論 文 の 内 容 の 要 旨

(Thesis Summary)

論文題目　Study on Interface and Crystallization of Materials in Organic Solar Cells

(有機薄膜太陽電池における材料の界面と結晶性に関する研究)

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In organic electronic devices such as organic solar cells (OSCs), interface of materials is of vital importance. A critical process for electricity generation in OSCs is the formation of free charges. However, unlike silicon solar cell in which the photogenerated charge pairs can be thermally activated into the free carriers due to its high dielectric constant, organic semiconductors generally have a very low dielectric constant (~3), giving rise to a large binding energy of electron-hole pairs generated by light. Instead of being separated, these strongly bonded pairs (excitons) diffuse to the interface of p-type (donor (D)) and n-type (acceptor (A)) materials and separated by the energy offsets of the highest occupied molecular orbitals (HOMO) and the lowest unoccupied molecular orbitals (LUMO) between two materials. This process is critical to achieve the current generation in OSCs and therefore makes D/A interface indispensable in the device. On the other hand, the major energy loss of OSCs also takes place at D/A interface through geminate and bimolecular charge recombination. Furthermore, open circuit voltage (V_{OC}) of the device is largely affected by the D/A interfacial energy levels (E_{DA}, energy difference between LUMO of D and HOMO of A). From these points above, investigating how D/A interfacial property affects the performance of OSCs could give important guideline to further push the efficiency of the device. In this thesis, conceptually new ideas for improving efficiency of OSCs via purposely modifying D/A interface and crystallization of materials are proposed. The observed change of device performance was correlated to the photo-physical processes of charge transfer, separation and recombination, providing a new methodology to enhance efficiency of OSCs. The strategies purposed in this thesis for improving efficiency of device are listed in the following paragraphs.

1.Manipulating molecular dipole moments at D/A interface by external stimuli

The D/A interfacial energy levels play a crucial role in determining V_{OC} of OSCs. The

maximum V_{OC} can be related to E_{DA} at this interface. Generally, V_{OC} could be changed by different combination of materials utilizing different energy levels. In prior to this study, however, a new way of manipulating V_{OC} of OSCs was provided by insertion of dipole moment at D/A interface, shifting interfacial energy levels (E_{DA}). This clearly shows that the performance of OSCs could be strongly affected by the D/A interfacial properties. Furthermore, it is possible that these interfacial properties could be changed by external stimuli after the fabrication of the devices. In this study, V_{OC} of bilayer OSCs with D/A interfacial dipole moment was reversibly controlled by using external electric field, which was correlated to the reorientation of dipole moment at D/A interface. This could clarify the relationship between the interfacial properties and the device performance, and also produce a new type of optoelectronic device that responds to various external stimuli.

The *J-V* characteristics under dark showed that as the applied bias became more negative, the reverse saturation current density decreased and the turn-on voltage for the diode increased. Under light irradiation, V_{OC} increased from 0.34 to 0.51 V as the negative bias voltage increased, whereas J_{SC} decreased from 1.40 to 1.15 mA cm^{-2}. On the other hand, after V_{OC} of the PCBM/FC_8//P3HT device (chemical structures of materials were shown in Figure 1a) was increased from 0.34 to 0.51 V by applying a negative bias (−8.5 V), the positive bias voltages from +3 to +5.5 V were applied to the same device. The dark *J-V* characteristics shown in Figure 2c were the reverse of those caused by the negative bias: the reverse saturation current density was increased in the negative voltage region and the turn-on voltage was decreased. Under the light irradiation, V_{OC} gradually decreased when the positive bias voltages were applied and a V_{OC} of 0.36 V was obtained after a bias of +5.5 V was applied.

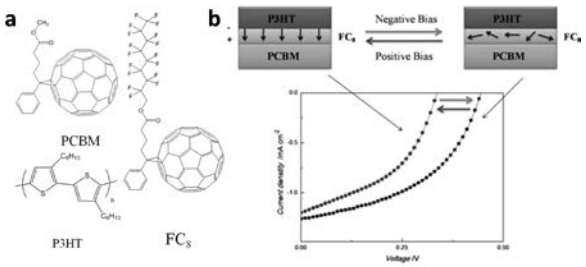

Figure 1 (a) Chemical structures of PCBM, P3HT and FC_8, (b) Reversible control of V_{OC} in PCBM/FC8//P3HT device via applying positive and negative bias in turn.

In order to demonstrate the reversible control of V_{OC} in the PCBM/FC_8//P3HT device, a negative (−7.5 V) and then a positive (+6 V) bias voltage were applied to the device by turn repeatedly. Figure 1b shows V_{OC} of the PCBM/FC_8//P3HT device switched reversibly between 0.32 and 0.44 V. This process could be repeated for over 3 turns. These results show that the change in V_{OC} was caused by the FC_8 layer at the D/A interface (shifting E_{DA}) and was reversibly controlled by the bias directions.

2. Effect of D/A distance on device performance and use of energy transfer process.

The J_{SC} and V_{OC} are two key factors that have critical influence on the device performance of

OSCs. The energy levels of the donor and acceptor materials are crucial for achieving a high J_{SC} and V_{OC}. However, the interfacial structures between the organic materials substantially affect the J_{SC} and V_{OC} through the energy of the charge transfer (CT) states and the charge separation and recombination reaction kinetics. Precise control of these processes via interfacial modification therefore could enhance device performance in terms of J_{SC} and V_{OC}. In this study, the effect of D/A distance on device performance was analyzed by an equivalent circuit model, and energy transfer process via dye doping at D/A interface was also investigated. The results showed that separating the donor and acceptor layer in bilayer OSCs with a thin insulating layer (CYTOP, chemical structures is provided in Figure 2d) increases the energy of the CT state by weakening the Coulomb interaction at the interface and also suppresses photoinduced CT and recombination.

