



Theoretical study on the electronic, structural, properties and reactivity of a series of mono-, di-, tri- and tetrafluorothiophenes as monomers for new conducting polymers

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ABSTRACT

Electrical and structural properties of mono-, di-, tri- and tetrafluorothiophenes and their radical cations have been studied using density functional theory and B3LYP method with 6-311++G** basis set. The effects of the number and position of the substituent of fluorine atoms on the properties of the thiophene ring have been studied using optimized structures obtained for these molecules and their radical cations. Vibrational frequencies, spin-density distribution, size and direction of dipole moment vector, ionization potential, electric polarizability, HOMO–LUMO gaps and NICS values of these compounds have been calculated as well. The analysis of these data showed that double bonds in 3-fluorothiophene are more delocalized and it is the best possible candidate monomer among all fluorothiophenes for the synthesis of corresponding conducting polymers with modified characteristics.

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1. Introduction

Electrically conducting 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 nano structures (nano-rods, -tubes, -wires and -fibers) since they incorporate the advantages of organic conductors with low-dimensional systems and so create interesting physico-chemical properties and potentially useful applications [4–7]. The varieties of such studies have been reported in the literature that includes: surfactants [8–11], liquid crystals [12], polyelectrolytes [13], nano-wire seeds [14], aniline oligomers [15], bulky organic dopants [16–21]. 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 them. The influence of water on polymerization process of thiophene as well as on the redox switching properties has been studied [23,24]. 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 [25,26]. Polythiophene has a solubility of 75% (w/w) in chloroform and a conductivity of 220 s cm^{-1} [22].

The effect of the 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 will be 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 electro active polymer (CEP), with the best conductivity when it is created from α - α' linkage [22]. In polythiophenes, the mechanism of polymerization involves the formation of the radical cations which react with another monomer to develop the polymeric structure (Fig. 1).

The objective of the present research is to study the electrical and structural properties of all fluorothiophenes (shown in Fig. 2) and their radical cations using DFT-B3LYP and DFT-UB3LYP methods.

The electropolymerization 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 thiophene ring. Vibrational frequencies with analyses of their IR intensities and NMR shielding constants will be used to characterize and predict the molecular and spectroscopic properties of fluorothiophenes.

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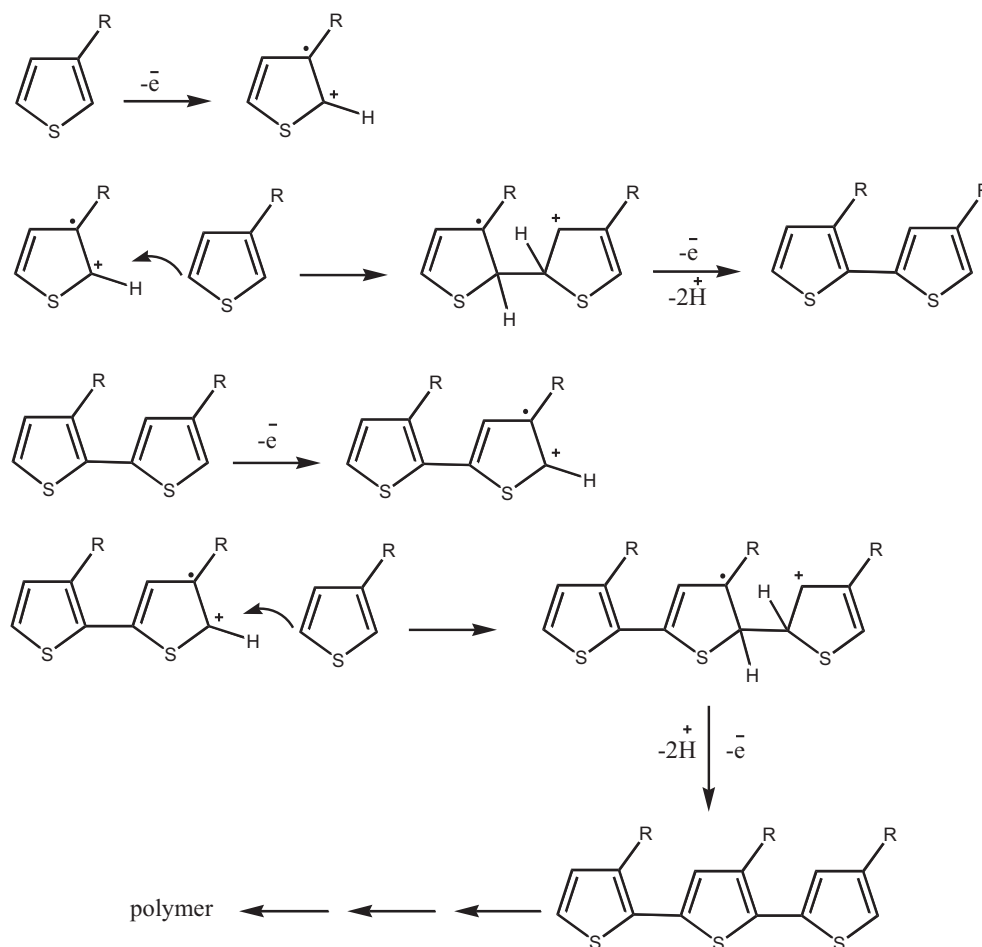


