DOI: 10.1002/ ((please add manuscript number))

Full Paper

Triarylphosphine Oxide as Cathode Interfacial Material for Inverted Perovskite Solar Cells

Kai Wang, Marios Neophytou, Erkan Aydin, Mingcong Wang, Thomas Laurent, George T. Harrison, Thomas D. Anthopoulos, Jiang Liu, Wenzhu Liu, Michele De Bastiani, Jafar I. Khan, Frédéric Laquai and Stefaan De Wolf**

Dr. K. Wang, Dr. M. Neophytou, Dr. E. Aydin, Dr. M. Wang, Mr. T. Laurent, Dr. G. Harrison, Prof. T. D. Anthopoulos, Dr. J. Liu, Dr. W. Liu, Dr. M. Bastiani, Dr. J. Khan, Prof. F. Laquai and Prof. S. De Wolf

King Abdullah University of Science and Technology (KAUST), KAUST Solar Center (KSC), Physical Sciences and Engineering Division (PSE), Thuwal 23955-6900, Kingdom of Saudi Arabia

E-mail: kai.wang@kaust.edu.sa; stefaan.dewolf@kaust.edu.sa

Keywords: (*p-i-n* perovskite solar cell, interface engineering, organic molecule, cathode interlayer, semi-transparent solar cell)

Metal halide perovskite solar cells (PSCs) in the inverted planar *p-i-n* configuration often employ phenyl-C₆₁-butyric acid methyl ester (PC₆₁BM) as electron transport layer, onto which Ag is deposited as outer electrode. However, the energy offset between PC₆₁BM and Ag imposes an energy barrier for electron extraction, which reduces the performance of the device. In this work, to improve the contact quality of this stack, we introduced a small organic molecule (2-(1,10-phenanthroline-3-yl)naphthalen-6-yl)diphenylphosphine oxide (DPO) as a cathode interfacial material (CIM), inserted between PC₆₁BM and Ag. In devices with the indium tin oxide ITO/NiO_x/methylammonium lead iodide (MAPbI₃)/PC₆₁BM/CIM/Ag configuration, we find that this results in fill factor (FF) and short-circuit current density values (*J*_{SC}) that are up to ~34% and ~1 mA/cm² higher, respectively, compared to DPO-free control devices. Inserting additional thin ZnO nanoparticle layers between the PC₆₁BM and DPO layers further improved the contact quality, resulting in FF and *J*_{SC} values up to 79.8% and 21 mA/cm²,

respectively, leading to a power conversion efficiency (PCE) of 18.2%. Semi-transparent PSCs, utilizing DPO as an interlayer between the ITO and a ZnO nanoparticle buffer layer, were also realised. Resultant devices exhibit improved performance compared to DPO-free control devices. This proves that DPO withstands the sputtering of ITO, and may thus find application in perovskite-based tandem solar cells. We conclude thus that DPO acts as an excellent cathode modifier, opening new device-engineering opportunities for *p-i-n* PSCs, especially in their semi-transparent implementation.

1. Introduction

Organic-inorganic metal halide PSC have recently emerged as one of the most promising photovoltaic technologies, thanks to their unique properties such as high absorption coefficient, steep absorption onset, long exciton diffusion length and potential to combine such properties with low processing cost.^[1-3] Within a few years, the power conversion efficiency (PCE) of PSCs has been boosted from 3.8% to 23.7%.^[4] These record devices are mostly in the *n-i-p* configuration, where the perovskite (*i* layer) is deposited on the underlying electron transport layer (ETL, *n*-type).^[5-10] This configuration often employs mesoporous materials for the extraction of photo-generated electrons – a legacy of dye-sensitized technology. However, the mesoporous ETLs require high processing temperatures, which may limit its application range. Moreover, only a limited choice of materials is available for its ETLs and hole transport layers (HTL, *p*-type). In parallel, PSCs have also been fabricated in the inverted *p-i-n* architecture, namely *inverted*, where the perovskite is deposited on the underlying HTLs.^[11] Inverted PSCs are found more convenient in literature as they do not require any sintering step, making them suitable for manufacturing flexible devices as well as multi-junction solar cells.^[12-14] Notably, this configuration usually also features less hysteresis in its current-voltage response, thanks to better passivation of the electronic trap states at the perovskite surface by the employed ETLs (often fullerene derivatives, such as phenyl-C61-butyric acid methyl ester, PC₆₁BM).^[15-19]

To improve the performance of *p-i-n* PSCs, several strategies are currently being pursued, such as improving the optoelectronic properties of the HTLs and ETLs, compositional tuning of the perovskite absorber, and interfacial engineering.^[20-27] Examples of interfacial engineering are the modification of the band offsets at the perovskite/extraction layer interface to favor charge extraction, as well as decreasing non-radiative carrier recombination. Through this methodology, the long-term stability of the devices has also been improved in literature.^[28-29] Interfacial engineering can be used to modify the electronic properties of the *n*-contact stack of the devices as well. Indeed, the energy offset between the lowest unoccupied molecular orbital (LUMO) energy level of PC₆₁BM (~3.9 eV) and work function of the commonly used Ag cathode (~4.7 eV) represents a limiting factor to further improve the efficiency of *p-i-n* devices.^[30-32] This energy offset imposes an extraction barrier between PC₆₁BM and Ag, reducing the performance of the device. Moreover, Ag interaction with PC₆₁BM and Ag diffusion through the perovskite layer negatively affect the stability of the devices. To address this issue, many different types of CIMs, including inorganic metal oxides (*e.g.* ZnO,^[33] TiO₂,^[22, 34] Ti(Nb)O_x,^[10] SnO₂^[35]), metals and alkaline salts (*e.g.* Ca,^[36] Ba,^[37] LiF), polymers (*e.g.* PN4N,^[38] PPDIN6,^[39] PEIE^[40]) and organic small molecules (*e.g.* BCP,^[8, 41] PDINO,^[33] Bphen^[42]), have been studied either by using solution- or vacuum-based techniques. Organic small molecules have an inherent advantage for their ease of synthesis and purification, as well as their well-defined structure and better tolerance to moisture. Their solution process-ability makes them readily available for low-temperature and cost-efficient processing. Additionally, they have higher synthetic modularity than polymers, due to the symmetry requirements of the monomers used in poly-condensation reactions, as testified by the growing interest in organic photovoltaics based on non-fullerene acceptors.^[43-44] Therefore, chemical modification of the organic small-molecule structure is a straightforward route for interfacial engineering in PSCs. However, organic small-molecule interface materials that could lead to PCE>18% in planar *p-i-n* PSC are yet rarely reported.^[45-50]

In this work, we demonstrate that DPO can work as an effective, low cost, solution processed CIM. We tested DPO, sandwiched between PC₆₁BM and the Ag electrode, in PSCs with the ITO/NiO_x/MAPbI₃/PC₆₁BM/CIM/Ag device configuration. Inverted devices with DPO CIM result in an open circuit voltage (V_{OC}) of 1050 mV, a short-circuit current (J_{sc}) of 21.5 mA/cm², and a high fill factor (FF) of 79.7%, corresponding to a maximum PCE of 18.2% for the champion cell, whereas the control device without DPO CIM yields an average PCE of only 11.3±0.65%. Moreover, utilizing DPO as CIM on semi-transparent PSC, underneath of the transparent electrode, provided absolute 1.3 mA/cm² current gain. This proves that DPO can withstand ITO sputtering conditions, and making this material a promising candidate in perovskite-based tandem applications.

