electron density is the number of electrons per unit volume for a given state. It is dependent only on three coordinates independently of the number of electrons of the system written as:

$$N = \int \rho(r)dr \quad (4)$$

2.2.1.1. The Hohenberg–Kohn Theorems

Hohenberg and Kohn received in 1998 the Noble Prize for simplifying the many body problems by introducing DFT. Instead of electron wave function, they used density functional to solve the problem (Hohenberg and Kohn, 1964). Based on those two theorems, the first Hohenberg-Kohn theorem (Hohenberg and Kohn, 1964) says that all the properties of a molecule in a ground electronic state are determined by the ground state electron density function ρ_0(x, y, z). Example for the energy

$$E_0 = F\rho_0 = E\rho_0 \quad (5)$$

Where F is functional (is a rule that transforms a function into a number).

The second Hohenberg–Kohn theorem (Hohenberg and Kohn, 1964) it says that any trial electron density function will give energy higher than (or equal to, if it were exactly the true electron density function) the true ground state energy this theorem can thus be stated as:

$$E_v[\rho_t] \geq E_0[\rho_0] \quad (6)$$

Where ρ_t is a trial electronic density and $E_0[\rho_0]$ is the true ground state energy, corresponding to the true electronic densityρ_0.

2.2.1.2. The Kohn-Sham Formalism

(Kohn and Sham. 1965) developed, with the introduction of atomic orbitals, a formalism that is the foundation for the current application of DFT in the computational chemistry field. This formalism yields a practical way to solve the Hohenberg-Kohn theorem for a set of interacting electrons, starting from a virtual system of non-interacting electrons having an overall ground-state density equal to the density to some real system of chemical interest where electrons do interact. The two basic ideas behind the KS approach are the first Kohn–Sham theorem tells us that it is worth looking for a way to calculate molecular properties from the electron density or to express the molecular energy as a sum of terms, only one of which, a relatively small term, involves the “unknown” functional.

The second theorem suggests that a variational approach might yield a way to calculate the energy and electron density to use an initial guess of the electron density in the KS equations to calculate an initial guess of the KS orbitals and energy levels. The total energy functional can be written as (Levine, 1991).

$$E[\rho_0] = -\frac{1}{2}\sum_{i=1}^{2n}\int \langle \psi_1^{KS}(1)\nabla_1^2\psi_1^{KS}(1)\rangle - \sum_{\text{nucleiA}} ZA\int \frac{\rho_0(r_1)}{r_{1A}}dr_1 + \frac{1}{2}\iint \frac{\rho_0(r_1)\rho_0(r_2)}{r_{12}}dr_1dr_2 + E_{XC}[\rho_0] \quad (7)$$

Where the sum is over all the occupied Kohn-Sham orbital and is known once these orbital have been computed. The first term in equation represent the kinetic energy of the electron; the second term represent the nucleus-electron attraction potential energies; the third term represent the columbic interaction between the total charge distribution (summed over all orbital) at r_1 $and r_2$; the last term is the exchange correlation energy of the system which is also a functional of the density and takes in to account all non-classical electron- electron interaction. The exact ground state charge density ρ at location r is given by

$$\rho(r) = \sum_{i=1}^{2n}\left|\psi_i^{KS}(r)\right|^2 \quad (8)$$

Density functional theory (DFT) proposed by Kohn-Sham has been the most popular computational method used to study electronic structures of molecules and periodic structures for chemists and physicists due to its relatively low computational cost with respect to the other high level methods including electron correlations. DFT methods may be classified into three different categories: (I) Local density approximation (LDA) (ii) Generalized gradient approximation (GGA) and (iii) meta-generalized gradient approximation (M-GGA). GGA and M-GGA methods may include Hartree-Fock exchange term to form a hybrid type of the functional. This term improves the functional to get the results, which have higher degree of agreement with the experimental results (Schultz *et al*., 2005; Sousa *et al*., 2007).

2.2.2. Basis Set

A basis set is a set of functions from which the state (system) wave function (electron probability density) is constructed. In general, a basis set is an assortment of mathematical functions used to solve a differential equation. In quantum chemical calculations, the term basis set is applied to a collection of contracted Gaussians representing atomic orbitals, which are optimized to reproduce the desired chemical properties of a system. Most modern computational codes use the 'Basis Set Approximation' to solve the Schrödinger equation. This involves expressing the molecular orbital's as a linear combination of a set of mathematical functions called the basis set. An infinite basis set will give the best possible result for a given level of theory although, in practice, only a finite basis set is possible.

Larger basis sets include more and a greater range of basis functions. Therefore, larger basis sets can better refine the approximation to the true molecular wave function, but require correspondingly more computer resources. Alternatively, accurate wave functions maybe obtained from different treatments of electrons in atoms. Generally, a trade-off between speed and accuracy is necessary, as there is an N dependence on the basis set size (O'Boyle, 2004).

2.2.2.1. Single-ζ , Multiple-ζ , Split-Valence

The STO-3G basis set is what is known as a 'single-ζ' basis set, or, more commonly, a 'minimal' basis set and 3G level represents (3 Gaussians to represent 1 STF). This nomenclature implies that there is one and only one basis function defined for each type of orbital core through valence (González *et al*., 2017).

In split valence basis sets, additional basis functions (one contracted Gaussian plus some primitive Gaussians) are allocated to each valence atomic orbital. The resultant linear combination allows the atomics to adjust independently for a given molecular environment, the most widely used split-valence basis sets are include 3-21G, 6-21G, 4-31G, 6-31G and 6-311G, the first number indicates the number of primitives used in the contracted core function and the number after the hyphen indicate the number of primitives used in the valance functions; if it is a double digit number, it is a valence-double – ζ basis and if there are three digits, then it is valence-triple- ζ.

Thus ‘6-21G’ describes an inner shell atomic orbital with a contracted Gaussian composed of six primitive Gaussians, an inner valence shell with a contracted Gaussian composed of two primitives, and an outer valence shell with one primitive. The following are examples of commonly used splitvalence basis sets with polarized and diffused functions: 3-21G, 3-21G* (Polarized), 3-21+G (Diffuse functions), 3-21+G* (With polarization and diffuse functions), 6-31G, etc (Cramer, 2004;McQuarrie, 2005).

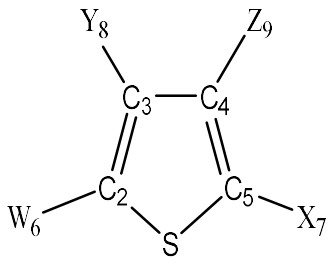
Basis sets in which there are multiple basis functions corresponding to each atomic orbital, including both valence orbital’s and core orbital’s or just the valence orbital’s, are called double, triple, or quadruple-zeta basis sets. Double zeta basis sets use two basis functions to describe valence electrons whereas triple zeta basis sets use three basis functions, and so forth. Basis sets developed by Pople and coworkers are denoted by the number of Gaussian functions used to describe inner and outer shell electrons. Here is a list of commonly used multiple zeta basis sets: cc-pVDZ, cc-pVTZ, cc-pVQZ, cc-pV5Z, etc. where the acronym stands for ‘correlation-consistent polarized Valence (Double/Triple/ quadruple etc.) Zeta. They are double/triple/zeta for the valence orbital’s only and include successively larger shells of polarization functions (p, d, f, g, etc.) that can yield convergence of the electronic energy to the complete basis set limit (Jensen, 2004; McQuarrie, 2005).

2.3. Theoretical Study of Factor Affecting Efficacy of Electroplymerization

2.3.1. Functional Coefficient

It is used to predict the bonding-characteristic behavior and aromaticity of molecule in their corresponding polymer chains and to determine the extent of the π-conjugation character of these polymers(Sabzyan and Omrani, 2003).Heterocyclic compounds are organic compounds that contain a ring structure and heteroatom in addition to carbon; it may be aromatic or non-aromatic heterocycles. Among these, Furan, pyrrole and thiophene are the most common five membered aromatic heterocycles. They show aromatic delocalization involving the unshared electrons located on respective heteroatom of the ring system. The nitrogen atom of pyrrole is of ideal size to permit extension of the conjugation around the entire ring leading the maximum aromatic character among the three (Cordell and Boggs, 1981). Through the same argument of size alterations, furan and thiophene become less aromatic than pyrrole.

Beigi and Jameh-Bozorghi in 2011 reported 3-fluorothiophene (Figure 5) which has the smallest value of the Fn coefficient, where Fn-coefficient calculated from (Fn=$\frac{R34}{R23+R45/2}$).



T: W=X=Y=Z=H	Thiophene
A: W=Cl, X=Y=Z=H	2-chlorothiophene
B: Y=Cl, W=X=Z=H	3-chlorothiophene
C: W=Y=Cl, X=Z=H	2,3-dichlorothiophene
D: W=Z=Cl, X=Y=H	2,4-dichlorothiophene
E: W=X=Cl, Y=Z=H	2,5-dichlorothiophene
F: Y=Z=Cl, W=X=H	3,4-dichlorothiophene
G: W=Y=Z=Cl, X=H	2,3,4-trichlorothiophene
H: W=X=Y=Cl, Z=H	2,3,5-trichlorothiophene
I: W=X=Y=Z=Cl	2,3,4,5-tetrachlorothiophe

Figure 5. All possible mono-, di-, tri- and tetrachlorothiophenes structures

Therefore, it can be suggested that the double bonds in 3-chlorothiophene are more delocalized. on the other hand they have been calculated the spin-density distribution over the ring atoms of fluorosubstituted thiophene instead of chloro substituted thiophene(Figure 5)and electroplymerization of 3-fluorothiophene can be more favorable ratio with respect to other molecules due to monomer of 3-fluorothiophene has the maximal spin density on positionC3.

2.3.2. Atomic Charge Distribution

Calculation of atomic charges plays an important role in determining the coupling position for electroplymerization process for each molecular radical cation is obtained from α-α’ (C2-C5) linkages (Wallace *et al*., 2009),so it can be said that in a compound, the electroplymerization rate will be higher with greater atomic positive charge in position α. It can also be said that in a compound, the electroplymerization rate will be higher with greater atomic negative charge in position α’. Beside of this, it is application for quantum mechanical calculations to molecular systems. It is the net electronic and nuclear charge on each atom is frequently used by chemists to rationalize observed chemical behavior.

In reality, this is not a measurable physical property, since the electrons are a diffuse charge distribution that can arbitrarily be assigned to any atomic center (Gunasekaran *et al*., 2008). Because the atomic charges affect dipole moment, molecular polarizability, electronic structure and a lot of properties of molecular systems (Sidir *et al*., 2010).

The charge distributions over the atoms suggest the formation of donor and acceptor pairs involving the charge transfer in the molecule. Mulliken charges are calculated by determining the electron population of each atom as defined in the basic functions. The most widely used charge partitioning scheme are Mulliken populations, which assign charge to an atomic center based on the total electron density in basis functions located on that center**.** A related problem is that Mulliken Populations are extremely basis set dependent. Seemingly, innocuous basis set changes can lead to very large shifts in Mulliken populations, even when the basis sets are very large, charge distributions calculated by the Mulliken (Mulliken, 1955).

The substituting group sin the β-position, by donating or withdrawing electrons, influence the electron distribution within the heterocycle ring and more importantly, activate carbon α and α' positions**.** On the other hand prevents the β-couplings and causes an increase in the crystallinity of the polymer. However, the steric effect of β-substitution cannot be ignored. For instance, 3, 4-dimethylpyrrole produces polymers with lower conductivities and lower mean conjugation length relative to pyrrole (Diaz *et al*., 1981). However, the substituents in position 3- or 4- of the pyrrole ring can also affect the electron density of the heterocycle.

2.3.3. Ionization Potential

The energy needed to remove one or more electrons from a neutral molecule to form a positively charged ion is a physical property that influences the chemical behavior of the molecule. By definition, the ionization energy of an element is the energy needed to remove the outer most electrons from a neutral molecule in the gas phase (Clark, 1985).

$$M \rightarrow M^{\cdot +} + e^{-}$$

Two approaches have been applied for computational prediction of the ionization potential of a process. The first one is, based on Koopman's theorem, which states that the IP is equal to the absolute value of the HOMO (Koopmans, 1933).

$$IP_K = |HOMO| \quad (9)$$

Although this method is relatively simple and practical, this method underestimates the IP. The error originates because the kohn-Sham orbital's (Kohn and Sham, 1965; Hohenberg and Kohn, 1964), are not real electronic orbital's but rather mathematical constructions. This is evidenced by more accurate prediction of IP by HF methods, which calculate the electronic orbital's and associated energy eigen values in a real sense (Vaschetto and Retamal, 1997). In the second approach, the ionization energy is calculated from the energy differences between the neutral monomer and the radical cations:

$$IP_V = E\ (cation) - E\ (neutral) \quad (10)$$

It is important to note for calculation of IP values in solvents, zero-point energy corrected values of the corresponding species in solvent are utilized. This, approach requires independent computation of the monomer and corresponding cations and hence is computationally demanding. However, this approach eliminates the systematic error associated with DFT based techniques mentioned above.

Ionization constitutes the important parameter controlling the kinetics of polymerization and reactivity of fragments. Too high ionization energy leads to a number of side processes, and too small does not lead to the expected polymerization product (Doskocz *et al*., 2006).Ionization potential (IP) is one of the fundamental quantities to characterize the electronic structures of molecules. As precise IP values have recently become available for molecules in the solution phase (Jagoda-Cwiklik*etal*., 2008; Slavíček *et al*., 2009), significant shifts have been observed for molecules in aqueous solutions from those in the gas phase. These results strongly indicate that the electronic structures of the molecules are significantly influenced by solvation.

The choice of the solvent and electrolyte is of particular importance in electrochemistry since both solvent and electrolyte should be stable at the oxidation potential of the monomer and provide an ionic ally conductive medium. Organic solvents like acetonitrile or propylene carbonate have very large potential windows (Bard and Faulkner, 1980), and high relative permittivities, which allow a good dissociation of the electrolyte and thus a good ionic

conductivity. Since pyrrole has a relatively low oxidation potential (Rodriguez *et al*., 1997), electroplymerization can be carried out in aqueous electrolytes, which is not possible for thiophene or benzene.

Polythiophene are normally produced from non-aqueous media because the monomer is more soluble in them. The influence of water on polymerization process of thiophene as well as on the redox switching properties has been studied (Lukkari *et al*., 2000; Asami *et al*., 2006). It has been, recently shown that the attachment of a range of electron-donating or electron-withdrawing groups through a conjugated linker has a dramatic effect on polymerization potential and subsequent photovoltaic performance (Chen *et al*., 2005; Silvestri and Marrocchi, 2010).

Substitution effects influence the position of the oxidation potentials of the polymers and the structure of the polymers plays a dominant role in determining the physical properties of conducting polymers. Although electron-donating substituents lower oxidation potentials just as they do in the monomers (Rubio *et al*., 1995; DiCésare *et al*., 1999; Zhang *et al*., 2004), the electron withdrawing substituents raise them (Monk *et al*., 1995; Shi *et al*., 2002). The chain length of the substituted alkyl or alkoxy groups have also an effect on the electrochemical properties of polymers derived from the 3-alkyl substituted polythiophene.

2.3.4. Bandgap

A bandgap is defined as the difference between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energy levels in the monomer:

$$E_{gap} = E_{LUMO} - E_{HOMO}(eV) \quad (11)$$

Its value decreases when the chain length of a conductive polymer (or the length of the π-conjugated system) increases. Therefore, it seems that bandgap values of a polymer cannot be determined exactly from their monomers.

However, the study of bandgap values of monomers may be used to predict the comparative bandgap behavior of the corresponding polymers and bandgap values are smaller this shows that the conductivity of that compound is greater (Tang, 2005; Jensen, 2007). Low bandgap

conjugated polymers are of interest for their intrinsic conductivity in electronic devices and also in devices such as light emitting diodes and solar cells. The bandgaps in conjugated polymers are governed by their chemical structures; therefore, the detailed bandgap theoretical calculations were carried out on the polymer structures.

The decrease in the bandgap is due to the electronic substituent effect created by the introduction of the alkyl side chains and is larger than the steric hindrance imparted by the alkyl side chains (Colladet *et al*., 2007). Hence, these steric hindrances are usually neglected, where alkyl substituents induce obvious steric hindrances and increased bandgaps for PTh copolymers. In some, report the substituent case for increasing or decreasing of the bandgap of ring, where alkyl attached to the molecular backbone can lead to a decrease in the bandgap in PTh (Gierschner *et al*., 2007). This behavior is a result of the electron-releasing effect created by the introduction of the alkyl side chains.

In other report, a large bandgap implies high kinetic stability and low chemical reactivity because it is energetically unfavorable to add electrons to a high-lying LUMO. Meanwhile, a molecule with a small frontier orbital gap is more Polarizable, is generally associated with a high chemical reactivity, low kinetic stability, and is termed as soft molecule (Fleming,1982).(Table 1) summarizes the energy bandgap of intrinsic thiophene monomers at HF, DFT (BLYP, B3LYP, B3P86, and LSDA) with various combinations of basis sets.

Table 1. Bandgap in eV of thiophene at various levels of theory (Dguigui *et al.,* 2012)

Methods	Basis set			
	6-31G	6-31G(d)	6-31+G	6-31G(d,p)
RHF	12.60(eV)	12.68(eV)	11.42(eV)	12.67(eV)
BLYP	5.49(eV))	5.44(eV)	6.08(eV)	5.46(eV)
B3LYP	7.39(eV)	7.29(eV)	6.98(eV)	7.31(eV)
B3P86	7.57(eV)	7.45(eV)	7.55(eV)	7.46(eV)
LSDA	6.70(eV)	6.53(eV)	6.63(eV)	6.52(eV)
Experimental value: 5.23(eV)				

The energy gaps between highest occupied and lowest unoccupied molecular orbital (i, e. E_{gap}) were calculated for thiophene using Hartree-Fock (HF) and density functional methods (DFT) with various combinations of basis sets. As expected, the restricted Hartree-Fock (RHF)

energy bandgap of thiophene monomer is overestimate compared to experimental value because of the neglect the correlation contribution. The improvement of the bandgap was obtained in applying a higher-level basis set, the absolute error is 6.19 – 7.45 (eV). Hybrid density functional (B3LYP and B3P86) overestimate the difference between E_{gap} respectively by up 2.16 (eV) and 2.34 (eV). The pure DFT (BLYP) yielded a good agreement with the experiment, the absolute error is 0.21(eV) with basis set6-31G*.

