Nanoplatelet Modulation in 2D/3D Perovskite Targeting Efficient Light Emitting Diode

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SUPPLEMENTARY TEXT

ST1 Estimation of crystallite size

The empirical Scherrer formula is used to estimate the crystal domain size:

$$D = \frac{K\lambda}{\beta cos\theta}$$

Where D refers to the mean size of the ordered (crystalline) domains, K refers the shape factor which has a value ~0.9, λ is the wavelength of Cu-$K_{\alpha1}$ X-ray (λ=1.546 Å), β is the line broadening at FWHM in radians and θ is the incident angle of X-ray

ST2. Calculation of lattice spacing (d) and <n>

According to Bragg's Law:

$$2dsin\theta = n\lambda \; ,$$

Where d is lattice spacing, θ is incident angle of X-ray, λ is wavelength of X-ray (for GIXRD is 1.24 Å) and n is the reflection order (here, we define as 1).

So, the lattice spacing d can be given as:

$$d = \frac{n\lambda}{2sin\theta} \; ,$$

As θ and q have a relationship as $q = \frac{4\pi sin\theta}{\lambda}$,

The d can be calculated from q:

$$d = \frac{2\pi}{q} \; .$$

Using the formula above, we can calculate the lattice spacing (d) for <n>=1 is 19.02 Å. As we get the (020) peak for <n>=2 is 5.06 nm^{-1}, the calculated d for (010) which is located at 2.53 nm^{-1} is 24.83 Å.

ST3. Calculation of trap states

The current-voltage (*J*-*V*) characteristics for the hole-only device is shown in **Figure S13**. At low voltages (< V_{TFL}, V_{TFL} is the trap-filled limit voltage), an ohmic response is indicated according to the linear *J*-*V* relation (red line). A trap-filling part (blue line) was drawn by abruptly increase of the current injection at a voltage (> V_{TFL}) when all the traps are been filled. In this region, the trap density was calculated using following relation. [1, 2]

$$n_t = \frac{2V_{TFL}\varepsilon\varepsilon_0}{eL^2}$$

where ε is relative dielectric constant (~4 for $CsPbBr_3$)[3], ε_0 is the vacuum permittivity, e is the electron charge, and L is the thickness of our perovskite (~ 50 nm). V_{TFL} of 60%-NMABr (FABr) (0.65 V) is lower than that of 60%-NMABr (0.85 V), which indicates reduction in trap density of perovskite after addition of FABr. The trap densities were calculated to be 1.5×10^{17} cm^{-3} for 60%-NMABr and 1.1×10^{17} cm^{-3} for 60%-NMABr (FABr).

ST4. EQE Calculation Method

External quantum efficiency (EQE) is defined as the ratio of the number of photons generated by the LED device per second (N_P (V)) to the number of electron-hole pairs injected into the device per second (N_e (V)) at a bias of V.

$$EQE = \frac{N_P(V)}{N_e(V)} = \frac{N_P}{I(V)/e} \times 100\%$$

Here, I (V) is the current (A) passing through a LED device at a certain bias (V), e is the elementary charge which is $1.6 \times 10^{-19}\,C$.

The N_P can be calculated by:

$$N_P(V) = \frac{\Phi_e}{E_{average} \times 1.6 \times 10^{-19}}$$

Where Φ_e is the radiant flux (W). $E_{average}$ refers to the average photon energy for the whole EL spectrum at a bias whose unit is eV. Here, a conversion factor (1.6×10^{-19} J eV^{-1}) is needed for calculation.

The relationship between radiant flux (Φ_e, unit: W) and luminous flux (Φ_v, unit: lm) can be described as:

$$\Phi_v = K_m \int \Phi_{e,\lambda} V(\lambda) d\lambda$$

Where V (λ) is the luminosity function, representing the average spectral sensitivity of human visual perception of brightness. λ is the wavelength (nm). K_m is a constant, which has a value of 683 lm W^{-1} at 555 nm.

Thus, Φ_e can be given by:

$$\Phi_e = \int \frac{\Phi_{v,\lambda}}{K_m V(\lambda) d\lambda}$$

The perovskite LED can be assumed as a Lambertian radiator according to its angular intensity light distribution profile, and the device shows uniform emission in over 1 cm^2, as shown in Figure.S12b. So $\Phi_{v,\lambda}$ = πAL, where π is the solid angle, A is the active area (m^2) of a working LED devices; L is the luminance (cd · m^{-2}) measured by PR670. Then Φ_e is given by:

$$\Phi_e = \frac{\pi AL}{K_m \int V(\lambda) d\lambda}$$

The relationship between the photon energy ($E_{average}$, unit: eV) and the photon wavelength (λ, unit: nm) is photon wavelength (nm) = 1240/photon energy (eV). Then, $E_{average}$ is calculated by following equation:

$$E_{average} = \frac{\int F(\lambda) \frac{\lambda}{1240} d\lambda}{\int F(\lambda) d\lambda}$$

F(λ) is the photon radiometric value (W · sr^{-1} · m^{-2}) collected by PR670.