2. Results and Discussion

Figure 1a shows the chemical structure of the DPO molecule. **Figure 1b** exhibits the device stack of the fabricated opaque PSCs schematically. The cross-sectional SEM image in **Figure 1c** depicts that a well-defined layered planar structure is formed. Such device stack consists of a 25 nm compact NiO_x film and following 350 nm MAPbI₃ and 60 nm PC₆₁BM layers. Since the thickness of the DPO layers is <10 nm which is measured by spectroscopic ellipsometry as shown in **Figure S4**, it is not clearly visible in the SEM image.

Figure 1. (a) The molecular structure of DPO. (b) Device structure of the opaque PSCs. The arrow indicates the side of illumination. (c) Cross-sectional SEM image of the opaque PSC using DPO as CIM.

The energetic band alignment of the contact stacks is generally regarded as the most critical parameter governing the charge transfer processes in PSCs. **Figure 2a** shows the relative band edges of the individual layers of the studied device stack. As-prepared NiO_x films show a valence band maximum (VBM) of -5.4 eV, which matches well with that of the MAPbI₃ absorber layer (**Figure 2a**),^[17, 51] indicating the efficient charge transfer at the hole-collecting electrode. On the other hand, the work function (WF) mismatch between PC₆₁BM and Ag causes a potential barrier at their shared interface which is detrimental for device performance. Here, to overcome the inherent energy loss between PC₆₁BM and Ag cathode, thin layers of ZnO-np and DPO were inserted as CIM. We measured WF changes of Ag with and without DPO layer by ultraviolet photoelectron spectroscopy (UPS). As shown in **Figure 2b-d**, the secondary electron cut-off point was determined by linear extrapolation (black dashed lines) between the sharp decay and baseline and demonstrates a shift of ca. 1.24 eV upon addition of DPO. The work function is found to range from 4.6 ± 0.1 eV for Ag to 3.4 ± 0.1 eV with DPO. The analysis of the onset of the occupied states for the DPO/Ag spectrum by using a linear extrapolation of the first convoluted peak results in a VBM of 2.7 ± 0.1 eV. The lowering of the WF of the Ag cathode in the presence of DPO can reduce the barrier of PC₆₁BM/Ag interface, and thus enhance the electron extraction efficiency at the interface. As shown in earlier work, proper interfacial layer could reduce the work function by the formation of interfacial dipoles between the metal and the organic interfacial layer. This is likely related to a strong interaction exists at the interface between P=O and Ag, and also between rigid phenanthrolyl moiety and Ag, which can promote good electrical contact properties between DPO and Ag cathode.^[52-53] The VBM of ZnO (7.6 eV) is sufficient to block holes from the MAPbI₃ layer. The XRD pattern of MAPbI₃ (**Figure S1**) shows an intense signal corresponding to the perovskite alpha-phase without secondary phases, or PbI₂ traces, confirming the presence of well-crystallized films which are matching well with the crystalline structure in earlier reports.^[54-56]

UV-vis absorption spectra taken from MAPbI₃/PC₆₁BM/ZnO and MAPbI₃/PC₆₁BM/DPO stacks reveal that ZnO-np and DPO layers have a very high transparency compared to PC₆₁BM (**Figure S2-S3**). Such broadband transparency is of high importance for semitransparent PSCs, such as used in perovskite-based tandems, especially on their light-incident side.

Figure 2. (a) Relative band edges of the materials present in our fabricated devices. (b) Secondary electron cut-off region and (c) valence band region in UPS spectra.

J-V characteristics of the fabricated devices are shown in **Figure 3**, and their photovoltaic characteristics are listed in **Table 1**. The control device with PC₆₁BM/Ag as *n*-contact exhibits an average PCE of 11.3%, with a V_{OC} of 1030 mV, J_{SC} of 19.1 mA/cm², FF of 57.6% measured under reverse scan, with notable hysteresis. This low FF is mainly due to a high series resistance (R_s) of 10.8 Ω cm²; the shunt resistance (R_{sh}) is 0.7 k Ω cm² (**Figure S5**). This high series resistance likely is due to the inherent Schottky barrier present at the interface between PC₆₁BM and Ag. With the insertion of a ZnO layer between PC₆₁BM and Ag cathode, the average PCE increases to 15.0%, with a V_{OC} of 1030 mV, J_{SC} of 20.2 mA/cm², and FF of 72.3%. The series resistance (R_s) is now 5.7 Ω cm² and the shunt resistance (R_{sh}) is 2.9 k Ω cm² under reverse scan. The higher J_{SC} , FF, and R_{sh} values are indirect indicative of a pinhole-free interface. However, statistically these device architecture shows a substantial absolute PCE variation, expressed by standard deviations of ± 0.65 and $\pm 0.7\%$ in its PC₆₁BM and PC₆₁BM/ZnO implementation, respectively. To further explore the role of the CIM layer thickness, the effect of the solution concentration of the DPO was studied systematically. *J-V* characteristics of such devices (**Figure 3b** and **Table S1**) revealed that the optimum solution concentration is 1 mg/ml which

results in 5-6 nm DPO layer, measured on a polished crystalline silicon substrate by SE (**Figure S4**). After inserting the DPO layer, the average PCE increased to 16.5%, with a V_{OC} of 1040 mV, J_{SC} of 20.5 mA/cm², and FF of 77.3%. The devices with DPO exhibit negligible hysteresis compared to the reference PC₆₁BM device (**Figure S5**). The PCE improvement mainly results from the enhancement of FF, which, is most likely because of a better Ohmic contact. The dark current density of the solar cells with and without DPO is shown in **Figure 3d**, it exhibits the reduced R_s and enhanced R_{sh} with insertion of DPO. Besides, the dark current density of DPO based device under reverse bias was about one order of magnitude smaller than that of control device, suggesting the modified cathode interface can decrease the leakage current, which might aroused from the reduced charge recombination and improved electron transport by reducing the injection barrier at the cathode interface. To evaluate the effect of DPO on the electron transport process of device, we fabricated the electron only devices to investigate the PC₆₁BM/with or without DPO/Ag (**Figure 3e**). In comparison, a greatly higher current intensity is obtained upon introduction of DPO layer, confirming the improved electron transport through DPO modified cathode. To study the effect of DPO on the built-in potential (V_{bi}), we performed the capacitance-voltage (C - V) characteristics at 1kHz of the devices with and w/o DPO in the dark at room temperature. Normally, the junction capacitance shows bias dependence according to Mott-Schottky analysis, $C^{-2} = 2(V_{bi}-V)/(A^2q\epsilon\epsilon_0N)$, where C is capacitance, A is the device area, ϵ is the relative dielectric constant of the perovskite, ϵ_0 is the permittivity of vacuum, N is doping density of perovskite, V_{bi} is the built-in potential, V is the applied voltage, and q is the elementary charge. V_{bi} can be extracted from the intersection of the $(1/C^2)$ line with the horizontal axis. As shown in figure, the V_{bi} value shows negligible difference (0.93 V for the w/o device and 0.94 V for DPO based device), consistent with that no V_{oc} change observed in the solar devices (**Figure 3f**). It is of note that the combination of ZnO-np and DPO layers results in slightly better performance, compared to devices with only DPO as CIM (yielding an average PCE of 17.4%, V_{OC} of 1040 mV, J_{SC} of 21.0 mA/cm², and FF of 79.8%). The champion

