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Investigations on Optoelectronic Properties of New low Gap Compounds Based on Pyrrole as Solar Cells Materials

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Abstract

In this paper theoretical study by using DFT method on three conjugated compound based on 2-styryl-5-phenylazo-pyrrole is reported. These dyes contain one carboxy, two carboxy and one sulfonic acid anchoring groups, the aim is to investigate their effects on the electronic structure. The theoretical knowledge of the HOMO and LUMO energy levels of the components is cannot be ignored in investigating suitable materials for organic solar cells so the HOMO, LUMO and gap energies of the studied compound have been calculated and reported. These properties suggest these materials as good candidates for organic solar cells.

Keywords:*p-conjugated molecules, Organic solar cells, DFT, low band-gap, Electronic properties, HOMO, LUMO.*

Introduction

Organic p-conjugated molecules and polymers have good properties such as thermal and photochemical stability ad high charge mobility, which make them promising candidates for research on optoelectronic device technology [1], such as LEDS [2], Transistors (TFTs) [3] and low-cost solar cells [4]. Polyheterocyclic compound have attracted much interest for potential applications in opto-electronic devices due to their electronic and photonic properties [1].

Whereas obtained polymers are highly amorphous, oligomers are not amorphous and

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can be synthesized as well defined compounds. Recently, many researchers have become interested in synthesizing short-chain OLED compounds based on conjugated oligmers [5]. On the other hand, since the discovery of the ultrafast and ultra-efficient photo induced electron transfer between p-conjugated systems and fullerene derivatives, [6] a considerable interest for hetero-junction solar cells based on interpenetrating networks of conjugated systems and C_{60} derivatives has been generated [7]. Roquet *et al.* [8] reported the relationships between the nature of acceptor groups in the molecule and the photovoltaic performances. The results showed that introducing electron-acceptor groups into the donor structure induces an extension of the photo-response in the visible spectral region, an increase of the maximum external quantum efficiency and an increase of the open circuit voltage under white light illumination.

The use of low band gap materials is a viable method for better harvesting of the solar spectrum and increasing the materials and the devices efficiency [9]. The control of the band gap parameter of these materials is a research issue of ongoing interest. This band gap engineering gives this material its desired electrical and optical properties and the reduction of the band gap to approximately zero is expected to give an intrinsically conducting material. The most efficient strategy has been applied to design molecules which alternated donor-acceptor repeating units that are expected to have small gaps [10]. Recent work in this area has been focused on the synthesis and design of new molecules combining donor and acceptor blocks, or conjugated systems with narrow band gaps [11].

Theoretical analysis of the electronic structure of conjugated systems can establish the relationships between molecular structure and electronic properties. Theoretical studies on the electronic structures of p-conjugated compounds have 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 of conjugated systems [12]. We note that theoretical knowledge of the HOMO and LUMO energy levels of the components is crucial in studying organic solar cells. So, we can save time and money in choosing the adequate organic materials to optimize photovoltaic devices 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 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.

In this article, a theoretical study on using DFT method for three conjugated compounds containing pyrrole rings, as shown in Figure 1, is reported. These dyes contain one carboxy, two carboxy and one sulfonic acid anchoring groups. The aim is to complete characterization of these compounds and to investigate the effects on the electronic structure. We have also investigated the effect of doping in these new conjugated compounds with the DFT method at UB3LYP level with 6-31G(d) basis set. Our attention focused on the study on the geometries and electronic properties in neutral and doped state. The HOMO, the LUMO and the gap energies of these compounds have been calculated and reported in this paper. A systematic theoretical study of such compounds has not been reported as we know. These new series of organic compounds have been successfully recently synthesized by J.A. Mikroyannidis et al. [13].

