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# Sputtered NiO Interlayer for Improved Self-Assembled Monolayer Coverage and Pin-Hole Free Perovskite Coating for Scalable Near-Infrared-Transparent Perovskite and 4-Terminal All-Thin-Film Tandem Modules

Radha K. Kothandaraman, Severin Siegrist, Marion Dussouillez, Maximillian Krause, Huagui Lai, Johnpaul K. Pious, Shiro Nishiwaki, Evgeniia Gilshtein, André Müller, Antonio Cabas Vidani, Sandra Jenatsch, Beat Ruhstaller, Quentin Jeangros, Romain Carron, Ayodhya N. Tiwari, and Fan Fu\*

The use of carbazole-based self-assembled monolayer (SAM) as a hole transport layer (HTL) has led to the efficiency advancement in p-i-n perovskite solar cells (PSCs). However, PSCs with SAM HTL display a large spread in device performance even on small-area substrates owing to poor SAM surface coverage and dewetting of the perovskite ink. Efforts to improve the uniformity in device performance of SAM-based PSCs have been confined to spin-coating method, which lacks high-throughput capabilities and leads to excessive material wastage. Herein, a scalable bilayer HTL stack with sputtered NiO and blade-coated SAM is utilized to achieve improved SAM coverage and accomplish uniform coating of perovskite absorber on 5 cm  $\times$  5 cm substrates. Fully scalable p-*i*-n PSCs with efficiency close to 19% with a minimal spread in device performance are achieved. To showcase the upscaling potential, near-infrared-transparent perovskite mini-modules with efficiency close to 15% and 13% are achieved on an aperture area of 2.56 and 12.96 cm<sup>2</sup>. Together with low-bandgap (1.0-1.1 eV) Cu(In,Ga)Se<sub>2</sub> (CIGS) mini-modules, the first fully scalable 4-terminal perovskite-CIGS tandem mini-module with an efficiency of 20.5% and 16.9% on an aperture area of 2.03 and 10.23 cm<sup>2</sup> is demonstrated.

R. K. Kothandaraman, S. Siegrist, M. Krause, H. Lai, J. K. Pious, S. Nishiwaki, E. Gilshtein, A. Müller, R. Carron, A. N. Tiwari, F. Fu Laboratory for Thin Films and Photovoltaics

Empa-Swiss Federal Laboratories for Materials Science and Technology Überlandstrasse 129, 8600 Dübendorf, Switzerland E-mail: Fan.Fu@empa.ch

M. Dussouillez, Q. Jeangros Sustainable Energy Center Centre Suisse d'Electronique et de Microtechnique (CSEM) Jaquet-Droz 1, 2002 Neuchâtel, Switzerland

A. Cabas Vidani, S. Jenatsch, B. Ruhstaller Fluxim AG

Katharina-Sulzer-Platz 2, 8400 Winterthur, Switzerland

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## 1. Introduction

Perovskite solar cells (PSCs) have shown remarkable progress over the past decade, achieving efficiencies of over 26% on smallarea devices.<sup>[1]</sup> The excellent optoelectronic properties, tunable bandgap, and lowtemperature processability of perovskite materials have made them ideal candidates for tandem applications.<sup>[2]</sup> In particular, PSCs with a planar inverted p–*i*–n architecture have gained enormous attention due to their favorable polarity for tandem integration with established single-junction solar cells.<sup>[3–6]</sup>

The recent improvements in power conversion efficiency (PCE) of PSCs with a p-*i*-n device architecture and 2-terminal (2T) perovskite-based tandem solar cells can be attributed to the use of the new generation of the hole transport layer (HTL), known as a self-assembled monolayer (SAM).<sup>[4,7,8]</sup> The SAM is an ultra-thin

HTL with an excellent hole extraction capability that enables efficient charge transport and reduced recombination losses at the interface to achieve high-performance PSCs.<sup>[4]</sup> Several promising SAM-based HTLs such as 2PACz, MeO-2PACz, Me-4PACz, and 4PADCB have been extensively used as HTLs to achieve high-efficiency small-area PSCs with an active area of  $<1 \,\mathrm{cm}^{2,[3,4,9,10]}$  However, the spread in device performance is severe even on 2.5 cm × 2.5 cm substrates raising concerns over uniformity of SAM deposition.<sup>[3,7]</sup>

The large spread in device performance with SAM-based PSCs can be attributed to two main reasons: non-uniform surface coverage of SAM and non-polar SAM surface hindering conformal growth of perovskite absorber.<sup>[9,11]</sup> Although SAM HTLs have been shown to exhibit excellent hole-extraction capability, the growth of the perovskite absorber on SAM's surface is non-optimal due to dewetting issues resulting in pin-holes and voids.<sup>[3,11]</sup> Further, the non-uniform SAM coverage leads to poor open-circuit voltage ( $V_{OC}$ ) in devices and, in severe cases, results

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in shunt due to direct contact of the perovskite absorber with the electrode. A dense and compactly packed HTL is required for efficient and uniform charge extraction. Several studies have identified that the SAM exhibits a weak anchoring on transparent conductive oxide (TCO) substrates such as indium tin oxide (ITO) leading to non-homogeneous distribution.<sup>[12–14]</sup> Recently, bilayer HTL stack based on nickel oxide (NiO) and SAM have gained attention due to reduced spread in device performance, improved fabrication yield, and reproducibility.<sup>[14-18]</sup> The anchoring of SAM onto NiO surface has shown to be superior compared to ITO surface due to a tridentate bonding, leading to a morehomogeneous surface coverage.<sup>[14,17,19]</sup> Further, the high-surface energy of the NiO surface improves the wettability of perovskite ink resulting in optimal growth of perovskite absorber.<sup>[17]</sup> However, most of these works use spin-coating to coat either NiO or SAM or both the layers, making the process non-ideal for high-throughput and large-scale manufacturing. Although a recent work demonstrates PSCs with a fully scalable bilaver HTL stack, challenges associated with PSC's upscaling using standalone SAMs or NiO HTL were not highlighted.<sup>[18]</sup>

