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Tandem Organic Solar Cells with an Inverted Structure

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Abstract

In this dissertation, systematic study on organic solar cells (OSCs) with inverted and tandem structures and a new polymer based solar cell is presented. An inverted device has been demonstrated using low work function (LWF) metal Ca modified ITO as cathode and MoO_3 modified Ag as anode. In tandem devices, an efficient Al/ MoO_3 intermediate layer achieving optical and electrical sub-cell connection, has been developed and employed in various types of tandem devices, including polymer/small molecule and polymer/polymer double- and triple-tandem devices with improved or comparable efficiencies. Subsequently, inverted tandem OSCs with $\text{MoO}_3/\text{Ag}/\text{Al}/\text{Ca}$ intermediate layer have been realized for the first time, exhibiting good performance. Optical and structural properties of these intermediate layers have been studied in details, along with their applications in corresponding devices. The intermediate layer is rather crucial for realization of conventional and inverted tandem devices. Furthermore, new polymer F6T2 based solar cells have been studied in terms of the effect of the weight ratio of F6T2 to PCBM on the photo-physics, morphology, and electrical characteristics.

Conventional OSCs suffer interface instability due to the usage of PEDOT:PSS at anode side and LWF metals as cathode. Inverted structure could solve these problems by reversing cathode and anode via interfacial modification. Interfacial layers used for modifying ITO as cathode have significantly affected the realization and performance of inverted devices. An ultrathin Ca as a simple interfacial layer is found to effectively modify ITO as cathode; meanwhile, MoO_3 as a buffer layer modifies Ag anode. The functions of Ca and

MoO₃ have been discussed correspondingly. The effect of Ca layer thickness, MoO₃ layer thickness, and P3HT:PCBM thickness as active layer has been investigated systematically.

Intermediate layers effectively connecting sub-cells are of great significance in tandem devices. In this dissertation, an efficient intermediate layer of Al(1 nm)/MoO₃(15 nm) has been found and developed, which shows satisfactory optical and electrical properties, especially the role of protecting prior-deposited active layer. Then, this intermediate layer has been applied in conventional polymer/small molecule and polymer/polymer double- and triple-tandem devices with summated V_{oc} and improved or comparable efficiency.

It is expected that combining inverted and tandem structures would be an effective approach to achieve the improvement of device efficiency and interface stability. Inverted tandem OSCs have been implemented for the first time, followed by detail optimization. The intermediate layer in inverted tandem device is as critical as that in conventional one. Various intermediate layers consisting of ultrathin metals and metal oxide layers have been compared. The results indicate that MoO₃(7.5 nm)/Ag(1 nm)/Al(1 nm)/Ca(3 nm) is optimal with excellent transparency and electrical connection, including the protection for prior-deposited layer and the voltage summation. Moreover, the effect of Ca layer thickness as part of intermediate layer, MoO₃ thickness as anode buffer layer, and sub-cell thickness on the device performance has been discussed in both experiment and simulation.

BHJ OSCs based on a new polymer F6T2 are presented. The investigation on photo-physics, morphology, and electrical characteristics via changing

the weight ratio of F6T2 to PCBM has been performed. Low LUMO level of F6T2 provides enough driving force for exciton separation, and therefore the charge transfer from F6T2 to PCBM is energetically favored. Nanoscale phase separation in two composites has also been found within a range of 10-20 nm. The optimized weight ratio (1:2) obtained for this blend results from a proper balance between light absorption and charge transport.

In summary, this dissertation addresses the fabrication and characterization of OSCs with inverted and tandem structures, and their combination. The work done will offer opportunities or approaches to further improve the device performance and lifetime for commercialization of OSCs.

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ABBREVIATIONS

OSCs	Organic solar cells
OLEDs	Organic light-emitting diodes
OTFTs	Organic thin film transistors
BHJ	Bulk heterojunction
HOMO	Highest occupied molecular orbital
LUMO	Lowest unoccupied molecular orbital
V_{bi}	Built-in voltage
E_g	Energy band gap
L_D	Exciton diffusion length
J_{sc}	Short-circuit current density
V_{oc}	Open-circuit voltage
FF	Fill factor
PCE	Power conversion efficiency
AM 1.5G	Air Mass 1.5 Global
I - V	Current-Voltage
IPCE	Incident photon-to-electron conversion efficiency
LWF	Low work function
AFM	Atomic force microscopy
HWF	High work function
SEM	Scanning electron microscope
FE-SEM	Field emission scanning electron microscope
XPS	X-ray photoelectron spectroscopy
SAM	Self-assembled monolayer
MIM	Metal-insulator-metal
PEDOT:PSS	Poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate)
ITO	Indium tin oxide
NiO	Nickel(II) oxide
MoO ₃	Molybdenum oxide
V ₂ O ₅	Vanadium oxide
WO ₃	Tungsten trioxide

LiF	Lithium fluoride
TiO ₂	Titanium oxide
ZnO	Zinc oxide
Cs ₂ CO ₃	Cesium carbonate
MDMO-PPV	Poly[2-methoxy-5-(3,7-dimethyloctyloxy)]-1,4-phenylenevinyl
MEH-PPV	Poly(2-methoxy-5-(2'-ethylhexyloxy)-1, 4-phenylenevinylene)
P3HT	Poly(3-hexylthiophene)
PPV	Polyphenylenevinylene
PCPDTBT	Poly[2,6-(4,4-bis-(2-ethylhexyl)-4 <i>H</i> -cyclopenta[2,1- <i>b</i> ;3,4- <i>b'</i>]dithiophene)- <i>alt</i> -4,7-(2,1,3-benzothiadiazole)]
PFDTBT	Poly((2,7-(9,9-dioctyl)-fluorene)- <i>alt</i> -5,5-(4,7-di-2-thienyl-2,1,3-benzothiadiazole)
PTBEHT	Poly(5,7-di-2-thienyl-2,3-bis(3,5-di(2-ethylhexyloxy)phenyl)-thieno[3,4- <i>b</i>]pyrazine)
PSBTBT	Poly[(4,40-bis(2-ethylhexyl) dithieno[3,2- <i>b</i> :20,30- <i>d</i>]silole)-2,6-diyl- <i>alt</i> -(2,1,3 benzothiadiazole)-4,7-diyl]
PDMS	Polydimethylsiloxane
PTE	Polyoxyethylene tridecyl ether
PC ₆₀ BM	1-(3-methoxycarbonyl)-propyl-1-phenyl-(6,6)C ₆₁
PC ₇₀ BM	1-(3-methoxycarbonyl)-propyl-1-phenyl-(6,6)C ₇₁
CuPc	Copper phthalocyanine
ZnPc	Zinc phthalocyanine
SnCl ₂ Pc	Tin phthalocyanine dichloride
F ₁₆ CuPc	Copper hexadecafluorophthalocyanine
PTCBI	3,4,9,10 perylenetetracarboxylic bisbenzimidazole
MTDATA	4,4',4''-tris(<i>N</i> -3-methylphenyl- <i>N</i> -phenyl-amino)triphenylamine
F ₄ -TCNQ	(2,5-cyclohexadine-1,4-diylidene)-dimalononitrile
TIPD	Titanium (diisopropoxide)bis(2,4-pentanedionate)
C ₆₀	Fullerene
BPhen	Bathophenanthroline

CHAPTER 1 ORGANIC SOLAR CELLS

1.1 *Motivation*

1.1.1 Introduction

With the limit of traditional energy resources causing climate change and environmental pollution, demand for clean and renewable energy is rising. Solar energy is the primary energy fueling all activities on earth. Photovoltaic effect is regarded as an ideal energy conversion technology, converting solar radiation into direct electricity for our daily life.

Conventional solar cells are made of inorganic materials such as silicon with high cost and complex fabrication techniques. As a promising alternative to inorganic solar cells, organic solar cells (OSCs) have attracted extensive interests in the past few years due to their unique properties of low cost, easy process at low temperature, and flexibility. Generally, OSCs are built from organic semiconductor donor and acceptor materials. The absorption of organic semiconductors can be tuned to match solar radiative spectrum by chemical design and synthesis. The capability of being solution-processed makes OSCs the most potential for manufacture by printing or coating techniques. Thus it is quite possible to realize large-area and low-cost OSCs replacing/complementing current inorganic solar cells.

In order to achieve commercialization, OSCs have to satisfy the basic and standard requirements, such as cost, efficiency, and lifetime. Recently, the power conversion efficiency (PCE) of OSCs has reached 7% or higher by using

novel materials and device structures.[1-3] However, it is still necessary to further improve device efficiency and stability.

1.1.2 Operation Principles and Device Structure

Figure 1-1 The basic working principle of organic solar cells. The energy level diagrams of (a) Bilayer; (b) Bulk heterojunction. The solid blue line is presenting the energy levels of donor material, and the dash red line is presenting the energy levels of acceptor material. In the diagrams, A, B, C, D, and E corresponds to light absorption, exciton formation and diffusion, exciton dissociation into free charge carriers, charge transport in their corresponding layers or pathways, and charge collection by electrodes, respectively.[4-7]

Physical processes in OSCs, as shown in Figure 1-1, consists of (A) light absorption, (B) exciton formation and diffusion, (C) exciton dissociation into free charge carriers, (D) charge transport, and (E) charge collection by electrodes.[8-9] Single layer, bilayer, and bulk heterojunction (BHJ) are typical device structures (Figure 1-2).

Figure 1-2 Device structures: (a) Single layer; (b) Bilayer; (c) Bulk heterojunction.

➤ Single layer

It is known that each organic molecule is stable due to the strong covalent bonding between atoms. The intermolecular interaction of van der Waals force is weaker than either of covalent or ionic bonds, so it is easy to change their mechanical, optical, and electronic properties by chemical approaches. Small molecule and polymer organic materials have in common a conjugated π -electron system formed by the p_z -orbitals of sp^2 -hybridized C-atoms in the molecules. The π -bonds are much weaker than the σ -bonds that form the backbone of molecules. Therefore, the lowest electronic excitations of conjugated molecules are the π - π^* transitions (seen in Figure 1-3) with energy band gaps ranging from 1.5 to 3 eV, which leads to light absorption and emission in the visible range.

Figure 1-3 The energy levels of a π -conjugated molecule. The lowest electronic excitation is between the bonding π -orbital and the antibonding π^* -orbital.

Conventional single layer device is regarded as a metal-insulator-metal (MIM) diode, made of a photoactive layer sandwiched by two electrodes with different work functions,[10-11] as shown in Figure 1-2 (a). After the light is harvested by the photoactive layer, the excitons are generated at the p-type donor material due to the electron transitions from π -HOMO to π^* -LUMO bands.[6] Subsequently, the excitons diffuse inside the donor material; meanwhile, the exciton recombination could also take place. In such device, the built-in potential that provides a driving force for exciton dissociation originates from the work function difference of electrodes[10-11] or from a Schottky-type potential barrier at one of metal/organic contacts.[12] However, this potential is not big enough to efficiently separate excitons before they diffuse to the electrodes and dissociate due to large exciton binding energy and short exciton diffusion length ($L_D \sim 20$ nm) compared to layer thickness (generally more than 100 nm). Therefore, dissociated free charge carriers will contribute less to the

photocurrent and also the low charge mobility increases the probability of charge recombination, leading to high resistance and low fill factor (FF).

➤ **Bilayer**

A typical bilayer device is comprised of a donor and an acceptor sandwiched by two electrodes, as shown in Figure 1-2 (b). Upon light absorption, the excitons are formed at the donor materials, followed by the diffusion to the interface of donor and acceptor. This diffusion has to compete with the charge recombination during the diffusion process since the excitons generated beyond this distance will decay fast. Therefore, the optimal thickness of active layer depends on the exciton diffusion length, which confines optical density in the devices and the amount of light absorbed. Such heterojunction is thought to improve exciton dissociation efficiency since the potential difference at the donor/acceptor interface provides sufficient driving force to separate the excitons, followed by electron and hole transport through acceptor and donor, respectively. The first bilayer device was reported by Tang *et al.*, [13] which overcame the limitation of single layer device by creating efficient donor/acceptor interface for exciton dissociation and individual charge transport path. However, the open-circuit voltage (V_{oc}) is determined by the nature of organic materials rather than by electrode work functions in single layer device. Noticeably, only at the donor/acceptor interface can the exciton dissociate, therefore the excitons formed away from this interface farther than L_D , are prone to decay via recombination, not contributing to photocurrent and meanwhile causing large series resistance.

➤ **Bulk heterojunction (BHJ)**

Similarly to the process in the former two structures, the light absorption and exciton formation will take place mainly in donor materials. In order to increase interfacial areas between donors and acceptors for solving the bottleneck of exciton diffusion and improving dissociation efficiency, the concept of BHJ was introduced,[14-15] as shown in Figure 1-2 (c), where donor and acceptor materials are intimately mixed with nanoscale phase separation in a 10-20 nm scale, leading to interpenetrating networks. This structure can also reduce the recombination due to the photoinduced charge transfer in a time scale of 45 fs,[16] rather faster than other competing relaxation processes in a time scale of 1 ns.[17] Ideally, all excitons can reach dissociation sites within their lifetimes and dissociate into free charge carriers. BHJ structure requires percolated pathways for electrons and holes transporting to their individual electrodes, i.e. bicontinuous, nanoscale, and interpenetrating networks.[14-15] Therefore, the morphology of active layer is vital to obtain good device performance.[8, 18-20] Such BHJ can be available by co-evaporating donor and acceptor small molecules,[21-23] or mixing donor and acceptor polymers in solution.[8, 16, 18, 24-25]

1.1.3 Main Parameters and Routes for Efficiency Improvement

Figure 1-4 The typical I - V characteristic of an organic solar cell under illumination.

The typical I - V characteristic of an OSC is shown in Figure 1-4. The PCE of a solar cell is calculated by

$$PCE = \frac{V_{oc} J_{sc} FF}{P_{in}}, \quad FF = \frac{(VJ)_{\max}}{V_{oc} J_{sc}}$$

where V_{oc} is the open-circuit voltage, J_{sc} is the short-circuit current density, FF is the fill factor, $(VJ)_{\max}$ is the maximum product of V and J , and P_{in} is the incident light power. Therefore, in order to enhance device efficiency, J_{sc} , V_{oc} , and FF are of paramount importance.

1. J_{sc}

The photocurrent is reflected by the number of created charges collected at the electrodes; therefore, it has a close relationship with quantum efficiency

of the device. Internal quantum efficiency (IQE, η_{IQE}) is the quantum efficiency without light reflection at the substrate surface. Hence, it can be defined as

$$\eta_{IQE} = \eta_A \eta_{ED} \eta_{CT} \eta_{CC}$$

If the light reflection is taken into account, we have the external quantum efficiency (EQE, η_{EQE}),

$$\eta_{EQE} = (1 - R) \eta_{IQE} = (1 - R) \eta_A \eta_{ED} \eta_{CT} \eta_{CC}$$

where η_A is the light absorption efficiency, η_{ED} is the exciton dissociation efficiency, η_{CT} is the charge transport efficiency, η_{CC} is the charge collection efficiency, and R is the light reflection at the substrate surface.

In short, the J_{sc} improvement can be achieved by increasing the corresponding efficiencies in the processes of light absorption, exciton diffusion/dissociation, charge transport, and charge collection.

In order to obtain high η_A , one way to go is to broaden the absorption range of active layer to make full use of solar light. The absorption coefficients of photoactive materials are relatively high ($> 10^5 \text{ cm}^{-1}$),[7] compared to those of inorganic materials. However, most organic semiconductors exhibit wide band gap energy with 2 eV or higher, leading to a mismatch of organic materials' absorption and solar emission spectra. On the other hand, the photons that are not absorbed will lose their energy via heat, not contributing to photocurrent. Therefore, organic materials with low band gaps, broad absorption range, and matched absorption spectrum with solar spectrum are significantly potential candidates in order to absorb a large fraction of solar light, such as PCPDTBT,[26-28] PCDTBT,[29] and PSBTBT,[30] especially those extending

to infrared range.[29-40] Moreover, PC₇₀BM can replace PC₆₀BM since it makes an increased absorption in the visible range, exhibiting an enhanced EQE.[29, 41] Another approach is to incorporate inorganic nanocrystals such as CdSe, PbSe, and CdS in organic polymers for absorbing wavelengths beyond 1000 nm.[42-43] From the device structure point of view, the light absorption can be maximized by using tandem structure that stacks two or more cells in series with complementary absorption spectra. This will be discussed in Chapter 2 and 4.

The η_{ED} improvement can be reached by reducing exciton quenching and enhancing exciton dissociation. It is acceptable that the excitons dissociation occurs only at the donor/acceptor interface. If the donor or acceptor layer is so thick that excitons could partially diffuse to the opposite direction of donor/acceptor interface, such as cathode/organic layer or anode/organic layer contacts. Subsequently the excessive excitons are likely quenched by means of non-radiative decays.[44] Hence it necessitates an insertion of buffer layer or blocking layer to prevent excitons from diffusing to unexpected interfaces.[45-47] On the other hand, η_{ED} is related to L_D that is mainly determined by exciton lifetime. It is confirmed that η_{ED} can be enhanced by introducing BHJ blend with a nanoscale phase separation (less than L_D). Obviously, forward and back charge transfer competes between the LUMOs of donor and acceptor. Since the charge transfer at the donor/acceptor interface is ultrafast, a few hundred times faster than any other process, a back charge transfer is not permitted.[16, 48] In addition, BHJ blend can significantly raise the donor/acceptor interfacial areas. Hence the quantum efficiency for exciton dissociation approaches 100%.[48]

Generally, organic semiconductors exhibit low charge carrier mobility within the range from 10^{-5} to $100 \text{ cm}^2/\text{Vs}$. [6] The formation of interpenetrating networks plays a crucial role in the η_{CT} improvement for BHJ device, facilitating charge transport through the percolated bicontinuous pathways correlated with phase separation of two components. [18, 24, 49] The phase separation is relevant to crystallization of polymer or fullerene, [18] usage of solvents due to large difference of polymer solubilities, solvent evaporation rate, surface interactions, [50-55] weight ratios of polymer donor to acceptor, [49, 56] concentration of blend solution, [24] molecular weight of materials, [57] postannealing treatment, [8, 20, 58] and processing additives. [59-60] It is also found that an initial phase separation is coarsening, leading to better charge transport capability. For temperature-controlled morphology, there is a great limit due to inevitable degradation of the polymers under high annealing temperature. The glass transition temperature of organic materials has to be considered in order to stabilize device, requiring a detail optimization for annealing temperature of assigned polymer blends. As a consequence, all above suggest that an optimum domain size of phase separation between donor and acceptor would be desired so as to balance exciton dissociation and charge transport.

The charge collection is sensitive to the interfaces of organic layers and electrodes. It is better to reduce contact resistance by lowering the potential barrier at the interfaces. Therefore, for achieving the improvement of charge collection efficiency η_{CC} , it is necessary to insert buffer layers between active layer and electrodes in order to obtain energy level alignment. [61]

On the anode side, ITO work function can be increased to match the HOMO of organic active layer by oxygen plasma, UV-ozone, chemical treatments, and molecular monolayer modification. These treatments effectively adjust work function by removing carbon from ITO surface, forming surface dipoles, or modifying the surfacial electronic structure.[62] PEDOT:PSS is the most commonly used as a hole-transporting layer, behaving as a highly transparent and conductive buffer layer.[63] P-type-like or transition metal oxides have been introduced to improve the ITO/active layer contact, such as NiO,[64] MoO₃,[65-67] V₂O₅,[65] and WO₃[46] due to their proper work function and good hole-transporting behavior.

On the cathode side, low work function (LWF) metals such as Ca or Mg and an ultrathin LiF layer are inserted between cathode and organic layers to lower the work function.[63, 68] Metal oxides and alkali metal compounds can also modify organic layer/cathode interfaces, such as TiO₂,[29, 69-70] ZnO,[71-72] and Cs₂CO₃. [73-74] These layers not only assist electron transport and collection, but also act as a spacer to adjust the optical field distribution in the entire device. In addition, such buffer layer is also used to block the exciton from diffusing to the metal cathode and to prevent the damage of active layer during metal deposition.

In short, enhancement in J_{sc} can be achieved by absorption efficiency, exciton dissociation efficiency, charge transport efficiency, and charge collection efficiency through adopting low band gap materials with broad absorption spectra, enhancing exciton diffusion length and charge carrier mobility, forming controllable nanoscale morphology, and aligning energy level at the interfaces.

Another parameter related to the photocurrent is Incident-Photon-to-electron Conversion Efficiency (IPCE), which is a spectral response presenting the ratio of the number of electrons generated under the short-circuit condition to the number of incident photons. It characterizes the capability of the device converting photons to electrons, where J_{sc} can be yielded from the integral of the product of IPCE and AM 1.5G solar spectrum. It is defined as

$$IPCE(\lambda) = \frac{1240J_{sc}(\lambda)}{\lambda P_{in}(\lambda)}$$

where $P_{in}(\lambda)$ is the incident light power at a particular wavelength λ , $J_{sc}(\lambda)$ is the short-circuit current density at that wavelength, and λ is the wavelength of light in nm.

2. V_{oc}

In the MIM device, the V_{oc} is considered to be determined by the work function difference of electrodes.[75] On the other hand, the difference between HOMO of donor and LUMO of acceptor is another important factor, described as HOMO (D) - LUMO (A), on which V_{oc} is linearly dependent.[10] A simple relation between the HOMO of donor and the V_{oc} in polymer:PCBM based devices is derived as $V_{oc} = (1/e)(|E_{HOMO,Donor}| - |E_{LUMO,PCBM}|) - 0.3V$, where e is the elementary charge and the value of 0.3 V is an empirical factor.[76] However, charge carrier losses at electrodes could lower the V_{oc} ,[77] indicating that V_{oc} is sensitive to the energy levels of organic materials, the work functions of electrodes, and their interfaces. Hence, a good contact between organic layers and electrodes via interfacial engineering, guarantees a reasonable V_{oc} .

Vandewal *et al.*[78-80] demonstrated that the charge transfer absorption and emission are related, confirming that the V_{oc} depends on the formation of weak ground-state charge-transfer complex between polymer and fullerene. The V_{oc} can be improved by suppressing the charge-transfer band oscillator strength or by eliminating extra non-radiative pathways to improve carrier lifetime, both of which reduce the dark current. At the point of V_{oc} , the photocurrent generated by the absorption of sunlight balances with the recombination current, resulting in emission of photons by the excited charge-transfer complexes.

