

Support Information of “Phase transformation  
between CsPbBr<sub>3</sub> and Cs<sub>4</sub>PbBr<sub>6</sub> nanocrystals  
mediated by a cationic oligomeric ligand and water,  
and their water resistance”

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**Table S2.** Curve fitting results of the ARXPS narrow scans of CsPbBr<sub>3</sub> NCs/OA–OAm, DDAB, 12-6-12, and 12-6-12-6-12 measured using  $\theta = 90^\circ$  and  $20^\circ$ .

**Figure S3.** Cs-Pb-Br ternary phase diagram assumed from literature data.

**Figure S4.** PL spectra of as-synthesized CsPbBr<sub>3</sub> NCs/12-6-12 and 12-6-12-6-12 NCs (i.e., 1st formation) and those obtained via the ligand- and water-mediated phase transformation (i.e., 2nd formation).

**Figure S5.** Photographs and PXRD patterns of the samples obtained by phase transformation of CsPbBr<sub>3</sub> NCs: (i) as-synthesized CsPbBr<sub>3</sub> NCs, (ii) Cs<sub>4</sub>PbBr<sub>6</sub> transformed by addition of 12-6-12-6-12 (20 mM) to (i), (iii) CsPbBr<sub>3</sub>/Cs<sub>4</sub>PbBr<sub>6</sub> obtained by dropping water on (ii), and (iv) Cs<sub>4</sub>PbBr<sub>6</sub> transformed by addition of 12-6-12-6-12 (20 mM) to (iii).

## **1. Materials and methods**

### **1.1 Synthesis of 12-6-12**

20 mL acetonitrile, 1,6-dibromohexane (4.5 mmol), and dimethyldodecylamine (9.0 mmol) were added in a 100 mL flask, and it was refluxed at 85 °C for 24 h. Subsequently, a white powder was obtained by evaporation of the resultant solution using a rotary evaporator. The obtained product was purified through recrystallization in a mixture of ethanol and ethyl acetate. The product was collected by filtration and dried under vacuum at room temperature.

### **1.2 Synthesis of 12-6-12-6-12**

10 mL methanol, bis(hexamethylene)triamine (7.0 mmol), formaldehyde (73.5 mmol), and formic acid (147 mmol) were added in a 200 mL flask, and it was refluxed at 110 °C for 24 h. The reaction was quenched by adding the NaOH aqueous solution (0.80 M) to the resultant solution until pH = 12. Then, an organic layer was extracted using 25 mL water and 50 mL diethyl ether. Dehydrated with anhydrous Na<sub>2</sub>SO<sub>4</sub>, the organic layer was evaporated. Subsequently, the crude product (1.52 g), 1-bromododecane (16.8 mmol), and 15 mL acetonitrile were refluxed in a 200 mL flask at 85 °C for 30 h. The resultant product was evaporated and purified by recrystallization in a mixture of ethanol and ethyl acetate. A white powder was collected by filtration and dried under vacuum at room temperature.

### **1.3 Synthesis of CsPbBr<sub>3</sub> NCs**

The synthesis of CsPbBr<sub>3</sub> NCs was performed according to the method reported elsewhere. PbBr<sub>2</sub> (1.13 mmol), 0.5 mL oleic acid (OA), and 30 mL 1-octadecene (1-ODE) were added to a 100 mL flask, and it was refluxed with a hot bath at 120 °C for 30 min under N<sub>2</sub> atmosphere. 3.0 mL OA

and 3.0 mL oleylamine (OAm) were added to the solution. The temperature was then raised to 180 °C and kept for 1 h. Cesium oleate (Cs-OA) was prepared from a mixture of 0.63 mmol Cs<sub>2</sub>CO<sub>3</sub>, 10 mL 1-ODE, and 0.63 mL OA in a 50 mL flask, which was refluxed at 120 °C for 30 min, followed by at 150 °C for 1 h under N<sub>2</sub> atmosphere. Then, 2.4 mL Cs-OA was swiftly injected into the PbBr<sub>2</sub> solution. After 5 s, the solution turned yellowish-green color and was quickly cooled down in a cold bath. Pristine CsPbBr<sub>3</sub> NCs were precipitated by centrifugation at 13000 rpm for 10 min. Subsequently, the precipitate was washed with 3.0 mL toluene/ethyl acetate (1:2) solution, and it was precipitated by centrifugation at 13000 rpm for 10 min. This operation was repeated at least three times. Finally, the obtained precipitate was dispersed in 3.0 mL toluene.