In this work, we demonstrate a fully scalable deposition route to fabricate p-i-n perovskite solar cells, and achieve uniform device performance using bilayer HTL stack comprising sputtered NiO and blade-coated SAM. We elucidate the role of bilayer HTL stack in comparison to standalone HTL in improving the uniformity in device performance of PSCs. To evaluate the uniformity in device performance, all the devices are fabricated on a  $5 \text{ cm} \times 5 \text{ cm}$  substrate with pixels distributed across the coated area (Figure S1, Supporting Information). First, we evaluated the efficacy of SAM as a standalone HTL in PSCs and fine-tuned their deposition procedure to achieve efficiencies close to 20%. However, we observed a large spread in device performance owing to non-optimal SAM surface coverage and pin-hole-rich perovskite absorber on the hydrophobic SAM surface. To resolve these challenges, we employed a sputtered NiO interlayer to enable an improved SAM surface coverage and realize pinhole-free uniform perovskite coating. We characterize these improvements in uniformity through surface-sensitive characterizations and provide insights into the role of the sputtered NiO. We understand the influence of HTL on charge-transfer dynamics at the perovskite/HTL interface by various optoelectronic characterizations. To demonstrate uniformity and upscalability potential, we fabricate near-infrared (NIR)-transparent perovskite mini-module on an aperture area of 2.56 and 12.96 cm<sup>2</sup> with PCEs of 14.9% and 12.5%, respectively. Finally, we utilize our perovskite mini-module together with low-bandgap (1.0-1.1 eV) Cu(In,Ga)Se<sub>2</sub> (CIGS) mini-module in a 4-terminal (4T) tandem architecture and achieved tandem efficiencies of 20.5% and 16.9% with aperture area of 2.56 and 10.23 cm<sup>2</sup>, respectively. To the best of our knowledge, this is the first demonstration of a 4-T perovskite-CIGS tandem module with a fully scalable process reported in the literature.

## 2. Result and Discussion

For perovskite deposition, a gas-quenching assisted bladecoating process is used to facilitate uniform drying of the wetfilm and to have fine control over nucleation and super-saturation

regime over a large-area substrate. To achieve uniform perovskite films and controlled crystallization over a large area, the perovskite inks were formulated using solvent system based on N.Ndimethylformamide (DMF) and N-methyl pyrrolidone (NMP). Compared to widely used DMF and Dimethyl sulfoxide (DMSO) based perovskite inks, the DMF-NMP solvent system provides excellent substrate-solvent interaction (Figure S2, Supporting Information) to achieve conformal spread of the perovskite ink on the substrate surface eliminating microscale pin-hole formations.<sup>[20]</sup> Further, the low-vapor pressure of NMP prevents rapid nucleation and crystallization during the gas-quenching process through the formation of a stable intermediate film, and later upon thermal annealing results in perovskite film without any pin-holes or voids (Figure S3, Supporting Information). An optimal amount of bulk additives such as PbCl<sub>2</sub> and KPF<sub>6</sub> were included in the ink formulation to improve the crystallinity and optoelectronic properties of the coated perovskite film.<sup>[21]</sup>

The schematic representation of the processing sequence and device architecture employed in this work is shown in **Figure 1**a,b. All the constituent layers in the PSC stack are deposited using scalable processes. The SAM HTL and perovskite absorber ( $Cs_{0.17}FA_{0.83}PbI_3$ , 1.57 eV) are deposited by blade-coating, NiO by sputtering,  $C_{60}$ /bathocuproine (BCP), and copper (Cu) by thermal evaporation. All the devices were fabricated on a 5 cm  $\times$  5 cm ITO/glass substrate, with 16 pixels uniformly distributed across the sample dimension to probe spread in device performance, as shown in Figure S1 (Supporting Information).

We first evaluate the efficacy of SAM as a standalone HTL. The MeO-2PACz SAM was chosen for blade-coating optimization due to its excellent band alignment with the mid-band gap (1.57–1.62 eV) perovskite absorber.<sup>[4]</sup> To determine suitable coating conditions for the HTL, we fixed the blading gap at 200 µm, solution concentration to  $0.1 \text{ mg mL}^{-1}$  (in anhydrous ethanol), and varied the coating speed. Unlike perovskite deposition, the wet-film was allowed to rest on the substrate for a few seconds and transferred to a hot plate for annealing without any gasquenching. Figure S4 (Supporting Information) shows the effect of SAM's blading speed on the *I*-V performance of the PSCs. Devices with blade-coated MeO-2PACz show a huge spread in device performance with numerous shunted cells, indicating severe inhomogeneity issues. At a fixed blading speed of  $60 \text{ mm s}^{-1}$ , we further screened different concentrations of MeO-2PACz and studied their influence on device performance (Figure S5, Supporting Information). At a higher MeO-2PACz concentration  $(0.3 \text{ mg mL}^{-1})$ , only a few pixels were functional, and others led to shunts, resulting in a severe spread in device performance. These shunts are dominated by pin-holes and nonconformal surface coverage of the overlying perovskite absorber due to poor wetting of the perovskite ink on the hydrophobic surface. From the contact angle measurements (Figure S6, Supporting Information), it is apparent that a high MeO-2PACz concentration makes the surface hydrophobic and hinders the uniform spread of perovskite ink onto the substrate. At very-low MeO-2PACz concentrations, an improved wetting of perovskite ink is observed. However, the spread of V<sub>OC</sub> and fill factor (FF) in these devices is severe, possibly due to a compromised surface coverage of the MeO-2PACz molecule. Despite shunting issues, several pixels achieve close to 20% PCE on

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**Figure 1.** a) Schematic representation of fabrication route and b) device architecture of fully scalable p-i-n solar cells used in this work. c) Box chart indicating PV parameters of PSCs using different HTLs such as bladed MeO-2PACz, standalone sputtered NiO, and bilayer NiO/MeO-2PACz HTL. The devices were fabricated on 5 cm × 5 cm substrates with an active area of 0.1 cm<sup>2</sup> and the data points are from reverse J-V scan.

