New π-Conjugated Materials Based on Thienopyrazine As Organic Dye Sensitizers for Organic Photovoltaic Device Applications

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Abstract. In this work, new organic donor-π-acceptor molecules based on thienopyrazine is designed and reported. Diverse side based electron groups were presented to evaluate their impacts on the electronic and photovoltaic properties. The calculations of ground state were done by employing the DFT-B3LYP/6-31G(d,p) and the TD-DFT method for the excitation properties of the produced molecules. The results indicated that the “HOMO” and “LUMO” level are slightly changed and this suggests that there are different structures, playing important roles in improving the electronic and photovoltaic properties and in improving the electron accepting ability. The attained values of band gap together with the open circuit voltage are parameters that can be manipulated to improve the quality of solar cell applications. Moreover, the results showed that these molecules can be used for a solar cell as organic sensitizers due to probability of the electron injection process from the molecules to the conduction band of PC60BM, PC70BM or TiO2, in addition to the help of the compounds in designing more effective functional photovoltaic organic materials.

Keywords: Thienopyrazine, DFT, π-conjugated, Open circuit voltage, LHE.

1. Introduction

The dye-sensitized of solar cells system (DSSCs) is one of the greatest hopeful photovoltaic devices for transforming energy rising from solar to electricity. In 1991, the DSSCs are firstly developed by O'Regan and Grätzel, which are among the inexpensive alternatives to establish solar cells[1,2]. The dye-sensitizers show a significant role in DSSCs that have an important impact on the transport efficiency of electrode and photoelectric conversion [2,3]. Many attempts have been focused on developing materials that are stable applications having easily work, conductions’ states, relatively modest to produce an inexpensive cost and use of flexible and lightweight materials such as electroluminescent devices, batteries, photovoltaic and organic field effect transistors [2,3,4]. The research of novel materials based on π-conjugated molecules as dye-sensitized of solar cells has developed as one of the most remarkable topics in the fields of physics, chemistry and material sciences [5]. The properties of π-conjugated molecules have paid a great and an important attention for their use in apparent conductors, light emitting diodes, semi-conductor layers and photovoltaic cells in the field of effect transistors. A key feature of these new semiconductors is that employment of the chemical properties allows control of the band gap [4,5,6]. A prolific approach includes the combination of hetero atomic moieties into the conjugated structures. Benzothiaphosphole or benzoazaphosphole is a sample of conjugated
coordinate heterocyclic organophosphorus composites which are analogous to benzothiazole or benzoxazole, a unique tunable band gap, electro-optical properties and easy device fabrications. In recent times, these materials found a greater significance in different technological applications [6,7,8]. Additional developments in dye-sensitizers design will perform a crucial part in the ongoing optimization of DSSCs, and it will be influenced by the quantitative information of DSSCs [2,9]. In this work, eight π-conjugated molecules design based on thienopyrazine by using density function theory (DFT), where introduced different electron side groups to examine their effects on the properties and electronic structure of new compounds. Consequently, the theoretical examinations of the physical properties and structure of DSSCs are very significant in order to disclose the correlation between the performance, structures and the properties. It is furthermore useful to design and synthesis new dye-sensitizers with greater performance.

2. Computational Methods

The calculations and designs of all π-conjugated molecules series have been implemented via the Gaussian 09 package with the Gauss View 5.0.8 programs in the gas phase [10]. The relaxed structures and electronic structure of compounds were calculated through taking the DFT at the three parameters (B3LYP) hybrid functional “Lee-Yang-Parr” with a 6-31G (d,p) basis sets for all atoms in the ground state [11,12]. The excited states properties, oscillator strengths and excited transition states structures were in relations of excitation transitions between the occupied and virtual orbitals of the new molecules structures investigated through the time dependent DFT [11,13]. Actually, these computation methods have been effectively functional to other conjugated compounds [14].

