The DFT Chemical Investigations of Optoelectronic and Photovoltaic Properties of Short-Chain Conjugated Molecules

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The research in the short-chain organic π-conjugated molecules has become one of the most interesting topics in the fields of chemistry. These compounds have become the most promising materials for the optoelectronic device technology. The use of low band gap materials is a viable method for better harvesting of the solar spectrum and increasing its efficiency. The control of the band gap of these materials is a research issue of ongoing interest. In this work, a quantum chemical investigation has been performed to explore the optical and electronic properties of a series of different short-chain compounds based on thiophene. Different electron side groups were introduced to investigate their effects on the electronic structure. The theoretical knowledge of the HOMO and LUMO energy levels of the components is basic in studying organic solar cells, so, the HOMO, LUMO, Gap energy and the photovoltaic properties of the studied compounds have been calculated and reported. These properties suggest these materials as a good candidate for organic solar cells.

INTRODUCTION

Over the past decade, thiophene-based electronic materials have been extensively investigated. The ease in the chemical modification of their structures can potentially allow us to fine-tune their optical and electronic properties [1]. These properties strongly depend on the degree of electronic delocalization present in these materials, effective conjugation length and the introduction of substituents. Whereas obtained polymers as highly amorphous, oligomers are not amorphous and can be synthesized as well defined compounds. Recently, many researchers are interested in the synthesis of short-chain compounds based conjugated oligomers, which finds application in OLED [2]. These materials offer advantages over polymeric systems in terms of easy synthesis and purification, and generally exhibit high charge carrier mobility. Therefore designing and

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synthesizing molecules with interesting properties play a crucial role in technology. At the same time it is important to understand the nature of the relationship between the molecular structure and the electronic properties to provide guidelines for the development of new materials. To this end, theoretical analysis of the electronic structure of conjugated systems can establish the relationships between molecular structure and electronic properties [3]. The theoretical knowledge of the electronic structures has given great contributions to the rationalization of the properties of known materials and to the properties prediction those of yet unknown ones. In this context, quantum-chemical methods have been increasingly applied to predict the band gap and other electronic properties of conjugated systems [4]. We note that theoretical knowledge of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels of the components is crucial in studying organic solar cells [5]. So, we can save time and money by choosing the adequate organic materials

to optimize photovoltaic device's properties. The HOMO and LUMO energy levels of the donor and of the acceptor components for photovoltaic devices are very important factors to determine whether the effective charge transfer will happen between donor and acceptor. The offset of band edges of the HOMO and LUMO levels will prove responsible for the improvement of all photovoltaic properties of the organic solar cells.

Recently [6] A. Marrocchi *et al.* have described the synthesis of a series of compounds based on thiophene (Fig. 1). Oligothiophene derivatives may exhibit large charge carrier mobility and excellent stability. To the best of your knowledge, a systematic theoretical study of such compounds has not been reported. The theoretical knowledge of the HOMO and LUMO energy levels of the components is a basis in studying organic solar cells, so, the HOMO, LUMO and Gap energy of the studied compounds have been calculated and reported. Their properties suggest they are good candidates for organic solar cells.

THEORETICAL METHODOLOGY

DFT method of three-parameter compound of Becke (B3LYP) [7] was used in all the study of the neutral and polaronic compounds. The 6-31G (d) basis set was used for all calculations [8-11]. To obtain the charged structures, we started from the optimized structures of the neutral form. The calculations were carried out using the GAUSSIAN 03 program [12]. The geometry structures of neutral and doped molecules were optimized under no constraint. We have also examined the HOMO and LUMO levels; the energy gap is evaluated as the difference between the HOMO and LUMO energies. The ground state energies and oscillator strengths were investigated using the ZINDO/s, calculations on the fully optimized geometries. In fact, these calculation methods have been successfully applied to other conjugated polymers [13].

