



High Phase Stability in CsPbI₃ Enabled by Pb–I Octahedra Anchors for Efficient Inorganic Perovskite Photovoltaics

Yong Wang, Gaoyuan Chen, Dan Ouyang, Xinjun He, Can Li, Ruiman Ma, Wan-Jian Yin,* and Wallace C. H. Choy*

CsPbI₃ inorganic perovskite has exhibited some special properties particularly crystal structure distortion and quantum confinement effect, yet the poor phase stability of CsPbI₃ severely hinders its applications. Herein, the nature of the photoactive CsPbI₃ phase transition from the perspective of PbI₆ octahedra is revealed. A facile method is also developed to stabilize the photoactive phase and to reduce the defect density of CsPbI₃. CsPbI₃ is decorated with multifunctional 4-aminobenzoic acid (ABA), and steric neostigmine bromide (NGBr) is subsequently used to further mediate the thin films' surface (NGBr-CsPbI₃(ABA)). The ABA or NG cation adsorbed onto the grain boundaries/surface of CsPbI₃ anchors the PbI₆ octahedra via increasing the energy barriers of octahedral rotation, which maintains the continuous array of corner-sharing PbI₆ octahedra and kinetically stabilizes the photoactive phase CsPbI₃. Moreover, the added ABA and NGBr not only interact with shallow- or deep-level defects in CsPbI₃ to significantly reduce defect density, but also lead to improved energy-level alignment at the interfaces between the CsPbI₃ and the charge transport layers. Finally, the champion NGBr-CsPbI₃(ABA)-based inorganic perovskite solar cell delivers 18.27% efficiency with excellent stability. Overall, this work demonstrates a promising concept to achieve highly phase-stabilized inorganic perovskite with suppressed defect density for promoting its optoelectronic applications.

comparable to the silicon solar cells. However, the volatile organic compositions in OIHPs are always a potential threat to the long-term stability of the PSCs' devices. Recently, all-inorganic perovskites have attracted considerable attention because of their excellent chemical components stability.^[5–8] In particular, the CsPbI₃ inorganic perovskite with desirable bandgap (≈ 1.7 eV) and excellent light absorption properties exhibits great potential for tandem solar cell integration with other sub-cells, such as silicon and low-bandgap perovskite.^[9–13] Moreover, compared to the orientated and rotating organic cation (MA⁺) (MA: methylammonium) in OIHPs, the isotropic Cs cation has no hydrogen bond and orientation, and they cannot rotate like organic cations, which offer CsPbI₃ inorganic perovskite some unique properties including crystal structure distortion and quantum confinement effect and so on.^[14–18] Because of quantum confinement effect, previously reported polycrystal CsPbI₃ thin films exhibit a blueshift in comparison with the single crystal CsPbI₃ (≈ 1.63 eV);^[17] Jin

Organic–inorganic hybrid perovskites (OIHPs) with the chemical formula of ABX₃ have undergone an unprecedented development and emerged as a revolutionary class of light-absorbing semiconductors.^[1–4] Especially, the certified efficiency of perovskite solar cell (PSC) has approached 25.2%, which is

and co-workers have also achieved pure-blue-color perovskite light-emitting diode with exceptionally high external quantum efficiency (EQE) of 9.5%.^[19]

However, CsPbI₃ is still facing serious phase stability issues, in which the black-phase CsPbI₃ tends to transform into the non-photoactive δ phase under humid or thermal stress conditions.^[20–21] There are some strategies including quantum dots, dimension engineering, B- or X-site doping/alloying and organic cation surface termination that have been developed to stabilize the black-phase CsPbI₃.^[22–28] Recently, Zhao and co-workers successfully fabricated highly thermodynamically stable β -CsPbI₃ perovskite with a slight distort of PbI₆ octahedra in comparison with cubic phase CsPbI₃.^[13] Steele et al. used substrate clamping and biaxial strain to prepare γ -CsPbI₃ with a larger distort of PbI₆ octahedra and render the black-phase CsPbI₃ stability at room temperature.^[29] Both of these two works imply that the stability of black-phase CsPbI₃ may be related to the distortion level of PbI₆ octahedra. Nevertheless, the underlying mechanism to further stabilize photoactive CsPbI₃ is still unclear.

In this work, a facile method was first developed to anchor PbI₆ octahedra and stabilize photo-active phase as well as to

Dr. Y. Wang, Dr. D. Ouyang, X. He, Dr. C. Li, R. Ma, Prof. W. C. H. Choy
Department of Electrical and Electronic Engineering
The University of Hong Kong
Pokfulam Road, Hong Kong 999077, China
E-mail: chchoy@eee.hku.hk

G. Chen, Prof. W.-J. Yin
College of Energy
Soochow Institute for Energy and Materials Innovations (SIEMIS)
and Jiangsu Provincial Key Laboratory for Advanced Carbon Materials
and Wearable Energy Technologies
Soochow University
Suzhou 215006, China
E-mail: wjiyin@suda.edu.cn

