

Theoretical study of new materials based on thiophene for Solar Cells

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Summary

The search for renewable energy currently leads the development of photovoltaic cells where organic conductive materials can play a vital role due to their ability to separate the electron-hole pairs and carry these loads to the electrodes in specific electronic configurations.

In this work, Theoretical study on the geometries, electronic properties and absorption spectra of these five conjugated compounds based on thiophene are studied by Density Functional Theory (DFT) method at B3LYP level with 6-31G(d,p) basis set. The absorption properties were calculated starting at the optimized structures are calculated using TD-B3LYP/6-31G(d,p) method. The HOMO, LUMO, Gap energy, Voc, ionization potentials (IP)/electron affinities (EA) and λ_{max} of these compounds have been calculated and reported in this paper. The objective of this study; is to evidence the relationship between chemical structure of these organic materials and their properties optoelectronic and photovoltaic of ways has conceive thereafter the compounds with effective character for solar cells.

Introduction

Solar energy has proven capacity to match the world's increasing energy needs [1]. Although several types of inorganic and organic materials, including semiconductors [2] and conducting polymers [3] are introduced in the materials of solar cell. Low band gap conjugated polymers are promising for the development of organic solar cells because of their improved solar light harvesting ability [4]. Organic semiconductors incorporated into solar cells have gained more and more attention due to the increasing energy needs in the world. Bulk heterojunction polymer solar cells (PSCs), which are based on solution-processable conjugated polymer donor and fullerene derivative acceptor materials, have attracted much attention in recent years, due to their advantages of easy fabrication, simple device structure, low cost, light weight, and capability to be fabricated into flexible devices. To date, power conversion efficiencies (PCEs) of 10% have been achieved for bulk heterojunction (BHJ) organic solar cells (OSCs) through the molecular structure modification and device optimization [5]. In this context, we present herein theoretical study of the structural and optoelectronic properties of new donor systems based on thiophene Ti (i=1, 2., 5) shown in Figure 1, The geometries, electronic properties and absorption of these studied compounds are studied by using density functional theory (DFT) and (TD-DFT) with the aim to evidence the relationship between molecular structure and optoelectronic properties. The theoretical knowledge of the HOMO and LUMO energy levels of the components is basic in studying organic solar cells so the HOMO, LUMO, ionization potentials (IP)/electron affinities (EA), gap energies and Voc (open circuit voltage) of the studied compounds have been calculated and reported. The obtained properties suggest these materials as a good candidate for organic solar cells.

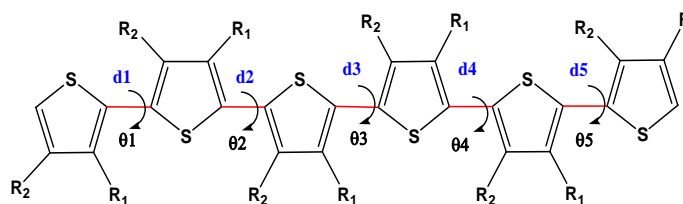


Fig:1: Structure of the studied molecules.

Compounds	R1	R2
T1	CH3	H
T2	C6H5	H
T3	mCH3-O-C6H5	H
T4	CH2-O-CH3	H
T5	(CH2)-O-(CH2)2-O-CH3	H

Theory and/or Method

DFT method of three-parameter compound of Becke (B3LYP)[6] was used in all the study of the neutral and polaronic compounds. The 6-31G (d,p) basis set was used for all calculate ions [7]. To obtain the charged structures, we start from the optimized structures of the neutral form. The molecular geometries and the electron density of states distribution of the compounds were simulated by using density functional theory (DFT). The DFT calculations were performed using Gaussian 09 [8] with a hybrid B3LYP correlation functional and a split valence 6-31G (d,p) basis set[9]. The HOMO, LUMO, ionization potentials (IP)/electron affinities (EA), and the gap energies were deduced from the stable structures, where the energy gap is the difference between LUMO and HOMO levels. The absorption properties were calculated starting at the optimized structures using TD-DFT/B3LYP calculations.

Results and discussion

The results of the optimized structures (fig.1) for all studied compounds so that they have similar conformations (quasi planar conformation). We found that the modification of several groups attached to the basic molecule does not change the geometric parameters.

