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Methylammonium-free, high-performance and stable perovskite solar cells on a planar architecture

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Currently, perovskite solar cells (PSCs) with high performances >20% contain Br, causing a suboptimal bandgap, and the thermally unstable methylammonium (MA) molecule. Avoiding Br and especially MA can, therefore, result in more optimal bandgaps and stable perovskites. We show that inorganic cation tuning, using Rb and Cs, enables highly crystalline formamidinium-based perovskites without Br or MA. On a conventional, planar device architecture, using polymeric interlayers at the electron and hole transporting interface, we demonstrate an efficiency of 20.35% (stabilized), one of the highest for MA-free perovskites, with a drastically improved stability reached without the stabilizing influence of mesoporous interlayers. The perovskite is not heated beyond 100°C. Going MA-free is a new direction for perovskites that are inherently stable and compatible with tandems or flexible substrates which are the main routes commercializing PSCs.

Perovskites with an ABX₃ structure (A = Cs, methylammonium (MA), formamidinium (FA); B = Pb, Sn; X = Cl, Br, I) have sky-rocketed in recent years with power conversion efficiencies (PCEs) at now 22.7% which is close to established technologies such as GaAs, CdTe, and silicon (1). Currently, high-performance perovskite solar cells (PSCs) with efficiencies >20%, including all reported world-records, contain unstable MA (2–6).

One important trend to achieve PCEs >20% has been the usage of more complex perovskite compositions ranging from double cation (MAFA, CsFA) (7–9), triple cation (CsMAFA) (6), to Rb-modified perovskites (5, 10–12). Interestingly, FA is used as the majority cation in almost all current high efficiency PSCs because FA, compared to MA, is thermally more stable (8, 13) and has a more optimal, redshifted bandgap since it is the largest organic cation to still fit into a 3D perovskites (14). Unfortunately, the relatively large size of FA also induces a distorted lattice resulting in a photoinactive “yellow phase” at room temperature while the photoactive “black phase” can only be observed at elevated temperatures (8). Therefore, obtaining phase-stable, black phase FA-perovskites at room temperature has become the implicit or explicit objective of the perovskite research field. Avoiding yellow phase impurities motivated the development of the above-mentioned optimized processing techniques and elaborate multication, multihalide mixtures. Especially the addition of Br has been crucial to suppress yellow phase impurities. Accordingly, Br often constitutes up to 20% of the

precursor compositions within most high-performance PSCs (5, 6, 15, 16).

However, using the halide position to improve crystallization comes at a cost: Br blueshifts the bandgap disproportionately. We illustrate this point in Fig. 1A, where we show the Shockley-Queisser limit for the theoretical, maximum PCE and short-circuit current (J_{sc}) as a function of the bandgap (E_g) (17). By interchanging Br with I in MAPbI₃Br_{1-x} compounds, a bandgap range from 1.58 eV (MAPbI₃) to 2.28 eV (MAPbBr₃), spanning 700 meV, is achieved (18).

In stark contrast, the cation interacts only moderately with the metal-halide cage and accordingly has a relatively small bandgap shift of only 100 meV from MAPbI₃ (1.58 eV) to FAPbI₃ (1.48 eV) (18). The instability of MAPbI₃ is reported by various works showing film degradation because of degassing MA (13, 20–23). In Fig. 1B, we illustrate the volatile nature of the MA molecule itself using the reported degradation pathway of CH₃NH₃I into CH₃I and NH₃ at temperatures as low as 80°C (the iodine atom is omitted in the figure for simplicity) (19). Therefore, MA remains a principled risk factor for long-term stability and should thus be avoided (although the exact timescales of MA degradation require further research). To substantiate this point further, Supplementary Note 1 (together with figs. S1 to S4) shows the XRD and respective UV vis spectra before and after annealing at 130°C for 3 hours of MA-containing perovskite films, i.e., MAPbI₃, Cs₅MAFAPbI₃, MAFAPbI₃ and Rb₅Cs₅MAFAPbI₃; and non-MA perovskite films, i.e., FAPbI₃, Rb₅FAPbI₃, Cs₁₀FAPbI₃ and

$\text{Rb}_5\text{Cs}_{10}\text{FAPbI}_3$. All MA-based perovskites exhibit strong degradation as evidenced by the growth of the PbI_2 peak at 12° , a behavior which does not occur for the non-MA perovskites. While thin films are not full devices, they nevertheless provide a clear motivation to avoid MA in all future compositions ensuring perovskites with intrinsic long-term stability that is required for decade-long stable solar cells. Industry cannot afford the long-term risk factor of MA. However, currently almost all reported PCEs $>20\%$, including all world-records, use MA (2–6) whereas perovskites without MA are currently often below 20% and frequently use high-temperature steps (2, 5, 24).

