Supporting Information

Monodisperse and Brightly Luminescent $CsPbBr_3/Cs_4PbBr_6$ Perovskite Composite Nanocrystals

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Experimental Section

Chemicals.

Cesium bromide (CsBr, 99.9%, Aldrich), lead(II) bromide ($PbBr_2$, 98%, Aldrich), 2-Methylimidazole (MeIM, 98%, Aladdin), oleic acid (OA, 90%, Aldrich), oleylamine (OAm, 70%, Aldrich), *N,N*-dimethylformamide (DMF, 99.8%, Aladdin), cyclohexane (>99.5%, Aladdin), toluene (TOL, 99.5%, Sinopharm Chemical Reagent Co., Ltd, China). All reagents were used as received without further purification.

Synthesis of $CsPbBr_3$ embedded in Cs_4PbBr_6 composite (CPB_{113}/CPB_{416}) NCs.

Typically, $PbBr_2$ (0.1 mmol), CsBr (0.4 mmol), and MeIm (0.1mmol) were added to a mixture solution of 0.2 mL OA, 0.5 mL OAm, and 10 mL DMF. The solution was kept stirring for 1h, 4h, or 24h. After is, 0.2 mL the solution was quickly injected into toluene (5 mL) solution under vigorous stirring for 1min. Finally, the CPB_{113}/CPB_{416} NCs were centrifuged at 5000 rpm for 5min and washed twice by toluene. The NCs powders were obtained by drying under vacuum and stored under ambient condition.

Synthesis of $CsPbBr_3/Cs_4PbBr_6$ composite (CPB_{113}/CPB_{416}) NCs without using MeIm.

Similar as the CPB_{113}/CPB_{416} NCs preparation approach, the CPB_{113}-CPB_{416} NCs were synthesized by without using MeIm.

Synthesis of $CsPbX_3$ embedded in Cs_4PbX_6 composite (CPX_{113}/CPX_{416}) NCs.

Similar as CPB_{113}/CPB_{416} NCs preparation approach, $CsPb(Br/Cl)_3$ embedded in $Cs_4Pb(Br/Cl)_6$ ($CPBC_{113}/CPBC_{416}$) NCs and $CsPb(Br/I)_3$ embedded in $Cs_4Pb(Br/I)_6$

($CPBI_{113}$/$CPBI_{416}$) NCs were performed by blending appropriate reagents (CsCl, $PbCl_2$, CsI, PbI_2, CsBr, and $PbBr_2$) in DMF solution.

Optical properties characterization. UV/vis absorption spectra were collected by using a Cary 5000 UV/vis/NIR spectrophotometer (Varian Instruments). The PL spectra and the decay curves were measured by Edinburgh instruments FLS920. The PLQYs were performed at an excitation wavelength of 365 nm on the Hamamatsu instruments C9920.

The PL decay can be fitted by the double-exponential equation

$$I = A_1 e^{(-t/\tau_1)} + A_2 e^{(-t/\tau_2)} \qquad \text{(S1)}$$

Where τ_1 and τ_2 are the fast and slow lived PL lifetime. A_1 and A_2 are the corresponding fitting parameters. The average PL lifetime can be further evaluated by the following equation:

$$\tau_{avg} = (A_1\tau_1^2 + A_2\tau_2^2) / (A_1\tau_1 + A_2\tau_2) \qquad \text{(S2)}$$

X-ray diffraction (XRD) patterns. The powder X-ray diffraction was measured on a Rigaku D/MAX 2200 VPC using a Cu Kr radiation (λ = 1.5405Å).

Transmission electron microscope (TEM) images were acquired on a FEI Tecnai G2 Spirit instrument with an accelerating voltage of 120 kV. High resolution TEM (HR-TEM) images and energy dispersive spectra (EDS), high angle annular dark field scanning transmission electron microscopy (HAADF-STEM) images, and elemental mapping images were acquired on a JEOL-JEM 2100F transmission electron microscope an accelerating voltage of 200 kV and an energy dispersive detector.

