THEORETICAL DESIGN OF FULLERENE DERIVATIVES AS ELECTRON ACCEPTORS FOR BULK HETEROJUNCTION SOLAR CELLS

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Abstract

In this paper semiempirical quantum chemical methods were used to optimize the geometry and to calculate the LUMO level of different fullerene derivatives used as electron acceptors in bulk heterojunction solar cells. The calculated LUMO levels were successfully correlated with the open circuit voltage of devices realized using poly[2-methoxy-5-(3,7-dimethyloctyloxy)]–1,4-phenylenevinylene as electron donor, showing the possibility to use a theoretical approach to design new acceptor molecules.

1. Introduction

The use of photovoltaic technology to obtain energy directly from the sunlight is considered an interesting solution to solve the energy needing. Although silicon-based solar cells dominate the present-day market, polymer solar cells (PSC) have evolved as a promising cost-effective alternative [1, 2]. These solar cells have some important advantages, such a potential low cost of fabrication, ease of processing, mechanical flexibility, and versatility of chemical structure from advances in organic chemistry [3, 4]. Actually, power conversion efficiencies surpassing 5% have been demonstrated using a bulk heterojunction (BHJ) [5] of poly(3-hexylthiophene) (P3HT) (donor material) and [6,6]-phenyl C61-butyric acid methyl ester (PCBM) (acceptor material) [6]. A schematic representation of this kind of the device structure is shown in Fig. 1.

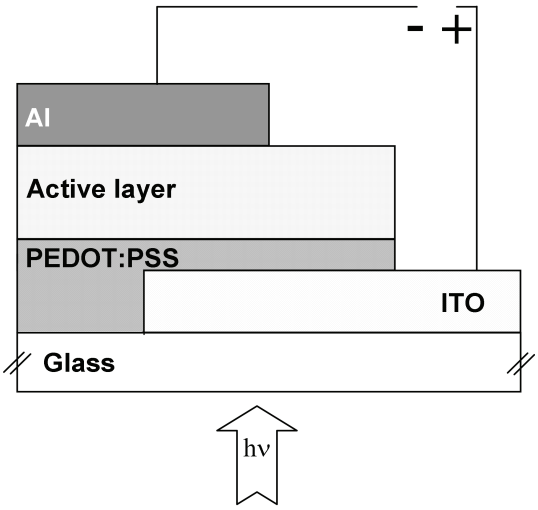


Fig. 1. Schematic device structure of a polymer/fullerene bulk heterojunction solar cells. The active layer is sandwiched between two contacts: an indium-tin-oxide electrode coated with a hole transport layer PEDOT:PSS and an aluminium top electrode.

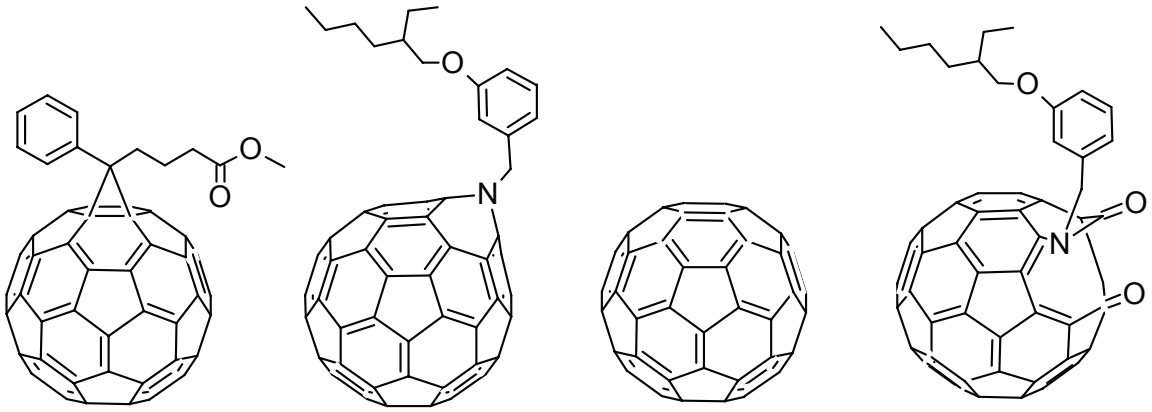


Fig. 2. Chemical structures of the investigated fullerene derivatives: [6,6]-phenyl C61-butyric acid methyl ester (**1**), N-3-(2-ethylhexyloxy)benzyl azafulleroid (**2**), C60 (**3**) and N-3-(2-ethylhexyloxy)-benzyl ketolactam (**4**).