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reduce the defect density of CsPbI_3 . Meanwhile, we systematically demonstrated the relationship between the distortion level of PbI_6 octahedra and phase transition of CsPbI_3 inorganic perovskite, and revealed the nature of this photoactive CsPbI_3 phase transition from the perspective of PbI_6 octahedra. We proposed to incorporate 4-aminobenzoic acid (ABA) into CsPbI_3 perovskite ($\text{CsPbI}_3(\text{ABA})$). The as-fabricated thin films were further surface mediated by the steric neostigmine bromide (NGBr) (NGBr- $\text{CsPbI}_3(\text{ABA})$). The ABA/NG cation would adsorb onto the grain boundaries/surface of CsPbI_3 and anchor PbI_6 octahedra, which suppressed PbI_6 octahedra rotation via enhancing the energy barrier. Furthermore, the carboxyl and amine groups in ABA associating with surface steric organic cation NG^+ could passivate shallow- or deep-level defects, i.e., the undercoordinated Pb_2^+ and Cs^+ vacancy. By the co-cation of ABA incorporation and steric NG cation surface termination, the CsPbI_3 exhibited both enhanced phase stability and suppressed defects density (reducing from $8.63 \times 10^{15} \text{ cm}^{-3}$ to $3.72 \times 10^{15} \text{ cm}^{-3}$). Moreover, the addition of ABA and NGBr led to better matching of energy levels at the interfaces between CsPbI_3 and charge transport layers. With the interesting properties, the NGBr- $\text{CsPbI}_3(\text{ABA})$ -based inorganic PSCs devices exhibited an efficiency of 18.27% with excellent stability.

Figure 1a shows the typical crystal structure of CsPbI_3 inorganic perovskite and chemical structure of ABA and NGBr multifunctional molecules. The ABA incorporation or NGBr surface mediation will not affect on the absorption, as shown in Figure 1b. The absorption edges of these thin films are located at $\approx 736 \text{ nm}$, which is the tetragonal phase CsPbI_3 .^[13,30] The bromine salt treatment usually blueshifts the absorption edge dependent on the diffusion length of Br ion and degree of ion exchange with iodine ion.^[25,31] However, in present work, the steric NG cation with a large topological polar surface area confines bromine (Br) anion diffusion during the post-treatment process. The Br is only concentrated on the surface of CsPbI_3 as confirmed by the time-of-flight secondary-ion mass spectrometry (TOF-SIMS) in Figure S1, Supporting Information, leading to ignorable effect on the absorption. The X-ray diffraction (XRD) patterns of CsPbI_3 , $\text{CsPbI}_3(\text{ABA})$, NGBr- CsPbI_3 , and NGBr- $\text{CsPbI}_3(\text{ABA})$ samples exhibit diffraction peaks at 14.19° and 28.64° (Figure 1c), which are the characteristic (110), (220) crystal planes diffraction of tetragonal phase CsPbI_3 .^[13,32] The intensity of XRD peaks for the $\text{CsPbI}_3(\text{ABA})$ thin film is stronger than that for the pristine CsPbI_3 sample, suggesting that ABA incorporation enhances the CsPbI_3 perovskite thin films overall crystallinity. The further NGBr surface mediation has neglectable effect on the crystallinity.

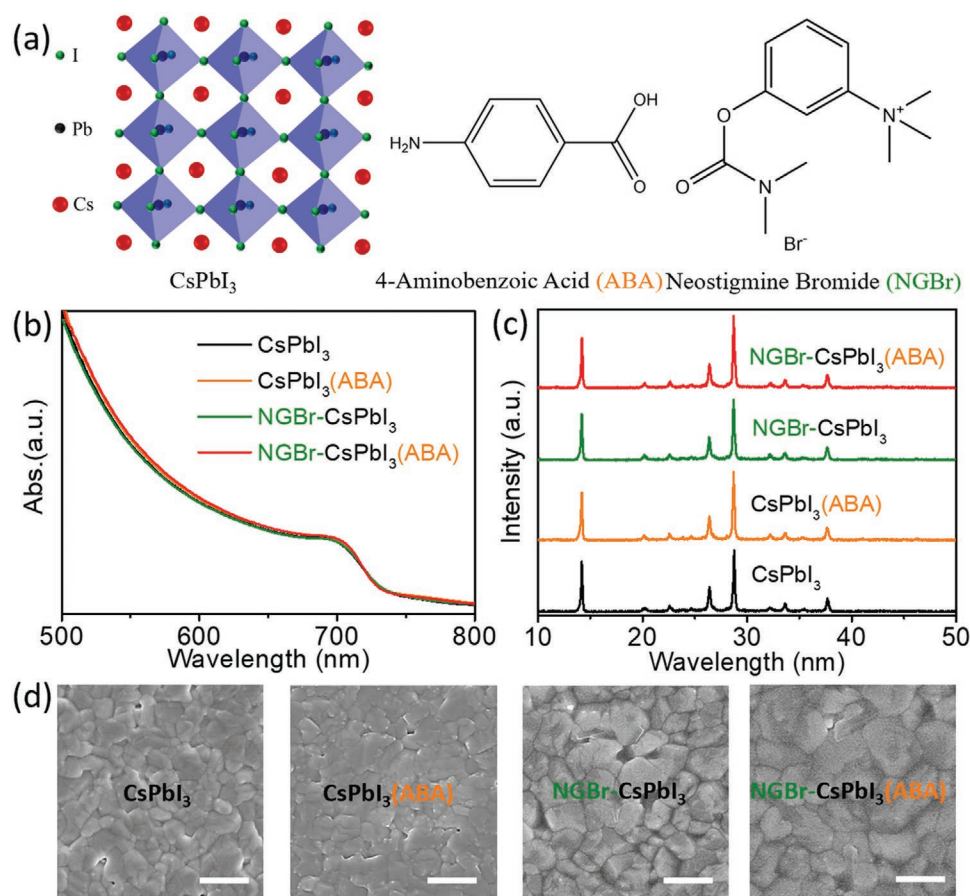


Figure 1. a) Crystal structure of typical CsPbI_3 inorganic perovskite and chemical structure of organic molecules ABA and NGBr. b) UV-vis spectra and c) XRD patterns for the CsPbI_3 , $\text{CsPbI}_3(\text{ABA})$, NGBr- CsPbI_3 , and NGBr- $\text{CsPbI}_3(\text{ABA})$ thin films. d) Corresponding top-view SEM images, scale bars represent 1 μm .

