

## Electronic Supplementary Information

### Nanocomposite of CsPbBr<sub>3</sub> Perovskite Nanocrystals in an Ammonium Bromide Frame with Enhanced Stability

Sunqi Lou,<sup>a</sup> Tongtong Xuan,<sup>\*b</sup> Caiyan Yu,<sup>a</sup> Mengmeng Cao,<sup>a</sup> Chao Xia,<sup>a</sup> Jing Wang,<sup>\*b</sup>  
and Huili Li<sup>\*a</sup>

<sup>a</sup>Engineering Research Center for Nanophotonics & Advanced Instrument, Ministry  
of Education, School of Physics and Materials Science, East China Normal University,  
Shanghai 200062, China.

<sup>b</sup>Ministry of Education Key Laboratory of Bioinorganic and Synthetic Chemistry,  
State Key Laboratory of Optoelectronic Materials and Technologies, School of  
Chemistry, School of Materials Science and Engineering, Sun Yat-Sen University,  
Guangzhou 510275, China

*\*Corresponding author:*

**Prof. Huili Li**

***E-mail:* hlli@phy.ecnu.edu.cn;**

***Tel:* +86-21-62235465;**

***Fax:* +86-21-62234321.**

**Prof. Jing Wang**

***E-mail:* ceswj@mail.sysu.edu.cn;**

***Tel:* +86-02-84112112.**

**Dr. Tongtong Xuan**

***E-mail:* xuantt@mail.sysu.edu.cn;**

***Tel:* +86-20-84110189.**

## Experimental Section

### 1. Chemicals

Lead chloride ( $\text{PbCl}_2$ , 99.999%), oleic acid (OA, 90%), 1-octadecene (ODE, 90%), oleylamine (OAm, 80-90%), trioctylphosphine (TOP, 90%) were purchased from Alfa Aesar. Cesium carbonate ( $\text{Cs}_2\text{CO}_3$ , 99.9%) and lead bromide ( $\text{PbBr}_2$ , 98%) were purchased from Aldrich. Ammonium chloride ( $\text{NH}_4\text{Cl}$ , 99.0%), Ammonium bromide ( $\text{NH}_4\text{Br}$ , 99.0%), Ammonium iodide ( $\text{NH}_4\text{I}$ , 99.0%), Sodium chloride ( $\text{NaCl}$ , 99.0%), Lead iodide ( $\text{PbI}_2$ , 99.99%) and toluene (analytical reagent) were purchased from Sinopharm Chemical Reagent Co., Ltd. All reagents were used as received without further experimental purification.

### 2. Preparation of Cs-oleate

$\text{Cs}_2\text{CO}_3$  (0.814 g), OA (2.5 mL) and ODE (40 mL) were added into a 100 mL 3-neck flask, dried for 1h at 120°C and then heated under  $\text{N}_2$  to 150°C to ensure full solubility of  $\text{Cs}_2\text{CO}_3$ . Since Cs-oleate precipitates out of ODE at room-temperature, it must be preheated to 100 °C before injection.

### 3. Synthesis of $\text{CsPbX}_3$ (X=Cl, Br, I) NCs

ODE (5 mL), OA (1.5 mL for  $\text{PbCl}_2$  and 0.5 mL for  $\text{PbBr}_2$ ), OAm (1.5 mL for  $\text{PbCl}_2$ , and 0.5 mL for  $\text{PbBr}_2$ ) and 0.188 mmol of  $\text{PbX}_2$  were loaded into a 50 mL 3-neck flask and dried under vacuum at 120 °C for 1h. After degassing, filling the  $\text{N}_2$  and keeping the temperature at 120°C for 2h. A hot syringe was used to swiftly inject 0.4 mL of the Cs precursor into the lead halide precursor solution at elevated temperatures (140°C for  $\text{CsPbBr}_3$  and  $\text{CsPbI}_3$ , 180°C for  $\text{CsPbCl}_3$ ) and a certain period of time later the reaction mixture was cooled down by an ice water bath. For obtaining  $\text{CsPbCl}_3$  NCs, a higher temperature of 180 °C and 1 mL of trioctylphosphine are necessary to solubilize  $\text{PbCl}_2$ . After reaction, the aggregated NCs were separated by centrifugation. After centrifugation, the supernatant was discarded and the precipitate was redispersed in dried 6 mL toluene.