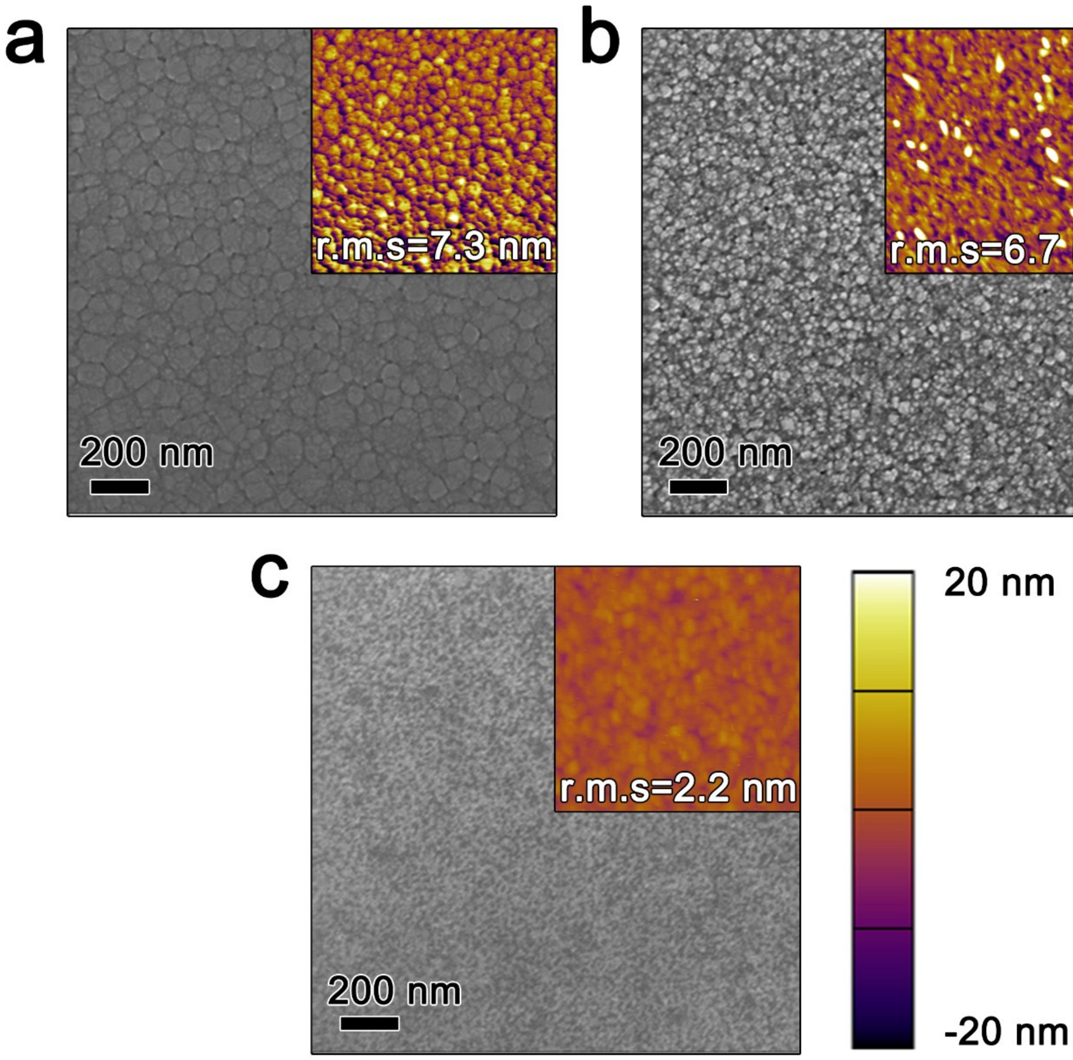

Figure S1 SEM (scale bar: **200 nm**) images of a) 20%-NMABr, b) 40%-NMABr, c) 80%-NMABr perovskite films. The insets are AFM (2 μm × 2 μm) images of different perovskite films spin-coatted on PVK at Si substrate with a scale bar of -20 nm to 20 nm.

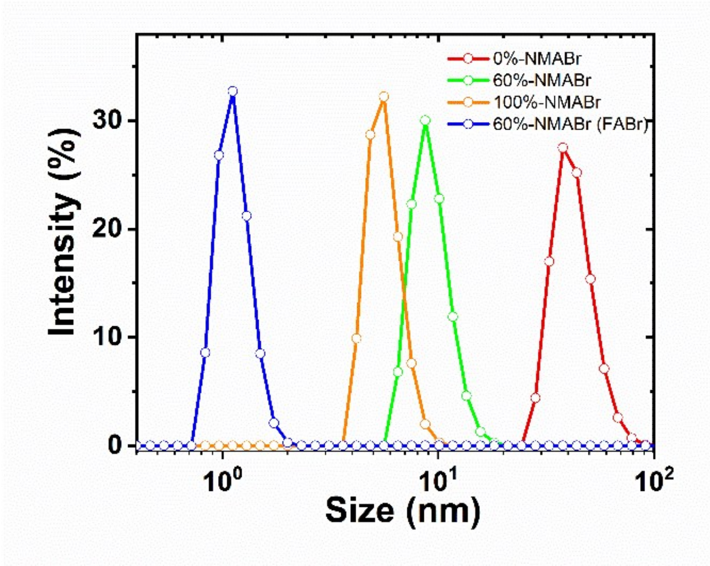

Figure S2 DLS measurement of different perovskite precursors dissolved in DMSO.

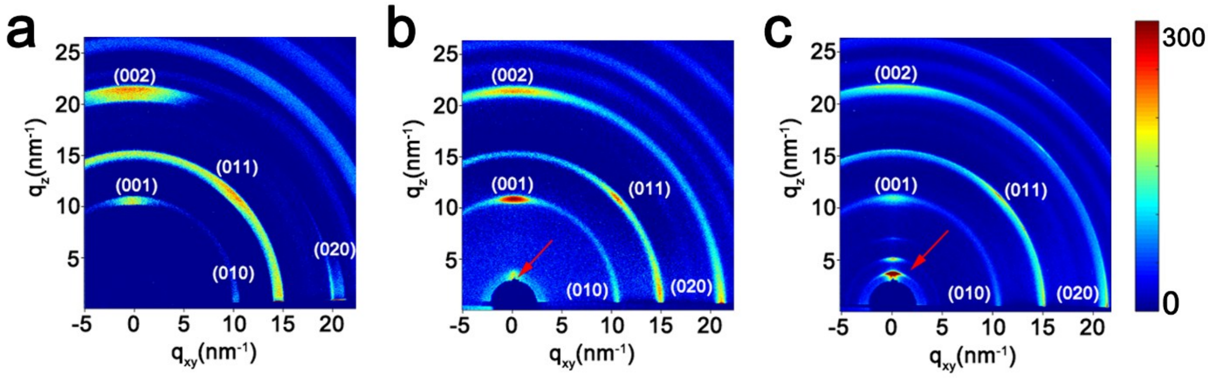

Figure S3 GIXRD diffraction rings of a) 20%-NMABr, b) 40%-NMABr and c) 80%-NMABr perovskite films. The red arrows in the 2D GIXRD images highlight diffraction peaks from the separation distance between discrete RP layers.

