



Molecular design of new π -conjugated materials based on thiadiazolothienopyzine for organic solar cells

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Abstract

In this paper and in order to guide the synthesis of novels materials with low band gaps, Theoretical study by using DFT method on six conjugated compound containing based on thiadiazolothienopyzine is reported. 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 and Gap energy of the studied compounds have been calculated and reported. These properties suggest these materials as a good candidate for organic solar cells.

Keywords: π -conjugated molecules, organic solar cells, DFT, low band-Gap, electronic properties, HOMO, LUMO.

1. Introduction

The research in the organic π -conjugated molecules and polymers has become one of the most interesting topics in fields of chemistry physics and materials science. Thanks to their specific properties, these compounds become the most promising materials for the optoelectronic device technology [1], such as LEDs [2], Transistors (TFTs) [3] and solar cells [4]. Polythiophenes have attracted much interest for potential application in opto-electronic devices due to their electronic and photonic properties [1]. Whereas polythiophenes obtained as highly amorphous, oligothiophenes are not amorphous and can be synthesized as well defined compounds. Recently, many researchers have become interested in synthesizing short-chain OLED compounds based on oligothiophenes [5]. On the other hand and since the discovery of the ultra fast and ultra efficient photo induced electron transfer between p-conjugated systems and fullerene derivatives [6] considerable interest for hetero-junction solar cells based on interpenetrating networks of conjugated systems and C60 derivatives has been generated [7]. Roquet et al [8] reported the relationships between the nature of acceptor groups in the molecule and the photovoltaic performance. The results show that the introduction of electron-acceptor groups in 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 its efficiency [9]. The control of this parameter of these materials is research issue of ongoing interest. This band gap engineering gives this material its desired electrical and optical properties, reduction of band gap to approximately zero is expected to give an intrinsically conducting material. The most efficient strategy has been applied to design molecules which alternate 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 conjugated compound have made great contributions to the rationalization of the properties of known materials and the prediction those of yet unknown ones. In this context and in order to guide the synthesis of novels materials with low band gaps, 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 basic 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 acceptor components for photovoltaic devices are very important factors to determine whether effective charge transfer will happen between donor and acceptor. The offset of ban edges of HOMO and LOMO levels will prove responsible for the improvement of all photovoltaic properties of the organic solar cells.

In this paper, Theoretical study by using DFT method on six conjugated compound containing thiophene ring, as shown in fig.1 is reported. Different electron side groups were introduced to investigate their effects on the electronic structure; The HOMO, LUMO and Gap energy of these compounds have been calculated and reported in this paper. A systematic theoretical study of such compound has not been reported as we know.

