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High stability bilayered perovskites through crystallization driven self-assembly

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Keywords: bilayered perovskite • air stability • mixed-dimensionality • phase separation • self-assembly

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Abstract

In this manuscript we reveal the formation of bilayered hybrid perovskites of a new lower dimensional perovskite family, $(\text{CHMA})_2(\text{MA})_{n-1}\text{Pb}_n\text{I}_3$ with $n = 1$ to 5 , with high ambient stability *via* its crystallization driven self-assembly process. The spun-coated perovskite solution tends to crystallize and undergo phase separation during annealing, resulting in the formation of 2D/3D bilayered hybrid perovskites. Remarkably, this 2D/3D hybrid perovskites possess striking moisture resistance and displays high ambient stability up to 65 days. The bilayered approach in combining 3D and 2D perovskites could lead to a new era of perovskite research for high efficiency photovoltaics with outstanding stability; with the 3D perovskite providing excellent electronic properties while the 2D perovskite endows it moisture stability.

Introduction

In the past few years, there has been a tremendous research effort in MAPbI₃ (MA⁺ = CH₃CH₂⁺) perovskite solar cells, pushing the power conversion efficiency to over 20 %.¹⁻² However, its moisture-sensitive nature remains a concern for large-scale commercialization.³⁻⁶ Partial substitution of the MA⁺ cations with hydrophobic organic cations (e.g. phenylethylammonium and butylammonium) will lead to the formation of a lower dimensional perovskite which enhances the moisture resistance of the conventional MAPbI₃ perovskite.⁷⁻⁸ Nevertheless, the power conversion efficiency of 2D perovskite solar cells is still far lower than their 3D counterpart, due to the larger bandgap and challenges of charge transport in the layered structure.⁹⁻¹⁰

Figure 1. Schematic illustration of different dimensionality in (CHMA)₂(MA)_{n-1}Pb_nI_{3n+1} perovskites.

Perovskite structures with different dimensionalities are shown in Figure 1. The general chemical formula for multidimensional perovskites is A_mB_{n-1}M_nX_{3n+1}, where A is a larger organic cation [m = 1 for di-ammonium cation (NH₃⁺-R-NH₃⁺) and m = 2 for mono-ammonium cation (R-NH₃⁺)]¹¹⁻¹⁴ that induces the formation of layered structure, B is a smaller cation (usually MA⁺, FA⁺, Cs⁺)¹¹ that fits into the space provided within the inorganic layers, M is a

divalent metal cation (Pb^{2+} , Sn^{2+} , Ge^{2+} , Cu^{2+} , etc.),^{11, 15-17} X is a halide ion (Cl, Br, or I),^{14, 18-19} while n represents the number of inorganic lattices between the larger organic cation layers. 2D perovskites can be conceptually derived from the 3D perovskites by replacing the smaller cations with larger organic cations. The interlayer distance between the inorganic lattices can be controlled through the choice of appropriate organic cations whereas the number of inorganic lattices (n) can be controlled by varying the stoichiometric ratios of the A and B cations.²⁰⁻²³

Ideally, in open-circuit condition, the photoexcited electrons and holes in the light absorbing layer should recombine and emit as external luminescence to balance the incident photon received from sunlight. Thus, a good light absorber should also be a good light emitter and its external luminescence can be considered as an indicator of its nonradiative recombination and optical losses.²⁴⁻²⁶ Previously, highly flexible cyclohexylmethylammonium ($\text{CHMA}^+ = \text{C}_6\text{H}_{11}\text{CH}_2\text{NH}_3^+$) cation was successfully incorporated between the lead halide lattices to form a layered perovskite which showed significantly strong photoluminescence (PL).²⁷⁻²⁸ Among the cyclohexane-based derivatives, the methyl group has been proven to be the optimum bridge between the ammonium and cyclohexyl moieties and exhibits the highest PL quantum efficiency among cyclohexylammonium lead halide perovskites.²⁷ We obtained a PL quantum efficiency of about 25 % for $(\text{CHMA})_2\text{PbI}_4$ 2D perovskite thin films, suggesting that CHMA^+ cations can be a potential candidate in creating perovskites suitable for photovoltaic applications.

There are numerous studies and reviews discussing the instability of perovskites under ambient, humid environment and in encapsulated devices. Perovskites can mainly decompose through the action of several factors such as high temperatures (140 - 200 °C),²⁹ UV light exposure³⁰⁻³¹ and humid environment³²⁻³⁷ which could lead to the deterioration of the power conversion efficiencies of the solar devices. The decomposition of perovskite usually occurs in

the presence of moisture or in environments with high humidity.⁵ Hence, several sealing techniques have been implemented to reduce the interaction between perovskites and moisture.³⁸⁻
⁴⁰ However, a small amount of moisture is sufficient to degrade the perovskite even in encapsulated solar cells with sealing techniques commonly used for OLEDs (organic light emitting diode).⁴¹ Thus, developing moisture insensitive perovskites is essential in strengthening the stability of perovskites in ambient condition.

In this work, a new lower dimensional perovskite family $(\text{CHMA})_2(\text{MA})_{n-1}\text{Pb}_n\text{I}_{3n+1}$ with $n = 1$ to 5 is synthesized and characterized. This new series of lower dimensional perovskites possesses a unique feature of forming a bilayer perovskite structure *via* a simple single-step deposition method. This novel bilayer perovskite structure exhibits good air stability and device efficiency which offers a new insight to combine different perovskite properties for hybrid perovskite solar cells.

