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DFT studies of all fluorothiophenes and their radical cations as candidate monomers for conductive polymers

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Abstract

In this paper, electronic, structural, and spectroscopic properties of mono-, di-, tri-, and tetrafluorothiophenes and their radical cations are studied using the density functional theory and B3LYP method with 6-311++G** basis set. Also the effects of the number and position of the substituent on the electrochemical properties of the thiophene ring have been studied using optimized structures obtained for these molecules and their cations, vibrational frequencies and nuclear chemical shielding constants of these compounds have been calculated and analyzed. The results of this study including charge and spin-density distribution, size and direction of the dipole moment vector, ionization potential, electric polarizability and NICS show that among all of these compounds 3-fluorothiophene as candidate monomer for new conductive polymers, possesses the most suitable conditions for electropolymerization.

Keywords: DFT-B3LYP; Dipole moment; Fluorothiophenes; Conductive polymers.

1. Introduction

Electrically-conductive polymers such as advanced materials and the new class of '*synthetic metals'* have drawn high attention in the last years [1]. The 2000 Nobel Prize in Chemistry recognized the discovery of conducting polymers and over 25 years of progress in this field [2, 3]. There has been growing interest in research on conducting polymer nanostructures (nano-rods, -tubes, -wires, and -fibers) since they incorporate the advantages of organic conductors with low-dimensional systems and so create interesting physicochemical properties and potentially useful applications [4–7].The variety of such studies have been reported in the literature that and these include: surfactants [8–11], liquid crystals [12], polyelectrolytes [13], nanowire seeds [14], thiophene oligomers [15-21]. Among intrinsic conducting polymers with conjugated double bonds, polythiophenes (PTHs) and related derivatives are suitable for commercial applications [22].

Polythiophenes are normally produced from non aqueous media because the monomer is more soluble in theme. The influence of water on polymerization process of thiophene as well as the redox switching properties has been studied here [23, 24]. The presence of water as low as 1% causes mislinkages and a subsequent deterioration in polymer properties [24]. We have recently shown that the attachment of a range of electron-donating or electron-withdrawing

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groups through a conjugated linker has a dramatic effect on polymerization potential and subsequent photovoltaic performance [25, 26]. Polythiophene has a solubility of 75 (w/w)% in chloroform and a conductivity of 220 S cm^{-1} [22].

The effect of temperature on polymerization process of thiophene has been investigated as well [27]. Results show that when polymerization is carried out at 15–20 °C, polymers with optimal properties are obtained. Ultrasonication has been used to improve the efficiency (improved yield, lowering of polymerization potentials) of electropolymerization process of polythiophene [28].

Thiophene is oxidized to form a conducting electroactive polymer (CEP), with the greatest conductivity obtained from α-α' (C_2-C_5) linkages [22]. As in polythiophenes, the mechanism of polymerization involves formation of radical cations that react with one another or the starting monomer to develop the polymeric structure (Fig. 1).

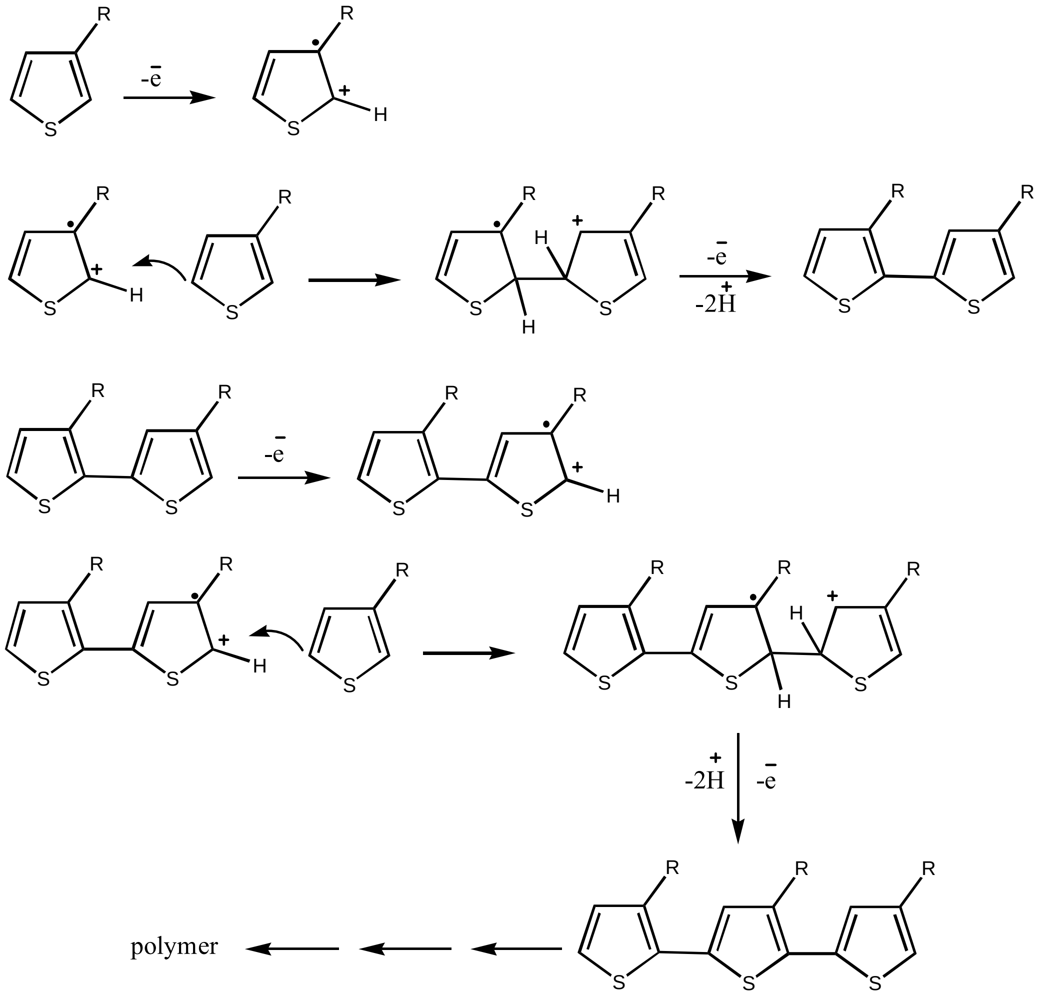
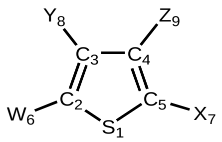