MeO-2PACz bladed with 0.1 mg mL<sup>-1</sup> concentration, leaving further scope for improvement in uniformity. These results indicate that SAM as a standalone HTL would not be sufficient in view of upscaling. To improve the uniformity, we employed sputtered NiO HTL into the device stack for PSC fabrication. PSCs with both standalone NiO HTL and bilayer HTL (NiO/ MeO-2PACz) were fabricated and compared with the PSCs on standalone MeO-2PACz, as shown in Figure 1c.

PSCs on NiO and NiO/MeO-2PACz (bilayer HTL) show reduced spread in device performance indicating improved conformal coverage of all the constituent layers in the device stack. We note that PSCs with standalone NiO HTL show inferior device performance in all the 3 PV parameters with severe losses in  $J_{SC}$  and FF, achieving a maximum device efficiency of 11%. With MeO-2PACz inclusion, the bilayer HTL-based PSCs exhibit improved performance, nearing 19% efficiency. These PSCs achieve a maximum  $V_{OC}$  of 1.10 V,  $J_{SC}$  of 22 mA cm<sup>-2</sup>, FF of 82%, and efficiency of 18.7%. While the bilayer HTL enhances mean PV parameters compared to standalone MeO-2PACz PSCs, minor losses in  $J_{SC}$  and FF slightly reduce the maximum achievable efficiency. In the next section, we elucidate the origin of improved uniformity in device performance with the introduction of sputtered NiO interlayer.

## 2.1. The Origin of Improved Uniformity in PSCs with Sputtered NiO HTL

The mechanism underlying SAM's anchoring to metal oxide surface is attributed to the condensation reaction and is well-documented in the literature.<sup>[7,19,22]</sup> Briefly, the phosphonic acid present in the SAM molecule acts as a binding group and attaches to surface hydroxyl present in the underlying substrate to form a self-limiting monolayer.<sup>[23]</sup> As the surface chemistry of the underlying substrate plays a pivotal role in anchoring of SAM, X-ray photoelectron spectroscopy (XPS) was employed to characterize the ITO and NiO surface.

Figure 2a–d compares the O 1s spectrum of ITO and NiO substrate before and after MeO-2PACz deposition. Post MeO-2PACz deposition, a shift in binding energy (Table S1, Supporting Information) (=0.2 eV) for O 1s peak to a higher energy level is observed on both the substrates indicating a strong

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Figure 2. a–d) O1s XPS spectra of ITO and NiO substrate before (bottom) and after (above) SAM deposition. e) Contact angle measurement of perovskite ink on different HTL-coated ITO substrates.

coordination through electron transfer. Further, the contribution of C–O group from the MeO-2PACz layer is evident in the O 1s spectrum for both samples. By comparing the P 2p spectrum (Figure S7, Supporting Information) on both ITO and NiO substrate, we found a higher integrated (Table S2, Supporting Information) P 2p intensity in the case of NiO substrate (2.8 at% of P) compared to ITO substrate (2.5 at% of P). The improved

intensity of the P 2P signal indicates an improved coverage of MeO-2PACz HTL on NiO substrate. Similarly, an increase in phosphorous intensity is observed in energy-dispersive X-ray spectroscopy (EDX) (Figure S8, Supporting Information) and time-of-flight secondary ion mass spectrometry (ToF-SIMS) analysis, suggesting an improved coverage of MeO-2PACz on the NiO substrate compared to the ITO substrate. The improved coverage and anchoring of SAM on NiO could possibly be attributed to the high surface hydroxyl concentration on the NiO substrate.<sup>[14,15,19]</sup> Comparing the fraction of different components in the O 1s XPS spectra prior to the SAM deposition, the NiO substrate (55.7%) exhibits a higher hydroxyl to metal oxide fraction compared to bare ITO substrate (45%) suggesting more anchoring sites for enhanced SAM absorption. The high surface hydroxyl group concentration facilitates a strong tridentate binding of SAM molecule on the NiO substrate to achieve ordered, dense, and uniform anchoring compared to a bidentate binding on ITO substrate.<sup>[16,17,19]</sup> Further, post MeO-2PACz deposition, an improved (-OH) intensity in the O 1s spectrum is observed on NiO substrate compared to the ITO substrate. The improved binding also reduces the surface roughness (Figure S9,

Supporting Information) resulting in a smoother surface for NiO/ SAM bilayer HTL (Root mean square (RMS) roughness – 3.02 nm) compared to ITO/MeO-2PACz HTL (RMS roughness – 3.67 nm).

The contact angle measurement of perovskite ink on different substrates is shown in Figure 2e. For layers processed with meniscus-assisted methods such as blade and slot-die coating, one of the factors that determine the layer conformality is the substrate-ink interaction. Apart from the solvent system used to formulate the perovskite ink, a high surface energy of the substrate is essential to accomplish an excellent substrate-ink interaction to pin the meniscus to the substrate surface for uniform spread of the dispensed ink. A poor substrate-ink interaction would lead to pinholes in the final films and, in severe cases, could result in complete dewetting of the ink, leading to poor coatings. The perovskite ink on the SAM-coated ITO substrates shows a contact angle close to 20°. The relatively higher contact angle results in poor coverage and hinders the pinning of the perovskite ink to the underlying substrate, subsequently leading to small pin-holes in the final perovskite films. These pinholes induce direct contact between the HTL and ETL creating shunts, affecting device performance. However, on both standalone NiO and bilayer HTL, we observe a much-improved wetting of the perovskite ink resulting in a six-fold and three-fold decrease in contact angle, respectively, to achieve conformal coverage of the ink on the underlying substrate. The high surface hydroxyl present on the NiO substrate helps in improving the wetting of the ink to achieve pin-hole-free perovskite absorber coating, resulting in a uniform device performance on large-area substrates.

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performance.

