

Electronic levels of small molecules for organic solar cells: A computational study

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Abstract

Currently significant progress has been made for the small molecules, indeed, achieved comparable performance compared to polymer in electronic devices mainly due to the many advantages of small molecules over the polymers. Designing better small molecules for electronic applications are required a comprehensive understanding of the structure-properties relationship and the factors affecting it. Valuable information can be generated directly toward understanding by systematically theoretical and experimental studies (band gap, HOMO, LUMO energy levels and geometry). Hybrid density functional B3LYP level of theory is a very good method for predicting the reliable geometry, electronic structure and properties of conjugated systems. In the present work, we have calculated the band gaps, highest occupied molecular orbital (HOMO), lowest unoccupied molecular orbital (LUMO) and geometry of a series of small molecules based on oligothiophene, benzodithiophene and dithienosilole unit using the hybrid density functional (B3LYP/6-31G(d)) level of theory and correlated with experimental values. The study provides details for the effect of the extended conjugation, two-dimension conjugation, substitution on geometry, HOMO, LUMO and band gaps of the small molecules. Copyright © 2017 VBRI Press.

Keywords: Density functional calculations, small molecules, photovoltaic, band gap, geometry.

Introduction

Organic photovoltaic cells (OPVs) are promising alternatives to silicon-based solar cells and possess light weight, low-cost, colour, semi-transparency, solution processable technique and to be fabricated into flexible devices [1]. Though power conversion efficiencies (PCEs) and lifetime of OPV devices based on solution processed bulk heterojunction (BHJ) have not yet reached these of their inorganic counterparts [2]. Currently, two types of electron donor materials, namely polymers and small molecules are used in BHJ solar cells. Last two decades, polymer-based solution processed BHJ solar cells research has been widely studied, and attracted scientific and commercial interest due to a rapid increase in PCE over 10% and lifetime [3, 4]. Although, the main disadvantages for polymeric solar cells are reproducibility of OPV performance due to intrinsic batch to batch variation of degree of polymerization, polydispersity and lower hole mobility for possible commercial applications [5].

Given many advantages of small molecules over the polymers used as a donor materials in solar cells such as (i) reproducibility of OPV performance due to their

defined molecular structure; (ii) purity; (iii) easily tuned the optoelectronic properties and (iv) intrinsic higher mobility. It is surprising that very little is reported about small molecules based solar cells up to end of last decade because of non-availability of suitable molecules with appropriate energy levels and film-forming properties for OPV devices. Although, currently, the significant progress has been made for the small molecules based solar cells by design and synthesis of suitable molecules and the studies indicated that small molecules based solar cells could play a major role for OPV devices, indeed, achieved comparable performance compared to polymer based solar cells [6 - 8].

Designing better small molecules as donor materials for solar cells requires a comprehensive understanding of the structure properties relationship, electronic structure of molecules and the factors affecting it. By systematically theoretical and experimental studies of a series of small molecule on band gap, highest occupied molecular orbital (HOMO), lowest unoccupied molecular orbital (LUMO) energy levels and geometry, a valuable information can be generated directly toward understanding and designing suitable molecules for solar cells. Recently, Bendikov and co-workers has been

shown, using hybrid density functional B3LYP level of theory, is a very good method for predicting reliable geometry, electronic structure and properties of conjugated systems [9,10]. To the best of our knowledge, no systematic studies have been reported for application of DFT to small molecules used in high performance solar cells.

Here, we have studied well known small molecules for organic solar cells using the hybrid density functional B3LYP/6-31G(d) level of theory, which should allow a direct comparison to be made with experimental values. In the present work, a series of high-efficiency small molecules using oligothiophene, benzodithiophene and dithienosilole unit were calculated. We have shown that, the band gaps, HOMO, LUMO and geometry of small molecules can be predictable and correlated with experimental values.

Experimental

Computational modellings

All calculations were performed using density functional theory (DFT) with the B3LYP hybrid functional [11] and the 6-31G(d) basis set. The Gaussian 03 program was used for all computations [12]. The geometries of all molecules were fully optimized using a hybrid density theory. All alkyl chains in the small molecules were replaced by ethyl group to save the time for calculation.

Results and discussion

For the better understanding of the structure-properties relationship, correlation between experimental and theoretical values, and evaluation of optoelectronic properties for small molecule, we have considered a series of oligothiophene, benzodithiophene and dithienosilole based small molecules for organic solar cells [13]. Indeed, few small molecules are well known and most studied for high efficient BHJ organic solar cells.

