

Compositional and Interfacial Engineering Yield High-Performance and Stable p-i-n Perovskite Solar Cells and Mini-Modules

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ABSTRACT: Through the optimization of the perovskite precursor composition and interfaces to selective contacts, we achieved a p-i-n-type perovskite solar cell (PSC) with a 22.3% power conversion efficiency (PCE). This is a new performance record for a PSC with an absorber bandgap of 1.63 eV. We demonstrate that the high device performance originates from a synergy between (1) an improved perovskite absorber quality when introducing formamidinium chloride (FACI) as an additive in the "triple cation" Cs_{0.05}FA_{0.79}MA_{0.16}PbBr_{0.51}I_{2.49} (Cs-MAFA) perovskite precursor ink, (2) an increased open-circuit voltage, V_{OC} , due to reduced recombination losses when using a lithium fluoride (LiF) interfacial buffer layer, and (3) high-quality hole-selective contacts with a self-assembled monolayer (SAM) of [2-(9H-carbazol-9-yl)ethyl]phosphonic acid (2PACz) on ITO electrodes. While all devices exhibit a high performance after fabrication, as determined from current–density voltage, J-V, measurements, substantial differences in device



performance become apparent when considering longer-term stability data. A reduced long-term stability of devices with the introduction of a LiF interlayer is compensated for by using FACl as an additive in the metal-halide perovskite thin-film deposition. Optimized devices maintained about 80% of the initial average PCE during maximum power point (MPP) tracking for >700 h. We scaled the optimized device architecture to larger areas and achieved fully laser patterned series-interconnected mini-modules with a PCE of 19.4% for a 2.2 cm² active area. A robust device architecture and reproducible deposition methods are fundamental for high performance and stable large-area single junction and tandem modules based on PSCs.

KEYWORDS: self-assembled monolayer, interface modification, FACl additive, triple cation perovskite, p-i-n solar cell, laser-interconnection, module

1. INTRODUCTION

Hybrid organic—inorganic lead halide perovskites solar cells (PSCs) have been demonstrated to yield impressive power conversion efficiencies above 25% for small area devices,¹ enthralling high aspiration for next-generation solar cell technology.^{2–9} The scalability and stability of high-performing PSCs are challenges for the commercial prospects of this technology. Therefore, great efforts have been made in process optimization to make high-quality thin films,^{10,11} optimizing the device structure,^{3,12} interface engineering,^{13–18} and the incorporation of new potential transport materials as well as perovskite materials.^{19,20} Efficient perovskite devices have been successfully made with both p-i-n and n-i-p architectures. Here, p and n denote a hole- and electron-selective contact layer, and the perovskite layer is assumed to be an intrinsic "i" semiconductor layer. The order of letters in these abbreviated

notations indicate the sequence of layers as deposited during device preparation.

For perovskite solar cells of the p-i-n type, lower PCEs have been achieved compared to those of n-i-p solar cells, which we attribute to fewer research groups working on their optimization. The p-i-n architecture becomes of increasing importance as a top cell in 2-terminal tandem solar cells based on silicon for the following reasons:^{21–23} p-i-n devices can be manufactured with only low-temperature processing steps involved, which reduces the risk of potential performance losses in the silicon bottom

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Figure 1. (a) False-colored cross-sectional SEM image of the perovskite solar cell device architecture investigated in this work. (b) Schematic device layout of p-i-n perovskite solar cells based on 2PACz as a hole-selective self-assembled monolayer. (c) Perovskite layer as $Cs_{0.05}FA_{0.79}MA_{0.16}PbBr_{0.51}I_{2.49}$ optionally with FACl as an additive studied herein together with the effect of lithium fluoride as an interfacial buffer layer between the perovskite and C_{60} was investigated here.

cell, charge-selective layers in p-i-n are comparatively less absorptive, and p-i-n devices commonly exhibit low currentdensity–voltage hysteresis.²⁴ Lately, promising strategies to reduce nonradiative recombination and improve the opencircuit voltage, $V_{\rm OC}$, in PSCs including interface passivation^{6,25,26} and the use of inorganic additives in the perovskite bulk material^{27–29} have been developed.

