

Electronic Supplementary Information

Universal Surface Tailoring of Perovskite Nanocrystals via Organic Pseudohalide Ligands Applicable to Green and Blue Light-Emitting Diodes

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Experimental Details

Materials

Lead(II) bromide (PbBr_2 , 99.999 %), lead(II) chloride (PbCl_2 , 99.999 %), cesium carbonate (Cs_2CO_3 , 99.995 %), octadecene (ODE, 90 %), oleic acid (OA, 90%), oleylamine (OAm, 70%), trioctylphosphine (99.9 %), toluene (99.8 %) were purchased from Sigma-Aldrich. Octane (≥ 98 %), sodium tetrafluoroborate (NaBF_4 , 97 %) were purchased from Alfa Aesar. Didodecyldimethylammonium bromide (DDAB, >98 %) was purchased from Tokyo Chemical Industry. All chemicals were used as received.

Preparation of DDA- BF_4 ligands

DDA-Br (1 mmol, 462 mg) was dissolved in 10 ml of toluene. In another vial, NaBF_4 (1 mmol, 110 mg) was dissolved in 10 ml of deionized water and poured into DDA-Br solution. Reaction was carried out under ultrasonication for 30 min. After sonication, opaque solution was centrifuged at 4000 rpm for 10 min. Then, the upper solution was carefully taken and dried over MgSO_4 . After concentrating in rotary evaporator, off-white powder of DDA- BF_4 was obtained by precipitation in cold hexane (338 mg, Yield = 72 %).

Synthesis of CsPbBr_3 and $\text{CsPbBr}_{3-x}\text{Cl}_x\text{NCs}$

CsPbBr_3 NCs were synthesized from the literature. For Cs-oleate precursor, Cs_2CO_3 (0.25 mmol, 0.0814 g) and OA (0.25 mL) were added to ODE (4 mL) and dried under N_2 flow for 1 hour at

120 °C. The temperature was kept at 150 °C before injection. In another 3-neck flask, PbBr₂ (0.276 g, 0.75 mmol) (for CsPbBr_{3-x}Cl_x NCs, PbBr₂ (0.184 g, 0.50 mmol) and PbCl₂ (0.069, 0.25 mmol)) OA (2 mL), and OAm (2 mL) were mixed and dried under N₂ flow for 1 hour at 120 °C. The solution was heated to 170 °C after completely dissolve PbBr₂. For CsPbBr_{3-x}Cl_x NCs, 1 mL or TOP was added for complete dissolution of PbCl₂. Then, 1.6 mL of warm Cs-oleate solution was quickly injected. After for 5 s, the flask was cooled by dipping into ice water bath. For purification, crude solution was centrifuged at 8,000 rpm for 20 min. A half of the precipitate was redispersed in octane (as pristine CsPbBr₃ NCs) and another half was dispersed again in toluene for further ligand exchange. To remove insoluble impurities, one more centrifuge was carried out at 4,000 rpm for 5 min. Then, the bright green supernatant was collected.

DDA-BF₄ treatment of CsPbBr₃ NCs

Various amount of DDA-BF₄ were dissolved in toluene (1 mL) and added to the CsPbBr₃ NCs toluene solution (1 mL). After stirring for 30 min, 3 mL of anhydrous ethyl acetate was added and centrifuged at 8,000 rpm for 10 min. The supernatant was discarded, and green precipitate was redissolved in anhydrous octane. Another centrifuge at 4,000 rpm for 5 min were carried out and insoluble impurities were removed and stored in N₂ atmosphere. Final concentration was ~20 mg ml⁻¹.

Device Fabrication

The device configuration were as follows: glass/ITO/PEDOT:PSS/poly-TPD/PeNCs/TPBi/LiF@Al. Patterned ITO glass substrates (sheet resistance of $15 \Omega \text{ cm}^{-2}$, AMG Corp.) were sonicated in deionized water, acetone, and isopropyl alcohol each for 15 min. After sonication, the substrate was further cleaned with UV-ozone plasma for 15 minutes. Then, PEDOT:PSS was spun-cast onto the ITO substrates at 4000 rpm for 30 sec and baked at $140 \text{ }^\circ\text{C}$ for 10 min in ambient conditions. Next, poly-TPD was spun-cast at 4000 rpm for 30 sec and baked under the same condition. The substrate was transferred into nitrogen-filled glovebox and perovskite NCs (20 mg mL^{-1}) were spun-cast at 2000 rpm for 30 sec and annealed at $60 \text{ }^\circ\text{C}$ for 20 min. Finally, TPBi (40 nm), LiF (1 nm), and Al (100 nm) were deposited using a thermal evaporation system through a shadow mask under a high vacuum chamber. All layers in HOD (glass/ITO/PEDOT:PSS/poly-TPD/PeNCs/Al) and EOD (glass /ITO/PeNCs/TPBi/LiF@Al) were fabricated at the same conditions as LEDs.

Characterization

For characterizing organic materials, ^1H -nuclear magnetic resonance (^1H -NMR) (500 MHz FT-NMR spectrometer, Bruker) and Fourier-transform infrared spectroscopy (FT-IR) (CARY 600 spectrometer, Agilent Tech.) were used. FT-IR spectra were obtained in specular mode with a resolution of 4 cm^{-1} . The obtained data were plotted using spectrum analysis software (OMNIC, Nicolet). For optical characterization, V-670 UV-visible/NIR spectrometer (JASCO Corp.) and F-7000 Fluorescence spectrophotometer (Hitachi) were used for absorption and emission spectra. Time-resolved photoluminescence (TRPL) signals were obtained out by using a time-correlated

single-photon counting (TCSPC) method. The samples in the solutions or films were excited by a 520 nm pulse (LDH-P-C-520, Picoquant). The TRPL signals emitted from the samples were spectrally-resolved by a monochromator and were finally detected by a photomultiplier tube (PMT). The instrumental function of our TRPL experimental setup is of about 0.2 ns. For structural characterization, scanning electron microscopy (SEM) images were acquired with a Hitachi S4800 operating at an acceleration voltage of 500 V to 30 kV, and Transmission electron microscopy (TEM) images were obtained using an FEI Tecnai 20 microscope operating at 200 kV. Atomic force microscopy (AFM) topographic images were measured using NX-10, Park Systems. X-ray diffraction patterns were acquired using Rigaku SmartLab with Cu K α radiation (40 kV, 150 mA). X-ray photoelectron spectroscopy (XPS) analysis was carried out with an Axis Supra spectrometer (Kratos Analytical, U.K.). Ultraviolet photoelectron spectroscopy (UPS) measurements were conducted with an AXIS-NOVA and Ultra DLD using a He I (21.2 eV for UPS) discharge lamp. Time-of-flight secondary ion mass spectrometry (TOF-SIMS) were recorded using TOF.SIMS5 (ION-TOF, Germany) at the Advanced Analysis Center located in Korea Institute of Science and Technology (KIST). Device characteristics such as J - V - L , CE, PE, EQE, and EL spectra were measured using a Keithley SMU 236 instrument and Spectrascan PR-655 colorimeter.