Bandgaps and effective conjugation lengths of furan polymers have been estimated by extrapolating vertical excitation energies of trimers through pentamers to infinite chain length (Ma *et al.,* 2002). The excitation energies varied from 6.31 to 1.69 eV, the experimental value being 2.35 eV. These authors applied time dependent density functional theory with the B3LYP functional. Surprisingly, theoretical data indicate that α-β-linked PFu has the largest bandgap, the highest ionization potential, and the lowest electron affinity (Bakhshi and Ray, 1988).

2.3.5. Dipole Moment

The dipole moment (μ in Debye) is another important electronic parameter used to describe the polarity of the molecule. This parameter helps in the understanding of interaction between atoms in the same or different molecules. Dipole moment increases with the increase in electro negativity of atoms. Chemical reactivity usually increases with an increase in dipole moment. It is an important factor in the chemical and electrochemical synthesis of conducting polymers based on the choice of proper solvent (Skotheim and Elsenbaumer, 1998).

The electro polymerization and characteristics of monomers (conductivity and solubility) are related to the stability of their radical cations, which it is closely dependent on the type and configuration of the substituent on the ring. It is necessary to know the dipole moments of monomer to be able to predict their electro polymerization properties. The size of the dipole moment vector for monomers is greater high solubility in polar solvents. These characteristics increase the efficiency of electrochemical polymerization processes of these monomers (Jameh-Bozorghiand Beigi, 2011).

(Sabzyan and Omrani, 2005) reported that analysis of the calculated electric dipole moments for fluoro substituted pyrrole instead of chloro substituted thiophene in (Figure 5)have been studied; among this molecules 3-fluoropyrroleand3,4-difluoropyrrole have the greatest dipole moments compared with their corresponding isomers. Significantly, larger dipole moments of these two molecules support possibility of higher admittance to the excess electric charge (Sabzyan and Omrani, 2003).

2.3.6. Solvation Energy

Solvent effects attract considerable attention because most of the chemical processes occur in the solution phase. Aprotic solvents appear to be the best for Ppy preparation. Among these solvents, acetonitrile is the most commonly used. In acetonitrile, the addition of a small quantity of water has a big influence on the kinetics of the reaction and the properties of the polymer formed (Funt and Diaz, 1991). This effect is due to the stabilization of the cation radical intermediate by the water molecules, which have a larger polarity than acetonitrile. It is defined as:

$$\Delta(\Delta G) = \Delta G_{solvent} - \Delta G_{vacuum} \quad (12)$$

3. MATERIALS AND METHODS

3.1. Computational Methods

Ground state geometry optimizations of the thiophenes, furans, pyrroles and their radical cations were performed at density functional theory level (Hohenberg and Kohn, 1964 and Kohn and Sham, 1965) B3LYP (Becke–Lee–Young–Parr composite of exchange-correction functional) (Becke, 1988; Lee *et al*., 1988; Parr and Yang, 1989) with 6-31G(d,p) and 6-31G++G(d,p) basis set (Becke, 1988; Becke, 1993) using Intel (R) Core (TM) i7-4790 CPU @ 3.60 GHz, 4 GB RAM with 32 bit, computer model OPTIPLEX7020 with Window 7 Profession, Gaussian 09 program package (Frisch *et al.,* 2009) and Gauss View .5.0.8.

The effect of basis set is also considered. In all cases, frequency calculations were performed at the same level of the theory to ensure the absence of imaginary vibrational frequency. The response of the electrochemical parameters to solvation was studied in solvents of various polarities such as, cyclohexane, dichloromethane, acetonitrile and water. Polarizable continuum model (PCM) using the integral equation formalism variant (IEF-PCM) was used to treat solvent effects, which creates the solute cavity via a set of overlapping spheres (Mennucci, 2002).

The atomic charge distribution, Dipole mount (μ) and Bond lengths (Å) are directly taken from optimized structure. Bonding characteristic behaviors of parent monomers/radical cations and their derivatives rings in their corresponding polymer chains were predicted according to function coefficient formula (in equation 13). Two approaches have been applied for computational prediction of the ionization potential of a process. The first one, which states that, the IP is equal to the absolute value of the HOMO. In the second approach, the ionization energy was calculated from the energy differences between the neutral monomer and the radical cations. For convenience, symbol IPk for ionization potential predicted using Koopman's theorem and the symbol IPv for the second approach were used.

HOMO-LUMO gap was obtained by subtracting the energy of the highest occupied molecular orbital's from the energy of the lowest unoccupied molecular orbital's and thermodynamic stability of compound determined according to solvation energy formula (in equation 12). All calculations were carried out at Haramaya University, chemistry department research laboratory.

4. RESULTS AND DISCUSSION

4.1. Structural Analysis of Thiophenes, Pyrroles, Furans and their Radical Cations

The ground state geometry optimizations of the parent monomers/radical cations and their derivatives were performed at DFT /B3LYP/6-31G (d,p) and 6-31G ++G (d,p) level of theory. From the optimized structure of the compounds, bond lengths were extracted; the values are listed in appendix (Tables 1-10). Based on bond lengths information Fn-Coefficient of parent monomers/radical cations and their derivatives calculation have been determined according to Eq. (13) as shown below.

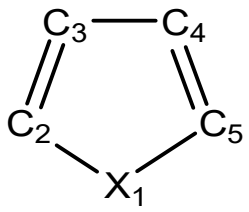


Figure 6. Stricture of five-member heterocycles

Where X_1=S=thiophene, N=pyrrole, O=furan

$$F_n = \frac{R34}{R23 + R45/2} \tag{13}$$

Where R34 is the length of C3–C4 bond and [(R23 + R45)/2] is the average length of C2–C3 and C4–C5 bonds in the thiophene, Pyrrole, furan as shown above (Figure 6).

As it is observed from (Table 2), the parent monomers in the presence of substituent such as -NH_2, -CH_3, -H, -CN and -NO_2 the Fn-Coefficient was higher than their radical cations excepted (-H) substituted thiophene because, thiophene monomer was stable by resonance compared to (-H) substituted furan and pyrrole, this shows that for thiophene oxidation is not necessary for stability. Among the substitutents in the parent monomers/radical cations having NO_2, substituent has smaller Fn-Coefficient value as it is compared to other substituent in using different common types of solvents (cyclohexane, dichloromethane, acetonitrile and water).

Table 2. Calculated Fn-Coefficient for thiophenes, pyrroles, furans, and there radical cations (presented in italic) in solvents of varying polarity by using DFT/B3LYP/6-31G (d, p).

Molecule	Vacuum	Cyclohexane	Dichloromethane	Acetonitrile	Water
3-aminopyrrole	1.034	1.034	1.033	1.033	1.033
	1.023	*1.024*	*1.024*	*1.024*	*1.025*
3-methylpyrrole	1.038	1.037	1.037	1.037	1.036
	0.971	*0.970*	*0.967*	*0.967*	*0.967*
Pyrrole	1.034	1.034	1.033	1.033	1.033
	0.958	*0.959*	*0.957*	*0.957*	*0.957*
3-cyanopyrrole	1.039	1.039	1.039	1.039	1.039
	0.975	*0.968*	*0.963*	*0.962*	*0.962*
3-nitropyrrole	1.032	1.033	1.033	1.033	1.033
	0.956	*0.955*	*0.955*	*0.955*	*0.955*
3-aminofuran	1.055	1.056	1.056	1.056	1.056
	1.029	*1.031*	*1.034*	*1.034*	*1.014*
3-methylfuran	1.059	1.060	1.060	1.060	1.060
	0.988	*0.987*	*0.987*	*0.986*	*0.986*
Furan	1.055	1.055	1.056	1.056	1.056
	0.977	*0.974*	*0.978*	*0.978*	*0.978*
3-cyanofuran	1.058	1.058	1.058	1.059	1.059
	0.990	*0.986*	*0.982*	*0.982*	*0.982*
3-nitrofuran	1.053	1.051	1.051	1.051	1.051
	0.980	*0.980*	*0.972*	*0.972*	*0.972*
3-aminothiophene	1.050	1.050	1.051	1.052	1.052
	1.038	*1.039*	*1.040*	*1.041*	*1.041*
3-methylthiophene	1.050	1.051	1.051	1.052	1.052
	1.050	*0.986*	*0.986*	*0.985*	*0.985*
thiophene	1.046	1.046	1.047	1.047	1.047
	1.098	*1.097*	*1.097*	*1.097*	*1.097*
3-cyanothiophene	1.049	1.049	1.049	1.049	1.049
	0.992	*0.983*	*0.976*	*0.974*	*0.974*
3-nitrothiophene	1.044	1.044	1.044	1.044	1.044
	0.967	*0.967*	*0.967*	*0.967*	*0.968*

However, the presence of NH_2 constituents in the molecule makes the Fn-Coefficient higher value on furan and pyrrole radical cation. In case of thiophene, (–H) substituent have high Fn-Coefficient in different solvent polarity. Based on solvent effect, the existences of NH_2constituents in molecular radical cations have smaller Fn-Coefficient in vacuum. Conversely, molecular radical cations substituted with -CH_3, -CN and -NO_2, have shown smaller Fn-Coefficient solvent polarity. The solvent polarities have no significant effect in both parent monomer/radical cations. The structural properties of Fn-Coefficient calculated by

DFT/B3LYP/6-31++G (d, p) levels and DFT/B3LYP/ 6-31G (d, p) level are in agreement but the result obtained from first level slightly increase because it accounts the lone pair electron of heteroatom in parent monomer (Pyrrole, furan and thiophene).

Table 3. Calculated Fn-coefficient for thiophenes, pyrroles, furans and their radical cations (presented in italic) in solvents of varying polarity by using DFT/B3LYP/6-31++G (d, p).

Molecule	Vacuum	Cyclohexane	Dichloromethane	Acetonitrile	Water
3-aminopyrrole	1.035	1.032	1.032	1.032	1.031
	1.022	*1.023*	*1.024*	*1.024*	*1.024*
3-methylpyrrole	1.036	1.036	1.035	1.035	1.035
	0.971	*0.970*	*0.968*	*0.968*	*0.967*
Pyrrole	1.033	1.033	1.032	1.032	1.032
	0.959	*0.958*	*0.958*	*0.957*	*0.957*
3-cyanopyrrole	1.038	1.038	1.038	1.038	1.038
	0.975	*0.967*	*0.962*	*0.961*	*0.961*
3-nitropyrrole	1.032	1.032	1.037	1.033	1.032
	0.955	*0.955*	*0.955*	*0.955*	*0.955*
3-aminofuran	1.054	1.055	1.055	1.055	1.055
	1.029	*1.031*	*1.033*	*1.034*	*1.034*
3-methylfuran	1.058	1.058	1.059	1.058	1.059
	0.987	*0.987*	*0.987*	*0.987*	*0.987*
Furan	1.054	1.055	1.055	1.055	1.055
	0.977	*0.978*	*0.978*	*0.975*	*0.981*
3-cyanofuran	1.057	1.060	1.058	1.058	1.058
	0.990	0.985	*0.985*	*0.981*	*0.981*
3-nitrofuran	1.050	1.050	1.051	1.051	1.051
	0.977	*0.972*	*0.972*	*0.972*	*0.972*
3-aminothiophene	1.048	1.048	1.049	1.049	1.049
	1.038	*1.039*	*1.040*	*1.040*	*1.040*
3-methylthiophene	1.048	1.049	1.049	1.050	1.050
	0.988	*0.987*	*0.986*	*0.986*	*0.986*
thiophene	1.044	1.044	1.045	1.045	1.045
	1.097	*1.097*	*1.096*	*1.096*	*1.096*
3-cyanothiophene	1.047	1.047	1.047	1.047	1.047
	0.991	*0.981*	*0.974*	*0.973*	*0.973*
3-nitrothiophene	1.043	1.043	1.043	1.043	1.043
	0.972	*0.967*	*0.968*	*0.968*	*0.968*

From Tables 2 and 3, shown that when compare all molecular radical cations; pyrrole has smaller Fn-Coefficient than furan and thiophene. On the other hand, electro withdrawing (-CN and -NO_2) substituent showed smaller Fn-Coefficient than the electro donating (NH2 and -

CH_3) substituent in all molecular radical cations. Because of smaller Fn-Coefficient in the molecular radical cation pyrrole and electro-withdrawing substituent (-CN and -NO_2) among those -NO_2substituent favors to form more delocalized π-bond system and creates stable environment. It is known that the stability of the pyrrole and NO_2 substituent radical cations has an important role in the electroplymerization process related report observed on (Beigi and Jameh-Bozorghi., 2011).

4.1.2. Comparison of Pyrrole, Furan and Thiophene with Experimental Results

The structural parameters (bond lengths) of pyrrole, furan and thiophene obtained in this work were listed with reported experimental result in the literatures as present in Table 4.

Table 4. Optimized bond lengths (Å) and Fn-coefficient (presented in italic) for neutral thiophene, pyrrole and furan in vacuum compared with experimental results.

Parameter	This work	This work	Exp' t
	6-31G(d p)	6-31G++(d p)	
Pyrrole			(Nygaard*etal.,*1969)
S1-C2	1.3751	1.37650	1.370
C2-C3	1.3781	1.38080	1.382
C3-C4	1.4247	1.42644	1.417
C4-C5	1.3781	1.38080	1.382
C5-S1	1.3751	1.37650	1.370
F_n Coefficient	*1.0338*	*1.0331*	*1.0253*
Furan			(Montero*etal*.,1994)
O1-C2	1.3640	1.36554	1.362
C2-C3	1.3605	1.36269	1.361
C3-C4	1.4353	1.43670	1.431
C4-C5	1.3605	1.36269	1.361
C5-O1	1.3640	1.36554	1.362
F_n Coefficient	*1.055*	*1.0543*	*1.0514*
Thiophene			(Cuff and Kertesz,1997)
N1-C2	1.7358	1.73537	1.714
C2-C3	1.3671	1.37018	1.370
C3-C4	1.4298	1.43073	1.423
C4-C5	1.3671	1.37018	1.370
C5-N1	1.7358	1.73537	1.714
F_n Coefficient	*1.0459*	*1.0442*	*1.0387*

As shown (Table 4), calculated Fn-coefficient of pyrrole, furan and thiophene by using 6-31++G (d, p) basis set was possible to estimate satisfactory result comparable with the experimental values than 6-31G (d, p) basis set.

4.2. Atomic Charge Distribution Analysis

The main purpose in this section was to determine a molecule have higher rate of polymerization, which means to indicate the greater atomic positive charge in position α greater atomic negative charge in position α' and appropriate site for electroplymerization to occur according to (Beigi and Jameh-Bozorghi, 2011). As a result radical–radical cation coupling that is the first step of the polymerization can take place at α and α' (C_2 and C_5) positions in (Figure 6). Using the Mulliken atomic charge distribution over the ring atoms of parent monomers/radical cations and their derivatives are calculated and summarized in Table 5 and 6.

According to the results presented in Table 5 α-α' carbons (C_2 and C_5) positions in parent monomers/radical cations have equal charges. On the other hand, the accumulation of atomic positive charge decreased in parent monomer and increased in radical cation going to more polar without equality is altered, but with attachment ofNO_2, CN, NH_2, CH_3 substituent to the parent monomer/radical cations, this equality is altered. The difference between α and α' positions depend on, the type of substituent and polarity of solvent. As shown the substituent effect on atomic charge accumulation in parent monomer, increase in electron-donating substituent (-NH2 and -CH3) and decrease in electron withdrawing substituent (NO_2 and CN) in solvent of polarity, which means parent monomer with electron-donating substituent and more polar solvent (water)are more reactive and less stable than their radical cation. On the other hand, after the removal of electron from the parent monomer the accumulation of atomic charge decreased in both electro (donating and withdrawing) substituent and solvent of polarity.

Parent monomers with electron-donating substituent NH_2 and CH_3) is less atomic positive charge in position α and greater atomic positive charge in position α' in pyrrole and furan, for thiophene the same trend but atomic charge accumulation is negative.

Table 5. Milliken charge distribution on α-α' for thiophenes, pyrroles, furans and their radical cation (presented in italic) in solvents of varying polarity by using DFT/B3LYP/6-31G (d, p).