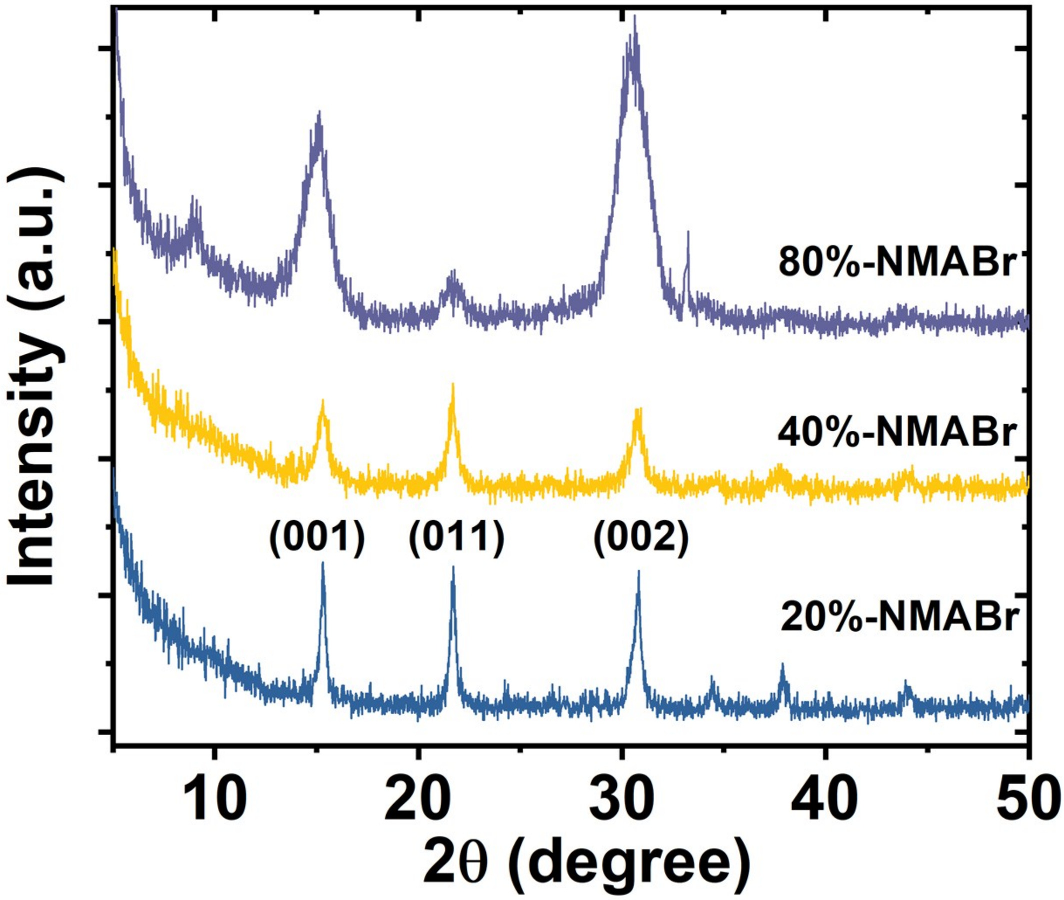

Figure S4 θ-2θ XRD spectra of the perovskite films with 20%-, 40%- and 80%-NMABr, respectively.

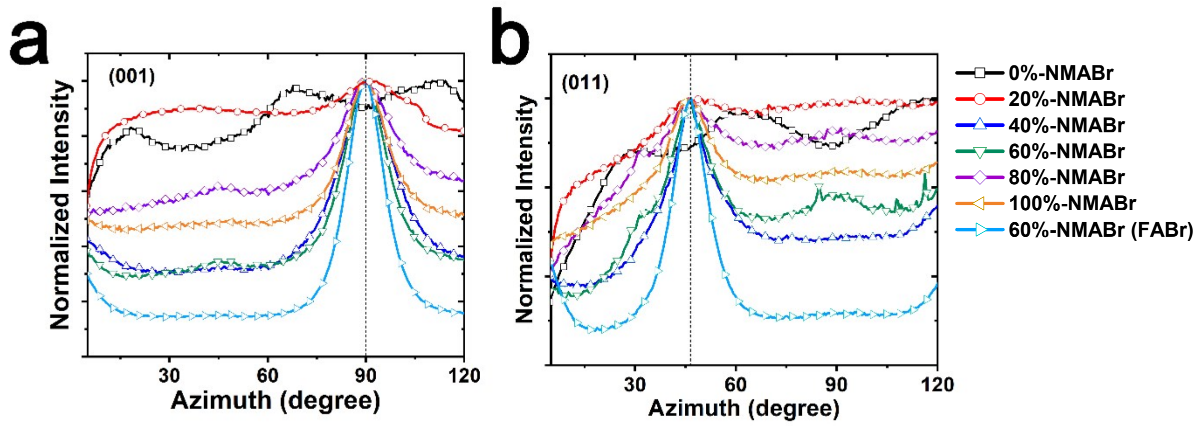

Figure S5 Radially integrated intensity plots along a) q= 11.05 nm^{-1}, assigned to (001) ring; b) q= 15.61 nm^{-1}, assigned to (011) ring of GIXRD diffraction intensity rings of perovskite films with 0%-, 20%-, 40%-, 60%-, 80%-, 100%- NMABr and 60%-NMABr (FABr), respectively.

