

## *Electronic Supplementary Information*

### **Prevention of Ion Migration in Lead Halide Perovskites upon Plugging the Anion Vacancies with PbSe Islands**

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## Experimental Section

**Materials.** Cesium carbonate ( $\text{Cs}_2\text{CO}_3$ , 99%, Sigma-Aldrich), lead bromide ( $\text{PbBr}_2$ , 99.99%, Sigma-Aldrich), lead iodide ( $\text{PbI}_2$ , 99.9%, Sigma-Aldrich), selenium powder (99.99%, Sigma-Aldrich), Ammonium molybdate tetrahydrate ( $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ , 98%, SRL), 1-butanethiol ( $\text{C}_4\text{H}_{10}\text{S}$ , >98%, Merck), oleyl amine (OLAM, Technical grade 70%, Sigma-Aldrich), 1-octadecene (ODE, 90%, Sigma-Aldrich), oleic acid (OA, 90%, Sigma-Aldrich), toluene ( $\text{C}_6\text{H}_5\text{CH}_3$ , 99%, Qualigens), poly (methyl methacrylate) (PMMA, CDH), ethyl acetate ( $\text{C}_4\text{H}_8\text{O}_2$ , 99.5%, Fischer Scientific) were used as received.

**Synthesis of  $\text{MoSe}_2$  nanosheets.**  $\text{MoSe}_2$  NSs were synthesized according to our previously published procedure.<sup>1</sup>

**Preparation of Cs-oleate.** Cs-Oleate was synthesized by mixing 0.203 g of  $\text{Cs}_2\text{CO}_3$  with 10 ml ODE and 625  $\mu\text{L}$  of OA. The mixture was then dried under vacuum at 120 °C for 30 minutes and further heated at 150 °C in an inert atmosphere until a clear solution was obtained.<sup>2,3</sup>

**Synthesis of  $\text{CsPbBr}_3$ -PbSe nanocrystals (NCs).** To synthesize the  $\text{CsPbBr}_3$ -PbSe nanoheterostructures (NHSs), a mixture of  $\text{PbBr}_2$  (69 mg, 0.188 mmol) and  $\text{MoSe}_2$  (5.0 mg, 0.0196 mmol) or Se (3.0 mg, 0.04 mmol) was dispersed in 10 ml of ODE and was put under vacuum for 45 minutes at 120 °C. After that, 0.5 ml of dried OA and 0.5 ml of dried OLAM were injected at 120 °C under an inert atmosphere. Once  $\text{PbBr}_2$  was solubilized at 150 °C, the temperature was raised to 180 °C, and 0.4 ml of Cs-Oleate was rapidly injected into the reaction mixture. Within 10 seconds of Cs-Oleate injection, the reaction was quenched by placing the mixture in an ice bath followed by addition of 10 ml of toluene. The resulting  $\text{CsPbBr}_3$ -PbSe NHSs were purified twice with ethyl acetate. The obtained product was dispersed in toluene for further analysis.

**Synthesis of  $\text{CsPbBr}_3$  nanocrystals (NCs).** Synthesis of  $\text{CsPbBr}_3$  NCs is similar to that of  $\text{CsPbBr}_3$ -PbSe NHSs, with the only difference being the absence of a selenium source. In the

case of CsPbBr<sub>3</sub> NCs, PbBr<sub>2</sub> was mixed with 10 ml of ODE. The subsequent steps for both CsPbBr<sub>3</sub> NCs and CsPbBr<sub>3</sub>-PbSe NHSs were carried out in a similar manner. Similarly, CsPbI<sub>3</sub> was synthesized using PbI<sub>2</sub> with a procedure similar to the synthesis of CsPbBr<sub>3</sub> NCs.

#### **PbSe decorated CsPbX<sub>3</sub> films.**

All films were processed under ambient conditions. Glass substrates were sonicated in soap solution, then acetone, and then isopropanol for 10 min each, followed by a 15 min UV-ozone treatment. The 50  $\mu$ L NC solution (20mg/mL) in toluene was deposited into 30 second cycle at 3000 rpm. The films were then annealed at 60 °C for 10 minutes to remove toluene and used further for heterostructure formation.

