Simplified Compact Perovskite Solar Cells with Efficiency of 19.6% via Interface Engineering

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For the commercialization of perovskite solar cells (PSCs), it is more appealing to develop high-performance simplified PSCs where perovskite films are just sandwiched between the back and front electrodes, in order to simplify the fabrication process and to reduce the cost. However, to date, this kind of devices shows rather low performance, and there are few researches on this subject. Herein, we report on a kind of compact PSCs (CPSCs) that are free of independent charge transport layers (CTLs). The devices are realized by the use of organic monolayer-modified effective electrodes, along with the use of [6,6]-phenyl-C61-butyric acid methyl ester (PCBM)-assisted anti-solvent technique to obtain ultra-thin (~10 nm) PCBM-embedded perovskite films. Compared to control devices, CPSCs achieve a promising champion power conversion efficiency of 19.6% with largely reduced hysteresis. Moreover, the unencapsulated CPSC shows good stability under ambient atmosphere, with only 10% efficiency loss after 60 days' storage. This work indicates that, by delicate design, CPSCs with smaller materials consumption in device architecture can perform competitively as conventional PSCs. Further reduction in the actual usage of costly CTL materials can be expected upon our CPSCs by developing more facile and economic methods to prepare ultra-thin CTLs.

1. Introduction

Organometal halide perovskite (PVK) materials have shown great potential for their applications in photovoltaics due to their excellent photoelectric properties and the rapid growth of power conversion efficiency (PCE). To date, the certified PCE of perovskite solar cells (PSCs) has been over 25% after a few short years study, which has exceeded that of conventional thin-film solar cells. In general, charge transport layers (CTLs), that is, electron transport layer (ETL) and hole transport layer (HTL) are regarded as essential to PSCs which exhibit top efficiencies (>21%) from devices with regular and inverted architectures. Particularly, perovskite precursor engineering and additional surface modification/passivation layers are further employed to suppress charge recombination for higher efficiencies. Under these efforts, although breakthrough of PCE is continuously achieved, the compositional and structural complexity in PSCs would inevitably increase the fabrication difficulties and cost, which would be disadvantageous to the commercialization of PSCs in the near future. Therefore, it is a crucial necessity to explore simplified architectures for highly efficient and economical planar PSCs.

Currently, there are mainly two strategies to fabricate simplified PSCs (SPSCs) that have only one CTL or are free of CTL. The first strategy is to remove the CTL directly from conventional five-layered device with the structure of electrode/HTL/PVK/ETL/electrode (SL-PSC). However, this would cause serious shunt losses due to direct contact between perovskite and electrode, thus leading to rather low open-circuit voltage ($V_{oc} < 1$ V) and PCE ($<15\%$) of devices. The second strategy is developed based on the first one. These SPSCs are fabricated by removing independent ETL or HTL, whereas further treatments are employed, either by surface treatment of electrode (ITO or FTO) to obtain effective electrode or by perovskite engineering. Benefitting from these treatments, better energy level alignment between perovskite and electrode is achieved, and the issue with respect to direct contact between them can be effectively addressed. For example, recently, an organic monolayer (ML) was used to prepare the effective ITO substrate (ML-ITO), of which the energy level matches much better with perovskite than the common ITO substrate. As a result, largely increased $V_{oc}$ from 0.75 V to 1.12 V and PCE from 9.5% to 19.4% were achieved. The evident increase in $V_{oc}$ is mainly due to the suppression of interfacial charge recombination at the surface of effective electrode. Apart from this, precursor engineering is also helpful in promoting the performance of SPSCs. Wu et al. incorporated functional small molecules into perovskite...
precursors and found that the additive could improve the conductivity of perovskite films and their electronic contact with electrode; thus, a promising efficiency of 20.2% ($V_{oc} = 1.10 \text{ V}$) was achieved from a HTL-free SPSC. Although the efficiency has been improved a lot as stated above, the current SPSCs still keep one of independent CTLs, for example, either ETL or HTL, within the devices.\textsuperscript{[16,17,21,24–27]} Clearly, it is much more attractive to the photovoltaic community if the perovskite film is just sandwiched between two electrodes; meanwhile, these devices exhibit competitive performance as the conventional PSCs that are with ETL and HTL.\textsuperscript{[28]} However, to date, there are no successful efforts reported on a prototype of high-performance SPSCs (PCE> 15%) that are free of independent CTLs.