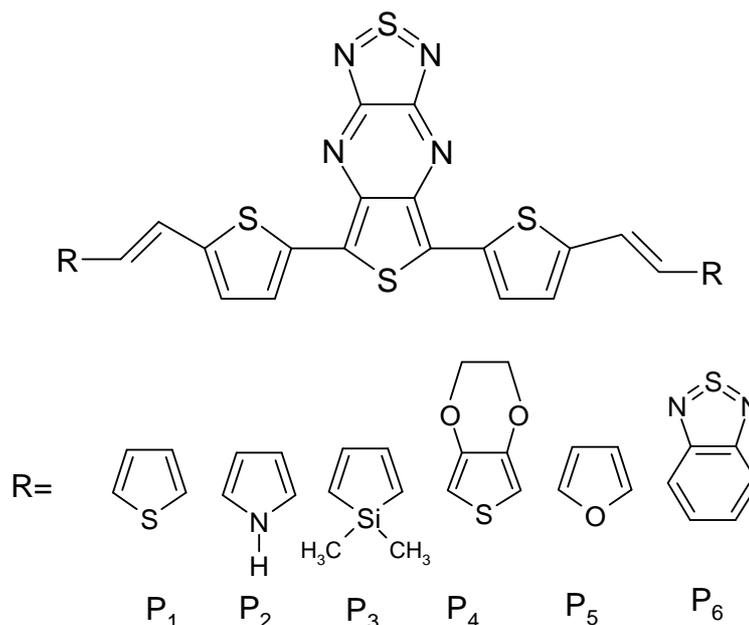


Fig. 1: The sketch map of studied structures

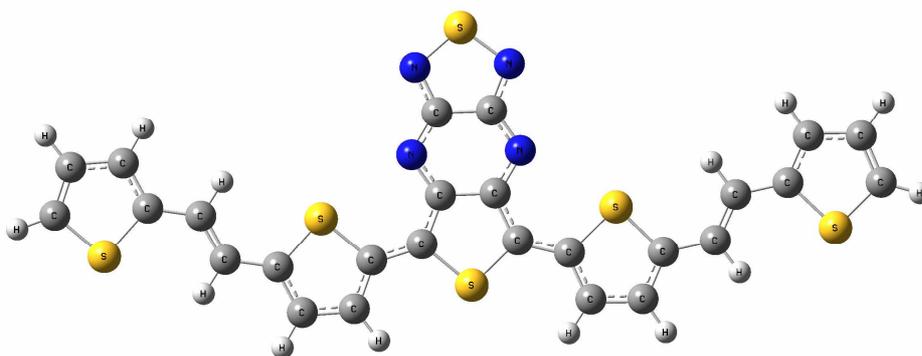
2. Theoretical methodology

The geometries of the studied compounds have been fully optimized at Density Functional Theory (Becke's Three Parameter Hybrid Functional using the Lee, Yang and Parr Correlation Functional B3LYP) [13]. The basis set 6-31G(d) was used for all atoms. All the optimizations were done without constraint on dihedral angles. The ground state energies and oscillator strengths were investigated using ZINDO calculations on the fully DFT optimized geometries. The calculations were carried out using the Gaussian 03 program [14]

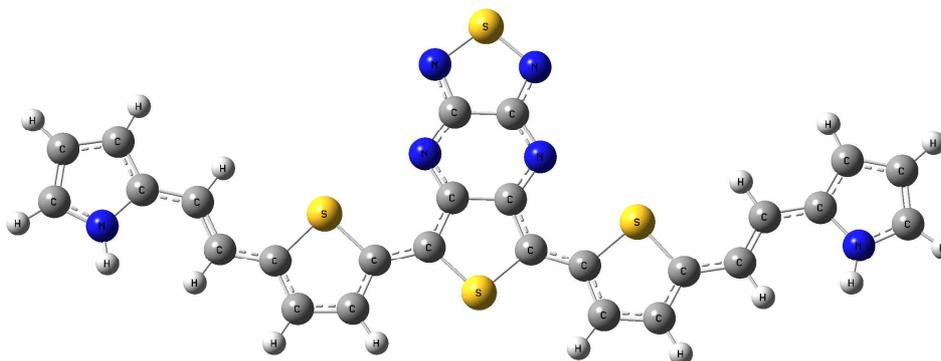
3. Results and discussion

The sketch map of studied structures is depicted in fig.1 and the optimized geometries obtained by B3LYP/6-31G(d) of the studied molecules are plotted in fig 2. Table 1 lists the theoretical electronic properties parameters (HOMO, LUMO, Gap). Calculated band Gaps were in the range 0.7-0.9 eV.

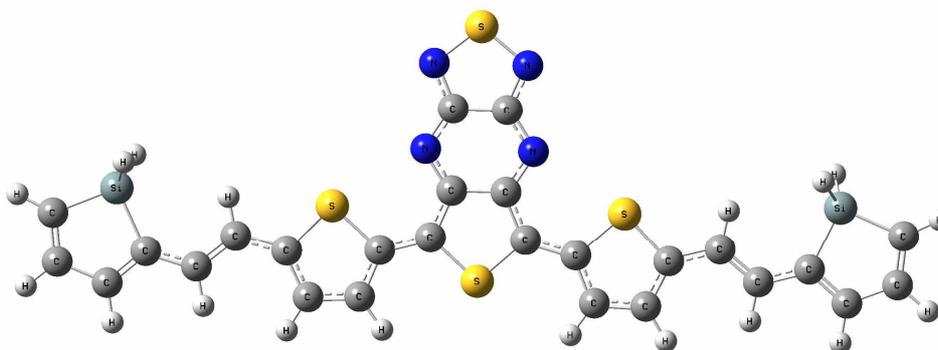
The calculated parameters (LUMO, HOMO, Gap) of, P2, P3, P4 and P5 are (-3.532, -4.423, 0.791 eV), (-3.724, -4.571, 0.847 eV), (-3.564, -4.361, 0.797 eV) and (-3.668, -4.513, 0.845 eV)) respectively. As compared with P1 (-3.722, -4.585, 0.863 eV), when we substituted the two thiophene rings by other heterocyclic compounds (pyrrole, silol, ethylenedioxythiophene, furan) , we showed systematic destabilization of the HOMO and LUMO levels and reduction of band Gap. This destabilization is attributed to the electron-donating substituted groups. On the other hand, the calculated parameters (LUMO, HOMO, Gap) of P6 are (-3.846, -4.754, 0.908 eV). As compared with P1 (-3.722, -4.585, 0.863 eV), the substitution by an electron withdrawing group (benzo[1,2,5]thiazole) leads to a systematic stabilization of the HOMO and LUMO levels and increase of the band Gap.