(a)

0

-5

-10

#### 2.2. Influence of Different HTL on PV Performance of PSCs

section, we will elaborate on the effect of various HTL on device

Figure 3a shows the *I–V* characteristics of champion PSCs with different HTL and the corresponding PV parameters are tabulated in Table 1. Although the PSCs with standalone NiO and bilayer HTL show improved uniformity in device performance, the champion devices with NiO-based HTL display penalty in PV performance in all the PV parameters compared to standalone MeO-2PACz PSCs.

PSCs with standalone NiO and bilayer HTL deliver a lower J<sub>SC</sub> compared to devices with MeO-2PACz. The lower J<sub>SC</sub> in NiO-based HTL can be attributed to a reduced spectral response in the UV region, as shown in Figure 3b. The parasitic absorption in the NiO hampers the external quantum efficiency (EQE) response in the UV region and affects the J<sub>SC</sub> in PSCs with standalone NiO and bilayer HTL. Apart from a poor spectral response in the UV region, a broadband reduction is also noticed in PSCs with standalone NiO HTL indicating problems pertaining to the perovskite/HTL interface.

To understand the influence of HTL on charge transfer and recombination characteristics photoluminescence (PL)

MeO-2PACz

NiO

→NiO/MeO-2PACz (b)

J<sup>0.6</sup>

Table 1. Photovoltaic parameters of the champion perovskite solar cells fabricated with different HTL.

Different HTLs	V <sub>oc</sub> [V]	$J_{\rm SC}$ [mA cm <sup>-2</sup> ]	FF [%]	PCE [%]
Standalone MeO-2PACz	1.05	22.6	83.2	19.9
Standalone NiO	0.99	16.8	68.1	11.3
NiO/MeO-2PACz	1.05	21.7	82.0	18.7

(Figure 3c) and time-resolved photoluminescence (Figure 3d) (TRPL) characterization were performed on perovskite absorber fabricated with different HTLs on ITO substrate. Perovskite on MeO-2PACz HTL exhibits an initial fast decay showcasing excellent charge-extraction capability and a slower second decay indicating a prolonged charge-carrier lifetime. The corresponding bi-exponential parameter fit is tabulated in Table S3 (Supporting Information). Whereas, for perovskite absorber on NiO HTL, a significantly lower PL intensity with a monoexponential charge-carrier decay is observed. The inferior PL intensity and short carrier lifetime of perovskite absorber on NiO can be attributed to the defect-rich surface defects on the HTL surface, and are responsible for low ISC achieved in PSCs with NiO HTL. In the case of NiO/MeO-2PACz HTL, a significant improvement in the PL intensity occurs, indicating suppression of non-radiative recombination pathways with the insertion of the MeO-2PACz layer. Similar to the bladed MeO-2PACz, perovskite on NiO/MeO-2PACz HTL displays a bi-exponential decay, signifying excellent charge-extraction at the interface and prolonged

(C)

nts) 4000

(COL

600

5000



absorber on different HTL evaluated through c) PL, d) TRPL, e) Mott-Schottky plot, and f) grain-size distribution analysis with ImageJ software based on SEM top view image.

NiO MeO-2PACz

NiO/MeO-2PACz



carrier lifetime in the bulk. However, both the carrier lifetime and PL intensity displayed in the case of NiO/MeO-2PACz are lower compared to the perovskite absorber on MeO-2PACz HTL.

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Several studies have indicated the presence of secondary and hydrate phases on the NiO surface (Ni<sup>3+</sup> states) that act as detrimental recombination centers at the NiO/perovskite interface.<sup>[24–27]</sup> Surface modification using spacer layers including ammonium<sup>[28,29]</sup> and metal halide salts<sup>[30]</sup> and polymer layer<sup>[31]</sup> have shown to suppress interface recombination by avoiding direct contact with NiO and perovskite interface and enhance the device performance. Also, modifying the NiO surface with SAM has also been shown to effectively suppress the interface recombination.<sup>[15,32]</sup> The enhanced PL intensity and improved TRPL lifetime for perovskite absorber on bilayer HTL originates due to passivation of NiO surface defects by MeO-2PACz HTL. The surface chemistry of NiO substrate before and after deposition of MeO-2PACz is shown in Figure S10 (Supporting Information). Post MeO-2PACz deposition, a shift in binding energy of the Ni 2P peak is observed (Table S1, Supporting Information), indicating a strong coordination between NiO and MeO-2PACz. The spectra can be deconvoluted into high energy peak (856 eV) and lower energy peak (852 eV) corresponding to Ni<sup>3+</sup> and Ni<sup>2+</sup> states. After the adsorption of MeO-2PACz, we observe a reduction in the ratio of Ni<sup>2+</sup> to Ni<sup>3+</sup> states from 1:2 to 1:1, indicating a suppression of Ni<sup>3+</sup> states due to the incorporation of the SAM molecule, and possibly passivating the defective NiO/perovskite interface. Further, the MeO-2PACz layer acts as a spacer between NiO and perovskite and mitigates the direct contact between them to prevent detrimental effects. The indication of suppressed nonradiative recombination with the incorporation of MeO-2PACz can also be observed by the reduction in the reverse saturation current density (Figure S11, Supporting Information) on the PSCs with the bilayer HTL.