Herein, we report on a kind of highly efficient compact PSCs (CPSCs) realized by sandwiching [6,6]-phenyl-C61-butyric acid methyl ester (PCBM)-embedded perovskite film (PVK-PCBM) between ML-modified effective electrode and metal electrode with the structure of ML-ITO/PVK-PCBM/BCP-Ag. The main novelty of this work is that ultra-simplified devices without independent CTLs have been successfully fabricated. Compared to the three-layered SPSCs free of CTL (ML-ITO/PVK/BCP-Ag, 3L-SPSCs) and the four-layered SPSCs without of independent HTL (ML-ITO/PVK/PCBM/BCP-Ag, 4L-SPSCs), the designed CPSCs achieved rather competitive performance; they deliver a champion PCE of 19.6% with a promising $V_{oc}$ of 1.13 V and negligible hysteresis; and the unencapsulated devices show improved stability under ambient atmosphere, with only 10% efficiency loss after 60 days’ storage. To the best of our knowledge, this is the highest efficiency among the 3L-SPSCs. Beyond that, both the efficiency and $V_{oc}$ are comparable to those from the best 4L-SPSCs or even conventional 5L-PSCs ever reported.\textsuperscript{[16,17,21,30]}

2. Results and Discussion

Figure 1 illustrates the fabrication process of CPSC in comparison with conventional 5L-PSC where both HTL and ETL are within the device. For CPSC, the effective electrode functionalized by an organic monolayer (ML-ITO) of 4,4’-cyclohexylidenebis[N,N-bis(4-methylphenyl)benzamidine] (TAPC) was used directly for the deposition of CH$_3$NH$_3$PbI$_3-x$Cl$_x$ (MAPbI$_3$-Cl$_x$) based on our previous report.\textsuperscript{[22]} After that, a modified anti-solvent technique, that is, appropriate PCBM being dissolved in chlorobenzene,\textsuperscript{[21]} was employed to prepare the perovskite film, atop which a rather thin PCBM layer would be formed concurrently. Following that, the counter electrode was thermally evaporated directly onto the annealed perovskite film to complete device fabrication (Figure 1b). Note that the PCBM-assisted anti-solvent technique has been proved to be effective to quench the perovskite precursors and to improve the surface topography of perovskite films.\textsuperscript{[23]} Compared with conventional 5L-PSC (Figure 1a), it is clearly notable that the device structure and fabrication process of CPSC have been simplified significantly by removing extra independent CTLs, which are of great potential for the development of cost-effective commercialized PSCs.

The introduction of ML in CPSC can raise the effective work function of ITO with the assistance of interface dipole via Sn-N bonds. The energy level alignment between ITO and perovskite is optimized with a barrier-free contact, which favors efficient charge transfer. Consequently, HTL can be removed successfully by ML-modified effective electrode; this procedure is well described in our previous work and will not be repeated here.\textsuperscript{[22]} On the other hand, PCBM has been widely used in inverted PSCs because it functions effectively both as electron collection material and defect (like grain boundary, GB) passivator to achieve high-quality perovskite films\textsuperscript{[31,13]} However, the PCBM layer that is formed simply by spin coating method on the annealed perovskite film may provide insufficient passivation (Figure 1a), and it normally suffers from resistive losses as the formation of thicker layers (>50 nm).\textsuperscript{[31]} In contrast, a much thinner PCBM layer with full coverage is applied in CPSC, and sufficient passivation is expected (studied in the following) due to the easier diffusion of PCBM into GBs as a result of concurrent film formation process of perovskite and PCBM (Figure 1b).\textsuperscript{[26,31]} These advantages are expected to provide CPSCs with competitive performance.

