

A Switchable Interconnecting Layer for High Performance Tandem Organic Solar Cell

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The all-solution-processed switchable interconnecting layer (ICL) for both inverted and normal tandem organic solar cells (OSCs) is reported for the first time here. The fundamental challenges in the literature arise from mixing multiple functionalities into a single layer. For a widely used ICL composed of an electron transport layer (ETL)/a hole transport layer (HTL), ETL needs not only to efficiently extract electrons from an underneath photoactive layer, but also to fulfill optical, mechanical, chemical and electrical requirements to function as effective tunneling junction ICL with HTL atop. Taking on multiple functionalities for a single ETL makes ETL in ICL highly coupled and difficult to be replaced. This is also the case for HTL. Here, this study demonstrates an all-solution-processed switchable ICL, ETL/recombination layer (RL)/HTL and HTL/RL/ETL, for both normal and inverted tandem OSCs. In switchable ICL, ETL and HTL simply serve as carrier transport layers as they did in single OSCs. Electrical recombination, mechanical protection and chemical separation functionalities are realized by RL alone. This strategy shifts the views of ICL for tandem OSCs from conventionally complicated ETL/HTL tunneling junction ICL, where both ETL and HTL play several different roles, towards simplified ICL where ETL and HTL play a distinct decoupled role, advancing ICL for more adaptable tandem OSCs.

1. Introduction

Organic solar cells (OSCs) have the potential to replace fossil fuels at a more economic cost than conventional inorganic solar cells. The most challenging issues in OSCs lie in its higher power conversion efficiency (PCE), reliable larger area fabrication production, and longer device stability. Among the above three factors, the most important is the higher PCE. Different technologies have been developed to improve the PCE of OSCs, such as synthesizing efficient photoactive polymer to utilize more solar energy, developing effective interface materials and incorporation of plasmonic effects to further improve

light harvesting.^[1–26] However, the two major energy loss mechanisms, the sub-band transmission loss and thermalization loss, can never be minimized unless the structure of tandem OSCs is utilized. The challenges for developing high performance tandem OSCs lie in two aspects: (i) efficient photoactive materials with complementary absorption range and (ii) qualified interconnecting layer (ICL). For the former, various materials with complementary absorption range have been developed.^[24,27–31] For the latter, the ICL should simultaneously fulfill the following three requirements: (1) optically minimizing light absorption; (2) electrically allowing efficient electron and hole recombination without the formation of counter diode; (3) mechanically, the ICL should be robust enough to protect underlying layers from being dissolved by sequential spin-coating of second photoactive layer.^[23,27,32]

Although there are studies on effective two-layer ICL, such as poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS)/zinc oxide (ZnO) and PEDOT:PSS/titanium dioxide (TiO₂), the successful combination of other different efficient electron transport layer (ETL) and hole transport layers (HTL) from single OSCs as the ICL for tandem OSCs has been greatly limited due to the failure of simultaneously fulfillment of the above optical, electrical and mechanical requirements.^[33–35] There are various efficient carrier transport layers (CTLs) developed for single-junction OSCs. For ETLs, there are transparent transition metal oxides, such as ZnO and TiO₂, and polymer dipole layers, such as poly[(9,9-bis(3'-(N,N-dimethylamino)propyl)-2,7-fluorene)-alt-2,7-(9,9-dioctylfluorene)] (PFN).^[4,5,36–38] While for HTLs, there are transparent metal oxides such as nickel oxide (NiO_x), molybdenum trioxide (MoO₃), vanadium oxide (V₂O₅) and conductive polymers such as PEDOT:PSS.^[39–41] However, the combination of different efficient ETL and HTL from single OSCs to be efficient ICL in tandem OSCs has been severely limited by the failure of simultaneously achieving the above requirements.^[27,28,42] Among the three requirements, the quasi-fermi level splitting resulted counter-diode effect is the most challenging one. There are typically two methods that solve the counter-diode effect. One is utilizing both heavily doped ETL and HTL to form tunneling junction, such as PEDOT:PSS/ZnO.^[25,29,33,35,43,44] However, this excludes most ETL and HTL that can act as efficient ICL. The other is to evaporate a thin layer of metal as recombination site

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between ETL and HTL, such as $\text{MoO}_x/\text{Ag}/\text{ZnO}$ and $\text{MoO}_x/\text{Ag}/\text{PFN}$.^[45–50] Nonetheless, this ICL introduces the expensive high vacuum process and would normally result in some loss of V_{oc} , J_{sc} as well as FF due to incomplete separation between ETL and HTL, and ICL absorption loss.

Besides the limitation of the two typical strategies to form efficient basic ICL for tandem OSCs, there are three major challenges hindering the future development of advanced ICL. Firstly, an advanced ICL should be switchable, that is to be incorporated in both normal and inverted tandem structure configuration. However, the switchable ICL has never been reported in literature, majorly due to multilayer solvent incompatibility, the lack of ETL and HTL materials with the duality property for functioning efficiently as CTLs in both normal and inverted single-junction OSCs, and the formation of counter-diode effect. Secondly, though PEDOT:PSS's mechanical protection function in ICL is well recognized as compared to other ICL without PEDOT:PSS, the incorporation PEDOT:PSS as efficient HTL on top of photoactive layer still remains a critical issue, which is majorly due to the acidic and water solvent-based nature of PEDOT:PSS. So far, PEDOT:PSS on top of Poly(3-hexylthiophene-2,5-diyl) regioregular (P3HT) system has been well recognized while that of other polymers have seldom been reported.^[35,51,52] On one hand, the hydrophilic PEDOT:PSS should be modified by surfactant additives to allow good film formation on top of the hydrophobic photoactive layer. The addition of surfactant would further reduce the work function (WF) of PEDOT:PSS, resulting in reduced V_{oc} and FF. On the other hand, the water and acidic nature would introduce extra surface recombination site, resulting in poor photovoltaic performance. Thus, the incorporation of PEDOT:PSS as part of ICL on top of high performance polymer other than P3HT is still a challenging issue in the area of tandem organic photovoltaics (OPV). Thirdly, the ETL/HTL tunneling junction ICLs put multiple constraints, including electrical, optical, mechanical and chemical requirements on each single layer. The failure to meet any of the above requirements excludes their possibility to be utilized in the ETL/HTL tunneling junction-based ICL, making them heavily coupled and extremely difficult to be replaced by other potential superior CTL materials. For example, in PEDOT:PSS/ TiO_2 ICL, replacing PEDOT:PSS with other efficient HTLs, such as NiO_x , MoO_3 , or V_2O_5 , results in ICL with strong counter-diode; replacing TiO_2 with other efficient ETLs, such as PFN and other polymeric-based ETL, most of which would also introduce S-shaped current density–voltage (J – V) characteristics. Hence, a simplified ICL structure where ETL and HTL play distinct function as they did in single OSCs is of great importance for the future development of tandem OSCs researches as well as industrial commercialization.

