

Probing Charge Transfer in Organic Photovoltaic Cells by Directly Exciting Single Electron

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In this paper, we use the first principle quantum chemistry method to calculate the electronic structures of the charge transfer excited state in P3HT/PC₆₀BM heterojunction and amphiphilic oligothiophene-C60 dyad (AMPHI). With the separation distances smaller than 4.0 Å, when PC₆₀BM molecule is placed in the middle of poly(3-hexylthiophene) (P3HT) oligomer chain hole distributes at the bridge electronic state; if the PC₆₀BM molecule is then shifted to the side of P3HT chain, electron resides at the bridge electronic state. When the separation distances are larger than or equivalent to 4.0 Å, the bridge electronic state disappears. The bridge electronic state doesn't occur either in AMPHI probably because of the large separation distance between donor and acceptor in this molecule. The calculated maximum binding energy of the charge transfer state in P3HT/PC₆₀BM heterojunction is about 0.4 eV, in good agreement with experiments.

Key Words: Charge transfer state, Binding energy, Bridge electronic state, Organic photovoltaic cell.

INTRODUCTION

Charge transfer processes in an electron donor (D) and an electron acceptor (A) heterojunction have attracted much attention in recent years¹⁻³. In a D-A heterojunction, excitons generated by the absorption of incident light in D or A dissociate at the interface followed by the charge separation⁴ or the formation of charge transfer state⁵. In the charge transfer state, electron in acceptor and hole in donor are bound with each other as a pair *via* the Coulombic attraction across the D-A interface⁶⁻⁸. The existence of interfacial charge transfer state has been proved by many experiments, such as the photoluminescence spectroscopies, transient absorption spectroscopies and pump/probe photocurrent spectroscopies⁹⁻²⁰. This charge transfer state is believed as the crucial intermediate process in charge separation of organic photovoltaic cells²¹.

In a general molecular picture, the charge transfer state can be formed by two ways: (a) Electron in the exciton transfers from the lowest unoccupied orbital (LUMO) of donor to the LUMO of acceptor and Coulombically bound with the left hole. (b) Alternatively, hole in the exciton transfers from the highest occupied orbital (HOMO) of acceptor to the HOMO of donor and bound to the left electron as a pair^{22,23}. In the former case, the driving force is the energy difference between LUMO energy level of donor and acceptor; while in the latter case, the energy difference between HOMO energy level of acceptor and donor acts as the driving force²⁴⁻²⁶.

In fact, there is the third mechanism in forming the D-A interfacial charge transfer state. In this case, the electron in the HOMO of donor is directly excited to the LUMO of acceptor^{18,21}. Often the molecular vibrations are excited at the same time, forming the so-called hot charge transfer state. The charge transfer state is generated by the D-A bimolecular absorption of the incident phonon at the interface. This picture is of important significance for the quantum theoretical calculations on the electronic structures of interfacial charge transfer state. In a practical quantum chemistry calculation, one doesn't need to distinguish the way in which the charge transfer state is generated. One only needs to think about the electronic structures of the D-A heterodimer at the interface.

Quantum chemistry time dependent density functional theory (TDDFT) method is usually employed in obtaining the electronic properties of the charge transfer state¹⁸, since in essence the charge transfer state is an excited state. However, TDDFT calculations only give the information of various electronic configurations. It can not give out the information of the new energy levels of the electron and hole in the charge transfer state. Therefore, other two ways that can give this kind of information are of interest in discussing the orbital relaxation in the charge transfer state. One is the constrained density functional theory method²¹, in which one positive charge is set on the donor molecule and one negative charge is set on the acceptor molecule. However, this method is challenged by another approximate density functional theory

method²⁷. This approximate density functional method taken by Kanai and Grossman²⁸ in the research of poly(3-hexylthiophene) (P3HT) and C60 blends gives the possibility of adiabatic partial charge transfer.

In this paper, we employ the standard density functional theory (DFT) method to investigate the electronic structures of charge transfer state in P3HT and fullerene derivative PC₆₀BM heterojunction and those in a fused molecule, amphiphilic oligothiophene-C60 dyad (AMPHI)²⁹, as shown in Fig. 1. The former is the case of the inter-molecular charge transfer, while the latter is the case of intra-molecular charge transfer. In our DFT calculations, we do not change the functional, as done by Kanai and Grossman²⁸ and thus the more complicated functional, such as B3LYP³⁰⁻³³ can be employed. This is of important significance for the convincing quantum chemistry calculations on the electronic structures of the charge transfer state.