RESULTAS AND DISCUSSION

Molecular Design and Geometric Structures

The optimized structures of all studied compounds are illustrated in Fig. 2. For saying about the effect of increasing additional π-bridge conjugated thiophene, 1, 2, 3, 4, T, TB
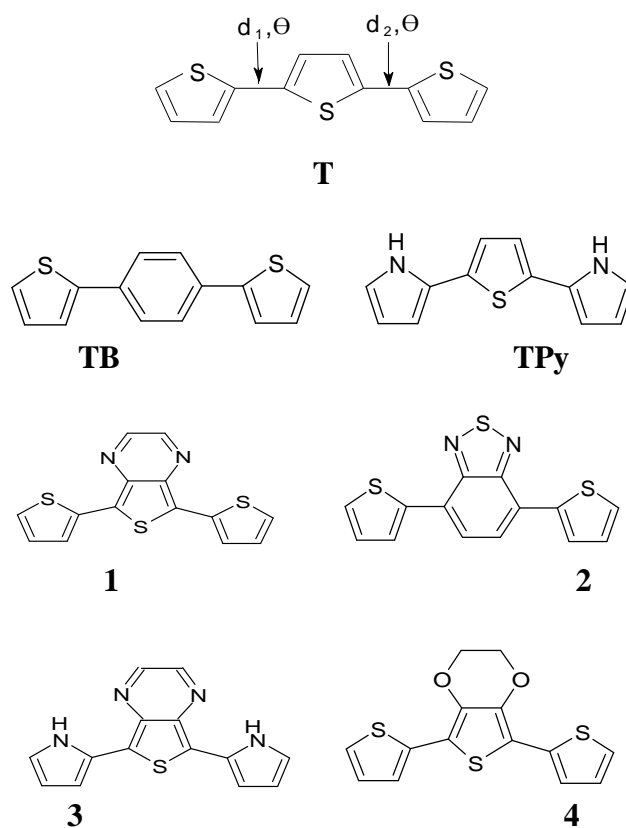

Fig. 1. The sketch map of studying structures (T, TB, TPy, 1, 2, 3 and 4).

et TPy are studied. All the molecular geometries have been calculated with the hybrid B3LYP function combined with 6-31G (d) basis sets. It was found in other works [14] that the DFT-optimized geometries were in excellent agreement with the data obtained from X-ray analyses.

The results of the optimized structures for all studied compounds show that they have similar conformation (quasi planar conformation) (see Fig. 2). We found that the consecutive units have similar dihedral angles (180°) and inter-ring distances (d_1 = 1.439 Å, d_2 = 1.439 Å). The incorporation of several groups does not change much these parameters (Table 1).