Fig. 1. Polymerization of thiophene (where R = H or a substituent) [32].

Theoretical studies indicate that neutral polythiophene has a nondegenerate ground state, with mesomeric aromatic and quinoidal structures of nonequivalent energy [29]. Oxidative doping leads to the formation of two bands in the band gap corresponding to a polaron (radical cation). However, both calculations and measurements of UV-visible spectra during increasing doping suggest that the polarons are unstable when compared with spinless bipolarons (dictions) [30-31].

The aim of the present research is study the electronic and structural properties of all fluorothiophene monomers (shown in Fig. 2) and their singly ionized cations, using DFT-B3LYP methods.



T: W=X=Y=Z=H	thiophene
A: W=F, X=Y=Z=H	2-fluorothiophene
B: Y=F, W=X=Z=H	3-fluorothiophene
C: W=Y=F, X=Z=H	2,3-difluorothiophene
D: W=Z=F, X=Y=H	2,4-difluorothiophene
E: W=X=F, Y=Z=H	2,5-difluorothiophene
F: Y=Z=F, W=X=H	3,4-difluorothiophene
G: W=Y=Z=F, X=H	2,3,4-trifluorothiophene
H: W=X=Y=F, Z=H	2,3,5-trifluorothiophene
I: W=X=Y=Z=F	2,3,4,5-tetrafluorothiophene

Fig. 2. All possible mono-, di-, tri-, and tetrafluorothiophene isomers.

The electropolymerization of monomers (conductivity and solubility) are related to the stability of their radicals cations, which itself is closely dependant on the type and configuration of the substituent on the thiophene ring. Vibrational frequencies with analyses of their IR intensities and NMR shielding constants can also be used to characterize and predict molecular and spectroscopic properties.

2. Computational procedures

Initially, structures of representative mono-, di-, tri-, and tetra-fluorothiophenes were fully optimized using B3LYP/6-311++G** method [33-36]. The geometries are optimized using standard gradient techniques with default parameters set in G98W. Atomic charges are calculated using NBO method [37-39]. Dipole moments and polarizability are calculated for all neutral species. Vibrational frequencies with their IR intensities are calculated with a scale factor of 0.8929. These vibrational analyses showed that all structures were fully optimized.

3. Results and discussion

3.1. Structural analysis of fluorothiophenes

In this section, the electronic and structural properties of fluorothiophenes and their related radicals cation have been studied. Because of the stabilizing effects of the delocalization of sulfure nonbonding p electrons participating in the π-conjugation system of the thiophene ring, it is expected that the favored structure corresponds to a thiophene ring molecular plane.

In agreement with this expectation, results of the present calculations show that all fluorothiophenes have planar structures (the optimized values of all dihedral angles in all of the species studied in this research are either 0 or 180°). The optimized structural parameters obtained at B3LYP/6-311++G** level of theory for all fluorothiophenes and their cations are listed in Tables 1 and 2.

To predict the bonding-characteristic behavior of fluorothiophene rings in their corresponding polymer chains and to determine the extent of the π-conjugation character of these polymers, we have used the *Fn* coefficient defined in equation 1 for each thiophene ring in isolated fluorothiophenes and in the tetramer of 3-fluorothiophene, (Fig. 3).

$$\mathbf{Fn} = \frac{\mathbf{2R34}}{\mathbf{R23+R45}} \qquad \mathbf{(1)}$$

where R34 is the length of C_3-C_4 bond (formally double bond) in the thiophene ring at form radical cation, and [(R23 + R45)/2] is the average length of C_2-C_3 and C_4-C_5 bonds (formally single bonds) at form radical cation. The value of the *Fn* coefficient gives a measure of relative importance of aromatic character with respect to quinoid character [40].

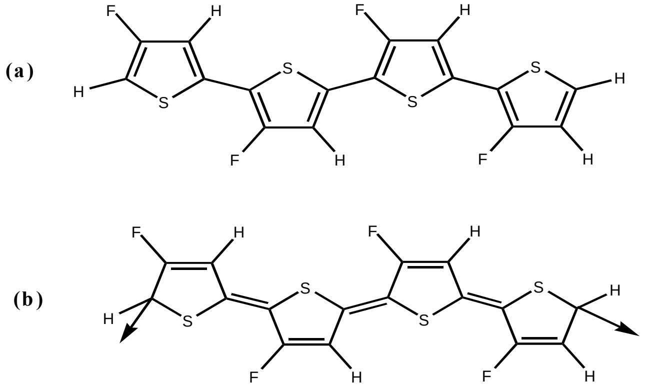


Fig. 3. **(a)** Molecular structure of tetra(3-fuorothiophene), the B tetramer, and **(b)** quinoid structure of the propagating radical cation polymer chain [22].