Here, a first kind of switchable ETL/RL/HTL ICL, specifically the $\text{ZnO}/\text{modified PEDOT:PSS (M-PEDOT:PSS)}/\text{phosphomolybdic acid hydrate (PMA)}$ and $\text{PMA}/\text{M-PEDOT:PSS}/\text{ZnO}$ ICL for both normal and inverted structure of tandem OSCs, has been proposed and demonstrated. Unlike the ETL and HTL on tunneling junction-based ICL in which each of them have to fulfill several requirements as described above, the PMA works solely as HTL while the ZnO works solely as ETL as they did in single cell. The M-PEDOT:PSS acts as elec-

trical recombination layer (providing efficient recombination for carriers from adjacent ETL and HTL), mechanical protection layer (preventing underlying photoactive from being dissolved by the solvent of second photoactive layer) as well as chemical separation layer (preventing possible chemical reaction from direct contact of different ETL and HTL) in the ICL. Our results show that the inverted tandem OSCs with $\text{PMA}/\text{M-PEDOT:PSS}/\text{ZnO}$ as ICL and the normal tandem OSCs with switched ICL of $\text{ZnO}/\text{M-PEDOT:PSS}/\text{PMA}$ have been realized with almost doubled V_{oc} and FF over 60%. Based on this switchable ICL, the performance of tandem OSCs using Poly[[4,8-bis[(2-ethylhexyl)oxy]benzo[1,2-b:4,5-b']dithiophene-2,6-diyl]-[3-fluoro-2-[(2-ethylhexyl)carbonyl]thieno[3,4-b]thiophenediyl]] (PTB7):[6,6]-Phenyl-C71-butyric acid methyl ester (PC_{70}BM) and poly(2,5-bis(2-decyltetradecyl)-pyrrolo[3,4-c]pyrrole-1,4-(2H,5H)-dione-3,6-diyl-alt-3'',4'-difluoro-2,2':5',2'':5'',2'''-quaterthiophene-5,5'''-diyl) (PDPP4T-2F): PC_{70}BM as active layers in inverted and normal structure achieve 10.34% and 10.46% PCE, respectively. Notably, both high performance inverted and normal tandem OSCs reach almost the same PCE which demonstrate the feasibility of the switchable ICL. This ETL/RL/HTL ICL not only fulfills the basic optical, electrical, and mechanical ICL requirements, but also provides critical advanced advantages: (1) this ICL functions as qualified switchable ICL in both inverted and normal tandem OSCs; (2) the M-PEDOT:PSS sandwiched between ZnO and PMA successfully prevents chemical reaction from direct contact of PMA on top of ZnO , showing that an appropriate RL can act as a chemical separation layer allowing for replacement of other potentially reacting HTL and ETL in ICL; in the meantime, the water detriments from M-PEDOT:PSS to photoactive layer has been successfully blocked by the ZnO and PMA layer in normal and inverted tandem OSCs devices; (3) this strategy shifts our views from the conventional complicated ETL/HTL tunneling junction ICL, where each CTL plays multiple roles, to the simplified ICL model where each CTL plays distinct role as they did in single OSCs, making it easier for the future advancement of ICL with new HTL and ETL material.

2. Results and Discussion

To demonstrate the $\text{PMA}/\text{M-PEDOT:PSS}/\text{ZnO}$ and $\text{ZnO}/\text{M-PEDOT:PSS}/\text{PMA}$ as qualified ICL for both inverted and normal structure for high performance tandem OSCs, the following experiments have been conducted. Firstly, the PMA and ZnO roles as efficient HTL and ETL in single junction P3HT: PC_{60}BM has been demonstrated. Secondly, several inverted and normal single OSCs with different equivalent ETL and HTL have been fabricated and the results reveal that $\text{PMA}/\text{M-PEDOT:PSS}/\text{ZnO}$ and $\text{ZnO}/\text{M-PEDOT:PSS}/\text{PMA}$ are qualified ICLs and provide extra advantages compared to PMA/ZnO (having poor mechanical protection) and ZnO/PMA (having undesirable chemical reaction) ICLs. Thirdly, high performance tandem OSCs with over 10% PCE based on $\text{PMA}/\text{M-PEDOT:PSS}/\text{ZnO}$ and $\text{ZnO}/\text{M-PEDOT:PSS}/\text{PMA}$ ICL have been demonstrated for both inverted and normal structures with PTB7: PC_{70}BM as front subcell and PDPP4T-2F: PC_{70}BM as bottom subcell.

2.1. ICL Properties

For single inverted and normal P3HT:PC₆₀BM OSCs, PMA and ZnO work as efficient HTL and ETL, respectively. For inverted single device, the device structure, *J*-*V* characteristics, and photovoltaic performance for ITO/ZnO/P3HT:PC₆₀BM/PMA/Ag are shown in **Figure 1** and **Table 1** as Device A, achieving a good PCE of 3.86% with 0.59 V *V*_{oc}, 10.69 mA cm⁻² *J*_{sc}, and 60.94% FF. For normal single device, the device structure, *J*-*V* characteristics, and photovoltaic performance for ITO/PMA/P3HT:PC₆₀BM/ZnO/Al are shown in **Figure 1** and

Table 1 as Device E, achieving a good PCE of 3.81% with 0.64 V *V*_{oc}, 9.24 mA cm⁻² *J*_{sc}, and 64.13% FF.

Based on the above results, different tandem and single devices in both inverted and normal structures have been fabricated to demonstrate PMA/M-PEDOT:PSS/ZnO and ZnO/M-PEDOT:PSS/PMA as efficient ICL for tandem OSCs.