The morphologies of MAPbI$_{3-x}$Cl$_x$ films covered by thick/thin PCBM layers are characterized by scanning electron microscopy (SEM), as shown in Figure 2. The crystal size of as-prepared perovskite is in the range of 300–500 nm, and the film thickness is ca. 400 nm with the crystals basically growing throughout the film (Figure 2a and b), which is favorable to charge transport and collection efficiency.\textsuperscript{[34,35]} In 4L-SPSC, a rather thick PCBM ETL is formed by spin coating method on the annealed perovskite film to construct MAPbI$_{3-x}$Cl$_x$/PCBM composite (Figure 2c and d) on ML-ITO. It normally requires relative thicker PCBM film to guarantee a full coverage on the perovskite film; otherwise, it easily leads to larger shunt losses.\textsuperscript{[28,31]} From the high-contrast cross-sectional SEM image, the PCBM layer can be clearly distinguished and its thickness can be estimated due to the difference in film conductivity between perovskite and PCBM. As shown in Figure 2d, a PCBM layer of ca. 90 nm is formed on the MAPbI$_{3-x}$Cl$_x$ film, which is consistent with previous reports by spin coating method.\textsuperscript{[31]} For CPSC, it is clear that a thin but compact PCBM layer is embedded into the perovskite film (MAPbI$_{3-x}$Cl$_x$/PCBM composite) on ML-ITO by anti-solvent assisted
During the annealing process, the thin PCBM layer can act as an anchor layer to prevent the MA cation from escaping, ensuring stoichiometric balance at the interface of perovskite crystal lattice. Such interface with reduced non-radiative recombination sites is beneficial to charge transfer. The absorption spectra (Figure 3b) of these two composites show little difference, indicating that PCBM treatment on MAPbI$_3$-Cl$_x$ does not affect the bandgap of perovskite. Ultraviolet photoelectron spectra were measured to study the energy level alignment (Figure S1). It is found that the energy level offset ($\Delta E$) between the conduction band of perovskite and the lowest unoccupied molecular orbital of PCBM is reduced from 0.1 eV of the MAPbI$_3$-Cl$_x$/PCBM composite to 0.05 eV of the MAPbI$_3$-Cl$_x$-PCBM one; thus, charge transfer between perovskite and PCBM would be largely improved.

In order to investigate charge transfer properties between perovskite and PCBM, steady-state and time-resolved photoluminescence (PL and TRPL) spectra were carried out, as shown in Figure 3c and d. The pristine MAPbI$_3$-Cl$_x$ film displays a strong PL peak at 764 nm. In comparison, markedly reduced PL intensities are observed for the MAPbI$_3$-Cl$_x$/PCBM and MAPbI$_3$-Cl$_x$-PCBM composites. By comparing the maximum emission intensity of the composite to that of pristine MAPbI$_3$-Cl$_x$ film, quenching efficiency is calculated, which is 74.6% and 91.2% for MAPbI$_3$-Cl$_x$/PCBM and MAPbI$_3$-Cl$_x$-PCBM composites, respectively. Therefore, charge transfer is more efficient in CPSC as compared with 4L-SPSC. This is due to increased interface area for charge transfer and reduced charge recombination in the MAPbI$_3$-Cl$_x$/PCBM and MAPbI$_3$-Cl$_x$-PCBM composites, respectively. Consequently, the improved charge transfer, along with much thinner PCBM layer for enhanced charge transport, would be favorable to promoting charge collection efficiency for higher short circuit current density ($J_{sc}$) in CPSCs.

