

Supporting Information

Engineering Color-Stable Blue Light-Emitting Diodes with Lead-Halide Perovskite Nanocrystals

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Experimental details:

Chemicals. Lead acetate trihydrate ($\text{Pb}(\text{OAc})_2 \cdot 3\text{H}_2\text{O}$, Sigma Aldrich), Cesium carbonate (Cs_2CO_3 , fluorochem), Oleic acid (OLA, Sigma Aldrich), Trioctyl phosphine (TOP, STREM), Bromine (Br_2 , Sigma Aldrich), Potassium permanganate (KMnO_4 , Fluka), Hydrochloric acid (HCl , Merck), 1-Octadecene (ODE, Sigma Aldrich), 3-(N,N-dimethyloctadecylammonio)-propanesulfonate (Sigma Aldrich), toluene (Sigma-Aldrich) were used as received.

Preparation of cesium oleate solution (Cs-oleate, 0.4 M in ODE). 1.628 g of Cs_2CO_3 (10 mmol, 2 eq. Cs) and 5 mL of OLA (16 mmol, 0.8 eq.) were evacuated in a three-neck flask along with 20 mL of ODE at room temperature until the first gas evolution subsides and then further evacuated at 25-120 °C for 1 hour.

Preparation of lead (II)-oleate solution (Pb-oleate, 0.5 M in ODE). 4.6066 g of $\text{Pb}(\text{OAc})_2 \cdot 3\text{H}_2\text{O}$ (12 mmol, 1 eq.) and 7.6 mL of OLA (24 mmol, 2 eq.) were evacuated in a three-neck flask along with 16.4 mL of ODE at room temperature until the first gas evolution subsides and then further evacuated at 25-120 °C for 1 hour.

Preparation of TOPBr_2 solution (0.5 M in toluene). TOP (6 mL, 13 mmol) and Br_2 (0.6 mL, 11.5 mmol) were reacted under inert atmosphere and diluted with toluene (18.7 mL) once the reaction was cooled to room temperature.

Preparation of TOPCl_2 solution (0.5 M in toluene). TOP (30 mL, 0.067 mol) was reacted at 0°C with Cl_2 gas (ca. 0.34 mol), which was produced in situ by the reaction of concentrated HCl (85 mL, 0.6725 mol) and potassium permanganate (106.27 g) and brought to the reaction vessel by argon gas flow after being cleaned from residual HCl by water. The resulting transparent product was diluted with toluene (93 mL).

Preparation of $\text{CsPb}(\text{Br}/\text{Cl})_3$ nanocrystals. The Pb-oleate (5 mL, 2.5 mmol) and Cs-oleate (4 mL, 1.6 mmol) solutions and 3-(N,N-dimethyloctadecylammonio)-propanesulfonate (0.43 g, 1

mmol) were mixed with 10 mL 1-octadecene and heated to 120°C under vacuum, where the atmosphere was changed to Argon. The temperature was further elevated to 150 °C where a mixture of TOPBr₂ and TOPCl₂ was injected (5 mL, 30% TOPCl₂, 5 mmol of halides). The reaction mixture was immediately cooled to room-temperature.

Isolation and purification of CsPb(Br/Cl)₃ nanocrystals. To the crude solution (24 mL) 24 mL of acetone were added and the NCs were precipitated by centrifugation at 29'500×g (g is the standard gravity) for 10 minutes. The NCs were then dispersed in 10 mL of toluene. The NCs in were precipitated with 20 mL of ethylacetate and centrifugation at 29'500×g for 1 minute. During the following second and third purification step 5 mL of toluene were used for redispersion and 10 mL of ethylacetate for the precipitation under identical centrifugation conditions. The final colloidal solution in toluene (ca. 10 mL) was centrifuged at 29'500×g for 1 minute to remove fractions which were not colloidally stable. The typical concentration of the final solution was estimated by mass and was between 10 and 20 mg/mL.

Characterization. For powder X-ray diffraction (XRD) patterns a Stoe IPDS II with an image plate detector, Cu-Kα radiation ($\lambda = 1.54186 \text{ \AA}$), graphite monochromator, fiber optics and a modified sample holder was used. Transmission electron microscopy (TEM) images were collected using Hitachi HT7700 microscope operated at 100 kV and using a Philips CM 12 microscope operating at 120 kV. TEM images were processed using Image J (or new Fiji). UV-Vis absorption spectra for colloidal solutions were collected using a Jasco V670 spectrometer in transmission mode. A Fluorolog iHR 320 Horiba Jobin Yvon spectrofluorometer equipped with a PMT detector was used to acquire steady-state photoluminescence (PL) spectra from solutions. PL quantum yields of thin films were determined in a Horiba Fluoromax equipped with an integrating sphere. Time-resolved PL measurements were performed by exciting the sample with a 405 nm

diode laser. The PL was detected by a single photon avalanche diode (PicoQuant PDM, 50 ps time resolution) coupled at the exit port of the monochromator. TRPL traces were recorded by using a time-correlated single photon counting (TCSPC) module (PicoQuant, PicoHarp 300).

