

Self-Stabilized Quasi-2D Perovskite with an Ion-Migration-Inhibition Ligand for Pure Green LEDs

Dezhong Zhang,[#] Chunyu Liu,[#] Jiayun Sun, Qi Xiong, Xiangtian Xiao, Dongyu Li, Benzhen Lyu, Haibin Su, and Wallace C. H. Choy*



Cite This: *ACS Energy Lett.* 2024, 9, 1133–1140



Read Online

ACCESS |



Metrics & More

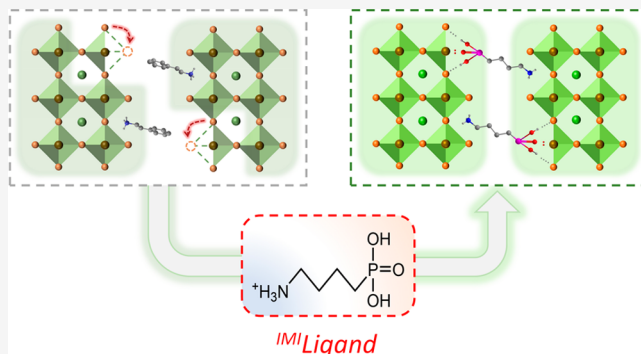


Article Recommendations



Supporting Information

ABSTRACT: Perovskite light-emitting diodes (PeLEDs) have recently achieved a great breakthrough in external quantum efficiency (EQE). However, the operational stability of pure primary color PeLEDs lags far behind because of serious ion migration. Herein, a self-stabilized quasi-2D perovskite is constructed with a strategically synthesized ion-migration-inhibition ligand (^{IMI}ligand) to realize highly stable and efficient pure green PeLEDs approaching the standard green light of Rec. 2020. The ^{IMI}ligand takes the role to not only eliminate migration pathways and anchor halide ions to suppress the ion migration but to also further enhance the crystalline orientation and energy transfer in quasi-2D perovskites. Meanwhile, the self-stabilized quasi-2D perovskite overcomes the degradation of electrical performance caused by conventional exogenous passivation additives. Ultimately, the figure of merit of the pure green quasi-2D PeLEDs is at least double that of previous works. The devices achieve an EQE of 26.2% and operational stability of 920 min at initial luminance of 1000 cd m⁻².



Metal halide perovskites have been considered to be one of the most promising candidates for next-generation light-emitting diode (LED) technology in light of their superior optoelectronic properties, such as narrow emission width, widely tunable band gap, and high photoluminescence quantum yields (PLQYs).^{1–9} Quasi-2D perovskites, as an important category of perovskites with improved exciton binding energy by forming multiquantum well structures, offer interesting properties for light emission.^{10–13} Recently, significant achievements have been made to improve the external quantum efficiency (EQE) of quasi-2D perovskite LEDs (PeLEDs).^{14–16} However, enhanced operational stability, particularly for pure primary (red-green-blue) color PeLEDs, is in urgent demand to satisfy the requirement of their further applications for display technologies.^{2,17–19}

It is well known that ion migration exists in perovskite-based optoelectronic devices^{20–22} and has been widely recognized as the primary source causing the poor operational stability of PeLEDs. Halide anions with low activation energies are acknowledged as the most mobile ions in perovskites^{21,23–25} and will be strongly stimulated by the driving bias voltage and Joule heat during operation.^{26–29} For quasi-2D perovskite emitters, because of the partition by the organic spacer ligands,

the grain size of perovskites will be reduced, thereby resulting in rich grain boundaries and structural defects in the films,^{17,30} which will provide more pathways for ion migration. Therefore, defect passivation and halide ion anchoring in quasi-2D perovskites are highly desirable for stable PeLEDs.

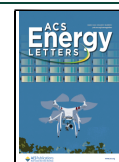
Passivating the halide vacancy defects is a commonly adopted strategy to improve the performance and stability of quasi-2D PeLEDs,^{13,15,31–34} especially incorporating exogenous passivation additives into the perovskite films to inhibit ion migration.²⁷ Different types of organic chemicals, including small molecules and polymers with Lewis base groups, such as P=O, C=O, S=O, and C–O–C, have been employed as the additives.^{31–36} However, some associated structures of alkyl or other low-conductive structures are inevitably brought in simultaneously, which hinders the carrier transport in perov-