3. Results and Discussion

3.1 Geometric Structures

Figure 1. represents sketch map geometric and relax structures of the eight π-conjugated molecules based on thienopyrazine under study labeled “M1, M2, M3, M4, M5, M6, M7 and M8” that are suggested as a dye-sensitized for solar cells. The calculations showed that there are no founding imaginary frequencies; this means that the relaxed geometries are energy minima. The virial ratio (-V/T) lies in the experimental value for hydrogen atom (2.0032); the results are due to that DFT takes in the account of all the corrections of the interaction between electrons in the structure and efficient theoretical DFT method in determining the geometrical optimization for structure. This result means that the suitable choice of basis was used to describe the molecules under study. The calculated bond length and bond angles between carbon and hydrogen atoms are compatible with experimental values of the aromatic carbon rings as well as the values of N-C distances. In addition, N-C-C angles are in a good agreement with the pyridine, pyrimidine and pyrazine [15,16]. In general, the result shows that the range bond lengths (C=C)= 1.3788-1.4212Å, (C-C)= 1.3621-1.570Å, (C-H)= 1.0890-1.0915Å, (N-C)= 1.30721-1.3206Å, (N=N)= 1.3366 -1.3386Å, (S-C)= 1.7872-1.7725Å and (O-C)=1.299-13005Å exhibits a delocalized π-bond character for molecules M1-M8[17]. As the geometric parameters investigating, it can be seen that, there is no important changes in the structure parameters. This deviation can be expected due to the strict interaction coming from the presence of molecule at the terminal ends of the thienopyrazine.
3.2 The Electronic Properties

The frontier molecular orbital energies “highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO)” and the energy gap (Egap) are very significant factors to govern whether effective charge transfer will occur between donor and acceptor. Moreover, the HOMO, LUMO and Egap play a very significant character in determining stability of the compound, optical, chemical reactivity and electrical properties. It is concluded that the adaptation of structure pushes up/down the “HOMO” and “LUMO” energy in covenant with their electron donor/acceptor property. Figure 2. indicates the electronic structures of orbitals “HOMO and LUMO” of the compounds Mi (i=1-8) and all these new molecules have good electron separated states. The conjugated compounds are described by gap between HOMO and LUMO level, which is the outcome of an important degree of inter-molecular charge transfer from the end overlaying electron (donor) groups to the effective electron (acceptor) groups through a π-conjugated path. The use of π-conjugated molecules arrangements based on thienopyrazine is a selection for qualities that are current to the thienopyrazine ring [18]. The information about the electronic properties and optical of these novel molecules can assist in the intention of new molecules with optimized characterizations for the design solar energy conversion. Table 1. states the electronic properties (E_{HOMO}, E_{LUMO} and E_{gap}) for the studied molecules Mi (i=1-8), PC60BM, PC70BM and TiO2 that are involved in the comparison purposes. The energy gaps were found in the range of 1.9856–2.4101eV. We noted the E_{gap} of the studied compounds that increase in order M3<M5<M2<M8<M6<M7. Furthermore, we showed that the E_{gap} of the molecules (M3, M2 and M5) are the low values. We can explain that these results by the electron donating affect the substituents groups.
Table 1. The electronic properties ($E_{\text{HOMO}}$, $E_{\text{LUMO}}$ and $E_{\text{gap}}$) for the studied molecules $M_i$ ($i=1-8$).

| Molecular | $E_{\text{HOMO}}$ (eV) | $E_{\text{LUMO}}$ (eV) | $E_{\text{gap}}$ (eV) |
|-----------|----------------|----------------|----------------|
| M1        | -5.441         | -3.259         | 2.181          |
| M2        | -5.421         | -3.319         | 2.101          |
| M3        | -5.203         | -3.217         | 1.985          |
| M4        | -5.407         | -3.292         | 2.114          |
| M5        | -5.314         | -3.178         | 2.136          |
| M6        | -5.684         | -3.353         | 2.330          |
| M7        | -5.706         | -3.296         | 2.410          |
| M8        | -5.485         | -3.275         | 2.210          |
| PC60BM    | -6.1           | -3.700         | ------         |
| PC70BM    | -5.8           | -3.83          | ------         |
| TiO$_2$   | -5.928         | -3.9           | ------         |

Figure 2. The contour plots of frontier molecular orbital of all molecules under study.

