

Supporting Information

High Performance and Stable Pure-Blue Quasi-2D Perovskite Light-Emitting Diodes by Multifunctional Zwitterionic Passivation Engineering

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Section 1: Materials and methods.

Materials and Chemical. 2-Phenylethylamine hydrochloride (PEACl, 99.5%), cesium bromide (CsBr, 99.9%), lead chloride (PbCl₂, 99.99%), lead bromide (PbBr₂, 99.99%), Poly(N-Vinylcarbazole) (PVK, 99.99%), 1,3,5-tris (1-phenyl-1H-benzimidazole-2-yl) benzene (TPBi, 99%) and lithium fluoride (LiF, 99%) were purchased from Xi'an Polymer Light Technology Corp. Polyvinylpyrrolidone (PVP, 99.99%), dimethyl sulfoxide (DMSO, 99.9%) and chlorobenzene were purchased from Sigma-Aldrich. 3-(benzyltrimethylammonio) propanesulfonate (3-BAS, 99%) was purchased from Aladdin. All the materials were used without further purification.

Perovskite precursor solution preparation. For precursor, PEACl, CsBr, PbCl₂ and PbBr₂ with a molar ratio of 0.08: 0.10: 0.025: 0.075 were prepared in DMSO (the concentration of Pb²⁺ is 0.1 M). The 3-BAS additive was dissolved in DMSO with 10 mg/ml for use. The ratio of 3-BAS in 3-BAS-based perovskite precursor is 10% (vol/vol), respectively. Finally, the perovskite precursor solutions were stirred overnight before use.

Device fabrication. Before the 5 minutes UV-ozone treatment, indium tin oxide (ITO) (1.5 cm×1.5 cm) glass substrates were sequentially cleaned by acetone, alcohol, detergent, deionized water and alcohol under the ultrasonic bath and then dried by drying tunnel. Then, the samples were transferred into an N₂-filled glovebox. PVK was spin-coated onto the ITO substrates at 4000 rpm, followed by annealing at 130 °C for 15 min. The perovskite films were fabricated by spin-coating the precursor solutions at 3000 rpm, followed by annealing on a preheated hotplate at 65 °C for 20 min. Finally, TPBi (40 nm), LiF (1 nm), and Al (130 nm) were deposited by thermal evaporation under vacuum pressure below 1×10^{-5} mbar with the evaporation rate of 1.0, 0.1, and 5 Å s⁻¹, respectively. The active device area was defined as 0.07 cm² by the overlapping area of Al and ITO electrodes.

Perovskite film and device characterizations. The film morphology and cross-section image were measured by scanning electron microscopy (SEM, Philips XL30 FEG) and tapping mode atomic force microscopy (AFM, NT-MDT Ntegra Prima). Top-view SEM measurement was taken by FEI Quanta 450 FEG. The film absorption spectra were measured by UV-Vis absorption spectrometer (UV-2600, SHIMADZU). Energy level alignment was evaluated

based on ultraviolet photoelectron spectroscopy (UPS, ESCALAB Xi+). The XEUSS SAXS/WAXS system was used to perform the GIWAXS measurement. The incidence angle of X-ray beam with the wavelength of 1.54 Å was set to be 0.2° for the perovskite thin films prepared on Si substrates. Contact angles were performed using a drop shape analyzer (DSA100). Microscopic PL imaging was applied to investigate the ion migration in the perovskite film under a constant bias (4.0 V) and a 365 nm light source (Lx POL, LABOMED). J - V - L and EQE curves of the PeLEDs were recorded simultaneously by a commercialized system (XPQYEQE-350-1100, Guangzhou XiPu Optoelectronics Technology Co., Ltd.) which was equipped with an integrated sphere (GPS-4P-SL, Labsphere) and a photodetector array (S7031-1006, Hamamatsu Photonics). Transient EL measurements were performed by using the commercially available Paios system (FLUXiM AG). The square wave signal is generated by signal generator (SDG 2082X), and the wave form was measured by oscilloscope (SDS1102X-E). PLQYs of the perovskite films were measured by a commercialized PLQY measurement system from Ocean Optics with a 365 nm LEDs excitation. FTIR spectra (NICOLET iS10) and X-ray photoelectron spectrometer (XPS, EscaLab 250Xi, Thermo Fisher) were used to evaluate the interaction between the 3-BAS and the Pb-(Cl/Br) framework. Time-resolved PL (TRPL) decay spectra were obtained using Edinburgh FL980 fluorescence spectrophotometer with a picosecond diode laser as the excitation wavelength at 371.6 nm. TRPL decay curves were fitted by a triexponential decay function:

$$A(t) = A_1 \exp\left(-\frac{t}{\tau_1}\right) + A_2 \exp\left(-\frac{t}{\tau_2}\right) + A_3 \exp\left(-\frac{t}{\tau_3}\right)$$

The average lifetimes were calculated based on:

$$\tau_{avg} = \frac{A_1\tau_1^2 + A_2\tau_2^2 + A_3\tau_3^2}{A_1\tau_1 + A_2\tau_2 + A_3\tau_3}$$

