Supporting Information

## Highly stable hetero-structured supercell, greenemitting cesium lead bromide by ligand-mediated phase control

G. Krishnamurthy Grandhi<sup>1</sup>, N. S. M. Viswanath<sup>2</sup>, Han Bin Cho<sup>1</sup>, Seong Min Kim<sup>1</sup> and Won Bin Im<sup>1</sup>, \*

<sup>1</sup>Division of Materials Science and Engineering, Hanyang University, 222 Wangsimni-ro,

Seongdong-gu, Seoul, 04763, Republic of Korea

<sup>2</sup>School of Materials Science and Engineering, Chonnam National University, 77 Yongbong-ro,

Buk-gu, Gwangju, 61186, Republic of Korea

\*E-mail: imwonbin@hanyang.ac.kr

## Characterization and spectroscopic techniques

The structure and size determination of the NCs were carried out using X-ray diffraction (XRD) technique and transmission electron microscopy (TEM). The XRD was performed on the thin films of the synthesized NCs, recorded on Shimadzu X-ray diffractometer using Cu K<sub>a</sub> radiation. All the patterns were recorded at a slow rate of 1° per minute to get a high signal to noise ratio. The structural information was derived from Rietveld refinement using the General Structure Analysis System (GSAS) software suite.<sup>1</sup> The visualization system for electronic and structural analysis (VESTA) program was used to draw the crystal structures.<sup>2</sup> The phase fractions of samples with dual-phase were estimated using Rietveld refinement of XRD results considering full refinement of crystallographic and instrumental parameters as implemented in the GSAS program suite. Energy dispersive X-ray (EDX) analysis was performed using a scanning electron microscope (Hitachi S-4700) at the Korea Basic Science Institute (KBSI), Gwangju, South Korea. The low and high-resolution TEM images were recorded using FEI Tecnai F20 (200 kV) at the Korea Basic Science Institute (KBSI), Gwangju, South Korea. The samples for TEM measurements were prepared by dispersing the NCs in n-hexane or n-octane. It is worth mentioning that cesium lead bromide NCs were usually not stable under irradiation with high-energy electron beams and tend to decompose within a short period of time. XPS was performed on the thin films of hybrid-I and hybrid-II CsPbBr<sub>3</sub>/Cs<sub>4</sub>PbBr<sub>6</sub> NCs using VG Multilab 2000 instruments to obtain the Cs:Pb:Br values on the sample surface (probing depth is up to 10 nm), employing Al as the target anode for the X-ray generation. The energy of the X-ray photon (Al  $K_{\alpha}$ ) is 1480 eV with a line width of 0.5 eV. UV-visible absorption spectra of various aliquots dissolved in hexane were obtained using Thermo Scientific Evolution 201 UV-visible spectrometer. Steady-state PL spectra in n-octane or hexane of the NCs were collected using a Hitachi F-4500 fluorescence spectrophotometer. The PL

lifetime measurements were carried out on the FLSP920 spectrometer, Edinburgh Instruments at Korea Advanced Institute of Science and Technology (KAIST), Seoul, South Korea. A laser was used as excitation source ( $\lambda_{ex} = 375$  nm). The internal quantum efficiency (absolute PL QY) of the NCs was conducted in an integrated sphere (QE-2000, Otsuka electronics) with an excitation wavelength at 440 nm.

**Stability experiments.** Photostability experiments were conducted by continuously illuminating the NC films using the using xenon lamp, in the PL instrument. The PL spectra were collected at regular intervals. Mild and harsh UV conditions were created by using slit widths (excitation) of 5 nm and 20 nm respectively. The variation of PL intensity during the heating-cooling cycles were measured using a connection to a Hitachi F-4500 fluorescence spectrometer with an integrated heater, temperature controller, and thermal sensor. For thermal stability studies, a thin film of hybrid-II CsPbBr<sub>3</sub>/Cs<sub>4</sub>PbBr<sub>6</sub> NCs annealed for 11 days at 120°C and 160°C on a hot plate in the ambient air, light, and oxygen. It is to be noted that we made sure that the NC film is in good contact with the hot plate throughout the heating process. Typically, thin films were obtained by drop-casting of concentrated solutions of the NCs onto glass substrates.

**Fabrication of prototype WLED.** Prototype WLED devices were fabricated by integrating the hybrid-II CsPbBr<sub>3</sub>/Cs<sub>4</sub>PbBr<sub>6</sub> NCs with a commercial blue phosphor, Sr<sub>3</sub>MgSi<sub>2</sub>O<sub>8</sub>: Eu<sup>2+</sup> and a commercial red phosphor, K<sub>2</sub>SiF<sub>6</sub>: Mn<sup>4+</sup> on a near UV LED chip ( $\lambda_{max} = 395$  nm). The devices were then encapsulated in a phosphor/silicone resin mixture, followed by curing it at 120°C for one hour. The EL characteristics of the WLED device were measured in an integrating sphere under direct current forward-bias condition.



