

1 **Efficient Sky-blue Perovskite Light-emitting Diodes via Photoluminescence**
2 **Enhancement**

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1 **Abstract: The efficiencies of green and red perovskite light emitting diodes (PeLEDs) have been**
2 **increased close to their theoretical upper limit, while the efficiency of blue PeLEDs is lagging far**
3 **behind. Here, we report enhancing the efficiency of sky-blue PeLEDs by overcoming a major hurdle**
4 **of low photoluminescence quantum efficiency in wide bandgap perovskites. Blending**
5 **phenylethylammonium chloride into cesium lead halide perovskites yields a mixture of two-**
6 **dimensional and three-dimensional perovskites, which enhances photoluminescence quantum**
7 **efficiency from 1.1% to 19.8%. Adding yttrium (III) chloride into the mixture further enhances**
8 **photoluminescence quantum efficiency to 49.7%. Yttrium is found to incorporate into the three-**
9 **dimensional perovskite grain, while is still rich at grain boundaries and surfaces. The yttrium on**
10 **grain surface increases the bandgap of grain shell, which confine the charge carriers inside grains**
11 **for efficient radiative recombination. Record efficiencies of 11.0 % and 4.8% were obtained in sky-**
12 **blue and blue PeLEDs, respectively.**

13 Perovskite light-emitting diodes (PeLEDs) have drawn tremendous research interest in recent years
14 due to the attractive properties of metal halide perovskite materials such as earth-abundance, solution
15 process capability, large carrier mobility, and excellent color purity.¹⁻¹² The versatile bandgap tuning of
16 perovskite materials (ABX₃) via composition tuning of A, B and X sites makes them applicable in whole
17 visible light range. The application of all inorganic cesium-based perovskite significantly enhances the
18 material stability under electric field.^{13, 14} Very impressive progresses have been made in enhancing the
19 efficiencies of perovskite LEDs in the past few years.³⁻¹² External quantum efficiencies (EQEs) approaching
20 20 % have been reported for both green and red PeLEDs, which rival those from optimized organic
21 phosphorescence light emitting diodes.³⁻⁹ However, blue emission PeLEDs, which are important for display
22 and lighting applications, have efficiency much lower than green and red PeLEDs. The highest reported
23 EQE for sky-blue PeLEDs is still less than 10 %.¹⁵⁻¹⁸ One convenient way to make blue emission perovskite
24 films is to incorporate chlorine (Cl) into Br based perovskites, while one critical issue for the Cl:Br mixed
25 or pure Cl based perovskite films is their small photoluminescence quantum efficiency (PLQE) below 20%,

1 which is much lower than the green or red emission perovskite films with typical PLQE of 70%.^{3-9, 19, 20} Since
2 only about a quarter of light could be extracted out of PeLED devices made on glass substrates due to the
3 mismatched refractive index,²¹ the highest EQE for the blue devices will be limited to less than 5%,
4 assuming perfect charge balance can be achieved in the devices. The exact reason for the low PLQEs in
5 chlorinated perovskite films is not clear. One way used in previous studies to increase PLQE was adopting
6 quantum dots or two-dimensional (2D) layered perovskites, in which strong quantum confinement could
7 significantly improve the film PLQE to over 80%.²² However, due to the inferior charge transport in these
8 films, high EQE sky-blue PeLEDs are still rarely reported.

9 In this manuscript, we report significantly enhanced PLQE of sky-blue emission polycrystalline
10 perovskite films from 1.1% to 49.7% by incorporating PEACl and YCl₃ into three-dimensional (3D)
11 CsPbBr₃ perovskite films, where PEACl is phenylethylammonium chloride (C₆H₅C₂H₄NH₃Cl) and YCl₃ is
12 Yttrium (III) chloride. The sky-blue PeLEDs with 2% YCl₃ showed high EQE of 11.0% and maximum
13 brightness of 9040 cd m⁻². Blue PeLED with 4.8% EQE was obtained by adding 10% YCl₃ in the perovskite
14 film, with a device CIE coordinate of (0.10, 0.13).