(a) In order to utilize PMA and ZnO as ICL in inverted single device, Device B with PMA/ZnO as equivalent ETL has been fabricated. As compared with Device A, Device B shows slightly decreased FF from 60.94% to 58.66%, resulting in a

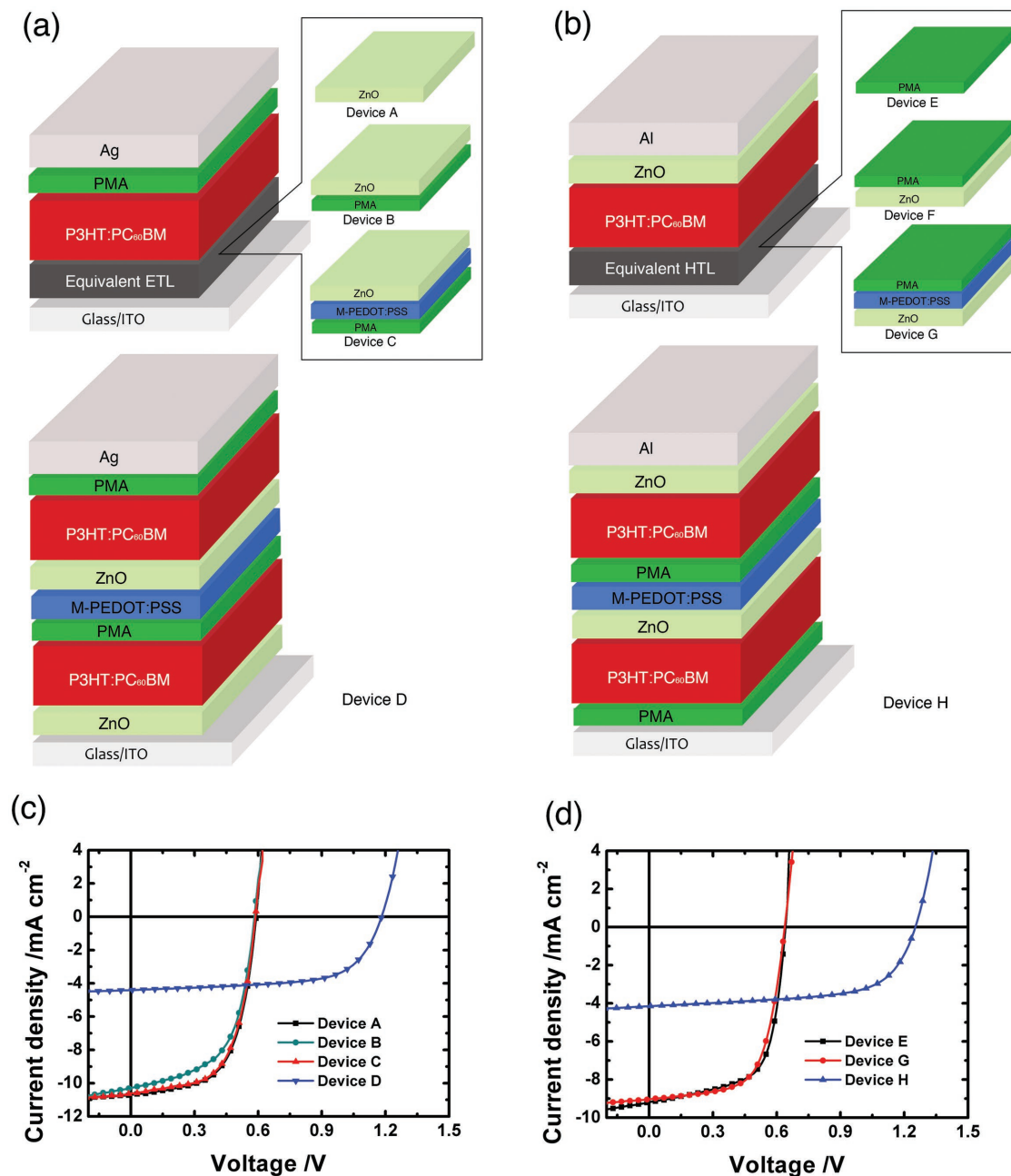


Figure 1. a) Inverted single (with equivalent ETL) and tandem P3HT:PC₆₀BM OSCs and their c) *J*-*V* characteristics. b) Normal single (with equivalent HTL) and tandem P3HT:PC₆₀BM OSCs and their d) *J*-*V* characteristics.

Table 1. Photovoltaic performance of inverted single and homo-tandem OSCs devices for P3HT:PC₆₀BM based OSCs.

Device	Structure	J_{sc} [mA cm ⁻²]	V_{oc} [V]	FF [%]	PCE [%]
A	ITO/ZnO/P3HT:PC ₆₀ BM/PMA/Ag	10.69 ± 0.107	0.59 ± 0.001	60.94 ± 0.548	3.86 ± 0.068
B	ITO/PMA/ZnO/P3HT:PC ₆₀ BM/PMA/Ag	10.28 ± 0.206	0.58 ± 0.005	58.66 ± 1.253	3.52 ± 0.123
C	ITO/PMA/M-PEDOT:PSS/ZnO/P3HT:PC ₆₀ BM/PMA/Ag	10.56 ± 0.117	0.59 ± 0.002	60.97 ± 0.426	3.81 ± 0.034
D	ITO/ZnO/P3HT:PC ₆₀ BM/PMA/M-PEDOT:PSS/ZnO/P3HT:PC ₆₀ BM/PMA/Ag	4.39 ± 0.106	1.18 ± 0.004	64.65 ± 0.233	3.35 ± 0.085

Table 2. Photovoltaic performance of normal single and homo-tandem OSCs devices for P3HT:PC₆₀BM based OSCs.

Device	Structure	J_{sc} [mA cm ⁻²]	V_{oc} [V]	FF [%]	PCE [%]
E	ITO/PMA/P3HT:PC ₆₀ BM/ZnO/Al	9.24 ± 0.124	0.64 ± 0.001	64.13 ± 0.368	3.81 ± 0.059
F	ITO/ZnO/PMA/P3HT:PC ₆₀ BM/ZnO/Al	/	/	/	/
G	ITO/ZnO/M-PEDOT:PSS/PMA/P3HT:PC ₆₀ BM/ZnO/Al	9.08 ± 0.115	0.64 ± 0.002	64.24 ± 0.501	3.73 ± 0.057
H	ITO/PMA/P3HT:PC ₆₀ BM/ZnO/M-PEDOT:PSS/PMA/P3HT:PC ₆₀ BM/ZnO/Al	4.08 ± 0.106	1.25 ± 0.002	63.22 ± 0.294	3.22 ± 0.097

PCE of 3.52%. No appearance of typical S-shaped J - V characteristics has been observed, implying no obvious formation of counter-diode between PMA/ZnO. However, when fabricating tandem OSCs based on PMA/ZnO ICL, the mechanical solvent protection is insufficient and the bottom P3HT:PC₆₀BM has been damaged to some extent. Indeed, these results also reconfirm the difficulty of utilizing the two-layer ICL to simultaneously fulfill the critical several requirements as stated in introduction. In order to provide better mechanical protection, M-PEDOT:PSS layer has been sandwiched between PMA and ZnO. The resulting single inverted OSC as Device C with ITO/PMA/M-PEDOT:PSS/ZnO/P3HT:PC₆₀BM/PMA/Ag structure achieves a PCE of 3.81% with 0.59 V V_{oc} , 10.56 mA cm⁻² J_{sc} , and 60.97% FF. Based on the PMA/M-PEDOT:PSS/ZnO ICL, an inverted tandem OSC has been fabricated as Device D. With the additional M-PEDOT:PSS layer as recombination layer as well as mechanical protection layer, Device D shows a PCE of 3.35% with 1.18 V V_{oc} , 4.39 mA cm⁻² J_{sc} , and 64.65% FF. The doubled V_{oc} with no loss and FF over 60% demonstrates that ICL provides equivalent ohmic contact for efficient carrier recombination.