**Figure S1.** Variation of phase fraction of CsPbBr<sub>3</sub> as a function of OlAm to OlAc ratio for the NCs synthesized with Cs to Pb ratio of 1:1. The phase fraction values were determined by performing Rietveld refinement on the corresponding XRD patterns. Rietveld refined parameters are presented in Table S2–S4.



**Figure S2.** The size distribution curves for (a)  $CsPbBr_3$ , (b)  $CsPbBr_3 + Cs_4PbBr_6$ , (c)  $Cs_4PbBr_6$  and (d) CsBr NCs. They correspond to the TEM images presented in Figure 1c–f.



Figure S3. CsBr NCs synthesized with Cs to Pb ratio of 5:1 and excess OlAm.



**Figure S4.** Phase switching of blue-light emitting mixed-halide NCs (Cs:Pb=5:1 and Br:Cl=55:45) as a function of OlAc concentration. (a) XRD patterns, (b) absorption spectra, and (c) PL spectra of the NCs synthesized with 2 mL (bottom) and 10 mL (top) of OlAc during their synthesis.



**Figure S5.** Phase switching of cesium lead bromide NCs (Cs:Pb = 2.5:1.0) as a function of OlAm/OlAc ratio. (a) UV-vis absorption spectra of the NCs and the inset shows the reduction in PL intensity of the NCs upon increasing OlAm/OlAc ratio during the synthesis. (b) XRD patterns of the NCs as a function of OlAm/OlAc ratio. Asterisk, circle, and diamond symbols represent the XRD peaks and absorption bands, correspond to CsPbBr<sub>3</sub>, Cs<sub>4</sub>PbBr<sub>6</sub>, and CsBr phases, respectively.

This data further suggests that the phase of the NCs shifted from  $CsPbBr_3$  to  $Cs_4PbBr_6$  as a function of OlAm to OlAc ratio regardless of Cs to Pb feed ratio.



**Figure S6.** Effect of OlAm concentration on the phase and PL efficiencies of cesium lead halide NCs synthesized with Cs:Pb = 1:1. (a) XRD patterns of NCs of different phases along with the reference XRD patterns and (b) the corresponding PL spectra corrected with the absorbance value at 440 nm. (c) The magnified version of the panel (b). (d) Normalized PL spectra of the NCs with varying OlAm concentration. (e) Photographs of the NC solutions as a function of OlAm concentration under room light (above) and 365 nm light (below). Excitation wavelength,  $\lambda_{ex} = 440$  nm for panels (b) and (c) and  $\lambda_{ex} = 320$  nm for panel (d).



**Figure S7.** Characterization of CsPbBr<sub>3</sub> NCs prepared with two different concentrations of OlAc. (a) XRD patterns, (b) absorption spectra, (c) PL spectra ( $\lambda_{ex} = 440$  nm), and (d) PLE spectra ( $\lambda_{em} = 525$  nm) of the NCs synthesized with a fixed OlAm concentration and using 3 mL (bottom) and 10 mL (top) of OlAc respectively. (e) and (f) are the corresponding TEM images.

The XRD patterns of these two samples are similar and show the reflections of CsPbBr<sub>3</sub> only (Figure S7a). So, XRD data suggests the absence of impurities in both the samples and hence indicates the phase-purity. Nevertheless, the absorption spectrum of NCs synthesized with 3 mL of OlAc consists of Cs<sub>4</sub>PbBr<sub>6</sub> absorption feature, while, 10 mL of OlAc produced impurity-free CsPbBr<sub>3</sub> NCs (Figure S7b). This agrees with the dip present in the corresponding PLE spectrum (Figure S7d) which is at its absorption maximum, further suggesting the existence of Cs<sub>4</sub>PbBr<sub>6</sub> impurity phase in the former case. The impurity phase was also not detected by either PL spectroscopy (Figure S7c) or TEM (Figure S7e,f). Therefore, these findings demonstrate that a combination of spectroscopic and structural techniques will be necessary in determining the phase-purity of the cesium lead bromide NCs but not only XRD or TEM measurements.



**Figure S8.** (a) The PL QY of the NCs synthesized with increasing OlAm concentration and with Cs:Pb = 1:1. (b) The PL QY of the NCs synthesized with increasing OlAc concentration and with Cs:Pb = 5:1. In both cases, the  $CsPbBr_3 + Cs_4PbBr_6$  mixed-phase NCs exhibited the highest PL QY among the samples. (c) The time-resolved PL spectra of NCs synthesized with increasing OlAm concentration and with Cs:Pb = 1:1. The inset shows the corresponding PL decay time variation. The PL decay time is higher for NCs rich in  $Cs_4PbBr_6$ -phase. The rest of the PL decay parameters are given in Table S5. 113, 416, 113+416, and 113/416 represent CsPbBr\_3, Cs\_4PbBr\_6, CsPbBr\_3 + Cs\_4PbBr\_6 mixed-phase and CsPbBr\_3/Cs\_4PbBr\_6 hybrid NCs, respectively.