device reaches up to 18.2% PCE, with a V_{OC} of 1040 mV, J_{SC} of 21.4 mA/cm^2 , and FF of 82.1%, which stands state-of-the-art performance in the NiO_x based inverted PSCs field (**Table S2**). Moreover, as seen in the box diagram of **Figure 3g**, the device which has DPO-modified contacts shows better reproducibility (with a lower standard deviation) than others. To validate the enhancement of J_{SC} for the DPO-based devices, external quantum efficiency (EQE) measurements were taken (**Figure 3h**). The integrated J_{SC} from the EQE spectra yielded J_{SC} values of 19.21 mA/cm^2 for the control device, 21.04 mA/cm^2 for the $\text{PC}_{61}\text{BM}/\text{DPO}$ device and 21.30 mA/cm^2 for the $\text{PC}_{61}\text{BM}/\text{ZnO}/\text{DPO}$ device respectively. These values are in a good agreement with those obtained from J - V measurements. The quantum efficiency of the DPO based devices is remarkably higher than that of the control device through the spectral perovskite absorption range, suggesting enhanced electron extraction and collection at the DPO/Ag interface,

Figure 3. (a) J - V characteristics of the planar PSCs of the reference devices, ZnO/Ag , DPO/Ag and $\text{ZnO}/\text{DPO}/\text{Ag}$ based devices. (b) J - V curves under illumination of AM 1.5 of the DPO

based PSCs with different concentration of the DPO solution. (c) Hysteresis test for the planar PSCs with optimal DPO interfacial layer with a scan rate of 100 mV^{-1} . (d) Dark J - V curves of corresponding solar cells. (e) Capacitance-voltage (C - V) characteristics based on Mott-Schottky analysis at 1k HZ for the devices. (f) Dark J - V curves of the devices with a configuration of ITO/SnO₂/PC₆₁BM/with or w/o DPO/Ag. (g) Statistics of PCE of reference devices, ZnO/Ag, DPO/Ag and ZnO/DPO/Ag based devices collected over 4 different batches (device parameters are collected from 25 individual solar cells) (h) EQE spectra for the corresponding solar cells of for the control device, PC₆₁BM/DPO device and PC₆₁BM/ZnO/DPO device respectively, and the J_{SC} values calculated from the EQE data. (i) Steady-state photocurrent and PCE of the ZnO/DPO based PSCs at V_{mpp} of 0.88V.

Table 1. The photovoltaic parameter with a standard variation of V_{OC} , J_{SC} , FF , and PCE of devices with MAPbI₃, measured at the reverse scan, results were collected from 20 devices for each condition.

Cathode configuration	V_{OC} [mV]	J_{SC} [mA/cm ²]	FF [%]	PCE_{ave} (PCE_{max}) [%]	R_s [$\Omega \text{ cm}^2$]	R_{sh} [k $\Omega \text{ cm}^2$]
PC ₆₁ BM/Ag	1030±20	19.1±0.59	57.6±0.44	11.3±0.65 (13.0)	10.8	0.7
PC ₆₁ BM/ZnO/Ag	1030±30	20.2±0.57	72.3±0.32	15.0±0.70 (16.3)	5.7	2.9
PC ₆₁ BM/DPO/Ag	1030±30	20.5±0.54	77.3±0.28	16.5±0.51 (17.5)	5.4	4.2
PC ₆₁ BM/ZnO/DPO/Ag	1040±20	21.0±0.42	79.8±0.22	17.4±0.38 (18.2)	4.1	4.5

considering the similar absorption spectra of MAPbI₃/ PC₆₁BM and MAPbI₃/PC₆₁BM/DPO layer (see **Figure S2**). We also performed stabilized current measurements under maximum power point conditions and found that DPO modified electrodes enable devices with enhanced light stability. We obtained a stabilized 17.9% PCE and photocurrent of 20.7 mA/cm^2 over 180 s (**Figure 3i**).

The surface morphology of the underlying layer is critical for the formation of high-quality contacts. To study the influence of various interface layers on the morphology of perovskite films, we performed atomic force microscopy (AFM) and scanning electron microscopy (SEM) measurement for the perovskite layer with and without PC₆₁BM, PC₆₁BM/ZnO, PC₆₁BM/DPO and PC₆₁BM/ZnO/DPO layers. The AFM images in **Figure 4** exhibit a root-mean-square (RMS) roughness of 6.5 nm for the pure MAPbI₃ film. The deposition of PC₆₁BM on top of MAPbI₃ dramatically reduces RMS roughness to 2.3 nm. Additional deposition of a ZnO-np film on top of perovskite/ PC₆₁BM layer increases significantly the RMS roughness, back to 6.5 nm. As shown in **Figure 4c**, the nanoparticles tend to aggregate on top of the perovskite/PC₆₁BM layer,

forming micron-sized island-like features with large surface roughness. In contrast, deposition of DPO on top of the perovskite/PC₆₁BM layer induces an even smoother surface with an RMS roughness of 1.4 nm, indicating efficient filling of the voids present on the PC₆₁BM surface. Similarly, DPO deposition reduces the surface roughness of PC₆₁BM/ZnO stack (**Figure 4e**). The good coverage of DPO layer likely resolves the non-ideal contact between Ag and PC₆₁BM, lowering the potential barrier.

Figure 4f shows a top-view SEM image of the related MAPbI₃ composite film. The MAPbI₃ film depicts a uniform and compact coverage with several hundred nanometers grain size. PC₆₁BM covers the perovskite film conformably. Consistently with the AFM results, **Figure 4h** confirms that ZnO on top of perovskite/PC₆₁BM causes a much rougher surface, which deteriorates device performance. **Figure 4i-j** shows that the DPO coating on perovskite/PC₆₁BM and perovskite/PC₆₁BM/ZnO layer gives a homogeneous and high-quality coverage on the film, in turn, leading to better contact with the Ag electrode, improving device performance. Moreover, we performed static water contact angle (θ) experiments to study the modification of the surface wettability by DPO. The pristine PC₆₁BM film displays an intensely hydrophobic surface with a θ value of 72.2°. Depositing DPO on top of PC₆₁BM significantly enhances the hydrophilicity with a θ value of 56.1° (**Figure S6**). To this end, Cao *et al.* demonstrated that increased hydrophilicity enhances the wettability and compatibility with the top metal cathode, which is beneficial to decrease the contact resistance at the cathode interface which, in turn, increases the FF.^[57]