Albrecht and co-workers demonstrated the use of carbazolbased phosphonic acid self-assembled monolayers to replace polymer hole-selective in p-i-n solar cells, reaching PCEs of >20%.²³ At the electron-selective contact, introducing a thin layer of LiF was shown to mitigate interfacial recombination losses at the C_{60} /perovskite interface, resulting in an improve-ment of the V_{OC} in PTAA-based PSCs.^{6,30} The incorporation of additives into the perovskite precursor solution is one of the potential strategies to improve the crystallinity and quality by positively affecting thin-film formation. A wide range of additives has been studied, including metal halides salts,^{31,32} fullerene derivatives,^{33,34} polymers,³⁵ halide salts,³⁶ and 2D materials,⁹ Among these, halide salt additives such as cesium iodide (CsI),³⁷ rubidium iodide (RbI),³⁸ and MACl³⁶ have been studied. Kim et al. reported that MACl as an additive acts as a stabilizer to maintain the original perovskite crystal structure.³⁶ Recently, Tavakoli and co-workers utilized formamidinium chloride (FACl) as an additive perovskite thin-film preparation and observed the suppression of surface defects, as well as improved crystallinity and grain size in n-i-p, configured PSCs.³⁵

We here demonstrate the unique synergistic effect of utilizing both FACl as an additive in perovskite thin-film preparation and LiF as an interfacial layer in p-i-n perovskite devices on the basis of a self-assembled monolayer (SAM) hole-selective contacts of 2PACz ([2-(9*H*-carbazol-9-yl)ethyl]phosphonic acid).^{23,40} These three strategies combined enabled us to demonstrate record efficiencies for p-i-n perovskite solar cell devices of up to 22.3%. These results are the highest for SAM-based p-i-n perovskite solar cells, on par with the recently published record for p-i-n solar cells⁹ and the highest performance of a perovskite solar cell with 1.63 eV in both polarities. Devices exhibited an improved steady-state device performance of 22% using SnO₂/ Cu as the counter electrode. The synergistic effect of the three approaches combined to reach high-performance devices became very apparent when comparing the longer-term device performance during maximum power point (MPP) tracking for >700 h under continuous simulated AM1.5G illumination in an inert atmosphere. Having identified the device configuration with the best long-term performance, we made some laser-patterned series interconnected mini-modules with a 2.2 cm² active area, reaching a maximum power conversion efficiency, PCE, of 19.4%. We are highlighting the importance of evaluating device architectures on the basis of longer-term performance rather than the initial PCE derived from J-V measurements to enable identifying device architectures and components that are most viable to develop efficient perovskite device technology on larger areas.

2. RESULTS AND DISCUSSION

2.1. Perovskite Solar Cell Performance. A cross-sectional scanning electron microscopy (SEM) image is shown in Figure 1a, and a schematic picture in Figure 1b illustrates the p-i-n perovskite solar cell devices (PSCs) with the layer stack glass/ITO/SAM/perovskite/LiF/ C_{60} /SnO₂/Cu investigated herein. An estimated energy level diagram is depicted in Figure S1 derived from the valence and conduction band level energies of each component. Figure 1c illustrates the three main modifications that synergistically led to the high device performance reported here: (1) adding FACl to precursor solutions in perovskite layer deposition, (2) introducing LiF as an interfacial buffer layer, and (3) utilizing SAM-based hole-selective contacts.

The devices were built in a superstrate configuration on conducting indium-doped tin oxide glass substrates (ITO, with 150 nm thickness). As a p-type-selective contact, self-assembled monolayers (SAMs) of the carbazole-based phosphonic acid 2PACz, shown in Figure 1c, were deposited on glass ITO substrates by spin-coating. These solutions form self-assembled monolayers that act as a p-type-selective contacts and can be assumed to be approximately 1-3 nm. As a photoabsorbing layer, the "triple cation" perovskite was deposited as specified in the Supporting Information (SI). The composition of the p e r o v s k i t e l a y e r w a s e s t i m a t e d t o b e $Cs_{0.05}FA_{0.79}MA_{0.16}PbBr_{0.51}I_{2.49}$ from the ratio of precursor salts, and the layer thickness was determined to be about 600 nm from cross-sectional SEM images (Figure 1c-3). We here investigated the effect of using formamidinium chloride (FACI) as an