#### **Heterostructure fabrication (on glass substrate)**

PbSe decorated CsPbBr<sub>3</sub> NCs films were prepared as previously described. PbSe decorated CsPbI<sub>3</sub> NCs were then spin coated on the already deposited PbSe capped CsPbBr<sub>3</sub> films as previously described. For long term PL studies, a thin film of PMMA was spin coated on top of heterostructure to protect the CsPbI<sub>3</sub> from moisture.

#### **Ion migration in solution**

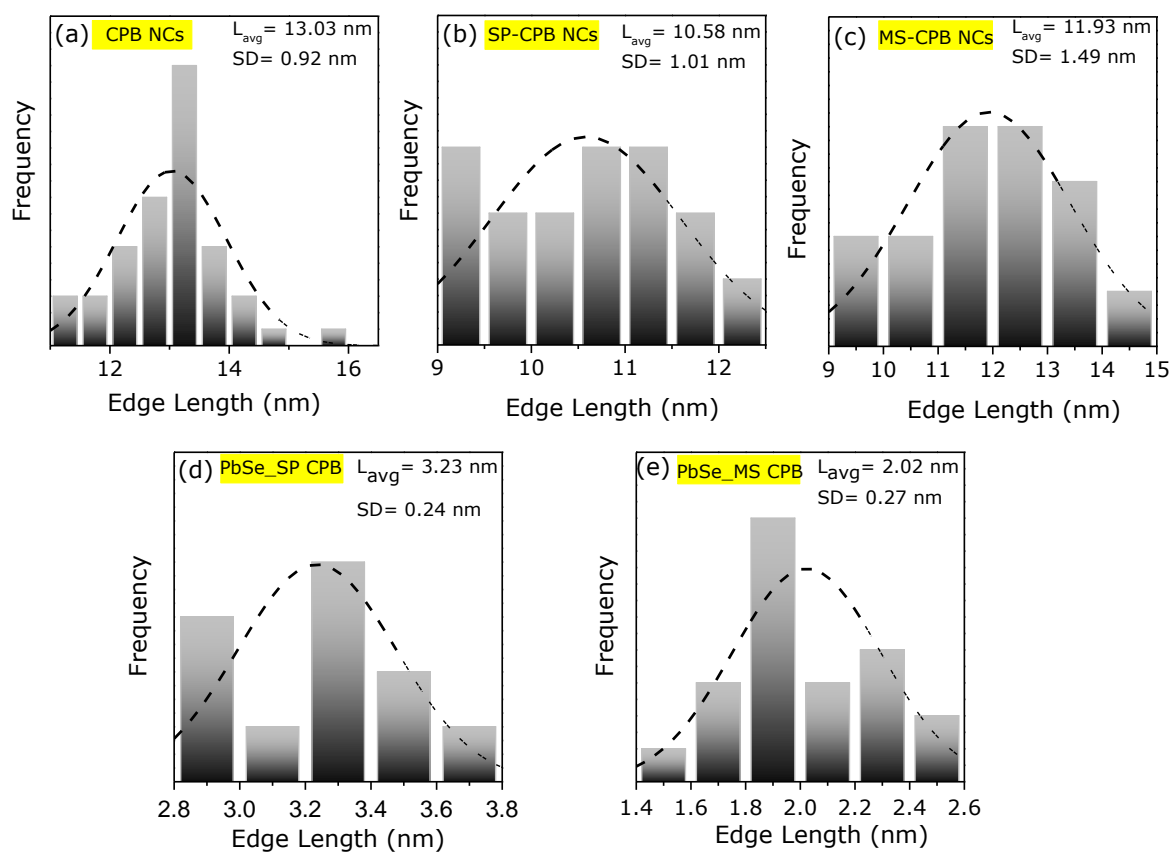
Ion migration is studied by monitoring the change in the PL intensity in a mixture of SP-CPB (20 mg/mL) and SP-CPI (20mg/mL) in toluene, prepared at a 1:1 concentration ratio. Initially, 2  $\mu$ L of this solution is added to a cuvette containing 2 mL of toluene for PL measurements. Similarly, pristine CPB and CPI NCs solutions are mixed in toluene in 1:1 concentration ratio, and we tracked the change in PL intensity with time.

