

High-Quality Pure-Phase MA-Free Formamndinium Dion-Jacobson 2D Perovskites for Stable Unencapsulated Photovoltaics

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It is generally difficult to achieve high quality in low-*n*-value (MA-free) FA-based Dion-Jacobson (DJ) 2D perovskites due to their low crystallinity, random well-width distribution of multiple quantum wells (QWs) with disordered orientation, which has seriously hindered further advances in photovoltaics. Meanwhile, pure-phase DJ 2D perovskites with uniform QWs width and fixed low-*n* values are highly desirable for high efficiency and stability. Herein a novel 4APP(FA)₃Pb₄I₁₃-based quasi-DJ-2D perovskite is presented first, where 4APP is 4-aminopiperidinium. The remarkable rigidity of 4APP and its strong hydrogen bonding with the perovskites prolong the perovskite intrinsic stability. The tri-solvent engineering approach is further established by matching solvent properties to achieve pure-phase DJ-2D perovskites with uniform QWs width structure and finely oriented crystal grains, which enhance the power conversion efficiency of unencapsulated solar cells by 48%, representing one of the highest values in MA-free DJ 2D perovskite with *n* ≤ 4. Remarkably, the unencapsulated devices retain 95% of their initial PCE after 2000 h of operation under 1-sun illumination at 40 °C, and 3000 h exposure in the air at 85 °C and 60–90% relative humidity (RH). The simultaneous control of rigidity and phase purity in DJ-2D perovskites will open up new directions for fundamental research and application exploration.

incorporation of bulky organic spacers into single inorganic perovskite slabs, the stability of PSCs has recently been significantly improved; this allows the single-layer inorganic perovskites to be sandwiched by organic molecules, resulting in the formation of the 2D perovskites.^[6–8] 2D Perovskites are commonly classified as Ruddlesden–Popper (RP) and Dion–Jacobson (DJ) phase 2D perovskites materials, in which the typical organic spacer cations are monoammonium or diammonium respectively.^[6,9]

In the early stages, the superior stability of RP phase 2D perovskites compared to 3D counterparts attracted many scientists. This was attributed to their layered structure and hydrophobic spacer cations.^[8,10–14] However, their chemical stability is still limited by the inter-layer van der Waals (vdW) gap of organic layers.^[10] DJ 2D perovskites have recently gained great attention by eliminating vdW gaps.^[15–17] In comparison with RP, these 2D perovskites are more stable, and robust, and offer greater

structural and chemical stability.^[18]

The first example of DJ 2D perovskites, for example 4AMP(MA)₃Pb₄I₁₃ and 3AMP(MA)₃Pb₄I₁₃ where 4AMP is 4-(aminomethyl)piperidinium and 3AMP 4-(aminomethyl)piperidinium is reported by Mao et al.,^[17] Since then, a number of MA-based DJ 2D perovskites and their PSCs

1. Introduction

The power conversion efficiency (PCE) of perovskite solar cells (PSCs) with the record-certified value reaching 26.0% is close to that of single-crystal silicon solar cells.^[1–3] However, chemical stability continues to be the fundamental challenge.^[4,5] Through the

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DOI: 10.1002/aenm.202302774

have been demonstrated with high stability.^[8,16,19–21] Despite significant progress in MA-based 2D PSCs the low thermal stability of MA poses a threat to their future.^[22]

In recent years, FA-based perovskites have demonstrated remarkable optoelectronic properties and thermal stability.^[22,23] The polar MA cations (dipole moment of 2.29 D) found in MA-based perovskites are intrinsically unstable due to their high volatility and (photo) reactivity. FA, with a dipole moment of 0.21 D, offers a more uniform electron density distribution during operation, which renders it more photochemically and thermally stable.^[24] In addition, the larger size of FA (2.79 Å) leads to an increased lattice size and degree of space filling, which is accompanied by stronger hydrogen bonding. Consequently, FA-based perovskites show narrower bandgaps, which are close to the thermodynamic optimum for single-junction solar cells. However, the black perovskite phase (α -FAPbI₃) is not thermodynamically stable at ambient temperature and forms the δ -FAPbI₃ (yellow) phase which is not appropriate for photovoltaics.^[25] One of the strategies to overcome these instabilities is to use FA-based DJ 2D perovskite, which was found to be more stable toward ambient conditions and ion migration. The interaction of single organic hydrophobic ligands with the opposite perovskite layers contributes to templating the α -FAPbI₃ phase setting a new route for FA-based PSCs.^[22,23,26] Li et al. developed the first FA-based DJ 2D perovskites (PDMA)(FA)₂Pb₃I₁₀ ($n = 3$, PDMA = 1,4-phenylenedimethan ammonium), which maintain over 60% of initial PCE after 500 h operation under 1-sun illumination and more than 85% of its initial PCE when exposed to ambient air with a relative humidity of 30–40% for 1440 hr.^[27] Nonetheless, FA-based DJ 2D perovskites need further development in terms of stability and obtaining high-quality pure-phase films.

Several strategies have been proposed to improve the quality of FA-based DJ 2D perovskites, for example, additive engineering (FACl),^[28] secondary A-site cation,^[29] and solvent engineering etc. For example, Cheng et al. used FACl additive for (PDA)(FA)₃Pb₄I₁₃ and PA as a secondary cation, for example, (PDA_{0.9}PA_{0.2})(FA)₃Pb₄I₁₃ in FA-based DJ 2D perovskites. DJ 2D perovskites based on FACl additives maintained 86% of initial PCE under dark inert conditions for 1000 h, and 85% in humid conditions (30–40% RH) for 540 h. While PDA_{0.9}PA_{0.2})(FA)₃Pb₄I₁₃-based device retains 90% of the initial efficiency after aging at 85 °C for 800 h.^[28,29] However, so far, the operational stability test in addition to the humidity stability test for most of the reported FA-based 2D perovskite remains unexplored, and yet PCE is still far behind its MA-based counterpart.