Figure 2. Statistical comparisons of the photovoltaic parameters of (a) short circuit current density together with antireflective coating, (b) opencircuit voltage, (c) fill factor, and (d) resulting power conversion efficiency (J_{SC} , V_{OC} , FF, and PCE) derived from current density–voltage (J–V) measurements of perovskite solar cells (ITO |2PACz |CsMAFAPb(Br, I)₃ (+FACl opt.) |(LiF opt.)|C₆₀|SnO₂|Cu) (i) using FACl as an additive in perovskite absorbing layer, (ii) introducing LiF as an interfacial layer between perovskite and C₆₀ layer, (iii) and SAM-based hole-selective contacts as a pristine measured under simulated AM 1.5G illumination. (e) Current density–voltage (J–V) characteristics of best-performing perovskite solar cells with different integrations of FACl and LiF layers. (f) External quantum efficiency (EQE) spectra of perovskite solar cells with corresponding integrated current densities. (g) Maximum power point tracking (MPPT) measured for 100 s at the fixed voltage near the maximum power point (MPP) derived from J–V measurements.

additive mixed-in with the perovskite precursor solution and observed an improved layer crystallinity of the absorber layer (Figure 1c-1). A 23 nm thick layer of the n-type-selective contact C_{60} was deposited by thermal evaporation with the layer thickness determined by the quartz microbalance in our evaporation setup. A 20 nm thick SnO₂ layer was deposited by atomic layer deposition (ALD) with the layer thickness measured by ellipsometry. Optionally, 1 nm of lithium fluoride (LiF) was introduced as an interfacial layer between perovskite and a C_{60} electron transport layer (ETL) by thermal evaporation to reduce nonradiative losses (Figure 1c-2). Finally a copper counter electrode with 100 nm thickness deposited via thermal evaporation.

In the optimization of devices, we carried out several series of solar cell batches. The statistical comparison of their photovoltaic performance metrics of short circuit current, J_{SC} , opencircuit voltage, V_{OC} , fill factor, FF, and resulting power conversion efficiency, PCE, obtained from the current density–voltage, J-V, measurements are summarized in Figure 2a–d. We compared batches of devices using all three concepts of device interface and perovskite layer modification outlined in Figure 1c: (1) FACl as an ink additive, (2) LiF as a buffer layer, and (3) 2-PACs as SAM. The pristine PSCs delivered an average J_{SC} of 21.8 mA·cm⁻², V_{OC} of 1.13 V, FF of 78.2%, and PCE of 19.0%. Here, we optimized a better performance with this 2PACz as a p-type-selective contact comparable to previously published values.²³ We introduced a LiF buffer layer between the perovskite and C₆₀ electron transport layer, ETL, which has been previously shown to increase the V_{OC} by reducing nonradiative recombination.⁶ When introducing a LiF layer

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perovskite layer additive		5 vol% FACl		5 vol% FACl
buffer layer			1 nm LiF	1 nm LiF
ETM/top contact	SnO ₂ /Cu	SnO ₂ /Cu	SnO ₂ /Cu	SnO ₂ /Cu
$J_{\rm SC} ({\rm mA \ cm^{-2}})_{\rm average}$	21.8 ± 0.50	21.7 ± 0.6	21.8 ± 0.19	21.9 ± 0.48
$J_{\rm SC} ({\rm mA \ cm^{-2}})_{\rm max}$	22.3	22.4	22.0	22.7
$V_{ m OC}$ (V) _average	1.13 ± 0.01	1.138 ± 0.01	1.16 ± 0.02	1.17 ± 0.03
$V_{\rm OC}$ (V) $_{\rm max}$	1.15	1.15	1.18	1.18
FF (%)_average	78.2 ± 2.8	79.0 ± 2.2	78.9 ± 2.1	80.0 ± 1.82
FF (%)_max	79.5	82.7	80.2	83.3
PCE (%)_average	19.0 ± 1.37	19.7 ± 1.11	19.7 ± 1.46	20.5 ± 1.56
PCE (%)_max	20.4	21.2	20.9	22.3
PCE_{MPP} (%)	20.3	21.1	20.6	22.0