3.3. The Photovoltaic Properties

In order to study the photovoltaic characteristics of the investigated molecules, it is scientifically necessary to assess the possibility of electronic transition from the excited state to the LUMO “conduction band” the acceptor from molecules. It is significant to note from Table 1. that the LUMO energies of the new studied molecules dyes are greater than that of the LUMO energies “conduction...
band” of the acceptor PC60BM (-3.7eV), PC70BM (-3.83eV) and TiO2 (-3.9eV) [19-21]. The HOMO energy levels of all examined molecules are higher than the PC60BM (-6.1eV), PC70BM(-5.8eV) and TiO2(-5.928eV) conduction band edge, highlighting that the photoexcited electron transfers from M(i=1-8) molecules to PC60BM, PC70BM and TiO2 that may be adequately efficient to be advantageous in photovoltaic devices. The open circuit voltage $V_{oc}$ has been discovered to be linearly depended on the energy the HOMO of the donor and the energy of LUMO of the acceptor [19,20].

Table 2. clarifies the calculation of the VOC for investigating the correlation between VOC and energy of LUMO of the studied dyes based on electron injection from LUMO level to the conduction band of PC60BM, PC70BM or TiO$_2$ as in the following equation [20,21]:

$$V_{oc} = |E_{HOMO} \text{(Donor)}| - |E_{LUMO} \text{(Accepter)}| - 0.3$$

(1)

The resulted values of $V_{oc}$ to the Eq. (1) in the range (1.203-1.706 eV) for PC60BM; (1.073-1.576 eV) for PC70BM and (1.506-1.003 eV). These values of molecules are efficient for a probable electron injection. Consequently, all the current dyes can be used as sensitizers for solar cells since the process of electron injection is possible from the studied compound to the LUMO of PC60BM, PC70BM and TiO$_2$.

Table 2. The $V_{oc}$ (eV), $\alpha$ (eV) and LHE of the studied days Mi(i=1-8).

| Molecular | PC60BM | PC70BM | TiO$_2$ | LHE |
|-----------|--------|--------|--------|-----|
|           | $V_{oc}$ (eV) | $\alpha$ (eV) | $V_{oc}$ (eV) | $\alpha$ (eV) | $V_{oc}$ (eV) | $\alpha$ (eV) |
| M1        | 1.441  | 0.440  | 1.311  | 0.570  | 1.241  | 0.640  | 0.858 |
| M2        | 1.421  | 0.380  | 1.291  | 0.510  | 1.221  | 0.580  | 0.638 |
| M3        | 1.203  | 0.482  | 1.073  | 0.612  | 1.003  | 0.682  | 0.401 |
| M4        | 1.407  | 0.407  | 1.277  | 0.537  | 1.207  | 0.607  | 0.748 |
| M5        | 1.314  | 0.522  | 1.184  | 0.652  | 1.114  | 0.722  | 0.839 |
| M6        | 1.684  | 0.346  | 1.554  | 0.476  | 1.484  | 0.546  | 0.882 |
| M7        | 1.706  | 0.403  | 1.576  | 0.533  | 1.506  | 0.603  | 0.917 |
| M8        | 1.485  | 0.424  | 1.355  | 0.554  | 1.285  | 0.624  | 0.912 |

In Table 2, the parameter $\alpha$ (eV) represent the variance between the LUMOs energies of the studied molecules and the LUMOs energies of PC60BM, PC70BM and TiO$_2$. The calculated values of $\alpha$ are in the range from 0.346 to 0.522eV/PC60BM, from 0.476 to 0.652eV/PC70BM and from 0.546 to 0.722 eV/TiO$_2$. These values suggest that the photoexcited electron transfers from the molecules Mi to PC60BM, PC70BM and TiO2 that may be efficient to be useful as an active layer in organic solar cells devices [22].

