## **Supporting information**

## Organic titanates: A model for activating a rapid room-

### temperature synthesis of shape-controlled CsPbBr<sub>3</sub> nanocrystals

### and their derivatives

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#### **Experimental section**

#### Materials and chemicals:

Cesium carbonate (Cs<sub>2</sub>CO<sub>3</sub>, Aladdin, 99.9%), oleic acid (OA, Aladdin, AR), 1octadecene (ODE, Aladdin, 90%), ethanol, oleylamine (OAm, Aladdin, 80%-90%), lead chloride (PbCl<sub>2</sub>, Aladdin, 99.99%), lead bromide (PbBr<sub>2</sub>, Adamas, 99%), lead iodide (PbI<sub>2</sub>, Aladdin, 98%), tetraethyl titanate (TE-Ti, Aladdin), tetraisopropyl titanate (TI-Ti, Aladdin), tetrabutyl titanate (TB-Ti, Aladdin) and toluene were used as received without further purification.

#### Synthesis of CsPbBr<sub>3</sub> NCs:

In a facile synthesis, 10 ml ODE was loaded into a 20 ml reagent bottle. Then, 0.5 ml OA, 0.5 ml OAm and a certain amount of organic titanates (TE-Ti, TI-Ti, and TB-Ti) were injected in the bottle in sequence. Then, 0.3 mmol of PbBr<sub>2</sub> and 0.1 mmol of  $Cs_2CO_3$  were added into the above solution under vigorous stirring. Bright green emission could be observed in a few minutes after the addition of PbBr<sub>2</sub> and  $Cs_2CO_3$ . The crude NCs were first separated via a high speed centrifugation at 10000 rpm for 5 min. After centrifugation, the supernatant was discarded, and the precipitates were redispersed in toluene. The toluene colloidal solution was centrifuged once more at 10000 rpm for 5 min. The supernatant was discarded again, and the precipitates were re-dispersed in toluene to form long-term stable colloidal solutions. All above operations were implemented at room temperature.

#### Scale up synthesis of CsPbBr<sub>3</sub> nanocrystals:

10 ml OA, 10 ml OAm and 20ml TI-Ti was added in 200 ml ODE. Then, 6 mmol PbBr<sub>2</sub> and 2 mmol  $Cs_2CO_3$  was added rapidly under vigorous stirring. After continue stirring for 2 hours to guarantee the complete reaction, the resulting yellow precipitates were collected by the centrifugation and washed by toluene for one time.

The obtained precipitate was dried in the vacuum oven at 50 °C. All of synthesis processes were completed under ambient conditions. The final yellow CsPbBr<sub>3</sub> nanocrystals powder produced by this scale up reaction weighted about 0.32 g (Fig. S1).

#### Anion-exchange reactions:

Metal halide solids ( $ZnCl_2$  and  $ZnI_2$ ) without any pretreatment were used as the anion sources. 1 ml CsPbX<sub>3</sub> toluene colloidal solution was diluted to 5 ml in a 20 ml reagent bottle. With continuous stirring, 10 mg metal halide solid were swiftly added into the colloidal solution. The anion-exchange reaction process could be monitored by the color change of colloidal solution under ultraviolet radiation.

### Measurement and characterization:

**Absorbance:** UV-VIS absorption spectra were collected using a SHIMADZU UV-2450 spectrometer.

**Photoluminescence (PL) measurement:** FLS920 Fluorescence Spectrometer was used to acquire PL spectra.

**Powder X-ray diffraction (XRD) patterns** were collected with a Rigaku miniflex600 with Cu K $\alpha$  irradiation ( $\lambda$ = 1.5418 Å).

**Transmission electron microscopy (TEM)** images were recorded using a Tecnai G2 S-Twin F20 with 200 kV accelerating voltage.

**X-ray Photoelectron Spectroscopy (XPS)**: The surface composition measurement was performed with X-ray photoelectron spectroscopy (ESCALAB250), and all the spectra were calibrated by C 1s peak at 284.6 eV.



**Fig. S1**. Photograph of large scale synthesized CsPbBr<sub>3</sub> powder (a) under natural light and (b) under UV light (365 nm) irradiation.



**Fig. S2.** XRD pattern of the powder sample obtained by a relatively large scale reaction. Green lines at the bottom are standard XRD of CsPbBr<sub>3</sub> (PDF#75-0412).



Fig. S3. (a) TEM image of the CsPbBr<sub>3</sub> NCs using TI-Ti as activating agent after storing in air condition for a week. (b) Photograph of the CsPbBr<sub>3</sub> NCs solution under UV light irradiation (365 nm) after storing the NCs solution in the ambient moisture conditions (RH = 30-50%).



**Fig. S4.** A comparison of photographs for the as-obtained product solution without (a) and with (b) UV light (365 nm) irradiation by adding inorganic titanate (BaTiO<sub>3</sub> solid) and organic titanate (TI-Ti), repectively. The solution prepared in presence of BaTiO<sub>3</sub> as activator does not exhibit any light emission, suggesting that inorganic titanates could not promot the formation of CsPrBr3 NCs at room temperature.