On the other hand, it is interesting to study how the p-doped π-conjugated molecule becomes the ultimate responsible of charge transport. As said before, to obtain the optimized oxidized structure, we started from the optimized structure of the neutral form. We can conclude that during
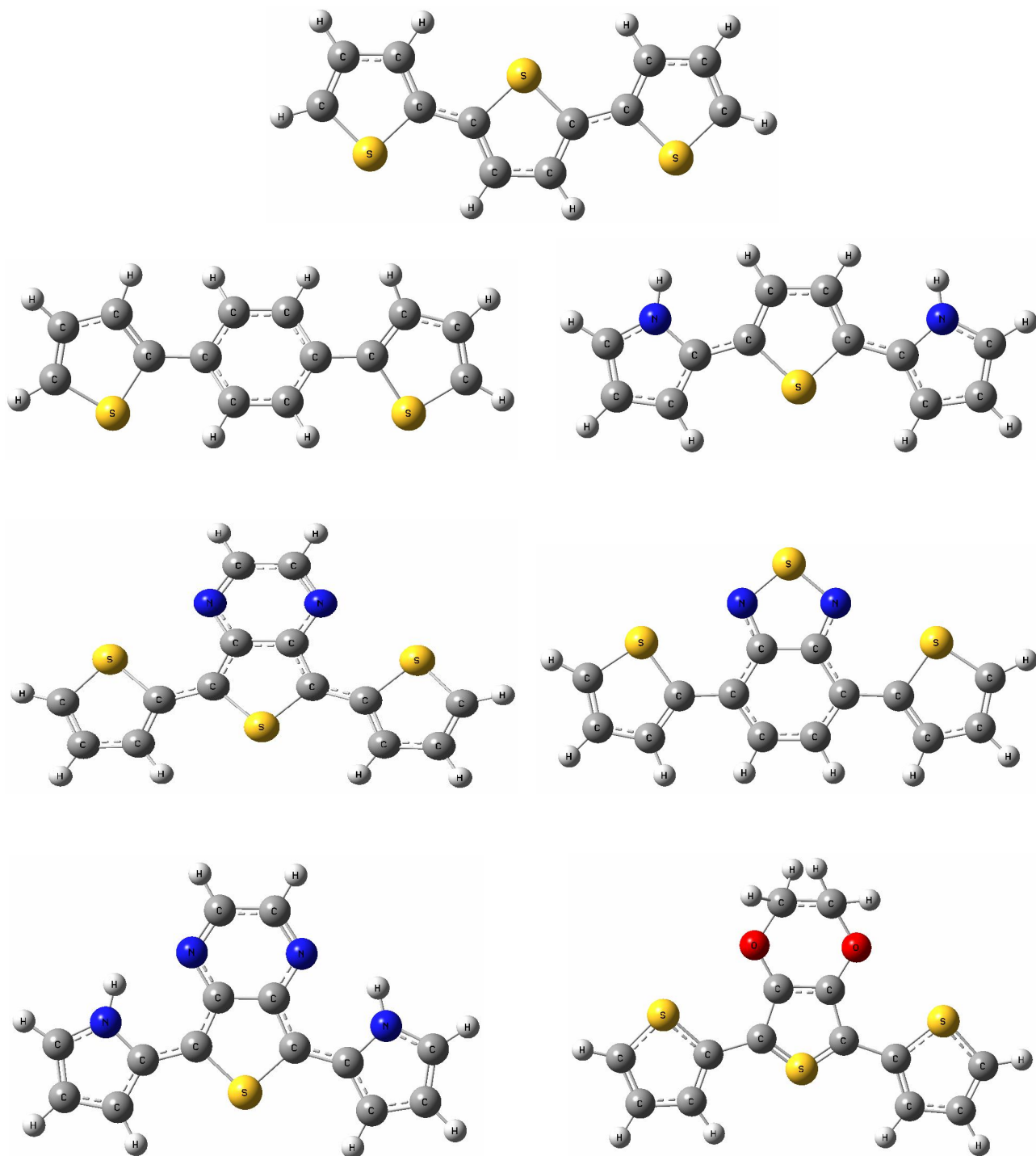
Fig. 2. Optimized structure of the studied compound obtained by B3LYP/6-31G (d).

Table 1. Geometrical Parameters of Study Compounds 1 to TPy Obtained by B3LYP/6-31G (d) in their Neutral (N) and Doped (D) States

distances molecules	d_1 (Å)	d_2 (Å)
1 (N)	1.439	1.439
1 (D)	1.406	1.406
2 (N)	1.459	1.459
2 (D)	1.423	1.423
3 (N)	1.435	1.435
3 (D)	1.402	1.402
4 (N)	1.442	1.442
4 (D)	1.411	1.411
T (N)	1.446	1.446
T (D)	1.413	1.413
TB (N)	1.465	1.465
TB (D)	1.430	1.430
TPy (N)	1.445	1.445
TPy (D)	1.411	1.411

the doping process and for all studied compounds the simple bonds become shorter, while the double ones become longer. The inter-rings bonds (d1 and d2) normally simple become shorter (Table 1); a quinoid-like distortion emerges as a result of the oxidation. These results are consistent with the *ab initio* HF and DFT calculations performed by J. Casado *et al.* [15] and S.M Bouzzine *et al.* [16] for substituting oligothiophenes. The optimized geometry of the cationic compound indicates the formation of the positive) polaron defect localized in the middle of the molecule and extending over the adjacent repeat units. The charged species are characterized by a reversal of the single double C-C bond pattern; the geometry process thus induces the appearance of a strong quinoid character within the molecule.

