Supporting Information

Hierarchical Arrays of Cesium Lead Halide Perovskite Nanocrystals through Electrophoretic Deposition

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Photoluminescence Quantum Yield Measurement

Photoluminescence quantum yield (PLQY) at room temperature of $PbSO_4$-Oleate capped $CsPbBr_3$ was calculated by taking Fluorescein dye as reference dissolved in 0.1 M NaOH. The nanocrystals were dispersed in hexane. The PLQY of $PbSO_4$-Oleate capped $CsPbCl_3$ and $CsPbI_3$ were then calculated relative to that of $CsPbBr_3$. To calculate the PLQY the following equation was used:

$$QY_s = QY_{ref} \cdot \frac{F_s}{F_{ref}} \cdot \frac{A_{ref}(\lambda_{exc})}{A_s(\lambda_{exc})} \cdot \frac{n_s^2}{n_{ref}^2}$$

Where,

$QY_s =$ Unknown PL quantum yield of sample.

QY_{ref} = Known PL quantum yield of reference.

F_s = Integrated PL intensity; *i.e*. area under the PL curve of the sample at fixed excitation wavelength.

F_{ref} = Integrated PL intensity; *i.e.* area under the PL curve of the reference at fixed excitation wavelength.

$A_{ref}(\lambda_{exc})$= Absorbance value of the reference in its absorbance spectrum at that fixed PL excitation wavelength.

$A_s(\lambda_{exc})$= Absorbance value of the sample in its absorption spectrum at that fixed PL excitation wavelength.

n_s = Refractive index of the solvent in which sample is dispersed.

n_{ref}= Refractive Index of the solvent in which reference is dispersed.

Concentration of Deposited Film Calculations

The concentration of $PbSO_4$-Oleate capped nanocrystals was calculated in the following manner for $CsPbBr_3$ capped NC's

$$A = \varepsilon c l$$
$$1.47 = 3.83 \times 10^6 M^{-1} cm^{-1} \times c \times 1\ cm$$
$$c \cong 0.39\ \mu M$$
$$volume\ of\ solution = 3.1\ mL$$
$$\frac{0.39\ \mu moles}{1{,}000\ mL} \times 3.1\ mL = 1.2\ nmoles$$
$$Area\ of\ deposition = 1.5\ cm^2$$
$$\frac{Concentration}{Area} = \frac{1.2\ nmoles}{1.5\ cm^2} = 0.8\ \frac{nmoles}{cm^2}$$

Where

A **=** The absorbance of the film. This was calculated by taking the absorbance of the solution at t = 0 (before any EPD) and absorbance at t = t (after EPD). These values can be seen in **Figure 2C and 2D**.

ε = The molar absorptivity. Values for molar absorptivity were taken from reference 2.

c = concentration of the deposited nanocrystals

l = length of the cuvette (1 cm)

This procedure was repeated for $PbSO_4$-Oleate capped $CsPbI_3$ nanocrystals where the molar absorptivity was $2.4 \times 10^6\ M^{-1}cm^{-1}$. The concentration for these films were found to be $0.9\ \frac{nmoles}{cm^2}$