Table 1. Photovoltaic Parameters Obtained from *J*–*V* Scans under Simulated 1 Sun Illumination along with MPP-Tracked Values of CsMAFA Perovskite Solar Cells Comparing a LiF Interlayer and FACI Additive

between the perovskite absorber and C_{60} layer, we found that the average performance of 2PACz-based PSCs increased due to an increased $V_{\rm OC}$ improvement (average 1.16 V) to 19.7%. Nevertheless, this improvement in $V_{\rm OC}$ was offset by the reduction of other PV parameters like FF and $J_{\rm SC}$, leading to no substantial increase in the PCE.

PSCs utilizing only FACl as an additive in the perovskite precursor solutions improve the average FF up to 79%, which led to an improved PCE of 19.7%. The $V_{\rm OC}$ and $J_{\rm SC}$ remain unchanged compared to the pristine device. The most significant improvement in PSC performance was obtained when both FACl was added in the perovskite precursor solution and the LiF interlayer was introduced at the interface of the perovskite absorber and C_{60} layer. PSCs comprising both showed an average PCE of 20.5% due to improvements in both average values of the FF (80%) and $V_{\rm OC}$ (1.17 V), as summarized in Table 1. For all devices, a negligible current density voltage (J-V) hysteresis between forward and reverse scan directions at a scan rate of 330 mV/s (calculated from the settings of 40 ms delay time, 20 ms integration time, and 20 mV voltage step size) was observed.

The J-V curves of best-performing 2PACz-based PSCs including pero+FACl, perolLiF, and (pero+FACl)lLiF along with the pristine device, measured under simulated AM 1.5G illumination, are shown in Figure 2e. As discussed above, the (pero+FACl)lLiF-based PSCs delivered a maximum PCE of 22.3% compared to the pristine device with a PCE of 20.4%, as given in Table 1. The external quantum efficiency (EQE) spectra of pero+FACl and (pero+FACl)lLiF-based champion PSCs are shown in Figure 2f. The $J_{SC, EQE}$, calculated by integrating the EQE spectrum with respect to the AM1.5G reference solar spectrum, yielded a negligible difference (<1%) compared to the J_{SC} derived from the J-V scan under AM 1.5G illumination.

The PCEs reported here are among the highest published for p-i-n perovskite devices and present a record for a perovskite solar cell with an absorber bandgap of 1.63 eV, $^{1,9,23,41-47}$ irrespective of device architecture, as summarized in Figure S2 and Table S1 in the Supporting Information. These results are of particular interest for tandem devices based on silicon, for which the optimal bandgap of a top cell absorber was calculated to be 1.62–1.68 eV.⁴⁸

The steady-state maximum power point efficiency for bestperforming (pero+FACl)|LiF-based PSC, measured for 100 s, was about 22% for an active area of 0.105 cm² (masked), as shown in Figure 2g, in comparison with the MPP of other representative PSCs of different device architecture investigated here. J-V curves of devices under dark conditions, measured in both forward and reverse, are shown in Figure S3. We observed that the J-V curves of PSCs with FACl show negligible hysteresis under dark conditions compared to the J-V of devices prepared without the additive. We calculated the ideality factors for both the device prepared without and with FACl additive from their dark J-V curves (see Figure S4), showing that the latter exhibits a lower ideality factor of 1.25 compared to the former (1.45). This demonstrates that the addition of FACl in the perovskite precursor ink leads to devices with better charge extraction and therefore higher FF values.