3. *FF*

FF is the ratio of the maximum output power (the product of photocurrent and applied voltage) to the product of J_{sc} and V_{oc} , reflecting the practical fraction of charge carriers reaching the electrodes. There is a drastic competition between charge recombination and charge transport.[6] As a result, the product of lifetime τ and mobility μ determines the distance that charge carriers can drift under an electric field E , $L_d = \mu \times \tau \times E$. Hence, $\mu \times \tau$ should be maximized to reduce charge recombination.[6] Series resistance (R_s) and parallel resistance (R_p) in the equivalent circuit (Figure 1-5) of an OSC largely influence the FF. Generally speaking, R_s likely caused by low intrinsic charge mobilities and low electrode conductivity should be minimized, which can be overcome by using highly conductive semitransparent substrates and introducing buffer layers for interfacial modification. On the other hand, it is necessary to free the devices from “short-circuits” in order to maximize R_p probably caused by imperfectly selective electrodes, which can be implemented by electrode modification.

Figure 1-5 The equivalent circuit for an organic solar cell. The series resistance and parallel resistance are R_s and R_p , respectively. J_s and J_{ph} are the reverse saturation and photocurrent densities, respectively.[6]

To summarize, the performance improvement of an OSC should be optimized and achieved through improving all parameters abovementioned. Therefore, further study on fundamental mechanisms and various improvement approaches is absolutely necessary.

1.2 Objectives

This dissertation addresses the fabrication and characterization of OSCs with inverted and tandem structures. Effective intermediate layer Al/MoO₃ connecting sub-cells has been developed and employed in polymer/small molecule and polymer/polymer double- and triple-tandem cells. More importantly, inverted tandem devices with MoO₃/Ag/Al/Ca as intermediate layer have also been realized for the first time, exhibiting comparable performance. The optical and structural properties of these intermediate layers have been studied in details, accompanied with their applications in corresponding devices. These intermediate layers are crucial for the realization of conventional and inverted tandem OSCs.

One of the main objectives of this work is to explore a new combination of intermediate layer used for conventional and inverted tandem OSCs. Conventional intermediate layer involves PEDOT:PSS causing the issues associated with interface instability due to its acidic nature. In order to overcome the issues, one should be developed to satisfy the prerequisites for a functional intermediate layer. Replacing PEDOT:PSS layer with p-type-like or transition metal oxides is regarded as a potential alternative due to their hole-transporting behavior and protection for prior-deposited polymer layers. The optimization and characterization of these intermediate layers used in both conventional and inverted tandem cells have been done. Subsequently, they have been applied to connect the sub-cells with small molecules or polymers as active layers, exhibiting extremely exciting flexibility. Either efficiency improvement or high V_{oc} has been achieved. Finally, a new polymer based solar cell has been investigated from the view of the relation between morphology and weight ratio.

The major technical difficulty in realization of tandem device is the choice of intermediate layer, especially for inverted tandem device. In this work, we will describe the fabrication and characterization of conventional and inverted tandem devices. The key point in tandem device is the functional intermediate layer, connecting sub-cells and ensuring doubled or multiplied V_{oc} in order to achieve the enhancement of device efficiency. The optical and structural properties of intermediate layers we developed have been compared and investigated.

1.3 *Major contributions*

This dissertation presents the investigation on realization and characterization of tandem OSCs with an inverted structure. Effective intermediate layers used in both conventional and inverted tandem devices have been developed with detailed characterizations in terms of optical, structural, and electrical properties. Moreover, new donor polymer F6T2 based solar cells have also been investigated on the effect of weight ratio of donor to acceptor on the morphology of BHJ blend, as well as the optical and electrical characterizations.

Major contributions are summarized as follows:

- An ultrathin Ca layer has been used to modify ITO as cathode in inverted OSCs, where MoO₃ has also been used to modify Ag as anode. The functions of Ca and MoO₃ have been discussed. Moreover, the effect of Ca layer thickness, MoO₃ layer thickness, and P3HT:PCBM thickness as active layer has been investigated in details.
- Intermediate layer Al/MoO₃ has been found and developed, exhibiting rather excellent optical, structural, and protecting properties. This layer has been used in conventional polymer/small molecule and polymer/polymer double- and triple-tandem devices. For polymer/small molecule tandem device with complementary absorption materials, the device has obtained an improved efficiency compared to single device. For polymer/polymer tandem devices with identical materials as the active layer, the V_{oc} has been doubled or tripled in spite of no much efficiency improvement.

- Inverted tandem OSCs have been realized for the first time and optimized in details. Different combinations of metals and metal oxide layers have been compared, showing an effective and optimal one of $\text{MoO}_3/\text{Ag}/\text{Al}/\text{Ca}$ that is highly transparent and reasonably smooth. The thickness effect of Ca layer as part of intermediate layer, MoO_3 as anode buffer layer, and sub-cells on the device performance has been investigated from both experiment and simulation points of view, concluding an optimal combination in our case.
- New donor F6T2 based BHJ polymer solar cells have been demonstrated. The effect of the weight ratio of F6T2 to PCBM on the photo-physics, morphology, and electrical characteristics has been studied. This charge transfer from F6T2 to PCBM is energetically favored due to low LUMO level of F6T2, providing enough driving force. Nanoscale phase separation in two composites has also been found within a range of 10-20 nm. The optimized weight ratio for this blend results from the balance between light absorption and charge transport.

1.4 Organization

This dissertation mainly includes 7 chapters.

Chapter 1 starts with the motivation, briefing of current research status, operation principles, and main parameters of OSCs. The routes for each parameter improvement have been discussed, providing various methods to enhance the efficiency. Then, the objectives of the research have been given.

Chapter 2 reviews current advance of inverted single devices and conventional tandem devices. Inverted structure is regarded as an effective way to overcome interface instability and meanwhile to improve charge transport in BHJ device due to the composite gradient distribution. Tandem structure consisting of multiple sub-cells with complementary absorption materials could maximize the light absorption and obtain the efficiency improvement via current matching.

Inverted OSCs with LWF metal Ca modified ITO as cathode and metal oxide MoO_3 buffered Ag as anode have been fabricated and presented in Chapter 3. Ca modified ITO functions well for electron transport and collection. The optimization has been done through the variation of Ca, active layer, and MoO_3 layer thicknesses due to the change of optical field distribution.

In Chapter 4, various tandem OSCs with Al/ MoO_3 as intermediate layer have been demonstrated, including polymer/small molecule and polymer/polymer double- or triple-tandem ones. Optical and structural properties of this intermediate layer have been characterized. Moreover, the optical and electrical characteristics of these tandem devices have been also investigated in details.

Chapter 5 describes the realization of inverted tandem OSCs for the first time. Different combinations of metals and metal oxide have been compared, among which $\text{MoO}_3/\text{Ag}/\text{Al}/\text{Ca}$ has been found the most effective, connecting sub-cells efficiently. This intermediate layer is potentially used for the efficiency improvement of inverted tandem devices with complementary absorption ma-

terials, overcoming the issues associated with charge transport/collection and interface instability.

New donor polymer based BHJ solar cells have been demonstrated in Chapter 6. The effect of the weight ratio of donor to acceptor on the photo-physics and morphology of blend films has been investigated, and meanwhile the electrical characteristics of these blend based solar cells have been also discussed, exhibiting pretty good device performance.

The dissertation ends in Chapter 7 with conclusions for the results and plan for future works.

CHAPTER 2 REVIEWS ON INVERTED AND TANDEM ORGANIC SOLAR CELLS¹

2.1 *Reviews on Inverted Organic Solar Cells*

2.1.1 Introduction

BHJ active layer sandwiched between anode and cathode is used to harvest light in conventional device in order to increase exciton dissociation efficiency. For further improvement of charge collection efficiency, buffer layers in both electrode sides are introduced, such as PEDOT:PSS between anode and BHJ layer or LWF metals between cathode and BHJ layer. However, conventional devices have drawbacks in device stability due to naturally acidic PEDOT:PSS and easily oxidized LWF metals.

de Jong *et al.* found that ITO/PEDOT:PSS interface is very sensitive to air due to the hygroscopic nature of PSS allowing absorbance of water that facilitates the etching of ITO layer[81] and increases sheet resistance of PEDOT:PSS layer.[82-83] LWF metals such as Li, Ca, Ba, and Al, are also sensitive to air and easily oxidized, increasing contact resistance and degrading device performance. Oxygen and water diffused into the device react with organic materials, preceded mainly through microscopic pinholes in electrode or possibly through metal grains.[63, 84-85]

¹ The main context of this Chapter has been published as: De Wei Zhao, Aung Ko Ko Kyaw, Xiao Wei Sun, “Organic Solar Cells with Inverted and Tandem Structures”, In:Energy Efficiency and Renewable Energy through Nanotechnology, Editor(s): Ling Zang, Springer Publishers, 2010.

In order to overcome the problem associated with LWF metal cathode, metal oxides, such as TiO_2 and ZnO , can be inserted between organic layer and cathode, acting as electron-transporting layer and protection layer to prevent oxygen and water from diffusing into organic layer.[86] As a result, the device without encapsulation exhibits relatively long stability, compared to those without metal oxides. However, the issue of ITO/PEDOT:PSS interface still remains. A potential alternative is to introduce p-type-like or transition metal oxides such as NiO ,[64] MoO_3 ,[65] V_2O_5 ,[65] and WO_3 ,[23] to replace PEDOT:PSS as hole-transporting layer.

Figure 2-1 Device structure of a typical inverted OSC.

An effective approach to address the issues is to construct inverted structure, as shown in Figure 2-1, in which charge transport and collection happen in opposite direction compared to that in conventional structure. Stable high work function (HWF) metals like Au or Ag can be used as the top anode electrode, avoiding metal oxidation and eliminating ITO/PEDOT:PSS interface in-

stability. In addition, charge transport and collection are proposed to be enhanced due to the observation that vertical phase separation occurs with a donor-enriched top surface and an acceptor-enriched bottom surface in BHJ polymer layer. The vertical distribution favors charge transport/collection in inverted structure.[87]

Only after being modified can ITO serve as the cathode, requiring a functional interfacial layer with a proper Fermi level or work function. N-type metal oxides such as TiO_2 and ZnO are good candidates for this purpose since they have similar energy levels with the acceptor (PCBM) used in BHJ layer. Hence, through optimizing the electron-transporting buffer layer via the increase of its conductivity and the energy level alignment at polymer/electrode interfaces, inverted device efficiency is anticipated to be improved. In the following section, inverted devices based on both polymer and small molecules will be reviewed in terms of interfacial layers.

2.1.2 Transition Metal Oxide as Interfacial Layer

Transition metal oxides offer a unique opportunity to fabricate solution-processed devices with large area and potentially low cost. Their electrical and optical properties, such as work function, conductivity, and transmittance in the visible range, are essential for application of optoelectronic devices. The interface modification of organic layer/electrode by inserting a transition metal oxide has made great progress in OLEDs[88] and OTFT.[89] Recently, the most commonly used interfacial layers are TiO_2 or ZnO film, and their nanostructures. Herein, various forms of interfacial layers will be discussed.

Titanium Oxide (TiO₂)

➤ Film

With the vacuum level as the reference energy level, TiO₂ is a transition metal oxide with a conduction band of - 4.4 eV suitable for modifying ITO due to the matching with the LUMO of PCBM (around - 4.0 eV[76]) and a high valence band of - 7.5 eV blocking hole extraction by ITO side.[70]

Waldauf *et al.*[90] reported inverted devices based on solution-processed TiO₂ as the electron-transporting layer, PEDOT:PSS as the hole-transporting layer, and P3HT:PCBM as the photoactive layer, exhibiting an improved FF compared to conventional devices owing to efficient hole-blocking by TiO₂ that reduces leakage current. PEDOT:PSS degrades the devices caused by its hygroscopic nature.[91-93] Hence, transition metal oxides are necessarily required as hole-transporting and exciton-blocking layers in inverted devices. Tao *et al.*[94] thermally evaporated MoO₃ as the hole-transporting layer and sol-gel processed TiO₂ as the electron-transporting layer in inverted devices with different metals (Au, Ag, and Al) as top electrode. The devices with MoO₃ have significantly higher V_{oc} than those without MoO₃, and the V_{oc} is independent on the work function of metal electrode. Schmidt *et al.*[95] reported a semitransparent inverted device with MoO₃/ITO as anode (ITO/TiO₂/P3HT:PCBM/MoO₃/sputtered-ITO), showing that a relatively thick MoO₃ (40 nm) protects the deterioration originating from sputtered ITO, ensuring the charge extraction and leading to increased FF (60%).

In addition to MoO_3 , other transition metal oxides are also used such as V_2O_5 and WO_3 , making a reasonable V_{oc} of 0.6 V obtainable in inverted devices. They serve to protect damage from top electrode deposition, to adjust optical field distribution as an optical spacer, to prevent oxygen or water from entering active layer as a barrier, to suppress leakage current, and to enhance built-in potential.[87, 96-97]

➤ **Nanostructures**

Nanostructured TiO_2 is also employed as an interfacial layer in inverted devices,[98-99] where nanostructured TiO_2 distributed in blend film provide additional donor/acceptor interface, i.e. the contact between TiO_2 and donor polymer, facilitating exciton dissociation and photocurrent generation. It is certain that well-ordered nanostructure metal oxides here bring two advantages: one is to increase the interfacial areas between donor and acceptor; the other one is to provide vertical straight pathway for electron transport and collection. On the other hand, hole transport is also enhanced due to vertical channel confinement of polymer chains between nanostructure arrays or in the pores.[5] Moreover, light harvesting can be enhanced due to multiple active layers or light trapping inside the layers. However, one concern that the exciton recombination occurs at the surface of nanostructure metal oxides influences photocurrent generation and interfacial resistance.[100]

More importantly, it is challenging to fabricate the nanostructures with highly ordered alignment and controllable pore size, determining the distribution of polymer chains between nanostructures or the infiltration inside nanostructures.

Coakley *et al.*[101] presented the increase in charge carrier mobility of polymer by 20 times due to the vertical channel confinement of polymer chains in the pores along the direction perpendicular to the substrate. Since high degree of π -stacking of twisted polymer chains does not occur in strongly confined pores (ca. 8 nm), straight pores with larger size are required in order to achieve good hole transport.[5, 102] Mor *et al.*[98] used TiO₂ nanotubes as interfacial layer, which have a length of 270 nm and a pore size of 50 nm, allowing the infiltration of P3HT:PCBM blend and the formation of coiled interacting chains as that in bulk polymer film. Due to the additional sites at P3HT/TiO₂ interface for exciton dissociation, the J_{sc} and EQE of this device are rather high (12.4 mA/cm² and maximum 80% at 538 nm respectively). Yu *et al.*[99] prepared TiO₂ nanotubes with 15 nm pore by anodizing 100 nm Ti film on ITO at 20 V for 27 min and then annealing at 500 °C for 1 h. The anodization time determines the formation of nanotubes and the degree of π -stacking of polymer chain inside the pores.

Zinc Oxide (ZnO)

➤ Film

ZnO is another transition metal oxide, which Fermi level is suitable for collecting electrons and valence band is capable of effectively blocking hole extraction by ITO side. Pinhole-free ZnO film as an interfacial layer is also desired to prevent short-circuits in inverted devices.

White *et al.*[103] reported an inverted device of ITO/ZnO/P3HT:PCBM/Ag. Solution-processed crystalline ZnO (work function

of 4.3 eV) as interfacial layer makes V_{oc} approach 0.556 V, indicating that only slight energy loss exists during the charge transfer. Efficient hole-blocking by ZnO layer at ZnO/P3HT interface results in high diode rectification. Kyaw *et al.*[104] systematically studied the effect of sol-gel ZnO on inverted device performance (FTO/ZnO/P3HT:PCBM/Au). The authors obtained conformal and pinhole-free film by controlling the concentration of sol at low levels (0.5 and 0.3 M). Through inserting a MoO_3 hole-transporting layer between organic layer and Ag anode, optimized device achieves maximum PCEs.[105]

Except for solution-process, ZnO film is also prepared by atomic layer deposition in flexible inverted devices.[106] This layer-by-layer deposition at atomic scale by incorporating reactant gas into reaction zone makes conformal and pinhole-free film obtainable at low temperature ($< 100^\circ\text{C}$), leading to lower resistivity of ZnO layer and more hydrophobic surface, beneficial to the adhesion of polymer films. In addition to polymer solar cells, inverted structure has been used in small molecule solar cells (ITO/ZnO/CuPc:C₆₀/CuPc/PEDOT:PSS/Ag), where ZnO acts as interfacial layer and CuPc:C₆₀ as active layer.[107]

➤ Nanostructures

ZnO nanostructures such as ZnO nanorods,[96, 108] are also applied in inverted devices. Similar to that in nanostructured TiO_2 based inverted devices, additional interfaces between ZnO and donor material increase interfacial areas and facilitates exciton dissociation.

Hau *et al.*[109] demonstrated inverted devices with spin-coated ZnO nanoparticles as interfacial layer and electron-transporting layer. The J_{sc} of in-

verted device is higher than that of conventional device due to the additional interface between ZnO and P3HT. Olson *et al.*[108] used ZnO nanofiber by hydrothermal method to modify ITO in inverted device (ITO/ZnO nanofiber/P3HT:PCBM/Ag). It has been compared that 20% of photocurrent for this inverted device is contributed from ZnO:P3HT heterojunction. Takanezawa *et al.*[110] replaced ZnO nanofibers with ZnO nanorods in inverted devices with an improved PCE. Similarly, 17% of photocurrent is estimated to come from ZnO:P3HT heterojunction.

Therefore, it can be concluded that nanostructure metal oxides serve not only as an electron-transporting media but also as an acceptor, allowing the formation of additional heterojunctions and increasing the photocurrent reasonably.

2.1.3 Alkali Metal Compound as Interfacial Layer

Recently, alkali and alkali-earth metal compounds have also been introduced as electron injection/transport layers in organic devices due to their low work functions and insensitivity to oxygen and moisture.[93, 111] Among these compounds, Cs_2CO_3 is the most commonly used because it can be easily fabricated by thermal evaporation or solution process[68] and also can reduce the work function of ITO due to strong dipole moment,[112] reducing energy barrier for electron collection and therefore contact resistance.[113]

Li *et al.*[114] compared conventional and inverted devices with Cs_2CO_3 (1 nm) as electron-transporting layer and V_2O_5 (10 nm) as hole-transporting layer. A strong dipole layer formed at ITO surface due to the electron-donating

ability of metal species alters the work function of ITO; therefore, the inverted device exhibits a better efficiency. Further, Liao *et al.*[115] demonstrated a highly efficient inverted device with a low temperature annealed Cs_2CO_3 , in which the PCE is improved largely with annealing temperature. Upon annealing at 170 °C, Cs_2CO_3 can decompose into doped cesium oxide Cs_2O with the decrease of work function from 3.45 to 3.06 eV, accountable for device efficiency improvement.

2.1.4 Summary

In order to overcome interface instability and improve charge transport/extraction due to the vertical phase separation in BHJ devices, inverted structure is regarded as an effective approach. To lower the work function of ITO, interfacial layers are essentially needed to match the Fermi level of the acceptor. Transition metal oxides such as TiO_2 and ZnO are able to be utilized due to their proper optical and electrical properties. They are usually in forms of film and nanostructure. The conformal and closely packed metal oxide film could prevent short-circuits. Vertical and highly ordered metal oxide nanostructures could facilitate the charge transport and collection. In particular, the contact between nanostructured metal oxides and donor polymer would provide additional heterojunction, increasing interfacial areas and exciton dissociation. In addition, Cs_2CO_3 has already been used to modify ITO suitable for electron collection due to decomposition of Cs_2CO_3 into LWF oxide upon annealing, beneficial to the Fermi level pinning and reduction of energy barrier. Therefore,

inverted structure is potential in application of OSCs for improvement of device efficiency and device stability.

2.2 Reviews on Tandem Organic Solar Cells

2.2.1 Introduction

Although the efficiency of conventional and inverted devices has remarkably advanced,[8, 30-31, 58] improvement is still needed for commercialization. Most organic semiconductors have wide band gaps, causing large loss of solar light. A thick layer can absorb photons as much as possible, yet low charge mobility limits the thickness of active layer compared to that in inorganic materials. In order to enhance the light absorption, materials with low band gap and broad absorption range have been designed.[30-31, 36, 116] Combining two active layers with complementary absorption spectra can achieve a full coverage of solar spectrum in a relatively thin device. Thus the device performance is expected to improve via stacking complementarily absorbing materials as active layer with a proper thickness.

Figure 2-2 Device structure of a typical tandem OSC.

A tandem structure[67, 117-119] consisting of two complementary absorbers in series, as shown in Figure 2-2, offers a few merits: (1) a broad absorption spectrum due to usage of complementarily absorbing materials, ensuring high J_{sc} ; (2) summation of the V_{oc} 's of individual cells; (3) higher optical density over a wider fraction of solar spectrum than that of a single cell without increasing internal resistance,[118] guaranteeing a reasonable FF.

In the following section, the design and operation of tandem devices will be discussed. Subsequently, device realization will be reviewed, in which the intermediate layer and device performance will be highlighted and compared.

2.2.2 Device Design and Operation: Theory and Limits

2.2.2.1 Design Rules

From the theoretical point of view, a model has been built to predict tandem device efficiency with estimates approaching a promising 15%, [120] on the assumptions that a few ideal properties of materials such as HOMO, LUMO, and band gap, which will assist the realization of highly efficient tandem devices. Moreover, a very important assumption for all calculations is a constant EQE for the absorbed wavelengths. Dennler *et al.* [120] considered three cases: the first one is a tandem cell that has a P3HT:PC₆₀BM based bottom cell and variable donor based top cells; and the second one is a tandem cell that has a PCPDTBT:PC₆₀BM based top cell and variable donor based bottom cells. The conclusions for both have been drawn that tandem cell in series is able to reach an enhanced efficiency only at the situation that the performance

of the donor materials based single cell is achieved under their maximum potential capability. This has been proven by Kim's work.[118] The third case is that the calculation is completed via fixing $E_{\text{LUMO1}} = E_{\text{LUMO2}} = -4.3$ eV like PC₆₀BM as acceptor and varying donor materials. The maximum efficiency of 15% was proposed to approach by stacking a bottom cell with a donor E_g of 1.6 eV and a top cell with a donor E_g of 1.3 eV.

Dennler *et al.*[121] performed optical calculations, highlighting two points: (1) the interference effect is evident in the top cell, on the contrary, no strong interference effect appears in the bottom cell; (2) the proper acceptors should be carefully selected in order to optimize tandem device performance, since acceptors PC₆₀BM and PC₇₀BM have different absorption ranges that could lead to matched and enhanced photocurrent.