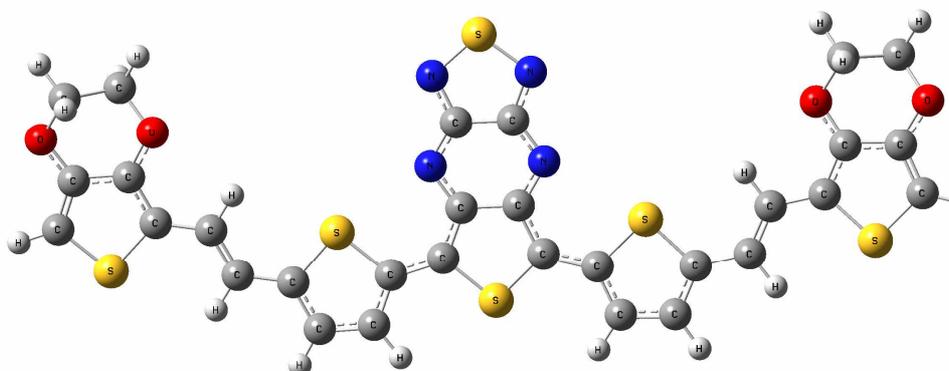
P1



P2



P3



P4

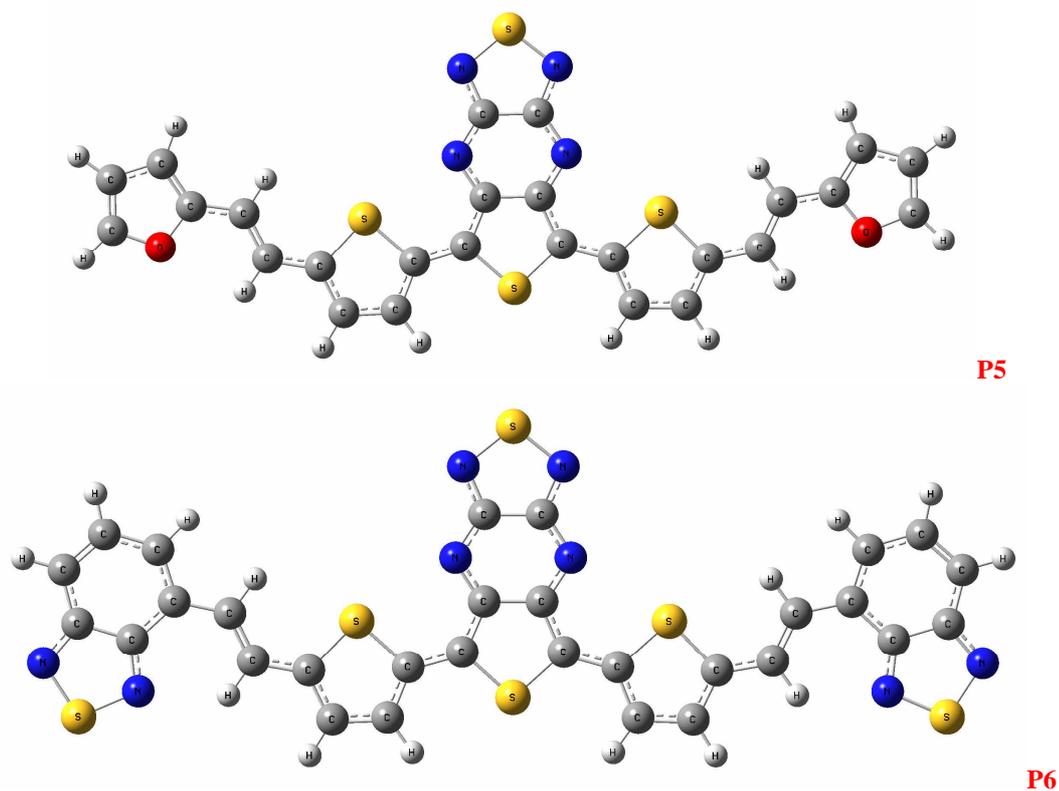


Fig.2: optimized geometries obtained by B3LYP/6-31G(d) of the studied molecules

Table 1: Theoretical electronic properties parameters (HOMO, LUMO, Gap) obtained by B3LYP/6-31G(d) of the studied molecules