15 **Results**

16 **Photoluminescence enhancement by YCl₃ in perovskite films**

17 We fabricated and studied perovskite films with two different compositions in this study: 3D
18 CsPbBr_{2.4}Cl_{0.6} film and 2D-3D mixed CsPbBr₃:PEACl film (molar ratio is 1:1 in precursor solution). Details
19 about the film fabrication could be found in the Methods section. Chlorine was added in these films so that
20 both films emit sky-blue light, with PL peaks at 486 nm for CsPbBr_{2.4}Cl_{0.6} film and 487 nm for
21 CsPbBr₃:PEACl (1:1) film (Fig. 1a). The corresponding Commission Internationale de l'Eclairage (CIE)
22 coordinates are (0.06, 0.26) and (0.08, 0.25), respectively (Fig. 1b). Under the UV lamp, CsPbBr₃:PEACl
23 (1:1) film exhibits much brighter PL emission than the CsPbBr_{2.4}Cl_{0.6} film (Fig. 1c). Figure 1d shows PLQEs
24 of CsPbBr_{2.4}Cl_{0.6} film and CsPbBr₃:PEACl (1:1) film under different incident laser intensities. Maximum

1 PLQE of CsPbBr₃:PEACl (1:1) film (19.8%) is much higher than that of CsPbBr_{2.4}Cl_{0.6} film (1.1%).
2 Phenylethylammonium halide incorporation in 3D perovskites usually introduces layered phases in the
3 films which has been demonstrated as an effective method to increase the PLQEs of green perovskite
4 films.^{23, 24} Therefore, we focused on CsPbBr₃:PEACl (1:1) perovskite in this study because of its higher
5 PLQE compared with 3D CsPbBr_{2.4}Cl_{0.6} film. PL spectra of perovskite films with different CsPbBr₃:PEACl
6 ratios are shown in Supplementary Figure 1, which shows blue shift of PL peak from 522 nm for CsPbBr₃
7 film to 487 nm for CsPbBr₃:PEACl (1:1). Further increasing PEACl ratio in the films to CsPbBr₃:PEACl
8 (1:2) results in much lower PL intensity and very broad emission band with multiple peaks, which might
9 be from self-trapped exciton emission of different layered phases.²⁵ XRD study of the CsPbBr₃:PEACl (1:2)
10 film in Supplementary Figure 2 clearly shows more layered phases are formed with the increased PEACl
11 ratio in the films.

12 The PLQE of 19.8% in CsPbBr₃:PEACl (1:1) film still limits the EQE of sky-blue PeLED to be
13 less than 5%, considering a typical out-coupling efficiency around 20% in perovskite LEDs.²¹
14 Encouragingly, we found that adding 2% YCl₃ in the CsPbBr₃:PEACl (1:1) film further increased PLQE to
15 49.7%, as shown in Fig 1d. Here, the yttrium ratio is defined as the molar ratio of Y to Pb in the precursor
16 solution. The photographs in Fig 1c and Supplementary Figure 3 clearly shows the PEACl:CsPbBr₃ (1:1)
17 films with YCl₃ have much stronger PL emission than the film without YCl₃. The maximum PLQEs of
18 PEACl:CsPbBr₃ (1:1) films with 2%, 5%, 10% YCl₃ are 49.7%, 37.9% and 31.2%, respectively, which are
19 much higher than the film without YCl₃. Adding YCl₃ in the PEACl:CsPbBr₃ (1:1) film also blue shifts the
20 PL peak (Supplementary Figure 3). PEACl:CsPbBr₃ (1:1) films with 2%, 5% and 10% YCl₃ exhibit PL
21 peak at 485, 483 nm and 477 nm, respectively. The decreased PLQE in 5% and 10% YCl₃ perovskite films
22 compared with 2% YCl₃ perovskite film might be caused by the formation of YCl₃ clusters which may
23 hinder perovskite grain growth.(Supplementary Figure 4) Adding 2 % YCl₃ in the 3D CsPbBr_{2.4}Cl_{0.6} film
24 also significantly increases the film PLQE from 1.1% to 8.5 %, as shown in Fig. 1d. The photographs in
25 Supplementary Figure 5 illustrate the PL of CsPbBr₃ film was significantly improved by YBr₃ treatment.

