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Electronic properties of two-dimensional molecular sheets of chemically decorated fullerenes under an external electric field

Fullerene can form various derivatives by attaching the functional groups[1] onto the covalent network, and be manipulated optical and electronic properties by π-electron network arrangement, which is totally different from that of the pristine fullerene, making them constituent materials for the optical, optoelectronic, magnetic, and photovoltaic devices. Fullerenes and fullerene derivatives are widely used for electron acceptors in organic thin film solar cells due to their deep lowest unoccupied (LU) states[2] resulting in the high open voltage to the electron donor materials[3]. [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) and silylmethylfullerenes (SIMEF) are widely used for an electron acceptor in organic photovoltaic devices. However, microscopic mechanism of the electron accumulation at the p/n-junction and the electron transport in such as packed structure are not elucidated yet. Therefore, in the present work, we aim to investigate the electronic properties of molecular sheet of PCBM and SIMEF, which form interface with counter electrodes, using the density functional theory combined with the effective screening medium method.

We use the density functional theory with local density approximation for investigating the geometric and electronic structures of the molecules under the electric filed which inject electrons into the molecules. Ultrasoft pseudopodtentials are adopted to treat the interaction between electrons and nuclei. Valence wavefunctions and charge density are expanded by the plane wave with the cutoff energy of 25 and 225 Ry, respectively. To inject excess electron by the external electric field, we consider the structural model shown in Fig. 1 in which the electrons are injected into the molecular sheet via a planar gate electrode, which is simulated by the effective screening medium with the infinite relative permittivity. To investigate the effect of the molecular arrangement on the carrier accumulation and the electron transport, we consider two different molecular arrangements with respect to the gate electrode.

Figure 2 shows the electrostatic properties of the molecules under the zero electric field. As shown in Fig. 2, in both molecules, the potential at the tail region is lower than that at the head region, indicating that the molecules possess electric dipole moment, arising from their asymmetric shapes by the attached functional groups onto fullerene. The dipole moment is expected to affect the carrier injection into these molecules with respect to their mutual molecular arrangement to the electrode. Figure 3 shows isosurfaces of accumulated electron in the molecules with head-to-tail and tail-to-head molecular arrangement. We find that the accumulated electrons are localized on the bowl region under the head-to-tail arrangement, while they are extended throughout the molecule in the tail-to-head arrangement. In accordance with the carrier distribution, an induced electric field around the molecules under the external electric field also depends on the molecular arrangement as shown in Fig. 4. The accumulated electron distributed on the molecular feather leads to the substantial electric field concentration around them because of its sharpen shape.

References

[1] Y. Matsuo and E. Nakamura, Chem. Rev., 108 (2008) 3016.
[2] Y. Matsuo, Y. Sato. T. Niinomi, I. Soga, H. Tanaka and E. Nakamura, J. Am. Chem. Soc., 131 (2009) 44.
[3] J. Zhao, Y. Li, G. Yang, K. Jiang, H. Lin, H. Ade, W. Ma and H. Yan, Nature Energy, 1 (2016) 15027.

Figures

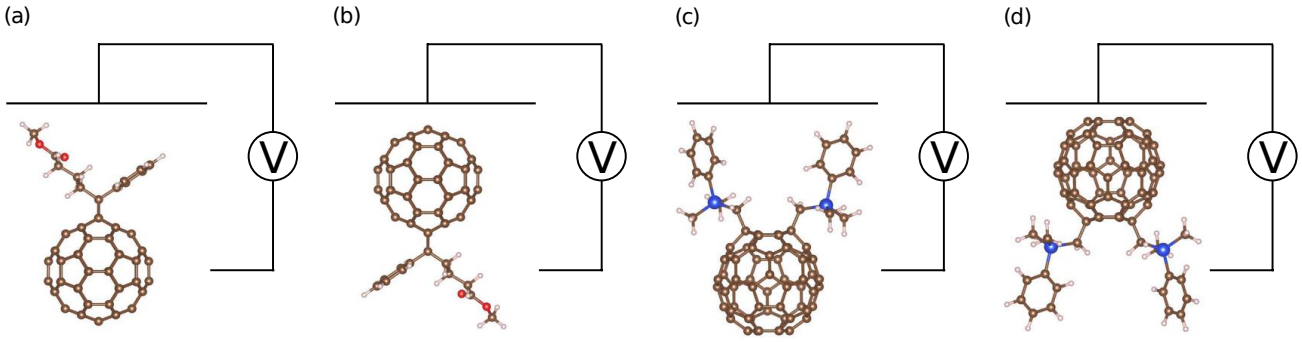

Figure 1: Geometric structures of (a), (b) PCBM and (c), (d) SIMEF and the structural model of (a), (c) tail-to-head and (b), (d) head-to-tail to simulate the heterointerface.