Results and Discussion

The series of $(\text{CHMA})_2(\text{MA})_{n-1}\text{Pb}_n\text{I}_{3n+1}$ perovskites was obtained by mixing stoichiometric amounts of CHMAI, MAI and PbI_2 in dimethylformamide (DMF) to achieve $n = 1$ to 5. For $(\text{CHMA})_2\text{PbI}_4$ ($n = 1$), the perovskite readily formed a smooth and compact film after the spin-coating process. X-ray diffraction patterns of $(\text{CHMA})_2\text{PbI}_4$ ($n = 1$) shows the dominant (00l) ($l = 2, 4, 6, 8$, etc.) reflections, indicating the preferential growth along the (110) direction in its self-assembly process (Figure 2a). Strong peaks of (00l) reflections of $n = 1$ and $n = 2$ and the signature (110) reflection of MAPbI_3 indicate the coexistence of $n = 1$, $n = 2$ and MAPbI_3 in all the films in which $n > 1$. As the content of MA^+ cations increases in $(\text{CHMA})_2(\text{MA})_{n-1}\text{Pb}_n\text{I}_{3n+1}$ ($n = 2$ to 5), the relative intensity of the corresponding (00l) reflections reduces, while the relative intensity of the signature (110) reflection peak of MAPbI_3 increases. It can hence be

deduced that the increasing amount of MA^+ cations induce the formation of MA-rich higher dimensional perovskites in the self-assembly process.

Figure 2. (a) XRD patterns and (b) optical absorption spectra for $\text{CHMA}_2(\text{MA})_{n-1}\text{Pb}_n\text{I}_{3n+1}$ ($n=1-5$) thin film samples. (c) Cross-sectional view SEM images of $(\text{CHMA})_2(\text{MA})_3\text{Pb}_4\text{I}_{13}$. (d) AFM image $(\text{CHMA})_2(\text{MA})_3\text{Pb}_4\text{I}_{13}$, showing the surface roughness of 13.79 nm. (e) Proposed formation process of bilayer structure.

Figure 2b shows the optical absorption of $(\text{CHMA})_2(\text{MA})_{n-1}\text{Pb}_n\text{I}_{3n+1}$ perovskites and MAPbI_3 . For $(\text{CHMA})_2\text{PbI}_4$, the absorption peak λ_{abs} was found at 508 nm which is in agreement with the previous report.²⁷ This optical absorption feature is attributed to the excitonic band which results from the localization of excitons in the inorganic part in the perovskite.^{21-22, 42-43}

When the dimensionality of $(\text{CHMA})_2(\text{MA})_{n-1}\text{Pb}_n\text{I}_{3n+1}$ perovskites increases from $n = 2$ to 5, the optical absorption results clearly shows the combination of absorption band at around 508, 565, 608 and 641 nm which represents the optical absorption from $n = 1, 2, 3$ and 4 dimensional perovskites respectively. The formation of mixed-dimensional perovskite are commonly seen in single step deposition methods as the self-assembly process of the perovskite formation is not properly controlled during the spin coating process.^{23, 44} Interestingly, when the dimensionality is increased beyond $n = 1$, there is a significant increase in the absorption beyond 700 nm. This is not common for lower dimensional perovskites where the absorption generally falls below 700 nm.⁴³ The increase in the optical absorption beyond 700 nm is attributed to the presence of higher dimensional perovskite (MAPbI_3) in the film in agreement with the XRD pattern discussed earlier.

FESEM images of top and cross-sectional view of $(\text{CHMA})_2(\text{MA})_3\text{Pb}_4\text{I}_{13}$ ($n = 4$) are shown in Figure S1 and Figure 2c. The top view image reveals the compact and smooth surface of the perovskite thin film confirmed by atomic force microscopy (AFM), showing a surface roughness of 13.79 nm (see Figure 2d). Surprisingly, the cross-sectional FESEM image of $(\text{CHMA})_2(\text{MA})_3\text{Pb}_4\text{I}_{13}$ indicates a porous underlayer below the compact and smooth upper layer. This clearly shows the presence of bilayer structure in the perovskite film as supported by XRD and UV-Vis measurements. From the cross-sectional FESEM image, it can also be seen that the top layer was formed without cracks although the bottom layer is porous. The proposed formation of the perovskite film is illustrated in Figure 2e, showing that the top layer was formed right after the spin-coating process, due to the different solubility of the organic cations which drives the formation of the top layer. Further phase separation starts to occur during the annealing process subsequent to spin coating, creating voids in the bottom layer. This is

supported by the appearance of a reddish transparent film during the spin-coating process which turns to opaque dark colour after annealing at 100 °C. By comparing the optical absorption of the perovskite film before and after annealing (see Figure S2a), it can be concluded that the higher dimensional perovskite (bottom layer) was formed after the crystallization of the lower dimensional perovskite (top layer). Surface stoichiometry measurements utilizing X-ray photoelectron spectroscopy (XPS) also confirms the bilayer hybrid structure in $(\text{CHMA})_2(\text{MA})_{n-1}\text{Pb}_n\text{I}_{3n+1}$ perovskites (see Figure S3).

However, the formation of bilayer perovskite was not observed when the precursors were mixed in DMF:DMSO (1:1) solvent mixture and pure DMSO solvent. Instead, a compact perovskite layer was observed in the cross-sectional FESEM images (see Figure S4) and no diffraction pattern of 3D perovskite was found for the perovskite thin films fabricated from DMF:DMSO (1:1) mixture and pure DMSO solution (see Figure S5). Upon spin-coating, the perovskite films did not turn red but remained faint yellow in appearance. The films then became reddish transparent after annealing at 100 °C. The absence of absorption above 700 nm for the perovskite deposited from the DMSO solution (see Figure S2b) indicates only the formation of lower dimensional perovskite. The presence of DMSO in the precursor solution could have induced the formation of $\text{PbI}_2 \cdot \text{MAI} \cdot \text{DMSO}$ adduct which prevented phase separation, resulting in a single compact layer. This Lewis-acid base adduct approach has been reported in controlling the morphology and the grain size of perovskite films.⁴⁵⁻⁴⁶

Ambient stability is important for perovskites to be commercialized successfully. MAPbI_3 tends to be hydrolysed into PbI_2 and MAI which subsequently degrades into methylamine and hydroiodic acid.³ To compare the ambient stability of MAPbI_3 and $(\text{CHMA})_2(\text{MA})_{n-1}\text{Pb}_n\text{I}_{3n+1}$, perovskite thin films were prepared and stored under 50 % relative

humidity for 65 days. Monitoring changes in their optical absorption, it is clear the air-stability in $(\text{CHMA})_2(\text{MA})_{n-1}\text{Pb}_n\text{I}_{3n+1}$ perovskites is significantly better than conventional MAPbI_3 under the same exposure condition (see Figure S6). MAPbI_3 perovskite gradually degraded to form a yellow colour film, whereas the $(\text{CHMA})_2(\text{MA})_{n-1}\text{Pb}_n\text{I}_{3n+1}$ perovskites retain the original optical absorption even after a prolonged exposure to moisture. The upper 2D perovskite capping layer could provide moisture shielding to the 3D perovskites underneath, enhancing the overall ambient stability. We have also examined the stability of 2D perovskite ($\text{CHMA}_2\text{PbI}_4$) under different environments through X-ray diffraction as illustrated in Figure S10. No significant change (indicating the absence of PbI_2) was observed, pointing to the robustness and high stability of 2D perovskite.