Fig. 1. Polymerization of thiophene (where R = H or a substituent) [29].

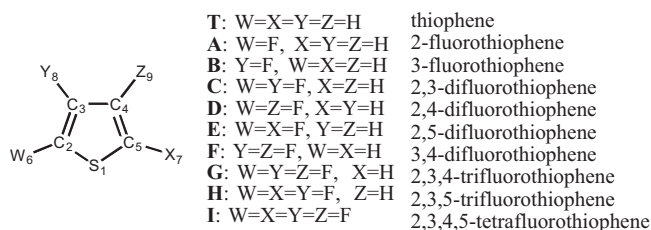


Fig. 2. All possible mono-, di-, tri- and tetrafluorothiophenes studied in this work.

2. Computational procedures

First of all, structures of representative mono-, di-, tri- and tetrafluorothiophenes were optimized using B3LYP/6-311++G** method [30–33]. The geometries of these compounds were optimized using standard gradient techniques with default parameters set in G98W. The vibrational analysis showed that all structures correspond to local minima in potential energy surface.

3. Results and discussion

3.1. Structural analysis of fluorothiophenes

In this section, the electrical and structural properties of fluorothiophenes and their related radical cations have been studied. Because of the stabilizing effects of the delocalization of

non-bonding p electrons of sulfur atom, it is expected that the thiophene molecules possess a plane structure.

In agreement with this expectation, results of the present calculations show that all fluorothiophenes possess planar structures (the optimized values of all dihedral angles of all structures are either 0° or 180°). The optimized structural parameters obtained at B3LYP/6-311++G** level of theory for all fluorothiophenes and UB3LYP/6-311++G** level of theory for all radical cations are listed in Table 1.

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 F_n coefficient defined in Eq. (1) for each thiophene ring [34]:

$$F_n = \frac{R_{34}}{(R_{23} + R_{45})/2} \quad (1)$$

where R_{34} is the length of C_3 – C_4 bond (formally single bond) and $[(R_{23} + R_{45})/2]$ is the average length of C_2 – C_3 and C_4 – C_5 bonds (formally double bonds) in the thiophene ring. The calculated values of the F_n coefficient for thiophene, all fluorothiophenes and their radical cations are listed in Table 1. As shown in this table, F_n coefficient has the following trend for all molecules:

$$\mathbf{B} > \text{Thiophene} > \mathbf{C} > \mathbf{F} > \mathbf{D} > \mathbf{A} = \mathbf{G} > \mathbf{H} > \mathbf{I} > \mathbf{E}$$

And for all molecular radical cations, values of the F_n coefficient has the following trend:

$$\mathbf{B} > \text{Thiophene} > \mathbf{A} > \mathbf{C} > \mathbf{E} > \mathbf{G} = \mathbf{H} > \mathbf{F} = \mathbf{I} > \mathbf{D}$$

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

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

Corresponding values for the related radical cations optimized with UB3LYP/6-311++G** are given in the lower row with italic fonts. See Fig. 2 for definitions of bond lengths and angles.