The calculated values of the *Fn* coefficient for all fluorothiophenes and their cations are listed in Table 1. As shown in this table, molecule **B** and their cation have the smallest values of the *Fn* coefficient. Therefore, it can be suggested that the quinoid character of monomer **B** is greater than that of other fluorothiophenes.

Table 1
B3LYP/6-311++G** optimized values of bond lengths (Å) and the *Fn c*oefficient for thiophene and fluorothiophenes.

Molecule	S1-C2	S1-C5	C2-C3	C3-C4	C4-C5	Fn
Thiophene	1.733	1.733	1.366	1.428	1.366	1.045
	1.728	*1.728*	*1.422*	*1.376*	*1.421*	*0.968*
A	1.739	1.743	1.357	1.431	1.363	1.052
	1.755	*1.722*	*1.413*	*1.377*	*1.420*	*0.972*
B	1.733	1.733	1.361	1.421	1.365	1.042
	1.681	*1.785*	*1.438*	*1.379*	*1.416*	*0.966*
C	1.739	1.741	1.359	1.423	1.362	1.046
	1.725	*1.754*	*1.439*	*1.383*	*1.392*	*0.977*
D	1.738	1.745	1.356	1.426	1.357	1.051
	1.782	*1.700*	*1.385*	*1.386*	*1.431*	*0.984*
E	1.751	1.751	1.351	1.438	1.351	1.064
	1.750	*1.750*	*1.410*	*1.379*	*1.410*	*0.978*
F	1.734	1.734	1.358	1.424	1.358	1.049
	1.733	*1.734*	*1.413*	*1.387*	*1.412*	*0.982*
G	1.738	1.744	1.358	1.427	1.355	1.052
	1.754	*1.728*	*1.415*	*1.386*	*1.411*	*0.981*
H	1.753	1.747	1.354	1.431	1.352	1.058
	1.734	*1.768*	*1.430*	*1.383*	*1.390*	*0.981*
I	1.750	1.751	1.353	1.435	1.353	1.061
	1.752	*1.752*	*1.413*	*1.388*	*1.413*	*0.982*

Corresponding values for the related cations are given in the lower row with italic fonts. See Fig. 2 for definitions of bond lengths and angles.

This shows that double bonds in this molecule are more delocalized. Consequently, quinoid structures, as in Fig. 2, involved in polymer chain growth are more probable for this monomer. This means that, compared with other fluorothiophenes, the said monomer has a higher capacity for electropolymerization as well as higher electric conductance.

3.2. Charge- and spin-distribution analysis

Natural Bond Orbital charges in this series of fluorothiophenes and their cations has been calculated and reported in Table 3. In addition, the spin-density distribution over the ring atoms of the fluorothiophene radical cations have been calculated and presented in Table 4. The analysis of these data, shows that the for all fluorothiophene radical cations, the positive charge is distributed manly on the positions $\mathbf{C_2}$ in Fig. 2.

It confirmed this not that propagation of the polymer chain through the $\mathbf{C_2}$ carbon (are given in the literature) is the favored choice. The more value of negative charge on the $\mathbf{C_2}$ positions for monomer **B** ratio on the thiophene shows that the rate of polymerization for 3-fluorothiophene is greater than thiophene. Also as shown in Table 4, it is obvious that the monomer **B** have the minimal spin density on the $\mathbf{C_2}$ positions among all of fluorothiophene cation radicals. This means that the electropolymerization rate of 3-fluorothiophene (monomer **B)** is greater than thiophene and other fluorothiophenes.

Table 2

B3LYP/6-311++G** optimized values of bond angles for thiophene and fluorothiophenes.

Molecule	C2-S1-C5	S1-C2-W	S1-C5-X	S1-C2-C3	S1-C5-C4	C3-C4-C5	C2-C3-Y	C5-C4-Z
Thiophene	118.4	120.8	120.8	119.5	119.5	118.7	120.6	120.6
	120.1	*120.0*	*120.0*	*119.5*	*119.5*	*120.8*	*119.6*	*119.6*
A	116.6	123.2	120.3	118.9	116.9	119.2	120.1	120.8
	118.4	*122.6*	*119.1*	*119.1*	*116.2*	*121.4*	*119.2*	*119.4*
B	118.7	120.9	120.4	119.6	121.5	117.0	120.5	122.6
	120.5	*119.3*	*120.2*	*119.3*	*121.6*	*119.4*	*118.9*	*121.6*
C	118.3	120.9	120.8	119.7	119.7	121.4	119.3	119.3
	119.9	*120.0*	*120.0*	*119.6*	*119.6*	*122.9*	*118.5*	*118.5*
D	117.3	123.1	119.6	119.3	118.4	117.9	119.6	122.6
	119.2	*122.1*	*118.8*	*119.1*	*117.9*	*120.4*	*118.3*	*121.3*
E	116.4	123.2	120.3	119.1	117.2	121.7	118.7	119.6
	118.3	*122.5*	*119.2*	*119.2*	*116.4*	*123.3*	*118.4*	*118.3*
F	116.9	122.9	120.3	120.9	116.9	117.4	122.0	120.6
	118.6	*122.9*	*118.6*	*121.3*	*116.3*	*119.8*	*121.4*	*118.8*
G	115.0	122.5	122.5	116.4	116.4	119.8	120.1	120.1
	117.1	*121.4*	*121.4*	*115.8*	*115.8*	*122.3*	*118.9*	*118.9*
H	118.5	120.9	120.5	119.8	121.5	119.3	119.9	120.8
	120.3	*119.5*	*120.2*	*119.4*	*121.5*	*121.2*	*118.4*	*120.4*
I	119.1	120.4	120.4	121.6	121.6	115.5	122.2	122.2
	121	*119.5*	*119.5*	*121.4*	*121.4*	*118.3*	*120.9*	*120.9*

Corresponding values for the related cations are given in the lower row with italic fonts. See Fig. 2 for definitions of bond lengths and angles.