In order to examine how the emission of perovskites can be influenced by its dimensionality, PL was recorded for all the samples. When illuminating with 350 nm light from the top, emission was observed ranging from 515 to 540 nm for all the perovskite films ($n = 1$ to 5) and the PL signals were slightly blue shifted as n increases (see Figure 3a). These PL signals indicate the presence of lower dimensional perovskite in all the films. To further confirm the presence of the bilayer perovskite structure, the PL signals of the bilayer perovskite films were decoupled by exciting the top and bottom of the substrates using excitation wavelengths of 450 and 650 nm (see the illustration in Figure 3b). When the representative sample $[(\text{CHMA})_2(\text{MA})_2\text{Pb}_3\text{I}_{10}, (n = 3)]$ was excited by 450 nm light from the top, a 520 nm PL signal was obtained (Figure 3c). Interestingly, when PL was measured from the bottom using the same excitation wavelength, only a 780 nm PL signal was detected, indicating the presence of higher dimensional perovskite in the bottom layer. When the sample was excited from the top, most of the photons from the excitation light (450 nm) were first absorbed by the lower dimensional

perovskite in the top layer and does not excite the higher dimensional perovskites in the bottom layer, resulting in only 520 nm PL signal being detected. However, when the sample was excited from the bottom (with 450 nm), most of the incident photons were absorbed by the higher dimensional perovskite in the bottom layer and is unable to excite the top layer, revealing the PL peak at 780 nm.

The sample was further investigated by collecting the PL signal using excitation wavelength of 650 nm. PL signal at 780 nm was detected in both top and bottom side measurement, affirming the existence of lower dimensional perovskite in the top layer. The incident 650 nm photons could not be absorbed by the lower dimensional perovskite due to its lower photon energy. The top layer became effectively “transparent”, and therefore the incident photons could pass through the top layer and excite the higher dimensional perovskite, showing only the emission from the bottom layer. The lower PL intensity when exciting from the bottom is due to the light scattering caused by the underlying mesoporous-TiO₂ layer and glass substrate. Similar behaviour was observed in MAPbI₃ films when exciting from the top and bottom side of the substrate (Figure S7). It shows that the PL signal was significantly reduced if the excitation was carried out from the bottom of the substrate. Thus the significantly strong signal at 780 nm obtained for the representative sample [(CHMA)₂(MA)₂Pb₃I₁₀], by exciting from the bottom of the substrate, was emitted from the bottom layer.

Figure 3. (a) PL signals were blue shifted as n is increased (excitation wavelength = 350 nm). (b) Schematics of PL measurement excited from top and bottom side of the sample with 450 nm and 650 nm wavelength. (c) PL obtained by illuminating from the top and bottom side of the sample using excitation wavelength of 450 nm (blue) and 650 nm (red) for the representative sample, $(\text{CHMA})_2(\text{MA})_2\text{Pb}_3\text{I}_{10}$.

The solar cells fabricated using these bilayer perovskites were measured under AM 1.5G solar illumination and the photovoltaic parameters summarized in Table 1. The simplest 2D perovskite, $(\text{CHMA})_2\text{PbI}_4$ ($n = 1$), does not perform well as the organic layer (CHMA^+) in the layered perovskite prohibits the charge transport in the vertical direction to the substrate, and hence limits the performance of the device. Similar device performances were also observed in other 2D perovskite ($n = 1$).⁸ When the dimensionality of perovskite was increased from $n = 1$ to $n = 2$ and 3, short circuit current density J_{SC} was improved from 0.08 to 0.45 mA cm^{-2} , due to the narrower band gap and reorientation of the perovskite which would slightly enhance the

charge transport in the mixed dimensional perovskite system.⁸ However, the open circuit voltage V_{OC} was reduced significantly from 831 mV to about 500 mV, probably due to the surface recombination induced by the 2D-3D bilayer interface. As a result, the overall power conversion efficiencies (PCE) for $n = 2$ and $n = 3$ devices were limited to about 0.1 %.

Table 1. Device performances for $(CHMA)_2(MA)_{n-1}Pb_nI_{3n+1}$ ($n = 1$ to 5).

	V_{OC} (mV)	J_{SC} (mA cm ⁻²)	FF (%)	PCE (%)
$n = 1$	831 ± 37	0.08 ± 0.01	34.08 ± 4.03	0.02 ± 0.00
$n = 2$	431 ± 54	0.13 ± 0.02	40.10 ± 2.70	0.02 ± 0.01
$n = 3$	558 ± 14	0.45 ± 0.12	36.91 ± 2.43	0.09 ± 0.02
$n = 4$	735 ± 19	10.65 ± 0.46	48.49 ± 4.39	3.78 ± 0.11
$n = 5$	761 ± 13	12.46 ± 0.55	58.62 ± 2.11	5.55 ± 0.13

As the dimensionality was increased further to $n = 4$ and 5, the PCE was significantly improved to 3.78 % and 5.55 %, respectively. The $(CHMA)_2(MA)_4Pb_5I_{16}$ ($n = 5$) perovskite had a J_{SC} of 12.46 mAcm⁻², V_{OC} of 761 mV and FF of 58.62 %. The thickness of the lower dimensional top layer was reduced to such an extent that the efficient charge transport from higher dimensional bottom layer to the hole transporting layer was possible, leading to the gigantic improvement in J_{SC} (see Figure S8). The increase of fill factor (FF) from about 40 % to 60 % can also be attributed to the reduction of lower dimensional layer thickness which reduced the series resistance within the absorber layer. The complete statistics of the solar cell parameters are depicted in the Figure S9. Incident photon-to-current efficiency (IPCE) shown in Figure 4d indicates a photocurrent response at 570 and 780 nm, clearly evidencing the contribution of both lower and higher dimensional perovskites to the current density of the devices. The stability of solar cells was examined and illustrated in Figure S12. The solar cells based on bilayered

perovskites were stored at > 60 % relative humidity at 25 °C without encapsulation. The devices exhibit decent stability under high humidity condition and retained its initial power conversion efficiency. This clearly indicates the importance of having a 2D perovskite capping layer on top of the 3D perovskite, providing better moisture shielding effect.