Supplementary Figures

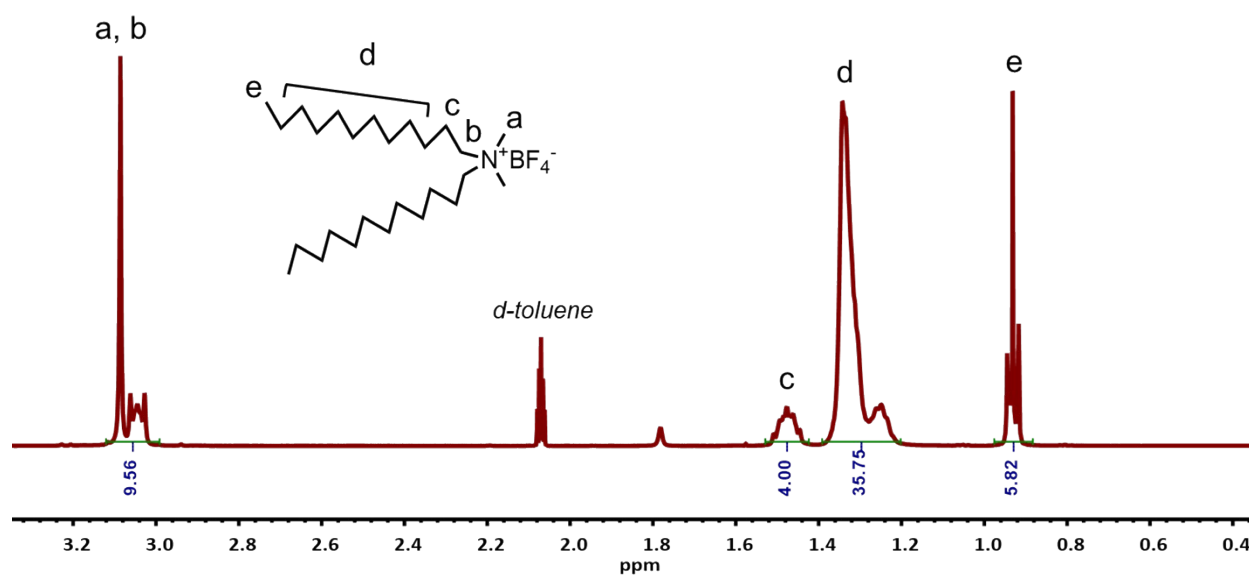


Figure S1. $^1\text{H-NMR}$ spectrum of DDA- BF_4 ligands (dissolved in d -toluene).

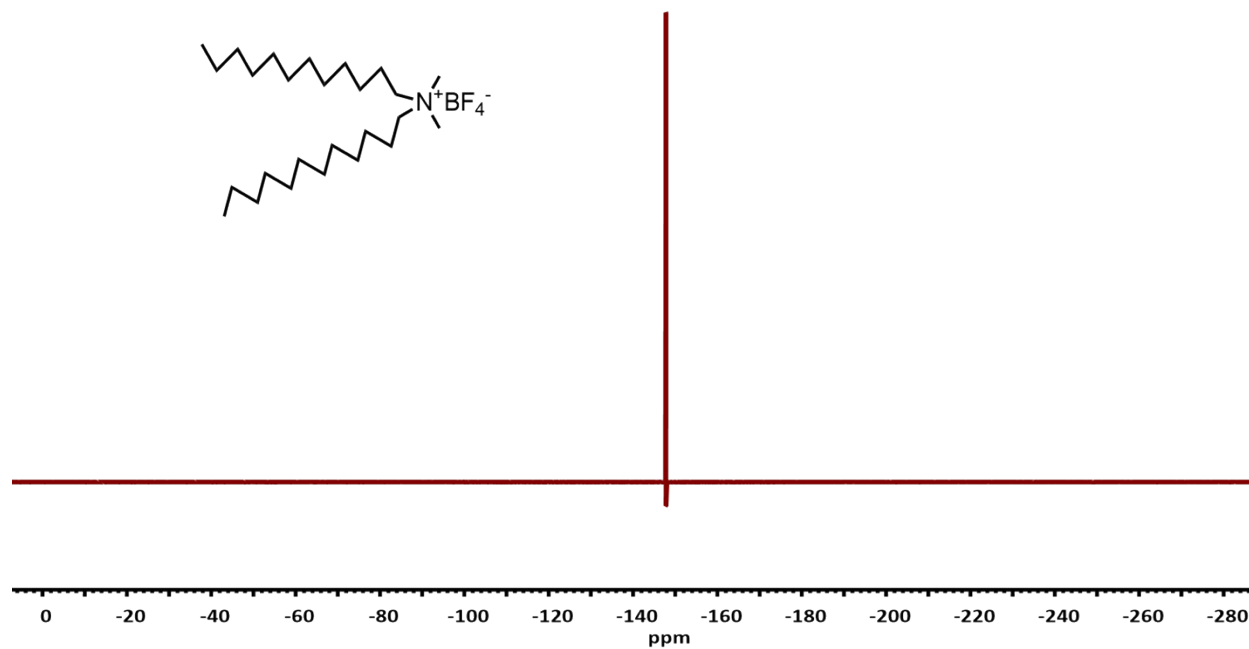


Figure S2. $^{19}\text{F-NMR}$ spectrum of DDA- BF_4 ligands (dissolved in d -toluene).

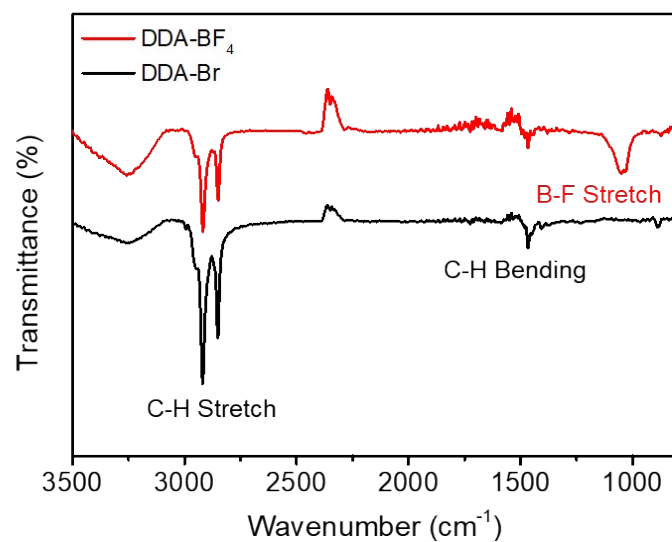


Figure S3. FT-IR spectra of DDA-Br and DDA-BF₄ ligand.