Charge- and spin-density distributions have similar trends with the number and position of the substituted fluorine atoms. On the basis of the results obtained in this study, one can conclude that among of all fluorothiophenes, 3-fluorothiophene can be electropolymerized much easier under suitable conditions [41].

Table 3
Charge distribution on sulfur and carbon atoms in the B3LYP/6-311++G** optimized structures of thiophene and fluorothiophenes (and their radical cations).

Molecule	δS_1	δC_2	δC_3	δC_4	δC_5
Thiophene	0.447	-0.550	-0.011	-0.191	-0.140
	(0.559)	(-0.133)	(-0.174)	(-0.174)	(-0.133)
A	0.384	0.237	-0.333	-0.239	-0.393
	(0.537)	(0.428)	(-0.230)	(-0.155)	(-0.166)
B	0.436	-0.467	0.360	-0.305	-0.376
	(0.619)	(-0.271)	(0.524)	(-0.315)	(-0.150)
C	0.403	0.166	0.289	-0.289	-0.378
	(0.546)	(0.357)	(0.437)	(-0.281)	(-0.156)
D	0.402	0.252	-0.378	0.376	-0.468
	(0.571)	(0.431)	(-0.346)	(0.494)	(-0.253)
E	0.352	0.239	-0.318	-0.318	0.239
	(0.503)	(0.410)	(-0.213)	(-0.213)	(0.410)
F	0.452	-0.452	0.315	0.315	-0.452
	(0.580)	(-0.183)	(0.364)	(0.365)	(-0.183)
G	0.418	0.179	0.244	0.329	-0.456
	(0.558)	(0.379)	(0.320)	(0.377)	(-0.217)
H	0.370	0.166	0.303	0.364-	0.251
	(0.518)	(0.347)	(0.431)	(-0.321)	(0.417)
I	0.383	0.177	0.257	0.257	0.177
	(0.524)	(0.360)	(0.332)	(0.332)	(0.360)

Table 4
Distribution of spin density over sulfur and carbon atoms in the B3LYP/6-311++G** optimized structures of thiophene and fluorothiophene radical cations.

Molecule	S_1	C_2	C_3	C_4	C_5
Thiophene	0.131-	0.547	0.046	0.046	0.548
A	-0.099	0.432	0.052	0.068	0.515
B	0.030	0.395	0.293	-0.170	0.428
C	-0.094	0.423	0.193	-0.101	0.489
D	-0.007	0.396	-0.090	0.176	0.484
E	-0.099	0.416	0.078	0.078	0.416
F	-0.105	0.554	0.004	0.001	0.554
G	-0.083	0.429	0.026	0.008	0.538
H	-0.074	0.432	0.148	-0.041	0.382
I	-0.088	0.426	0.034	0.033	0.426

3.3. Electric dipole moments

Orientations of the polymer chains in the condensed phase are the most important parameters affecting the electric charge transport properties of polymers, so that the electrical conductivity of a polymer chain is altered when its orientation and consequently its symmetry and non isotropic interactions are changed [40, 41].

Chemically synthesized PTHs powders exhibit a partially crystalline structure in which the chains align and pack in a herringbone arrangement (Fig. 4) in the crystalline regions [42]. These overall interactions can be well expressed in terms of interactions between local dipole moments of monomers. The local alignment of monomers' dipole moments in solution with respect to the orientation of the polymer chain determines the electrochemical properties of the polymer formed on electrode surface. In addition, the orientation of monomer in the double layer of the solution in an electropolymerization cell depends on both size and direction of the dipole moment vectors of both monomers and polymer chain [40].

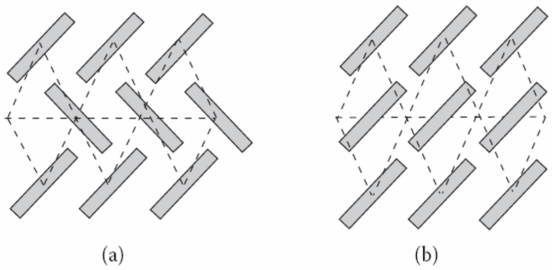


Fig. 4. Illustration of stacking arrangements proposed for polythiophene (PTH). Oriented chains extend into and out of the page: (a) herringbone stacking arrangement, (b) lamellar stacking arrangement.

It is, therefore, necessary to study the dipole moments of these fluorothiophenes to be able to predict their electropolymerization properties. The size of the dipole moment vector and its components calculated for fluorothiophenes in this study are presented in Table 5. Analysis of calculated dipole moments shows that the size and direction of the dipole moment vector depend mainly on the position (symmetry) of substituents. Furthermore, the orientation of the dipole moment vector is toward the sulfur atom for all fluorothiophenes. It can also be seen from Table 5 that the size of the dipole moment vector for monomer **B** is greater than thiophene. It can then be concluded that the solubility of 3-fluorothiophene in polar solvents is higher than thiophene.

Table 5

Electric dipole moments, polarizability tensor elements, and ionization potentials calculated at the B3LYP/6-311++G** level of theory for the optimized structures of thiophene and fluorothiophenes.

