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Investigations of New Low Gap Conjugated Compounds Based on Thiophene-Phenylene as Solar Cells Materials

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Abstract

The research in new organic π-conjugated molecules with specific properties has become one of the most interesting topics in fields of materials chemistry. These materials are promising for optoelectronic device technology such as solar cells. On the other hand, 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 this parameter of these materials is research issue of ongoing interest. In this work, quantum chemical investigation has been performed to explore the optical and electronic properties of a series of different compounds based on thiophene-phenylene. 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, Thiophene-phenlyne, Organic solar cells, DFT, Low band-gap, Electronic properties, HOMO, LUMO.*

Introduction

The π-conjugated materials based on thiophene and phenylenes were of broad interest in many areas of research in the last decade, for their interesting applications in organic electronics [1]. Among these applications, optoelectronic device technology, such as LEDS [2], Transistors (TFTs) [3] and low-cost solar cells [4]. Many researchers have become interested in synthesizing short-chain compounds based

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on conjugated molecules because they are not amorphous and can be synthesized as well defined structures [5]. More, the short conjugated molecules based on thiophene and phenylene units have attracted much attention because of their unique electronic properties, to their high photoluminescence quantum efficiency and thermal stability [6]. In order to obtain materials with more predominant capability, the development of novel structures is now being undertaken following the molecular engineering guidelines. One of the most important factors of controlling physical properties is the band-gap, which is a current topic of research; In particular materials with a low band-gap are desired in optoelectronic applications. Many experimental and theoretical attempts have been made to modify the chemical structures [7].

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. 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 [8]. Theoretical studies on the electronic structures of π-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 [9]. 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. Several syntheses of compounds designed as photo-sensitizers in dye-sensitized solar cells are described. In these studies the authors showed the effect of diversifying electron donors, π-spacers and electron acceptors on the performance of DSC's based on organic dyes [10]. The number of anchoring group is another parameter which affects the efficiency of the material.[11]. Among the donor groups, triphenylamine and its derivatives have displayed promising properties in the development of synthesis of dye sensitized solar cells. TPA- based compounds can be viewed as tridimensional (3D) systems, which can lead to amorphous materials with isotropic optical and charge-transport properties. Thus, organic small molecules based on a 3D system are viewed as one of the promising photovoltaic materials for OSCs [12]. Furthermore, the carboxylic acid group is by far the most employed group for attachment of the sensitizers to the semiconductor surface. The carboxylic function is normally used as the electron acceptor group for the attachment of the dye on the TiO_2 surface [13]. The anatase structure is preferred over other polymorphs for solar cell applications because of its higher electron mobility, low dielectric constant and lower density [14]. Due to these advantages, we designed a series of no symmetrical branched molecules based on diphenylamine as a central core and cyanoacrylic acid as the end group connected with different π-spacer groups. The designed compounds include two arms with diphenylamine as donor unit (D), cyanoacrylic acid as acceptor unit (A). The fundamental composition of D-π-A for most organic solar cells, which is propitious to obtain optimal performance, is considered. Thiophene is chosen as a π-spacer in one arm. As for the second arm, one form thiadiazolothienopyrazine (TTP), benzothiadiazole-pyrazine (BTP) and benzopyrazine-pyrazine (BPP) is chosen (Fig. 1). These Different electron π-conjugated groups were introduced to investigate their effects on the electronic structure.

In this work, quantum chemical investigation has been performed to explore the geometric, electronic and optical properties of these novel compounds with the aim to evidence the relationship between molecular structure and optoelectronic properties. This investigation was used to drive next syntheses towards compounds more useful as active materials in optoelectronic. On the other hand, 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 Voc (open circuit voltage) of the studied compounds have been calculated and reported. These properties suggest these materials as a good candidate for organicdye-sensitized solar cells.