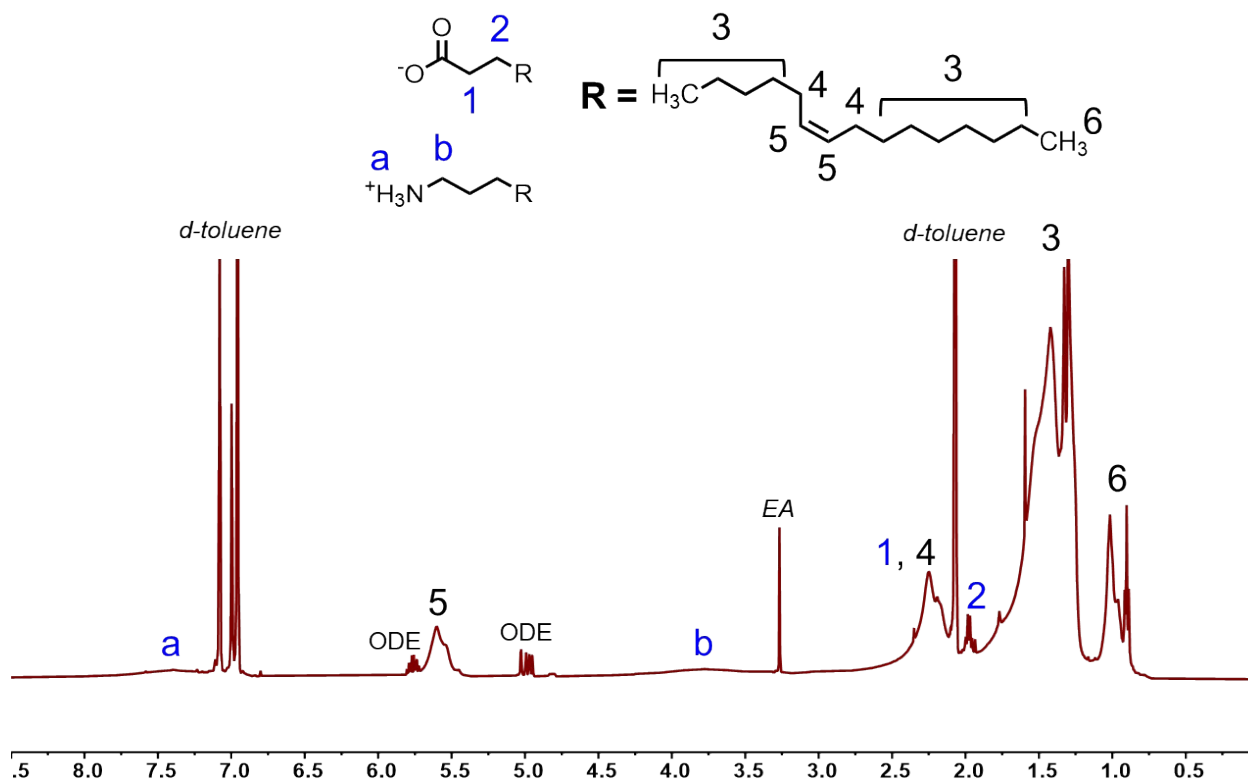


Figure S4. ¹H-NMR spectra of pristine CsPbBr₃ NCs (dissolved in *d*-toluene).

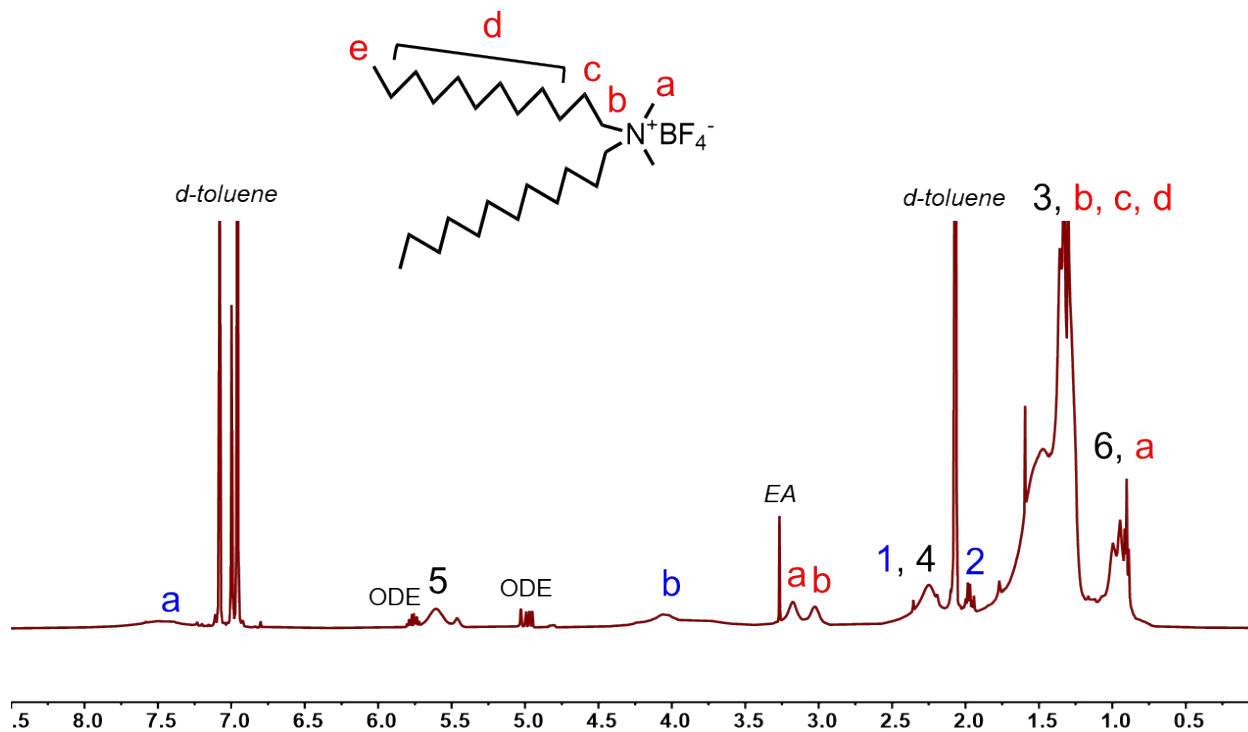


Figure S5. $^1\text{H-NMR}$ spectra of $\text{CsPbBr}_3\text{-BF}_4$ NCs (dissolved in d -toluene).