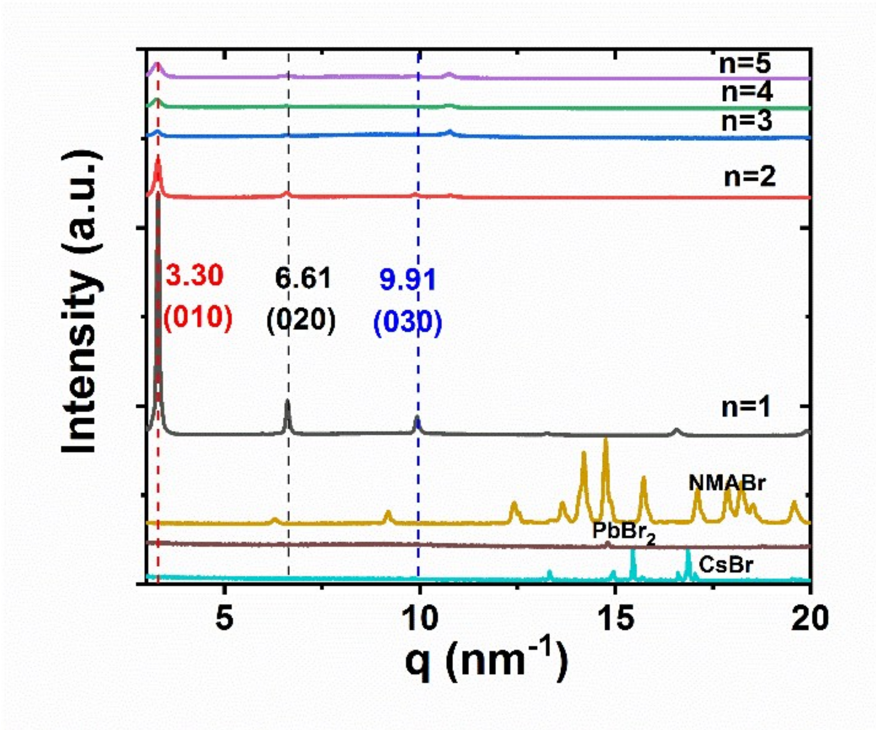

Figure S6 θ-2θ XRD spectra of layered $NMA_2Cs_{n-1}Pb_nBr_{3n+1}$ perovskite films with different <n> values using NMABr as organic spacer. The layered $NMA_2Cs_{n-1}Pb_nBr_{3n+1}$ perovskite films with different <n> values are prepared according to chemical component formula.

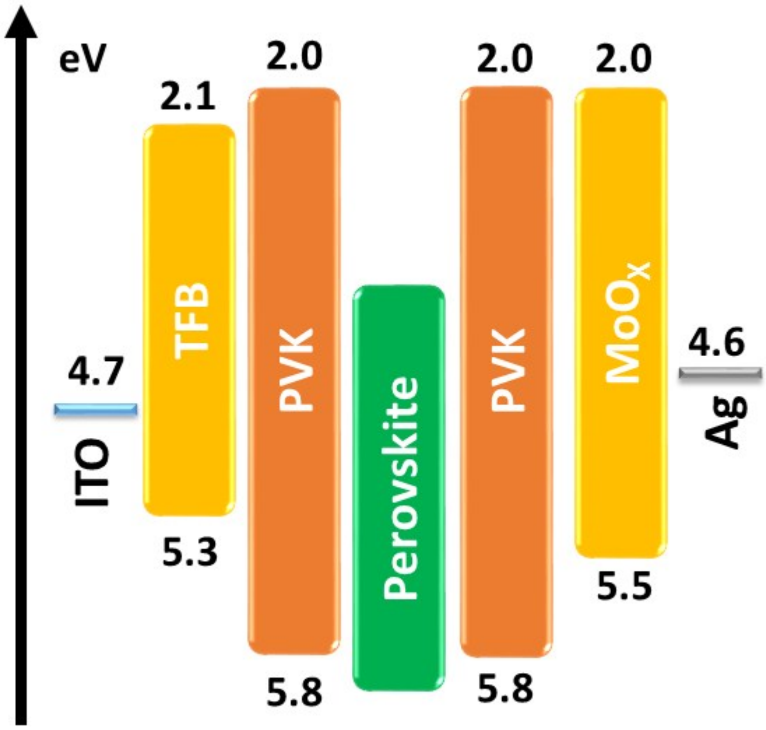

Figure S7 Energy band diagram of the hole only device for measuring hole transport properties of perovksite layer. PVK (8 mg/ml in CB) is spin-coatted on the surface of perovskite to prevent the injection of electrons. MoO_x/Ag are evaporated as electrode with a thickness of 20 nm/100 nm respectively.

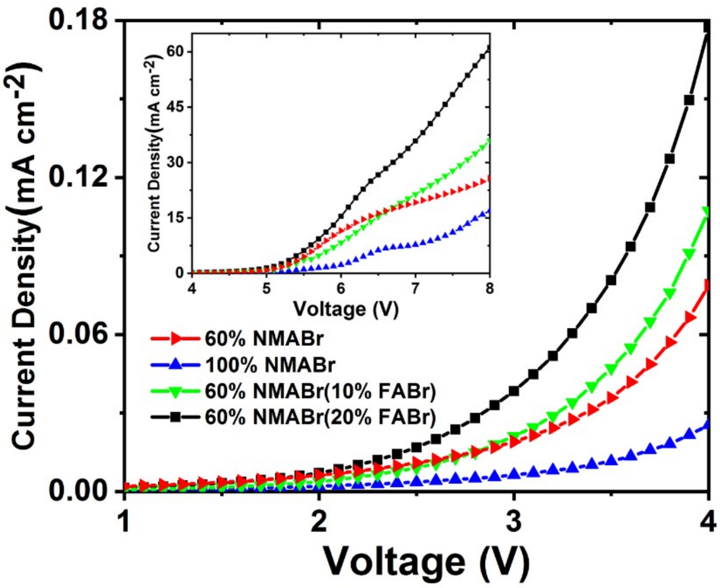

Figure S8 Current density-voltage characteristics of hole-only PeLED devices with 60%-NMABr, 60%-NMABr (10% FABr), 60%-NMABr (20% FABr) and 100% NMABr perovskites (Inset: Current density at the range of 4-8 V)..

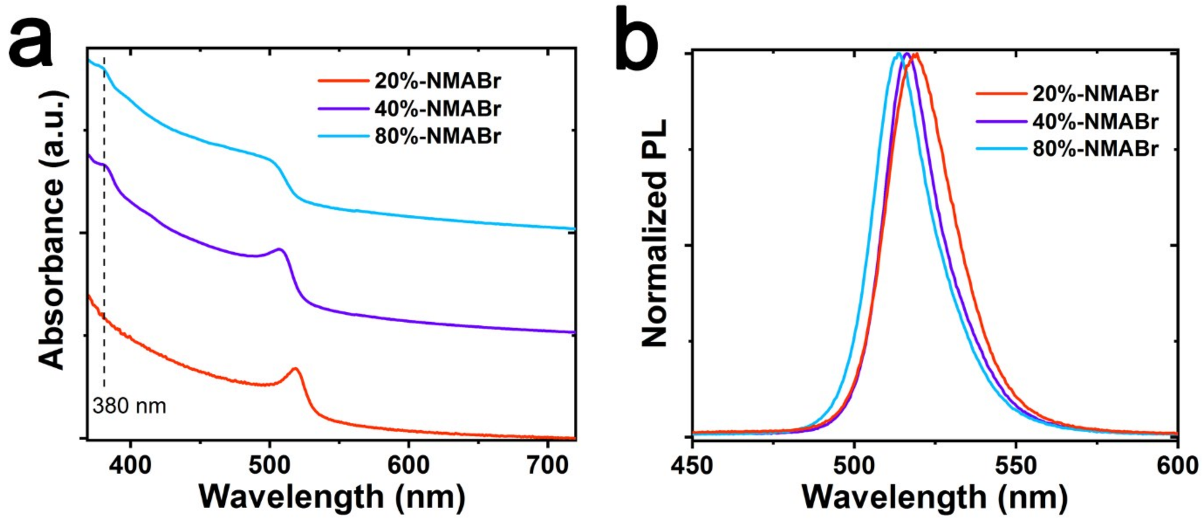

Figure S9 a) UV-vis absorption and b) PL spectra of 20%-NMABr, 40%-NMABr and 80%-NMABr perovskite films.