Next we used steady-state photoluminescence (PL) and time-resolved PL to study the effect of DPO CIM insertion on the charge transport and recombination processes. **Figure S7** shows that PL intensity of pristine perovskite film dramatically decreased when PC₆₁BM coated. PL quenching is also observed for samples with additional deposition of DPO, as shown by time-resolved (TR) PL measurements. **Figure 5a** shows 2D pseudo-color transient PL spectra of MAPbI₃/PC₆₁BM and MAPbI₃/PC₆₁BM/DPO samples. Both films show the characteristic

perovskite PL peak at 771 nm. The PL decay process was parametrized by a bi-exponential decay function, $f(t) = \sum A_i \exp(-t/\tau_i) + B$, where A_i is the weight factor of each exponential decay function, τ_i is the decay time (inverse decay rate), and B a constant offset. The results are summarized in **Figure 5b** and **Table S3**. The PL decay of each sample can be described by a fast decay component (τ_1) and a slow decay component (τ_2), which have previously been shown to depend on the carrier transport to the interface layer and the perovskite's radiative charge recombination channel, respectively.^[35,58] For the perovskite/PC₆₁BM sample, the fast decay lifetime (τ_1) is 5.77 ns and the slow decay lifetime (τ_2) is 16.04 ns. The presence of DPO on top of the perovskite/PC₆₁BM layer changes these lifetimes to 5.20 and 14.83 ns, respectively. Based on this small variation in PL decay times for samples with and without DPO, we can conclude that the presence of DPO does not significantly alter aforementioned carrier decay processes, in other words does not have a negative impact on carrier extraction and recombination. This indicates there is no obvious interaction between perovskite/PCBM and DPO interface, which is in line with the increased device performance – especially the FF – is more related to the better contact of the electron-collecting DPO/Ag stack.

Figure 4. AFM image (5 $\mu\text{m} \times 5 \mu\text{m}$) of (a) perovskite film, (b) perovskite/PC₆₁BM film, (c) perovskite/PC₆₁BM/ZnO film, (d) perovskite/PC₆₁BM/DPO film and (e) perovskite/PC₆₁BM/ZnO/DPO film. The root-mean-square roughness (RMS) is indicated on the AFM images. SEM images of (f) perovskite film, (g) perovskite/PC₆₁BM film, (h) perovskite/PC₆₁BM/ZnO film, (i) perovskite/PC₆₁BM/DPO film and (j) perovskite/PC₆₁BM/ZnO/DPO film.

We also carried out a shelf-stability test on the devices without encapsulation in ambient conditions at $\sim 23^\circ\text{C}$ and under a relative humidity of $\sim 25\%$ with the cells stored in the dark. The cells' performance was then assessed at fixed time intervals before being stored again. **Figure 5c** shows the PCE decay versus exposure time for the control and DPO-based optimal devices. Notably, the degradation of the control device is very fast as it loses 80% of its initial PCE after 200 h. Meanwhile, the perovskite/PC₆₁BM/ZnO/DPO device retains approximately 80% of its initial PCE for almost 200 h, implying a better shelf stability. The perovskite/PC₆₁BM/ZnO device shows slightly slower degradation speed of the reference perovskite/PC₆₁BM device, while perovskite/PC₆₁BM/DPO device exhibits a better stability, retains $\sim 72\%$ of its initial PCE after 200h, close to the perovskite/PC₆₁BM/ZnO/DPO device (Figure S8). The chemical reaction between perovskite film and metal (*e.g.*, Ag) electrode can happen under humid environment or when in direct contact with each other, which is the major factor leading to the self-degradation of PSCs.^[59] The migrating halide ions I⁻ may corrode the Ag electrode, producing silver iodide (AgI). It has been reported ammonium based interlayer between PC₆₁BM and Ag could form Ag-N bond after device fabrication, and it eliminated after aging with the formation of N-I ion bond pair.^[46, 58, 60] Here, we argue that the presence of the DPO layer between Ag and PC₆₁BM layer could trap the moving I⁻ ions and suppress the reaction of Ag and I⁻ ion, hence preventing corrosion of the Ag electrode and improving the long-term device stability.

Figure 5. (a) Streak camera images of MAPbI₃/PC₆₁BM and MAPbI₃/PC₆₁BM/DPO samples deposited on quartz substrates. The images show the evolution of the spectra as a function of time excited at 532 nm (fluence = $2.5 \mu\text{J}/\text{cm}^2$, laser frequency = 1 kHz). (b) Time-resolved

photoluminescence spectra for perovskite/PC₆₁BM and perovskite/PC₆₁BM/DPO films. The initial carrier concentration was calculated as $5 \times 10^{17} \text{ cm}^{-3}$, calculated according to the quotation of $n = Fa/(hc/\lambda)$. F is the laser fluence decided by the pulse energy and the focus area. We neglected the surface reflection and assumed that each photon can excited one electron-hole pair. α is absorption coefficient, h is Plank constant, c is speed of light and λ is wavelength. (c) PCE decay of control device and DPO based device as a function of storage time in an ambient environment with low relative humidity (~25%).

In order to demonstrate the potential application of DPO CIM in high-performance device architectures such as perovskite-based tandem solar cells, we fabricated semi-transparent PSCs by replacing the evaporated metal electrode with a sputter-deposited ITO as sketched in **Figure 6a**. In such devices, the ZnO-np layer acts as a protection layer to sputter damage of the soft, underlying layers.^[61-62] Notably, inserting DPO between these ZnO-np layers and the ITO transparent electrodes enabled an absolute 1.3 mA/cm^2 current gain (**Figure 6b**), which is also confirmed by EQE measurements (**Figure 6c**). The corresponding device parameters are summarized in **Table 2**. The stabilized photocurrents of 19.2 and 18.2 mA/cm^2 are recorded over 600 s under voltage bias for perovskite cells with and without the DPO buffer layer, respectively (**Figure 6d**). Overall, the device characteristics reveal that DPO modification of the ITO/ZnO-np interface provides enhanced semi-transparent device performance. This underlines the promise of such interfacial layers for ultra-high performance devices such as perovskite-based tandem solar cells.

Figure 6. (a) Schematic drawing of the fabricated semi-transparent devices. (b) J - V characteristics of the device with and without DPO buffer layer. (c) EQE spectra together with integrated current density (18.7 and 16.9 mA/cm^2 for with DPO and w/o DPO based devices, respectively). (d) Stabilized J_{SC} values of the devices at 0.88 V and 0.80 V for the devices with DPO and w/o DPO, respectively.

Table 2. The photovoltaic parameter of the semi-transparent perovskite solar cells with and without DPO.

	V_{oc} [mV]	J_{sc} [mA/cm^2]	FF [%]	PCE [%]
with DPO (R)	1070	19.1	73.6	15.0
with DPO (F)	1070	19.2	72.2	14.8
w/o DPO (R)	1060	17.8	71.9	13.6
w/o DPO (F)	1060	17.9	70.3	13.5

3. Conclusions

In summary, we successfully fabricated efficient p - i - n MAPbI₃-based perovskite solar cells using DPO as an n -contact interfacial material, inserted between PC₆₁BM and the Ag electrode. The PCE is largely improved from 11.3 to 16.5% using the DPO interfacial layer. Combining DPO with ZnO-np layer enabled further PCE improvement, with the latter reaching a maximum

value of 18.2% thanks to notable enhancement on FF (from 57 to 79.8%). The reason for this improvement is likely linked to the lowering of interface barrier due to the presence of DPO, which leads to improved electron extraction at the PC₆₁BM/Ag interface, and thus a lower contact resistivity. Besides, the DPO-based devices also show higher device stability than the control devices. Finally, we find that the DPO interfacial layers effectively withstand ITO sputtering, and provide enhanced J_{SC} on semi-transparent PSCs. This result may lead to improved PCE for perovskite-based tandem solar cells.

