

Supporting Information for:

Direct Synthesis of Quaternary Alkylammonium Capped Perovskite Nanocrystals for Efficient Blue and Green Light-Emitting Diodes

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Methods

Materials and chemicals. Diisooctylphosphinic acid (DOPA), cesium carbonate (Cs_2CO_3 , 99.9%), mesitylene, didodecyldimethylammonium bromide (DDAB), toluene, chlorobenzene (99.8%), cyclohexane, acetone, ethyl acetate were purchased from Sigma-Aldrich. Lead (II) bromide (PbBr_2 , 98%) was purchased from ABCR; didodecyldimethylammonium chloride (DDAC) from TCI. ITO coated glass was supplied by Zhuhai Kaivo Optoelectronic Technology Co., Ltd. Hellmanex detergent solution was supplied by Ossila. PEDOT:PSS (Clevios P VP.AL 4083) was purchased from Heraeus. PolyTPD (Poly[N,N'-bis(4-butylphenyl)-N,N'-bisphenylbenzidine]), PVK (Poly[9-vinylcarbazole]), and 3TPYMB 3,3',3''-[Borylidynetris(2,4,6-trimethyl-3,1-phenylene)]tris[pyridine] were purchased from Lumtec. Lithium fluoride (99.9%) was procured from Alfa Aesar. B2PYMPM (4,6-Bis(3,5-di(pyridin-2-yl)phenyl)-2-methylpyrimidine), B3PYMPM (4,6-Bis(3,5-di(pyridin-3-yl)phenyl)-2-methylpyrimidine), TPBi (1,3,5-Tris(1-phenyl-1Hbenzimidazol-2-yl)benzene), aluminum pellets (99.9%) were provided by Angstrom Engineering. All of the materials were used as received without further purification.

Preparation of cesium diisooctylphosphinate precursor solution (Cs-DOPA, 0.144 M). Cs_2CO_3 (200 mg, 0.614 mmol) was mixed with toluene (7.5 mL) and diisooctylphosphinic acid (DOPA, 1 mL, 3.154 mmol) in a vial. The mixture was stirred and heated to ca. 125 °C on a hot plate, until it became clear and then cooled to room temperature.

Synthesis of CsPbBr_3 nanocrystals. PbBr_2 (55 mg, 0.15 mmol) and DDAB (61 mg, 0.132 mmol) were added to 4 mL mesitylene in a 25 mL flask. With vigorous magnetic stirring, the mixture was heated to 150 °C until it became clear and Cs-DOPA precursor solution of 0.4 mL was swiftly injected using a 1-mL syringe with a 1.6x 40 mm needle. After 10s the reaction mixture was cooled down to RT with a water/ice bath.

Synthesis of CsPb(Br_{1-x}Cl_x)₃ nanocrystals. PbBr₂ (66 mg, 0.18 mmol) and various quantities of DDAB and/or DDACl (for exact quantities see Table S1 below) were added to 4 mL mesitylene in a 25 mL flask, stirring at 1400 rpm. The mixture was rapidly heated to 150 °C until it became clear and Cs-DOPA precursor solution (0.4 mL) was injected using a 1-mL syringe with a 1.6x40 mm needle. After 10 s, the reaction mixture was cooled down to RT with a water/ice bath.

Table S1. Precursor ratio in the synthesis, elemental analysis

PL peak of NC solution	DDAC	DDAB	DDAC: DDAB ratio	CsPb(Br _{1-x} Cl _x) ₃	SEM-EDS chloride content
462 nm	58 mg (0.139 mmol)	-	1:0	$x=0.39$	$x=0.41$
476 nm	42 mg (0.1 mmol)	25 mg (0.054 mmol)	6.5:3.5	$x=0.24$	$x=0.3$
487 nm	33.5 mg (0.08 mmol)	24 mg (0.052 mmol)	6.1:3.9	$x=0.19$	$x=0.24$
499 nm	20 mg (0.048 mmol)	38 mg (0.082 mmol)	3.7:6.3	$x=0.11$	$x=0.14$
515 nm	-	61 mg (0.132 mmol)	0:1	$x=0$	

Purification of CsPbBr₃ nanocrystals. 0.5 mL of toluene and 1 mL acetone were added to the 0.5 mL of crude solution, followed by the centrifugation for 3 min at 10 krpm (10283 x g). Supernatant was discarded and the precipitate was redispersed in 0.5 mL of cyclohexane and 0.5 mL toluene. Then NCs were again precipitated by 1 mL acetone, centrifuged 3 min at 10 krpm (10283 x g) and re-dispersed in 0.5 mL cyclohexane. Obtained colloidal solution of CsPbBr₃ was filtered with a PTFE-syringe filter (pore size 0.2 µm) and used for the fabrication LEDs.