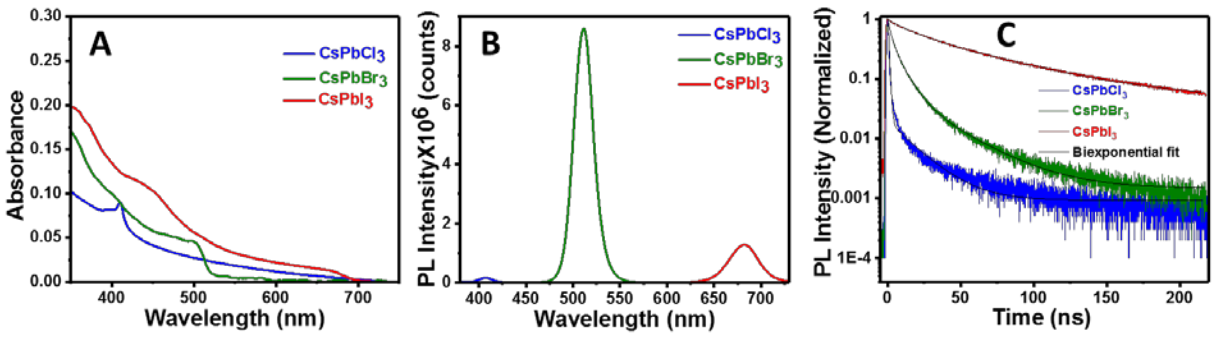

Figure S1: (A) Absorbance spectra (B) Emission spectra of $PbSO_4$-Oleate capped $CsPbX_3$ nanocrystals in hexane for determination of photoluminescence quantum yield. (C) Emission decay spectra of $PbSO_4$-Oleate capped $CsPbX_3$ nanocrystals dispersed in hexane monitored at their emission peak maxima ($CsPbCl_3$= 407 nm, $CsPbBr_3$= 511 nm and $CsPbI_3$= 682 nm) .

Table S1: Photoluminescence quantum yield values along with average lifetime and calculate radiative and non-radiative rate constant **($\tau = 1/(k_r + k_{nr})$ and $\Phi = k_r/(k_r + k_{nr})$** for $PbSO_4$-Oleate capped $CsPbX_3$ nanocrystals.

Sample	Quantum Yield, ϕ(%)	τ_{avg} (ns)	k_r (ϕ/τ_{avg})(ns^{-1})	k_{nr} (ns^{-1})
$CsPbCl_3$	0.02	5.7	0.0035	0.1719
$CsPbBr_3$	0.73	17.5	0.0417	0.0154
$CsPbI_3$	0.12	56.1	0.0021	0.0157

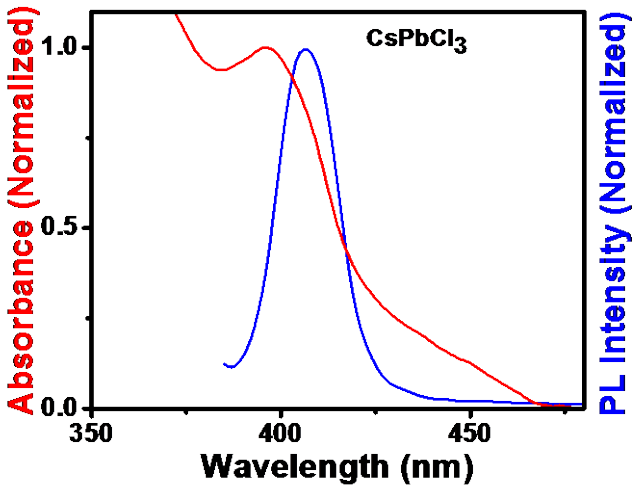

Figure S2: UV-Vis absorbance and Emission spectra of $PbSO_4$-Oleate capped $CsPbCl_3$ nanocrystals. (Excitation wavelength was 370 nm)