#### **1.4 Ligand exchange process**

CsPbBr<sub>3</sub> NCs (0.7 μM) were dispersed in 2.0 mL dichloromethane containing 0.2 mL OA. Then, 0.4 mL dichloromethane containing the oligomeric ligand (25 mM for 12-6-12 and 17 mM for 12-6-12-6-12) was added to the CsPbBr<sub>3</sub> NCs solution with stirring at 900 rpm for 5 min. After the addition of 4.0 mL ethyl acetate, the resulting solution was precipitated by centrifugation at 13000 rpm for 10 min. The precipitate obtained was dispersed in 3.0 mL toluene and precipitated again by centrifugation. The supernatant solution was extracted and used as the sample. In the case of the ligand exchange using didodecyldimethylammonium bromide (DDAB), toluene was used as the solvent, and the concentration of the DDAB solution was set at 50 mM.

#### **1.5 Water resistance test**

0.5 mL ultrapure water was added to a glass cuvette, and then 2.0 mL CsPbBr<sub>3</sub> NCs solution of which absorbance at 500 nm was set at 0.5 was slowly added to it. The solution was vigorously

stirred at 200 rpm, and its photoluminescence (PL) with an excitation wavelength of 365 nm was observed using a C10083CA spectrometer (Hamamatsu Photonics K.K.) for 360 min. After that, the oil phase was extracted and dried on a powder X-ray diffraction (PXRD) glass holder by vacuum at room temperature for the PXRD measurement. The time evolution of the relative PL intensity was averaged over at least two experiments.

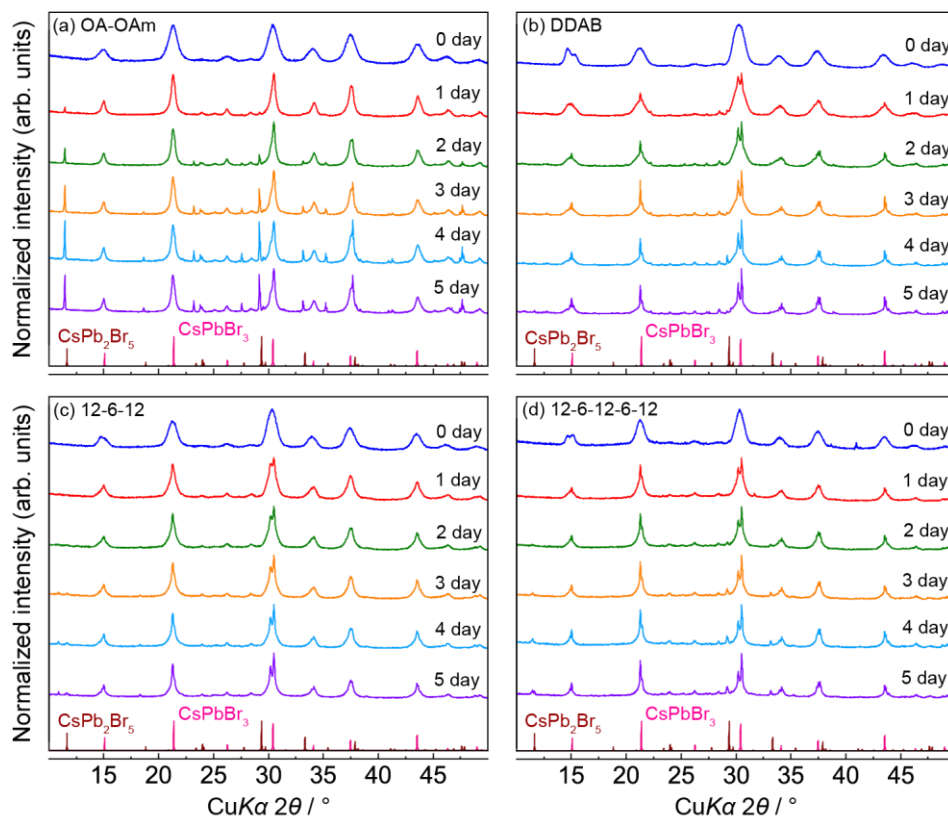
Moisture resistance test was carried out using CsPbBr<sub>3</sub> NCs dried on a PXRD glass holder by vacuum at room temperature. The glass holder was stored in a closed glass chamber for five days, where retained a lot of a saturated K<sub>2</sub>SO<sub>4</sub> solution at 30 °C to keep 97% relative humidity. The PXRD pattern of the sample was measured every 24 h.

