New compounds based on anthracene for organic solar cells applications

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Abstract

The specific properties of organic-conjugated molecules and polymers are of great importance since they have become the most promising materials for the optoelectronic device technology such as solar cells. 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 the parameter of these materials is a research issue of on going interest. In this work, quantum chemical investigation was performed to explore the optical and electronic properties of a series of different compounds based on anthracene. Different electron side groups were introduced to investigate their effects on the electronic structure. The theoretical knowledge of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels of the components is basic in studying organic solar cells; so the HOMO, LUMO, Gap energy and open circuit voltage (Voc) of the studied compound shave been calculated and reported. These properties suggest these materials as good candidate for organic dye-sensitized solar cells.

Key words: π-Conjugated molecules, anthracene, organic solar cells, density function theory (DFT), low band-gap, electronic properties.

1. Introduction

The π-conjugated molecules and polymers based on heterocylcic ring and characterized by an extended π-conjugation is of broad interest in many areas of research, for their applications in organic electronics [1, 2]. Particularly in the last decade, optoelectronic device technology [1, 2], such as light-emitting diode (LEDS) [3], thin film transistors (TFTs) [4,5] and low-cost solar cells [6,7] are among these applications. Obtained polymers are highly amorphous, while oligomers are not amorphous and can be synthesized as well defined compounds. Recently, many researchers have become interested in synthesizing short-chain organic OLED compounds based on conjugated oligomers [8, 9]. Considerable efforts have been directed towards the study of the electro-optic properties of these conjugated systems, with the aim to exploit their potential as materials for stable and easy processable devices [10- 12]. These materials offer advantages over polymeric systems in terms of easy synthesis and purification, and generally exhibit high charge carrier mobility. Therefore, designing and synthesizing molecules with interesting properties play a crucial role in technology [13, 14]. 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 [15]. 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 π-conjugated compounds have given great contributions to the rationalization of the properties of known materials and to the properties prediction of those yet unknown. In this context, quantum-chemical methods have been increasingly applied to predict the band gap of conjugated systems [16- 20]. We note that theoretical knowledge of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels of the components is crucial in studying organic solar cells. So, we can save time and money by choosing the adequate organic materials to optimize photovoltaic device's 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 the 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. Recently, Marrocchi et al. [21] described the synthesis of a series of anthracene-containing semiconductors (Figure 1).
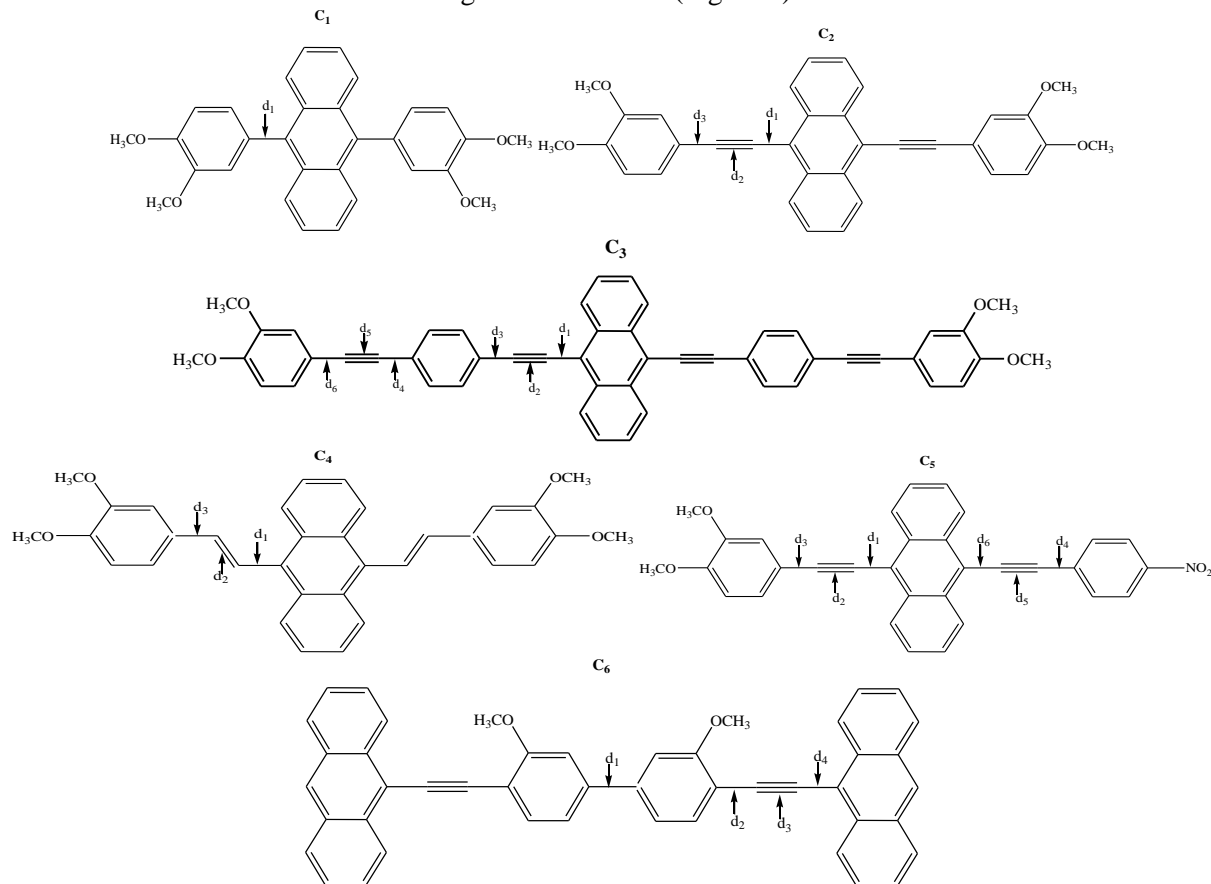
Figure 1: The sketch map of studying structures (C1, C2, C3, C4 C5 and C6)