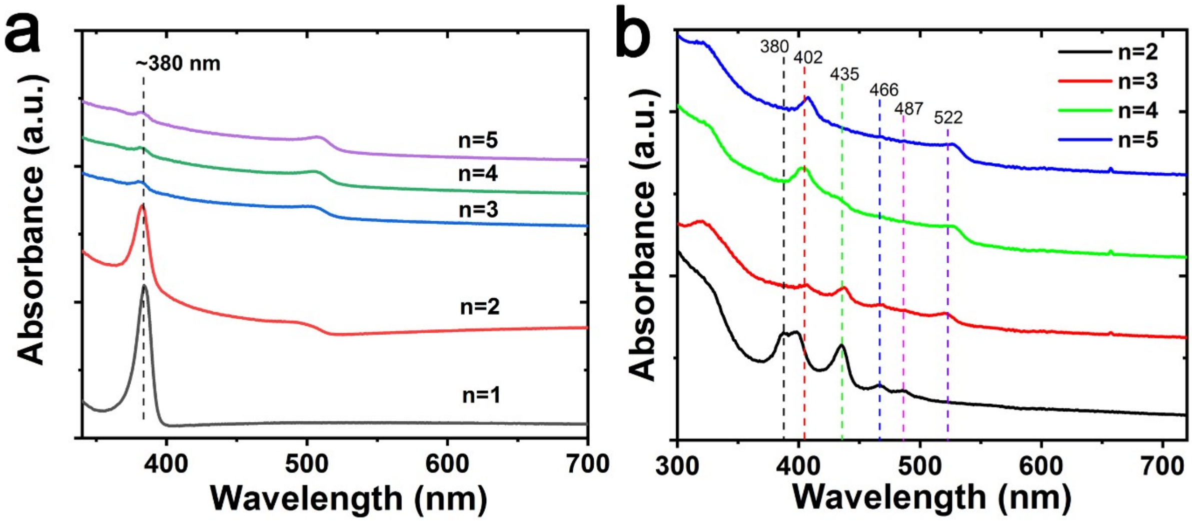

Figure S10 a) UV-vis absorption spectra of layered $NMA_2Cs_{n-1}Pb_nBr_{3n+1}$ perovskites with different <n> values using NMABr as organic ligand. b) UV-Vis absorption spectra of layered $NMA_2FA_{n-1}Pb_nBr_{3n+1}$ perovskites with different <n> values using NMABr as organic ligand. The layered perovskite films with different <n> values are prepared according to chemical component formula.

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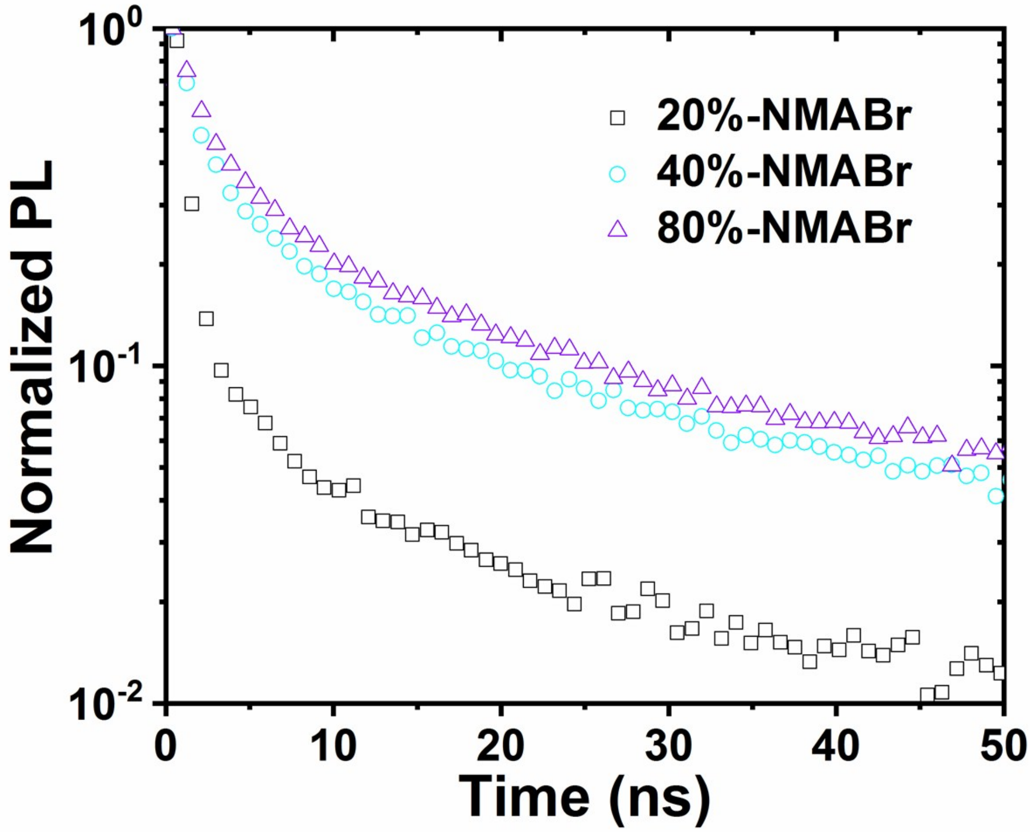

Figure S11 PL decay lifetimes of perovskite films with 20%, 40%, 80% NMABr on quartz, respectively. The PL is probed by a 370-nm-wavelength laser.