Picosecond transient absorption experiments were performed under ambient conditions by using a Helios pump-probe system (Ultrafast Systems LLC) combined with an amplified femtosecond laser system (Coherent). Optical parametric amplifier (TOPAS-800-fs) provided a 380 nm pump pulse (≈ 1 nJ pulse⁻¹ at the sample), which was excited by a Ti: sapphire regenerative amplifier (Legend Elite-1K-HE; 800 nm, 35 fs, 7 mJ pulse⁻¹, 1 kHz) and seeded with a mode-locked Ti:S-5 sapphire laser system (Micra 5) and a Nd: YLF laser (Evolution 30) pumped. Focusing the 800 nm beams (split from the regenerative amplifier with a tiny portion,

≈ 400 nJ pulse⁻¹) onto a sapphire plate produced the white light continuum (WLC) probe pulses (420-780 nm and 820-1600 nm). The pulse-to-pulse fluctuation of the WLC is corrected by a reference beam split from WLC. A motorized optical delay line was used to change the time delays (0-8 ns) between the pump and probe pulses. The instrument response function (IRF) was determined to be ≈ 100 fs by a routine cross-correlation procedure.

The kinetics curve is fitted by a multiple-exponential function: $A(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2) + A_3 \exp(-t/\tau_3)$, where A_1 , A_2 and A_3 are amplitudes, τ_1 is the fast decay time constant assigned to the carrier transferring from smaller-n-phases to larger-n-phases in perovskite films, τ_2 and τ_3 are the slow decay time constants.

First-Principles calculations. We performed the first-principles calculations in the frame of density functional theory (DFT) with the Vienna ab initio simulation package (VASP).^{50,51} The exchange-correlation energy is described by the Perdew-Burke-Ernzerhof (PBE) form of generalized-gradient approximation (GGA) exchange-correlation energy functional.⁵² The structure optimization of CsPbBr₃ perovskite has been carried out by allowing all atomic positions and lattice parameters to vary and relax until the energy difference of successive atom configurations was less than 10^{-6} eV. The force on each atom in the relaxed structures was less than 0.015 eV \AA^{-1} . The cutoff energy for the plane-wave basis set was set to 400 eV. The k-point spacing was set to be smaller than 0.03 \AA^{-1} over Brillouin zone (BZ).

Charge Difference Density of 3-BAS-doped CsPbBr₃ (001) surface. To intuitively observe the interfacial binding between 3-BAS molecule and CsPbBr₃ (001) surface, their charge density difference (CDD) was calculated according to

$$\Delta\rho = \rho_{system} - \rho_{CsPbBr_3} - \rho_{3-BAS}$$

where ρ_{system} is the charge density of the 3-BAS-incorporated CsPbBr₃ (001) surface and ρ_{CsPbBr_3} and ρ_{3-BAS} are the charge densities of CsPbBr₃ (001) surface and 3-BAS molecule, respectively.

Adsorption energy. To calculate the adsorption energies of 3-BAS molecule on CsPbBr₃ (001) surface with uncoordinated Pb²⁺ defect, we first construct the corresponding surfaces with 3-, 3- and 4- times unit cell in the x, y and z periodic directions, respectively. In order to obtain the

most stable structures, their structure optimizations were performed by fixing middle 2 layers and setting the thickness of 15 Å in vacuum. The optimization of the exchange correlation functional and convergence conditions is consistent with that of bulk, while the k-point mesh was changed to $1 \times 1 \times 1$. Then, the adsorption energies were calculated by the following equation:

$$\Delta E = E_{system} - E_{slab} - E_{adsorption}$$

Where E_{system} , E_{slab} and $E_{adsorption}$ represent the total energies of the adsorption system, substrate surface and adsorbate, respectively.

Defect formation energy before and after passivation. The Br defect formation energies before and after passivation were calculated by the following equation:

$$\Delta E_{defect} = E_{defect-system} + E_t[Br] - E_{perfect-system}$$

where, $E_{defect-system}$, $E_t[Br]$ and $E_{perfect-system}$ represent the total energies of the defect system, isolated Br atom and perfect system, respectively.

Section 2: Supplementary figures.

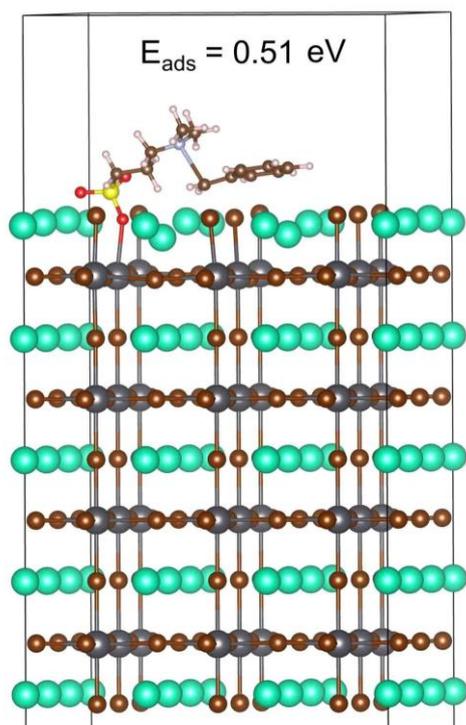


Fig. S1 Surface configuration after relaxation at the 3-BAS/CsPbBr₃ interface.