### 4. Synthesis of $\text{CsPbBr}_3\text{-NH}_4\text{Br}$ nanocomposites

$\text{CsPbBr}_3\text{-NH}_4\text{Br}$  (loading of 0.062 mmol of  $\text{CsPbX}_3$  (X=Cl, Br) NCs to 1 g of  $\text{NH}_4\text{Br}$  in theory) was synthesized via an anion exchange procedure and physical

absorption. In order to differentiate, the products were named as CPBr-NB-AE and CPBr-NB-PA, respectively. In detail, 4 mL dry toluene was poured into a reagent bottle containing 2 mL CsPbX<sub>3</sub> NCs solution, and then 1 g NH<sub>4</sub>Br was added in the ambient condition for an anion exchange or physical absorption. After rest for a period of time (24h for the CPBr-NB-PA), the precipitates were separate collected through centrifugation at 1000 rpm for 3 min, and the CPBr-NB nanocomposites were obtained by vacuum drying. For the water stability tests, the content of the CsPbBr<sub>3</sub> NCs in the CPBr-NB-AE nanocomposites was kept nearly same with the pure CsPbBr<sub>3</sub> powder. The concentration of the CsPbBr<sub>3</sub> is  $6.3 \times 10^{-3}$  mmol/mL for CPBr-NB-AE and  $6.0 \times 10^{-3}$  mmol/mL for CsPbBr<sub>3</sub>, respectively. Both samples were dispersed in 5 mL deionized water during the test.

#### 5. Packaging of White LEDs

CPBr-NB-AE nanocomposites and red K<sub>2</sub>SiF<sub>6</sub>:Mn<sup>4+</sup> phosphor were mixed with silicone resin B and silicone resin A (A: B = 1: 2; wt%). After bubbles were removed, the mixture was dropped onto a blue chip and then thermally cured for 2 h at 150 °C in an oven. Followed previously step, we can fabricate white LEDs for optical properties test. The optical properties of the fabricated devices were determined using an integrating sphere with an analyzer system (Ocean Optics Co., Ltd.).

#### 6. Characterization

The absorption and transmittance spectra of as-prepared NCs and nanocomposites were measured by using a UV/vis spectrophotometer (Hitachi U-3900). Photoluminescence (PL) spectra and external quantum yield (QY) were measured by using a fluorescence spectrophotometer (Horiba Jobin Yvon, FluoroMax-4) containing an integrating sphere unit (Horiba Jobin Yvon, F3029). For the temperature-dependent photoluminescence measurement, the sample was bedded in a sample cavity and heated to the desired temperature by a high-temperature fluorescence controller (Tianjin Orient KOJI Co., Ltd., TAP-02). X-ray diffractometer (XRD), using Cu K $\alpha$  radiation ( $\lambda = 1.5405 \text{ \AA}$ ) at a voltage of 40 k and a current of 40 mA with  $2\theta$  scanning mode. The surface morphology, structure, composition and energy dispersive spectrometer (EDS) of the samples were characterized by Feld-emission scanning electron microscopy

(FESEM, Hitachi S-4800). The morphology and particle size of samples were observed by a JEM-2100 high-resolution transmission electron microscope (HRTEM, JEOL, Japan). X-ray photoelectron spectroscopy (XPS) measurements were carried out on a multifunctional imaging electron spectrometer (Thermo ESCALAB 250XI). And fourier transformation infra-red (FTIR) spectra were taken by using a fourier transformation infra-red spectrometer (Bruker, EQUINOX 55). respectively.