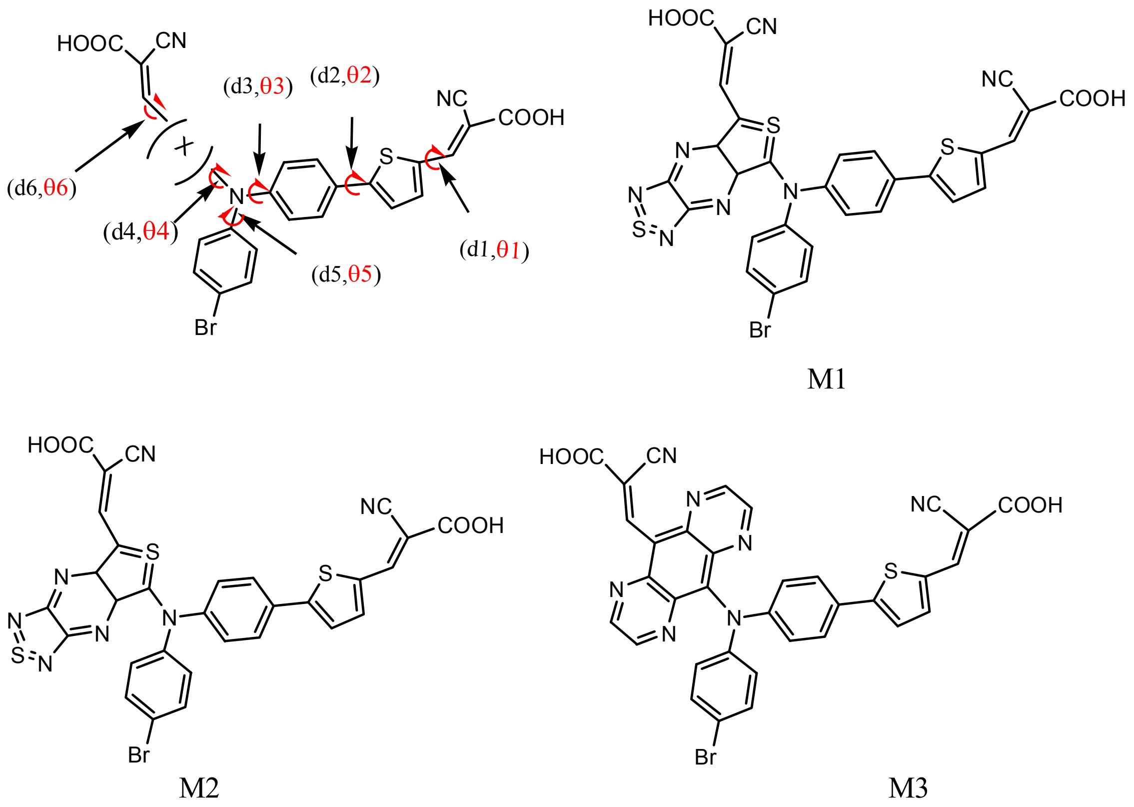


Figure 1. The sketch map of studied structures (M1, M2 and M3).

Theoretical methodology

The calculations were carried out using the GAUSSIAN 03 program [15]. The geometries of the studied molecules were optimized using density functional theory (DFT) with the B3LYP density functional and the 6-31G* basis set [16]. All optimizations were done without constraint on dihedral angles.The time-dependent DFT (TD-DFT) at B3LYP level was carried out to study the excited state of molecules[17].We have also examined HOMO and LUMO levels; the energy gap is evaluated as the difference between the HOMO and LUMO energies. The 3 lowest spin-allowed singlet transitions were involved to simulate the absorption spectra,The maximum absorption, excitation energies and oscillator strengths were investigated using the TD-DFT at B3LYP level. The graphical molecular orbital were generated with the Gauss View software program (version 3.07)

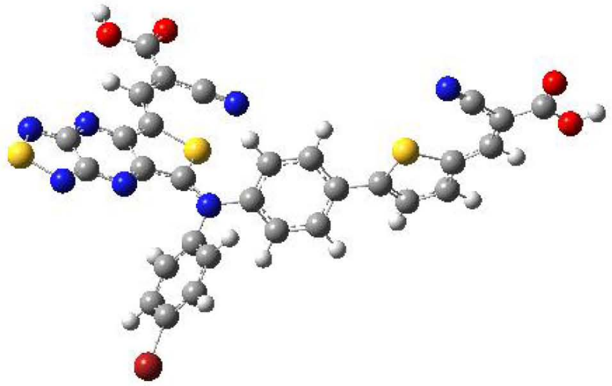
Results and discussion

Geometric properties

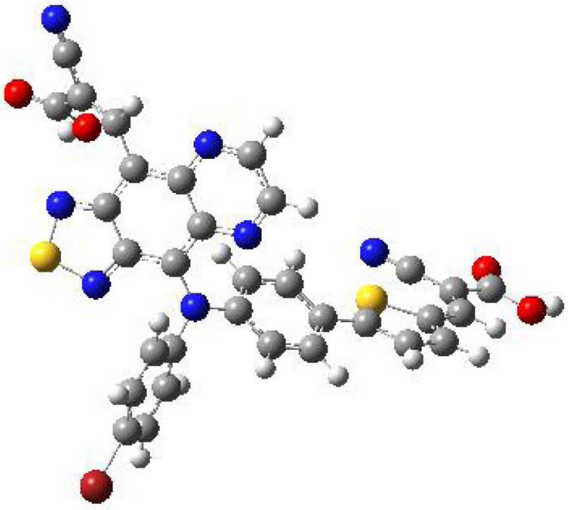
The optimized structures of all studied compounds are illustrated in figure 2. All the molecular geometries have been calculated with the hybrid B3LYP function combined with 6-31G (d) basis sets using *Gaussian 03* program suite. It was found in other works