Purification of CsPb(Br_{1-x}Cl_x)₃ nanocrystals. 0.5 mL of toluene and 0.75 mL acetone were added to the 0.5 mL crude solution followed by the centrifugation for 3 min at 10 krpm (10283 x g). The supernatant was discarded and the precipitate was redispersed in 0.5 mL of cyclohexane and 0.5

mL of toluene. Then NCs were again precipitated by 1 mL acetone, centrifuged for 3 min at 10 krpm ($10283 \times g$) and the resulting precipitate was redispersed in 0.5 mL of cyclohexane. Obtained colloidal solution of $\text{CsPb}(\text{Br}_{1-x}\text{Cl}_x)_3$ NCs was filtered through a PTFE-syringe filter (pore size $0.2 \mu\text{m}$) and used for the fabrication of LEDs.

Device fabrication. Substrates with pre-patterned indium tin oxide ($<17 \text{ Ohm/sq}$) were cleaned by sequentially sonicating in Hellmanex (2% in water), deionized water, acetone, and isopropanol for 10 minutes at each stage, and then treated with UV ozone for 10 minutes. PEDOT:PSS 4083 was filtered through $0.45 \mu\text{m}$ hydrophilic syringe filter and spin-coated at 4000 rpm for 25 s, followed by annealing for 30 mins at 130°C in air. Then the substrates were transferred into the nitrogen-filled glovebox, where polyTPD (2 mg/ml in chlorobenzene) was spin-coated at 2000 rpm for 40 s and annealed at 130°C for 25 min. For blue LED fabrication, additional PVK layer was spin-coated at 2000 rpm for 40 s (using 2 mg/ml solution in chlorobenzene) and annealed at 130°C for 20 min. The perovskite NCs solutions were spin-coated at 2000 rpm for 40 s. While remaining in N_2 atmosphere, the substrates were transferred into the thermal evaporator with a base pressure of 10^{-7} mBar, where 15 nm of B2PYMPM, 45 nm of TPBi, and 1.2 nm of LiF were thermally evaporated onto the substrates with the following rates: 0.5, 0.5, and 0.1 As^{-1} . Finally, 100 nm of aluminum were evaporated through the shadow mask (installed without breaking the vacuum) at $2\text{-}5 \text{ As}^{-1}$, defining 0.16 cm^2 pixel area by overlap with ITO. The device performance was measured under ambient conditions without any encapsulation.

Characterization. Optical absorption spectra were measured with Jasco V770 spectrometer in transmission mode (samples diluted ~ 1000 times in cyclohexane). Photoluminescence (PL) spectra were measured in a 90-degree configuration using Horiba Fluoromax-4P+ equipped with a photomultiplier tube and a monochromatized 150W Xenon lamp as an excitation source. All spectra were corrected to take into account the spectral sensitivity of the setup. Powder XRD

patterns were recorded using a powder diffractometer (STOE STADI P) with Cu K α 1 radiation. The diffractometer was operated in a transmission mode with a germanium monochromator and a silicon strip detector (Dectris Mythen). TEM images were captured using a JEOL JEM-2200FS microscope operated at 200 kV. Cross-section SEM image of LED was captured using FEI Nova Nano SEM 230 microscope at 5kV after ion beam milling by Hitachi IM4000. The halide ratios were determined with FEI Quanta 200F using energy-dispersive X-ray spectroscopy (EDAX Octane Super). The QY of the samples was measured in Hamamatsu Quantaurus-QY Plus UV-NIR absolute PL spectrometer (C13534-11) equipped with an integrating sphere. The films for QY measurements were prepared by drop-casting 10 μ l of the sample mixed with 50 μ l of the cyclohexane on the square 10mm x 10mm cleaned glass substrates. Time-resolved PL traces were measured with a time-correlated single-photon counting technique at the PL peak with Picoquant FT-300 lifetime spectrometer and 355 nm picosecond laser (1 MHz repetition rate) as an excitation source; the instrument response function of the measurement setup was 220 ps.