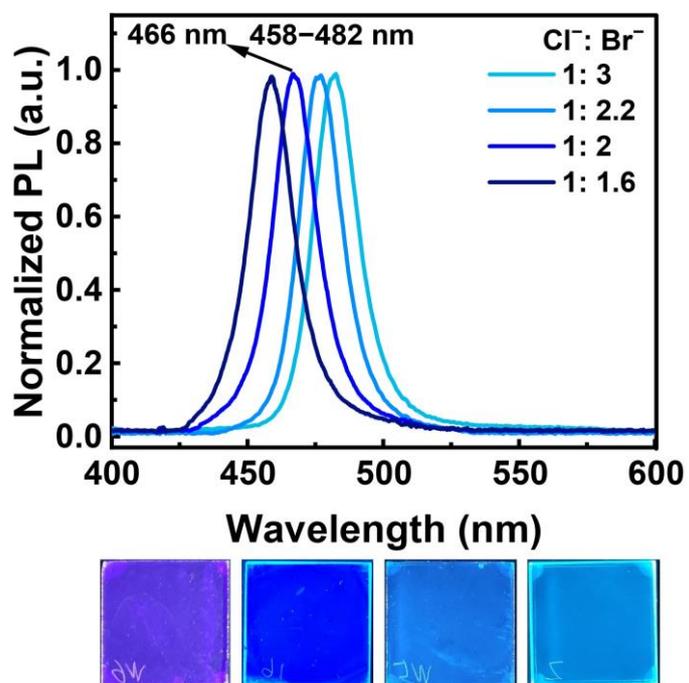


Fig. S2 Normalized PL spectra with different ratios of Cl⁻: Br⁻ in the perovskite films.

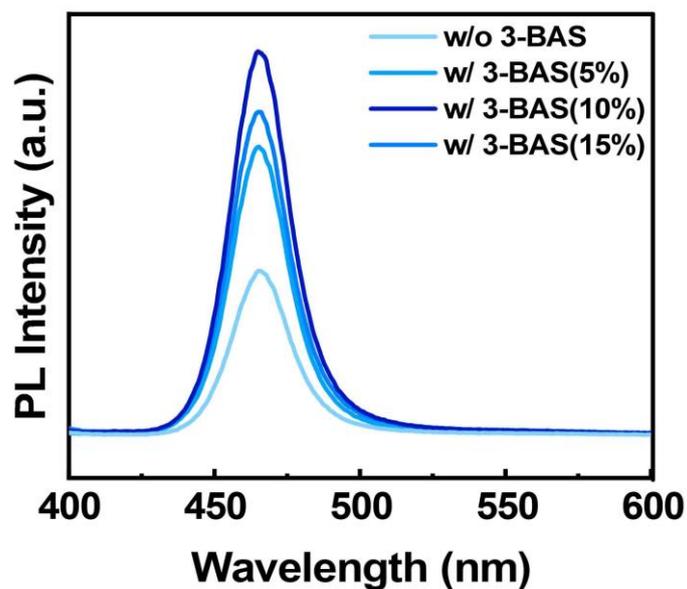


Fig. S3 Steady-state PL spectra of the quasi-2D control and targeted perovskite films (5, 10, 15 vol%).

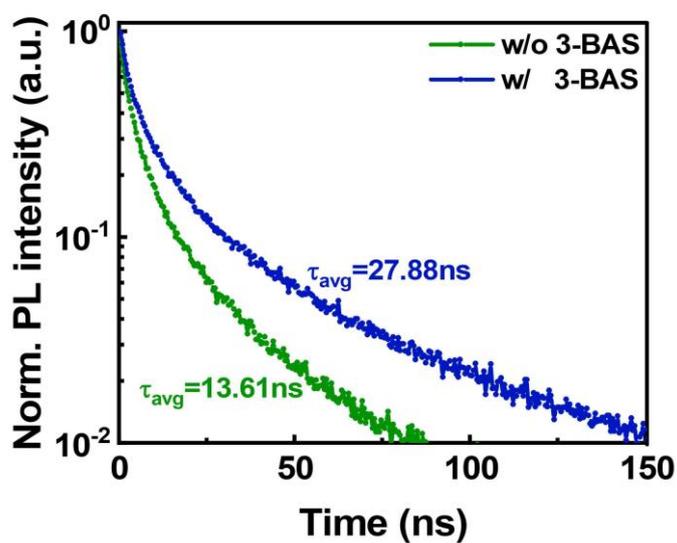


Fig. S4 TRPL spectra of the quasi-2D control and targeted perovskite films.

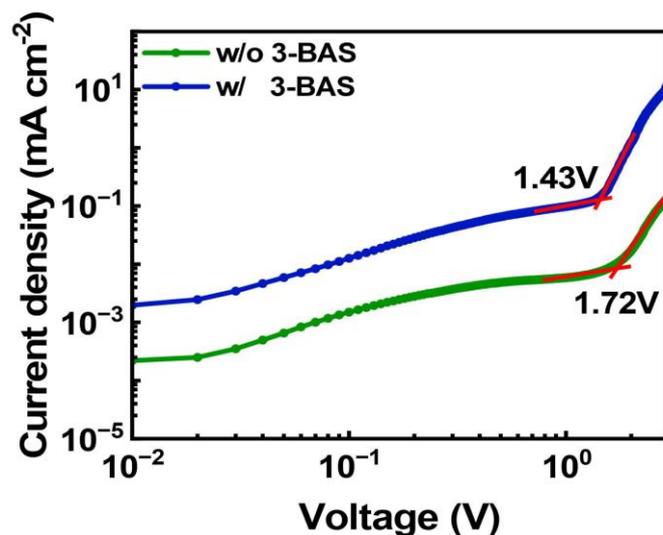


Fig. S5 J - V curves of the hole-only control and 3-BAS-treated devices with the structure of ITO/PVK/perovskite/MoO_x/Ag.