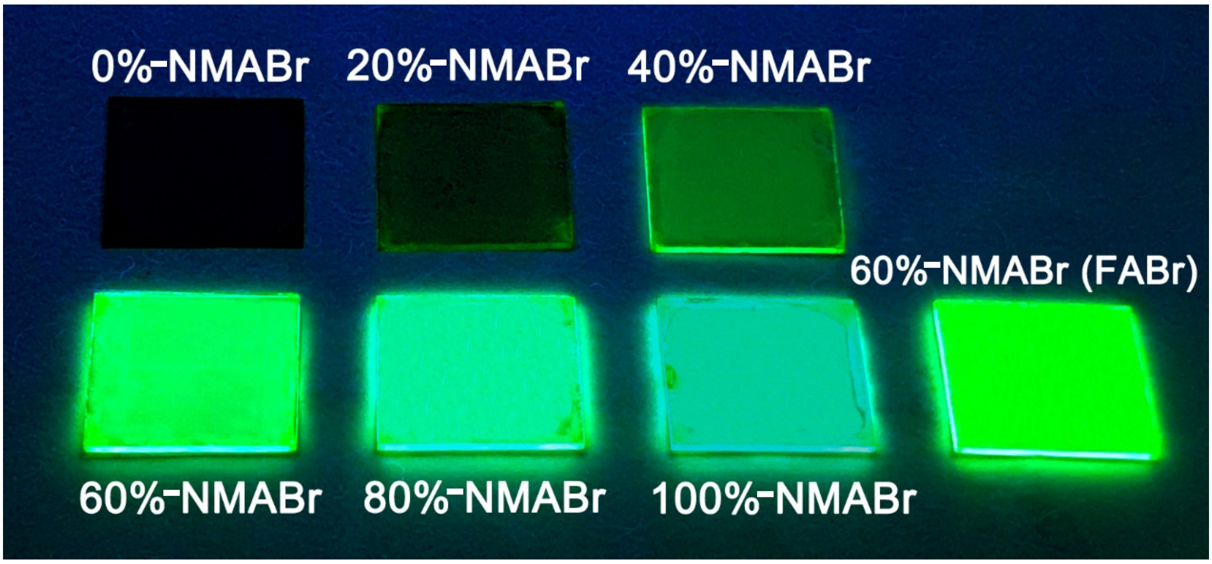

Figure S12 Photographs of perovskite films with 0%-, 20%-, 40%-, 60%-, 80%-, 100%- NMABr and 60%-NMABr (FABr) under 365 nm ultraviolet light illumination.

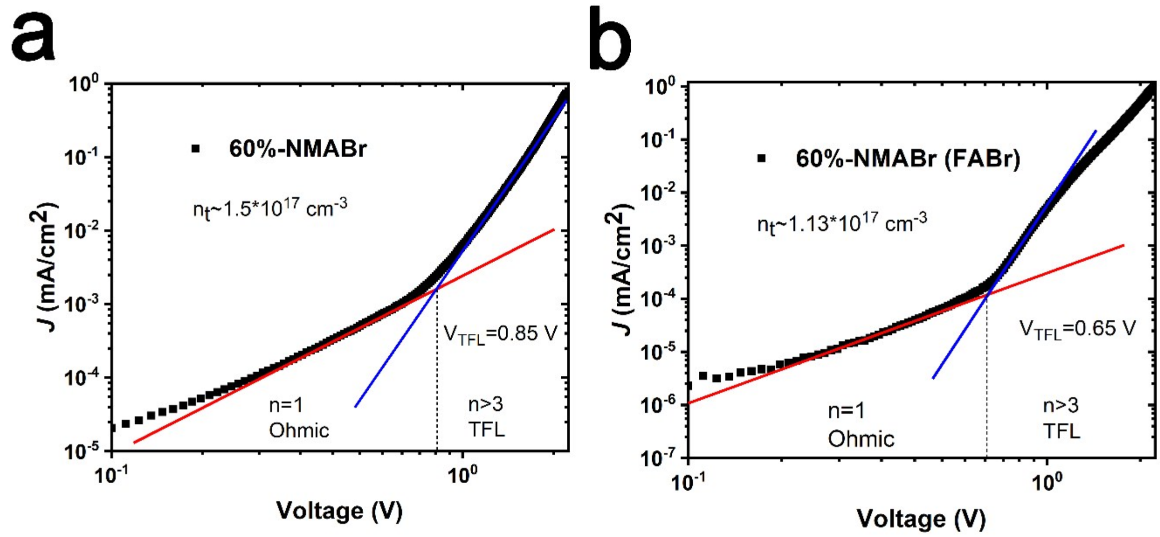

Figure S13 Current (*J*)-voltage characteristics of hole-only device (ITO/Perovskite/MoOx/Ag).

J-V characteristic of hole only device a) 60%-NMABr and (b) 60%-NMABr (FABr).

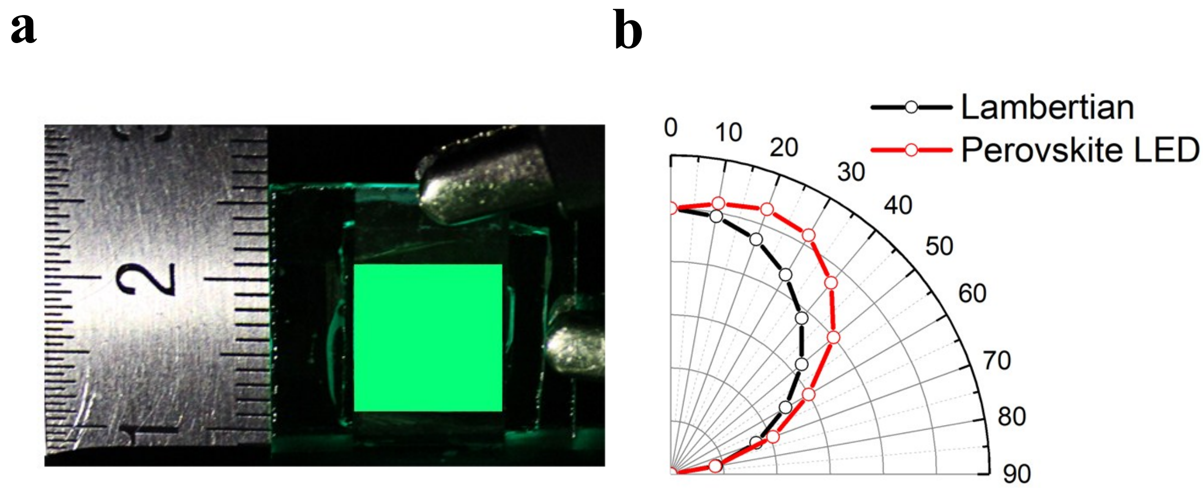

Figure S14 a) A photograph of a 60% NMABr (FABr) based LED device with an emitting size of 1×1 cm^2 operated at a bias of 3.5 V. b) Angular intensity profile a perovskite LED based on perovskite film with 60%-NMABr (FABr). The angular dependent Lambertian emitter profile is calculated by an equation of $I = I_0 \cos\theta$. Here, I is light intensity at an angle of θ. I_0 is the light emitting light intensity at normal direction. I_0 is assumed to be “1”.