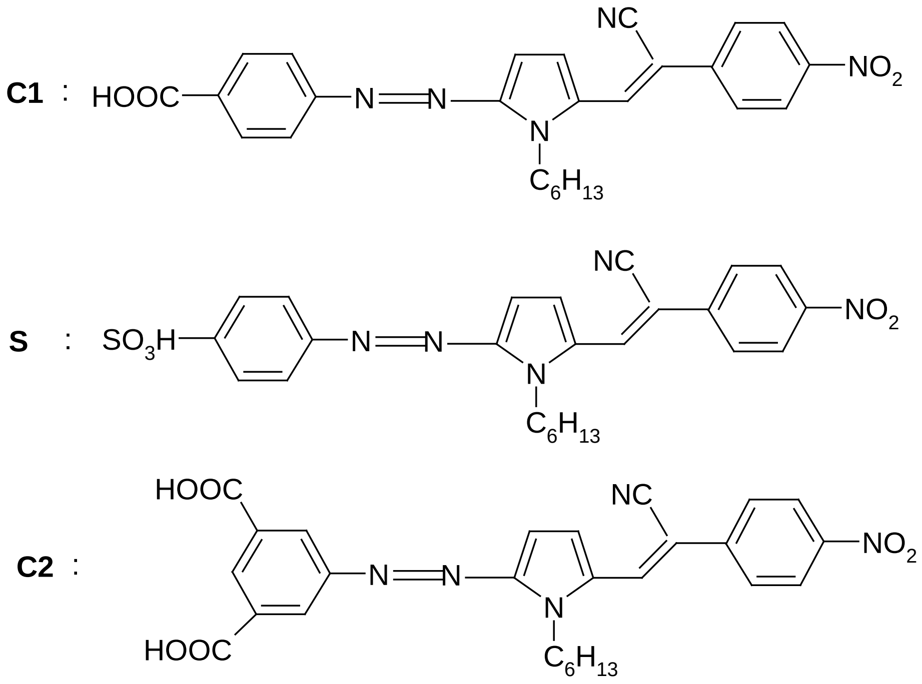


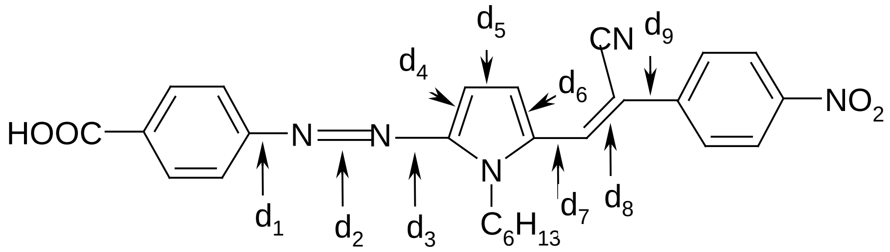
Figure 1. The sketch map of studied structures (C1, S and C2).

Methodology

DFT method of three-parameter compound of Becke (B3LYP) [14] was used in all the study of the neutral, polaronic and bipolaronic compounds. The 6-31G(d) basis set was used for all calculations [15–18]. To obtain the charged structures, we start from the optimized structures of the neutral form. The calculations were carried out using the GAUSSIAN 03 program [19]. The geometries structures of neutral and doped molecules were optimized under no constraint. We have also examined 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 [20].

Table 1. Geometric parameters of compounds C1, C2 and S obtained by B3LYP/6-31G(d) in their neutral and doped (polaronic and bipolanic) states.



di(Å)/C1	d_1	d_2	d_3	d_4	d_5	d_6	d_7	d_8	d_9
Neutral	1.424	1.259	1.387	1.408	1.390	1.406	1.440	1.368	1.482
Polaronic	1.374	1.257	1.318	1.434	1.366	1.439	1.446	1.367	1.476
Bipolaronic	1.346	1.267	1.296	1.467	1.350	1.455	1.409	1.400	1.446

di (Å)/S	d_1	d_2	d_3	d_4	d_5	d_6	d_7	d_8	d_9
Neutral	1.424	1.259	1.386	1.407	1.391	1.407	1.444	1.367	1.482
Polaronic	1.376	1.258	1.315	1.436	1.365	1.441	1.445	1.368	1.475
Bipolaronic	1.349	1.266	1.299	1.466	1.351	1.456	1.408	1.402	1.444