4. Experimental Section

Material Preparation. Unless stated otherwise, all materials were purchased and used without further treatment. DPO was purchased from 1-Material (Canada). PbI₂ was purchased from TCI (Japan). Methylammonium Iodide (CH₃NH₃I) was purchased from GreatCell Solar (Australia). 6,6-phenyl C₆₁ butyric acid methyl ester (PC₆₁BM) was purchased from Xi'an Polymer Light Technology Cory. The 1.2 M MAPbI₃ perovskite precursor solution was prepared by mixing CH₃NH₃I and PbI₂ with a molar ratio of 1:1 dissolved in dimethylformamide (DMF) and dimethyl sulfoxide (DMSO) (4:1 by volume) and stirred overnight at room temperature in the N₂ filled glove box (<1 ppm of H₂O and O₂). The solution of PC₆₁BM was prepared in chlorobenzene (20 mg/ml), and DPO was prepared in anhydrous isopropanol with different concentrations as explained in the main text. ZnO-np is purchased from Avantama (Switzerland). For the *p* layer, NiO_x sol-gels were prepared as follows: Nickel acetate tetrahydrate was dispersed in 2-methoxyethanol with a concentration of 50 mg/ml to get a dark green solution; then ethanolamine was slowly added into the solution until precipitation. The obtained green solution was heated at 50 °C for 20 min. The NiO_x precursors were filtered by 0.45µm PTFE syringe filter before spin coating.

Device fabrication. The patterned ITO coated glass substrates (15 ohm/sq., Xin-Yan Technologies, China) were ultrasonically cleaned with toluene, acetone, and isopropanol for 10 min, then rinsed with water prior to UV-ozone treatment for 10 min. Then, NiO_x sol-gels were spin coated at 3000 rpm on cleaned ITO substrate at room temperature. Immediately after, deposited films were annealed at 300 °C for 20 min in ambient air. The NiO_x-coated ITO glasses were then transferred into an N₂ filled glovebox (<1 ppm of H₂O and O₂). As-prepared perovskite solution was spin-coated on top of the NiO_x layer at 4000 rpm for 30 s with an acceleration of 1000 rpm/s. While spinning, chlorobenzene (100 µl) was dropped on the substrate, after six seconds. Soon after, films were then annealed at 100 °C for 10 min. After cooling down to room temperature, the PC₆₁BM solution was deposited on top of the perovskite film via spin-coating at 3000 rpm for 30 s. Then, ZnO-np or DPO solution was spin-coated on top of PC₆₁BM films. Devices were completed by the thermal evaporation of a 100 nm silver contacts at 10⁻⁶ m Torr. Measured opaque and semi-transparent solar cells had 0.10 and 0.16 cm² active area, respectively. Opaque devices were measured without an aperture. For semi-transparent device fabrication, the NiO_x layer was deposited on pre-cleaned ITO substrates via RF magnetron sputtering with high uniformity as defined in the previous study.^[56] All the sequent layer deposition keeps the same recipe as the opaque devices, an ultra-thin layer of DPO was spin-coated at 5000 rpm for 30 seconds from a 1 mg/ml solution in isopropanol. 100 nm of ITO was sputtered as a transparent electrode at 1.95 W/cm² power density and 1.96 % O₂ partial pressure.

Characterization methods. The current-voltage (*J-V*) curves were measured using a solar simulator (ABET Technologies Sun 3000) with a source meter (Keithley 2420) at 100 mW cm⁻² illumination (AM 1.5G). The light intensity was calibrated by a c-Si reference cell (RERA Solutions, calibrated at Radboud University Nijmegen). Scanning rate was 100 mV s⁻¹ and voltage step was 10 mV. No preconditioning protocol is used before the *J-V* measurements. The reverse scan was from 1.2 to -0.1 V and the forward scan was from -0.1 to 1.2 V. X-Ray

diffraction (XRD) analysis was performed on a Bruker D8 Advance X-ray powder diffractometer using the Cu-K α radiation ($\lambda = 1.54071 \text{ \AA}$). Atomic force microscope (AFM) from Bruker was used to image the perovskite absorber layers morphology. Surface and cross-sectional images of the samples were taken by a Carl Zeiss AURIGA CrossBeam workstation using in-lens detectors. A 5 kV voltage was used to accelerate the electrons, and the working distance was 5 mm. The surface work function of DPO layer was measured by ultraviolet photoelectron spectroscopy (UPS). Absorption and transmission spectra were recorded by a Perkin-Elmer Lambda 950 with integrating sphere. EQE spectra were gained through the measurement of solar cell spectra response measurement system QE-R3011 (Enli Technology Ltd., Taiwan). Ultraviolet photo-electron (UPS) measurements were performed in an Omicron multi-probe UHV chamber equipped with a ISE-5 cold cathode ion gun for sputter cleaning (Ar^+) a monochromated Al K α 1486.29 eV X-ray (0.75 mm diameter spot) source and a hemispherical electron analyzer (Sphera II) with photo-electrons collected at 90 degrees with respect to the sample plane. The UPS source was a non-attenuated He(1) lamp (500 V, 90 mA, 5×10^2 mbar) of energy 21.22 eV. The analyzer system's Fermi level was determined using a clean evaporated silver sample (carbon below XPS noise level), and the sample placed in electrical contact by mounting with tight Ta clips to the sample holder. All UPS spectra were recorded with an analyzer spot of 60 μm , diameter and constant analyzer retarding pass energy of 5 eV at 0.01 eV/s sweep rate. The secondary electron cut-off and the valence band onset were determined by linear extrapolation from the slope of onsets inter-section with the baseline. A high-resolution Hamamatsu streak camera system (Hamamatsu, C10910) was used for time-resolved photoluminescence (TRPL) measurements. Our pump source was a picosecond pulse laser operating at 532 nm with a repetition rate of 1 kHz. Then it was focused to pump the perovskite samples which were placed in a sealed nitrogen chamber to prevent any changes due to the exposure to oxygen and humidity. The PL emission was spectrally and temporally resolved using a spectrograph and streak camera system.

Supporting Information

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

Acknowledgements

The research reported in this publication was supported by funding from King Abdullah University of Science and Technology (KAUST) under award no. OSR - CARF URF/1/3079 - 33 - 01.