2.2.2.2 Device Operation

If an intermediate layer could perfectly ensure efficient recombination of holes and electrons from sub-cells, there is no voltage loss across this intermediate layer. Therefore, the V_{oc} of tandem cell in series should be the summation of the V_{oc} 's of the individual cells, i.e. $V_{\text{oc, tandem}} = V_{\text{oc, 1}} + V_{\text{oc, 2}} + V_{\text{oc, 3}} \dots$

Figure 2-3 (a) A case that a tandem cell, consisting of a cell with lower J_{sc} and much higher FF and the other cell with high J_{sc} and much low FF, has a J_{sc} of the tandem cell ($J_{sc, \text{tandem}} = \text{Min} [J_{sc,1}, J_{sc,2}]$). (b) A case that a tandem cell, consisting of one cell with much lower J_{sc} and FF as well as the other cell with much higher J_{sc} and FF, has a J_{sc} of the tandem cell ($J_{sc, \text{tandem}} = \text{Max} [J_{sc,1}, J_{sc,2}]$).[122]

Ameri *et al.*[122-123] reviewed that the FF of individual cells significantly determines the overall efficiency of tandem cell. Figure 2-3 shows the comparison for two cases using different combinations of the individual cells. One case, as shown in Figure 2-3 (a), is that one cell has a lower J_{sc} and much higher FF whereas the other cell has a high J_{sc} and much low FF, resulting in the J_{sc} of the tandem cell ($J_{sc, \text{tandem}} = \text{Min} [J_{sc,1}, J_{sc,2}]$).[120] The other case, as shown in Figure 2-3 (b), is that one cell has much lower J_{sc} and FF while the other cell has much higher J_{sc} and FF, leading to an extremely low FF and the J_{sc} of the tandem cell ($J_{sc, \text{tandem}} = \text{Max} [J_{sc,1}, J_{sc,2}]$).[122]

2.2.3 Realization of Tandem Organic Solar Cells

For tandem devices, the intermediate layer plays significant roles in device realization and performance, and should possess the following properties: (1) low electrical resistance; (2) high optical transparency in the visible and infrared ranges; (3) low barriers for charge recombination; (4) easy fabrication; and (5) protection for prior-deposited active layer in solution-processed tandem devices. Herein, various combinations of functional intermediate layers will be reviewed. According to the fabrication techniques of active layers and intermediate layers, tandem OSCs can be divided into three types.

- Small molecule/small molecule tandem organic solar cells, where thermally evaporated organic small molecules are used as both bottom and top cells.
- Polymer/small molecule tandem organic solar cells, in which solution-processed polymer BHJ is used as the bottom cell and thermally evaporated small molecules as the top cell.
- Polymer/polymer solution-processed tandem organic solar cells, where solution-processed polymer BHJs are used as both bottom and top cells by spin-coating.

2.2.3.1 Small Molecule/Small Molecule Tandem Organic Solar Cells

This type of tandem device consists of multiple layers of pure donors and acceptors or their mixtures. The whole process is carried out by thermal evaporation under high vacuum, guaranteeing sequential multiple layers with high-quality interfaces.

(a)

(b)

Figure 2-4 (a) The structure of tandem device with 0.5 nm Ag nanocluster as recombination center, made of CuPc and PTCBI as donor and acceptor, respectively.[124] (b) The structure of hybrid PM-heterojunction tandem device.[125]

In 1990, Hiramoto *et al.*[126] reported the first small molecule/small molecule tandem device with phthalocyanine (H₂Pc) (50 nm) and perylene tetracarboxylic derivative (Me-PTC) (70 nm) as active layers. An inserted thin Au (2 nm) between the sub-cells, acting as the effective recombination center, results in a doubled V_{oc} of 0.78 V for tandem cell, compared to that for single cell (0.44 V).

Yakimov *et al.*[124] presented the first multiple heterojunctions (CuPc and PTCBI as donor and acceptor respectively) based tandem devices with 0.5 nm Ag nanoclusters as the recombination center, as shown in Figure 2-4 (a). When Ag is incorporated between two sub-cells, the V_{oc} is summated to be 0.9 V, while the V_{oc} of individual cell is 0.45 V. The increase in Ag thickness dra-

matically decreases J_{sc} with unchangeable V_{oc} due to the reduced light reaching top cell. It is noted that final photocurrent in tandem device depends on how efficient charges can recombine at the Ag nanocluster.[117, 124] Any excessive current generated in one cell will induce the unbalanced charges at the intermediate layer, resulting in performance degradation.

A few unique techniques have been developed by Xue and Forrest *et al.*[21, 125] to enhance single and tandem device performance. An “asymmetric” tandem device, i.e. front and back cells absorb different ranges of light, as shown in Figure 2-4 (b), which has a PCE of nearly 6% under 100 mW/cm². Such high efficiency is primarily attributed to (1) a better acceptor C₆₀ with longer L_D of 40 nm and higher carrier mobility; (2) a mixed donor-acceptor layer, so-called “hybrid planar-mixed heterojunction (PM-HJ)” structure,[21] sandwiched between pure donor and acceptor layers, increasing donor/acceptor interfacial area and enhancing exciton dissociation; (3) application of BCP and PTCBI as blocking layer and electron-transporting layer, respectively. It is worth mentioning that m-MTDATA layer is p-doped by inserting Ag nanoclusters, not only increasing conductivity but also reducing Ohmic losses in the intermediate layer. The highly conductive transporting layer also helps to adjust the optical field distribution in the device by changing thickness, and furthermore thick layer can make the devices stable and reduce the probability of short-circuit.[117]

Triple-tandem cells with different absorption spectrum materials as active layers were reported by Triyana *et al.*,[127] exhibiting an improved PCE due to balanced carriers in sub-cells. In order to improve the charge transport,

Cheyne *et al.*[128] used pentacene/ C_{60} to stack double-tandem cells. Through comparison of intermediate layers based on different metals, it was found that thin Al causes S-shaped I - V curves due to a barrier for charge extraction at the intermediate layer, however, incorporating a thin Au or Ag layer makes the S-shape disappear and the V_{oc} increase. Yu *et al.*[129] explored an all-organic intermediate layer in ZnPc: C_{60} based tandem devices. The $SnCl_2Pc/F_{16}CuPc$ intermediate layer has advantages in higher transparency and lower sublimation temperature, serving as an effective recombination center due to highly accumulated electron density in $F_{16}CuPc$ layer, reduced barrier height, and probable tunneling at the $F_{16}CuPc/ZnPc$ interface.

2.2.3.2 Polymer/Small Molecule Tandem Organic Solar Cells

This type of tandem device is fabricated by both solution process and high-vacuum process. Generally, it can be easily realized by stacking two sub-cells with complementary absorption ranges without damaging prior-deposited active layer.

Figure 2-5 The structure of polymer/small molecule tandem OSC, where the bottom cell consists of a stratified bilayer of P3HT and PCBM, and the top cell is fabricated by the evaporation of ZnPc, C₆₀ and their mixture[130]

Dennler *et al.*[130] stacked tandem devices with a P3HT/PCBM bilayer as bottom cell and small molecules ZnPc/C₆₀ multiple layers as top cell, as shown in Figure 2-5, in which the bottom cell mainly absorbs the light from 375 to 630 nm and the top cell from 600 to 800 nm, resulting in a broadened absorption spectrum. A thin Au (1 nm) intermediate layer makes the V_{oc} of tandem cell approach 1.02 V, the summation of that of bottom cell (0.55 V) and that of top cell (0.47 V). As a result, the PCE of 2.3% with $J_{sc} = 4.8 \text{ mA/cm}^2$ and FF = 50% is obtained compared to single cells (2.6% and 2.2%). However, the tandem device performance is limited by the low photocurrent and reduced FF. Colsmann *et al.*[131] presented tandem devices with P3HT/PCBM heterojunction as bottom cell and small molecules CuPc/C₆₀ as top cell with an intermediate layer of BPhen:Li/Au/MTDATA:F4-TCNQ, consisting of two doped organic layers (either doped layer is mandatory for the operation of tandem device) and a thin noble metal layer. The summated V_{oc} is achieved; however, the tandem device performance is low due to the poor individual single devices.

Figure 2-6 The structure of the tandem cell with different intermediate layers: Al/Au and Al/WO₃. [132]

Janssen *et al.* [132] used a thin metal oxide WO₃ (3 nm) layer instead of Au (10 nm) layer in intermediate layer of Al(1 nm)/WO₃(3 nm) to connect P3HT:PCBM bottom cell and CuPc:C₆₀ top cell, as shown in Figure 2-6. Both tandem cells exhibit summated V_{oc} s. However, the intermediate layer Al/WO₃ has much higher transparency than Al/Au, allowing more light to arrive at the CuPc:C₆₀ top cell. Therefore, the maximum PCE of tandem device with Al/WO₃ reaches 3.0% at 160 mW/cm² and 4.6% at 16 mW/cm², higher than those with Al/Au.

Polymer/small molecule tandem cell is superior due to the absence of solvents for the vacuum-deposited top cell, avoiding the contaminations and damages against the bottom cell.

2.2.3.3 Polymer/Polymer Solution-Processed Tandem Organic Solar Cells

Polymer OSCs are typically prepared by using spin-coating, printing, and doctor-blading. For polymer/polymer tandem devices, the main issue lies in

that the prior-deposited active layer is easy to be destroyed by the following top layer since polymers are able to be dissolved in most organic solvents like chlorobenzene or chloroform. Therefore, except for optical and electrical connections, the intermediate layer must possess a special property of protecting prior-deposited layer. This issue may be overcome by using different combinations of intermediate layers, which will be reviewed in the following section.

➤ **ITO/PEDOT:PSS as Intermediate Layer**

Figure 2-7 The structure of tandem cell with ITO/PEDOT:PSS as intermediate layer.[133]

Kawano *et al.*[133] reported a tandem device made of two identical BHJ MDMO-PPV/PCBM as active layer and ITO/PEDOT:PSS as intermediate layer, as shown in Figure 2-7. The ITO deposition by dc magnetron sputtering without substrate heating prevents the bottom active layer from damage. It is important that highly transparent ITO layer allows enough light to reach top cell, ensuring increased photocurrent. The tandem device with a 20 nm ITO has a $V_{oc} = 1.34$

V , $J_{sc} = 4.1 \text{ mA/cm}^2$, $FF = 56\%$, and $PCE = 3.1\%$. Since the obtained V_{oc} is smaller than the summation, it is necessary to optimize the intermediate layer to achieve proper energy level alignment between sub-cells, probably by using LWF materials or thin metal, taking structural continuity, chemical and mechanical stability against the solution process into account.[133]

➤ **Metals/PEDOT:PSS as Intermediate Layer**

Figure 2-8 The structure of tandem cell consisting of PFDTBT:PCBM as the bottom cell and PTBEHT:PCBM as the top cell, connected by Al/Au/PEDOT:PSS intermediate layer.[134]

Hadipour *et al.*[134] firstly reported solution-processed tandem devices made of two BHJ cells with complementary absorption spectra, where PFDTBT:PCBM (wide band gap polymer) bottom cell mainly absorbing the short-wavelength light[134] and PTBEHT:PCBM (low band gap polymer) top cell mainly absorbing the long-wavelength light are connected by LiF/Al/Au/PEDOT:PSS intermediate layer,[116, 134] as shown in Figure 2-8. LiF(0.5 nm)/Al(0.5 nm) acts as the cathode for bottom cell, forming an Ohmic

contact between PCBM and LiF/Al to extract electrons, and Au(15 nm)/PEDOT:PSS(60 nm) acts as the anode for top cell, providing a stable Ohmic contact for hole extraction. 15 nm Au is employed to protect the bottom cell. Due to multiple thin layers, there might be an optical cavity formed by the interference of incident and reflected light. Finally, the optimal device has a 110 nm bottom cell (PFDTBT:PCBM, 1:4) and a 90 nm top cell (PTBEHT:PCBM, 1:4), yielding a PCE of 0.57% with $V_{oc} = 1.5$ V, $J_{sc} = 0.9$ mA/cm², and FF = 55%.

➤ **Metal Oxides/PEDOT:PSS as Intermediate Layer**

Figure 2-9 The structure of double-tandem cell with ZnO/PEDOT:PSS intermediate layer. The active layers are made of MDMO-PPV:PCBM and P3HT:PCBM for the bottom and top cells, respectively.[135]

Gilot *et al.*[135] presented fully solution-processed multiple tandem devices with a ZnO(nanoparticles)/PEDOT:PSS intermediate layer, MDMO-PPV:PCBM and P3HT:PCBM as active layers, as shown in Figure 2-9. ZnO layer, spin-coated onto the active layer, serves as the electron-transporting layer

and PEDOT:PSS as the hole-transporting layer, at the interface of which electrons and holes recombine. The high offset of work functions between ZnO and PEDOT:PSS causes poor charge recombination. In order to form an Ohmic contact, ZnO layer is n-doped by exposure to UV light for a few seconds, resulting in the increased V_{oc} of triple-tandem cell with MDMO-PPV:PCBM from 1.40 V to 1.92 V. However, the V_{oc} is lower than the summation of individual cells' (0.84 V), likely attributed to large voltage drop across ZnO/PEDOT:PSS interface, leading to poor overall efficiency. This approach offers a potential opportunity to fabricate fully solution-processed tandem devices with ideally complementary absorption spectra.

Figure 2-10 The structure of double-tandem cell with TiO_2 /PEDOT:PSS as intermediate layer.[118]

TiO_2 *et al.*[118] can be used to fabricate fully solution-processed tandem devices. The intermediate layer, comprised of highly transparent TiO_2 (cathode for bottom cell) and highly conductive PEDOT:PSS PH500 (anode for top cell), serves as the recombination center and the protection layer. The tandem cell, shown in Figure 2-10, consists of a 130 nm thick layer of

PCPDTBT:PCBM (1:3.6) as the bottom cell and a 170 nm thick layer of P3HT:PC₇₀BM (1:0.7) as the top cell with complementary absorption spectra, absorbing in the entire visible range and a small part of infrared range of solar spectrum, which guarantees appropriate photocurrent generation in both cells. Therefore, the resultant tandem cell achieves the highest PCE of 6.7% under 20 mW/cm² and 6.3% under 100 mW/cm².

Sista *et al.*[136] recently presented an efficient tandem device with an improved intermediate layer of Al/TiO₂:Cs/PEDOT:PSS 4083, P3HT:PC₇₀BM as bottom cell absorbing the light ranging from 400 to 600 nm, and PSBTBT:PC₇₀BM as top cell from 600 to 800 nm, exhibiting a well-complementary absorption spectrum. In the intermediate layer, an ultra thin Al is thermally evaporated for improving both wettability and electrical contact between P3HT:PC₇₀BM and TiO₂. Forming densely packed network of nanocrystals, TiO₂ protects prior-deposited active layer, blocks holes, and collects electrons. Upon exposure to UV light, the TiO₂/PEDOT:PSS 4083 interface transits from Schottky to Ohmic contact, leading to no energy barrier and facilitating efficient electron tunneling. Moreover, by comparison for tandem devices with PEDOT:PSS 4083 and PEDOT:PSS PH500 as part of intermediate layer, tandem device with PEDOT:PSS PH500 gives a higher J_{sc} than that with PEDOT:PSS 4083 and however no difference in EQE appears. This is because the active area for PEDOT:PSS PH500 based tandem device is slightly larger than the electrode overlap due to high conductivity of PEDOT:PSS PH500. Thus, the active area should be carefully concerned when PEDOT:PSS PH500 is used.

Overall, the PCE of tandem device reaches 5.84% with a $J_{sc} = 7.44 \text{ mA/cm}^2$, $FF = 63.2\%$, and $V_{oc} = 1.25\text{V}$.

It is clear that PEDOT:PSS has to be involved in most of intermediate layers. Since PEDOT:PSS needs to be dried and treated outside glove box and at high temperature, this process will damage prior-deposited polymer layer, causing the degradation of tandem device. Therefore, a superior intermediate layer, processed in air-free environment without high temperature treatment, is necessary for efficiency improvement of tandem devices.

2.2.4 Summary

Different types of tandem OSCs have been discussed and reviewed in terms of operation, design, and realization. This structure potentially improves the efficiency by increasing light absorption and adopting a proper thickness of active layer. In tandem structure, the intermediate layer, connecting sub-cells optically and electrically, plays crucial roles in the device performance. It should be possessed with a few unique properties as mentioned-above, serving as efficient recombination center for the charges extracted from sub-cells. By carefully optical and electrical optimization, the tandem device can achieve a summated V_{oc} and reasonable J_{sc} . Additionally, low series resistance caused by this intermediate layer would result in a relatively high or comparable FF . Therefore, the overall PCE of tandem device is expected to be enhanced, larger than those in single devices.

Tandem structure is providing an approach to further improve the efficiency by stacking multiple cells with complementary absorption spectra.

2.3 Conclusion

For efficiency improvement of OSCs, except for developing materials with broad absorption range and high carrier mobility, adopting effective device structures is essentially vital to maximize the capability of achieving optimal device performance based on well-known organic semiconductors. Inverted structure, in which the charge transport/collection is opposite to that in conventional structure, provides stable and robust devices. Moreover, tandem structure consisting of multiple cells with complementary absorption spectra is able to enhance the light harvesting via a proper thickness of active layer. These two structures could effectively overcome the initial issues associated with interface instability and light loss.

Interfacial layer, employed between active layer and electrodes, is rather crucial to understand the charge collection behavior in inverted devices. The energy level at electrode/active layer interfaces should be matched so that voltage or charge loss during charge transfer would be minimized. One advantage of inverted structure is vertical phase separation in BHJ blend, facilitating charge transport and collection. Combining nanostructure metal oxides with BHJ blend is another potential approach to improve the photocurrent by increasing effective interfacial areas. However, it suffers from charge recombination at the surface of metal oxides via charge trapping sites created by hydroxyl groups, leading to low contribution to final photocurrent. Through tuning work function of electrodes, manipulating phase separation in BHJ blend, and incor-

porating nanostructure metal oxide, inverted devices with better air-stability and higher efficiency could be achieved.

Intermediate layer, connecting sub-cells, plays a significant role in the realization and efficiency improvement of tandem device. It should be highly transparent, highly conductive, and protective. The choice of intermediate layer is not merely material exploration, yet it accounts for efficiency improvement of tandem device, where the intermediate layer should serve as efficient recombination center for the extracted charges from sub-cells. In fact, the photocurrent in tandem device is limited mainly by large overlapping of absorption spectra of the materials used in sub-cells, which could be solved by designing and synthesizing excellent organic semiconductors with broad absorption range and high carrier mobility. Therefore, through tuning the band gaps of donors and the sub-cell thickness, matched photocurrent would be implemented.

In summary, inverted and tandem structure based devices, aiming to fulfill the commercial requirements, have approached an exciting and potential level. Such kind of devices will push forwards the realization of flexible and large-area devices with low cost.

CHAPTER 3 INVERTED ORGANIC SOLAR

CELLS WITH CALCIUM AS ELEC-

TRON-TRANSPORTING LAYER¹

3.1 *Introduction*

Organic solar cells are attracting much attention due to their potential as a low-cost and flexible energy conversion device.[87, 137] As mentioned in Chapter 1, the device operation includes light absorption, exciton diffusion/dissociation, charge transport, and charge collection. Therefore, efficiency improvement can be accomplished by enhancing various efficiencies in the corresponding processes.

In order to increase the light absorption, a few classes of organic materials with broad absorption ranges have been developed.[29-31] We can simply increase the thickness of photoactive layer. However, the thickness is ultimately limited by the short L_D and low charge carrier mobility. Therefore, the balance between the light absorption and the charge transport plays a crucial role in the efficiency improvement. Tandem structure is able to enhance the light harvesting by stacking multiple cells with complementary absorption spectra.[67, 118-119] For the improvement of diffusion/dissociation efficiency, BHJ blend of donors and acceptors is generally used. Thus the formation of the nanoscale morphology facilitates charge transport in the interpenetrating networks.[18, 24,

¹ The main results of this Chapter have been published as: D. W. Zhao, P. Liu, X. W. Sun,* S. T. Tan, L. Ke, and A. K. K. Kyaw, *Appl. Phys. Lett.* **95**, 153304 (2009), and D. W. Zhao, S. T. Tan, L. Ke, P. Liu, A. K. K. Kyaw, X. W. Sun,* G. Q. Lo, and D. L. Kwong, *Sol. Energy Mater. Sol. Cells* **94**, 985-991 (2010).

49] Moreover, in order to improve the charge collection, functional layers are inserted to modify the interfaces of active layers and electrodes. For the anode, PEDOT:PSS is the most commonly used as the hole-transporting layer. P-type-like or transition metal oxides have also been introduced to improve the ITO anode/active layer contact, such as NiO,[64] MoO₃,[65, 67, 119] V₂O₅,[65] WO₃,[46] due to their proper work function and good hole-transporting behavior. For the cathode, modification by Ca,[63] LiF,[68] TiO₂,[29, 69-70] ZnO,[72, 135] and Cs₂CO₃,[73-74] has been reported to improve the electron transport and extraction.

However, PEDOT:PSS is an acidic water-based solution, which would cause interface instability to the photoactive layer and corrosion to ITO.[63, 87] In addition, LWF metals are easily oxidized. To overcome the instability issue in conventional device, one feasible approach is to construct an inverted configuration,[87] where ITO serves as the cathode and a HWF metal as the anode. It should be pointed out that only modified ITO can serve as the cathode for electron extraction. The functional layers for modifying ITO mainly focus on metal oxides such as TiO₂[94] and ZnO,[105, 138] and alkali-metal-compound such as Cs₂CO₃. [114-115] Large-area inverted devices with ZnO can also be realized by roll-to-roll processing each layer.[139-142] As an alternative, modifying ITO by a LWF metal would be an effective approach to lower the work function of ITO. On the other hand, the contact between anode and active layer should be significantly improved by a buffer layer such as PEDOT:PSS,[143] V₂O₅,[65, 87] and WO₃[97] in order to reduce the exciton quenching and then increase the charge collection efficiency. Except for the roles of hole transport

and extraction, such an anode buffer layer also acts as an optical spacer, adjusting the effective optical field distribution.[144]

3.2 Fabrication of Device

All cells were fabricated on ITO coated glass substrates with a sheet resistance of 20 Ω /square. The substrates were cleaned in an ultrasonic bath with detergent, deionied-water, acetone, and isopropyl alcohol successively for 15 min. After being dried in a laboratory oven, the ITO surfaces were treated by oxygen plasma for 5 min. A Ca layer was first thermally evaporated under a base vacuum of 9.0×10^{-5} Pa. Then, a blend solution made of P3HT (Rieke Metals, Inc.) and PCBM (American Dye Sources Inc.) with a weight ratio of 1:0.8 in chlorobenzene (30 mg/mL) was spin-coated onto Ca coated ITO substrate to form the active layer in a glove box filled with N₂. Subsequently, MoO₃ and Ag were evaporated sequentially (9.0×10^{-5} Pa), followed by post-annealing at 160 °C for 10 min. Finally, the cells with an active area of 0.1 cm² were encapsulated before taking out from the glove box.