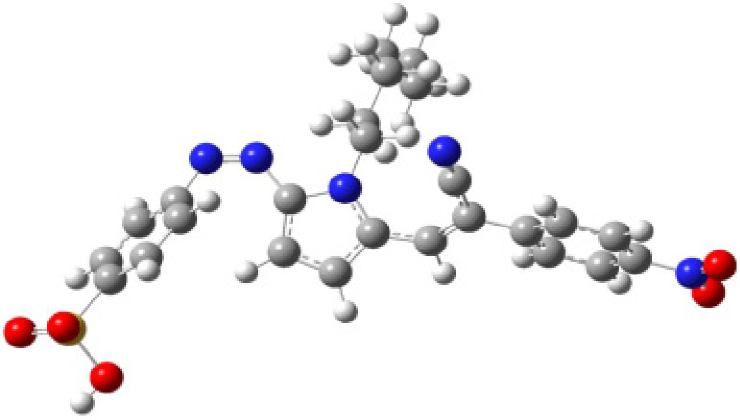
di (Å)/C2	d_1	d_2	d_3	d_4	d_5	d_6	d_7	d_8	d_9
Neutral	1.415	1.272	1.370	1.402	1.389	1.407	1.440	1.369	1.481
Polaronic	1.384	1.272	1.331	1.436	1.364	1.443	1.433	1.386	1.471
Bipolaronic	1.359	1.241	1.289	1.457	1.350	1.462	1.408	1.400	1.445

Results and discussion

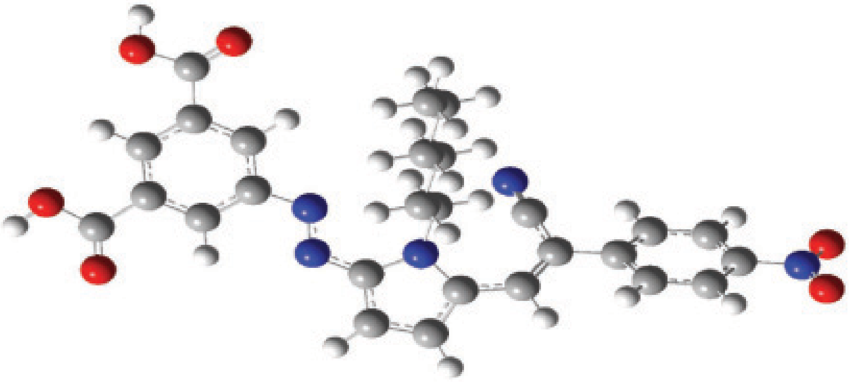
Geometric properties

For all molecules, geometrical parameters were obtained after total optimization by B3LYP/6-31G(d). It was found in other works [21] that the DFT-optimized geometries were in excellent agreement with the data obtained from X-ray analyses. To investigate the effect of the substituents on the geometries and electronic properties, the optimized structures of several studied compound (C1, C2 and C3) were compared. The results of the optimized structures for all studied compounds show that they have similar conformations (quasi planar conformation) (see Figure 2). We found that the consecutive units have similar dihedral angles (180°) and inter-ring distances (d_1=1.424 Å, d_2=1.259 Å, d_3=1.387 Å, d_7=1.440 Å, d_8=1.3689 Å , d_9=1.482 Å). The incorporation of several groups does not change these parameters.

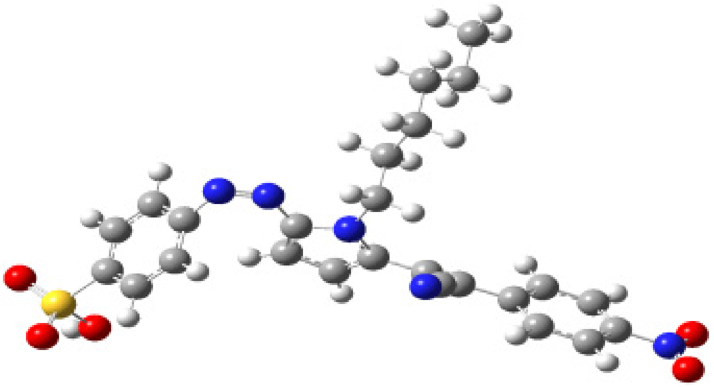
On the other hand, since the p-doped π-conjugated molecule becomes the ultimate responsible of charged transport; it is interesting to study this phenomenon in our case. As mentioned before, to obtain oxidized optimized structure, we started from the optimized structure of the neutral form. We can conclude that during the doping process and for all studied compounds the simple bonds become shorter, while the double ones become longer. The inter-rings bonds are longer than normal double bonds. 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. [22] and S.M Bouzzine et al [23] for substituted oligothiophenes. The optimized geometry of the dicationic compound indicates the formation of the positive bipolaron 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 C¾C bond pattern; the geometry process thus induces the appearance of a strong quinoid character within the molecule.