Molecule	Vacuum		Cyclohexane		Dichloromethane		Acetonitrile		Water	
	α	*α'*	*α*	*α'*	*α*	*α'*	*α*	*α'*	*α*	*α'*
3-aminopyrrole	.035	.075	.025	.067	.014	.056	.01	.053	.009	.053
	.178	*.129*	*.181*	*.127*	*.181*	*.122*	*.183*	*.127*	*.184*	*.120*
3-methylpyrrole	.037	.074	.029	.066	.018	.056	.015	.053	.015	.053
	.195	*.176*	*.202*	*.182*	*.211*	*.188*	*.213*	*.190*	*.214*	*.190*
Pyrrole	.070	.070	.063	.063	.054	.054	.051	.051	.051	.051
	.198	*.198*	*.204*	*.204*	*.210*	*.210*	*.165*	*.165*	*.212*	*.212*
3-cyanopyrrole	.098	.081	.099	.078	.100	.076	.101	.075	.101	.075
	.246	*.180*	*.257*	*.200*	*.268*	*.221*	*.271*	*.227*	*.272*	*.228*
3-nitropyrrole	.113	.082	.115	.081	.120	.081	.121	.081	.122	.081
	.245	*.211*	*.255*	*.225*	*.268*	*.241*	*.272*	*.246*	*.273*	*.247*
3-aminofuran	.086	.129	.077	.122	.066	.113	.063	.111	.062	.110
	.253	*.179*	*.257*	*.176*	*.269*	*.170*	*.270*	*.169*	*.271*	*.169*
3-methylfuran	.088	.128	.081	.121	.072	.113	.069	.110	.069	.110
	.255	*.236*	*.263*	*.242*	*272*	*.245*	*.274*	*.250*	*.275*	*.250*
Furan	.129	.129	.122	.122	.115	.115	.113	.113	.112	.112
	.263	*.263*	*.316*	*.316*	*.276*	*.276*	*.278*	*.278*	*.278*	*.278*
3-cyanofuran	.155	.129	.158	.127	.161	.125	.162	.124	.163	.124
	.309	*.237*	*.320*	*.254*	*.332*	*.275*	*.336*	*.280*	*.337*	*.281*
3-nitrofuran	.174	.124	.178	.124	.183	.123	.185	.124	.185	.124
	.311	*.247*	*.311*	*.247*	*.333*	*.293*	*.337*	*.297*	*.338*	*.298*
3-aminothiophene	-.347	-.299	-.345	-.304	-.362	-.310	-.364	-.311	-.365	-.312
	-.249	*-.287*	*-.243*	*-.286*	*-.236*	*-.287*	*-.351*	*-.288*	*-.233*	*-.288*
3-methylthiophene	-.338	-.300	-.343	-.305	-.349	-.310	-.351	-.312	-.351	-.313
	-.338	*-.300*	*-.206*	*-.227*	*-.196*	*-.219*	*-.193*	*-.217*	*-.192*	*-.217*
Thiophene	-.298	-.298	-.302	-.302	-.308	-.308	-.309	-.309	-.310	-.310
	-.304	*-.304*	*-.300*	*-.300*	*-.297*	*-.297*	*-.296*	*-.296*	*-.296*	*-.296*
3-cyanothiophene	-.307	-.281	-.279	.309	-.278	-.311	-.277	-.312	-.277	-.312
	-.172	*-.245*	*-.159*	*-.224*	*-.147*	*-.201*	*-.144*	*-.195*	*-.144*	*-.194*
3-nitrothiophene	-.315	-.292	-.290	-.316	-.288	-.317	-.288	-.318	-.288	-.318
	-.277	*-.262*	*-.181*	*-.201*	*-.172*	*-.187*	*-.169*	*-.183*	*-.169*	*-.183*

However, the atomic positive charges on the carbon atoms (α-α') of parent monomer increased after oxidation and became increasing atomic positive charge and the trend is opposite. Parent monomer/radical cations with electron-withdrawing (NO_2 and CN) substituent and molecular radical cation with electron-donating substituent (NH_2 and CH_3) have a greater atomic positive

charge in α and less atomic positive charge in α'. This is encouraging radical–radical cation coupling. Table 6 shown that, atomic charge distribution calculated by DFT/B3LYP/6-31++G (d, p) levels, the results obtained are in agreement with the results at the DFT/B3LYP/ 6-31G (d, p) level but the values are slightly increase.

Table 6. Milliken charge distribution on α-α' for thiophenes, pyrroles, furans and their radical cations (presented in italic) in solvents of varying polarity by using DFT/B3LYP/6-31++G (d, p).

Molecule	Vacuum		Cyclohexane		Dichloromethane		Acetonitrile		Water	
	α	*α'*	*α*	*α'*	*α*	*α'*	*α*	*α'*	*α*	*α'*
3-amino pyrrole	.059	-.433	.044	-.427	.028	-418	.024	-.415	.023	-.415
	.186	*-.400*	*.193*	*-.407*	*.200*	*-.409*	*.202*	*-.409*	*.203*	*-.409*
3-methyl pyrrole	-.011	-.361	-.020	-.362	-.026	-.363	-.027	-.363	-.027	-.364
	.152	*-.244*	*.154*	*-.248*	*.154*	*-.245*	*.154*	*-.249*	*.154*	*-.249*
Pyrrole	-.188	-.188	-.190	-.190	-.191	-.191	-.191	-.191	-.191	-.191
	-.061	*-.061*	*-.061*	*-.061*	*-.060*	*-.060*	*-.059*	*-.059*	*-.059*	*-.059*
3-cyano pyrrole	.237	-.295	.234	-.298	.233	.301	.234	.302	.234	-.302
	.268	*-.198*	*.277*	*.188*	*.288*	*-.185*	*.290*	*.185*	*.291*	*-.185*
3-nitro pyrrole	.377	-.411	.385	-.303	.395	-.429	.399	-.431	.400	-432
	.462	*-.293*	*.494*	*-.298*	*.530*	*-.314*	*.540*	*-.317*	*.542*	*-.318*
3-amino furan	.085	-.313	.077	-.308	.068	-.301	.066	-.299	.065	-.299
	.226	*-.273*	*.236*	*-.282*	*.249*	*-.288*	*.253*	*-.290*	*.254*	*-.290*
3-methyl furan	-.124	-.163	-.118	-.166	-.109	-.171	-.118	-.166	-.105	-.172
	.096	*-.029*	*.100*	*-.030*	*.105*	*-.028*	*.106*	*-.027*	*.106*	*-.027*
Furan	-.098	-.098	-.096	-.096	-.094	-.094	-.093	-.093	-.093	-.093
	.045	*.045*	*.047*	*.047*	*.052*	*.052*	*.163*	*.163*	*.054*	*.054*
3-cyano furan	.169	-.069	.052	-.056	.189	-.075	.192	-.076	.193	-.076
	.221	*.043*	*.225*	*-.168*	*.226*	*-.168*	*.230*	*.066*	*.230*	*.066*
3-nitro furan	.421	-.331	.442	-.334	.469	-.336	.475	-.337	.476	-.337
	.528	*-.204*	*.536*	*-.193*	*.577*	*-.195*	*.589*	*-195*	*.591*	*-.195*
3-amino thiophene	.006	-.390	-.015	-.393	-.044	-.397	-.053	-.399	-.055	-.399
	.068	*-.329*	*.080*	*-.330*	*.096*	*-.331*	*.101*	*-.332*	*.102*	*-.332*
3-methylthiophene	-.412	-.153	-.423	-.166	-.436	-.184	-.440	-.190	-.440	-.191
	.063	*-.043*	*.083*	*-.032*	*.102*	*-.020*	*.107*	*-.017*	*.108*	*-.017*
Thiophene	-.215	-.215	-.224	-.224	-.235	-.235	-.238	-.238	-.239	-.239
	-.176	*-.176*	*-.176*	*-.176*	*-.180*	*-.180*	*-.181*	*-.181*	*-.181*	*-.181*
3-cyano thiophene	-.015	-.059	-.010	-.065	-.006	-.074	-.005	-.077	-.005	-.078
	.108	*.070*	*.134*	*.093*	*.158*	*.116*	*.164*	*.121*	*.165*	*.123*
3-nitro thiophene	.252	-.351	.265	-.356	.280	-.363	.285	-.365	.286	-.366
	.470	*-.197*	*.526*	*-.168*	*.584*	*-.155*	*.600*	*-.152*	*.604*	*-.151*

The reason is most propabily 6-31++G (d, p) basis set was accounts the lone pair electron of heteroatom in parent monomer (Pyrrole, furan and thiophene).

From Tables 5 and 6, shown that, among electron-withdrawing substituent (NO_2 and CN), NO_2 substitute with pyrrole, furan and thiophene and polar solvents have smaller charge accumulation. Based on this, they have a greater atomic positive charge (less atomic negative charge) in position of α and less atomic positive charge (greater atomic negative charge) in α'. Because of this, they have higher rate of polymerization and radical-radical coupling for initiation step of the polymerization, related report observed (Beigi and Jameh-Bozorghi, 2011).

4.3. Ionization Potential

The first step in the electro polymerization of conducting polymers is formation of intermediate radical cations from monomers, which can be considered as an ionization reaction (Nikoofard and Sabzyan, 2007), so stability of intermediate radical cations has an important role in the electro polymerization process. Therefore, it is useful to calculate electronic energy deference between the neutral monomer (as the initial species) and positively charged monomer (as the intermediate). This energy difference is proportional to ionization potential (IP) of the monomer.

Basis set dependent ionization potentials (IP_V) of pyrrole and its derivatives in solvents of different polarities were presented in Table 7-8.The corresponding IP_K values were presented in parenthesis. In general, the predicted IPv values are closer to the experimental values while the IPk values systematically underestimate the ionization potentials. However, IPv and IPk show a good correlation as presented in Figure 7. This correlation was found to show no dependence on the basis set utilized. In all cases a correlation coefficient $R>0.98$ is obtained.

While electron-withdrawing solvents increase the ionization potential, electron-donating groups decrease the value and hence contributing their easier oxidation step. The ionization potential also decreases in solvated environment. This was evidenced by generally smaller values of the IPs in solvents than the corresponding values in vacuum. A general decrease in the IP with increasing solvent polarity was observed. Comparison of the computed values with

available experimental data also shows a fair agreement. In this respect, the ionization potential of pyrrole in acetonitrile environment predicted by the calculation (5.61eV) gives comparable result with the experimental value (5.64 eV) from Waltman *et al.,* (1984).

Table 7. Comparison of IPv and IPk (presented in parenthesis) for pyrrole family in solvents of varying polarity by using DFT/B3LYP/6-31G (d, p) in eV.

Molecule	Vacuum	Cyclohexane	Dichloromethane	Acetonitrile	Water
3-amino pyrrole	6.600	5.538	4.758	4.594	4.564
	(4.713)	(4.798)	(4.911)	(4.946)	(4.953)
3-methyl pyrrole	7.495	6.407	5.588	5.411	5.379
	(5.377)	(5.436)	(6.261)	(5.548)	(5.553)
Pyrrole	7.799	6.648	5.790	5.607	5.574
	(5.502)	(5.567)	(5.652)	(5.678)	(5.683)
	8.28[a]			5.64[b]	
3-cyano pyrrole	8.486	7.323	6.407	6.203	6.165
	(6.417)	(6.373)	(6.336)	(6.328)	(6.327)
3-nitro pyrrole	8.733	7.549	6.613	6.403	6.365
	(6.692)	(6.635)	(6.597)	(6.577)	(6.575)

[a] Experimental value: (kishimoto *et al*., 1996).
[b] Experimental value: (Waltman *et al.,* 1984).

On the other hand, the DFT calculation slightly underestimates the IP in vacuum (7.7988 eV) compared to the experimental values by Kishimoto *et al*., (1996) 8.28 eV. Comparisons between the computed ionization potentials were compared with those from Koopmans method, results were presented in Table 7.

Table 8. Comparison of IPv and IPk (value presented in parenthesis) for pyrrole family in solvents of varying polarity by using DFT/B3LYP/6-31++G (d, p) in eV.

Molecule	Vacuum	Cyclohexane	Dichloromethane	Acetonitrile	Water
3-amino pyrrole	6.884	5.818	5.038	4.874	4.844
	(5.103)	(5.171)	(5.278)	(5.313)	(5.320)
3-methyl pyrrole	7.721	6.630	5.809	5.633	5.601
	(5.723)	(5.765)	(5.841)	(5.866)	(5.872)
Pyrrole	8.035	6.883	6.025	5.840	5.810
	(5.880)	(5.927)	(6.001)	(6.025)	(6.030)
3-cyano pyrrole	8.719	7.545	6.620	6.413	6.375
	(6.752)	(6.686)	(6.632)	(6.621)	(6.619)
3-nitro pyrrole	8.992	7.798	6.854	6.643	6.604
	(7.054)	(6.977)	(6.914)	(6.900)	(6.914)

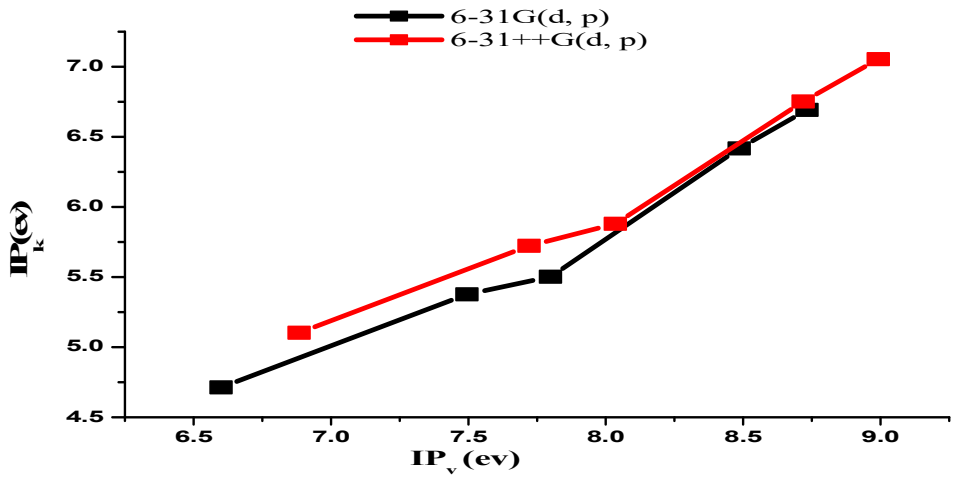


Figure 7. Basis set dependent correlation between IPv and IPk of pyrrole derivatives in vacuum at DFT/B3LYP level.

Figure 8 presents the plot of the Hammet substituent constant $\sigma_p = \sigma_I + \sigma_R$ (Hansch *et al.*, 1991) versus ionization potential (IPv) of the pyrrole family. Here σ_I and σ_R represent field inductive and resonance effects of the substitutents.

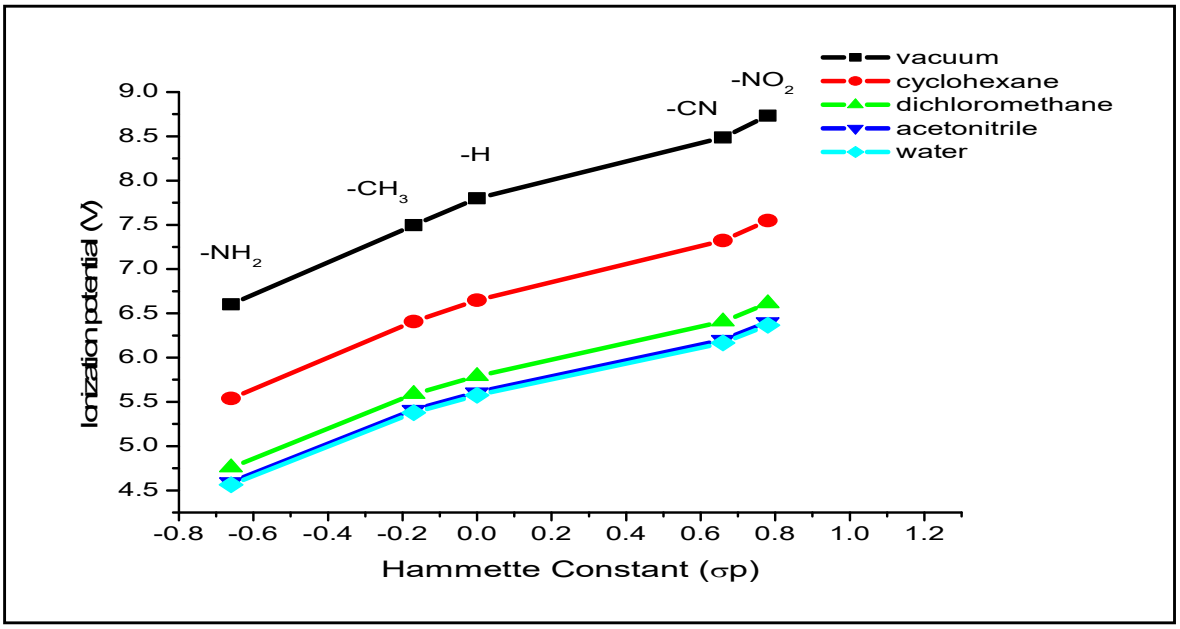


Figure 8. Plot of ionization potential of pyrrole derivatives versus Hammett substituent constant in solvents of different polarities by using DFT/B3LYP/6-31G (d, p).

While the two methods' predictions of IP show large discrepancies in vacuum, the discrepancies become smaller in solvent environments. For example, the two methods show good prediction of the IP in acetonitrile solvent which is very close to the experimental result. Nevertheless, the Koopmans theorem shows series limitations when predicting the solvent effect. In this method, for a given species, a progressive increase of the IP were predicted with increasing solvent polarity whereas both the experiment and the computation based on energy differences between the cation and the neutral monomer predicted an opposite trend. On the other hand, the method predicts the correct trend with respect to the substituent effect.

In a similar fashion, we have presented the computed ionization potentials of furan derivatives in solvents of different polarities (Table 9-10). Experimental values were also included wherever available. The substituent effect on the ionization potential of the species in solvents of different polarities were presented in Figure 9.

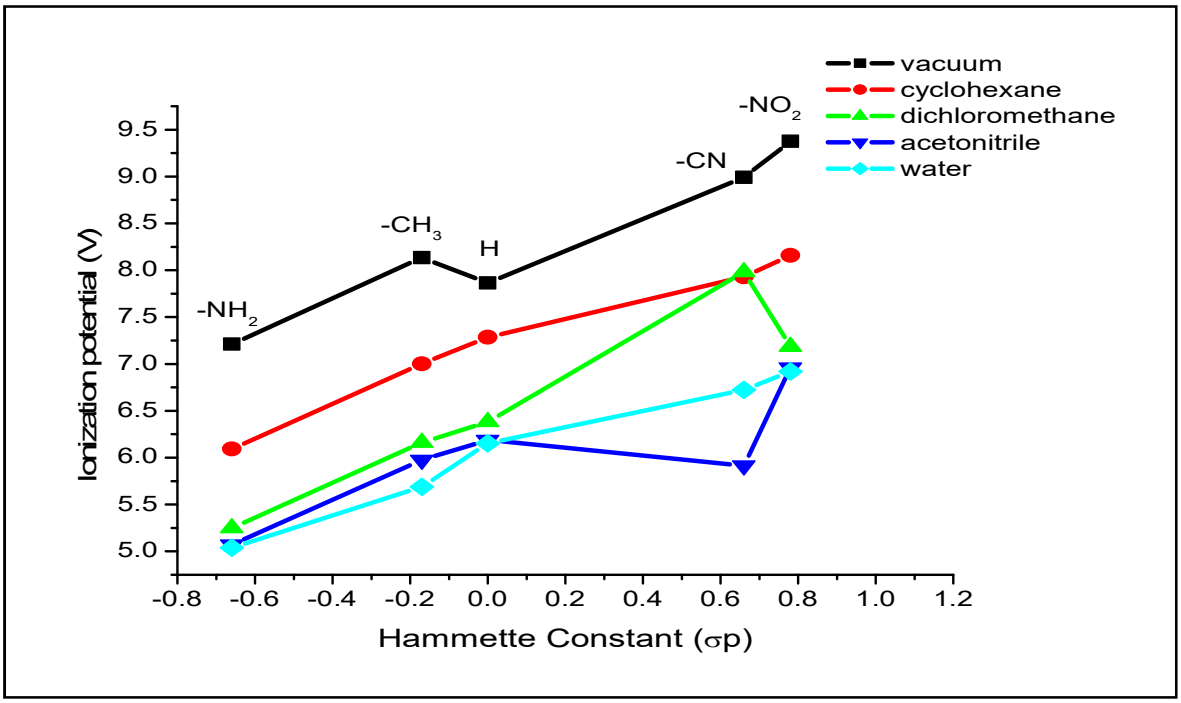


Figure 9. Plot of ionization potential of furan versus Hammett substituent constant in solvents of different polarities by using DFT/B3LYP/6-31G (d,p) method.