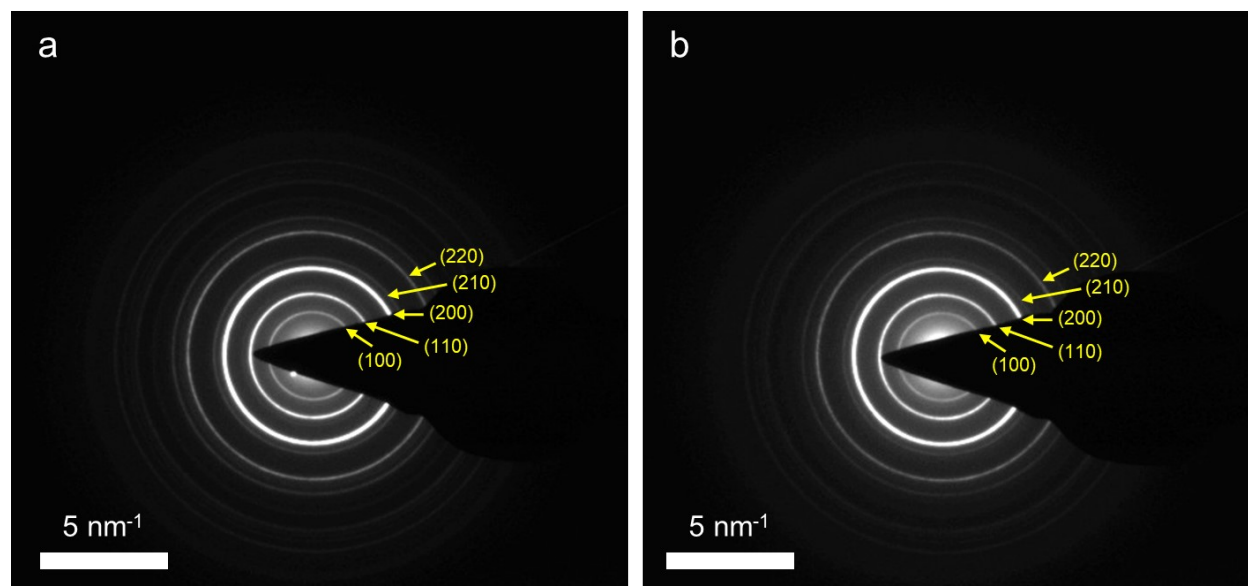


Figure S6. Selected area electron diffraction patterns of (a) CsPbBr_3 NCs and (b) $\text{CsPbBr}_3\text{-BF}_4$.

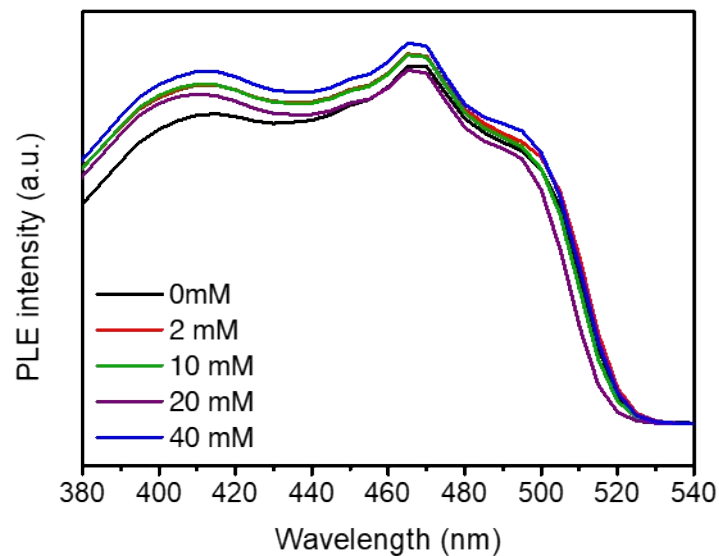


Figure S7. PLE spectra of DDA-BF₄ treated CsPbBr₃ NCs.

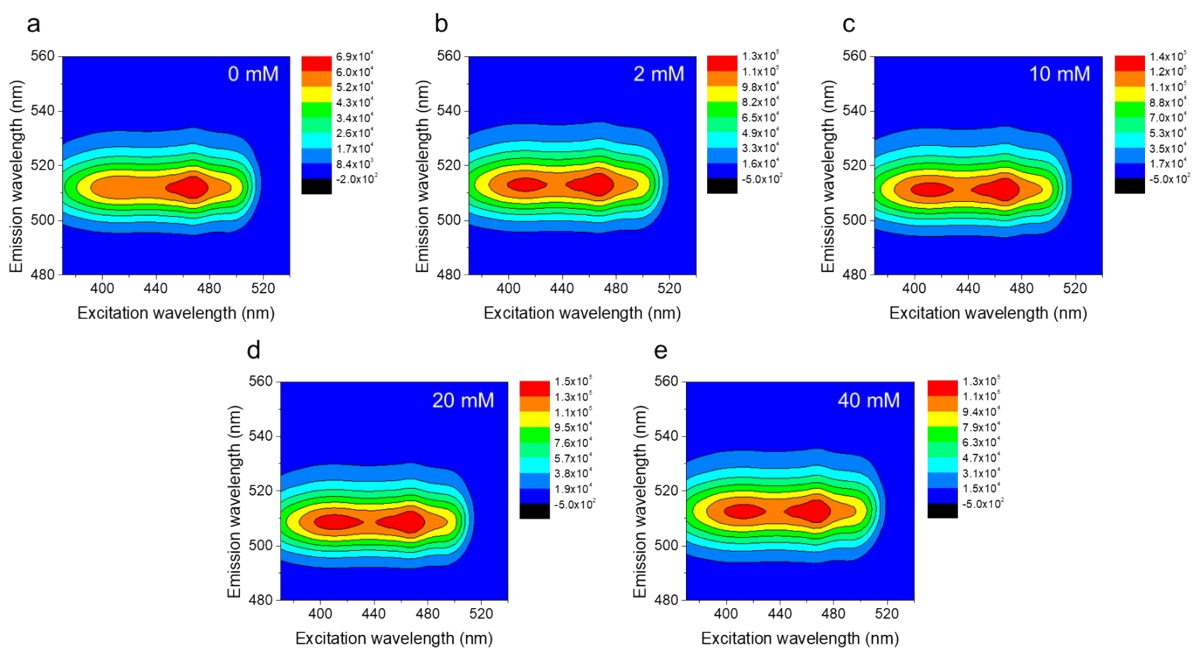


Figure S8. 2D PLE maps of (a) pristine CsPbBr₃ NCs, (b) 2 mM treated, (c) 10 mM treated, (d) 20 mM treated, and (e) 40 mM treated CsPbBr₃-BF₄.