C1



C2



S

Figure 2. Optimized structures of studied compounds C1, C2 and S.

Electronic parameters

Table 2 lists the theoretical electronic parameters of the studied conjugated compounds. In the case of compounds C1 and C2, one remark that they exhibit destabilization of the HOMO and LUMO levels in comparison with those of compound S due to electron-attracting substitution of carboxy –COOH group comparing to sulfonic - SO_3H group; while in the case of C2 there is a net stabilization of the LUMO level comparing to that of C1 which is due to the presence of two carboxy groups. The band gap of C2 is much smaller than that of the other substituted compounds. This may be attributed to the number of electron-attracting carboxy side groups. Concerning the comparison between the two compounds Ci (i=1,2) and S, it suggests that the replacement of sulfonic group SO_3H by carboxy group COOH leads to the destabilisation of both the HOMO level and LUMO levels with decrease in the energy Gap. This is in agreement with what it was found in experimental results [13].

Table 2. Values of HOMO (eV), LUMO (eV) and Eg (eV) energies calculated for, S, C1 and C2 obtained by B3LYP/6-31G(d).

Compounds	HOMO(eV)	LUMO(eV)	Eg(eV)
S	-6,265	-3,247	3,018
C1	-6,034	-3,152	2,883
C2	-6,032	-3,204	2,828

The calculated band gap E_{gap} of the studied compound increases in the following order C2<C1<S. Figure 4 shows detailed data of absolute energy of the frontier orbitals for C1, C2 and S, ITO, PCBM (C_{60}) and aluminum (Al) is included for comparison purposes. It is deduced that substitution of phenylene pushes up/down the HOMO/LUMO energies in agreement with their electron acceptor character. To evaluate the possibilities of

electron transfer from the excited studied molecules to the conductive band of PCBM, the HOMO and LUMO levels were compared. As shown in Table 2, the change of the electron-donor shows a great effect on the HOMO and on the LUMO levels. The experiment phenomenon was quite consistent with previous literature [24], 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 HOMO level of PCBM.