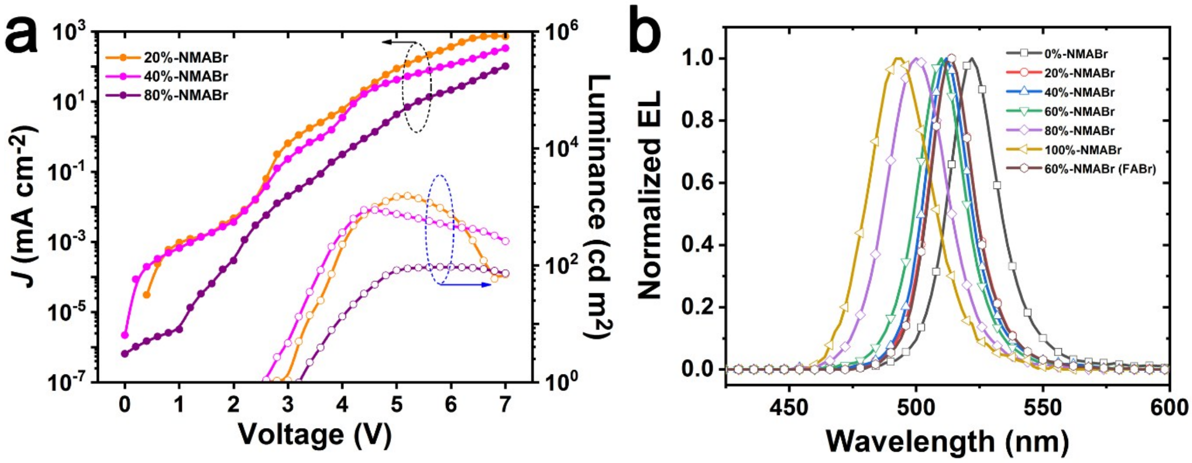

Figure S15 a) I-V-L curves for LED devices based on perovskite films with 20%-, 40%-, 80%-NMABr. b) EL peaks of the LED devices based on the perovskite films with 0%-, 20%-, 40%-, 60%-, 80%-, 100%- NMABr and 60%-NMABr (FABr).

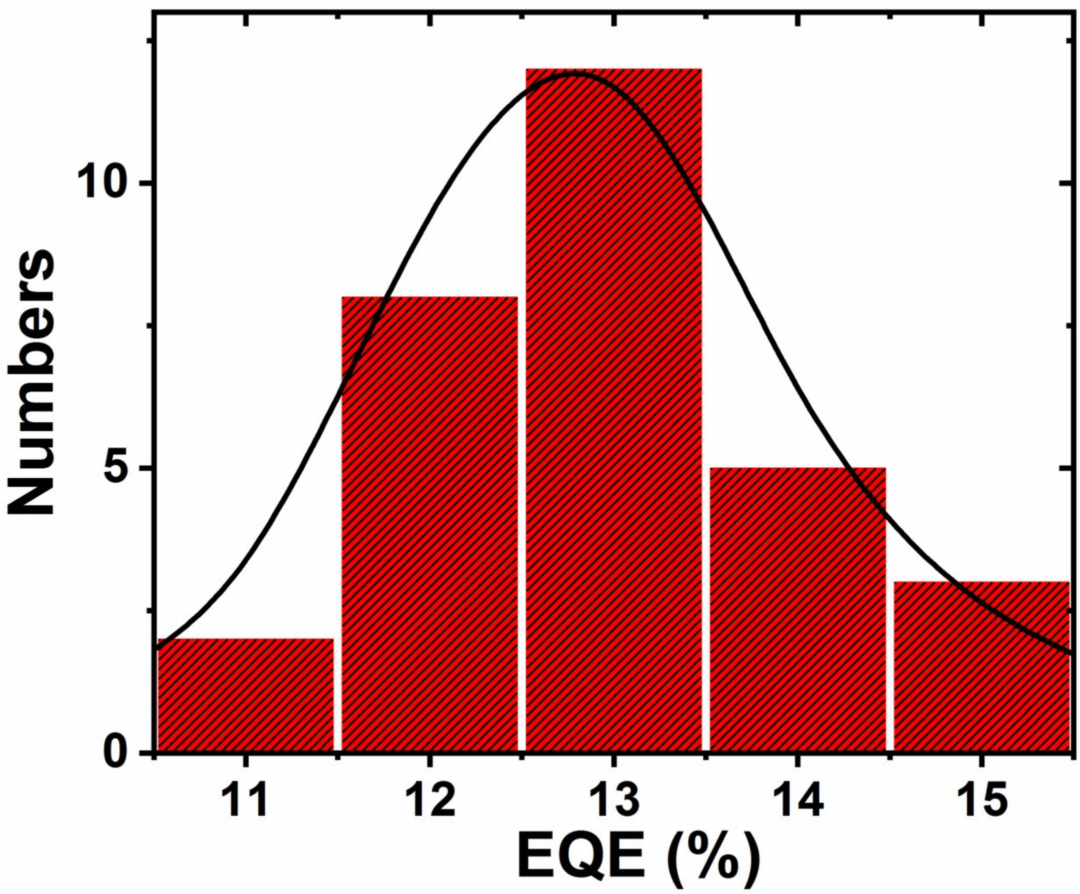

Figure S16 EQE distribution of 30 devices based on 60%-NMABr (FABr) perovskite LED.