Apart from carrying out characterization on layers, the whole devices were subjected to further electrical studies to evaluate the role of different HTLs on charge-transfer kinetics. Figure 3e shows the Mott-Schottky plot for devices with different HTL. The built-in potential for NiO devices is much lower (1.01 V) in comparison to devices on bilaver HTL (1.05 V) and MeO-2PACz HTL (1.04 V). The higher built-in potential in NiO/ MeO-2PACz and MeO-2PACz devices facilitates faster charge extraction and charge separation enabling reduced charge accumulation at the HTL/Perovskite interface.<sup>[33]</sup> The short transient photocurrent (TPC) decay time (Figure S12a, Supporting Information) on devices with NiO/MeO-2PACz and MeO-2PACz HTL indicates a faster charge extraction. Similar to the Mott-Schottky characterization, the device with NiO/MeO-2PACz HTL delivers the highest implied  $V_{OC}$  and photoluminescent quantum yield (Figure S12b, Supporting Information) among the fabricated devices. Concurrently, a longer decay time in the transient photovoltage (TPV) measurement (Figure S12c, Supporting Information) is displayed for devices with the bilayer HTL compared to standalone NiO indicating a lower carrier recombination rate and suppressed interface recombination. However, as indicated with TRPL and TPC measurement, the charge-extraction at the HTL/perovskite interface is hindered in the case of bilayer HTL with the inclusion of NiO. The impedance spectroscopy (Figure S12d, Supporting Information) clearly

To understand the influence of different HTLs on the perovskite growth, morphology, and crystallinity scanning electron microscopy (SEM), ultraviolet-visible (UV-vis), and X-ray diffraction (XRD) analyses were carried out. Figure S13 (Supporting Information) shows the SEM top view of the perovskite absorber on different HTL, and the corresponding grain-size distribution is plotted in Figure 3f. The grain-size distribution reveals that the perovskite grown on bare NiO substrate shows relatively smaller grains compared to the MeO-2PACz and bilaver HTL. This is reasonable as perovskite grown on any hydrophilic surface tends to nucleate faster resulting in smaller size crystal domain. Also, an increase in perovskite grain size on bilayer HTL confirms that the NiO surface is altered post-incorporation of MeO-2PACz. A minor change in absorbance is noticed with different HTLs attributed to the difference in reflectance with the insertion of NiO HTL, as shown in Figure S14 (Supporting Information). Although XRD analysis (Figure S15, Supporting Information) shows no significant difference in the perovskite peak on different HTLs, the fraction of PbI<sub>2</sub> in comparison to the perovskite peak is significantly higher for perovskite on standalone NiO HTL indicating possible decomposition due to undesirable redox reaction between Ni<sup>3+</sup> and perovskite absorber at the HTL/ perovskite interface.

Figure S16 (Supporting Information) shows the light-soaking stability assessment of encapsulated PSCs with MeO-2PACz and bilayer HTL upon continuous light-soaking conditions in a lowhumid atmosphere. We do not carry out any stability assessment on PSCs with NiO HTL as the detrimental degradation pathways at the NiO/perovskite interface are established in our results, and further documented extensively in literature. PSCs with MeO-2PACz HTL exhibit superior stability retaining over 90% of their initial efficiency over a period of 400 h. With bilayer HTL, after a stable maximum power point (MPP) performance over 150 h, a decline in device performance is observed. The device retains close to 75% of its initial performance at the end of 400 h. A dedicated study on the stability of sputtered NiO-based PSCs attributes the performance loss in sample with NiO HTL to the formation of an electrical barrier at the perovskite/HTL that scales with the HTL thickness.<sup>[34]</sup> In future work, the thickness of the NiO HTL could be optimized keeping stability and device performance as the figure of merit.

## 2.3. NIR-Transparent Perovskite Mini-Module for Tandem Application

Perovskite photovoltaic devices with NIR-transparency are gaining research attention as they offer the possibility for integration in avenues such as agrivoltaics,<sup>[35]</sup> building-integrated photovoltaics,<sup>[36,37]</sup> and tandem application.<sup>[5]</sup> Also, they show superior device stability compared to their opaque counterpart by mitigating metal contact-induced degradation through replacement with robust TCO electrodes.<sup>[38]</sup> However, very few works have been carried out to demonstrate NIR-transparent perovskite minimodules due to design constraints.<sup>[39–44]</sup> The use of transparent conductive electrodes with high resistance on both the front and rear sides dictates judicious module layout design to mitigate



resistive losses. Design considerations pertaining to NIR-transparent module layout optimization have been discussed in our previous work and can be referred to for further clarification.<sup>[42]</sup>

In this work, to demonstrate the uniformity of our solar cell stack, we chose to fabricate NIR-transparent perovskite minimodules and utilize them for tandem application. The copper electrode was replaced with a sputtered Indium Zinc oxide (IZO) TCO to facilitate NIR-transparency. To mitigate sputter damage on the perovskite absorber, an atomic layer deposition (ALD) SnO<sub>2</sub> buffer layer was used instead of BCP. The schematic representation of the monolithically interconnected NIRtransparent perovskite mini-module demonstrated in this work is shown in **Figure 4**a. A typical P1-P2-P3 interconnection scheme is used to achieve series interconnection of solar cell strips to mini-modules. High-precision laser patterning allowed us to achieve a narrow interconnection width (Figure 4b) close to 200  $\mu$ m. The module design was optimized to achieve a geometric fill factor (GFF) close to 95%.

To assess the uniformity over the deposited area, several small mini-modules along the blading directions were scribed out. The mini-module comprised 8 monolithically interconnected



**Figure 4.** a) Schematic representation of NIR-transparent perovskite mini-module with monolithic interconnection scheme. b) Confocal microscope image of interconnection area with indication of P1, P2, and P3 patterning lines. c) J-V characteristics and d) MPP efficiency plot of NIR-transparent perovskite mini-module with area of 2.56 and 12.96 cm<sup>2</sup>. The small-area and large-area mini-module comprise of 8 and 12 subcells, respectively. e) Schematic representation of bifacial NIR-transparent perovskite module with an indication of illumination direction. f) J-V characteristics of NIR-transparent perovskite module illuminated from film (black) and glass (red) side.

 Table 2. Photovoltaic parameters of NIR-transparent perovskite solar

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cells/mini-modules on different areas.