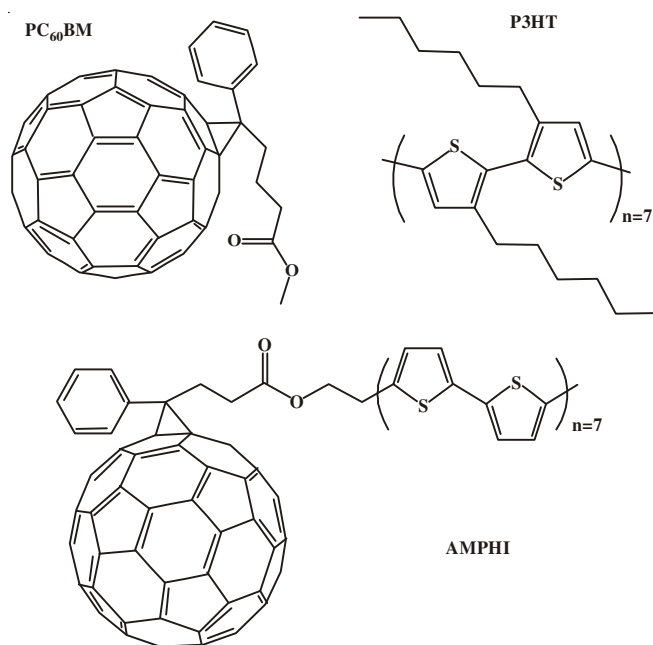


Fig. 1. Selected systems under study

COMPUTATIONAL METHOD

The geometries of the selected molecules are optimized by the hybrid density functional B3LYP with the basis set of 6-31G* in the Gaussian 09 package. The oligomer of P3HT with 7 repeating units (for simplicity, in the next description we just use P3HT to represent this oligomer without confusion), as shown in Fig. 1, is utilized in all the calculations of electronic structures. The ground state HOMO and LUMO orbital of the P3HT/PC₆₀BM heterojunction and AMPHI are exchanged and the quadratically convergent self-consistent-field method is employed all the time. In this paper we only take account of the adiabatic process of electronic excitation. Thus, the geometrical relaxation of charge transfer state is neglected due to the consideration that in a superfast charge dissociation and charge separation processes at the organic photovoltaic heterojunction interface this atomic relaxation is not the key process.

The key point in present DFT calculations is to directly excite one electron from HOMO or lower occupied orbital to the LUMO or higher unoccupied orbital. This is implemented by exchange the corresponding occupied orbital and the unoccupied orbital to construct the new density matrix. After the self consistent process, the electronic energy levels of the original single excited electronic configuration are fully relaxed, giving the correct electronic structures of charge transfer state. In this paper, the geometries of P3HT-PC₆₀BM heterodimer are set as following: the PC₆₀BM molecule is put on the top of the P3HT backbone with a six-membered carbon ring parallel to the π -conjugation plane of P3HT. The distance between the six-membered carbon ring of PC₆₀BM and the P3HT conjugation plane is referred to as the separation distance between PC₆₀BM and P3HT in following discussion. In one case, the PC₆₀BM molecule is at the middle of the oligomer backbone; in another case, PC₆₀BM molecule was shifted towards the end of the thiophene chain with respect to the first case.

RESULTS AND DISCUSSION

First, we scan the potential curve of PC₆₀BM-P3HT heterodimer with respect to the different distance between PC₆₀BM and P3HT. From Fig. 2, we find that the distance between PC₆₀BM and P3HT with the lowest total energy of PC₆₀BM-P3HT heterodimer is 4.0 Å. Due to the different experimental method in making the PC₆₀BM/P3HT bulk heterojunction, there may be a distribution of distance between PC₆₀BM and P3HT around the lowest energy equilibrium geometry. Hence, we investigate different cases of the electronic structures of the charge transfer state, the separation distance being set in the range of 3.0-5.5 Å with an interval of 0.5 Å. This is because in a real vibration of the PC₆₀BM-P3HT dimer with a higher vibrational quantum number, the distance between PC₆₀BM and P3HT can vary with a bigger deviation against the equilibrium distance.