(b) In order to utilize PMA and ZnO in normal tandem OSCs, Device F with ITO/ZnO/PMA/P3HT:PC₆₀BM/PMA/ZnO/Al structure has been fabricated. However, depositing PMA solution on top of ZnO would result in undesirable chemical reaction that makes ZnO/PMA ICL impossible to form well-defined layers. The acidic PMA solution would react vigorously with the basic oxide of ZnO as the following equation



This excludes the utilization of ZnO/PMA as ICL in tandem OSCs. The reaction between HTL and ETL is also one of the most common obstacles to employ different HTL and ETL as part of the potential ICL. Here, the M-PEDOT:PSS layer has been inserted between ZnO and PMA as in Device G. This device with ZnO/M-PEDOT:PSS/PMA as equivalent HTL achieves comparable device performance with a PCE of 3.73% with 0.64 V V_{oc} , 9.08 mA cm⁻² J_{sc} , and 64.24% FF as shown in Table 2. Based on ZnO/M-PEDOT:PSS/PMA ICL,

Device H (normal tandem OSC with structure of ITO/PMA/P3HT:PC₆₀BM/ZnO/M-PEDOT:PSS/PMA/P3HT:PC₆₀BM/ZnO/Al) has been fabricated and achieving a PCE of 3.22% with 1.25 V V_{oc} , 4.08 mA cm⁻² J_{sc} , and 63.22% FF. The V_{oc} with an ignorable 0.03 V loss and 63.22% FF with no S-shaped J - V characteristics demonstrates ZnO/M-PEDOT:PSS/PMA as a qualified ICL for normal tandem OSCs. The M-PEDOT:PSS layer not only plays the role of recombination layer and mechanical protection layer but also provides effective chemical separation of PMA from direct contact with ZnO that otherwise will lead to immediate reaction, which potentially broadens the selection of other superior HTL or ETL as part of ICL for future tandem development.

In order to further clarify the electrical role of M-PEDOT:PSS, the following devices have been fabricated and their J - V characteristics and photovoltaic performance are shown in Figure 2 and Table 3.

Device K1: glass/ITO/P3HT:PC₆₀BM/ZnO/Al;
Device K2: glass/M-PEDOT:PSS/P3HT:PC₆₀BM/ZnO/Al;
Device K3: glass/M-PEDOT:PSS/PMA/P3HT:PC₆₀BM/ZnO/Al.

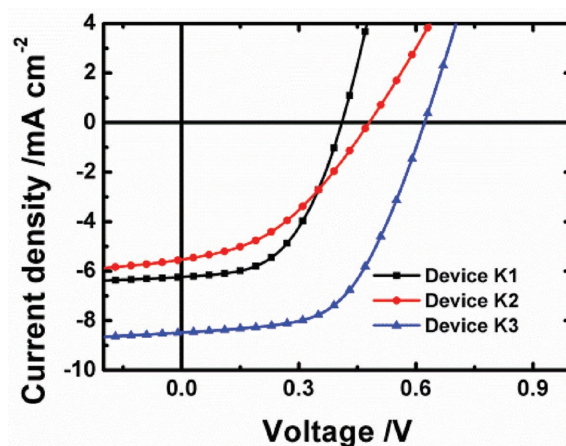


Figure 2. The J - V characteristics of different single devices to identify M-PEDOT:PSS's role as transparent electrode rather than HTL.

Table 3. Photovoltaic performance with different transparent electrodes without PMA as HTL.

Device	Structure	J_{sc} [mA cm ⁻²]	V_{oc} [V]	FF [%]	PCE [%]
K1	glass/ITO/P3HT:PC ₆₀ BM/ZnO/Al	6.11 ± 0.164	0.41 ± 0.011	50.86 ± 1.233	1.29 ± 0.079
K2	glass/M-PEDOT:PSS/P3HT:PC ₆₀ BM/ZnO/Al	5.48 ± 0.164	0.48 ± 0.005	40.07 ± 0.546	1.05 ± 0.033
K3	glass/M-PEDOT:PSS/PMA/P3HT:PC ₆₀ BM/ZnO/Al	8.50 ± 0.157	0.62 ± 0.001	53.22 ± 0.739	2.81 ± 0.086

The M-PEDOT:PSS with a conductivity of 500 S cm⁻¹ serves as transparent electrode in Devices K2 and K3. This is supported by the fact that Device K1 (ITO as transparent electrode and no HTL, 1.29% PCE with 0.41 V V_{oc} , 6.11 mA cm⁻² J_{sc} , and 50.86% FF) and Device K2 (with M-PEDOT:PSS and no HTL, 1.05% PCE with 0.48 V V_{oc} , 5.48 mA cm⁻² J_{sc} , and 40.07% FF) show similar features of J - V characteristics resulted from the lack of HTL layer. While Device E (ITO as transparent electrode and PMA as HTL, 3.81% PCE with 0.64 V V_{oc} , 9.24 mA cm⁻² J_{sc} , and 64.13% FF) and Device K3 (with M-PEDOT:PSS and PMA as HTL, 2.81% PCE with 0.62 V V_{oc} , 8.50 mA cm⁻² J_{sc} , and 53.22% FF), after PMA inserted as HTL, show comparable J - V characteristics. The above devices demonstrate that electrically, the M-PEDOT:PSS serves as efficient transparent electrode and thus takes the role as RL in the three-layer ICL rather than efficient HTL.

In addition, the transmission of ICL is of great importance for the current matching of series connected configuration of tandem OSCs. Typically, the average transmission above 90% from 350 to 1000 nm is highly favored for a qualified ICL. Undesirable transmission loss would make bottom subcell the current limiting cell in the series connected tandem configuration, leading to an unnecessarily PCE loss for tandem OSCs. The transmission spectra of ZnO, M-PEDOT:PSS, and PMA layers are shown in Figure 3. It is worth noting that all of them show an average transmission above 92% from 370 to 1000 nm, making them the optically favorable film as ICL for tandem OSCs.

To sum up, we have demonstrated the PMA/M-PEDOT:PSS/ZnO and its switching counter-part ZnO/M-PEDOT:PSS/PMA as qualified ICL to simultaneously fulfill optical, electrical, mechanical and chemical requirements for inverted and

normal structured P3HT:PC₆₀BM tandem OSCs. The role of M-PEDOT:PSS has been identified as carrier recombination layer rather than HTL, mechanical protection layer, chemical separation layer in this structure. This three-layer ETL/RL/HTL makes the switchable ICL realizable, which otherwise would be extremely difficult to develop based on the only two-layer ETL/HTL ICL structure with lots of other issues need to be taken into consideration.