Compounds	E_{LUMO} (eV)	E_{HOMO} (eV)	E_{gap} (eV)
P1	-3,722	-4,585	0,863
P2	-3,532	-4,323	0,791
P3	-3,724	-4,571	0,847
P4	-3,564	-4,361	0,797
P5	-3,668	-4,513	0,845
P6	-3,846	-4,754	0,908

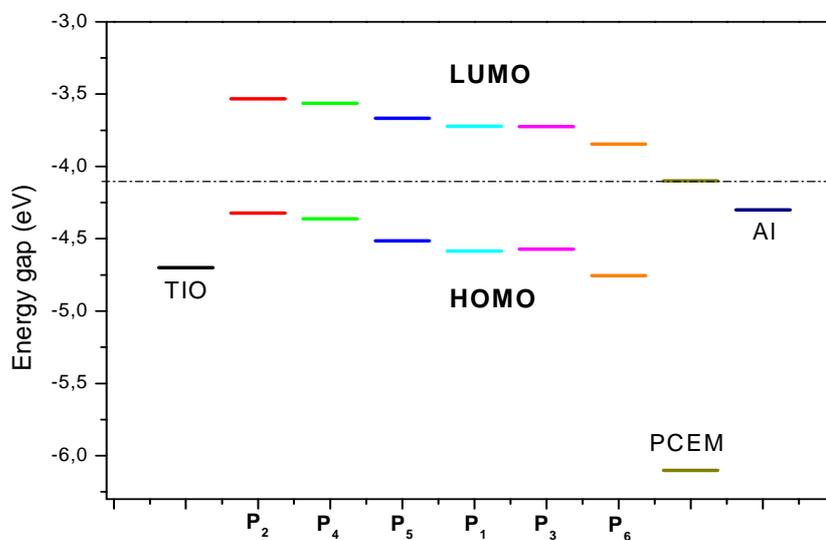


Fig. 3 : Data of absolute energy of the frontier orbital HOMO & LUMO for P1, P2, P3, P4, P5, P6 and ITO, PCEM