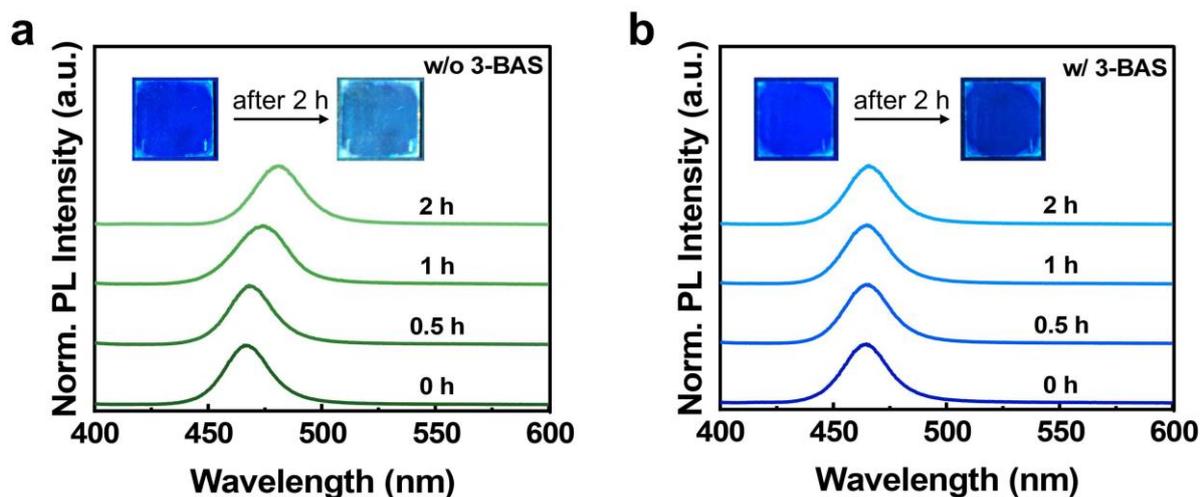


Fig. S6 Stability evolution of PL spectra of the (a) control and (b) targeted pure-blue perovskite films in the ambient environment (40% RH and 25 °C). The insets are the photographs of the pure-blue perovskite films under UV lamp illumination.

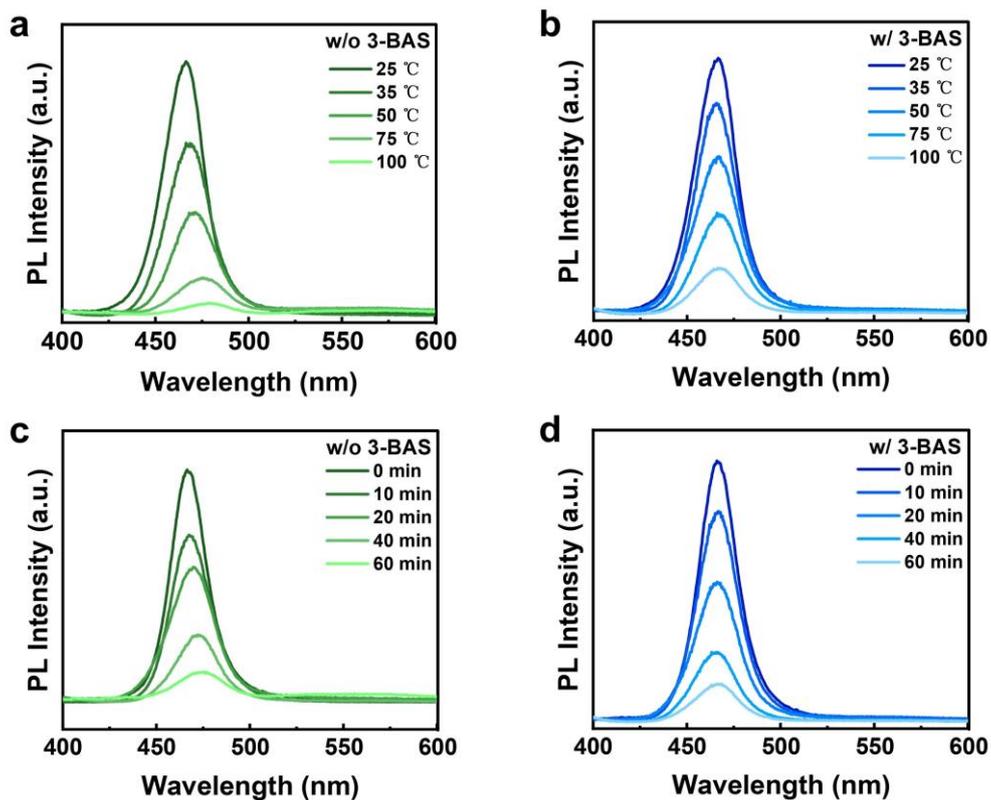


Fig. S7 Temperature-dependent PL spectra of the (a) control and (b) targeted perovskite films. UV-light dependent PL spectra the (c) control and (d) targeted perovskite films (365 nm, 5 mW).