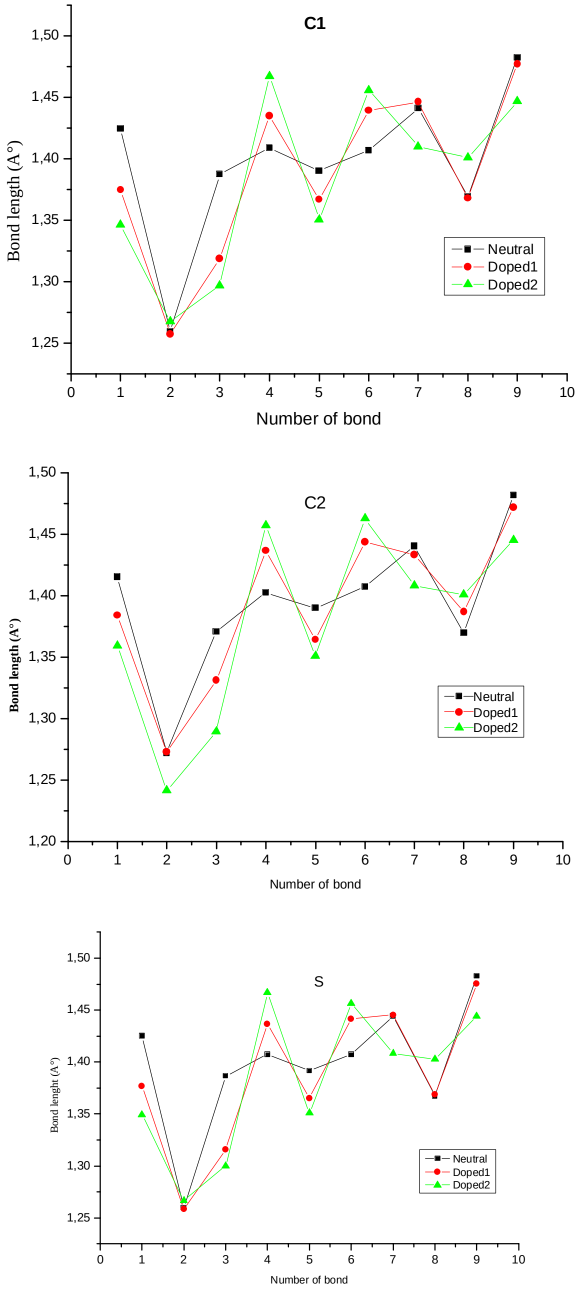


Figure 3. Optimized CC bond lengths of neutral, polaronic and bipolaronic of compound C1, C2 and S calculated by the B3LYP/6-31G(d).

As shown in Figure 4, both HOMO and LUMO levels of the studied molecules agreed well with the requirement for an efficient photosentizer. On the one hand, the HOMO levels of the studied compounds were 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 [25].

The difference between the energy of conduction band (LUMO) of PCBM and the energy of HOMO of the studied molecules (C1, C2, S) range from 2.1 ev (S) to 1.93eV (C1 and C2) these values are sufficient for a possible efficient electron injection. Therefore, the three studied molecules can be used as sensitizers because the electron injection process from the excited molecule to the conduction band of PCBM and the subsequent regeneration is possible in organic sensitized solar cell.