Received: November 10, 2023

Revised: January 17, 2024

Accepted: February 20, 2024

Published: February 23, 2024



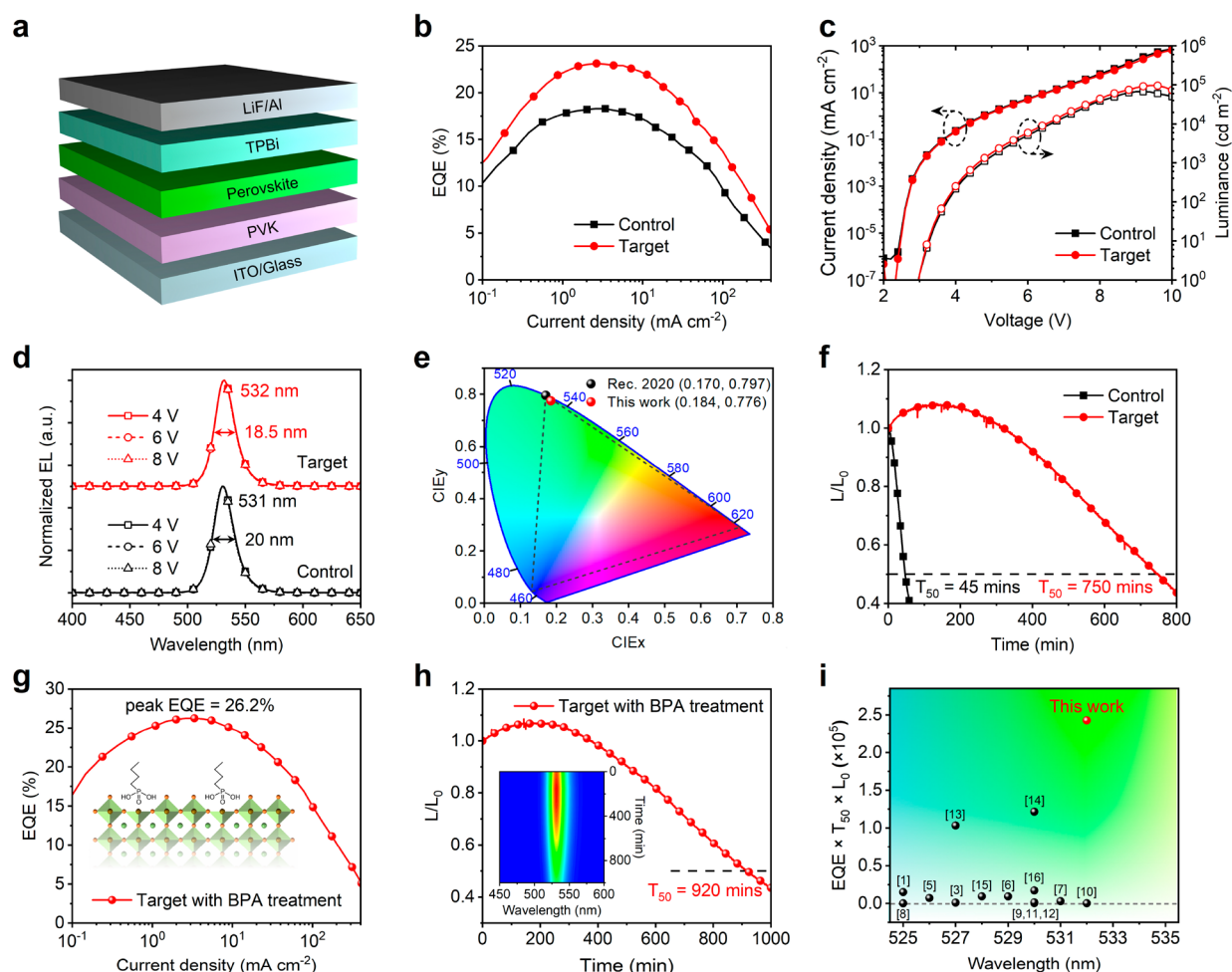


Figure 1. (a) Device structure diagram. (b) EQE curves and (c) current density–voltage–luminance characteristics of control and target devices. (d) Normalized EL spectra of devices under different applied voltages. (e) CIE coordinate of the target devices. (f) Operational stability at $L_0 = 1000 \text{ cd m}^{-2}$. (g) EQE of the target device with further BPA treatment; inset shows the schematic diagram of BPA treatment. (h) Operational stability of target device with further BPA treatment; inset shows the time-dependent EL spectra. (i) Comparison of the figure of merit of our device with reported high-performance pure green PeLEDs; the references in (i) are listed in Table S1.

skite films.^{34,37–41} Exogenous additives with better conductivity, such as conjugated molecules, have also been studied,^{27,37} but it is still difficult to match their conductivity with the high conductivity of perovskites. Recently, as a necessary component in the quasi-2D perovskite, organic spacer ligands have been further designed to be equipped with functional groups. Dual functional group ligands equipped with ammonium and with either sulfonic or carboxyl groups have been used to self-passivate defects and improve the phase distribution in quasi-2D perovskite films.^{16,42} The incorporation of these passivation ligands avoids the electrical performance degradation of the quasi-2D perovskite. However, it is very important to point out that all of the reported ligands have not yet shown commendable effects in inhibiting ion migration and improving the operational stability of PeLEDs.

In this work, we strategically synthesize butylphosphonic acid 4-ammonium (BAPA) as the ion-migration-inhibition ligand (^{IMI}ligand) to partially replace the common phenethylammonium (PEA) ligands to construct self-stabilized quasi-2D perovskites without additives. The ^{IMI}ligand of BAPA offers both the elimination of migration pathways and the anchoring to halide ions to fully inhibit ion migration in quasi-2D perovskites. In addition, we also find the significant

contribution of the ^{IMI}ligand on the enhanced crystalline orientation of perovskites and the reduced van der Waals gap to enhance energy transfer in quasi-2D perovskites and, thus, enhance the emission properties of the quasi-2D perovskite. Given the successful construction of the self-stabilized quasi-2D perovskite, we demonstrate the pure green PeLEDs approaching the standard green light of Rec. 2020 with the figure of merit doubled compared with previous reported works, the peak EQE to be 26.2%, and an obviously improved operational lifetime of 920 min at an initial luminance (L_0) of 1000 cd m^{-2} .

The pure green quasi-2D PeLEDs are fabricated with the device structure shown in Figure 1a. BAPA ligands are introduced to construct the self-stabilized quasi-2D perovskites by replacing PEA. An enhanced EQE over 23% for the target device (with 20% BAPA ligands) is obtained (Figure 1b and Figure S1a,b), as well as an increased peak luminance (Figure 1c). The current density and luminance curves plotted on a linear scale are shown in Figure S2. Notably, the turn-on voltage and current density of the devices do not change significantly even when more BAPA ligands are introduced (Figure S1c,d). Both control (with 100% PEA ligands) and target devices present stable electroluminescence (EL) spectra

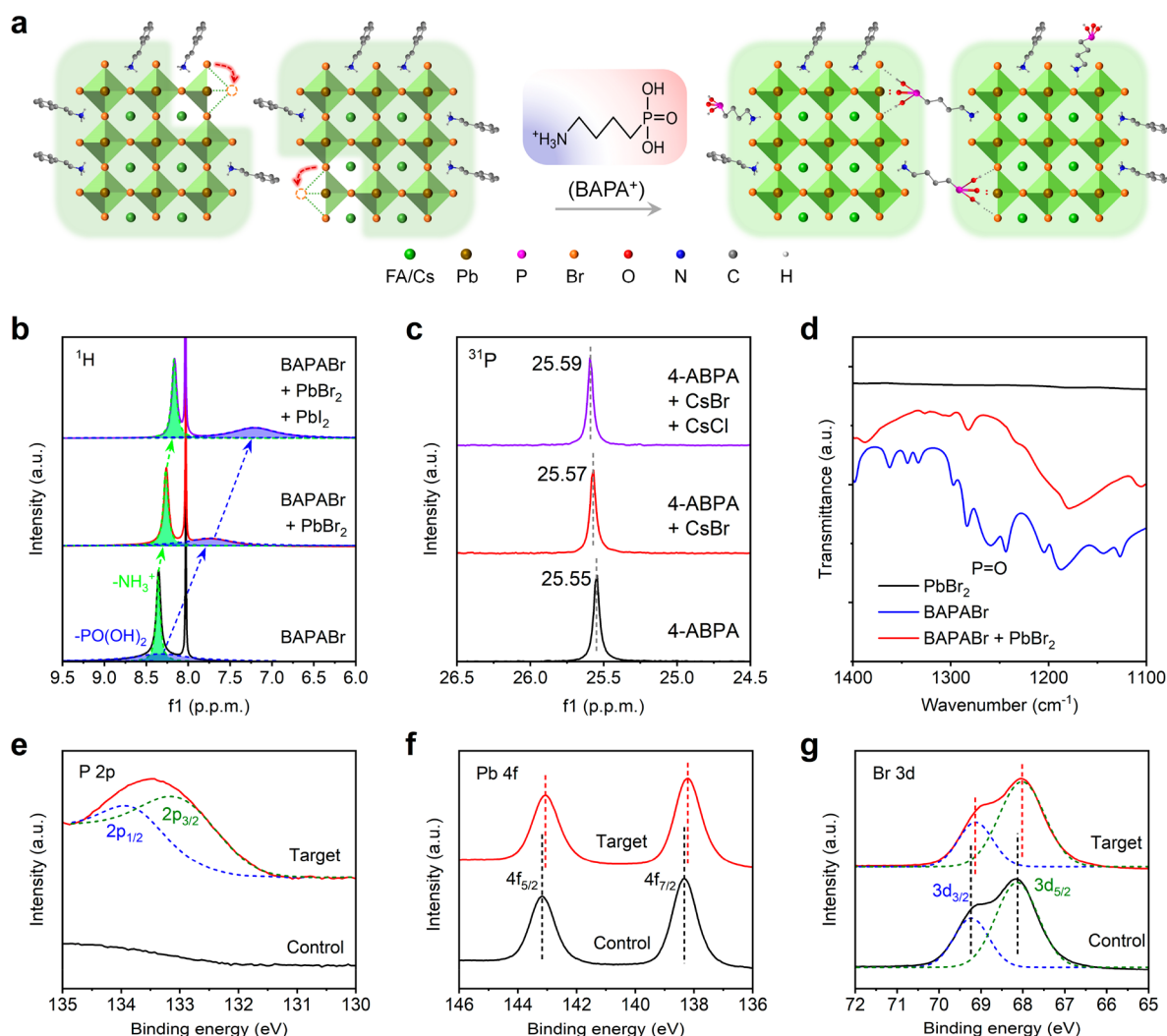


Figure 2. (a) Schematic illustration of quasi-2D perovskite structures before and after the introduction of BAPA ligands. (b) ¹H NMR spectra of pure BAPABr, with PbBr₂, and further with PbI₂ dissolved in deuterated DMF. (c) ³¹P NMR spectra of pure 4-ABPA, with CsBr, and further with CsCl dissolved in D₂O. XPS spectra of (e) P 2p, (f) Pb 4f, and (g) Br 3d peaks of control film and target film with BAPA ligands.