Typical 3L-SPSCs, 4L-SPSCs, and CPSCs were fabricated for comparison. The detailed J-V curves and parameters are shown in Figure 4 and Table 1, and the statistical distribution of J-V parameters is shown in Figure S2. At first, we tried to fabricate the most simplified 3L-SPSCs; however, the device exhibits abnormal J-V curve and its performance is rather poor (Figure 4a), which is mainly due to serious recombination and large shunt losses.\(^{26}\) To address this issue, the perovskite film embedded by a rather thin PCBM layer was employed in replacement of pristine MAPbI$_3$-Cl$_x$ to fabricate CPSCs. As a result, significantly enhanced $V_{oc}$, $J_{sc}$, and fill factor (FF) were achieved. Clearly, CPSC shows enhanced diode characteristics, method (Figure 2 e and f). This PCBM layer is rather thin (~10 nm) that perovskite crystals underneath are still distinguishable, and is rather compact which will be effective to suppress the shunt losses, similar to the results from PCBM-modified perovskite films.\(^{12}\) Moreover, such a thin layer is to the advantage of charge diffusion by largely reducing the transport resistance. As a result, the unique MAPbI$_3$-Cl$_x$-PCBM thin layer is to the advantage of charge diffusion by largely reducing perovskite is disadvantageous to the layer is formed atop the quasi-perovskite

X-ray diffraction (XRD) patterns were recorded to disclose the effect of PCBM layer on the structure of perovskite films (Figure 3a). The MAPbI$_3$-Cl$_x$/PCBM composite of 4L-SPSC exhibits a tetragonal perovskite structure with the diffraction peaks at 14.2°, 28.5°, and 32.0° being assigned to (110), (220), and (310) lattice plane, respectively. Moreover, it can be seen that an evident peak appears at 12.7°, which is belonged to the (001) plane of cubic PbI$_2$.\(^{11}\) The appearance of PbI$_2$ peak is mainly due to the volatile nature of the organic cation CH$_3$NH$_3$+ (MA) that easily escapes from the perovskite crystal lattice during thermal annealing process.\(^{136}\) Therefore, the following spin-coated PCBM ETL on the annealed perovskite film actually cannot suppress the volatilization of MA effectively. This would easily lead to the formation of deep level under-coordinated lead ions or metallic lead defects on the surface, which mainly serve as non-radiative recombination centers to increase energy losses.\(^{12}\) Besides, the non-stoichiometric perovskite is disadvantageous to the film stability. In contrast, for the MAPbI$_3$-Cl$_x$-PCBM composite of CPSC, a thin but compact PCBM layer is formed atop the quasi-perovskite film before thermal annealing.
indicating that such PCBM layer works effectively as hole blocking layer, although its thickness (~10 nm) is much smaller than that of conventional spin-coated PCBM layers (>50 nm).\textsuperscript{13,21} The performance of 4L-SPSC based on spin-coated PCBM layer (ca. 90 nm, Figure 2d) is inferior to that of CPSC. The reason is mainly due to that, in CPSC, there is relative higher charge collection efficiency due to efficient charge transfer and short charge transport distance, as well as sufficient defect passivation on the perovskite (vide infra); these features can significantly promote $V_{oc}$ and $J_{sc}$. In addition, the improved charge transport would result in shorter transit time, which has been proved to be key to the enhancement of FF.\textsuperscript{127} Benefiting from these advantages, a champion PCE of 19.6% was achieved from the CPSCs, with $V_{oc}$, $J_{sc}$, and FF of 1.13 V, 21.4 mA cm$^{-2}$, and 81.0%, respectively (Figure 4b). To the best of our knowledge, this is currently the highest efficiency of CPSCs. This efficiency is also comparable to that from HTL-free SPSCs,\textsuperscript{16,25} indicating that, by delicate design, independent HTL and ETL are not indispensable in PSCs.

The external quantum efficiency (EQE) spectrum of the champion device was demonstrated in Figure 4c. The integrated $J_{sc}$ is 21.0 mA cm$^{-2}$, which is in good agreement with that from $J$-$V$ measurement. The CPSC shows good stability upon continuous light exposure, as shown in Figure 4d. A steady-state efficiency of 19.1% was obtained after biasing at the maximum power point for 300 s, which is consistent with the $J$-$V$ result. Apart from PCE, long-term stability of devices is another factor that is highly concerned for the practical application. For the stability test, the CPSC without encapsulation was stored under ambient atmosphere (25 °C and 40% relative humidity). It is found that the device still retained nearly 90% of its initial efficiency after 60 days’ storage (Inset to Figure 4d). In contrast, about 20% loss was observed from the 4L-SPSC within 10 days. In addition to improving the moisture stability, it has also been reported that PCBM coverage on the surface of perovskite film is favorable to the device thermal stability.\textsuperscript{38} Therefore, these results indicate that the designed CPSCs exhibit not only promising PCEs, but also competitive stability, as compared with the conventional inverted PSCs with independent HTLs and ETLs.\textsuperscript{39}