2.2. High Performance Tandem Devices

The PMA/M-PEDOT:PSS/ZnO and its counter-part ZnO/M-PEDOT:PSS/PMA are qualified ICL for homo-tandem P3HT:PCBM. In order to demonstrate our ICL for high performance tandem OSCs, PTB7 with absorption edge around 800 nm and PDPP4T-2F with absorption edge around 900 nm are utilized as photoactive layer for the top and bottom subcells, respectively.

2.2.1. Inverted Tandem OSCs

The J - V characteristics and the corresponding photovoltaic performance of inverted single OSC device with structure of ITO/ZnO/PTB7:PC₇₀BM/PMA/Ag are shown in Figure 4 and Table 4, respectively. The optimized Device I1 with 100 nm photoactive layer thickness achieves a PCE of 7.79% with 0.72 V V_{oc} , 17.02 mA cm⁻² J_{sc} , and 63.49% FF. The inverted single OSC with photoactive layer of PDPP4T-2F:PC₇₀BM, based on which the bottom subcell of inverted tandem OSC would be fabricated, has been demonstrated here with a PCE of 7.91%. The PDPP4T-2F polymer is a good donor candidate for bottom subcell of tandem OSCs to fulfill complementary absorption with 300 to 900 nm absorption range and efficient EQE in the range of 700 to 900 nm. A mixed solvent of chloroform:chlorobenzene:chloronaphthalene is used for PDPP4T-2F:PC₇₀BM in order to form well established nanoscale phase separation morphology to promote exciton dissociation and charge transport.^[30] The photovoltaic performance and EQE of Device I3 (ITO/ZnO/PDPP4T-2F:PC₇₀BM/MoO₃/Ag) are shown in Figure 4 and Table 4 respectively. Device I3 shows 7.91% PCE with 0.76 V V_{oc} , 15.51 mA cm⁻² J_{sc} , and 67.05% FF. The Thickness of PDPP4T-2F:PC₇₀BM photoactive layer is around 100 nm. Figure 4d shows above 50% averaged EQE from 700 to 900 nm. The good photovoltaic performance and EQE makes PDPP4T-2F the favored bottom subcell in the tandem OSCs structure.

In order to balance the J_{sc} of two subcells to maximize the total current in the series connected configuration of tandem OSCs, a thinner PTB7:PC₇₀BM photoactive layer with a

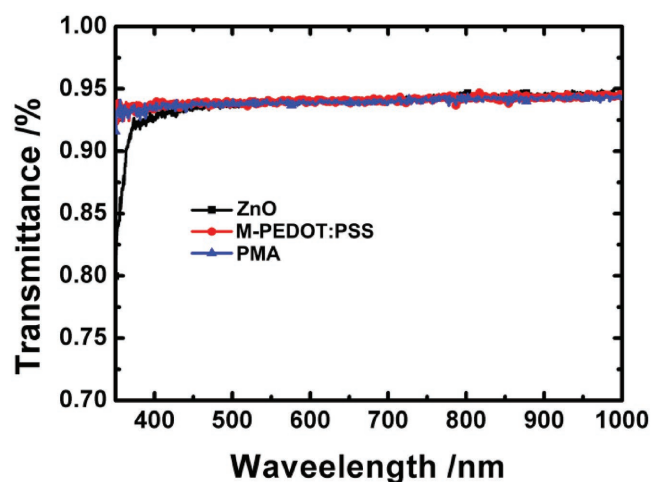


Figure 3. Transmission spectrum of ZnO, M-PEDOT:PSS, and PMA layer.

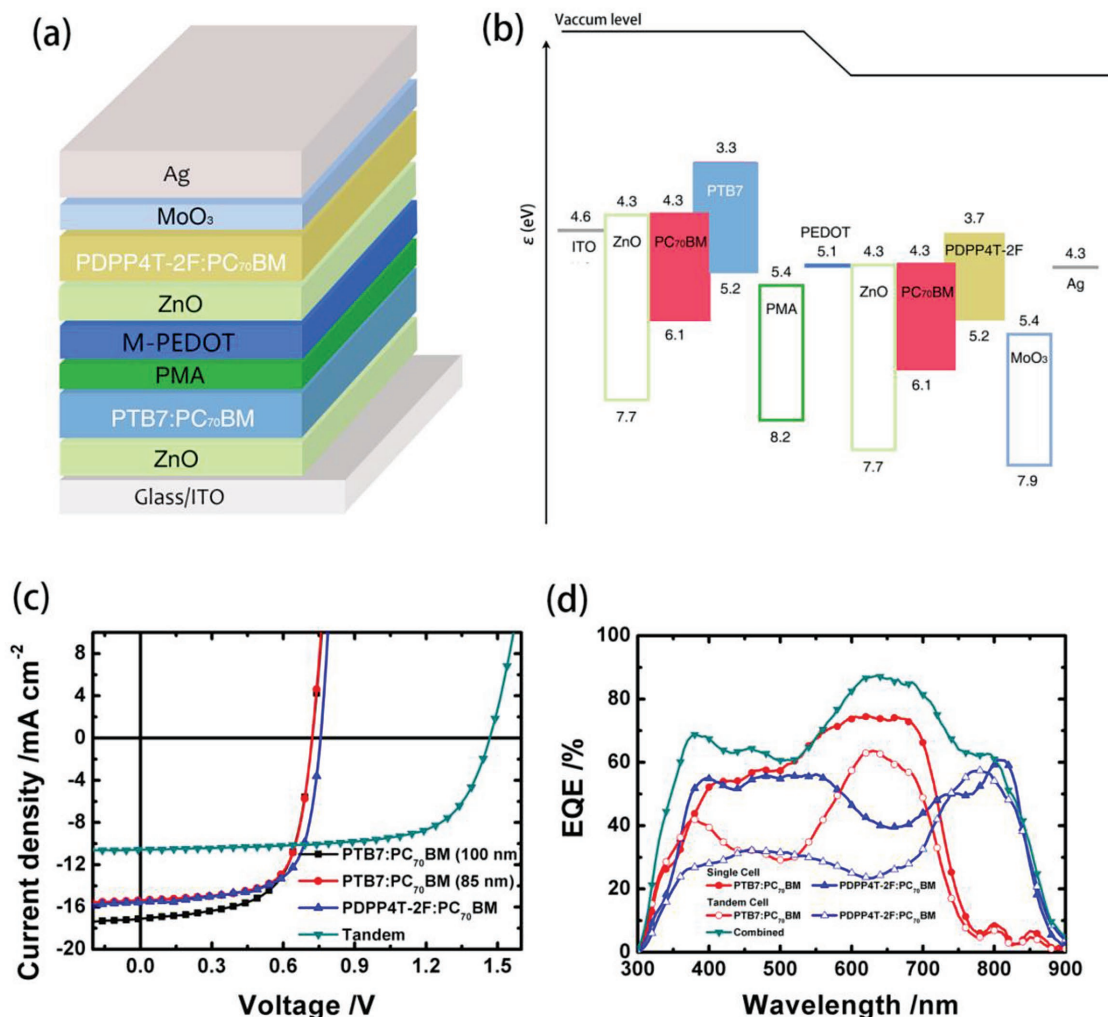


Figure 4. a) Devices structure and b) band diagram of inverted tandem OSCs with PMA/M-PEDOT:PSS/ZnO as ICL. c) J - V characteristics and d) EQE of inverted single and tandem OSCs.