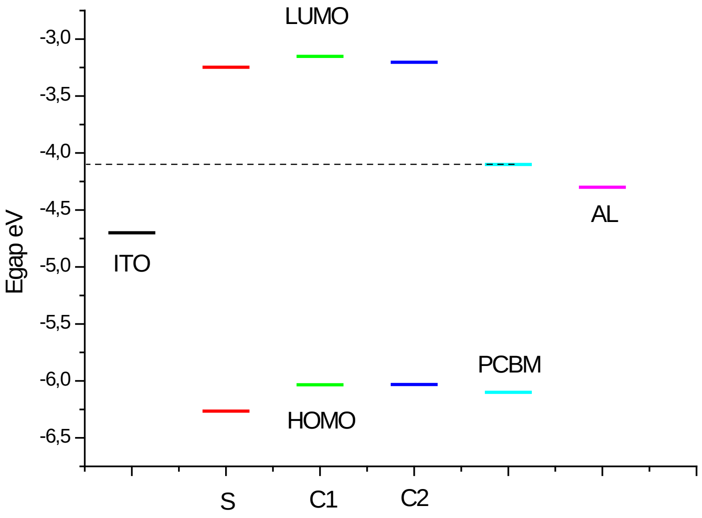


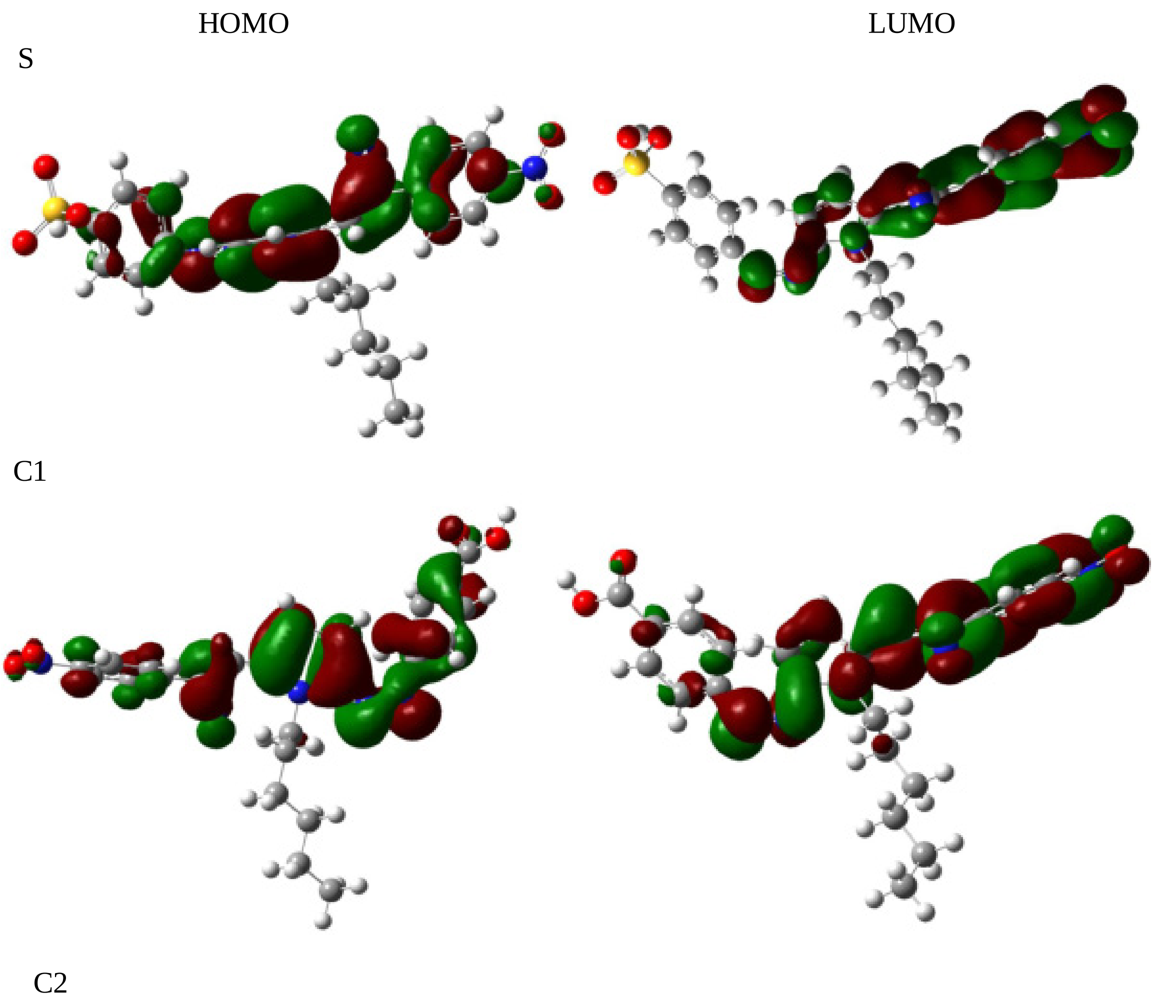
Figure 4. Data of the absolute energy of the frontier orbitals HOMO and LUMO for S, C1 and C2 and ITO, PCBM and the aluminum (Al).

On the other hand, since the p-doped π-conjugated molecule becomes the ultimate responsible of charged transport, the values of the energy of the HOMO, LUMO, DE_N (HOMO, LUMO) for several compounds in their neutral, polaronic and bipolaronic forms were determinate and presented in Table 3. Available values of the gap energy in neural state are presented also in this Table for comparison. Traditionally and until now, charged stated in conjugated molecules have been discussed in terms of one-electron band model. We note that the energy gap decreases when passing from the neutral to the doped form for all oligomers.

Table 3. Values of Gap energy (eV) of the several studied compounds S, C1 and C2, respectively in their neutral, polaronic and bipolaronic forms.

Studied Compounds	E_{gap}(eV) neutral form	E_{gap}(eV) Polaronic form	E_{gap}(eV) Bipolaronic form
S	3,018	2,220	1,479
C1	2,439	2,214	1,498
C2	2,828	2,709	1,675

Finally, it is important to examine the HOMO and the LUMO for these compounds because the relative ordering of occupied and virtual orbital provides a reasonable qualitative indication of excitations properties [26]. In general, as shown in Figures 5 and 6 (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 whereas it is the opposite in the case of doped forms.