To assess differences in the transient response of the device, we performed transient analysis during maximum power point tracking (TrAMPPT) measurements of samples with and without FACl additives. This methodology was described elsewhere^{29,49} and allows us to extract the time constants and amplitudes of the transient current response upon a voltage perturbation as well as the steady-state current density (ΔI_{ss}) during maximum power point tracking. As summarized in the SI (Figure S5c) the p-i-n devices investigated all exhibit a fast response, in agreement with negligible hysteresis indices of <0.1 even at fast scan rates (Figure S5d) and J-V curves in different delay times, as in Figure S6. We find that the addition of FACl suppresses the amplitude of current transients, which we interpret as passivation of ion vacancies that else give rise to capacitive effects. Additional short-term MPP traces are shown in Figure S7 for devices with and without FACl additive in the precursor solution but with a LiF interlayer; also, the mediumterm MPP efficiency was measured for 11 h, as shown in Figure S7b. These measurements indicate the substantially higher stability of devices comprising both the FACl additive and LiF interlayer, as further discussed in Section 2.4.

By carrying out J-V measurements under different illumination conditions, we found that solar cell samples prepared with the FACl additive in the precursor solution and a LiF layer exhibited a higher $V_{\rm OC}$ for all illumination intensities and a higher FF in particular at higher illumination intensities, as shown in Figure S8.

2.2. FACI Additive in Perovskite Thin-Film Fabrication. To rationalize the dramatic differences observed in the devices upon adding FACI to the precursor solutions, we investigated the differences between the perovskite thin films. From the EQE onset shown in Figure 2f, the absorption onset does not seem to change dramatically for samples prepared with additional FACI in the precursor solution. This becomes even clearer when looking at the derivative of the EQE shown in Figure S9. To analyze differences in the sample morphology, scanning electron



Figure 3. (a and b) Top view SEM images of 2PACz-based Cs-MAFA perovskite layer with and without FACl additive, and (c) grain size distribution of 2PACz-based Cs-MAFA perovskite layer with and without FACl additive. (d) GIWAXS patterns of intensity versus 2θ of 2PACz-based Cs-MAFA perovskite layer with and without the FACl additive. (e) Optical images captured under blue light emission of 2PACz-based Cs-MAFA perovskite films with and without FACl deposited on quartz substrates.

microscope (SEM) and grazing-incidence wide-angle X-ray scattering (GIWAXS) measurements were carried out. The analysis of the SEM images showed the surface morphology of the perovskite film prepared with and without FACl in the precursor solution, as shown in Figure 3a,b. Figure 3c shows the statistics of the grain size derived from the SEM image analysis, showing that the average grain size is significantly higher (309 nm) for samples prepared from a precursor solution with the FACl additive compared to samples prepared without it (238 nm). The addition of 5 vol% FACl has a definitive effect on grain size. Analogously, GIWAXS measurements were performed on samples without and with the FACl additive in the perovskite processing. The 2D GIWAXS scattering images are shown in Figure S10. As we did not observe a substantial difference in sample orientation and texture, in Figure 3d, we compared the integrated diffraction pattern with respect to the diffraction angle. The FACl additive leads to a very slight increase in lattice spacing, indicated by a shift in the peak positions of the main peaks attributed to the cubic perovskite phase. We hypothesize that this is likely due to some substitution of methylammonium (MA) with the larger formamidinium cations and that MA might be leaving the thin film as MACl during annealing as reported elsewhere.⁵⁰ In previous reports, it was found that a reduction in the amount of the MA-cation in perovskite composition led to better stability of the perovskite solar cells measured under AM 1.5G illumination.⁵¹ Chloride ions have been postulated to passivate defects at the grain boundaries, and growth from halide-rich conditions may prevent ion migration. We observed that the intensity of the α -phase perovskite peaks exhibits higher values, indicating a better crystallinity of the perovskite. The fullwidth at half-maximum (FWHM) values for the (100) perovskite peaks were 0.22 and 0.26 for samples prepared with

and without FACl perovskite, respectively, suggesting that FACl improves the crystallinity of the perovskite layer. Opposite to our expectations, samples prepared with the FACl additive exhibited an increased peak attributable to a crystalline PbI_2 phase, which might be one of the reasons for the higher PCE as PbI_2 has been postulated to passivate grain boundaries.⁵² We are currently conducting more in-depth work to illuminate the role of FACl and other ink additives in perovskite absorber growth kinetics, the stoichiometry, and the crystallinity of resulting thinfilm composition on the performance and stability of perovskite devices.