Table 9. Comparison of IPv and IPk (value presented in parenthesis) for furan family in solvents of varying polarity by using DFT/B3LYP/6-31G (d, p) in eV.

Molecule	Vacuum	Cyclohexane	Dichloromethane	Acetonitrile	Water
3-amino furan	7.211	6.093	5.249	5.073	5.040
	(5.296)	(5.338)	(5.400)	(5.421)	(5.424)
3-methyl furan	8.134	7.000	6.161	5.9744	5.6901
	(5.953)	(5.992)	(6.047)	(6.065)	(6.069)
Furan	7.865	7.287	6.383	6.1880	6.153
	(6.122)	(6.156)	(6.205)	(6.220)	(6.223)
	8.9 [c]			5.94[d]	
3-cyano furan	8.990	7.930	7.983	5.914	6.723
	(7.004)	(6.933)	(6.863)	(6.845)	(6.842)
3-nitro furan	9.375	8.158	7.184	6.962	6.921
	(7.275)	(7.190)	(7.103)	(7.080)	(7.076)

[c] Experimental value: (Klapstein *et al*., 1990)
[d] Experimental value: (Demirboğa and Önal,1999)

Table 10. Comparison of IPv and IPk (value presented in parenthesis) for furan family in solvents of varying polarity by using DFT/B3LYP/6-31++G (d, p) in eV.

Molecule	Vacuum	Cyclohexane	Dichloromethane	Acetonitrile	Water
3-amino furan	7.472	6.351	5.513	5.331	5.299
	(5.656)	(5.683)	(5.740)	(5.760)	(5.764)
3-methyl furan	8.336	7.214	6.360	6.173	6.140
	(6.267)	(6.291)	(6.339)	(6.355)	(6.359)
Furan	8.692	7.493	6.589	6.432	6.359
	(6.460)	(6.478)	(6.517)	(6.530)	(6.533)
3-cyano furan	9.421	8.084	7.170	6.954	6.914
	(7.313)	(7.293)	(7.211)	(7.115)	(7.111)
3-nitro furan	9.614	8.3885	7.404	7.179	7.137
	(7.612)	(7.507)	(7.403)	(7.375)	(7.370)

In general, a higher ionization potential was predicted for furan and derivatives relative to their pyrrole analogues. However, except from slight irregularities in dichloromethane, the ionization potential shows similar trend with respect to substituent and solvent effects; i.e. electron donating group and polar solvents favors easy oxidation. Comparison of the two computational methods in (Table 9), i.e. IPv vs. IPk shows that the Koopmans prediction still show larger discrepancy in vacuum, while the discrepancy decrease in solvated environment. Moreover, the Koopmans prediction fails to reproduce the solvent effect on IP like the case of

pyrrole discussed above. Similar line of analyses was followed for thiophene systems. (Table 11-12) presents computed ionization potentials of thiophene derivatives in solvents of various polarities. Experimental values were also included wherever available.

Table 11. Comparison of IPv and IPk (value presented in parenthesis) for thiophene family in solvents of varying polarity by using DFT/B3LYP/6-31G(d, p) method in eV.

Molecule	Vacuum	Cyclohexane	Dichloromethane	Acetonitrile	Water
3-amino thiophene	7.164 (5.341)	6.072 (5.378)	5.268 (5.437)	5.100 (5.456)	5.069 (5.460)
3-methyl thiophene	8.1477 (6.177)	7.061 (6.208)	6.243 (6.261)	6.065 (6.278) 6.30***	6.033 (6.282)
thiophene	8.969 (6.350) 8.96**	7.819 (6.375)	6.953 (6.421)	6.767 (6.436) 6.50***	6.733 (6.440)
3-cyano thiophene	9.048 (7.100)	7.891 (7.037)	6.973 (6.973)	6.766 (6.957) 6.90***	6.723 (6.954)
3-nitro thiophene	9.417 (7.001)	7.969 (7.276)	7.160 (7.187)	6.940 (7.164) 7.13***	6.921 (7.160)

**Experimental value: (Kishimoto *et al*., 1996),
***Experimental value: (Waltman *al.,* 1984)

Table 12. Comparison of IPv and IPk (value presented in parenthesis) for thiophene family in solvents of varying polarity by using DFT/B3LYP/6-31++G (d, p) in eV.

Molecule	Vacuum	Cyclohexane	Dichloromethane	Acetonitrile	Water
3-amino thiophene	7.390 (5.637)	6.295 (5.663)	5.490 (5.717)	6.418 (5.738)	5.292 (5.742)
3-methyl thiophene	8.325 6.435	7.222 (6.445)	6.401 (6.486)	6.223 (6.502)	6.191 (6.505)
thiophene	9.129 (6.625)	7.974 (6.633)	7.105 (6.667)	6.918 (6.680)	6.884 (6.685)
3-cyano thiophene	9.229 (7.363)	8.065 (7.281)	7.138 (7.200)	6.929 (7.180)	7.084 (7.176)
3-nitro thiophene	9.455 (7.651)	8.301 (7.541)	7.342 (7.434)	7.124 (7.406)	6.418 (7.401)

The results shows that the DFT calculation based on equation 10predicts the trends observed for both solvation and substituent effects similar to the cases of pyrrole and furan. On the other hand, the Koopman's method miserably fails to predict the solvent effect, even though a better agreement with experiment was observed in acetonitrile solvent by the method.

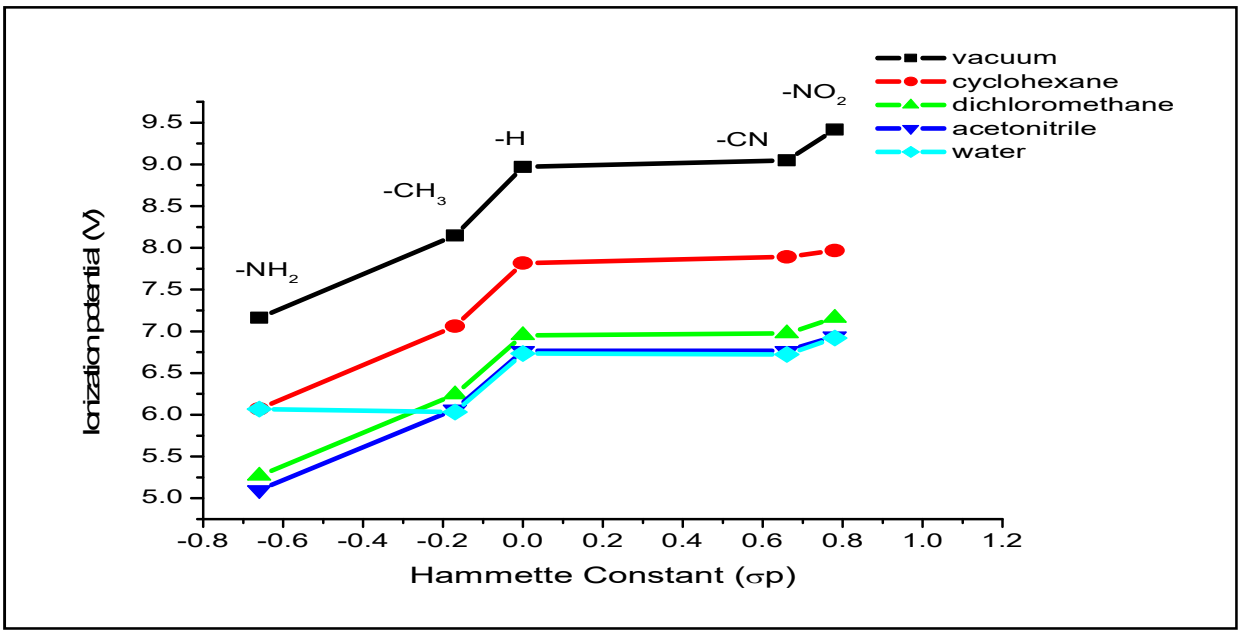


Figure 10. Plot of ionization potential of thiophene versus Hammett substituent constant in solvents of different polarities.

Based on the comparison of substituent effect on electrochemical oxidation potentials, higher in (-NO_2) substituent than other used in this work. It can be stated that the electrochemical stability of -NO_2 substituent of pyrrole, furan and thiophene is greater than other substituent in solvents of polarity. However, the stability is decreased vacuum to water; the stability of intermediate radical cations has an important role in the electroplymerization process (Beigi, 2012).

4.4. Bandgaps

Bandgap is an important parameter determining molecular electrical transport properties and electric admittance (being charged under applied electric filed) because it is a measure of the electron density. The energy of highest occupied molecular orbital (E_{HOMO}) and energy of the lowest unoccupied molecular orbital (E_{LUMO}) of parent monomers/radical cations and their

derivatives were performed at DFT /B3LYP/6-31G (d, p) and 6-31G++G (d, p) level of theory, the value are listed in Appendix Tables 11-12. Based on this information bandgap of parent monomers/radical cations and their derivatives have been determined by (equation11).

As it is indicated from Table 13, parent monomer with electron withdrawing (-NO_2 and -CN) substituent has lower bandgap. However, with electro donating (-NH_2,-H, CH_3) substituent on the parent monomer has the higher bandgap; this indicated that electro donating substituent makes high kinetic stability and low chemical reactivity parent monomer. Moreover, the radical cation bandgap is lower when we compared to the parent monomer. In the case of solvent effect on the parent monomer, the polar solvent slightly decreases the bandgap as compared to non-polar solvents. The effect of solvent on the radical cation is similar with that of the parent monomer. Therefore, the presence of (-NO_2 and -CN) on molecular radical cations improves the conductivity and enhances the reactivity of these molecules (Tang, 2005; Jensen, 2007). Among those-NO_2substituted pyrrole; furan and thiophene are smaller than other compounds. This shows that the conductivity of -NO_2 substituted pyrrole, furan and thiophene are greater than other molecules. Related report was observed in (Jameh-Bozorghi and Beigi, 2011).

Table 13. Bandgap for thiophenes, pyrroles, furans and there radical cation (presented in italic) in solvents of varying polarity by using DFT/B3LYP/6-31G (d, p) in eV.

Molecule	Vacuum	Cyclohexane	Dichloromethane	Acetonitrile	Water
3-aminopyrrole	6.848	6.866	6.886	6.892	6.893
	2.490	*2.489*	*2.488*	*2.488*	*2.487*
3-methylpyrrole	4.873	4.700	4.511	4.459	4.449
	2.779	*2.801*	*2.823*	*2.829*	*2.829*
Pyrrole	6.221	6.159	6.079	6.055	6.051
	3.004	*2.999*	*2.992*	*2.998*	*2.989*
3-cyanopyrrole	6.821	6.833	6.079	6.853	6.854
	2.482	*2.558*	*2.663*	*2.690*	*2.695*
3-nitropyrrole	6.226	6.244	6.267	6.274	6.276
	1.957	*2.308*	*2.716*	*2.830*	*2.851*
3-aminofuran	6.628	6.623	6.618	6.616	6.616
	2.743	*2.753*	*2.766*	*2.770*	*2.053*
3-methylfuran	4.922	4.780	4.626	4.583	4.575
	2.912	*2.921*	*2.928*	*2.930*	*2.934*
Furan	6.072	6.030	5.976	5.961	5.958
	3.019	*3.087*	*3.020*	*3.020*	*3.020*
3-cyanofuran	6.604	6.597	6.588	6.586	6.585
	2.558	*2.701*	*2.719*	*2.720*	*2.724*
3-nitrofuran	6.058	6.038	6.017	6.011	6.010
	2.025	*2.109*	*2.714*	*2.721*	*2.583*
3-aminothiophene	6.122	6.120	6.117	6.117	6.117
	2.324	*2.343*	*2.369*	*2.377*	*2.379*
3-methylthiophene	4.778	4.826	4.675	4.633	4.625
	2.243	*2.473*	*2.498*	*2.505*	*2.507*
thiophene	5.715	5.708	5.687	5.680	5.679
	1.464	*1.473*	*1.486*	*1.490*	*1.491*
3-cyanothiophene	6.089	6.084	6.079	6.078	6.078
	2.242	*2.281*	*2.356*	*2.382*	*2.387*
3-nitrothiophene	5.383	5.366	5.348	5.344	5.343
	0.796	*2.033*	*2.387*	*2.489*	*2.509*

Table 14 also contain the bandgap calculated by DFT/B3LYP/6-31++G (d, p) levels, it has shown a similar trend with that of DFT/B3LYP/6-31G (d, p) level. In the case of 6-31++G (d, p) basis set, the values are slightly decrease do to inclusion of diffusion function (++) on the basis set.

Table 14. Bandgap for thiophenes, pyrroles, furans and there radical cation (presented in italic) in solvents of varying polarity by using DFT/B3LYP/6-31++G (d, p) in eV.

Molecule	Vacuum	Cyclohexane	Dichloromethane	Acetonitrile	Water
3-aminopyrrole	4.815	4.969	5.128	5.169	5.177
	2.460	*2.456*	*2.453*	*2.453*	*2.452*
3-methylpyrrole	5.425	5.575	5.712	5.741	5.746
	2.746	*2.764*	*2.783*	*2.787*	*2.789*
Pyrrole	5.530	5.704	5.880	5.922	5.930
	2.965	*2.955*	*2.945*	*2.485*	*2.944*
3-cyanopyrrole	5.991	6.027	5.941	5.914	5.909
	2.472	*2.553*	*2.662*	*2.688*	*2.693*
3-nitro pyrrole	4.657	4.458	4.238	4.178	4.238
	2.054	*2.439*	*2.857*	*2.856*	*2.855*
3-amino furan	5.262	5.409	5.575	5.620	5.629
	2.718	*2.727*	*2.740*	*2.743*	*2.745*
3-methyl furan	6.099	6.169	6.250	6.273	6.277
	2.885	*2.893*	*2.901*	*2.903*	*2.903*
Furan	6.355	6.351	6.347	6.346	6.345
	2.989	*2.987*	*2.986*	*2.986*	*2.986*
3-cyano furan	5.954	5.936	5.893	5.838	5.835
	2.474	*2.616*	*2.690*	*2.719*	*2.724*
3-nitro furan	4.715	4.552	4.369	4.318	4.308
	2.055	*2.239*	*2.632*	*2.744*	*2.765*
3-aminothiophene	5.199	5.209	5.203	5.202	5.202
	2.315	*2.327*	*2.327*	*2.334*	*2.336*
3-methylthiophene	6.263	5.923	5.919	5.918	5.918
	2.130	*2.439*	*2.463*	*2.469*	*2.471*
thiophene	5.961	5.961	5.961	5.961	5.961
	1.459	*1.469*	*1.484*	*1.488*	*1.489*
3-cyanothiophene	5.630	5.619	5.593	5.584	5.582
	2.272	*2.273*	*2.357*	*2.389*	*2.392*
3-nitrothiophene	4.761	4.600	4.413	4.360	4.349
	2.163	*2.164*	*2.561*	*2.675*	*2.697*

From Tables 13 and 14, we can also see that, the basis set dependency on the bandgap values comparison with other theoretical value. As shown in Table 1 of the literature the bandgap of thiophene monomer absolute error using density functional methods DFT/B3LYP with various combinations of basis sets is 6-31G, 6-31G(d) and 6-31+G (2.16, 2.22 and 2.32 respectively) and in Table 13 and 14, 6-31G (d, p) and 6-31++G (d, p) (0.89 and 0.73 respectively). The bandgap value of (Table 13 and 14) have good agreement with the experimental value present in Table 1. This indicated that improvement of the bandgap is obtained in applying a higher-

level basis set, the other thing is the functional also another advantage for improvement of the bandgap value. Because BLYP is good agreement with the experimental value, than B3LYPfunctional in higher-level basis set (Table 5 and 6).

4.5. Dipole Moment

The dipole moment (μ in Debye) is one of electronic parameter used to describe the polarity of the molecule. In this section, we have attempt to determine polarity of the parent monomer/radical cation and their derivatives at the DFT/B3LYP/6-31G (d, p) and DFT/B3LYP/6-31++G (d, p) calculations were carried out for all the compounds and the dipole moments (μ) of the compounds are determined. The dipole moments (μ) value subtracting from the information of optimized structure of those molecule with different common types of solvent (cyclohexane, dichloromethane, acetonitrile and water) and the results are listed in Tables 15 and16.

As shown (Table 15), all monomers have smaller dipole moment compared to their radical cation except amino substituted pyrrole, furan and thiophene. Among, the radical cations the higher dipole moment is observed in electron withdrawing substituent (-NO_2 and -CN) with polar solvents than the other substituents. Besides of this, smaller dipole moment shown in (-NH_2) substituent for pyrrole, (-CH_3) for thiophene and furan. This finding demonstrates monomers that have large dipole moment are highly soluble in polar solvents for example in thiophene family, in pyrrole family and in furan family, which could enhance the efficiency of electro polymerizations. Variation in dipole moment of furan, pyrrole and thiophene most probably due to the nature of the monomer and their heteroatom.

Table 15. Dipole moment (μ in Debye) for thiophenes, pyrroles, furans and there radical cations (presented in italic) in solvents of varying polarity by using DFT/B3LYP/6-31G (d, p).

