Higher fullerenes as electron acceptors for polymer solar cells: A quantum chemical study

P. Morvillo *

ENEA, C.R. Portici, Loc. Granatello, 80055 Portici (NA), Italy

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ABSTRACT

In the present study, we have used quantum chemical methods to study the energy levels of the frontier orbitals of higher fullerene derivatives (from C_{70} to C_{84} and having the same addend as in [6,6]-phenyl C_{61}-butyric acid methyl ester) with the aim to understand if they can be used as electron acceptors in bulk heterojunction polymer–fullerene solar cells. Higher fullerenes have a stronger and broader absorption compared to C_{60} and they can improve the current output of the corresponding devices. The geometries of all the compounds were optimized with the density functional theory at the B3LYP/3-21G* level of calculation. The lowest unoccupied molecular orbital (LUMO) levels of the investigated compounds correlate well with the reduction potentials (obtained by cyclic voltammetry) of the already prepared species. We found that the LUMO level depends not only on the fullerene size (number of carbons of the cage) and constitutional isomer, but also on the position and, in some cases, the addend orientation. This issue should be considered because for a proper device operation, a well-defined LUMO is required. The position of the LUMO level of some higher fullerene derivatives can be suitable for low-bandgap polymers.

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1. Introduction

Since the discovery [1] and isolation of macroscopic quantity of fullerenes [2], these molecules have received an increasing interest in material science due to the remarkable electrochemical and photophysical properties [3]. The most intensively studied and available fullerene, is the football shaped C_{60}: it is a good electron acceptor, and its triply degenerate low-lying lowest unoccupied molecular orbital (LUMO) allows for the reversible addition of up to six electrons [4]. The ultrafast photoinduced electron transfer from a π-conjugated polymer to C_{60} [5] has established fullerene derivatives as the most important n-type materials for polymer solar cells [6–10]. The best efficient and extensively studied device architecture is based on the bulk heterojunction approach [11–13]. It consists of a blend of electron donating material, e.g. a p-type conjugated polymer, and an electron accepting material (n-type), such as fullerene derivatives; the thin photoactive layer is sandwiched between two electrodes with different work functions forming ohmic contacts to the respective p- and n-type semiconductors. Most bulk heterojunction solar cells are based on a blend of regioregular poly(3-hexylthiophene) (P3HT) (electron donor) and [6,6]-phenyl-C_{61}-butyric acid methyl ester ([60]PCBM) (electron acceptor).

Actually a power conversion efficiency (PCE) above 5% has been reached for such device under 1 sun AM1.5 illumination [14]. However, for commercial applications, a further increase of PCE is needed but other aspects like stability/degradation of the devices [15–20] and large-area processing [21–24] are equally important.

The conversion of light into electricity in the polymer-fullerene solar cells involves four different steps: (i) photons are absorbed from the active layer, resulting in the formation of excitons, (ii) the excitons diffuse to the interface region of donor–acceptor, (iii) dissociation of excitons with the formation of free charges and (iv) transport of the charges under an electric field to the anode (holes) and cathode (electrons) to supply an external current [25]. To break up the exciton, the relative positions of donor LUMO and acceptor LUMO are crucial. Usually the LUMO of the donor polymer needs to be 0.3–0.5 eV higher than the LUMO of the acceptor molecule [26,27], but if we consider the energy levels of the P3HT:PCBM system, this difference is around 1.1 eV. By the way, the maximum V_{oc} of a BHJ solar cell is related to the difference between the highest occupied molecular orbital (HOMO) of the electron donor and the LUMO of the electron acceptor [28–31]. This is true only for devices with ohmic contacts: in this case, the Fermi levels of the electrodes are pinned to the energy levels of the relevant molecular orbitals [30]. Instead, the V_{oc} of devices with non-ohmic contacts is related to the work function difference of the electrodes as described from the MIM model [32]. For this reason, the V_{oc} of the P3HT:PCBM device can be further increased: it has been estimated that the

* Tel.: +390817723260; fax: +390817723345.
  E-mail address: pasquale.morvillo@enea.it

efficiency can reach the value of 8.4% if the difference between the LUMO level of the donor and the LUMO level of the acceptor is reduced to 0.5 eV [33]. Moreover, low-bandgap polymers (which have the potential to increase the power conversion efficiency because they can absorb light until the infrared range, harvesting more solar energy), can have HOMO and LUMO levels shifted compared to P3HT [9,34]. In particular, when the LUMO level increases, a suitable electron acceptor must be used in order to keep a sufficient driving force for the exciton dissociation and to minimize the loss of V_{oc}. As a general rule, to optimize the V_{oc} of polymer fullerene devices, it is necessary to find a proper acceptor molecule with a suitable LUMO level for the used polymer.

In this paper, we investigated, using quantum chemical methods, the energy levels of the frontier orbitals of higher fullerene derivatives (from C_{70} to C_{84} and having the same addend as in [60]PCBM) with the aim to verify if they can be used as electron acceptors in polymer solar cells. Higher fullerene derivatives have a stronger and broader absorption compared to [60]PCBM and they can improve the current output of the corresponding polymer-fullerene devices [35,36]. In the last years, [70]PCBM and [84]PCBM have already been proposed as electron acceptors in BHJ solar cells [35,36]. It has been shown that devices realized using [70]PCBM as electron acceptor have a higher current output compared to the ones based on the analogous [60]PCBM, due to the increase in absorption [35]. For this reason, it can be interesting to verify if the position of the LUMO levels of other higher PCBM fullerenes is suitable for the LUMO levels of the donor polymers used in BHJ solar cells and if it can be useful to prepare other acceptors like [76]PCBM and [78]PCBM.