thickness of 85 nm (Device I2) as compared to that of 100 nm (Device I1) is fabricated as the top subcell in tandem OSCs. The J - V characteristics and single cell photovoltaic performance of 85 nm PTB7:PC₇₀BM OSC are shown in Figure 4c and Table 4, respectively. As compared to Device I1 with optimized 100 nm PTB7:PC₇₀BM photoactive layer, Device I2 shows a decreased J_{sc} from 17.02 to 15.27 mA cm⁻², an improved FF from 63.49% to 69.05%, and a slight reduced PCE from 7.79% to 7.58%. This could be explained by the decreasing of photoactive layer thickness. On one hand, thinner photoactive layer decreases photon absorption, resulting in lower photon current. On the

other hand, it improves charge collection ability and reduces charge recombination due to shorter traveling path, resulting in a higher FF.

The tandem OSCs based on the ICL of PMA/M-PEDOT:PSS/ZnO is demonstrated here with PTB7:PC₇₀BM (85 nm) and PDPP4T-2F:PC₇₀BM (100 nm) as top and bottom subcells, respectively. The device structure and band diagram are shown in Figure 4a,b, respectively. The device fabrication process is described in the Experimental Section. The ZnO plays the role of efficient ETL in both PTB7:PC₇₀BM and PDPP4T-2F:PC₇₀BM. PMA (part of ICL) and MoO₃ play

Table 4. Photovoltaic performance of inverted single and tandem high performance OSC devices.

Device	Structure	J_{sc} [mA cm ⁻²]	V_{oc} [V]	FF [%]	PCE [%]
I1	ITO/ZnO/PTB7:PC ₇₀ BM (100 nm)/PMA/Ag	17.02 ± 0.184	0.72 ± 0.002	63.49 ± 0.276	7.79 ± 0.089
I2	ITO/ZnO/PTB7:PC ₇₀ BM (85 nm)/PMA/Ag	15.27 ± 0.143	0.72 ± 0.003	69.05 ± 0.153	7.58 ± 0.092
I3	ITO/ZnO/PDPP4T-2F:PC ₇₀ BM (100 nm)/MoO ₃ /Ag	15.51 ± 0.201	0.76 ± 0.004	67.05 ± 0.304	7.91 ± 0.129
I4	ITO/ZnO/PTB7:PC ₇₀ BM/PMA/M-PEDOT/ZnO/PDPP4T-2F:PC ₇₀ BM/MoO ₃ /Ag	10.48 ± 0.134	1.47 ± 0.003	67.06 ± 0.225	10.34 ± 0.115

the role of efficient HTL in PTB7:PC₇₀BM and PDPP4T-2F:PC₇₀BM, respectively. The PMA/M-PEDOT:PSS/ZnO ICL plays the important role as efficient and robust connecting unit for both top and bottom subcells in the tandem OSCs. In addition, it is worth noting that the direct contact of the water solvent-based M-PEDOT:PSS on top of most of photoactive layer including PTB7:PC₇₀BM would greatly degrade PTB7:PC₇₀BM OSC performance by introducing extra surface recombination. However, in our PMA/M-PEDOT:PSS/ZnO ICL, the PMA successfully excludes the direct contact from M-PEDOT:PSS to PTB7:PC₇₀BM layer, resulting in a good *J*-*V* performance. The M-PEDOT:PSS improves the mechanical protection and electrical carrier recombination capability without introducing much optical loss in the ICL. The photovoltaic performance and *J*-*V* characteristics of tandem OSCs device composed of 85 nm PTB7:PC₇₀BM as top subcell, 100 nm PDPP4T-2F:PC₇₀BM as bottom subcell, and PMA/M-PEDOT:PSS/ZnO as ICL are shown in Figure 4 and Table 4, respectively. The tandem OSC shows 1.47 V *V*_{oc}, which is the addition *V*_{oc} of two subcells with almost ignorable loss. In addition, the 67.06% FF indicates that both the efficient charge recombination in ICL and good current matching of subcells in the tandem OSC are fulfilled. The failure to match either requirement would results in S-shaped *J*-*V* curve or non-S-shaped *J*-*V* curve with poor FF, which is not the case in PMA/M-PEDOT:PSS/ZnO-based tandem OSCs. Finally, the tandem OSC achieves a PCE of 10.34%, which is 24.18% and 23.39% improvement compared to the optimized PCE of PTB7:PC₇₀BM and PDPP4T-2F:PC₇₀BM subcell, respectively.

2.2.2. The Normal Single and Tandem OSCs

Besides the successful incorporation of all-solution-processed PMA/M-PEDOT:PSS/ZnO as efficient ICL in inverted high performance tandem OSCs, here the normal high performance tandem OSCs based on ZnO/M-PEDOT:PSS/PMA ICL is also demonstrated with PTB7:PC₇₀BM and PDPP4T-2F:PC₇₀BM as top and bottom subcells.

In normal single OSC for PTB7:PC₇₀BM photoactive layer, Device N1 with structure of ITO/PMA/PTB7:PC₇₀BM (100 nm)/ZnO/Al is fabricated. The *J*-*V* characteristics and photovoltaic performance of Device N1 are shown in Figure 5c and Table 5, respectively. The device shows 8.35% PCE with 0.75 V *V*_{oc}, 16.37 mA cm⁻² *J*_{sc}, and 68.08% FF. A thinner normal single OSC (Device N2) with 80 nm PTB7:PC₇₀BM photoactive layer is also optimized for current balance in tandem OSCs, showing 7.81% PCE with 0.75 V *V*_{oc}, 14.87 mA cm⁻² *J*_{sc}, and 69.89% FF. A normal optimized single OSC with PDPP4T-2F:PC₇₀BM photoactive layer (Device N3) shows 7.51% PCE with 0.76 V *V*_{oc}, 15.14 mA cm⁻² *J*_{sc}, and 65.19% FF. In addition, from the EQE of both Device N2 and Device N3 as shown in Figure 5d, the averaged EQE of normal single PTB7:PC₇₀BM is above 60% from 350 to 750 nm while that of PDPP4T-2F:PC₇₀BM is above 50% from 700 to 900 nm, indicating their promising capabilities as front and bottom subcell in normal tandem OSCs device respectively.