1 Efficiency and stability of sky-blue PeLEDs with YCl₃.

2 We fabricated PeLEDs with the device structure shown in Fig. 2a to evaluate the impact of the
3 PLQE enhancement on device efficiency. PEACl:CsPbBr₃ (1:1) perovskite films with different amount of
4 YCl₃ were fabricated between hole transporting layer (HTL) poly(3,4-ethylenedioxythiophene) polystyrene
5 sulfonate (PEDOT:PSS) and electron transporting layer (ETL) 2,2',2''-(1,3,5-Benzinetriyl)- tris(1-phenyl-
6 1-H-benzimidazole) (TPBI). A photo of an operating sky-blue PeLED is shown in Fig. 2b which shows
7 bright sky-blue emission. Figure 2c-e show current density (J)-bias (V), luminance (B)-bias (V) and EQEs
8 curves of the PEACl:CsPbBr₃ (1:1) devices with different ratios of YCl₃. It was found that adding PEACl
9 in the perovskite film improved the film morphology by forming pinhole-free and smooth film, as shown
10 by the scanning electron microscopy (SEM) images in Supplementary Figure 4. The pin-hole free
11 perovskite film reduced leakage current and improve efficiency in the device, as CsPbBr₃ device showed
12 large current leakage (Fig. 2c-e). The device with PEACl:CsPbBr₃ (1:1) has an EQE of 5.6 % and maximum
13 brightness of 5,183 cd m⁻². Adding 2 % YCl₃ in perovskite film significantly increases EQE and maximum
14 luminance to 11.0% and 9040 cd m⁻², respectively. Figure 2f shows statistic EQEs of PEACl:CsPbBr₃ (1:1)
15 devices without and with 2% YCl₃, which clearly demonstrates the efficiency enhancement by adding YCl₃
16 in the devices. Angular emission intensity of the PeLEDs follows a Lambertian profile, as shown in
17 Supplementary Figure 6. Further increasing the YCl₃ ratio to 5% and 10% reduced device EQEs to 8.7%
18 and 4.8%, respectively. The device with 10% YCl₃ shows EL peak at 477 nm with a CIE coordinate of
19 (0.10, 0.13), which comes to blue light region, as shown in Fig.1d and Supplementary Figure 7. The EQE
20 variation of devices with different YCl₃ ratios closely follows the trend of PLQE change in Fig 1d,
21 indicating the limiting factor for the efficiency of these sky-blue emission PeLEDs is the PLQE of the
22 perovskite films, while the electron and hole current has been well balanced through controlling the
23 thickness of the charge transport layers in this work. (Supplementary Figure 8-9)

24 It has been widely reported that mixed-halide perovskites, such as CsPb(Br_{0.5}Cl_{0.5})₃, undergo a
25 quick phase segregation under electric field, caused by charge enhanced ion migration.^{22, 26-29} Such phase

1 segregation can generate bromine-rich domains and chlorine-rich domains in CsPb(Br_{0.5}Cl_{0.5})₃ films,
2 resulting in severe change of electroluminescent (EL) spectrum during the operation of PeLEDs.^{22, 26-29} We
3 tested the EL spectrum and luminance stabilities of the most efficient sky-blue PeLEDs to evaluate whether
4 such the phase segregation occurs in these mixed perovskite films. In striking contrast, we found the EL
5 spectra are very stable for the PEACl:CsPbBr₃ (1:1) LEDs with YCl₃. Figure 2g shows the EL emission
6 spectra of the sky-blue PeLED under constant bias of 3.2 V for 120 min. The device shows a stable EL
7 emission with a peak at 485 nm. Supplementary Figure 10 also shows negligible EL spectrum variation of
8 the device under varied biases. The EL luminance stability of PeLEDs was also tested by fixing the applied
9 voltage bias of 3.2 V, with an initial luminance around 100 cd m⁻², as shown in Fig. 2h.

10 The significantly improved spectrum stability in PEACl:CsPbBr₃ (1:1) films with 2% YCl₃
11 compared with 3D perovskite materials was ascribed to the dramatically suppressed ion migration in these
12 films, since phase segregation occurs via ion migration.^{28, 30} To verify it, we studied the activation energies
13 of ionic conduction in both CsPbBr_{2.4}Cl_{0.6} and PEACl:CsPbBr₃ (1:1) films using an established method.^{31,}
14 ³² As shown in Fig. 2i, the ion conduction activation energy of 3D CsPbBr_{2.4}Cl_{0.6} film in the dark is around
15 0.26 eV which is consistent with previously reported values.³³ In striking contrast, we found that ionic
16 conduction is negligible in the PEACl:CsPbBr₃(1:1) film in the temperature range up to 350 K. The derived
17 small activation energy of 0.04 eV can be assigned to electronic conduction. This indicates that the ion
18 migration in the PEACl:CsPbBr₃(1:1) films is significantly suppressed by the presence of layered
19 perovskites, in consistent with previous study.^{34, 35} In addition, adding 2% YCl₃ in 3D CsPbBr_{2.4}Cl_{0.6} film
20 also increased ion migration activation energy from 0.26 eV to 0.75 eV.