## 1.6 Characterization

Ultraviolet-visible (UV-vis) absorbance spectra of the prepared samples were recorded using a V-570 spectrometer (JASCO Co.). Their crystal phase was characterized by powder X-ray diffraction (PXRD) on an Ultima IV diffractometer (Rigaku Co.) with CuK $\alpha$  ( $\lambda = 1.5406 \text{ \AA}$ ) radiation source. Their microstructure was observed using a transmission electron microscope (TEM) JEM-2100 (JEOL, Ltd) with a tungsten electron source excited by an accelerating voltage of 200 kV. The luminescence of the samples was characterized with a photoluminescence spectrometer FP-6500 (JASCO Co.) using the excitation wavelength of 365 nm. Angle-resolved X-ray photoemission spectroscopy (ARXPS) spectra were measured using a JPS-9030 spectrometer (JEOL, Ltd.) equipped with AlK $\alpha$  X-ray source ( $h\nu = 1486.6 \text{ eV}$ ). The angle of the sample to the probe direction is referred as to the take-off angle (TOA,  $\theta$ ). Photoemission spectra were observed with  $\theta = 90^\circ$  (i.e., normal emission) and  $20^\circ$ . The pass energy was set at 30.0 eV for all spectra, with the instrumental resolution of electron energy being 0.2 eV. The sample was spin-coated on an indium

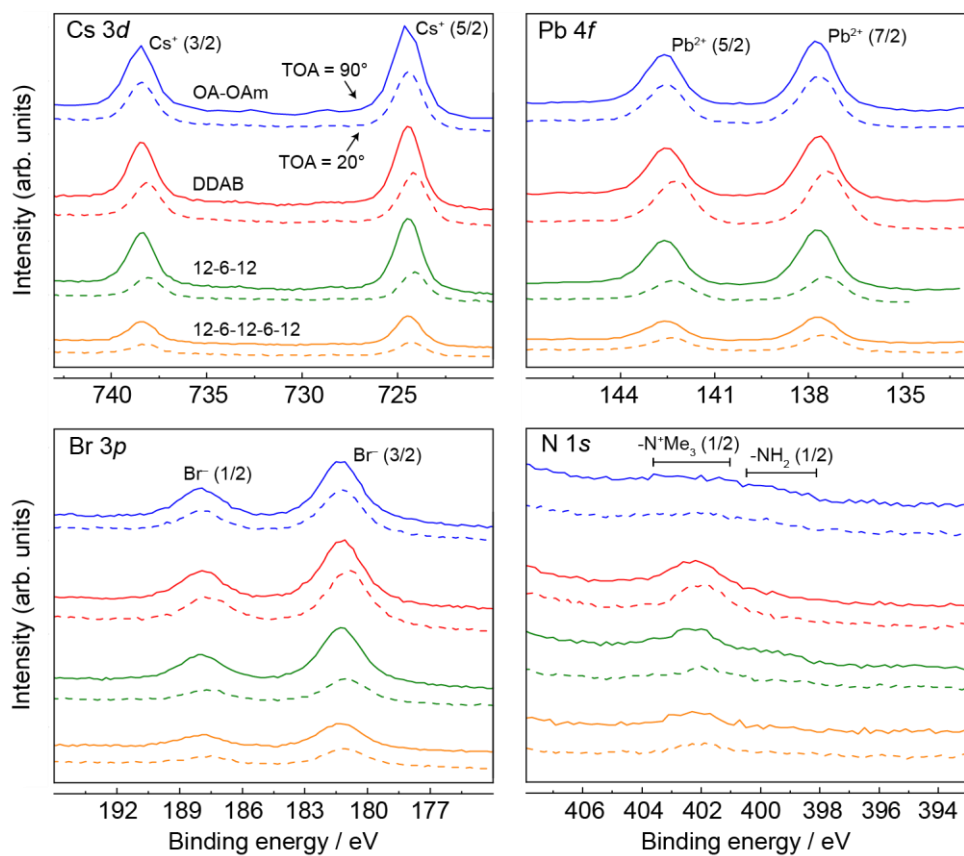
tin oxide (ITO) coated glass substrate. The observed spectra were fitted by mixed Gaussian-Lorentzian functions using the least squares method to calculate the peak intensities and relative shifts of peak positions. Then, the binding energy of every observed signal was calibrated assuming 284.8 eV of the standard C1s signal. For elemental analyses, the peak area of each XPS narrow scan calculated by the curve fitting was normalized by the photo-ionized probabilities of the corresponding orbital reported in the literature.<sup>1</sup> The high-resolution hard X-ray photoemission spectroscopy (HAXPES) was measured at a Japanese synchrotron radiation facility, BL-46XU of super photon ring 8 GeV (SPring-8). The energy of the incident X-ray beam from an undulator was 7.94 keV with a Si (111) double crystal and a Si (444) channel-cut monochromator. The slit size was 0.5 mm × 30 mm. The Scienta Omicron R4000 was used as an analyzer with a pass energy of 200 eV and  $\theta = 80^\circ$ . The measurement was performed at room temperature. The largest difference between XPS and HAXPES is the escape depth of photoelectrons, which is about several nm and a few tens nm for XPS and HAXPES, respectively. Hence, HAXPES is bulk sensitive compared to XPS.

