Supporting Information

Designing of blue, green, red CsPbX₃ perovskite-codoped flexible films with water resistant and elimination of anion-exchange for tunable white light emission

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**Experiments**

**Chemicals.** Cs$_2$CO$_3$ (99.9 %, Aldrich), 1-octadecene (ODE, 90 %, Aldrich), oleic acid (OA, 90 %, Sigma-Aldrich), PbCl$_2$ (99.99 %, Aldrich), PbBr$_2$ (99.99 %, Aldrich), PbI$_2$ (99.9 %, Aldrich), n-trioctylphosphine (TOP, Aldrich, 97 %), oleylamine (OAm, Aldrich, 70 %), hexane (99.9 %, Fisher Scientific), ethanol (Aldrich), Polyvinylpyrrolidone (PVP, Sigma-Aldrich, Mw ~1,300,000), silicone resin [A and B (OE6630), Dow Corning Co.]. All chemicals were used as received without further purification.

**Preparation of Cs-oleate precursor.** Cs-oleate solutions were prepared via a reported approach developed by Protesescu *et al.*$^1$ Cs$_2$CO$_3$ (0.814 g), OA (2.5 mL) and ODE (40 mL) were added into a 100 mL 3-neck flask, dried under N$_2$ for 1 h at 120 ºC and then heated under N$_2$ to 150 ºC until all Cs$_2$CO$_3$ reacted with OA. Since Cs-oleate precipitates out in ODE at room-temperature, it must be preheated to 100 ºC before injection.

**Synthesis of CsPbBr$_3$ QDs.$^1$** ODE (10 mL) and 0.188 mmol of PbBr$_2$ (0.069 g) were loaded into a 25 mL three-neck flask and dried under N$_2$ at 120 ºC for 1 h. Dried OA (0.5 mL) and OAm (0.5 mL) were injected at 120 ºC under N$_2$ flow. After complete solubilisation of a PbBr$_2$ salt, the temperature was raised to 190 ºC and Cs-oleate solution (0.4 mL of stock solution prepared as described above) was swiftly injected and the reaction mixture was cooled down by a water bath after 5s. The aggregated NCs were separated by centrifugation, the supernatant was discarded and the precipitate was redispersed in hexane for further use.

**Synthesis of Blue CsPb(Br$_{0.5}$Cl$_{0.5}$)$_3$ QDs.$^2$** 20 mL of ODE, 0.1104 g of PbBr$_2$, 0.083 g of PbCl$_2$, 2.6 mL of OA, and 2.6 mL of OAm were mixed in a 50 mL three-necked bottle. Water and oxygen were removed under N$_2$ for 30 min at 120 ºC. The temperature was increased to 190 ºC in an N$_2$ environment. This condition was maintained for approximately 10 min at 190 ºC. Afterward, 1.6 mL of Cs-oleate precursor, which was also pre-heated at 100 ºC, was injected into the prepared solution. After 5 s, the three-necked bottle was placed in a water bath and cooled to room temperature. The formed crude QDs were isolated by centrifugation. The supernatant was discarded and the precipitate was dispersed in hexane. For CsPb(Br$_{0.5}$Cl$_{0.5}$)$_3$,
higher temperature of 170 °C and 1 mL of trioctylphosphine (TOP) are required to dissolve PbCl₂.

**Synthesis of Red CsPb(Br₀.₄I₀.₆)₃ QDs.** 20 mL of ODE, 0.1104 g of PbBr₂, 0.2064 g of PbI₂, 2.6 mL of OA, and 2.6 mL of OAm were mixed in a 50 mL three-necked bottle. Water and oxygen were removed under N₂ for 30 min at 120 °C. The temperature was increased to 190 °C in a N₂ environment. This condition was maintained for approximately 10 min at 190 °C. Afterward, 1.6 mL of Cs-oleate precursor, which was pre-heated at 100 °C, was injected into the prepared solution. After 5 s, the three-necked bottle was placed in a water bath and cooled to room temperature. The crude solution was centrifuged. The precipitate was dispersed in a hexane.