It should be noted that $n \geq 4$ among the different n numbers of 2D perovskite materials has shown to be the most efficient with the best stability.^[10,22,30] However, 2D perovskites with $n \geq 4$, fabricated through solution methods typically have multiple QWs, with random well width distributions (different n numbers), which, as with impurity phases and structural disorder, lead to trap-assisted recombination, resulting in decreased device performance.^[31,32] Additionally, multiple phases can result in inefficient charge injection into emission centers, forming multiple photoluminescence (PL) peaks with coexisting and unstable emission characteristics.^[32–34] It worsens in low- n FA-based 2D perovskites as more spacer cations are involved in crystallization, also, FA cations interact strongly with [PbI₆]⁴⁻ octahedrons, as well as with dimethyl sulfoxide (DMSO).^[11,35] For highly effi-

cient and stable solar cells, the fabrication of a pure-phase FA DJ 2D perovskite with uniform QWs width remains a major scientific challenge. Pure-phase films exhibiting uniform QWs width of DJ 2D perovskites with fixed n values are more efficient and stable. This is due to the fact that the conductive perovskite layers are uniformly distributed and equally protected by the hydrophobic organic layer.^[22,34,36]

In this work, first we investigate a series of (MA-free) FA-based quasi-DJ 2D perovskites with various cyclic organic spacers (A) including 4APP (4-(aminomethyl)piperidinium), 4AMP (4-(aminomethyl)piperidinium), AMPY (4-(aminomethyl)pyridinium) and PP (piperidinium) and comprehensively study their influences on the stability and efficiency. Importantly, we find that organic spacer-perovskite interaction and rigidity of organic spacer will significantly affect quasi-DJ 2D perovskite stability. The 4APP-based perovskite films have the highest Young's modulus and hardness value ($E = 29.99$ GPa and $H = 1.19$ GPa) compared with PP ($E = 11.11$ GPa and $H = 0.36$ GPa) 4AMP ($E = 18.63$ GPa and $H = 0.64$ GPa) and 4AMPY ($E = 20.11$ and $H = 0.5$). As a result, the FA-based DJ 2D perovskites with 4APP as an organic template between the perovskite layers, exhibit a more rigid lattice, resulting high quality intrinsically stable FA-based quasi-DJ 2D perovskite. Remarkably, the 4APP-based quasi-DJ 2D perovskites thin films show very little change after heating for over 3000 h at 85 °C and 30 min at 250 °C in an ambient environment with a relative humidity of over 60–90%. For boosting the performance in photovoltaics of 4APP-based perovskites, we further develop a tri-solvent system composed of gamma-butyrolactone (GBL), dimethylformamide (DMF), and dimethyl sulfoxide (DMSO). We unveil that, the different boiling points, D_N (Gutmann's donor), numbers and dielectric constants of these solvents are crucial to the fabrication of high quality (high phase purity, uniform QWs structure, enhanced crystal grain orientation, and improved film morphology) FA-based DJ 2D perovskites films. As a result, the PCE of the tri-solvent engineered PSCs significantly improved by 48% over the control device for FA-free DJ 2D perovskites with $n = 4$. Particularly, the unencapsulated devices maintain 95% (T_{95}) of their initial PCEs when operated at maximum power (MPP) at 40 °C for over 2000 h, damp heated at 85 °C for over 3000 h in the air (with relative humidity 60–90%), presenting the highest stability among the reported MA-free DJ 2D PSCs.

2. Results and Discussion

2.1. Novel Organic Spacers and their MA-Free FA-Based DJ 2D Perovskites

We synthesized four different kinds of FA-based quasi-DJ 2D perovskites materials, with a general formula of (A)(FA)₃Pb₄I₁₃, by introducing the inter-related spacers of A = 4APP (4-(aminomethyl)piperidinium), 4AMP (4-(aminomethyl)piperidinium), 4AMPY (4-(aminomethyl)pyridinium) and PP (piperidinium) (Figure 1a) in which 4APP and PP are newly demonstrated. Throughout this work, we target to study the $n = 4$ phase (nominally $n = 4$) quasi-DJ 2D perovskites, for example PP(FA)₃Pb₄I₁₃, 4APP(FA)₃Pb₄I₁₃, 4AMP(FA)₃Pb₄I₁₃ and 4AMPY(FA)₃Pb₄I₁₃. Precursor solutions of these quasi-DJ 2D perovskites were

