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Electronic Interfacial Properties of Bathocuproine with Metal and Fullerene for Organic Solar Cells

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Abstract

Organic solar cells (OSCs) belong to third generation solar cells. They have many advantages, such as low cost, easy fabrication, and compatibility with large-scale and flexible substrates by means of low-cost printing and coating technologies. OSCs have made significant progress in the past two decades, and the power conversion efficiency (PCE) has been achieved to be 11.1%. However, the market only has a few manufacturers that have been able to offer this young technology. This is caused by the relatively low PCE and the poor stability as compared to the silicon solar cells.

To further improve the performance of OSCs, it is essential to understand the deep physics concealing in the cell. An OSC consists of several layers, which are sandwiched between two electrodes such as an indium tin oxide (ITO) anode and a metal cathode. As a result, there are many interfaces in OSCs where charge carriers have to cross them. The study of electronic structure is an important matter because the electronic structure affects directly the charge transport and extraction. Considering such an important point, the study of electronic structure should be executed in detail to understand and improve the device characteristics.

The mechanisms of the energy level alignment (ELA) of organic semiconductor interfaces have been investigated extensively to understand the fundamental physics of organic-conductor and organic-organic interfaces and to improve the performance of organic devices. However, the interfacial electronic structure and the ELA mechanisms are still not comprehensively understood. The interfaces, including organic/organic and organic/metal in OSCs play essential roles to the cell performance by separating excitons and extracting free charges. Unfortunately, the common model for organic/organic and organic/metal interfaces are not yet established.

A buffer layer is indispensable in OSCs. The most commonly used buffer layer between acceptor and cathode layer is bathocuproine (BCP). The insertion of BCP layer can greatly improve the PCE. Several interpretations have been proposed to explain the working mechanism, such as functioning as an exciton-blocking layer, reducing nonradiative recombination of excitons at the C₆₀/Al interface, increasing the built-in field, avoiding the formation of aluminum carbide and

acting as an optical spacer. However, the clear mechanism has not yet extensively understood. Therefore, it is of importance to understand the electronic properties of BCP-related interfaces. Gaining insight into the electronic properties of BCP with metal and C₆₀ is necessary to understand the mechanism of BCP, and therefore to improve the cell performance. This thesis aims to clarify the working mechanism of BCP buffer layer in OSCs by systematically studying the electronic properties of C₆₀/BCP/metal interfaces as a function of thickness of intermediate BCP layer and work function of metal.

First, the thickness dependence of energy level alignment of C₆₀/BCP/Ag interfaces was studied. The thicknesses of organic materials strongly affect the performance of OSCs because of the short exciton diffusion length, low carrier mobility, high resistance and unique carrier hopping mechanism in organic materials. It has been demonstrated that the performance of OSCs is dependent on the thickness of BCP layer and a thick BCP buffer layer deteriorates to the device performance. Moreover, it has been reported that the shape of current-voltage (*J-V*) curve of OSC depends on the BCP layer thickness. The thick-BCP induced S-shaped *J-V* curve leads to a low fill factor and poor device performance. Therefore, it is critical to study the energy level alignment of C₆₀/BCP/Ag heterostructures as a function of BCP layer thickness to determine the role of BCP and clarify the origin of the S-shaped *J-V* curve. The results show that the interfacial properties are strongly dependent on the thickness of BCP intermediate layer. When BCP layer is thin, Ag and BCP can weakly interact, resulting in the formation of Ag-BCP complex. When C₆₀ layer is subsequently deposited on this complex, the interaction between Ag-BCP complex and C₆₀ produces gap states at the C₆₀/complex interface. This interaction drives the flat energy levels, and therefore the energetic difference of the lowest unoccupied molecular orbital (LUMO) levels between BCP and C₆₀ is low. When BCP layer is thick, the interaction at interfaces, such as BCP/Ag interface and C₆₀/complex interface, would be suppressed. In this case, energy band bending at C₆₀/BCP interface was observed, which is owing to charge transfer from BCP to C₆₀ when forming the interface. This band bending generates a considerable barrier for electrons transport (as high as 1.4 eV). In a word, the electronic properties of C₆₀/BCP/Ag heterostructures are strongly dependent on the thickness of the BCP layer. When BCP layer is thin, the energy levels are flat, which is beneficial to the OSCs. When the BCP layer is thick, energy band bending occurs at the C₆₀/BCP interface, which generates a considerable barrier for electrons transport. This will induce charge accumulation at the C₆₀/BCP interface in OSCs and therefore lead to S-shaped *J-V* curve.