**Preparation of electrospinning solution.** PVP solution: 1.5 g of PVP (Mₜₜ = 1.3 × 10⁶) was added in 10 mL of ethanol, and the solution was stirred overnight to form a homogeneous solution with a concentration of 15 wt %. QDs/PVP solution: 0.25 g of QDs powder was dispersed in 5 mL of PVP solution by sonicating and the mixture was stirred for 3 h. The QDs was dissolved forming a homogeneously dispersed QDs/PVP solution with a QDs loading of 20 wt %.

**Preparation of PVP nanofibers.** The QDs/PVP solution (20 wt %) was transferred to the electrospinning setup and spun at a flow rate of 1 mL/h with a spinneret of 0.8 mm in diameter. A high voltage of 10 kV was applied and the distance between the collector and the spinneret was set at 15 cm. The thus obtained fibers were collected on various substrates (aluminum foil, nonwoven fabric or stainless steel mesh). The electric voltage was adjusted (8–12 kV) for solutions with different concentrations. The temperature and relative humidity were kept at 25 ºC and 35 %.

**Packaging of LEDs.** In this procedure, 10 mm × 20 mm rectangle of PVP-CsPbX₃ was coated with 0.5 g of silicone resin A. The composite nanofibrous mats were then heated to 40°C for 1 h, and then double equal of silicone resin B (1.0 g) was coated again. In order to eliminate air bubbles, the mixture was placed into a vacuum oven for 30 min at 50 °C to form a composite sol, which was deposited to form the down-conversion layer.

**Characterizations**
Transmission Electron Microscope (TEM). TEM images were carried out using a FEI Tecnai F30 (USA) transmission electron microscope equipped with a thermionic gun operated at an acceleration voltage of 120 kV. Samples were prepared by diluting the QDs solution in toluene (20 μL in 1 mL), and then dropping diluted QDs colloidal suspensions onto a copper grid coated with carbon film, followed by evaporation of the solvent.

Scanning Electron Microscope. The morphologies were investigated by the Tescan Mira 3XM electronmicroscope. An electron beam accelerated to 3 kV was used with an in-lens detector.

X-ray Powder Diffraction (XRD). XRD measurements were performed on a Rigaku D/max - 2400 Advance X-ray powder diffractometer equipped with Cu – Kα radiation (λ = 1.540 Å). The QDs were redispersed in 50 μL of toluene and then dropped on a 2 cm by 1 cm glass slide, followed by evaporation of the solvent.

Optical Absorption Spectroscopy (Abs). UV – Vis spectra were recorded on a Shimadzu UV-1750 spectrophotometer at room temperature. Samples were prepared by diluting 20 μL of the QDs solution in 1 mL of toluene, in 1 cm path length quartz cuvettes with airtight screw caps.

Photoluminescence measurements (PL). The steady-state PL emission spectra were recorded on a Shimadzu RF-5301 spectrophotometer. Samples were the same as those using for absorption spectra. They were excited at 365 nm at room temperature. The absolute photoluminescence quantum yield (PLQY) was carried out on an FLS 920 spectrometer. The PL decay process was measured on FLS 920 lifetime system equipped with Supercontinuum Laser system at room temperature.

Confocal microscopy. Fluorescence microscopic images were viewed under a fluorescent microscope (Leica DR) equipped with a digital camera (ORCA-ER, Hamamatsu). Photos were processed by using Photoshop software (Adobe, CA).

Thermal stability. For the thermal stability test at 298–373 K, the samples were placed in a lead holder, and the temperature was controlled by a THMS-600 device (Linkam Scientific Instruments Ltd.).

Principle of the time-resolved PL decay. The PL decay curve can be well- fitted with a triexponential function:
\[ A(t) = A_1 \exp\left(-\frac{t}{\tau_1}\right) + A_2 \exp\left(-\frac{t}{\tau_2}\right) + A_3 \exp\left(-\frac{t}{\tau_3}\right) \]

where \( A, A_1, A_2, \) and \( A_3 \) are constants, \( t \) is time, and \( \tau_1, \tau_2, \) and \( \tau_3 \) represent the decay lifetimes corresponding to the intrinsic exciton relaxation, the interaction between excitons and phonons, and the interaction between excitons and defects, respectively. The average lifetime \( (\tau_{\text{ave}}) \) can be calculated as

\[
\tau_{\text{ave}} = \frac{A_1 \tau_1^2 + A_2 \tau_2^2 + A_3 \tau_3^2}{A_1 \tau_1 + A_2 \tau_2 + A_3 \tau_3}
\]

For example, the obtained CsPbBr\(_3\) quantum dots exhibit three lifetimes \( (\tau) \): \( \tau_1 \) of 7.4 ns accounting for 47.9\%, \( \tau_2 \) of 42.9 ns accounting for 27.8\%, and \( \tau_3 \) of 205.1 ns accounting for 24.3\%, respectively, which reveals the high ratio of radiative recombination to nonradiative transitions. The average lifetime of each sample was derived (see Table S2).