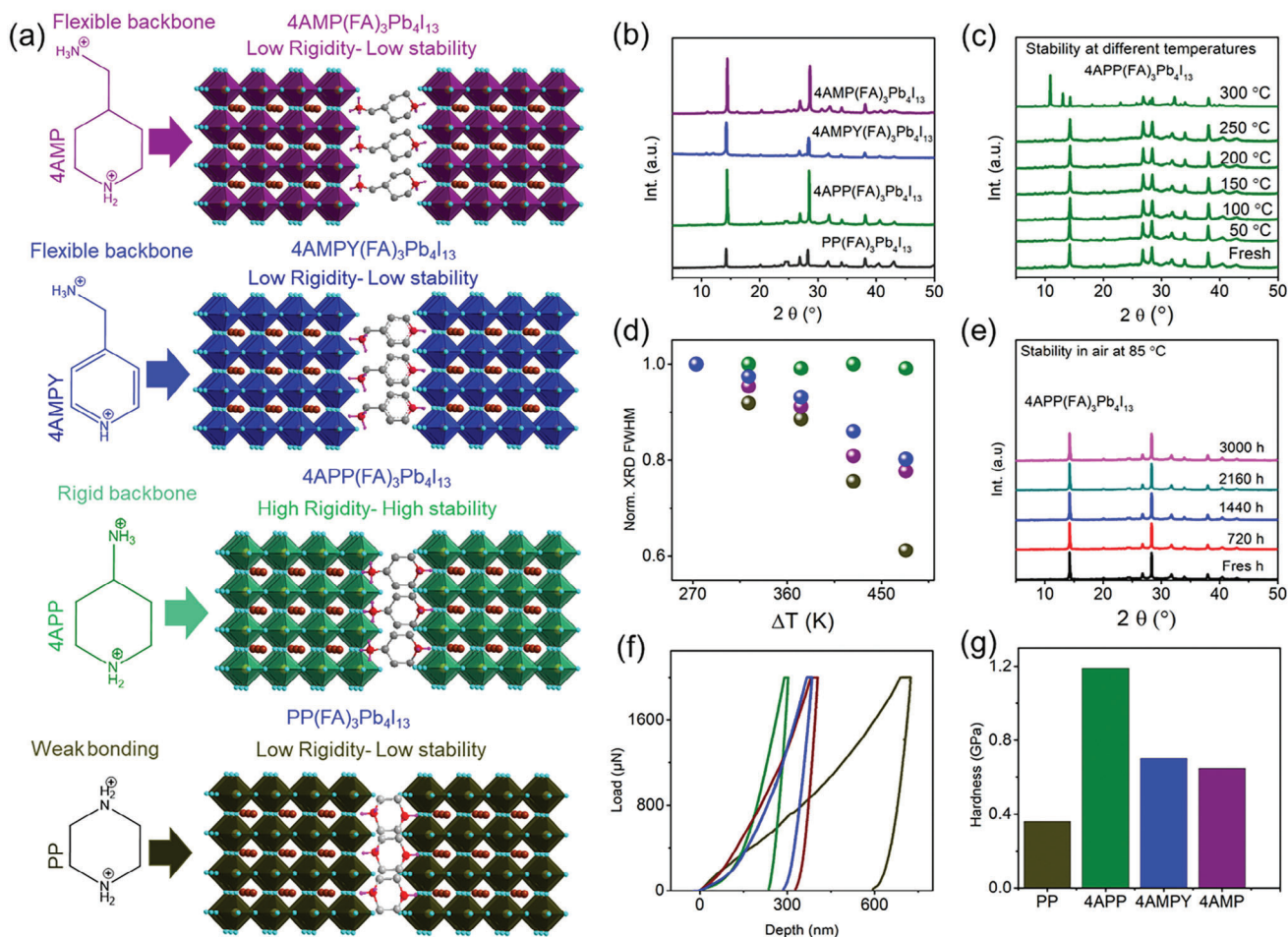


Figure 1. Schematic structures and stability analysis of different MA-free DJ 2D perovskites. a) Schematic illustration of (A)(FA)₃Pb₄I₁₃-based DJ 2D perovskites and chemical structure of all organic spacers studied in this work. b) XRD spectra of (A)(FA)₃Pb₄I₁₃-based quasi-DJ 2D perovskites films. c) Thermal stability test of 4APP(FA)₃Pb₄I₁₃-based perovskites at different temperature 0–300 °C in air for 0.5 h d) Normalized FWHM of XRD versus temperature of (A)(FA)₃Pb₄I₁₃-based quasi-DJ 2D perovskites e) Long-term thermal stability test of 4APP(FA)₃Pb₄I₁₃-based perovskites film at 85 °C in air for 3000 h f) Load versus indentation (P–h) curves and g) hardness for (A)(FA)₃Pb₄I₁₃-based quasi-DJ 2D perovskites.

prepared by stoichiometric reactions between PbI₂, FAI, and AI₃ in a mixed solvent of GBL, DMF, and DMSO (see Experimental section for detail). The thin films of all FA-based quasi-DJ 2D perovskites were formed by using the hot casting-annealing method. First, the substrate was preheated at 130 °C (hot plate temperature) and then quickly transferred to the spin coating chuck. After spin coating for 10 s a brown dark film was obtained. This film changed to completely black after annealing for 5 min at 130 °C. The details can be found in the Experimental Section.

UV–vis absorption and photoluminescence (PL) spectroscopies were carried out to compare the optical properties of different (A)(FA)₃Pb₄I₁₃-based quasi-DJ 2D perovskites films. The absorption spectra of all series, exhibit clear excitonic features similar to those of other 2D perovskites,^[27] and become less prominent for the 4APP and PP with decreasing spacer size and *n* value until they eventually disappear for *n* = ∞ (3D perovskites) (Figures S1 and S2a, Supporting Information). As shown in Figure S2b (Supporting Information), the PL spectra of these materials follow an analogous trend to the absorption spectra. A clear blue shift in PL emission energy is observed on

4AMP-based perovskites, as the ligand size is increased (from PP to 4AMP), which is due to increases in dielectric mismatch and quantum confinement effects in 2D perovskites because the 2D hybrid perovskite structures are natural quantum wells with semiconducting perovskite slabs alternating with dielectric organic slabs.^[37–40] A blue shift, can also be seen when changing from 4AMPY (aromatic) to 4AMP (aliphatic). This is due fact that aromatic cations exhibit a higher dielectric constant than aliphatic barriers due to the presence of the delocalized π -electron cloud. Consequently, the dielectric mismatch and quantum confinement effect in quantum-well structures of aromatic-based 2D perovskites are reduced.^[41–44]

Additionally, we measure the transient PL of all four quasi-DJ 2D perovskites (Figure S2c, Supporting Information). 4APP quasi-DJ 2D perovskites films show a longer average lifetime (25 ns) than those based on the other three (5 ns for PP(FA)₃Pb₄I₁₃, 16 ns for 4AMP(FA)₃Pb₄I₁₃, and 10 ns for 4AMPY(FA)₃Pb₄I₁₃), indicating a slower carrier combination, which is more desirable for photovoltaics.^[17] To understand the effect of the organic spacer cations on the crystal structure

of these quasi-DJ 2D perovskites, we conducted powder X-ray diffraction (XRD) analysis for $n = 4$ (Figure 1b). Diffraction spectra of all FA-based quasi-DJ 2D perovskites (nominally $n = 4$) exhibit two major peaks showing scattering from crystallographic planes (111) and (202) at diffraction angles (2θ) of 14.24° and 28.22° , respectively.^[45] When the organic spacer size increases (Figure S3, Supporting Information), both peaks shift to a larger angle, which is due to a change in crystal lattice constant and thus unit cell size.^[46]

Among the four organic spacers, we find that 4APP has a number of advantages in the construction of high-quality FA-based 2D perovskites. For example: 4APP is among the shortest cyclic diammonium organic spacers with the highest number of hydrogen bonds compared to 4AMP, AMPY, and PP. This is critical to the spacer-perovskite interaction, ensuring 2D perovskites' intrinsic stability. A strong hydrogen bond between inorganic perovskites and the positively charged NH_3^+ and NH_2^+ groups causes the inorganic perovskites to become more compact and thus more stable as a result.^[9,34] Second, the alkylamine tail (NH_3^+) and NH_2^+ group are directly connected to the ring, making the 4APP backbone more rigid than that of 4AMP and 4AMPY, thereby providing less flexibility (softness) and freedom between opposite layers and neighbors organic spacers.^[8] Overall our results show that a rigid 4APP backbone together with strong spacer-perovskite interactions make the perovskite difficult to deform once formed.

To prove our claims, first, we have systematically investigated the stability of thin films under various harsh conditions. The XRD patterns of quasi-DJ 2D perovskites $(\text{A})(\text{FA})_3\text{Pb}_4\text{I}_{13}$ at various temperatures (Figure 1c; Figure S4, Supporting Information) in air with RH between 60% and 90% to assess the thermal stability and the resistance to moisture and oxygen of all $n = 4$ thin films. In order to forecast the relative change of the main peak at around 14.21° , we calculated the evolution of full width half maximum (FWHM) with increasing temperatures (50°C increments) (Figure 1d). It can be seen that the FWHM of PP, 4AMP, and 4AMPY-based quasi-DJ 2D perovskites begins to decrease and the 2D perovskite phase completely disappears at 200°C . We believe that the change in FWHM here is caused by the thermal expansion of the crystal grains, with a greater expansion suggesting soft and chemically unstable stable lattices.^[47] In contrast, 4APP-based DJ 2D perovskites, even after 200 and 250°C , have almost unchanged FWHM, suggesting a more rigid crystal structure and chemical stability. We further extend the heat stability for over four months at 85°C in the air for 4APP-based perovskite films. Surprisingly, even though after two months of continuous heating, 4APP-based perovskite is stable and did not show any sign of decomposition (Figure 1e).