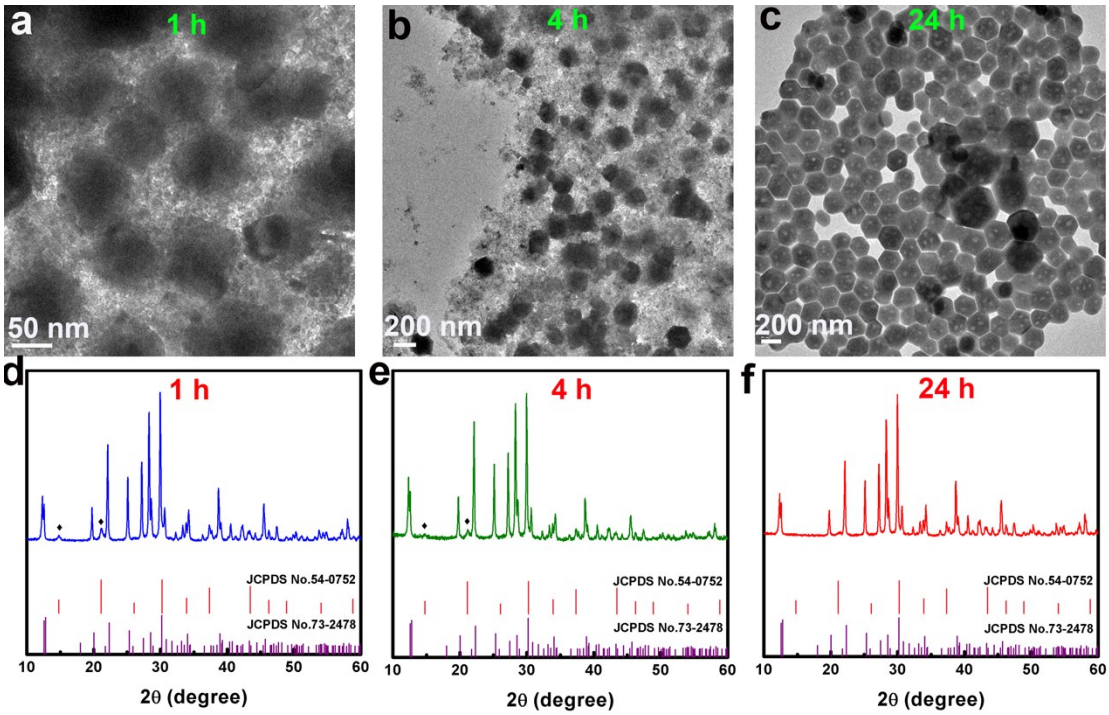

Fig. S1. The TEM images (a-c) and XRD patterns (d-f) of $CsPbBr_3$-Cs_4PbBr_6 composite NCs synthesized

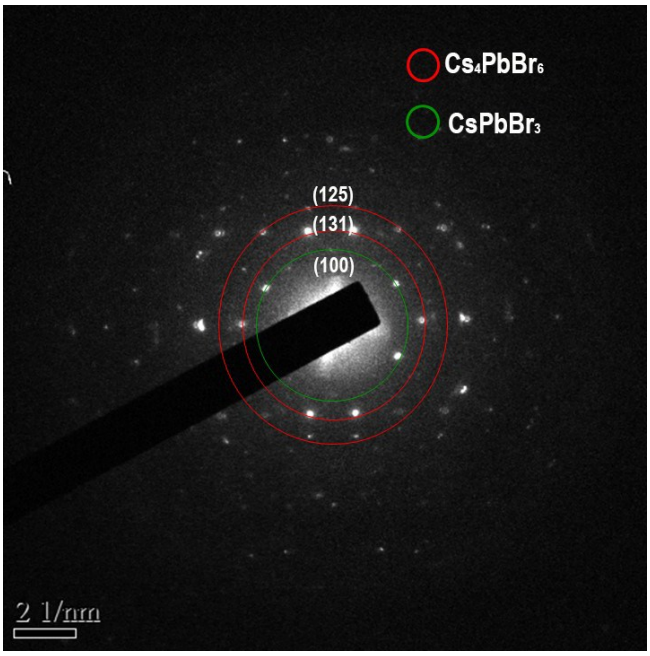

Fig. S2. The SAED images of CPB_{113}/CPB_{416} NCs.