To confirm the reasonable of interfacial properties of C₆₀/BCP/Ag in device, inverted OSC with structure of ITO/BCP/C₆₀/SubPc/MoO₃/Ag was fabricated. The open-circuit voltage (V_{OC}), short-circuit current (J_{SC}), fill factor (FF) and overall PCE of the cell are 1.03 V, 3.06 mA/cm², 29.3 % and 0.93 % under illuminated condition. Unfortunately, the *J-V* curve shows an anomalous S-kink, leading to low fill factor. To improve the device performance, inverted OSC with Ag-doped BCP buffer layer was fabricated, because the formation of Ag-BCP complex seems very important for the device from the discussion aforementioned. And this complex can be apparently formed by

co-evaporation of Ag and BCP. Then, the doping concentration was optimized. The thickness of Ag-doped BCP layer was fixed at 10 nm.

The results show that the transmittance is strongly dependent on the Ag content. When the molar ratio (MR) of Ag and BCP is 1:1, the transmittance is nearly the same as the BCP layer. When the MR is up to 1:1, the transmittance decreases with increasing the MR . This decrease can be ascribed to the formation of Ag nanoparticles. Next, the exciton quenching properties were characterized by photoluminescence (PL) measurement. The result show that the PL peak intensity of C_{60} layer on Ag-doped BCP layer with $MR=1:1$ is the same as the quartz/ C_{60} and quartz/BCP/ C_{60} samples. When the MR is above 1:1, the PL intensity gradually decreases with increasing the MR , suggesting that Ag-doped BCP layer with $MR=1:1$ has no influence on the exciton quenching of C_{60} layer. The decrease of the peak intensity is caused by the formation of C_{60} /metal interface, because metals can render recombination centers more likely and strongly enhance the quenching rate due to charge transfer process. As we all know, the morphologic properties are very important for device performance. The morphology measurement shows that the root mean square (RMS) roughness of ITO, BCP on ITO and Ag-doped BCP on ITO are 2.1, 0.9, and 1.3 nm, respectively. The surface of BCP and Ag-doped BCP layers is much smoother than the bare ITO. When C_{60} layer is directly deposited on bare ITO layer, the RMS roughness is 2.1 nm. However, the RMS roughness of C_{60} layer on BCP deteriorates to be 5.9 nm. In contrast, when C_{60} layer is deposited on Ag-doped BCP layer, the RMS roughness of C_{60} layer is only 1.8 nm. The smooth surface of C_{60} layer will make a good interface contact, and therefore facilitate the carrier dissociation in OSCs. This indicates that Ag-doped BCP layer is helpful to the growth of C_{60} layer and result in a smooth morphology of C_{60} layer. Additionally, we have demonstrated that the electrical conductivity of BCP layer can be greatly increased by metal doping. The Ag-doped BCP with $MR=1:1$ shows 3×10^{-2} S/m of conductivity, which is more than 5 orders magnitude higher than pure BCP with 6×10^{-8} S/m of conductivity.

Therefore, the Ag-doped BCP layer has good conductivity, high transparence, no influence on exciton quenching and can result in smooth surface of subsequently deposited C_{60} layer. All of these properties meet the demand of cathode buffer layer in inverted structure cell. The performance of cell with Ag-doped BCP with $MR=1:1$ shows the V_{OC} of 0.87 V, the J_{SC} of 3.51 mA/cm^2 , the FF of 45.2 % and overall PCE of 1.38 %. Importantly, the S-kink disappeared in the $J-V$ curve for the cell with Ag-doped BCP, so the FF was drastically increased and the PCE was improved by 48 %. The absence of the S-kink in $J-V$ curve may be caused by the favorable energy level alignment at C_{60} /Ag-doped BCP. To confirm it, the interfacial properties of C_{60} /Ag-doped BCP and C_{60} /BCP were studied by ultraviolet photoemission spectroscopy (UPS) measurement.