Figure 4. Cross-sectional FESEM images of solar cells fabricated from (a) $(\text{CHMA})_2\text{PbI}_4$ ($n = 1$) and (b) $(\text{CHMA})_2(\text{MA})_3\text{Pb}_4\text{I}_{13}$ ($n = 4$). (c) J - V characteristics of solar cells fabricated from $(\text{CHMA})_2(\text{MA})_{n-1}\text{Pb}_n\text{I}_{3n+1}$ ($n = 1, 2, 3, 4$ and 5). The IV characteristics are recorded in the reverse scanning direction (from V_{oc} to J_{sc}) with sweeping rate of 100 mV/s under AM 1.5G (100 mW cm⁻²) illumination. (d) IPCE and integrated current density of $(\text{CHMA})_2(\text{MA})_3\text{Pb}_4\text{I}_{13}$ ($n = 4$) and $(\text{CHMA})_2(\text{MA})_4\text{Pb}_5\text{I}_{16}$ ($n = 5$) solar cells.

Conclusion

In conclusion, the photophysical properties and its photovoltaic application of a series of 2D perovskites, $(\text{CHMA})_2(\text{MA})_{n-1}\text{Pb}_n\text{I}_{3n+1}$, were characterized and studied. A unique formation

of bilayer perovskite through a simple single-step deposition was triggered by the different rate of crystallization of organic cations. This bilayer perovskites exhibit higher ambient stability compared to the conventional 3D MAPbI₃ under the same condition due to the presence of top layer which comprises of lower dimensionality perovskite and served as a moisture resisting layer. This work provides a new insight into intrinsic bilayer perovskite formation through careful design of the organic components in the perovskite structure to achieve a more stable and highly efficient perovskite material for photovoltaics.

EXPERIMENTAL SECTION

Synthesis of cyclohexylmethylammonium iodide (CHMAI)

5 g of cyclohexanemethylamine (98 %, Sigma Aldrich) was first dissolved in 15 ml ethanol and cool it in an ice-bath for 15 mins. 6.4 ml of hydriodic acid (57 wt. % in H₂O) was added dropwise into the solution and kept it stirring for 2 hours. The solution was then dried under rotary evaporator at 60 °C. The resulting powder was recrystallized using ethanol and diethyl ether for 5 times. White crystalline powder was obtained by suction filtration and washed thoroughly with diethyl ether. The powder was further dried under vacuum and stored in glove box for use.

Device fabrication

The (CHMA)₂(MA)_{n-1}Pb_nI_{3n+1} perovskite solar cell devices were fabricated on fluorine-doped tin oxide (FTO) transparent conducting substrates with mesoporous TiO₂ scaffold. The FTO substrates (Pilkington, TEC 15) were cut and cleaned by sequential 15 minutes sonication in soap solution (Decon), deionized water and ethanol. Subsequently, the substrates were dried by N₂ gun and treated by ozone plasma for 15 minutes. A compact TiO₂ blocking layer with

thickness of approximately 50 nm was deposited on the cleaned substrates by spray pyrolysis of a precursor solution on a 450°C hot plate. The precursor solution is a solution of titanium diisopropoxide bis(acetylacetonate) (75% in 2-propanol, Sigma-Aldrich), acetylacetone and absolute ethanol with volume ratio of 6:4:90. After cooling down to room temperature, the substrates were treated in a 50 mM TiCl_4 solution (5 M TiCl_4 from Wako Pure Chemical Industries, >99 %, diluted with deionized water) at 70 °C for 30 minutes. A 300 nm-thick mesoporous TiO_2 scaffold was deposited by spin-coating a TiO_2 paste onto the dense TiO_2 -coated substrates. The TiO_2 paste was prepared by diluting a commercial TiO_2 paste (Dyesol 30NRD) and absolute ethanol with a weight ratio of 2:7 and stirred until all the paste was dissolved. The paste was spin-coated at 4500 rpm for 30 s, followed by a three-step annealing procedure at 125 °C, 375 °C and 500 °C, each for 30 minutes.

The $(\text{CHMA})_2(\text{MA})_{n-1}\text{Pb}_n\text{I}_{3n+1}$ ($n = 1, 2, 3, 4$, and 5) solution were prepared by mixing the stoichiometric ratios, namely 2:n-1:n, of CHMAI, MAI (Dyesol) and PbI_2 (99 %, Acros Organics) in DMF (anhydrous, 99.8 %, Sigma-Aldrich). In the case of perovskite films fabricated from DMF: DMSO (1:1) and DMSO solvent (anhydrous, $\geq 99.9\%$, Sigma-Aldrich), DMF is replaced by the respective solvents and the perovskite films are made in the same fabrication condition. For the preparation of $(\text{CHMA})_2(\text{MA})_{n-1}\text{Pb}_n\text{I}_{3n+1}$ films, 30 μl of the corresponding solution was spin-coated on a mesoporous- TiO_2 substrate at 4000 rpm for 30 s. Subsequently, the substrate was placed on a hot plate for annealing at 100 °C for 15 minutes.