when the bias voltage is increased (Figure 1d). Importantly, the target PeLEDs demonstrate pure green EL emission at 532 nm, which corresponds to the CIE coordinate (0.184, 0.776), which is very close to the Rec. 2020 standard (Figure 1e). More impressively, the operational stability is significantly improved with a half-life time (t_{50}) prolonged from 45 min for the control device to over 750 min for the target device at an L_0 of 1000 cd m⁻² at the optimized amount of 20% BAPA (Figure 1f). The lifetime of devices will decrease when BAPA concentration is further increased (Figure S1e).

The improved stability and EQE of the quasi-2D PeLEDs with the proposed ^{IMI}ligand of BAPA are comparatively analyzed with the perovskite formed from the combination of the commonly used butyl ammonium (BA)-only ligands and butylphosphonic acid (BPA) (single functional group) additive (Figure S3a) with different ratios. Our results show that although the associated structures are necessary to enable the additive to have appropriate and stable physical and chemical properties, the incorporation of associated structures of alkyl by the exogenous BPA additive could hinder the carrier transport in perovskite films. As shown in Figure S3b, the perovskite films with the BPA show improved PL intensity

when the amount of BPA increases because of the interaction between phosphonic acid groups and defects of perovskites. However, the EQE and operational stability of devices are much inferior to those of the target device with the ^{IMI}ligand of BAPA (Figure S4). The current density decreases (Figure S4b), and the turn-on voltage of devices (Figure S4c) increases severely, which implies that the electrical properties of perovskite films with additives deteriorate significantly. When the same amount of phosphonic acid (20%) is introduced by the exogenous passivation additive of BPA, the current density reduces by more than an order of magnitude, and the turn-on voltage unexpectedly increases from 3 to 4.6 V compared with the ^{IMI}ligand of BAPA. From the characteristics of single-carrier devices (Figure S5), the transport of both electrons and holes is severely reduced. These results further validate the unique advantages of the self-stabilized quasi-2D perovskite with the ^{IMI}ligand of BAPA in electrical properties (which cannot be realized by the single functional group ligand/additive). Interestingly, when BPA is further employed as the additive in antisolvent, both the control and target films become brighter (Figure S6). A high EQE of 26.2% for the target device with the BPA treatment (Figure 1g) and a peak

luminance exceeding 1×10^5 cd m⁻² with the pure green emission at 532 nm (Figure S7a, b) are eventually demonstrated. Figure S7c shows the EQE statistics of the control and target devices with further BPA treatment. The improvement can be explained by the coordination of defects by P=O at the emission region of the film,^{13,27,38} as shown in the inset of Figure 1g, which is also evidenced by the Fourier transform infrared spectroscopy (FTIR) spectra in Figure S8. Meanwhile, the lifetime of both the control and target samples with BPA treatment is further prolonged to the best value of 920 min (Figure S9b and Figure 1h).

Ultimately, we further demonstrate that the champion PeLEDs show a substantial enhanced “figure of merit,” which is defined as EQE $\times$ lifetime $\times L_0$ because good PeLEDs shall simultaneously show high EQE and long lifetime at a large L_0 , as shown in Figure 1i. The champion device shows a figure of merit reaching a value of $\sim 2.5 \times 10^5$ (at least double that of previous works at pure green region) and achieves the t_{50} lifetime of 920 min with a L_0 of 1000 cd m⁻², as well as a t_{50} of 185 and 50 min with a higher L_0 of 4500 and 9800 cd m⁻² respectively (Figure S10), without any spectral shift in the EL emission during operation (inset of Figure 1h). Other reported high-performance PeLEDs with pure green emission (EL peak position between 525 and 535 nm, full-width at half-maximum < 25 nm) are further summarized and compared in Table S1 and Figure S11a,b.

The formation scheme of the quasi-2D perovskites without and with BAPA ligands is shown in Figure 2a. The BAPA ligands are expected to interact with Pb-related defects and anchor with Br ions and simultaneously interact with the perovskite framework. To prove the formation scheme as illustrated, the chemical interaction of BAPA ligands is explored first. The ¹H nuclear magnetic resonance (NMR) spectra (Figure 2b) show changes in the resonance signals arising from the NH₃⁺ and P–OH protons of BAPABr with PbBr₂. The NH₃⁺ proton signals show an upfield shift from 8.35 to 8.26 ppm, and the signals arising from the P–OH protons also demonstrate a significant shift from 8.32 to 7.73 ppm. This can be rationalized in terms of the strong coordination between BAPA ligands and Pb. The hydrogen bond of P=O...H–O and P=O...H–N in neat BAPABr solution will be replaced by the interaction of P=O:Pb when in situ adding PbBr₂, which reduces the shielding effect for protons of NH₃⁺ and P–OH, thereby upfield-shifting the signals. To prove the existence of P–OH...Br, excess PbI₂ is further added into the solution, and the I[–] induces a further upfield chemical shift of $\Delta\delta = -0.42$ ppm (from 7.73 to 7.21 ppm) because of the weaker shielding effect of the P–OH...I compared with the P–OH...Br. Simultaneously, the signals arising from protons of NH₃⁺ also show an upfield shift, which proves that the NH₃⁺ will form a hydrogen bond with halogen and, thus, interact with the perovskite frameworks.⁴³ To more clearly verify the formation of the hydrogen bond between P–OH and halogen, the parent amine [4-aminobutylphosphonic acid (4-ABPA)] of BAPABr is studied, and the corresponding ³¹P NMR spectra are shown in Figure 2c. The addition of CsBr leads to downfield-shifted signals from 25.55 to 25.57 ppm, thereby indicating the formation of P–OH...Br, which decreases the electron density of P. The signals are further downfield-shifted with the presence of CsCl because of the stronger electron-withdrawing ability of Cl, which is solid evidence for the existence of bonding interaction between P–OH and halogen. To further prove the interaction of P=O

with Pb, FTIR spectra were obtained and are shown in Figure 2d. We observe an infrared peak at ca. 1250 cm⁻¹ originating from the P=O stretching vibration for pristine BAPABr, while it exhibits a notable weakening with PbBr₂, which fully indicates the coordination of P=O with Pb²⁺.^{13,44,45} The chemical interaction brought by BAPA ligands in the perovskite films is also verified by X-ray photoelectron spectroscopy (XPS) measurements. P 2p spectra (Figure 2e) prove the existence of BAPA ligands, and in the Pb 4f and Br 3d spectra (Figure 2f,g), the peaks shift toward lower binding energy, which can be attributed to changes in electron cloud density,^{35,46} thereby suggesting an interaction brought by the functional phosphonic acid groups. Therefore, the BAPA ligands have been shown to interact with Pb-related defects by P=O, anchor with Br ions by P–OH, and simultaneously interact with the perovskite frameworks by NH₃⁺.