Received: ((will be filled in by the editorial staff))

Revised: ((will be filled in by the editorial staff))

Published online: ((will be filled in by the editorial staff))

References

- [1] A. Kojima, K. Teshima, Y. Shirai, T. Miyasaka, *J. Am. Chem. Soc.* **2009**, *131*, 6050.
- [2] N. Jeon, J. Noh, W. Yang, Y. Kim, S. Ryu, J. Seo, S. Seok, *Nature* **2015**, *517*, 476.
- [3] W. Yang, B. Park, E. Jung, N. Jeon, Y. Kim, D. Lee, S. Shin, J. Seo, E. Kim, J. Noh, S. Seok, *Science* **2017**, *356*, 1376.
- [4] N. Jeon, H. Na, E. Jung, T. Yang, Y. Lee, G. Kim, H. Shin, S. Seok, J. Lee, J. Seo, *Nat. Energy* **2018**, *3*, 682.
- [5] M. Michael, J. Lee, T. Miyasaka, T. Murakami, H. J. Snaith, *Science* **2012**, *338*, 643.
- [6] H. Jung, N. G. Park, *Small* **2015**, *11*, 10.
- [7] L. Meng, J. You, T. Guo, Y. Yang, *Acc. Chem. Res.* **2016**, *49*, 155.
- [8] X. Zheng, B. Chen, J. Dai, Y. Fang, Y. Bai, Y. Lin, H. Wei, X. Zeng, J. Huang, *Nat. Energy* **2017**, *2*, 17102.
- [9] D. Luo, Z. Wang, A. Sadhanala, Q. Hu, R. Su, R. Shivanna, G. Trindade, J. Watts, Z. Xu, T. Liu, K. Chen, F. Ye, P. Wu, L. Zhao, J. Wu, Y. Tu, Y. Zhang, X. Yang, W. Zhang, R. Friend, Q. Gong, H. Snaith, R. Zhu, *Science* **2018**, *360*, 1442.
- [10] W. Chen, Y. Yue, J. Liu, W. Zhang, X. Yang, H. Chen, E. Bi, I. Ashraful, M. Grätzel, L. Han, *Science* **2015**, *350*, 944.

- [11] N. Wijeyasinghe, A. Regoutz, F. Eisner, T. Du, L. Tseteris, Y. Lin, H. Faber, P. Pattanasattayavong, J. Li, F. Yan, M. McLachlan, D. Payne, M. Heeney, T. D. Anthopoulos, *Adv. Funct. Mater.* **2017**, 27, 1701818.
- [12] B. Chen, Y. Bai, Z. Yu, T. Li, X. Zheng, Q. Dong, L. Shen, M. Boccard, A. Gruverman, Z. Holman, J. Huang, *Adv. Energy Mater.* **2016**, 6, 1601128.
- [13] X. Yin, P. Chen, M. Que, Y. Xing, W. Que, C. Niu, J. Shao, *ACS nano* **2016**, 10, 3630.
- [14] C. Sun, Z. Wu, H. Yip, H. Zhang, X. Jiang, Q. Xue, Z. Hu, Y. Shen, M. Wang, F. Huang, Y. Cao, *Adv. Energy Mater.* **2016**, 6, 1501534.
- [15] J. H. Heo, H. Han, D. Kim, T. K. Ahn, S. H. Im, *Energy Environ. Sci.* **2015**, 8, 1602.
- [16] P.-W. Liang, C.-C. Chueh, S. T. Williams, A. K. Y. Jen, *Adv. Energy Mater.* **2015**, 5, 1402321.
- [17] S. Ye, W. Sun, Y. Li, W. Yan, H. Peng, Z. Bian, Z. Liu, C. Huang, *Nano lett.* **2015**, 15, 3723.
- [18] C. Bi, Q. Wang, Y. Shao, Y. Yuan, Z. Xiao, J. Huang, *Nat. Commun.* **2015**, 6, 7747.
- [19] T. Liu, K. Chen, Q. Hu, R. Zhu, Q. Gong, *Adv. Energy Mater.* **2016**, 6, 1600457.
- [20] W. Yu, F. Li, H. Wang, E. Alarousu, Y. Chen, B. Lin, L. Wang, M. Hedhili, Y. Li, K. Wu, X. Wang, O. Mohammed, T. Wu, *Nanoscale* **2016**, 8, 6173.
- [21] Y. Bai, Q. Dong, Y. Shao, Y. Deng, Q. Wang, L. Shen, D. Wang, W. Wei, J. Huang, *Nat. Commun.* **2016**, 7, 12806.
- [22] P. Docampo, J. M. Ball, M. Darwich, G. E. Eperon, H. J. Snaith, *Nat. Commun.* **2013**, 4, 2761.
- [23] H. Chen, W. Fu, C. Huang, Z. Zhang, S. Li, F. Ding, M. Shi, C.-Z. Li, A. K. Y. Jen, H. Chen, *Adv. Energy Mater.* **2017**, 1700012.
- [24] X. Huang, K. Wang, C. Yi, T. Meng, X. Gong, *Adv. Energy Mater.* **2016**, 6, 1501773.
- [25] P. W. Liang, C. Y. Liao, C. C. Chueh, F. Zuo, S. T. Williams, X. K. Xin, J. Lin, A. K. Jen, *Adv. Mater.* **2014**, 26, 3748.

- [26] J. Peng, J. I. Khan, W. Liu, E. Ugur, T. Duong, Y. Wu, H. Shen, K. Wang, H. Dang, E. Aydin, X. Yang, Y. Wan, K. J. Weber, K. R. Catchpole, F. Laquai, S. De Wolf, T. P. White, *Adv. Energy. Mater.* **2018**, 8, 1801208.
- [27] M. De Bastiani, E. Aydin, T. Allen, D. Walter, A. Fell, J. Peng, N. Gasparini, J. Troughton, D. Baran, K. Weber, T. P. White, S. De Wolf, *Adv. Electron. Mater.* **2019**, 5, 1800500.
- [28] C. Cui, Y. Li, Y. Li, *Adv. Energy Mater.* **2016**, 1601251.
- [29] W. Deng, X. Liang, P. S. Kubiak, P. J. Cameron, *Adv. Energy Mater.* **2018**, 8, 1701544.
- [30] Q. Wang, Q. Dong, T. Li, A. Gruverman, J. Huang, *Adv. Mater.* **2016**, 28, 6734.
- [31] C.-C. Chueh, C.-Z. Li, A. K. Y. Jen, *Energy Environ. Sci.* **2015**, 8, 1160.
- [32] H. Kim, K.-G. Lim, T.-W Lee, *Energy Environ. Sci.* **2016**, 9, 12-30.
- [33] J. Min, Z.-G. Zhang, Y. Hou, Q. Ramirez, T. Przybilla, C. Bronnbauer, F. Guo, K. Forberich, H. Azimi, T. Ameri, E. Spiecker, Y. Li, C. J. Brabec, *Chem. Mater.* **2014**, 27, 227.
- [34] Y. Yu, R. S. Chiang, H. Hsu, C. C. Yang, C. P. Chen, *Nanoscale* **2014**, 6, 11403.
- [35] Z. Zhu, Y. Bai, X. Liu, C. C. Chueh, S. Yang, A. K. Jen, *Adv. Mater.* **2016**, 28, 6478.
- [36] A. T. Barrows, A. J. Pearson, C. K. Kwak, A. Dunbar, A. R. Buckley, D. G. Lidzey, *Energy Environ. Sci.* **2014**, 7, 2944.
- [37] L. Gil-Escrig, C. Momblona, M. Sessolo, H. J. Bolink, *J. Mater. Chem. A* **2016**, 4, 3667.
- [38] Q. Xue, Z. Hu, J. Liu, J. Lin, C. Sun, Z. Chen, C. Duan, J. Wang, C. Liao, W. M. Lau, F. Huang, H.-L. Yip, Y. Cao, *J. Mater. Chem. A* **2014**, 2, 19598.
- [39] J. Li, Q. Dong, N. Li, L. Wang, *Adv. Energy Mater.* **2017**, 7, 1602922.
- [40] J. Werner, L. Barraud, A. Walter, M. Bräuninger, F. Sahli, D. Sacchetto, N. Tétreault, B. Paviet-Salomon, S.-J. Moon, C. Allebé, M. Despeisse, S. Nicolay, S. De Wolf, B. Niesen, C. Ballif, *ACS Energy Lett.* **2016**, 1, 474.
- [41] Y. Lin, L. Shen, J. Dai, Y. Deng, Y. Wu, Y. Bai, X. Zheng, J. Wang, Y. Fang, H. Wei, W. Ma, X. C. Zeng, X. Zhan, J. Huang, *Adv. Mater.* **2017**, 1604545.