After cooling down to room temperature, hole transporting materials, 2,2',7,7'-tetrakis-(N,N-di-4-methoxyphenylamino)-9,9'-spirobifluorene (spiro-OMeTAD, Merck livilux SHT-263) solution, was deposited by spin-coating at 4000 rpm for 30 s. The spiro-OMeTAD solution was prepared by dissolving spiro-OMeTAD in chlorobenzene (100 mg ml^{-1}), with addition of 15.92

μl of tert-butylpyridine (96 % from Sigma-Aldrich) and 9.68 μl of lithium bis(trifluoromethylsulfonyl)imide (Li-TFSI stock solution, 520 mg ml^{-1} in acetonitrile) were added directly to spiro-OMeTAD solutions. Co-dopant tris(2-(1H-pyrazol-1-yl)-pyridine)cobalt(III) tris(trifluoromethylsulfonyl)imide (FK 102 Co(III) TFSI salt, Dyesol) was predissolved into acetonitrile and added into the hole-transport material solution at 15 mol % concentration. The as-prepared solution was spin-coated onto the perovskite film at 4000 rpm for 30 s. About 100 nm of gold electrode was deposited through a mask with 0.2 cm^2 using a thermal evaporator.

Film fabrication for characterization

Thin film samples of $(\text{CHMA})_2(\text{MA})_{n-1}\text{Pb}_n\text{I}_{3n+1}$ ($n = 1, 2, 3, 4$, and 5) perovskites were prepared in a similar way as the perovskite layer in the devices. 50 μl of perovskite solution was spin-coated onto a 25 x 25 x 4 mm^3 glass with 300 nm-thick TiO_2 scaffold at 4000 rpm for 30 s, followed by post-annealing at 100 $^\circ\text{C}$ for 15 minutes. These thin film samples were used for X-ray diffraction, UV-visible spectroscopy, photoluminescence measurement and moisture stability test.

Characterization

X-ray diffraction measurements were conducted on a Bruker AXS D8 ADVANCE system with Cu $\text{K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). An incident angle of 5° was set to record the XRD spectra, with step size of 0.05° and delay time of 1s for each step. Optical absorption was measured by a UV-3600 UV-VIS-NIR spectrophotometer (Shimadzu) in the wavelength range of 300-800 nm. SEM images of the perovskite films and devices were taken by a field emission scanning electron

microscope (FESEM) JEOL JSM-7600F. For the moisture stability, perovskite films deposited on glass substrates with 300 nm thick mesoporous-TiO₂ were placed inside a dry cabinet with relative humidity control to 50 % and periodically analysed by UV-vis spectroscopy. The photovoltaic characteristics of the solar cell devices were measured in the reverse scanning direction (from V_{OC} to J_{SC}) with sweeping rate of 100 mV/s under AM 1.5G (100 mW cm⁻²) spectrum by a solar simulator (Newport 91190A) with a 450W xenon lamp (model 81172, Oriel) calibrated with a Si reference cell (Oriel PN91150). The devices were characterized through a 0.25 cm² black mask. Incident photon-to-current efficiency (IPCE) was measured using a PVE300 (Bentham), with dual Xenon/quartz halogen light source, measured in DC mode and no bias light was used in the wavelength range of 300-800 nm. PL spectra were recorded by exciting the perovskite films with a standard 450-W Xenon CW lamp. The signal was recorded with a spectrofluorometer (Fluorolog 3, HORIBA Jobin Yvon Technology) and analysed with FluorEssence software. The bottom side excitation measurements were done by placing the sample with substrate facing the incident excitation light. 450 nm and 650 nm excitation wavelength were used in the top and bottom side measurement to identify the composition of top and bottom layer of the bilayer perovskite films. The micro-PL setup is based on fiber coupled microscope system, where the excitation path and the emission collection from the side, using a VIS-NIR microscope objective (10x, NA= 0.65). The samples were excited with 5-MHz-repetition-rate, picosecond-pulse light sources at 405 nm (Picoquant P-C-405B) light-emitting diode. The beam spot size was about 10 mm. Time-resolved decay curves were collected using an Acton monochromator (SpectraPro 2300), fiber coupled to the microscope, to filter the desired wavelength, and detected by Micro Photon Devices single-photon avalanche photodiode. The signal was then acquired by a time-correlated single photon counting card. The temporal

resolution is ~ 5 ps. The decay curves were fitted with double exponential function. The decay curves were fitted with double exponential function. PLQE is measured using an integrated sphere and a fiber spectrometer (Ocean Optics USB 4000). The excitation source is 405 nm blue laser (Cobolt MLD™). The XPS was measured in a home-made UHV system with the base pressure below 1×10^{-9} torr. A hemispheric electron analyzer (Omicron, EA125) was used to detect the photoelectron excited by a monochromatic Al K α radiation ($h\nu = 1486.7$ eV) or UV light (He I, $h\nu = 21.2$ eV).

ASSOCIATED CONTENT

Supporting Information.

The Supporting Information is available free of charge on the ACS Publications website at DOI:

Supplementary characterizations and statistics of fabricated perovskite solar cells.

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Notes

The authors declare no competing financial interest.