We further conducted nanoindentation experiments on all FA-based quasi-DJ 2D perovskite films in order to compare and confirm their rigidity (Figure S5, Supporting Information). Our results indicate that the organic spacer, indeed affects the resulting mechanical properties, especially the hardness and thus stability of FA-based quasi-DJ 2D perovskites. Figure 1f presents a typical load-indentation curve for all FA-based quasi-DJ 2D perovskites films having $n = 4$. There are a few small typical discontinuities known as "pop-ins" (Figure S6, Supporting Information). Similar pop-ins have also been reported in nanoindentation of other 2D and 3D perovskites.^[48] In 3D perovskites, pop-in events

are related to plastic deformation caused by the nucleation and propagation of slip dislocations. However, it can also occur with 2D crystals due to layer kinking, layer delamination, and layer fracture. We determine the Young's modulus and hardness of all FA-based quasi-DJ 2D perovskites films using the Oliver and Pharr method (See more detail in Experimental Section). Hardness measures the material resistance to plastic deformation. As shown Figure 1g and Figure S7 (Supporting Information), 4APP-based perovskites films show the highest Young's modulus and hardness values ($E = 29.99\text{ GPa}$ and $H = 1.19\text{ GPa}$) compared with PP ($E = 11.11\text{ GPa}$ and $H = 0.36\text{ GPa}$) 4AMP ($E = 18.63\text{ GPa}$ and $H = 0.64\text{ GPa}$) and 4AMPY ($E = 20.11$ and $H = 0.5$). While 4AMP and 4AMPY show small Young's moduli and hardness values (alkyl chain length (softer organic part) increases), they can be easily deformed.^[48,49] The PP-based perovskite film has the lowest Young's modulus and hardness, possibly because one hydrogen is absent at one end, causing a poor interaction with the perovskites. Consequently, our results indicate that 4APP-based perovskites are more compact and harder and cannot be easily deformed which are important for achieving highly stable perovskite as described in later sections.

2.2. Tri-Solvent Engineering for High-Quality Pure-Phase DJ 2D Perovskite

Generally, it is difficult to achieve high quality in low- n -value (MA-free) FA-based DJ 2D perovskites, as FA cations interact strongly with $[\text{PbI}_6]^{4-}$ octahedrons, or interact with dimethyl sulfoxide (DMSO), which is the most commonly used solvent. These quasi-DJ 2D perovskites have low crystallinity, and random well-width distribution of multiple quantum wells (QWs) with disordered orientation, which has seriously hindered further advances in photovoltaics.^[29,34] However, pure-phase films exhibiting uniform QWs width of DJ 2D perovskites with fixed n values are more efficient and stable. This is due to the fact that the conductive perovskite layers are uniformly distributed and equally protected by the hydrophobic organic layer.^[34] We developed a novel tri-solvent system with GBL, DMF, and DMSO to improve thin film morphology, crystal grain orientation, and phase purity of our champion rigid and stable 4APP-based perovskites for improved photovoltaic applications.

We choose these solvents based on their boiling point, dielectric constant, and Gutmann's donor number (D_N) (Table 1). The boiling point will affect the crystallization process and a solvent with a high boiling point contributes to slow down the crystallization process and will be beneficial to the growth of high-quality phase pure perovskites films with large crystal grain, thus prolonging carrier lifetime and device performances.^[50] Dielectric constant indicates a solvent ability to dissolve any ionic compound by screening coulomb attraction between its ionic species, while D_N describes the coordination ability of the solvent with the cations such as the divalent cation of Pb^{2+} at the center of the lead halide precursor.^[51,52] The high dielectric constants of DMSO and DMF make them ideal for the synthesis of 3D perovskite precursors. When using classic DMF mixed with DMSO solvent for fabrication of FA-based DJ 2D perovskites, DMF quickly evaporates due to its low boiling point and D_N number than DMSO. Meanwhile, DMSO interacts strongly with the perovskite

Table 1. Summary of different properties of three solvent used in this work.

Name of solvent (Abbreviation)	Boiling point [°C]	Gutmann's donor number [D_N] Kcal mol ⁻¹	Dielectric constant	Binding Energy [B.E] [eV]
Gamma-butyrolactone (GBL)	204	18	39	-3.258
Dimethylformamide (DMF)	153	27	37	-3.391
Dimethyl sulfoxide (DMSO)	189	30	49	-3.514

precursor such as PbI_2 , owing to its high D_N number and binding energy that will help the formation of perovskites through forming complex intermediates (e.g., $\text{DMSO} \cdot \text{PbI}_2$ and $(\text{DMSO})_2 \cdot \text{PbI}_2$).

However, there is a concern that the intermediates will be unexpectedly trapped in the film as residuals.^[50] We postulate that the intermediate residuals not only produce small grains, polycrystalline forms, and large structural disorders like those in 3D perovskites,^[53] but also cause low n phases in 2D perovskites and thus affect phase purity. In addition, DMSO can cause large pinholes at the perovskite buried interface, reducing photovoltaic performances and accelerate the degradation process.^[54] To address the concerns, we introduce GBL with a higher boiling point (204 °C) than DMSO (189 °C) but lower D_N number and binding energy in the tri-solvent system for delaying the crystallization process which promotes the effective removal of DMSO-intermediate phases and forms FA-based 2D perovskites with better crystallinity as to be further verified below.

To probe our hypothesis of the contribution of suitable amount of GBL in the tri-solvent system, we prepared four different types 4APP-base perovskites thin film obtained from different DMF:

DMSO: GBL solvent ratios, for example, (7:3:0 (without GBL) and 6:3:1, 4:3:3, and 2:3:5 with different GBL ratio. As shown in **Figure 2a**, surface and cross-sectional scanning electron microscopy (SEM) measurements reveal strong dependencies between the GBL ratios and the film uniformity and coverage. 4APP-based DJ 2D perovskites obtained from 7:3:0 solvent mixture (without GBL) have an inhomogeneous surface with many cracks. In contrast, the grain size increases after mixing GBL (6:3:1), with few pinholes. An increase in the GBL ratio (4:3:3) dramatically enlarges crystal grains with uniform surfaces. It should be noted that further increasing the GBL ratio (2:3:5), lots of cracks appear on the film surface, implying poor crystallinity, attributed to excess of GBL which causes the crystals to re-dissolve.