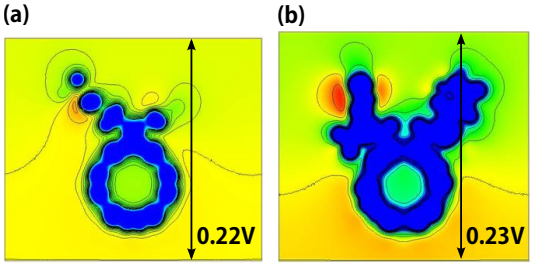

Figure 2: Contour plot of the electrostatic potential of (a) PCBM and (b) SIMEF without the external electric field.

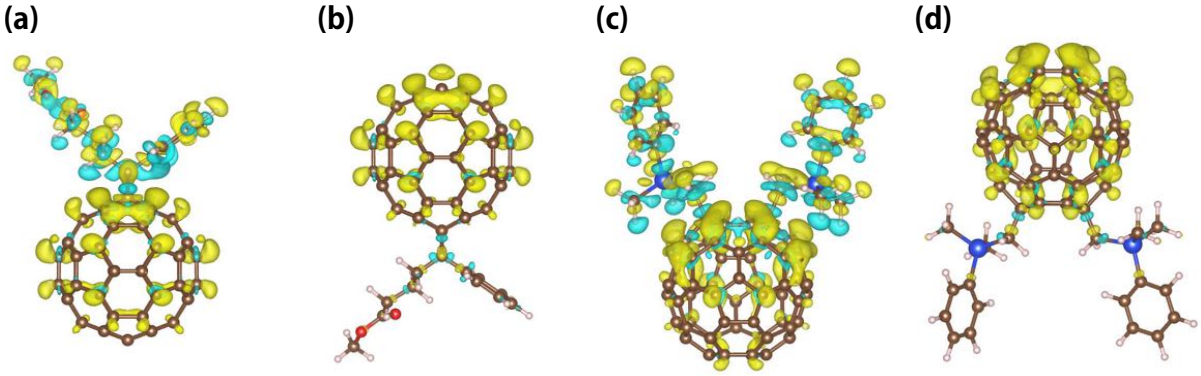

Figure 3: Isosurfaces of accumulated electrons of (a), (b) PCBM and (c), (d) SIMEF with two different molecular arrangements to the electrode under the external electric field.

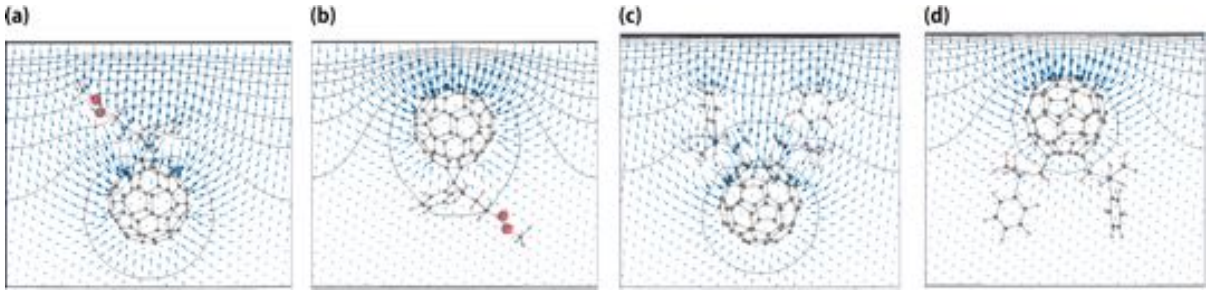

Figure 4: Contour plots of electrostatic potential and vector plots of the induced electric field under the electron accumulation.