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### Hydrogen-bond-bridged intermediate for perovskite solar cells with enhanced efficiency and stability

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1 **Hydrogen Bond-Bridged Intermediate for Perovskite Solar Cells with Enhanced**  
2 **Efficiency and Stability**

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17

18 **Keywords:** intermediate phase, crystallization, perovskite solar cells, non-radiative  
19 recombination

20 **Abstract:** Improving the intrinsic film quality of metal halide perovskites is very  
21 critical to increase the power conversion efficiency (PCE) and long-term stability of  
22 perovskite solar cells. Herein, we report a multifunctional, non-volatile additive that  
23 can be used to modulate the kinetics of perovskite film growth through a hydrogen  
24 bond-bridged intermediate phase. The additive enables the formation of large  
25 perovskite grains and coherent grain growth from bottom to the surface of the film. The  
26 enhanced film morphology results in significantly reduced non-radiative  
27 recombinations, thus boosting the PCE of inverted (p-i-n) solar cells to 24.8% (24.5%

1 certified) with a low energy loss of 0.36 eV. The unencapsulated devices exhibit  
2 improved thermal stability with a  $T_{98}$  lifetime beyond 1000 hours under continuous  
3 heating at  $65 \pm 5$  °C in an N<sub>2</sub>-filled glovebox. This effective approach can also be  
4 applied to wide-bandgap perovskites and larger-area devices to show reduced voltage  
5 loss and high efficiency.

6

7 Organic-inorganic hybrid perovskites have garnered great attention due to their  
8 impressive optoelectronic properties.<sup>1</sup> Combining compositional and interfacial  
9 engineering strategies, the record power conversion efficiency (PCE) of perovskite  
10 solar cells (PVSCs) has now achieved 25.7%.<sup>2,3</sup> However, the high-efficiency devices  
11 reported are mostly of conventional (n-i-p) architecture,<sup>4-6</sup> while inverted (p-i-n)  
12 PVSCs still show inferior performance despite their low-temperature processability and  
13 better compatibility in fabricating tandem and flexible devices.<sup>7-11</sup> The major challenge  
14 stems from the severe energy loss in inverted PVSCs, especially the non-radiative  
15 recombination loss associated with defects embedded at the interfaces and grain  
16 boundaries.<sup>12</sup> A high-quality perovskite film with intrinsically low defect density is thus  
17 critical in determining the achievable efficiency and stability for PVSCs.<sup>13</sup>

18 In the typical one-step solution process, the perovskite precursors dissolved in polar  
19 aprotic solvents are spin-coated onto the substrate. The introduction of an antisolvent  
20 then quickly extract the residual solvents and template perovskite crystal growth  
21 through intermediate phases.<sup>14</sup> Various volatile solvents and organic salts have been  
22 employed as additives to tune the intermediate compositions for modulating the  
23 crystallization kinetics.<sup>15-17</sup> Huang *et al.* added *N*-methyl-2-pyrrolidone (NMP) in the  
24 perovskite precursors to form PbI<sub>2</sub>-NMP adduct for promoting the black phase  
25 formation at room temperature.<sup>16</sup> Kim *et al.* used methylammonium chloride (MACl)  
26 to facilitate the formation of an intermediate phase for stabilizing the perovskite  $\alpha$ -  
27 phase.<sup>17</sup> However, these additives may volatilize during annealing, creating voids at the  
28 perovskite-substrate interface, inducing unavoidable recombination loss and fast  
29 degradation of perovskite.<sup>18</sup>

1        Herein, we report the formation of a hydrogen bond-bridged intermediate by adding  
2 a multifunctional molecule (4-guanidinobenzoic acid hydrochloride, GBAC) into  
3 perovskite precursor to modulate the crystallization kinetics and serve as an effective  
4 non-volatile passivation linker in the annealed film. Combining crystallography, *in-situ*  
5 photoluminescence (PL) characterizations, and density functional theory (DFT)  
6 calculations, we reveal the crystal growth kinetics is regulated by additional energies  
7 required for hydrogen-bond breakage and cation exchange between the intermediate  
8 phase and perovskite. Therefore, the obtained perovskite films exhibit significantly  
9 enhanced crystallinity with larger grains. Besides, the additives can form tight packs at  
10 the grain boundaries due to  $\pi$ - $\pi$  interaction of the aryls to effectively passivate the  
11 defects in perovskites. The derived inverted PVSCs achieved a champion PCE of 24.8%  
12 with an open-circuit voltage ( $V_{OC}$ ) of 1.19 V, short-circuit current density ( $J_{SC}$ ) of 24.55  
13 mA/cm<sup>2</sup> and fill factor ( $FF$ ) of 84.78%. A certified PCE of 24.5% was obtained from  
14 the Japan Electrical Safety & Environment Technology Laboratories (JET), being  
15 among the highest for inverted PVSCs reported (**Supplementary Table 1**). We also  
16 applied this strategy to fabricate wide-bandgap and large-area PVSCs, paving the way  
17 for developing multijunction and scalable perovskite photovoltaics.