Light-emitting diode (LED) materials. Indium-tin oxide coated glass substrates (ITO, Kaivo, $<17 \text{ } \Omega/\text{sq}$), Poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS, Heraeus Clevios AI 4083), Poly[N,N'-bis(4-butylphenyl)-N,N'-bisphenylbenzidine] (Poly-TPD, Luminescence Technology Corp.), 4,4'-Bis(9-carbazolyl)-1,1'-biphenyl (CBP, Angstrom Engineering), Tris(4-carbazoyl-9-ylphenyl)amine (TCTA, Luminescence Technology Corp.), polystyrene (Sigma-Aldrich), 4,6-Bis(3,5-di(pyridin-3-yl)phenyl)-2-methylpyrimidine (B3PYMPM, Luminescence Technology Corp.), 2,2',2''-(1,3,5-Benzinetriyl)-tris(1-phenyl-1-H-benzimidazole) (TPBi, Angstrom Engineering), lithium fluoride (LiF, Angstrom Engineering), aluminum pellets (Al, Angstrom Engineering), chlorobenzene (Sigma-Aldrich) were used as received.

LED fabrication. The LEDs were fabricated by spin-coating PEDOT:PSS on pre-patterned, cleaned ITO-coated glass substrates in ambient conditions. After annealing the spin-coated PEDOT:PSS layer at 130 °C in air, the substrates were transferred into a nitrogen glovebox, where sequentially Poly-TPD (1.5 mg/mL in chlorobenzene), CBP (0.5 mg/mL in chlorobenzene) and the CsPb(Br/Cl)₃ NCs (8 mg/mL in toluene) mixed with polystyrene (1.0 mg/mL) were spin-coated (The CsPb(Br/Cl)₃ NC-dispersion was filtered and its concentration determined before use). The Poly-TPD and CBP layer were annealed at 130°C and 120°C, respectively, before the next layer was spin-coated. Afterwards, the substrates were transferred into a high-vacuum chamber for evaporation of B3PYMPM (50 nm, 0.5 Å/s), LiF (1.2 nm, 0.1 Å/s) and Al (100 nm, 2 – 5 Å/s).

LED performance measurements. The current-density and photon-power of the LEDs were measured as a function of voltage using a Keysight 2902b source measurement unit and a calibrated photodiode (FDS1010-CAL, Thorlabs) under ambient conditions. The size of the photodiode ($10 \times 10 \text{ mm}^2$) is much larger than that of the active pixel size ($4 \times 4 \text{ mm}^2$) of the LEDs. Electroluminescence (EL) spectra were recorded using a CCS200 CCD spectrometer (Thorlabs). The luminance and external quantum efficiency (EQE) were calculated from the LED's photon-power and EL spectrum using the photodiode sensitivity. For the calculation of the luminance a Lambertian emission profile was assumed. LED transient spectra were measured with a Keysight 2902b source measurement unit and the CCS200 CCD spectrometer.

Hole-transporting materials:

The need for two hole-transporting layers (HTLs) is emphasized in the Figure S1, where we show peak EQE values for two sets of experiments performed each in the same run. The first set of experiments (left in Figure S1) was performed on devices with either only Poly-TPD or Poly-TPD and CBP as hole-transporting materials. The second set of experiments used TCTA as the only HTL or as the second one on top of Poly-TPD. With the combination of Poly-TPD and TCTA, the LEDs gave on average similar results to Poly-TPD and CBP.