The current-voltage (*I-V*) characteristics were measured with a Keithley 2400 sourcemeter under simulated 100 mW/cm² (AM 1.5G) irradiation from a solar simulator (Solar Light Company Inc.). The film thickness was measured with a surface profiler (Tencor P15). The IPCEs, i.e. spectral responses, were measured using a 200 W Xenon lamp light source with a motorized monochromator (Oriel). Tapping mode AFM (D5000, Veeco) was used to characterize

the surface roughness of the active layers prepared by spin-coating polymer solution onto Ca coated ITO glass.

3.3 Optical Properties

Figure 3-1 The transmittance spectra of the films Ca(x nm)/P3HT:PCBM(85 nm) with $x = 0, 0.5, 1, 2,$ and 3 nm.

Figure 3-1 shows the transmittance spectra of Ca/P3HT:PCBM(85 nm) films (with ITO/glass substrate absorption extracted for all curves) with different Ca thickness. In order to avoid the oxidization of Ca when measuring the transmittance spectra, we overcoated Ca by an 85 nm P3HT:PCBM layer. With the increase of Ca thickness, the transmittance of the film does not change much in the absorption range of active layer (from 400 to 650 nm), indicating that such an ultra thin Ca layer has a high transparency.

3.4 Electrical Characterization and Optimization

The device structure and energy level diagram of the corresponding device are shown in Figure 3-2. The inverted devices have a structure of ITO/Ca/P3HT:PCBM/MoO₃/Ag(100 nm) with different thicknesses of Ca, P3HT:PCBM, and MoO₃ layers.

Figure 3-2 (a) The device structure of ITO/Ca/P3HT:PCBM/MoO₃/Ag with different thicknesses of Ca, P3HT:PCBM, and MoO₃ layers. (b) The energy level diagram of inverted OSCs.

3.4.1 Device Optimization with Different Thick Ca

Figure 3-3 The I - V characteristics of inverted cells with 3 nm MoO_3 and different thicknesses of Ca under 100 mW/cm^2 illumination. The corresponding Ca thickness, FF, and PCE are shown in the format of (Ca thickness, FF, PCE).

The I - V characteristics of these inverted devices with 3 nm MoO_3 and different thicknesses of Ca under 100 mW/cm^2 are shown in Figure 3-3. Without Ca, the cell is a hole-only device, exhibiting nearly no photovoltaic effect. The efficiency increases significantly when Ca is inserted. The J_{sc} and FF increase first and then decrease as the Ca thickness increases. As a result, the optimal thickness of Ca layer is 1 nm, and its corresponding PCE reaches 3.55%. Similar to Cs_2CO_3 in inverted OSCs,[87] Ca ($\sim 2.9 \text{ eV}$) firstly lowers the work function of ITO ($\sim 4.8 \text{ eV}$). The obtained V_{oc} approaches $\sim 0.60 \text{ V}$ for the cells with Ca layer. This demonstrates that the work function of Ca is pinned to the Fermi level of PCBM via the surface states. Then, an Ohmic contact is favored

between Ca and PCBM.[62, 145] Meanwhile, in contrast, a rectifying contact between Ca and P3HT will be formed,[62, 145] which will block the hole collection on the ITO side. Hence, ITO covered with Ca acts well as a cathode for electron collection.

Figure 3-4 The I - V characteristics of the devices with CaO and Ca as the electron-transporting layers under 100 mW/cm^2 .

Since Ca is used to modify the work function of ITO and it is easily oxidized, we fabricated a CaO modified ITO on purpose to check if the corresponding device can still work properly. The CaO layer was obtained by purposely oxidizing the Ca deposited under high vacuum (expose the Ca to dry air). All the other layers are exactly the same. Figure 3-4 shows the comparison of the I - V characteristics of two devices (ITO/Ca/P3HT:PCBM/MoO₃/Ag and ITO/CaO/P3HT:PCBM/MoO₃/Ag). It is obvious that the device with CaO (0.5

nm) exhibits rather poor performance compared to that with Ca (0.5 nm). In this way, we can indirectly confirm that Ca was not oxidized (at least not fully oxidized). Therefore it can be concluded that Ca still primarily remains in its metallic state.

3.4.2 Device Optimization with 1 nm Ca

Figure 3-5 (a) The I - V characteristics of inverted cells with 1 nm Ca and different thicknesses of MoO₃ under 100 mW/cm². The corresponding MoO₃ thickness, FF, and PCE are shown in the format of (MoO₃ thickness, FF, PCE). (b) IPCEs of inverted cells with different thicknesses of MoO₃ layer.

Figure 3-5 (a) shows the I - V characteristics of various OSCs with 1 nm Ca and different MoO₃ thicknesses under 100 mW/cm². Obviously, in the absence or for a very thin layer of MoO₃ (0 or 1 nm), the J_{sc} and FF are close ex-

cept for a large difference in V_{oc} . For the cell with 3 nm MoO_3 , the PCE remarkably increases to 3.55% with $J_{sc} = 8.28 \text{ mA/cm}^2$, $V_{oc} = 0.65 \text{ V}$, and $\text{FF} = 65.9\%$. As the thickness of MoO_3 layer increases to 5 nm, the PCE slightly reduces to 3.34% with $J_{sc} = 7.93 \text{ mA/cm}^2$, $V_{oc} = 0.65 \text{ V}$, and $\text{FF} = 64.7\%$. However, the cell with 15 nm MoO_3 exhibits a rather low PCE of 0.11% ($J_{sc} = 2.13 \text{ mA/cm}^2$ and $\text{FF} = 11.0\%$). The IPCE spectra of these inverted OSCs are shown in Figure 3-5 (b). We can see that the cell with 3 nm MoO_3 has the best spectral response.

Herein, besides acting as a hole transporting/extraction layer,[67, 105, 119] this MoO_3 layer functions as a protection layer preventing damage to the active layer caused by the metal deposition.[7] Thus, the MoO_3 layer has to be thick enough to serve this purpose. Due to its high energy bandgap ($\sim 3 \text{ eV}$),[146] MoO_3 also serves as an exciton-blocking layer to prevent the exciton from diffusing to Ag anode side and subsequent exciton quenching there,[119] beneficial to a high photocurrent. Furthermore, the higher reflection by Ag anode compared to Al cathode in conventional cell helps to contribute a larger J_{sc} as well.[147]

Figure 3-6 The simulated optical field distribution (for 520 nm illumination) as a function of the distance from ITO/P3HT:PCBM interface in these inverted cells. These cells have the structures of ITO/Ca(1 nm)/P3HT:PCBM(85 nm)/MoO₃(x nm)/Ag(100 nm) with x = 0, 1, 3, 5, and 15. The ultra thin Ca is neglected in the simulation.

To understand the effect of MoO₃ as an optical spacer on the J_{sc} , we then simulated the optical field distribution for a single wavelength illumination (520 nm, the maximum absorption peak of P3HT:PCBM blend) in the inverted cells with different MoO₃ thicknesses.[148] The simulation result is shown in Figure 3-6. It can be seen that the intensity maximum resides close to the center of the active layer, however, the relative optical intensity decreases with the increase of MoO₃ thickness. Particularly, for the cell with 15 nm MoO₃, the maximum peak across the active layer shifts to the anode side, showing some light leakage at the thicker MoO₃ and Ag anode side. This implies that a relatively thin MoO₃ layer is necessary for optimal performance of the cell, consistent with the experimental results.

It has to be pointed out that V_{oc} changes drastically with the thickness of MoO_3 layer [Figure 3-5 (a)]. Without MoO_3 , V_{oc} is only 0.39 V. It can be explained by the non-Ohmic contact between P3HT:PCBM and Ag anode, i.e. the V_{oc} is correlated with the work function difference of the electrodes.[75] In this case, $V_{oc} = 0.39$ V is in agreement with the work function difference of Ag (~ 4.4 eV) and ITO (~ 4.8 eV). With a 1 nm MoO_3 deposited, the P3HT:PCBM layer cannot be covered completely by MoO_3 , therefore, the charge carrier loss exists at the Ag anode,[77] lowering the V_{oc} to 0.59 V. As the thickness of MoO_3 layer increases to 3 and 5 nm, full and uniform coverage of the active layer is established and meanwhile Ohmic contact is formed, hence the V_{oc} is determined by the difference of HOMO of P3HT and LUMO of PCBM,[10] and a reasonable V_{oc} of 0.65 V is obtained. However, with further increase of the MoO_3 thickness to 15 nm, the V_{oc} reduces to 0.45 V, likely caused by the voltage loss across the thick MoO_3 layer. This is different from the trend in the conventional structure where the MoO_3 thickness does not affect the V_{oc} much.[65]

Moreover, it can be seen clearly from Figure 3-5 (a), that R_s , R_p , and final FF are sensitive to the MoO_3 thickness in our inverted cells. With a very thin MoO_3 layer (0 and 1 nm), the active layer may not be fully covered by MoO_3 , leading to surface charge recombination at Ag anode,[94] and hence a smaller R_p (245.8 and 367.8 $\Omega \cdot \text{cm}^2$ respectively). In this case, R_p is the determining factor for a relatively small FF (40.3% and 41.6% respectively). For a thicker MoO_3 layer (15 nm), a larger R_s (1121.5 $\Omega \cdot \text{cm}^2$) is introduced by MoO_3 layer itself, leading to a poor FF of 11%, i.e. R_s is the determining factor of FF.

Only with intermediate MoO_3 thickness (3 and 5 nm), the R_p is large (1052.6 and 1116.1 $\Omega\cdot\text{cm}^2$ respectively) and R_s is small (9.4 and 9.7 $\Omega\cdot\text{cm}^2$ respectively), leading to a high FF (65.9% and 64.7% respectively).

3.4.3 Device Optimization with 0.5 nm Ca

As discussed above, ultrathin Ca and MoO_3 are highly transparent,[67, 119] therefore, these two layers cause little light loss in our inverted devices.[149] In order to minimize the light loss caused by Ca layer, the inverted devices have been optimized by using 0.5 nm Ca to modify the ITO for electron extraction and meanwhile block the hole collection by ITO side.[62, 145, 149]

It has been reported that the TiO_2 or ZnO layer can perform multiple roles in conventional and inverted OSCs.[69-71, 144] In order to investigate the roles of MoO_3 layer in our cells, the inverted cells with different thicknesses of MoO_3 and P3HT:PCBM layers were compared. Figure 3-7 shows the I - V characteristics of various OSCs (P3HT:PCBM = 85, 140, and 205 nm) with 0.5 nm Ca and different MoO_3 thickness under 100 mW/cm^2 . The dependence of the photovoltaic parameters on the MoO_3 thickness is plotted in Figure 3-8. It can be seen clearly from Figure 3-8, that these devices exhibit obvious difference with the variance of active layer and MoO_3 layer thickness. The J_{sc} for the devices with a thin P3HT:PCBM (85 nm) is much more sensitive to the MoO_3 thickness than that for the devices with a thicker P3HT:PCBM (140 and 205 nm) [Figure 3-8 (a)]. The V_{oc} for all devices is around 0.6 V, shown in Figure 3-8 (b), except for devices with 85 or 140 nm P3HT:PCBM and 10 nm MoO_3 . Addi-

tionally, in Figure 3-8 (c), the FF decreases as the thickness of P3HT:PCBM layer increases, indicating that a thicker active layer induces a high intrinsic resistance, affecting the charge carrier transport. Meanwhile, a distinct change in FF with the thickness of MoO₃ layer is also displayed at a fixed thickness of P3HT:PCBM. Thus the devices with 85, 140, and 205 nm P3HT:PCBM reach the

Figure 3-7 The I - V characteristics of inverted devices with P3HT:PCBM (a) 85 nm, (b) 140 nm, and (c) 205 nm, and different thicknesses of MoO₃ layer under 100 mW/cm^2 illumination.

highest PCEs of 3.86%, 3.04%, and 3.15%, respectively, at the optimal MoO₃ thickness of 5, 7.5, and 7.5 nm as shown in Figure 3-8 (d). The results indicate that thickness difference leads to a different optimal MoO₃ thickness.

Figure 3-8 The dependence of each parameter on the MoO_3 thickness in the inverted devices with 85, 140, and 205 nm P3HT:PCBM active layer, (a) J_{sc} ; (b) V_{oc} ; (c) FF; and (d) PCE.

Obviously, from Figure 3-8 (a), the J_{sc} varies with the thicknesses of MoO_3 and active layers. In order to understand the influence of MoO_3 layer thickness on the photocurrent, we simulated the optical field distribution for 520 nm light illumination (the peak absorption wavelength of P3HT:PCBM blend) in the inverted cells with different MoO_3 thicknesses,[148] as shown in Figure 3-9. As reported,[69-70] in order to increase the photocurrent for the devices with a fixed thickness of active layer, TiO_2 was inserted between the photoactive layer and the top electrode as an optical spacer, redistributing the maximum light intensity across the active layer. It primarily originates from the in-

interference effect between the incident light and the reflected light from the metal electrode. In our inverted devices, Ag used as the top electrode enhances the interference effect within the active layer.[147] For the devices with 85 nm P3HT:PCBM [Figure 3-9 (a)], the relative intensity of the optical field distribution across the active layer changes more with the MoO₃ thickness than that for the devices with 140 and 205 nm P3HT:PCBM [Figure 3-9 (b) and (c)]. This is consistent with the J_{sc} results of I - V characteristics shown in Figure 3-8 (a). Moreover, it has to be pointed out that the relative optical intensity increases as MoO₃ thickness increases for 140 nm P3HT:PCBM device, exhibiting an increased J_{sc} from 7.36 to 7.65 mA/cm², different from the trend for 85 or 205 nm P3HT:PCBM device. The J_{sc} for the device with 85 nm P3HT:PCBM firstly increases and then decreases with the increase of MoO₃ thickness, showing a highest J_{sc} of 8.56 mA/cm² at 5 nm MoO₃. In addition, the J_{sc} for the device with 205 nm P3HT:PCBM does not change so much (ranging between 8.0 and 8.5 mA/cm²). This indicates the MoO₃ thickness has a significant impact on the photocurrent of the devices with thin active layer (85 nm) compared with that of the devices with thicker active layers (140 and 205 nm), i.e. for thick active layers, MoO₃ cannot be absolutely considered as an optical spacer due to its low capability of redistributing the optical field across the active layer. Thus, an optical spacer is not always beneficial to the enhancement of absorption efficiency and further the device performance.[150]

Figure 3-9 The normalized simulation of the optical field distribution (for 520 nm illumination) as a function of the distance from ITO/P3HT:PCBM interface in these inverted cells: (a) 85 nm P3HT:PCBM, (b) 140 nm P3HT:PCBM, (c) 205 nm P3HT:PCBM. These cells have the structures of ITO/Ca(0.5

nm)/P3HT:PCBM/MoO₃(x nm)/Ag(100 nm) with x = 3, 5, 7.5, and 10. The ultra thin Ca is neglected in the simulation.

Figure 3-10 The simulated optical field distribution (for 520 nm illumination) as a function of the distance from ITO/P3HT:PCBM interface in these inverted cells: (a) 85 nm P3HT:PCBM, (b) 140 nm P3HT:PCBM, (c) 205 nm P3HT:PCBM. The green dash is the interface between ITO and P3HT:PCBM layer. These cells have the structures of ITO/Ca(0.5 nm)/P3HT:PCBM/MoO₃(5 nm)/Ag(100 nm). The ultra thin Ca is neglected in the simulation.

Furthermore, the J_{sc} is also correlated with the thickness of the active layer. Figure 3-10 shows the simulation of the optical field distribution in the devices with different thick P3HT:PCBM and 5 nm MoO₃. It can be observed that the maximum intensity for thin active layer (85 nm) is higher than that for thick active layer (140 and 205 nm); correspondingly, the J_{sc} of 8.56 mA/cm² for 85 nm device is larger than those of 140 and 205 nm devices. Moreover, the optical field peak for 85 nm device situates in the center of the active layer,

while for 140 nm layer device, the field is close to Ag anode side, and for 205 nm layer device, the field is split into two peaks sitting closer to two electrodes. Although the maximum intensity for 205 nm P3HT:PCBM device is slightly lower than that of 140 nm P3HT:PCBM device, two absorption profiles (peaks) may contribute more to the photocurrent. As a result the J_{sc} of 8.23 mA/cm² for 205 nm device is larger than that of 7.49 mA/cm² for 140 nm device. It indicates the optical interference effect becomes more pronounced as the reflected light intensity increases due to the decrease in active layer thickness. In contrast, the interference effect is weaker for the thicker active layer, as evidenced by an almost unchanged relative intensity of optical field distribution shown in Figure 3-10.

Figure 3-11 The IPCEs of inverted devices with P3HT:PCBM (a) 85 nm, (b) 140 nm, and (c) 205 nm, and different thicknesses of MoO₃ layer.

Figure 3-11 shows the IPCEs of these inverted devices with different thicknesses of P3HT:PCBM and MoO₃ layers. The spectral response characterizes the capability of the devices converting the photons to electrons, where the J_{sc} can be yielded from the integral of the product of the IPCE and AM 1.5G solar spectrum. It is evident that the IPCEs reflect an identical trend with that of the I - V characteristics (Figure 3-7).

Figure 3-12 The AFM images of P3HT:PCBM films deposited with different thicknesses of MoO₃ layers deposited: (a) 85 nm/0 nm; (b) 85 nm/3 nm; (c) 85 nm/5 nm; (d) 205 nm/0 nm; (e) 205 nm/3 nm; (f) 205 nm/5 nm. All image sizes are $2 \times 2 \mu\text{m}^2$. The height scale is 10 nm.

Table 3-1 The summary of the surface roughness (RMS and Rmax) of the P3HT:PCBM films (85 and 205 nm) with different thicknesses of MoO₃ layers.

P3HT:PCBM thickness	MoO ₃ thickness (nm)	RMS (nm)	Rmax (nm)
85 nm	0.0	0.807	6.795
	3.0	0.619	5.617
	5.0	0.601	4.804
205 nm	0.0	0.721	8.358
	3.0	0.643	7.348
	5.0	0.603	5.767

It is obtainable that the optimal thickness of MoO₃ layer shifts from 5 nm for 85 nm P3HT:PCBM device to 7.5 nm for 140 or 205 nm P3HT:PCBM devices. In order to further clarify this phenomenon, the AFM images of 85 and 205 nm P3HT:PCBM films with different thicknesses of MoO₃ layers deposited

are shown in Figure 3-12. The surface root-mean-square (RMS) roughness and peak-to-valley (Rmax) roughness are tabulated in

Table 3-1. Obviously, all the films are rather smooth with the RMS less than 1 nm. However, the Rmax varies significantly as the thickness of MoO₃ layer increases. The 85 nm P3HT:PCBM film exhibits a decreased Rmax from 6.795 nm to 4.804 nm. Meanwhile, the Rmax for 205 nm P3HT:PCBM film decreases from 8.358 nm to 5.767 nm, both with 5 nm thick MoO₃. It is also displayed that the Rmax for 205 nm P3HT:PCBM film is slightly larger than that for 85 nm P3HT:PCBM film despite the deposition of 5 nm MoO₃. Thus, except for the adjustment of optical field distribution, the shift of optimal MoO₃ thickness for the devices with different thickness of active layer could also be caused partially by the maximum surface roughness, which would make the incomplete coverage of the active layer by MoO₃ and cause certain leakage currents in some weak spots. Furthermore, the MoO₃ layer has to be thick enough to serve as a protection layer, preventing Ag metal diffusion into the active layer.[7]

As the MoO₃ thickness further increases to 10 nm, the V_{oc} drops obviously, as shown in Figure 3-8 (b), implying that a relatively thick MoO₃ layer causes voltage loss. It is worth mentioning that the reduction of V_{oc} becomes more significant with the decrease in the thickness of active layer. This can be understood that a thicker active layer has a high internal resistance, where the V_{oc} is built upon. With a thinner MoO₃ thickness, the voltage loss on the MoO₃ is less.

Furthermore, although 0.5 nm Ca can work well as expected, there are probably weak spots on the cathode side due to an ultrathin Ca layer, similar to an ultrathin LiF (0.5 – 1.0 nm) used in conventional devices. As a result, different from the cell with a 1 nm Ca,[149] the cell with a thinner Ca (0.5 nm) requires a slightly thicker MoO₃ layer to reduce the shunt resistance by avoiding current leakage, evidenced by the FFs obtained in Figure 3-8 (c). Therefore, the shift in optimal layer thickness of MoO₃ is reasonable.[149]

3.5 Roles of MoO₃ Layer

It is worth pointing out that the MoO₃ layer in our inverted devices functions multiple roles as follows:

- (1) Anode buffer layer: facilitate hole transport and collection by Ag anode.
- (2) Exciton-blocking layer: prevent the excitons from quenching at the interface of active layer and Ag anode.
- (3) Protection layer: protect the damages from Ag deposition and diffusion.
- (4) Optical spacer: adjust the optical field distribution in the thin active layer.

Hence, MoO₃ is suitable for application in inverted devices.

3.6 Summary

Inverted OSCs using an ultra thin Ca layer as the electron-transporting layer and MoO₃ as the hole-transporting layer have been realized. ITO electrode

modified by a thin Ca acts as the cathode. The Ca layer has high transparency. On the other hand, MoO₃ layer between photoactive layer and Ag anode improves the photocurrent and the FF, serving as an exciton-blocking, hole-transporting, and protection layer. In addition, it can also act as an optical spacer in relatively thin device to adjust optical field distribution. Through optimization the highest PCE for the device with 0.5 nm Ca, 85 nm P3HT:PCBM, and 5 nm MoO₃ reaches 3.86%. This detailed investigation provides a reference for usage of MoO₃ layer in inverted devices.