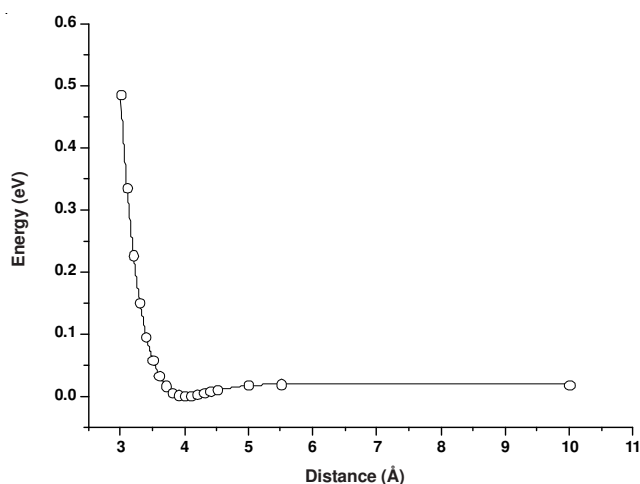


Fig. 2. Potential curve of the ground state in P3HT/PC₆₀BM heterojunction with respect to the separation distances (the point with minimum energy is set as the reference point)

Electronic structures of heterojunction: Fig. 3 showed the energy level diagram of the ground state electronic structures (at the top) and that of the charge transfer state electronic structures (at the bottom) of the PC₆₀BM-P3HT

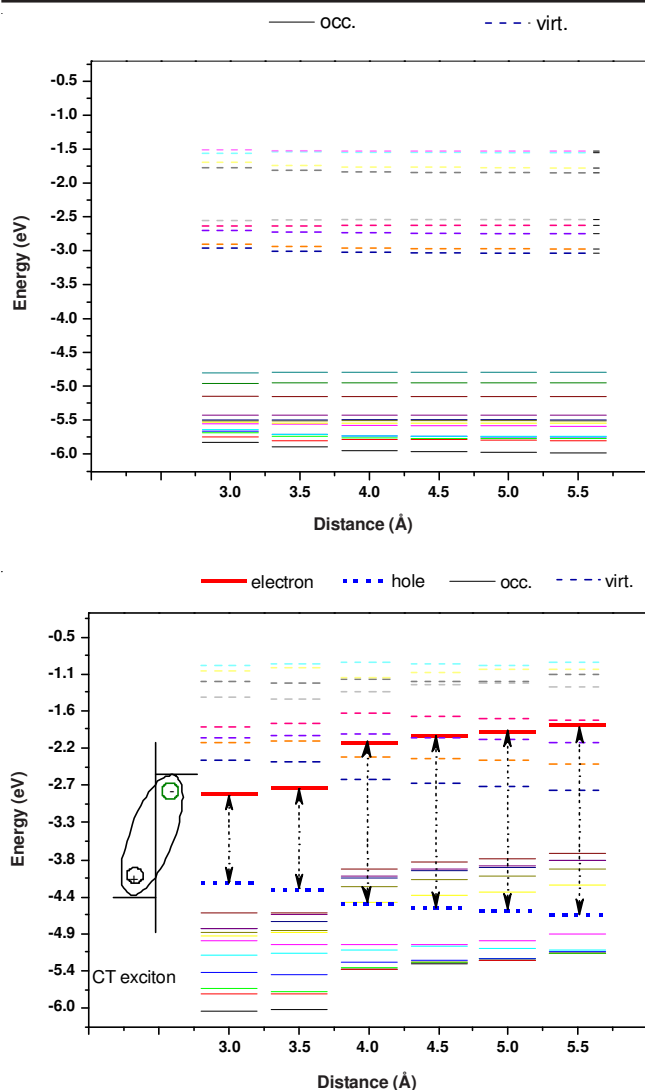


Fig. 3. Separation distance dependent distribution of electronic energy levels of P3HT/PC₆₀BM heterojunctions in the ground state (top) and in the charge transfer state (bottom)

heterodimer with different separation distances. We can find that the ground state energy level distribution converges quickly as the separation distance increasing from 3.0 to 5.5 Å. But in the charge transfer excited state, the electronic structures are far from convergence as shown at the bottom of Fig. 3. At the distances of 3.0 and 3.5 Å which are smaller than the equilibrium distance of 4.0 Å, the excited electron and the left hole redistribute, residing in between the occupied orbitals and the virtual orbitals. When the distances are larger than or equivalent to the equilibrium distance (the cases of 4.5, 5.0 and 5.5 Å), the electron enters into the region of virtual orbitals and the hole into the region of occupied orbitals. This behaviour of energy levels indicates that the equilibrium distance of the charge transfer state in PC₆₀BM-P3HT heterodimer is between 3.5 and 4.0 Å. This smaller equilibrium distance of the charge transfer state is as expected, since after charge transfer the PC₆₀BM with negative charge and the P3HT with positive charge coulombically attract with each other. Although the electron and hole enter into the region of unoccupied and occupied energy levels, we find that the orbital of electron and that of hole still corresponds to LUMO of PC₆₀BM and

HOMO of P3HT, respectively, as the cases of the distances smaller than 4.0 Å. This is further discussed from the analysis of electrostatic potential of electron and hole orbital as in the following section.