Electronic Parameters

Electronic structures are fundamental to the interpretation and understanding of the absorption spectra. The calculated energies of the frontier orbitals (four

occupied and four unoccupied orbitals) and the energy gaps between the HOMO and LUMO are listed in Table 2.

As shown in Table 2, one remarks that, in one hand, the studied molecules (1, 2, 3, 4, T, TB and TPy) exhibit destabilization of HOMO levels in comparison with those of compound TB (-5.418 eV) and, on the other hand, the studied molecules (1, 2, 3, 4, T, TB and TPy) exhibit stabilization of LUMO levels in comparison with those of compound TPy (-0.925 eV). The values of the HOMO and LUMO energies change significantly, this change depends on the nature of the moiety attached. This implies that different structures play key roles on electronic properties and the effect of the motifs branched to the central ring on the HOMO and LUMO energies is clearly seen. We have found respectively -4.98 eV and -2.61 eV for 1; -5.28 eV and -2.61 eV for 2; -4.52 eV and -2.45 eV for 3; -4.84 eV and -1.47 eV for 4; -5.11 eV and -1.68 eV for T; -5.41 eV and -1.38 ev for TB; -4.57 ev and -0.92 ev for TPy). In addition, the E_{gap} varies slightly from 4.03 eV to 2.07 eV, depending on the different structures. They are studied in the following order TB > Tpy > T > 4 > 2 > 1 > 3.

To study the photovoltaic properties and to evaluate the possibilities of electron transfer from the studied molecules to the conductive band of an acceptor (PCBM), the HOMO and LUMO levels are compared. As shown in Table 2, the change of molecular structure affects greatly on the HOMO and LUMO levels. The experiment phenomenon is quite consistent with previous literature [17-18], which reported that the increase of the HOMO levels may suggest a negative effect on organic solar cell performance due to the broader gap between the HOMO level of the organic molecules and the LUMO level of PCBM (V_{oc}). As shown in Fig. 3, both the HOMO and LUMO levels of the studied molecules agree well with the requirement for an efficient photosentizer. On the one hand, the HOMO levels of the studied compounds are higher than that of PCBM. Knowing that in organic solar cells, the open circuit voltage is found to be linearly dependent on the HOMO level of the donor and the LUMO level of the acceptor [19].

The maximum open circuit voltage (Voc) of the organic solar cell is related to the difference between the HOMO of the electron donor and the LUMO of the electron acceptor, taking into account the energy lost during the photo-charge generation [16]. The theoretical values of open-circuit

Table 2. Energy Values of E_{LUMO} (ev), E_{HOMO} (ev) and the Open Circuit Voltage V_{oc} (ev)

Molecules	$E_{(LUMO)}$ (eV)	$E_{(HOMO)}$ (eV)	Gap= $(E_{(LUMO)} - E_{(HOMO)})$ (eV)	*α_i (eV)	Voc (eV)
1	-2.614	-4.983	2.369	0.612	1.457
2	-2.614	-5.282	2.668	0.612	1.756
3	-2.450	-4.520	2.070	0.776	0.994
4	-1.470	-4.846	3.376	1.756	1.320
T	-1.688	-5.119	3.431	1.538	1.593
TB	-1.388	-5.418	4.030	1.838	1.892
TPy	-0.925	-4.574	3.649	2.301	1.048
PCBM	-3.226	-5.985			

