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Supporting Information

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Keywords: perovskite light-emitting diodes; high efficiency; blue emission; stability; ion migration
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Supplementary Figure S12. Transient absorption contour maps of the PFNBr-modified perovskite film on nanosecond timescales.

In order to gain insights into the energy transfer processes in the blue quasi-2D perovskites, transient absorption (TA) spectroscopy was performed for the PFNBr-modified perovskite film. As shown in Figure 2b and Supplementary Figure S10, three distinctive ground state bleach (GSB) peaks at 414 nm, 445 nm and 456 nm are observed. According to the second derivative of the steady state absorption in Figure 2a, the first two sharp bleaches agree well with the quasi-2D perovskite absorption features of the bilayer ($n = 2$) and trilayer ($n = 3$) phases, whereas the third broad bleach feature is attributed to the spectrally overlapped signals of the $n \geq 4$ components. The bandgap of these quasi-3D components with $n \geq 4$ can be determined by the boundary between the band edge bleach feature and the bandgap renormalization feature at the early times (0.1 ps). The latter appears at 474 nm for our perovskites, as shown in Figure 2b, and this bandgap is related to the emissive species. Figure 2c shows the dynamic evolution of the three bleach bands (414 nm, 445 nm and 456 nm) and the band edge of the emissive spices (474 nm). At time zero, the three bleach bands build up very fast and simultaneously, indicating that the initial photoexcitations are formed.
in all three domains under 400 nm excitation. Following the fast buildup, the bilayer \((n = 2)\) shows a dominant ultrafast decay with a time constant of 0.43 ps, corresponding to the depopulation of \(n = 2\) component. This agrees well with a second-stage fast buildup of the other two bleach bands. After fast charge delocalization from the quasi-2D \((n = 2, 3)\) to quasi-3D domains, charge carriers within the quasi-3D domains undergo fast cooling processes to the band edge with a time constant of approximately 1 ps, confirmed by the buildup of the 474 nm bleach and the recovery of the bandgap renormalization signal. The cooling process is also accompanied by a small red-shift of the large-\(n\) bleach peak (Figure 2b). Since excitons are more tightly bound in quasi-2D perovskites, they are less susceptible to local defects. These bound electron-hole pairs can be concentrated effectively towards the quasi-3D domains on sub-ps timescales, leading to an efficient energy migration process.

**Supplementary Figure S13.** Excitation-intensity-dependent PLQY of the perovskite films with and without PFNBr modification; the PLQY of the perovskite film with PFNBr modification is as high as 82 % under the excitation intensity of 0.2 mW cm\(^{-2}\).

**Supplementary Figure S14.** The capacitance behaviour of the devices. a, Capacitance versus frequency plot for the devices with and without PFNBr modification. b, Mott–Schottky curves for the devices with and without PFNBr modification.

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Supplementary Table S1. Comparison of our blue perovskite LEDs with other reported blue perovskite LEDs.

| EL Peak (nm) | EQE (%) | Reference                  |
|--------------|---------|----------------------------|
| 485          | 11.2    | This Work                  |
| 476          | 8.0     |                            |
| 467          | 3.2     |                            |
| 458          | 1.9     |                            |
| 483          | 9.5     | Nat. Photon. 2019, 13, 760 |
| 474          | 4.0     |                            |
| 485          | 11.0    | Nat. Commun. 2019, 10, 5633|
| 477          | 4.8     |                            |
| 488          | 12.1    | Nat. Commun. 2020, 11, 4165|
| 480          | 4.1     |                            |
| 480          | 5.7     | Nat. Commun. 2019, 10, 1027|
| 478          | 2.8     |                            |
| 490          | 1.5     | Nat. Commun. 2018, 9, 3541 |
| 476          | 1.3     | Nat. Commun. 2019, 10, 1868|
| 473          | 8.8     | Nat. Commun. 2020, 11, 6428|
| 479          | 12.3    | Nat. Nanotech. 2020, 15, 668|
| 477          | 11.0    | Nat. Commun. 2021, 12, 361 |
Supplementary Table S2. Turn-on voltages for all the relevant devices.

| Emission Peak (nm) | Perovskite based LEDs | Turn-on voltage (V) |
|--------------------|------------------------|---------------------|
| 485 nm             | w/o PFNBr              | 2.62                |
|                    | With PFNBr             | 2.55                |
| 476 nm             | w/o PFNBr              | 2.46                |
|                    | With PFNBr             | 2.48                |
| 468 nm             | w/o PFNBr              | 2.75                |
|                    | With PFNBr             | 2.61                |
| 458 nm             | w/o PFNBr              | 3.3                 |
|                    | With PFNBr             | 2.9                 |

The slightly lower turn-on voltages for devices with emission at 476 nm can be attributed to the fabrication processes such as spin-coating process, thermal annealing process and evaporation process, meanwhile, the measurement error such as delay time after each driven current point, it may be impacted by transient capacitance, also probably induces the slight difference.
Supplementary Table S3. Estimated the grain size for quasi-2D and 3D phases.

| Thin film                                      | Diffract Peak (2θ) | FWHM (rad) | Grain Size (nm) |
|------------------------------------------------|--------------------|------------|-----------------|
| Perovskite without PFNBr modification          | 5.37 /2D (002)     | 0.0050     | 30.8            |
| Perovskite without PFNBr modification          | 4.04 /2D (002)     | 0.0032     | 48.1            |
| Perovskite without PFNBr modification          | 15.96/3D (100)     | 0.0115     | 13.5            |
| Perovskite with PFNBr modification             | 5.34 /2D (002)     | 0.0065     | 23.7            |
| Perovskite with PFNBr modification             | 4.01 /2D (002)     | 0.0089     | 17.3            |
| Perovskite with PFNBr modification             | 15.89/3D (100)     | 0.0195     | 7.9             |
Supplementary Note 1

The binding affinity ($E_{\text{bind}}$) of the cationic polymer to the perovskite surface is computed as

$$E_{\text{bind}} = E_{\text{tot}} - E_{\text{slab}} - E_{\text{ligand}}$$

where $E_{\text{tot}}$ is the total energy of the passivated perovskite supercell, $E_{\text{slab}}$ is the energy of the perovskite slab with a pair of Cs vacancy, and $E_{\text{ligand}}$ the energy of the ligand.

The formation energy of the halide vacancy $E[V_{\text{halide}}^+]$ for a perovskite slab is computed\(^1\) as

$$E[V_{\text{halide}}^+] = E_{\text{tot}}[V_{\text{halide}}^+] - E_{\text{tot}}[\text{bulk}] + \mu_{\text{halide}} + E_F + E_{\text{corr}}$$

Where $E_{\text{tot}}[V_{\text{halide}}^+]$ is the total energy of the supercell containing the halide vacancy, $E_{\text{tot}}[\text{bulk}]$ is the total energy for the equivalent supercell without the defect. $\mu_{\text{halide}}$ is the chemical potential for the halide atom which is the same for the passivated and unpassivated slab. $E_F$ is the Fermi level of the electron referenced to the VBM. $E_{\text{corr}}$ is the correction term for the charged defect calculation in the periodic 2D supercell, which were computed using sxdefectalign2D code\(^2\).

Reference

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