NIR-transparent perovskite mini-modules	V <sub>oc</sub> [V]	J <sub>SC</sub> [mA cm <sup>-2</sup> ]	FF [%]	PCE [%]	Area [cm <sup>2</sup> ]
Small-area mini-module (8 subcells)	9.01	2.3	71.1	14.9	2.56
Large-area mini-module (12 subcells)	12.40	1.6	62.0	12.5	12.96

subcells with subcell width of 4 mm, resulting in an aperture area of 2.56 cm<sup>2</sup>. Figure S17 (Supporting Information) displays the box plot summarizing PV performance across 16 mini-modules fabricated on 4 different 5 cm × 5 cm substrates. The mini-modules demonstrate excellent uniformity with minimal spread in the PV performance, displaying  $V_{\rm OC}$  close to 9 V. The  $V_{\rm OC}$  of a single subcell matches well with the small-area cell  $V_{\rm OC}$  implying uniform properties across the coated film. Further, the excellent GFF enabled us to achieve minimal loss in  $J_{\rm SC}$  compared to the small-area cells.

We further upscaled the active area of our mini-module from 2.56 to 12.96 cm<sup>2</sup> and the J-V characteristics and MPP efficiency plots of the best-performing mini-modules are shown in Figure 4c with PV parameters tabulated in **Table 2**.

The photograph of the representative modules is shown in Figure S18 (Supporting Information). Champion mini-module on 2.56 cm<sup>2</sup> aperture-area achieves a  $V_{OC}$  of 9.02 V,  $I_{SC}$  of 2.3 mA cm<sup>-2</sup>, FF of 71.1%, resulting in a PCE of 14.9%. With an increase in active area to  $12.96 \text{ cm}^2$ , the device performance dropped to 12.5% mainly originating from a reduction in  $V_{\rm OC}$  and FF. Electroluminescence imaging (EL) (Figure S19, Supporting Information) performed on the large-area module displays a reduced luminescent intensity signal at the exterior edge of the module. The drop in signal at the end corresponds to a problem pertaining to solvent back-flow in the blade-coater. Further, on both the mini-modules, the FF is affected due to poor shunt resistance originating from delamination of our brittle top electrode upon scribing (Figure 4b). Further optimization on P3 scribe would enable improvement in FF resulting in improvement in PCE. Nevertheless, the mini-modules display a steady-state efficiency (Figure 4d) of 14.6% (2.56 cm<sup>2</sup>) and 12.5% ( $12.96 \text{ cm}^2$ ). To evaluate bifaciality of the module, the *I–V* performance of mini-module from both glass and film sides were measured (Figure 4e). The mini-module performs with a PCE of 14% and 13.7% with film-side and glass-side illumination respectively, achieving a bifaciality (Figure 4f) factor close to 98%.

The best-performing mini-modules were combined with CIGS bottom module of the respective area to demonstrate



**Figure 5.** a) Schematic representation of 4T perovskite-CIGS tandem mini-module demonstrated in this work. b) J-V characteristics of perovskite-top mini-module, CIGS bottom mini-module in a 4-terminal tandem configuration on small-area mini-modules with an overlapping area of 2.03 cm<sup>2</sup> and c) large-area mini-modules with an overlapping area of 10.23 cm<sup>2</sup>. The NIR-transparent perovskite module is placed as a filter on top of CIGS mini-module to carry out 4T tandem measurement. d) Efficiency versus area plot of 4T perovskite-CIGS tandem solar cells and modules reported in the literature. This work demonstrates the first fully scalable 4T perovskite-CIGS tandem mini-module, and also exhibits upscaling capability by achieving modules with aperture area of over 10 cm<sup>2</sup>.

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Mini-module (with indication of number of subcells)	V <sub>oc</sub> [V]	$J_{\rm SC}$ [mA cm <sup>-2</sup> ]	FF [%]	PCE [%]	Area [cm <sup>2</sup> ]
CIGS standalone mini-module (5)	3.66	6.6	56.5	13.7	2.03
NIR-transparent perovskite mini-module (8)	9.02	2.3	71.1	14.9	2.56
CIGS bottom mini-module	3.47	2.6	61.9	5.6	2.03
Tandem mini-module (5)				20.5	2.03
CIGS standalone mini-module (7)	3.81	4.6	63.5	11.1	10.23
NIR-transparent perovskite mini-module (12)	12.40	1.6	62.0	12.5	12.96
CIGS bottom mini-module (7)	3.66	1.8	66.3	4.4	10.23
Tandem mini-module				16.9	10.23

Table 3. Photovoltaic parameters of the perovskite-CIGS tandem mini-module compared to the standalone CIGS mini-module.

the perovskite-CIGS 4T tandem module (**Figure 5**a). To enhance their applicability for tandem application, an anti-reflection coating was applied on the film side of the module to minimize reflection losses and achieve NIR-transmittance (Figure S20, Supporting Information) of over 70% in the range of 800–1000 nm. The perovskite mini-module was placed as a filter on top of the CIGS mini-module to carry out 4T tandem J-Vmeasurements. In a 4T tandem architecture with CIGS bottom module, we achieve an efficiency of over 20% on 2 cm<sup>2</sup> and 16.9% on 10 cm<sup>2</sup>. The J-V characteristics of the 4T tandem module are shown in Figure 5b,c, and the corresponding PV parameters are summarized in **Table 3**. Compared to single-junction standalone perovskite and CIGS mini-module, the 4-terminal tandem mini-module results in an improved performance.

Figure 5d displays the PCE of 4T perovskite-CIGS tandem solar cells and modules reported in the literature. The thin-film tandem technology displays excellent PCE of close to 30%, show-casing its potential.<sup>[45]</sup> However, all the works have utilized the spin-coating technique in the fabrication of perovskite top cells. In this work, we demonstrate the first fully scalable 4T perovskite-CIGS tandem module with a promising efficiency on 2 and 10 cm<sup>2</sup>, making them the first reported demonstration of large-area 4T perovskite-CIGS mini-module.

## 3. Conclusion

We demonstrated fully scalable p-*i*-n PSCs achieving PCE close to 20%. Problems pertaining to poor surface coverage of MeO-2PACz on ITO substrate and non-uniform deposition of perovskite absorber on the hydrophobic SAM surfaces were resolved using a bilayer HTL consisting of sputtered NiO and blade-coated MeO-2PACz HTL. The insertion of NiO HTL facilitated intimate binding with SAM molecule, thus improving SAM's surface coverage and the hydrophilic surface improved the wetting of perovskite ink which results in pin-hole-free perovskite absorber. Both these attributes make NiO HTL as an essential component to achieve uniform and conformal coverage of SAM and perovskite absorber.