Figure 3. a) XRD and b) absorption spectra of MAPb$_{1-x}$Cl$_x$/PCBM and MAPb$_{1-x}$Cl$_x$-PCBM composites. The symbol “●” identifies the diffraction peak of PbI$_2$. c) PL and d) TRPL spectra of pristine MAPb$_{1-x}$Cl$_x$, MAPb$_{1-x}$Cl$_x$-PCBM and MAPb$_{1-x}$Cl$_x$-PCBM composites grown on ITO substrate.

Figure 4. a) $J$-$V$ curves of devices with forward and reverse scan, b) champion efficiency, c) EQE, and d) steady-state PCE upon continuous light exposure achieved from CSPSC. Inset to d) shows the stability of 4L-SPSC and CPSC stored under ambient atmosphere.
Table 1. Summary of average and champion photovoltaic parameters of devices.

<table>
<thead>
<tr>
<th>Device Type</th>
<th>V_{oc} (V)</th>
<th>J_{sc} (mA cm$^{-2}$)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3L-SPSCs (w/o PCBM)</td>
<td>0.88 ± 0.03</td>
<td>14.2 ± 0.7</td>
<td>442 ± 8.9</td>
<td>55 ± 1.0</td>
</tr>
<tr>
<td>4L-SPSCs (90 nm PCBM)</td>
<td>1.05 ± 0.02</td>
<td>18.4 ± 0.5</td>
<td>741 ± 1.7</td>
<td>144 ± 0.4</td>
</tr>
<tr>
<td>3L-SPSCs (10 nm embedded PCBM)</td>
<td>1.12 ± 0.01</td>
<td>21.4 ± 0.5</td>
<td>781 ± 1.3</td>
<td>186 ± 0.4</td>
</tr>
<tr>
<td>CPSCs</td>
<td>1.34</td>
<td>19.0</td>
<td>753</td>
<td>15.2</td>
</tr>
<tr>
<td></td>
<td>1.35</td>
<td>21.4</td>
<td>810</td>
<td>19.6</td>
</tr>
</tbody>
</table>

To investigate charge recombination characteristics of the simplified devices, light intensity ($I$)-dependent $V_{oc}$ and space-charge-limited current (SCLC) spectra were recorded (Figure 5a and b). The extracted parameters are listed in Table 2. As all the photogenerated charge carriers eventually recombine with each other under open-circuit condition, the variation of $V_{oc}$ upon $I$ can provide the information about recombination characteristics within devices. The relationship between $I$ and $V_{oc}$ is described as:

$$\frac{dV_{oc}}{d \log I} = 2.303 \frac{n k_B T}{q}$$

where $n$, $k_B$, $T$, and $q$ are ideality factor, Boltzmann constant, absolute temperature, and elementary charge, respectively. By linear fitting of $V_{oc}$ upon $I$ (Figure 5a), $n$ was calculated with the value of 1.34 and 1.80 for CPSC and 4L-SPSC, respectively. All the $n$ values are larger than unity, suggesting that non-radiative recombination is existed in both devices. However, the smaller $n$ in CPSC indicates less charge recombination within the device as compared with that in 4L-SPSC.