The crystallization of quasi-2D perovskites changes because of chemical interactions of BAPA ligands. The 2D grazing incidence X-ray diffraction (GIXRD) image of the control film (Figure 3a) exhibits diffraction rings along certain extended arc

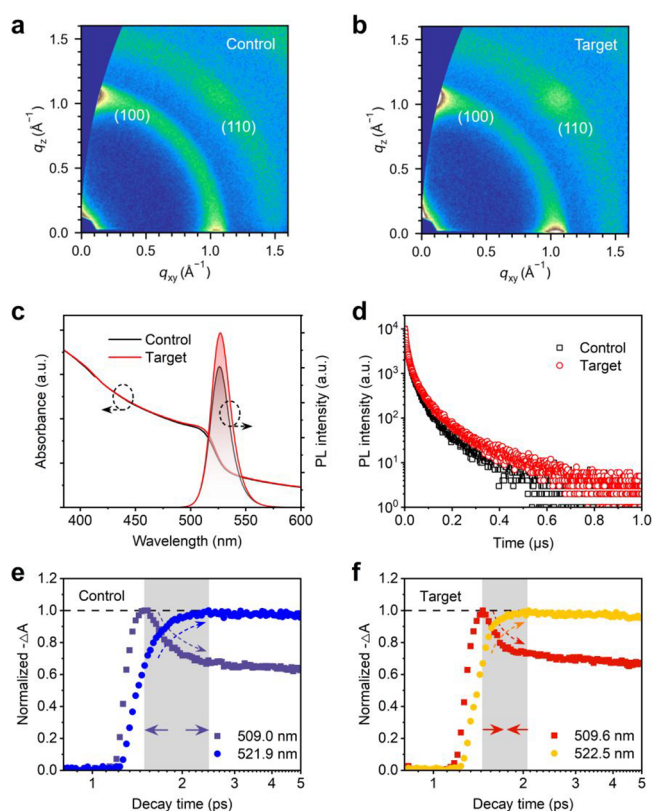


Figure 3. 2D-GIXRD images of (a) control and (b) target films. (c) Absorbance and PL spectra of the films. (d) PL decay curves of the films. TA kinetics probed at selected wavelengths for (e) control and (f) target films.

segments, which indicates considerable random crystal orientation in the film. In contrast, the target film shows discrete Bragg spots along the same rings (Figure 3b), which suggests an enhanced crystalline orientation of the perovskite. This could be related to the dual-terminal interaction of ligands in the perovskite.^{42,47} When we replace the BAPA ligands with equimolar amounts of BA ligands and BPA additives, the orientation of the perovskite is similar to the control sample (Figure S12). In addition, the diffraction signals

begin to weaken significantly when incorporating excessive BAPA ligands of more than 30% (Figure S13), which should be responsible for the drop in EQE and operational stability of PeLEDs. The weakened crystallinity of perovskites is caused by the strong coordination between excessive phosphonic acid groups and Pb^{2+} . To verify the formation of quasi-2D perovskite phases with BAPA ligands, a thicker perovskite film with 100% BAPA ligands is prepared (see the details in Experimental Section in the Supporting Information), which results in a wider phase distribution in the film. The GIXRD image (Figure S14) shows the obvious presence of low-order quasi-2D perovskite phases in the film, and the similar results also occur in thicker control film (with 100% PEA ligands) and some perovskites with other reported ligands,^{48,49} thereby proving that quasi-2D perovskites can be constructed via the BAPA ligands. For film morphology, the target quasi-2D perovskite film is similar to the control film (Figure S15), and both exhibit small surface roughness (Figure S16). The energy-dispersive X-ray (EDX) mapping of surface and cross-sectional scanning electron microscopy (SEM) images of target films in Figure S17 shows the uniform distribution of the BAPA ligand in the perovskite films.

For the optical properties, the control and target films demonstrate almost the same absorbance spectra (Figure 3c). As the ratio of BAPA ligands in perovskite increases, the absorption edge, as well as the PL emission, gradually red shift (Figure S18) corresponding to the decrease in the band gap of perovskite. Similarly, a slight red shift is also observed when 20% of PEA is replaced by BA ligands (Figure S19). This is because of the different distortion of the perovskite framework caused by changing ammonium cationic ligands in the quasi-2D perovskite.^{50,51} On the basis of the defect passivation effect, the PL intensity of the target film is significantly higher than that of the control film (Figure 3c), which is accompanied by an increase in the PL lifetime (Figure 3d). The PL emission of the target film exhibits a slightly narrower full width at half-maximum (fwhm) (Figure S18d) corresponding to the narrower EL emission from the target device, which is also closely related to the defect passivation. The PLQYs of perovskite films with different contents of BAPA ligands are shown in Figure S20. The PLQY values of different films are also consistent with the EQE distribution of the corresponding devices.

To investigate the changes in photogenerated exciton/carrier transfer dynamics with the introduction of BAPA ligands, transient absorption (TA) spectroscopy are performed. The TA spectra of perovskite films at different time scales are shown in Figure S21a,b. Similar to the steady-state absorption spectra, the TA spectra also show a slight red-shift after the introduction of the BAPA ligands. When prolonging the decay time, the peaks arising from low- n (n is the order of quasi-2D perovskite) phases decrease, which is accompanied by a gradual growth of the high- n peaks, thereby indicating energy transfer from low- n to high- n phases.^{11,52} To further study the transfer process, time traces of low- n peaks (509.0 nm for control film and 509.6 nm for target film) and high- n peaks (521.9 nm for control film, and 522.5 nm for target film) are extracted, as shown in Figure 3e,f. A faster energy transfer process is found in the target sample, which is due to the stronger interlayer interaction and reduction of the van der Waals gap in quasi-2D perovskites by ligands with dual-terminal interactions.^{42,47} It is beneficial for improving the

emitting performance and carrier transportation of the quasi-2D perovskite film.