Molecule	Electric dipole moment (D)			Polarizabilities (Å)				Ionization potentio (ev)
	μ_x	μ_y	μ_{tot}	α_{xx}	α_{yy}	α_{zz}	α_{xy}	IP
Thiophene	0.0000	-0.5169	0.5169	67.093	73.851	41.017	0.012	8.75
A	0.9839	-1.4169	1.7250	73.793	68.155	39.942	0.938	8.67
B	0.5027	-1.3471	1.4379	68.469	72.277	39.803	2.962	8.87
C	-1.4527	-2.1682	2.6098	73.132	68.886	38.996	-1.857	8.82
D	-0.6594	-0.2523	0.7061	73.350	68.554	38.836	-1.605	8.84
E	-0.0002	-1.1812	1.1812	69.054	73.074	38.836	-0.029	8.64
F	-1.7507	-1.5012	2.3062	71.527	70.283	38.866	4.207	9.21
G	0.3141	-2.3909	2.4115	70.207	73.147	38.115	3.112	9.10
H	-0.4070	-0.9900	1.0704	73.656	69.145	37.989	-0.333	8.79
I	1.0104	-1.1765	1.5508	71.963	72.814	37.476	-2.669	9.03

$\boldsymbol{\mu_z}$, $\boldsymbol{\alpha_{xz}}$, and $\boldsymbol{\alpha_{yz}}$ are essentially zero for all compounds because of the planar structure. The nonzero values of $\boldsymbol{\alpha_{xz}}$ and $\boldsymbol{\alpha_{yz}}$ obtained for symmetric compounds and the negative values of $\boldsymbol{\alpha_{xz}}$ are due to computational errors.

3.4. Ionization potentials

The ionization potential energies calculated for the optimized structures of fluorothiophenes are listed in Table 5. Because ionization potential energies are directly proportional to the electrochemical oxidation potentials of the compounds, it can be said that the electrochemical stability of monomer **B** is greater than thiophene and all their related isomers.

3.5. Electric polarizabilities

Values of exact electrical polarizabilities for B3LYP/6-311++G** optimized structures of all fluorothiophenes have been calculated and listed in Table 5. Static and dynamic multipole polarizabilities of halogencontaining compounds are important properties needed for modeling of solvent effects on their reactions in solution.

These values are also used to interpret light scattering and intensities of vibrational Raman spectra of such compounds [40, 43].

The zero values obtained for polarizabilities α_{xz}, and α_{yz} are consequences of the planar structure, whereas small values of α_{xy} polarizabilities indicate that the delocalization strength of the π system of the ring dominates the anisotropic effects of substituents for asymmetric fluorothiophenes. Values of the α_{xy} polarizabilities for symmetric (C_{2V}) fluorothiophenes; **E**, **F** and **I** should essentially be zero.

3.6. Vibrational spectra

The vibrational frequencies for all fluorothiophenes were calculated using optimized structures at B3LYP/6-311++G** level of theory. These vibrational analyses showed that all structures all fully optimized.

Calculated IR absorption frequencies and intensities for all fluorothiophenes are presented in Table 6. To facilitate the comparison the frequencies are divided into low-frequency (below 1000 cm^{-1}) and high-frequency groups (above 1000 cm^{-1}) to facilitate the comparison. According to analysis of frequencies listed in Table 6, it can be suggested that compound **B** has higher low-frequency values among all fluorothiophenes. This means that the compound has the largest force constants for their bending modes of vibration [41].

Higher values of low frequencies obtained for **B** can be regarded as higher protection from thermal decomposition for **B** compound compared with that of other fluorothiophenes. Furthermore, this indicates that the relative thermal stabilities of these molecules are higher than those of their corresponding isomers. In terms of the Zero-Point Energy (ZPE), it can be said that the ZPE for molecule **B** (that is 36.62077 kcal mol^{-1}) is greater than others molecules.

Displacements of C_5 and H_7 atoms (in Fig. 2) for vibration with the highest intensity in the IR spectrum of fluorothiophenes have been compared in Table 7. It can be seen that the displacement of C_5 atom for compound **B** is greater than thiophene and other isomers. It is important to note that the displacements are given on the basis of respective standard Cartesian coordinates of molecules, which may be evidently different from each other. The displacement of H_7 atom for **B** is only greater than **C**. Furthermore, the force constant for C_5-H_7 bond in molecules **B**, must be greater than that for their corresponding isomers due to their higher relative stabilities.

On the basis of the vibrational analysis carried out in this study, it can be predicted that electropolymerization of fluorothiophenes can be enhanced, or even controlled, by use of appropriate selective IR radiation.

Table 6
B3LYP/6-311++G** calculated IR transition wave numbers in cm^{-1} (intensities in km/mol) for thiophene and fluorothiophenes.