We upscaled our process by fabricating NIR-transparent perovskite mini-module suitable for tandem application. The standalone single-junction NIR-transparent perovskite mini-module displayed 14.9% and 12.5% PCE on 2.56 and 12.96 cm<sup>2</sup>, respectively with an excellent bifaciality of 97.8%.

Further, in combination with the CIGS bottom mini-module, we realize the first fully scalable perovskite-CIGS 4-terminal tandem mini-module with record efficiency of 20.5% and 16.9% on aperture area of 2.03 and 10.23 cm<sup>2</sup>, respectively.

## 4. Experimental Section

*Materials*: All materials were used without further purification. Chemicals such as formamidinium iodide (FAI), lead iodide (PbI<sub>2</sub>), cesium Iodide (CsI), lead chloride (PbCI<sub>2</sub>), and MeO-2PACz were purchased from Tokyo Chemical Industry. Dimethylformamide (DMF, 99.8% anhydrous), dimethyl sulfoxide (DMSO, 99.9% anhydrous), N-methyl-2-pyrrolidone (NMP, 99.5% anhydrous), KPF<sub>6</sub>, and copper were purchased from Sigma-Aldrich. C<sub>60</sub> and BCP were purchased from Xi'an Polymer Light Technology. Anhydrous Ethanol was purchased from VWR Chemicals. All the materials were weighed in a glove box filled with high-purity N<sub>2</sub>.

Perovskite Solution Preparation: Perovskite (Cs<sub>0.17</sub>FA<sub>0.83</sub>PbI<sub>3</sub>) solution with 1.2 M concentration was prepared as follows. 10% PbCl<sub>2</sub> and 1.5% KPF<sub>6</sub> were used as additive. FAI (171.28 mg), CsI (53 mg), and PbI<sub>2</sub> (553.2 mg) along with PbCl<sub>2</sub> and KPF<sub>6</sub> were weighed and mixed in 900  $\mu$ L of DMF and 100  $\mu$ L of NMP. The perovskite precursors were prepared in a glove box under N<sub>2</sub> and were stirred overnight. Before use, the solution was filtered with a polytetrafluoroethylene 0.2  $\mu$ m filter.

Fabrication of PSC: ITO-coated glass substrates (15  $\Omega/\Box$ , sheet resistance) were cleaned sequentially using acetone, ethanol, and isopropanol for 15 min in ultrasonic cleaner. After drying with N<sub>2</sub> flow, the substrates were transferred to sputter chamber for HTL deposition. NiO with a thickness of 20 nm was sputtered in an Oerlikon Clusterline cluster tool after oxygen plasma cleaning in an RIE chamber (power 250 W, O<sub>2</sub> flow 50 sccm, working pressure 100 mTorr, time 60 s). The chuck temperature and sputtering power were set at 60 °C and 150 W, respectively with an Ar gas flow of 150 sccm. Prior to device fabrication, the NiO films were annealed in air at 300 °C for 30 min. More detailed information on NiO deposition can be found elsewhere.<sup>[34]</sup>

The samples were transferred to a N<sub>2</sub>-filled glove-box for blade-coating MeO-2PACz and perovskite absorber. For perovskite blading, 300  $\mu$ m blading gap with 7 mm s<sup>-1</sup> blading speed was used. A perovskite solution of 55  $\mu$ L was used to coat on 5 cm  $\times$  5 cm substrate. A dummy sample was placed after the main sample to prevent back-flow during blade-coating process. An N<sub>2</sub> air knife with 1.4 mbar pressure was used to dry the wet film, and samples were transferred immediately to a hot plate for annealing. A two-step annealing was followed in which the films were annealed at 70 °C for 5 min and 150 °C for 10 min. After cooling down, the substrates were then transferred into a vacuum chamber for thermal evaporation of C60 (23 nm), BCP (7 nm), and copper (100 nm) electrode. For NIR-transparent perovskite solar cells and module, the samples were transferred to Fiji G2 ALD deposition system, and the ALD process was performed at a substrate temperature of 100 °C with argon as carrier gas at a base pressure of 0.4 mbar to deposit ALD SnO<sub>2</sub> layer.



Tetrakis (dimethylamino)tin (IV) (TDMASn) (Strem) and H<sub>2</sub>O were used as the precursor, and TDMASn was kept at 65 °C while H<sub>2</sub>O remained unheated. A 200 cycle of SnO<sub>2</sub> was found to be optimum as a buffer layer for the development of NIR-transparent mini-modules. The growth rate was determined by ellipsometry on Si (100) reference substrates and linear growth was observed with a growth rate of 1.05. Å per cycle. The substrates were then transferred to sputter chamber for the deposition of IZO electrode at a pulsed DC power of 200 W. A 200 nm thick IZO electrode with a sheet resistance of  $32 \Omega/\Box$  was used to complete the devices. For bestperforming devices, an electron beam evaporated MgF<sub>2</sub> layer was deposited on the film side as anti-reflection coating. Scribing parameters and module layout used in this work are similar to our previous work.<sup>[42]</sup>

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Fabrication of CIGS Mini-Module: Cu(In,Ga)Se<sub>2</sub> (CIGS) absorber layer was deposited in a 3-stage coevaporation growth process on a molybdenum (Mo) coated flexible polyimide (PI) (for small-area module) or glass (for large-area module) substrate, and underwent an alkali postdeposition treatment. More details on the fabrication process can be found elsewhere.<sup>[46]</sup> The stacking sequence of the completed solar cell is PI/Mo/CIGS/CdS/i-ZnO/ZnO:Al/InO:Zn/MgF<sub>2</sub>. The mini-modules were fabricated on a 5 cm × 5 cm large PI or Glass substrate with three individual units. Each module interconnects six 0.5 cm<sup>2</sup> cells. In the laser scribing process (P1 step), the Mo was patterned with an IR laser (1.23 J cm<sup>-2</sup>). Second, the CIGS absorber, CdS, i-ZnO, and thin AZO layer were segmented (P2 step) by a quasi-continuous 1070 nm laser. Third, a highly conductive thick IZO was deposited and scribed again (P3 step) with an IR laser (0.46 J cm<sup>-2</sup>). Finally, the Mo layer was removed by mechanical scribing to separate the individual units (PT step).