The LED device performance was measured with FDS1010 silicon photodiode (Thorlabs) through Keysight B2902A Precision Source/Measure Unit with 50V/s sweep speed, while electroluminescence spectra were measured using CCS200 fiber CCD spectrometer (Thorlabs) at various constant voltages. Luminance was recalculated from the electroluminescence spectra in the assumption of Lambertian source.

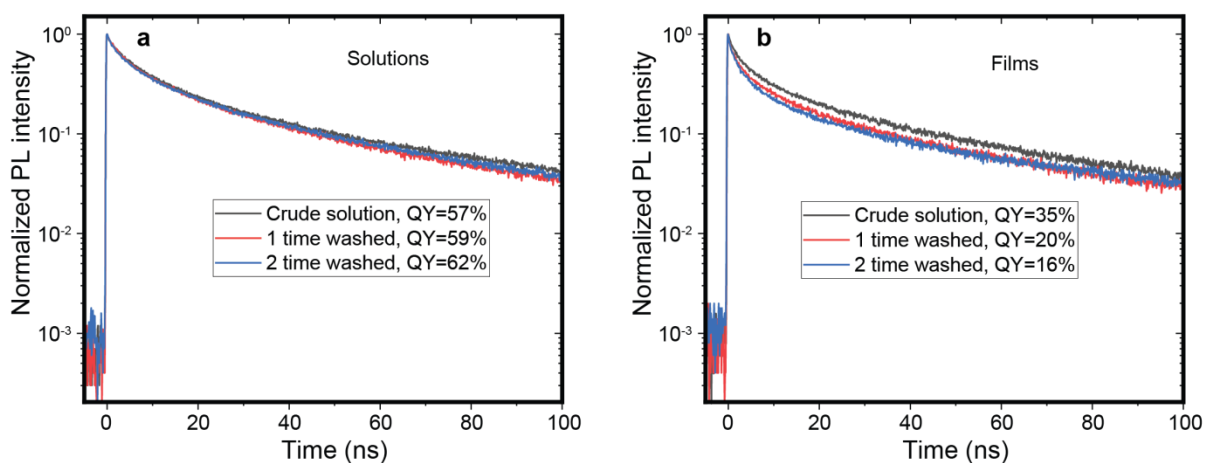


Figure S1. (a) Time-resolve PL spectra of the colloidal solutions and (b) corresponding drop-cast films of $\text{CsPb}(\text{Br}_{1-x}\text{Cl}_x)_3$ NCs, $x=0.11$, directly after synthesis (crude solution) and after washing steps.

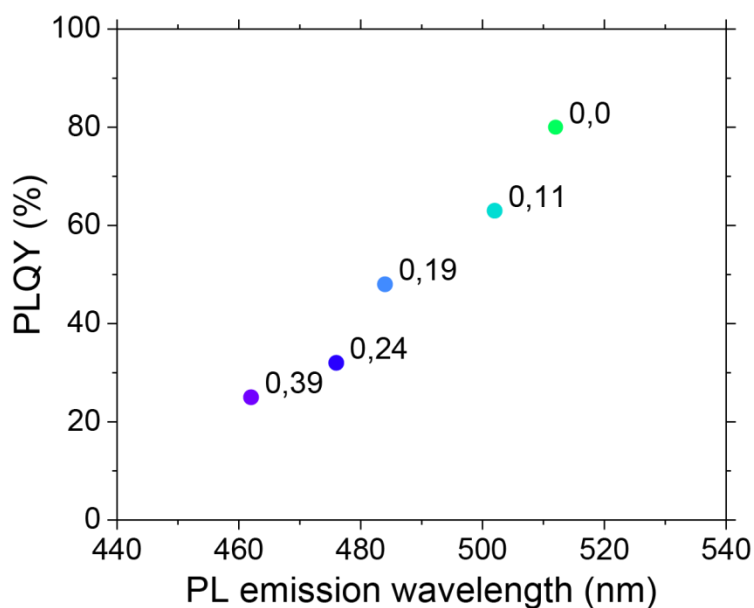


Figure S2. Solution PL quantum yield and PL peak position of $\text{CsPb}(\text{Br}_{1-x}\text{Cl}_x)_3$ NCs for different Cl-content (x) indicated near the corresponding points on the graph.