Table 2
Distribution of spin density over sulfur and carbon atoms in UB3LYP/6-311++G** optimized structures of thiophene and fluorothiophenes 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

As this table shows, 3-fluorothiophene has the smallest value of the F_n coefficient. Therefore, it can be suggested that the double bonds in 3-fluorothiophene are more delocalized.

3.2. Spin density distribution analysis

Electropolymerization process for each molecular radical cation is obtained from $\alpha-\alpha'$ (C₂–C₅) linkages [29], so it can be said that in

Table 3
Electric dipole moments, polarizability tensor elements and ionization potentials calculated at B3LYP/6-311++G** level of theory for the optimized structures of thiophene and fluorothiophenes.

Molecule	Electric dipole moment (D)			Polarizabilities (Å)					Ionization potentials (eV)
	μ_x	μ_y	μ_{tot}	α_{xx}	α_{yy}	α_{zz}	α_{xy}	α_{ave}	
Thiophene	0.0000	-0.5169	0.5169	67.093	73.851	41.017	0.012	60.654	8.75
A	0.9839	-1.4169	1.7250	73.793	68.155	39.942	0.938	60.630	8.67
B	0.5027	-1.3471	1.4379	68.469	72.277	39.803	2.962	60.183	8.87
C	-1.4527	-2.1682	2.6098	73.132	68.886	38.996	-1.857	60.338	8.82
D	-0.6594	-0.2523	0.7061	73.350	68.554	38.836	-1.605	60.247	8.84
E	-0.0002	-1.1812	1.1812	69.054	73.074	38.836	-0.029	60.321	8.64
F	-1.7507	-1.5012	2.4115	71.527	70.283	38.866	4.207	60.225	9.21
G	0.3141	-2.3909	2.3062	70.207	73.147	38.115	3.112	60.490	9.10
H	-0.4070	-0.9900	1.0704	73.656	69.145	37.989	-0.333	60.263	8.79
I	1.0104	-1.1765	1.5508	71.963	72.814	37.476	-2.669	60.751	9.03

μ_z , α_{xz} , and α_{yz} are essentially zero for all compounds because of the planar structure. The values of α_{ave} have been calculated using the $\alpha_{ave} = (1/3)(\alpha_{xx} + \alpha_{yy} + \alpha_{zz})$ relation.

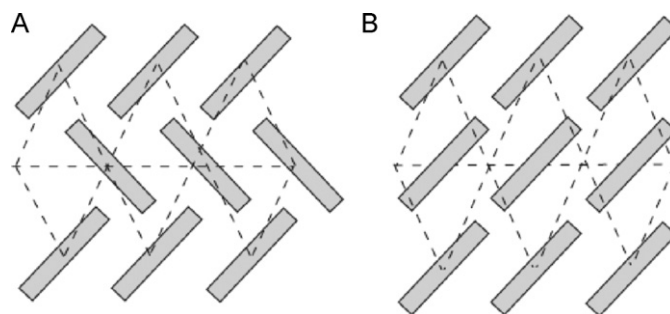


Fig. 3. Illustration of stacking arrangements proposed for polythiophene (PTH). Oriented chains extend into and out of the page: (a) herringbone stacking arrangement; (b) lamellar stacking arrangement.

a compound the greater spin density in positions C₃ and C₄ is, the higher electropolymerization rate will be [29].

The spin-density distribution over the ring atoms of fluorothiophene radical cations have been calculated and presented in Table 2. As shown in this table, it is obvious that monomer B has the maximal spin density on position C₃. This means that the electropolymerization of 3-fluorothiophene (B) can be more favorable ratio with respect to other molecules.

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.

Chemically synthesized PTHs powders exhibit a partially crystalline structure in which the chains align and pack in a herringbone arrangement (Fig. 3) in the crystalline regions [35].

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 monomers 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 chains [36].

It is 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 3.