Oligothiophene based small molecules

The chemical structures of the oligothiophene based small molecules **M1** [14], **M2** [15] and **M3** [16] in this study are depicted in Fig. 1. Oligothiophene with electron accepting end group have been one of the widely investigated small molecules for the BHJ solar cells. The small molecules **M1-M3** were calculated at B3LYP/6-31G(d) level of theory. Importantly, the optimized geometry of **M1-M3** are not planer with average dihedral angle is about 25 degree, as shown in Fig. 2. The calculated band gap, HOMO and LUMO energy levels are presented in Table 1. It was observed that as increases in the conjugation length of the small molecule the band gap of the molecule decreases significantly. For example, the band gap of terthiophene **M1** is about 0.40 and 0.46 eV higher compared to quinquethiophene **M2** and septithiophene **M3** respectively (Table 1), whereas no significant band gap difference between **M2** and **M3** was observed.

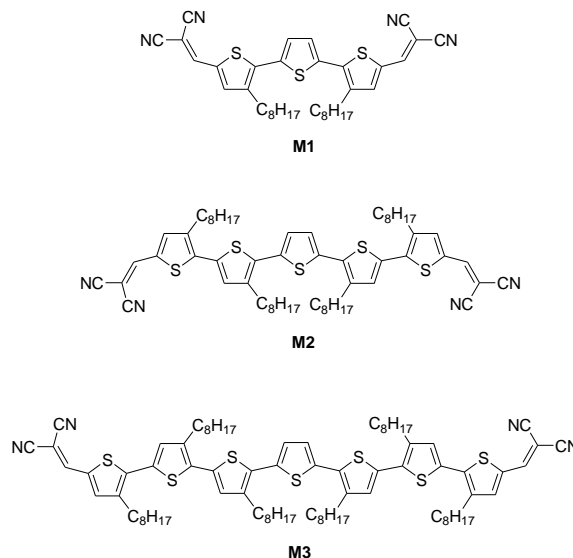


Fig. 1. Chemical structures of **M1-M3**.

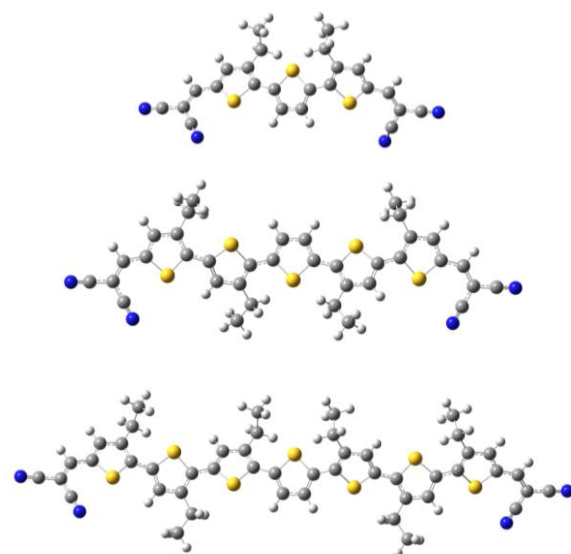


Fig. 2. Optimized structures of (top) **M1**, (middle) **M2** and (bottom) **M3** are calculated at B3LYP/6-31G(d).

This may be due to the linear prediction which is not particularly accurate for longer conjugation system and previously this type observation was reported. The experimental band gaps of the small molecules **M1**, **M2** and **M3** are reported in literature as presented in Table 1. It was mentioned here that PCE is about 3.70% was reported for **M3** in solution processable BHJ solar cells [16,17]. The calculated band gaps of **M1** ($E_g = 2.71$ eV), **M2** ($E_g = 2.31$ eV) and **M3** ($E_g = 2.25$ eV) are about 0.81, 0.57 and 0.57 eV higher than that of experimental band gap of **M1** ($E_g = 1.90$ eV), **M2** ($E_g = 1.74$ eV) and **M3** ($E_g = 1.68$ eV) respectively. The large deviation of band gap trend is seen in these molecules **M1-M3**, which is anticipated due to the strong electron withdrawing group attached to the terminal thiophene ring and that should be destabilized/ vary the HOMO/LUMO levels [14].

Table 1. Calculated (at B3LYP/6-31G(d)) HOMO, LUMO energy levels, band gaps and experimental band gaps values for small molecules **M1-M3**.