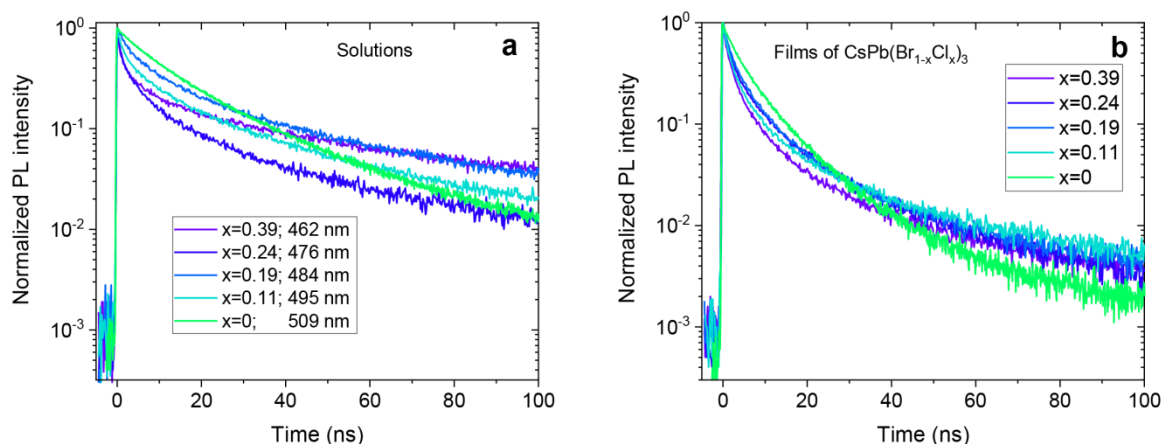


Figure S3. (a) Time-resolve PL spectra of the colloidal solutions and (b) corresponding drop-cast films of $\text{CsPb}(\text{Br}_{1-x}\text{Cl}_x)_3$ NCs. x represents Cl-content in the synthesis, wavelength shows PL peak position in the solution.