1. Optoelectronic properties

The experiment showed that the HOMO and LUMO energies were obtained from an empirical formula based on the onset of the oxidation and reduction peaks measured by cyclic voltametry [10]. But in theory, the highest occupied molecular orbital (HOMO), the lowest unoccupied molecular orbital (LUMO) energy levels, can be calculated by DFT calculations. In order to have the electronic properties of all molecules, we calculated HOMO and LUMO energy levels and the band gap (E_{gap}) energies of the studied molecules. In Table 1, we listed the calculated energies for the HOMO and LUMO energies of T1 to T5 at neutral and doped compounds. It can also be found that, the HOMO and LUMO energies of the studied compounds are slightly different. This implies that different structures play key roles on electronic properties and the effect of slight structural variations, especially the effect of the motifs branched to the molecule on the HOMO and LUMO energies is clearly seen. In addition, energy (E_{gap}) of the studied molecules differs slightly from 2, 68 eV to 3,25 eV for neutral molecule and 2,31 eV to 2,39 eV for the polaronic cationic molecule and 0,96 to 1,18 for the polaronic anionic depending on the different structures. The doping allows us to raise the conjugation and the ionic conductivity and consequently reduces energy (Gap) of the molecules.

2. Frontier Molecular Orbitals

The electronic and optical properties of molecules are related to the values of FMOs and E_{gap} . Thus, in order to gain insight into the influence of the optical and electronic properties, the distribution patterns of

the FMOs for the designed molecules are studied, and the electronic density contours of the designed molecules in ground states.

Table 1: The HOMO energy (E_{HOMO}), LUMO energy (E_{LUMO}), and energy gap (E_{gap}) in eV for ground and Doped states computed at the B3LYP/6-31G (d,p) level of theories.

Compounds	Neutral stats			cationic states			anionic states		
	E_{HOMO} (eV)	E_{LUMO} (eV)	Egap (eV)	E_{HOMO} (eV)	E_{LUMO} (eV)	Egap (eV)	E_{HOMO} (eV)	E_{LUMO} (eV)	Egap (eV)
T1	-4,62	-1,93	2,68	-7,34	-4,95	2,39	-0,04	0,94	0,98
T2	-5,00	-1,81	3,19	-7,10	-4,79	2,31	-0,51	0,49	1,00
T3	-4,92	-1,67	3,25	-6,95	-4,63	2,32	-0,43	0,54	0,96
T4	-4,96	-1,77	3,19	-7,25	-4,86	2,39	-0,27	0,85	1,11
T5	-5,01	-1,87	3,15	-7,29	-4,98	2,32	-0,48	0,70	1,18

3. Photovoltaic properties

Photovoltaic cells, or solar cells, take advantage of the photoelectric effect to produce electricity. PV cells are the building blocks of all PV systems because they are the devices that convert sunlight to electricity. Commonly known as solar cells, individual PV cells are electricity-producing devices made of semiconductor materials. The process of conversion is based on photovoltaic effect, by which electrons and holes are produced as the result of photoexcited electron transfer between donor and acceptor, followed by the transport of created charges to the electrodes [11]. The structure of an organic photovoltaic device bulk-heterojunction PV devices were fabricated with a typical structure of ITO/PEDOT:PSS/Donors:PCBM/Al. (Fig.3). work we studied the photovoltaic properties of the studied molecules Ti (i= 1-5) as donor blended with [6.6]-phenyl-C61-butyric acid methyl ester (PCBM) and these Derivatives (C60, C70, C76, C78-C2V, C78-D3, C84-D3, C84-D2, C84-D2d) which are the most broadly used as an acceptor in solar cell devices.