CHAPTER 4 TANDEM ORGANIC SOLAR CELLS WITH AL/MOO₃ AS INTERMEDIATE LAYER¹

4.1 Introduction

For conventional OSCs, there is large light loss due to relatively narrow absorption range of organic materials compared to solar spectrum. To increase light absorption, one efficient way is to broaden the light absorption range. Tandem structure consisting of two or more cells with complementary absorption spectra is believed to be an effective approach to enhance the light absorption and the device efficiency.[118, 125, 130-135, 151] In tandem devices, the intermediate layer is crucial and should possess the following properties: (1) low electrical resistance; (2) high optical transparency in the visible and infrared range; (3) low barriers for both electron and hole extractions; (4) easy-fabrication process; and (5) the protection for the prior-deposited active layer in solution-processed devices. Thin metals can be used as semitransparent intermediate layer such as Ag[125] and Al/Au.[134] However, such intermediate layer alone is not suitable for solution-processed tandem devices (thickness is not enough for protecting the prior-deposited polymer layer) or light loss is usually high. Recently, the combination of n-type metal oxides (e.g. TiO₂[118] and ZnO[135]) and PEDOT:PSS has been applied as the intermediate layer for

¹ The main results of this Chapter have been published as: D. W. Zhao, X. W. Sun, * C. Y. Jiang, A. K. K. Kyaw, G. Q. Lo, and D. L. Kwong, *Appl. Phys. Lett.* 93, 083305 (2008), and D. W. Zhao, X. W. Sun, * C. Y. Jiang, A. K. K. Kyaw, G. Q. Lo, and D. L. Kwong, *IEEE Electron Device Lett.* 30, 490 (2009)

solution-processed tandem devices, where n-type metal oxide and PEDOT:PSS serve as the electron- and hole-transporting layer respectively, and the charge recombination occurs at the interface between n-type oxide and PEDOT:PSS. However, such intermediate layers need to be fabricated in an oxygen and moisture environment (outside the glove box) with baking, harmful to the organic layer of bottom cell.[6] For ZnO/PEDOT:PSS intermediate layer, PEDOT:PSS is a water-based acidic solution, which could dissolve ZnO. Thus PEDOT:PSS solution has to be modified to be neutral.[135]

There are other p-type-like metal oxides, such as NiO, MoO₃, V₂O₅ and WO₃, with HWF and good hole conductivity, which have been used previously for hole injection in OLEDs[152-155] and anode buffer layer in single OSCs.[23, 64-65] These oxide films can be generally deposited by thermal evaporation which does not do harm to the prior-deposited organic layers. However, there is a lack of study of tandem OSCs using a combination of p-type-like metal oxide layer and metal as the intermediate layer,[132] especially for solution-processed tandem cells.

Moreover, for a standard P3HT:PCBM single device, the V_{oc} is only around 0.60 V. Tandem devices stacked in series can raise the V_{oc} by summing those of sub-cells. A few double-tandem polymer cells with identical active layers have been demonstrated with increased V_{oc} , using identical MEH-PPV:PCBM ($V_{oc} = 1.64$ V)[156] and MDMO-PPV:PCBM ($V_{oc} = 1.34$ V)[133] BHJ. However, there are problems associated with tandem structure such as incompletely stacking cells[156] and large voltage drop.[133] A good intermediate layer has to meet the challenges of stacking solution-processed polymer

layers repeatedly and reducing light loss caused by the added intermediate layer. For triple-tandem polymer cell, to date, only one has been reported where solution-processed ZnO/PEDOT:PSS intermediate layer was used to connect identical MDMO-PPV:PCBM active layers.[135] However, the resulting V_{oc} of the devices without UV irradiation is much lower than expected due to large voltage loss across ZnO/PEDOT:PSS layer. And the FF suffers remarkable decrease induced by high series resistance. Thus, an intermediate layer with simple and controllable processes, high transparency, efficient electric-connection, and protection of prior-deposited polymer layer is desired.

4.2 *Fabrication of Device*

All cells were fabricated on ITO coated glass substrates with a sheet resistance of 20 Ω /square. PEDOT:PSS was firstly spin-coated onto pre-cleaned ITO-glass with a thickness of 40 nm, and baked at 120 °C for 20 min. For polymer cell, the active layer was fabricated by spin-coating the blend solution, made of P3HT (Rieke Metals, Inc.) and PCBM (Nano-C) with a weight ratio of 1:0.8 in chlorobenzene (18 mg/mL). For small molecule cell, MoO₃, CuPc, C₆₀, and BPhen layers were deposited sequentially by thermal evaporation in organic deposition chamber (5.0×10^{-5} Pa). Al and Ag were deposited by e-beam and thermal evaporations in metal deposition chamber (2.0×10^{-4} Pa), respectively. The active area was 0.1 cm². For comparison, all single cells were fabricated in the same run as the tandem cell.

The I - V characteristics were measured with a Keithley 2400 Sourceme-
ter in dark and under illumination of a solar simulator operating at various light

intensities ranging from 50, 100 (AM1.5G), 150, 200 to 300 mW/cm². The absorption and transmittance spectra of these films were characterized by a HP 8453 UV-VIS Spectrometer. The thickness was measured with a surface profiler (Tencor P15). The film morphology was evaluated by AFM (NanoScope IIIa). The IPCEs (spectral response) were measured by using a 200 W Xenon lamp light source with a motorized monochromator (Oriel).

4.3 Optical and Structural Properties of Intermediate Layer

Figure 4-1 The absorption spectra of the bottom film P3HT:PCBM (120 nm), top film CuPc(7.5 nm)/CuPc:C₆₀(12.5:12.5 nm)/C₆₀(27.5 nm) and tandem film P3HT:PCBM(120 nm)/LiF(0.5 nm)/Al(1 nm)/MoO₃(15 nm)/CuPc(7.5 nm)/CuPc:C₆₀(12.5:12.5 nm)/C₆₀(27.5 nm) films. And the transmittance spectrum of the Al(1 nm)/MoO₃(15 nm) intermediate layer.

Figure 4-1 shows the absorption spectra of P3HT:PCBM, CuPc/CuPc:C₆₀/C₆₀ and P3HT:PCBM/LiF/Al/MoO₃/CuPc/CuPc:C₆₀/C₆₀ films used in the bottom single, top single and tandem cells, respectively. It is obvious that the bottom film mainly covers the visible range from 400 to 650 nm, while the top film absorbs complementarily from 650 to 750 nm. By stacking these two films together, the absorption spectrum is broadened (see the tandem film curve in Figure 4-1). In addition, the transmittance spectrum of Al(1 nm)/MoO₃(15 nm) intermediate layer is also shown in Figure 4-1. Compared to the commonly used Al/Au intermediate layer with only 80% of transmittance in the visible range,[132, 156] it can be seen that the transmittance is almost 98% in the range from 350 to 900 nm, ensuring enough light to be absorbed by the top cell. Hence, this intermediate layer with high transparency satisfies the optical requirement as outlined in the beginning.

Figure 4-2 AFM images of (a) P3HT:PCBM; (b) P3HT:PCBM/Al(1 nm); (c) P3HT:PCBM/Al(1 nm)/MoO₃(15 nm) films. The scan size in all images is $1 \times 1 \mu\text{m}^2$. The scale bar is 200 nm.

Figure 4-2 shows the AFM images of P3HT:PCBM, P3HT:PCBM/Al(1 nm), and P3HT:PCBM/Al(1 nm)/MoO₃(15 nm) films. The 1 nm thick Al should be in the form of nanocluster as pointed out by other researchers.[124]

The RMS surface roughness of P3HT:PCBM/Al film [Figure 4-2 (b)] is 0.861 nm slightly higher than that of P3HT:PCBM film (0.662 nm) [Figure 4-2 (a)]. However, with the deposition of 15 nm MoO₃, the roughness of P3HT:PCBM/Al/MoO₃ [Figure 4-2 (c)] reduces to 0.366 nm, indicating that the Al/MoO₃ intermediate layer is structurally smooth.

4.4 Electrical Characterization and Optimization

Upon these optical and structural properties of Al/MoO₃ intermediate layer, it is applied to realize different types of tandem devices.

4.4.1 Polymer/Small Molecule Double-Tandem Organic Solar Cells

The resulting structure of polymer/small molecule double-tandem cell is shown in Figure 4-3, with a structure of ITO/PEDOT:PSS(40 nm)/P3HT:PCBM(120 nm)/LiF(0.5 nm)/Al(1 nm)/MoO₃(15 nm)/CuPc(7.5 nm)/CuPc:C₆₀(12.5:12.5 nm)/C₆₀(27.5 nm)/BPhen(8 nm)/Ag(80 nm). And the corresponding bottom and top cells have the structures of ITO/PEDOT:PSS(40 nm)/P3HT:PCBM(120 nm)/LiF(0.5 nm)/Al(100 nm) and ITO/MoO₃(15 nm)/CuPc(7.5 nm)/CuPc:C₆₀(12.5:12.5 nm)/C₆₀(27.5 nm)/BPhen(8 nm)/Ag(80 nm), respectively.

Figure 4-3 The resulting structure of the polymer/small molecule double-tandem cell.

Figure 4-4 (a) The *I-V* characteristics of the tandem cells with 15 nm MoO₃ and different Al thicknesses. (b) The *I-V* characteristics of the tandem cells with an optimized 1 nm Al and different MoO₃ thicknesses. The cells for the polymer/small molecule double-tandem cell were post-annealed at 140 °C for 5 min.

Figure 4-4 shows the comparisons of the *I-V* characteristics of polymer/small molecule double-tandem cells with different thicknesses of Al [Figure 4-4 (a)] and MoO₃ [Figure 4-4 (b)]. It is evident that the tandem cell with 1 nm Al [Figure 4-4 (a)] and 15 nm MoO₃ [Figure 4-4 (b)] intermediate layer obtains the best performance. Reduced device performances are presented

with other combined Al and MoO₃ thicknesses since (1) too thin Al (or MoO₃) does not effectively act as recombination center (or electrical connection), without the summation of V_{oc} s; (2) thicker Al (or MoO₃) will cause increased light loss or high series resistance, which leads to poor J_{sc} or decreased FF. Therefore, the intermediate layer was optimized as 1 nm Al and 15 nm MoO₃.

Figure 4-5 The I - V characteristics of bottom single, top single cells and polymer/small molecule tandem cell under 100 mW/cm^2 . The cells for the polymer/small molecule tandem cell were post-annealed at 140°C for 5 min. The corresponding FF and PCE are shown in the format of (FF, PCE).

The I - V characteristics of bottom single, top single and tandem cells in polymer/small molecule double-tandem structure are shown in Figure 4-5 with their corresponding FFs and PCEs under 100 mW/cm^2 . The PCEs of the bottom and top single cells are 2.11% and 1.68%, respectively. With the Al(1 nm)/MoO₃(15 nm) intermediate layer, the tandem cell has a PCE of 2.82% with $V_{oc} = 1.01 \text{ V}$, $J_{sc} = 6.05 \text{ mA/cm}^2$, and FF = 46.2%. The V_{oc} (1.01 V) of the tan-

dem cell is the summation of the V_{oc} 's of the bottom single cell (0.63 V) and top single cell (0.45 V), which demonstrates that the tandem cell is connected electrically by this Al/MoO₃ intermediate layer. It is known that matched J_{sc} of bottom and top single cells is important for the tandem cells in series. It can be found in Figure 4-5 that the J_{sc} (7.83 mA/cm²) of top single cell is slightly higher than that (6.54 mA/cm²) of bottom one, demonstrating that the nearly matched photocurrent density between the bottom and top cells can be available in such tandem cell. Overall, the PCE of the tandem cell is higher than either of the individual single cells due to the increase of V_{oc} .

Figure 4-6 The I - V characteristics of polymer/small molecule double-tandem cell under different illuminations. The cells for the polymer/small molecule double-tandem cell were post-annealed at 140 °C for 5 min.

It should be pointed out that although the V_{oc} in the bottom P3HT:PCBM single cell is comparable to the literature,[9] the J_{sc} and FF are lower, which might be due to low annealing temperature (this low annealing temperature is preferred for the top small molecule OSC).[8] Figure 4-6 shows

the I - V characteristics of the polymer/small molecule double-tandem cell under different illuminations. It is seen clearly that its V_{oc} increases with the intensity of illumination because of the increase of the V_{oc} of both bottom and top single cells. Despite the FF reduces from 47.20% (at 50 mW/cm²) to 43.3% (at 300 mW/cm²) monotonically, the maximum PCE reached 3.88% at 300 mW/cm² primarily due to the enhanced V_{oc} .

4.4.2 Polymer/Polymer Double-Tandem Organic Solar Cells

Figure 4-7 The resulting structure of the polymer/polymer double-tandem cell

This intermediate layer is further applied in a solution-processed polymer/polymer double-tandem cell (P3HT:PCBM for both bottom and top cells) with a structure of ITO/PEDOT:PSS(40 nm)/P3HT:PCBM(70 nm)/Al(1 nm)/MoO₃(15 nm)/P3HT:PCBM(70 nm)/Al(100 nm). With a 15 nm thick MoO₃ layer, dissolving of the prior-deposited polymer (bottom cell) is avoided during spin-coating of the top cell polymer, i.e. a complete coverage of the bottom cell is made.

Figure 4-8 The I - V characteristics of the bottom single cell, top single cell, polymer/polymer double-tandem cell under 100 mW/cm^2 . The corresponding FF and PCE are shown in the format of (FF, PCE).

The I - V characteristic of the polymer/polymer double-tandem cell under 100 mW/cm^2 is shown in Figure 4-8. For comparison, the I - V characteristics of the bottom and top single cells are also presented. We can see that reasonable performance is obtained ($V_{oc} = 1.17 \text{ V}$ and $\text{PCE} = 2.23\%$) for this solution-processed polymer double-tandem cell.

4.4.3 Polymer/Polymer Triple-Tandem Organic Solar Cells

The identical polymer blend (P3HT:PCBM) was used as the three active layers to further constitute the triple-tandem cell, as shown in Figure 4-9. To realize tripled V_{oc} and relatively high efficiency, the thicknesses of each active layer were carefully adjusted so as to optimize the optical field distributed in

each cell, resulting in maximum light absorption and matched J_{sc} in each sub-cell.

Figure 4-9 The resulting structure of the polymer/polymer triple-tandem cell.

Figure 4-10 (a) The I - V characteristics of first (70 nm), second (85 nm), third (50 nm) single, double- and triple-tandem cells under 100 mW/cm². The corresponding FF and PCE are shown in the format of (FF, PCE). (b) The transmittance spectra of the first single film (70 nm), double-tandem film (70 nm/85 nm), and triple-tandem film (70 nm/85 nm/50 nm).

Figure 4-10 (a) compares the I - V characteristics of all cells covered in the triple-tandem cell under 100 mW/cm². The PCEs of the first (70 nm), second (85 nm) and third (50 nm) single cells are 1.94%, 2.64%, and 1.76%, respectively. The double-tandem cell has the PCE of 2.19% with V_{oc} of 1.19 V and J_{sc} of 3.71 mA/cm². The triple-tandem cell achieves a V_{oc} of 1.73 V with J_{sc} = 2.41 mA/cm², FF = 48.4% and PCE = 2.03%. The V_{oc} almost triples that of a single cell (0.62 V), demonstrating a relatively good Ohmic contact between Al

and MoO₃ layer.[135] Figure 4-10 (b) shows the transmittance spectra of first (70 nm), double-tandem (70 nm/85 nm) and triple-tandem (70 nm/85 nm/50 nm) films. Obviously, the triple-tandem cell absorbs more solar irradiation in the main absorption range of P3HT/PCBM blend. However, as we are using the same polymer materials for the stacked device, the light intensity becomes weaker and weaker when it passes through the first and second cells. Hence the third cell will have much less light passing through, which correspondingly leads to less or no reflected light by Al cathode. As a result, the photocurrent generated in each sub-cell will reduce largely due to the only incident absorption (almost no reflection absorption). It is known that the final current in serially connected cells is determined by the smallest current; therefore, the current from tandem cell is scaled down. Consequently, compared to a $J_{sc} = 4 - 7$ mA/cm² of a single cell, a J_{sc} of 2.41 mA/cm² for a triple-tandem cell is pretty good [Figure 4-10 (a)]. Meanwhile, the J_{sc} is expected to be enhanced by stacking different polymer layers with less overlapping absorptions. It can be also seen from Figure 4-10 (a) that the FF reduces as the number of the cells increases, which might be attributed to the increase of the series resistance in the multiple-tandem cell. However, the intermediate layer connecting triple-tandem cell does not results in large reduction of FF, still high here compared to that in the previously reported triple-tandem cell.[135] The overall PCE of triple-tandem cell (2.03%) is comparable to those of the single cells and double-tandem cell. To further improve the power efficiency, the way to go is to apply different polymers with complimentary absorption spectra. Thus this interme-

diode layer is feasible for such multiple cells stacked in polymer OSCs and polymer-based light-emitting diodes.

Figure 4-11 The IPCE spectra of each single, double-tandem, and triple-tandem cells.

The spectral response (IPCEs) of each single, double-tandem, and triple-tandem cells are illustrated in Figure 4-11. Since the identical materials are used as the active layer in sub cells, a light bias commonly used for the IPCE measurement of tandem device with complementary absorption spectra is not possible in our case. The IPCE spectrum reflects the contribution of each component of the blend to the photocurrent. All spectra are similar to the absorption spectrum of P3HT film, indicating that the excitons in P3HT phase primarily contribute to the photocurrent. However, the IPCE spectra of the second and third single devices are slightly different from that of first single device at around 450 nm due to the usage of MoO₃ and PEDOT:PSS as ITO buffer layer respectively. With the increase of the number of sub cells, the capability of conversion of harvested photons into extracted charges becomes weak at all wavelengths

across the absorption spectrum of the active layers due to the reduction of the photocurrent in each sub cell.

Figure 4-12 The photo image of a LED light up by this polymer/polymer triple-tandem cell (a) under 100 mW/cm², (b) device under test, and (c) under 300 mW/cm².

Furthermore, this triple-tandem cell with only 0.1 cm² active areas can turn on a red light-emitting diode under 100 and 300 mW/cm² illuminations, as shown in Figure 4-12. Since the V_{oc} of the triple-tandem cell can increase from 1.73 V (under 100 mW/cm²) to 1.87 V (under 300 mW/cm²), the LED grows brighter. Compared to the triple-tandem cell, only one single cell cannot achieve such high V_{oc} . On the other hand, three separate devices connected in series, like the formation of a Si-based cell array by integrating solar cells serially, could enhance the V_{oc} ; however, they would cause large room loss in small size-limited PSCs. Therefore, our tandem cell is advantageous compared to three individual cells connected in series in that it has a three times smaller footprint beneficial for area-limited applications.

4.4.4 Polymer/Small Molecule Triple-Tandem Organic Solar Cells

Figure 4-13 The resulting structure of the polymer/small molecule triple-tandem cell.

The resulting structure of the polymer/small molecule triple-tandem cell is shown in Figure 4-13, with a structure of ITO/PEDOT:PSS(40 nm)/P3HT:PCBM(70 nm)/Al(1 nm)/MoO₃(15 nm)/P3HT:PCBM(100 nm)/Al(1 nm)/MoO₃(15 nm)/CuPc(7.5 nm)/CuPc:C₆₀(12.5:12.5 nm)/C₆₀(27.5 nm)/BPhen(8 nm)/Ag(80 nm). For comparison, the bottom first single, double-tandem, and top single cells were fabricated in the same run as the triple-tandem cell, with the structures of ITO/PEDOT:PSS(40 nm)/P3HT:PCBM(70 nm)/Al(100 nm), ITO/PEDOT:PSS(40 nm)/P3HT:PCBM(70 nm)/Al(1 nm)/MoO₃(15 nm)/P3HT:PCBM(100 nm)/Al(100 nm), and ITO/MoO₃(15 nm)/CuPc(7.5 nm)/CuPc:C₆₀(12.5:12.5 nm)/C₆₀(27.5 nm)/BPhen(8 nm)/Ag(80 nm), respectively.

Figure 4-14 The absorption spectra of the bottom first cell (P3HT:PCBM(70 nm)), double-tandem cell (P3HT:PCBM(70 nm)/Al(1 nm)/MoO₃(15 nm)/P3HT:PCBM(100 nm)), top cell (CuPc(7.5 nm)/CuPc:C₆₀(12.5:12.5 nm)/C₆₀(27.5 nm)), and triple-tandem cell (P3HT:PCBM(70 nm)/Al(1 nm)/MoO₃(15 nm)/P3HT:PCBM(100 nm)/Al(1 nm)/MoO₃(15 nm)/CuPc(7.5 nm)/CuPc:C₆₀(12.5:12.5 nm)/C₆₀(27.5 nm)).

Figure 4-14 shows the absorption spectra of these single cells, double-tandem, and triple-tandem films used in their corresponding cells, respectively. It is evident that the bottom film and double-tandem films mainly cover the visible range from 400 to 650 nm, while the top film absorbs complementarily from 650 to 750 nm. With two identical active layers stacked, the absorption intensity increases correspondingly, not showing any change of spectrum shape. As the top film is deposited, the absorption spectrum is broadened. The absorption spectrum of the triple-tandem film with Al(1 nm)/MoO₃(15 nm) intermediate layer corresponds to a simple superposition of features from the absorption spectra of the bottom double-tandem and top films, thus indicating that the enhanced absorption is achievable in such constructed tandem device.

Figure 4-15 (a) The I - V characteristics of the bottom first single, double-tandem, top single, and polymer/small molecule triple-tandem cells under 100 mW/cm². (b) The comparison of I - V characteristics of polymer/small molecule triple-tandem cell and our previous all polymer triple-tandem cell.

Table 4-1 The summary of the I - V characteristics of the bottom double-tandem cell, top small molecule single cell, and triple-tandem cells under 100 mW/cm².

Cells	V_{oc} (V)	J_{sc} (mA/cm ²)	FF (%)	PCE (%)
Bottom 1 st single cell	0.63	5.47	56.4	1.94
Bottom Double-Tandem cell	1.17	3.55	49.5	2.05
Top Small-Molecule cell	0.45	7.83	47.6	1.68
All Polymer Triple-Tandem cell[67]	1.73	2.41	48.4	2.03
Polymer-Small Molecule Triple-Tandem cell	1.51	3.02	47.7	2.18

Figure 4-15 (a) shows the I - V characteristics of the bottom first single cell, top small molecule single cell, double-tandem cell, and triple-tandem cell under 100 mW/cm². The corresponding data are summarized in Table 4-1. The bottom double-tandem polymer cell has a PCE of 2.05% with $J_{sc} = 3.55$ mA/cm², $V_{oc} = 1.17$ V, and FF = 49.5%, comparable with our reported other double-tandem polymer cells. The PCEs of bottom first single cell and top single cell are 1.94% and 1.68%, respectively. Furthermore, the PCE of 2.18% is

obtained for polymer/small molecule triple-tandem cell, which is higher than that of all polymer triple-tandem cells, as shown in Figure 4-15 (b). This efficiency enhancement mainly originates from an increased J_{sc} to 3.02 mA/cm² due to the complementary absorption of the low bandgap top small molecule (CuPc:C₆₀) with P3HT:PCBM.[119] Since the photocurrent extracted from tandem cell depends on the smallest one generated among all sub-cells stacked in series, a matched photocurrent in all sub-cells is crucial. By replacing the top P3HT:PCBM active layer with a complementary absorption layer of CuPc:C₆₀, the interference effect (at the P3HT:PCBM absorption range) becomes more pronounced as compared to the case in all polymer triple-tandem cell. Meanwhile, the photocurrent in the top small molecule cell is larger due to the complementary absorption of small molecule to polymer. Therefore, it indicates that the complementary absorption benefits to higher photocurrent generated in both bottom double-tandem and top small molecule cells.