Table S1. The photoluminescent quantum yield of the CPBr-NB-AE nanocomposites.

time	0.5h	3h	6h	12h	24h	48h
PL quantum yield (%)	41.42	43.00	61.89	62.13	64.21	54.88

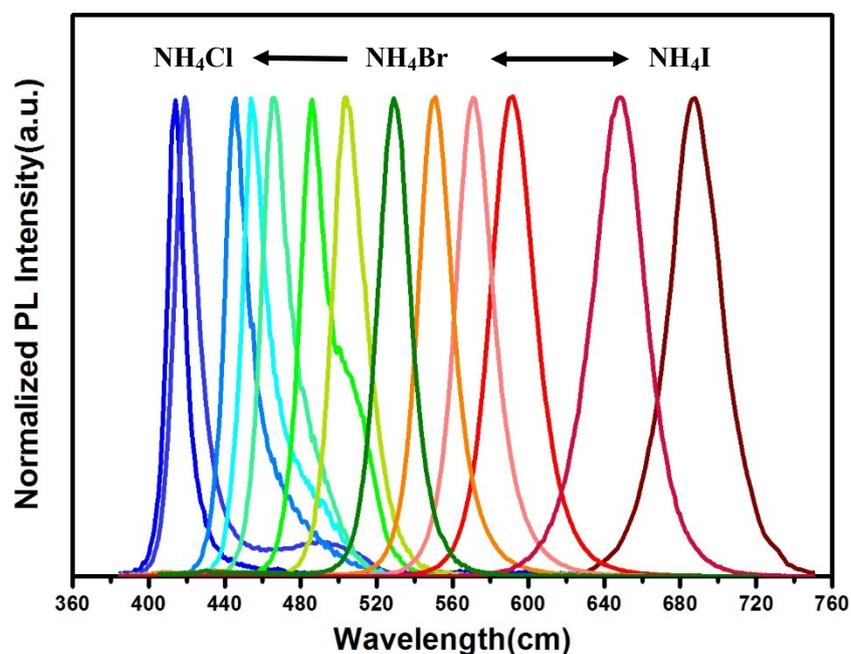


Figure. S1 PL spectra of the exchanged CsPbX<sub>3</sub> NCs by NH<sub>4</sub>X (X = Cl,Br,I)

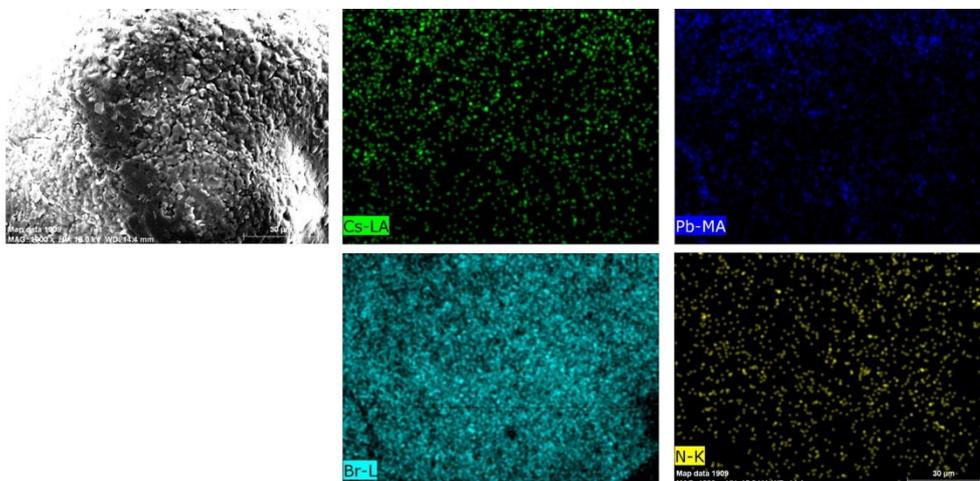


Figure. S2 elemental mappings of CPBr-NB-AE.