**The characterization of as-synthesized CsPbX\(_3\) perovskite QDs.** It is thus clear that all the monodispersed QDs have cubic and uniform shapes. Their mean diameter size was 10.5 nm for CsPb(\(\text{Br}_{0.5}\text{Cl}_{0.5}\))\(_3\), 11.3 nm for CsPbBr\(_3\), and 14.7 nm for CsPb(\(\text{Br}_{0.4}\text{I}_{0.6}\))\(_3\), as obtained by nanoparticle statistics (Fig. S1). The high-resolution TEM (HR-TEM) image of green CsPbBr\(_3\) QDs, shown in Fig. S2, displays the single-crystalline nature of the cubic phase with \( d \)-spacing of 5.8 Å. This is consistent with (100) planes of CsPbBr\(_3\). Elemental analyses were performed using an energy dispersive X-ray analyzer (EDX) to confirm the elemental composition ratios of the three CsPbX\(_3\) QDs (Fig. S3). As shown in Fig. S4, the three synthesized CsPbX\(_3\) QDs exhibit blue emission (455 nm) for CsPb(\(\text{Br}_{0.5}\text{Cl}_{0.5}\))\(_3\), green emission (516 nm) for CsPbBr\(_3\), and red emission (614 nm) for CsPb(\(\text{Br}_{0.4}\text{I}_{0.6}\))\(_3\). For backlight applications, the CIE coordinates of blue (0.15, 0.03), green (0.08, 0.76), and red (0.65, 0.35) are shown in Fig. S4d. The wide color gamut spectra of RGB QDscan be attributed to the narrow emission wavelength.
**Figure S1. Nanosize measurement.** The histograms of size distribution of a) blue CsPb(\(\text{Br}_{0.5}\text{Cl}_{0.5}\))\(_3\), b) green CsPbBr\(_3\), and c) red CsPb(\(\text{Br}_{0.4}\text{I}_{0.6}\))\(_3\) perovskite NCs, and d) Particle size of RGB perovskite QDs.
Figure S2. Structural characterization. a) X-ray diffraction patterns of CsPb(Br_{0.5}Cl_{0.5})_3, CsPbBr_3, and CsPb(Br_{0.4}I_{0.6})_3 QDs compared with standard JCPDS, b) crystal structure of cubic CsPbBr_3, and c) high-resolution TEM images of CsPbBr_3 perovskite QDs.
Figure S3. EDX spectra of a) blue CsPb(Br\textsubscript{0.5}Cl\textsubscript{0.5})\textsubscript{3}, b) green CsPbBr\textsubscript{3}, and c) red CsPb(Br\textsubscript{0.4}I\textsubscript{0.6})\textsubscript{3} perovskite QDs.
Figure S4. Photographs and characterization by UV-Vis spectroscopy. a,b) Photographs of colloidal perovskite QDs dispersed in a) hexane under sunlight, b) hexane under UV-light (365 nm). c, Photoluminescence and UV-Vis spectra of CsPb(Br$_{0.5}$Cl$_{0.5}$)$_3$, CsPbBr$_3$, and CsPb(Br$_{0.4}$I$_{0.6}$)$_3$ QDs. d, Color gamut spectra of RGB perovskite QDs.
Figure S5. Morphological images of PVP-CsPbX3 composite nanofibers. 