21 **Phase Composition study in CsPbBr₃:PEACl (1:1) film**

22 To understand the role of PEACl, we studied phase composition of the PEACl:CsPbBr₃ (1:1) film
23 by performing X-ray diffraction (XRD) measurements. The XRD pattern of PEACl:CsPbBr₃ (1:1) film in
24 Fig.3a shows mixed phases of $n=1$, $n=2$ and $n\geq 3$ perovskites, and each peak is indexed. Most XRD peaks
25 of the PEACl:CsPbBr₃ (1:1) film can be assigned to $n=1$ phase based on reported XRD pattern of

1 (PEA)₂PbBr₄ single crystal.³⁶ The XRD peak intensity of the $n=1$ phase is much stronger than the other
2 phases, indicating $n=1$ layered phase may prefer to lay down in parallel to the substrate. The Cl:Br ratio in
3 $n=1$ layered phase is estimated to be 1:4 based on the XRD and PL peak positions, as shown in
4 Supplementary Figure 11-12. The XRD peak at 4.3° is most likely from $n=2$ phase based on the analysis of
5 lattice constants. The XRD diffraction peak of $n\geq 3$ phase locates at a larger diffraction angle of 31.1° than
6 (202) plane of CsPbBr₃ (30.7°), while it's very close to (202) plane of 3D perovskite with a composition of
7 CsPbBr_{2.4}Cl_{0.6}, as shown in Supplementary Figure 13. Hereinafter we refer the $n\geq 3$ phase in the
8 PEACl:CsPbBr₃ (1:1) film as 3D phase. As shown in Fig. 3b, the PL spectrum from PEACl:CsPbBr₃ (1:1)
9 film at room temperature only has one emission peak around 489 nm. Reducing the temperature to 173 K
10 leads to two additional peaks in the PL spectrum at 392 nm and 419 nm, which are most likely from $n=1$
11 and $n=2$ phases, respectively.³⁷ The PL emission around 490 nm in the PEACl:CsPbBr₃ (1:1) perovskite
12 films should be from 3D phase with a composition approximately CsPbBr_{2.4}Cl_{0.6}. The absorbance spectrum
13 of PEACl:CsPbBr₃ (1:1) film in Fig. 3c also shows two obvious peaks at 390 nm and 418 nm, which are
14 close to the PL emission peaks of $n=1$ and $n=2$ phases.

15 Since the PL emission from the PEACl:CsPbBr₃ (1:1) perovskite film at room temperature has only
16 one peak from the 3D phase, there should be efficient energy transfer from layered perovskites to 3D
17 perovskite. To verify it, we performed transient absorption (TA) measurement to study the charge carrier
18 dynamics in PEACl:CsPbBr₃ (1:1) perovskite films. As shown in Fig. 3d, the bleach peak around 485 nm
19 belongs to the 3D phase in the PEACl:CsPbBr₃ (1:1) film. The bleach peak evolved in the first 2 ps after
20 light excitation, suggesting a fast energy transfer from layered perovskites to 3D phase (Fig. 3e). After 2
21 ps, the energy funneling is complete, followed by charge recombination in 3D perovskite. The energy
22 transfer from layered phases to 3D phase functions as an energy and carrier concentrator to enhance
23 radiative recombination efficiency for higher PLQE, which has been reported in red emission 2D-3D mixed
24 perovskite films.³⁸ The promoted radiative recombination should give rise to higher PLQE observed in the
25 PEACl:CsPbBr₃ (1:1) perovskite films.

1 Mechanism of PLQE enhancement by YCl_3

2 We investigated the distribution of yttrium in the $\text{CsPbBr}_{2.4}\text{Cl}_{0.6}$ and $\text{PEACl}:\text{CsPbBr}_3$ (1:1) films
3 in order to understand its functions in PLQE enhancement. We first examined whether yttrium ions
4 incorporated into the 3D perovskite phase. We grew single crystals of CsPbBr_3 with the presence of YCl_3
5 in the solution. The Y distribution in the crystal was studied by inductively coupled plasma (ICP) mass
6 spectrometry which is a sensitive technique to detect trace metal ions as low as particle per quadrillion. The
7 details about crystal growth can be found in the Methods section.^{39, 40} The single crystal was sliced into
8 small pieces and the compositions of the crystal at different depth were measured. As shown in Fig. 4a, the
9 Y/Pb ratio in the crystal center is 0.5%, demonstrating yttrium ions could incorporate into CsPbBr_3
10 perovskite crystals. In addition, it was interesting to find the Y/Pb ratio gradually increase from the crystal
11 center to surface, yielding an yttrium concentration gradient in the crystal. A gradient distribution of Y ions
12 can be explained by the enhanced chemical pressure in the solution during the growth of crystal, because
13 more Y ions excluded into solution during crystal growth increase its concentration in solution. Similar to
14 single crystal growth, the larger amount of Y added in solution for thin film growth should also cause a
15 concentration gradient, as illustrated in Fig. 4b. Absorption and PL study on thin films in Fig 4c and 4d
16 revealed the bandgap of CsPbBr_3 was increased by Y incorporation. We also found a high density of yttrium
17 on the perovskite film surface using surface-sensitive X-ray photoelectron spectroscopy (XPS)
18 measurements. The XPS spectra of $\text{PEACl}:\text{CsPbBr}_3$ (1:1) films with different ratios of YCl_3 are shown in
19 Supplementary Figure 14. The Y $3d_{3/2}$ peak at 160.4 eV obviously increases with yttrium incorporation in
20 the films. The Y/Pb ratios on the surfaces of the films derived from XPS spectra are shown in Fig. 4e. The
21 Y/Pb ratios on the film surfaces are 3-7 times higher than the corresponding Y/Pb ratios in the precursor
22 solution, indicating that yttrium ions accumulate on the film surfaces or grain boundaries.