**Figure S9.** "Considerably" pure  $Cs_4PbBr_6$  NCs, synthesized with an equimolar ratio of Cs and Pb and an excess of Olam in hexane and DMF as the solvents. (a) XRD pattern and (b) PL spectra of NCs excited at two different wavelengths.

These NCs exhibit a weak or negligible green emission under 440 nm excitation. Moreover, the PL spectrum shows almost no green PL under 320 nm excitation but dominated by a 370 nm emission peak, attributed to emission arises from  $Pb^{2+}$  ions of  $Cs_4PbBr_6$ . This data indicates that small amounts of  $CsPbBr_3$ -impurity are present in the sample.



**Figure S10**. (a) The stoichiometry of hybrid-I and hybrid-II NCs acquired by EDX spectroscopy and obtained by taking an average of the data collected at three different areas (b) of the NC film.



**Figure S11.** The PL spectra corresponding to the photostability data presented in Figure 4a. The variation of PL intensity for thin films of (a) CsPbBr<sub>3</sub>, (b) Br-rich hybrid CsPbBr<sub>3</sub>/Cs<sub>4</sub>PbBr<sub>6</sub> and (c) Br-poor hybrid CsPbBr<sub>3</sub>/Cs<sub>4</sub>PbBr<sub>6</sub> NCs as a function of UV (365 nm) irradiation time. Excitation wavelength,  $\lambda_{ex} = 440$  nm for all the PL spectra.



**Figure S12.** The variation of the PL intensity of CsPbBr<sub>3</sub> and hybrid CsPbBr<sub>3</sub>/Cs<sub>4</sub>PbBr<sub>6</sub> NCs in thin film form under harsh UV radiation (365 nm) as a function of time. Excitation wavelength,  $\lambda_{ex} = 440$  nm for all the PL spectra.

Sample	OlAc (mL)	OlAm (mL)
Pure CsPbBr <sub>3</sub>	10.2	0.1
89% Cs <sub>4</sub> PbBr <sub>6</sub> + 11% CsPbBr <sub>3</sub> +	1.95	0.5
95% Cs <sub>4</sub> PbBr <sub>6</sub> + 5% CsPbBr <sub>3</sub>	1.85	1
Pure Cs <sub>4</sub> PbBr <sub>6</sub>	0.2	1.25
CsBr	0.2	4

**Table S1.** The amounts of OlAc and OlAm used for NCs synthesized with Cs:Pb = 1:1.

OlAm:OlAc	1.0:3.5	1.0:1.65
space group	<i>R</i> <sup>3</sup> <i>c</i>	Pbnm
composition	Cs <sub>4</sub> PbBr <sub>6</sub>	Cs <sub>4</sub> PbBr <sub>6</sub>
Wt. fraction	95%	89%
<i>a</i> /Å	13.72(2)	8.227(1)
b/Å	13.72(2)	8.245(7)
c/Å	17.2912(5)	11.743(3)
V/Å <sup>3</sup>	2818.61(8)	796.78(5)
Ζ	6	4
space group	Pbnm	R <sup>3</sup> c
composition	CsPbBr <sub>3</sub>	CsPbBr <sub>3</sub>
Wt. fraction	5%	11%
a/Å	8.208(3) 13.71	
b/Å	/Å 8.251(1) 13.718	
<i>c</i> /Å	11.743(5)	17.295(3)
$V/\text{\AA}^3$	796.68(8)	2818.68(5)
Ζ	4	6
$\chi^2$	2.49	1.77

**Table S2**. Structural parameters of cesium lead halide NCs synthesized with varying OlAm to OlAc ratio and an equimolar ratio of Cs and Pb, calculated using the Rietveld refinement. The number in the parentheses are the estimated standard deviation of the last significant figure.

primary phase: Cs <sub>4</sub> PbBr <sub>6</sub>						
atomic p	arameters					
atom	site	x	у	Ζ	occupancy	100×U <sub>iso</sub> [Å]
Pb	6 <i>b</i>	0	0	0	1.0	0.0118(5)
Cs1	6 <i>a</i>	0	0	1⁄4	1.0	0.0483(11)
Cs2	18e	0.3727(23)	0	1/4	1.0	0.0338(11)
Br	36 <i>f</i>	0.1943(8)	0.0300(26)	0.1014	1.0	0.0377(18)
secondary phase: CsPbBr <sub>3</sub>						
atom	site	x	у	Ζ	occupancy	100×U <sub>iso</sub> [Å]
Pb	4 <i>b</i>	0.5	0	0	1.00	0.1349(19)
Cs	4 <i>c</i>	0.9286(3)	1/2	0.2500	1.00	0.0414(15)
Br1	4 <i>c</i>	0.0856(6)	0.4376(9)	0.2500	1.00	0.0458(13)
Br2	8 <i>d</i>	0.8710(2)	0.1229(3)	0.0532(9)	1.00	0.0015(19)