#### **Phosphor converted light emitting diode (pc-LED)**

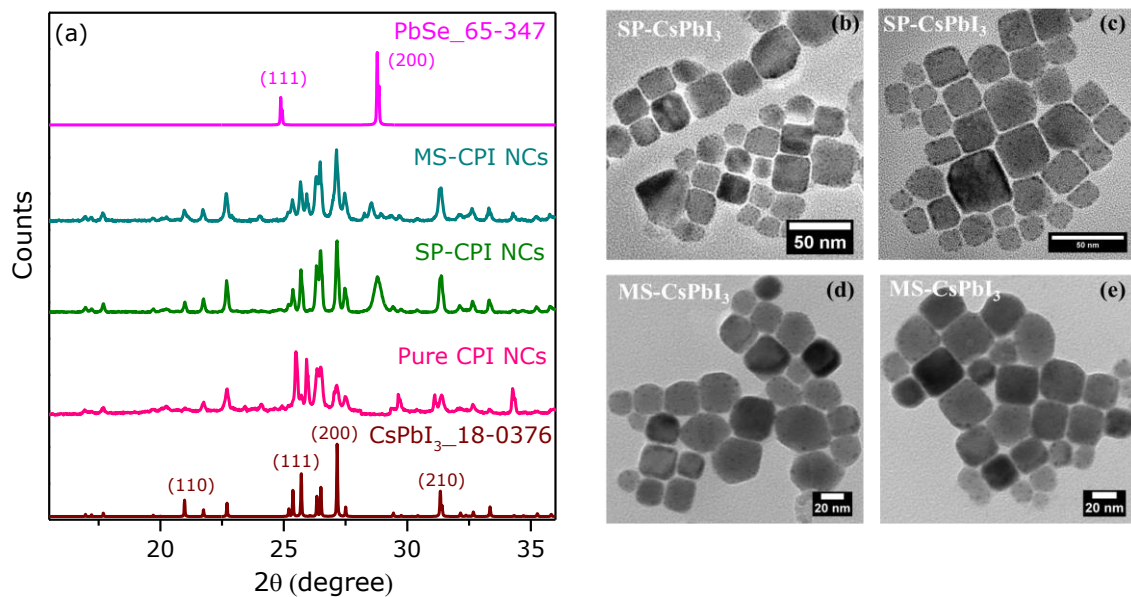
Pc-LEDs were fabricated by coating SP-CsPbBr<sub>3</sub> and subsequently SP-CsPbI<sub>3</sub> on top of a commercially available violet emitting LED (405 nm).<sup>4</sup> First, 10 weight % poly (methyl methacrylate) (PMMA) in toluene was mixed with both SP-CsPbBr<sub>3</sub> and SP-CsPbI<sub>3</sub> sample. Then the obtained paste was coated on top of the UV LEDs to get the pc-LED. Keithley 2450

Source meter was used to operate the pc-LED at 3.4 V and 0.1 mA current. Spectra and intensity of emitted radiation from pc-LED are measured by using Avantes open spectrometer.

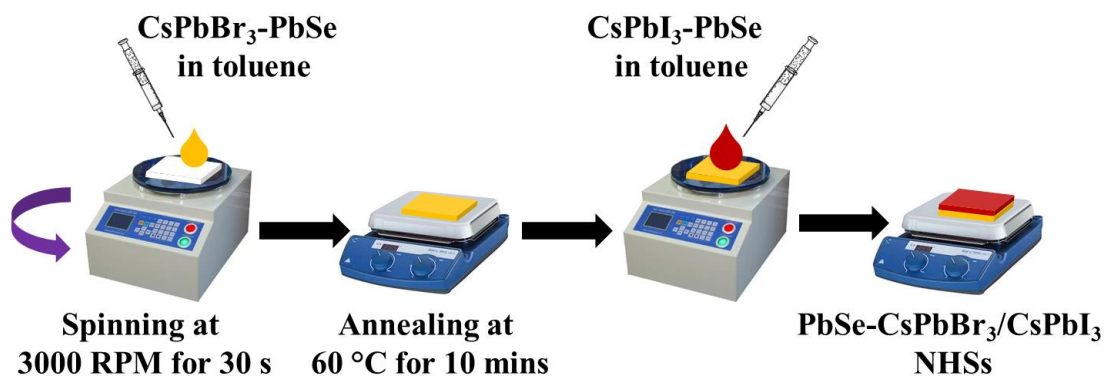
**Characterization Techniques.** Absorption measurements were performed for thin films using Perkin Elmer Lambda 1050 UV/vis/NIR spectrophotometer. The photoluminescence spectra (PL) of the same samples were collected on a Avantes open spectrometer. PL spectra was recorded by using an excitation wavelength of 400 nm. The lifetime decay curves were recorded at the PL emission maxima using HORIBA Deltaflex TM (380 nm). A Light emitting diode of 380 nm was used for lifetime measurements. The instrument response function was determined using a blank substrate. All the decay curves were fitted multiexponentially using  $I(t) = \sum_i \alpha_i e^{-t/\Gamma_i}$  where  $I(t)$  is total intensity at time  $t$  and  $\alpha_i$  and  $\Gamma_i$  are the amplitude and decay time of the  $i$ th component respectively. For average lifetime calculation, we used the equation  $\Gamma_{avg} = \sum_i^n (\alpha_i \Gamma_i^2 / \alpha_i \Gamma_i)$ . For all optical measurements, thin films on a glass substrate were used. Powder X-Ray diffraction (PXRD) pattern was taken on Bruker D8 Advance diffractometer using Ni-filtered Cu K $\alpha$  radiation. Field-emission scanning electron microscopy and Elemental Dispersive X-ray Spectroscopy (FESEM-EDX) measurements were carried out using JEOL-7800F Prime instrument. Transmission electron microscopy (TEM) images were collected using JEOL JEM-2010 microscope working at accelerating voltage of 120 keV, TALOS F200S G2 microscope at 200 keV. Dilute suspension of NCs in toluene was drop casted on the 200-mesh carbon coated Cu grids to prepare the sample.



