## Nanocubic mixed-halide perovskite superlattices for bright red light-emitting diodes

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## Experimental

Materials: All solvents and chemicals were purchased from commercial suppliers and used as received without further purification. Octadecene (ODE, 90%), oleylamine (OAm, 80-90%), oleic acid (OA, 90%), hexane (99.5%) and methyl acetate (MA, 99%) were purchased from Anhui Zesheng Technology Co., Ltd. Poly[N,N'-bis(4-(Poly-TPD, butylphenyl)-N,N'-bis(phenyl)-benzi M<sub>w</sub>>20000) and 1,3,5-Tris(Nphenylbenzimidazol-2-yl)benzene (TPBi, 99.999%) were purchased from Xi'an Polymer Technology Corp. Poly(3,4-ethylenedioxythiophene)-Light poly(styrenesulfonate) (PEDOT: PSS, 4083) was purchased from Yingkou Advanced Election Technology Co., Ltd. 1-Octadedecylamine (ODA, 90%), 1-hexadecylamine (HDA, 90%) and 1-aminotetradecane (TDA, 96%) were purchased from Heowns Biochem Technologies,LLC,Tianjin. Lead iodide (PbI2, 99.99%) was purchased from Sigma Aldrich. Cesium carbonate (Cs<sub>2</sub>CO<sub>3</sub>, 99.9%) and lithium fluoride (LiF, 99.99%) were purchased from Shanghai Macklin Biochemical Co., Ltd.

**Preparation of cesium-oleate precursor**: 10 mL of ODE, 0.8 mL of OA, and 100 mg of  $Cs_2CO_3$  were added to a flask and stirred at 120 °C for one hour under a vacuum until  $Cs_2CO_3$  was entirely dissolved. The flask was then cooled to 100 °C.

**Preparation and purification of CsPb(I<sub>x</sub>Br<sub>1-x</sub>)<sub>3</sub> NCs:** 10 mL of ODE, (75, 90, 105, 120, 135, 150 mg) of PbI<sub>2</sub> and (60, 48, 36, 24, 12, 0 mg) of PbBr<sub>2</sub> were added to a flask and agitated at 120 °C under vacuum for 1 hour. After that, 1 mL of OAm and 1 mL of OA were added to the mixture, and the temperature was set to 160-165 °C in a nitrogen atmosphere. 1.5 mL of cesium oleate was injected into the mixture when the precursor was fully dissolved. After waiting 10 seconds, we transferred the flask to an ice bath. The crude solution was then transferred to centrifuge tubes and centrifuged at 8,000 rpm for 5 minutes after adding 20 mL of MA. The NCs were decentralized with 1 mL of hexane. For the fabrication of LEDs and surface ligand engineering, 3 mL of MA was added to 1 mL of the NC solution and centrifuged at 1,000 rpm for 1 minute. The NCs were redispersed in 1 mL of hexane.

**Preparation and purification of CsPb**( $I_{0.6}Br_{0.4}$ )<sub>3</sub> NCs with different ligands: 10 mL of ODE, 90 mg of PbI<sub>2</sub>, and 48 mg of PbBr<sub>2</sub> were added to a flask and agitated at 120 °C under vacuum for 1 hour. After that, 810 mg of ODA (720 mg of HDA, 630 mg of TDA) and 1 mL of OA were added to the mixture, and the temperature was set to 160-165 °C in nitrogen. 1.5 mL of cesium oleate was injected into the mixture when the precursor was fully dissolved. After waiting 10 seconds, we transferred the flask to an ice bath. Purification was performed identically to the above method.

**Preparation and purification of**  $CsPb(I_xBr_{1-x})_3$  **superlattices:** The nanocrystal solution is mixed with hexane at a volume ratio 1:2 (original solution: hexane). The mixture is then placed in a low-vacuum environment and slowly evaporated at 40°C. Once precipitates form in the solution, the mixture is centrifuged at 3000 rpm for 3 minutes. The centrifuged precipitate was redispersed in 1.0 mL hexane for subsequent characterization and device fabrication.