## 2. Results and discussion



**Figure S1.** PXRD patterns of CsPbBr<sub>3</sub> NCs / (a) OA–OAm, (b) DDAB, (c) 12-6-12, and (d) 12-6-12-6-12 stored in a 97% relative humidity at 30 °C for five days. The bottom purplish- and dark-red lines indicate simulated PXRD profiles of CsPbBr<sub>3</sub> and CsPb<sub>2</sub>Br<sub>5</sub>, respectively.





**Figure S2.** ARXPS narrow scans of CsPbBr<sub>3</sub> NCs/OA–OAm, DDAB, 12-6-12, and 12-6-12-6-12. The solid and dot lines indicate the spectra measured using TOA ( $\theta$ ) = 90° and 20°, respectively.

**Table S1.** Curve fitting results of the HAXPES narrow scans of CsPbBr<sub>3</sub> NCs/OA–OAm, DDAB, 12-6-12, and 12-6-12-6-12: (a) binding energies of the deconvoluted peaks and (b) results of atomic ratio calculations using the fitted peak areas. The atomic ratios were assumed using the photoelectron ionization probability reported in the literature.<sup>2</sup>

(a) Binding energies (/eV) of the deconvoluted peaks.

Ligand	Cs 3 <i>d</i>		Pb 4 <i>f</i>		Br 3 <i>p</i>		N 1 <i>s</i>			O 1 <i>s</i>		
	Cs <sup>+</sup> (5/2)	Pb <sup>0</sup> (7/2)	Pb <sup>2+</sup> (7/2)	Br <sup>-</sup> (3/2)	-NH <sub>2</sub>	-N <sup>+</sup> Me <sub>3</sub>	ITO	OH	O-C=O			
OA–OAm	725.34	–	138.87	182.37	400.65	402.85	530.91	532.20	533.51			
DDAB	725.25	137.14	138.87	182.37	–	403.20	530.85	531.90	533.22			
12-6-12	725.27	–	138.82	182.42	–	403.33	530.87	532.11	533.42			
12-6-12-6-12	725.32	–	138.87	182.37	–	403.27	530.87	531.91	533.03			

(b) Results of atomic ratio calculations.

Ligand	Cs 3 <i>d</i>	Pb 4 <i>f</i>	Br 3 <i>p</i>	N 1 <i>s</i>
	Cs <sup>+</sup> (5/2+3/2)	Pb <sup>2+</sup> (7/2+5/2)	Br <sup>-</sup> (3/2+1/2)	-NH <sub>2</sub> and -N <sup>+</sup> Me <sub>3</sub> (1/2)
Observed peak areas				
OA-OAm	325434	95590	301664	7758
DDAB	231484	71872	189895	3594
12-6-12	178617	41751	160484	2994
12-6-12-6-12	183501	51025	173183	3481
Calculated atomic ratios				
OA-OAm	1.12		3.24	0.41
DDAB	1.06		2.71	0.25
12-6-12	1.41	1.0	3.95	0.46
12-6-12-6-12	1.19		3.49	0.35