However, one major problem for the use of BHJ solar cells in commercial applications is the relatively small device efficiencies that have been reached up to now.

The power conversion efficiency (η) of a photovoltaic cell is directly proportional to short circuit current (I_{sc}), the open circuit voltage (V_{oc}), and the fill factor (FF) (Eq. 1)

$$\eta = \frac{I_{sc} * V_{oc} * FF}{P_{inc}}, \tag{1}$$

where P_{inc} is the incident power irradiation.

The maximum V_{oc} of a BHJ solar cells is related to the difference between the highest occupied molecular orbital (HOMO) of the electron donor and the lowest unoccupied molecular orbital (LUMO) of the electron acceptor [7-11]. For an efficient charge transfer from the donor polymer to the acceptor fullerene, the relative position of donor LUMO and acceptor LUMO is also crucial. So it is possible to increase the V_{oc}, by raising the LUMO level of the electron acceptor molecule. In other words, to maximize the V_{oc} in BHJ solar cells, it is necessary to find the appropriate acceptor for each donor polymer used. On the other hand, a lot of time is required to investigate experimentally new structures for acceptors with the aim to optimize the LUMO for a given donor polymer and maximize the V_{oc}. So it can be useful to implement a theoretical approach to study the influence of the LUMO level of the acceptor on the V_{oc} of the device.

Recently, we have shown the possibility to tune the LUMO level of the acceptor to increase the V_{oc} of a BHJ solar cells using a quantum chemical approach [10, 11]. We have correlated the theoretical LUMO levels of several fullerene derivatives calculated using the density functional theory, with the V_{oc} of polymer-fullerene solar cells.

The aim of this work is to investigate whether semiempirical quantum chemical methods are still reliable in the prediction of LUMO levels of fullerene derivatives successfully used as electron acceptors in BHJ solar cells. We also try to correlate the values of the LUMO obtained with this level of theory with the V_{oc} of BHJ solar cells with poly(2-methoxy-5-(3',7'-dimethyloctyloxy)-1,4-phenylenevinylene) (MDMO-PPV) having similar device structure.

2. Computational details

The geometric structures of all the investigated fullerene derivatives (**1**-**4**) (Fig. 2) were optimized under no constraints using different semiempirical quantum chemical methods

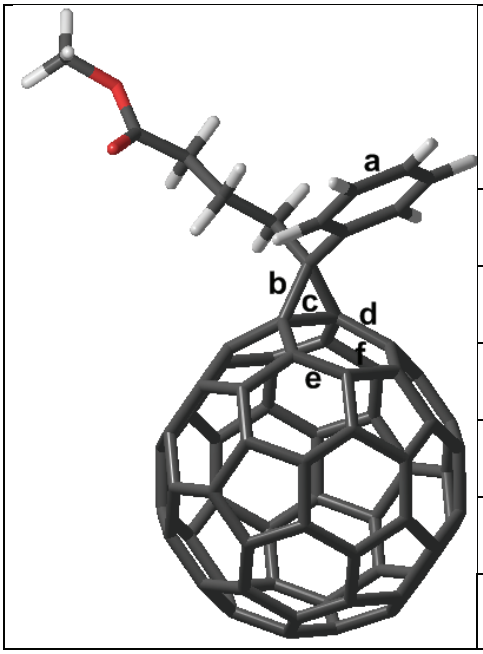
(MNDO [12], PM3 [13], PM6 [14]). To assess the reliability of these methods, comparisons with higher-level methods have also been made. The geometries were also optimized using density-functional calculations with 3-21G* basis set [15, 16] and Becke's three-parameter functional (which defines the exchange functional as the linear combination of Hartree-Fock, local and gradient-corrected exchange terms) in combination with the correlation functionals of Lee, Yang and Parr (B3LYP) [17, 18]. Single point calculations at the same level of theory were carried out with the aim to investigate the energy levels of the frontier orbitals.

