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Research paper

Electronic properties of electron-doped [6,6]-phenyl-C61-butyric acid methyl ester and silylmethylfullerene

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ABSTRACT

Electronic properties of electron-doped chemically decorated C_{60} fullerenes, [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) and silylmethylfullerene (SIMEF), by a planar electrode were studied using density functional theory combined with the effective screening medium method to simulate the heterointerface between the chemically decorated C_{60} and cationic counter materials. We find that the distribution of accumulated electrons and induced electric field depend on the molecular arrangement with respect to the external electric field of the electrode. We also show that the quantum capacitance of the molecule is sensitive to molecular arrangement owing to the asymmetric distribution of the accumulated electrons.

1. Introduction

Over the past three decades, fullerenes have been keeping a premier position in nanoscale sciences and technologies, because of the diversity of their geometry and corresponding electronic properties. Fullerenes have been widely applied as starting materials for various derivatives that form constituents of devices. The structural variation of fullerene arises from the multiple possible arrangements of twelve pentagons with various numbers of corresponding hexagons in a hollow-cage network topology [1–3]. Owing to strong correlation between the geometry of fullerenes and their electronic properties, the detailed electronic structure depends not only on fullerene cage size but also on the local atomic arrangement. For example, the electronic structures of the 24 isomers of C_{84} are completely different from each other, depending on variations in their covalent network topology, even though each isomer has the same cage size [5,4]. It has been pointed out that the π electronic structures of fullerenes can be characterized as a spherical harmonic Y_{lm}: The electronic states associated with π electrons tend to bunch up or become degenerate with each other, reflecting their approximately spherical distribution in the fullerene cage. Thus, the π electron states are often naively regarded as an electron system confined to the spherical shell with a nanometer scale diameter [6]. In addition, fullerenes commonly possess a deep lowest unoccupied (LU) state compared with that of other carbon nanomaterials and hydrocarbon molecules, owing to the twelve pentagonal rings embedded in their cages [7]. Thus, fullerenes can act as electron acceptors for electrochemical applications.

Pristine fullerenes have a moderate chemical reactivity arising from the high curvature of the molecule and can be derivatized by covalently attaching atoms [8–11] or functional groups [12–19] to the cage. The spherical π electron network of fullerenes can also be modulated by chemisorption of atoms and molecules, and these derivatives are known to possess unusual electronic structures, which are completely different from those of pristine fullerenes. These materials are also of great interests as constituents for optical, optoelectronic, magnetic, and photovoltaic devices. For organic thin film photovoltaic devices, chemically decorated fullerenes act as an electron acceptor in blends with appropriate donor molecules. These devices can show large open voltages owing to the deep lowest unoccupied state of the fullerene [20–25] and remarkable power conversion efficiency of up to 11 percent [26]. Experiments are steadily developing the structure and enhancing the performance of organic thin film photovoltaic devices based on fullerene derivatives. However, the microscopic mechanism of carrier generation and detail of the nanostructure at the heterointerfaces remain unclear. This lack of understanding motivated our study to clarify the electronic properties of electron-doped fullerene derivatives interfacing with cationic materials. Thus, in this work, we aim to clarify the electronic properties of chemically decorated fullerenes at heterointerfaces with electron doping by an electrode to simulate the cationic materials, using density functional theory combined with the effective screening

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medium method. We considered [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) and silylmethylfullerenes (SIMEF), which are widely used as accepter molecules in organic thin film solar cells. Our calculations indicated that the distribution of accumulated electrons and the induced electric field upon electron injection are sensitive to the molecular arrangement with respect to the positively charged planar electrode, reflecting the distribution of the LU state of the PCBM and SIMEF.

2. Methods and models

In the present work, theoretical calculations were performed using density functional theory (DFT) [27,28] implemented in the STATE package [29]. To express the exchange correlation potential among the interacting electrons, the local density approximation was applied with the Perdew-Wang functional form fitting to the Quantum Monte Carlo results on the homogeneous electron gas [30,31]. We used an ultrasoft pseudopotential to describe the interactions between the valence electrons and the ions generated by the Vanderbilt scheme [32]. The valence wave functions and deficit charge density were expanded by a plane-wave basis set with cutoff energies of 25 and 225 Ry, respectively. The Γ point sampling was adopted to perform the Brillouin zone integration. Structural optimization was performed until the remaining force acting on each atom was less than 5 mRy/Å. To investigate the electronic properties of an individual electron-doped molecule, each molecule was well separated from its periodic images in a cuboidal cell with lattice parameters of $a = b = 21.77$ and $c = 25$ Å for PCBM and $a = b = 22.03$ and $c = 24$ Å for SIMEF. We adopted the effective screening medium (ESM) [33] method to solve the Poisson equation including the excess electrons injected by the electrode within the framework of the DFT with the plane-wave basis set.