We performed time-resolved and absolute photoluminescence measurements with and without the FACl additive in the synthesis of perovskite films deposited on quartz substrates (shown in Figure 3e and Figure S11). The photoluminescence quantum yield (PLQY) for samples prepared with the FACl additive is 1.4% and that without is 1.2%, which is comparable. The quasi Fermi level splitting (QFLS) values were calculated to be 1.22-1.23 eV, showing that the FACl additive in thin-film fabrication is not expected to increase the $V_{\rm OC}$ of the PSCs. Time-resolved PL measurements (as shown in Figure S11) showed negligible differences in the PL decay kinetics comparing samples prepared without and with FACl in the perovskite precursor solution. This is in accordance with the device performance metrics summarized in Table 1, showing that the addition of FACl does not change the $V_{\rm OC}$ dramatically but seems to positively affect the FF.

2.3. Effect of FACI Additive and LiF Interlayer. Figure 4a shows the QFLS values of the perovskite films sandwiched between glassIITOl2PACz and a C_{60} layer system using only FACl, only LiF, both FACl and LiF (pero+FACl)ILiF, and pristine perovskite film. We have also merged the average values

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Figure 4. (a) Quasi Fermi level splitting (QFLS) of perovskite films sandwiched between glass/ITO/2PACz and a C_{60} layer system using only FACl, only LiF, both FACl and LiF, and pristine perovskite film along with the mean value of V_{OC} from the *J*–*V* scans. (b) Photoluminescence spectra of the respective sample variations. (c and d) Modulated SPV (surface photovoltage) measurements of 2PACz-based Cs-MAFA perovskite film utilizing with and without FACl and a LiF layer.

of the $V_{\rm OC}$ measured from the J-V curves for each system on the same left axis, as shown. Here, we can correlate the average QFLS values with the V_{OC} for each system. GlassIITO|2PACz| perovskitelC₆₀ showed a mean QFLS of 1.14 eV for 1 sunequivalent illumination intensity. The utilization of FACl in perovskite (glass|ITO|2PACz|(perovskite+FACl)|LiF|C₆₀) improved the QFLS up to 1.165 eV. Figure 4b shows the absolute photoluminescence (PL) signal measured on perovskite thin films sandwiched between glass|ITO|2PACz and a C₆₀ layer for the four different cases of the perovskite thin film with and without the FACl additive as well as with and without the LiF interlayer. While the FACl additive does not exhibit a systematic effect, the absolute PL is certainly increased when including a LiF interlayer, consistent with a higher observed open-circuit voltage due to a higher quasi Fermi level splitting calculated from the absolute PL measurement. All the results can be directly correlated to the perovskite solar cell devices. LiF is necessary to mitigate interface recombination with C_{60} ; however, LiF leads to devices being unstable under continuous MPP tracking. Our data demonstrate that the recombination properties of the absorbers do not change with FACl, but it suppresses the degradation induced by LiF.

Further, we performed modulated surface photovoltage (SPV) spectroscopy measurements to determine the electronic disorder of the perovskite thin films⁵³ with and without incorporation of the FACl additive and a LiF layer. Figure 4c shows the spectra of modulated SPV amplitude versus photon energy for different perovskite layers on glassIITOl2PACzl(pero +FACl_{opt.})|LiF_{opt.}|C₆₀ substrates. The tail energy (E_T) was calculated from the slope of the SPV spectra near the band energy for each substrate.⁵⁴ As shown in Figure 4d, we obtained average $E_{\rm T}$ values of 26, 21.7, 22.5, and 20 meV for pristine (neither FACl nor LiF), CsMAFA mixed with the FACl additive only, perovskite and a LiF buffer layer, and both with FACl and a LiF layer, respectively. The small tail energy values represent lower sub-bandgap defect densities near the band edge, which allow for reducing the recombination losses at the interface, and consequently, these lead to improving the performance of the respective PSCs.⁵³