- [42] L.-L. Jiang, S. Cong, Y.-H. Lou, Q.-H. Yi, J.-T. Zhu, H. Ma, G.-F. Zou, *J. Mater. Chem. A* **2016**, *4*, 217.
- [43] C. B. Nielsen, S. Holliday, H. Y. Chen, S. J. Cryer, I. McCulloch, *Acc. Chem. Res.* **2015**, *48*, 2803.
- [44] Y. Lin; X. Zhan, *Adv. Energy Mater.* **2015**, *5*, 1501063.
- [45] A. Kara, G. Oylumluoglu, M. Z. Yigit, M. Can, J. J. Kim, E. K. Burnett, G. Arellano, S. Buyukcelebi, F. Ozel, O. Usluer, A. L. Briseno, M. Kus, *ACS Appl. Mater. Interfaces* **2018**, *10*, 30000.
- [46] C. Wang, P. Liu, H. Ju, Q. Yuan, D. Han, Y. Wang, D. Y. Zhou, L. Feng, *ACS Appl. Mater. Interfaces* **2018**, *10*, 15933.
- [47] Y. Li, Y. Zhao, Q. Chen, Y. M. Yang, Y. Liu, Z. Hong, Z. Liu, Y. T. Hsieh, L. Meng, Y. Li, Y. Yang, *J. Am. Chem. Soc.* **2015**, *137*, 15540.
- [48] Z. Zhou, S. Pang, Z. Liu, H. Xu, G. Cui, *J. Mater. Chem. A* **2015**, *3*, 19205.
- [49] F. Wu, W. Gao, H. Yu, L. Zhu, L. Li, C. Yang, *J. Mater. Chem. A* **2018**, *6*, 4443.
- [50] J. Miao, Z. Hu, M. Liu, A. Umair, O. Goto, W. Lu, T. Yang, Y. Liang, H. Meng, *Org. Electron.* **2018**, *52*, 200.
- [51] Z. Yin, Q. Yao, X. Dai, Y. Zhou, Y. Zhang, Y. Zhou, S. Luo, J. Li, N. Wang, H. Lin, *ACS Appl. Mater. Interfaces* **2017**, *9*, 2439.
- [52] H. Zhang, W.-Y. Tan, S. Fladischer, L. Ke, T. Ameri, N. Li, M. Turbiez, E. Spiecker, X.-H. Zhu, Y. Cao, C. J. Brabec, *J. Mater. Chem. A* **2016**, *4*, 5032.
- [53] W.-Y. Tan, R. Wang, M. Li, G. Liu, P. Chen, X.-C. Li, S.-M. Lu, H. L. Zhu, Q.-M. Peng, X.-H. Zhu, W. Chen, W. C. H. Choy, F. Li, J. Peng, Y. Cao, *Adv. Funct. Mater.* **2014**, *24*, 6540.
- [54] J. Cao, H. Yu, S. Zhou, M. Qin, T.-K. Lau, X. Lu, N. Zhao, C.-P. Wong, *J. Mater. Chem. A* **2017**, *5*, 11071.

- [55] E. Ugur, A. D. Sheikh, R. Munir, J. I. Khan, D. Barrit, A. Amassian, F. Laquai, *ACS Energy Lett.* **2017**, *2*, 1960.
- [56] E. Aydin, J. Troughton, M. De Bastiani, E. Ugur, M. Sajjad, A. Alzahrani, M. Neophytou, U. Schwingenschlögl, F. Laquai, D. Baran, S. De Wolf, *ACS Applied Energy Materials* **2018**, *1*, 6227.
- [57] G. Chen, F. Zhang, M. Liu, J. Song, J. Lian, P. Zeng, H.-L. Yip, W. Yang, B. Zhang, Y. Cao, *J. Mater. Chem. A* **2017**, *5*, 17943.
- [58] W. Chen, G. Zhang, L. Xu, R. Gu, Z. Xu, H. Wang, Z. He, *Materials Today Energy* **2016**, *1*, 10.
- [59] Y. Kato, L. K. Ono, M. V. Lee, S. Wang, S. R. Raga Y. Qi, *Adv. Mater. Interfaces* **2015**, *2*, 1500195.
- [60] M. De Bastiani, G. Dell'Erba, M. Gandini, V. D'Innocenzo, S. Neutzner, A. R. S. Kandada, G. Grancini, M. Binda, M. Prato, J. M. Ball, M. Caironi, A. Petrozza, *Adv. Energy Mater.* **2016**, *6*, 1501453.
- [61] K. A. Bush, C. D. Bailie, Y. Chen, A. R. Bowring, W. Wang, W. Ma, T. Leijtens, F. Moghadam, M. D. McGehee, *Adv. Mater.* **2016**, *28*, 3937.
- [62] E. Aydin, M. De Bastiani, X. Yang, M. Sajjad, F. Aljamaan, Y. Smirnov, M. N. Hedhili, W. Liu, T. G. Allen, L. Xu, E. Van Kerschaver, M. Morales-Masis, U. Schwingenschlögl, S. De Wolf, *Adv. Funct. Mater.* **2019**, 1901741.

The small organic molecule DPO is explored as cathode interfacial material to reduce the extraction barrier between PC₆₁BM and Ag. With the better contact quality thanks to this molecule, both opaque and semi-transparent *p-i-n* perovskite solar cell achieve improved performance and stability.

Keyword: *p-i-n* perovskite solar cell, interface engineering, organic molecule, cathode interlayer, semitransparent solar cell

Kai Wang,* Marios Neophytou, Erkan Aydin, Mingcong Wang, Thomas Laurent, George T. Harrison, Thomas D. Anthopoulos, Jiang Liu, Wenzhu Liu, Michele De Bastiani, Jafar I. Khan, Frédéric Laquai and Stefaan De Wolf*

Triarylphosphine Oxide as Cathode Interfacial Material for Inverted Perovskite Solar Cells

Supporting Information

Triarylphosphine Oxide as Cathode Interfacial Material for Inverted Perovskite Solar Cells

Kai Wang, Marios Neophytou, Erkan Aydin, Mingcong Wang, Thomas Laurent, George T. Harrison, Thomas D. Anthopoulos, Jiang Liu, Wenzhu Liu, Michele De Bastiani, Jafar I. Khan, Frédéric Laquai and Stefaan De Wolf**

Figure S1. XRD patterns of the glass/NiO_x/MAPbI₃ samples.

Figure S2. UV-Vis absorption spectra of perovskite, perovskite/PC₆₁BM, perovskite/PC₆₁BM/ZnO and perovskite/PC₆₁BM/DPO films.

Figure S3. The transmittance (T) and absorbance (A) spectra of the DPO film, measured with an integrating sphere.

Figure S4. The thickness of DPO layer measured by ellipsometer. The concentration of DPO solution is 1 mg/ml and it was spin-coated on Si substrate.