23 We examined possible mechanisms that explain the function of YCl_3 in PLQE enhancement.
24 Previous study showed organic ligands of layered perovskites have strong impact on the electron-phonon
25 interaction and thus PLQE of perovskites.⁴¹ To find out possible impact of Y incorporation on electron-

1 phonon interaction, we studied the temperature dependent PL full width at half-maximum (FWHM) of
2 PEACl:CsPbBr₃(1:1) films with or without YCl₃, which is a well-established method to derive electron-
3 phonon interaction.⁴¹⁻⁴³ As shown in Supplementary Figure 15, the PL FWHMs of samples with and without
4 YCl₃ shows a same trend at varied temperatures, which indicates that YCl₃ does not notably change charge-
5 phonon interaction strength. We did notice that addition of YCl₃ reduced FWHM of PL spectra at all
6 temperatures. This result implies YCl₃ can reduce the non-radiative recombination centers in
7 PEACl:CsPbBr₃(1:1) films,⁴¹ which is confirmed by more than two times longer PL decay lifetime after
8 adding YCl₃, as shown in Supplementary Figure 16. Simulation was performed in CsPbBr₃ perovskite
9 incorporated with YCl₃ to find out why Y³⁺ ions reduce non-radiative charge recombination. Based on the
10 model, the way of Y³⁺ incorporation in CsPbBr₃ is most likely by replacing Pb²⁺ and simultaneously forming
11 a Cs⁺ vacancy to compensate the charge difference. As shown in Fig.4f, density function theory calculation
12 reveals Y³⁺ incorporation increases the bandgap of perovskite, since Y *4d* level is well above the Pb *6p*
13 states, and the Cl *3p* states are slightly lower than Br *3p* states. Therefore, the yttrium incorporated region
14 at the shell of the grains impose an energy barrier which confines charge carriers inside the grains, as is
15 illustrated in Fig. 4b. This charge confinement minimizes nonradiative recombination that generally occurs
16 at grain boundaries and surfaces due to local large density of defects.

17 **Discussion**

18 In conclusion, we demonstrated sky-blue PeLED with EQE of 11% and blue PeLED with EQE of
19 4.8%, by overcoming the limitation from the low PLQE of wide bandgap perovskites. The combination of
20 layered perovskite formation and YCl₃ incorporation enhances the PLQE from 1.1 % to 49.7%, which also
21 enhance the material stability by suppressing ion migration. This study reveals that the low PLQE in most
22 Cl:Br based perovskites films limits the LED efficiency. Further research to improve the PLQY of wide
23 bandgap perovskite films to 100% should increase the EQE of sky-blue emission PeLEDs to over 20%.

24

1 **Methods**

2 **Material and solution preparation.** PEACl was synthesized by reacting equal molar of phenethylamine
3 (Sigma) with hydrochloric acid solution (Alfa Aesar 37%) under nitrogen at ice bath for 2 hours with
4 stirring. After reaction, the white precipitate PEACl was recovered by rotary evaporation at 80 °C and
5 recrystallized by diethyl ether for three times. The PEACl powders were finally collected and dried at room
6 temperature in a vacuum oven for 24 h. CsPb, PbBr and YCl₃ were purchased from Sigma Aldrich and
7 TPBI was purchased from Lemtec. The perovskite precursor solution was prepared by mixing CsPbBr₃
8 solution, PEACl solution and YCl₃ solution with desired ratios. CsPbBr₃ solution (0.25 M) was prepared
9 by mixing 106 mg CsBr and 183.5 mg PbBr₂ in 2 mL DMSO. The CsPbBr₃ solution was filtered before
10 using. PEACl solution (1 M) was prepared by mixing 158 mg PEACl in 1 mL DMSO. YCl₃ solution (0.25
11 M) was prepared by mixing 49 mg YCl₃ in 1 mL DMSO.