The greatly improved operational stability is closely related to the suppression of ion migration. To reveal the ion migration behavior, we investigate the frequency-dependent capacitance of PeLEDs (Figure 4a,b). Obviously, the control

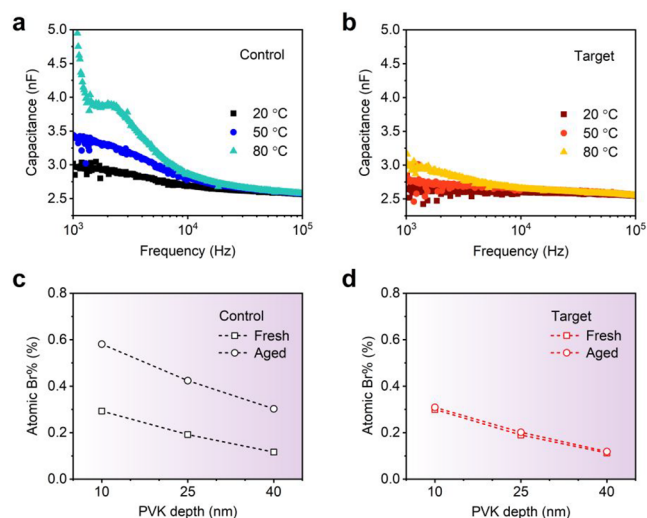


Figure 4. Frequency-dependent capacitance plot of (a) control and (b) target samples at different temperatures. Br contents of fresh and aged (c) control samples and (d) target samples at different depths of PVK layers.

device shows increasing capacitance near 1 kHz, and the additional capacitance originates from the mobile ions that accumulate at contact interfaces because of the severe ion migration.^{29,53–56} As the test temperature increases, a larger capacitance is observed because of the thermal-induced enhancement of ion migration. For the target sample, the additional capacitance is insignificant even after heating. In addition, Figure S22 presents the time-dependent capacitance decay profiling. The decay process from a much higher capacitance is collected for the control device, which implies the easy ion migration and accumulation in the control device is driven by prebias. For the target device, the capacitance generated by the same prebias is obviously lower, which further proves that ion migration is suppressed. Furthermore, forward and reverse current density–voltage scans are also carried out to investigate the hysteretic behavior, as current–voltage hysteresis is known to be related to the ionic transport in perovskite devices.^{40,57} More pronounced hysteresis is observed in the control PeLEDs compared with target devices (Figure S23a,b).

To more intuitively demonstrate the ion migration and redistribution behavior, depth-dependent XPS measurements of poly(9-vinylcarbazole) (PVK) hole transport layers are carried out. We find that during operation, Br^- will migrate toward the anode and into the PVK layer, as shown in the schematic diagram in Figure S24. For fresh and aged (driven at 5 V for 60 min) PeLEDs, the top layers above PVK are removed, and XPS measurement is applied to the PVK samples. The Pb 4f and Br 3d peaks at different depths for the fresh and aged control samples are shown in Figure S25a,b. The Pb signals can be detected because the perovskite precursor solution can be impregnated into the PVK layer during the perovskite fabrication process. Notably, the Pb

content is similar in fresh and aged control samples, while the Br content increases significantly after device aging. Figure 4c shows the comparison of Br content at different depths in fresh and aged PVK samples, thereby indicating the severe Br[−] migration from perovskite to PVK. The Br/Pb ratio of the fresh sample is slightly higher than 3 at different depths of the PVK layer (Figure S26a), which is similar to the proportion in the perovskite used here. Whereas the Br/Pb ratio in the aged sample is much higher than the fresh one, thereby further proving that the additional Br originates from ion migration. For target samples, there is no obvious change in the Br content after the same aging process, as shown by the Br content in Figure 4f and Br/Pb ratios in Figure S26b, which is direct evidence that the ion migration in the target sample is effectively suppressed, thus contributing to the significantly improved operational stability of quasi-2D PeLEDs.

In summary, we have constructed a self-stabilized quasi-2D perovskite with the ^{IMI}ligand of BAPA to realize highly stable and efficient pure green PeLEDs. The BAPA ligands significantly inhibit the ion migration and redistribution, as confirmed by the direct experimental confirmation of the substantial drop of ion generation/accumulation and almost no change of Br ion across the device during operation. Equally important, the self-stabilized quasi-2D perovskite with the ^{IMI}ligand exhibits excellent energy transfer, optical, and electrical properties simultaneously, which cannot be realized by conventional exogenous passivation additives. Consequently, the figure of merit of the champion PeLEDs is at least doubled compared with other reported results. The EQE exceeds 26%, and the operational lifetime is extended to 920 min at $L_0 = 1000 \text{ cd m}^{-2}$. The work not only provides valuable guidance for suppressing ion migration in perovskites and enhancing the optoelectronic properties but also paves a novel way for realizing stable and efficient PeLEDs for advancing true color display applications.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsenerylett.3c02418>.

Experimental section, EQE curves, current density–voltage curves, luminance–voltage curves, operational stability, PLQY values, electron-only and hole-only devices, EL spectra, FTIR spectra, comparison of EQE and operation lifetime, 2D-GIXRD images, SEM images, AFM images, absorbance and PL spectra, TA spectra, capacitance properties, XPS spectra, and Br/Pb ratios in the films (PDF)

■ AUTHOR INFORMATION

Corresponding Author

Wallace C. H. Choy – Department of Electrical and Electronic Engineering, The University of Hong Kong, Hong Kong 000000, China; orcid.org/0000-0002-9535-4076; Email: chchoy@eee.hku.hk

Authors

Dezhong Zhang – Department of Electrical and Electronic Engineering, The University of Hong Kong, Hong Kong 000000, China

Chunyu Liu – Department of Electrical and Electronic Engineering, The University of Hong Kong, Hong Kong

000000, China; State Key Laboratory of Integrated Optoelectronics, College of Electronic Science and Engineering, Jilin University, Changchun 130012, China

Jiayun Sun – Department of Electrical and Electronic Engineering, The University of Hong Kong, Hong Kong 000000, China; Department of Electronic and Electrical Engineering, Southern University of Science and Technology, Shenzhen 518055, China

Qi Xiong – Department of Electrical and Electronic Engineering, The University of Hong Kong, Hong Kong 000000, China

Xiangtian Xiao – Department of Electrical and Electronic Engineering, The University of Hong Kong, Hong Kong 000000, China

Dongyu Li – Department of Electrical and Electronic Engineering, The University of Hong Kong, Hong Kong 000000, China

Benzheng Lyu – Department of Electrical and Electronic Engineering, The University of Hong Kong, Hong Kong 000000, China

Haibin Su – Department of Chemistry, The Hong Kong University of Science and Technology, Hong Kong 000000, China; orcid.org/0000-0001-9760-6567

Complete contact information is available at: <https://pubs.acs.org/doi/10.1021/acsenerylett.3c02418>

Author Contributions

#D.Z. and C.L. contributed equally.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work is supported by University Grant Council of the University of Hong Kong Grants (Grant# 202011159254 and 202111159113), General Research Fund (Grant# 17211220, 17200021, and 17200823), and Collaborative Research Fund (Grant No. C7035-20G) from the Research Grants Council (RGC) of Hong Kong Special Administrative Region, China.