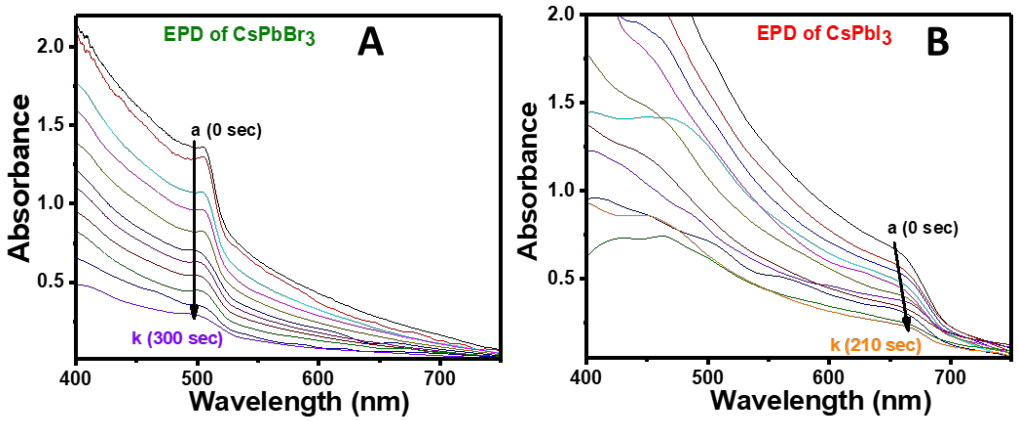

Figure S3: Absorbance spectra of (A) $PbSO_4$-Oleate capped $CsPbBr_3$ nanocrystals (B) $PbSO_4$-Oleate capped $CsPbI_3$ nanocrystal solutions recorded at different times during electrophoretic deposition.

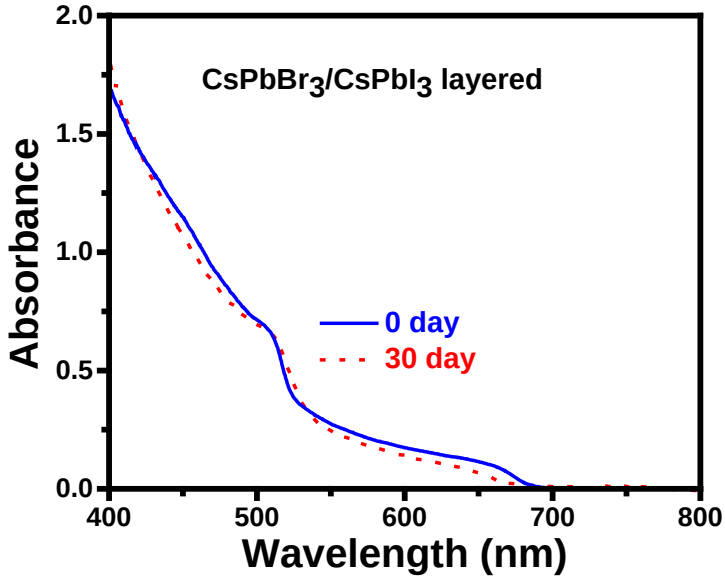

Figure S4: UV-Vis absorbance spectra showing the stability of the $PbSO_4$-Oleate capped $CsPbBr_3/CsPbI_3$ layered film stored under ambient condition. The excitonic peaks for bromide and iodide were preserved indicating no intermixing of the nanocrystals.