The SCLC measurement was carried out on electron-only devices with the structure of ITO/SnO$_2$/composite/BCP-Ag, where the composite was MAPb$_{1-x}$Cl$_x$/PCBM or MAPb$_{1-x}$Cl$_x$-PCBM (Figure 5b). The plot at low bias voltage shows a linear relation, indicating an ohmic contact response. Further increasing the bias voltage leads to a sharp rise in the current, which suggests that the injected electrons start to fill up thetrap states of perovskite, that is, the trap-filled limit (TFL) region, until reaching the SCLC region. As is known, the onset voltage of TFL region ($V_{TFL}$) correlates tightly with the trap density in the perovskite film, and a smaller trap density is normally accompanied by a smaller $V_{TFL}$. As shown in Figure 5b, it is evident that the $V_{TFL}$ is smaller in the MAPb$_{1-x}$Cl$_x$/PCBM composite-based device, which is in agreement with the result from Figure 5a. However, the electron mobility ($\mu$) of perovskite film shows no difference (Table 2), as compared between the linear fitting to the SCLC region of respective device, suggesting that PCBM treatment does not influence the electron mobility of perovskite. Based on the results from Figure 5a and b, conclusion can be drawn that the reduced trap assisted recombination in the MAPb$_{1-x}$Cl$_x$/PCBM composite of CPSC stems from the decrease in trap density therein.

To confirm this, admittance spectroscopy was further measured (Figure 5c), which has been widely applied as a powerful technique to quantitatively study the trap density ($N_T$) of perovskite.$^{11,33}$ From the admittance spectroscopy, $N_T$ can be calculated from the equation described as,

$$N_T(E_{\omega}) = \frac{V_{th} \frac{dC}{d\omega} \omega}{qW \phi_0 k_B T}$$

where $\omega$, $C$, and $E_{\omega}$ are angular frequency, capacitance, and variance between trap energy and valence band edge, respectively. The built-in potential ($V_{bi}$) and depletion width ($W$) are obtained from the Mott-Schottky analysis as described elsewhere.$^{11}$ The calculated results shown in Figure 5c demonstrate that $N_T$ is reduced significantly in CPSC, with the reduction of one order of magnitude ($E_{\omega} = 0.15$ eV) in comparison with that from 4L-
The result indicates more sufficient defect passivation in the further simplified device, which is mainly due to better interfacial contact between the perovskite and PCBM to passivate GBs (Figure 1) and the suppression of MA volatilization on the surface of perovskite to reduce deep level under-coordinated lead ions or metallic lead defects on the surface (Figure 3a). The reduced $N_F$ in CPSC would lead to decreased charge recombination, which is favorable to the device $V_{oc}$ and stability.\[11\]

To further study the charge transfer and recombination behaviors in devices, electrochemical impedance spectroscopy (EIS) was studied. Figure 5d shows the Nyquist plots of 4L-SPSC and CPSC. Two semicircles appear in the Nyquist plots of both devices, where the one at high frequency is relative to the selective contact resistance ($R_N$) for charge transport, and the other one at low frequency is associated with the recombination resistance ($R_{rec}$).\[14\] The parameters $R_N$ and $R_{rec}$ can be obtained by the equivalent circuit (Figure S3). Clearly, the CPSC exhibits smaller $R_N$ and larger $R_{rec}$ (Table 2). This result suggests improved charge transfer and suppressed recombination, and it mainly originates from largely reduced thickness of the PCBM layer and trap density in the perovskite film. Therefore, in the CPSC, the enhanced charge transfer and shortened charge transport distance are beneficial to charge collection for higher $J_{sc}$ and FF, while the reduced trap density endows the device less recombination for increased $V_{oc}$.

The designed CPSCs are promising to work as competitively as conventional 1L-PSCs ever reported,\[16,25,29,10\] although the amount of charge transport materials contained in CPSCs is much less. Firstly, we have successfully demonstrated a prototype of high-performance CPSCs (PCE>15%) that are free of independent HTLs. However, the current fabrication process still requires large amount of charge transport materials owing to the anti-solvent technique for the preparation of PCBM-embedded perovskite layer. Therefore, further efforts have been ongoing to develop effective methods to reduce practical usage of the costly charge transport materials in CPSCs. It should be noted that the entire fabrication for CPSCs can be solution processed in a low temperature (PCE have successfully demonstrated a prototype of high-performance CPSCs designed for the development of cost-effective and highly efficient PSCs.