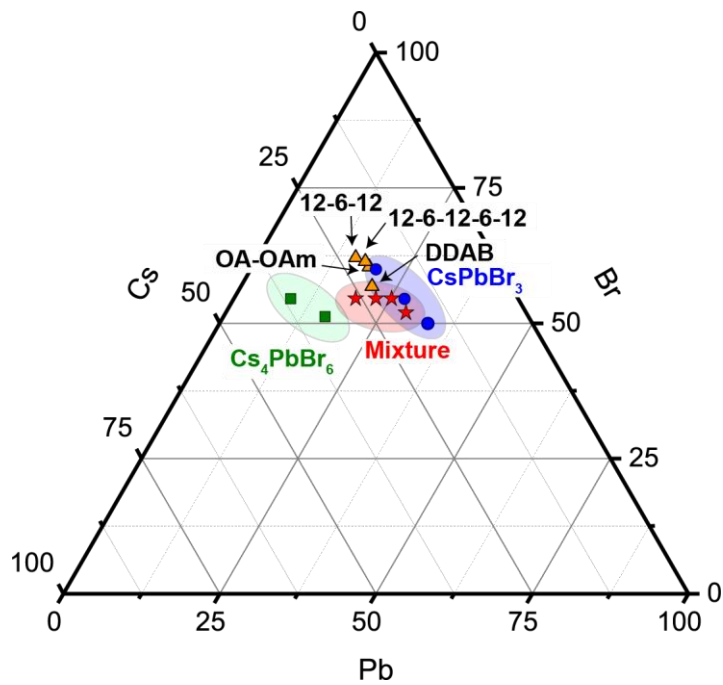
**Table S2.** Curve fitting results of the ARXPS narrow scans of CsPbBr<sub>3</sub> NCs/OA–OAm, DDAB, 12-6-12, and 12-6-12-6-12 using  $\theta = 90^\circ$  and  $20^\circ$ : (a) binding energies of the deconvoluted peaks and (b) results of atomic ratio calculations using the fitted peak areas. The atomic ratios were assumed using the photoelectron ionization probability reported in the literature.<sup>1</sup>

(a) Binding energies (/eV) of the deconvoluted peaks observed with each  $\theta$ .

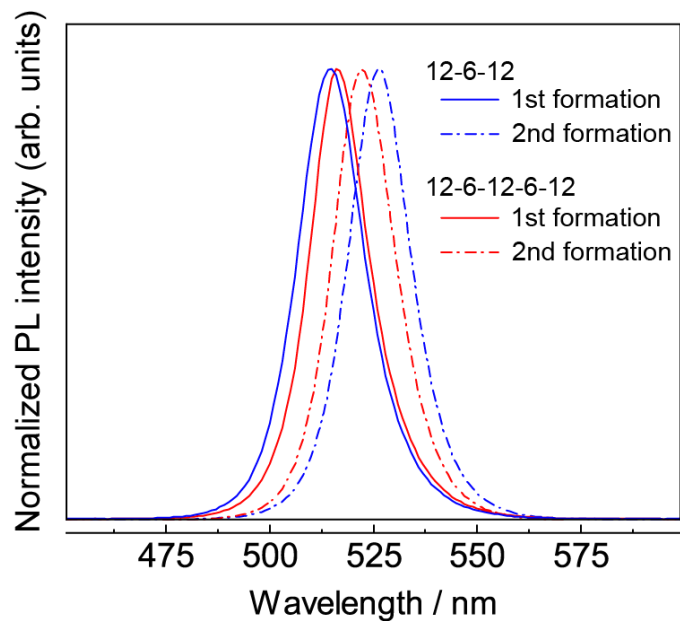
Ligand	Cs 3 <i>d</i>		Pb 4 <i>f</i>		Br 3 <i>p</i>		N 1 <i>s</i>			
	Cs <sup>+</sup> (5/2)		Pb <sup>2+</sup> (7/2)		Br <sup>-</sup> (3/2)		-NH <sub>2</sub>		-N <sup>+</sup> Me <sub>3</sub>	
	90°	20°	90°	20°	90°	20°	90°	20°	90°	20°
OA–OAm	724.5	724.4	137.8	137.7	181.3	181.2	399.7	–	402.5	401.6
DDAB	724.5	724.2	137.7	137.4	181.3	181.0	–	–	402.1	402.0
12-6-12	724.5	724.2	137.7	137.5	181.3	181.0	399.5	–	402.3	401.7
12-6-12-6-12	724.5	724.3	137.7	137.5	181.3	181.1	–	–	402.2	402.0

(b) Results of atomic ratio calculations.