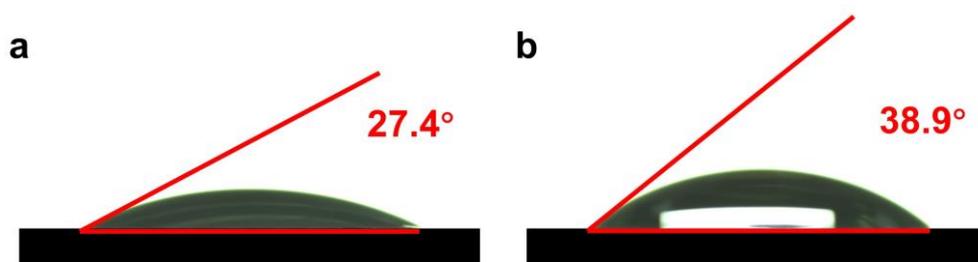


Fig. S8 Water contact angles of the (a) control and (b) targeted perovskite films.

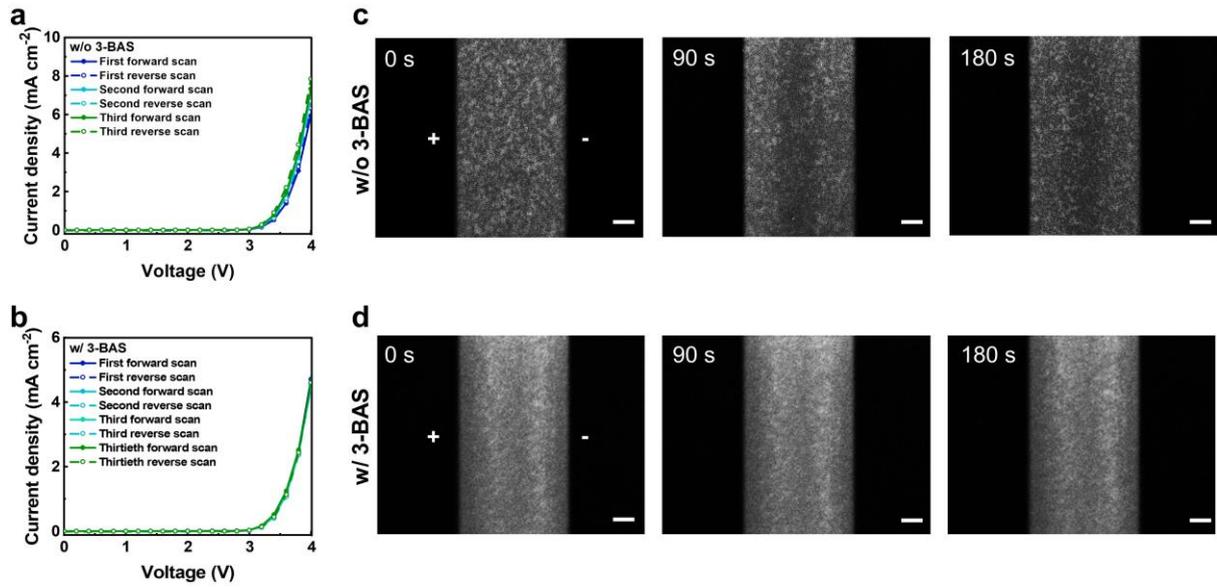


Fig. S9 Forward and reverse scanning current density-voltage curves with a scan rate of 0.02 V s^{-1} for the (a) control and (b) targeted PeLEDs. Time-dependent PL images of the (c) control and (d) targeted films at 4 V bias using wide-field PL imaging microscopy. The polarity of the external electric field is marked by the '+' and '-' symbols. The perovskite samples were excited by a 365 nm light source (scale bars=10 μm).