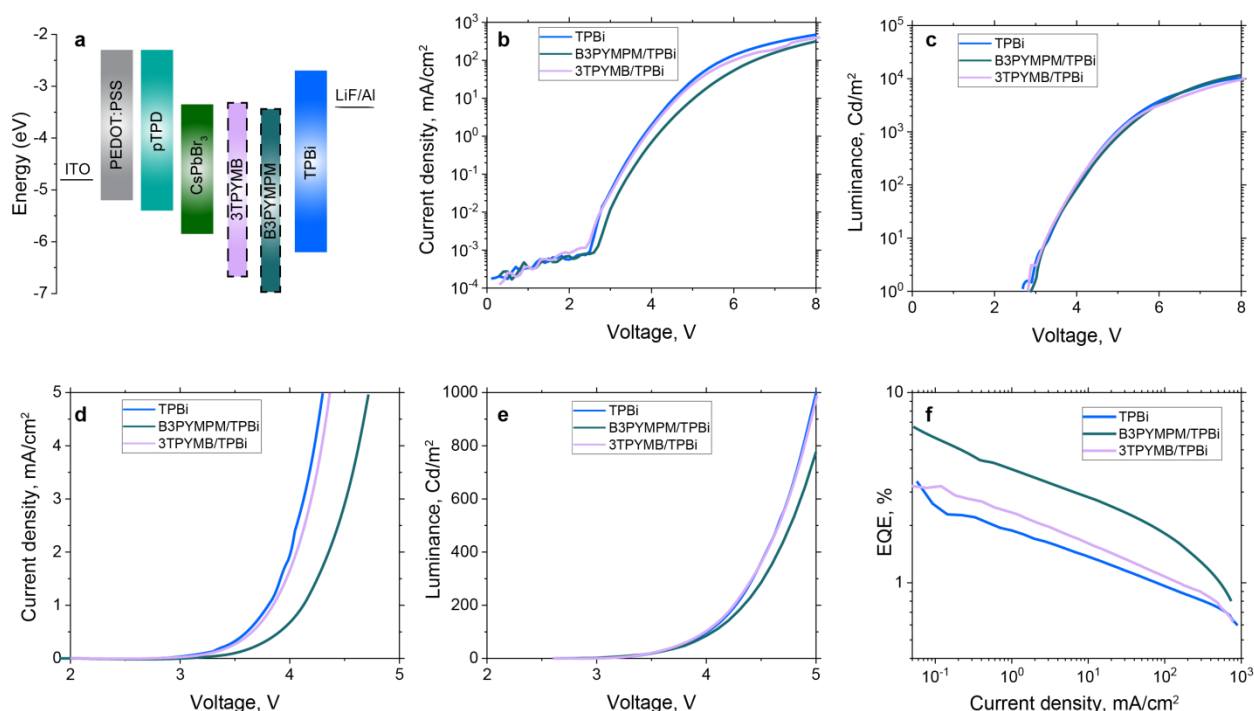


Figure S4. Tests of various HBLs for LEDs based on CsPbBr_3 NCs. Performance of the device structures without any HBL, and with B3PYMPM or 3TPYMB as HBLs. (a) Energy level of the layers vs. vacuum. (b) Current density vs. voltage. (c) Luminance vs. voltage. (d, e) Same as (b, c), but zoomed near turn-on voltage. (f) EQE of the devices vs. current density.