PC GAMESS software package [19, 20] was used for MNDO, AM1, PM3 and DFT 3-21G*/B3LYP and MOPAC2007 package [21] for PM6 method.

3. Results and discussion

The geometry of the fullerene derivatives (**1-4**) was optimized using semiempirical methods (MNDO, PM3 and PM6) and the DFT (B3LYP/3-21G*). In Table I, we show the structure of PCBM (**1**) optimized using DFT B3LYP/3-21G* method. Selected bond lengths calculated with the above cited methods are reported together with the experimental values.

Table I. PCBM structure optimized using DFT B3LYP/3-21G* method.



Bond length (Å)	Method				
	MNDO	PM3	PM6	B3LYP 3-21G*	EXP. [22]
a	1.405	1.391	1.398	1.397	1.372
b	1.549	1.515	1.525	1.523	1.515
c	1.594	1.552	1.603	1.630	1.625
d	1.515	1.497	1.501	1.495	1.483
e	1.391	1.375	1.376	1.381	1.377
f	1.487	1.474	1.482	1.483	1.471

Selected bond lengths calculated using different semiempirical (MNDO, AM1, PM3, PM6) and DFT (B3LYP/3-21G*) methods are reported in the table. Experimental bond distances from ref. [22] are reported for comparison.

As we can see, the DFT theory and the semiempirical PM6 method predict fairly well the geometry of this compound.

To verify whether the semiempirical methods are still reliable in the prediction of the acceptor strength of **1-4**, we try to correlate the LUMO levels of the investigated species with the reduction potential obtained by cyclic voltammetry measurements. As shown in Fig. 3, the first and second reduction potentials of the fullerene derivatives [7] exhibit remarkable linear relationships with their LUMO energy levels obtained by different theoretical methods (MNDO, PM3, PM6 and B3LYP/3-21G*). The third reduction potentials [7] correlate better

with the LUMO+1 energy levels than with the LUMO energy levels, indicating that the energy gaps between the LUMO and LUMO+l should be taken into account to explain the electroreductions of these fullerenes. As we can see from the correlation coefficients reported inside the plots of Fig. 3, the semiempirical PM6 method gives the best correlation coefficients among semiempirical methods, and it is very close to the one obtained using the DFT B3LYP/3-21G* method.