*α_i(eV) = $E_{(LUMO)}$ (Donor) - $E_{(LUMO)}$ (PCBM) (eV) (The donor compounds is 1, 2, 3, 4, T, TB and TPy).
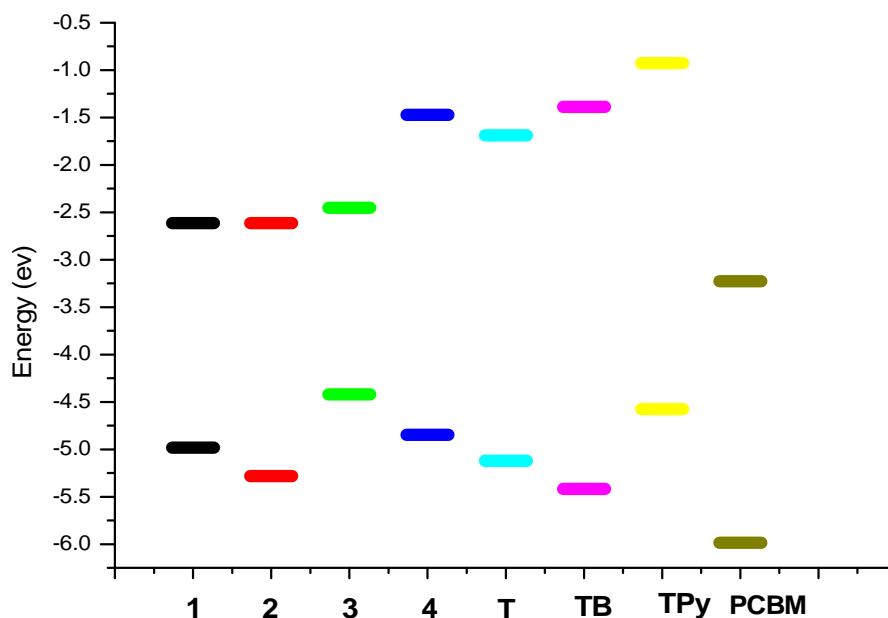

Fig. 3. Data of the absolute energy of the frontier orbitals HOMO and LUMO for the studied molecules and PCBM.

voltage Voc have been calculated from the following expression:

$$Voc = ||E_{HOMO}(D)| - |E_{LUMO}(A)| - 0.3$$

The obtained values of open-circuit voltage Voc of the studied molecules range from 0.99 eV to 1.89 eV, these values are sufficient for a possible efficient electron injection. Therefore, all the studied molecules can be used as sensitizers because the electron injection process from the excited molecule to the conduction band of fullerene derivative [6,6]-phenyl-C61-butyric acid methyl ester

(PCBM) and the subsequent regeneration is possible in an organic sensitized solar cell.

Finally, it is important to examine the HOMO and LUMO for these compounds because the relative ordering of occupied and virtual orbital provides a reasonable qualitative indication of excitations properties [20]. In general, as shown in Fig. 4 (LUMO, HOMO), the HOMOs of these oligomers in the neutral form possess a π-bonding character within subunit and a π-antibonding character between the consecutive subunits, while the LUMOs possess a π-antibonding character within subunit and a π-bonding character between the subunits which is the opposite in the case of doped forms.

Absorption and Electronic Properties

Based on the optimized molecular structures with B3LYP/6-31G(d) method. We have calculated the UV-Vis spectra of the studied compounds m1, 2, 3, 4, T, TB and TPy using ZINDO/s method. As illustrated in Table 3, we can find the values of calculated wavelength λ_{max} and for comparison experimental ones excitation to the S_1 state corresponds almost exclusively to the promotion of an electron from the HOMO to the LUMO orbital. The absorption wavelengths arising from $S_0 \rightarrow S_1$ electronic transition increase progressively with increasing of conjugation lengths. It is reasonable, since HOMO→LUMO transition is predominant in $S_0 \rightarrow S_1$ electronic transition; the results show a decrease of the LUMO and an increase of the HOMO energy.

These values are calculated by ZINDO method starting from optimized geometry obtained at B3LYP/6-31G(d) level. However, we believe that the bulk of intermolecular effect must be taken into account. Another point is that the position of λ_{max} shows a bathochromic shift when passing from molecule TB to molecule 3 with the following order TB (346.73 nm) < 2 (353.98 nm) < 1 (401.87 nm) < 3 (403.67 nm) < Tpy (428.13 nm) < T (441.83 nm) < 4 (453.19 nm). These results are due to the increasing of the extended conjugation through the system of aryl groups and multiple bonds. Those interesting points are seen both in the theoretical and experimental results.