To further investigate the effect of tri-solvent systems on the crystallographic orientation of the 4APP-based DJ 2D perovskites films, we conducted 2D grazing-incidence X-ray scattering (2D-GIXRD) measurements (Figure 2b). The 2D-GIXRD map of DJ 2D perovskites films fabricated from 7:3:0 solvent mixture (without GBL) showed characteristic continuous Debye-Scherrer rings and a few low-intensity Bragg spots with some low angle

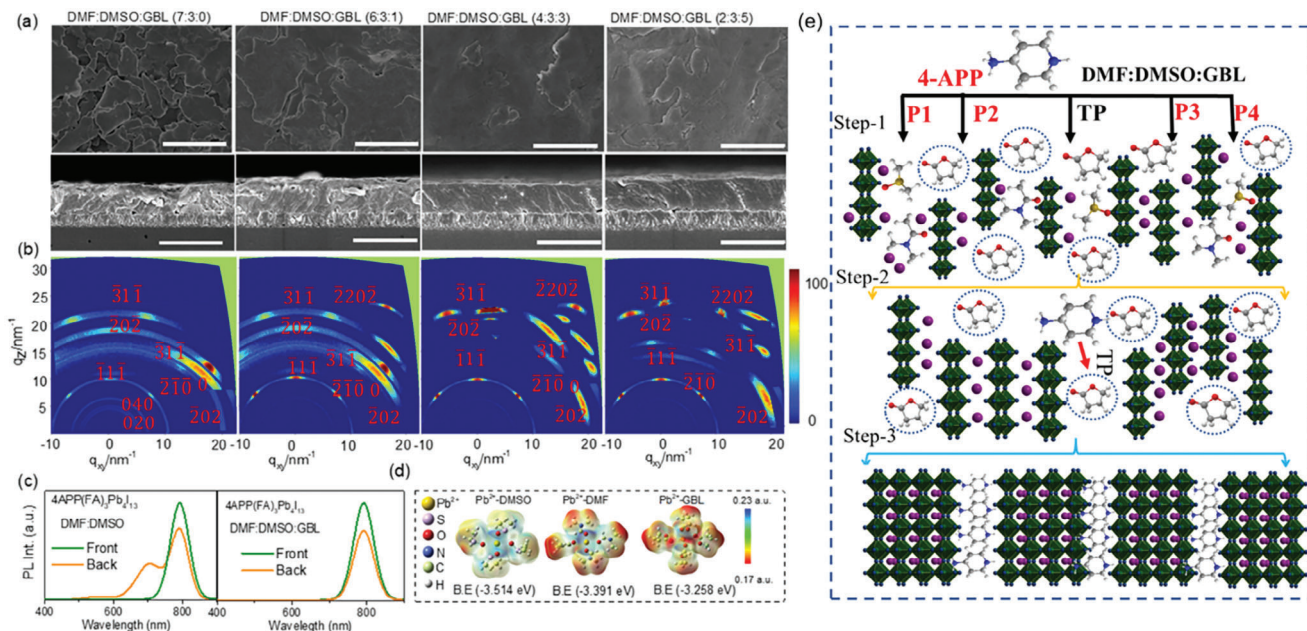


Figure 2. Crystallinity and phase purity of 4APP-based DJ 2D perovskite. Surface and cross-sectional SEM images, where the scale bar is 1 μm a) and 2D GIWAXS maps b) of 4APP-based DJ 2D perovskite films fabricated from different solvent ratios. c) PL spectra obtained from film side and back side of 4APP-based DJ 2D perovskite films fabricated from 7:3:0/without GBL (right) and 4:3:3 with GBL (left). d) Electrostatic potential plots of GBL, DMSO and DMF with PbI_2 . e) Formation mechanism of pure-phase 4APP-based DJ 2D perovskites film via tri-solvent (DMF: DMSO: GBL) engineering, where P1-P4 represent the different possible positions and TP indicates the target position for 4APP organic ligands.

(040, 060 peaks) diffraction rings indicating small n values, This indicating formation of mixture of 2D perovskites phases with random well-width distribution of multiple QWs and disordered orientation.^[55,45] When the GBL amount increases to become 6:3:1 solvent mixture, the perovskite films show strong Bragg spots and a weak diffraction ring. Interestingly, the diffraction rings for the 4:3:3 based perovskites film completely change into sharp Bragg spots of (111) along the q_z direction and (202) along the q_y direction, indicating a highly preferentially oriented crystal plane relative to the substrate, facilitating charge transport in devices. In contrast, with the further increase of GBL like the case of 2:3:5, the perovskites films show diffraction rings instead of Bragg spots, implying random orientation of the crystal domains again.^[56] As a result, the highly vertically oriented 4APP-based DJ 2D perovskite is achieved with the optimum DMF: DMSO: GBL ratio of 4:3:3 as shown in Figure 2e (step-3).

To confirm the good (vertical) phase purity of our champion 4APP-based 2D perovskites film, we measured the PL spectra of samples with different GBL ratios to determine whether the tri-solvent affects phase purity. When excited from both sides, samples with optimum GBL ratio (4:3:3) do not exhibit any differences in PL spectra, but those without GBL exhibit additional peaks (Figure 2c). As a result, the additional peaks are likely caused by intermediates/ low n phases formed by excess DMSO solvent (as discussed above). We also conducted PL measurements on both the front and back of PP, 4AMP, and 4AMPY films similar to 4APP, which are synthesized from DMF: DMSO: GBL and DMF: DMSO: GBL. Interestingly, as shown in Figure S8 (Supporting Information), the control (DMF: DMSO) PL spectra of PP, 4AMP, and 4AMPY for $n = 4$ have additional peaks when excited from the back side, in contrast to DMF.DMSO.GBL perovskites film, which does not exhibit any additional peaks upon excitation from the back, confirming solvent engineering's generalizability.