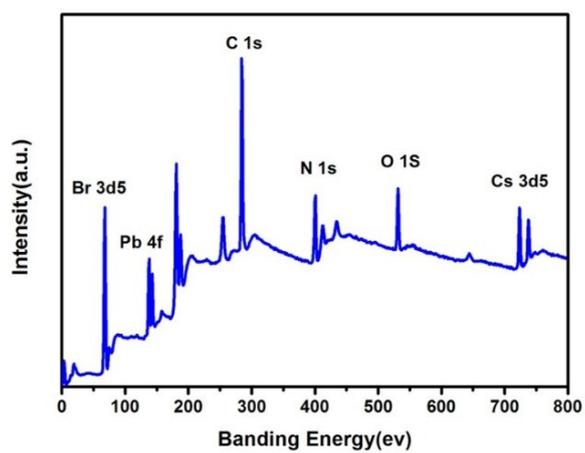


Figure. S3 XPS image of the CPBr-NB-AE.

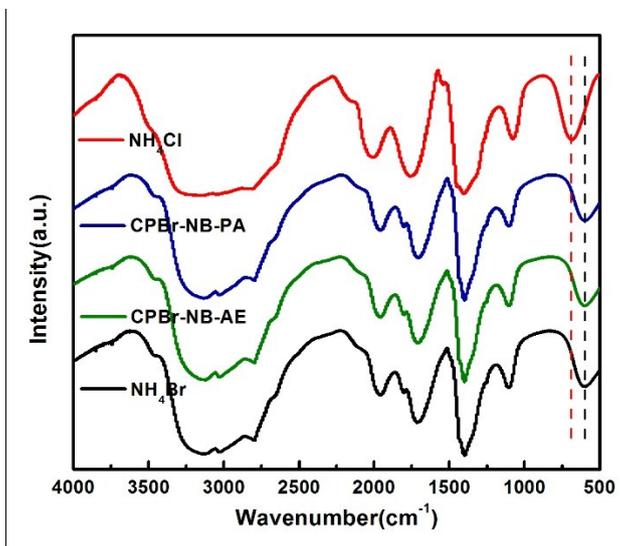


Figure. S4 FTIR spectra of the NH<sub>4</sub>Br, CPBr-NB-AE, CPBr-NB-PA and NH<sub>4</sub>Cl (the red dotted line indict the vibrations of N-Cl and the blank dotted line is N-Br).