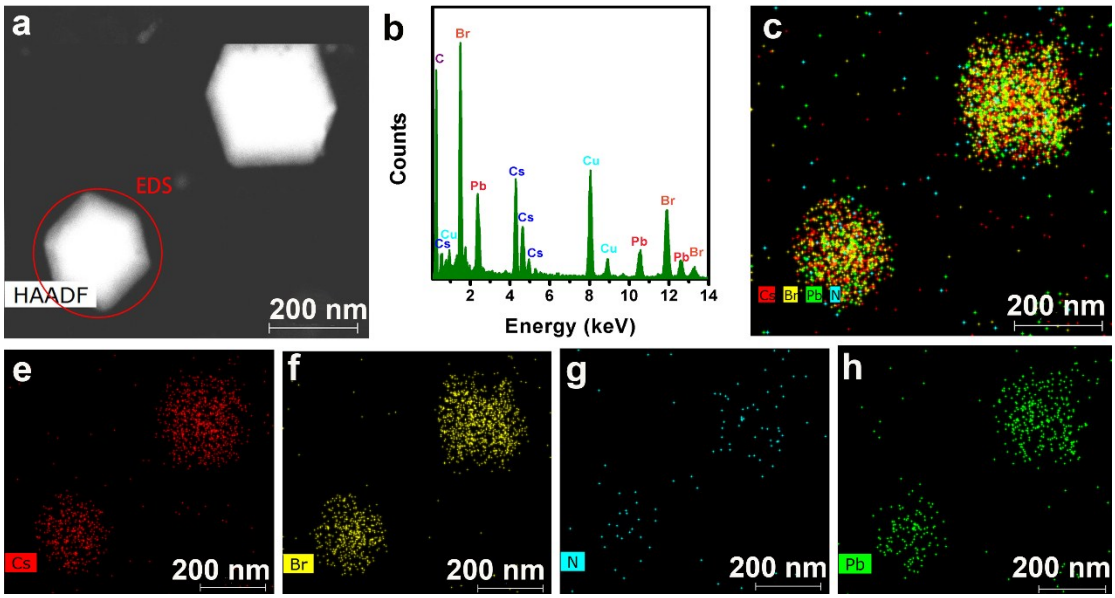

Fig. S3. HAADF-STEM image (a), EDS spectrum (b), and elemental mappings (c-h) of as-prepared CPB_{113}/CPB_{416} NCs.

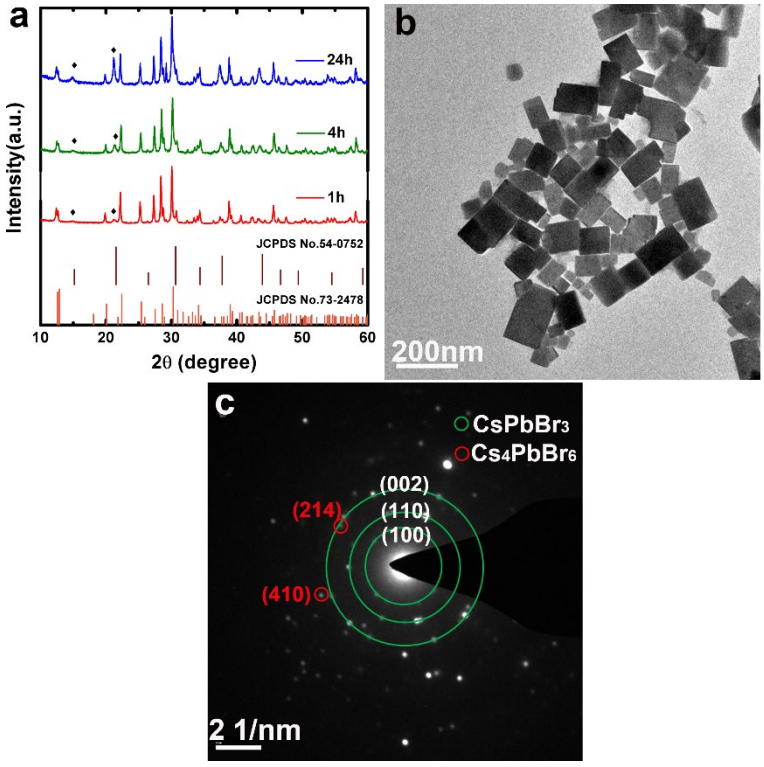

Fig. S4. The XRD patterns (a), TEM image, (b), and SAED (c) of $CsPbBr_3$-Cs_4PbBr_6 composite NCs prepared by without using MeIm as capping ligands.