Molecule	Vacuum	Cyclohexane	Dichloromethane	Acetonitrile	Water
3-aminopyrrole	1.921	2.104	2.346	2.424	2.439
	1.775	*1.975*	*2.223*	*1.975*	*2.311*
3-methylpyrrole	1.713	1.891	2.109	2.174	2.187
	2.653	*2.993*	*3.390*	*3.502*	*3.524*
Pyrrole	1.902	2.106	2.360	2.436	2.450
	1.788	*2.001*	*2.262*	*2.336*	*2.353*
3-cyanopyrrole	6.387	7.089	7.886	8.109	8.152
	7.270	*8.486*	*9.786*	*10.128*	*10.192*
3-nitro pyrrole	6.496	7.241	8.145	8.413	8.465
	9.894	*10.810*	*11.821*	*12.102*	*12.157*
3-aminofuran	1.852	2.009	2.206	2.266	2.278
	3.504	*3.859*	*4.294*	*4.422*	*4.447*
3-methylfuran	0.932	1.027	1.142	1.175	1.182
	0.398	*0.345*	*0.305*	*0.298*	*0.296*
Furan	0.628	0.683	0.752	0.773	0.777
	1.114	*1.262*	*1.150*	*1.156*	*1.158*
3-cyanofuran	3.916	4.328	4.770	4.888	4.910
	4.555	*5.462*	*6.450*	*6.707*	*6.752*
3-nitrofuran	3.977	4.387	4.858	4.991	5.017
	6.419	*6.119*	*8.618*	*8.815*	*8.853*
3-aminothiophene	1.940	2.129	2.366	2.435	2.449
	3.927	*4.328*	*4.834*	*4.989*	*5.020*
3-methylthiophene	0.984	1.104	1.244	1.283	1.291
	0.817	*0.735*	*0.646*	*0.622*	*0.618*
thiophene	0.623	0.692	0.771	0.792	0.798
	1.082	*1.047*	*0.990*	*0.970*	*0.966*
3-cyanothiophene	4.092	4.555	5.067	5.208	5.235
	4.090	*5.098*	*6.255*	*6.567*	*6.626*
3-nitrothiophene	4.189	4.671	5.245	5.413	5.445
	6.166	*7.795*	*8.643*	*8.877*	*8.922*

Table 16 also contain the dipole moments (μ) calculated by DFT/B3LYP/6-31++G (d, p) levels, it has shown a similar trend with that of DFT/B3LYP/6-31G (d, p) level. On the other hand, the value calculated by 6-31++G (d, p) basis set has slightly decrease do to inclusion of diffusion function (++) on the basis set. From Tables 15 and 16, which shown as the dipole moments of the molecular radical cation with electron withdrawing (NO_2 and CN) substituent are largely affected by solvent polarity.

Table 16. Dipole moment (μ in Debye) for thiophenes, pyrroles and furans and there radical cations (presented in italic) in solvents of varying polarity by using DFT/B3LYP/6-31++G (d, p).

Molecule	Vacuum	Cyclohexane	Dichloromethane	Acetonitrile	Water
3-amino pyrrole	1.873	2.105	2.430	2.542	2.564
	1.747	*1.957*	*2.222*	*2.301*	*2.317*
3-methyl pyrrole	1.651	1.836	2.069	2.139	2.153
	2.611	*2.963*	*3.379*	*3.497*	*3.520*
Pyrrole	1.912	2.137	2.423	2.510	2.527
	1.780	*2.006*	*2.285*	*2.368*	*2.384*
3-cyano pyrrole	6.571	7.353	8.258	8.516	8.565
	7.438	*8.750*	*10.167*	*10.543*	*10.614*
3-nitro pyrrole	6.898	7.782	8.902	9.247	9.316
	10.224	*11.235*	*12.389*	*12.719*	*12.783*
3-amino furan	1.831	2.018	2.264	2.344	2.360
	3.499	*3.875*	*4.347*	*4.488*	*4.515*
3-methyl furan	1.085	1.211	1.366	1.211	1.421
	0.472	*0.416*	*0.367*	*0.357*	*0.354*
Furan	0.728	0.503	0.899	0.928	0.934
	1.171	*1.197*	*1.233*	*1.326*	*1.247*
3-cyano furan	4.037	5.667	5.652	5.129	5.155
	4.687	*4.456*	*4.993*	*7.026*	*7.081*
3-nitro furan	4.288	4.783	5.375	5.549	5.583
	6.889	*8.247*	*9.074*	*9.305*	*9.349*
3-amino thiophene	1.796	1.983	2.224	2.297	2.312
	3.796	*4.195*	*4.703*	*4.860*	*4.892*
3-methyl thiophene	0.958	1.075	1.209	1.247	1.254
	0.789	*0.698*	*0.598*	*0.571*	*0.566*
thiophene	0.537	0.591	0.649	0.663	0.666
	1.047	*1.047*	*0.939*	*0.917*	*0.912*
3-cyano thiophene	4.371	4.912	5.526	5.698	5.731
	4.307	*5.421*	*6.713*	*7.062*	*7.129*
3-nitro thiophene	4.682	5.290	6.049	6.280	6.326
	6.742	*8.292*	*9.276*	*9.556*	*9.611*

The electric dipole moments and their components have the greatest dipole moments on 3-NO_2 substituent with polar solvent compared with their corresponding monomer. Hence 3-NO_2 substitute with polar solvent larger dipole moments of these three molecules support possibility of more soluble in polar solvents and higher admittance to the excess electric charge; they have increase efficiency of electroplymerization (Sabzyan and Omrani, 2003).

4.5. Thermodynamic Property

Solvation energy is one of the thermodynamic properties used to determine the thermodynamic stability of compound. The solvent effects are included here to ensure that the calculations are compatible with the typical conditions. Thermodynamic stability of the parent monomer/radical cations and their derivatives with different common types of solvent at the DFT/B3LYP/6-31G (d, p) and 6-31++G (d, p) calculations were carried out for all the compounds. Based on this information, the solvation energy of the compounds are calculated by using (equation 12) and values were listed in Tables 17 and18.

Table 17. Solvation energy are (ΔGsol and ΔG'sol refers to solvation energy of the neutral and cations respectively) in solvents of varying polarity by using DFT/B3LYP/6-31G (d, p) in eV.

	Cyclohexane		Dichloromethane		Acetonitrile		Water	
Molecule	ΔG_{sol}	$\Delta G'_{so}$	ΔG_{sol}	$\Delta G'_{so}$	ΔG_{sol}	$\Delta G'_{so}$	ΔG_{sol}	$\Delta G'_{so}$
		1		1		1		1
3-amino pyrrole	-0.3	-1.16	-0.35	-2.25	-0.15	-2.26	-0.26	-2.3
3-methyl pyrrole	-0.3	-1.15	-0.34	-2.04	-0.15	-2.24	-0.26	-2.27
pyrrole	-0.06	-1.22	-0.14	-2.15	-0.16	-2.35	-0.17	-2.39
3-cyano pyrrole	-0.1	-1.3	-0.3	-2.38	-0.13	-2.63	-0.26	-2.67
3-nitro pyrrole	-0.1	-1.4	-0.14	-2.5	-0.06	-2.7	-0.2	-2.8
3-amino furan	-0.2	-1.1	-0.35	-2.12	-0.08	-2.33	-0.2	-2.37
3-methyl furan	-0.2	-1.17	-0.5	-2.05	-0.08	-2.24	-0.19	-2.62
furan	-0.65	-1.23	-0.69	-2.17	-0.7	-2.38	-0.7	-2.42
3-cyano furan	-0.2	-1.28	-0.18	-1.39	-0.07	-2.58	-0.17	-2.62
3-nitro furan	-0.1	-1.3	-0.23	-2.3	-0.03	-2.6	-0.08	-2.7
3-amino thiophene	-0.1	-1.1	-0.2	-2.0	-0.1	-2.2	-0.2	-2.3
3-methyl thiophene	-0.1	-1.1	-0.2	-2.0	-0.1	-2.2	-0.2	-2.2
thiophene	-0.1	-1.2	-0.1	-2.1	-0.1	-2.3	-0.1	-2.3
3-cyano thiophene	-0.1	-1.3	-0.2	-2.3	-0.1	-2.5	-0.2	-2.6
3-nitro thiophene	-0.1	-1.4	-0.1	-2.3	-0.1	-2.7	-0.1	-2.7

As shown in Table 17, all monomers have smaller solvation energy than their radical cations. Among these radical cations, the higher solvation energy was observed on electron

withdrawing substituents comparing with the other. However, solvation energy increase in both parent monomers and molecular radical cations (effect is higher) with solvent polarity, which means the effect of solvent in all parent monomer is much less than that of molecular radical cations. This is may be the delocalization of the radical cations through the double bonds as depicted in the above (Table 2 and 3).The solvation energy calculated by DFT/B3LYP/6-31++G (d, p) levels. The results obtained in Table 18 are in agreement with the results obtained at the DFT/B3LYP/6-31G (d, p) level. On the other hand, the values are slightly increasing, because, 6-31++G (d, p) basis set was accounts the lone pair electron of heteroatom in parent monomer (Pyrrole, furan and thiophene).

Table 18. Solvation energy are (ΔGsol and ΔG'sol refers to solvation energy of the neutral and cation respectively) in solvents of varying polarity by using DFT/B3LYP/6-31G (d, p) in eV.

Molecule	Cyclohexane		Dichloromethane		Acetonitrile		Water	
	ΔG_{sol}	$\Delta G'_{sol}$	ΔG_{sol}	$\Delta G'_{sol}$	ΔG_{sol}	$\Delta G'_{sol}$	ΔG_{sol}	$\Delta G'_{sol}$
3-amino pyrrole	-0.10	-1.17	0.23	-2.08	-0.27	-2.28	-0.28	-2.32
3-methyl pyrrole	-0.06	-1.15	-0.13	-2.05	-0.16	-2.25	-0.16	-2.28
pyrrole	-0.06	-1.22	-1.14	-2.15	-0.17	-2.36	-0.17	-2.40
3-cyano pyrrole	-0.15	-1.32	-0.32	-2.42	-0.37	-2.67	-0.38	-2.72
3-nitro pyrrole	-0.16	-1.35	-0.35	-2.49	-0.41	-2.76	-0.42	-2.81
3-amino furan	-0.08	-1.20	-0.18	-2.14	-0.21	-2.35	-0.22	-2.39
3-methyl furan	-0.04	-1.16	-0.08	-2.06	-0.09	-2.26	-0.10	-2.29
furan	-0.04	-1.24	-0.08	-2.18	-0.09	-2.41	-0.10	-2.43
3-cyano furan	-2.05	-1.30	-0.20	-2.37	-0.23	-2.62	-0.24	-2.66
3-nitro furan	-0.10	-1.32	-0.21	-2.42	-0.25	-2.68	-0.25	-2.73
3-amino thiophene	-0.08	-1.17	-0.17	-2.07	-0.20	-2.27	-0.21	-2.30
3-methyl thiophene	-0.03	-1.12	-0.07	-2.0	-0.09	-2.18	-0.09	-2.21
thiophene	-0.03	-1.19	-0.07	-2.10	-0.09	-2.30	-0.09	-2.30
3-cyano thiophene	-0.1	-1.26	-0.27	-2.30	-0.24	-2.54	-0.24	-2.58
3-nitro thiophene	-0.1	-1.29	-0.27	-2.37	-0.25	-2.62	-0.27	-2.67

From Tables 17 and 18, we can also see that, the potential effect of solvent in electro withdrawing substituent (NO_2 and CN) monomer is higher than that of electron donating substituted (NH_2 and CH_3) monomer. Among these NO_2- substituted pyrroles, furans and thiophenes have lower change in solvation energy than others. That means polar solvents favor formation of stable intermediate radical cation of pyrroles, furans and thiophenes. Their stability is key role in the electroplymerization process related report observed on (Waltman *et al.,* 1984; Vaschetto and Retamal, 1997; Jameh-Bozorghiand Shirani, 2011).

5. SUMMARY, CONCLUSIONSAND RECOMMENDATIONS

5.1. Summary and Conclusions

Electrical, thermodynamic and structural properties of neutral thiophene, pyrrole, furan and their radical cations as a function of substituent and solvent polarity were studied using the density functional theory and B3LYP method with 6-31G(d, p) and 6-31++G(d, p) basis set in solution phase using Polarized Continuum Model (PCM) method. Electrochemical parameters such as function coefficient (Fn), atomic charge distribution, ionization potential, bandgap, dipole moment and solvation energy were calculated and analyzed.

Analysis of the data showed that,NO_2 substituted; pyrrole, furan and thiophene have higher ret of polymerization and they encourage radical-radical coupling do to greater atomic positive charge in position of α and smaller atomic positive charge in α'. A similar trend was observed in both vacuum and polar solvents (effect is high). Based on function coefficient (Fn) observation, the data showed that NO_2 substituted pyrrole, furan and thiophene have smaller Fn values and have no significant effect on solvent polarity. Therefore, it can be suggested that double bonds in nitro substituted; pyrrole, furan and thiophene are more delocalized than the other substituents. However geometry optimization and calculated Fn-coefficient for parent monomer in 6-31++G(d, p) basis set has been found in a good agreement with experimental data than 6-31G(d, p).

Two approaches have been applied for computational prediction of the ionization potential. The first approach is Koopman's theorem (IPk) and the second approach is IPv. The results of ionization energy of monomers obtained using IPv method was in good agreement with experimental data in the literature. For example, calculated ionization potential of pyrrole in acetonitrile environment predicted (5.61eV) gives comparable result with the experimental value (5.64 eV). It also recorded that the DFT calculation slightly underestimates the IP in vacuum (7.7988 eV) compared to the experimental values (8.28 eV) than in solution. Besides, the DFT calculation demonstrates bandgap of the monomers is relatively higher than their radical cation. These radical cations with solvent polarity and electron withdrawing substituent make its value lower.

Furthermore, the study showed both the dipole moment and the solvation energy in the monomer and there radical cation (effect is high) increase with polarity and electron withdrawing substituent.

Generally the charge density, Fn, bandgap and dipole moment and solvation energy follows the order of pyrrole > furan > thiophene. Therefore, the DFT investigations of the various experimental parameters are affected by the nature of the solvent and substituents attached to the heterocycle ring. The efficiency of polymerization determined by the first step of oxidation can be optimized using different substituent having different strength of electron donating and withdrawing nature and solvents of different polarity i.e. nucleaphilic and electrophilic properties. Accordingly, from the theoretical results it seems NO_2 substitute hypothetical pyrrole, furan and thiophene is the best candidate monomer among other all the considered substituted monomers, for the synthesis of corresponding conducting polymers and for maximizing the efficiency electroplymerization.

5.2. Recommendations

Based on this thesis work, the following are recommended for future investigation.

- Introducing mixed solvents in different proportion using PCM model is recommended to calculate experimental parameters important in electroplymerization and for comparison purposes between single and mixed solvents.
- This work can be extended by employing higher basis sets to get accurate value of various parameters.

6. REFERENCES

Andersson, M.R., Selse, D., Berggren, M., Järvinen, H., Hjertberg, L.T., Inganäs, O., Wennerström, O. and Österholm, J.E. 1994. Regioselective polymerization of 3-(4-octylphenyl) thiophene with FeCl3. *Macromolecules*, 27(22): 6503-6506.

Andersson, M.R., Thomas, O., Mammo, W., Svensson, M., Theander, M. and Inganäs, O. 1999. Substituted polythiophenes designed for optoelectronic devices and conductors. *Journal of Materials Chemistry*, 9(9):1933-1940.

Ando, S. and Ueda, M. 2002. Density functional theory calculations of the local spin densities of 3-substituted thiophenes and the oligomerization mechanism of 3-methylsulfanyl thiophene. *Synthetic metals*, 129(2): 207-213.

Asami, R., Fuchigami, T. and Atobe, M. 2006. Development of a novel environmentally friendly electroplymerization of water-insoluble monomers in aqueous electrolytes using acoustic emulsification. *Langmuir*, *22*(24): 10258-10263.

Atkins and Friedman, R.S. 1996. Molecular Quantum Mechanics. *Calculation of Quantum Me chanics.* Purdue University, Fort Wayne, USA.

Baerends, E.J. and Gritsenko, O.V. 1997. A quantum chemical view of density functional theory. *The Journal of Physical Chemistry A*, 101(30): 5383-5403.

Bakhshi, A.K. and Ray, N.K. 1988. A b-initio study of the electronic structure and conduction properties of mislinked heterocyclic polymers. *The Journal of Chemical Physics*, 88(1): 386-393.

Balint, R., Cassidy, N.J. and Cartmell, S.H. 2014. Conductive polymers: towards a smart biomaterial for tissue engineering. *Acta Biomaterials,* 10: 2341–2353.

Bard, A.J., Faulkner, L.R., Leddy, J. and Zoski, C.G. 1980. *Electrochemical methods: fundamentals and applications*. New York, wiley, USA.

Becke, A.D. 1988. Density-functional exchange energy approximation with correct asymptotic behavior. *Physical Review,* 38(6): 3098-3100.

Beigi, H.S. 2012. Density functional theory study on the structural, reactivity, and electronic properties of all mono-, di-, tri-, tetra-, and pentafluoroanilines as monomers for conducting polymers *Canadian Journal of Chemistry*, 90: 902–914.

Beigi, H.S. and Jameh-Bozorghi, S. 2011. Theoretical study on the electronic, structural, properties and reactivity of a series of mono-, di-, tri- and tetrachlorothiophenes as well

as corresponding radical cation forms as monomers for conducting polymers. *Central Journal Chemistry,* 5: 1-13

Buchała, T., Chudoba, A. and Roszak, S. 2016. Oxidation properties of b-substituted pyrroles Struct. *Journal of Physical Chemistry*, 27: 185–189.

Chen, J., Officer, D.L., Pringle, J.M., MacFarlane, D.R., Too, C.O. and Wallace, G.G. 2005. Photo electrochemical solar cells based on polyterthiophenes containing porphyrins using ionic liquid electrolyte. *Electrochemical and Solid-State Letters*, 8(10): 528-A530.

Clark, T., 1985. *A handbook of computational chemistry: A practical guide to chemical structure and energy calculations*. Wiley-Interscience.

Colladet, K., Fourier, S., Cleij, T.J., Lutsen, L., Gelan, J., Vanderzande, D., Huong Nguyen, L., Neugebauer, H., Sariciftci, S., Aguirre, A. and Janssen, G. 2007. Low bandgap donor− acceptor conjugated polymers toward organic solar cells applications. *Macromolecules*, 40(1): 65-72.

Cordell, F.R. and Boggs, J.E., 1981. Structure and degree of aromatic character in furan, pyrrole, and thiophene. *Journal of Molecular Structure: THEOCHEM*, 85(1-2): 163-178.