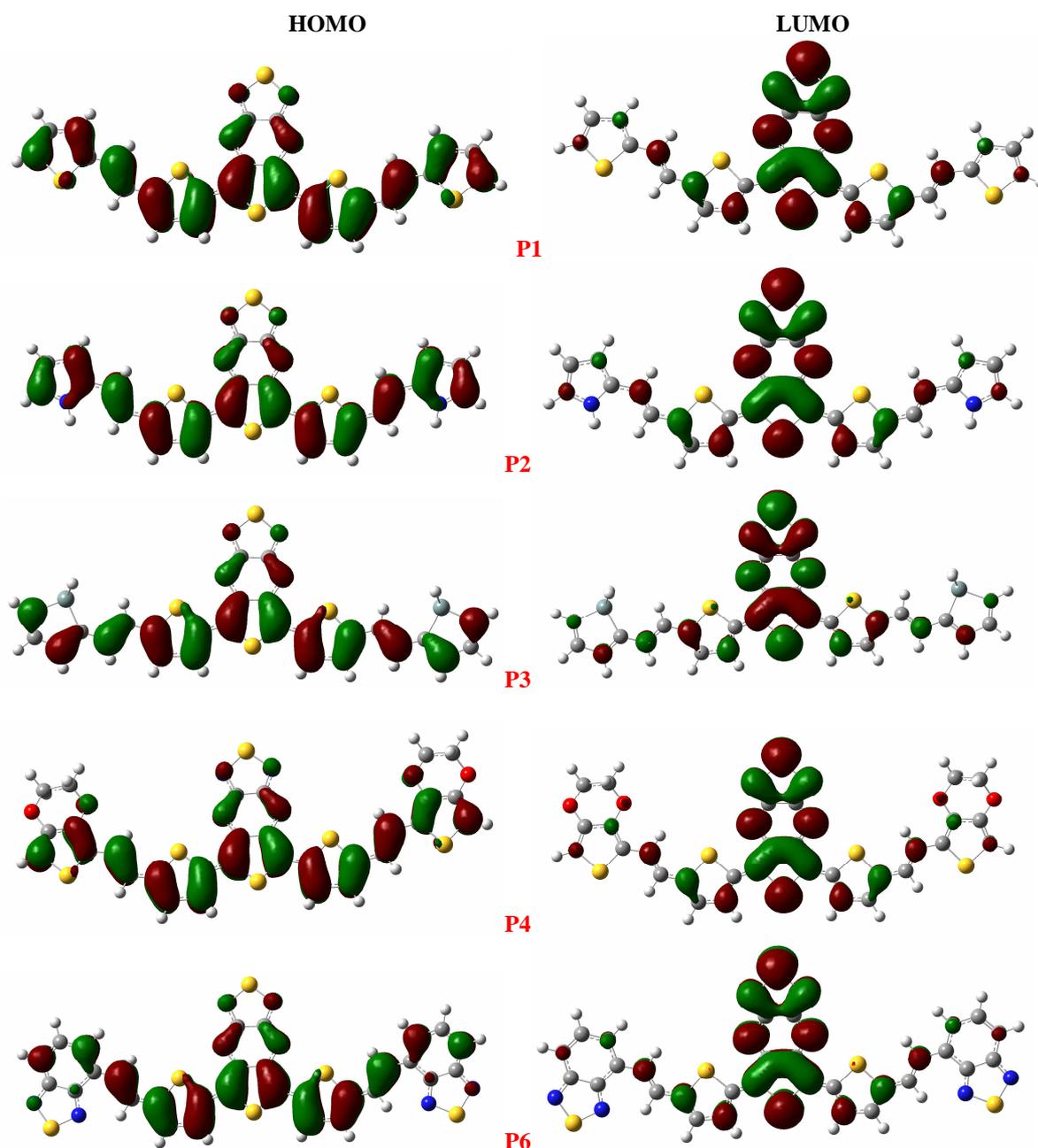


Fig. 4. Sketch of B3LYP/6-31G(d) calculated energies of the HOMO, LUMO level of studied molecules.

The calculated band gap E_{gap} of the studied compound increases in the following order $P2 < P4 < P5 < P3 < P1 < P6$. Fig. 3 shows detailed data of absolute energy of the frontier orbital for P1, P2, P3, P4, P5, P6 and ITO, PCEM (C60), Al is included for comparison purposes. It is deduced that substitution of thiophene by another aromatic or heterocyclic rings pushes up/down the HOMO/LUMO energies in agreement with their electron donor/acceptor character. To evaluate the possibilities of electron transfer from the excited studied molecules to the conductive band of PCEM. The HOMO and LUMO levels were compared. As shown in table 1, the change of the electron-donor shows a great effect on the HOMO and LUMO levels. The experiment phenomenon was quite consistent with previous literature [15], 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 PCEM. As shown in Fig.3, both HOMO and LUMO levels of the studied molecules agreed well with the requirement for an efficient photosensitizer. On one hand, the HOMO levels of the studied compounds P_i ($i=1-6$) were higher than that of PCEM. On the other hand, the LUMO levels are higher than that of PCEM (conduction band of C60). The difference E_{gap} between the energy of conduction band (LUMO) of PCEM and the energy of LUMO of the studied molecules P_i ($i=1-6$) range from 0.25-0.56.eV (Table 2). Provided that energy gap of 0.2 eV is necessary for efficient electron injection, these driving forces are sufficiently large for effective electron injection. Therefore, the six studied molecules can be

used as sensitizers because the electron injection process from the excited molecule to the conduction band of PCEM and the subsequent regeneration are feasible in organic sensitized solar cell.

We have demonstrated that there is a systematic change of the HOMO and LUMO energies into the backbone causing a destabilisation for HOMO and LUMO levels and lowering the energy band gap. On the other hand, it will be useful to examine the HOMO and the LUMO for these studied molecules because the relative ordering of occupied and virtual orbital provides a reasonable qualitative indication of excitation properties and provides also the ability of electron hole transport. In general, and as plotted in figure 4, (LUMO, HOMO); the HOMO possesses an antibonding character between the consecutive subunits. On the other hand, the LUMO of all studied compounds generally shows a bonding character between the subunits

4. Conclusion

The six studied molecules can be used as sensitizers because the electron injection process from the excited molecule to the conduction band of PCEM and the subsequent regeneration are feasible in organic sensitized solar cell. Actually related experimental works also confirmed the above computational results. This calculation procedure can be used as a model system for understanding the relationship between electronic properties and molecular structure and also can be employed to explore the potential EL device and their application; Presumably, the procedures of theoretical calculations can be employed to predict the electronic properties on the other materials, and further to design novel materials for organic solar cells.

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