### 18 **Characterization of Perovskite Films**

19        We introduced GBAC as an additive into the perovskite precursor solution, which  
20 can interact with the uncoordinated lead and organic/inorganic vacancies via Lewis  
21 acid-base reactions with the carboxyl and guanidium groups.<sup>19</sup> To verify our hypothesis,  
22 we first conducted Fourier transform infrared (FTIR) spectrometry to study the  
23 interactions between GBAC and organic species in perovskite. As shown in **Fig. 1a and**  
24 **Supplementary Fig. 1**, the N-H stretching peak shifted from 3352 to 3378 cm<sup>-1</sup> for  
25 FA<sup>+</sup>/MA<sup>+</sup> and the C=N stretching peak in FA<sup>+</sup> also shifted from 1713 to 1709 cm<sup>-1</sup> upon  
26 adding GBAC, suggesting the formation of hydrogen bonds between GBAC and  
27 organic cations.<sup>20</sup> These indicate that the interplay between GBAC and FA<sup>+</sup>/MA<sup>+</sup> in  
28 perovskite helps strengthen the film stability, especially the thermal stability mainly  
29 governed by the organic species. We then verified this through thermogravimetric

1 analysis (TGA) (Supplementary Fig. 2), where the impeded decomposition of target  
2 film suggests more energy is required to disrupt the interaction between GBAC and  
3 perovskite,<sup>21</sup> ameliorating the film thermal stability.

4 We performed high-resolution X-ray photoelectron spectrometry (XPS) to study the  
5 surface chemistry of perovskites (Supplementary Fig. 3). We clearly observed the peak  
6 corresponding to GBAC  $\pi$ - $\pi$  interaction (293.10 eV, C 1s spectrum) and increased C=O  
7 peak area (O1s spectrum) in target film, further validating the existence of GBAC linker  
8 in perovskite (Supplementary Figs. 4 and 5). In the Pb4f spectrum (Fig. 1b), the binding  
9 energy of 4f<sub>5/2</sub>, 4f<sub>7/2</sub> for divalent Pb<sup>2+</sup> shifted from 141.92 and 137.09 eV to 141.59 and  
10 136.76 eV, respectively, due to the electrostatic interaction between the guanidium  
11 group and PbI<sub>6</sub><sup>4-</sup>. We further recorded the steady-state photoluminescence (PL) and  
12 time-resolved photoluminescence (TRPL) profiles of perovskite films to reveal how  
13 GBAC affects film quality and charge-transport dynamics (Supplementary Fig. 6). The  
14 target film exhibits 6-times stronger PL intensity and 3-times longer PL lifetime than  
15 those of control film, agreeing well with the FTIR and XPS results that GBAC  
16 suppresses the defect-induced non-radiative recombination to reduce energy loss for  
17 improving photovoltaic performance.

18 To understand how GBAC addition affects the film morphology, we collected  
19 scanning electron microscope (SEM) images of perovskite films. The target film shows  
20 considerably larger grains (~1  $\mu$ m) and fewer residual PbI<sub>2</sub> sheets than the control film  
21 (Figs. 1c and d), with a coherent bottom-to-surface grain growth which can facilitate  
22 the transport of carriers to electrodes. Besides good film morphology, the crystallinity  
23 of target film is significantly improved (Fig. 1e). The decreased PbI<sub>2</sub> sheets in SEM  
24 images was also confirmed by the X-ray powder diffraction (XRD) patterns, suggesting  
25 GBAC can interact with the uncoordinated Pb<sup>2+</sup> and modulate film growth to obtain  
26 fully grown grains. Moreover, the addition of GBAC significantly helps modulate the  
27 crystal orientation within the film for facilitating charge transport (Supplementary Fig.  
28 7).

29 Atomic force microscopy (AFM) characterization reveals a lower surface roughness

1 after GBAC addition (Supplementary Fig. 8). We also applied Kelvin probe force  
2 microscopy (KPFM) to evaluate the distribution of surface potential of perovskite films,  
3 which shows an increasement of 200-300 mV in the target film (Fig. 1f and  
4 Supplementary Fig. 9), indicating a Fermi level ( $E_f$ ) closer to the conductive band  
5 edge.<sup>22</sup> The higher work function measured by KPFM matches well with the results  
6 obtained from the ultraviolet photoelectron spectrometry (UPS), showing a 0.25 eV  
7 shift of  $E_f$  by adding GBAC (Supplementary Fig. 10). The more n-characteristic film  
8 surface stems from the modified surface termination after adding GBAC,<sup>23</sup> enabling  
9 more efficient charge transfer between perovskite and electron-transporting materials  
10 (Supplementary Fig. 11).

### 11 ***In-situ* Characterization of Film Formation**

12 To gain more insights into the remarkably enhanced film quality, we adopted *in-situ*  
13 PL spectrometry to understand the role of GBAC during film formation.<sup>24-26</sup> The  
14 evolution of PL peak position in both control and target films show similar trends in the  
15 long-term stage (0-750 s) (Supplementary Figs. 12-14). However, the initial peak  
16 position of the wet target film was slightly blue-shifted compared to that of the control  
17 film due to additional chloride from GBAC (Figs. 2a and b). Also, the target film  
18 exhibits a much slower shift with negligible fluctuation in the initial stage (0-10 s)  
19 compared to those of the control sample, implying that the crystallization process was  
20 significantly retarded by adding GBAC (Fig. 2b).<sup>24</sup> Moreover, the PL peaks of the target  
21 film are more symmetric compared to the control film, indicating a more uniform  
22 distribution of crystallite sizes, which facilitates the significantly increased grain sizes  
23 as shown in SEM images (Figs. 1c and d).<sup>26</sup>

24 We then analyzed the evolution of PL peak intensity, which show typical PL  
25 quenching in both films but more severe in the control film (Figs. 2c and d).<sup>25,26</sup> Such  
26 PL quenching originates from the continuously increased Urbäch energy, indicating the  
27 gradual formation of defects in the microstructures of perovskites.<sup>25</sup> However, it is  
28 considerably inhibited in the target film, showing a much lower defect density and  
29 better ambient stability than the control film (Fig. 2d).<sup>27</sup> The initial stages (0-2 s for