Cramer, C. J. 2004. *Essentials of Computational Chemistry*, 2 nd Edition, John Willey and Sons,

Cuff L and Kertesz M. 1997. Evidence of quinonoid structures in the vibrational spectra of thiophene based conducting polymers: Poly(thiophene), poly(thieno[3,4-b]benzene), and poly(thieno[3,4-b]pyrazine). *Journal of Chemical Physics,* 106: 5541-5553.

Davison, E. 2000. Computational Transition Metal Chemistry *Chemical Reviews*, 100(2): 351.

Demirboğa, B. and Önal, A.M., 1999. Electrochemical polymerization of furan and 2-methylfuran. *Synthetic metals*, 99(3): 237-242.

Dguigui, K., El Hallaoui, M. and Mbarki, S. 2012. Ab-initio and DFT study of polythiophene energy bandgap and substitutions effects. *Ijrras*, 12: 427-430

Diaz, A.F., Castillo, J.I., Logan, J.A. and Lee, W.Y., 1981. Electrochemistry of conducting Polypyrrole films. *Journal of Electro analytical Chemistry and Interfacial Electrochemistry*, 129(1-2): 115-132.

DiCésare, N., Belletête, M., Leclerc, M. and Durocher, G. 1999. Intermolecular Interactions in conjugated oligothiophenes. 2. quantum chemical calculations performed on crystalline structures of terthiophene and substituted terthiophenes. *The Journal of Physical Chemistry*, 103(7): 803-811.

Doskocz, J., Doskocz, M., Roszak, S., Soloducho, J. and Leszczynski, J. 2006. Theoretical studies of symmetric five-membered heterocycle derivatives of carbazole and fluorene: precursors of conducting polymers. *The Journal of Physical Chemistry*, 110(51): 13989-13994.

Fleming, I., 1982. Frontier Orbitals and Organic Chemical Reactions. *Wiley, New York. Fukui, K., Science*, 218: 747-754.

Foresman, J.B. and Frisch, Æ. 1993. *Exploring chemistry with electronic structure methods: a guide to using Gaussian*. Gaussian, Incorporated.

Frisch, M.J., Trucks, G.W., Schlegel, H.B., Scuseria, G.E., Robb, M.A., Cheeseman, J.R. et al., 2009. Gaussian 09, Revision A.1, Gaussian, Inc, Wallingford CT,

Funt, B.L. and Diaz, A.F. 1991. Organic electrochemistry: an introduction and a guide, 1337

Gierschner, J., Cornil, J. and Egelhaaf, H.J. 2007. Optical bandgaps of π-conjugated organic materials at the polymer limit: experiment and theory. *Advanced materials*, 19(2): 173-191.

González, L., Tejedor, R.M., Royo, E., Gaspar, B., Munarriz, J., Chanthapally, A., Serrano, J.L., Vittal, J.J. and Uriel, S. 2017. Two-dimensional arrangements of bis (haloethynyl) benzenes combining halogen and hydrogen interactions. *Crystal Growth & Design*, 17(12): 6212-6223.

Gunasekaran, S., Kumaresan, S., Arunbalaji, R., Anand, G. and Srinivasan, S. 2008. Density functional theory study of vibrational spectra, and assignment of fundamental modes of dacarbazine. *Journal of Chemical Sciences*, 120(3): 315-324.

Hansch, C., Leo, A. and Taft, R.W. 1991. A Survey of Hammett Substituent Constants and Resonance and Field Parameters, *Chemical Reviewers*. 91:165-195

Hehre, W.J., 2003. *A guide to molecular mechanics and quantum chemical calculations* (2). Irvine, CA: Wave function.

Hepburn, A.R., Maud, J.M. and Marshall, J.M. 1991. Conductive polymers-synthesis, properties and applications. *Metals and materials, 7(12): 747-752*.

Hohenberg, P. and Kohn, W. 1964. Inhomogeneous electron gas. *Physical review*, *136*(3B): p.B864.

Hutchison, G.R, Zhao, Y.J. and Delley, B. 2003. Electronic structure of conducting polymers: limitations of oligomer extrapolation approximations and effects of heteroatoms. *Physical Review,* 68: 35204.

Jagoda-Cwiklik, B., Slavíček, P., Nolting, D., Winter, B. and Jungwirth, P. 2008. Ionization of aqueous cations: Photoelectron spectroscopy and ab initio calculations of protonated imidazole. *The Journal of Physical Chemistry*, 112(25): 7355-7358.

Jameh-Bozorghi, S. and Beigi, S.H. 2011.Theoretical study on the electronic, structural, properties and reactivity of a series of mono-, di-, tri- and tetrafluorothiophenes as monomers for new conducting polymers. *Journal of Fluorine Chemistry*, 132: 190–195

Jensen, F. 2004. *Introduction to Computational ChemistrySecond Edition*, John Willey and Sons

Jensen, F., 2007. Introduction to Computational Chemistry John Wiley & Sons Ltd. *West Sussex, Chapter*, *6*: p.257.

Kamran, M., Ullah, H., Anwar-ul-Haq, A.A., Bilal, S., Tahir, A.A. and Ayub, K. 2015.Combined experimental and theoretical study of poly (aniline-co-pyrrole) oligomer*Polymer,* 72: 30-39.

Kassim, A., Basar, Z.B. and Mahmud, H. 2002. Effects of preparation temperature on the conductivity of polypyrrole conducting polymer. *Journal of Chemical Science,* 114:155–162.

Kishimoto, N Yamakado, H. and Ohno, K. 1996. Jornail of Physical Chemistry. Penning Ionization of Thiophene, Furan, and Pyrrole by Collision with He (23S) Metastable Atoms, 100: 8204-8211

Klapstein, D., MacPherson, C.D. and O'Brien, R.T. 1990. The photoelectron spectra and electronic structure of 2carbonyl furans, *Canadian Journal Chemistry*, 68, 747

Klapstein, D., MacPherson, C.D. and O'Brien, R.T., 1990. The photoelectron spectra and electronic structure of 2-carbonyl furans. *Canadian journal of chemistry*, *68*(5): 747-754.

Kohn, W. and Sham, L.J. 1965. Self-consistent equations including exchange and correlation effects. *Physical review*, 140(4A): p.A1133.

Koopmans, T. 1933. Ordering of wave functions and eigenenergies to the individual electrons of an atom. *Physical*, 1: 104-113.

Lacroix, J.C., Maurel, F. and Lacaze, P.C., 2001. Oligomer−Oligomer versus Oligomer−Monomer C2−C2‘ Coupling Reactions in Polypyrrole Growth. *Journal of the American Chemical Society*, 123(9): 1989-1996.

Lange, U., Roznyatovskaya, N.V. and Mirsky, V.M. 2008. Conducting polymers in chemical sensors and arrays, *Anaytical ChimicaActa,* 614: 1– 26.

Lukkari, J., Viinikanoja, A., Paukkunen, J., Salomäki, M., Janhonen, M., Ääritalo, T. and Kankare, J. 2000. Oxidation induced variation in polyelectrolyte multilayers prepared from sulfonated self-dopable poly (alkoxythiophene). *Chemical Communications*, (7): 571-572.

Ma, J., Li, S. and Jiang, Y. 2002. A Time-Dependent DFT Study on Bandgaps and Effective Conjugation Lengths of Polyacetylene, Polyphenylene, Polypentafulvene, Polycyclopentadiene, Polypyrrole, Polyfuran, Polysilole, Polyphosphole, and Polythiophene. *Macromolecules*, 35 (3): 1109–1115.

MaMcClain, M.D., Whittington, D.A., Mitchell, D.J. and Curtis, M.D. 1995. Novel Poly (3-alkylthiophene) and Poly (3-alkylthienyl ketone) Syntheses via Organomercurials. *Journal of the American Chemical Society*, 117(13): 3887-3888.

McCullough, R.D. 1998. The chemistry of conducting polythiophenes. *Advanced Materials*, 10(2): 93-116.

McQuarrie, D. A. 2005. *Quantum Chemistry*, Viva Books P. L. C., New Delhi.

Mennucci, B. and Tomasi, J. 1997. Continuum solvation models: A new approach to the problem of solute’s charge distribution and cavity boundaries. *The Journal of chemical physics*, 106(12): 5151-5158.

Monk, P.M., Mortimer, R.J. and Rosseinsky, D.R. 2008. *Electrochromism: fundamentals and applications*. John Wiley & Sons.

Montero, L.A., Gonzalez-Jonte, R., Diaz, L.A. and Alvarez-Idaboy, J.R. 1994. Theoretical model of furan and 2-furancarboxaldehyde. The molecular structure and vibrational spectra, including isotopic effects. *The Journal of Physical Chemistry*, 98(22): 5607-5613.

Mulliken, R.S. 1955. Electronic population analysis on LCAO–MO molecular wave functions. I. *The Journal of Chemical Physics*, 23(10): 1833-1840.

Nikoofard, H. and Sabzyan H. 2007. DFT study of molecular structure and electronic properties of fluoromethylpyrrole oligomers including di-, tri- and tetramer. *Journal of Fluorine Chemistry,* 128: 668-673

Nygaard, U., Nielsen, J.T., Kirchheiner, J., Maltesen, G., Rastrup-Andersen, J. and Sørensen, G.O. 1969. Microwave spectra of isotopic pyrroles. Molecular structure, dipole moment, and 14N quadrupole coupling constants of pyrrole. *Journal of Molecular Structure*, 3(6): 491-506.

O'Boyle, N.M. 2004. *Surface studies and density functional theory analysis of ruthenium polypyridyl complexes* Doctoral dissertation, Dublin City University.

Orio, M., Pantazis, D.A, Neese, F. 2009. Density functional theory. *Photosynthesis Research,* 102: 443–453.

Otero, T.F. and Nalwa, H.S. 1997. ``Handbook of Organic Conductive Molecules and Polymers", 4-10.

Parr, R.G. and Yang, W. 1989. Density Functional Theory of Atoms and Molecules, *Oxford University Press, New York.*

Ponce Ortiz, R., Malavé Osuna, R., Ruiz Delgado, M.C., Casado, J., Jenekhe, S.A., Hernandez, V. and Lopez Navarrete, J.T. 2005. Spectroscopic and DFT studies of donor–acceptor molecules containing phenylquinoline and phenothiazine moieties in various redox states. *International journal of quantum chemistry*, 104(5): 635-644.

Rodriguez, J., Grande, H.J. and Otero, T.F. 1997. Handbook of organic conductive molecules and polymers. *John Wiley & Sons Ltd: New York*, *2*.

Rubio, M., Merchán, M., Orti,E. and Roos, B. O. 1995. A theoretical study of the electronic spectrum of bithiophene. *The Journal of chemical physics*, 102(9): 3580-3586.

Sabzyan, H. and Omrani, A. 2003. Ab-initio and DFT study of all mono-, di-, tri-, and tetrafluoropyrroles and their cations: Predicting structural, spectroscopic, electropolymerization, and electrochemical properties. *The Journal of Physical Chemistry*, 107(33): 6476-6482.

Sabzyan, H. and Omrani, A. 2005. Ab-initio and density functional study of electrical and thermochemical properties of mono-, di-, tri-, and tetrafluoropyrroles and their cations and anions Journal of Molecular Structure: THEOCHEM, 713: 43–49

Schilinsky, P., Waldauf, C. and Brabec, C.J., 2002. Recombination and loss analysis in polythiophene based bulk heterojunction photodetectors. *Applied Physics Letters*, 81(20): 3885-3887.

Schultz, N.E., Zhao, Y. and Truhlar, D.G. 2005. Density functionals for inorganometallic and organometallic chemistry. *The Journal of Physical Chemistry*, 109(49): 11127-11143.

Shi, G., Xu, J. and Fu, M. 2002. Raman spectroscopic and electrochemical studies on the doping level changes of polythiophene films during their electrochemical growth processes. *The Journal of Physical Chemistry*, 106(2): 288-292.

Sıdır, İ., Sıdır, Y.G., Kumalar, M. and Taşal, E. 2010. Ab initio Hartree–Fock and density functional theory investigations on the conformational stability, molecular structure and vibrational spectra of 7-acetoxy-6-(2,3-dibromopropyl)-4, 8-dimethylcoumarin molecule. *Journal of Molecular Structure*, 964(1-3): 134-151.

Silvestri, F. and Marrocchi, A., 2010. Acetylene-Based materials in organic photovoltaics. *International journal of molecular sciences*, 11(4): 1471-1508.

Skotheim, T.A., R.L. Elsenbaumer and J.R. Reynolds, 1998. Handbook ofconducting polymers. *New York: Marcel Dekker*

Slavíček, P., Winter, B., Faubel, M., Bradforth, S.E. and Jungwirth, P., 2009. Ionization energies of aqueous nucleic acids: photoelectron spectroscopy of pyrimidine nucleosides and ab initio calculations. *Journal of the American Chemical Society*, 131(18):6460-6467.

Sousa, S.F., Fernandes, P.A. and Ramos, M.J. 2007. General performance of density functionals. *The Journal of Physical Chemistry A*, 111(42): 10439-10452.

Tang, C.L., 2005. *Fundamentals of quantum mechanics: for solid state electronics and optics*. Cambridge University Press.

Taras-Goslinska, K. and Jonsson, M. 2006. Solvent effects on the redox properties of thioethers. *The Journal of Physical Chemistry*, 110(30): 9513-9517.

Taye Beyene, Ahmed Mustefa, Shimelis Admasse. 2007. Computational Investigation of Conducting Polythiophenes and Substituted Polythiophenes. MSc Thesis, Addis Ababa University, Addis Ababa, Ethiopia.

Ullah, H., Shah, A.A., Ayub, K. and Bilal, S.J. 2013. Density Functional Theory Study of Poly(*o*-phenylenediamine) Oligomers. *The Journal of Physical Chemistry,* 117: 4069-4078

Ullah, H., Shah, A.A., Bilal, S. and Ayub, K. 2014. Doping and de-doping processes of polypyrrole: DFT study with hybrid Functionals. *Journal of Physical Chemistry*, 118: 17819–17830

Vaschetto, M.E. and Retamal, B.A. 1997. Substituents effect on the electronic properties of aniline and oligoanilines. *The Journal of Physical Chemistry*, 101(37): 6945-6950.

Wallace, G.G., Spinks, G.M. Kane-Maguire L.A.P. and Teasdale PR. 2009. In Conductive electroactive polymers: *Intelligent polymer systems Queensland: CRC Press* 77-226.

Waltman, R.J., Diaz, A.F. and Bargon, J. 1984. Substituent effects in the electropolymerization of aromatic heterocyclic compounds. *The Journal of Physical Chemistry*, 88(19): 4343-4346.

Winokur, M.J. Skotheim, T.A. and Reynolds (Eds.), J.R. 2007. Handbook of ConductingPolymers. Conjugated Polymers. Theory, Synthesis, Properties and Characterisation,3rd edition, CRC Press, Boca Raton, 1–17.

Yamamoto, T. J. 1981. Use of Polymer-Iodine Adducts as Positive Electrodes of Cells. *Journal of the Chemical Society, Chemical Communications*, 187-188.

Young, D. 2004. *Computational chemistry: a practical guide for applying techniques to real world problems*. John Wiley & Sons.

Yurtsever, E. 2001. A quantum mechanical study of the electrochemical polymerization of pyrrole. *Synthetic metals*, 119(1-3): 227-228.

Zhang, G., Pei, Y., Ma, J., Yin, K. and Chen, C.L., 2004. Packing structures and packing effects on excitation energies of amorphous phase oligothiophenes. *The Journal of Physical Chemistry,* 108(22): 6988-6995.

7. APPENDIX

7.1. Appendix Tables

Appendix Table 1. Optimized values of bond lengths (Å) and the Fn-coefficient for pyrroles, furans, thiophenes and their radical cations (presented in italic) in vacuum by using B3LYP/6-31G (d, p).

Molecule	X1-C2	C2-C3	C3-C4	C4-C5	C5-X1	Fn
3-aminopyrrole	1.385	1.382	1.428	1.379	1.368	1.034
	1.338	*1.441*	*1.434*	*1.363*	*1.401*	*1.023*
3-methylpyrrole	1.377	1.380	1.430	1.377	1.374	1.038
	1.344	*1.458*	*1.390*	*1.404*	*1.385*	*0.971*
Pyrrole	1.375	1.378	1.425	1.378	1.375	1.034
	1.363	*1.434*	*1.374*	*1.434*	*1.363*	*0.958*
3-cyanopyrrole	1.364	1.388	1.434	1.372	1.379	1.039
	1.335	*1.457*	*1.394*	*1.401*	*1.390*	*0.975*
3-nitropyrrole	1.361	1.382	1.422	1.372	1.384	1.033
	1.357	*1.432*	*1.370*	*1.434*	*1.367*	*0.956*
3-aminofuran	1.375	1.367	1.439	1.361	1.356	1.055
	1.325	*1.433*	*1.434*	*1.354*	*1.388*	*1.029*
3-methylfuran	1.366	1.363	1.441	1.359	1.363	1.059
	1.337	*1.436*	*1.396*	*1.391*	*1.367*	*0.988*
Furan	1.364	1.360	1.435	1.360	1.364	1.055
	1.350	*1.416*	*1.383*	*1.416*	*1.350*	*0.977*
3-cyanouran	1.351	1.371	1.443	1.356	1.368	1.058
	1.325	*1.436*	*1.400*	*1.391*	*1.374*	*0.991*
3-nitrofuran	1.348	1.366	1.434	1.357	1.374	1.053
	1.335	*1.418*	*1.383*	*1.405*	*1.364*	*0.980*
3-aminothiophene	1.741	1.373	1.437	1.364	1.733	1.050
	1.691	*1.430*	*1.444*	*1.352*	*1.772*	*1.038*
3-methylthiophene	1.737	1.369	1.436	1.365	1.736	1.050
	1.736	*1.369*	*1.436*	*1.365*	*1.736*	*1.050*
thiophene	1.736	1.367	1.430	1.367	1.736	1.046
	1.733	*1.363*	*1.496*	*1.363*	*1.733*	*1.098*
3-cyanothiophene	1.722	1.378	1.437	1.363	1.737	1.049
	1.688	*1.448*	*1.404*	*1.384*	*1.771*	*0.992*
3-nitrothiophene	1.720	1.370	1.426	1.363	1.742	1.044
	1.721	*1.421*	*1.374*	*1.421*	*1.741*	*0.967*

Appendix Table 2. Optimized values of bond lengths (Å) and the Fn-coefficient for pyrroles, furans, thiophenes and their radical cations (presented in italic) in cyclohexane by using B3LYP/6-31G (d, p).