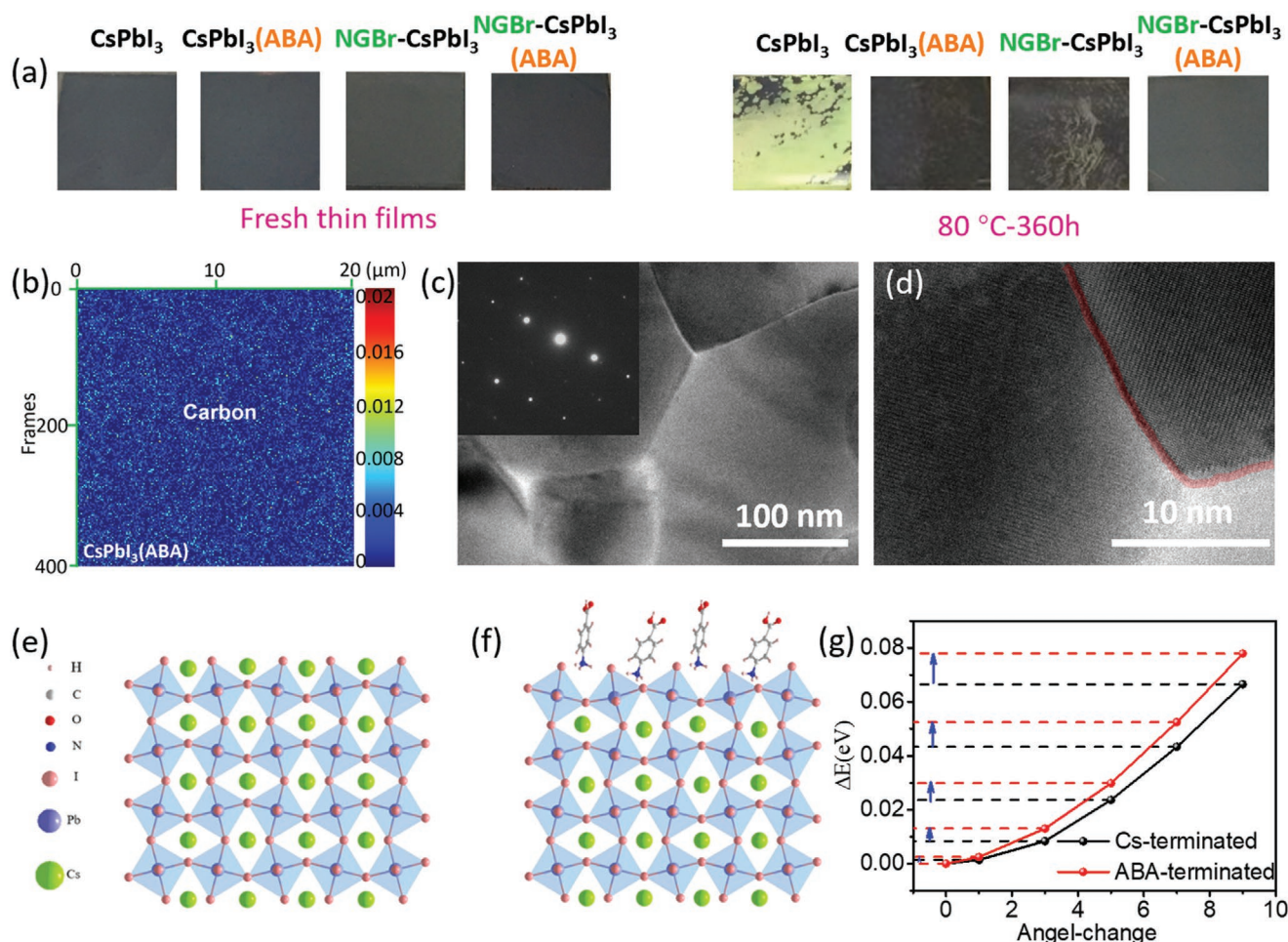


Figure 2. a) Phase stability of CsPbI₃, CsPbI₃(ABA), NGBr-CsPbI₃, and NGBr-CsPbI₃(ABA) thin film heated on a hotplate at 80 °C in a N₂ glovebox. b) Cross-section of carbon elemental profile of CsPbI₃(ABA) measured by TOF-SIMS. c) Bright-field TEM image of CsPbI₃(ABA) thin film. d) HRTEM image of the grain boundaries. e, f) Surface models of CsPbI₃ without (e) and with (f) ABA. g) The total energies of Cs-terminated and ABA-terminated slabs as a function of angle-change. Taking the energy of angle-change = 0 as zero.

Scanning electron microscopy (SEM) was used to investigate the morphologies of these CsPbI₃ thin films, as shown in Figure 1d. The ABA incorporation and NGBr mediation have a slight effect on the grain sizes and morphologies of CsPbI₃ thin films. The pristine CsPbI₃ thin film exhibits inhomogeneous crystal grains ranging from 300 to 600 nm with some pinholes. The CsPbI₃(ABA) thin film has fewer pinhole, larger and more uniform grains (600–800 nm). Both the NGBr-CsPbI₃ and NGBr-CsPbI₃(ABA) thin films show larger and denser grains, which is possibly attributed to the surface grain re-growth because of the bromine enriched on the surface of CsPbI₃ perovskite.^[31]

We further studied the phase stability of these CsPbI₃ thin films, as shown in Figure 2a and Figures S2 and S3, Supporting Information. The NGBr-CsPbI₃(ABA) thin films show very good humidity resistance contributed by the hydrophobic benzene (Figure S2, Supporting Information). In the fields of PSCs, the moisture effect can be well addressed by the encapsulation methods.^[33–34] We then investigated the phase stability of these samples under thermal stress condition. The CsPbI₃ thin films show the signals of yellow phase (δ -CsPbI₃)

after annealing at 80 °C for $\approx$ 144 h, as shown in Figure 2a and Figure S3, Supporting Information. However, both the CsPbI₃(ABA) and NGBr-CsPbI₃ thin films exhibit improved phase stability, which keep unchanged at 80 °C for $\approx$ 288 h. Especially, the simultaneous ABA incorporation and NGBr mediation offer excellent CsPbI₃ phase stability (Figure 2a).