■ REFERENCES

- (1) Liu, X.-K.; Xu, W.; Bai, S.; Jin, Y.; Wang, J.; Friend, R. H.; Gao, F. Metal halide perovskites for light-emitting diodes. *Nat. Mater.* **2021**, *20*, 10–21.
- (2) Quan, L. N.; Rand, B. P.; Friend, R. H.; Mhaisalkar, S. G.; Lee, T.-W.; Sargent, E. H. Perovskites for next-generation optical sources. *Chem. Rev.* **2019**, *119*, 7444–7477.
- (3) Cho, H.; Jeong, S.; Park, M.; Kim, Y.; Wolf, C.; Lee, C.; Heo, J. H.; Sadhanala, A.; Myoung, N.; Yoo, S.; Im, S. H.; Friend, R. H.; Lee, T. W. Overcoming the electroluminescence efficiency limitations of perovskite light-emitting diodes. *Science* **2015**, *350*, 1222–1225.
- (4) Cao, Y.; Wang, N.; Tian, H.; Guo, J.; Wei, Y.; Chen, H.; Miao, Y.; Zou, W.; Pan, K.; He, Y.; Cao, H.; Ke, Y.; Xu, M.; Wang, Y.; Yang, M.; Du, K.; Fu, Z.; Kong, D.; Dai, D.; Jin, Y.; Li, G.; Li, H.; Peng, Q.; Wang, J.; Huang, W. Perovskite light-emitting diodes based on spontaneously formed submicrometre-scale structures. *Nature* **2018**, *562*, 249–253.
- (5) Jiang, Y.; Sun, C.; Xu, J.; Li, S.; Cui, M.; Fu, X.; Liu, Y.; Liu, Y.; Wan, H.; Wei, K.; Zhou, T.; Zhang, W.; Yang, Y.; Yang, J.; Qin, C.; Gao, S.; Pan, J.; Liu, Y.; Hoogland, S.; Sargent, E. H.; Chen, J.; Yuan, M. Synthesis-on-substrate of quantum dot solids. *Nature* **2022**, *612*, 679–684.
- (6) Kim, J. S.; Heo, J.; Park, G.; Woo, S.; Cho, C.; Yun, H. J.; Kim, D.; Park, J.; Lee, S.; Park, S.; Yoon, E.; Greenham, N. C.; Lee, T.

Ultra-bright, efficient and stable perovskite light-emitting diodes. *Nature* **2022**, *611*, 688–694.

(7) Chen, W.; Huang, Z.; Yao, H.; Liu, Y.; Zhang, Y.; Li, Z.; Zhou, H.; Xiao, P.; Chen, T.; Sun, H.; Huang, J.; Xiao, Z. Highly bright and stable single-crystal perovskite light-emitting diodes. *Nat. Photonics* **2023**, *17*, 401–407.

(8) Liu, A.; Bi, C.; Li, J.; Zhang, M.; Cheng, C.; Binks, D.; Tian, J. High color-purity and efficient pure-blue perovskite light-emitting diodes based on strongly confined monodispersed quantum dots. *Nano Lett.* **2023**, *23*, 2405–2411.

(9) Sun, Y.; Ge, L.; Dai, L.; Cho, C.; Orri, J. F.; Ji, K.; Zelewski, S. J.; Liu, Y.; Mirabelli, A. J.; Zhang, Y.; Huang, J.; Wang, Y.; Gong, K.; Lai, M. C.; Zhang, L.; Yang, D.; Lin, J.; Tennyson, E. M.; Ducati, C.; Stranks, S. D.; Cui, L.; Greenham, N. C. Bright and stable perovskite light-emitting diodes in the near-infrared range. *Nature* **2023**, *615*, 830–835.

(10) Byun, J.; Cho, H.; Wolf, C.; Jang, M.; Sadhanala, A.; Friend, R. H.; Yang, H.; Lee, T.-W. Efficient visible quasi-2D perovskite light-emitting diodes. *Adv. Mater.* **2016**, *28*, 7515–7520.

(11) Yuan, M.; Quan, L. N.; Comin, R.; Walters, G.; Sabatini, R.; Voznyy, O.; Hoogland, S.; Zhao, Y.; Beauregard, E. M.; Kanjanaboos, P.; Lu, Z.; Kim, D. H.; Sargent, E. H. Perovskite energy funnels for efficient light-emitting diodes. *Nat. Nanotechnol.* **2016**, *11*, 872–877.

(12) Wang, N.; Cheng, L.; Ge, R.; Zhang, S.; Miao, Y.; Zou, W.; Yi, C.; Sun, Y.; Cao, Y.; Yang, R.; Wei, Y.; Guo, Q.; Ke, Y.; Yu, M.; Jin, Y.; Liu, Y.; Ding, Q.; Di, D.; Yang, L.; Xing, G.; Tian, H.; Jin, C.; Gao, F.; Friend, R. H.; Wang, J.; Huang, W. Perovskite light-emitting diodes based on solution-processed self-organized multiple quantum wells. *Nat. Photonics* **2016**, *10*, 699–704.

(13) Ma, D.; Lin, K.; Dong, Y.; Choubisa, H.; Proppe, A. H.; Wu, D.; Wang, Y.-K.; Chen, B.; Li, P.; Fan, J. Z.; Yuan, F.; Johnston, A.; Liu, Y.; Kang, Y.; Lu, Z.-H.; Wei, Z.; Sargent, E. H. Distribution control enables efficient reduced-dimensional perovskite LEDs. *Nature* **2021**, *599*, 594–598.

(14) Wang, K.; Lin, Z.-Y.; Zhang, Z.; Jin, L.; Ma, K.; Coffey, A. H.; Atapattu, H. R.; Gao, Y.; Park, J. Y.; Wei, Z.; Finkenauer, B. P.; Zhu, C.; Meng, X.; Chowdhury, S. N.; Chen, Z.; Terlier, T.; Do, T.-H.; Yao, Y.; Graham, K. R.; Boltasseva, A.; Guo, T.-F.; Huang, L.; Gao, H.; Savoie, B. M.; Dou, L. Suppressing phase disproportionation in quasi-2D perovskite light-emitting diodes. *Nat. Commun.* **2023**, *14*, 397.

(15) Liu, Z.; Qiu, W.; Peng, X.; Sun, G.; Liu, X.; Liu, D.; Li, Z.; He, F.; Shen, C.; Gu, Q.; Ma, F.; Yip, H.-L.; Hou, L.; Qi, Z.; Su, S.-J. Perovskite light-emitting diodes with EQE exceeding 28% through a synergistic dual-additive strategy for defect passivation and nanostructure regulation. *Adv. Mater.* **2021**, *33*, 2103268.

(16) Liu, S.; Guo, Z.; Wu, X.; Liu, X.; Huang, Z.; Li, L.; Zhang, J.; Zhou, H.; Sun, L.-D.; Yan, C.-H. Zwitterions narrow distribution of perovskite quantum wells for blue light-emitting diodes with efficiency exceeding 15%. *Adv. Mater.* **2023**, *35*, 2208078.

(17) Zhang, L.; Sun, C.; He, T.; Jiang, Y.; Wei, J.; Huang, Y.; Yuan, M. High-Performance Quasi-2D Perovskite Light-Emitting Diodes: from Materials to Devices. *Light: Sci. Appl.* **2021**, *10*, 61.

(18) Kong, L.; Zhang, X.; Zhang, C.; Wang, L.; Wang, S.; Cao, F.; Zhao, D.; Rogach, A. L.; Yang, X. Stability of perovskite light-emitting diodes: existing issues and mitigation strategies related to both material and device aspects. *Adv. Mater.* **2022**, *34*, 2205217.

(19) Woo, S.-J.; Kim, J. S.; Lee, T.-W. Characterization of stability and challenges to improve lifetime in perovskite LEDs. *Nat. Photonics* **2021**, *15*, 630–634.

(20) Yuan, Y.; Huang, J. Ion migration in organometal trihalide perovskite and its impact on photovoltaic efficiency and stability. *Acc. Chem. Res.* **2016**, *49*, 286–293.

(21) Kamat, P. V.; Kuno, M. Halide ion migration in perovskite nanocrystals and nanostructures. *Acc. Chem. Res.* **2021**, *54*, 520–531.