12 **Perovskite light emitting diode fabrication.** The indium tin oxide (ITO)-coated glass substrates were
13 sequentially cleaned in detergent, distilled water, acetone and isopropanol by sonication. The cleaned
14 substrates were treated in ultraviolet ozone for 15 min. Then PEDOT:PSS (AI 4083) aqueous solution was
15 spin-coated at 3500 round per minute (RPM) for 40 s and baked at 125 °C for 30 min in ambient air. After
16 that, the substrates were transferred into a nitrogen-filled glove box and perovskite solution was spin-coated
17 on top of substrate at 4000 RPM for 40 s. 500 µL chloroform was poured onto perovskite film 20 s after the
18 spin coating started. The perovskite films were annealed at 90 °C for 20 min. Finally, the fabrication of
19 PeLEDs was completed by thermally evaporate TPBi (40 nm), LiF (less than 1 nm) and Al (100 nm)
20 electrode. The device area was 0.10 cm² as defined by the overlapping area of the ITO and Al electrode.

21 **Perovskite film and device characterizations:** Absorption and photoluminescence (PL) spectra were
22 measured by Evolution 201 UV-Visible Spectrophotometer and iHR320 Photoluminescence Spectroscopy,
23 respectively. Scanning electron microscopy (SEM) was measured by FEI Helios 600 system. XPS was
24 measured by Kratos Axis Ultra DLD X-ray Photoelectron Spectrometer. The surface compositions of
25 samples were analyzed by the Processing software on the system. The current (*J*)-voltage (*V*)-luminance

1 characterizations of the devices were performed in N₂ glovebox without encapsulation. A Keithley 2400
2 source meter was used to measure the J-V data from 0 V to 7 V with a voltage scanning speed around 0.2
3 V s⁻¹. The luminance of the device was recorded simultaneously by Konica Minolta, LS-160 or a calibrated
4 silicon photodiode (Hamamatsu, S2387 1010R) with an area of 10mm*10mm. The photodiode was placed
5 on top of the LED in close contact to collect light. The EQE was calculated using Lambertian profile and
6 the obtained electroluminescence spectrum.

7 **Photoluminescence quantum efficiency measurements** were measured by following previous established
8 method.⁴⁴ An integrating sphere (Labsphere QE sphere) was connected with a PL spectrometer (Ocean
9 Optics QEpro) by an optical fiber. A continuous wave 403 nm laser was used to excite the sample. The
10 incident laser intensity was changed by neutral density filters and the intensity was measured by a power
11 meter (Newport 843R). The samples for PLQE measurement were encapsulated and the measurement was
12 performed in air at room temperature. The PLQE results were confirmed by our collaborator at Xi'an Jiao
13 Tong University (Supplementary Figure 17). Edinburgh FLS980 fluorescence spectrometer system was
14 used in collaborator's PLQE measurement. The Edinburgh FLS980 fluorescence spectrometer has an
15 integrating sphere with a diameter of 150 mm. The excitation light was a monochromatic 365 nm light and
16 the intensity is 0.5 mW cm⁻².

17 **Inductively coupled plasma mass spectrometry** was carried out using a Thermo Element XR-Optical
18 laser ablation source with a double focusing magnet sector. Standards were prepared from THERMO-54
19 and MSPB calibration standards from Inorganic Ventures and calibration curves were produced for yttrium
20 (Y) to lead (Pb) from 25 parts per trillion to 500 parts per billion. CsPbBr₃ with 2% YCl₃ crystals were
21 grown by inverse temperature crystallization method which has been widely used to grow high quality
22 perovskite crystals. Four surfaces of the crystals polished by sand paper to expose the crystal internal. Then
23 the crystal was cleaved into about 1 mm thin piece by using operation blades. To prevent contamination,
24 each sample was sealed in different vials and the blade was carefully cleaned after each cutting. The samples
25 were then dissolved in 1 mol% HNO₃ (prepared from Fisher Chemical Nitric Acid TraceMetal Grade and

1 NERL 18 MΩ water). The solutions were then further diluted with 18 MΩ water to reach a concentration
2 within the range of the calibration curve. Solutions were injected into the nebulizer and injected into the
3 instrument for analysis. Each sample was followed by a washing period with 1 mol% HNO₃ in 18 MΩ
4 water before the next sample. Using the calibration curves produced, the ratio of yttrium (Y) to lead (Pb)
5 was determined.