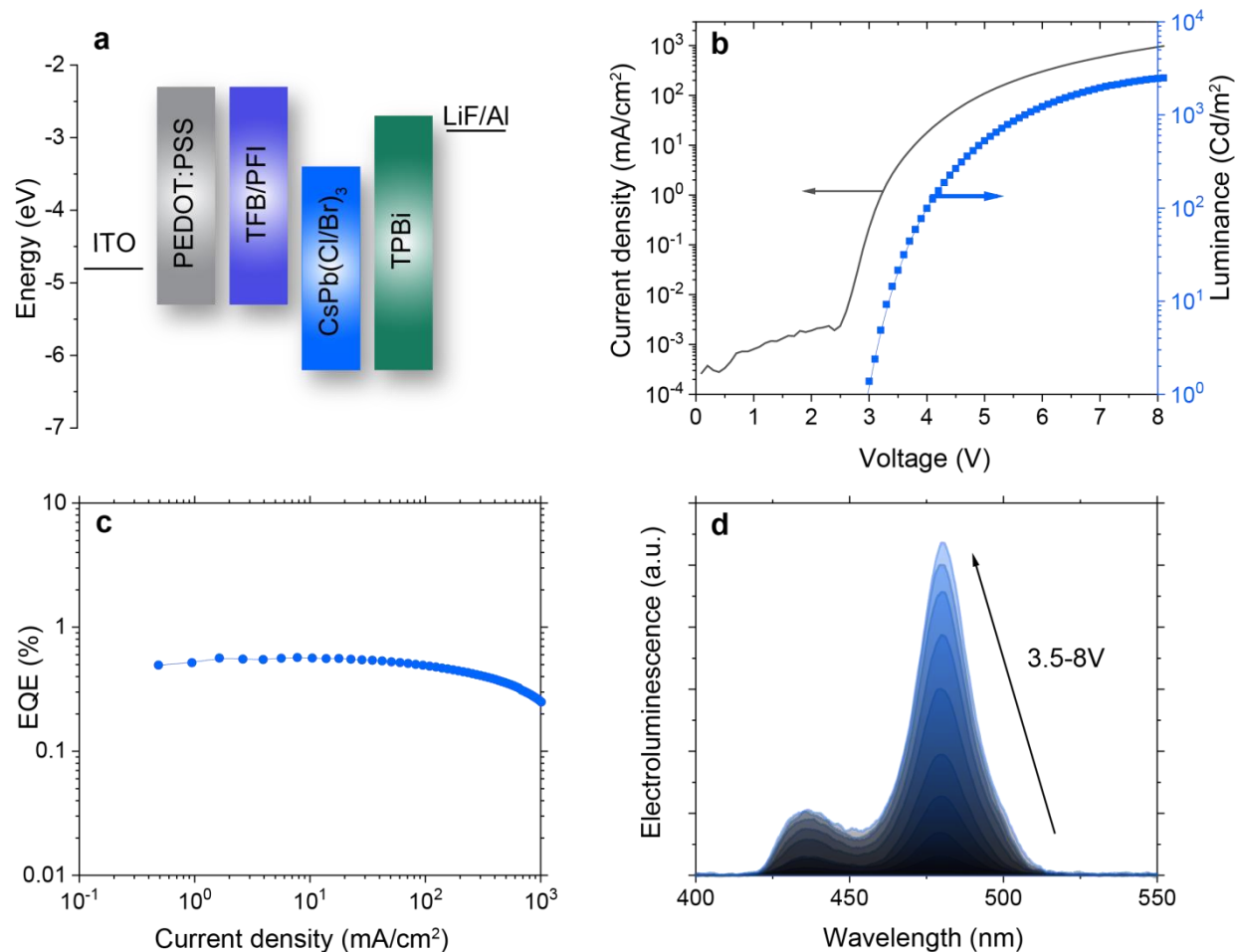


Figure S5. Performance of the LED based on CsPb(Br_{1-x}Cl_x)₃ NCs emitting at 480 nm. (a) Energy diagram vs. vacuum. (b) Current density and luminance vs. voltage. (c) External quantum efficiency of the device vs. current density. (d) Electroluminescence spectra at different driving voltages. Peak at 430 nm corresponds to the emission of TFB.

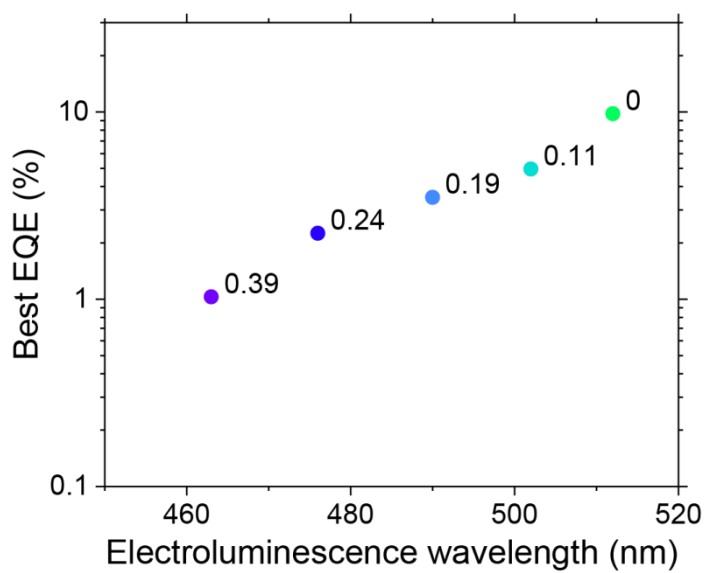


Figure S6. Comparison of the best external quantum efficiencies of the LEDs based on CsPb(Br_{1-x}Cl_x)₃ NCs with different Cl-content (x) indicated near the corresponding points on the graph.