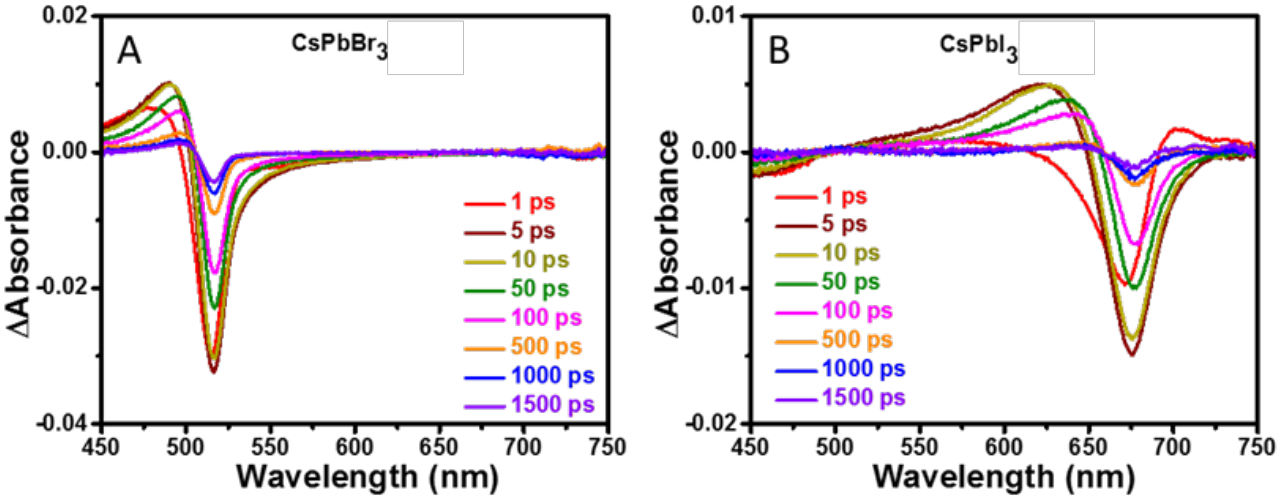

Figure S5: Transient absorption spectra recorded following 387 nm laser pulse excitation of $PbSO_4$-Oleate capped (A) $CsPbBr_3$ and (B) $CsPbI_3$ films (electrophoretically deposited).

Table S2: (Time correlated single photon counting) TCSPC decay analysis of $PbSO_4$-Oleate capped $CsPbBr_3$, $CsPbI_3$, and $CsPbBr_3/CsPbI_3$ layered films (Exc. = 370 nm).
Emission originating from $CsPbBr_3$ was monitored at 520 nm and that of $CsPbI_3$ was at 675 nm.

$CsPbBr_3$ emission @520 nm

Sample	A_1(%)	τ_1(ns)	A_2(%)	τ_2(ns)	τ_{avg}(ns)
$CsPbBr_3$	76	1.1	24	12.4	9.9
$CsPbBr_3/CsPbI_3$layered	93	1.0	7	8.2	3.7

$CsPbI_3$ emission @675 nm

Sample	A_1(%)	τ_1(ns)	A_2(%)	τ_2(ns)	τ_{avg}(ns)
$CsPbI_3$	92	4.9	8	29.5	13.4
$CsPbBr_3/CsPbI_3$ layered	90	5.3	10	29.6	14.6