Molecule	X1-C2	C2-C3	C3-C4	C4-C5	C5-X1	Fn
3-aminopyrrole	1.384	1.383	1.429	1.380	1.367	1.034
	1.338	*1.439*	*1.434*	*1.362*	*1.399*	*1.024*
3-methylpyrrole	1.377	1.381	1.431	1.381	1.377	1.036
	1.343	*1.457*	*1.387*	*1.405*	*1.382*	*0.969*
pyrrole	1.375	1.379	1.426	1.379	1.375	1.034
	1.361	*1.433*	*1.373*	*1.433*	*1.361*	*0.958*
3-cyanopyrrole	1.361	1.389	1.434	1.372	1.379	1.039
	1.339	*1.453*	*1.387*	*1.411*	*1.380*	*0.968*
3-nitropyrrole	1.358	1.385	1.423	1.372	1.383	1.033
	1.356	*1.430*	*1.369*	*1.437*	*1.362*	*0.955*
3-aminofuran	1.377	1.367	1.440	1.361	1.357	1.056
	1.326	*1.431*	*1.435*	*1.352*	*1.389*	*1.031*
3-methylfuran	1.368	1.363	1.442	1.359	1.364	1.059
	1.337	*1.435*	*1.395*	*1.392*	*1.366*	*0.987*
furan	1.365	1.361	1.436	1.361	1.365	1.055
	1.325	*1.405*	*1.368*	*1.405*	*1.325*	*0.974*
3-cyanofuran	1.350	1.371	1.443	1.356	1.370	1.058
	1.328	*1.433*	*1.395*	*1.397*	*1.368*	*0.986*
3-nitrofuran	1.347	1.367	1.431	1.356	1.375	1.051
	1.335	*1.418*	*1.383*	*1.405*	*1.364*	*0.980*
3-aminothiophene	1.742	1.374	1.438	1.364	1.734	1.050
	1.692	*1.428*	*1.445*	*1.352*	*1.770*	*1.039*
3-methylthiophene	1.738	1.369	1.437	1.365	1.737	1.051
	1.700	*1.446*	*1.398*	*1.388*	*1.763*	*0.986*
thiophene	1.737	1.367	1.430	1.367	1.737	1.046
	1.732	*1.362*	*1.495*	*1.362*	*1.732*	*1.097*
3-cyanothiophene	1.721	1.378	1.437	1.363	1.737	1.049
	1.694	*1.445*	*1.396*	*1.394*	*1.760*	*0.983*
3-nitrothiophene	1.718	1.371	1.427	1.363	1.742	1.044
	1.726	*1.416*	*1.375*	*1.426*	*1.729*	*0.967*

Appendix Table 3. Optimized values of bond lengths (Å) and the Fn-coefficient for pyrroles, furans, thiophenes and their radical cations (presented in italic) in dichloromethane by using B3LYP/6-31G (d, p).

Molecule	X1-C2	C2-C3	C3-C4	C4-C5	C5-X1	Fn
3-aminopyrrole	1.384	1.384	1.429	1.382	1.367	1.033
	1.337	*1.438*	*1.435*	*1.363*	*1.398*	*1.025*
3-methylpyrrole	1.376	1.382	1.431	1.379	1.373	1.037
	1.342	*1.456*	*1.385*	*1.407*	*1.379*	*0.967*
pyrrole	1.374	1.380	1.426	1.380	1.374	1.033
	1.359	*1.434*	*1.373*	*1.434*	*1.359*	*0.957*
3-cyanopyrrole	1.359	1.391	1.435	1.373	1.378	1.039
	1.343	*1.449*	*1.382*	*1.421*	*1.370*	*0.963*
3-nitropyrrole	1.355	1.388	1.425	1.372	1.384	1.033
	1.355	*1.429*	*1.369*	*1.439*	*1.358*	*0.955*
3-aminofuran	1.378	1.368	1.441	1.361	1.359	1.056
	1.329	*1.428*	*1.437*	*1.351*	*1.389*	*1.034*
3-methylfuran	1.369	1.363	1.442	1.359	1.365	1.059
	1.338	*1.433*	*1.393*	*1.392*	*1.366*	*0.986*
furan	1.366	1.361	1.436	1.361	1.366	1.056
	1.350	*1.413*	*1.382*	*1.413*	*1.350*	*0.978*
3-cyanfouran	1.349	1.372	1.444	1.356	1.371	1.059
	1.332	*1.428*	*1.391*	*1.403*	*1.361*	*0.982*
3-nitrofuran	1.345	1.368	1.431	1.356	1.377	1.051
	1.342	*1.412*	*1.376*	*1.419*	*1.351*	*0.972*
3-aminothiophene	1.743	1.374	1.440	1.364	1.735	1.051
	1.693	*1.427*	*1.445*	*1.351*	*1.770*	*1.040*
3-methylthiophene	1.739	1.370	1.438	1.365	1.738	1.051
	1.700	*1.445*	*1.396*	*1.389*	*1.760*	*0.986*
thiophene	1.738	1.367	1.431	1.367	1.738	1.047
	1.731	*1.361*	*1.494*	*1.361*	*1.731*	*1.097*
3-cyanothiophene	1.721	1.379	1.438	1.363	1.738	1.049
	1.704	*1.441*	*1.389*	*1.406*	*1.745*	*0.976*
3-nitrothiophene	1.717	1.372	1.428	1.363	1.743	1.044
	1.727	*1.414*	*1.375*	*1.428*	*1.723*	*0.967*

Appendix Table 4. Optimized values of bond lengths (Å) and the Fn-coefficient for pyrroles, furans, thiophenes and their radical cations (presented in italic) in acetonitrile by using B3LYP/6-31G (d, p).

Molecule	X1-C2	C2-C3	C3-C4	C4-C5	C5-X1	Fn
3-aminopyrrole	1.384	1.384	1.429	1.382	1.367	1.033
	1.338	*1.439*	*1.434*	*1.362*	*1.399*	*1.024*
3-methylpyrrole	1.376	1.382	1.431	1.380	1.373	1.037
	1.342	*1.456*	*1.385*	*1.408*	*1.378*	*0.967*
pyrrole	1.374	1.380	1.427	1.380	1.374	1.033
	1.359	*1.434*	*1.373*	*1.434*	*1.359*	*0.957*
3-cyanopyrrole	1.358	1.392	1.436	1.373	1.378	1.039
	1.344	*1.448*	*1.381*	*1.424*	*1.367*	*0.962*
3-nitropyrrole	1.354	1.389	1.426	1.372	1.384	1.033
	1.355	*1.429*	*1.369*	*1.439*	*1.356*	*0.955*
3-aminofuran	1.379	1.368	1.441	1.361	1.360	1.056
	1.329	*1.428*	*1.437*	*1.351*	*1.390*	*1.035*
3-methylfuran	1.370	1.362	1.442	1.360	1.366	1.060
	1.338	*1.432*	*1.393*	*1.392*	*1.366*	*0.986*
furan	1.367	1.361	1.437	1.361	1.367	1.056
	1.350	*1.413*	*1.382*	*1.413*	*1.350*	*0.978*
3-cyanofuran	1.348	1.372	1.444	1.356	1.372	1.059
	1.332	*1.428*	*1.391*	*1.404*	*1.354*	*0.982*
3-nitrofuran	1.345	1.369	1.431	1.356	1.377	1.051
	1.342	*1.412*	*1.376*	*1.419*	*1.351*	*0.972*
3-aminothiophene	1.744	1.374	1.440	1.364	1.736	1.052
	1.694	*1.427*	*1.445*	*1.351*	*1.769*	*1.041*
3-methylthiophene	1.740	1.370	1.438	1.365	1.738	1.052
	1.700	*1.444*	*1.396*	*1.389*	*1.760*	*0.985*
thiophene	1.738	1.367	1.431	1.367	1.738	1.047
	1.731	*1.361*	*1.493*	*1.361*	*1.731*	*1.097*
3-cyanothiophene	1.720	1.379	1.438	1.363	1.738	1.049
	1.706	*1.439*	*1.388*	*1.409*	*1.741*	*0.975*
3-nitrothiophene	1.716	1.373	1.428	1.362	1.743	1.044
	1.727	*1.414*	*1.375*	*1.429*	*1.721*	*0.967*

Appendix Table 5. Optimized values of bond lengths (Å) and the Fn-coefficient for pyrroles, furans, thiophenes and their radical cations (presented in italic) in water by using B3LYP/6-31G (d p).

Molecule	X1-C2	C2-C3	C3-C4	C4-C5	C5-X1	Fn
3-aminopyrrole	1.384	1.384	1.429	1.382	1.367	1.033
	1.337	*1.438*	*1.436*	*1.363*	*1.398*	*1.025*
3-methylpyrrole	1.376	1.382	1.431	1.380	1.373	1.037
	1.342	*1.456*	*1.385*	*1.408*	*1.378*	*0.967*
pyrrole	1.374	1.381	1.427	1.381	1.374	1.033
	1.359	*1.434*	*1.373*	*1.434*	*1.359*	*0.957*
3-cyanopyrrole	1.358	1.392	1.436	1.373	1.378	1.039
	1.344	*1.447*	*1.381*	*1.424*	*1.366*	*0.962*
3-nitropyrrole	1.353	1.389	1.426	1.372	1.384	1.033
	1.355	*1.429*	*1.369*	*1.439*	*1.356*	*0.955*
3-aminofuran	1.379	1.368	1.441	1.361	1.359	1.056
	1.379	*1.408*	*1.438*	*1.428*	*1.329*	*1.014*
3-methylfuran	1.370	1.363	1.442	1.360	1.366	1.059
	1.338	*1.432*	*1.393*	*1.392*	*1.366*	*0.986*
furan	1.367	1.361	1.437	1.361	1.367	1.056
	1.351	*1.413*	*1.382*	*1.413*	*1.351*	*0.978*
3-cyanofuran	1.348	1.372	1.444	1.356	1.372	1.059
	1.332	*1.424*	*1.391*	*1.408*	*1.320*	*0.982*
3-nitrofuran	1.345	1.369	1.432	1.356	1.377	1.051
	1.342	*1.412*	*1.376*	*1.419*	*1.350*	*0.972*
3-aminothiophene	1.744	1.374	1.440	1.364	1.736	1.052
	1.694	*1.427*	*1.445*	*1.351*	*1.769*	*1.041*
3-methylthiophene	1.740	1.370	1.438	1.365	1.438	1.052
	1.701	*1.444*	*1.396*	*1.389*	*1.760*	*0.985*
thiophene	1.738	1.367	1.432	1.367	1.738	1.047
	1.730	*1.361*	*1.493*	*1.361*	*1.730*	*1.097*
3-cyanothiophene	1.720	1.379	1.438	1.363	1.738	1.049
	1.706	*1.438*	*1.387*	*1.409*	*1.740*	*0.974*
3-nitrothiophene	1.716	1.373	1.428	1.362	1.743	1.044
	1.727	*1.413*	*1.375*	*1.429*	*1.721*	*0.968*

Appendix Table 6. Optimized values of bond lengths (Å) and the Fn-coefficient for pyrroles, furans, thiophenes and their radical cations (presented in italic) in vacuum by using B3LYP/6-31++G (d p).

Molecule	X1-C2	C2-C3	C3-C4	C4-C5	C5-X1	Fn
3-aminopyrrole	1.386	1.384	1.428	1.382	1.369	1.033
	1.339	*1.441*	*1.434*	*1.364*	*1.401*	*1.023*
3-methylpyrrole	1.379	1.382	1.431	1.380	1.375	1.036
	1.345	*1.459*	*1.390*	*1.404*	*1.386*	*0.971*
pyrrole	1.376	1.381	1.426	1.381	1.376	1.033
	1.364	*1.434*	*1.375*	*1.434*	*1.364*	*0.959*
3-cyanopyrrole	1.365	1.389	1.434	1.375	1.380	1.038
	1.337	*1.460*	*1.394*	*1.403*	*1.390*	*0.975*
3-nitropyrrole	1.361	1.385	1.424	1.374	1.385	1.032
	1.358	*1.432*	*1.370*	*1.436*	*1.367*	*0.955*
3-aminofuran	1.377	1.368	1.439	1.363	1.357	1.054
	1.326	*1.433*	*1.434*	*1.355*	*1.389*	*1.029*
3-methylfuran	1.369	1.364	1.442	1.362	1.364	1.058
	1.337	*1.437*	*1.397*	*1.393*	*1.368*	*0.987*
furan	1.365	1.363	1.437	1.363	1.365	1.054
	1.351	*1.416*	*1.384*	*1.416*	*1.351*	*0.977*
3-cyanofuran	1.352	1.372	1.443	1.358	1.370	1.058
	1.326	*1.436*	*1.400*	*1.393*	*1.373*	*0.990*
3-nitrofuran	1.349	1.368	1.431	1.358	1.376	1.050
	1.338	*1.419*	*1.382*	*1.409*	*1.362*	*0.977*
3-aminothiophene	1.741	1.375	1.437	1.368	1.732	1.048
	1.691	*1.430*	*1.444*	*1.353*	*1.772*	*1.038*
3-methylthiophene	1.737	1.372	1.437	1.368	1.735	1.049
	1.698	*1.449*	*1.401*	*1.388*	*1.767*	*0.988*
thiophene	1.735	1.370	1.431	1.370	1.735	1.044
	1.734	*1.364*	*1.497*	*1.364*	*1.734*	*1.097*
3-cyanothiophene	1.722	1.380	1.437	1.366	1.736	1.047
	1.687	*1.448*	*1.404*	*1.386*	*1.772*	*0.991*
3-nitrothiophene	1.718	1.372	1.427	1.365	1.742	1.043
	1.712	*1.425*	*1.380*	*1.413*	*1.747*	*0.972*

Appendix Table 7. Optimized values of bond lengths (Å) and the Fn-coefficient for pyrroles, furans, thiophenes and their radical cations (presented in italic) in cyclohexane by using B3LYP/6-31++G (d p).

Molecule	X1-C2	C2-C3	C3-C4	C4-C5	C5-X1	Fn
3-aminopyrrole	1.386	1.384	1.429	1.384	1.368	1.032
	1.339	*1.440*	*1.435*	*1.364*	*1.400*	*1.023*
3-methylpyrrole	1.379	1.383	1.432	1.381	1.374	1.036
	1.344	*1.458*	*1.388*	*1.406*	*1.383*	*0.969*
pyrrole	1.376	1.382	1.427	1.382	1.376	1.033
	1.362	*1.434*	*1.374*	*1.434*	*1.362*	*0.958*
3-cyanopyrrole	1.363	1.391	1.435	1.375	1.380	1.038
	1.341	*1.453*	*1.386*	*1.414*	*1.379*	*0.967*
3-nitropyrrole	1.358	1.388	1.425	1.374	1.385	1.032
	1.357	*1.431*	*1.370*	*1.439*	*1.362*	*0.955*
3-aminofuran	1.379	1.369	1.440	1.363	1.359	1.055
	1.327	*1.431*	*1.435*	*1.354*	*1.389*	*1.031*
3-methylfuran	1.370	1.364	1.443	1.362	1.365	1.058
	1.338	*1.435*	*1.396*	*1.393*	*1.367*	*0.987*
furan	1.367	1.363	1.437	1.363	1.367	1.055
	1.351	*1.415*	*1.383*	*1.415*	*1.351*	*0.978*
3-cyanofuran	1.348	1.368	1.442	1.353	1.369	1.060
	1.329	*1.433*	*1.395*	*1.398*	*1.367*	*0.985*
3-nitrofuran	1.347	1.370	1.432	1.358	1.377	1.050
	1.343	*1.415*	*1.378*	*1.419*	*1.353*	*0.972*
3-aminothiophene	1.742	1.376	1.438	1.368	1.733	1.048
	1.691	*1.429*	*1.445*	*1.353*	*1.771*	*1.039*
3-methylthiophene	1.698	1.447	1.400	1.388	1.764	0.987
	1.738	*1.372*	*1.438*	*1.368*	*1.736*	*1.049*
thiophene	1.736	1.370	1.431	1.370	1.736	1.044
	1.734	*1.364*	*1.497*	*1.364*	*1.734*	*1.097*
3-cyanothiophene	1.721	1.380	1.438	1.366	1.737	1.047
	1.695	*1.446*	*1.395*	*1.397*	*1.758*	*0.981*
3-nitrothiophene	1.717	1.374	1.428	1.365	1.742	1.043
	1.727	*1.417*	*1.376*	*1.429*	*1.727*	*0.967*

Appendix Table 8. Optimized values of bond lengths (Å) and the Fn-coefficient for pyrroles, furans, thiophenes and their radical cations (presented in italic) in dichloromethane by using B3LYP/6-31++G (d p).

Molecule	X1-C2	C2-C3	C3-C4	C4-C5	C5-X1	Fn
3-aminopyrrole	1.386	1.385	1.429	1.385	1.368	1.032
	1.338	*1.439*	*1.436*	*1.365*	*1.399*	*1.024*
3-methylpyrrole	1.378	1.384	1.432	1.383	1.374	1.036
	1.343	*1.457*	*1.387*	*1.408*	*1.380*	*0.968*
pyrrole	1.375	1.383	1.428	1.383	1.375	1.033
	1.360	*1.435*	*1.374*	*1.435*	*1.360*	*0.958*
3-cyanopyrrole	1.360	1.393	1.436	1.375	1.379	1.038
	1.345	*1.448*	*1.382*	*1.424*	*1.368*	*0.962*
3-nitropyrrole	1.354	1.391	1.427	1.373	1.385	1.033
	1.356	*1.429*	*1.370*	*1.440*	*1.357*	*0.955*
3-aminofuran	1.381	1.369	1.441	1.363	1.361	1.055
	1.330	*1.429*	*1.437*	*1.352*	*1.391*	*1.033*
3-methylfuran	1.372	1.364	1.443	1.362	1.367	1.059
	1.339	*1.434*	*1.395*	*1.393*	*1.367*	*0.987*
furan	1.368	1.363	1.438	1.363	1.368	1.055
	1.351	*1.414*	*1.383*	*1.414*	*1.351*	*0.978*
3-cyanofuran	1.370	1.385	1.498	1.363	1.482	1.090
	1.350	*1.373*	*1.444*	*1.357*	*1.373*	*1.058*
3-nitrofuran	1.345	1.371	1.433	1.357	1.379	1.051
	1.343	*1.413*	*1.377*	*1.420*	*1.351*	*0.972*
3-aminothiophene	1.743	1.376	1.439	1.368	1.734	1.049
	1.693	*1.427*	*1.446*	*1.353*	*1.770*	*1.040*
3-methylthiophene	1.740	1.372	1.438	1.369	1.737	1.049
	1.699	*1.446*	*1.398*	*1.389*	*1.762*	*0.986*
thiophene	1.737	1.371	1.432	1.371	1.737	1.045
	1.732	*1.362*	*1.494*	*1.362*	*1.732*	*1.096*
3-cyanothiophene	1.720	1.381	1.438	1.366	1.737	1.047
	1.705	*1.440*	*1.388*	*1.409*	*1.742*	*0.974*
3-nitrothiophene	1.714	1.376	1.429	1.365	1.743	1.043
	1.728	*1.414*	*1.376*	*1.431*	*1.720*	*0.968*

Appendix Table 9. Optimized values of bond lengths (Å) and the Fn-coefficient for pyrroles, furans, thiophenes and their radical cations (presented in italic) in acetonitrile by using B3LYP/6-31++G (d p).