Based on the normal single OSCs, normal tandem OSCs with ZnO/M-PEDOT:PSS/PMA ICL is fabricated with structure of ITO/PMA/PTB7:PC₇₀BM/ZnO/M-PEDOT:PSS/PMA/PDPP4T-2F:PC₇₀BM/Ca/Al as Device N4. Its schematic device structure and band diagram are shown in Figure 5. The device fabrication process is described in the Experimental Section. The *J*-*V* characteristics and photovoltaic performance of Device N4 are shown in Figure 5c and Table 5, respectively. Device N4 shows 10.46% PCE with 1.49 V *V*_{oc}, 10.25 mA cm⁻² *J*_{sc}, and 68.52% FF. The tandem *V*_{oc} shows an ignorable loss of 0.02 V and a good FF, which indicates the efficient recombination of electron and hole in ZnO/PEDOT/PMA ICL. The normal tandem OSC shows 19.41% and 27.82% PCE improvement as compared to the optimized normal single PTB7:PC₇₀BM and PDPP4T-2F:PC₇₀BM OSCs.

To sum up, based on PMA/M-PEDOT:PSS/ZnO and ZnO/M-PEDOT:PSS/PMA ICL, high performance tandem OSCs with PTB7:PC₇₀BM and PDPP4T-2F:PC₇₀BM as top and bottom subcells have been realized in its inverted and normal structure, respectively, with summed ignorable loss *V*_{oc}, high FF, and almost the same PCE above 10%. This demonstrates PMA/M-PEDOT:PSS/ZnO and ZnO/M-PEDOT:PSS/PMA are qualified switchable ICL for high performance tandem OSCs.

3. Conclusion

A new kind of switchable ETL/RL/HTL all-solution-processed ICL, that is the PMA/M-PEDOT:PSS/ZnO together with ZnO/M-PEDOT:PSS/PMA ICL as its symmetric inverse counterpart, has been demonstrated as the qualified ICL for both inverted and normal tandem OSCs. The high performance tandem OSCs based on this switchable ICL achieve the summed *V*_{oc} with ignorable loss in both inverted and normal structures. The conventional tunneling junction-based ETL/HTL ICL structure, which requires both ETL and HTL not only fulfill efficient CTL for extraction of carrier from photoactive layer, but also should meet the optical, electrical, mechanical and chemical property for ICL, is heavily coupled and makes it extremely difficult to replace either layer in ICL without compromising being efficient ICL. In the proposed switchable three-layer ETL/RL/HTL and HTL/RL/ETL ICL, ETL and HTL only serve as CTL as they did in single OSCs and the electrical recombination, mechanical protection and chemical separation functionalities are all fulfilled by the RL alone. This three-layer switchable ICL structure simplifies the conventional ICL design strategy based on ETL/HTL tunneling junction, providing a general ICL design guide to incorporate other efficient ETL and HTL from single OSCs to be qualified ICL in tandem OSCs.

4. Experimental Section

Material Preparation and Synthesizing: PTB7 and PC₇₀BM were purchased from Solarmer Materials Inc. Neutral PEDOT:PSS and PMA were purchased from Sigma Aldrich, Inc. PDPP4T-2F was provided by Hou's group. ZnO nanoparticles were synthesized according to the previous report.^[53,54]

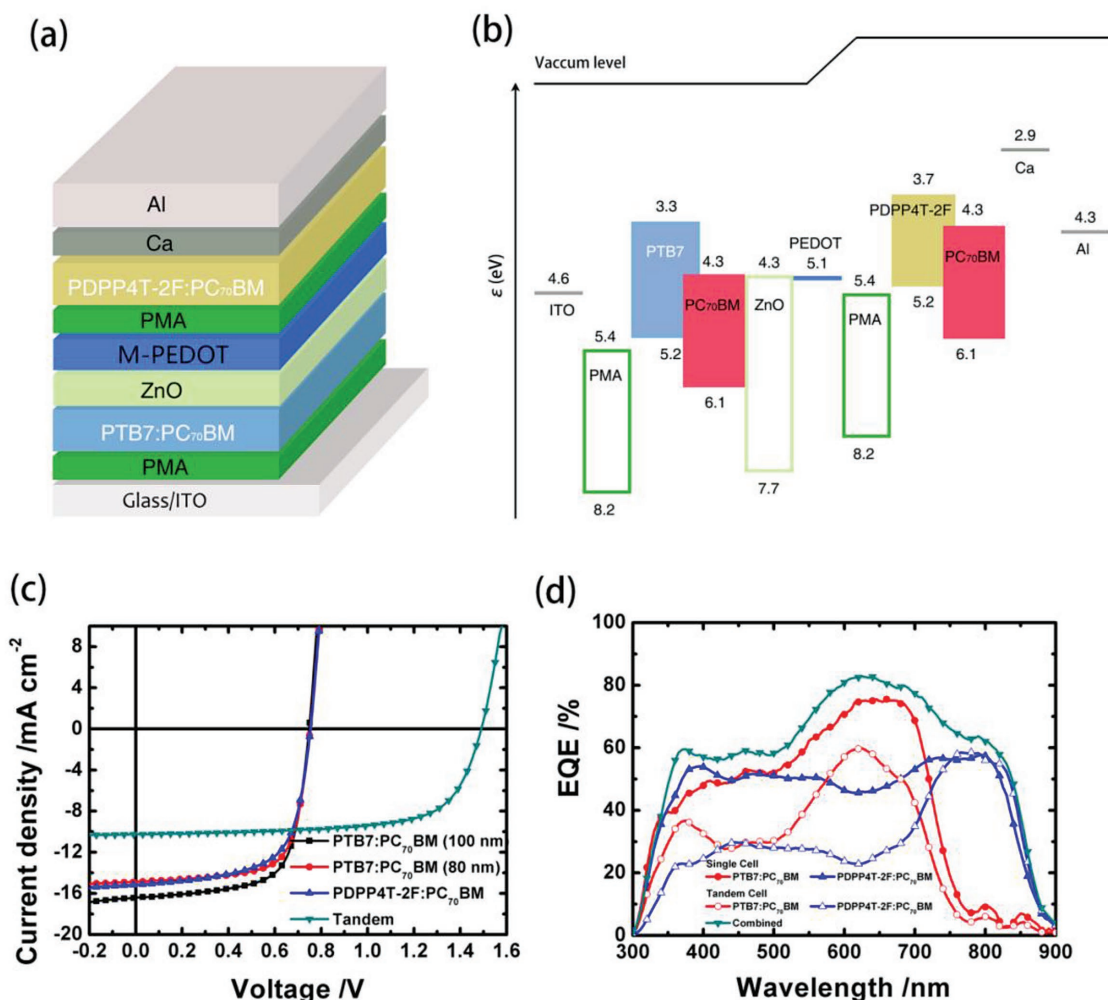


Figure 5. a) Devices structure and b) band diagram of normal tandem OSCs with ZnO/M-PEDOT:PSS/PMA as ICL. c) J - V characteristics and d) EQE of normal single and tandem OSCs.