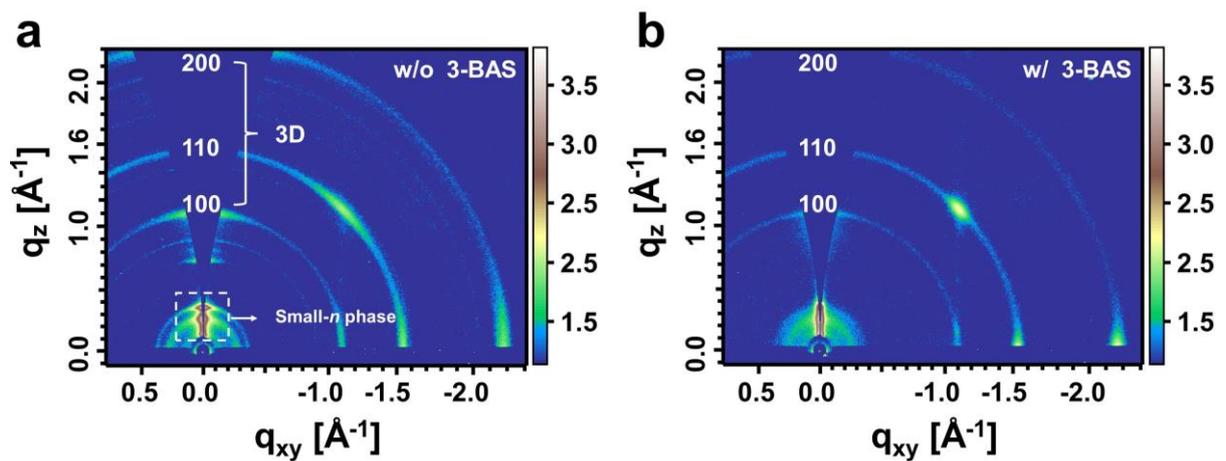


Fig. S10 2D GIWAXS patterns of the a) control and b) targeted perovskite films.

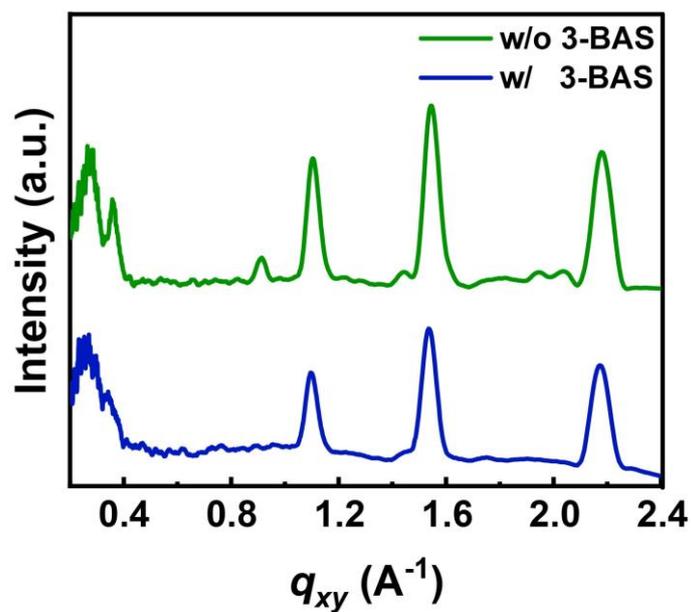


Fig. S11 In-plane cut-line profile of GIWAXS for the control and targeted perovskite films.

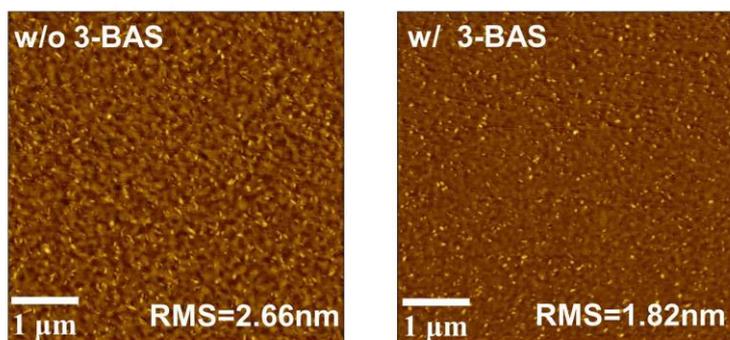


Fig. S12 AFM surface images of the quasi-2D control and targeted perovskite films (size: $5 \mu\text{m} \times 5 \mu\text{m}$).

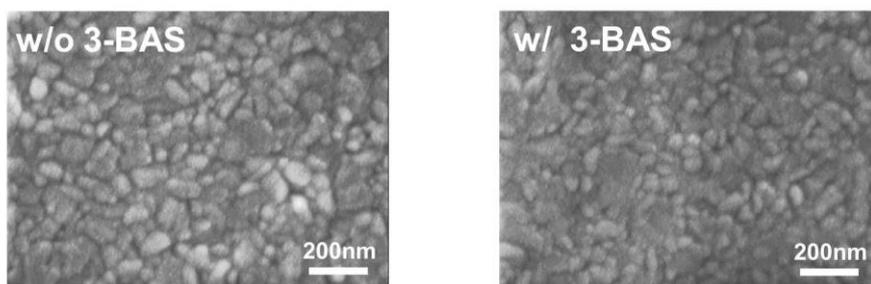


Fig. S13 Top-view SEM images of the quasi-2D control and targeted perovskite films.