Table 4
B3LYP/6-311++G** calculated IR absorption frequencies 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)	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)

An analysis of calculated dipole moments shows that the orientation of the dipole moment vector is toward sulfur atom for all fluorothiophenes. The size and direction of the dipole moment vector is more dependent on the position (symmetry) of substituent than its number. It can also be seen in Table 3 that the dipole moments for all compounds have the following trend:

C > F > G > A > I > B > E > H > D > Thiophene

The size of the dipole moment vector for monomers **C** and **F** is greater than other compounds. Therefore, compounds **C** and **F** have a high solubility in polar solvents. These characteristics increase the efficiency of electrochemical polymerization processes of these monomers. Moreover it can be seen in Table 3 that thiophene has a low solubility in polar solvents.

3.4. Ionization potentials

The first step in the electropolymerization of conductive polymers is formation of intermediate radical cations from monomers which can be considered as an ionization reaction [37]:



where M and $M^{\bullet+}$ denote monomer and its radical cation, respectively. So, stability of intermediate radical cations has an important role in the electropolymerization process. Therefore, it is useful to calculate electronic energy difference 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. Calculated values of IP for fluorothiophenes based on Eq. (2) are presented in Table 3. The trend of electrochemical stability of these monomers is:

F > G > I > B > D > C > H > Thiophene > A > E

Since ionization potential energies are directly proportional to the electrochemical oxidation potentials of the compounds, it can be said that the electrochemical stability of monomer **F** is greater than other compounds.

3.5. Electric polarizabilities

Values of polarizabilities of compounds containing halogen are used to interpret light scattering and intensities of vibrational

Raman spectra [34]. Values of exact electrical polarizabilities and average of polarizabilities (α_{ave}) for thiophene and all fluorothiophenes have been calculated and listed in Table 3. Based on this table, it can be claimed that with an increase in the number of fluorine atoms on the thiophene ring, polarization values will increase as well. The zero values obtained for polarizabilities α_{xz} , and α_{yz} are consequences of the planar structure.

The small values of α_{xy} polarizabilities indicate that the delocalization strength of the π -system of the ring dominates the anisotropic effects of substituent for asymmetric fluorothiophenes.

3.6. Vibrational spectra

The vibrational frequencies for all fluorothiophenes were calculated using optimized structures at B3LYP/6-311++G** level of theory. Calculated IR absorption frequencies and intensities for all fluorothiophenes are presented in Table 4. To facilitate the comparison the frequencies are divided into low-frequency (below 1000 cm^{-1}) and high-frequency groups (above 1000 cm^{-1}). According to analysis of frequencies listed in Table 4, it can be suggested that thermal decomposition has the following trend:

Thiophene > B > A > D > F > C > E > H > G > I

Thiophene and 3-fluorothiophene have the highest low-frequency values among all of these compounds; this means that thiophene and 3-fluorothiophene have the largest force constants for their bending modes of vibration. Higher values of low frequencies obtained for thiophene and 3-fluorothiophene can be regarded as a higher protection from thermal decomposition for these molecules.

The calculated Zero-Point vibrational Energy (ZPE) values for thiophene and all fluorothiophenes are listed in Table 5. Having in mind the contents of the table it can be said that ZPE for thiophene is greater than other compounds, as a result the relative thermal stability of thiophene is higher than other compounds.

3.7. NICS analysis

Nuclear Independent Chemical Shift (NICS) at GIAO/B3LYP/6-311++G** [38–43] and magnetic susceptibilities at CSGT/B3LYP/6-311++G** level of theory [44–48] in Angstrom upper than thiophene ring were calculated and listed in Table 6. Negative values of NICS represent the magnetic shielding and electric

Table 5

Zero-Point vibrational Energy in kcal/mol, calculated at B3LYP/6-311++G** level of theory for the optimized structures of thiophene and fluorothiophenes.

Molecule	ZPE
Thiophene	41.64
A	36.65
B	36.62
C	31.68
D	31.60
E	31.61
F	31.67
G	26.71
H	26.64
I	21.70

Table 6

Calculated NICS values (ppm) at GIAO/B3LYP/6-311++G** and magnetic susceptibilities (cgs-ppm) at CSGT/B3LYP/6-311++G** for thiophene and fluorothiophenes.