2.3. Formation Mechanism of Pure-Phase FA-Based DJ 2D Perovskites Films

While preparing DJ perovskite films based on FA, we tested the function of GBL as a mediator, cosolvent/additive to retard fast crystallization (slow crystallization), form an intermediate phase, and be easily removed by thermal annealing, due to small D_N number and its low binding energy with perovskite/ PbI_2 compared to DMF and DMSO. A detailed formation mechanism of pure-phase FA-based 2D perovskites is shown in Figure 2e. In the precures solution (step-1) the presence of GBL facilitate the solubility of 2D perovskite (ligands- 4APP) due to its high dielectric constant but partially helps in the solubility 3D perovskites ($FA_3Pb_4I_{13}$), specially PbI_2 due to its low D_N number.^[51] The DMF and DMSO evaporated completely during initial perovskite crystallization (step-2) via host casting-annealing stages (see Experimental section for detail), but some GBL-perovskite intermediates appear to exist, due to their high boiling points. An XRD analysis shows some low-angle peaks at around 8° after 1 min of annealing (Figure S9, Supporting Information), which confirms this. Upon further annealing, GBL is eliminated and low-angle peaks disappear. In step 3, the organic ligands reach their target

positions (TP) and form high-oriented perovskite QWs as demonstrated by GIWAXS, SEM, and PL spectra analysis.

By contrast, using classic DMF: DMSO only 2D perovskites solution (Figure S10, Supporting Information), DMF and DMS evaporated quickly (fast crystallization) and the 4APPs were randomly distributed in different positions (P1-P4), which resulted in random well-width distributions with disordered orientations^[57] (as discussed above).

Overall based on SEM, 2D-GIRXD, and PL results, we conclude that a high-quality vertically oriented pure-phase 4APP-based DJ 2D perovskite thin film can be obtained using an optimal amount of GBL tri-solvent without any changes to crystal structure when compared to the perovskite layer that is made using traditional DMF: DMSO bi-solvent system.

2.4. Device Performances and Stability

We fabricate devices with FTO/ NiO_x /(4APP(FA)₃Pb₄I₁₃/PCMB/Ag structures from our optimized, stable and rigid 4APP(FA)₄-based DJ 2D perovskites (Figure 3a). A representative cross-sectional SEM image of the device shows a 4APP-based DJ 2D perovskite layer with a thickness of 650 nm as in Figure 3b. The device delivers a champion PCE of 17.27% with open-circuit voltage (V_{oc}) = 1.01 V, short-circuit current density (J_{sc}) = 22.01 mA cm⁻², and fill factor (FF) = 0.71 as shown in Figure 3c. The device also shows negligible hysteresis. The performances of the control device are shown in Figure S11 (Supporting Information). For the control PSCs prepared from the bi-solvent of DMF: DMSO, the device performances are V_{oc} = 0.87 V, J_{sc} = 19.7 mA cm⁻², FF = 0.677, and PCE = 11.7%. Therefore, the PCE of the tri-solvent-engineered PSCs is significantly (48%) better than of the control devices. A statistical analysis of PCEs derived from fifty devices is presented in Figure 3d. The J_{sc} value obtained from the EQE is in line with the value provided by the J - V curves, proving its validity (Figure 3e), proving their validity. Figure 3f depicts the stabilized power output under maximum power point which is in good agreement with the J - V scan. In addition, we fabricate devices with PP, 4AMP, and 4AMPY (Table S2, Supporting Information), where the PCEs of all ligands-based PSCs improve significantly, again demonstrating our solvent engineering's generalizability.

We further evaluate the stability of all four types of FA-based DJ 2D devices without encapsulation under various aging conditions. We first assessed the thermal stability of devices based on 4APP, 4AMP, and 4AMPY at 85 °C in ambient environment. PP, 4AMP, and 4AMPY devices retained 29%, 36%, and 46% respectively after 2016 h and completely died after that, while the 4APP-based devices exhibited greater thermal resistance and retained almost 95% PCE after over 3000 h at 85 °C (Figure 4a). We further evaluated the compatibility of those devices under ambient conditions with humidity ranging from 60 to 90% RH (Figure 4b). In contrast with PP, 4AMP, and 4AMPY devices, which lost almost 80%, 57%, and 53% of their PCEs, 4APP-based devices retained 95% of their initial PCEs after 3500 h. Finally, we tested the operational stability under 1-sun illumination at maximum power point for over 2000 h.^[58] Figure 4c presents that the 4APP-based device can maintain over 95% of its original PCE after 2000 h continuous operation. These results indicate that DJ 2D PSCs

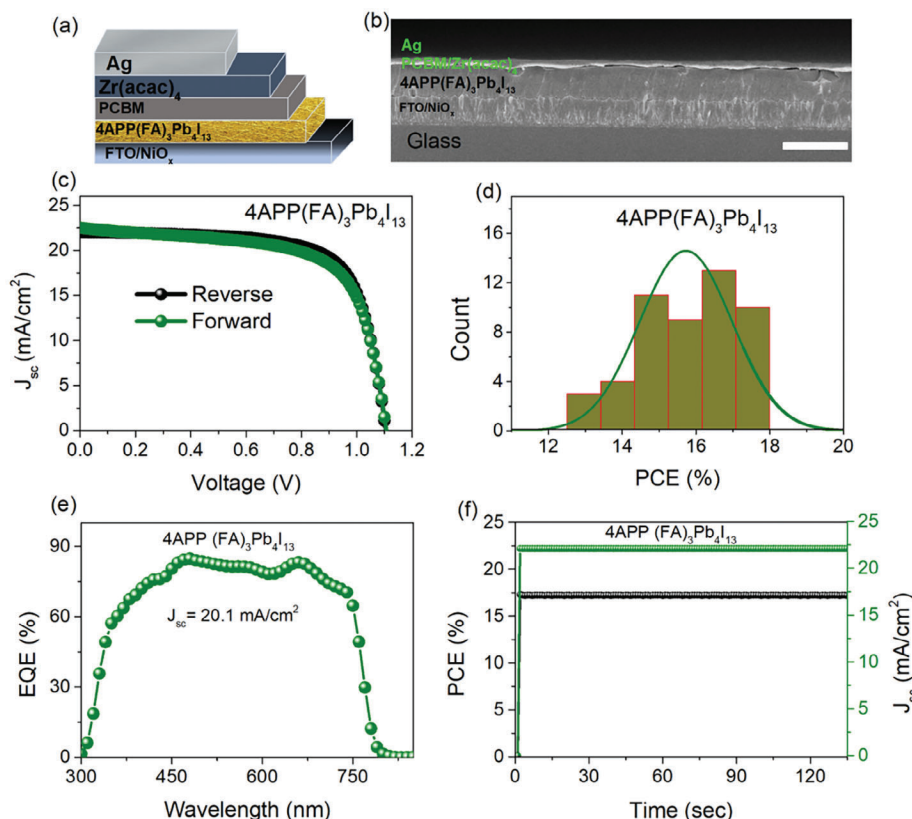


Figure 3. Fabrication and performances of MA-free DJ 2D perovskites solar cell. Device structure a) cross-sectional SEM images where the scale bar is 2 μm b) fabricated in this work. Forward and reverse J - V curves c) statistical PCE distribution of 50 devices d) EQE spectra and, stabilized PCE and J_{sc} of the champion 4APP-based DJ 2D PSCs.

based on the 4APP have astonishing stability highest among the reported DJ 2D FA-based 2D PSCs (Table S3, Supporting Information).