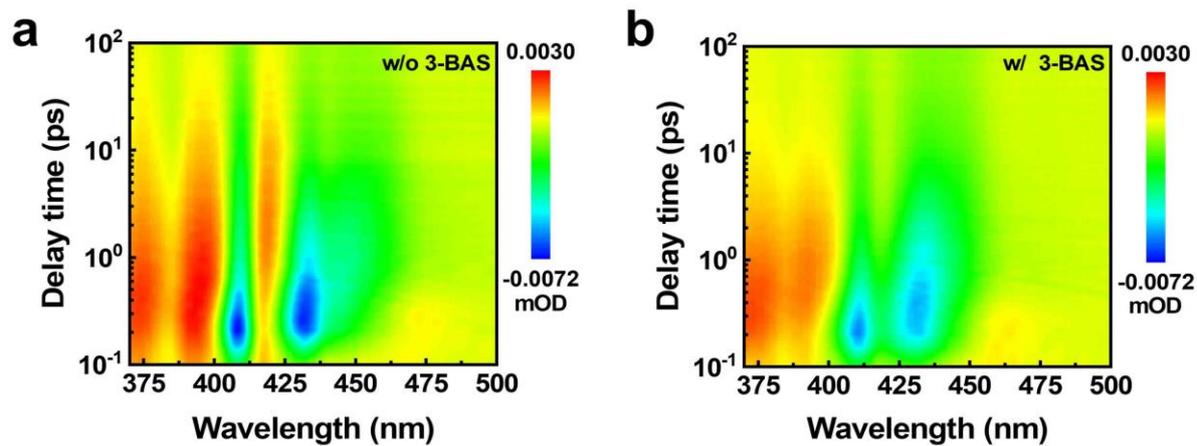


Fig. S14 TA color maps of the quasi-2D (a) control and (b) targeted perovskite films.

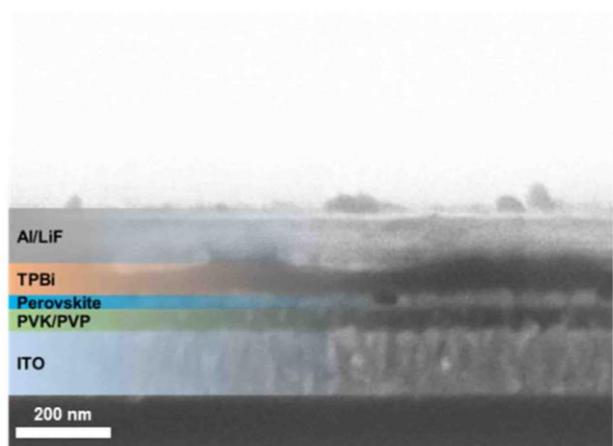


Fig. S15 Cross-section SEM image of the PeLEDs.

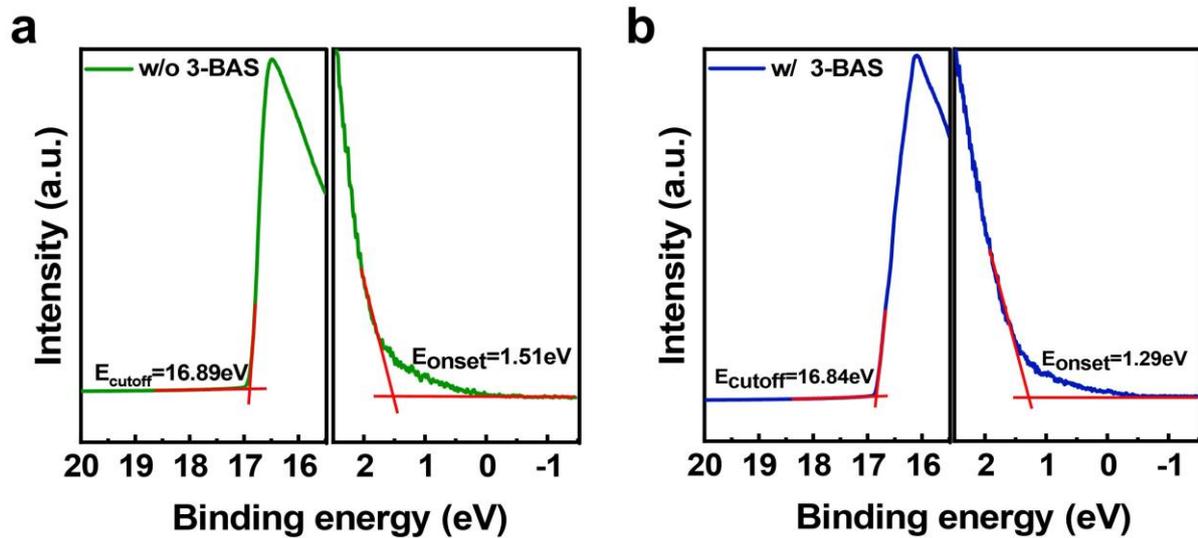


Fig. S16 UPS results for the quasi-2D (a) control and (b) targeted perovskite films.

By obtaining the tangent-line secondary cutoff and onset edges data from UPS measurements, the valence band maximum (VBM) of the perovskite films is calculated using the following formula:

$$VBM = hv - (E_{cutoff} - E_{onset})$$

where hv represents the energy of the UV light source of HeI (21.22 eV). The value of the conduction band minimum (CBM) can be obtained using the following formula:

$$CBM = VBM - E_g$$

where E_g represents the optical band gap value calculated from UV-vis absorption of the perovskite films. The optical band gaps of the control and targeted films were determined to be 2.62 and 2.65 eV, respectively. Taking all the above calculations into account, the energy levels of perovskite films can be obtained.