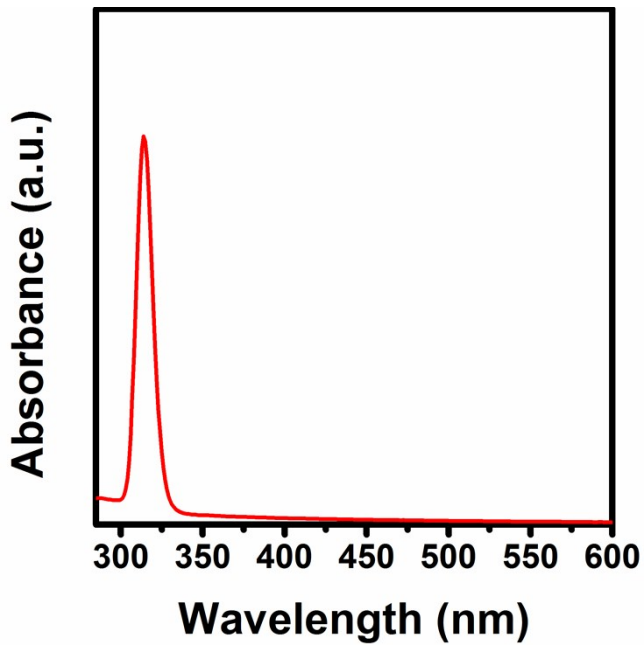

Fig. S5. The absorption spectrum of Cs_4PbBr_6 NCs.

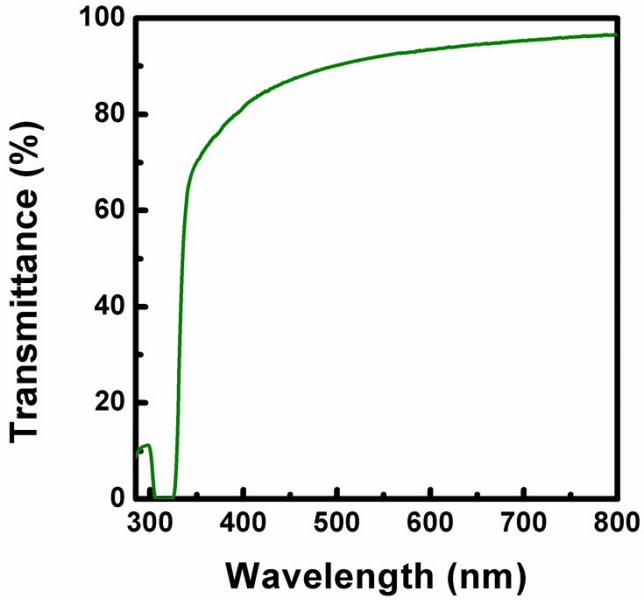

Fig. S6. The transmittance of Cs_4PbBr_6 NCs.

Tab. S1. The comparison of PLQY of the composite perovskite solids.

Composition	Size	PLQY (%)	Ref.
Cs_4PbBr_6	-	45	[1]
Cs_4PbBr_6	>1 μm	40-45	[2]
$CsPbBr_3$-Cs_4PbBr_6	~ 1 μm	-	[3]
Cs_4PbBr_6	~30 nm	54	[4]
CPB_{113} in CPB_{416}	-	55	[5]
Cs_4PbBr_6	~100 μm	40	[6]
CPB_{113} in CPB_{416}	~ 200 nm	83	This work

Tab. S2. The lifetimes, fitting parameters of CPB_{113}/CPB_{416} NCs.