[18, 9] 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 conformations (quasi planar conformation) (see Fig. 2). We found that the consecutive thiophene phenylene units have dihedral angles θ2 (130,8° for M1, 140,42° for M2 and 143,46° for M3) and inter-ring distances (d1=1.429 Å, d2=1.464 Å, d3=1.434 Å for M1; d1=1.427 Å, d2=1.462 Å, d3=1.420 Å for M2; d1=1.426 Å, d2=1.461 Å, d3=1.416 Å for M3). We note firstly that the dihedral angle increases from M1 to M3 and on the other hand, the incorporation of several groups does not change inter-ring distances d1 and d2 but a slight increase in the distance d3 is observed going from M1 to M3. This is probably due to greater extension of conjugation in the case of compound M3.

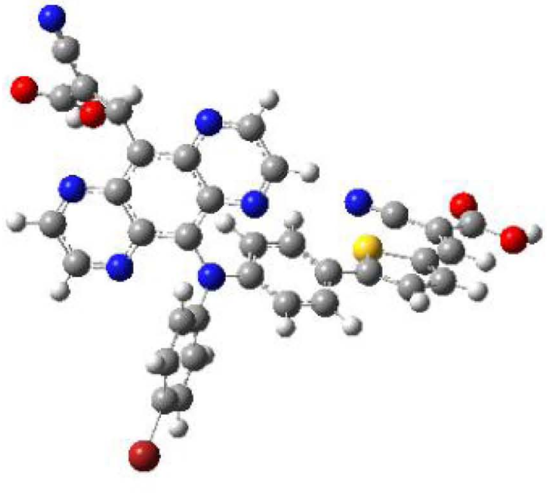
In the D-π-A system, the π-conjugated group is employed as the bridge of intramolecular charge transfer. Thus the bond length between donor moiety and acceptor π-spacer and between π-spacer and acceptor group can elucidate the interaction amid the D-π-A system. Indeed, a short bond length favors the intramolecular charge transfer. Data in table1 show that d4 is the shortest bond for all the studied compounds, this bond shows more C=C character especially for M1.this result shows that the interaction between diphenylamino group and TTP is more slightly important.



M1



M2



M3

Figure 2. Optimized structures of studied compounds (M1, M2 and M3).

Table 1. Geometric parameters of compoundsM1, M2 & M3obtained by B3LYP/6-31G(d) in their neutral states.

Molecule	d1	d2	d3	d4	d5	d6
M1	1.42933	1.46436	1.43480	1.36978	1.43453	1.41059
M2	1.42701	1.46208	1.42063	1.39709	1.42793	1.45162
M3	1.42622	1.46152	1.41635	1.40479	1.42526	1.45811

Molecule	θ1	θ2	θ3	θ 4	θ 5	θ 6
M1	27.15080	-131.80433	56.65777	-151.93	51.29	1.80
M2	-21.03037	140.4281	-40.13386	131.19	134.03	150.78
M3	-20.69239	143.46359	-37.70883	125.79	135.23	147.68

Absorption and Electronic properties

From the optimized structure obtained with the method B3LYP/6-31G(d) of each studied compound, we have calculated the UV-Vis spectra of M1, M2 and M3 using time-dependent density functional theory (TDDFT) method. As illustrated in table2, we can find the values of calculated wavelength λ_{max}, lowest excited energies, oscillator strengths (f), and compositions in terms of molecular orbital contributions. 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 $S0 \rightarrow S_1$ electronic transition increase progressively with the increasing of conjugation lengths.