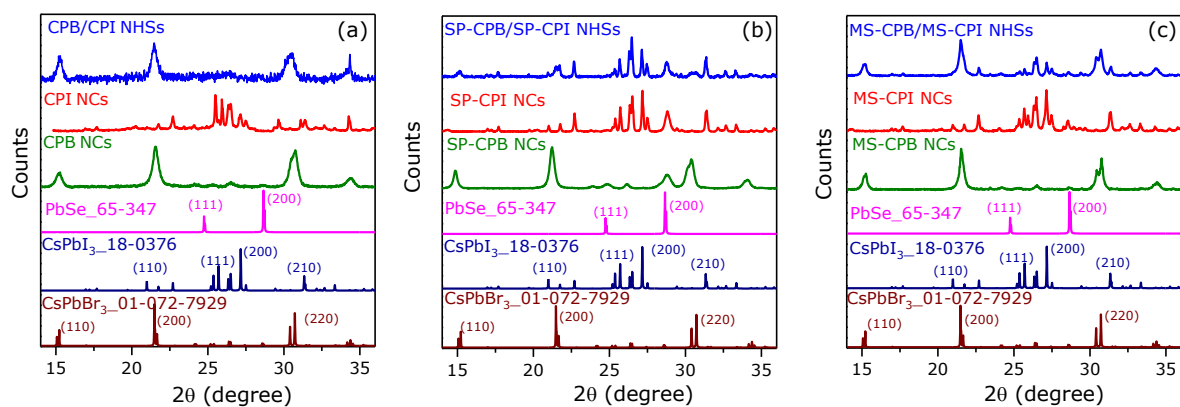
**Figure S1.** Histograms corresponding to (a) pristine CPB NCs, (b) SP-CPB NCs, and (c) MS-CPB NCs, showing size distribution of CPB in all cases; (d), (e) histograms showing size distribution of PbSe particles in SP-CPB and MS-CPB NCs, respectively.