2. Computational methodology

The density function theory (DFT) has proven to be an important tool in quantum chemistry to describe the electronic structure of molecules at a reduced computational cost [37]. Recently, we have shown the possibility to apply the DFT to calculate the LUMO levels of different C_{60} fullerene derivatives successfully used as electron acceptors in polymer solar cells [38]. The theoretical LUMO levels (calculated for isolated molecules in vacuo) correlate well with the first reduction potential of these species (experimentally determined with cyclic voltammetry) and with the open-circuit voltage of the corresponding photovoltaic devices based on the blend of poly[2-methoxy-5-(3,7-dimethy-loctyloxy)]-1,4-phenylenevinylene (MDMO-PPV) with the acceptor molecules [38]. This correlation allow us to foresee the possible V_{oc} of a BHJ solar cell based on a new acceptor fullerene, once we know the theoretical LUMO level.

The geometric structures of the investigated fullerene derivatives were preliminarily optimized under no constraints using the PM3 semiempirical method [39]. The harmonic vibrational frequencies calculated at PM3 theory level were employed to confirm that the PM3-optimized geometries correspond to minima on the potential energy surfaces. Then the PM3 optimized geometries were subjected to further geometry optimization and energy calculation using density-functional theory with 3-21G* basis set [40,41] 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) [42,43]. Since these supramolecules contain over 60 atoms, a smaller basis set is chosen to save computation time. Indeed, this method has proved to be very adapted to study macromolecular systems with fullerene units [44]. Afterwards, we investigated the localization of the frontier orbitals using a single point calculation at the same level of theory. The prediction of the

geometries of fullerenes using DFT B3LYP/3-21G* is fairly good [44] although this agreement is accredited to fortuitous error cancellation from exchange-correlation functional and basis set [45].

All calculations were carried out using the PC GAMESS/Firefly package [46], which is partially based on the GAMESS (US) [47] source code.

3. Results and discussion

3.1. Higher fullerenes

Higher fullerenes are fullerenes containing more than 60 atoms of carbons [48]. After C_{60}, the next possible fullerenes that follow the isolated pentagon rule (IPR) [49] are C_{70}, C_{72}, C_{74}, C_{76}, C_{78}, C_{82}, C_{84}. While fullerenes up to C_{76} have only one IPR isomer, there is a dramatic increase in the number of possible fullerene isomers with expanding cage size. The number of IPR isomers are 5 for C_{78}, 7 for C_{80}, 9 for C_{82} and 24 for C_{84} [48]. In this paper, we have restricted our investigation to higher fullerenes commercially available (C_{70}, C_{76}, C_{78}-C_{2v}, C_{78}-D_3, C_{84}-D_2 and C_{84}-D_{2d}).

Using the methodology described above, we optimized the structure of the investigated fullerenes (**1–7**, Fig. 1) and we calculated the energy of the LUMO levels using the DFT B3LYP/3-21G* level of theory. The theoretical LUMO levels (Table 1) are
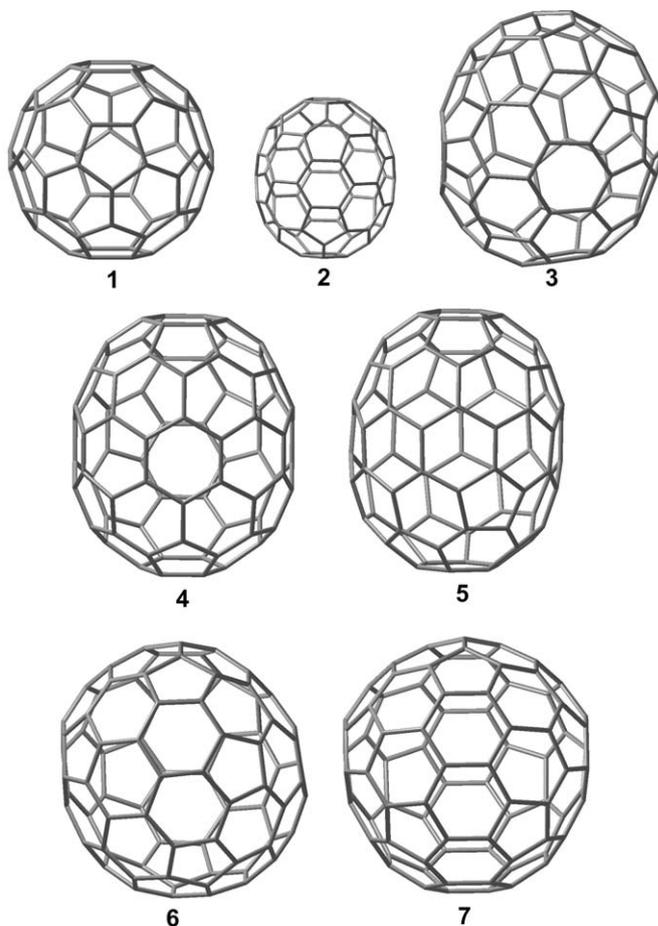

Fig. 1. Structures of the investigated fullerenes optimized at DFT/B3LYP/3-21G* level of theory: C_{60} (**1**), C_{70} (**2**), C_{76} (**3**), C_{78}–C_{2v} (**4**), C_{78}–D_3 (**5**), C_{84}–D_2 (**6**), C_{84}–D_{2d} (**7**).