Table 2. Absorption wavelength λ_{max} (nm), Excitation energies and oscillator strengths obtained by the TD-DFT method.

molecule	λ_{max} (nm)	E_{tr} (eV)	f	Contribution	Character
M1	769.11	1.6120	0.1231	59.91% H→L	CT
				12,75% H→L+2	π→π*
M2	605.59	2.0473	0.3345	61,37% H→L	CT
				14,10% H-4→L	π→π*
M3	606.05	2.0458	0.2874	64,74% H→L	CT

Data in Table 3 shows that there is a bath chromic effect in this order (M2→M3→M1),this effect is obviously due to insertion of differentπ-spacers (BTP, BPP and TTP). The band gaps of conjugated compound are governed by their chemical structures. Therefore, the detailed band gap theoretical calculations were carried out on the studied compound structures. The experiment showed that the HOMO and LUMO energies were calculated from an empirical formula proposed by J.L. Brédas et al. [19], based on the onset of the oxidation and reduction peaks measured by cyclic voltammetry. But theoretically speaking, the HOMO and LUMO energies can be calculated by DFT calculations. However, it is noticeable that solid-state packing effects are not included in the DFT calculations, which tends to affect the HOMO and LUMO energy levels in a thin film compared to an isolated molecule as considered in the calculations. All band gaps were obtained by B3LYP/6-31 G (d). The HOMO, LUMO and HOMO–LUMO gaps energies are computed in Table 3. The values of HOMO and LUMO energies of M1 to M3 shows that, which are −6.32 and -4.22; -5.71 and -3.81; -5.64 eV and -3.58eV respectively, shows significant difference between M1 and the two other compounds, but there is slight difference between M2 and M3.

This implies that different structures play key roles on electronic properties and enhancing the electron-accepting ability. In addition, the energies of Egap M1-M3 differ slightly from 1.9 eV to 2.1 eV depending on the different structures. The calculated band gap Egap of the studied compound increases in the following order M2<M3<M1.

Table 3. Values of HOMO (eV), LUMO (eV) and Eg (eV) energies calculated for, M1, M2 and M3 obtained by B3LYP/6-31G(d).

molecule	En (HOMO) (eV)	En (LUMO) (eV)	En (Gap) (eV)
M1	-6.3252	-4.2210	2.104
M2	-5.7176	-3.8175	1.900
M3	-5.6430	-3.5819	2.061

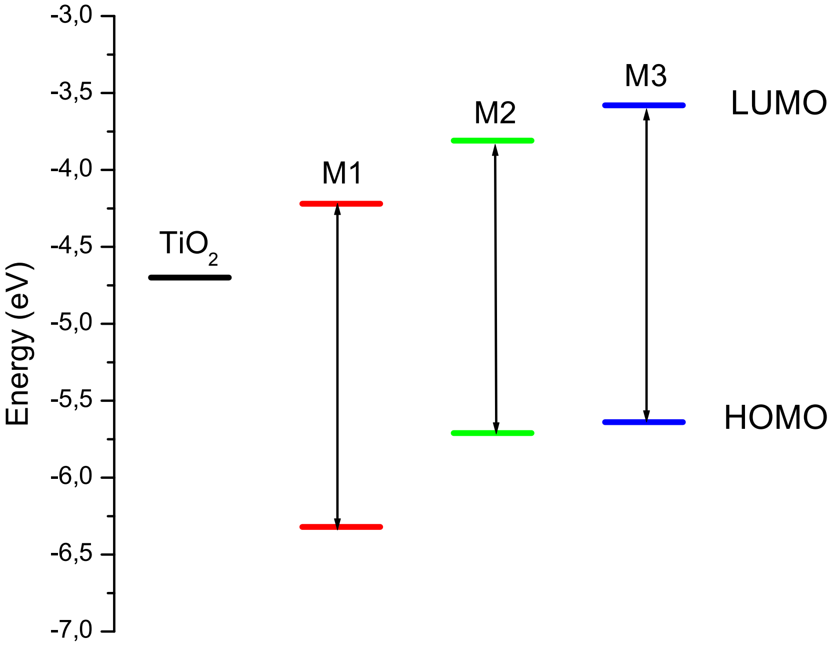


Figure 3. Schematic energy levels of the studied compounds M1, M2, M3 and the conduction band edge of TiO_2

The HOMO and the LUMO energy levels of the donor and acceptor components are very important factors to determine whether effective charge transfer will happen between donor and acceptor. Figure 3 shows detailed data of absolute energy of the frontier orbitals for studying compounds and the conduction band edge of TiO2 is included for comparison purposes. It is deduced that the nature of donor or acceptor pushes up/down the HOMO/ LUMO energies in agreement with their electron character. To evaluate the possibilities of electron transfer from the excited studied molecules to the conductive band of Titania, the HOMO and LUMO levels were compared. To effectively inject the electron into the CB of TiO2, the LUMO levels of the dyes must be sufficiently more negative than the conducing band energy (Ecb) of semiconductor, -4.7 eV (vs. NHE) [20]. As shown in figure 3, the LUMOenergy of the compound M3is higher than that of the conductive band of Titania providing sufficient thermodynamic driving for electron injection from the excited dyes M3 to TiO2 and suggesting this material for applications in photovoltaic devices [21].