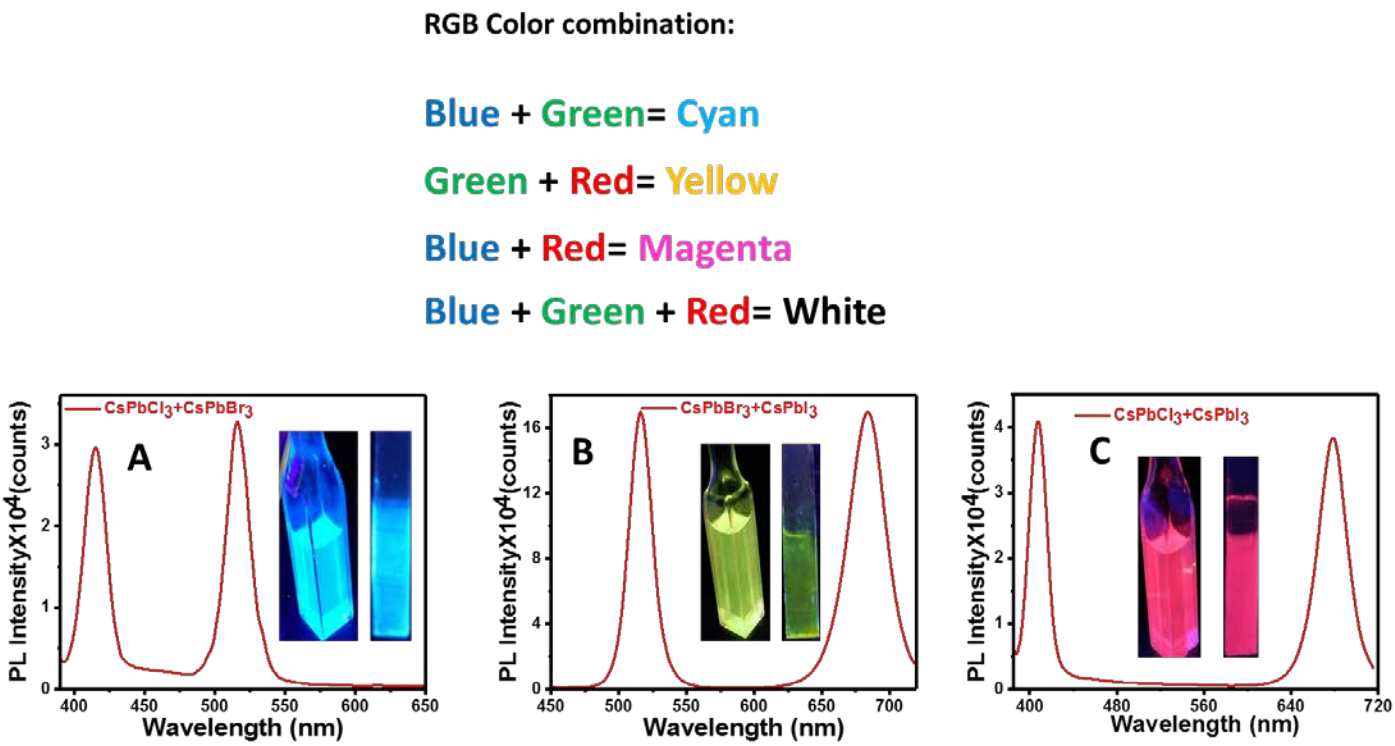

Figure S6: Scheme showing RGB (Red, Green, and Blue) color combination. $PbSO_4$-Oleate capped nanocrystals were mixed and (A) cyan light was generated by mixing $CsPbCl_3$ and $CsPbBr_3$, (B) yellow light was generated by mixing $CsPbBr_3$ and $CsPbI_3$, and (C) magenta light was generated by mixing $CsPbCl_3$ and $CsPbI_3$. Insets show the photographs of the colloidal solutions and the deposited films on FTO/TiO_2 under UV light.

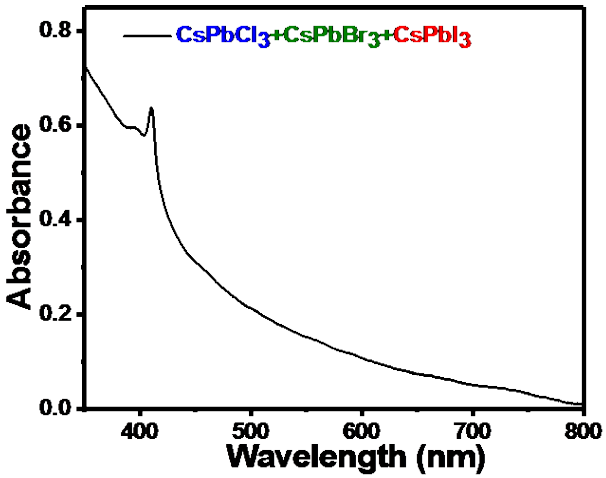

Figure S7: UV-Vis absorbance spectra for the mixed $PbSO_4$-Oleate capped $CsPbX_3$ nanocrystals, which emits white light. $CsPbCl_3$ excitonic peak is more dominant as it was added in excess compared to bromide or iodide counterpart to account for low quantum yield and charge transfer.