Figure S5. Hysteresis test for the planar PSCs of (a) ITO/NiO_x/MAPbI₃/PC₆₁BM/Ag, (b) ITO/NiO_x/MAPbI₃/PC₆₁BM/ZnO/Ag and (c) ITO/NiO_x/MAPbI₃/PC₆₁BM/DPO/Ag.

Figure S6. Static water contact angle images of (a) perovskite/PC₆₁BM film and (b) perovskite/PC₆₁BM/DPO film.

Figure S7. Room temperature steady-state photoluminescence spectra for perovskite film, perovskite/PC₆₁BM and perovskite/PC₆₁BM/DPO films.

Figure S8. PCE decay of control device and ZnO based device (a) and DPO based device (b) as a function of storage time in an ambient environment with low relative humidity (~25%).

Table S1. The average photovoltaic parameter of the solar cells with DPO deposited from its isopropanol solutions with different concentrations (reverse scan). Thickness values represent SE results.

DPO (wt%)	V _{OC} [V]	J _{SC} [mA/cm ²]	FF [%]	PCE [%]
0	1.03	19.3	57.5	11.6
0.25 (3-4 nm)	1.02	20.4	70.2	14.6
0.75 (4-5 nm)	1.03	21.0	74.4	15.9
1 (5-6 nm)	1.04	20.8	77.2	16.6
1.5 (7-8 nm)	1.05	19.7	73.7	15.3
2.5 (9-10 nm)	1.04	19.4	45.9	8.9

Table S2. Summary of different NiO_x-based perovskite solar cells in this work and literatures

Device configuration	V _{OC} [V]	J _{SC} [mA/cm ²]	FF [%]	PCE [%]	Refs.
ITO/NiO/MAPbI ₃ /PC ₆₁ BM/ZnO/DPO/Ag	1.05	21.6	80.2	18.2	this work
ITO/NiO/MAPbI ₃ /C60/Bis-C60/Ag	1.03	21.8	78	17.6	S1
ITO/NiO(NPs)/MAPbI ₃ /PC ₆₁ BM/Ag	1.04	21.2	75	16.5	S2
ITO/NiO/MAPbI ₃ /ZnO/Al	1.01	21.0	76	16.1	S3
ITO/NiO/PEDOT/MAPbI ₃ /PC ₆₁ BM/Ag	1.04	20.1	72	15.1	S4
ITO/NiO(ALD)/PEDOT/MAPbI ₃ /PC ₆₁ BM/Ag	1.02	21.1	73	15.6	S5
ITO/NiO/DEA/MAPbI ₃ /C ₆₀ /PN4N/Ag	1.13	20.4	80	18.1	S6
ITO/NiO/MAPbI ₃ /PC ₆₁ BM/Ag	1.09	20.2	74	16.3	S7
ITO/NiO-UVO(NPs)/MAPbI ₃ /PCBM/BCP/Ag	1.03	20.6	74	15.9	S8
ITO/NiO/FA _x PEA _{1-x} PbI ₃ /PCBM/bis-C ₆₀ /Ag	1.03	21.7	76	17.2	S9
ITO/ Cu-NiO/MAPbI ₃ /C ₆₀ /BCP/Ag	1.12	22.2	80	20.1	S10
ITO/PLD-NiO/MAPbI ₃ /PCBM/LiF/Al	1.06	20.2	81	17.3	S11
ITO/ NiO/MAPbI ₃ /PCBM/LiF/Al	1.03	19.0	69	13.4	S12
ITO/ sputter-NiO/MAPbI ₃ /PCBM/BCP/Ag	1.08	20.7	79	17.6	S6

Table S3. Summary of lifetime parameter from Time-Resolved PL spectra by fitting with bi-exponential decay function.

$$f(t) = \sum A_i \exp(-t/\tau_i) + B$$

	τ_1 (ns)	A_1 (%)	τ_2 (ns)	A_2 (%)	τ_{avg} (ns)
Perovskite/PC ₆₁ BM	5.77	70.2	16.04	28.2	11.16
Perovskite/ PC ₆₁ BM/DPO	5.20	68.3	14.83	28.9	10.44

τ_{avg} is calculated from the equation $\tau_{\text{avg}} = \frac{\sum A_i \tau_i^2}{\sum A_i \tau_i}$

References

- [S1] H. Zhang, J. Cheng, F. Lin, H. He, J. Mao, K. S. Wong, A. K. Y. Jen, W. C. H. Choy, *ACS Nano* **2016**, *10*, 1503.
- [S2] J. Ciro, D. Ramírez, M. A. Mejía Escobar, J. F. Montoya, S. Mesa, R. Betancur, F. Jaramillo, *ACS Appl. Mater. Interfaces* **2017**, *9*, 12348.
- [S3] J. You, L. Meng, T.-B. Song, T.-F. Guo, Y. (Michael) Yang, W.-H. Chang, Z. Hong, H. Chen, H. Zhou, Q. Chen, Y. Liu, N. De Marco, Y. Yang, *Nat. Nanotechnol.* **2015**, *11*, 75.
- [S4] I. J. Park, M. A. Park, D. H. Kim, G. Do Park, B. J. Kim, H. J. Son, M. J. Ko, D. K. Lee, T. Park, H. Shin, N. G. Park, H. S. Jung, J. Y. Kim, *J. Phys. Chem. C* **2015**, *119*, 27285.
- [S5] S. Seo, I. J. Park, M. Kim, S. Lee, C. Bae, H. S. Jung, N.-G. Park, J. Y. Kim, H. Shin, *Nanoscale* **2016**, *8*, 11403.
- [S6] Q. Xue, Y. Bai, M. Liu, R. Xia, Z. Hu, Z. Chen, X. F. Jiang, F. Huang, S. Yang, Y. Matsuo, H. L. Yip, Y. Cao, *Adv. Energy Mater.* **2017**, *7*, 1602333.
- [S7] X. Yin, J. Liu, J. Ma, C. Zhang, P. Chen, M. Que, Y. Yang, W. Que, C. Niu, J. Shao, *J. Power Sources* **2016**, *329*, 398.
- [S8] J. Kim, H. R. Lee, H. P. Kim, T. Lin, A. Kanwat, A. R. bin Mohd Yusoff, J. Jang, *Nanoscale* **2016**, *8*, 9284.
- [S9] N. Li, Z. Zhu, C. C. Chueh, H. Liu, B. Peng, A. Petrone, X. Li, L. Wang, A. K. Y. Jen, *Adv. Energy Mater.* **2017**, 1601307.
- [S10] W. Chen, Y. Wu, J. Fan, A. B. Djurisić, F. Liu, H. Tam, A. Ng, C. Surya, W. Chan, D.

Wang, Z. He, *Adv. Energy Mater.* **2017**, 1703519.

[S11] J. H. Park, J. Seo, S. Park, S. S. Shin, Y. C. Kim, N. J. Jeon, H. W. Shin, T. K. Ahn, J. H. Noh, S. C. Yoon, C. S. Hwang, S. Il Seok, *Adv. Mater.* **2015**, 27, 4013.

[S12] U. Kwon, B. Kim, D. Nguyen, J. Park, N. Ha, S. Kim, S. Ko, S. Lee, D. Lee, H. Park, *Sci. Rep.* **2016**, 6, 30759.