**Hole-only devices fabrication:** The hole-only devices were fabricated with a structure of ITO/PEDOT: PSS/Poly-TPD/Perovskite/MoO<sub>3</sub> /Al. The spin-coating conditions for the PEDOT:PSS, Poly-TPD, and perovskite layers were maintained at the same values as those employed in the LED device fabrication process. The MoO<sub>3</sub> and Al layers were successively deposited using a thermal evaporation system. MoO<sub>3</sub> (10 nm, 0.1–0.2 Å/s), and Al (120 nm, 8–10 Å/s) were sequentially deposited by thermal evaporation. The effective luminous area of the LEDs is  $2.5 \times 2.5$  mm<sup>2</sup>.

**LED fabrication:** ITO glass was ultrasonically washed with deionized water, propanone, and ethanol, then dried with nitrogen and cleaned using a UV-ozone. All the devices were fabricated with a typical multilayer structure consisting of ITO/PEDOT: PSS/Poly-TPD/Perovskite/TPBi/LiF/Al. The PEDOT: PSS solution was filtered through 0.22  $\mu$ m hydrophilic filters before use. The PEDOT: PSS was spin-coated onto the ITO at 4,000 rpm and annealed at 140 °C for 10 minutes in air. The Poly-TPD chlorobenzene solution (6 mg mL<sup>-1</sup>) was spin-coated onto the PEDOT: PSS at 4,000 rpm and annealed at 140 °C for 10 minutes in a nitrogen glove box. The TDA-capped CsPb(I<sub>0.6</sub>Br<sub>0.4</sub>)<sub>3</sub> NCs (superlattices) solution was spin-coated onto the Poly-TPD film at 2,000 rpm for 40 s and annealed for 5 min at 60 °C. The TPBi, LiF, and Al layers were successively deposited using a thermal evaporation system. TPBi (40 nm, 1–2 Å/s), LiF (1 nm, 0.1–0.2 Å/s), and Al (100 nm, 8–10 Å/s) were sequentially deposited by thermal evaporation. The effective luminous area of the LEDs is 2.5 × 2.5 mm<sup>2</sup>.

**Characterization.** Ultraviolet-visible (UV–vis) absorption spectra were measured by a Thermo Evolution 300 UV–vis spectrometer. Steady-state photoluminescence (PL) spectra were performed using a Horiba Fluorolog system with an excitation wavelength of 365 nm and a 395 nm nano-LED source. X-ray diffraction (XRD) patterns were characterized by a Rigaku Miniflex 600 with Cu K $\alpha$  radiation ( $\lambda = 1.54178$  Å). A transmission electron microscope (TEM) was used, with a JEM-F200 operating at an accelerating voltage of 200 kV. The energy level was obtained using a Thermo ESCALAB 250Xi ultraviolet photoelectron spectroscopy (UPS) system. The Valence band spectra were measured with a monochromatic He I light source (21.22 eV) and a VG Scienta R4000 analyzer. The luminescence-current density-voltage (L-J-V) characteristics were recorded by a commercial system (Keithley 2400 source meter and photodetector, Guangzhou Jinghe Equipment Co., Ltd) under an Ar atmosphere. The response time of the photodetector is about 50 ns, and the scan length was set to 0.2 V. The electroluminescence (EL) spectra and CIE coordinate measurements were conducted and recorded using a Chroma meter CS-2000.

**Calculations of defect density:** Through corresponding simulations of the high-frequency region (f = 1 kHz) in the Nyquist plot of perovskite LEDs, the geometric capacitance (C<sub>g</sub>) of these devices can be determined. Impedance tests were conducted on LEDs to calculate the relative permittivity  $\varepsilon_r$  using the following formula:

$$\varepsilon_r = \frac{C_g d}{\varepsilon_0 S}$$

Where, *d* represents the thickness of the film.  $\varepsilon_0$  represents vacuum dielectric constant and *S* represents the area of the film.