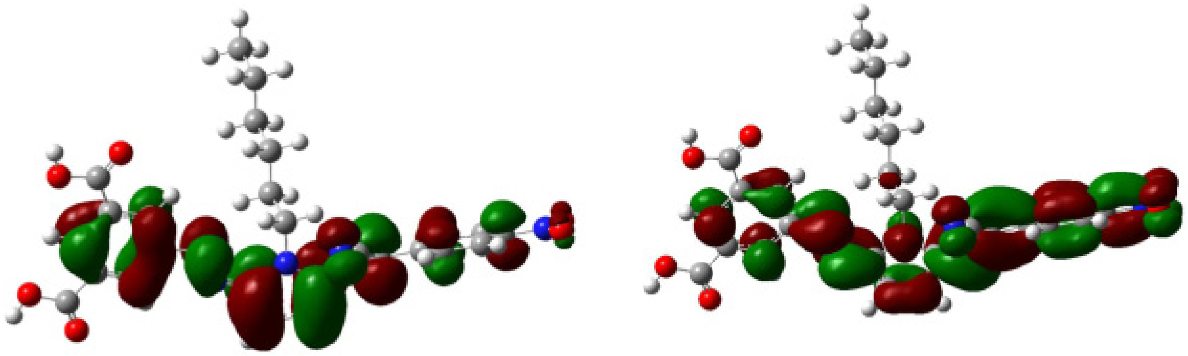
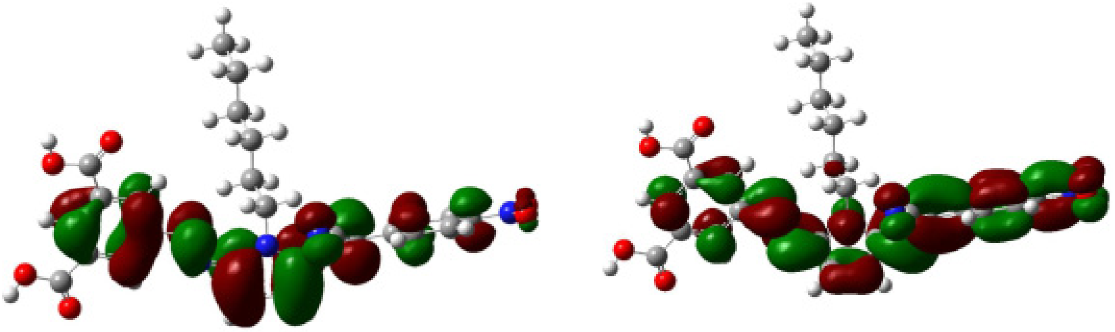
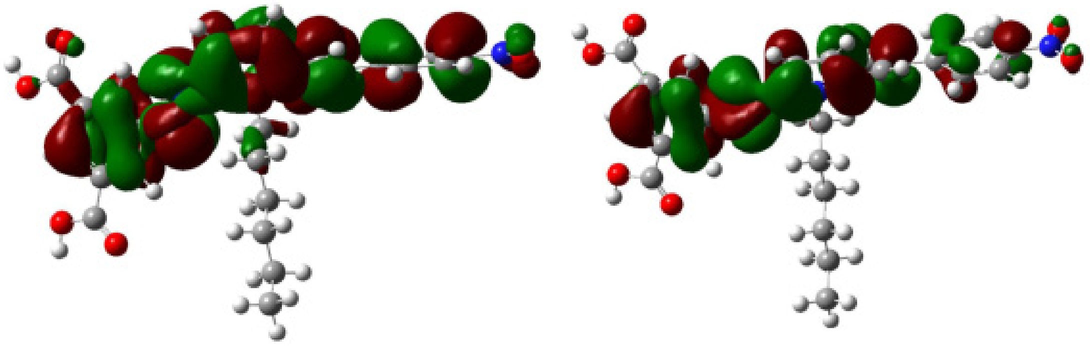