To simulate the PCBM and SIMEF located at the heterointerface with cationic donor molecules in an organic photovoltaic device, we considered a structural model of PCBM and SIMEF located below a planar electrode by 4.0 Å vacuum spacing simulated by an effective screening medium, which can dope electrons into PCBM and SIMEF by inducing a counter charge on the electrode surface (Fig. 1). To investigate the effect of molecular arrangement on the electron accumulation, we considered two molecular orientations, the tail-to-head and head-to-tail arrangements, of PCBM and SIMEF with respect to the electrode. Under the theoretical setup, we inject up to 1 electron with a gate voltage, which corresponded approximately to 3.5 and 1.5 V for the tail-to-head and head-to-tail arrangements, respectively. During the calculations under the conditions with an excess electron, the geometries of PCBM and SIMEF were kept the same as those with zero electric field, because the forces acting on each atom were smaller than the defined criterion for the force cutoff.

3. Results and discussion

Fig. 2 shows the electrostatic potential of PCBM and SIMEF without an excess electron. The electrostatic potential at the head (C_{60}) moiety is higher than that at the tail (functional groups) moiety by 0.22 and 0.23 V for PCBM and SIMEF, respectively, owing to the asymmetric shape and composition of the fullerene derivatives. This result indicates that the PCBM and SIMEF have an intrinsic dipole moment between the head and tail moieties, with a value of 0.60 and 0.63 D for PCBM and SIMEF, respectively. These values are smaller than those of pentamethyl C_{60} and pentaphenyl C_{60} by approximately 1.3 and 0.3, respectively [34]. Thus, the electrostatic properties of the electron-doped molecules may be expected to be sensitive to their relative molecular arrangement with a respect to a cationic counter material, as for the case of pentaorgano C_{60} under an external electric field.

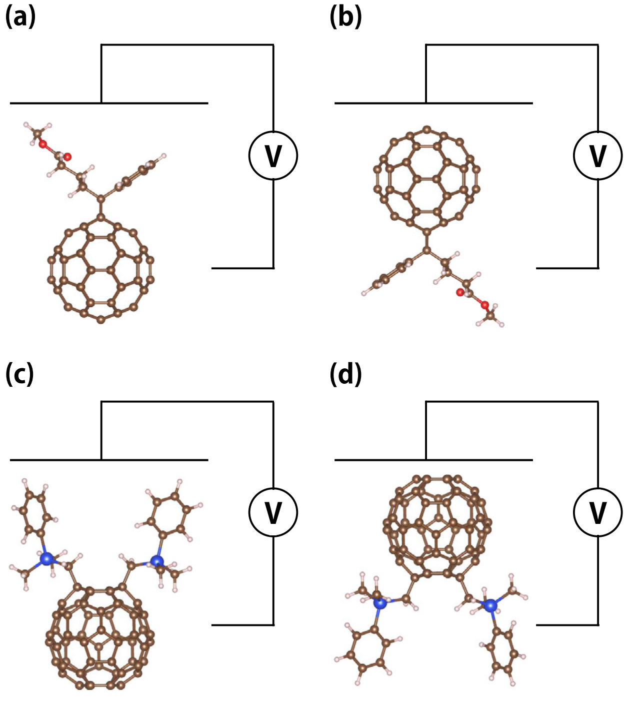

Fig. 1. Schematic structures of PCBM with (a) tail-to-head and (b) head-to-tail arrangements to the electrode. Schematic structures of SIMEF with (c) tail-to-head and (d) head-to-tail arrangements to the electrode. Brown, red, blue, and white balls denote C, O, Si, and H atoms, respectively. Horizontal lines just above the fullerenes indicate the planar electrode. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

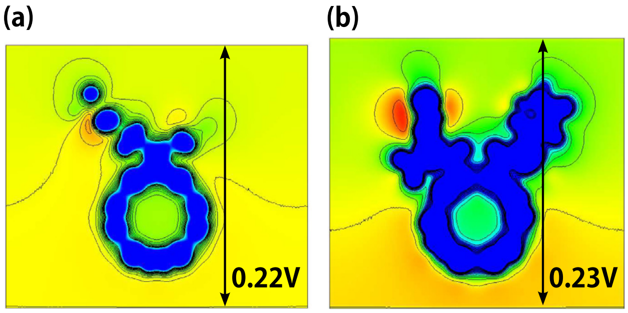

Fig. 2. Contour plots of the electrostatic potential of neutral (a) PCBM and (b) SIMEF. Each contour represents higher or lower by 0.01 in the density of the adjacent contour lines.

Fig. 3 shows the electronic energy levels of PCBM and SIMEF without an excess electron. The electronic structures around the Fermi level of these two molecules qualitatively exhibit the same features. The gaps between the highest occupied (HO) and LU states of the molecules were 1.58 and 1.43 eV for PCBM and SIMEF, respectively. Furthermore, the energy levels of the LU state of these molecules were the same, indicating that they may give the same open voltage when used as counter donor materials in photovoltaic devices. Note that the LU state of these molecules is deeper than that of typical polycyclic hydrocarbon molecules, which are commonly used as electron donors. Thus, a sufficient charge separation may be expected to allow for the application of PCBM and SIMEF as acceptors. The similarities of the electronic structure around the HO and LU indicate that the electronic states around the gap of these molecules are associated with states distributed on the C_{60}