Anthracene derivatives may exhibit large charge carrier mobility and excellent stability. To the best of our knowledge, a systematic theoretical study of such compounds has not been reported. This work shall further elucidate geometric and electronic properties with the aim to evidence the relationship between molecular structure and electronic properties, thus, driving towards the next syntheses compounds useful as active materials in optoelectronic; the quantum chemical investigation has been performed to explore the optical and electronic properties of a series of different compounds based on anthracene. 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 a basis in studying organic solar cells as the HOMO, LUMO and gap energy of the studied compounds have been calculated and reported. Their properties suggest they are good candidates for organic solar cells

2. Theoretical methodology

Density function theory (DFT) method of three-parameter compound of Becke [22] (B3LYP) was used in all the study of the neutral and polaronic compounds. The 6-31G(d) basis set was used for all calculations [23-26]. 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 [27]. The geometry structures of neutral molecules were optimized under no constraint. We have also examined HOMO and LUMO levels; the energy gap is evaluated as calculated by 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 [28].

3. Results end discussion

3.1. Molecular design and geometry structures

The optimized structures of all studied compounds are shown in Figure 2. It reveals that the π-electron delocalization between the different aromatic units is clear. For the effect of increasing additional conjugated, π-bridge are studied. The addition of end alkoxy chains to backbone might increase the materiel solubility. In addition, molecules C2 and C5 are designed in order to examine the effect of asymmetry in