Thus, a more ideal perovskite compound ought to avoid Br because of the “blue penalty” and MA for stability reasons. This leaves iodine as the preferred halide and the thermally more stable Rb, Cs, and FA as the preferred cations (see Fig. 1C) rendering RbCsFAPbI_3 perovskites particularly relevant. Hence, in this work, we explore $\text{Rb}_x\text{Cs}_y\text{FA}_{(100-x-y)}\text{PbI}_3$ compositions. We discover an optimized RbCsFAPbI_3 perovskite (without MA and Br) with a bandgap of 1.53 eV, close to the single-junction optimum, with high short-circuit currents comparing favorably with the previously used $\text{RbCsMAFAPb}(\text{Br}_{17}\text{I}_{83})_3$ perovskite (see red and blue open circles in Fig. 1A). We achieve a planar PSC with a short-circuit current of 25.06 mA cm^{-2} and a high PCE of 20.44% (stabilized at 20.35%) for planar PSCs which is among the highest non-MA containing results thus far reported. The perovskites do not require any heating beyond 100°C rendering them compatible with perovskite/silicon tandem solar cells or flexible solar cells which are among the most attractive pathways to commercialization.

We provide X-ray diffraction (XRD), photoluminescence (PL), and UV-visible absorption (UV-vis) data for $\text{Rb}_x\text{Cs}_y\text{FA}_{(100-x-y)}\text{PbI}_3$ perovskite films (on a planar substrate), written for convenience as $\text{Rb}_x\text{Cs}_y\text{FAI}$ in the following (x and y are in percentage throughout the manuscript). This nomenclature refers to the precursor solutions as outlined in the Supplementary Information (SI).

We start our investigation with the double-cation compounds $\text{Cs}_y\text{FA}_{(100-y)}\text{I}$ and $\text{Rb}_x\text{FA}_{(100-x)}\text{I}$. In Supplementary Note 2 (together with figs. S5 to S8), the XRD data for $\text{Cs}_y\text{FA}_{(100-y)}\text{I}$ (figs. S5 and S6) show the characteristic perovskite peak at 14° that shifts as more Cs is added. This corresponds to a blueshift in the PL and UV-vis data as shown in Fig. 2A and as previously reported (8, 25). For $\text{Rb}_x\text{FA}_{(100-x)}\text{I}$, the perovskite peak in the XRD data does not shift as strongly as for the Cs series (see figs. S7 and S8). This is consistent with the PL and UV-vis data (Fig. 2B) where only a very slight blueshift occurs for small Rb quantities (see Fig. 2B). As the amount of Rb is increased, only a very small blueshift in the PL occurs. Albeit, for $\text{Rb}_{15}\text{FA}_{85}\text{I}$, a more noticeable blueshift and broadening occur in the PL correlating with the occurrence of a second

phase in the XRD at 10° (fig. S7). In addition, in contrast to CsFA, the RbFAPbI_3 films require annealing at 150°C , close to the temperature needed to convert pure FAPbI_3 films. This is consistent with previous work (5, 26) confirming that there is no “black phase” for RbPbI_3 .

From SEM top view images in Fig. 2C, we observe that $\text{Cs}_x\text{FA}_{(100-x)}\text{I}$ films, starting with 5% Cs, have a relatively ordered film morphology with large grains. In contrast, Rb, likely due to the partial integration, has a less ordered film morphology resembling pure FAPbI_3 films. The last image on the right, $\text{Rb}_5\text{Cs}_{10}\text{FAI}$, has a regular film morphology. We display specifically $\text{Rb}_5\text{Cs}_{10}\text{FAI}$ because it shows the highest and most reproducible device results (see below).

We fabricate full devices on a planar stack of glass/FTO/ SnO_2 /perovskite/spiro/Au as reported previously (27). In Fig. 2D, cross-sectional SEM images are presented. The pure FAPbI_3 film is highly irregular and rough. For the CsFA series, starting with $\text{Cs}_5\text{FA}_{95}\text{PbI}_3$, the grains become monolithic throughout the film reaching from the top to the bottom contact. For the RbFA series, for all Rb concentrations, the films resemble FAPbI_3 which is not beneficial for the perovskite/hole transporter materials (HTM) interface. The $\text{Rb}_5\text{Cs}_{10}\text{FAI}$ compound has particularly monolithic, large grains.