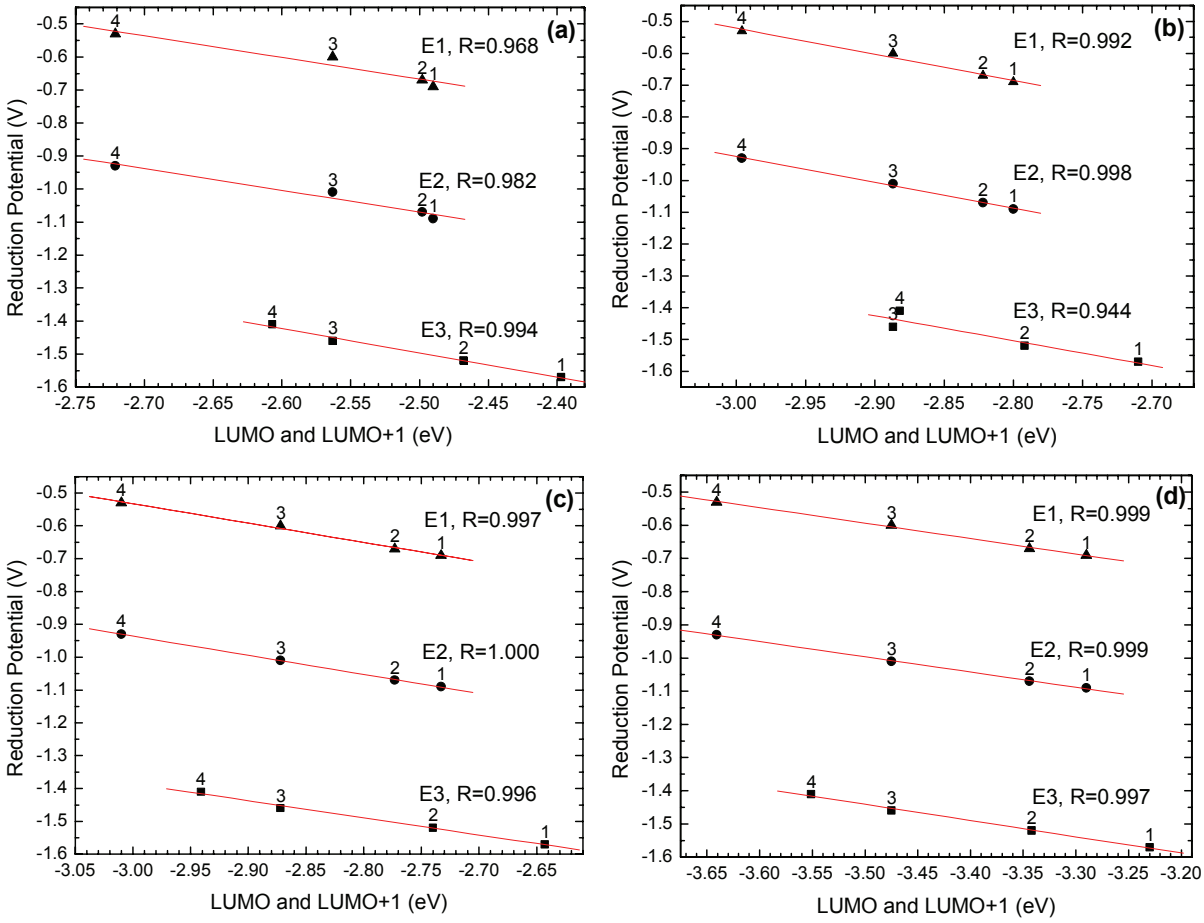


Fig. 3. Plots of the first (E1) and second (E2) reduction potential (V vs NHE) [7] versus the LUMO energy levels of **1**-**4** and the third reduction potential (E3) versus the LUMO+1 energy levels of **1**-**4**. The LUMO and LUMO+1 levels are calculated by (a) MNDO, (b) PM3, (c) PM6, and (d) B3LYP/3-21G* methods.

Recently, it has been shown that the V_{oc} of polymer-fullerene solar cells is directly related to the acceptor strength of fullerenes [7-11]. This observation has been proved using the fullerene derivatives **1**-**4** as electron acceptor in MDMO–PPV based BHJ solar cells (Fig. 2). In Fig. 4, we report the best V_{oc} for the photovoltaic devices based on the ITO/PEDOT:PSS/(MDMO-PPV):fullerene/Ca structure [7] versus the LUMO level calculated using different theoretical methods for the fullerene derivatives **1**–**4**. A linear relationship between experimental V_{oc} and theoretical LUMO level is found for all the used methods. Also in this case, the semiempirical PM6 method gives the best correlation coefficient among semiempirical methods and it is very close to the one obtained using the DFT B3LYP/3-21G* method. This is consistent with the better geometry obtained using PM6 method, compared with other semiempirical methods. We have to consider also that all the LUMO levels were

calculated for isolated molecules in the gas phase while V_{oc} are related to measurements made for solid state device and little deviations from linearity are expected.