1 control sample and 0-30 s for target sample) were then enlarged to clearly show the PL  
2 intensity evolution (Figs. 2e and f). The control film shows a typical four-stage “up-  
3 down-up-down” process with two states (Fig. 2e).<sup>25</sup> In state “I” (0-200 ms), the  
4 perovskite grains grow freely and are well crystallized/ordered, resulting in an  
5 increased PL intensity (“up”). When the solvent is almost entirely evaporated, the  
6 perovskite crystallites are exposed to the surrounding atmosphere and the surfaces of  
7 other crystallites, forming grain boundaries and triggering rapid PL quenching (“down”,  
8 200-400 ms). In state “II”, the small crystallites further grow and merge into larger ones  
9 upon annealing to reduce overall grain boundaries, resulting in increased PL intensity  
10 again (“up”, 400-600 ms). Such rapid film formation can also be attributed to the  
11 absorbed moisture accumulated within grain boundaries, inducing grain boundary creep  
12 and subsequent merging of adjacent grains to accelerate the film growth.<sup>28</sup> The partial  
13 recovery of PL intensity also comes from the passivation effect of excessive  $\text{PbI}_2$  at the  
14 perovskite grain boundaries.<sup>29</sup> Eventually, the film is vulnerable under ambient  
15 conditions and prone to decomposition. These result in a stabilized but almost one order  
16 of magnitude lower PL intensity than that of  $\text{PL}_{\text{max}}$  (“down”, after 600 ms). However,  
17 adding GBAC introduces an extra stage involving the intermediate-induced pre-growth  
18 process in the target sample (Fig. 2f).<sup>25,26</sup> The film formation is significantly slowed  
19 down, reaching its maximum PL intensity at  $\sim 20$  s and long-maintained. These results  
20 imply that adding GBAC can modulate the crystallization kinetics by forming an  
21 additional intermediate to enhance film quality, leading to larger grain sizes and high  
22 crystallinity.

### 23 **Film Growth with Hydrogen Bond-Bridged Intermediate**

24 To study the GBAC-induced intermediate phase, we grew the single crystal of  
25 GBAC- $\text{PbI}_2$ -DMF (Supplementary Table 2).<sup>30</sup> We observed strong cyclic hydrogen  
26 bonds between carboxylic acid and guanidino group, DMF and guanidino group,  
27 respectively (Fig. 3a). The DMF molecules locked by hydrogen bonds help isolate the  
28  $\text{PbI}_2$  sheets and GBAC layer, leading to a 1D organic-inorganic hybrid chain structure.  
29 Due to the strong dipole of GBAC and the electron delocalization in the guanidino



1 groups (Supplementary Fig. 15), these hydrogen bonds are very different from the  
2 typical linear hydrogen-bonded chains that serve as supramolecular synthons for  
3 layered perovskite structures.<sup>31</sup> This unique interaction mode helps build a bridge to  
4 connect the organic/inorganic components. Moreover, the interaction between GBAC  
5 and perovskite precursor components in solution was investigated by <sup>1</sup>H NMR  
6 spectrometry (Supplementary Figs. 16), of which the results echo well with those  
7 observed from XPS and FTIR measurements.<sup>8</sup> Through these studies, we have  
8 identified that GBAC can interact with solvent, organic, and inorganic components  
9 simultaneously in the precursor solution through both Coulomb interaction and  
10 hydrogen bonding, demonstrating its multifunctionality in solution.

11 We then conducted thermal analysis of single crystals to study the phase transition  
12 from the intermediate state to perovskite. The experimental XRD pattern of obtained  
13 transparent GBAC-PbI<sub>2</sub>-DMF crystals matches well with the XRD pattern simulated  
14 from single-crystal structure, confirming their composition (Supplementary Fig. 17).  
15 The simultaneous thermal analysis (STA) profile shows an intense endothermic peak at  
16 ~80 °C corresponding to hydrogen-bond breakage (Supplementary Fig. 18). At elevated  
17 temperature, DMF starts to evaporate, destabilizing the intermediate which then  
18 transforms into a new 1D structure composed of GBAC-PbI<sub>2</sub> (Fig. 3b and  
19 Supplementary Fig. 19). This GBAC-PbI<sub>2</sub> phase can only be identified in perovskite  
20 film with >4 mol% GBAC dosage (Supplementary Fig. 20 and 21), where small dosage  
21 of GBAC in turn functions as a passivation linker anchoring at the grain boundaries to  
22 reduce the defect density and enhance the film stability with its rigid stacking.<sup>9</sup>

23 To understand the impact of such hydrogen bond-bridged intermediate on film  
24 growth, periodic density functional theory (DFT) calculations were performed to  
25 understand if GBAC<sup>+</sup> can exchange with FA<sup>+</sup> spontaneously during the crystallization  
26 process. Due to the substantial hydrogen bonding, the formation energy of this  
27 intermediate (GBAC-PbI<sub>2</sub>-DMF) (-18.58 eV) is much lower than that of  $\delta$ -FAPbI<sub>3</sub> (-  
28 10.60 eV). Such extra stabilization is not thermodynamically favorable for crystal  
29 growth, since extra energy is required to enable the cation exchange between GBAC<sup>+</sup>