Lastly, in Fig. 2, E and F, we present XRD, and PL and UV-vis data for the $\text{Rb}_5\text{Cs}_y\text{FA}_{(95-y)}\text{I}$ series. The most blueshifted composition is for 15% Cs followed, surprisingly, by 3% Cs. Upon adding 5% and 10% Cs, the PL remains relatively close to that of pure FA-based perovskite. This is consistent with Rb and Cs interacting with one another. We posit Cs could be aiding Rb to modify the lattice more effectively, but it is also possible that for certain Rb/Cs ratios, RbCsPbI_3 perovskites form (see the occurrence of an additional phase at 10° in Fig. 2E for 10 and 15% Cs). These inorganic compounds could “lock up” excess I-halides and help forming a passivation layer for the remaining, pure FAPbI_3 perovskite that has a more optimal single-junction bandgap. This is most noteworthy for the $\text{Rb}_5\text{Cs}_{10}\text{FAI}$ compound which has a PL emission very close to FAPbI_3 in contrast to the non-Rb containing Cs_{10}FAI (see Fig. 2A).

From device data in Supplementary Note 3 (together with figs. S9 to S16), we observe relatively high performing CsFA (figs. S9 and S11) compounds which are not matched by the analogous RbFA series (figs. S10 and S12).

Importantly, the double-cation CsFA films, possibly due to the large mismatch between the small Cs and large FA, do not yield highly reproducible PSCs. While CsFA can occasionally reach high PCEs of 19.23% (fig. S9), we show in fig. S14A that the statistical baseline is lower (5). The Rb-modification again yields higher performing perovskites with PCEs toward 19.52% for $\text{Rb}_5\text{Cs}_{10}\text{FAI}$ (see fig. S13 for the RbCsFAI series). In fig. S14, we show that the best performing Cs_{10}FAI perovskite

improves significantly upon 5% Rb addition in terms of absolute efficiencies and especially reproducibility (an often neglected metric).

From Supplementary Note 3, we identify $\text{Rb}_5\text{Cs}_{10}\text{FAPbI}_3$ as a promising composition (see figs. S13 and S14) and therefore continue with this composition for the remainder of this study. We note that we successfully redshifted the bandgap as motivated in Fig. 1. This can be observed clearly in the EQE measurements in figs. S15 and S16 where the EQE follows the PL trends. Consequently, we measure a high short-circuit current density of 24.52 mA cm^{-2} as confirmed by EQE data showing an integrated J_{sc} of 24.01 mA cm^{-2} (fig. S16B), highlighting the inorganic cation tuning as a versatile tool to achieve more optimized, MA-free bandgaps.

The planar device architecture is used because it is inherently more compatible with flexible and tandem applications (none of the processing steps exceeds 100°C). Currently, planar PSCs show relatively high PCEs $>20\%$ and up to 21.4% (28–30) (all using MA) which is slightly lower than mesoporous-containing perovskites at 22.1% (also using unstable MA) (31). One reason for this is that planar PSCs are prone to exhibit shunting pathways between the highly monolithic perovskite grains (32). Accordingly, one of the main parameters lacking for planar PSCs is the fill factor (FF) (see Supplementary Note 2). In planar PSCs, any pinhole in the perovskite film results in a shunt-path enabling a direct pathway between electron and hole transporter. In contrast, an additional meso-layer avoids direct contact between the electron and hole transporter preventing pinholes from becoming detrimental shunt paths. Consequently, for planar PSCs, the perovskite layer itself needs to be formed nearly perfectly and thus the processing window for planar PSCs is much narrower than for meso PSCs. In addition, we posit that the formation of pinholes is less likely with a meso-layer because of a more uniform surface wettability for the liquid precursor in contrast to planar PSCs where surface wettability is a constant concern. Thus, an imperfect perovskite layer can be saved by the meso interlayer. In other words, meso PSCs are more forgiving of imperfections. Consequently, due to the challenging fabrication, planar PSCs have remained less efficient than meso PSCs. This results in fewer groups specializing on planar PSCs which, in turn, results in fewer reported results. At the moment, this is a vicious circle: because planar PSCs do not reach world records yet, groups are less willing to switch from meso to planar even though it is industrially more preferable (33). To change this, we aim here for high-performance, MA-free perovskites on a planar architecture requiring modifications of the planar architecture.