We then investigated the phase stability mechanism of CsPbI₃ using the case of ABA incorporation. The TOF-SIMS results in Figure 2b and Figure S4, Supporting Information, suggest that the ABA homogeneously distributes in the CsPbI₃ perovskite layer. Transmission electron microscopy (TEM) was further used to characterize the detailed microstructure of CsPbI₃(ABA) thin films. Figure 2c shows the corresponding bright-field TEM image. The typical selected-area electron diffraction pattern (SAEDP) further confirms that the as-achieved CsPbI₃ perovskite is tetragonal phase (the inset image in Figure 2c), which agrees with the XRD and UV-vis results in Figure 1. Figure 2d presents the high-resolution TEM images of the typical grain boundary regions. There is $\approx$ 1 nm relatively amorphous region between grain boundaries, which is clearly distinct from the high-crystalline state of CsPbI₃ perovskite grain.

These results indicate that ABA molecule homogeneously distributes at the grain boundaries of CsPbI₃(ABA) thin films, which is in good agreement with the TOF-SIMS results.

The above analysis shows that the ABA molecules are located at the grain boundaries while absorbing on the CsPbI₃ crystal surface. In solution, amino or carboxyl groups in ABA can be easily ionized with positive and negative charges, respectively.^[35] The mechanism of ABA-stabilized CsPbI₃ can be understood from the energetic and kinetic points of view. Energetically, the adsorption of ABA on CsPbI₃ surfaces or grain boundaries would reduce surface energy and thus stabilize CsPbI₃ grains. To further understand the details, we theoretically study Cs-terminated and ABA-terminated CsPbI₃ (Figure 2e,f) through the first-principles density functional theory (DFT) calculations. The formation energies (ΔH_f) of Cs-terminated (ΔH_f -Cs) and ABA-terminated (ΔH_f -ABA) slabs are calculated as follow:^[36–37]

$$\Delta H_f = \frac{E_{\text{Cs/ABA-terminated}} - nE_{\text{PbI}_2} - (n-1)E_{\text{CsI}} - 2E_{\text{CsI/(ABA)I}}}{n} \quad (1)$$

DFT-calculated formation energies for ΔH_f -Cs and ΔH_f -ABA surfaces are 0.058 eV and −0.218 eV, respectively. The ABA-terminated surface is, therefore, more stable than that of Cs-terminated one, which is ascribed to stronger ionic interaction between ligand ABA and CsPbI₃ crystal surface.^[37]

The crystal structure of black-phase CsPbI₃ is featured as corner-sharing octahedra, while the yellow phase is an edge-sharing octahedral structure. Therefore, octahedral rotation would happen during the phase transition from black to yellow phase. One may expect that the large ABA molecule and its strong ionic bonding to surface are able to hinder the octahedral rotation of PbI₆ at the surface, and therefore, prevent the phase transition from black to yellow phase. Accordingly, we investigated the effects of surfactant Cs and ABA on the rotation of PbI₆ octahedral in black-phase CsPbI₃. Figure S5, Supporting Information, reveals that the designated angles between PbI₆ octahedra on Cs-terminated surface are 113.83° and 65.15°, respectively. However, the corresponding angles between PbI₆ octahedra of ABA-terminated surface are 111.20° and 73.93°, respectively, being closer to ideal 90° for cubic phase, indicating that ABA can restrain the rotation distortion of octahedron. Thus, the framework of corner-sharing PbI₆ octahedra can be maintained owing to the strain introduced into CsPbI₃ crystal processed with ABA.^[29] We further studied the ability of ABA to inhibit the PbI₆ octahedral rotation (Figure 2g) via calculating the total energies of Cs- and ABA-terminated slabs as a function of angle change of surface PbI₆ octahedron. The values of angle change ranging from 1° to 9° with an interval of 2°. Figure 2g reveals that ABA possesses a stronger inhibitory effect on octahedral rotation because of the strong interaction between large ABA molecule and CsPbI₃ surface. To confirm the stability enhancement under thermal stress conditions, molecular dynamics simulations have been performed for Cs-terminated and ABA-terminated surfaces. As shown in Figure S6, Supporting Information, the variations of surficial angles are reduced because of the incorporation of ABA. Overall, the large ionic size of ABA increases the rotation barriers of PbI₆ octahedral and kinetically stabilizes the black-phase CsPbI₃.