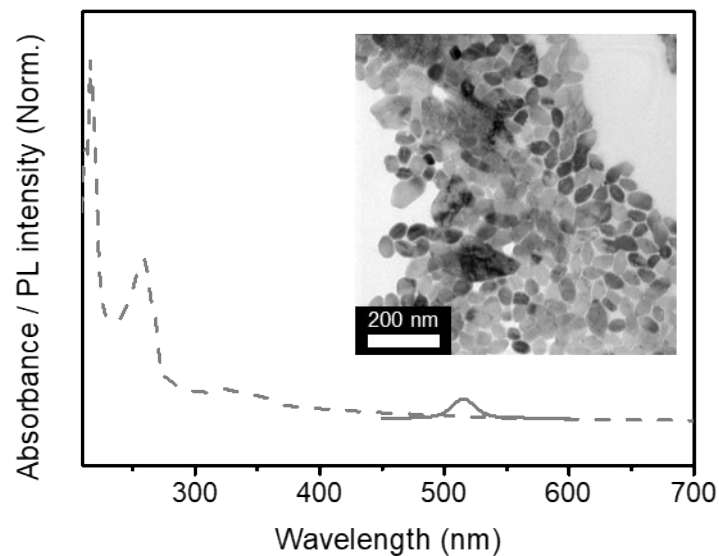


Figure S9. Absorbance and PL spectra of 100 mM DDA-BF₄ treated CsPbBr₃ NCs (inset : corresponding TEM images).

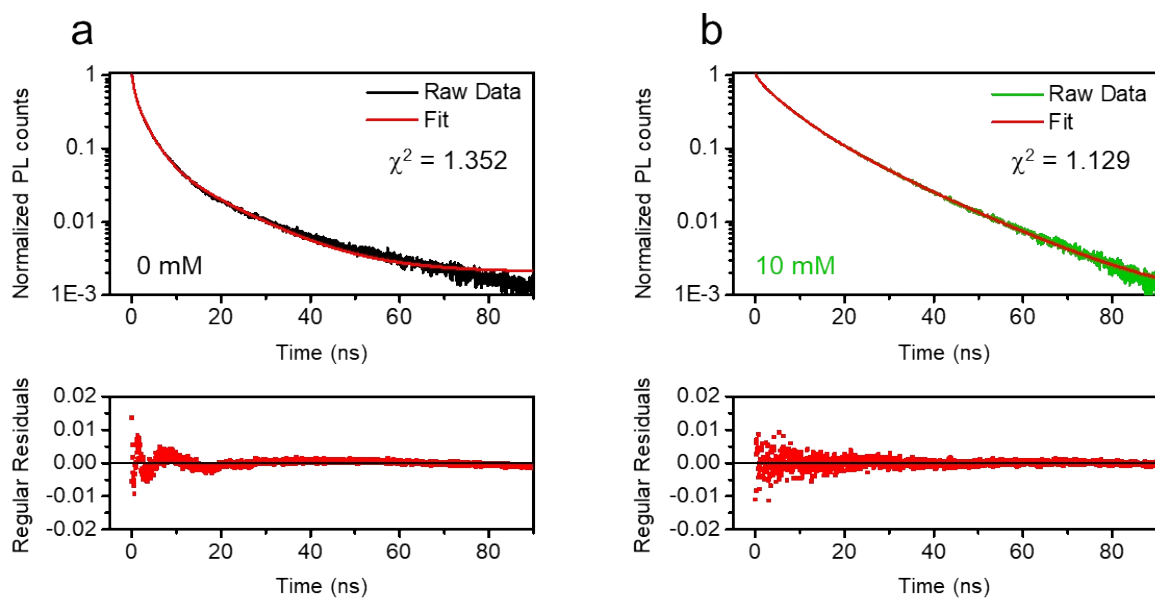


Figure S10. Triexponential fitting and regular residuals of time-resolved PL signals in Figure 1c for (a) pristine CsPbBr₃ and (b) CsPbBr₃-BF₄ (10 mM) (detailed fitting parameters are summarized in Table S1).

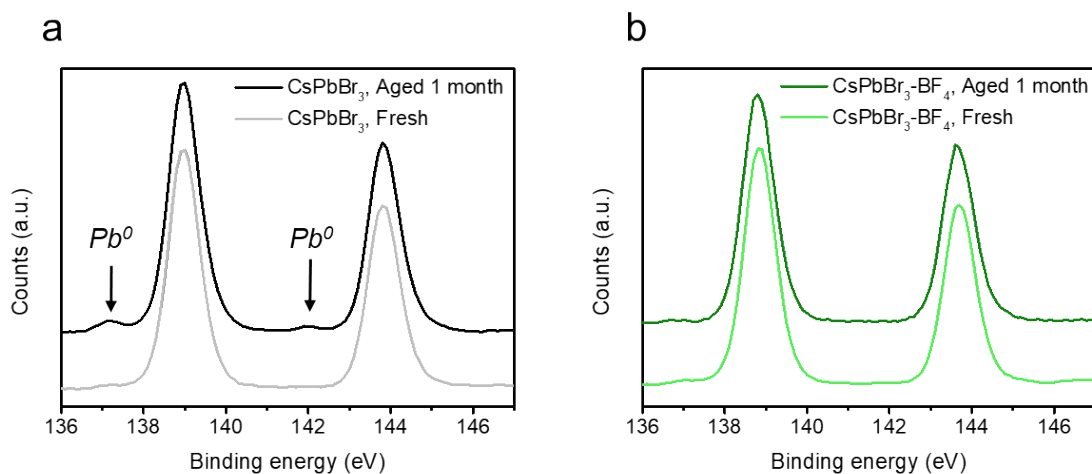


Figure S11. Comparison of Pb 4f XPS spectra of fresh (bottom) and one month aged (top) film. (a) Pristine CsPbBr₃ NCs which exhibits appearance of Pb⁰ peaks and (b) CsPbBr₃-BF₄.

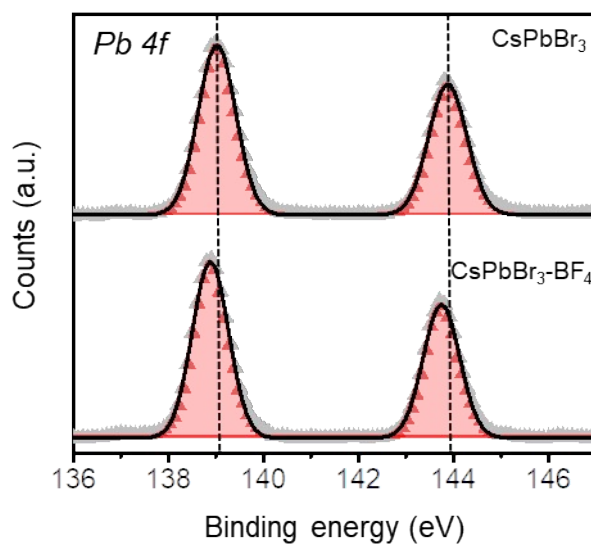


Figure S12. XPS spectra of CsPbBr₃ NCs (top) and CsPbBr₃-BF₄ (bottom) at Pb 4f core level.