1 and FA<sup>+</sup>.<sup>32</sup> During the subsequent thermal annealing, the hydrogen bonds in the GBAC-  
2 PbI<sub>2</sub>-DMF phase were broken to form GBAC-PbI<sub>2</sub> with an energy of -11.85 eV (Fig.  
3 3c). Although this significantly reduced the energy barrier (1.25 eV) is easier to  
4 overcome, it will still hinder the free exchange between GBAC<sup>+</sup> and FA<sup>+</sup>, thereby  
5 slowing down the crystallization process.<sup>33</sup>

6 In addition to thermodynamic control, the nucleation rate mediated by kinetic control  
7 can also be altered by increasing the activation energy of cation exchange.<sup>34</sup> Compared  
8 with the Lewis acid-base adduct formed between PbI<sub>2</sub> and DMF (-0.79 eV) (Fig. 3d),  
9 the stronger ionic bonding between GBAC and PbI<sub>2</sub> (-1.16 eV) will cost extra energy  
10 to overcome the saddling point (Supplementary Fig. 22 and 23).<sup>35,36</sup> Moreover, based  
11 on the Arrhenius equation, the inherent nucleation and growth kinetics originated from  
12 the high volatility of DMF and strong FA-precursor binding to DMF (-1.00 eV),<sup>37</sup> will  
13 also be hindered by the more stable GBAC-PbI<sub>2</sub> phase. Therefore, the crystal growth  
14 of perovskite can be both thermodynamically and kinetically modulated by this  
15 hydrogen bond-bridged intermediate (Supplementary Fig. 24). Due to strong  
16 interaction between GBAC and perovskite, the retarded film formation would also  
17 accumulate GBAC at the bottom interface (Supplementary Fig. 25). Eventually, rigidly  
18 stacked GBAC can form at grain boundaries due to  $\pi$ - $\pi$  interaction after DMF  
19 evaporation, functioning as a multifunctional passivation linker to enhance photovoltaic  
20 performance (Fig. 3e).<sup>9</sup>

## 21 Photovoltaic Performance

22 The inverted PVSCs with a device configuration of ITO/((2,7-dimethoxy-9H-  
23 carbazol-9-yl) methyl) phosphonic acid (DC-PA)<sup>22</sup>/Perovskite (with/without GBAC)/  
24 C60/bathocuproine (BCP)/Ag were fabricated to evaluate their photovoltaic  
25 performance (Fig. 4a, Supplementary Fig. 26 and 27, and Table S3). As shown in Fig.  
26 4b, the highest PCE of the control device is 22.8%, with a  $V_{OC}$  of 1.12 V,  $J_{SC}$  of 24.48  
27 mA/cm<sup>2</sup>, and  $FF$  of 83.01%. However, the champion PCE of the GBAC-treated device  
28 can be further improved to 24.8% ( $V_{OC}$  of 1.19 V,  $J_{SC}$  of 24.55 mA/cm<sup>2</sup>,  $FF$  of 84.78%),  
29 which is among the highest efficiencies reported so far for inverted PVSCs. The

1 stabilized power output of the target champion device is 24.4%, matching well with the  
2 PCEs from the  $J$ - $V$  measurement (Fig. 4c). The device performance was also validated  
3 at an independent laboratory (JET, Japan) to show a certified PCE of 24.5% ( $V_{OC}$ =1.19  
4 V,  $J_{SC}$ =24.45 mA/cm<sup>2</sup>,  $FF$ =84.20%) (Supplementary Fig. 28). The integrated  
5 photocurrent (24.38 mA/cm<sup>2</sup>) from the external quantum efficiency (EQE) spectrum  
6 also matches well with the values obtained from  $J$ - $V$  measurement (Fig. 4d). The  
7 bandgap of the perovskite is 1.55 eV as obtained by calculating the EQE derivative  
8 (Supplementary Fig. 29). Benefiting from the enhanced film quality and defect  
9 passivation aided by GBAC, the average  $V_{OC}$  was boosted from 1.12 V to 1.18 V (Fig.  
10 4e). The overall energy loss of the champion target device is reduced to 0.36 eV, which  
11 is very close to that of GaAs photovoltaics and represents one of the lowest energy  
12 losses in high PCE cases (Fig. 4f).<sup>38,39</sup> DFT calculations investigated the typical  $I_{Pb}$   
13 antisite defect on a  $PbI_2$ -terminated surface, revealing that the GBAC passivation can  
14 help reduce these deep-level charge carrier traps (Supplementary Fig. 30). The trap  
15 density was reduced from  $2.58 \times 10^{16}$  cm<sup>-3</sup> to  $1.53 \times 10^{16}$  cm<sup>-3</sup> after adding GBAC,  
16 further demonstrating the effectiveness of this strategy (Supplementary Fig. 31).

17 Since adding GBAC can modulate crystallization to improve film quality, this  
18 strategy can also be explored for fabricating large-area PVSCs (Supplementary Fig. 32).  
19 As shown in Fig. 4g, a large-area device (1.008 cm<sup>2</sup>) delivered a PCE of 22.7% ( $V_{OC}$  =  
20 1.18 V,  $J_{SC}$  = 24.83 mA cm<sup>-2</sup>,  $FF$  = 77.43%), which is also one of the highest efficiencies  
21 reported for similar size PVSCs (Supplementary Table 4). Besides, the  $V_{OC}$  and  $J_{SC}$   
22 values of this device are comparable with those obtained in small-area devices, showing  
23 great promise for device upscaling (Supplementary Fig. 33 and Supplementary Table  
24 5). To demonstrate the general applicability of this approach to different perovskite  
25 compositions, we also fabricated devices based on a larger bandgap perovskite (1.78  
26 eV). The average PCE showed increase from 15.70% to 16.61%, with averaged  $V_{OC}$   
27 improved from 1.19 V to 1.25 V, which is highly favorable for fabricating tandem  
28 photovoltaics (Supplementary Fig. 34).