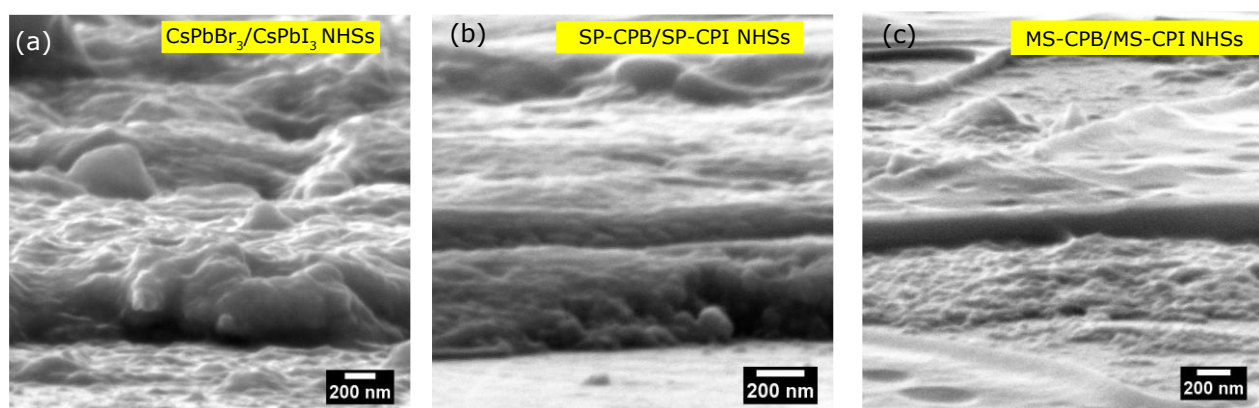
**Figure S2.** (a) XRD pattern of CPI NCs and MS/SP-CPI along with their reference pattern; TEM images of (b), (c) SP-CPI NCs; (d), (e) MS-CPI NCs, illustrating cubic morphology of CPI NCs, decorated with dot like PbSe particles.



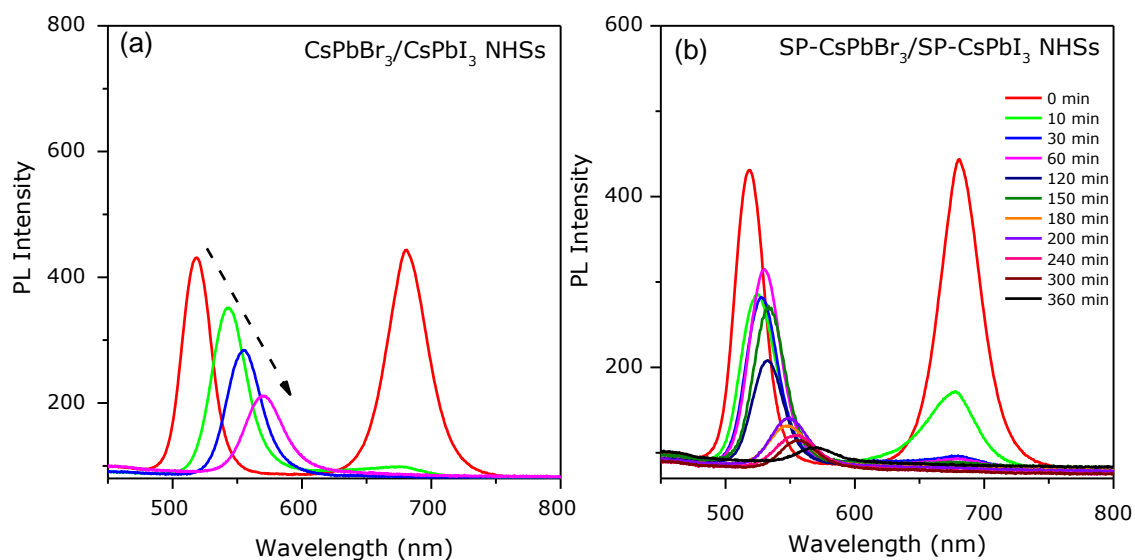
**Figure S3.** Schematic illustrating the sequential deposition of two perovskite layers on a glass substrate using spin coater.



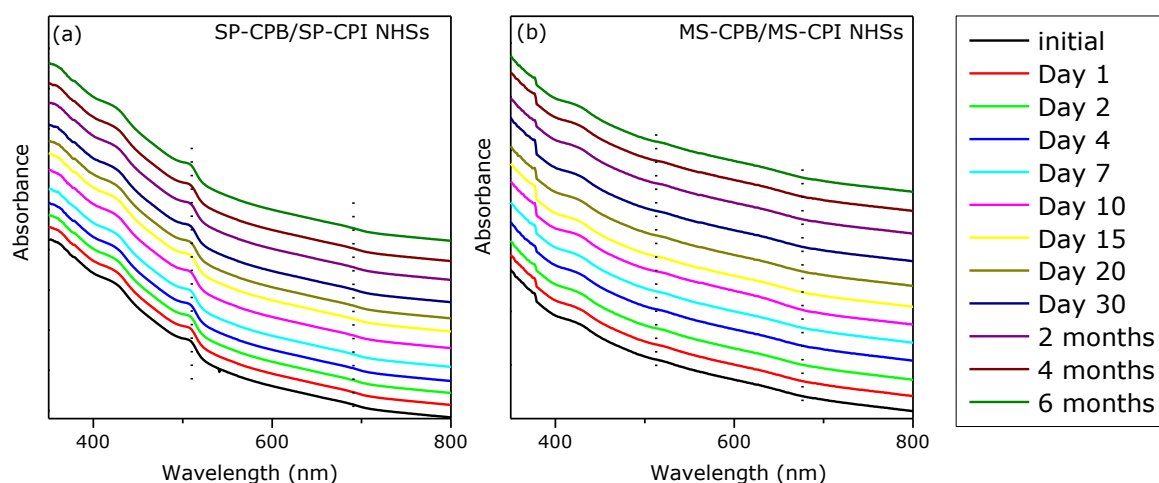
**Figure S4.** (a-c) XRD pattern of pristine CPB, SP/MS-CPB, CPI, SP/MS-CPI and their corresponding heterostructures along with their reference pattern.