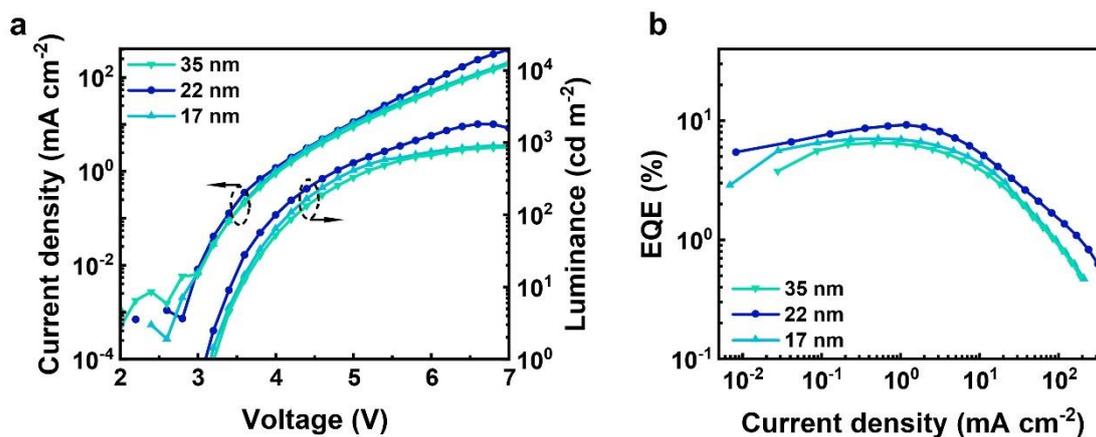


Fig. S17 (a) J - V - L and (b) EQE - J curves of PeLEDs with different perovskite film thicknesses.

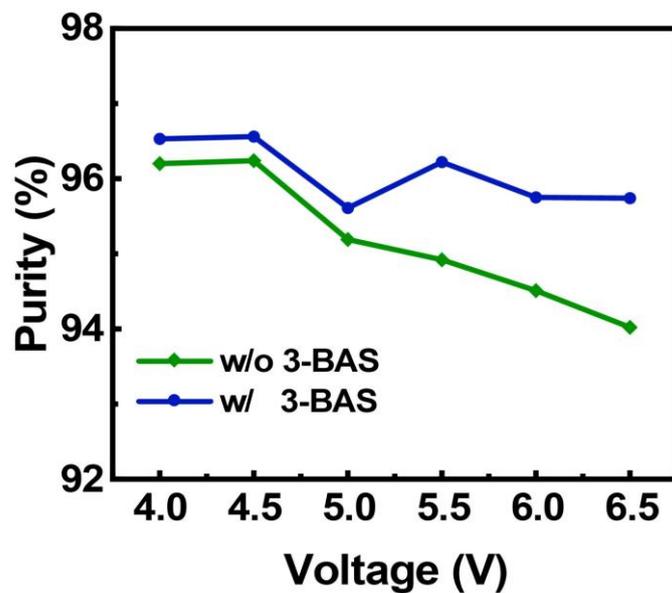


Fig. S18 The color purity of control and targeted PeLEDs.

Table S1 PL lifetime characteristics of the quasi-2D control and targeted perovskite films.

3-BAS	$\tau_1(\text{ns})$	A_1	$\tau_2(\text{ns})$	A_2	$\tau_3(\text{ns})$	A_3	$\tau_{\text{avg}}(\text{ns})$
w/o	1.39	0.35	4.82	0.47	20.59	0.18	13.61
w/	2.61	0.52	10.38	0.36	43.25	0.15	27.88

Table S2 The relevant TA parameters of the quasi-2D control and targeted perovskite films.

3-BAS		A_1	$\tau_1(\text{ns})$	A_2	$\tau_2(\text{ns})$	$\tau_{\text{avg}}(\text{ns})$
	n=2	0.89	0.38	0.33	16.13	15.17
w/o	n=3	0.62	1.38	0.39	12.69	11.03
	n \geq 4	0.75	5.39	0.17	42.67	29.22
	n=2	1.01	0.49	0.23	10.19	8.51
w/	n=3	0.58	2.57	0.32	13.12	10.37
	n \geq 4	0.47	4.15	0.35	17.07	13.92

Table S3 Performance summary for the pure-blue quasi-2D PeLEDs reported in literature.

References	Perovskite materials	EL Peak (nm)	Max. EQE (%)	Max. L. (cd m ⁻²)
12	p-F-PEA ₂ Cs _{n-1} Pb _n (Br _{0.55} Cl _{0.45}) _{3n+1}	468	11.87	710
15	(Cs/PEA)Pb(Cl/Br) ₃	468	3.2	1010
16	Rb _{0.1} Cs _{1.2} FA _{0.2} Pb(Cl _x Br _{1-x}) _{3.5}	467	5.5	330
53	PBA ₂ (Cs/MA/FA) _{n-1} Pb _n Br _{3n+1}	465	2.34	145
54	(Cs/FA/p-F-PEA)Pb(Cl/Br) ₃	469	4.14	451
55	DPPA-CsPbBr ₂ Cl	464	3.03	442
56	CsPbBr _{1.43} Cl _{1.57} :PEO:PVP:LiPF ₆	464	2.2	543
57	(Cs/FA/PEA)(Pb/Rb)(Cl/Br) ₃	466	4.4	~1000
57	(Cs/FA/DPEA)(Pb/Rb)(Cl/Br) ₃	468	6.5	~600
This work	PEA₂Cs_{n-1}Pb_n(Cl/Br)_{3n+1}	466	9.25	1806