(22) Li, Z.; Xiao, C.; Yang, Y.; Harvey, S. P.; Kim, D. H.; Christians, J. A.; Yang, M.; Schulz, P.; Nanayakkara, S. U.; Jiang, C.-S.; Luther, J. M.; Berry, J. J.; Beard, M. C.; Al-Jassim, M. M.; Zhu, K. Extrinsic ion

migration in perovskite solar cells. *Energy Environ. Sci.* **2017**, *10*, 1234–1242.

(23) Cho, H.; Kim, Y.-H.; Wolf, C.; Lee, H.-D.; Lee, T.-W. Improving the stability of metal halide perovskite materials and light-emitting diodes. *Adv. Mater.* **2018**, *30*, 1704587.

(24) Fu, X.; He, T.; Zhang, S.; Lei, X.; Jiang, Y.; Wang, D.; Sun, P.; Zhao, D.; Hsu, H.; Li, X.; Wang, M.; Yuan, M. Halogen-halogen bonds enable improved long-term operational stability of mixed-halide perovskite photovoltaics. *Chem.* **2021**, *7*, 3131–3143.

(25) Huang, Z.; Proppe, A. H.; Tan, H.; Saidaminov, M. I.; Tan, F.; Mei, A.; Tan, C.-S.; Wei, M.; Hou, Y.; Han, H.; Kelley, S. O.; Sargent, E. H. Suppressed ion migration in reduced-dimensional perovskites improves operating stability. *ACS Energy Lett.* **2019**, *4*, 1521–1527.

(26) Li, N.; Jia, Y. H.; Guo, Y. W.; Zhao, N. Ion Migration in Perovskite Light-Emitting Diodes: Mechanism, Characterizations, and Material and Device Engineering. *Adv. Mater.* **2022**, *34*, 2108102.

(27) Zhang, D.; Fu, Y.; Zhan, H.; Zhao, C.; Gao, X.; Qin, C.; Wang, L. Suppressing Thermal Quenching via Defect Passivation for Efficient Quasi-2D Perovskite Light-Emitting Diodes. *Light: Sci. Appl.* **2022**, *11*, 69.

(28) Dong, Q.; Lei, L.; Mendes, J.; So, F. Operational stability of perovskite light emitting diodes. *J. Phys.: Mater.* **2020**, *3*, 012002.

(29) Kim, H.; Kim, J. S.; Heo, J. M.; Pei, M.; Park, I. H.; Liu, Z.; Yun, H. J.; Park, M. H.; Jeong, S. H.; Kim, Y. H.; Park, J. W.; Oveis, E.; Nagane, S.; Sadhanala, A.; Zhang, L.; Kweon, J. J.; Lee, S. K.; Yang, H.; Jang, H. M.; Friend, R. H.; Loh, K. P.; Nazeeruddin, M. K.; Park, N. G.; Lee, T. W. Proton-transfer-induced 3D/2D hybrid perovskites suppress ion migration and reduce luminance overshoot. *Nat. Commun.* **2020**, *11*, 3378.

(30) Shao, Y.; Fang, Y.; Li, T.; Wang, Q.; Dong, Q.; Deng, Y.; Yuan, Y.; Wei, H.; Wang, M.; Gruverman, A.; Shield, J.; Huang, J. Grain boundary dominated ion migration in polycrystalline organic-inorganic halide perovskite films. *Energy Environ. Sci.* **2016**, *9*, 1752–1759.

(31) Ye, J. Z.; Byrnavand, M. M.; Martinez, C. O.; Hoye, R. L. Z.; Saliba, M.; Polavarapu, L. Interfacial Chemistry Triggers Ultrafast Radiative Recombination in Metal Halide Perovskites. *Angew. Chem., Int. Ed.* **2021**, *60*, 21636–21660.

(32) Quan, L. N.; Ma, D.; Zhao, Y.; Voznyy, O.; Yuan, H.; Bladt, E.; Pan, J.; García de Arquer, F. P.; Sabatini, R.; Piontkowski, Z.; Emwas, A.-H.; Todorović, P.; Quintero-Bermudez, R.; Walters, G.; Fan, J. Z.; Liu, M.; Tan, H.; Saidaminov, M. I.; Gao, L.; Li, Y.; Anjum, D. H.; Wei, N.; Tang, J.; McCamant, D. W.; Roeflaers, M. B. J.; Bals, S.; Hofkens, J.; Bakr, O. M.; Lu, Z.-H.; Sargent, E. H. Edge Stabilization in Reduced-Dimensional Perovskites. *Nat. Commun.* **2020**, *11*, 170.

(33) Ma, D.; Todorović, P.; Meshkat, S.; Saidaminov, M. I.; Wang, Y.-K.; Chen, B.; Li, P.; Scheffell, B.; Quintero-Bermudez, R.; Fan, J. Z.; Dong, Y.; Sun, B.; Xu, C.; Zhou, C.; Hou, Y.; Li, X.; Kang, Y.; Voznyy, O.; Lu, Z.-H.; Ban, D.; Sargent, E. H. Chloride Insertion-Immobilization Enables Bright, Narrowband, and Stable Blue-Emitting Perovskite Diodes. *J. Am. Chem. Soc.* **2020**, *142*, 5126–5134.

(34) Peng, X.; Yang, X.; Liu, D.; Zhang, T.; Yang, Y.; Qin, C.; Wang, F.; Chen, L.; Li, S. Targeted Distribution of Passivator for Polycrystalline Perovskite Light-Emitting Diodes with High Efficiency. *ACS Energy Lett.* **2021**, *6*, 4187–4194.

(35) Chu, Z.; Ye, Q.; Zhao, Y.; Ma, F.; Yin, Z.; Zhang, X.; You, J. Perovskite Light-Emitting Diodes with External Quantum Efficiency Exceeding 22% via Small-Molecule Passivation. *Adv. Mater.* **2021**, *33*, 2007169.

(36) He, H.; Mei, S.; Wen, Z.; Yang, D.; Yang, B.; Zhang, W.; Xie, F.; Xing, G.; Guo, R. Recent advances in blue perovskite quantum dots for light-emitting diodes. *Small* **2022**, *18*, 2103527.

(37) Jang, H.; Kim, Y. I.; Harit, A. K.; Ha, J. M.; Park, S.; Noh, Y. W.; Lee, A.; Kim, K. S.; Jung, J. W.; Woo, H. Y.; Song, M. H. Multifunctional conjugated molecular additives for highly efficient perovskite light-emitting diodes. *Adv. Mater.* **2023**, *35*, 2210511.

(38) Yang, X.; Zhang, X.; Deng, J.; Chu, Z.; Jiang, Q.; Meng, J.; Wang, P.; Zhang, L.; Yin, Z.; You, J. Efficient Green Light-emitting Diodes Based on Quasi-two-dimensional Composition and Phase

Engineered Perovskite with Surface Passivation. *Nat. Commun.* **2018**, *9*, 570.

(39) Ren, Z.; Sun, J.; Yu, J.; Xiao, X.; Wang, Z.; Zhang, R.; Wang, K.; Chen, R.; Chen, Y.; Choy, W. C. H. High-Performance Blue Quasi-2D Perovskite Light-Emitting Diodes via Balanced Carrier Confinement and Transfer. *Nano-Micro Lett.* **2022**, *14*, 66.