Recently, much progress has been made in improving perovskite interfaces through polymeric buffer layers that help passivating the perovskite, reduce recombination and mitigate the negative impact from pinholes as well as block metal

electrode migration at elevated temperatures (5, 34). This approach is used both for the electron-transporting layer (ETL)/perovskite and the HTM/perovskite interface, e.g., C60-SAM (35), PCBM (36), and PMMA (34). For example, mixing PCBM and PMMA was shown to benefit the ETL/perovskite interface (37). This method, however, still uses an undesirable high-temperature TiO_2 mesoporous layer. Therefore, we explore the potential of polymeric buffer layers for a planar ETL/perovskite interface using our optimized $\text{Rb}_5\text{Cs}_{10}\text{FAI}$ compound (see Supplementary Note 4 together with figs. S17 to S19). In fig. S17, we explore different concentrations of PCBM at the SnO_2 /perovskite interface realizing that no improvement is achieved compared to the control device without polymeric layers. We then investigate different concentrations of a mixed polymeric interlayer of PCBM:PMMA at the SnO_2 /perovskite interface (see fig. S18). For planar PSCs, we find that PCBM:PMMA with a 5:1 ratio increases the average FF with remarkable values up to 77% (when compared to the control device without polymer-modification). Importantly, the reproducibility, a very critical parameter for planar devices, is also improved as indicated by the lowered standard deviation.

Encouraged by this, we investigate the top interface between the HTL and the perovskite using a PMMA layer on devices that already have a PCBM:PMMA polymer mix at the ETL interface. We show the results for the double-polymer modified, planar PSCs in fig. S19. The additional PMMA layer improves the device architecture further. Perovskite films with and without a PMMA layer were characterized further using atomic force microscopy (fig. S20) and contact angle measurements (fig. S21). From these measurements we can conclude that the surface roughness is reduced and the contact angle increased using PMMA, indicating that the polymer layer indeed modified the interface.

While the devices with a 10:0.1 PCBM:PMMA show some of the highest PCE, the 5:1 PCBM:PMMA ratio exhibits more reproducible device parameters, especially in the FF. Thus, we use a double polymer-modified PSCs (pm-PSCs) with a 5:1 PCBM:PMMA mix at the ETL/perovskite and a PMMA layer between the perovskite/HTM as the most promising system for high performances and reproducibility.

In figs. S19 and S14B, we evaluate statistically the potential of the $\text{FTO}/\text{SnO}_2/\text{PCBM:PMMA}/\text{perovskite}/\text{PMMA}/\text{HTM}$ stack. We observe in fig. S19 a similar average J_{sc} at 24.67 mA cm^{-2} (control) and 24.51 mA cm^{-2} (polymer-modified), a similar V_{oc} from 1095 to 1083 mV, and an increase of the average FF from 68 to 74% translating into an improved average PCE from 18.20 to 19.71% . Most importantly, the polymer-modification improves reproducibility as especially noticeable in the FF.

In Fig. 3A, we show the champion device for pm-PSCs reaching a high stabilized power output of 20.35% (see table

S1 for the J - V parameters). The J_{sc} of 25.06 mA cm^{-2} is in good agreement with the integrated external quantum efficiency value of 24.48 mA cm^{-2} (Fig. 3B). (In addition, figs. S22 and S23 display a 0.5 cm^2 area device, and J - V parameters for differently sized masks, respectively). In Fig. 3C, we show the SEM image of a representative $\text{Rb}_5\text{Cs}_{10}\text{FAPbI}_3$ polymer-modified device. Moreover, in Fig. 3E, we show a Tauc plot with a bandgap of 1.53 eV for $\text{Rb}_5\text{Cs}_{10}\text{PbI}_3$ confirming once more that the inorganic cation tuning achieved the original goal of red-shifting the bandgap.

Stability is one of the most important obstacles remaining for PSCs to become attractive for industry. However, relatively few stability data sets exist for planar devices.