29 Finally, we investigated the stability of devices under an accelerated aging condition

1 based on recognized protocols.<sup>40</sup> The unencapsulated devices were aged under  
2 continuous heating at  $65 \pm 5$  °C (under N<sub>2</sub>). The target device showed a very small PCE  
3 decay (< 3%) after 1200 h, while that of the control device decreased nearly 30% during  
4 the same period (Fig. 4h). This shows that the interaction between GBAC and organic  
5 components (MA/FA) helps strengthen the film to avoid severe decomposition and  
6 sublimation under heating (Supplementary Fig. 35). The long-term operational stability  
7 of unencapsulated devices was also measured by tracking the true MPP under  
8 continuous 1-sun illumination (Supplementary Fig. 36) in an N<sub>2</sub>-filled glovebox. The  
9 target device maintained ~90% of its initial PCE after 500 h, while the control device  
10 decreased to ~30% of its original value (Supplementary Fig. 37). We also performed  
11 time-of-flight secondary ion mass spectrometry (ToF-SIMS) measurements to probe  
12 the compositional changes and ion migration related to the device degradation. The  
13 control devices show dramatic changes with ions migrated to the perovskite/ETL  
14 interface after aging (Supplementary Fig. 38). However, only negligible changes  
15 observed in the target sample aged under the same condition. Such improved device  
16 stability can be attributed to the enhanced film morphology and inhibited ion migration  
17 by adding GBAC. If GBAC can be used in conjunction with more efficient  
18 encapsulation techniques and optimal perovskite compositions, further improved PVSC  
19 efficiency and stability can be expected to meet the requirements for practical  
20 applications.<sup>41-43</sup>

## 21 **Conclusion**

22 In summary, we report an innovative strategy for achieving high-quality and stable  
23 perovskite films by employing a multifunctional, non-volatile additive, GBAC, which  
24 forms unique hydrogen bond-bridged intermediate phase to modulate the perovskite  
25 crystallization process and functions as efficient passivation linker simultaneously. We  
26 experimentally and theoretically unveil the mechanism of GBAC in assisting perovskite  
27 film formation, providing a design guideline for selecting suitable non-volatile  
28 additives to enhance the film quality. The greatly ameliorated optoelectronic properties  
29 are attributed to improved film morphology and crystallinity, effective defect

1 passivation, and more efficient charge transfer at the more n-characteristic film surface.  
2 Consequently, an impressive PCE of 24.8% (24.5% certified), low energy loss (0.36  
3 eV), and remarkable device stability were achieved in inverted PVSCs. Our approach  
4 can also be extended to fabricate wide-bandgap perovskite devices and upscale devices,  
5 providing a simple and effective way towards scalable and highly efficient PVSCs.

6

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14 by A. K.-Y. J. F. L. and X. D. conducted the film characterization, device fabrication, and device  
15 characterization. F. L. synthesized the single crystal and analyzed the results with S.-H. J. Z. S.  
16 performed the DFT calculations and was supervised by X. C. S. W. contributed to fabricating  
17 the large-bandgap device. Z. Z. helped collect the *in-situ* PL and was supervised by S. W. T. D.  
18 W. performed the PL and TRPL characterization. Y. L. conducted the UPS measurement. F. Q.  
19 helped conducted the <sup>1</sup>H NMR measurement. Z. Z. performed the AFM and KPFM  
20 characterization and was supervised by Z. Y. F. R. L., X. C. and A. K.-Y. J. revised the  
21 manuscript.

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23 **Additional information:** Supplementary information is available in the online version of the  
24 paper. Correspondence and requests for materials should be addressed to A. K.-Y. Jen.

25

26 **Figure 1. Chemical interaction and morphology characterization of the perovskite films.**

27 **a**, FTIR spectra of the control and target films. **b**, The Pb4f XPS spectra of control and target  
28 films. **c**, **d**, Surface (up) and cross-section (down) SEM images of the control (**c**) and target (**d**)  
29 perovskite films. The scale bars are 1  $\mu\text{m}$ . **e**, XRD patterns of the control and target films. \*

1 Denotes the diffraction peak of  $\text{PbI}_2$ , # denotes the diffraction peak of ITO. **f**, The statistical  
2 distribution of surface potential extracted from the KPFM images.

3

4 **Figure 2. Comparison of the film growth kinetics by *in-situ* PL.** **a, b**, Normalized *in-situ* PL  
5 peak position evolution of the control (**a**) and target (**b**) perovskite films. **c, d**, Normalized *in-*  
6 *situ* PL intensity evolution of the control (**c**) and target (**d**) perovskite films. **e, f**, Detailed  
7 analysis of PL intensity evolution of the control (**e**) and target (**f**) perovskite films. **e, f**, are  
8 enlarged from **c** and **d**, respectively. The titles of the x-axis and y-axis are “Wavelength (nm)”  
9 and “Time (ms)”, respectively, which are hidden to better display the evolution. All the figures  
10 use the same scale bar as shown at the left of **a**.