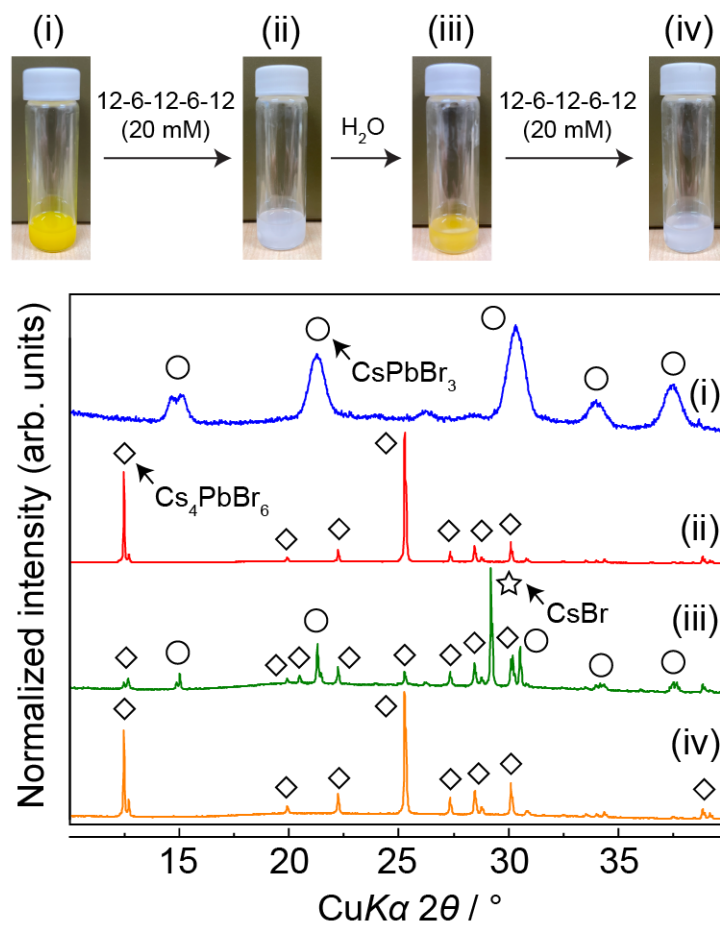
Ligand	Cs 3 <i>d</i>		Pb 4 <i>f</i>		Br 3 <i>p</i>		N 1 <i>s</i>	
	Cs <sup>+</sup> (5/2+3/2)		Pb <sup>2+</sup> (7/2+5/2)		Br <sup>-</sup> (3/2+1/2)		-NH <sub>2</sub> and -N <sup>+</sup> Me <sub>3</sub> (1/2)	
	Peak areas observed with each $\theta$							
	90°	20°	90°	20°	90°	20°	90°	20°
OA-OAm	12993	8041	5449	4148	3729	2863	344	146
DDAB	11522	7454	5389	4776	3809	3430	331	278
12-6-12	10374	4016	5042	2117	3490	1552	312	157
12-6-12-6-12	4230	2042	2128	1496	1658	1204	122	106
	Calculated atomic ratios							
OA-OAm	1.35	1.10			3.09	3.12	0.80	0.44
DDAB	1.21	0.88			3.20	3.25	0.78	0.73
12-6-12	1.16	1.07		1.0	3.13	3.31	0.78	0.94
12-6-12-6-12	1.12	0.77			3.52	3.64	0.73	0.89



**Figure S3.** Cs-Pb-Br ternary phase diagram assumed from literature data.<sup>3</sup> The triangle plots indicate the atomic concentrations of  $CsPbBr_3$  NCs determined by HAXPES.



**Figure S4.** PL spectra of as-synthesized CsPbBr<sub>3</sub> NCs/12-6-12 and 12-6-12-6-12 NCs (i.e., 1st formation) and those obtained via the ligand- and water-mediated phase transformation (i.e., 2nd formation). The latter were prepared by dropping water on Cs<sub>4</sub>PbBr<sub>6</sub> NCs that were transformed from CsPbBr<sub>3</sub> NCs by the addition of 12-6-12 or 12-6-12-6-12. The sample was dispersed in dichloromethane.



**Figure S5.** Photographs and PXRD patterns of the samples obtained at each step of the ligand- and water-mediated phase transformation of CsPbBr<sub>3</sub> NCs: (i) as-synthesized CsPbBr<sub>3</sub> NCs, (ii) Cs<sub>4</sub>PbBr<sub>6</sub> transformed by the addition of 12-6-12-6-12 (20 mM) to (i), (iii) CsPbBr<sub>3</sub>/Cs<sub>4</sub>PbBr<sub>6</sub> obtained by dropping water on (ii), and (iv) Cs<sub>4</sub>PbBr<sub>6</sub> transformed by the addition of 12-6-12-6-12 (20 mM) to (iii). The circle, diamond, and star marks in the figure indicate the diffraction pattern of CsPbBr<sub>3</sub>, Cs<sub>4</sub>PbBr<sub>6</sub>, and CsBr, respectively.



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