Molecule	Low – frequency range	High – frequency range
Thiophene	456(0.67) 572(0.0) 613(0.37) 690(0.0) 720(143) 744(0.41) 834(26.9) 877(1.63) 885(0.30) 919(0.0)	1051(3.15) 1105(4.45) 1106(0.0) 1275(***11.37***) 1393(0.71) 1443(11.2) 1551(0.24) 3196(3.85) 3210(3.7) 3243(0.04) 3246(1.20)
A	264(0.02) 362(0.75) 474(1.74) 544(7.78) 548(2.49) 685(85.23) 708(13.35) 729(2.85) 819(19.61) 846(17.82) 899(0.17)	1045(6.17) 1109(10.89) 1197(***130***) 1251(4.86) 1383(2.57) 1492(83) 1599(75) 3205(3.59) 3228(0.42) 3250(0.68)
B	270 (0.03) 395(1.41) 460(0.07) 542(6.82) 616(18.9) 656(2.43) 662(8.96) 774(99.18) 827(4.00) 860(15.41) 875(0.06) 967(38.7)	1090(9.56) 1167(33.05) 1245(29.6) 1429(78.7) 1457(1.52) 1590(***92***) 3221(0.05) 3250(0.66) 3262(5.12)
C	211(0.05) 268(1.23) 289(0.14) 415(0.11) 476(0.42) 516(4.00) 589(25.33) 634(7.84) 702(42.4) 725(20.3) 827(5.82) 860(2.94)	1010(102) 1110(21.98) 1212(76) 1257(45) 1422(44) 1500(57) 1659(***135***) 3221(0.12) 3254(2.07)
D	227(0.39) 289(0.37) 310(2.2) 430(0.07) 467(0.02) 534(10.4) 555(6.3) 610(17.5) 706(32.5) 729(13) 807(43) 847(15.2) 981(39) TABLE 6: B3LYP/6-311++G** Calculated IR Transition Wave	1132(117.8) 1177(0.77) 1213(95) 1426(96.96) 1531(57.77) 1624(***178***) 3242(2.8) 3267(7.6)
E	176(0.65) 394(1.09) 320(0.0) 410(1.22) 487(4.86) 497(10.49) 515(0.0) 675(12.3) 715(11.42) 716(25.5) 785(66.5) 849(0.0)	1029(7.83) 1184(4.62) 1204(***316***) 1230(50.64) 1352(9.84) 1571(68) 1631(115) 32231(1.99) 3234(1.73)
F	225(0.0) 268(0.13) 306(0.29) 448(0.18) 473(0.74)543(3.5) 601(5.3) 614(0.0) 705(0.0) 783(90) 803(23) 851(61) 870(1.16)	1138(48) 1193(43) 1200(42) 1455(54) 1529(***233***) 1619(13.8) 3262(8) 3265(5.7)
G	163(0.19) 255(0.28) 275(0.71) 290(1.5) 298(0.0) 465(0.85) 477(1.62) 507(2.3) 551(3.3) 653(3.9) 688(11.22) 705(41) 851(23) 965(94)	1131(169) 1182(32.4) 1260(15.2) 1469(***174***) 1568(113) 1677(104) 3268(11)
H	173(0.87) 232(0.54) 269(1.32) 285(0.0) 304(1.75) 449(1.6) 489(5.3) 496(7) 545(2.6) 602(1.17) 718(12.2) 736(25.7) 798(35.6)	1026(136) 1152(67) 1187(6.9) 1243(***274***) 1414(42) 1590(45) 1682(181) 3240(4.5)
I	159(0.0) 172(1.5) 245(0.0) 250(0.05) 274(2.2) 290(1.1) 291(0.06) 484(4.6) 488(1.2) 513(1.7) 532(1.12) 580(1.5) 630(0.0) 862(17)	1019(168) 1088(***268***) 1181(4.3) 1298(96.3) 1464(164) 1653(26) 1707(168)

Some specific vibrational modes may not be active in IR for certain compounds because of the selection rules arising from symmetrical characteristics

3.7. NMR chemical shifts

In this study, ^{1}H and ^{13}C chemical shieldings has been calculated for DFT-B3LYP/6-311++G** optimized geometries of all fluorothiophenes. The isotropic and anisotropic magnetic shieldings for these two nuclei have been calculated using GIAO and CSGT methods. The isotropic and anisotropic chemical shielding constants are defined as $\sigma iso = (\sigma_{xx} + \sigma_{yy} + \sigma_{zz})/3$ and $\Delta\sigma = \sigma_{zz} - (\sigma_{xx} + \sigma_{yy})/2$, respectively. The ^{1}H and ^{13}C chemical shieldings for TMS have also been calculated as references. On a comparative basis, relative shielding constant $\Delta\sigma_{X}$ (chemical shift δ_{X}) is defined as

$$\delta_{X} = \Delta\sigma_{X} = \sigma_{X}(\text{reference}) - \sigma_{X}\ (\text{fluorothiophene}) \qquad \textbf{(2)}$$

where δ_{X}(fluorothiophene) and δ_{X}(reference) are isotropic chemical shielding constants, δ_{iso}, of nucleus X in the fluorothiophene and in the reference molecules, respectively [40,41]. Values of relative shielding constants, $\Delta\delta_X$, or chemical shifts, δ_X, for different carbon nuclei in thiophene **T** and fluorothiophenes **A-I** are calculated and presented in Fig. 5.

Table 7
Analysis of C_5-H_7 displacement (in Å) for the most intense vibrational mode of Fluorothiophenes in the IR spectrum.

	C_5			H_7		
Molecule	Δx	Δy	Δr	Δx	Δy	Δr
Thiophene	-0.04	0.11	0.117	0.11	-0.42	0.434
A	0.06	0.06	0.085	0.24	0.03	0.242
B	0.05	0.23	0.235	-0.20	0.03	0.202
C	0.16	-0.02	0.161	0.05	0.11	0.121
D	-0.30	-0.01	0.300	0.06	-0.27	0.277
F	0.47	0.02	0.470	0.09	0.46	0.469
G	-0.11	0.10	0.149	0.14	0.37	0.396

Z displacements for C_5 and H_7 are zero for all compounds. The values of Δr have been calculated using the $(\Delta r)^2 = (\Delta x)^2 + (\Delta y)^2 + (\Delta z)^2$ relation.