In addition to the phase stability, the high-quality CsPbI₃ with suppressed defects is very important for various CsPbI₃ inorganic optoelectronic applications. We further used the steady photoluminescence (PL) to check the effect of ABA and NGBr on the excitonic quality of perovskite thin films (Figure 3a and S7). The PL intensities of CsPbI₃(ABA), NGBr-CsPbI₃, and NGBr-CsPbI₃(ABA) thin films obviously increase in comparison with the pristine CsPbI₃ thin films. Especially, the NGBr-CsPbI₃(ABA) thin films exhibit the strongest PL intensity with a PL peak at ≈732 nm, whereas the PL emission of the pristine CsPbI₃ thin films red shifts to ≈735 nm with a much weaker signal (Figure S7, Supporting Information). Such a blueshift of the PL peak associating with enhanced PL intensity is indicative of defects passivation effect and a reduction in the spontaneous radiative recombination via defects/trap states. Because of the lower Goldschmidt tolerance factor ($t = 0.847$) and simple solution processing techniques, the shallow- or deep-level defects, such as Cs⁺ vacancy and undercoordinated Pb²⁺, form in the pristine CsPbI₃ thin films during crystallization.^[28,38–40] Previous results indicated that amines and carboxylic acids can be used as ligands to effectively passivate the surface defects of perovskite nanocrystals.^[32,41] Therefore, we speculate that the carboxyl, amine groups in ABA and steric NG cation can effectively passivate the defects in CsPbI₃. The time-resolved PL (TRPL) results in Figure 3b and Figure S8, Supporting Information, support the similar results as steady PL. The carrier lifetimes of the perovskite thin films increase from CsPbI₃, CsPbI₃(ABA), NGBr-CsPbI₃, to NGBr-CsPbI₃(ABA) as listed in Table S1, Supporting Information. In particular, a very long average carrier lifetime of 28.74 ns is observed for the NGBr-CsPbI₃(ABA) sample, indicating a significant passivation effect from ABA and NGBr.

We further conducted transient photovoltage (TPV) measurement to evaluate the effect of ABA together with steric NG cation on the charge recombination of the CsPbI₃- and NGBr-CsPbI₃(ABA)-based PSCs. Laser pulses (532 nm, 50 Hz) were applied to the PSCs, which are soaked under AM 1.5G illumination of 100 mW cm^{−2}, at open circuit condition to generate a transient photovoltaic signal. As seen in Figure 3c, the charge-recombination lifetime of the device with ABA incorporation and NGBr surface mediation increases to 0.91 μs in comparison with the 0.06 μs of the CsPbI₃ ones. The longer lifetime indicates a significant reduction in the undesired charge-carrier recombination for the NGBr-CsPbI₃(ABA)-based PSC, which is consistent with the PL and TRPL results.

The aforementioned results of PL, TRPL, and TPV show that the functional groups of ABA and surface terminated NG cation can effectively passivate the defects/traps in CsPbI₃ perovskite layer. We further accurately quantify the defect in perovskite layer through space charge limited current (SCLC) methods (Figure 3d; Figure S9, Supporting Information). The trap state density (N_t) can be calculated by the trap-filled limit voltage (V_{TFL}) using the equation: $V_{\text{TFL}} = (e \times n_t \times L^2)/(2 \times \epsilon \times \epsilon_0)$.^[42] The N_t is the trap-state density, e is the elementary charge of the electron, L is the thickness of perovskite film, ϵ is relative dielectric constant, and ϵ_0 is vacuum permittivity. Both the CsPbI₃(ABA) and NGBr-CsPbI₃ devices show low trap densities (5.75×10^{15} cm^{−3}, 5.05×10^{15} cm^{−3}), while it is highly 8.63×10^{15} cm^{−3} in the pristine CsPbI₃ device. These results

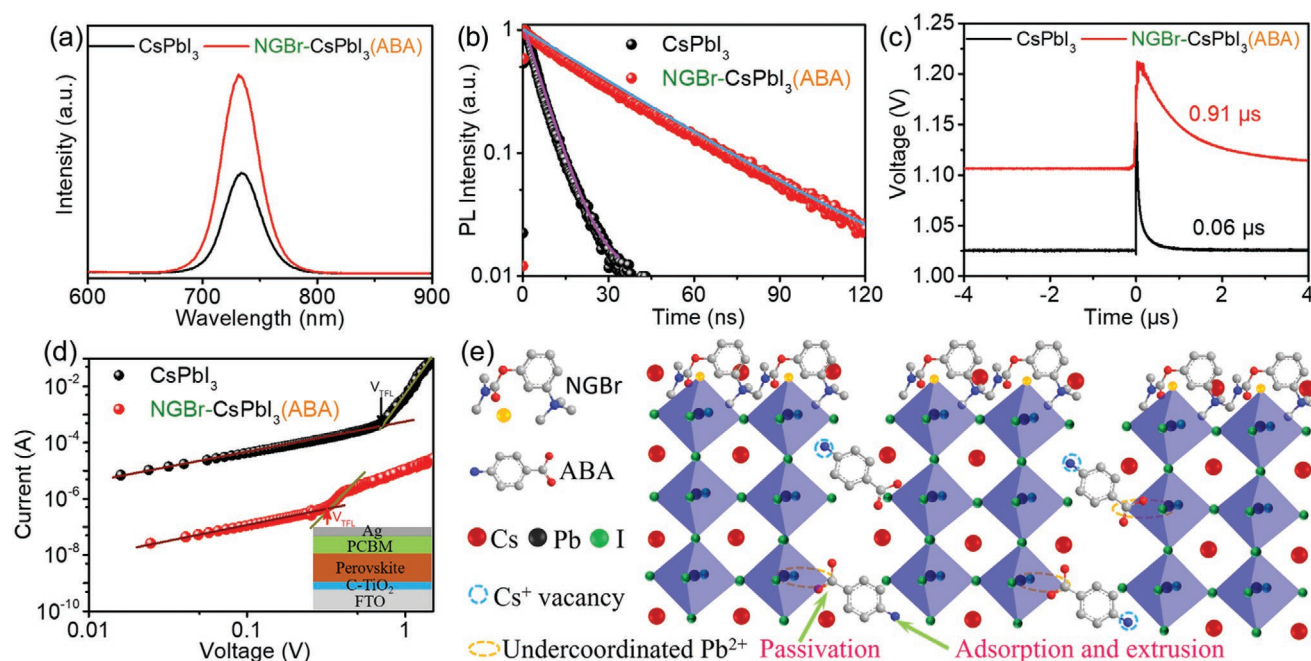


Figure 3. a) Steady-state PL and b) TRPL spectra of CsPbI₃ and NGBr-CsPbI₃(ABA) thin films. c) TPV of the CsPbI₃- and NGBr-CsPbI₃(ABA)-based PSCs. d) Dark *J*-*V* measurement of the electron-only device for CsPbI₃ and NGBr-CsPbI₃(ABA) perovskite thin films, the inset depicts the SCLC architecture. e) Schematic mechanism for the NGBr and ABA molecule interacted with CsPbI₃ inorganic perovskite.