Small mol.	HOMO (eV)	LUMO (eV)	Band gap calc. (eV)	Band gap expt. (eV)	Ref.
M1	-6.11	-3.40	2.71	1.90	14
M2	-5.46	-3.15	2.31	1.74	15
M3	-5.27	-3.02	2.25	1.68	16

Benzodithiophene based small molecules

In order to further evaluate the concept, we have considered the most successfully used benzodithiophene based small molecules **M4** and **M5** for calculation and their chemical structures are shown in **Fig. 3**. The series of benzodithiophene based small molecules have been widely investigated for their photovoltaic applications particularly in high performances BHJ solar cells. Moreover, benzodithiophene unit is an attractive building block for organic electronic materials due to the symmetrical, rigid, planar fused aromatic system, which enhances the electron delocalization, and promotes the π - π stacking in solid state. In addition benzodithiophene based materials having lower HOMO levels, which improved the stability and open circuit voltage (V_{oc}) [18,19]. The molecules **M4** and **M5** with PC₇₁BM show PCE of 7.51 and 4.56% respectively in solution processable BHJ solar cells [20,21]. The geometry and electronic structures of the molecules **M4** and **M5** were calculated at B3LYP/6-31G(d) level of theory and the optimized geometry are shown in **Fig. 4**. The calculated band gap, HOMO and LUMO energy levels of **M4-M5** are presented in **Table 2**. The calculated band gap for **M4** ($E_g = 2.28$ eV) and **M5** ($E_g = 2.31$ eV) are about 0.56 and 0.47 eV higher than that of experimental band gap of **M4** ($E_g = 1.72$ eV) [20] and **M5** ($E_g = 1.84$ eV) [21] respectively. Like, oligothiophene based small molecules **M1-M3**, the difference of band gap between calculated and experimental for **M4-M5** may be anticipated due to the strong electron withdrawing group attached to the molecules.

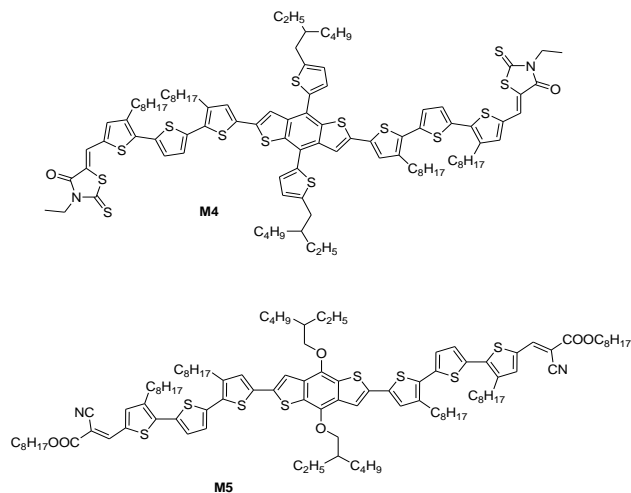


Fig. 3. Chemical structures of **M4** and **M5**.

Table 2. Calculated (at B3LYP/3-21G(d)) HOMO, LUMO energy levels, band gap and experimental band gap values for small molecules **M4-M5**.

Small mol.	HOMO (eV)	LUMO (eV)	Band gap calc. (eV)	Band gap expt. (eV)	Ref.
M4	-5.00	-2.72	2.28	1.72	20
M5	-5.03	-2.72	2.31	1.84	21

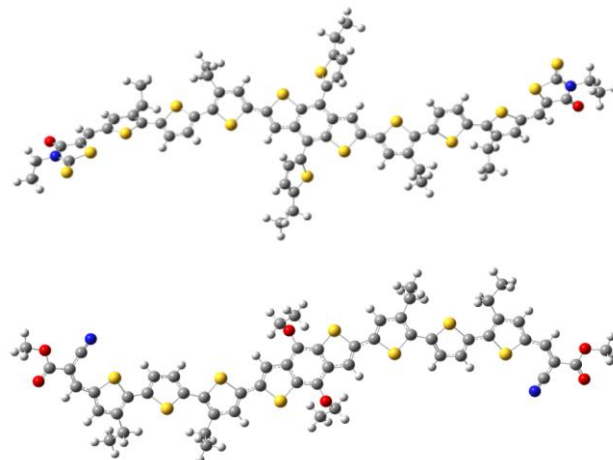


Fig. 4. Optimized structures of (top) **M4** and (bottom) **M5** are calculated at B3LYP/6-31G(d).

Dithienosilole based small molecules

In order to broaden the scope of the calculation we have considered the dithienosilole unit based small molecules since the dithienosilole core containing compounds are the leading small molecules for high efficient organic solar cells. Indeed, small molecules **M6-M8** [22-25] (**Fig. 5**) show considerable better performance in solar cells. The calculated band gap, HOMO and LUMO energy levels for **M6-M8** at the B3LYP/6-31G(d) level of theory are shown in **Table 3**. The substituent effect has been studied by considering the introduction of N atom in place of C atom at the phenyl ring in benzothiadiazole unit in **M7**.