It can be seen from Fig. 5-a that compound **B** has the highest magnetic shielding in position **C_2**, the same compound that has the higher capacity for electropolymerization (section 3.3). Figure 5-b shows changes in the values of chemical shifts for the hydrogen nucleus on the X position (X-^{1}H) of the fluorothiophenes (Fig. 2). As this Figure clearly shows, the highest values of the ^{1}H NMR chemical shift belong to the X-hydrogen nuclei of compounds **B**.

In addition, as the number of substituted fluorine atoms on the sulfur ring increases, NMR chemical shifts of all nuclei decrease. These NMR data can be used to probe the electropolymerization or chemical polymerization experimentally based on one or two characteristic nuclei.

3.8. Nuclear Independent Chemical Shift (NICS) Analysis

Nuclear Independent Chemical Shift (NICS) at GIAO/B3LYP/6-311++G** and Magnetic susceptibilities at CSGT/B3LYP/6-311++G** level of theory in rings center, 0.5 and 1 angstrom upper than polymer rings center were calculate for Fluorothiophenes (see Table 8). Negative NICS values represent magnetic shielding, electronic current and aromaticity in cyclic compounds. NICS results showed that compound **B** had the largest quantity of negative value in center of thiophene ring, therefore this compound has the largest electrical current and conductivity in center of thiophene ring, between thiophene and their corresponding isomers. Also, magnetic susceptibilities at CSGT/B3LYP/6-311++G** for thiophene and fluorothiophenes have been compared in Table 8.

3.9. Electronic properties

Energy gap between the highest occupied and the lowest unoccupied molecular orbital (HOMO and LUMO, respectively) known as the HOMO–LUMO gap or simply HLG, is a critical parameter determining molecular electrical transport properties [43] and electricadmittance (being charged under applied electric filed) because it is a measure of the electron density hardness [44]. A reasonable estimate of HLG values can be obtained from both HF and DFT calculations [45, 46].