**Figure S5.** (a-c) Cross-sectional FESEM image of CPB/CPI NHSs, SP-CPB/SP-CPI NHSs, and MS-CPB/MS-CPI NHSs, respectively.

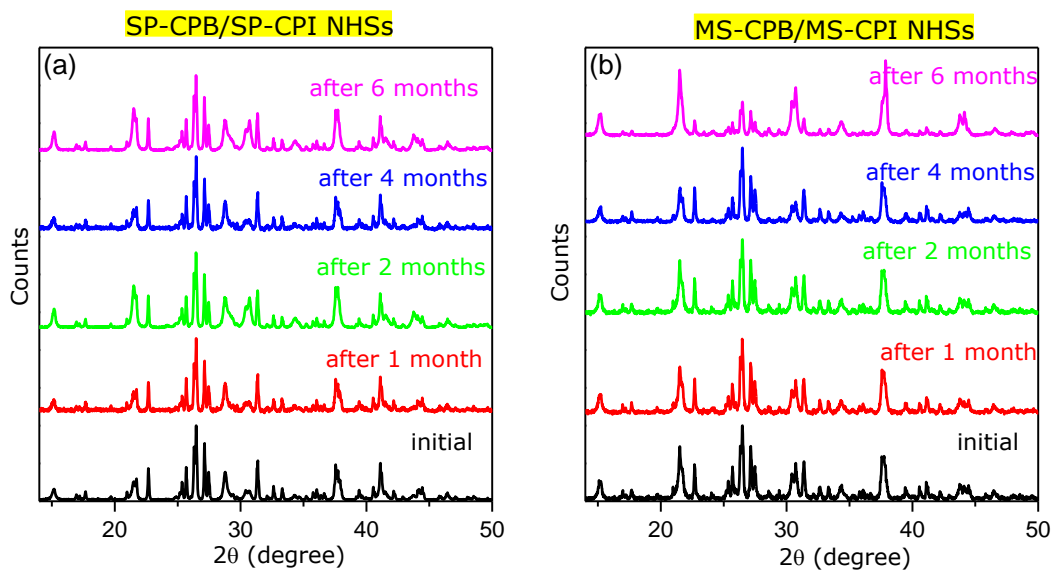


**Figure S6.** Change in the PL emission spectra of **(a)** pristine CsPbBr<sub>3</sub>/CsPbI<sub>3</sub> NHSs in toluene; **(b)** SP-CsPbBr<sub>3</sub>/SP-CsPbI<sub>3</sub> NHSs in toluene.