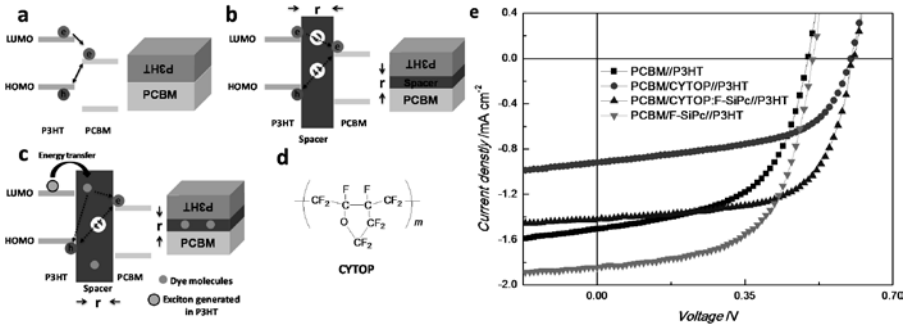

Figure 2 (a) P3HT/PCBM interface at which charge separation and recombination happened, (b) with a spacer at P3HT/PCBM interface, CT state become delocalized, and charge separation and recombination were also suppressed, (c) introducing small amount of charge separation center to promote energy transfer for charge separation, (d) chemical structure of CYTOP, (e) *J*-*V* curves of the four OSCs under the irradiation, PCBM//P3HT (■), PCBM/CYTOP//P3HT (●), PCBM/CYTOP:F-SiPc//P3HT (▲), and PCBM/F-SiPc//P3HT (▼).

Although these effects usually increase V_{OC} and decrease J_{SC}, the trade-off was avoided by doping the insulating layer with a dye to utilize energy transfer process. (Figure 2c) The increase in V_{OC} without the reduction in J_{SC} enhanced the conversion efficiency of the OSCs by 30% (Figure 2e).

The results were analyzed by an equivalent circuit model, expression of V_{OC} deduced from this model is: $V_{OC} \approx \frac{n\phi}{e} - \frac{nkT}{e}\ln\left(\frac{J_{00}}{J_{ph}(V_{OC})}\right)$, where n is the ideality factor, k is the Boltzmann constant, T is the temperature, e is the elementary charge, $J_{ph}(V_{OC})$ is the photogeneration rate of the charge density under open circuit conditions, J_{00} is the pre-exponential factor, ϕ is the energetic term for the thermal excitation generation of the charge carrier under dark conditions, and $n\phi$ is related to energy of CT state (E_{CT}). As the thickness of CYTOP layer increased, V_{OC} was enhanced and then saturated, J_{SC} on the other hand decreased. The equivalent circuit model showed the J_{00} decreased and $n\phi$ increased as the thickness increased, indicating suppressed

charge recombination and enhanced E_{CT}. This is due to weakened intermolecular coupling at D/A interface making CT state more delocalized. On the other hand, as concentration of dye doped in CYTOP layer increased, V_{OC} kept constant and then decreased, and J_{SC} increased monotonically. Dye doping in CYTOP layer promoted energy transfer and enhanced J_{SC}, but excessive dye could also promote charge recombination causing loss of V_{OC}.

3. Crystallization induced energy level changes in PCBM and its effect on OSC performance

In high performance OSCs, PCBM are often used as the electron acceptor in the combination with semiconducting polymers and oligomers as the donors. Crystallization of the materials in OSCs could largely affect the device performance through mixing morphology, efficiencies of the charge separation, recombination and collection in the organic thin films. However, how the crystallization of PCBM affects the energy levels and its electronic property has not been clear, although they have primary importance for the photovoltaic processes. In this study, the effect of the thermal annealing on the energy levels of PCBM films were investigated using ultraviolet photoelectron spectroscopy (UPS), x-ray photoelectron spectroscopy (XPS) and low-energy inverse photoemission spectroscopy (LEIPS). We observed that the thermal annealing at 150 °C induces reductions of both ionization potential (IP, 5.95 to 5.74 eV) and electron affinity (EA, 3.76 to 3.74 eV) with the narrowing of the HOMO-LUMO gap by 0.1 eV. These changes are associated with the crystallization and the reduction of the film thickness by 2.54%. Precise measurements of both IP and EA enabled us to evaluate the effects of the electrostatic polarization energy. The above phenomenon was also utilized in OSCs. A bilayer device with crystalline or amorphous PCBM layer showed V_{OC} difference of 0.12 V, which agrees well with the energy level change reveled by spectroscopy analysis. These results showed that crystalline PCBM in OSCs could have significantly different energy levels from the non-crystallized domains through the change of polarization energy, offering a new way to utilize crystalline PCBM for efficient OSCs.

In summary, D/A interfacial property was modified via various approaches in this research. The results showed that device performance of OSCs could be significantly altered by interfacial modification. It was demonstrated that by purposely modifying the interface in OSCs, a clearer picture of photo-physical process at interface could be revealed. Furthermore, by understanding these fundamental process in OSCs, a new route is provided to push the efficiency of device, and even pave the way for breaking its upper limit. The results obtained in this study could not only shed light on optimization of device structure, but also give guideline to the material design for more efficient OSCs.