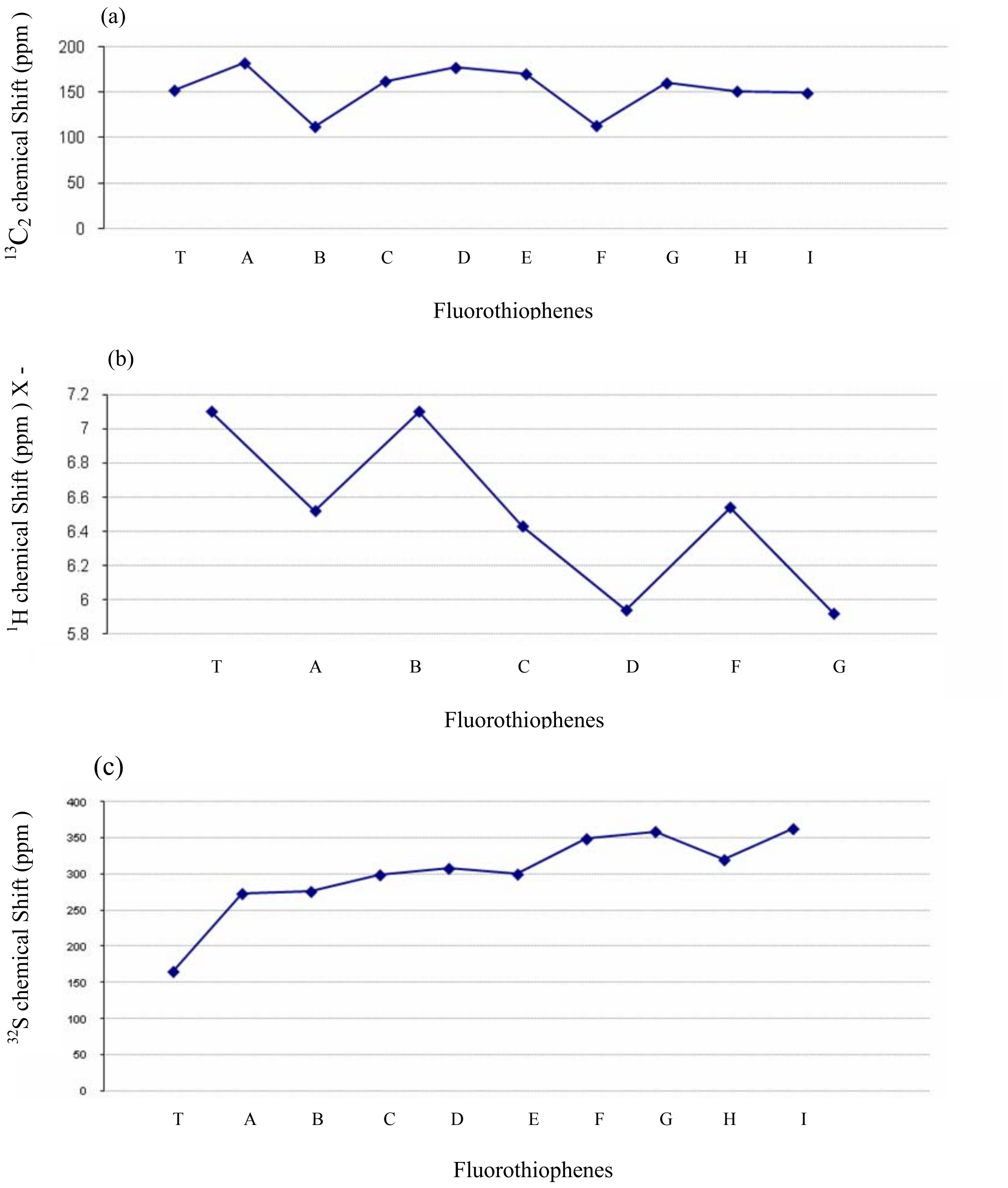


Fig. 5. GIAO calculated values of the chemical shifts for thiophen and fluorothiophenes (Fig. 2) based on B3LYP/6-311++G** optimized structure: (**a**) For ^{13}C chemical shifts of carbon atom at position C_2 (referenced to TMS), (**b**) For ^{1}H chemical shifts of hydrogen atom at position X (referenced to TMS). Obviously, compounds **E**, **H** and **I** are absent in the proton chemical shift data because of lack of X hydrogen and (**c**) For ^{32}S chemical shifts for sulfur atom in thiophene ring.

The HLG values determine also the voltage produced in a photovoltaic cell as well as the electromotive force (EMF) of an electrochemical cell when the polymer is used as its negative or as its positive electrode. Increase in the chain length of a conductive polymer (or the length of the π-conjugated system) decreases the HLG values of the polymer. Therefore, it seems that HLG values of a polymer cannot be determined exactly from those of their monomers. However, the study of HLG values of monomers may be used to predict the comparative band gap behavior of the corresponding polymers.

Table 8
Calculated NICS values at GIAO/ B3LYP/6-311++G** and magnetic susceptibilities at CSGT/B3LYP/6-311++G** for thiophene and fluorothiophenes.

Molecule	NICS(0)	NICS(0.5)	NICS(1)	χ
Thiophene	-11.91	-11.49	-9.28	-51.86
A	-13.02	-11.78	-8.89	-55.57
B	-14.3	-12.84	-9.59	-56.21
C	-15.40	-13.03	-8.99	-60.06
D	-15.30	-12.80	-8.66	-59.97
E	-14.21	-11.92	-8.12	-59.35
F	-16.90	-14.15	-9.59	-61.07
G	-18.53	-14.79	-9.27	-65.55
H	-16.68	-13.32	-8.36	-64.06
I	-19.91	-15.40	-9.06	-69.42

The HLG values of fluorothiophenes defined in Fig. 6 are calculated and listed in Table 9. It can be seen from this table that the HLG values for all of the fluorothiophenes is very good for transit than valance band to conducting band. As shown in this table it is obvious that for the 3-fluorothiophene HLG is smaller than thiophene. This shows that conductivity of 3-fluorothiophen is more than thiophene.

Table 9
The B3LYP/6-311++G** calculated values of energy gaps Li (defined in Fig. 6) including HOMO–LUMO gap (HLG) L1 for thiophene and fluorothiophenes(in kcal mol^{-1}).

Molecule	L_1	L_2	L_3	L_4	L_5	L_6
Thiophene	5.07	5.37	7.46	5.58	5.87	7.97
A	4.98	5.60	7.76	5.41	6.04	8.20
B	4.99	5.36	7.58	5.62	5.99	8.20
C	4.91	5.50	7.73	5.24	5.83	8.06
D	4.97	5.58	7.79	5.39	6.00	8.20
E	4.90	5.79	7.99	5.18	6.06	8.26
F	5.12	5.18	7.58	5.78	5.85	8.25
G	5.03	5.41	7.74	5.36	5.74	8.07
H	4.88	5.73	7.95	5.00	5.85	8.06
I	4.98	5.64	7.93	5.05	5.71	8.00

It should be noted here that HLG values are not the only parameters that determine electric conductance of a polymer film. Orientation and alignment of the monomers in the polymer chain are two other determining characteristics that play important roles in the electrical conductance.

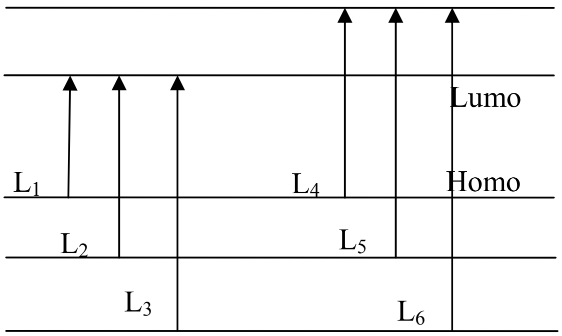


Fig. 6. Molecular orbital energy spacings, including HOMO–LUMO gap (HLG), studied in this research for thiophene and fluorothiophenes.

4. Conclusion

Density functional theory and B3LYP method with 6-311++G** basis set calculations have been carried out successfully to study the structural, electronic, electrochemical, and spectroscopic properties of all fluorothiophenes. Based on B3LYP/6-311++G** optimized structural parameters, especially the quinoid character, charge distribution, size and direction of the electric dipole moment vector, HLG, NICS analaysis, and vibrational frequencies, it was shown that compound **B** is a possible candidate to replace thiophene in the synthesis of corresponding conducting polymers with modified characteristics compared to polythiophene. Compared to thiophene, monomer **B** (3-fluorothiophene) is more soluble in water and has a lower potential energy to form cations. These characteristics increase the efficiency of electrochemical polymerization processes of this monomer. The feasibility of fluorothiophenes synthesis and experimental measurement of their molecular and thermochemical stability are interesting subjects to study. Furthermore, it has been shown that the prediction of polymer characteristics from the molecular properties of the constituting monomers is possible by quantum mechanical computations.

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