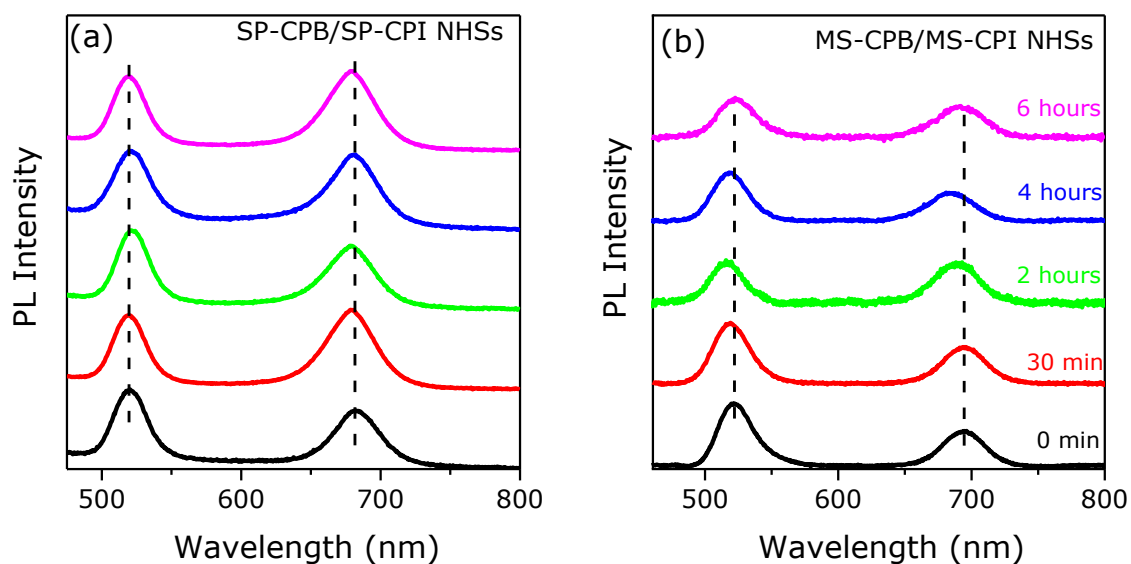


**Figure S7.** **(a), (b)** Absorption Spectra of SP-CPB/SP-CPI and MS-CPB/MS-CPI NHSs over the course of six months, showing no evidence of halide intermixing, whereas the control sample is completely mixed almost instantaneously.





**Figure S8.** (a), (b) PXRD pattern of SP-CPB/SP-CPI and MS-CPB/MS-CPI NHSs collected for a span of six months. The PXRD pattern corresponding to NHSs is stable for even after six months, which shows the highly crystalline stability of the NHSs.



**Figure S9.** Evolution of emission spectra with time upon heating at 100 °C (a) SP-CPB/SP-CPI NHSs; (b) MS-CPB/MS-CPI NHSs.

**Table S1.** Fluorescence decay parameters for CPB, SP/MS-CPB, and SP-CPB/SP-CPI and MS-CPB/MS-CPI heterostructure with  $\lambda_{em}= 518$  nm

<b>Sample</b>	<b>T<sub>1</sub> (ns)</b>	<b>A<sub>1</sub></b>	<b>T<sub>2</sub> (ns)</b>	<b>A<sub>2</sub></b>	<b>T<sub>3</sub> (ns)</b>	<b>A<sub>3</sub></b>	<b>T<sub>avg</sub> (ns)</b>
Pure CsPbBr <sub>3</sub> NCs	7.59	0.26	37.13	0.70	0.54	0.03	8.38
SP-CPB NCs	8.51	0.33	41.97	0.55	1.77	0.11	8.68
MS-CPB NCs	19.52	0.47	86.30	0.37	3.42	0.15	13.80
SP-CPB/SP-CPI NHSs	5.03	0.38	29.41	0.48	0.63	0.13	3.26
MS-CPB/MS-CPI NHSs	4.76	0.43	26.46	0.40	0.58	0.16	2.59

**Table S2.** Fluorescence decay parameters for CPI, SP/MS-CPI, and SP-CPB/SP-CPI and MS-CPB/MS-CPI NHSs heterostructure with  $\lambda_{em}= 692$  nm

<b>Sample</b>	<b>T<sub>1</sub> (ns)</b>	<b>A<sub>1</sub></b>	<b>T<sub>2</sub> (ns)</b>	<b>A<sub>2</sub></b>	<b>T<sub>3</sub> (ns)</b>	<b>A<sub>3</sub></b>	<b>T<sub>avg</sub> (ns)</b>
Pure CsPbI <sub>3</sub> NCs	21.93	0.34	57.41	0.58	4.37	0.06	24.45
SP-CPI NCs	26.21	0.37	102.99	0.56	3.26	0.05	27.97
MS-CPI NCs	33.70	0.43	131.03	0.44	6.64	0.12	28.60
SP-CPB/SP-CPI NHSs	34.89	0.43	132.71	0.45	7.04	0.10	32.01
MS-CPB/MS-CPI NHSs	40.52	0.43	154.80	0.45	8.15	0.11	36.76

## References.

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