Moreover, the V_{oc} of the polymer/small molecule triple-tandem cell reaches 1.51 V, nearly the summation of V_{oc} 's of double-tandem and top single cells. It has to mention that the V_{oc} (1.51 V) decreases since the small molecule cell has a smaller V_{oc} (0.45 V) compared to P3HT:PCBM blend (~ 0.6 V). However, the PCE of polymer/small molecule triple-tandem cell is increased to 2.18%. This demonstrates that stacked cells with complementary absorptions contribute effectively to the improvement of the efficiency despite a slightly reduced V_{oc} .

4.5 Roles of MoO₃ layer

In our tandem cell, MoO₃ has multiple functions of (1) anode for top cell, (2) hole-transporting, (3) exciton-blocking, and (4) layer protection.

Figure 4-16 The energy level diagram of the tandem OSC.

Take polymer/small molecule double-tandem cell as an example. Figure 4-16 shows the energy level diagram of the polymer/small molecule tandem cell. The holes collected/transported by MoO₃ and electrons generated from the bottom cell recombine at the Al/MoO₃ intermediate layer (1 nm Al, most likely in nanocluster form). MoO₃ has been used as a hole-injection layer for OLEDs,[154-155] and a replacement of PEDOT:PSS in polymer solar cells,[65] exhibiting a good hole transporting property. Moreover, MoO₃ has a function of exciton blocking. Due to higher energy band gap of MoO₃ (3.0 eV) than the exciton energy of CuPc (1.9 eV), excitons formed in the top cell will be blocked by MoO₃. Only after exciton dissociation (at the CuPc/C₆₀ interfaces), holes can be collected by MoO₃ layer, contributing to photocurrent. More importantly, this intermediate layer can also act well as the protection layer for the prior-deposited polymer layer.

4.6 Summary

We have demonstrated an effective intermediate layer made of 1 nm Al and 15 nm MoO₃ for tandem OSCs. Such an intermediate layer, which can be easily fabricated, is highly transparent in the entire solar spectrum, is structurally smooth, and is well protective for prior-deposited polymer layer in solution-processed polymer tandem cell. We have applied this intermediate layer in polymer/small molecule and solution-processed polymer double- and triple-tandem OSCs with good and repeatable results. The PCE of the polymer/small molecule double-tandem cell is 2.82% at 100 mW/cm² (3.88% at 300 mW/cm²), higher than either of the individual ones. The polymer/polymer triple-tandem cell has an enhanced V_{oc} of 1.73 V and a comparable PCE of 2.03%. Such a high V_{oc} by multiple-cells tandem structure will provide potential application of polymer solar cells in area-limited low-power electronics. By replacing the third polymer cell with a complementary absorption small molecule cell, the PCE of the polymer/small molecule triple-tandem cell reaches 2.18%. The results indicate that organic materials with complementary absorption spectra play a crucial role in the performance of tandem cells. In addition, this intermediate layer would be potentially applied in the multiple-tandem polymer cells with complementary absorptions.

CHAPTER 5 INVERTED TANDEM ORGANIC SOLAR CELLS WITH $\text{MOO}_3/\text{Ag}/\text{Al}/\text{Ca}$ INTERMEDIATE LAYER¹

5.1 Introduction

As mentioned in Chapter 2 and 3, the conventional BHJ architecture (with ITO on glass as the anode at the bottom and a LWF metal as anode atop) has limitations in device stability due to air-sensitive LWF metal cathode (e.g. Ca and Al) and also due to degradation of ITO/PEDOT:PSS interface caused by slightly acidic nature of PEDOT:PSS.[63, 109] Moreover, spin-coated P3HT:PCBM BHJ layer exhibits a vertical phase separation with a concentration gradient changing from PCBM-rich at the bottom (closer to the substrate) to P3HT-rich atop (farther away from the substrate),[87, 157-158] which obstructs charge transport and charge collection in the conventional structure. Inverted structure [with modified ITO on glass as the cathode (at the bottom) and a HWF metal as the anode (at the top)] overcomes the above problems associated with the conventional structure with demonstrated better performance.[87, 92, 105, 109, 138, 149, 159]

On the other hand, in Chapter 4, we have developed an efficient intermediate layer to implement various types of tandem devices. As discussed, tan-

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dem structure consisting of two or more cells with complementary absorption spectra,[66-67, 118, 125, 132, 134, 160] is considered as an effective approach to boost the efficiency by enhancing light absorption. Herein, an intermediate layer, connecting sub-cells optically and electrically, plays a crucial role in overall device performance.[66] Thus far, quite a few intermediate layers have been reported,[117] such as Ag nanoclusters,[125] Au,[130] Al/ WO_3 ,[132] ITO/PEDOT:PSS,[133] Al/Au/PEDOT:PSS,[134] ZnO/PEDOT:PSS,[135] TiO_x /PEDOT:PSS,[118] Al/ MoO_3 ,[66-67, 160] and Al/ TiO_2 :Cs/PEDOT:PSS.[136]

Combining tandem and inverted structures in one device will benefit in terms of both device efficiency and stability. It is worth mentioning that the “inverted structure” reported by Kim *et al.*[118] is still a conventional tandem structure with ITO anode at the bottom and LWF cathode atop, in which the inversion refers to swapping the high and low band gap materials. Thus, it is completely different from the inverted tandem structure to be discussed in this chapter, where we shall present inverted tandem devices with various combinations of metals (Ca/Al/Ag) and metal oxide (MoO_3) as intermediate layer, and further optimize the intermediate layer and two BHJ sub-cell thicknesses with experiment and simulations.

5.2 Fabrication of Device

All cells were fabricated on ITO coated glass substrates with a sheet resistance of $20 \Omega/\text{square}$. A Ca layer was first thermally evaporated in a base vacuum of 9.0×10^{-5} Pa. Then, a blend solution made of P3HT (Rieke Metals, Inc.)

and PCBM (American Dye Sources Inc.) with a weight ratio of 1:0.8 in chlorobenzene (30 mg/mL) was spin-coated to form the active layers for both bottom and top sub-cells in a glove box filled with N_2 . MoO_3 , Ag, Al, and Ca were evaporated in designed sequence and combinations to form the intermediate layer (9.0×10^{-5} Pa). Evaporated MoO_3/Ag was used as the anode for all single and tandem devices. A post-annealing at 160 °C for 10 min was always performed for all devices after the final MoO_3/Ag anode fabrication. All cells had an active area of 0.1 cm² and were encapsulated before taking out from the glove box. The *I-V* characteristics were measured with a Keithley 2400 source-meter under simulated 100 mW/cm² (AM 1.5G) irradiation from a solar simulator. The transmittance spectra of the samples were recorded using UV-VIS-NIR scanning spectrophotometer (UV-3101PC). The film thickness was measured with a surface profiler (Tencor P15). Tapping mode AFM (D5000, Veeco) was used to characterize the surface roughness of metal oxide layer, metal layers and spin-coated polymer on Ca coated ITO glass. Figure 5-1 (a) shows the structure of inverted tandem device, consisting of ITO/Ca/P3HT:PCBM/ $\text{MoO}_3/\text{Ag}/\text{Al}/\text{Ca}$ /P3HT:PCBM/ MoO_3/Ag . The devices with various intermediate layers, including MoO_3 (7.5 nm)/Ca(3 nm), MoO_3 (7.5 nm)/Al(1 nm)/Ca(3 nm), MoO_3 (7.5 nm)/Ag(1 nm)/Ca(3 nm), and MoO_3 (7.5 nm)/Ag(1 nm)/Al(1 nm)/Ca(3 nm), different thicknesses of Ca in intermediate layer MoO_3 (7.5 nm)/Ag(1 nm)/Al(1 nm)/Ca, MoO_3 buffer layer, and P3HT:PCBM active layers in sub-cells, were fabricated for comparison. Also the energy level diagram of the device is shown in Figure 5-1 (b).

(a)

(b)

Figure 5-1 (a) The device structure of the inverted tandem cell with $\text{MoO}_3/\text{Ag}/\text{Al}/\text{Ca}$ intermediate layer. (b) The energy level diagram of inverted tandem OSCs.

5.3 Optical and Structural Properties of Intermediate Layer

5.3.1 Optical Properties of Intermediate Layer

Figure 5-2 The transmittance spectra of different combinations of intermediate layers: $\text{MoO}_3(7.5 \text{ nm})/\text{Ca}(3 \text{ nm})$, $\text{MoO}_3(7.5 \text{ nm})/\text{Al}(1 \text{ nm})/\text{Ca}(3 \text{ nm})$, $\text{MoO}_3(7.5 \text{ nm})/\text{Ag}(1 \text{ nm})/\text{Ca}(3 \text{ nm})$, and $\text{MoO}_3(7.5 \text{ nm})/\text{Ag}(1 \text{ nm})/\text{Al}(1 \text{ nm})/\text{Ca}(3 \text{ nm})$, and also the absorption spectrum of the P3HT:PCBM film.

Figure 5-2 shows the transmittance spectra of different combinations of intermediate layers, including $\text{MoO}_3(7.5 \text{ nm})/\text{Ca}(3 \text{ nm})$, $\text{MoO}_3(7.5 \text{ nm})/\text{Al}(1 \text{ nm})/\text{Ca}(3 \text{ nm})$, $\text{MoO}_3(7.5 \text{ nm})/\text{Ag}(1 \text{ nm})/\text{Ca}(3 \text{ nm})$, and $\text{MoO}_3(7.5 \text{ nm})/\text{Ag}(1 \text{ nm})/\text{Al}(1 \text{ nm})/\text{Ca}(3 \text{ nm})$. The absorption spectrum of P3HT:PCBM film is also shown in Figure 5-2 for comparison. The measurements of absorption and transmittance spectra were conducted as follows: the light source is incident from the glass side for all film samples and the transmitted light is detected

from the other side. Therefore, each multilayer structure suffers the same reflectance loss at the air/glass interface. Any other reflectance losses existing at the layer/layer interface just reflect the situation in the real device. Obviously, MoO_3/Ca and $\text{MoO}_3/\text{Al}/\text{Ca}$ have a high transparency of 98% ranging from 300 to 800 nm.[66, 149] With the insertion of Ag (1 nm), the transmittance of $\text{MoO}_3/\text{Ag}/\text{Ca}$ and $\text{MoO}_3/\text{Ag}/\text{Al}/\text{Ca}$ decreases in the range from 400 to 600 nm, exhibiting a transmittance dip peaking at 485 nm. This implies that Ag nanocluster layer (1 nm) is slightly absorptive in this range due to localized surface plasmon resonance (LSPR).[161-164] However, the LSPR absorption does not occur for either MoO_3/Al or MoO_3/Ca interface. Considering that a post-annealing was performed for the devices, it is possible that an oxide layer (O deficient) between MoO_3 and Al (or Ca) is formed since either Al or Ca has a lower electronegativity value compared to Mo (the Pauling electronegativity of Al, Ca and Mo is 1.61, 1.00 and 2.16 respectively). Formation of such oxide layer will lead to a reduction in electron density, preventing LSPR from happening. Interestingly, the transparency of $\text{MoO}_3/\text{Ag}/\text{Al}/\text{Ca}$ is nearly the same as that of $\text{MoO}_3/\text{Ag}/\text{Ca}$, although 1 nm Al is added in between, demonstrating that the insertion of Al nanocluster layer has no or little effect on the transparency of the intermediate layer.

5.3.2 Morphology of Intermediate Layer

Figure 5-3 The surface morphology (AFM images) of different films used for the intermediate layer: (a) P3HT:PCBM, (b) P3HT:PCBM/ MoO_3 , (c) P3HT:PCBM/ MoO_3/Ag , (d) P3HT:PCBM/ $\text{MoO}_3/\text{Ag}/\text{Al}$, (e) P3HT:PCBM/ $\text{MoO}_3/\text{Ag}/\text{Al}/\text{Ca}$.

Figure 5-3 shows the surface morphology (tapping mode AFM images) of P3HT:PCBM(80 nm), P3HT:PCBM(80 nm)/ MoO_3 (7.5 nm), P3HT:PCBM(80 nm)/ MoO_3 (7.5 nm)/Ag(1 nm), P3HT:PCBM(80 nm)/ MoO_3 (7.5 nm)/Ag(1 nm)/Al(1 nm), P3HT:PCBM(80 nm)/ MoO_3 (7.5 nm)/Ag(1 nm)/Al(1 nm)/Ca(3 nm) films, as used in the inverted tandem cells. The P3HT:PCBM(80 nm) film displays a rather smooth surface with a RMS surface roughness of 0.703 nm. Obviously, deposited MoO_3 layer (7.5 nm) does not cause an increase in surface roughness (0.740 nm). With the deposition of metal layers (Ag, Al, and Ca) used for intermediate layer, the RMS surface

roughness increases to 0.829, 1.048, and 2.712 nm for P3HT:PCBM/ MoO_3/Ag , P3HT:PCBM/ $\text{MoO}_3/\text{Ag}/\text{Al}$, P3HT:PCBM/ $\text{MoO}_3/\text{Ag}/\text{Al}/\text{Ca}$ films, respectively. This indicates that ultrathin Ag and Al make the films slightly rougher due to aggregation of metal nanoclusters during their depositions. It has to be pointed out that the AFM measurement was performed in air, leading to oxidization of Ca layer, therefore, the surface roughness of P3HT:PCBM/ $\text{MoO}_3/\text{Ag}/\text{Al}/\text{Ca}$ film (2.712 nm) is remarkably higher than those of other films.

5.4 Electrical Characterization and Optimization

5.4.1 Comparison of Various Intermediate Layers

Figure 5-4 The comparison of the I - V characteristics of the inverted tandem cells with different combinations of intermediate layers. The device structure is ITO/Ca(1 nm)/P3HT:PCBM(85 nm)/intermediate layer/P3HT:PCBM(70 nm)/ MoO_3 (5 nm)/Ag(100 nm), where intermediate layer includes MoO_3 (7.5 nm)/Ca(3 nm), MoO_3 (7.5 nm)/Al(1 nm)/Ca(3 nm), MoO_3 (7.5 nm)/Ag(1 nm)/Ca(3 nm), and MoO_3 (7.5 nm)/Ag(1 nm)/Al(1 nm)/Ca(3 nm).

Figure 5-4 shows the comparison of the I - V characteristics of the inverted tandem cells with different combinations of intermediate layers. Although the V_{oc} for the cell with MoO_3/Ca intermediate layer approaches 0.79 V, it is much smaller than the V_{oc} summation of two inverted sub-cells due to large voltage loss across the MoO_3/Ca interface. For conventional tandem cell,[66, 136] an ultrathin Al is quite necessary. In the case of inverted tandem cell, the

insertion of 1 nm Al between MoO_3 and Ca increases the V_{oc} of inverted tandem cell to 1.19 V, equal to the sum of the V_{oc} values of inverted sub-cells. However, both inverted tandem cells with MoO_3/Ca and $\text{MoO}_3/\text{Al}/\text{Ca}$ exhibit an S-shaped I - V curve, similar to some previous reports.[128, 136] Such an S-shaped curve may be caused by the formed oxide layer as above-mentioned, which blocks charge extraction and recombination at the intermediate layer, resulting in rather poor FFs (27.9% and 31.2%) for both inverted tandem cells.

In contrast, with 1 nm Ag inserted between Ca (or Al/Ca) and MoO_3 , it is obvious that the S-shaped curve disappears. This indicates that the formation of the oxide layer between MoO_3 and Ca (or Al) is prevented by the insertion of Ag. As a consequence, the FF remarkably roars up to $\sim 60\%$, similar to those of inverted sub-cells. However, the V_{oc} (0.99 eV) of the inverted tandem cell with $\text{MoO}_3/\text{Ag}/\text{Ca}$ is lower than the summation of the V_{oc} 's of the inverted sub-cells, suggesting the existence of an energy barrier.[136] With an ultrathin Al incorporated between Ag and Ca, an Ohmic contact between both sub-cells is fully established, leading to removal of the charge extraction/recombination barrier. Hence, the V_{oc} of 1.18 V is obtained for the inverted tandem cell with $\text{MoO}_3/\text{Ag}/\text{Al}/\text{Ca}$, which is almost the exact summation of the V_{oc} 's (0.57 and 0.63 V) of the sub-cells, demonstrating no voltage loss across the intermediate layer. In addition, the slight increase in FF to 61.8% is ascribed to the fact that Al functions (work functions of Ag, Al, and Ca are 4.4, 4.3, and 2.9 eV respectively) as an energy step for efficient charge recombination sites of the holes extracted from bottom sub-cell through MoO_3/Ag and the electrons extracted from top sub-cell through Ca. Finally, the inverted tandem cell with

$\text{MoO}_3/\text{Ag}/\text{Al}/\text{Ca}$ has a PCE of 2.78% with a J_{sc} of 3.81 mA/cm^2 , V_{oc} of 1.18 V, and FF of 61.8%.

Figure 5-5 The I - V characteristics of the inverted bottom sub-cell, top sub-cell, and tandem cell with $\text{MoO}_3/\text{Ag}/\text{Al}/\text{Ca}$ intermediate layer under 100 mW/cm^2 . The bottom sub-cell is with a structure of $\text{ITO}/\text{Ca}(1 \text{ nm})/\text{P3HT}:\text{PCBM}(85 \text{ nm})/\text{MoO}_3(7.5 \text{ nm})/\text{Ag}$ and the top sub-cell is with a structure of $\text{ITO}/\text{Ca}(3 \text{ nm})/\text{P3HT}:\text{PCBM}(70 \text{ nm})/\text{MoO}_3(5.0 \text{ nm})/\text{Ag}$. The inset shows the summary of all device performance.

Figure 5-5 shows the I - V characteristics of inverted bottom sub-cell, top sub-cell, and tandem cell with $\text{MoO}_3/\text{Ag}/\text{Al}/\text{Ca}$ intermediate layer under 100 mW/cm^2 . The summarized performance is tabulated as the inset of Fig. 4. The

inverted bottom sub-cell has a PCE of 2.68% with $J_{\text{sc}} = 7.24 \text{ mA/cm}^2$, $V_{\text{oc}} = 0.57 \text{ V}$, and $\text{FF} = 64.9\%$. It is worth mentioning that the smaller V_{oc} (0.57 V) is attributed to the voltage loss across the relatively thick MoO_3 layer (7.5 nm).[149, 165] For the inverted top sub-cell, since a 3 nm thick Ca is used to modify the ITO substrate for electron extraction, there is some slight light loss. As a result, its PCE reaches 3.01% with $J_{\text{sc}} = 8.02 \text{ mA/cm}^2$, $V_{\text{oc}} = 0.63 \text{ V}$, and $\text{FF} = 59.6\%$. It is obvious that both inverted sub-cells have not achieved the best performance,[149, 165] as a few critical requirements for inverted tandem cell have to be satisfied, i.e. relatively thick MoO_3 in bottom sub-cell for protecting the prior-deposited polymer layer and relatively thick Ca in top sub-cell for forming a continuous film to collect electrons from the top sub-cell and also to avoid “short-circuit” points.

It is noted that the high FF (61.8%) of the inverted tandem cell is comparable to those of inverted single cells, and significantly larger than that of the conventional tandem cell.[66] The J_{sc} decreases since identical materials (P3HT:PCBM) are used as the active layer for the sub-cells. Overall, the PCE (2.78%) of inverted tandem cell is comparable to those (2.68% and 3.01%) of single cells due to the compensation of the doubled V_{oc} . It is promising that this intermediate layer could result in significantly improved performance for solution-processed inverted tandem cells with complementary absorption materials.

5.4.2 Effect of Contribution Layer in Intermediate Layer

Careful combination of multiple ultrathin metals and metal oxide is essential to realize effective connection of the sub-cells. MoO_3 layer plays mul-

multiple roles in inverted single devices,[149, 159] including transporting and extracting the holes, preventing the exciton quenching at the Ag electrode, protecting the active layer from damage caused by the Ag deposition, and adjusting the optical field distribution as an optical spacer in the device. Hence, the MoO_3 layer thickness significantly influences the device performance. In the case for intermediate layer in inverted tandem devices, if the MoO_3 layer is too thick, it will cause high series resistance and large voltage drop across this layer, leading to reduction of FF and V_{oc} . [149, 159] Meanwhile, if the MoO_3 layer is too thin, it cannot completely protect the prior-deposited polymer from being dissolved.[119] Therefore, the thickness of MoO_3 layer is optimized to be 7.5 nm, which could function well as both a connecting unit layer working as anode for bottom sub-cell and a protection layer.

It has been discussed that the metal layers are also crucial to implement efficient sub-cell connection and to achieve good device performance. For each metal layer (Ag, Al, and Ca), they contribute to low contact resistance and voltage drop at proper intermediate layer, leading to good FF and fully summated V_{oc} . Herein, we further continue optimizing the thickness of Ca as part of intermediate layer for inverted tandem devices since the thickness of Ca layer has great impact on single inverted device performance. In inverted single device, the optimal thickness of Ca is 0.5 or 1 nm.[149, 159]

Figure 5-6 The I - V characteristics of the inverted tandem cells (80 nm bottom sub-cell and 70 nm top sub-cell) with $\text{MoO}_3/\text{Ag}/\text{Al}/\text{Ca}$ intermediate layer by varying the thickness of Ca and 5 nm MoO_3 as anode buffer layer under $100 \text{ mW}/\text{cm}^2$.

Figure 5-6 shows the I - V characteristics of the inverted tandem cells (80 nm bottom sub-cell and 70 nm top sub-cell) with different thickness of Ca in intermediate layer and 5 nm MoO_3 as anode buffer layer. Obviously, the V_{oc} 's for all devices are similar, indicating that Ca acts effectively as cathode for the top sub-cell. When Ca layer is 1.5 and 3 nm, the device has a J_{sc} of 3.77 and 4.19 mA/cm^2 , respectively. However, the device with 1.5 nm Ca exhibits a higher photocurrent variation in the reverse bias region than that with a 3 nm Ca, implying the existence of slightly larger leakage current in the device with 1.5 nm Ca. This might be caused by relatively thin Ca layer (1.5 nm) which cannot form a continuous film on prior-deposited multiple layers. It can be observed that this 3 nm-thick Ca layer performs well. With further increase of Ca thick-

ness to 4.5 nm, the performance drops dramatically, in particular in FF, implying a large series resistance and bad current matching. As a consequence, the optimal device has a 3 nm Ca layer, exhibiting a PCE of 2.89% with $J_{\text{sc}} = 4.19 \text{ mA/cm}^2$, $V_{\text{oc}} = 1.17 \text{ V}$, and FF = 59.0%.