The properties of frontier molecular orbital of polymer donor are related to the open-circuit voltage (V_{oc}) of organic solar cells and optical properties [12]. In fact, the maximum V_{oc} of the BHJ solar cell was calculated from 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-charges generation [13]. The theoretical values of the V_{oc} were determined from the following expression (Eq:1) :

$$V_{oc} = |E_{\text{HOMO}}(\text{Donor})| - |E_{\text{LUMO}}(\text{Acceptor})| - 0.3 \quad (1)$$

The theoretical values of the open circuit voltage V_{oc} of the studied compounds calculated according to the equation (4) range from (0,62eV to 1,01 eV) for PCBM C₆₀(A); (0,85 eV to 1,24 eV) for PCBM C₆₀; (0,78 eV to 1.17 eV) for PCBM C₇₀; (0.53 eV to 0,92 eV) for PCBM C₇₆; (0.38 eV to 0.77 eV) for PCBM C_{78-C2V}; (0.32 eV to 0.71 eV) for PCBM C_{78-D3}; (0.32 eV to 0.71 eV) for PCBM C_{84-D2}; (0.34 eV to 0.73 eV) for PCBM C_{84-D2d}.

Absorption properties

The TD-DFT/B3LYP/6-31G (d,p) has been used on the basis of the optimized geometry to obtain the nature and the energy of the singlet-singlet electronic transitions of all the molecules study as reported in Table 6. All electronic transitions are of the $\pi-\pi^*$ type and no localized electronic transitions are exhibited among the calculated singlet-singlet transitions.

The corresponding simulated UV-Vis absorption spectra of all compounds, presented as oscillator strength against wavelength, are shown in Figure 2.

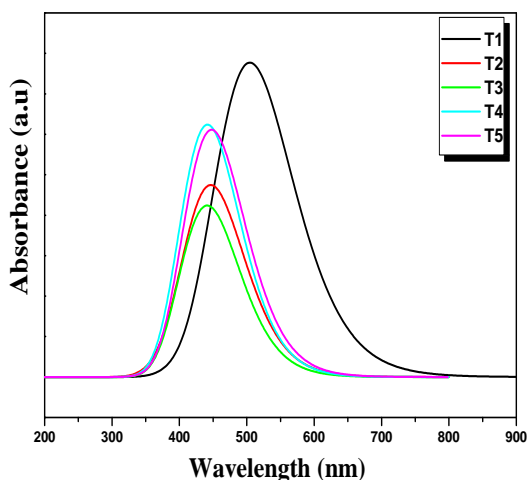


Fig. 2: Simulated UV–visible optical absorption spectra of title compounds with

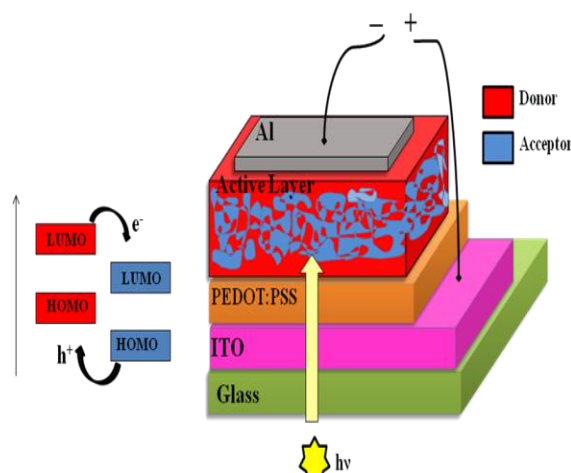


Fig. 3: Architecture of an organic photovoltaic device (BHJ).

Conclusions

In this study, the quantum chemical investigation on the geometries, electronic properties and absorption of these five molecules based on thiophene is performed in order to display the effect of molecular structure on the optoelectronic and photovoltaic properties of these materials.

These compounds we have analyzed the role of different electron-donor groups on the geometries, electronic structures and optical properties. Also, we have aimed to see the donor effects on the EHOMO, ELUMO, Egap, Voc, λ_{max} , EA and IP of the cell.

There are some design considerations when choosing an appropriate organic material. For these material would be a band gap differ slightly from 2.68 eV to 3.25 eV. On the other hand the best values of Voc indicated for the studied compounds blended with C60 or C70 and higher value are given for T5 blended with C60 (1.24 eV), and also The smaller IP of new designed compounds than thiophene are revealing that hole injection would increase. The upturns EA are illuminating that electron injection would increase by introducing the motifs (R1,R2) in the following tendency: T4<T1<T3<T2<T5.

It also makes the absorption maximum of these compounds are in the range 505, 21 to 441, 49 nm.

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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