To study the emission photoluminescence propreties of the studied compounds (1, 2, 3, 4, T, TB, TPy), the ZINDO-DFT/B3LYP method was applied to the geometry of the
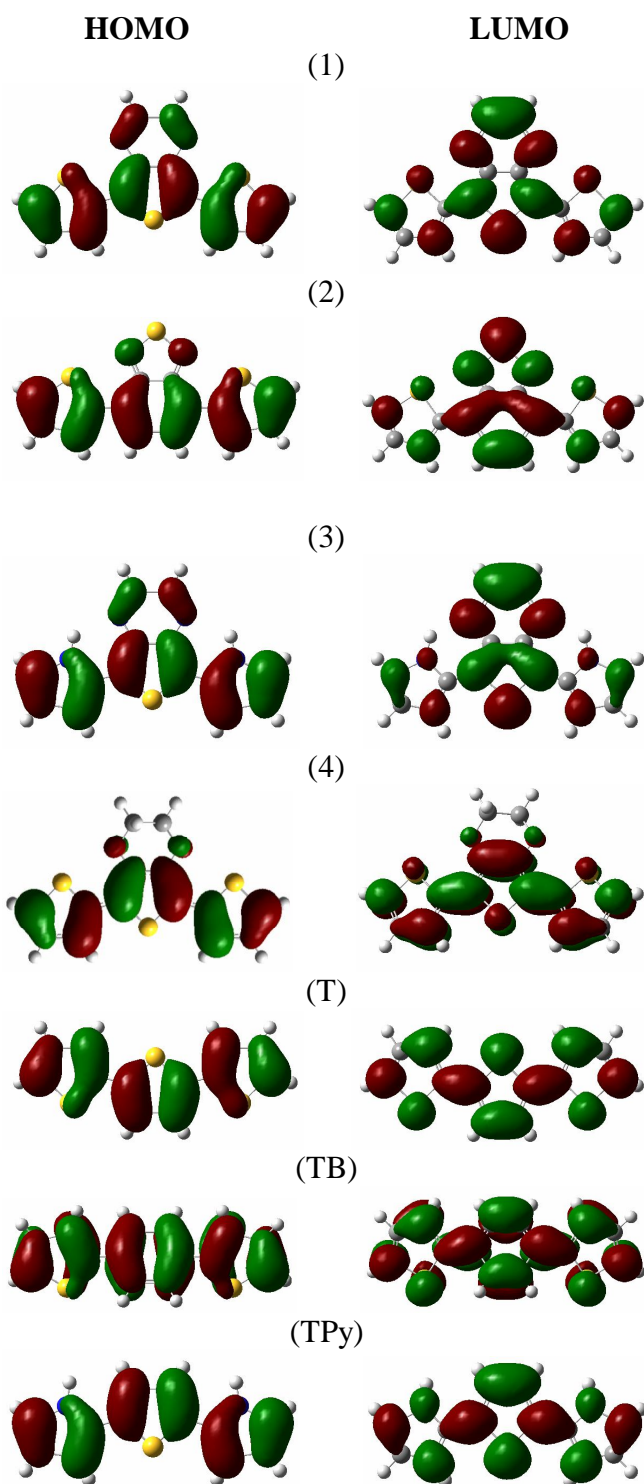
HOMO   **LUMO**

Fig. 4. The contour plots of HOMO and LUMO orbitals of the studied molecules in their neutral form.