6 **Time-resolved photoluminescence measurement** was performed on a Horiba DeltaPro fluorescence
7 lifetime system. The excitation was provided by a DeltaDiode (DD-405) pulse laser diode with a
8 wavelength of 404 nm. The TRPL curves were fitted to a monoexponential rate law:

$$9 \quad y = A \exp\left(-\frac{t}{\tau}\right) + y_0 \quad (1)$$

10 where A is the relative amplitudes and τ is the lifetimes. The samples for TRPL measurements were
11 perovskite films deposited on glass substrates without hole transporting layer. The fluence of TRPL
12 excitation laser and the generated carrier density were 2.0 nJ cm⁻² and 4.07×10^{14} cm⁻³, respectively.

13 **Temperature dependent conductivity measurement** for deriving ion migration activation energy was
14 performed in a Lakeshore probe station under a vacuum of 10⁻⁴ pa.^{31,32} The sample were placed on a copper
15 plate with its temperature being controlled by a heater and injected liquid N₂. A Keithley 2400 was used
16 for applying voltage bias and measuring the current. The samples for conductivity measurement have lateral
17 Au electrodes on perovskite film. Perovskite films were firstly fabricated on glass substrates by following
18 above mentioned method. Then 50 nm Au electrodes with spacing of 50 μm were thermally deposited using
19 a mask. Ion activation energy can be derived by fitting the conductivity curve with Nernst-Einstein equation:

$$20 \quad \sigma(T) = \frac{\sigma_0}{T} \exp\left(-\frac{E_A}{k_B T}\right) \quad (2)$$

21 where σ is conductivity, T is temperature, E_A is activation energy, k_B is Boltzmann constant.

22 **Transient absorption experiment** was conducted with a 45-fs, 4-mJ 800-nm Coherent Libra with a 1-kHz
23 repetition rate. Single-frequency 400-nm pump pulses were generated by the second harmonic generation

1 through a BBO crystal. The remaining 800-nm component was filtered by two 400-nm dielectric mirrors.
2 The pulse energies were controlled by a neutral density filter. Continuum probe pulses were generated in a
3 sapphire window and relayed to the sample with reflective optics. The spot size of the probe was adjusted
4 to match the 200- μm spot size of the pump. Signal detection was accomplished with a high-speed CMOS
5 array detector that is synchronized to the laser system.

6 **Temperature-dependent PL spectrum measurement** was performed by using iHR320
7 Photoluminescence Spectroscopy and a portal LINKAM thermal stage. The full width at half-maximum
8 (FWHM) of PL spectra was fitted by the following equation to derive electron-phonon interaction
9 strength.⁴¹⁻⁴³

$$10 \quad \Gamma(T) = \Gamma_0 + \frac{\Gamma_1}{\exp\left(\frac{\hbar\omega_1}{k_B T}\right) - 1} \quad (3)$$

11 where Γ_0 is temperature independent inhomogeneous broadening term, which arises from scattering due to
12 disorder and imperfections. Γ_1 represents electron-phonon coupling strength, primarily contributed by
13 longitudinal optical (LO) phonon scattering. ω_1 is homopolar phonon frequency which is 133 cm^{-1} for
14 Pb-Br-Pb stretch based on previous report. The electron-phonon coupling strengths (Γ_1) in Supplementary
15 Figure 15 were fitted to be 0.032 eV and 0.035 eV in PEACl:CsPbBr₃(1:1) films with or without YCl₃,
16 respectively. Γ_0 was reduced from 0.093 eV in PEACl:CsPbBr₃(1:1) film to 0.086 eV in
17 PEACl:CsPbBr₃(1:1) film with YCl₃.

18 **Density functional theory calculations** were performed using the VASP code^{45, 46} with projector
19 augmented-wave (PAW)⁴⁷ potentials. The PBE⁴⁸ exchange-correlation functional and a kinetic energy
20 cutoff of 300 eV were employed. Spin-orbit coupling was included in the calculations due to the heavy Pb
21 atoms. To model the surface passivation, we built a CsPbBr₃ slab with the top surface layer covered by
22 [YCl₆] octahedra. The cell size is 1.2 nm*1.2 nm*2.3 nm. A vacuum thickness of 15 Å was used to eliminate
23 spurious periodic interactions between the slabs. The bottom two layers of [PbBr₆] octahedra were fixed at

1 their relaxed bulk positions while all other atoms were relaxed with a force tolerance of 0.01 eV \AA^{-1} . A Γ -
2 centered k mesh of $4 \times 4 \times 1$ was used to sample the Brillouin zone.