comparison with the corresponding ones and also the effect of the electron accepting group (NO_2) and finally in order to examine the effect of the position of anthracene compounds, molecule C6 is designed. Finally, in order to study the effect of terminating anthracene moieties on the electronic properties, the doubled end-capped dianthryl compound C6 has also been considered. All the molecular geometries have been calculated with the Hybrid B3LYP function combined with 6-31G (d) basis sets using GAUSSIAN 03 program. It was found in other works [29] that the DFT-optimized geometries were in excellent agreement with the data obtained from X-ray analysis. The results of the optimized structures for all studied compounds show that they have similar conformation (quasi planar conformation) (Figure 2). We found that the consecutive units have similar dihedral angles (180°) and inter-ring distances (d1=1.424 Å, d2=1.259 Å, d3=1.387 Å, d7=1.440 Å, d8=1.3689 Å, d9=1.482 Å) (Table 1). The incorporation of several groups does not change these parameters.
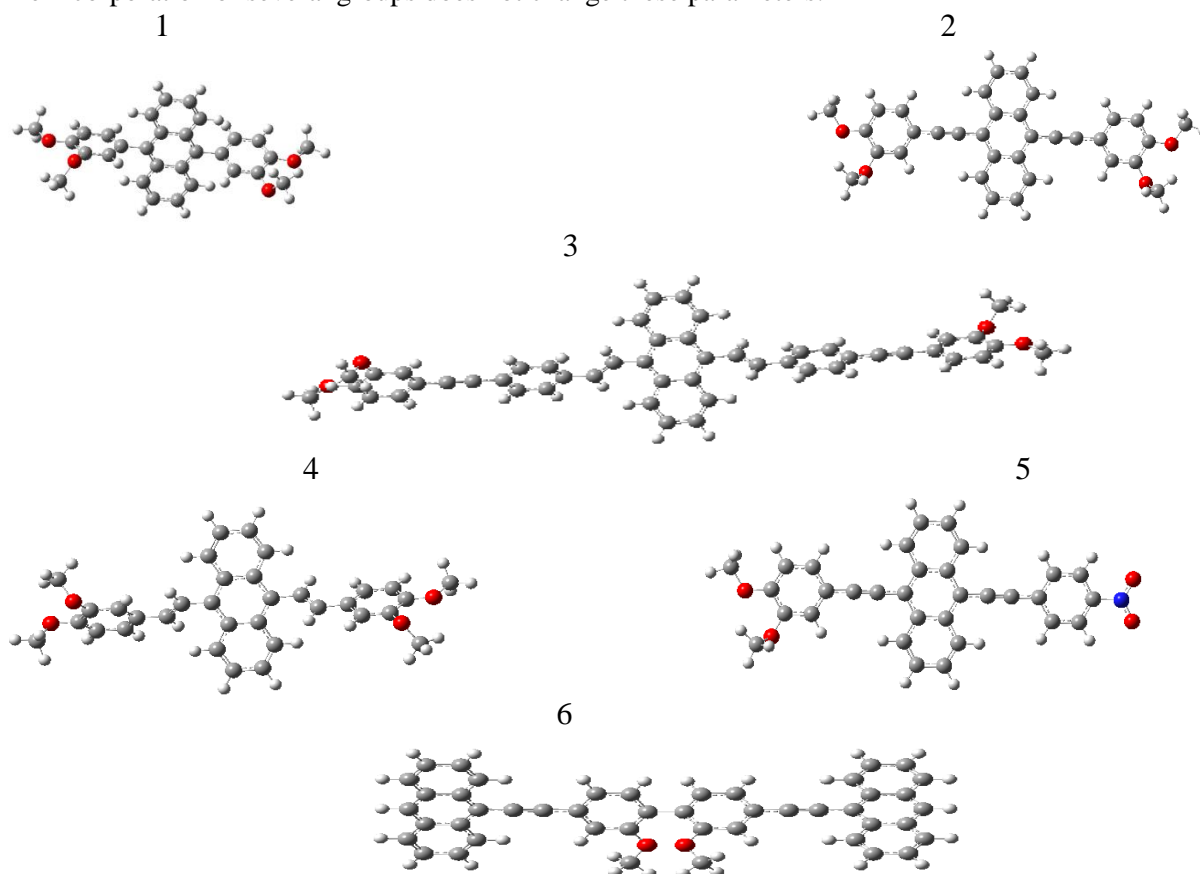
Figure 2: Optimized structure of C1, C2, C3, C4, C5 and C6 obtained by B3LYP/6-31(d) level.

Table 1: Geometrical parameters of study compounds C1 to C6 obtained by B3LYP/6-31G(d) in their neutral (N) state.

Compound state	d_1(Å)	d_2(Å)	d_3(Å)	d_4(Å)	d_5(Å)	d_6(Å)
C1(N)	1.497					
C2(N)	1.421	1.219	1.417			
C3(N)	1.422	1.217	1.421	1.464	1.349	1.475
C4(N)	1.467	1.384	1.467			
C5(N)	1.420	1.219	1.426	1.415	1.220	1.417
C6(N)	1.420	1.218	1.423	1.486		

Table 2: Values of HOMO (eV), LUMO (eV) and Gap energy (eV) energies calculated for, C1 to C6 obtained by B3LYP/6-31G (d).

Compound	C1	C2	C3	C4	C5	C6
HOMO-1	-6.75	-6.59	-6.66	-6.71	-6.85	-6.45
HOMO	-4.95	-4.67	-4.80	-4.77	-5.11	-4.93
GAP	3.47	2.57	2.78	2.95	2.35	2.90
LUMO	-1.48	-2.09	-2.02	-1.82	-2.75	-2.03
LUMO+1	0.57	0.53	-0.002	0.35	-0.25	0.17