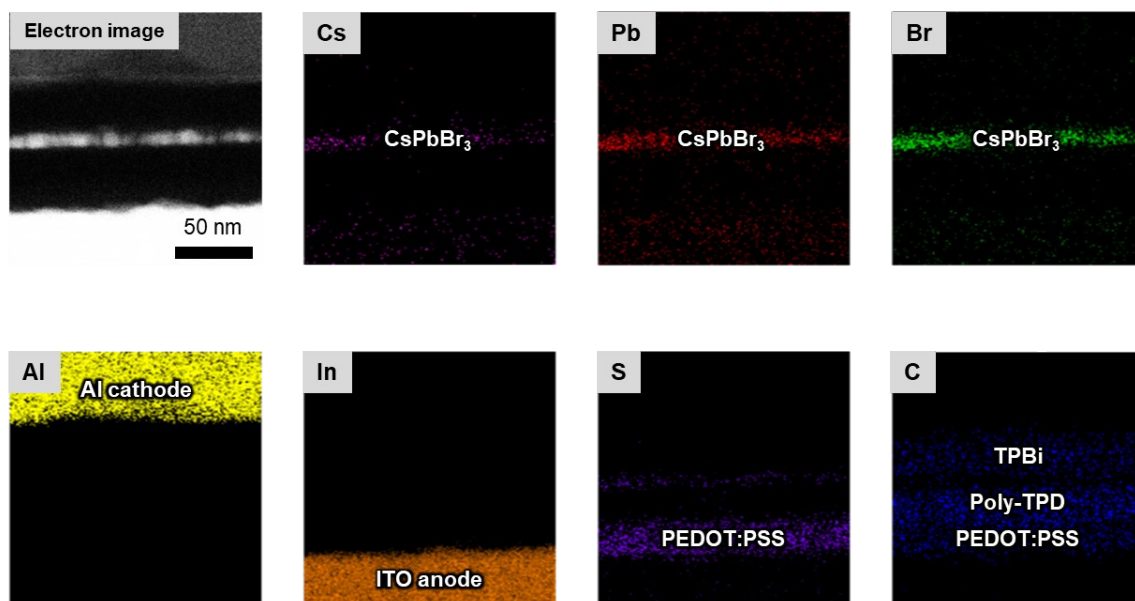


Figure S13. Energy-dispersive X-ray spectroscopy mapping images of multilayered LED in the cross-sectional view.

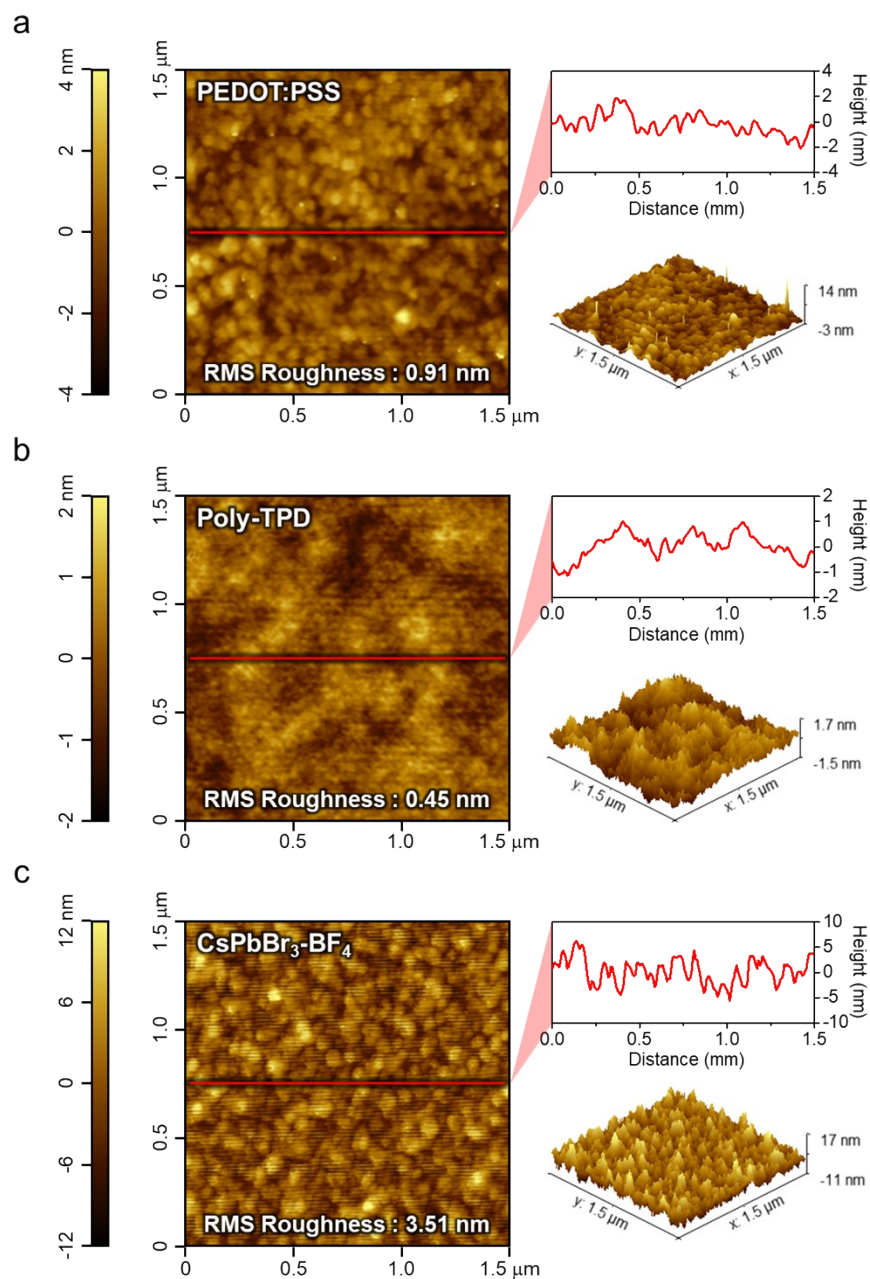


Figure S14. AFM topographic images with RMS roughness and height profiles of solution-processed films. (a) PEDOT:PSS film on ITO glass, (b) poly-TPD film on ITO glass/PEDOT:PSS, and (c) CsPbBr₃-BF₄ film on ITO glass/PEDOT:PSS/poly-TPD.