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References

1. Bi, D.; Tress, W.; Dar, M. I.; Gao, P.; Luo, J.; Renevier, C.; Schenk, K.; Abate, A.; Giordano, F.; Correa Baena, J.-P.; Decoppet, J.-D.; Zakeeruddin, S. M.; Nazeeruddin, M. K.; Grätzel, M.; Hagfeldt, A., Efficient luminescent solar cells based on tailored mixed-cation perovskites. *Sci. Adv.* **2016**, 2 (1), e1501170.
2. Yang, W. S.; Noh, J. H.; Jeon, N. J.; Kim, Y. C.; Ryu, S.; Seo, J.; Seok, S. I., High-performance photovoltaic perovskite layers fabricated through intramolecular exchange. *Science* **2015**, 348 (6240), 1234-1237.
3. Niu, G.; Guo, X.; Wang, L., Review of recent progress in chemical stability of perovskite solar cells. *J. Mater. Chem. A* **2015**, 3 (17), 8970-8980.
4. Niu, G.; Li, W.; Meng, F.; Wang, L.; Dong, H.; Qiu, Y., Study on the stability of CH₃NH₃PbI₃ films and the effect of post-modification by aluminum oxide in all-solid-state hybrid solar cells. *J. Mater. Chem. A* **2014**, 2 (3), 705-710.
5. Noh, J. H.; Im, S. H.; Heo, J. H.; Mandal, T. N.; Seok, S. I., Chemical Management for Colorful, Efficient, and Stable Inorganic-Organic Hybrid Nanostructured Solar Cells. *Nano Lett.* **2013**, 13 (4), 1764-1769.
6. Boix, P. P.; Agarwala, S.; Koh, T. M.; Mathews, N.; Mhaisalkar, S. G., Perovskite Solar Cells: Beyond Methylammonium Lead Iodide. *J. Phys. Chem. Lett.* **2015**, 6 (5), 898-907.
7. Smith, I. C.; Hoke, E. T.; Solis-Ibarra, D.; McGehee, M. D.; Karunadasa, H. I., A Layered Hybrid Perovskite Solar-Cell Absorber with Enhanced Moisture Stability. *Angew. Chem. Int. Ed.* **2014**, 53 (42), 11232-11235.
8. Cao, D. H.; Stoumpos, C. C.; Farha, O. K.; Hupp, J. T.; Kanatzidis, M. G., 2D Homologous Perovskites as Light-Absorbing Materials for Solar Cell Applications. *J. Am. Chem. Soc.* **2015**, 137 (24), 7843-7850.
9. Mitzi, D. B., Synthesis, structure, and properties of organic-inorganic perovskites and related materials. In *Progress in Inorganic Chemistry*, Vol 48, Karlin, K. D., Ed. 1999; Vol. 48, pp 1-121.
10. Ahmad, S.; Kanaujia, P. K.; Beeson, H. J.; Abate, A.; Deschler, F.; Credgington, D.; Steiner, U.; Prakash, G. V.; Baumberg, J. J., Strong Photocurrent from Two-Dimensional Excitons in Solution-Processed Stacked Perovskite Semiconductor Sheets. *ACS Appl. Mater. Interfaces* **2015**, 7 (45), 25227-25236.

11. Mitzi, D. B., Synthesis, structure, and properties of organic-inorganic perovskites and related materials. *Prog. Inorg. Chem.* **2007**, *48*, 1-121.
12. Lemmerer, A.; Billing, D. G., Lead halide inorganic-organic hybrids incorporating diammonium cations. *CrystEngComm* **2012**, *14* (6), 1954-1966.
13. Lemmerer, A.; Billing, D. G., Synthesis, characterization and phase transitions of the inorganic-organic layered perovskite-type hybrids $[(C_nH_{2n+1}NH_3)_2PbI_4]$, $n = 7, 8, 9$ and 10 . *Dalton Trans.* **2012**, *41* (4), 1146-1157.
14. Billing, D. G.; Lemmerer, A., Inorganic-organic hybrid materials incorporating primary cyclic ammonium cations: the lead iodide series. *CrystEngComm* **2007**, *9* (3), 236-244.
15. Zheng, Y.-Y.; Wu, G.; Deng, M.; Chen, H.-Z.; Wang, M.; Tang, B.-Z., Preparation and characterization of a layered perovskite-type organic-inorganic hybrid compound $(C_8NH_6CH_2CH_2NH_3)_2CuCl_4$. *Thin Solid Films* **2006**, *514* (1), 127-131.
16. Mitzi, D. B., Synthesis, crystal structure, and optical and thermal properties of $(C_4H_9NH_3)_2MI_4$ ($M = Ge, Sn, Pb$). *Chem. Mater.* **1996**, *8* (3), 791-800.
17. Mitzi, D. B.; Feild, C. A.; Harrison, W. T. A., Conducting Tin Halides with a Layered Organic-based Perovskite Structure. *Nature* **1994**, *369* (9), 467-469.
18. Kitazawa, N., Compositional modulation of two-dimensional layered perovskite $(RNH_3)_2Pb(Cl, Br, I)_4$ and its optical properties. *Jpn. J. Appl. Phys.* **1996**, *35* (12R), 6202.
19. Billing, D. G.; Lemmerer, A., Inorganic-organic hybrid materials incorporating primary cyclic ammonium cations: The lead bromide and chloride series. *CrystEngComm* **2009**, *11* (8), 1549-1562.
20. Mercier, N.; Louvain, N.; Bi, W., Structural diversity and retro-crystal engineering analysis of iodometalate hybrids. *CrystEngComm* **2009**, *11* (5), 720-734.
21. Cheng, Z.; Lin, J., Layered organic-inorganic hybrid perovskites: structure, optical properties, film preparation, patterning and templating engineering. *CrystEngComm* **2010**, *12* (10), 2646-2662.
22. Mitzi, D. B., Templating and structural engineering in organic-inorganic perovskites. *J. Chem. Soc. Dalton* **2001**, (1), 1-12.
23. Takeoka, Y.; Asai, K.; Rikukawa, M.; Sanui, K., Systematic studies on chain lengths, halide species, and well thicknesses for lead halide layered perovskite thin films. *Bull. Chem. Soc. Jpn.* **2006**, *79* (10), 1607-1613.
24. Miller, O. D.; Yablonovitch, E.; Kurtz, S. R., Strong Internal and External Luminescence as Solar Cells Approach the Shockley-Queisser Limit. *IEEE J. Photovolt.* **2012**, *2* (3), 303-311.
25. Yablonovitch, E., Inhibited spontaneous emission in solid-state physics and electronics. *Phys. Rev. Lett.* **1987**, *58* (20), 2059-2062.
26. Rau, U., Reciprocity relation between photovoltaic quantum efficiency and electroluminescent emission of solar cells. *Phys. Rev. B* **2007**, *76* (8), 085303.
27. Zhang, S.; Lanty, G.; Lauret, J.-S.; Deleporte, E.; Audebert, P.; Galmiche, L., Synthesis and optical properties of novel organic-inorganic hybrid nanolayer structure semiconductors. *Acta Mater.* **2009**, *57* (11), 3301-3309.
28. Zhang, S.; Audebert, P.; Wei, Y.; Al Choueiry, A.; Lanty, G.; Bréhier, A.; Galmiche, L.; Clavier, G.; Boissiere, C.; Lauret, J.-S., Preparations and characterizations of luminescent two dimensional organic-inorganic perovskite semiconductors. *Materials* **2010**, *3* (5), 3385-3406.
29. Aharon, S.; Dymshits, A.; Rotem, A.; Etgar, L., Temperature dependence of hole conductor free formamidinium lead iodide perovskite based solar cells. *J. Mater. Chem. A* **2015**, *3* (17), 9171-9178.