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 [22]. In general, as shown in Figures 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 .The HOMO is delocalized along the two arms of the three molecules with low contribution in arm containing thiophene and cyanoacrylic acid units concerning M1.The LUMO is delocalized over the cyanoacrylic acceptor moiety through the π-conjugated bridges group with low contribution in cyanoacrylic moiety in arm1 concerning M1. The examination of the HOMO and LUMO of the three organic dyes indicates that HOMO→LUMO excitation moves the electron distribution from the arm1 to the cyanoacrylic acid unit connected tricyclic group.

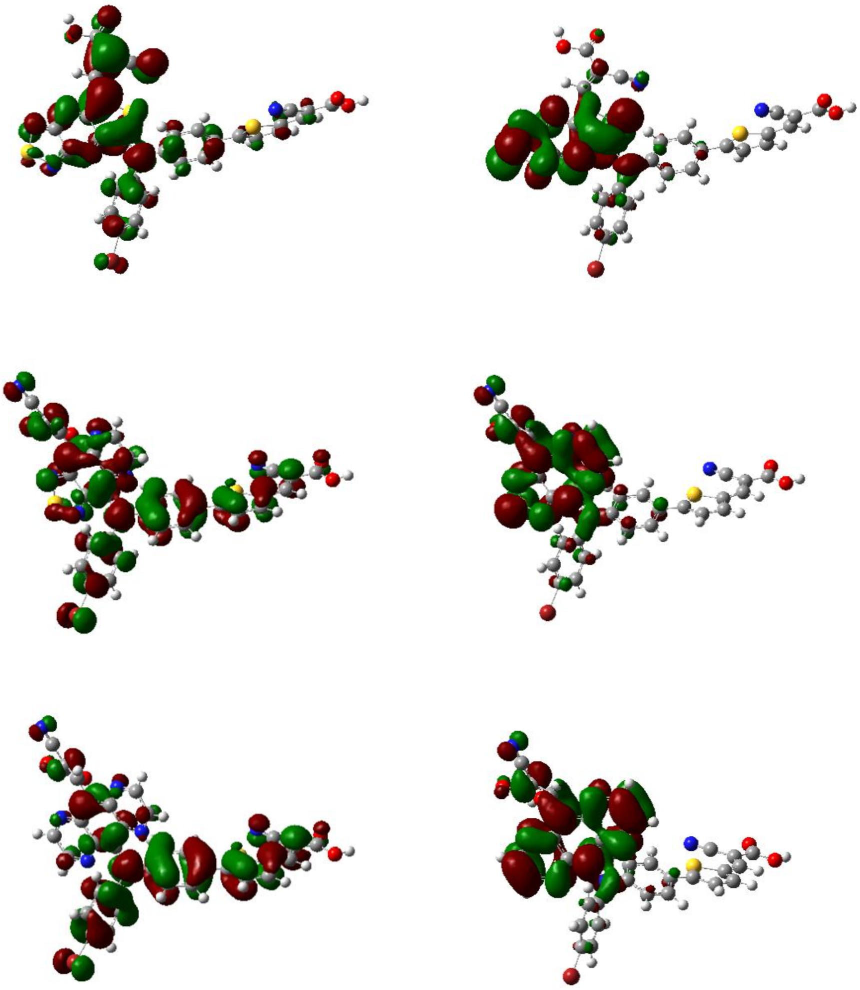


Figure 4. The contour plots of HOMO and LUMO orbitals of studied compounds M1, M2 & M3 in neutral form

Conclusions

In this study, theoretical analysis on the geometries and electronic properties of three various compounds based on thiophene-phenylene in order to display the effect of substituted groups a on the structural and optoelectronic properties of these materials. The concluding remarks are:

- The results of the optimized structures for all studied compounds show that they have similar conformations
- The calculated frontier orbital energies HOMO and LUMO and energy gaps showed that the energies gaps of the studied molecules differ slightly from 1.90eV to 2.06eV depending on the different structures. The calculated band gap Egap of the studied compound increases in the following order M2< M3< M1
- The LUMO energy of the compound M3is higher than that of the conductive band of Titania providing sufficient thermodynamic driving for

electron injection from the excited molecule M3 to TiO_2 and suggesting this material for applications in photovoltaic devices

- Thanks to small gap, all the studied molecules can be used for other electronic applications.
- 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.

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