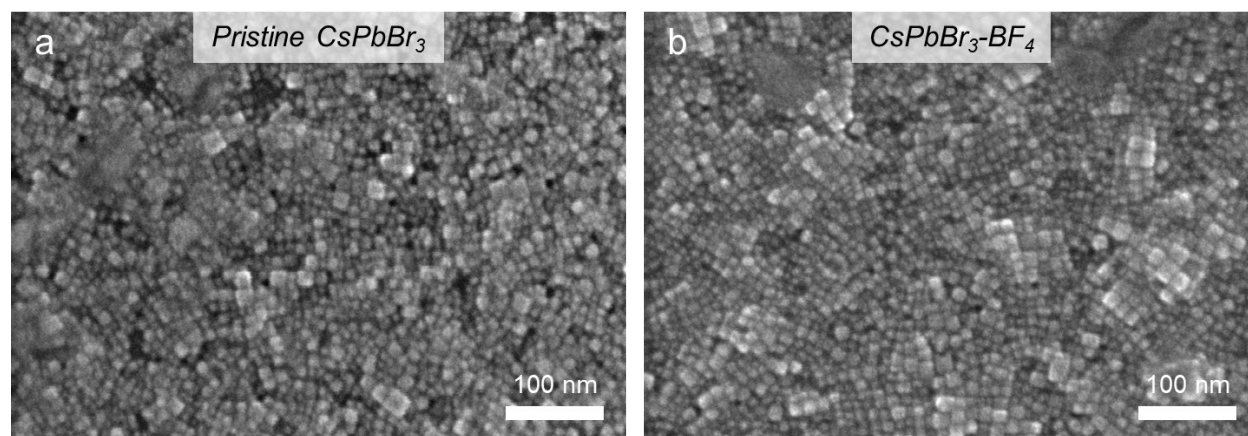


Figure S15. Planar SEM images of (a) pristine CsPbBr₃ and (b) CsPbBr₃-BF₄ films on ITO glass/PEDOT:PSS/poly-TPD.

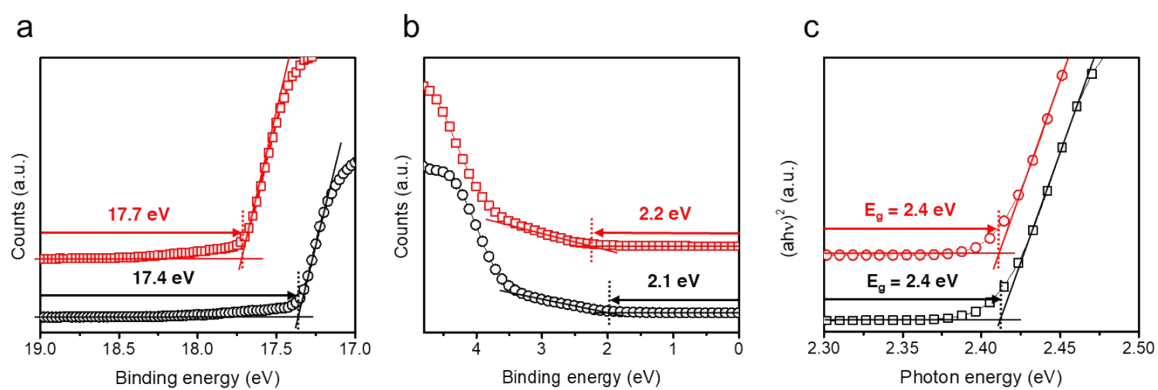


Figure S16. UPS spectra of pristine CsPbBr₃ NC (black, bottom) and CsPbBr₃-BF₄ (red, top) at (a) secondary electron cutoff and (b) valence band regime. (c) Corresponding Tauc plots for calculation of bandgap value of 2.4 eV.

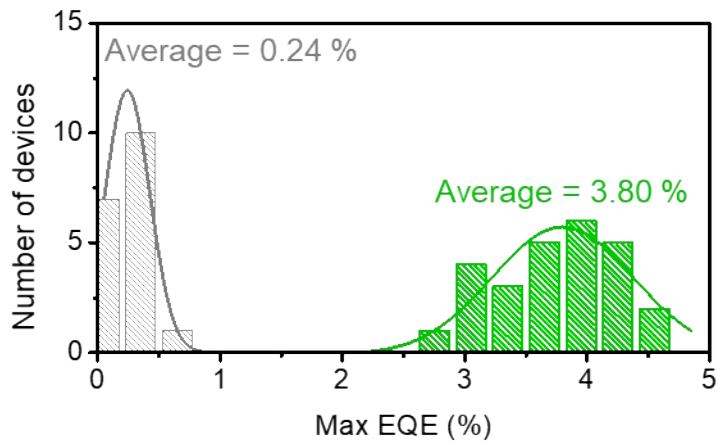


Figure S17. Histogram of maximum EQE for green-emitting PeLEDs based on pristine CsPbBr₃ (gray) and CsPbBr₃-BF₄ (green). Data were acquired from 23 devices and 26 devices respectively.

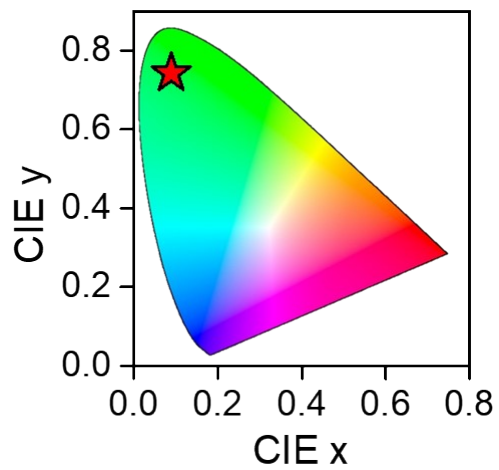


Figure S18. CIE color coordinates of our green-emitting PeLED.

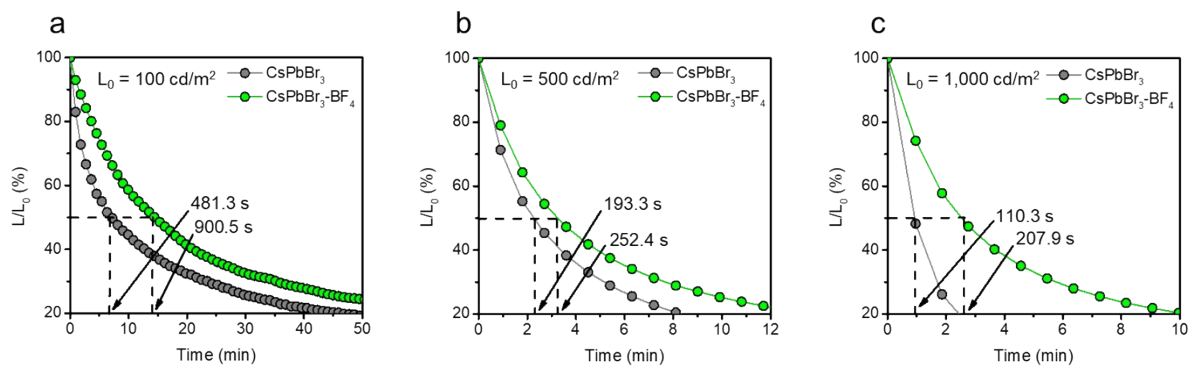


Figure S19. Operational lifetime of pristine CsPbBr₃ (gray) and CsPbBr₃-BF₄ (green) with an initial luminance of (a) 100 cd m⁻² (driving current densities for pristine CsPbBr₃ and CsPbBr₃-BF₄ were 9.85 and 0.65 mA cm⁻²) (b) 500 cd m⁻² (60.51 and 4.07 mA cm⁻²) and (c) 1000 cd m⁻² (229.14 and 8.75 mA cm⁻²).