By characterizing the current density-voltage (J-V) curves of hole-only devices, the trap-filling limit voltage ( $V_{TFL}$ ) can be determined. Subsequently, the defect density ( $N_t$ ) in perovskite thin films can be calculated using the following formula:

$$N_t = \frac{2\varepsilon_0 \varepsilon_r V_{TFL}}{qd^2}$$

Where, q represents the elementary charge.



Figure S1. PL spectra of  $CsPb(I_xBr_{1-x})_3$  NCs (X=0.5-1).



**Figure S2. (a-d)** TEM images of the original  $CsPb(I_xBr_{1-x})_3$  NCs. **(e-h)** TEM images of the original  $CsPb(I_xBr_{1-x})_3$  NCs after self-assembly. **(i-l)** PL spectra during the self-assembly process of  $CsPb(I_xBr_{1-x})_3$  NCs. (From left to right, x varies from 0.6 to 0.9).



**Figure S3. (a-c)** TEM images of original  $CsPb(I_{0.6}Br_{0.4})_3$  NCs prepared with different nucleation times. The inset is size distribution of  $CsPb(I_{0.6}Br_{0.4})_3$  NCs, where **d** represents the average particle size. **(d-f)** TEM images of  $CsPb(I_{0.6}Br_{0.4})_3$  NCs prepared with different nucleation times after self-assembly. **(g-i)** PL spectra during the self-assembly process of  $CsPb(I_{0.6}Br_{0.4})_3$  NCs.



Figure S4. HRTEM image of  $CsPb(I_{0.6}Br_{0.4})_3$  (a) nanocrystals and (b) superlattices.



Figure S5. XRD spectra of  $CsPb(I_{0.6}Br_{0.4})_3$  NCs with different surface ligands before and after self-assembly.



**Figure S6.** UPS spectra for cut-off edges ( $E_{cut-off}$ ) and Fermi edges ( $E_{Fermi}$ ) of CsPb( $I_{0.6}Br_{0.4}$ )<sub>3</sub> NCs and superlattices.



Figure S7. Optical bandgaps of  $CsPb(I_{0.6}Br_{0.4})_3$  NCs and superlattices.



**Figure S8. (a)** Band structure of pristine  $CsPb(I_{0.6}Br_{0.4})_3$  NCs and superlattices. **(b)** Device energy level diagrams for all functional layers of LEDs.



**Figure S9. (a)** Current density-voltage curve of hole-only devices with  $CsPb(I_{0.6}Br_{0.4})_3$  nanocrystals and superlattices as the luminescent layer under dark current. **(b)** Impedance diagrams of LEDs based on  $CsPb(I_{0.6}Br_{0.4})_3$  nanocrystals and superlattices. The applied potential was 3 V, the high frequency was 100 kHz, the low frequency was 100 Hz, and the amplitude was 0.005 V. The equivalent circuit was shown in the illustration, where Rs, Rct, and C represented series resistor, charge transfer resistor, and geometrical capacitance, respectively.



Figure S10. Time-resolved photoluminescence spectra of  $CsPb(I_{0.6}Br_{0.4})_3$  nanocrystals and superlattices.

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Sample	$\tau_1(ns)$	f1(%)	$\tau_2(ns)$	f2(%)	$\tau_{avg}(ns)$
Nanocrystal	10.2	68	26.3	32	15.4
Superlattice	14.6	61	35.0	39	22.6

Table S1. Fluorescence decay components of the  $CsPb(I_{0.6}Br_{0.4})_3$  nanocrystals and superlattices.



Figure S11. The distribution diagram of peak EQE of 16 LEDs.



**Figure S12.** Normalized luminance as a function of working time for LEDs (The measurements were conducted under a nitrogen atmosphere without encapsulation at a room temperature of 25°C).



Figure S13. EL spectra of LED based on  $CsPb(I_{0.6}Br_{0.4})_3$  (a) nanocrystal and (b) superlattice with different operation time at a driving voltage of 3.5 V.



Figure S14. The CIE coordinates of  $CsPb(I_{0.6}Br_{0.4})_3$  superlattice LED.