The results show that the energy levels are flat at C_{60} /Ag-doped BCP interface. Additionally, the highest occupied molecular orbital (HOMO) level of Ag-doped BCP is much higher than that of BCP. Therefore, the LUMO level of Ag-doped BCP approaches the E_F . For bulk C_{60} , the HOMO levels are nearly the same for both cases. Overall, the energy difference between the LUMO levels

of Ag-doped BCP and C₆₀ is 0.4 eV, while 1.5 eV for no doped case. The considerably large energy difference at BCP/C₆₀ interface will act as a barrier to block the electrons transportation from C₆₀ layer to BCP layer in device. So the electrons will be accumulated at the interface, and therefore lead to the S-shaped *J-V* curve. However, in the case of Ag-doped BCP, the transfer of free charges in devices will become much easier than that of BCP case. This is caused by the high electrical conductivity of Ag-doped BCP, small barrier height at C₆₀/Ag-doped BCP interface and the presence of gap states. In a word, OSC with Ag-doped BCP shows good performance because of the absence of S-kink in *J-V* curve. This is mainly caused by the favorable electronic properties of C₆₀/Ag-doped BCP interface. In Ag-doped BCP case, the barrier is as low as 0.4 eV, so the free charges can easily transfer and then be effectively extracted by the electrode. Additionally, the emergence of gap states can also facilitate the electrons transfer by providing additional transportation channels. This result also shows that Ag-doped BCP is an effective buffer layer for inverted structure OSCs.

As is well known, low work function (*WF*) metal is useful to be the cathode in OSCs. However, the electronic properties of BCP/metal interface are strongly dependent on the *WF* of metal by forming different dipole layer. Therefore, it is very important to study the interfacial properties of C₆₀/BCP/metal interfaces as a function of metal. To get a comparison with Ag case, Mg was selected as a low *WF* metal, which has a *WF* of 3.7 eV. The electronic properties of C₆₀/BCP/Mg interfaces were systematically studied.

From the UPS spectra, two small peaks can be clearly observed for BCP layer thickness of 2-16 Å on Mg, suggesting the presence of gap states. To derive the origin of gap state, X-ray photoemission spectroscopy (XPS) measurements were carried out to get a deeper insight at BCP/Mg interface. The results show that the C1s peak is not affected by BCP layer thickness. For N1s, two peaks can be observed for thin layers, whereas there is just one peak when the BCP layer thickness is up to 16 Å. This suggests the chemical interaction exists at BCP/Mg interface.

To further understand the electronic structure of the BCP on Mg, near edge X-ray absorption fine structure spectroscopy (NEXAFS) was carried out to characterize the molecular orientation. For thin BCP layer, with changing the incidence angle from normal to grazing, the intensity of π^* transitions gradually increase and the intensity of σ^* transitions gradually decrease. This suggests that BCP molecule shows lying-down configuration on substrate plane. For thick BCP layer, the peak features are different from thin BCP layer. The ratio of peak intensity of π^* and σ^* transitions has no any evolution with changing the incidence angle, suggesting that BCP molecules exhibit random orientation. The nominal thickness of 6-8 Å corresponds to a monolayer (*ML*) of BCP. Therefore, the BCP molecule orientation is parallel to the substrate in case that the film is thin like one 1-2 *MLs*, while disordered for multiple *MLs*. The orderly orientation can improve electron transport and increase mobility. In a word, strong chemical interaction between N atoms of BCP molecules exists at BCP/Mg interface. This interaction produces gap states, and therefore drives flat energy levels at C₆₀/BCP interface and highly ordered flat-lying orientation of BCP molecules,

which may be the reasons for improving the efficiency of OSCs with BCP buffer layer and low WF metal cathode.

In conclusion, the role of BCP buffer layer in OSCs was clarified. The energy difference of LUMO levels between BCP and C_{60} of C_{60} /BCP/metal interfaces are not dependent on the metal when the BCP layer is enough thick. The interaction between metal and BCP is very important for the electronic properties of C_{60} /BCP/metal interfaces. The low WF metal has strong interaction with BCP through N atoms and metal atoms. The interaction between metal and BCP can result in favorable interfaces for free charges transfer, and therefore enhancing the device performance. When this kind of interaction at C_{60} /BCP/metal interfaces is screened by enough thick BCP layer, the energy band bending will occur at the interface. This will result in charge accumulation and therefore lead to the unexpected S-shaped J - V curve. Additionally, metal-doped BCP was demonstrated to be as an effect cathode buffer layer to improve the cell performance and stability. This work provides wealthy information about the working mechanism of buffer layer in OSCs and the essence of controlling interfaces. With the help of deep understand of physics in OSCs, not only does the efficiency can be further improved, but also the span of OSCs will be improved, which will accelerate the pace of commercialization of organic photovoltaics.