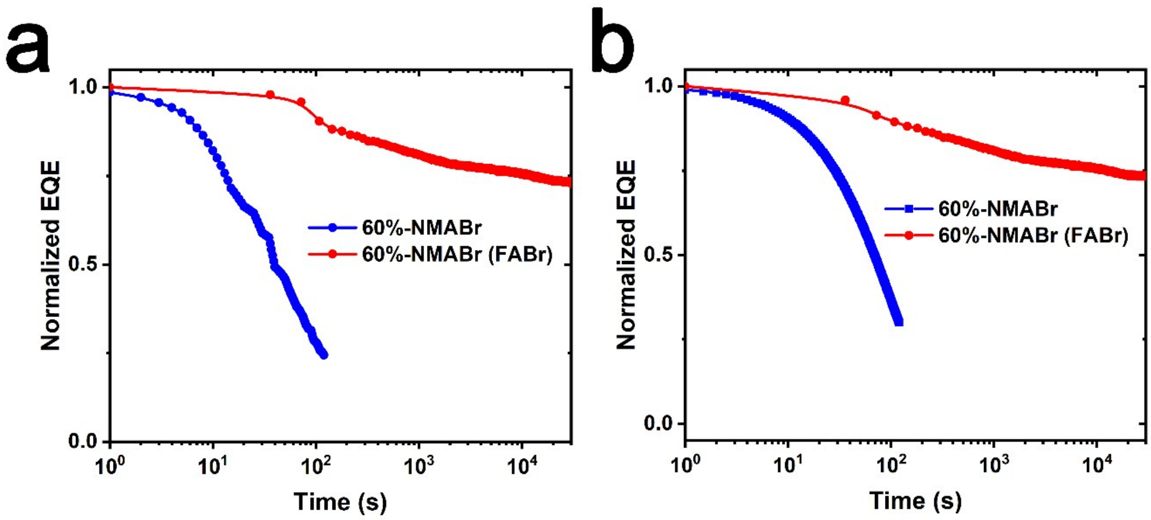

Figure S17 Time-dependent EQE under a) constant voltage of 3.5 V, b) constant current density of 0.2 mA cm^{-2} for the LEDs based on 60%-NMABr and 60%-NMABr (FABr) perovskite films.

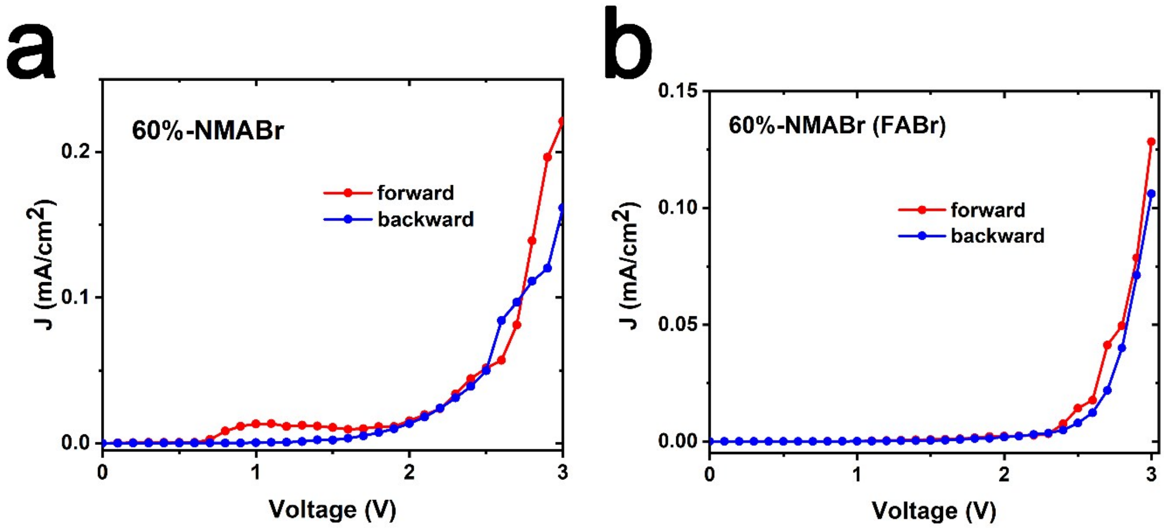

Figure S18 Forward (from 0 V to 3 V) and backward (from 3 V to 0 V) scan of a) 60%-NMABr perovskite and b) 60%-NMABr (FABr) perovskite film.

Table S1 Different chemical molar ratios for perovskite precursors dissolved in DMSO.

Molar Ratio (NMABr:CsBr:$PbBr_2$:FABr)	CsBr (mg/ml)	FABr (mg/ml)	$PbBr_2$ (mg/ml)	NMABr (mg/ml)
0:10:10:0	42.56	0	73.40	0
2:10:10:0	4.256	0	73.40	9.48
4:10:10:0	42.56	0	73.40	18.97
6:10:10:0	42.56	0	73.40	28.45
8:10:10:0	42.56	0	73.40	37.94
10:10:10:0	42.56	0	73.40	47.42
6:10:10:1	42.56	2.99	73.40	28.45
6:9:10:2	38.31	4.98	73.40	28.45

Table S2 Calculated crystallite size from (100) θ-2θ XRD diffraction according to the empirical Scherrer Equation.

Perovskite	Size (nm)
0%-NMABr	36.0
20%-NMABr	22.7
40%-NMABr	12.2
60%-NMABr	6.6
80%-NMABr	5.4
100%-NMABr	5.6
60%-NMABr (FABr)	6.9

Table S3 Electrical output characteristics of the perovskite with different amount of NMABr.

Perovskite	V_T (V)	CE ($cd\ A^{-1}$)	PE ($lm\ W^{-1}$)	L_{max} ($cd\ m^{-2}$)	EQE (%)	EL peak (nm)
20%-NMABr	3.0	3.8±0.5	3.0±0.4	1401.7±55.5	1.2±0.2	514
40%-NMABr	2.5	8.0±0.3	6.3±0.3	890.7±24.9	2.7±0.1	512
80%-NMABr	3.2	5.8±0.9	5.2±0.9	67.7±21.3	2.4±0.4	500

Table S4 A summary for reported output characteristics of representative green perovskite LEDs.

Emitters	Structures	EL peak (nm)	CE (cd A^{-1})	EQE (%)	Reference
$MAPbBr_3$	3D Film	517	0.3	0.1	[4]
$Cs_{0.87}MA_{0.13}PbBr_3$	3D Film	520	33.9	10.4	[5]
$CsPbBr_3$	QD	512	13.3	6.27	[6]
$MAPbBr_3$	2D	513	17.1	9.3	[7]
$CsPbBr_3$	2D	514	31.2	10.4	[8]
$FAPbBr_3$	2D	532	62.4	14.36	[9]
This work	2D/3D	514	46.8	14.9	

Reference

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