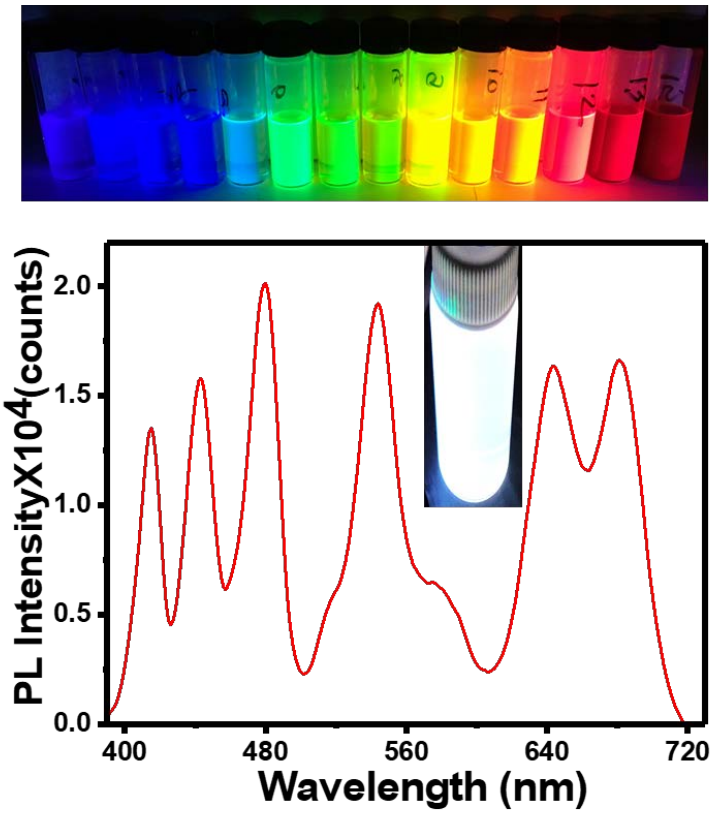

Figure S8: The photograph shows the $PbSO_4$-Oleate capped $CsPbX_3$ (X= Cl, Br, I) nanocrystals with varying compositions and thus emission covering the entire visible range. The spectrum shows the generation of white light by mixing different $CsPbX_3$ compositions to have a better color purity of white light. The inset shows the photograph of colloidal dispersion showing white emission under UV light.

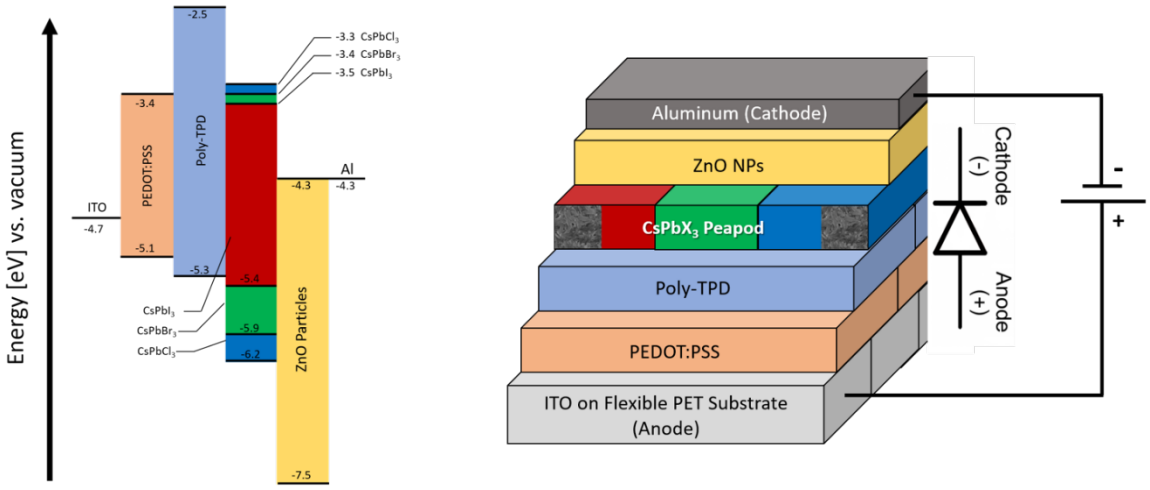

Figure S9: Band diagram and device stack showing how preliminary LEDs have been fabricated. The device architecture and procedures for fabrication were based on a previously reported method[1]. The active layer of $CsPbX_3$ was deposited via EPD onto the ITO substrate after deposition of PEDOT:PSS and Poly-TPD. Values for the conduction band minima and valence band maxima of the materials were taken from the literature.[10,46]

Figure S10: $CsPbBr_3$ and $CsPbX_3$ mixed halide film-based LEDs displaying characteristic green and white light emission. Left panel: LED based on $CsPbBr_3$ nanocrystals. Middle and Right panels: white light emission from $CsPbX_3$ LED.

References:

(10) Ravi, V. K.; Markad, G. B.; Nag, A. *ACS Energy Lett.* **2016**, *1*, 665.
(46)Zaiats, G.; Ikeda, S.; Kinge, S.; Kamat, P. V. *ACS Appl. Mater. & Interfaces* **2017**, *9*, 30741.