To understand whether the organic spacer or solvent engineering is responsible for the stability improvement, we study the typical thermal stability of 4APP(FA)₃Pb₄I₁₃-based DJ 2D perovskite devices fabricated from tri-solvent and bi-solvent (control) systems. As shown in Figure S12 (Supporting Information), the unencapsulated 4APP PSCs fabricated from tri-solvent and bi-solvent maintain almost identical their initial PCEs (95% for tri-solvent and 93% for bi-solvent) for over 3000 h at 85 °C in air. It is therefore evident that the stability of 4APP(FA)₃Pb₄I₁₃-based perovskite is intrinsically and primarily contributed from the rigid organic spacers and the strong hydrogen bonding with the perovskite materials in PSCs.

3. Conclusion

In summary, we have studied a series of organic spacers to achieve a very rigid and chemically stable (MA-free) FA-based DJ 2D perovskite, namely 4APP(FA)₃Pb₄I₁₃. The unencapsulated quasi-DJ 2D perovskites made from 4APP are exceedingly chemically stable under various harsh conditions, that is, exposure at 85 °C for over 3000 h and even 250 °C for 0.5 h. The improved stability is attributed to two aspects. First, the positively charged ends (NH₃⁺ groups) of the organic spacer are strongly linked with

the negatively charged ends of the inorganic perovskites layer through hydrogen bonds. Second, the 4APP rigid backbone and its strong spacer interactions with perovskite materials make it difficult to deform once the perovskite is formed. Equally important, we achieve high-quality pure-phase DJ 2D perovskite films with uniform QWs width structure and excellent crystal plane orientation by strategically introducing GBL to form a new tri-solvent engineering with DMF and DMSO. The optimized 4APP(FA)₃Pb₄I₁₃-based DJ 2D perovskites enhance the PCE of the solar cell by 48% as compared to the control. Importantly, the unencapsulated 4APP-based PSCs show a T_{95} of over 3000 h at 85 °C in the air with relative humidity (60–90%) with a negligible decline in the performance. Furthermore, the unencapsulated devices show impressive operational stability, with a T_{95} of 2000 h under 1-sun illumination at 40 °C in the air. The present work not only introduces a convenient approach for enriching novel new class of highly rigid diamine spacers but also advances the design and operation of organic spacers and solvents engineering to further enhance FA-based DJ 2D perovskites stability and efficiency.

4. Experimental Section

Materials: 4APP (4-(aminopiperidine), 98%), 4AMP (4-(aminomethyl) piperidine, 98%), AMPY (4-(aminomethyl)pyridine, 98%), PP (piperidine 99%), and lead iodide (PbI₂, 99%), were purchased from TCI. FAI was

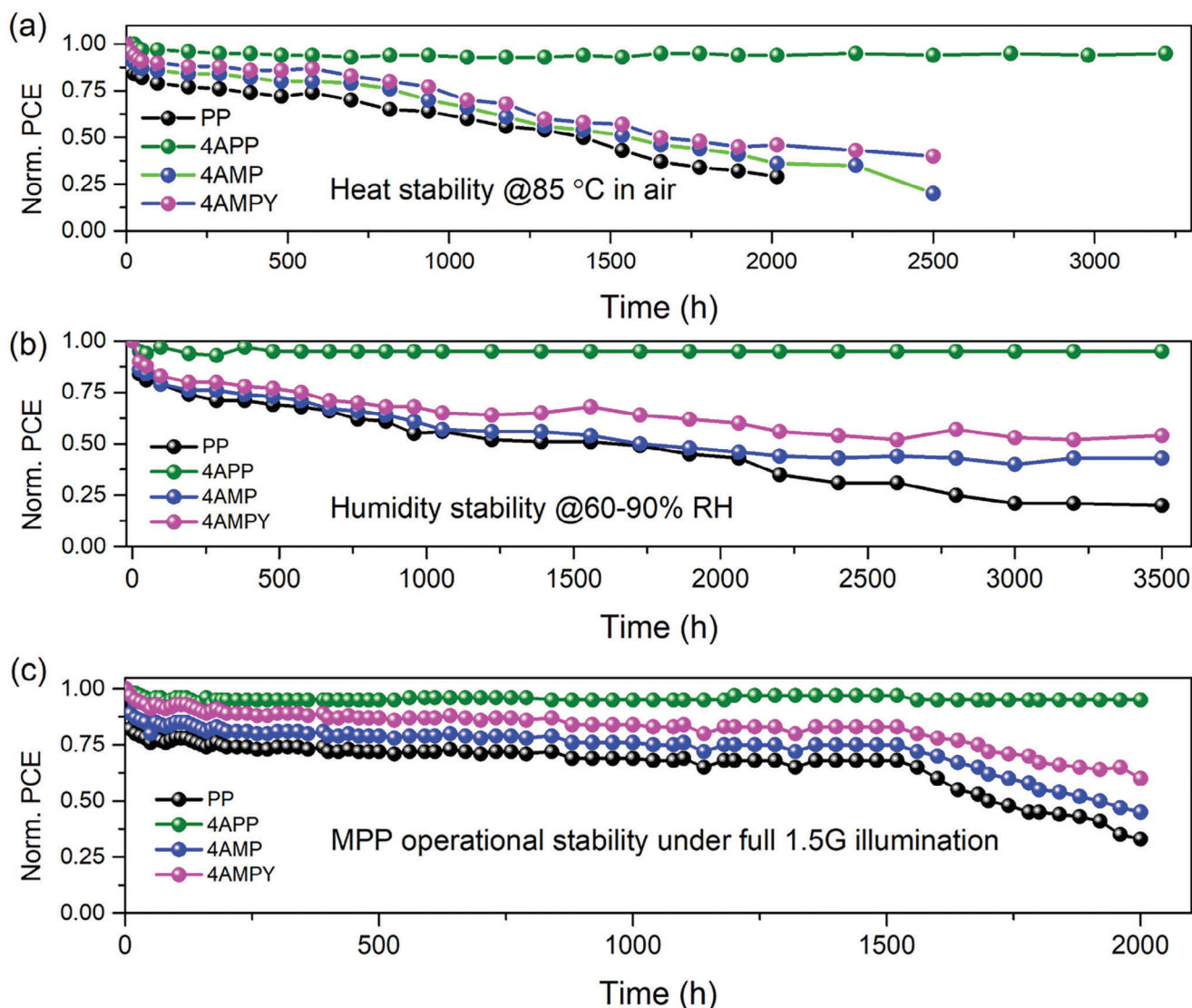


Figure 4. Stability of MA-free DJ 2D perovskite solar cells. Thermal stability test at 85 °C a) Humidity stability test at room temperature b) operational stability test at MPP under 1-sun illumination c) of unencapsulated (A)(FA)3Pb4I13-based devices in air with R.H = 60–90%.