Device Characterization: J-V Measurement: For the photocurrentvoltage (J-V) characteristics, the mini-modules were tested under standard AM 1.5G illumination and were measured using a Keithley 2400 source meter under four-contact mode. A certified monocrystalline silicon solar cell (RS-ID-5, Fraunhofer-ISE) was used to calibrate a class ABA solar simulator (LOT-QuantumDesign) to 1 sun AM 1.5G illumination. All the J-V measurements were carried out under backward scan conditions (from  $V_{OC}$  to  $J_{SC}$ ). The measurement stage was maintained at a steady state temperature by a cooling system. For carrying out the steady-state efficiency measurement, a MPP tracking system with perturb and observe algorithm method was used to record the efficiency as a function of time.

Device Characterization: EQE Measurement: The EQE of the minimodules was measured using an in-house developed setup. The probing beam was generated by a chopped white source (900 W, halogen lamp, 280 Hz) and a dual grating monochromatar. The beam size was adjusted to ensure an illumination area within the cell area. A monocrystalline silicon solar cell (RS-ID-5, Fraunhofer-ISE) was used as a reference cell. White bias light was applied during the measurement with an intensity of  $\approx 0.1$  sun.

Device Characterization: UV-vis Spectroscopy: The total transmittance (T) and reflectance (R) spectra were acquired using an UV-vis–NIR spectrophotometer (Shimadzu UV-3600) equipped with an integrating sphere.

Device Characterization: Confocal Measurement: Images were acquired with LEICA DCM8 with the bright field in default operation mode with  $5\times$ ,  $20\times$ , and  $50\times$  EPI-L objectives. Images were constructed using the smart area stitching correlation.

Device Characterization: EL: EL images were recorded by probing the perovskite mini-module in forward bias with 10 mA source current at a bias over open-circuit voltage condition with an acquisition time of 400 ms. The luminescence was measured using a high-resolution digital B/W CCD camera ORCA-ER from Hamamatsu.

Device Characterization: TRPL Measurement: TRPL was measured using the MicroTime 100 system from PicoQuant. A 639 nm pulsed laser diode (pulse width  $\approx 100 \text{ ps}$ ) was used. The excitation density was  $2 \cdot 10^{12} \text{ photons} \cdot \text{cm}^{-2} \text{pulse}^{-1}$  ( $\approx 3.1 \text{ J} \cdot \text{s}^{-1} \text{ cm}^{-2}$ ). The spot size was measured by a NanoScan2 beam profiler resulting in  $\approx 130 \, \mu\text{m}$  diameter. Acquisition times were 60 s and the pulse frequency was 0.5 MHz. For the fitting procedure, a biexponential decay was used.

Device Characterization: XPS: XPS was performed using a Quantum2000 system from Physical Electronics with a monochromatic Al K $\alpha$  source (1486.6 eV) and a base pressure below  $8 \times 10^{-9}$  mbar.

Survey spectra were recorded with an energy step size of 0.4 eV and a pass energy of 93.90 eV. The composition of the samples was analyzed using the Multipak software.

Device Characterization: EDX: The surface was studied using a multifunctional field emission scanning electron microscope (FEI Quanta 660i) combined with an oxford instruments EDX system. EDX mapping was performed using a 15 kV acceleration voltage with a current of 0.4 nA. A Gaussian filter was applied to the EDX mappings (standard deviation for the Gaussian Kernel:  $\Sigma = 2$  using Python)

*Device Characterization: SEM*: A Hitachi S-4800 scanning electron microscope was used for the imaging of the top view and cross-sections. A 5 kV acceleration voltage was used for a 10 mA probing beam.

Device Characterization: XRD: XRD patterns were measured with an X'Pert Pro in Bragg-Brentano geometry using Cu-K $\alpha$ 1 radiation ( $\lambda = 1.5406$  Å), scanning from 5° to 60° (2 $\theta$ ) with a step interval of 0.0167°.

Device Characterization: Contact Angle Measurement: Contact angle measurements were carried out on a drop shape analyzer (Krüss, DSA30E). Contact angles of droplets of deionized water and di-iodomethane were measured by a Young–Laplace fit of the drop shape. The free surface energy was calculated with the OWRK model.

Device Characterization: ToF-SIMS: Compositional depth profiles were measured by ToF-SIMS V system, ION-ToF. The primary beam was a 25 keV Bi<sup>+</sup> with total current of 0.39 pA and a raster size of  $50 \times 50 \ \mu\text{m}^2$ . The sputtering beam was a 50 nA, 2 keV  $O_2^+$  with an on-sample area of  $300 \times 300 \ \mu\text{m}^2$ .

Device Characterization: Stability Assessment: Stability tests were performed with the stress-test platform Litos from Fluxim AG. The platform is composed of four individual chambers with one sample per chamber. Illumination with white LEDs (no UV component) was set to 1 Sunequivalent intensity. The stage temperature was set to 25 °C in an atmosphere with reduced humidity of <10%. The humidity was continuously monitored in each chamber. Aging was performed under MPP tracking conditions and every 60 min, a *J*–*V* scan in reverse and forward direction was automatically acquired.

## Supporting Information

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

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### Conflict of Interest

The authors declare no conflict of interest.

#### **Data Availability Statement**

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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## Keywords

blade-coating process, mini-modules, monolithic interconnection, perovskite solar cells, scalable processing, tandem solar cells

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