We, therefore, measure stability as outlined in previous works (5, 28, 38). We use the $\text{Rb}_5\text{Cs}_{10}\text{FAPbI}_3$ composition with and without the polymer modification applying aging at room temperature for 1000 hours of continuous maximum power point tracking in a nitrogen atmosphere. Figure 3D shows that without polymeric buffer layers, the loss is significant (starting at 19.54% and finishing at 15.31% PCE). In stark contrast, the polymer-modified device has a only small losses. The absolute PCE starts at 19.04%, drops quickly to 18.3% after 35 hours (sometimes compared to a “burn-in”), and then exhibits a long-term component that stays relatively constant finishing at 18.16% PCE after 1000 hours. Thus, after the initial component, the efficiency loss is less than 2 rel%, which is among the best-reported stability data yet for planar PSCs (without using MA). The stability of the $\text{Rb}_5\text{Cs}_{10}\text{PbI}_3$ compound is confirmed in figs. S24 and S25 where additional devices, including mesoporous (see figs. S25 and S26), were aged under the same conditions for 500 hours. This stability data highlights the significance of the device architecture for the long-term stability of especially planar PSCs. Interestingly, this implies also that the mesoporous titania interlayer in the current world-record architectures not only contributes to higher performances but also higher stabilities. We posit that the higher stability is due to the meso-layer acting as a mechanic barrier against external degradation factors (such as moisture, vapors and a diffusing metal electrode) as well as the challenges for planar PSCs to deposit a nearly perfect, compact perovskite absorber, which is needed for high performances but also to protect against the mentioned external degradation factors. Thus, stabilizing planar architectures, without the help from protective mesoporous interlayers, is one of the key challenges for perovskite research. Therefore, especially the contacts, e.g., polymeric buffer layers, will play an important role in fortifying planar PSCs further in the future as clearly evidenced by Fig. 3D (39).

More generally, using only inorganic additives to phase stabilize the thermally relatively stable FA perovskites is a compositional design strategy that may be used to stabilize intermediate bandgaps as well, which is highly attractive for

tandem applications. Especially the prospect of a perovskite/silicon tandem has inspired much progress in the field. However, silicon solar cells are stable over many decades and therefore any unstable perovskite component, such as MA, must be avoided if PSCs were to be combined with silicon. Our work provides a direct pathway circumventing many of the drawbacks so far observed in MA and Br-containing perovskites.

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SUPPLEMENTARY MATERIALS

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Materials and Methods
SupplementaryText
Figs. S1 to S26
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Reference (40)

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Fig. 1. Disproportionate bandgap tuning and cation stability. (A) Shockley-Queisser limit for the theoretical, maximum power conversion efficiency (PCE) and short-circuit current (J_{sc}) as a function of the bandgap (E_g). A wide bandgap range is spanned from 1.48 eV (FAPbI₃) to 1.58 eV (MAPbI₃) to 2.28 eV (MAPbBr₃). The cation position (FA to MA) shifts the bandgap only moderately by 0.1 eV, whereas the halide position (I to Br) incurs a disproportionate “blue penalty” shifting the bandgap by 0.7 eV. The red open circle is the newly developed, non-MA, non-Br compound RbCsFAPbI₃ which is closer to more optimal bandgaps; whereas RbCsMAFAPb(Br₁₇I₈₃)₃ (blue open circle) (5), one of the currently highest performing compositions, has a suboptimal bandgap and contains unstable MA. (B) Illustration of the volatile nature of the MA molecule. One reported degradation pathway is CH₃NH₃ into CH₃ and NH₃ (the iodine atom is omitted for simplicity) at temperatures as low as 80°C as reported in (19). (C) In contrast, Rb, Cs, and FA are thermally more stable cations and therefore preferable for long-term stability.

Fig. 2. Inorganic cation tuning: UV-vis, PL, SEM, and XRD characterisation. PL and UV-vis data for the (A) $\text{Cs}_x\text{FA}_{(100-x)}\text{PbI}_3$ ($x = 0, 1, 5, 10, 15\%$), and the (B) $\text{Rb}_y\text{FA}_{(100-y)}\text{PbI}_3$ ($y = 0, 1, 5, 10, 15\%$) series. (C) Corresponding top view SEM images. The scale bar is 200 nm. (D) Corresponding cross-sectional SEM images for full devices. The scale bar is 200 nm. The last image on the right is the $\text{Rb}_5\text{Cs}_{10}\text{PbI}_3$ composition that results later in the highest device results. (E) XRD data, and (F) PL and UV-vis data for the $\text{Rb}_x\text{Cs}_y\text{FA}_{(100-x-y)}\text{PbI}_3$ series.

Fig. 3. Best performing device, J - V , EQE, SEM, and stability. (A) J - V curve with MPP of a Rb₅Cs₁₀FAPbI₃ device with polymer layers comprised of PCBM/PMMA at the SnO₂/perovskite interface, and PMMA at the perovskite/HTM interface. The planar device displays a stabilized power output of 20.35%. Corresponding EQE (B) and SEM image (C). (D) Stability for the Cs₁₀Rb₅FAPbI₃ device without polymer layers (green curve) and with polymer-modification (blue curve) aged at room temperature after 1000 hours of continuous maximum power point tracking in a nitrogen atmosphere. (E) Tauc plot resulting in a 1.53 eV bandgap for the optimized Rb₅Cs₁₀FAPbI₃ perovskite.