11

12 **Figure 3. Structure analysis and DFT calculations of the intermediate phase induced**  
13 **crystallization.** **a**, The Crystal structure of the GBAC- $\text{PbI}_2$ -DMF intermediate, the hydrogen  
14 bonds are marked in cyan-blue. **b**, The simulated XRD patterns of GBAC- $\text{PbI}_2$ -DMF and  
15 GBAC- $\text{PbI}_2$ . **c**, Formation energies of GBAC- $\text{PbI}_2$ -DMF, GBAC- $\text{PbI}_2$ , and  $\delta$ -FAPbI<sub>3</sub>  
16 compounds. **d**, The binding energies between  $\text{PbI}_2$  and DMF,  $\text{FA}^+$ , and  $\text{GBAC}^+$ , respectively. **e**,  
17 Schematic illustration of GBAC-assisted film growth. The brown arrows represent the breakage  
18 of hydrogen bonds, and the green arrows represent the cation exchange.

19

20 **Figure 4. Characterization of photovoltaic performance and stability of PVSCs.** **a**, Device  
21 architecture of the inverted PVSC. **b**,  $J$ - $V$  curves of the champion devices. **c, d**, Stable output  
22 (**c**) and EQE curve (**d**) of the target champion device. **e**, Box plot of the  $V_{\text{OC}}$  distribution for  
23 control and target PVSCs. The data from 20 cells were statistically analyzed. The box  
24 represents the median and the quartiles, and the whisker covers the minima up to  
25 maxima of the data points. The individual value of each data point is plotted as a point  
26 superimposed on the graph. **f**, The comparison of PCE and  $V_{\text{OC}}$  loss of inverted PVSCs  
27 reported in the literature (listed in Table S1). **g**,  $J$ - $V$  curve of the champion device with an active  
28 area of 1.008  $\text{cm}^2$ , the inset shows the photograph of the device. **h**, Intrinsic stability of

1 unencapsulated devices aged under  $65 \pm 5$  °C in N<sub>2</sub>-filled glove box. The data from 8 cells are  
2 collected and presented as mean values  $\pm$  SEM.  
3



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31

## 1 **Methods**

2 **Materials.** All the materials are used as received without further purification, including N,N-  
3 dimethylformamide (DMF, 99.99%, J&K), dimethyl sulfoxide (DMSO, 99.7%, J&K),  
4 isopropanol (IPA, 99.5%, J&K), chlorobenzene (CB, 99.9%, J&K). Cesium iodide (CsI),  
5 Cesium bromide (CsBr), methylammonium iodide (MAI), formamidinium iodide (FAI) and  
6 formamidinium bromide (FABr) were bought from Dysol (Australia). Lead iodide (PbI<sub>2</sub>,  
7 99.9985%) and Lead bromide (PbBr<sub>2</sub>, >98.0%) were bought from TCI (Japan).  
8 Methylammonium chloride, BCP (99.9%), and C60 were bought from Xi'an Polymer Light  
9 Technology Corp. (China). 4-Guanidinobenzoic acid hydrochloride (GBAC, 99%) was bought  
10 from Sigma Aldrich. Piperazinium iodide (PI)<sup>8</sup> and (2,7-dimethoxy-9H-carbazol-9-yl) methyl)  
11 phosphonic acid (DC-PA)<sup>22</sup> were synthesized according to previous reports.

12 **Synthesis of GBAC-PbI<sub>2</sub>-DMF Single Crystals.** PbI<sub>2</sub> and GBAC (1/1 by molar, 1.0 M) were  
13 dissolved in DMF, and stirred overnight at 50 °C. The turbid liquid was filtered and transferred  
14 into a 4 mL vial. The vial was then placed into a sealed bottle filled with 2 mL CB. The GBAC-  
15 PbI<sub>2</sub>-DMF single crystals were grown along with the slow diffusion of the vapor of the anti-  
16 solvent CB into the solution.

17 **Device Fabrication.** ITO glass (15 Ω/sq, 1.5 × 1.5 cm for regular device, 2.5 × 2.5 cm for  
18 large-area device) was progressively washed by sonication with detergent (Decon 90),  
19 deionized water, acetone, and isopropyl alcohol for 15 min, respectively. Washed ITO glass was  
20 dried in a 75 °C oven for over 12 hours. Then, the cleaned ITO substrates were dealt with UV  
21 ozone for 25 min and transformed into an N<sub>2</sub>-filled glovebox for film fabrication. DC-PA (2  
22 mg/mL in IPA) was dynamically spin-coated onto the cleaned ITO at 3000 r.p.m. for 30 s,  
23 followed by annealing at 100 °C for 15 min. The substrates were cool down to room temperature  
24 and washed with pure IPA. Then annealed at 100 °C for 5 min. 1.7 M perovskite precursor  
25 solutions were constructed by mixing FAI, PbI<sub>2</sub>, MAI, and CsI in DMF:DMSO mixed solvent  
26 (4:1/v:v) with a chemical formula of Cs<sub>0.06</sub>MA<sub>0.14</sub>FA<sub>0.80</sub>PbI<sub>3</sub>. 10 mol% MACl was added into  
27 the precursor solution. For target perovskite, 0.8 mol% of GBAC was added to the precursor  
28 solution and make sure it is well mixed with the precursor. 50 μL of the prepared precursor