**Table S3**. Rietveld refined parameters for NCs synthesized with an equimolar ratio of Cs and Pb and OlAm:OlAc = 1:4. The number in the parentheses are the estimated standard deviations of the last significant figure.

**Table S4**. Rietveld refined parameters for NCs synthesized with an equimolar ratio of Cs and Pb and OlAm:OlAc = 1:2. The number in the parentheses are the estimated standard deviations of the last significant figure.

primary phase: Cs <sub>4</sub> PbBr <sub>6</sub>						
rameters						
site	x	У	Ζ	occupancy	100×U <sub>iso</sub> [Å]	
6 <i>b</i>	0	0	0	1.0	0.0118(5)	
6 <i>a</i>	0	0	1/4	1.0	0.0483(11)	
18 <i>e</i>	0.3704(23)	0	1/4	1.0	0.0338(11)	
36 <i>f</i>	0.2034(8)	0.0347(26)	0.0944	1.0	0.0377(18)	
y phase: C	sPbBr <sub>3</sub>					
site	x	у	Z	occupancy	100×U <sub>iso</sub> [Å	
4 <i>b</i>	0.5	0	0	1.00	0.1349(23)	
4 <i>c</i>	0.9286(6)	1/2	0.87518(9)	1.00	0.0400(13)	
4 <i>c</i>	0.0856(3)	0.4376(7)	0.25	1.00	0.0476(11)	
L 0	0.0710(2)	0.1220(2)	0.0522(0)	1.00	0.04(7(10)	
	hase: $Cs_4P$ rameters site 6b 6a 18e 36f y phase: C site 4b 4c 4c 4c	hase: $Cs_4PbBr_6$ rameters   site x $6b$ 0 $6a$ 0 $6a$ 0 $18e$ 0.3704(23) $36f$ 0.2034(8)   y phase: CsPbBr <sub>3</sub> site x $4b$ 0.5 $4c$ 0.9286(6) $4c$ 0.0856(3) $8d$ 0.8710(2)	hase: $Cs_4PbBr_6$ rameters   site x y   6b 0 0   6a 0 0   18e 0.3704(23) 0   36f 0.2034(8) 0.0347(26)   y phase: CsPbBr <sub>3</sub> y   site x y   4b 0.5 0   4c 0.9286(6) $\frac{1}{2}$ 4c 0.0856(3) 0.4376(7)   8 d 0.9710(2) 0.1220(2)	hase: $Cs_4PbBr_6$ rameters   site x y z   6b 0 0 0   6a 0 0 1/4   18e 0.3704(23) 0 1/4   36f 0.2034(8) 0.0347(26) 0.0944   y phase: CsPbBr <sub>3</sub> site x y z   4b 0.5 0 0   4c 0.9286(6) 1/2 0.87518(9)   4c 0.0856(3) 0.4376(7) 0.25	hase: $Cs_4PbBr_6$ rameters   site x y z occupancy   6b 0 0 1.0   6a 0 0 1/4 1.0   18e 0.3704(23) 0 1/4 1.0   36f 0.2034(8) 0.0347(26) 0.0944 1.0   y phase: CsPbBr <sub>3</sub> site x y z occupancy   4b 0.5 0 0 1.00   4c 0.9286(6) 1/2 0.87518(9) 1.00   4c 0.0856(3) 0.4376(7) 0.25 1.00	

**Table S5.** The parameters obtained by fitting the PL decay curves (Figure S8c) to the exponential function.  $t_{slow}$  and  $t_{fast}$  represent the decay times for the slow and fast components of the decay curve, respectively.  $A_{slow}$  (%) and  $A_{fast}$  (%) represent the percentage contributions of the two components, respectively.

OlAm:OlAc	average lifetime (ns)	t <sub>slow</sub> (ns)	$t_{fast} (ns)$	A <sub>slow</sub> (%)	$A_{fast}$ (%)
1:100	5	9	4	24	76
1:5	7	20	5	34	66
1:2	8	51	7	27	73

## References

- 1. Toby, B. H. J. Appl. Crystallogr. 2001, 34, 210-213.
- 2. Momma, K.; Izumi, F. J. Appl. Crystallogr. 2008, 41, 653-658.