Charge transfer: We choose to show the representative cases of the electrostatic potential distributions of the electron orbital and hole orbital in the charge transfer state of PC₆₀BM/P3HT heterojunction. The charge transfer in AMPHI²⁹ is also discussed.

PC₆₀BM/P3HT Heterojunction: At the top of Fig. 4, we find that with the separation distance of 3.5 Å the so called bridge electronic state occurs in the hole orbital. In contrast, the electron has its complete density in PC₆₀BM. This indicates the partial charge transfer in the heterojunction as noticed by Kanai and Grossman²⁸. At the bottom of Fig. 4, the separation distance is set as 4.0 Å and do not find the bridge electronic state. The calculations were checked and found that in all cases with separation distances larger than 4.0 Å and there is no existence of the bridge electronic state. Fig. 5 showed that the electrostatic potential of electron orbital and hole orbital when the PC₆₀BM molecule is shifted to the left side of the P3HT chain. It is interesting to find that this time the electron orbital becomes the bridge electronic state, similar to the finding of Kanai and Grossman²⁸. We have noticed that the calculations

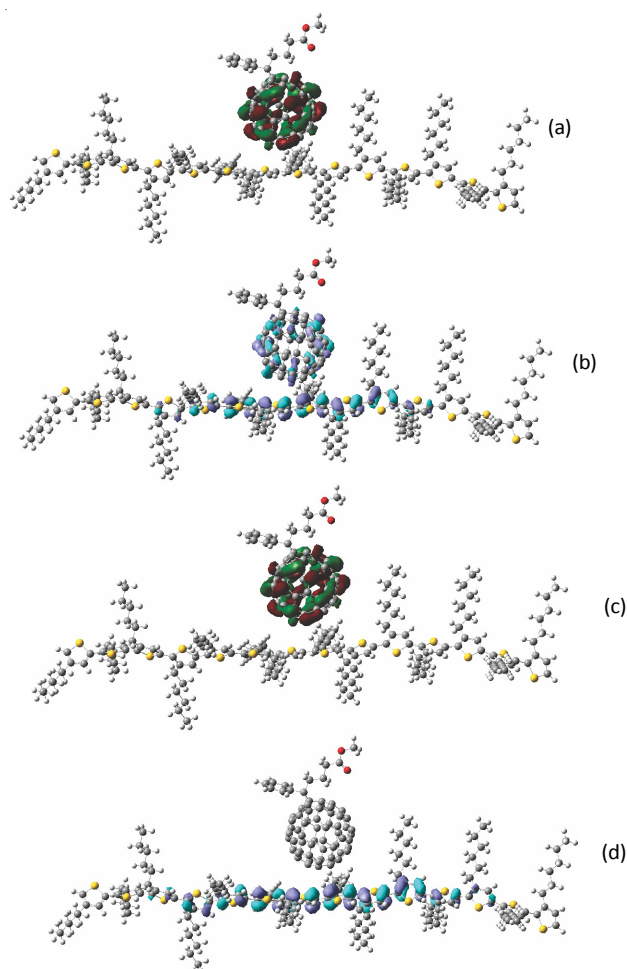


Fig. 4. Electrostatic potential distribution of electron (a), hole (b) with the separation distance of 3.5 Å and that of electron (c), hole (d) with the separation distance of 4.0 Å in . Note that the hole in (b) is of the property of bridge electronic state

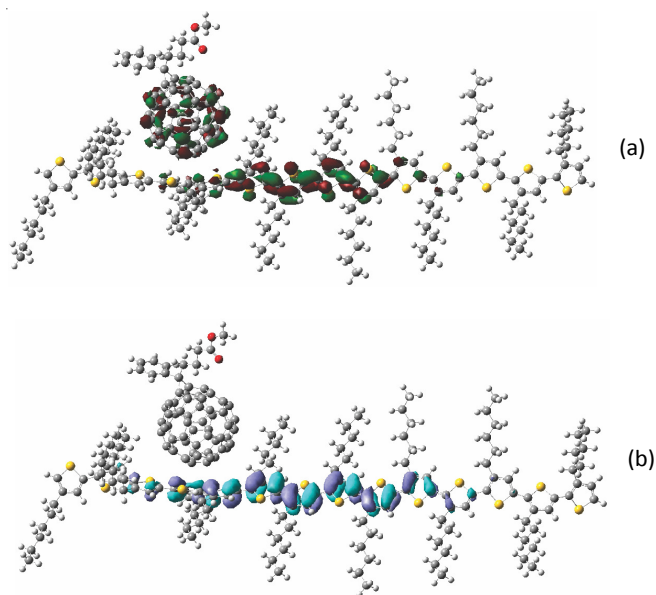


Fig. 5. Electrostatic potential distribution of electron (a) and hole (b) in P3HT/PC₆₀BM heterojunction with the separation distance of 3.5 Å and the PC₆₀BM molecule shifting to the left side of P3HT conjugation backbone. Note that in this time the electron locates in the bridge electronic state