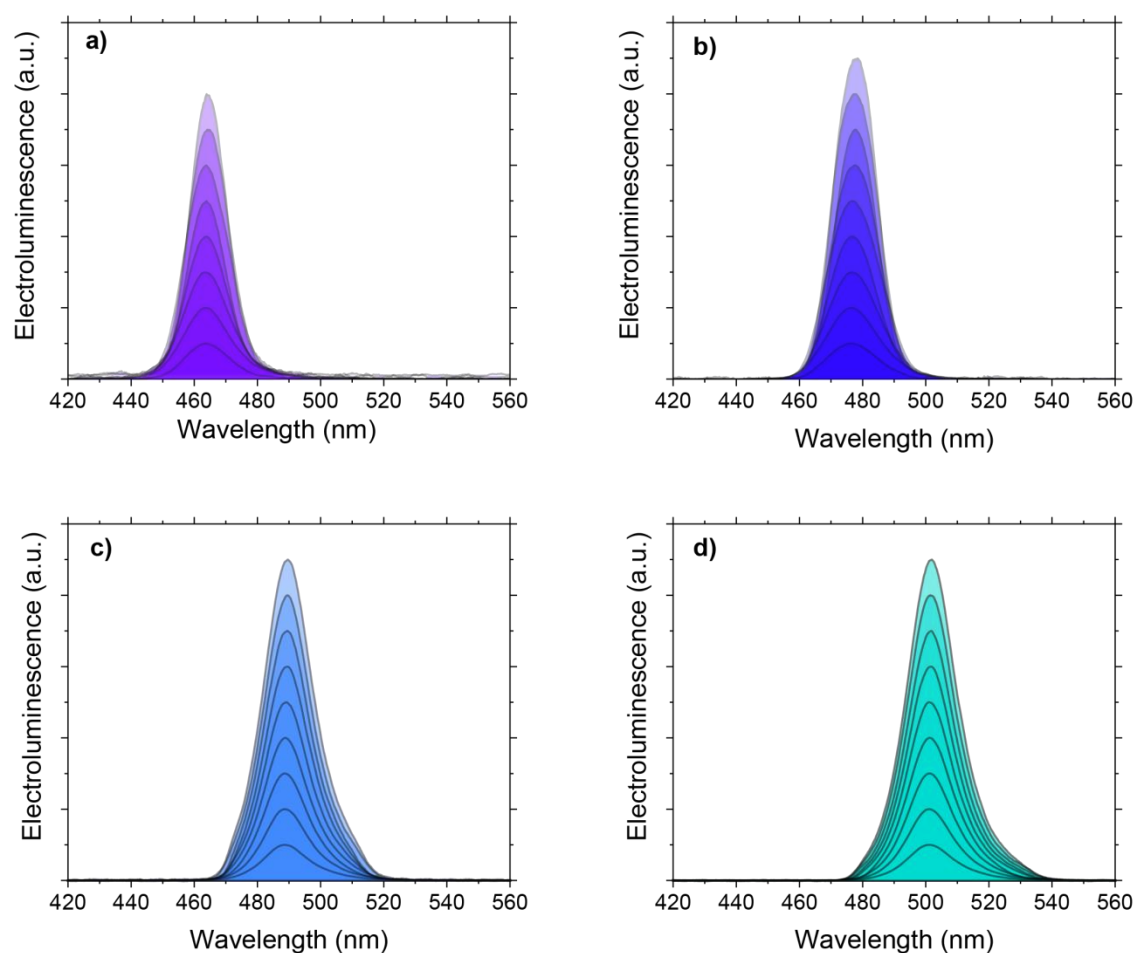


Figure S7. Electroluminescence spectra of the blue-emitting devices based on $\text{CsPb}(\text{Br}_{1-x}\text{Cl}_x)_3$ NCs at increasing bias from 3 V to 8V for (a) $x=0.39$, EL peak at 463 nm. (b) $x=0.24$, EL peak at 476 nm. (c) $x=0.19$, EL peak at 490 nm. (d) $x=0.11$, EL peak at 502 nm.

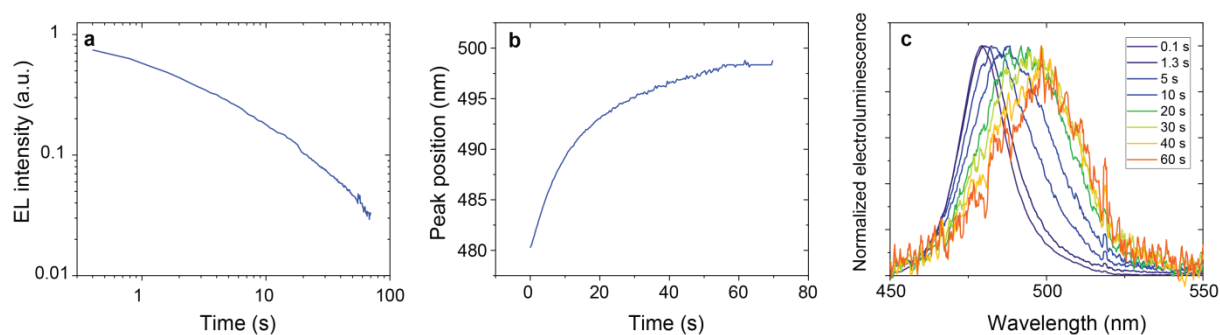


Figure S8. Stability test of the LED with $\text{CsPb}(\text{Br}_{0.76}\text{Cl}_{0.24})_3$ emissive layer operated at constant current density of 10 mA/cm^2 corresponding to initial brightness of 100 Cd/m^2 . (a) Peak intensity change during the operation. (b) Change of the EL peak position during the operation. (c) Normalized electroluminescence spectra evolution during constant current bias.

Table S2. Commission Internationale de l'Éclairage CIE 1931 color coordinates of the devices presented in this work. BT.2020 (Rec 2020) coordinates of the desired blue colour for display application (0.131; 0.046).

Chloride content, $\text{CsPb}(\text{Br}_{1-x}\text{Cl}_x)_3$	EL Peak, nm	x	y
$x=0.39$	463	0.131	0.059
$x=0.24$	476	0.102	0.144
$x=0.19$	490	0.075	0.767
$x=0.11$	502	0.058	0.298
$x=0$	515	0.033	0.577