30. Ito, S.; Tanaka, S.; Manabe, K.; Nishino, H., Effects of Surface Blocking Layer of Sb₂S₃ on Nanocrystalline TiO₂ for CH₃NH₃PbI₃ Perovskite Solar Cells. *J. Phys. Chem. C* **2014**, *118* (30), 16995-17000.
31. Leijtens, T.; Eperon, G. E.; Pathak, S.; Abate, A.; Lee, M. M.; Snaith, H. J., Overcoming ultraviolet light instability of sensitized TiO₂ with meso-superstructured organometal tri-halide perovskite solar cells. *Nat. Commun.* **2013**, *4*, 2885.
32. Frost, J. M.; Butler, K. T.; Brivio, F.; Hendon, C. H.; van Schilfgaarde, M.; Walsh, A., Atomistic Origins of High-Performance in Hybrid Halide Perovskite Solar Cells. *Nano Lett.* **2014**, *14* (5), 2584-2590.
33. Manser, J. S.; Saidaminov, M. I.; Christians, J. A.; Bakr, O. M.; Kamat, P. V., Making and Breaking of Lead Halide Perovskites. *Acc. Chem. Res.* **2016**, *49* (2), 330-338.
34. Tiep, N. H.; Ku, Z.; Fan, H. J., Recent Advances in Improving the Stability of Perovskite Solar Cells. *Adv. Energy Mater.* **2016**, *6* (3), 1501420.
35. Christians, J. A.; Miranda Herrera, P. A.; Kamat, P. V., Transformation of the Excited State and Photovoltaic Efficiency of CH₃NH₃PbI₃ Perovskite upon Controlled Exposure to Humidified Air. *J. Am. Chem. Soc.* **2015**, *137* (4), 1530-1538.
36. Leguy, A. M. A.; Hu, Y.; Campoy-Quiles, M.; Isabel Alonso, M.; Weber, O. J.; Azarhoosh, P.; van Schilfgaarde, M.; Weller, M. T.; Bein, T.; Nelson, J.; Docampo, P.; Barnes, P. R. F., Reversible Hydration of CH₃NH₃PbI₃ in Films, Single Crystals, and Solar Cells. *Chem. Mater.* **2015**, *27* (9), 3397-3407.
37. De Wolf, S.; Holovsky, J.; Moon, S.-J.; Loeper, P.; Niesen, B.; Ledinsky, M.; Haug, F.-J.; Yum, J.-H.; Ballif, C., Organometallic Halide Perovskites: Sharp Optical Absorption Edge and Its Relation to Photovoltaic Performance. *J. Phys. Chem. Lett.* **2014**, *5* (6), 1035-1039.
38. Habisreutinger, S. N.; Leijtens, T.; Eperon, G. E.; Stranks, S. D.; Nicholas, R. J.; Snaith, H. J., Carbon Nanotube/Polymer Composites as a Highly Stable Hole Collection Layer in Perovskite Solar Cells. *Nano Lett.* **2014**, *14* (10), 5561-5568.
39. Weerasinghe, H. C.; Dkhissi, Y.; Scully, A. D.; Caruso, R. A.; Cheng, Y.-B., Encapsulation for improving the lifetime of flexible perovskite solar cells. *Nano Energy* **2015**, *18*, 118-125.
40. Hwang, I.; Jeong, I.; Lee, J.; Ko, M. J.; Yong, K., Enhancing Stability of Perovskite Solar Cells to Moisture by the Facile Hydrophobic Passivation. *ACS Appl. Mater. Interfaces* **2015**, *7* (31), 17330-17336.
41. Han, Y.; Meyer, S.; Dkhissi, Y.; Weber, K.; Pringle, J. M.; Bach, U.; Spiccia, L.; Cheng, Y.-B., Degradation observations of encapsulated planar CH₃NH₃PbI₃ perovskite solar cells at high temperatures and humidity. *J. Mater. Chem. A* **2015**, *3* (15), 8139-8147.
42. Kawano, N.; Koshimizu, M.; Sun, Y.; Yahaba, N.; Fujimoto, Y.; Yanagida, T.; Asai, K., Effects of organic moieties on luminescence properties of organic-inorganic layered perovskite-type compounds. *J. Phys. Chem. C* **2014**, *118* (17), 9101-9106.
43. Wu, X.; Trinh, M. T.; Zhu, X. Y., Excitonic Many-Body Interactions in Two-Dimensional Lead Iodide Perovskite Quantum Wells. *J. Phys. Chem. C* **2015**, *119* (26), 14714-14721.
44. Tabuchi, Y.; Asai, K.; Rikukawa, M.; Sanui, K.; Ishigure, K., Preparation and characterization of natural lower dimensional layered perovskite-type compounds. *J. Phys. Chem. Solids* **2000**, *61* (6), 837-845.
45. Ahn, N.; Son, D.-Y.; Jang, I.-H.; Kang, S. M.; Choi, M.; Park, N.-G., Highly reproducible perovskite solar cells with average efficiency of 18.3% and best efficiency of

19.7% fabricated via Lewis base adduct of lead (II) iodide. *J. Am. Chem. Soc.* **2015**, *137* (27), 8696-8699.

46. Lee, J.-W.; Kim, H.-S.; Park, N.-G., Lewis Acid–Base Adduct Approach for High Efficiency Perovskite Solar Cells. *Acc. Chem. Res.* **2016**, *49* (2), 311-319.

High stability bilayered perovskites through crystallization driven self-assembly

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Abstract

In this manuscript we reveal a novel formation of bilayered hybrid perovskites of new lower dimensional perovskite family, $(\text{CHMA})_2(\text{MA})_{n-1}\text{Pb}_n\text{I}_3$ with $n = 1$ to 5 , with high ambient stability *via* its crystallization driven self-assembly process. The spun-coated perovskite solution tend to crystallize and undergo phase separation during annealing, resulting in the formation of 2D/3D bilayered hybrid perovskites. Remarkably, this 2D/3D hybrid perovskites possess striking moisture resistance and display high ambient stability up to 65 days. The bilayered approach in combining 3D and 2D perovskites could lead to a new era of perovskite research for high efficiency photovoltaics with outstanding stability: 3D for excellent electronic properties while 2D for moisture stability.