purchased from Dyesol. Gamma-butyrolactone (GBL, 99% extra dry) Dimethyl sulfoxide (DMSO, 99%, extra dry), Dimethylformamide (DMF 99% extra dry), isopropyl alcohol (IPA), Chlorobenzene (CB, extra dry, 99.8%) were purchased from Acros. PCBM was purchased from Solarmer Energy, Inc. HI (50% wt/wt in water), and Zirconium (IV) acetylacetonate (ZrAcac, 98%) were purchased from Sigma–Aldrich. NiO_x nanoparticles inks were prepared according to the previous reports.^[59,60]

Synthesis of 4APP I_2 , 4AMP I_2 , 4AMPY I_2 and PPI I_2 Salts: The diammonium iodide salts (A) I_2 (A = 4APP, AMP, AMPY, and PP) were prepared by adding dropwise 2 moles of hydroiodic acid (HI) to 1 mole equivalent of diamine, with continuous stirring at 0 °C for 2 h. By evaporating the solvent at 60 °C, the precipitate of diammonium iodide salts was recovered using a rotary evaporator. ethanol and diethyl ether were used three times to wash the precipitate. Afterward, the white powder was collected by suction filtration and dried under vacuum overnight in an oven at 60 °C.

Synthesis and Fabrication of MA-free DJ 2D Perovskites Films: 0.25 mmol of AlI_3 , 0.75 mmol of FAI, and 1 mmol of PbI_2 were used in a mixed solvent of DMF, GBL, and DMSO, with a volume ratio of 7:X:3:X (where X = 0, 1, 3, and 5). An ultrasonic washing procedure was applied to patterned

FTO-coated glasses during 15 min of washing with detergent, deionized water, acetone, and ethanol, followed by drying with nitrogen gas. Then the FTO glasses were treated by ultraviolet ozone for 20 min. In the next step, 50 μL of NiO_x (20 mg mL^{-1} in deionized water) were spin-coated on FTO glass at 2500 rpm for ≈ 50 s. FTO/ NiO_x substrates were transferred into a nitrogen-filled glovebox and preheated for 5 min at 130 °C on a hot plate. After transferring the substrates to the spin-coating chuck, DJ 2D perovskites were spin-coated on top of the NiO_x layer at 6000 rpm for 30 s. The film was then annealed at 130 °C for 5 min. After cooling the perovskite films to room temperature, a 20 mg mL^{-1} PC61BM solution in chlorobenzene spin-coated for 40 s on the DJ 2D perovskite surface, followed by a 2 mg mL^{-1} zirconium (IV) acetylacetonate solution in isopropanol at 4000 rpm for 40. Finally, the 120 nm Ag electrode was thermally evaporated on top of the device under a vacuum of 2×10^{-4} Torr in the high-vacuum deposition system with a device area of 0.08 cm^2 .

Measurements and Characterizations: The nanoindentation experiment was performed using a Berkovich indenter of a half angle of 65.3°. During nanoindentation, a maximum load of 2000 μN was applied and the distances between indents were at least 5 μm . The Nano-hardness was

defined by the maximum load over the residual indentation impression. Under a light intensity of 100 mW cm^{-2} calibrated with a standard silicon reference cell, the current density–voltage (J – V) characteristics of each solar cell with area 0.08 cm^2 were measured using Enlitech AM 1.5 G solar simulator, and data were collected using Keithley 2400. Perkin Elmer Lambda 750 UV–vis spectrometer was used to measure UV–vis absorption spectra of DH 2D perovskites films. A Hitachi S4800 FEG scanning electron microscope was used to measure the surface and cross-sectional morphology. Time-resolved photoluminescence spectra were recorded on an FLS920 fluorescence spectrometer (Edinburgh Instruments) in the air at room temperature. A picosecond pulsed diode laser (406.8 nm) was used as the excitation source. The 2D GIWAX maps were obtained at the Shanghai Synchrotron Radiation Facility (SSRF) using the beamline BL14B1, with a photon energy of 10 keV (wavelength 1.2398 angstrom) and an incident angle of 0.40° . Samples were prepared on Glass/FTO substrates for GI-XRD measurements.

Stability Tests: Long-term damp heat tests were conducted on unencapsulated devices and thin films inside a constant 85°C oven. A hot plate at a specific temperature was used to heat test unencapsulated devices and thin films at different temperatures. In order to test the long-term humidity stability of unencapsulated devices and thin films, both were stored in air with RH between 60% and 90%. Continuous maximum power point (MPP) operation under 1 Sun, AM 1.5G illumination was tested inside an environment chamber at 50 percent relative humidity and 40°C by determining the voltage at VMPP and then tracking the current output.

Supporting Information

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

Acknowledgements

The authors would like to acknowledge seed fund (grant nos. 202011159254 and 202111159113) from the University Grant Council of the University of Hong Kong, the General Research Fund (grant nos. 17211220, 17200021 and 17200823), and the Collaboration Research Fund (C7035-20G) from the Research Grant Council as well as Innovation and Technology Fund (MRP/040/21X) from Innovation and Technology Commission, Hong Kong Special Administrative Region, China. The authors would like to thank Prof. Aleksandra Djurisic from Department of Physics, for providing XRD facility for thin film analysis and stability test. The authors also would like thank Prof. Mingxin Huang from Mechanical engineering department, for providing Nanoindentation measurement facility for thin film analysis and hardness test.

Conflict of Interest

The authors declare no conflict of interest.

Author Contributions

W.C.H.C. supervised the project. S.A. and W.C.H.C. proposed the project. S.A., J.K., and X.H. conducted the experiments. M.G. conducted nanoindentation measurement. S.A. and Z.R. measured XRD. S.A. and W.C.H.C. prepared manuscript. All authors participated in the discussions for manuscript preparation.

Data Availability Statement

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

Keywords

chemical stability, device stability, DJ 2D perovskites, ligand spacers, rigidity, solvent engineering

Received: August 22, 2023

Revised: October 17, 2023

Published online:

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