a, b, SEM and HSEM images of PVP-CsPbX3 composite nanofibers. c, EDX line scanning of PVP-CsPbX3 composite nanofibers.
Figure S6. PL spectra of a) blue CsPb(Br_{0.5}Cl_{0.5})_3 and SR/PVP-CsPb(Br_{0.5}Cl_{0.5})_3, b) green CsPbBr_3 and SR/PVP-CsPbBr_3, and c) red CsPb(Br_{0.4}I_{0.6})_3 and SR/PVP-CsPb(Br_{0.4}I_{0.6})_3 perovskite QDs.
Figure S7. (a) PL Spectra of SR/PVP-CsPbX₃ before color filter. (b) Color gamut of QD-LED, phosphor-LED, and SR/PVP-CsPbX₃. (c) PL spectra of SR/PVP-CsPbX₃ mixed with multinozzle electrospun under the UV excitation; the inset spectrum reveals a photograph of white light LED and the color gamut spectra of SR/PVP-CsPbX₃ mixed with different molar ratios. (d) Time-resolved fluorescence decay profiles (triexponential fit) of CsPbBr₃ QDs, PVP-CsPbBr₃ and SR/PVP-CsPbX₃ (emission at 516 nm). (e) Fluorescence microscopic images of SR/PVP-CsPbX₃ electrospun with multi-nozzle equipment. (f) Fluorescence microscopic images of SR/PVP-CsPbX₃ electrospun with single-nozzle equipment. (g) A logo illustration of Lanzhou University with SR/PVP-CsPbX₃.
Figure S8. PL spectra of non-capped CsPbBr$_3$ (sample Green) and CsPb(Br$_{0.4}$I$_{0.6}$)$_3$ (sample Red) QDs, and of their 1:1 molar % mixture taken immediately after mixing (sample Mix) and after 5 min of reaction (sample Mix').
Figure S9. PL spectra of non-capped CsPb(Br$_{0.5}$Cl$_{0.5}$)$_3$ (sample Blue), CsPbBr$_3$ (sample Green) and CsPb(Br$_{0.4}$I$_{0.6}$)$_3$ (sample Red) QDs, and of their 1:1:1 molar % mixture taken immediately after mixing (sample Mix) and after 5 min of reaction (sample Mix').
Figure S10. PL spectra of SR/PVP-CsPbX₃ flexible films under continuous UV light irradiation; the inset photograph reveals a linear change of PL spectra of SR/PVP-CsPbX₃ flexible films at different emission peaks.
Figure S11. The XRD patterns of SR/PVP-CsPbX$_3$ flexible films were exposed to ambient air.
Figure S12. Time-resolved fluorescence decay profiles of 

a) Pb(Cl$_{0.5}$Br$_{0.5}$)$_3$ QDs, CsPb(Cl$_{0.5}$Br$_{0.5}$)$_3$ QDs in SR/PVP, CsPb(Cl$_{0.5}$Br$_{0.5}$)$_3$ QDs in SR/PVP-CsPbX$_3$, emission at 459 nm. 

b) CsPb(Br$_{0.4}$I$_{0.6}$)$_3$ QDs, CsPb(Br$_{0.4}$I$_{0.6}$)$_3$ QDs in SR/PVP, and CsPb(Br$_{0.4}$I$_{0.6}$)$_3$ QDs in SR/PVP-CsPbX$_3$, emission at 620 nm.
Figure S13. Microscopic images of a) blue, b) green, and c) red SR/PVP-CsPbX$_3$ under UV-light (365 nm) excitation.
Figure S14. Thermal cycling of a) SR/PVP-CsPbBr$_3$ and b) CsPbBr$_3$ QDs.
Table S1. Detailed XRD data of characteristic diffraction peaks with $2\theta$ values on CsPbX$_3$ QDs and SR/PVP-CsPbX$_3$ nanofibers.

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<th>Sample &amp; Plane</th>
<th>20 value</th>
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<tr>
<td></td>
<td>$(110)$</td>
<td>$(200)$</td>
<td>$(211)$</td>
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<tr>
<td>CsPbBr$_3$ QDs</td>
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<td>37.5°</td>
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Table S2. Detailed lifetime data of CsPbX$_3$ QDs, SR/PVP-CsPbX$_3$ with single nozzle electrospun and SR/PVP-CsPbX$_3$ with multi-nozzle electrospun.

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<th>Sample</th>
<th>$\tau_1$ (ns)</th>
<th>$A_1$ (%)</th>
<th>$\tau_2$ (ns)</th>
<th>$A_2$ (%)</th>
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<td>42.9</td>
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