Keywords: bilayered perovskite • air stability • mixed-dimensionality • phase separation • self-assembly

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Figure S1. Top view FESEM image of $(\text{CHMA})_2(\text{MA})_3\text{Pb}_4\text{I}_{13}$.

Figure S2. Optical absorbance and images of $(\text{CHMA})_2(\text{MA})_2\text{Pb}_3\text{I}_{10}$ fabricated from different solvent (a) DMF and (b) DMSO unannealed and annealed films.

Figure S3. Elemental scans (a) N 1s, (b) Pb 4f, (c) I 3d and (d) C 1s of MAPbI₃ (red), (CHMA)₂PbI₄ (green) and the representative n=3 bilayer perovskite (purple).

X-ray photoelectron spectroscopy (XPS) was performed to probe the surface composition of the bilayer perovskite. The surface sensitivity of this technique, which is down to tens of nanometers, makes it suitable to affirm the formation of lower dimensional perovskite structure at the top surface of the n = 3 bilayer perovskite. Measurements were performed on MAPbI₃, (CHMA)₂PbI₄ (n = 1) and the representative sample of bilayer perovskite, (CHMA)₂(MA)₂Pb₃I₁₀ (n = 3), for comparison of the chemical states at the bilayer perovskite surface to both the pure 3D and 2D structures. The N 1s, Pb 4f and I 3d elemental states in the three structures shown in Figure S3 show a single state corresponding to C-N, Pb-I and I-Pb respectively, but comparing the C 1s peak in the three samples in Figure 4d reveals that the bilayer perovskite surface is identical to the pure 2D structure, which is composed of C atoms in the cyclohexane and methyl group in a fixed intensity ratio of 6:1 respectively with fixed binding energy difference of 1.3 eV. Systematically shifted binding energy of the elemental peaks in bilayer perovskite, by -0.4 ± 0.2 eV compared to that of pure 2D perovskite could be attributed to the different amounts of charging in the two samples. XPS also provides information on the surface chemical stoichiometry of the system, which in **Table S1** shows that the stoichiometry of the (CHMA)₂(MA)₂Pb₃I₁₀ perovskite surface has I/Pb ratio of 4.8, C(in cyclohexane)/Pb ratio of 1.7, N/Pb of 1.8 and C(in methyl)/N of 1.0, consistent with the stoichiometry of

the 2D perovskite surface, having I/Pb, C(in cyclohexane)/Pb, N/Pb and C(in methyl)/N ratios of 4.3, 1.9, 1.7 and 1.2, respectively. The similarities in stoichiometry of the $n = 3$ bilayer perovskite with that of the pure 2D affirms that the top surface of bilayer perovskite consists of the lower dimensionality perovskite.

Table S1. Stoichiometry of various elements with respect to lead in the top surface of MAPbI₃ (top), (CHMA)₂PbI₄ (middle) and the representative bilayer perovskite in (CHMA)₂(MA)₂Pb₃I₁₀ (bottom), determined by XPS.

MAPbI₃	Result
I/Pb	3.4
C/Pb	1.1
N/Pb	1.1
C (in methyl)/N	1.0

(CHMA)₂PbI₄	Result
I/Pb	4.3
C (in cyclohexane)/Pb	1.9
N/Pb	1.7
C (in methyl)/Pb	1.2
Impure Pb	7.9

(CHMA)₂(MA)₂Pb₃I₁₀	Result
I/Pb	4.8
C (in cyclohexane)/Pb	1.7
N/Pb	1.8
C (in methyl)/Pb	1.0

Figure S4. Cross-sectional SEM images of spin-coating films: (a) $(\text{CHMA})_2(\text{MA})_2\text{Pb}_3\text{I}_{10}$ from DMF:DMSO (1:1) and (b) from DMSO.

Figure S5. Comparison of XRD patterns of MAPbI_3 (from DMF) perovskite thin film and $(\text{CHMA})_2(\text{MA})_2\text{Pb}_3\text{I}_{10}$ fabricated from different solvent (DMF and DMSO).

Figure S6. (a-f) Optical absorption of $(\text{CHMA})_2(\text{MA})_{n-1}\text{Pb}_n\text{I}_{3n+1}$ ($n = 1$ to 5) perovskites and MAPbI_3 . Samples were stored under 50 % relative humidity at 25 °C for 65 days and the respective photos were shown.

Figure S7. PL measurement of (a) mp-TiO₂ substrates and (b) MAPbI₃ with excitation from top and bottom. It shows that the PL signal was significantly reduced if the excitation was carried out from the bottom side of the substrate. Hence, this proves that the significantly strong signal at 780 nm obtained for the representative sample (CHMA)₂(MA)₂Pb₃I₁₀, by exciting from the bottom side of the substrate, was emitted from the bottom layer.

Figure S8. The comparison of top and bottom perovskite layers in (a) (CHMA)₂(MA)₂Pb₃I₁₀ and (b) (CHMA)₂(MA)₃Pb₄I₁₃.

Figure S9. Statistics of photovoltaic parameters from a total of 30 devices containing $(\text{CHMA})_2(\text{MA})_{n-1}\text{Pb}_n\text{I}_{3n+1}$ ($n = 1$ to 5) perovskites with under simulated AM 1.5 sunlight of 100 mW cm^{-2} illumination. The data are represented by using standard box plot where the box range is defined by the standard deviation.

Figure S10. XRD of 2D perovskite $(\text{CHMA})_2\text{PbI}_4$ stored under different environment, showing decent stability over 5 days.

Figure S11. PL decay measurement of 2D perovskite (CHMA₂PbI₄), indicating PL lifetime of 370 ps.

Figure S12. Stability test of bilayered perovskite solar cells. The devices are stored under > 60 % relative humidity at 25 °C without encapsulation. The IV curves were recorded under simulated AM 1.5 sunlight of 100 mW cm⁻² illumination.