Molecule	X1-C2	C2-C3	C3-C4	C4-C5	C5-X1	Fn
3-aminopyrrole	1.385	1.386	1.430	1.386	1.368	1.032
	1.338	*1.439*	*1.436*	*1.365*	*1.399*	*1.024*
3-methylpyrrole	1.378	1.384	1.433	1.383	1.373	1.035
	1.342	*1.457*	*1.386*	*1.408*	*1.380*	*0.968*
pyrrole	1.375	1.384	1.428	1.384	1.375	1.032
	1.360	*1.435*	*1.374*	*1.435*	*1.360*	*0.957*
3-cyanopyrrole	1.359	1.394	1.437	1.375	1.379	1.038
	1.346	*1.447*	*1.382*	*1.427*	*1.366*	*0.961*
3-nitropyrrole	1.352	1.393	1.428	1.373	1.386	1.033
	1.356	*1.429*	*1.371*	*1.441*	*1.356*	*0.955*
3-aminofuran	1.381	1.369	1.441	1.363	1.361	1.055
	1.330	*1.428*	*1.438*	*1.352*	*1.391*	*1.034*
3-methylfuran	1.370	1.364	1.443	1.362	1.365	1.058
	1.339	*1.433*	*1.394*	*1.392*	*1.367*	*0.987*
furan	1.369	1.363	1.438	1.363	1.369	1.055
	1.326	*1.404*	*1.368*	*1.404*	*1.326*	*0.975*
3-cyanofuran	1.349	1.373	1.445	1.357	1.373	1.058
	1.334	*1.427*	*1.390*	*1.406*	*1.359*	*0.981*
3-nitrofuran	1.344	1.371	1.433	1.357	1.379	1.051
	1.342	*1.412*	*1.377*	*1.420*	*1.350*	*0.972*
3-aminothiophene	1.744	1.376	1.439	1.368	1.735	1.049
	1.693	*1.427*	*1.446*	*1.353*	*1.770*	*1.040*
3-methylthiophene	1.740	1.373	1.439	1.369	1.737	1.050
	1.699	*1.446*	*1.398*	*1.389*	*1.761*	*0.986*
thiophene	1.738	1.371	1.432	1.371	1.738	1.045
	1.732	*1.362*	*1.493*	*1.362*	*1.732*	*1.096*
3-cyanothiophene	1.719	1.381	1.439	1.366	1.737	1.047
	1.708	*1.438*	*1.387*	*1.413*	*1.738*	*0.973*
3-nitrothiophene	1.714	1.376	1.429	1.364	1.743	1.043
	1.728	*1.413*	*1.377*	*1.431*	*1.718*	*0.968*

Appendix Table 10. Optimized values of bond lengths (Å) and the Fn-coefficient for pyrroles, furans, thiophenes and their radical cations (presented in italic) in water by using B3LYP/6-31++G (d p).

Molecule	X1-C2	C2-C3	C3-C4	C4-C5	C5-X1	Fn
3-aminopyrrole	1.385	1.386	1.430	1.386	1.368	1.032
	1.338	*1.439*	*1.436*	*1.365*	*1.398*	*1.024*
3-methylpyrrole	1.378	1.385	1.433	1.383	1.373	1.035
	1.342	*1.457*	*1.386*	*1.408*	*1.386*	*0.968*
pyrrole	1.375	1.384	1.429	1.384	1.375	1.032
	1.360	*1.435*	*1.374*	*1.435*	*1.360*	*0.957*
3-cyanopyrrole	1.359	1.394	1.437	1.375	1.379	1.038
	1.346	*1.447*	*1.381*	*1.427*	*1.365*	*0.961*
3-nitropyrrole	1.352	1.393	1.428	1.373	1.385	1.033
	1.355	*1.429*	*1.371*	*1.441*	*1.356*	*0.955*
3-aminofuran	1.382	1.369	1.441	1.363	1.361	1.055
	1.331	*1.428*	*1.438*	*1.352*	*1.391*	*1.034*
3-methylfuran	1.373	1.364	1.444	1.362	1.367	1.059
	1.339	*1.433*	*1.394*	*1.392*	*1.367*	*0.987*
furan	1.369	1.363	1.438	1.363	1.369	1.055
	1.352	*1.413*	*1.386*	*1.413*	*1.352*	*0.981*
3-cyanofuran	1.349	1.373	1.445	1.357	1.373	1.058
	1.33413	*1.427*	*1.390*	*1.406*	*1.359*	*0.981*
3-nitrofuran	1.34401	1.371	1.433	1.357	1.380	1.051
	1.34239	*1.412*	*1.377*	*1.420*	*1.350*	*0.972*
3-aminothiophene	1.74366	1.376	1.439	1.368	1.735	1.049
	1.69366	*1.427*	*1.446*	*1.352*	*1.770*	*1.040*
3-methylthiophene	1.73991	1.373	1.439	1.369	1.738	1.050
	1.69891	*1.446*	*1.398*	*1.389*	*1.761*	*0.986*
thiophene	1.73765	1.371	1.432	1.371	1.738	1.045
	1.73171	*1.362*	*1.493*	*1.362*	*1.732*	*1.096*
3-cyanothiophene	1.71929	1.382	1.439	1.366	1.737	1.047
	1.70850	*1.438*	*1.387*	*1.413*	*1.737*	*0.973*
3-nitrothiophene	1.713	1.376	1.429	1.364	1.743	1.043
	1.728	*1.413*	*1.377*	*1.431*	*1.718*	*0.968*

Appendix Table 11. Contains the energy of HOMO and LUMO for thiophenes, pyrroles, furans and their radical cations (presented in italic) in solvents of varying polarity by using B3LYP/6-31G (d p) level in electron volt unit.

Molecule	Vacuum		Cyclohexane		Dichloromethane		Acetonitrile		Water	
	E_{HOMO}	E_{LUMO}	E_{HOMO}	E_{LUMO}	E_{HOMO}	E_{LUMO}	E_{HOMO}	E_{LUMO}	E_{HOMO}	E_{LUMO}
3-aminopyrrole	-4.7133	1.5127	-4.7982	1.4457	-4.9114	1.3554	-4.9462	1.3282	-4.9533	1.3227
	-11.0053	-8.5752	-8.8244	-6.3357	-7.14005	-4.6524	-6.7768	-4.2891	-6.7109	-4.2235
3-methylpyrrole	-5.3767	1.4441	-5.4361	1.3970	-6.2608	-0.1818	-5.5476	1.3051	-5.5531	1.3007
	-12.3935	-9.6141	-10.1660	-7.3651	-8.4080	-5.6450	-8.0965	-5.2679	-8.0288	-5.1993
pyrrole	-5.5020	1.3464	-5.5672	1.2988	-5.6521	1.2340	-5.6780	1.2142	-5.6831	1.2104
	-13.0991	-10.0947	-10.7135	-7.7148	-8.9037	-5.9120	-8.5072	-5.5087	-8.4378	-5.4491
3-cyanopyrrole	-6.4173	-0.1967	-6.3729	-0.2136	-6.3362	-0.2571	-6.3283	-0.2732	-6.3272	-0.2765
	-13.0822	-10.6003	-10.8737	-8.3159	-9.1785	-6.5155	-8.8013	-6.1114	-8.7325	-6.0374
3-nitropyrrole	-6.6924	-1.8172	-6.6355	-1.9350	-6.5974	-2.0768	-6.5768	-2.1176	-6.5749	-2.1255
	-12.8071	-10.8501	-10.8245	-8.5164	-9.3991	-6.6832	-9.1028	-6.2731	-9.0495	-6.1982
3-aminofuran	-5.2960	0.7625	-5.3381	0.7001	-5.4004	0.6166	-5.4208	0.5910	-5.4241	0.5861
	-12.0158	-9.2729	-9.7178	-6.9645	-7.9773	-5.2113	-7.5983	-4.8284	-8.3618	-6.3090
3-methylfuran	-5.9531	0.6509	-5.9914	0.6054	-6.0475	0.5410	-6.0652	0.5208	-6.0687	0.5167
	-13.2360	-10.3235	-10.9456	-8.0241	-10.9268	-7.9989	-9.7033	-6.7735	-8.7306	-5.7961
furan	-6.122	0.6059	-6.1561	0.4672	-6.2048	0.4131	-6.2200	0.3962	-6.2230	0.3929
	-13.8877	-10.8683	-11.3788	-3.5119	-9.5839	-6.5640	-9.1760	-6.1561	-9.1020	6.0818
3-cyanofuran	-7.0040	-0.9314	-6.9332	-0.9034	-6.8630	-0.8868	-6.8451	-0.8841	-6.8418	-0.8838
	-13.8667	-11.3089	-9.8296	-7.1289	-9.6731	-6.9537	-9.6582	-6.9382	-9.3611	6.6374
3-nitrofuran	-7.2750	-2.3530	-7.1896	-2.4093	-7.1030	-2.4773	-7.0804	-2.4969	-7.0761	-2.5007
	-13.4869	-11.4615	-11.2996	-9.1910	10.9251	-8.7852	10.8534	8.6442	-9.3891	-6.8062
3-aminothiophene	-5.3408	0.0424	-5.3783	-0.0120	-5.4369	-0.0887	-5.4565	-0.1126	-5.4603	-0.1173
	-11.4593	-9.1352	-9.2650	6.9215	-7.6078	-5.2385	-7.2481	-4.8709	-7.1828	-4.8039

Appendix Table 12. Continued…

Molecule	Vacuum		Cyclohexane		Dichloromethane		Acetonitrile		Water	
	E_{HOMO}	E_{LUMO}	E_{HOMO}	E_{LUMO}	E_{HOMO}	E_{LUMO}	E_{HOMO}	E_{LUMO}	E_{HOMO}	E_{LUMO}
3-methylthiophene	-6.1768	-0.0876	-6.2080	-0.1238	-6.2608	-0.1818	-6.2785	-0.2005	-6.2821	-0.2043
	13.3628	-11.9295	-10.4109	-7.9382	-8.7338	-6.2358	-8.7659	-5.8606	-8.2993	-5.7925
thiophene	-6.3501	-0.2283	-6.3754	-0.2559	-6.4208	-0.3034	-6.4365	-0.3192	-6.4396	-0.3224
	-12.814	-11.3505	-10.4808	-9.0078	-8.7058	-7.2198	-8.3186	6.8285	-8.2481	-6.7572
3-cyanothiophene	-7.1000	-1.3845	-7.0366	-1.3290	-6.9735	-1.2860	-6.9575	-1.2773	-6.9545	-1.2757
	-13.2988	-11.0572	-11.0830	-8.8019	-9.3722	-7.0160	-8.9945	-6.6127	-8.9257	-6.5389
3-nitrothiophene	-7.3661	-2.4057	-7.2764	-2.4501	-7.1871	-2.5119	-7.1640	-2.5310	-7.1596	-2.5344
	-12.6994	-11.9054	-11.0310	-8.9978	-9.5586	-7.1710	-9.2481	-6.7591	-9.1923	-6.6837

Appendix Table 13. Contains the energy of HOMO and LUMO for pyrroles, thiophenes, furans and their radical cations (presented in italic) in solvents of varying polarity by using B3LYP/6-31++G (d p) level in electron volt unit.

Molecule	Vacuum		Cyclohexane		Dichloromethane		Acetonitrile		water	
	E_{HOMO}	E_{LUMO}	E_{HOMO}	E_{LUMO}	E_{HOMO}	E_{LUMO}	E_{HOMO}	E_{LUMO}	E_{HOMO}	E_{LUMO}
3-aminopyrrole	-5.1027	-0.2873	-5.1713	-0.2019	-5.2782	-0.1505	-5.3133	-0.1439	-5.3204	-0.1431
	-11.2275	*-8.7673*	*-8.9891*	*-6.5327*	*-7.3068*	*-4.8537*	*-6.9441*	*-4.4915*	*-6.8783*	*-4.4260*
3-methylpyrrole	-5.7229	-0.2982	-5.7653	-0.1899	-5.8415	-0.1292	-5.8665	-0.1254	-5.8717	-0.1252
	-12.4909	*-9.7450*	*-10.2642*	*-7.5001*	*-8.5662*	*-5.7830*	*-8.1942*	*-5.4067*	*8.1267*	*-5.3381*
pyrrole	-5.8801	-0.3505	-5.9267	-0.2229	-6.0007	-0.1211	-6.0252	-0.1031	-6.0301	-0.1001
	-13.1903	*-10.2256*	*-10.8073*	*-7.8519*	*-8.9991*	*-6.0540*	*-8.8585*	*-6.3735*	*-8.5338*	*5.5922*
3-cyanopyrrole	-6.7523	-0.7616	-6.6864	-0.6596	-6.6325	-0.6920	-6.6208	-0.7067	-6.6187	-0.7099
	-13.2158	*-107.442*	*-11.0131*	*-8.4598*	*-9.3167*	*-6.6549*	*-8.9371*	*-6.2486*	*-8.8674*	*-6.1743*
3-nitropyrrole	-7.0535	-2.3968	-6.9768	-2.5184	-6.9139	-2.6754	-6.9000	-2.7222	-6.9139	-2.6754
	-13.0743	*-11.0201*	*-11.1230*	*-8.6835*	*-9.7034*	*-6.8462*	*-9.2911*	*-6.4353*	*-9.2152*	*-6.3599*
3-aminofuran	-5.6556	-0.3937	-5.6834	-0.2748	-5.7400	-0.1649	-5.7596	-0.1396	-5.7637	-0.1350
	-12.1589	*-9.4405*	*-9.8647*	*-7.1373*	*-8.1273*	*-5.3876*	*-7.4990*	*-5.0056*	*-7.6807*	*-4.9362*
3-methylfuran	-6.2671	-0.1682	-6.2913	-0.1222	-6.3392	-0.0887	-6.3555	-0.0827	-6.3588	-0.0819
	-13.3184	*-10.4335*	*-11.0316*	*-8.1387*	*-9.2751*	*-6.3743*	*-8.8892*	*-5.9857*	*-8.8182*	*-5.9147*
furan	-6.4603	-0.1053	-6.4780	-0.1273	-6.5169	-0.1698	-6.5302	-0.1845	-6.5329	-0.1875
	-13.9650	*-10.9755*	*-11.5268*	*-8.5395*	*-9.6672*	*-6.6810*	*-9.4120*	*-6.4259*	*-9.1861*	*-6.2002*
3-cyanofuran	-7.3128	-1.3587	-7.2932	-1.3573	-7.225	-1.332	-7.1147	-1.2762	-7.1107	-1.2754
	-13.6963	*11.2225*	*-11.7165*	*-9.1004*	*-9.9507*	*-7.2527*	*-9.5548*	*-6.8353*	*-9.4821*	*-6.7585*
3-nitrofuran	-7.6124	-2.8972	-7.5066	-2.9549	-7.4026	-3.0333	-7.3754	-3.0569	-7.3703	-3.0618
	-13.6961	*-11.6411*	*-11.5793*	*-9.3406*	*-10.0843*	*-7.4524*	*-9.7706*	*-7.0266*	*-9.7140*	*-6.9485*

Appendix Table 14. Continued

Molecule	Vacuum		Cyclohexane		Dichloromethane		Acetonitrile		water	
	E_{HOMO}	E_{LUMO}	E_{HOMO}	E_{LUMO}	E_{HOMO}	E_{LUMO}	E_{HOMO}	E_{LUMO}	E_{HOMO}	E_{LUMO}
3-aminothiophene	-5.6369	-0.4381	-5.6630	-0.4544	-5.7174	-0.5148	-5.7378	-0.5358	-5.7419	-0.5399
	-11.5698	*-9.2552*	*-7.7213*	*-5.3939*	*-7.7213*	*-5.3939*	*-7.3613*	*-5.0268*	*-7.2960*	*-4.9601*
3-methylthiophene	-6.7025	-0.4391	-6.4448	-0.5222	-6.4861	-0.5671	-6.5017	-0.5831	-6.5049	-0.5864
	-12.6531	*-10.5232*	*-10.4775*	*-8.0383*	*-8.8010*	*-6.3384*	*-8.4331*	*-5.9637*	*-8.3662*	*-5.8954*
thiophene	-6.6249	-0.6634	-6.6331	-0.6721	-6.6666	-0.7059	-6.6799	-0.7189	-6.6826	-0.7216
	-12.8983	*-11.4389*	*-10.5695*	*-9.1001*	*-8.7986*	*-7.3145*	*-8.4122*	*-6.9237*	*-8.3420*	*-6.8527*
3-cyanothiophene	-7.3634	-1.7336	-7.2807	-1.6613	-7.2005	-1.6071	-7.1803	-1.5962	-7.1762	-1.5943
	-13.5961	*-11.324*	*-11.1889*	*-8.9161*	*-9.4838*	*-7.1270*	*-9.1074*	*-6.7215*	*-9.0386*	*-6.6470*
3-nitrothiophene	-7.6513	-2.8899	-7.5414	-2.9416	-7.4339	-3.0213	-7.4064	-3.0469	-7.4013	-3.0518
	13.6952	*-11.5324*	*-11.2963*	*-9.1325*	*-9.8617*	*-7.3008*	*-9.5619*	*-6.8870*	*-9.5083*	*-6.8111*