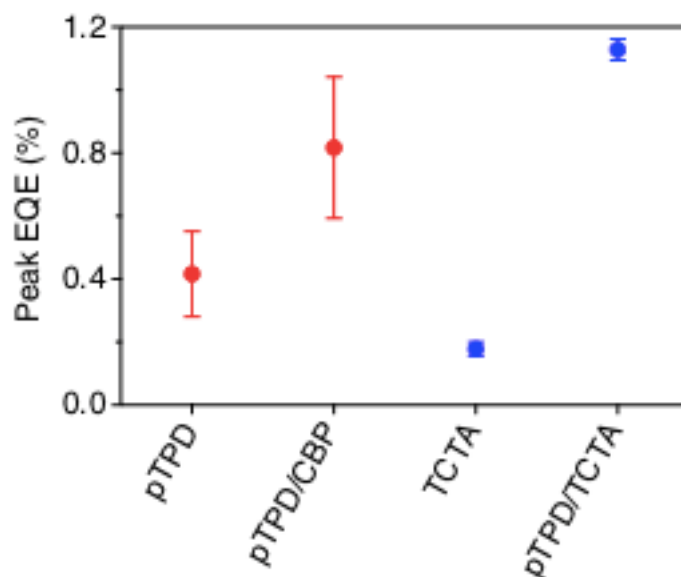


Figure S1. Peak EQE values for different HTLs. Left: only Poly-TPD compared to Poly-TPD/CBP (best device architecture) measured on the same day with the otherwise same device architecture and batch of NCs; right: only TCTA compared to Poly-TPD/TCTA (on average, similar performance to Poly-TPD/CBP was observed).

Statistics:

EQE distribution. For identical device configuration and similar NC concentrations (4 – 10 mg/mL), a distribution of EQE values as shown in the histogram of Figure S2 was observed. The width of the histogram bars is 0.2%. The distribution shows that 18 times an EQE of $1.0 \pm 0.1\%$ was obtained. The overlaid normal distribution also peaks at 1.0% with a standard deviation of 0.2%. The results represent four different NC batches.

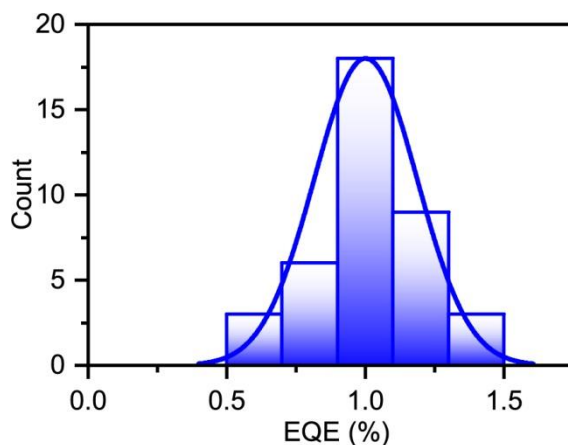


Figure S2. Distribution of EQE values observed for standard device configuration.

Color stability:

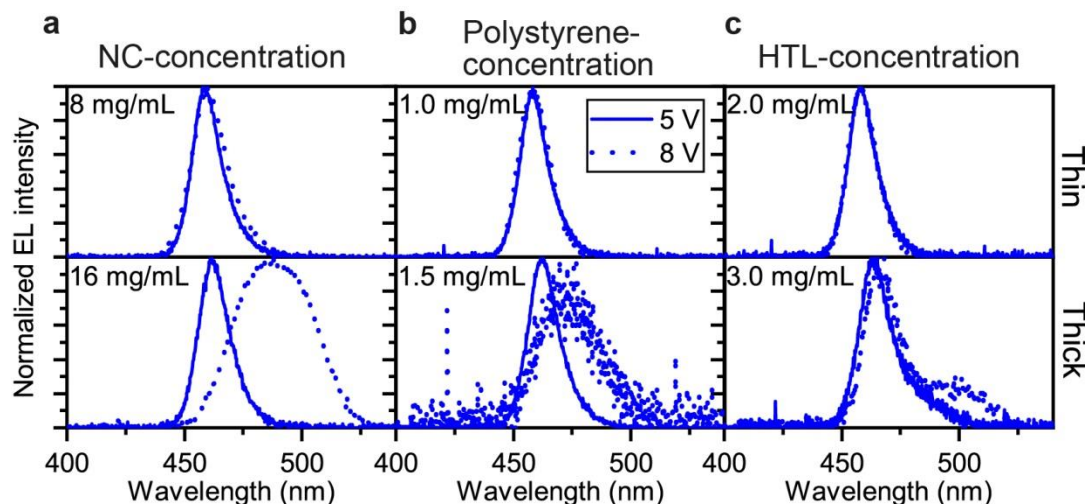


Figure S3. (a) Normalized EL spectra of LEDs with $\text{CsPb}(\text{Br},\text{Cl})_3$ NCs deposited from an 8 mg/mL (top) and 16 mg/mL (bottom) dispersion recorded at 5 V (solid line) and 8 V (dotted line), (b) normalized EL spectra of LEDs with $\text{CsPb}(\text{Br},\text{Cl})_3$ NCs (8 mg/mL) with added polystyrene (1.0 mg/mL, top; 1.5 mg/mL, bottom) recorded at 5 V (solid line) and 8 V (dotted line), (c) normalized EL spectra of LEDs with $\text{CsPb}(\text{Br},\text{Cl})_3$ NCs (8 mg/mL) and polystyrene (1.0 mg/mL) using concentrations of 1.5 mg/mL Poly-TPD and 0.5 mg/mL CBP (top) and of 2.0 mg/mL Poly-TPD and 1.0 mg/mL CBP (bottom) to make the HTLs recorded at 5 V (solid line) and 8 V (dotted line).

Conditions for stable color. In order to better understand the reasons for the color (in)stability of mixed lead-halide perovskites (LHPs) under LED operation, we looked at the thickness-dependence of the EL spectra through varying the concentrations of the spin-coated materials. Some of the corresponding results are shown in Figure S3. For devices without polystyrene added to the emitting layer (EML) of the LEDs, we observed stable EL wavelength up to 8 V for NC-concentrations below 10 mg/mL, albeit with low EQE of $\sim 0.1\%$. Making the EML thicker by using higher concentrations of NCs (e.g. 16 mg/mL) in toluene resulted in an increased EQE ($\sim 0.6\%$), but the EL was only stable up to 5.5 nm, and at 8 V was clearly shifted compared to 5 V (see Figure S3a). A similar trend is observed when the polystyrene-concentration is increased above 1.0 mg/mL with a constant NC concentration of 8 mg/mL NCs, Figure S3b. Up to 1.0 mg/mL polystyrene, the EL wavelength stays constant with increasing voltage while simultaneously the

EQE increases to 1.0%. For e.g. 1.5 mg/mL polystyrene, the EQE drops to 0.9% with unstable color (Figure 4b). Surprisingly, even thicker hole-transporting layers (HTLs) decrease the color stability. In Figure S3c, the EL spectra at 5 and 8 V are shown for thinner HTLs (Poly-TPD concentration: 1.5 mg/mL; CBP concentration: 0.5 mg/mL), and thicker HTLs (Poly-TPD concentration: 2.0 mg/mL; CBP concentration: 1.0 mg/mL) labelled by the sum of the two concentrations. Clearly, with the thicker HTLs a second EL band appears at ~500 nm, indicative of a bromide-rich phase. To summarize, in all cases when the total thickness of the device was increased, the EL wavelength was less stable, and EL from a bromide-rich phase appeared with increasing voltage or even became dominant. At the same voltage, the electric field at the NCs is smaller for a larger total layer thickness than for a thinner one. Thus, we believe it unlikely that the halide-demixing and associated color instability is caused solely by the external electric field. The results more likely point towards charge-imbalance in the EML as a cause of the instability. We plan to investigate this issue in detail for a future report.

Green LEDs:

Device architecture. Green LEDs were prepared on pre-patterned ITO by spin-coating PEDOT:PSS, then Poly-TPD, followed by sulfobetaine-capped CsPbBr₃ NCs (4 mg/mL) together with 1.0 mg/mL polystyrene. B3PYMPM (15 nm, 0.5 Å/s), TPBi (45 nm, 0.5 Å/s), LiF (1.2 nm, 0.1 Å/s) and Al (100 nm, 2 – 5 Å/s) were evaporated sequentially in high-vacuum. The work functions and bandgap energies are shown in Figure S4a, where CsPbBr₃ levels are taken from¹.

LED performance. The LEDs with sulfobetaine-capped CsPbBr₃ NCs with or without polystyrene in the EML emit at ~515 nm, as shown in the EL spectra in Figure S4b. The current density and the luminance are shown as a function of voltage in Figure S4c. Without polystyrene an earlier steep increase of the current density than with polystyrene is observed (2.5 vs. 3.0 V). The turn-on voltage, however, is the same for both samples, 3.0 V, indicating some “wasted”

current density in LEDs without polystyrene. Additionally, the peak luminance with polystyrene reaches over 7'000 cd/m², while without polystyrene only just above 3'000 cd/m² was attained.. These observations are also reflected in the EQE vs current density curve, Figure S4d, where the peak EQE reaches only 0.8% without polystyrene, but more than 6% with polystyrene. Previously, with different device architecture and without polystyrene, we obtained 2.5% EQE and peak brightness of 24'000 cd/m².²