1 solution was spin-coated at 1000 rpm for 10 s and 5000 r.p.m. for 30 s onto the DC-PA based  
2 ITO substrate, 170  $\mu\text{L}$  CB as anti-solvent was dripped on the film at 10 s before the end of the  
3 last procedure and then annealed at 100  $^{\circ}\text{C}$  for 30 min. After deposition of the perovskite active  
4 layer, 50  $\mu\text{L}$  of PI<sup>8</sup> (0.4 mg/mL, IPA) solution was spin-coated onto the film at 5000 rpm for 30  
5 s and annealed at 100  $^{\circ}\text{C}$  for 5 min. For wide-bandgap perovskite, 1.2 M precursor solution  
6 with a chemical formulation of  $\text{Cs}_{0.2}\text{FA}_{0.8}\text{Pb}(\text{I}_{0.6}\text{Br}_{0.4})_3$  was prepared from FAI, CsI, FABr, CsBr,  
7  $\text{PbI}_2$ , and  $\text{PbBr}_2$ , and dissolved in DMF:DMSO mixed solvents (4:1/v:v). 5 mol% excess of  $\text{PbI}_2$   
8 and 5 mol% MACl were added into the precursor solution. The target perovskite with 0.5 mol%  
9 GBAC was spin-coated onto the DC-PA/ITO substrates at 5000 r.p.m. with an accelerating  
10 speed of 1500 for 30 s. 150  $\mu\text{L}$  CB as anti-solvent was dripped on the film at 15 s before the  
11 ending and then annealed at 100  $^{\circ}\text{C}$  for 10 min. The films were then cooled down to room  
12 temperature and ready for thermal evaporation. 25 nm C60, 8 nm BCP and 100 nm silver  
13 electrode were evaporated under high vacuum ( $< 4 \times 10^{-6}$  Torr) sequentially.

14 **Characterizations.** The  $^1\text{H}$  NMR spectra were collected on a Bruker AVANCE III HD 300 MHz  
15 spectrometer in  $d_6$ -DMSO solution with TMS as a reference. The morphology of the samples  
16 was recorded by scanning electron microscopy (SEM, Philips XL30 FEG). Steady-state  
17 photoluminescence (PL) and time-resolved photoluminescence spectrum (TRPL) spectrum  
18 were conducted with an FLS980 spectrofluorometer (Edinburgh) with a pulsed excitation laser  
19 of 485 nm. XPS and UPS characterization were conducted in a VG ESCALAB 220i-XL surface  
20 analysis system equipped with a Hedischarge lamp ( $h\nu = 21.22$  eV) and a monochromatic Al-  
21  $\text{K}\alpha$  X-ray gun ( $h\nu = 1486.6$  eV), respectively. ToF-SIMS (ION TOF-SIMS5) was analyzed with  
22 positive mode (Bi) under 30 keV (1.00 pA) with an area of  $100 \times 100 \mu\text{m}^2$ . The sputter  
23 parameters for the device are  $\text{O}_2$  under 1 keV (100 nA) with an area of  $300 \times 300 \mu\text{m}^2$ , and the  
24 sputter parameter for the film sample is GCIB ion gun under 10 keV (10 nA) with an area of  
25  $800 \times 800 \mu\text{m}^2$ . X-ray diffraction (XRD) characterization was conducted on the D2 Phaser  
26 instrument with a Cu  $\text{K}\alpha$  (a wavelength of 1.5418  $\text{\AA}$ ) radiation. GIWAXS measurements were  
27 conducted using a Xeuss 2.0 SAXS/WAXS laboratory beamline with a Cu X-ray source (8.05  
28 keV, 1.54  $\text{\AA}$ ) and a Pilatus 3R 300K detector. The incidence angle is 1.0 $^{\circ}$ . *In-situ* PL spectra  
29 were characterized with home-built equipment. An excitation laser (315 nm) was introduced to

1 the sample through a fiber, and the PL spectra were detected by using a detector connected to  
2 an Ocean Optics USB2000. PL mapping was collected using WITec alpha300 M+ confocal  
3 microscopy (WITec GmbH). The excitation laser was a diode-pumped solid-state laser (532  
4 nm, cobalt Laser).  $J$ - $V$  characteristics were measured in an  $N_2$ -filled glove box by Keithley 2400  
5 source meter under AM 1.5G ( $100 \text{ mW cm}^{-2}$ ) irradiation using an EnliTech SS-F5 solar  
6 simulator (Enlitech, SS-F5, Taiwan). The light intensity was calibrated using a silicon solar cell  
7 (with a KG-2 filter) from the National Renewable Energy Laboratory. The device areas are  $0.04$   
8  $\text{cm}^2$  for regular devices and  $1.008 \text{ cm}^2$  for the large-size device, both are determined by metal  
9 aperture masks. A 150-nm thick magnesium fluoride layer was deposited on the back of the  
10 glass before measurements. EQEs were collected by an EnLi Technology (Taiwan) EQE  
11 measurement system. A National Renewable Energy Laboratory calibrated silicon solar cell  
12 was used to obtain the AM 1.5G solar simulator's light intensity. The devices used for the  
13 stability test were the same structure as that for the  $J$ - $V$  test. For thermal stability  
14 characterization, the devices were aged on the hotplate at  $65 \pm 5^\circ\text{C}$  in an  $N_2$ -filled glovebox and  
15 cooled down to room temperature before the  $J$ - $V$  test. For MPP tracking, the devices were  
16 tracked through the high throughput solar cell lifetime test system from CRYSCO cooperation  
17 with maximum power point tracking under LED simulated AM 1.5 spectrum. The light source  
18 is a SLED with a range from 400 nm to 1000 nm. The SLED source is equipped with a silicon  
19 photoelectric probe to monitor the change of the light intensity and adjust the intensity  
20 automatically with the control of the host. The intensity of the SLED source can be adjusted  
21 from  $0.1$  to  $1.2 \text{ kW/m}^2$ . The duration between the two tests is 300 s.