λ_{ex}/nm	A_1/%	τ_1/ns	A_2/%	τ_2/ns	τ_{avg}/ns
289	64.7	7.1	35.3	38.1	29.9
365	85.3	6.0	14.7	34.6	20.2

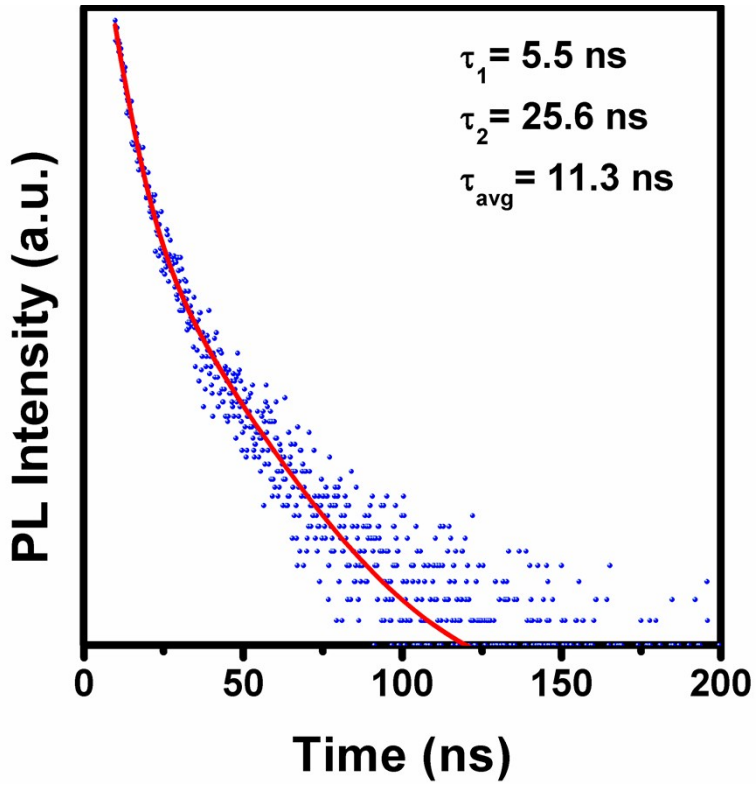

Fig. S7. Time-resolved PL decay of $CsPbBr_3$ NCs synthesized by hot-injection method.

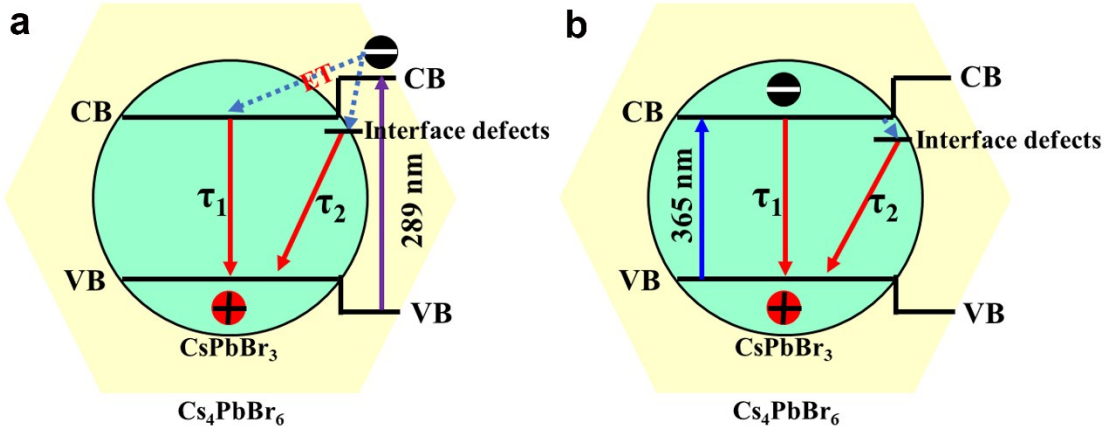

Fig. S8. Schematic illustration of the possible recombination in the CPB_{113}/CPB_{416} composite NCs excited by 289nm and 365 nm, respectively.