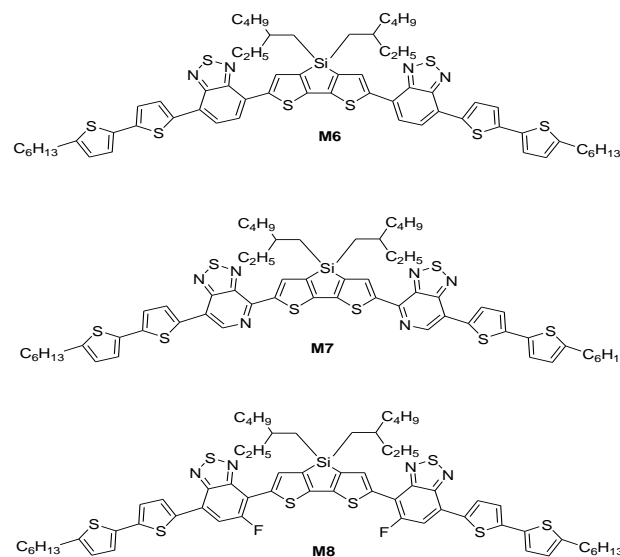


Fig. 5. Chemical structures of **M6-M8**.

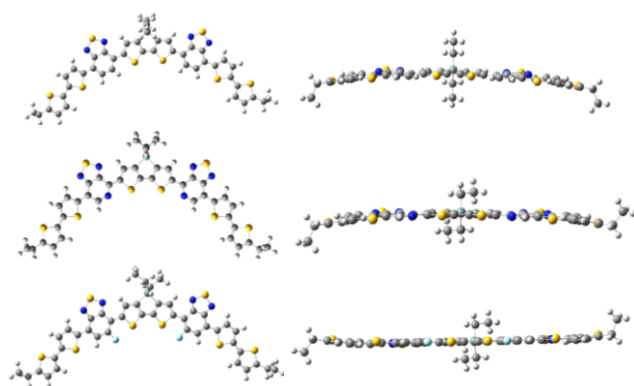


Fig. 6. Optimized structures of (top) both **M6**, (middle) **M7** and (bottom) **M8** are calculated at B3LYP/6-31G(d).

Such substitution causes a change in the band gap of about 0.13 eV (**M6**; $E_g = 1.90$ eV; **M7**; $E_g = 1.77$ eV). Whereas the replacement of H atom by F atom at benzothiadiazole unit (structure **M8**; $E_g = 1.98$ eV) has no significant change of band gap was observed compared to **M6**. In contrast to previous molecules, the calculated band gaps are in relatively good agreement with the experimental results (**Table 3**). This is due to aliphatic alkyl chains attached to the molecules **M6-M8** in contrast to electron withdrawing group attached to the molecules **M1-M5**. This type of screening might be useful to design suitable small molecules for organic electronic applications especially maximize the V_{oc} and short circuit current density (J_{sc}) for BHJ solar cells.

Table 3. Calculated (at B3LYP/6-31G(d)) HOMO, LUMO energy levels, band gaps and experimental band gaps values for small molecules **M6-M8**.

Small mol.	HOMO (eV)	LUMO (eV)	Band gap calc. (eV)	Band gap expt. (eV)	Ref.
M6	-4.68	-2.78	1.90	1.58	22
M7	-4.82	-3.05	1.77	1.60	23
M8	-4.68	-2.70	1.98	1.78	24

Conclusion

Small molecules are interesting organic electronic materials namely for organic solar cells applications. Indeed, high efficiency optoelectronic device have been developed by using oligothiophene, benzodithiophene, dithienosilole based small molecules. We have performed DFT calculation using B3LYP/6-31G(d) levels of theory on a series of the small molecules. This study shows that the theoretical calculation on small molecules can be used to predict the properties of known molecules as well as designing better new molecules for organic electronic applications. The study provides details for the effect of extended conjugation, two-dimension conjugation, substitution on geometry, HOMO, LUMO levels and band gap. We have compared the experimentally evaluated band gaps with our calculated band gaps for a series of molecules for better understanding. Finally, this

type of calculation is important for identifying leading molecules to pursue experimentally and the data for design and modelling studies to understand the structure–property relationship in organic electronic applications.

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Author’s contributions

Conceived the plan: AP, Shahjad; Performed the experiments: AP, Shahjad; Data analysis: Shahjad, RB, DB, AP; Wrote the paper: Shahjad, RB, DB AP. Authors have no competing financial interests.

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