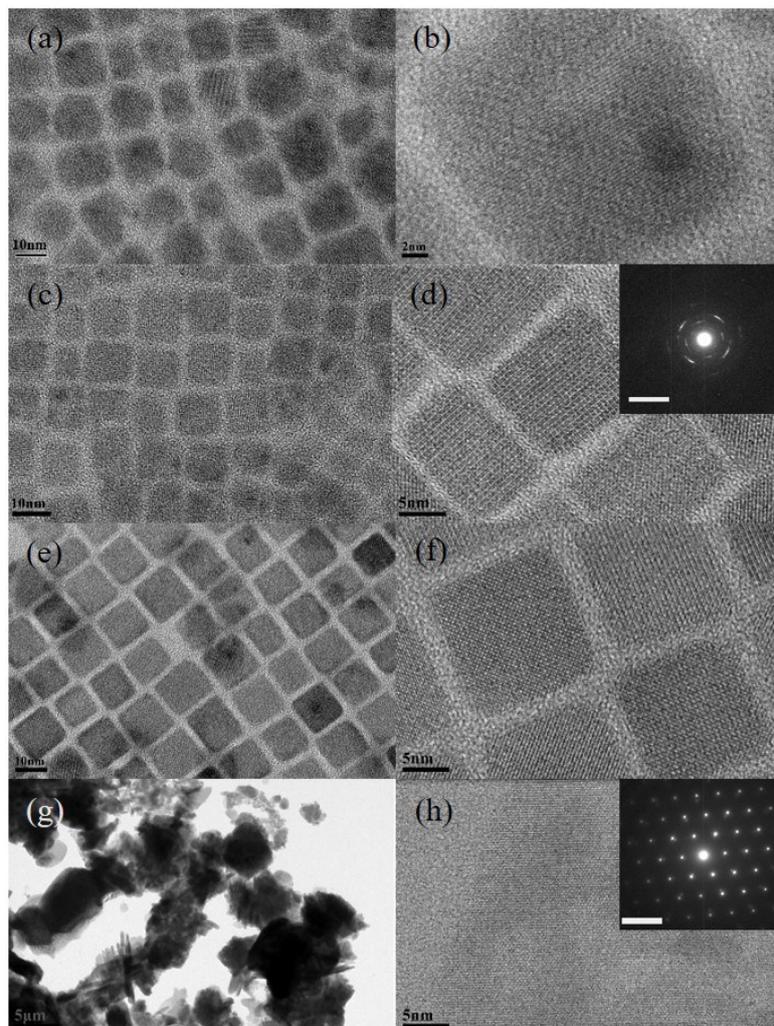


Figure. S5 TEM images of monodisperse perovskite NCs: (a, b) CsPbBr<sub>3</sub> NCs; (c, d) CsPbBr<sub>3</sub> NCs; (e, f) CsPbCl<sub>3</sub> NCs; (g, h) bulk CsPbBr<sub>3</sub> which got from the heat treat CPBr-NB-AE nanocomposites. The insets in right corner of the picture (d, h) show the diffraction spot of the CsPbBr<sub>3</sub> NCs and bulk CsPbBr<sub>3</sub>.

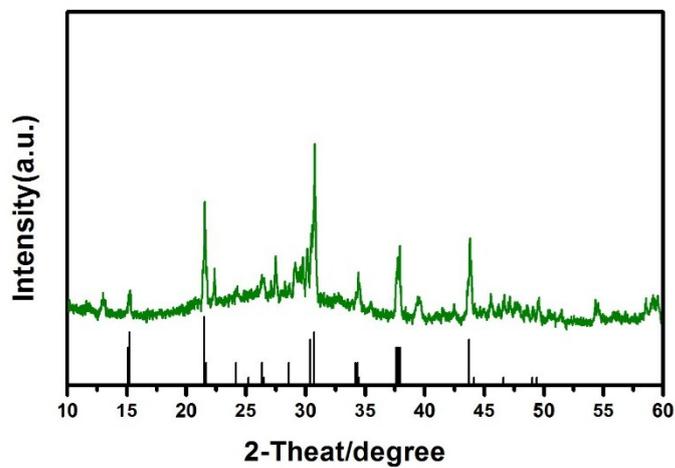


Figure. S6 XRD of the patterns of bulk CsPbBr<sub>3</sub> which got from the heat treat CPBr-NB-AE nanocomposites.

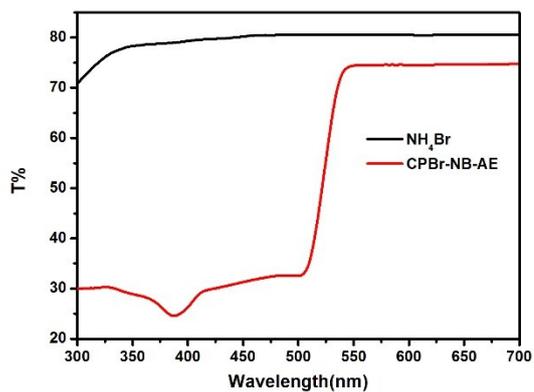


Figure. S7 transmittance spectra the CPBr-NB-AE nanocomposites and NH<sub>4</sub>Br.