Molecule	NICS	χ
Thiophene	-9.28	-51.86
A	-8.89	-55.57
B	-9.59	-56.21
C	-8.99	-60.06
D	-8.66	-59.97
E	-8.12	-59.35
F	-9.59	-61.07
G	-9.27	-65.55
H	-8.36	-64.06
I	-9.06	-69.42

current in cyclic compounds. NICS results showed that compounds **B** and **F** have the highest NICS values in 1 angstrom upper than thiophene ring. These compounds have the largest electrical current and the highest conductivity among all of other compounds. Based on this table, it can be claimed that the magnetic susceptibilities of these molecules increase with the number of the fluorine atoms.

3.8. 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 and electric admittance (being charged under applied electric field) because it is a measure of the electron density hardness. A reasonable estimate of HLG values can be obtained from both HF and DFT calculations [42,43]. The HLG values determine the voltage produced in a photovoltaic cell as well as the electromotive force (EMF) of an electrochemical cell [49]. Increase in the chain

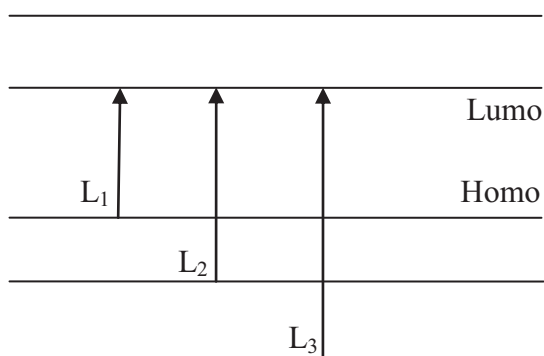


Fig. 4. Molecular orbital energy spacing, including HOMO–LUMO gap (HLG), studied in this research for thiophene and fluorothiophenes.

Table 7

The B3LYP/6-311++G** calculated values of energy gaps L_i (defined in Fig. 4) including HOMO–LUMO gap (HLG) L_1 for thiophene and fluorothiophenes (in kcal/mol).

Molecule	L_1	L_2	L_3
Thiophene	5.07	5.37	7.59
A	4.98	5.60	7.76
B	4.84	5.36	7.58
C	4.91	5.50	7.73
D	4.97	5.58	7.79
E	4.90	5.79	7.99
F	4.85	5.18	7.58
G	5.03	5.41	7.74
H	4.88	5.73	7.95
I	4.98	5.64	7.93

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 their monomers. However, the study of HLG values of monomers may be used to predict the comparative band gap behavior of the corresponding polymers.

The HLG values of fluorothiophenes defined in Fig. 4 are calculated and listed in Table 7. It can be seen in this table that the HLG values of 3-fluorothiophene (**B**) and 3,4-difluorothiophene (**F**) are smaller than other compounds. This shows that the conductivity of 3-fluorothiophene and 3,4-difluorothiophene are greater than other molecules.

It should be noted here that HLG values are not the only parameters which determine the electric conductivity of a polymer film, the orientation and alignment of the monomers in the polymer chain are two characteristics which play an important role in the electric conductivity as well.

4. Conclusion

B3LYP method with 6-311++G** basis set calculations have been carried out successfully to study the structural, electric and spectroscopic properties of all fluorothiophenes. Values of dipole moment, spin density distribution, ionization potential, vibrational frequencies, HLG and NICS have been calculated and analyzed. The analysis of the data showed that the 3-fluorothiophene has the smallest value of the F_n coefficient. Therefore, it can be suggested that double bonds in 3-fluorothiophene are more delocalized, electrochemical stability of thiophene and 3-fluorothiophene are greater than other compounds, Zero-Point Energy for thiophene is greater than other molecules, thermal stability of thiophene is higher than other compounds, the 3-fluorothiophene and 3,4-difluorothiophene possess the largest NICS value and these compounds possess the largest electrical current in the thiophene ring. Accordingly, compound **B** (3-fluorothiophene) is the best candidate monomer among other fluorothiophenes for the synthesis of corresponding conducting polymers with modified characteristics. The synthesis feasibility, experimental measurement and thermo chemical stability of these fluorothiophenes are interesting subjects for study.

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