5.4.3 MoO_3 Optimization as Anode Buffer Layer

Figure 5-7 The I - V characteristics of the inverted tandem cells (80 nm bottom sub-cell and 70 nm top sub-cell) under 100 mW/cm^2 with $\text{MoO}_3/\text{Ag}/\text{Al}/\text{Ca}(5 \text{ nm})$ intermediate layer and variable thickness of MoO_3 anode buffer layer.

It is worth mentioning that MoO_3 as anode buffer layer has a significant influence on inverted single devices with Ca as electron-transporting layer.[149, 159] Hence, it is still necessary to optimize the thickness of MoO_3 as anode buffer layer in the inverted tandem devices to prevent the exciton quenching and charge loss at the anode side. Figure 5-7 shows the I - V characteristics of the inverted tandem cells under 100 mW/cm^2 with $\text{MoO}_3/\text{Ag}/\text{Al}/\text{Ca}$ (Ca = 3 nm) intermediate layer and variable MoO_3 as anode buffer layer. When MoO_3 is 3 or

5 nm, the devices have identical V_{oc} of 1.17 V. However, 7 nm MoO_3 makes the V_{oc} drop to 1.13 V, primarily originating from the slightly reduced V_{oc} in single top cell caused by relatively thick MoO_3 layer.[149, 159] Moreover, the devices with all three thicknesses of MoO_3 exhibit similar FFs of around 59.0%. Since the current matching is obtained in stacked sub-cells for the device with 5 nm MoO_3 , [159] the device achieves a best J_{sc} of 4.19 mA/cm^2 . Overall, the thickness of MoO_3 layer as anode buffer layer is optimized to be 5 nm, demonstrating that it has a slight effect on inverted tandem device performance.

5.4.4 Optimization of Sub-cell Thickness

For a multiple-layer based solar cell, the layer thickness determines the degree of light absorption via the change of optical field distribution. Correspondingly, some approaches have been employed to effectively adjust the optical field distribution inside the entire device, such as varying layer thickness,[148, 159, 166-167] introducing an optical spacer that will not affect the initial electrical properties,[69-71, 151, 168] using highly reflective electrode to enhance the fraction of reflection light.[94, 147]

Tandem OSC is a typical multiple-layer based solar cell, where an optimal PCE can be obtained by changing the thickness of each sub-cell so as to attain a good current matching. In order to understand the effect of sub-cell thickness on the final photocurrent, we simulated the optical field distribution in the entire device and calculated the current density contributed by bottom and top sub-cells with different thicknesses using a transfer matrix method.[148, 169-170] The overall J_{sc} was set to be the smaller one of the top and bottom

sub-cells. For this simulation, complex refractive indexes of various layers were obtained from several sources.[169, 171-174] Figure 5-8 shows a 3D plot of the overall J_{sc} of inverted tandem cells as functions of bottom and top sub-cell layer thickness.

Figure 5-8 3D plot of the overall J_{sc} of the inverted tandem cells versus bottom and top sub-cell layer thicknesses.

Figure 5-9 The I - V characteristics of the inverted tandem cells under 100 mW/cm^2 with $\text{MoO}_3/\text{Ag}/\text{Al}/\text{Ca}$ intermediate layer and different thickness of active layers in sub-cells: (a) bottom cell=70 nm, 80 nm, and 100 nm, top cell=70 nm, (b) bottom cell=80 nm, top cell=70 nm, 80 nm, and 100 nm.

Figure 5-9 (a) shows the I - V characteristics of the inverted tandem cells with a fixed top sub-cell (70 nm) and variable thickness of bottom sub-cell (70, 80, and 100 nm) under 100 mW/cm^2 . With the top sub-cell thickness of 70 nm, the J_{sc} of inverted tandem device slightly decreases from 4.28 to 3.92 mA/cm^2 when the bottom sub-cell thickness increases from 70 to 100 nm. It is primarily attributed to the slight variation of optical field distribution, leading to the shift of current matching. This change is consistent with the trend shown in Figure 5-8. However, the 70 nm bottom sub-cell has to suffer relatively high resistance

caused by 7.5 nm MoO_3 as anode buffer layer compared to the 80 nm and 100 nm bottom sub-cells.[159] Therefore, the inverted tandem device with 70 nm bottom and top sub-cells has a lower FF (57.6%) than those with 80 or 100 nm bottom sub-cell and 70 nm top sub-cell (59.0% and 59.0% respectively). This is the main reason why the optimal inverted device is obtained by stacking 80 nm bottom and 70 nm top sub-cells. On the other hand, Figure 5-9 (b) shows the I - V characteristics of the inverted tandem cells with a fixed bottom sub-cell (80 nm) and variable thickness of top sub-cell (70, 80, and 100 nm) under $100 \text{ mW}/\text{cm}^2$. Similarly, the final photocurrent drops with the increase of top sub-cell thickness, exhibiting J_{sc} of 4.19, 4.07, and $3.90 \text{ mA}/\text{cm}^2$ for the devices with top sub-cell thickness of 70, 80, and 100 nm, respectively. Figure 5-8 shows a similar trend in photocurrent (the trend for 70 and 80 nm sub-cells). The results indicate that interference effect between the incident light and the reflected light from the metal electrode reduces due to the usage of identical active material in both sub-cells and the increase of active layer thickness. As a consequence, the optimized combination for inverted tandem devices is 80 nm and 70 nm for bottom and top sub-cells, respectively.

5.5 Summary

We have presented inverted tandem devices with different combinations of multiple metal layers (Ag, Al, and Ca) and a metal oxide MoO_3 layer as intermediate layer, in which an optimal one is given as $\text{MoO}_3/\text{Ag}/\text{Al}/\text{Ca}$ with high transparency and structural smooth. We have optimized the inverted tandem devices with $\text{MoO}_3/\text{Ag}/\text{Al}/\text{Ca}$ intermediate layer by tuning the thickness of Ca

as part of intermediate layer, MoO_3 as buffer layer, and P3HT:PCBM as active layer. This intermediate layer exhibits slight change in the surface roughness with the deposition of each layer. A 3 nm-thick Ca acts as cathode for top sub-cell, benefiting to the protection of the prior-deposited active layer. The optimal thickness of MoO_3 anode buffer layer is 5 nm for effectively preventing the exciton quenching and damages from Ag deposition. The optical field distribution in the device is tuned by the variance of sub-cell thickness for matching photocurrent. Finally, the best device performance is obtained with 80 nm bottom sub-cell, 70 nm top sub-cell, 3 nm Ca as part of intermediate layer, and 5 nm MoO_3 anode buffer layer. Our developed intermediate layer would provide a potentially efficient approach to achieve the performance improvement of inverted tandem devices with complementary absorbing materials as active layers, and meanwhile the issues associated with interface instability and charge transport/collection could be overcome.

CHAPTER 6 NEW POLYMER BASED ORGANIC SOLAR CELLS AND APPLICATIONS IN TANDEM DEVICES¹

6.1 Introduction

Conjugated polymer solar cells (PSCs) (e.g. P3HT and PPVs) have achieved potential efficiencies with BHJ structure, where a photoactive layer is casted from a mixture solution of polymer donor (D) and soluble fullerene-based acceptor (A) and sandwiched between two electrodes with different work functions.[8-9] A maximum PCE is predicted as 10% by designing new materials to address issues associated with light absorption, charge transfer, and charge transport.[76] In BHJ PSCs, the device performance is a result of balance between light absorption and charge transport.[31, 36, 116] Light absorption is primarily determined by the materials used, while efficient charge transport in D-A blend film can be facilitated by nanoscale bicontinuous pathways, which also increases the exciton dissociation efficiency by decreasing exciton diffusion distance and increasing the D-A interfacial areas.[18, 24, 49] It has been demonstrated that the charge transfer from the LUMO of donor to the LUMO of acceptor is extremely fast (- 45 fs).[16] This charge transfer is related with the LUMO difference of acceptor and donor, described as LUMO (D) - LUMO (A), determining the driving force for exciton dissociation at the interface.[34, 175-176] Therefore, for efficient exciton dissociation, such D-A LU-

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MO difference is required at least larger than the exciton binding energy of polymers (typically between 0.1 and 2 eV).[7] On the other hand, the difference between HOMO of donor and LUMO of acceptor is another important factor, described as HOMO (D) - LUMO (A), on which V_{oc} is dependent.[10] In addition, the V_{oc} is also considered to be determined by the work function difference of two electrodes in MIM device.[75] Hence, a conjugated polymer donor with suitable energy levels is necessary to maintain a relatively large V_{oc} and obtain efficient charge transfer. The performance of BHJ solar cells strongly depends on nanoscale morphology in the active layer. The phase separation occurring in polymer:PCBM blend[18] is determined to a great extent by the solvents used,[50-53] the weight ratios of polymer donor to fullerene,[49, 56] the concentration of the blend solution,[24] and post-annealing treatment.[8, 20, 58]

A conjugated polymer poly(9,9-dihexylfluorene)-*alt*-bithiophene) (F6T2) has been reported, giving rise to a PCE of 2.7% in the device with a F6T2:PCBM weight ratio of 1:4.[177] Detailed study on the thermal and hole-transporting properties of poly[2,7-(9,9-dihexylfluorene)-*alt*-bithiophene] (F6T2) and photovoltaic performance of BHJ solar cells has been reported,[178] in which the devices consist of F6T2 as the donor and PCBM as the acceptor with a weight ratio of 1:3 and exhibit a PCE of 2.4%. Obviously, the weight ratio in F6T2 based devices is also as crucial as that in other donor blends,[18, 24, 49] correlated with phase separation in two components. Thus, a comprehensive optimization for F6T2:PCBM based PSCs is necessitated.

In this chapter, we study a more complete solid-state photo-physical and morphological characterization of F6T2:PCBM blends with variable weight ra-

tios, and their corresponding single cells are also compared for achieving an optimal efficiency. In addition, F6T2:PCBM is used as a bottom cell to implement a polymer/small molecule tandem cell. Upon the insertion of an ultra thin Ca in Al/MoO₃ intermediate layer, the V_{oc} (1.27 V) of tandem device is the exact summation of those of both sub-cells.

6.2 Fabrication of Device

➤ Device fabrication

All devices were fabricated on ITO coated glass substrates with a sheet resistance of 20 Ω /square. The substrates were cleaned in an ultrasonic bath with detergent, deionied-water, acetone, and isopropyl alcohol successively for 15 min. After being dried in a laboratory oven, the ITO surfaces were treated by oxygen plasma for 5 min. F6T2 was synthesized as reported[178-179] and PCBM was purchased from Nano-C. F6T2 and PCBM were dissolved separately in chlorobenzene with 20 mg/mL and stirred at 60 °C for one day. Then, they were mixed together with designated weight ratios. PEDOT:PSS (Baytron P 4083), filtered with 0.45 μ m filter syringe, was firstly spin-coated onto pre-cleaned ITO-glass with a thickness of 40 nm, and baked at 125 °C for 30 min. Subsequently, the substrates were moved into a glove box filled with N₂. For single cells, the active layer was fabricated by spin-coating the blend solution onto PEDOT:PSS coated substrates. Ca(20 nm)/Ag(80 nm), Au (80 nm), Ag (80 nm) cathodes were thermally deposited on the top of the active layer under a vacuum of 9.0×10^{-5} Pa, where Al (100 nm) cathode was deposited by E-beam evaporation. For tandem device, the bottom active layer was prepared, followed

by the fabrication of intermediate layer Ca/Al/MoO_3 , deposited by thermal and E-beam evaporation. Then, CuPc, C_{60} , and BPhen were deposited sequentially by thermal evaporation to act as the top cell. Finally, the Ag (80 nm) cathode was deposited. The active area was 0.1 cm^2 . A series of the devices were repeated and compared three times; and around 90 devices were fabricated in total. For each comparison, the trend exhibits the same.

➤ Characterization

The optical absorption spectra were recorded using UV-VIS-NIR scanning spectrophotometer (UV-3101PC). The films used for absorption measurement were fabricated on PEDOT:PSS coated ITO-glass, where ITO/PEDOT:PSS acted as the reference. The photoluminescence (PL) spectra of pure F6T2, PCBM, various F6T2:PCBM blend thin films were measured using Fluorolog-3 spectrofluorimeter, excited by 450 nm light. The samples were prepared on quartz substrates. The thicknesses for all active layers were measured with a surface profiler (Tencor P15). SEM (JSM-5600) and tapping mode AFM (D5000, Veeco) were used to characterize the surface topography (phase separation and surface roughness) of the spin-coated F6T2:PCBM layers on PEDOT:PSS based ITO glass. The I - V characteristics were measured with a Keithley 2400 sourcemeter in dark or under 100 mW/cm^2 irradiation of a solar simulator. The IPCEs (spectral response) of the devices were measured using Oriel Merlin under short-circuit conditions, meanwhile, the tested devices were illuminated by a 200 W Xenon lamp light source with a motorized monochromator (Oriel), calibrated against a silicon solar cell.

6.3 Energy Level and Optical Properties

Figure 6-1 (a) The chemical structures of donor F6T2 and acceptor PCBM. (b) The structure of PSC.

Figure 6-2 The energy level diagram of F6T2:PCBM based PSC.

F6T2 was synthesized in the lab with a high molecular weight (M_w) of 52 400 and polydispersity index (PDI) of 1.99.[179] The chemical structures of donor F6T2 and acceptor PCBM used and the device structure are shown in

Figure 6-1. As reported, F6T2 possesses a LUMO of - 2.64 eV and HOMO of - 5.13 eV, exhibiting a high bandgap of 2.49 eV. Hence, the energy level diagram of the device can be drawn in Figure 6-2. In order to obtain good photovoltaic performance, both differences of HOMO (D) - LUMO (A) and LUMO (D) - LUMO (A) have to be considered. Large HOMO (D) - LUMO (A) difference is beneficial to a high V_{oc} . LUMO energy matching of donor and acceptor can supply sufficient driving force for exciton separation.[34, 175-176] In Figure 6-2, a large LUMO offset of 1.06 eV is observed (LUMO of PCBM: - 3.7 eV[65]), which is significantly larger than the exciton binding energy in F6T2. Therefore, photoinduced charge transfer process from F6T2 to PCBM is favored.

Figure 6-3 The normalized absorption spectra of pure F6T2, pure PCBM, and F6T2:PCBM blend films with different weight ratios.

Figure 6-3 shows the normalized absorption spectra of pure F6T2, pure PCBM, and blend F6T2:PCBM films with different weight ratios. The absorption spectrum of pure F6T2 film displays one main peak located at 450 nm and one slightly weak shoulder at 480 nm, covering an absorption range from 350 nm to 520 nm, comparable to those of PPV or its derivatives,[14] but narrower than that of P3HT.[9] Since the absorption range of F6T2 is relatively narrow, a small region of the solar spectrum is covered. It has to be pointed out that there are only 30% photon with energy higher than 1.9 eV in the whole solar spectrum.[180] Therefore, this F6T2:PCBM blend (2.49 eV bandgap) is able to absorb only a small fraction of solar light. For F6T2:PCBM blend in Figure 6-3, two peaks are distinguished, i.e. one peak at ~ 335 nm stems from PCBM and the other one at ~ 450 nm represents the contribution from F6T2. Obviously, the addition of PCBM results in a red-shifted F6T2 absorption with the absorption band edge extending to 600 nm. For the F6T2:PCBM (1:1) film, there exists a strong absorption of pristine F6T2, two times higher than that of PCBM. Further increasing PCBM, however, results in a gradual decrease in the F6T2 absorption intensity in comparison with parent F6T2. The absorption intensities of F6T2 level off when the weight ratio of F6T2:PCBM changes to 1:4, 1:5, and 1:6. This is reasonable when considering that conjugated polymer donors serve as the main absorber for solar photon flux and also as the hole transporting phase.

Figure 6-4 The normalized PL spectra of pure F6T2 and F6T2:PCBM (1:0.5, 1:1, 1:2, and 1:5) blend films. All the films were excited at the wavelength of 450 nm.

In order to investigate the effect of the PCBM concentration on the excited-state charge transfer, steady-state PL measurements were employed for F6T2:PCBM blend films with different weight ratios (pure F6T2, 1:0.5, 1:1, 1:2, and 1:5) and their corresponding normalized PL spectra are shown in Figure 6-4. To detect PL emission from F6T2, the blend films were excited with a wavelength of 450 nm (the maximum absorption peak of pure F6T2 shown in Figure 6-3). The PL emission of pure F6T2 film is mainly located at 560 nm, exhibiting a relatively narrow emission width (Figure 6-4). At a F6T2:PCBM weight ratio of 1:0.5, the PL emission from F6T2 dramatically decreases by over 99% of its emission quenched by the addition of PCBM. As the F6T2:PCBM weight ratio changes to 1:2, the PL emission from F6T2 is further reduced to 0.15% of the original level, indicating the effective PL quenching of F6T2 by PCBM, as

similar behavior observed in P3HT:PCBM[181] and MDMO-PPV:PCBM[182-183] systems. Because the overlap between the PL spectrum of F6T2 and the absorption spectrum of PCBM is rather small, the resonance energy transfer between them can be neglected.[184] Therefore, it is the charge transfer between F6T2 and PCBM that leads to the PL quenching with the photogenerated exciton dissociated into electrons and holes before luminescence can occur. From the quenched PL spectra, there exists a slight blue-shift for F6T2 emission, which can be explained by the origin of the residual emission from increasingly short-lived F6T2 excitations,[185] or the spectrum superposition of the residual F6T2 emission and the increased PCBM emission. In our F6T2:PCBM system, except for the large LUMO offset of 1.06 eV, the charge-transfer state has a HOMO (D) and LUMO (A) difference of 1.43 eV, smaller than the exciton energy of F6T2 (around 2 eV), which guarantees an energetically favorable charge transfer.[7] Thus, the exciton can be efficiently dissociated at the interface under photo-excitation.

6.4 Electrical Characterization and Optimization

Figure 6-5 The tapping mode AFM height images of F6T2:PCBM BHJ active layers with different weight ratios. (a) 1:1, (b) 1:2, (c) 1:3, (d) 1:4, (e) 1:5, and (f) 1:6. For all images, the height-scale is 10 nm and scan size is $2 \times 2 \mu\text{m}^2$.

Morphology of the BHJ active layer plays a crucial role in the performance of PSCs.[18, 24, 49, 87] Therefore, we have performed AFM and SEM measurements to investigate the influence of the amount of PCBM in the F6T2:PCBM blends on the morphological differences and phase separation. Considering the real device structure, the films used for measurement were fabricated onto PEDOT:PSS coated ITO substrates. Figure 6-5 shows the tapping mode AFM images of F6T2:PCBM BHJ active layers with different weight ratios. It can be seen that all the active layers have a rather smooth surface with a RMS surface roughness less than 1 nm. The active layers for the F6T2:PCBM weight ratios of 1:1, 1:2, and 1:3 display a slightly decreased surface roughness of 0.516 nm [Figure 6-5 (a)], 0.485 nm [Figure 6-5 (b)], and 0.439 nm [Figure 6-5 (c)], respectively. However, with further increase of PCBM concentration, a

small increase in the RMS roughness of the active layer for the F6T2:PCBM weight ratios of 1:4 (0.491 nm), 1:5 (0.544 nm), and 1:6 (0.599 nm) samples is observed, as shown in Figure 6-5 (d), (e), and (f), respectively. This could be attributed to PCBM aggregation caused by the high PCBM concentration.[18]

Figure 6-6 The SEM images of F6T2:PCBM BHJ active layers with different weight ratios of (a) pure F6T2, (b) 1:2, (c) 1:4, and (d) 1:6.

Figure 6-6 shows the SEM images of F6T2:PCBM BHJ active layers with different weight ratios. The pristine F6T2 exhibits no phase separation at all [Figure 6-6 (a)]. When the weight ratio of F6T2:PCBM is 1:2, the phase separation between F6T2 and PCBM domains occurs, though not quite clear [Figure 6-6 (b)]. For other weight ratios, the phase separation becomes more pronounced [island-like areas appear in Figure 6-6 (c) and (d)], similar to the

observed morphology in F6T2:PCBM (1:3) films.[178] It should be noted that the phase separation in our F6T2:PCBM blend is formed during the spin-coating process without any annealing treatments, not like that in P3HT:PCBM systems.[18, 49] The well-separated phases in F6T2:PCBM blends would contribute to good photovoltaic performance in such devices (discuss later). Interestingly, the phase separation in the F6T2:PCBM [1:4, Figure 6-6 (c)] active layer confirms the nanoscale F6T2 and PCBM domains with dimensions of 10 - 20 nm, which is suitable for efficient exciton dissociation.[18, 87]

Figure 6-7 Comparison of the I - V characteristics of F6T2:PCBM based polymer solar cells with different weight ratios under $100 \text{ mW}/\text{cm}^2$ illumination. (a) J_{sc} (closed

square) and FF (open square); (b) V_{oc} (open circle) and PCE (closed circle). The inset in Figure 6-7(a) shows the dependence of the V_{oc} of F6T2:PCBM (1:5) devices on the cathode metals used.

Figure 6-7 shows the comparison of the I - V characteristics of the F6T2:PCBM PSCs with different weight ratios under 100 mW/cm^2 . Although the PL quenching is rather complete at the F6T2:PCBM weight ratio of 1:1 (Figure 6-4), the J_{sc} and FF of the corresponding device are only 1.19 mA/cm^2 and 25.2%, respectively, which are possibly caused by the insufficient PCBM domains for the charge transport pathway. When the weight ratio of F6T2:PCBM changes to 1:2, the J_{sc} of the device is significantly increased to 5.2 mA/cm^2 . Further increase in PCBM concentration leads to a slight reduction of J_{sc} , probably due to mismatched electron transport mobility of PCBM and the hole transport mobility of F6T2[178] and also reduced light absorption by F6T2 (Figure 6-3). In contrast, the FF increases significantly from 25.2% to 56.9% as the weight ratio of F6T2:PCBM changes from 1:1 to 1:6. As a consequence, despite the fine quenching of F6T2 by only a small amount of PCBM (Figure 6-4), the efficient charge transport is still influenced by the PCBM volume. It can imagine that F6T2:PCBM (1:1) blend possesses less efficient charge transport, as proved by a rather low FF. For F6T2:PCBM (1:2) blend, FF of the device is still relatively low (53.1%), mainly due to insufficient fullerene percolated pathway. When the PCBM concentration increases further, FF increases accordingly (56%), indicating the improvement of the charge transport. The increase in FF is guaranteed by the relatively high hole mobility (ca. $8.4 \times 10^{-5} \text{ cm}^2/\text{Vs}$ at 310 K and $2.5 \times 10^5 \text{ V/cm}$)[178] and is also directly asso-

ciated with the presence of PCBM crystals in the blends and the high probabilities of electrons to escape beyond the capture radius.[186] As a consequence, the increase of the PCBM concentration results in a reduced J_{sc} , but significantly improved FF (competitive effect).