(40) Guo, B.; Lai, R.; Jiang, S.; Zhou, L.; Ren, Z.; Lian, Y.; Li, P.; Cao, X.; Xing, S.; Wang, Y.; Li, W.; Zou, C.; Chen, M.; Hong, Z.; Li, C.; Zhao, B.; Di, D. Ultrastable near-infrared perovskite light-emitting diodes. *Nat. Photonics* **2022**, *16*, 637–643.

(41) Zhang, D.; Fu, Y.; Liu, C.; Zhao, C.; Gao, X.; Zhang, J.; Guo, W.; Liu, J.; Qin, C.; Wang, L. Domain Controlling by Compound Additive toward Highly Efficient Quasi-2D Perovskite Light-Emitting Diodes. *Adv. Funct. Mater.* **2021**, *31*, 2103890.

(42) Ren, Z.; Yu, J.; Qin, Z.; Wang, J.; Sun, J.; Chan, C. C. S.; Ding, S.; Wang, K.; Chen, R.; Wong, K. S.; Lu, X.; Yin, W.; Choy, W. C. H. High-Performance Blue Perovskite Light-Emitting Diodes Enabled by Efficient Energy Transfer between Coupled Quasi-2D Perovskite Layers. *Adv. Mater.* **2021**, *33*, 202005570.

(43) Li, X.; Dar, M. I.; Yi, C.; Luo, J.; Tschumi, M.; Zakeeruddin, S. M.; Nazeeruddin, M. K.; Han, H.; Grätzel, M. Improved Performance and Stability of Perovskite Solar Cells by Crystal Crosslinking with Alkylphosphonic Acid Omega-Ammonium Chlorides. *Nat. Chem.* **2015**, *7*, 703–711.

(44) Li, H.; Shi, J.; Deng, J.; Chen, Z.; Li, Y.; Zhao, W.; Wu, J.; Wu, H.; Luo, Y.; Li, D.; Meng, Q. Intermolecular π - π Conjugation Self-Assembly to Stabilize Surface Passivation of Highly Efficient Perovskite Solar Cells. *Adv. Mater.* **2020**, *32*, 1907396.

(45) Zhao, Y.; Zhu, P.; Huang, S.; Tan, S.; Wang, M.; Wang, R.; Xue, J.; Han, T. H.; Lee, S. J.; Zhang, A.; Huang, T.; Cheng, P.; Meng, D.; Lee, J. W.; Marian, J.; Zhu, J.; Yang, Y. Molecular Interaction Regulates the Performance and Longevity of Defect Passivation for Metal Halide Perovskite Solar Cells. *J. Am. Chem. Soc.* **2020**, *142*, 20071–20079.

(46) Xu, W.; Hu, Q.; Bai, S.; Bao, C.; Miao, Y.; Yuan, Z.; Borzda, T.; Barker, A. J.; Tyukalova, E.; Hu, Z.; Kaweck, M.; Wang, H.; Yan, Z.; Liu, X.; Shi, X.; Uvdal, K.; Fahlman, M.; Zhang, W.; Duchamp, M.; Liu, J.-M.; Petrozza, A.; Wang, J.; Liu, L.-M.; Huang, W.; Gao, F. Rational Molecular Passivation for High-Performance Perovskite Light-Emitting Diodes. *Nat. Photonics* **2019**, *13*, 418–424.

(47) Shang, Y.; Liao, Y.; Wei, Q.; Wang, Z.; Xiang, B.; Ke, Y.; Liu, W.; Ning, Z. Highly stable hybrid perovskite light-emitting diodes based on Dion-Jacobson structure. *Sci. Adv.* **2019**, *5*, No. eaaw8072.

(48) Wang, C.; Han, D.; Wang, J.; Yang, Y.; Liu, X.; Huang, S.; Zhang, X.; Chang, S.; Wu, K.; Zhong, H. Dimension control of in situ fabricated CsPbClBr₂ nanocrystal films toward efficient blue light-emitting diodes. *Nat. Commun.* **2020**, *11*, 6428.

(49) Gu, H.; Xia, J.; Liang, C.; Chen, Y.; Huang, W.; Xing, G. Phase-pure two-dimensional layered perovskite thin films. *Nat. Rev. Mater.* **2023**, *8*, 533–551.

(50) Qing, J.; Ramesh, S.; Xu, Q.; Liu, X. K.; Wang, H. Y.; Yuan, Z. C.; Chen, Z.; Hou, L. T.; Sum, T. C.; Gao, F. Spacer cation alloying in Ruddlesden-Popper perovskites for efficient red light-emitting diodes with precisely tunable wavelengths. *Adv. Mater.* **2021**, *33*, 2104381.

(51) Jiang, J.; Chu, Z.; Yin, Z.; Li, J.; Yang, Y.; Chen, J.; Wu, J.; You, J.; Zhang, X. Red perovskite light-emitting diodes with efficiency exceeding 25% realized by co-spacer cations. *Adv. Mater.* **2022**, *34*, 2204460.

(52) Quan, L. N.; Zhao, Y.; García de Arquer, F. P.; Sabatini, R.; Walters, G.; Voznyy, O.; Comin, R.; Li, Y.; Fan, J. Z.; Tan, H.; Pan, J.; Yuan, M.; Bakr, O. M.; Lu, Z.; Kim, D. H.; Sargent, E. H. Tailoring the Energy Landscape in Quasi-2D Halide Perovskites Enables Efficient Green-Light Emission. *Nano Lett.* **2017**, *17*, 3701–3709.

(53) Futscher, M. H.; Lee, J. M.; McGovern, L.; Muscarella, L. A.; Wang, T.; Haider, M. I.; Fakhruddin, A.; Schmidt-Mende, L.; Ehrler, B. Quantification of ion migration in CH₃NH₃PbI₃ perovskite solar cells by transient capacitance measurements. *Mater. Horiz.* **2019**, *6*, 1497–1507.

(54) Pitarch-Tena, D.; Ngo, T. T.; Vallés-Pelarda, M.; Pauporté, T.; Mora-Seró, I. Impedance spectroscopy measurements in perovskite solar cells: device stability and noise reduction. *ACS Energy Lett.* **2018**, *3*, 1044–1048.

(55) Scheidt, R. A.; Kamat, P. V. Temperature-driven anion migration in gradient halide perovskites. *J. Chem. Phys.* **2019**, *151*, 134703.

(56) Shen, T. L.; Loganathan, A.; Do, T. H.; Wu, C.; Chen, Y.; Chen, Z.; Chiu, N.; Shih, C.; Wang, H.; Chou, J.; Hsu, Y.; Liu, C.; Chang, Y.; Fu, Y.; Lai, W.; Chen, P.; Wen, T.; Guo, T. Characterize and retard the impact of the bias-induced mobile ions in CH₃NH₃PbBr₃ perovskite light-emitting diodes. *Adv. Opt. Mater.* **2022**, *10*, 2101439.

(57) Xiao, Z.; Kerner, R. A.; Zhao, L.; Tran, N. L.; Lee, K. M.; Koh, T.-W.; Scholes, G. D.; Rand, B. P. Efficient perovskite light-emitting diodes featuring nanometre-sized crystallites. *Nat. Photonics* **2017**, *11*, 108–115.