2.2 Electronic parameters

Electronic structures are fundamental to the interpretation and understanding of the absorption spectra. The calculated frontier orbital energies (four occupied orbital and four unoccupied orbital) and energy gaps between HOMO and LUMO are shown in Table 2. As shown in Table 2, one can notice that all studied molecules (C2 to C6) exhibit destabilization of the LUMO and stabilization HOMO levels in comparison with those of compound C1. The HOMO and LUMO energies of C1 to C6 change significantly, (-4.96 and -1.48 eV, -4.67 and -2.09 eV, -4.80 and -2.02eV, -4.77 and -1.82eV, -5.11 and -2.76eV, and -4.93 and -2.03eV, respectively). It can also be found that, the HOMO and LUMO energies of the studied compound are slightly different. This implies that different structures play key roles on electronic properties and enhancing the electron-accepting ability and the effect of the symmetry of ethylene-thiophene branch on the HOMO and LUMO energies cannot be neglected. In addition, the energies of Egap C1 to C6 differ slightly from 2.35 to 3.47eV depending on the different structures. They are studied in the following order C1 > C4 > C6> C3 > C2 > C5.
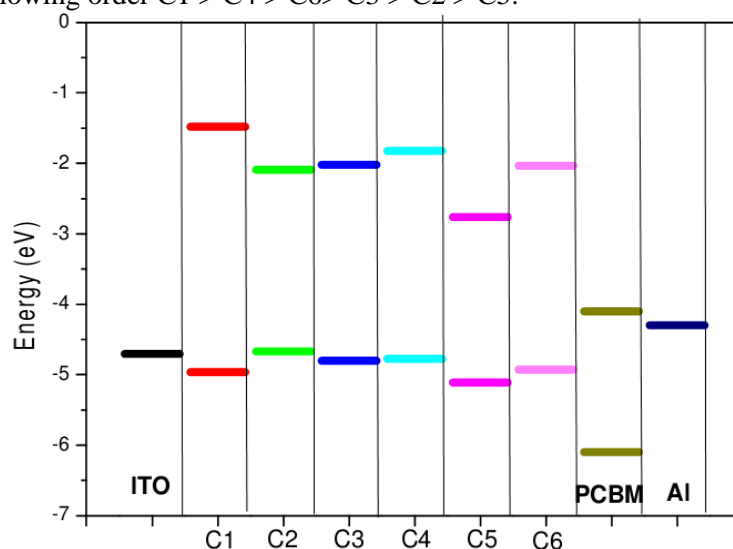
Figure 3. Data of the absolute energy of the frontier orbitals HOMO and LUMO for the studied molecules and ITO, PCBM and the Aluminum (Al).

It should be emphasized that C2 and C5 are asymmetric, one can see that the energies of HOMO and LUMO for the C5 molecule (HOMO: -5.11 eV, LUMO: -2.76 eV) are obviously lower than that of the molecule C2 (HOMO: -4.67 eV, LUMO: -2.09 eV) and the energy gap between HOMO and LUMO of C5 is also lower than that of C2 with a lower energy gap (2.35 eV). This may be attributed to the presence of electron-attracting NO2side groups. On the other hand, the comparison between C2 and C4 show that the replacement of two triple with two double bonds causes a decrease of band gap and a net destabilization of both HOMO and LUMO levels. This is in agreement with what was found in experimental results [21]. The calculated band gap Egap of the studied compound increases in the following order: C1 > C4 > C6 > C3 >C2 > C5. Figure 3 shows detailed data of absolute energy of the frontier orbitals for studying compounds, Indium tin oxide (ITO), [6.6]-phenyl-C61-butyric acid methyl ester (PCBM) (substituted C_{60}) and aluminum (Al) is included for comparison purposes. It was deduced that substitution 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, we have studied the photovoltaic properties of the compounds C1 as donor blended with PCBM, which is the most broadly used as an acceptor in solar cell devices. As shown in Table 3, 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 [30,31], 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 LUMO level of PCBM (open circuit voltage, Voc). The theoretical values of Voc were calculated from the following expression:

$$Voc = E_{HUMO} \text{ (Donor)} - E_{LUMO}\text{(Acceptot)} - 0,3$$

As shown in Figure 3, and knowing that in organic solar cells, the Voc is considered linearly as a function of the HOMO level and the donor level of the LUMO of the acceptor [32]. The Voc calculated molecules studied range from 1.14 to 1.58 eV with the acceptor PCBM and from 1.77 to 2.21 eV with the acceptor OMe-PCBM, these values are sufficient to efficient injection of electrons. Therefore, all molecules studied can be used as sensitizers because the process of injecting electrons from the excited molecule to the conduction band of the PCBM and PCBM-OMe and subsequent regeneration is possible in an organic sensitized solar cell.

Table 3. Energy values of ELUMO (ev), EHOMO (ev) and the Voc (ev).