indicate that both the ABA and surface terminated NG cation can significantly reduce the defects in CsPbI₃ perovskite. The NGBr-CsPbI₃(ABA) PSCs has only a low trap density of $3.72 \times 10^{15} \text{ cm}^{-3}$. We further used thermal admittance spectroscopy to measure the defect density, as shown in Figure S10, Supporting Information. The NGBr-CsPbI₃(ABA) devices exhibit lower trap density of states (tDOS) than that of CsPbI₃ ones almost over the whole trap depth region, suggesting significantly reduced trap density in the NGBr-CsPbI₃ thin films, which is consistent with the SCLC results. In fact, such significantly reduced defect density in the CsPbI₃ is not only favored for high-performance perovskite photoelectronic devices, but also beneficial to enhancing the photoactive phase stability via increasing the phase transition energy barrier from black phase to non-photoactive yellow phase.^[39,43]

The aforementioned results indicate that the incorporation of ABA or NGBr surface mediation can significantly reduce the defects density in the pristine CsPbI₃ thin films. X-ray photoelectron spectroscopy (XPS) was used to investigate the underlying defect passivation mechanism, as shown in Figures S11 and S12, Supporting Information. For the pristine CsPbI₃ sample, except for the dominant peaks (137.9 eV for 4f_{7/2} and 143 eV for 4f_{5/2}), two small peaks are observed at lower binding energy of 136.8 eV, and 141.9 eV refer to the defects of undercoordinated Pb²⁺. After the incorporation of ABA or NGBr mediation, the peaks related to undercoordinated Pb²⁺ disappear, while the peak due to Pb–O bonds is observed in the O 1s spectrum. These results that the carboxyl from ABA and NG⁺ coordinates with undercoordinated Pb²⁺. Meanwhile, the N 1s spectra in Figures S11 and S12, Supporting Information, indicate that the amine groups from those molecules can heal the defect caused by the Cs⁺ vacancies, which match well with previous results.^[14,16,44] Particularly,

for the case of only NGBr surface mediation, small shifts of Pb 4f, I 3d, and Br 3d in the NGBr-CsPbI₃ samples indicate the formation of Pb–Br bonds and further confirm the surface Br doping, as shown in Figure S12, Supporting Information. These results suggest that the carboxyl from ABA or NGBr will coordinate with undercoordinated Pb²⁺, while the amine groups can heal these Cs vacancies. Moreover, the NGBr surface mediation would also result in only surface Br doping.

According to the analysis above, we propose the mechanism of ABA and NGBr on the phase stability and defect density of CsPbI₃ perovskite as shown in Figure 3e. After participating in CsPbI₃ crystallization, ABA molecules located the boundaries adsorb on the surface of CsPbI₃ crystal grain and act as an anchor to suppress the rotation of PbI₆ octahedra through enhancing the energy barrier of octahedral rotation. Meanwhile, the NGBr surface mediation results in the surface bromine enrichment and NG⁺ cation surface termination, which can further reduce the surface energy. Upon their multiple actions, the CsPbI₃ shows excellent phase stability. Moreover, the carboxyl and amine groups in ABA together with surface terminated NG cation also interact with shallow- or deep-level defects in CsPbI₃ layer for reducing the defect density.

We further adopted the planar configuration of FTO/c-TiO₂/perovskite/spiro-OMeTAD/MoO₃/Au to fabricate PSCs. The PV parameters in Figure S13, Supporting Information, show that NGBr-CsPbI₃(ABA) PSCs perform better than the pristine CsPbI₃ ones. Figure 4a shows the current density–voltage (*J*-*V*) characteristics of champion PSCs based on CsPbI₃ and NGBr-CsPbI₃(ABA) thin films. The NGBr-CsPbI₃(ABA)-based device exhibits significantly improved power conversion efficiency (PCE) of 18.27% over 15.71% of CsPbI₃ ones. We also investigated the effect of individual ABA or NGBr incorporation