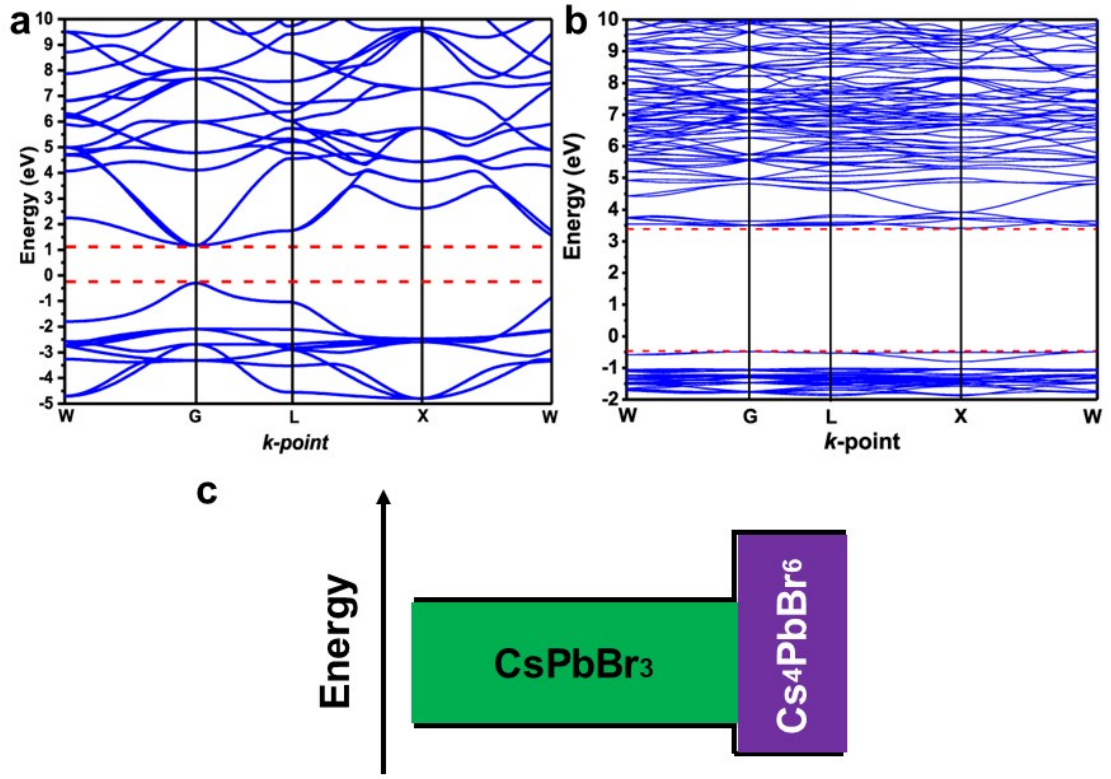

Fig. S9. The electronic band structures of $CsPbBr_3$ (a) and Cs_4PbBr_6 (b), respectively. (c) Schematic representation of Type I $CsPbBr_3/Cs_4PbBr_6$ core/shell structure.