Compound	E_{LUMO} (ev)	E_{HOMO} (ev)	V_{oc} (ev) (OMe-PCBM	V_{oc} (ev) (PCBM
C1	-1.488	-4.960	2.060	1.434
C2	-2.096	-4.672	1.772	1.146
C3	-2.025	-4.806	1.906	1.280
C4	-1.820	-4.774	1.874	1.248
C5	-2.760	-5.112	2.212	1.586
C6	-2.033	-4.939	2.039	1.413
OMe-PCBM	-2.9	-5.44	--	--
PCBM	-3.226	-5.985		

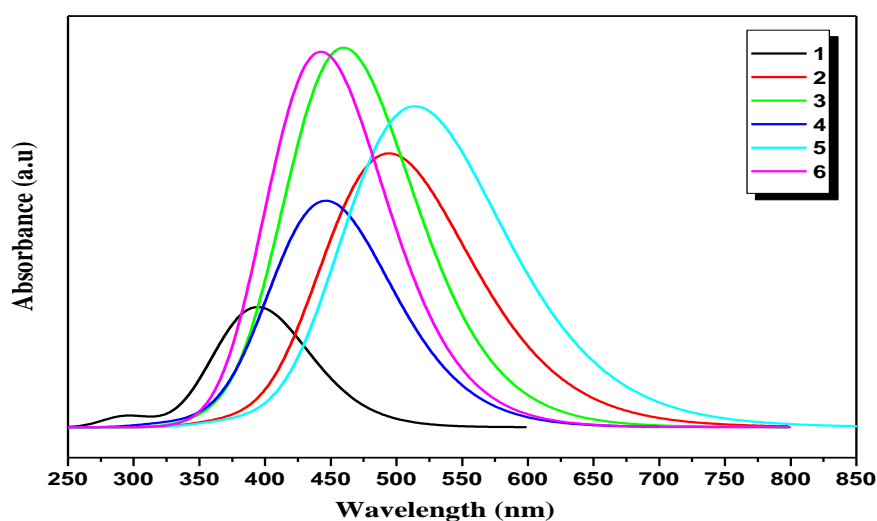*2.3 Absorption and electronic properties*
Based on the optimized molecular structures with B3LYP/6-31G(d) method, we have calculated the ultraviolet-visible (UV-Vis) spectra of the studied compounds C1, C2, C3, C4, C5 and C6 using ZINDO/s method. As shown in Table 5, we can find the values of calculated wavelength λmax and for comparison experimental ones excitation to the S1state corresponds almost exclusively to the promotion of an electron from the HOMO to the LUMO orbital. The absorption wavelengths arising from S0→S1electronic transition increase progressively with the increasing of conjugation lengths. It is reasonable, since HOMO→LUMO transition is predominant in S0→S1electronic transition; the results are a decrease of the LUMO and an increase of the HOMO energy.
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 experimental results.
We can remark for comparing calculated and experimental results [21] a linear relationship between calculated and experiment results. Therefore, the DFT theoretical calculations give a good description of the absorption 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 are in the vapor state. Another considered point is that the position of λmax shows a bathochromic shift when passing from C1 to C6, which also can be seen, respectively in C1 (397.54 nm), C2 (494.19 nm), C3 (460.17 nm), C4 (447.35 nm), C5 (514.20 nm) and C6 (442.76 nm) due to the increasing of the extended conjugation through the system of aryl groups and multiple bonds. The asymmetrically substituted compounds C5, containing a nitro-group, show absorption spectra red-shifted of about 20 nm with respect to the symmetric analogous to C2 and finally the presence of two anthracene units in C6 does not cause a significant red shift of the absorption. Those interesting points are seen both in the theoretical and experimental results.

Table 4. Absorption λabs(nm) obtained by the ZINDO method.

Compound	λ_{max}(nm) ZINDO	OS	λ_{max} exp (nm)	
			Chloroform	Cyclohexane
C1	397.54	0.4317	398	375, 395
C2	494.49	1.1089	475	478
C3	460.17	1.5308	464	460
C4	447.35	0.9057	418	413
C5	514.20	1.3002	494	492
C6	442.76	1.5183	444	439

Figure 5: Absorption spectrum of study compounds C1 to C6

Conclusion

In this study, theoretical analysis of the geometries and electronic properties of several various compounds based on the anthrance was performed using the DFT/B3LYP method. The effect of substituted groups on the structural and opto-electronic properties of these materials and the possibility of their application as organic solar cells are discussed. The concluding remarks are:

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

2) The calculated frontier orbital energies HOMO and LUMO and energy gaps showed that the energy gaps of the studied molecules differ slightly from 2.35 to 3.47 eV depending on the different structures. The calculated band gap Egap of the studied compound increases in the following order C1 > C4 > C6 > C3 > C2 > C5.

3) The replacement of two triple with two double bonds causes a decrease of band gap and a net destabilization of both HOMO and LUMO levels

4) All the 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 the 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 other materials, and to further to novel materials for organic solar cells.

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