3 **Data Availability**

4 The data that support the findings of this study are available from the corresponding author upon reasonable
5 request.

6

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8

9 **Author contributions:**

10 J. H. and Q. W. conceived the idea. Q. W. fabricated the devices and performed the device
11 efficiency measurement. Z. Y. conducted photoluminescence quantum yield measurement. N. Z.
12 and A. M. conducted transient absorption measurement. J. Z., Y. D., and X. X. conducted X-ray
13 diffraction measurement. P. R. conducted ICP measurement. X. W. and Y. Y. conducted the
14 simulation. Q. W. and J. H. wrote the paper.

15

16 **Competing interests**

17 The authors declare no competing financial or non-financial interests.

18

1 **Figure Captions**

2 **Fig. 1 Photoluminescence enhancement by PEACl and YCl₃ incorporation in perovskite films.** (a) PL
3 spectra of CsPbBr_{2.4}Cl_{0.6}, CsPbBr_{2.4}Cl_{0.6}:2%YCl₃, CsPbBr₃:PEACl (1:1) and CsPbBr₃:PEACl:2%YCl₃
4 films. (b) CIE coordinates of CsPbBr_{2.4}Cl_{0.6} (1), CsPbBr_{2.4}Cl_{0.6}:2%YCl₃ (2), CsPbBr₃:PEACl (1:1) (3) and
5 CsPbBr₃:PEACl:2%YCl₃ (4) films. CIE coordinates of CsPbBr₃:PEACl:2%YCl₃ (5) device and
6 CsPbBr₃:PEACl:10%YCl₃ (6) device were also shown. (c) A photograph of the films under UV lamp. The
7 composition of each film is labeled in the photograph. (d) Power dependent PLQEs of the perovskite films
8 with different compositions.

9 **Fig. 2 Efficiency and stability of sky-blue PeLEDs with YCl₃.** (a) Device structure of the PeLEDs. (b) A
10 photograph of the fabricated PeLED showing sky-blue EL emission under bias. Current density-bias (c),
11 luminance-bias (d), EQE-current density (e) curves of CsPbBr₃:PEACl (1:1) devices with different ratios
12 of YCl₃. c-e also show the performance of a CsPbBr₃ perovskite LED. (f) Statistic EQEs of sky-blue
13 PeLEDs with or without YCl₃ (g) Electroluminescence spectrum stability test of a sky-blue PeLED with
14 continuous bias of 3.2 V for 120 min. (h) Operational stability test of a sky-blue PeLED with initial
15 luminance around 100 cd m⁻². The stability test was conducted in N₂ glovebox without device encapsulation.
16 (i) Temperature dependent conductivity measurements to reveal the ion migration activation energies of
17 CsPbBr_{2.4}Cl_{0.6}, CsPbBr_{2.4}Cl_{0.6} with 2% YCl₃, CsPbBr₃:PEACl (1:1) films

18 **Fig. 3 Phase composition study of CsPbBr₃:PEACl (1:1) film and the function of layered phases.** (a)
19 XRD of CsPbBr₃:PEACl (1:1) film. (b) PL spectra of CsPbBr₃:PEACl (1:1) film at 273 K and 173 K. (c)
20 Absorbance of CsPbBr₃:PEACl (1:1) film. (d) Transient absorption (TA) spectra of CsPbBr₃:PEACl (1:1)
21 film at different timescales. (e) TA spectra as a function of delay time that probed selected wavelength of
22 480 nm corresponding to the distinct bleaching of 3D phase in CsPbBr₃:PEACl (1:1) film.

23 **Fig. 4 Mechanism of PLQE enhancement by YCl₃.** (a) ICP measurement results that show the Y/Pb ratios
24 in the different locations of the crystal. The crystal (inset) was cleaved into thin pieces (1 to 4) and Y/Pb

1 ratio of each piece was measured. (b) Schematic illustration of the yttrium gradient distribution in the
2 CsPbBr₃:PEACl (1:1) film and its function in increase the bandgap around the grain surface. Absorption (c)
3 and PL (d) of CsPbBr₃ films with or without YBr₃. (e) XPS measurement results that show the Y/Pb ratios
4 on the surface of CsPbBr₃:PEACl (1:1) films with different YCl₃ ratios of 0%, 2%, 5% and 10%. The Y/Pb
5 ratios on the film surface is higher than the corresponding Y/Pb ratios in the precursor solutions. (f) DFT
6 calculated PDOS of CsPbBr₃ with YCl₃.

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