The V_{oc} is believed to be determined by either the difference of donor HOMO and acceptor LUMO[10] or the work function difference of the electrodes.[75] In our F6T2:PCBM devices, the V_{oc} remains around 0.87 V for most devices except the one with the F6T2:PCBM weight ratio of 1:1 (0.99 V), as shown in Figure 6-7 (b). The high concentration of F6T2 leads to a relatively higher V_{oc} , similar to other conjugated polymer-fullerene systems.[14] As a result, the V_{oc} of F6T2:PCBM cells is not very sensitive to their weight ratios in the blend. In order to clarify the origin of the V_{oc} in the F6T2:PCBM system, different metals were used as the cathode. The results in the inset of Figure 6-7 (a) show only a slight variance of V_{oc} (Ca/Ag: 0.89 V; Al: 0.85 V; Ag: 0.82V; Au: 0.90 V), indicating the independence of the produced V_{oc} on the work function differences of the electrodes. Therefore, the V_{oc} depends on the difference of donor HOMO and acceptor LUMO in our F6T2:PCBM system, which is slightly smaller than the estimated value of 1.13 V.[76] Overall, except for the device with the F6T2:PCBM weight ratio of 1:1, the PCE is slightly decreased from 2.46% for the device with the F6T2:PCBM weight ratio of 1:2 to around 2.2% for the devices with other F6T2:PCBM weight ratios.

Figure 6-8 The IPCE spectra of the devices with different weight ratios. The inset shows their corresponding normalized IPCE spectra.

Additionally, the contribution of each component to the photocurrent generation can be revealed from the IPCE spectra as well. The IPCE spectra of devices with different F6T2:PCBM weight ratios are presented in Figure 6-8. These spectra are nearly identical with the F6T2 absorption spectrum, giving direct evidence that the excitons are mainly formed in F6T2 phase and there is efficient photoinduced charge transfer between F6T2 and PCBM.[184] In other words, for our F6T2:PCBM system, the light is mainly absorbed by the F6T2 phase, and the role of PCBM is to act as the electron acceptor and electron transport material. There are two peaks at 350 and 450 nm originated from PCBM and F6T2, respectively, and the spectral response of these devices primarily covers a range from 320 to 550 nm. The contribution from PCBM (350 nm) is enhanced with the increase of PCBM concentration (inset in Figure 6-8).

However, these IPCE spectra are rather narrow, compared to other conjugated polymer:PCBM based PSCs, which are caused by the narrow absorption range of F6T2. Therefore, the PCEs of these devices are not as high as that of other polymer:PCBM based devices, though the maximum value of IPCE reaches 65% at 450 nm.

6.5 Application in Tandem Device

Figure 6-9 (a) The absorption spectra of the bottom film (F6T2:PCBM), top film (CuPc:C₆₀), and tandem film (F6T2:PCBM/Al/MoO₃/CuPc:C₆₀). (b) The I - V characteristics of the bottom cell, top cell, and three tandem cells with different intermediate layers under 100 mW/cm². The bottom cell was made of F6T2:PCBM (1:5) BHJ, and the top cell was made of CuPc and C₆₀ bilayer. The I - V curve of the top cell was obtained by fabricating F6T2:PCBM layer on the glass side of the original top cell. The

tandem cell 1, 2, and 3 uses Al(1 nm)/MoO₃(15 nm), Ca(1 nm)/Al(1 nm)/MoO₃(15 nm), and Ca(2 nm)/Al(2 nm)/MoO₃(15 nm) as the intermediate layers, respectively.

Figure 6-10 The simulated optical field distribution (for 450 nm illumination) in single and tandem cells. The ultra thin Ca and Al in the intermediate layer of tandem cell are neglected in the simulation.

Table 6-1 The summary of *I-V* characteristics of the bottom cell, top cell (modified), and tandem cells with different intermediate layers under 100 mW/cm². For testing the similar performance of the single top cell to that of the top cell in the tandem structure, a bottom active layer (F6T2:PCBM = 50 nm) was fabricated onto the glass-side of the single top cell.

Cells	V_{oc} (V)	J_{sc} (mA/cm ²)	FF (%)	PCE (%)
Bottom cell	0.86	4.27	59.7	2.19
Top cell (modified)	0.43	3.59	60.2	0.93
Tandem cell 1 (Al(1 nm)/MoO ₃ (15 nm))	1.15	1.76	48.2	0.98
Tandem cell 2 (Ca(1 nm)Al(1 nm)/MoO ₃ (15 nm))	1.25	1.70	57.7	1.23
Tandem cell 3 (Ca(2 nm)Al(2 nm)/MoO ₃ (15 nm))	1.27	1.75	57.2	1.27

Organic semiconductors with complementary absorption spectra are essential to construct tandem OSCs.[134] Currently, P3HT:PCBM BHJ is the most commonly used bottom cell, however, it has a certain spectral overlapping with the top cells made of CuPc:C₆₀[119] or PCPDTBT:PCBM.[118] Hence, wide bandgap materials absorbing high energy photons below 600 nm are promising and potential to be applied in tandem devices. The F6T2:PCBM blend is a good choice to meet this requirement. Consequently, we introduced this F6T2:PCBM BHJ as the bottom cell to implement a polymer/small molecule tandem device, where small molecule CuPc:C₆₀ acts as the top cell. Previously, we have developed an effective intermediate layer of Al(1 nm)/MoO₃(15 nm) in both polymer/small molecule and solution-processed devices.[67, 119] Accordingly, a modified intermediate layer is designed to be Ca/Al/MoO₃(15 nm) here. The resulting structure of the tandem cell is ITO/PEDOT:PSS(40 nm)/F6T2:PCBM(50 nm)/intermediate layer/CuPc(20 nm)/C₆₀(40 nm)/BPhen(8 nm)/Ag(80 nm). For comparison, the bottom and top single cells were fabricated in the same run as the tandem cell, with the structures of ITO/PEDOT:PSS(40 nm)/F6T2:PCBM(50 nm)/Ca(20 nm)/Ag(80 nm) and ITO/MoO₃(15 nm)/CuPc(20 nm)/C₆₀(40 nm)/BPhen(8 nm)/Ag(80 nm), respectively.

Figure 6-9 (a) shows the absorption spectra of the bottom, top, and tandem films. It is evident that there is nearly no overlapping between the main absorption ranges of F6T2:PCBM (350 – 500 nm) and CuPc/C₆₀ (550 – 750 nm) films, exhibiting complementary absorption spectra. The absorption spectrum of the tandem film with Al(1 nm)/MoO₃(15 nm) intermediate layer added

corresponds to a simple superposition of features from the absorption spectra of the bottom and top films, thus indicating that the enhanced absorption is obtainable in such constructed tandem device. Figure 6-9 (b) shows the I - V characteristics of the single bottom cell, single modified top cell, and three tandem cells with different intermediate layers under 100 mW/cm^2 . Their corresponding data are summarized in Table 6-1. The bottom cell has a PCE of 2.19% with $J_{\text{sc}} = 4.27 \text{ mA/cm}^2$, $V_{\text{oc}} = 0.86 \text{ V}$, and $\text{FF} = 59.7\%$. In order to achieve the similar performance of the single top cell to that of the top cell in the tandem structure, a bottom active layer (F6T2:PCBM = 50 nm) was fabricated onto the glass-side of the single top cell. As a result, the modified top cell has a PCE of 0.93% with $J_{\text{sc}} = 3.59 \text{ mA/cm}^2$, $V_{\text{oc}} = 0.43 \text{ V}$, and $\text{FF} = 60.2\%$, slightly lower than that of the original top cell without this additional bottom active layer fabricated. It can be observed that the J_{sc} of the tandem cells is only around 1.70 mA/cm^2 , reduced to half of that of the modified top cell. The low photocurrent of the tandem cell primarily results from the large reduction of J_{sc} in the bottom cell since the interference effect is weakened with the top cell stacked, i.e. that the light reflected by cathode (Ag) is decreased largely, especially for the bottom cell. To understand this effect, we simulated the optical field distribution for a single wavelength illumination (450 nm, the maximum absorption peak of F6T2:PCBM blend) in both single and tandem cells,[148-149] as shown in Figure 6-10. With the top cell stacked, the relative intensity across F6T2:PCBM active layer is significantly reduced. Moreover, the second interference maxima has shifted to the ITO/PEDOT:PSS interface, away from the active layer of the bottom cell, resulting in less exciton generation and low photocurrent in the

bottom cell.[166] Hence it has to be pointed out that the complementary absorption of organic semiconductor materials is only one of the prerequisites for the efficiency enhancement in tandem cell, not the determining one. The photocurrent from each sub-cell in tandem cell is correlated with the light absorption (related to the effective optical field distribution in the photoactive layer). Since the photocurrent extracted from the tandem cell is determined by the smallest photocurrent generated among all sub-cells stacked in series, a matched photocurrent in all sub-cells is crucial. This should be realized by optimizing the thickness and architecture of sub-cells for a balanced photocurrent.

When the Al(1 nm)/MoO₃(15 nm) intermediate layer is used in tandem cell 1, the V_{oc} is only 1.15 V and the FF of 48.2% is also low. An ultra thin Ca of 1 nm inserted in the existing intermediate layer (tandem cell 2) results in the increase of V_{oc} to 1.25 V, about the sum of the V_{oc} 's of both sub-cells. Meanwhile, the FF is largely increased to 57.7%. Since the work function of Ca (2.9 eV) is lower than the Fermi level of PCBM (4.7 eV), the Ohmic contact is favorable between Ca and PCBM. On the contrary, the rectifying contact is formed between Ca and F6T2, which effectively blocks the hole collection by the cathode of bottom cell, compared with an intermediate layer without Ca layer. Thus, the modified intermediate layer (Ca/Al/MoO₃) functions well as the recombination center of charge carriers. Moreover, the improved contact lowers the series resistance of the tandem device, as shown in Figure 6-9 (b). Hence the FF increases significantly.

Overall, these enhanced parameters lead to an improved PCE of 1.23%, higher than that of the top cell (0.93%). With the introduction of a thicker Ca(2

nm)Al(2 nm)/MoO₃(15 nm) intermediate layer, the PCE of tandem cell 3 (1.27%) is slightly improved with a similar J_{sc} of 1.75 mA/cm² and slightly increased V_{oc} of 1.27 V.

6.6 Summary

We have presented efficient F6T2:PCBM BHJ PSCs and have demonstrated the potential application in tandem devices. The large LUMO difference between F6T2 and PCBM facilitates the charge transfer and exciton separation, elucidated by the PL quenching of F6T2 with PCBM mixed. The photocurrent and charge transport exhibit strong correlation to the morphology of F6T2:PCBM blends with different weight ratios. The single cell with a F6T2:PCBM (1:2) blend gives rise to the highest J_{sc} and overall efficiency of 2.46%. The results show that the improved charge transport occurs with the increase of PCBM concentration due to the interpenetrating networks induced by the fine phase separation. Optimization of the composite weight ratio reveals the important role played by the morphology for the charge transport properties of F6T2:PCBM BHJ devices.

Importantly, F6T2:PCBM single cell is further employed as the bottom cell in polymer/small molecule tandem cells by stacking CuPc:C₆₀ as the top cell. By inserting an ultra thin Ca into previous Al(1 nm)/MoO₃(15 nm) intermediate layer, the V_{oc} (1.27 V) of the tandem cell approaches the exact summation of those of bottom (0.86 V) and top (0.43 V) cells, indicating that the F6T2:PCBM is preferable to Ca contact without voltage loss across the intermediate layer. The PCE of tandem cell is larger than that of the top cell, but

lower than that of the bottom cell. The optimization of this tandem cell may provide some insights for the potential application of F6T2:PCBM single cell.

CHAPTER 7 CONCLUSION AND FUTURE WORKS

7.1 Conclusion

Inverted devices have been presented with an ultra thin Ca modified ITO cathode and MoO₃ modified Ag anode. This Ca layer is highly transparent. The MoO₃ layer functions as exciton-blocking, hole-transporting, and protection layer, facilitating photocurrent and FF. Moreover, it adjusts the optical field distribution in a relatively thin device. A maximum PCE of 3.86% has been obtained for the device with 0.5 nm Ca, 85 nm P3HT:PCBM, and 5 nm MoO₃.

In order to fully exploit the solar light and further enhance the light absorption efficiency, efficient tandem OSCs have been demonstrated, which consist of an Al(1 nm)/MoO₃(15 nm) intermediate layer that has high transparency and acts as a protective layer for prior-deposited polymer layer in solution-processed polymer tandem devices. Subsequently, this intermediate layer has been applied in polymer/small molecule and solution-processed polymer double- and triple-tandem devices. In polymer/small molecule double-tandem cell, the PCE of 2.82% achieved is higher than either of the individual ones. In polymer/polymer triple-tandem cell, an enhanced V_{oc} of 1.73 V and a comparable PCE of 2.03% have been achieved. Such a high V_{oc} by multiple-cells tandem structure is potentially useful in area-limited low-power electronics. Polymer/small molecule triple-tandem cell has also been fabricated with the third polymer cell replaced by a complementary absorption small molecule cell, producing an improved PCE of 2.18%. Therefore, the intermediate layer would be

the most potentially applied in the multiple-tandem polymer cells with ideal complementary absorption spectra.

A combination of inverted and tandem structures offers opportunities to efficiently improve light absorption efficiency, charge transport, and interface stability. Inverted tandem devices with various combinations of multiple metal layers (Ag, Al, and Ca) and a metal oxide layer (MoO_3) as intermediate layer have been accomplished. $\text{MoO}_3/\text{Ag}/\text{Al}/\text{Ca}$ is optimal with high transparency and structural smoothness. Inverted tandem devices with $\text{MoO}_3/\text{Ag}/\text{Al}/\text{Ca}$ intermediate layer have been optimized through varying the thickness of Ca as part of intermediate layer, MoO_3 as anode buffer layer, and P3HT:PCBM as active layer. The best device consists of 80 nm bottom cell, 70 nm top cell, 3 nm Ca as part of intermediate layer, and 5 nm MoO_3 anode buffer layer. In MoO_3 (7.5 nm)/Ag (1 nm)/Al (1 nm)/Ca (3 nm) intermediate layer, MoO_3 acts as the anode for bottom cell connecting unit and a protection layer. Ag and Al effectively reduce contact resistance and voltage drop at proper intermediate layer, leading to good FF and summated V_{oc} . Ca works as cathode for top cell, protecting the prior-deposited active layer. MoO_3 anode buffer layer (5 nm) effectively prevents the exciton quenching and damages from Ag deposition. Our intermediate layer would provide a potentially efficient approach to improve the device performance and to overcome the issues associated with interface instability and charge transport/collection.

Furthermore, efficient F6T2:PCBM BHJ PSCs have been presented. Large LUMO difference between F6T2 and PCBM benefits charge transfer and exciton dissociation, evidenced by the PL quenching of F6T2 with PCBM

mixed. The device performance is correlated with the morphology of F6T2:PCBM blends with different weight ratios. The device with a F6T2:PCBM (1:2) blend achieves a maximum PCE of 2.46% due to the balance between light absorption and charge transport. The results indicate that the charge transport is improved with the increase of PCBM concentration, leading to efficient interpenetrating networks. Additionally, polymer/small molecule tandem cells have been demonstrated, consisting of F6T2:PCBM as bottom cell and CuPc:C₆₀ as top cell. By inserting an ultra thin Ca into Al (1 nm)/MoO₃ (15 nm) intermediate layer, the V_{oc} (1.27 V) of the tandem cell approaches the exact summation of those of bottom (0.86 V) and top (0.43 V) cells, indicating that there is no voltage loss at the F6T2:PCBM and Ca interface.

7.2 Future works

In this dissertation, most results were based on P3HT:PCBM BHJ. The efficiency could be improved by enhancing efficiencies associated with photon absorption and charge generation processes. One effective approach is to use new materials with broad absorption spectrum and high charge carrier mobility.

Currently, P3HT:PCBM is the most commonly used in single or tandem devices. For tandem structure, complementarily absorbing organic materials with P3HT:PCBM are demanded to cover a wider solar spectrum in order to enhance light absorption efficiency. In the next step, we expect to be able to collaborate with professional experts and chemists on material synthesis. Once complementarily absorbing materials are made available, breakthrough could

be expected in tandem and inverted tandem devices with an efficiency of 10% and above.

In inverted structure, solution-processed interfacial layers such as ZnO and TiO₂ used for modifying ITO are required to complete inverted devices. Their Fermi levels should be tuned to match the LUMO level of acceptor, facilitating charge transfer and collection. On the other hand, solution-processed interfacial layers for anode modification are also needed to function as an exciton blocking layer reducing exciton quenching at the anode/photoactive layer, a buffer layer helping hole transport/extraction, an optical spacer adjusting effective light field distribution, and a protection layer preventing the damage from metal deposition.

Besides, for large-area and commercial productions, all solution-processed devices are desirable in order to reduce the cost. Hence, solution-processed intermediate layers are of great significance to implement all solution-processed tandem devices. As mentioned in this thesis, the usage of PEDOT:PSS causes interface instability, so an alternative solution-processed hole-transporting layer is a must. In the following study of tandem devices, we will focus on solution-processed intermediate layers, which must satisfy all requirements outlined in previous chapters.

Another equally paramount parameter for OSCs is lifetime or stability. The sensitivity to moisture, oxygen, UV light, and heat leads to serious degradations of organic materials and devices. So far, the focus on device stability is still not too much compared with device performance, although some progress has been made to a great degree. A typical device consists of multiple layers in

which each component and interface might potentially suffer from degradation through various chemical and physical ways. Therefore, degradation mechanisms should be understood deeply and investigated in order to overcome the instability and meanwhile extend the device lifetime. The study of degradation should be carried out in the following aspects:

➤ Photoactive materials

Organic photoactive materials are easily to be oxidized by oxygen, in particular, when the devices are under illumination. However, the devices must be exposed to solar light for operation. Therefore, it is challenging to synthesize and develop air-stable organic materials which have deep HOMO levels and low band gaps.

➤ Device structure

BHJ structure formed by mixing donor and acceptor materials offers an interpenetrating network for charge transport. Such morphology is usually obtained by means of annealing, solvent mixture, additives incorporation, etc, which make the morphology of blend film changeable with heating temperature and processing time, i.e. not at the thermodynamic equilibrium. Thus it is necessary to exploit an effective and stable morphology beneficial to both efficiency and stability. This morphology should provide bi-continuous pathways for charge transport in their individual phase. Moreover, it needs to be temperature-stable, especially under illumination when the device is heated up.

On the other hand, inverted structure benefits to the stability improvement due to the reverse of anode and cathode, where high work function metal as anode at top could sustain the oxidization.

➤ Electrodes

ITO as highly conductive and transparent anode shows a lack of Indium reserves in nature and damage of Indium to organic layer through diffusion. Additionally, ITO is prone to be etched by PEDOT:PSS when PEDOT:PSS adsorbs water to exhibit slight acid property. Currently, it is popular that an alternative to ITO is Gallium doped ZnO (GZO) which has a proper work function as anode and air-stability. More importantly, GZO can scale up to large areas and be mechanically flexible.

PEDOT:PSS as a hole transporting layer is a water-based solution, exhibiting hydrophilic and slightly acidic nature degrading organic layers. An alternative is necessary. Metal oxides with hole-transporting behavior as buffer layer are rather potential due to their appropriate work functions and stability against the air. Most metal oxides are deposited under high vacuum which raises the fabrication cost and hinders the realization of large-area devices. Therefore, solution-processed metal oxides as buffer layers could provide many opportunities and important insights on commercial OSCs.

Low work function metals used as cathode such as Al, Mg, Ca are prone to be oxidized and cause some dark spots degrading devices very fast. One way is to introduce inverted structure as mentioned before. The other way is to develop advanced encapsulation techniques to protect the devices from moisture and oxygen. Regarding the encapsulation, multilayer encapsulation is actually preferred due to the requirements for flexibility of OSCs.

To summarize, all the factors that might affect the device stability should be highlighted to extend the lifetime in order to realize the commerciali-

zation. And also through these investigations, a theoretical model of device degradation should be established. Deep insight and knowledge into degradation mechanism, which could disclose the relationship between degradation mechanisms and material design, preparation technique, heat effect during operation, annealing treatment, and encapsulation, are significantly beneficial to optimization of organic material design and device stability.

Journal publications

1. **D. W. Zhao**, L. Ke, X. W. Sun, A. K. K. Kyaw, S. T. Tan, G. Q. Lo and D. L. Kwong, "Optimization of inverted tandem organic solar cells", *Sol. Energy Mater. Sol. Cells*, **95**, 921–926 (2011).
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Conference presentations

1. IEEE PhotonicsGlobal at Singapore, Dec 08-11, 2008 Singapore. Poster presentation, **D. W. Zhao**, X. W. Sun, C. Y. Jiang, A. K. K. Kyaw, "Enhanced Open-Circuit Voltage in Tandem Polymer Solar Cell," in *2008 IEEE Photonicsglobal@Singapore*, pp. 217-219 (2008).
2. Material Research Society (MRS) Fall Meeting, Boston, United States, Nov 30 to Dec 4, 2009. Poster presentation, **D. W. Zhao**, X. W. Sun, L. Ke, S. T. Tan, "An Improved Triple-Tandem Organic Solar Cell," Proceedings of MRS 2009 Fall Meeting, 1212-S03-19 (2010). **DOI:** 10.1557/PROC-1212-S03-19.
3. 1st Annual Workshop on Energy Research, Energy Research Institute @ NTU, Singapore. Jun 16-17 2009. Poster presentation, "Efficient Tandem Organic Solar Cells."
4. 2nd Annual Workshop on Energy Research, Energy Research Institute @ NTU, Nanyang Technological University, Singapore. Jun 15-16 2010. Poster presentation, "Inverted Organic Solar Cells."

Awards

1. Green Talents Competition 2010, Germany (BMBF)

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