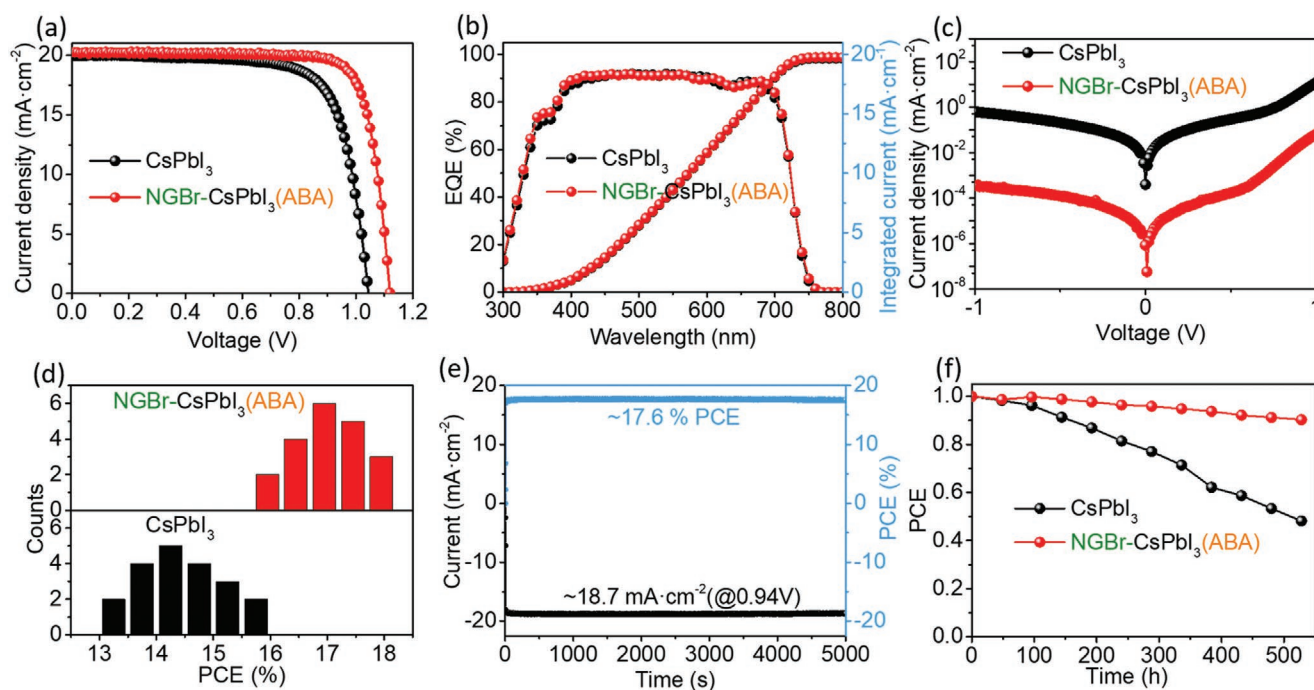


Figure 4. a) *J*-*V* characteristics of champion PSCs for the CsPbI₃- and NGBr-CsPbI₃(ABA)-based devices in reverse scan and b) corresponding EQE spectra. (effective cell area of 0.12 cm²). c) Corresponding dark *J*-*V* curves. d) Efficiency histogram of CsPbI₃- and NGBr-CsPbI₃(ABA)-based PSCs. e) Stabilized output curves for the champion NGBr-CsPbI₃(ABA)-based PSC. f) Photo-stability of CsPbI₃- and NGBr-CsPbI₃(ABA)-based PSC under continuous illumination conditions.

(Figure S14, Supporting Information). Their PV performances are better than CsPbI₃ ones, as shown in Figures S13 and S14 and Table S2, Supporting Information. The integrated current from the EQE spectra is 19.81 mA cm⁻² for the NGBr-CsPbI₃(ABA)-based devices is similar to that of CsPbI₃-based devices (≈19.68 mA cm⁻²), as shown in Figure 4b. Meanwhile, the similar TPC responses in Figure S15, Supporting Information, suggest that the ABA incorporation or surface terminated NG cation has a slight effect on the charge transport or charge collection efficiency, which is well consistent with *J*_{sc} and EQE results. These results indicate that the improved PV performance of NGBr-CsPbI₃(ABA) over CsPbI₃ can be attributed to the enhancement of the V_{oc} and FF. The improved energy level alignment at the interfaces between NGBr-CsPbI₃(ABA) and charge transport layer (Figure S16 and 17, Supporting Information) and desired charge-carrier dynamics (Figure 3) can account for such significant improvement of V_{oc} and FF in the NGBr-CsPbI₃(ABA)-based devices.

The TPV result in Figure 3c shows that the device with simultaneous ABA incorporation and NGBr mediation has a larger photovoltage of 1.106 V than the pristine CsPbI₃-based devices, which is in accordance with the *J*-*V* results. The dark current shown in Figure 4c indicates that NGBr-CsPbI₃(ABA)-based PSCs provide a smaller dark current density. It further confirms that the amino and carboxyl groups in ABA as well as surface terminated NG cation interact with the defects in CsPbI₃ layer, therefore leading to low defects density corresponding with the reduced leakage current.

In addition to the improved PV performance, the NGBr-CsPbI₃(ABA)-based PSCs also exhibits a narrow PCE distribution

(Figure 4d), suggesting improved reproducibility. The NGBr-CsPbI₃(ABA)-based devices has also shown smaller *J*-*V* hysteresis (Figure S18), therefore leading to a stable 17.6% output (Figure 4e). Finally, we investigated the stability of the encapsulated NGBr-CsPbI₃(ABA)-based PSCs devices in a dark box with a 60 ± 5% RH at 25 ± 5 °C, which show no decay after over 200 h storage, as shown in Figure S19, Supporting Information. In addition to the humidity stability, the NGBr-CsPbI₃(ABA)-based devices also show good photostability and retain 90% of its initial PCE after 500 h continuous white light LED illumination (Figure 4f), while the PCE of CsPbI₃-based PSCs drop to 50% of its initial PCE.

In summary, we propose a facile ABA incorporation combining with NGBr surface mediation to CsPbI₃ perovskite to simultaneously enhance the stability of photoactive phase and reduce the defect density. The comprehensive experimental and theoretical results indicate that ABA molecules absorb onto the surface of CsPbI₃ crystal grain and anchor the PbI₆ octahedra via increasing the energy barrier of octahedral rotation. The NGBr mediation will reduce the surface energy. Therefore, the CsPbI₃ perovskite with ABA incorporation and NGBr mediation exhibits excellent phase stability. Furthermore, the carboxyl and amino groups in ABA associated with surface terminated NG⁺ not only interact with shallow- or deep-level defects in CsPbI₃ layer (i.e., undercoordinated Pb₂⁺, Cs⁺ vacancy) to reduce the defect density, but also improves the interfacial properties at the interface between CsPbI₃ and charge transport layers. This allowed us to achieve efficiency of 18.27% for an inorganic PSCs, with excellent phase- and photo-stability.