22 **Single Crystal Analysis.** The single crystal structure of GBAC-PbI<sub>2</sub>-DMF was solved and  
23 refined using the Bruker SHELXTL Software Package. All non-hydrogen atoms were refined  
24 anisotropically, and all hydrogen atoms were refined as riding atoms. The crystal data and data  
25 collection and refinement parameters are listed in Table S1. CCDC 2141303 contains the  
26 supplementary crystallographic data of GBAC-PbI<sub>2</sub>-DMF, which can be obtained free of charge  
27 from the Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

28 **DFT calculations.** First-principles calculations based on DFT were performed with the Vienna  
29 Ab initio Simulation Package (VASP),<sup>44</sup> using the generalized gradient approximation of the

1 Perdew-Burke-Ernzerhof (PBE) functional<sup>45</sup> for the exchange-correlation functional. Valence-  
 2 core electron interactions were treated with the projector-augmented wave (PAW) method.<sup>46</sup>  
 3 We employed Grimme's DFT-D<sub>3</sub> scheme to include the van der Waals interactions,<sup>46</sup> and dipole  
 4 correction for slab calculations.<sup>47</sup> The cutoff energy of plane-wave expansions was set at 500  
 5 eV and the Hellmann-Feynman forces acting on atoms were converged below 0.01 eV Å<sup>-1</sup> for  
 6 all calculations. For the calculation of binding energies which is defined as  $E_{\text{PbI}_2\text{-molecule}} -$   
 7  $E_{\text{PbI}_2} - E_{\text{molecule}}$ ,  $1 \times 1 \times 1$   $\Gamma$ -centered k-point grid was adopted, and the convergence criteria for  
 8 the electronic wave function was  $1.0 \times 10^{-6}$  eV energy difference. For geometry optimizations  
 9 and energy calculations,  $4 \times 4 \times 4$   $\Gamma$ -centered k-point mesh for  $\delta$ -FAPbI<sub>3</sub>,  $2 \times 4 \times 2$   $\Gamma$ -centered k-  
 10 point mesh for GBAC-PbI<sub>2</sub>-DMF,  $3 \times 4 \times 2$   $\delta$ -centered k-point mesh for GBAC-PbI<sub>2</sub>, and  $5 \times 5 \times 5$   
 11  $\Gamma$ -centered k-point mesh for  $\alpha$ -FAPbI<sub>3</sub> were used respectively. The convergence criteria of the  
 12 energy difference was set to  $1.0 \times 10^{-5}$  eV. Note that the formation energy ( $\Delta E_{\delta\text{-FAPbI}_3}$ ) was  
 13 calculated using the equation,  $\Delta E_{\delta\text{-FAPbI}_3} = 2E_{\delta\text{-FAPbI}_3} - 2E_{\text{PbI}_2} - 4E_{\text{FAI}}$  for  $\text{PbI}_2 + \text{FAI} \rightarrow$   
 14  $\delta\text{-FAPbI}_3$ , where  $E_{\delta\text{-FAPbI}_3}$  is the energy of  $\delta$ -FAPbI<sub>3</sub>,  $E_{\text{PbI}_2}$  is the energy of PbI<sub>2</sub> calculated from  
 15 bulk PbI<sub>2</sub>,  $E_{\text{FAI}}$  is the energy calculated from gas phase FAI. The formation energy of bulk  
 16 GBAC-PbI<sub>2</sub> was calculated by the equation,  $\Delta E_{\text{GBAC-PbI}_2} = E_{\text{GBAC-PbI}_2} - 2E_{\text{PbI}_2} - 4E_{\text{GBAC}}$  for  
 17  $\text{PbI}_2 + \text{GBAC} \rightarrow \text{GBAC-PbI}_2$ , where  $E_{\text{GBAC}}$  is the energy calculated from gas phase GBAC. The  
 18 formation energy of intermediate phase GBAC-PbI<sub>2</sub>-DMF was calculated with the equation,  
 19  $\Delta E_{\text{GBAC-PbI}_2\text{-DMF}} = E_{\text{GBAC-PbI}_2\text{-DMF}} - 2E_{\text{PbI}_2} - 4E_{\text{GBAC}} - 8E_{\text{DMF}}$  for  $\text{PbI}_2 + \text{GBAC} +$   
 20  $\text{DMF} \rightarrow \text{GBAC-PbI}_2\text{-DMF}$ , where  $E_{\text{DMF}}$  is the energy of DMF molecules. For slab calculations,  
 21 the Brillouin zone was sampled with  $2 \times 2 \times 1$   $\Gamma$ -centered k-point mesh, and a vacuum of at least  
 22 30 Å was used to avoid the interaction of neighboring interfaces along the z-direction. The  
 23 electrostatic potentials ( $\phi$ ) of the interacting pairs were calculated using the Gaussian 09  
 24 package at the B3LYP/def2TZVP level with DFT-D3. The maximum  $\phi$  ( $\phi_{\text{max}}$ ) and minimum  $\phi$   
 25 ( $\phi_{\text{min}}$ ) of the interacting pairs were obtained with the help of Multiwfn code.<sup>48</sup> The structure  
 26 models were drawn with the VESTA software.<sup>49</sup> Some data processing was done by  
 27 VASPKIT.<sup>50</sup>

## 28 Data Availability

29 The authors declare all data supporting the findings of this study are available within the

1 manuscript and the Supplementary Information. The .cif files corresponding to single-crystal  
2 structures reported in this work are available from CCDC (2141303).

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