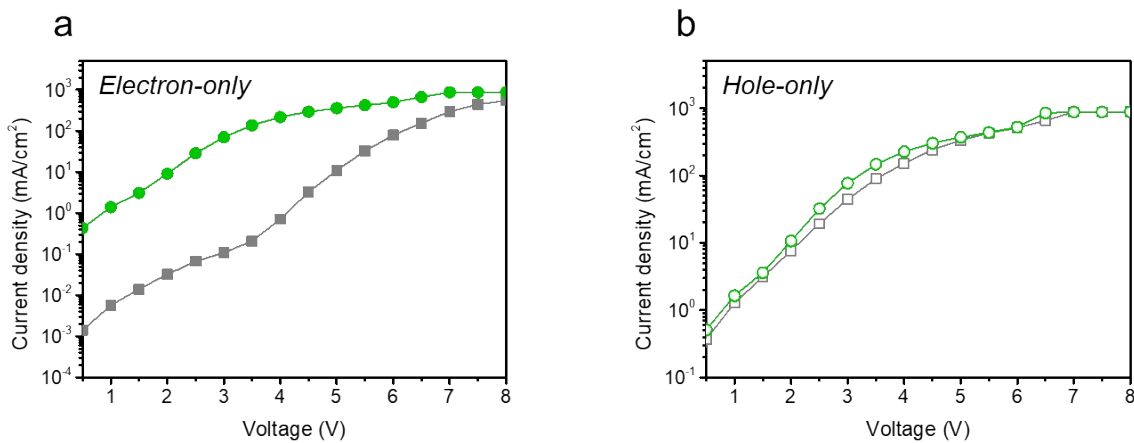


Figure S20. Current density-voltage (J - V) characteristics of hole-only devices (HOD) and electron-only devices (EOD) with CsPbBr₃ (gray square) and CsPbBr₃-BF₄ (green circle).

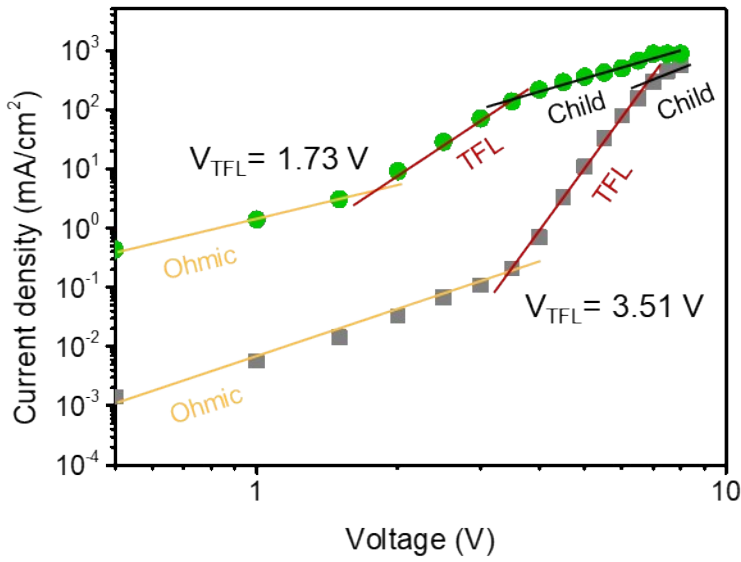


Figure S21. SCLC fit of EOD with CsPbBr₃ (gray square) and CsPbBr₃-BF₄ (green circle), showing ohmic, trap-filled limit (TFL), and Child region.

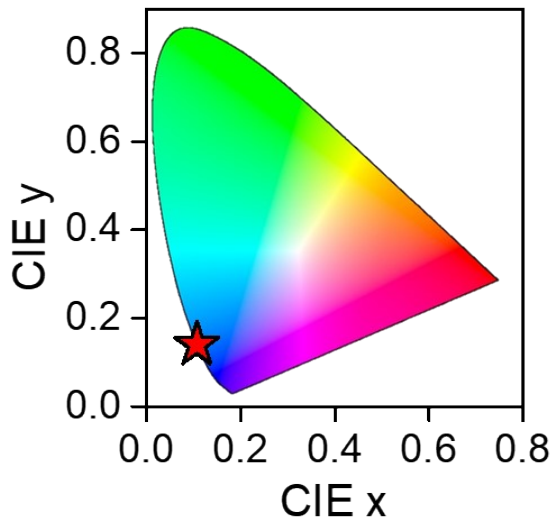


Figure S22. CIE color coordinates of our sky-blue-emitting PeLED.

Table S1. Result of a tri-exponential fit to the time-resolved PL signals of pristine CsPbBr₃ NCs and 10 mM treated CsPbBr₃-BF₄ displayed in Figure 2c.

Sample	A ₁ (%)	τ ₁ (ns)	A ₂ (%)	τ ₂ (ns)	A ₃ (%)	τ ₃ (ns)	τ _{avg} (ns)*	χ ²
CsPbBr ₃	0.43	0.97	0.36	3.46	0.06	11.23	3.30	1.352
CsPbBr ₃ -BF ₄	0.17	0.99	0.52	5.87	0.34	14.41	8.20	1.129

* $\tau_{avg} = \sum A_i \tau_i / \sum A_i$.

Table S2. Summary of green and sky-blue-emitting device performances.

Samples	V _{on} ^{a)} (V)	CE _{max} (cd A ⁻¹)	PE _{max} (lm W ⁻¹)	L _{max} ^{d)} (cd m ⁻²)	EQE _{max} (%)	λ _{EL} ^{f)} (nm)	λ _{FWHM} ^{g)} (nm)	CIE ^{h)} (x, y)
Pristine CsPbBr ₃	2.87	1.02	0.91	1,029	0.37	516	20	(0.09,0.74)
CsPbBr ₃ -BF ₄	2.62	15.62	16.36	5,474	4.79	516	20	(0.09,0.74)
Pristine CsPbBr _{3-x} Cl _x	3.38	0.22	0.17	153	0.21	484	19	(0.11,0.14)
CsPbBr _{3-x} Cl _x -BF ₄	2.84	2.33	2.44	207	2.01	484	19	(0.11,0.14)

^{a)} Turn-on voltage at 1 cd m⁻² luminance. ^{b)} Maximum CE. ^{c)} Maximum PE. ^{d)} Maximum luminance. ^{e)} Maximum EQE. ^{f)} EL peak wavelength. ^{g)} Full width at half maximum (FWHM) of EL. ^{h)} CIE coordinates at luminance of 1,000 cd m⁻² for green CsPbBr₃-based LED and 100 cd m⁻² for sky-blue CsPbBr_{3-x}Cl_x-based LED.