Table 3. Data Absorption Spectra Obtained by the ZINDO Method for the Compounds Studied in the Optimized Geometries at B3LYP/6-31G(d)

Molecules	λ_{max} (nm)	Eex(eV)	O.S (nm)	Transition	
1	401.87	0.67931	0.4048	HOMO	LUMO+1
2	353.98	0.66054	0.5446	HOMO	LUMO+1
3	403.67	0.68071	0.4988	HOMO	LUMO+1
4	453.19	0.68108	0.8948	HOMO	LUMO
T	441.83	0.68137	0.9668	HOMO	LUMO
TB	346.73	0.65207	1.0182	HOMO	LUMO
TPy	428.13	0.68391	0.9191	HOMO	LUMO

Table 4. Emission Wavelength λ_{max} (nm) and Oscillator Strengths (O.S.) Obtained by the ZINDO Method

Molecules	λmax (nm) (emission)	O.S.	Stokes Shift (SS)
1	450.90	0.5517	49.03
2	385.21	0.6240	31.23
3	454.92	0.6291	51.25
4	518.01	0.9412	64.82
T	511.87	1.0261	70.04
TB	437.90	1.2396	91.17
TPy	505.87	0.9672	77.74

lowest singlet excited state optimized at the OPT ZINDO level with 6-31G(d).

The normalized photoluminescence spectrum of the studied compounds shows a maximum at 437.90 nm with strongest intensity (1.2396) for TB, 505.87 nm (0.9672) for TPy, 511.87 nm (1.0261) for T, 518.01 nm (0.9412) for 4, 454.92 nm (0.6291) for 3, 450.90 nm (0.5517) for 1, and 385.21 nm (0.6240) for 2. We can also note that relatively high values of Stokes Shift (SS) are obtained for TB (91.17 nm). In fact, the Stokes Shift, defined as the difference between the absorption and emission maximums, is usually related to the band widths of both absorption and emission bands [21].

CONCLUSIONS

This study is a theoretical analysis of the geometries and electronic properties of three various short-chain compounds based on the thiophene which displays the effect of substituted group on the structural and opto-electronic properties of these materials. The concluding remarks are:
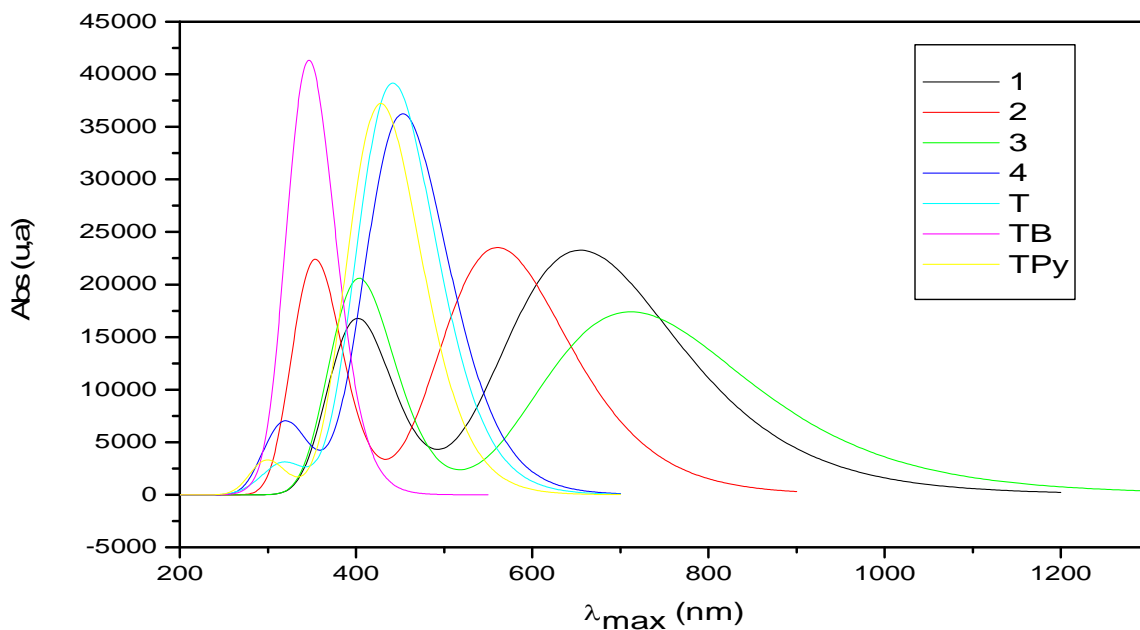
The results of the optimized structures for all studied