2.4. Stability Assessment. To assess the steady-state performance of devices, we carried out maximum power point tracking on representative devices manufactured without and with the FACl additive in the perovskite precursor ink. On each substrate, six pixels constituting single small area test devices



Figure 5. Stability evolution of perolLiF- and (pero+FACl)|LiF layer-based perovskite solar cells carried out in the inert atmosphere. Average maximum power point tracking with the standard deviation of five best-performing pixels of solar cells of each combination measured under continuous 1 sun illumination at 25 °C temperature (without using any filter) showing the (a and b) PCE and (c) J_{SC} , V_{OC} , and FF photovoltaic parameters for more than 700 h. (d) Cross-sectional SEM images of fresh devices compared to aged devices. (e) MPP tracking of encapsulated cells in air.

were defined by the pattern of the ITO substrate and evaporated Cu contacts, as described in the Experimental Section (see the Supporting Information). The average maximum power point (MPP) of these PSCs device measured under continuous 1 sun illumination at 25 °C temperature for more than 700 h, as shown in Figure 5a,b. The plots include the standard deviation of measurement values. The J_{SC} , V_{OC} , and FF values were also evaluated during the maximum power point (MPP) tracking and are shown in Figure 5c. The J-V scans as a function of illumination time are shown in Figure S12 of the Supporting Information. The device made without FACl additive (pero LiF) showed a dramatic performance drop during the first 100-200 h with a high degradation rate dominated by a loss in current and FF (see Figure 5c). The boost in the PCE in first 0-20 h is mainly due to an increase in V_{OC} , which might be attributed the insertion of ultrathin layer of LiF. While stressing the device over a longer time (>20 h), LiF facilitates charge

carrier extraction at the interfaces. The devices prepared without FACl in the precursor solution only maintained \sim 30% of their initial PCE after 700 h of continuous testing. In contrast, the efficiency of the PSCs prepared using FACl as an additive in the Cs-MAFA precursor solution and utilizing the LiF buffer layer maintained ~80% of initial PCE after 700 h of aging. This discrepancy becomes even clearer when comparing the integral lifetime energy yield, LEY, of the devices, as shown in Figure S14. The SEM image of the aged perovskite device with FACl additive employed in thin-film fabrication appears more analogous to the fresh device. Thus, FACl plays an important role in the long-term stability of perovskite solar cells. We also performed a shelf life test for our best encapsulated device (pero +FACl)ILiF. We recorded the MPP for one hour before and after storing the encapsulated device for 80 days in air and observed no loss in the PCE. We conclude that the combination of using FACl as an ink additive in perovskite deposition and LiF



Figure 6. (a) Current–voltage curves of perovskite solar cell module with an active area of 2.20 cm^2 measured in both forward and reverse directions. (b) Maximum power point tracking (MPPT) of module measured for 200 s at a voltage of 2.95 V. (c) Statistics of efficiency distribution achieved for mini-modules. (d) Photograph of a perovskite solar mini-module captured from the glass side.

as an interfacial layer results in PSCs with a high efficiency and stability. We postulate that the additional FACl compensates for cation and anion deficiencies that negatively affect device stability.

2.5. Perovskite Mini-Modules. Perovskite solar minimodules (PSMs) with the device structure of glass|ITO|2PACz| (pero+FACl)|LiF|C₆₀|SnO₂|Cu were fabricated. A photograph of the mini-module is depicted in Figure 6d. The PSM was designed with three interconnected cells in a series enabled by multiple scribing including P1, P2, and P3 via laser scribing techniques⁵⁶ (see details in the Supporting Information). We tested approximately 30 modules with the PCE distribution, as shown in Figure 6c. Most mini-modules performed with a PCE in the range 17-18%, as summarized in Figure 6c. The J-Vcharacteristics for the best-performing module measured in both forward and reverse directions under 1 sun illumination are shown in Figure 6a. The photovoltaic parameters such as V_{OC} I_{SC} , FF, and PCE values are summarized in the inserted table in Figure 6a. The PSM in a reverse scan delivered a $V_{\rm OC}$ of 3.50 V, indicating that each sub cell contributes an average $V_{\rm OC}$ of 1.16 V. The current was 15.76 mA. The maximum power point efficiency for the best-performing (pero+FACl)lLiF-based PSM, measured for 200 s, was about 19.2%, as shown in Figure 6b. We also tested mini-modules under continuous 1 sun illumination at 25 °C for more than 6 h (as shown in Figure S15) and realized no loss in the PCE.