The performance of a solar cell that is the conversion of solar to electric efficiency is reliant on light harvesting efficiency “LHE” that helps in light absorbance by the dye-sensitized PC60BM, PC70BM or TiO$_2$ film. The LHE can be counted with the assistance of oscillator strength ($f$) from TD-DFT method by using the following equation:

$$LHE = 1 - 10^{-f}$$

(2)

We can note from Table 2, that the highest LHE of eight dyes was 0.917 for M7 and M8 with value 0.912 than M6, M1, M5, M4, M2 and M3 that refer to the molecules M7 and M8, which could harvest more light leading to better performance of a cell.

The excitation state of the molecules was studied and investigated using TD-DFT/B3LYB with 6-31G (d, p) basis sets. The UV–Vis. spectra of the compounds represent the key factor for the molecules that can have applications since the photovoltaic materials is the examined compounds.
corresponding to the solar spectrum. The resultant simulated UV–Vis spectra of compounds Mi (i=1-8), obtainable as oscillator strength against wavelength, are displayed in Figure 3. As demonstrated in Table 3, the values of absorption energy are (E_{abs}) in eV, absorption wavelength (\lambda_{max}) in nm, oscillator strength (O.S), the main transitions (HOMO→ LUMO) and the molecular transition characters %. We can examine in Table 3, the calculated wavelength \lambda_{max} of the dyes under study increases as the following order: M2 > M4 > M5 > M3 > M2 > M1 > M8 > M7. This order according to properties and terminal molecular is connected to \pi-conjugated. This remarkable point is seen both by investigating electronic and absorption results. All current molecules have energy gaps as for semiconductor materials. Furthermore, the results indicated that the lowest singlet electronic excitation is described as a typical \pi→\pi^* transition.

Table 3. The excitation properties for the molecules using B3LYB/TD-DFT/6-31G (d, p).

| Molecular | E_{abs} (eV) | \lambda_{max} (nm) | O.S | Transitions | Transition Characters |
|-----------|--------------|--------------------|-----|-------------|----------------------|
| M1        | 2.1643       | 572.874            | 0.8494 | HOMO→ LUMO | 96%                  |
| M2        | 1.8178       | 682.872            | 0.4417 | HOMO→ LUMO | 89%                  |
| M3        | 1.9816       | 627.032            | 0.2227 | HOMO→ LUMO+1 | 87%               |
| M4        | 1.8117       | 681.351            | 0.6002 | HOMO→ LUMO | 98%                  |
| M5        | 2.1901       | 566.291            | 0.7935 | HOMO→ LUMO | 91%                  |
| M6        | 2.6189       | 471.121            | 0.9292 | HOMO→ LUMO | 98%                  |
| M7        | 2.5895       | 478.422            | 1.0814 | HOMO→ LUMO | 99%                  |
| M8        | 2.2112       | 561.269            | 1.0573 | HOMO→ LUMO | 97%                  |

Figure 3. The UV–Vis. spectra of the compounds Mi (i=1-8) at TD-DFT/B3LYB/6-31G (d, p).
4. Conclusions

As a conclusion, the calculated geometric properties were compatible with experimental values; this refers to the method that is used for the relaxation of all studied molecules that is a convenient and steady method. The HOMO, LUMO level, and energy gap were well controlled by the acceptor strength. It has been found that the range band gaps (2.410-1.985) eV within the semiconductor, making a correspondence to the solar spectrum of the absorbtion energy and wave length. In addition, the values of Voc range (1.203- 1.706)eV in the state of PCBM, 1.073-1.576eV in the case PC70BM and1.003-1.506 eV in the case TiO2; these values are enough for a possible efficient electron injection. Moreover, LHE is the efficiency of dye to response the light. The high LHE was 0.917 for molecular M7. Further, the UV–Vis. absorption properties are maximized in the range of 682.872–471.121 nm. An another result is that the acceptor strength and the stable geometry are meaningfully contributing to the electronic features of alternating donor-acceptor conjugated copolymers. Finally, the quantum calculations processes can be applied to calculate the electronic properties on other molecules, and additional to design new materials for organic solar cells applications.

5. References

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