In summary, CPSCs that are free of independent HTLs and ETLs are achieved by improved energy level alignment, enhanced charge collection efficiency, and reduced non-radiative recombination. This work demonstrates a potential strategy to assemble CPSCs for high-performance and cost-effective PSCs in the future.

### 4. Experimental Section

**Materials:** ITO glasses were acquired from Ying Kou You Xuan Trade Co., Ltd., China, and the sheet resistance was measured to be 15 $\Omega$ sq$^{-1}$. PbI$_2$ (99.9985%) was purchased from Alfa Aesar, United States. TAPC (>97%), MAI (>99.5%), PbCl$_2$(>99.99%), PC$_{61}$BM (>99%) and BCP (>99%) were purchased from Xi’an Polymer Light Technology Corp, China. All solvents, including DMF (>99.8%), DMSO (>99.9%) and chlorobenzene (>99.8%) were purchased from Sigma-Aldrich, United States. All reagents were used without further purification.

**Device fabrication:** The perovskite solar cells were fabricated on pre-patterned ITO substrates. The patterned ITO substrates were ultrasonically cleaned in sequence with detergent solution, deionized water, acetone, and isopropanol for 20 min in an ultrasonic bath. After drying with nitrogen flow, ITO substrates were treated by UV-ozone treatment for 20 min before a thin layer of TAPC was spin-coated at 4000 rpm for 25 s and then annealed at 110°C for 15 min. Before the deposition of perovskite films, solvent rinsing of TAPC films was carried out by adding 100 $\mu$L DMF onto the spinning TAPC coated ITO substrate (5000 rpm for 25 seconds) to wash away TAPC to form ML-ITO. The MAPb$_{1-x}$Cl$_x$ precursor solution was prepared by dissolving 1.17 M PbI$_2$, 0.13 M PbCl$_2$, and 1.3 M MAI in 1 mL DMF/DMSO co-solvent (9:1, v/v) and stirred for 2h at 70°C. PCBM solution (15 mg/mL) were prepared by dissolving PCBM in anhydrous chlorobenzene.

The perovskite films were obtained by dripping 30 $\mu$L MAPb$_{1-x}$Cl$_x$ precursor solution onto the ITO substrates at 700 rpm for 3s and 5000 rpm for 25 s. After spinning for 10s, 100 $\mu$L anhydrous chlorobenzene or PCBM solution was directly injected onto the substrates. All of the perovskite films deposited with or without PCBM in the dripping solvent were annealed at 120°C for 10 min in the glove box. Finally, BCP (8 nm) and Ag (100 nm) were thermally evaporated on top of the device through a shadow mask, with an effective area of 0.10 cm$^2$.

**Characterization:** J-V curves were measured under AM 1.5G one sun illumination (100 mW/cm$^2$) with a solar simulator (Enlitech SS-F7-3A) equipped with a 300 W Xenon lamp and a Keithley 2400 source meter. The light intensity was calibrated by an NREL standard Si solar cell. During measurement, the cell was covered by a mask with a 0.1 cm$^2$ aperture. The external quantum efficiency (EQE) values were measured under ambient atmosphere at room temperature using an EQE system (Enlitech QE-R3011) containing a Xenon lamp, a monochromator, a Si detector for calibration, and a dual-channel power. The morphology of perovskite films was characterized by scanning electron microscopy (SEM, ZEISS Merlin) at a 5 KV accelerating voltage. The electrochemical impedance spectroscopy (EIS) measurements were performed on an electrochemical workstation (Zahnner PP211) with applied bias voltage of 0.7 V under dark. X-ray diffraction spectra of perovskite films was performed on a Bruker D8 Discover X-ray diffractometer with Cu Ka radiation (1.54Å). The absorbance spectra of perovskite films were measured by a UV-Vis-NIR spectrometer equipped with an integrating sphere (PerkinElmer Lambda 950). Steady-state and time-resolved PL spectra were measured using an Edinburgh FLS5 spectroscopy system, and pulsed laser excitation at 405 nm. Admittance spectroscopy was recorded by an electrochemical workstation (CHI660, China) over the frequency range of 1 MHz-1 Hz.

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There are no conflicts of interest to declare.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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