Single-Junction Device Fabrication: ITO glass with a sheet resistivity of $15 \Omega \text{ square}^{-1}$ was cleaned by ultrasonication for 30 min in detergent water, deionized (DI) water, acetone, and ethanol sequentially followed by 15 min Ultraviolet Ozone (UVO) treatment. PMA was dissolved in isopropanol, and ZnO was synthesized in butyl alcohol. For inverted single OSCs, firstly, the ZnO layer was spin-coated on top of ITO at 2000 rpm with 10 min post-annealing at 80°C . Then, P3HT:PC₆₀BM (1:1) and PTB7:PC₇₀BM (1:1.5) in CB with various concentration were spin-coated on top of the ZnO film at different velocity. After that, PMA with optimized concentration was spin-coated atop. For PDPP4T-2F, PDPP4T-2F:PC₇₀BM (1:2) was dissolved in a mixture solvent of CF:CB:CN (v/v/v, 80:16:4). The mixture solution was heated overnight at 50°C with stirring. The solution was spin-coated on top of the ZnO film with various velocities. After that, MoO₃ was thermally evaporated atop as the HTL. Finally, 100 nm Ag was thermally

evaporated as the anode for all the single-junction devices. For normal single OSCs, PMA with different optimized concentration was spin-coated on top of ITO at 3000 rpm with no post-treatment. Then, P3HT:PC₆₀BM and PTB7:PC₇₀BM were spin-coated on top of PMA. After that, ZnO was spin-coated on top with 10 min post-annealing at 80°C and finished by thermal evaporation of 100 nm Al. For PDPP4T-2F:PC₇₀BM, 20 nm Ca and 100 nm Al were thermal evaporated sequentially to complete the device.

Tandem Device Fabrication: The modified M-PEDOT:PSS was made by diluting neutral PEDOT:PSS with DI water and ethylene glycol (v/v/v, 1:1:0.05). An extra amount (v/v, 0.2%:1) of Triton X-100 surfactant was further added, and the final solution was stirred at room temperature overnight. For inverted tandem OSCs, PTB7:PC₇₀BM was spin-coated on top of ZnO. After that, PMA was spin-coated at 3000 rpm for 40 s with no post-treatment. The modified M-PEDOT:PSS was spin-coated

Table 5. Photovoltaic performance of normal single and tandem high performance OSC devices.

Device	Structure	J_{sc} [mA cm^{-2}]	V_{oc} [V]	FF [%]	PCE [%]
N1	ITO/PMA/PTB7:PC ₇₀ BM (100 nm)/ZnO/Al	16.37 ± 0.112	0.75 ± 0.002	68.08 ± 0.26	8.35 ± 0.087
N2	ITO/PMA/PTB7:PC ₇₀ BM (80 nm)/ZnO/Al	14.87 ± 0.096	0.75 ± 0.005	69.89 ± 0.32	7.81 ± 0.058
N3	ITO/PMA/PDPP4T-2F:PC ₇₀ BM (100 nm)/Ca/Al	15.14 ± 0.137	0.76 ± 0.005	65.19 ± 0.148	7.51 ± 0.065
N4	ITO/PMA/PTB7:PC ₇₀ BM/ZnO/M-PEDOT/PMA/PDPP4T-2F:PC ₇₀ BM/Ca/Al	10.25 ± 0.071	1.49 ± 0.004	68.52 ± 0.252	10.46 ± 0.083

on top of PMA with 2000 rpm followed by 5 min annealing at 80 °C. Then, ZnO was spin-coated at 1500 rpm followed by 5 min annealing at 80 °C. After that, PDPP4T-2F:PC₇₀BM was spin-coated on top. The device was then finished by thermal evaporation of 10 nm MoO₃ and 100 nm Ag. For P3HT:PC₆₀BM homo-tandem device, 2500 and 3000 rpm spin-coating velocities were used for top and bottom photoactive subcells, respectively, followed by 5 min annealing at 80 °C. The device was completed by spin-coating of PMA atop followed by thermally evaporation of 100 nm Ag. The ICL sublayer thicknesses are 30, 55, and 20 nm for PMA, M-PEDOT:PSS and ZnO, respectively, in inverted tandem structures. For normal tandem OSCs, firstly, PMA was spin-coated on top of ITO glass with no post-treatment. Then, PTB7:PC₇₀BM was spin-coated on top of PMA. After that, ZnO was spin-coated atop with 10 min post-annealing at 80 °C. Then, the modified M-PEDOT:PSS was spin-coated atop with 2000 rpm followed by 5 min annealing at 80 °C. The ICL was completed by spin-coating of PMA at 3000 rpm. After that, PDPP4T-2F:PC₇₀BM was spin-coated on top. The device was then finished by thermal evaporation of 30 nm Ca and 100 nm Al. For P3HT:PC₆₀BM homo-tandem device, 3000 rpm spin-coating velocities were used for both top and bottom photoactive subcell followed by 5 min annealing at 80 °C. The device was completed by spin-coating of ZnO atop followed by thermally evaporation of 100 nm Al. The ICL sublayer thicknesses are 20, 55, and 5 nm for ZnO/-PEDOT/-PSS and MA, respectively, in normal tandem structures.

Device Characterization: The (*J*-*V*) characteristics were obtained by using a Keithley 2635 source meter and Newport AM 1.5G solar simulator with irradiation intensity of 100 mW cm⁻² under mask. The thicknesses of layers were measured by a Dekak Stylus Profiler. The incident photon-to-current efficiency (IPCE) measurement was performed by a system combining xenon lamp, monochromator, chopper, and a lock-in amplifier together with a calibrated silicon photodetector. For tandem IPCE measurement, 532 nm and 730 nm lasers were selected to light bias the front and bottom subcells. The transmission spectra of the film were measured by a goniometer combined with a charge-coupled device (CCD) spectrometer and integrating sphere.

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Conflict of Interest

The authors declare no conflict of interest.

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