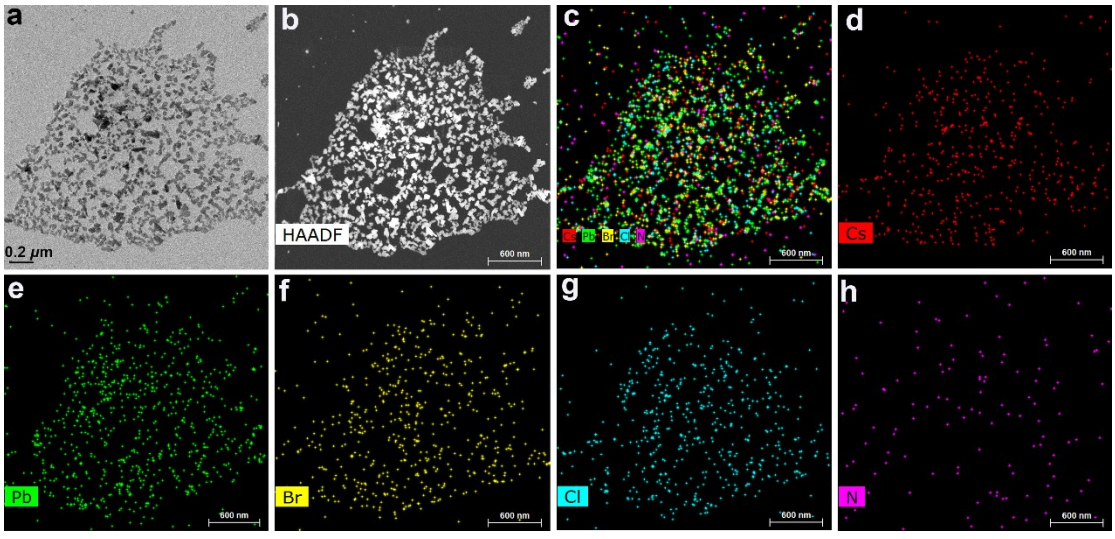

Fig. S10. The TEM image (a), HAADF-STEM image (b), and elemental mappings (c-h) of $CPBC_{113}/CPBC_{416}$ NCs.

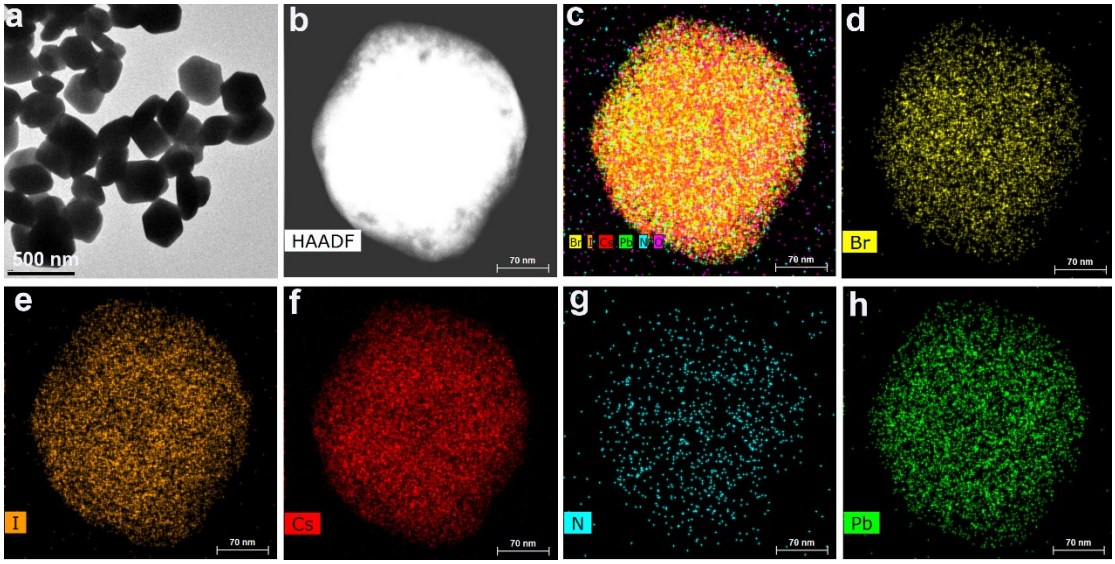

Fig. S11. The TEM image (a), HAADF-STEM image (b), and elemental mappings (c-h) of $CPBI_{113}/CPBI_{416}$ NCs.

Tab. S3. The PL peaks, FWHM, and PLQY of CPX_{113}/CPX_{416} NCs.

Sample	**PL peaks (nm)**	**FWHM (nm)**	**PLQY (%)**
Blue	460	17	40
Green	517	20	83
Red	625	59	32

Tab. S4. The lifetimes, fitting parameters of CPX_{113}/CPX_{416} NCs.

Sample	A_1	τ_1/ns	A_2	τ_2/ns	τ_{avg}/ns
Blue	14.4	3.23	0.3	25.4	6.5
Green	2.9	6.0	0.5	34.6	20.2
Red	0.9	16.9	0.5	67.3	51.4

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