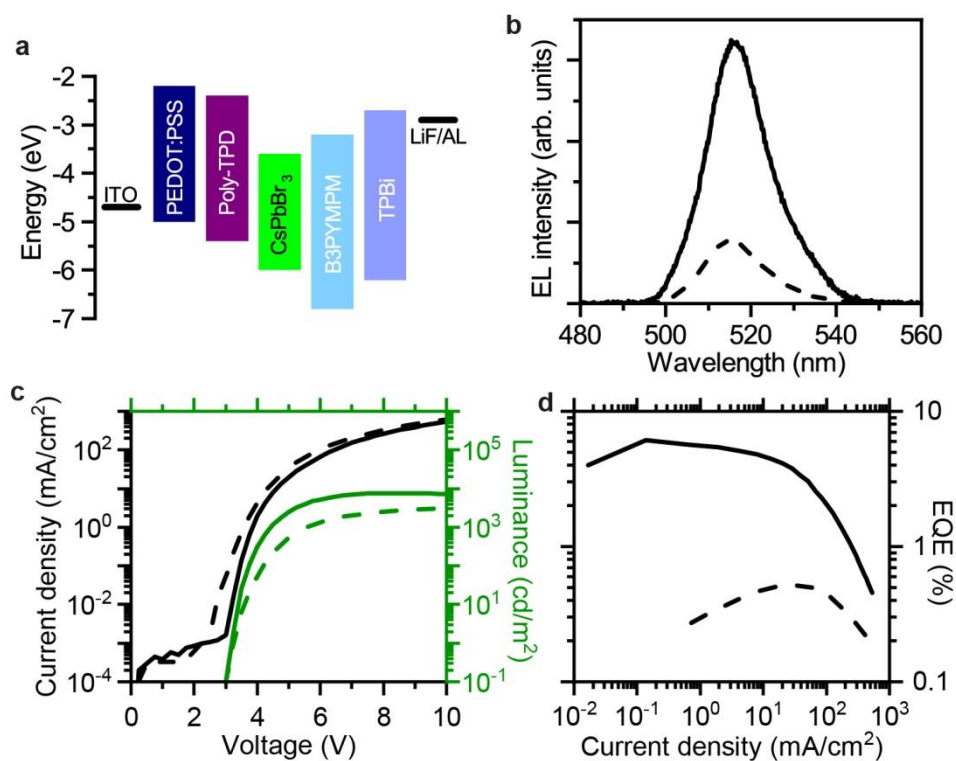


Figure S4. (a) Work function and bandgap of materials used in LED stack, energies vs. vacuum, (b) EL spectra between 4 and 10 V, (c) current density (black line) and luminance (green line) vs. voltage for green LED, (d) EQE vs. current density for the same LED. Dotted lines in (b), (c) and (d) are for devices without polystyrene.

Effect of polystyrene on optical properties:

As it was previously shown that low- k dielectric hosts, like polymers, can increase the exciton confinement potential,³ we also decided to investigate whether polystyrene influences the optical properties. We prepared thin-films of CsPb(Br/Cl)₃ NCs with and without the addition of polystyrene and measured their PL. The inset of Figure S5 shows that the PL spectrum of thin-films is virtually unchanged by the addition of polystyrene. The absolute quantum yields (29% without vs. 37% with polystyrene) and the decay of the PL with time (Figure S5) are also barely affected by polystyrene, indicating that its influence on the optical properties of the CsPb(Br/Cl)₃ NCs is negligible and cannot solely explain the improved LED performance.

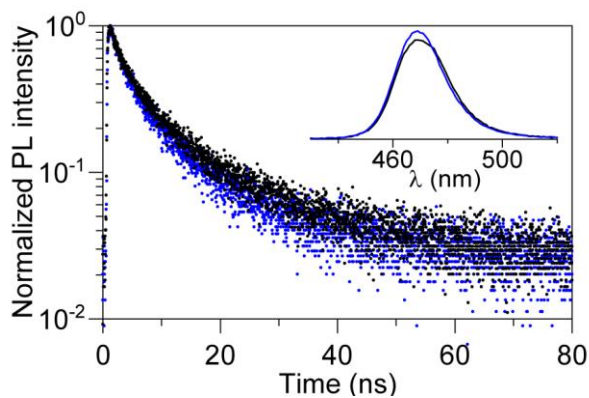


Figure S5. Time-resolved PL of spin-coated thin films of CsPb(Br/Cl)₃ NCs without (black dots) and with polystyrene (1.0 mg/mL, blue dots), inset: corresponding PL spectra.

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