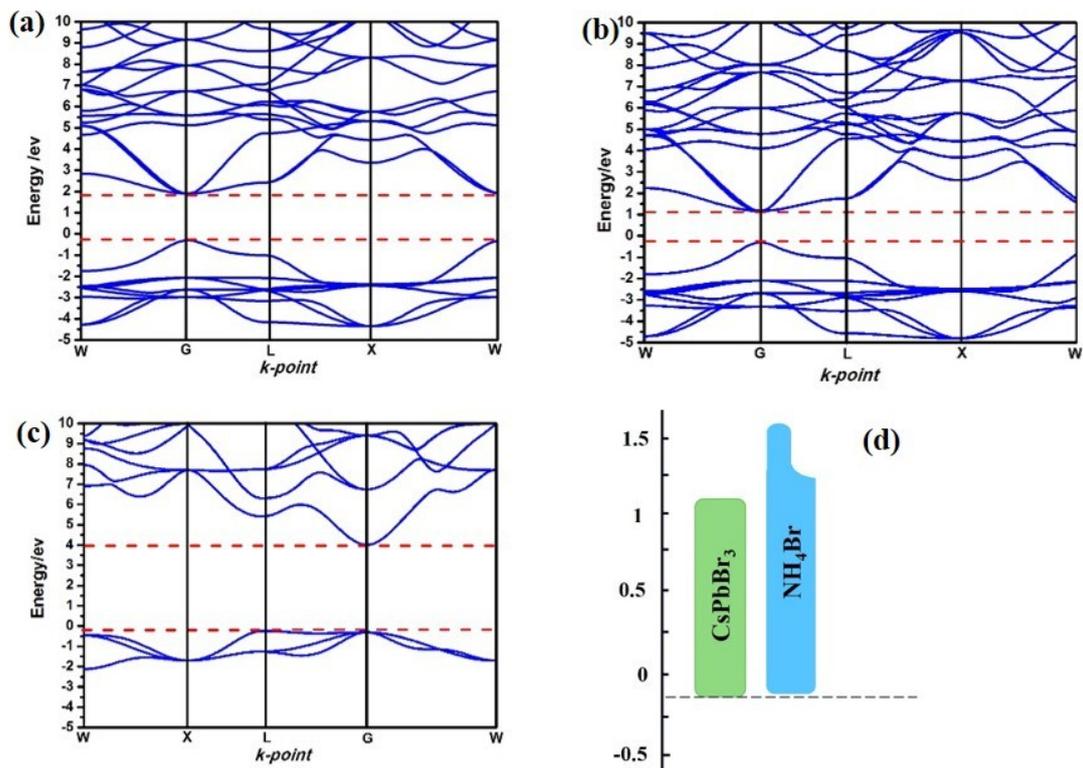


Figure. S8 Electronic state structures of energy band of the (a) CsPbCl<sub>3</sub>, (b) CsPbBr<sub>3</sub> (c) NH<sub>4</sub>Br and (d) the flat-band energy level diagram of the CsPbBr<sub>3</sub> NCs and NH<sub>4</sub>Br.

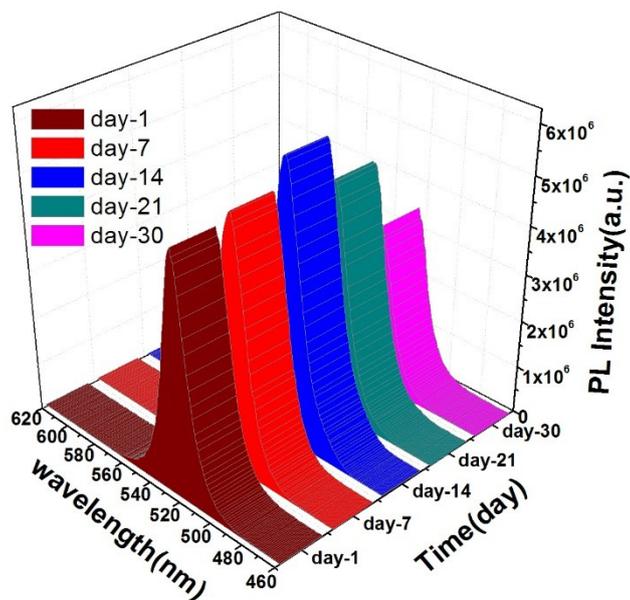


Figure. S9 PL spectra of the CPBr-NB-AE nanocomposites under the ambient condition maintaining for different time, which the humidity was  $\sim 45\%$  and the temperature was  $\sim 30^\circ\text{C}$ .