Experimental Section

Materials: CsI was purchased from Alfa Aesar. PbI_2 4-aminobenzoic acid, and neostigmine bromide were purchased from TCI Co., Ltd. SuperDry dimethylformamide (DMF) and isopropyl alcohol (IPA) were purchased from J&K scientific LTD.

The $\text{PbI}_2 \times \text{DMAI}$ ($x = 1.1\text{--}1.3$) was prepared by mixing PbI_2 and 57% w/w hydroiodic acid (molar ratio 1:1.4) in DMF with stirring for 6 h.^[13] The as-achieved solution was evaporated at 80 °C to remove the solutions. Finally, the resulting solid was centrifuged and washed twice with copious diethyl ether and ethyl alcohol, respectively. The collected powders were dried in a vacuum oven for 24 h.

Solar Cell Fabrication: The laser-patterned FTO (TEC-7) substrate was deposited with a ≈ 20 nm thick compact TiO_2 (c- TiO_2) layer. The stoichiometric CsI and $\text{PbI}_2 \times \text{DMAI}$ with 1:1 molar ratio were dissolved in DMF to prepare 0.7 M CsPbI_3 perovskite precursor. For the CsPbI_3 with ABA incorporation, 6 mm ABA was pre-dissolved in DMF solution. The CsPbI_3 perovskite layer was then spin-coated on 70 °C preheated c- TiO_2 /FTO substrate (3000 rpm, 30 s). The as-achieved precursor thin films were annealed at 200 °C for 6 min. For the NGBr-CsPbI_3 and $\text{NGBr-CsPbI}_3(\text{ABA})$ samples, the annealed CsPbI_3 and $\text{CsPbI}_3(\text{ABA})$ thin films were post-treated with 100 μL NGBr IPA solution (3000 rpm, 60s). Finally, the NGBr-CsPbI_3 and $\text{NGBr-CsPbI}_3(\text{ABA})$ thin films were annealed at 100 °C for 4 min. Subsequently, 60 μL layer of hole transport material (HTM) solution, consisting of 0.1 M spiro-MeOTAD, 0.035 M bis(trifluoromethane) sulfonamide lithium salt (Li-TFSI), and 0.12 M 4-*tert*-butylpyridine (tBP) in chlorobenzene/acetonitrile (10:1, v/v), was spin-coated on top of the annealed perovskite films at 4000 rpm for 25 s. Finally, a 6 nm of MoO_3 and 100 nm gold electrode on the top of the cell was prepared by thermal evaporation.

Characterization: The crystal structures of these perovskite thin films were characterized on a BRUKER D2 PHASER. The morphology was characterized by SEM (Hitachi S4800). High-resolution characterization was performed using a Philips Tecna G2 20 S-TWIN. The thin films for TEM studies were prepared using the same procedure as above, but were deposited directly onto the TEM grids (SPI). XPS spectra were acquired with a Kratos Axis UltraDLD spectrometer (Kratos Analytical-A Shimadzu Group Company) using a monochromatic Al K source (1486.6 eV). The Ultraviolet photoelectron spectroscopy (UPS) measurement was measured by a PHI 5000 Versaprobe III instrument. The UPS radiation was generated by a He-gas discharge lamp with energy of 21.22 eV. The J - V curves were measured with a Keithley 2635 source meter and the illumination intensity was 100 mW cm^{-2} (ABET AM 1.5G solar simulator). The scan range was 1.2 to -0.1 V. The light intensity was calibrated by a stand Si cell before test. The EQE was measured on a QE-3011 system (Enlitech).

Thermal Admittance Spectroscopy (TAS): The tDOS can be obtained from:^[45] $N_T(E\omega) = -\frac{1}{qk_B T} \frac{\partial C}{\partial \omega} \frac{V_{bi}}{W}$, where C is the capacitance, ω is the angular frequency, k is Boltzmann constant, and T is temperature. V_{bi} and W are built-in potential and depletion width, respectively, extracted from Mott-Shockley analysis. The applied angular frequency ω defines the energetic demarcation, $E_\omega = k_B T \ln\left(\frac{\omega\omega_0}{\omega_0}\right)$, where ω_0 is attempt-to-escape frequency.

Stability Test: The thermal stability of CsPbI_3 thin films were tested on an 80 °C hotplate. The unencapsulated PSCs were continuously illuminated in a white LEDs lamp (100 mW cm^{-2}) to measure the devices' photo-stability stability. Both the thermal and photo-stability tests were performed in an N_2 glove box.

Computational Details: In order to study the interaction mechanism between ABA and CsPbI_3 crystal interface, the generalized gradient approximation of Perdew–Burke–Ernzerhof (GGA-PBE) within the frame work of density functional theory were carried out on the basis of all-electron-like projector-augmented wave (PAW) potentials, as implemented in the Vienna Ab-initio Simulation Package (VASP). Monkhorst–Pack k -point meshes of $9 \times 5 \times 1$ were used for the (110) slabs of CsPbI_3 , and a plane-wave cutoff energy of 400 eV was used for the self-consistent calculations. Born–Oppenheimer MD simulations have been performed using VASP code. For MD simulations, the Brillouin

zone is sampled at the sole Γ -point. Slabs containing 264 atoms for Cs-terminated and 468 atoms for ABA-terminated are conducted for MD simulation in the NVT ensemble for 3 ps. Nosé–Hoover thermostats under temperature of 300 K were used to control the temperature and the time step was set to 1 fs.

Supporting Information

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

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

CsPbI_3 , defect density, inorganic perovskite, PbI_6 octahedra anchors, phase stability

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