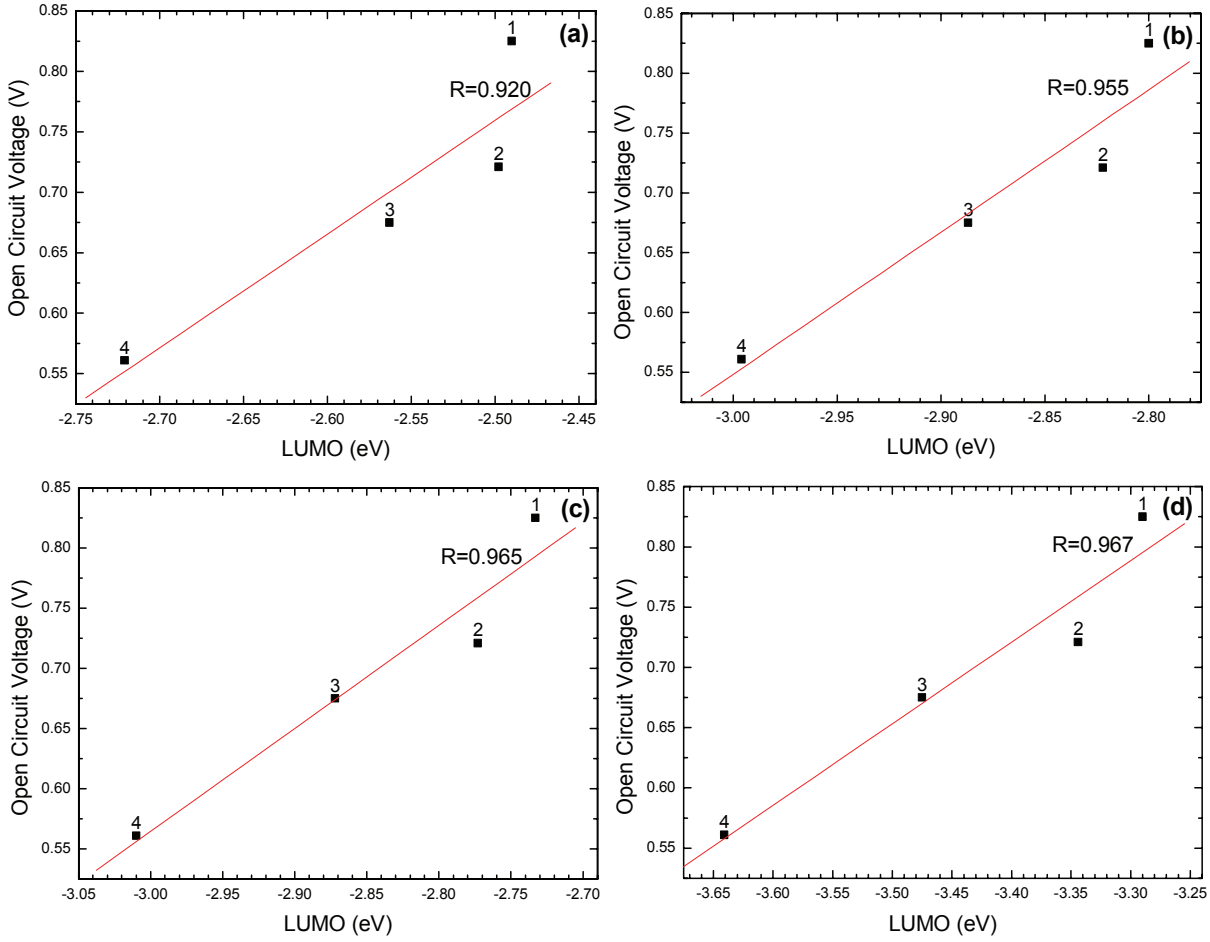


Fig. 4. Open circuit voltage of MDMO-PPV:fullerene (**1**-**4**) devices [7] versus theoretical LUMO levels of acceptors calculated by (a) MNDO, (b) PM3, (c) PM6, and (d) DFT B3LYP/3-21G* methods.

These results show that LUMO levels obtained by semiempirical methods (in particular, the PM6 method) can be successfully used for the estimation of V_{oc} in BHJ solar cells if the HOMO and LUMO levels of donor polymer are known. We have to remark that the V_{oc} depends not only on the position of the LUMO level of the acceptor but also on other factors like the injection barriers, the ideality factor, the recombination, the mobility, and the morphology of the blend.

4. Conclusions

In this work, we have studied the LUMO levels of fullerene derivatives using different semiempirical methods (MNDO, PM3, and PM6). The calculated LUMO levels correlate well with V_{oc} of organic solar cells based on the blend of MDMO-PPV:fullerene. Using PM6 methods, it is possible to obtain geometries comparable with experimental data. The correlation with V_{oc} is fairly good as using higher level calculations (DFT B3LYP/3-21G*).

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