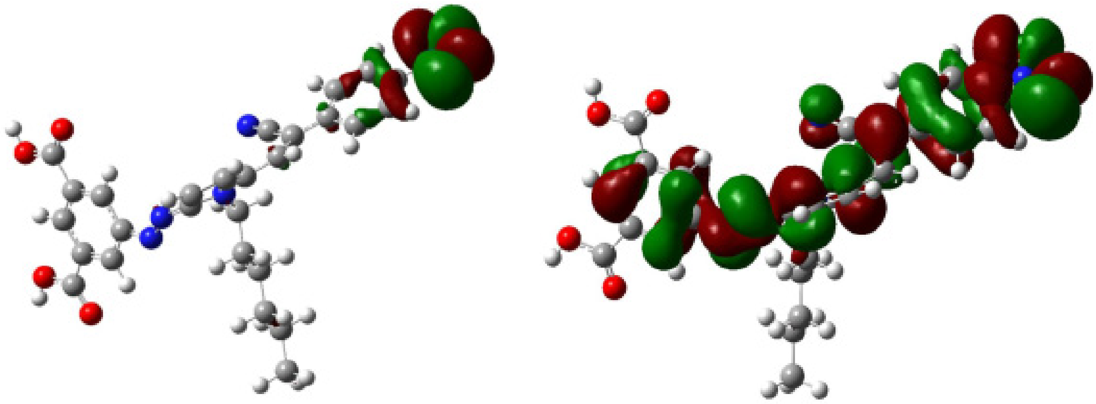
Figure 5. The contour plots of HOMO and LUMO orbitals of studied coupounds S, C1 and C2 in neutral form.



Neutral form



Polaronic state



Bipolaronic state

Figure 6. The contour plots of HOMO and LUMO orbitals of studied compound C2 in neutral, polaronic and bipolaronic forms.

Absorption and electronic properties

Based on the optimized molecular structures with B3LYP/6-31G(d) method. We calculated the UV-vis spectra of the studied compounds C1, C2 and S using ZINDO/s method. As illustrated in Table 4, we can find the values of calculated wavelength λmax 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 the increasing of conjugation lengths. It is reasonable, since HOMO→LUMO transition is predominant in $S_0 \rightarrow S_1$ electronic transition; the results are a decrease of the LUMO and an increase of the HOMO energy.

Table 4. Absorption λ_{abs} (nm) obtained by the ZINDO/DFT method.

Studied compounds	ZINDO method			λ_{max}(nm)Exp
	λ_{max}(nm)	f	activation energy (eV)	
S	505.36	0.229	2.45	602
C1	523.59	0.286	2.36	625
C2	508.43	0.015	2.43	615

These values are calculated by ZINDO method starting with optimized geometry obtained at B3LYP/6-31G(d) level. However, we believe that the bulk of intermolecular effect must be taken into account. This effect is the source of the deviation between the calculation and the experiment data. We can remark for comparing calculated and experimental results [13] a linear relationship between calculated and experiment results. Therefore, the DFT theoretical calculations give a good description of absorptions properties of the studied compound and can be employed to predict the electronic characteristics of other materials. It should be noted that the difference between theoretical and experimental values can be explained by the fact that the calculations assume that the molecules in the vapor state.

Another consider point in that the position of λmax shows a bathochromic shift when passing form S to C2, which also can be seen respectively in S (505,36 nm), C2(508,43 nm) and C1(523,59nm) This interesting point is seen both in the theoretical and experimental results.

On the other hand, when compared compound C1 and C2, we remark the red-shifted by 15 based on theoretical results and by 10 nm based on experimental results. This clearly indicated the significant influence of the number of carboxy groups that lead to enhance the conjugation.

Conclusion

In this study, theoretical analysis on the geometries and electronic properties of three various compounds based on 2-styryl-5-phenylazo-pyrrole is performed in order to display the effect of substituted groups and the doping process on the structural and opto-electronic properties of these materials. The concluding remarks are:

- The substitution in phenylene ring by the electron- withdrawing groups carboxy -COOH and solfonic - SO_3H on the phenylene ring destabilizes the HOMO and LUMO with a decrease in the energy gap and results in a red shifting in the absorption spectrum. Such theoretical results are in agreement with experimental ones.
- The replacement in phenylene of sulfonic group by carboxy group leads to the destabilisation of the HOMO and LUMO levels and decrease in the energy gap.
- For polaron and bipolaron oligomers, the obtained structures are completely planar. The gap energy decreases when passing from the neutral to the doped form for each oligomer. The quinoidic character is more accentuated when a second electron is removed.
- The three studied molecules can be used as sensitizers because the electron injection process from the excited molecule to the conduction band of PCBM and the subsequent regeneration are feasible in organic sensitized solar cell. This calculation procedure can be used as a model system for understanding the relationships between electronic properties and molecular structure and also can be employed to explore their suitability in electroluminescent devices and in related application. 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.

Acknowledgements

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