The module PCE of 19.4% on 2.2 cm² achieved here is the record for a perovskite solar cell mini-module reported in the literature. Li et al. reported record efficiencies for 21 cm² area perovskite modules with a PCE of 18.1% .⁵⁷ Microquanta has also shown one of the highest certified mini-module with an efficiency of 17.3% on a 17.3 cm² area. Toshiba has achieved the highest certified module PCE of 11.6% on an area of 802 cm².^{58,59} Further improvements of our mini-module performance can be achieved by further reducing the geometrical fill factor, which for this module was calculated to be ~91%. After introducing a robust device architecture and perovskite thin film deposition strategy, we now focus on scalable deposition strategies for all active layers in the perovskite device stack to manufacture larger area perovskite devices.

3. CONCLUSION

Using the combination of three different strategies to optimize the performance of perovskite solar cells, the addition of FACI into the perovskite precursor solution, introducing LiF as an interfacial layer, and using a self-assembled monolayer of a carbazol phosphonic acid as a hole-selective contact, we achieved high solar cell power conversion efficiencies. On average, the highest device performance was achieved when combining the FACl additive with the LiF interlayer resulting in a record power conversion efficiency of 22.3%. This is a record for a p-i-n perovskite solar cell with a bandgap of 1.63 eV. This is

of particular importance for the realization of efficient tandem solar cells based on silicon. The synergistic effects of combining these strategies became very apparent when considering the long-term performance of devices. Devices with both the FACl additive and LiF interlayer exhibited >80% of their initial steadystate performance after >700 h of MPP tracking. In comparison, devices prepared without the FACl additive maintained only 30% PCE after 700 h under continuous full illumination of simulated AM1.5G in a nitrogen atmosphere. Samples made with the FACl additive in the precursor solution resulted in thin films with better crystallinity and larger grain size, and FACl seems to counteract instability effects introduced with the LiF interlayer. We scaled the most promising device configuration to a mini-module device area with 2.2 cm² active area and achieved 19.2% power conversion efficiency. Evaluating devices on the basis of their longer-term performance and not on their initial performance becomes important when deciding which device architectures and components to prioritize in scaling the device technology to larger areas.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsami.0c17893.

Discussions of experimental details, further sample characterization, transient analysis during MPP-tracking (TrAMPPT) and discussion of devices hysteresis, life-time/levelized energy yield calculations (LEY), Figures of an estimated energy level diagram, extracted bandgaps from EQE spectras, J-V curves, ideality factors, PV parameters, 2D plots of GIWAXS intensity pattern, time-resolved PL measurements, light source spectra, comparison of lifetime energy yield, statistics of efficiency distribution of mini-modules, SEM image, and perovskite module MPP, table summarizing highest efficiency and stability of p-i-n perovskite solar cells reported in the literature (PDF)

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Author Contributions

J.D. was the main contributor to the experimental part of this work and fabricated and characterized the solar cells, analyzed the data, and prepared the first draft of the manuscript and figures. B.L. and A.A.-A. supported the solar cell fabrication and device analysis. M.F. and C.S. carried out laser patterning of the mini-modules. G.P. supported the fabrication of the devices. A.M. supported TrAMPPT data analysis. R.M., J.L., and D.M.T. contributed to in beam time GIWAX measurements. J.D. and I.L. supported SPV experiments. H.K. carried out long-term stability measurements. J.A.M, H.N, T.U., and L.K. analyzed the PL data. A.A., R.S., B.S., and S.A. contributed to the scientific content through scientific discussions. E.U. was the main responsible PI in this project and supervised the experimental work and contributed to the writing as well as revisions of this manuscript. All authors have read and given input to the final draft of this manuscript.

Notes

The authors declare no competing financial interest.

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