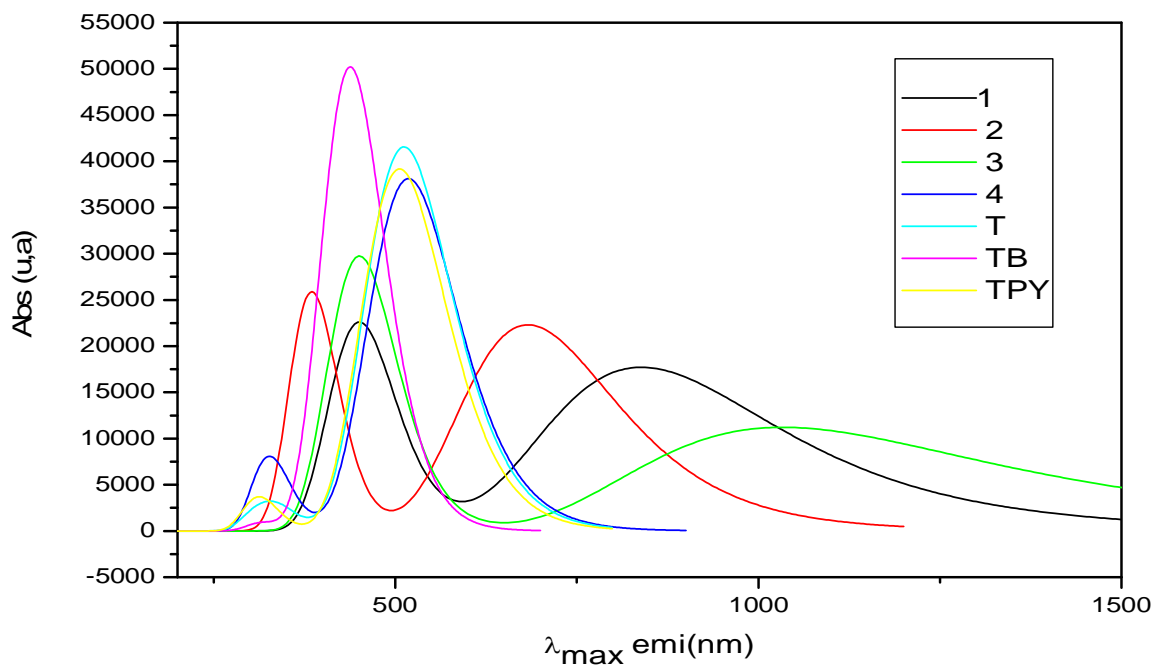**Fig. 5.** Simulated UV-visible optical absorption spectra of title compounds.

Fig. 6. Simulated emission spectra of title compounds.

compounds show that they have similar conformations (quasi planar conformation). We found that the incorporation of several groups does not change the geometric parameters.

The calculated energies of the frontier orbitals HOMO and LUMO and the energy gaps showed that the energy gaps of the studied molecules vary slightly from 2.070 eV to 4.03 eV depending on the different structures. The calculated band gap energy, E_{gap}, of the studied compounds increases in the following order TB > TPy > T > 4 > 2 > 1 > 3.

All the studied molecules can be used as sensitizers because the electron injection process from the studied molecule to the conduction band of PCBM and the subsequent regeneration are feasible in the organic sensitized solar cell.

This calculation procedure can be used as a model system for understanding the relationships between the electronic properties and the molecular structure and also can be employed to explore their suitability in electroluminescent devices and in related applications. Presumably, the procedures of theoretical calculations can be employed to predict and assume the electronic properties on yet prepared and efficiency proved the other materials, and further to design novel materials for organic solar cells.

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