of Kanai and Grossman²⁸ are performed in the primitive cell with a periodic boundary condition. The similar bridge electronic state between our calculations and those of Kanai and Grossman²⁸ may be due the constraint of the heterojunction in a relative smaller region. However, our calculations are performed without the periodic boundary condition and thus the localizations of electrostatic potential in the backbone of P3HT chain can be found.

Charge transfer in AMPHI: The AMPHI (Fig. 1) was studied as the photoconductive material by Li *et al.*²⁹. The geometrical feature of this molecule lies in that the electron donor and electron acceptor are chemically connected to form a fused molecule. In this case, the charge transfer happens in different parts of AMPHI, which is referred to as the intramolecular charge transfer. In this case we do not find the bridge electronic charge transfer state (Fig. 6). This may be because of the relative large spatial distance (*ca.* 9.0 Å) between the donor part and the acceptor part in the AMPHI molecule, which is similar to the cases discussed above.

Binding energies: According to our calculations, the convergence separation distance is *ca.* 15 Å. Therefore we set the total energy of the lowest excited state of PC₆₀BM-P3HT heterodimer at this separation distance as the reference zero point for calculating the binding energies of charge transfer states. As shown in Table-1, the maximum binding energy of 0.77 eV in the charge transfer state of PC₆₀BM/P3HT heterojunction

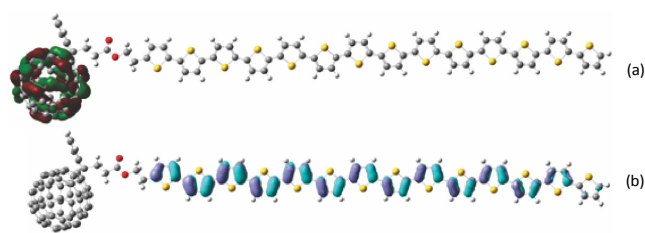


Fig. 6. Electrostatic potential distribution of electron (a) and hole (b) in the charge transfer state of AMPHI molecule

is at the separation distance of 3.5 Å. If we further consider the modification of the geometrical relaxation of PC₆₀BM (with one negative charge) and P3HT (with one positive charge), the maximum binding energy in the charge transfer state of PC₆₀BM/P3HT heterojunction is *ca.* 0.4 eV, in good agreement with the experiments²¹. On the other hand, one can see from Table-1 that the excitation energies always increase and should finally converge at the distance of infinity. The separation distance dependent behaviour in the excitation energy is parallel to that in the energy difference between excited electron and hole in the charge transfer state (Fig. 3).

Conclusion

In this paper, the first principle quantum chemistry method is employed in calculating the electronic structures of the charge transfer excited state in P3HT/PC₆₀BM heterojunction and AMPHI. Accordingly, the intermolecular charge transfer in P3HT/PC₆₀BM heterojunction and the intramolecular charge transfer in AMPHI are discussed. When PC₆₀BM molecule is placed in the middle of P3HT oligomer chain with the separation distances smaller than 4.0 Å, hole is of the property of bridge state. If the PC₆₀BM molecule is shifted to the side of P3HT chain, electron resides at the bridge electronic state. When the separation distances larger than or equivalent to 4.0 Å, the bridge state disappears. The bridge electronic state doesn't occur either in AMPHI because of the large separation distance between donor and acceptor in the molecule. After rectification, the calculated maximum binding energy of the charge transfer state in P3HT/PC₆₀BM heterojunction is *ca.* 0.4 eV, in good agreement with experiments.

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TABLE-1
LOWEST EXCITATION ENERGIES (E_{lex}) AND BINDING ENERGIES (E_{B}) OF THE CHARGE TRANSFER STATE (IN THE UNIT OF eV) WITH RESPECT TO THE DISTANCES BETWEEN P3HT AND PC₆₀BM (IN THE UNIT OF ANGSTROM). NOTE THAT BOTH E_{lex} AND E_{B} CONVERGE AT THE DISTANCE OF 15 ANGSTROM

	Distances						
	3.0	3.5	4.0	4.5	5.0	5.5	15.0
E_{lex}	1.59	1.69	1.89	1.96	2.01	2.07	2.51
E_{B}	0.45	0.77	0.63	0.56	0.49	0.44	0.00

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