**Fig. S5.** HRTEM image of CsPbBr<sub>3</sub> nanocrystals. The black dots marked by red circles are Pb species.



**Fig. S6.** Time-resolved photoluminescence decay data and their fitting curve for the light emission of CsPbBr<sub>3</sub> NCs.



**Fig. S7.** A comparsion of TEM images for reavling the effect of reaction time on the morphology of CsPbBr<sub>3</sub> NCs using TI-Ti as an activator.

TEM images were recorded for the products under different reaction time. As expected, the TEM images presented in Fig. S7 shows the evolution of CsPbBr<sub>3</sub> NCs in morphology and structure with the reaction time. Mixed nanodots and nanoplates is clearly seen for the product after a 15 minute reaction (Fig. S7a). When the reaction time increased to 30 min, nanodots and nanoplates grew to nanocubes, but a few nanoplates still existed in the product (Fig. S7b). Both the stacking of nanoplates and the growing of nanodots could evulate further to nanocubes. Due to the weaking or partly relieving of quantum confinement effect, the color of emission light change from bluish-green to green light accompaning the evolution of morphology. When the reaction time was set to 60 min, the amount of nanocubes increased obviously (Fig. S7c). For 180 min onward, nanoplates disappear almost and the uniform nanocubes were obtained (Fig. S7d). In the products reacting for 30, 60, and 180 min, most nanocubes were 20-30 nm in length, suggesting that the size of nanocube did not change apparently as the reaction time prolonging. Moreover, even continuing reaction for 180 min at room temperature, no CsPbBr<sub>3</sub> NCs with orthorhombic structure or other morphology was observed. That is to say, prolonging reaction time at room temperature does not promote NCs to continiously grow or have phase transition, but only make the morphology of nanocrystals more uniform.



**Fig. S8.** A comparsion of TEM images to examine the effect of TI-Ti content on the morphology of CsPbBr<sub>3</sub> NCs. Increasing the content of TI-Ti resulted in the morphology change from nanoparticles for 0.5 ml (a), nanocubes for 1 ml (b), to mixture of nanocubes and nanoplates for 1.5 ml (c) and 2 ml (d) when fixed the reaction time at 180 min.

To understand the the effect of TI-Ti content on the morphology of CsPbBr<sub>3</sub> NCs, the reaction time was fixed at 180 min, and the rest of the procedures were left unaltered. From Fig. S8, we can clearly see the huge disparities of morphology for the NCs. When 0.5 ml TI-Ti was added, only non-uniform nanoparticles with unfixed morphology (Fig. S8a) could be obtained. Increasing the addition to 1 ml, uniform nanocubes with size about 20 - 30 nm were formed (Fig. S8b). Continuously increasing the addition to 1.5 ml, the NCs consisted of lager size cubes along with nanoplates (Fig. S8c). Significantly, these cubes and nanoplates were covered by a lot of TiO<sub>2</sub> nanoparticles. As the addition of TI-Ti reached to 2 ml, more TiO<sub>2</sub> nanoparticles were produced to form a layer covering the CsPbBr<sub>3</sub> NCs (Fig. S8d). The presence of TiO<sub>2</sub> nanoparticles is attributed to hydrolysis of TI-Ti. The observation above suggests that the optimal addition of TI-Ti is 1 ml for preparing uniform CsPbBr<sub>3</sub> nanocubes.

Table S	<b>S1</b>	Binding	energy,	spin-	-orbita	l spl	litting,	and	full	width	at	half	maxii	mum
(FWHM	4)	of main	level f	or Cs	3d, P	b4f,	Ti2p	and	Br3d	of C	CsPł	oBr <sub>3</sub>	NCs	with
nanocul	be r	norpholo	gy after	reacti	on for	180	min in	n pres	ence	of TI-	Ti.			

Core levels		Binding Energy (eV)	Spin-Orbital Splitting (eV)	FWHM (eV)	
Cs3d	3d <sub>5/2</sub>	724.45	13.88	1.95	
	3d <sub>3/2</sub>	738.33		1.99	
Pb4f	$4f_{7/2}$	138.11	4.87	1.34	
	4f <sub>5/2</sub>	142.98		1.30	
Ti2p	2p <sub>3/2</sub>	458.42	5.69	1.65	
	2p <sub>1/2</sub>	464.11		2.64	
Br3d	3d <sub>5/2</sub>	67.97	1.03	1.31	
	3d <sub>3/2</sub>	69.00		1.49	



**Fig. S9.** PL emission spectrum of  $CsPbI_3$  NCs synthesized with  $Cs_2CO_3$  and  $PbI_2$  at room temperature for about 20 min. The inset is the photograph of  $CsPbI_3$  NCs solution.



**Fig. S10.** Elemental mapping for Pb, Cs, Br and Ti of CsPbBr<sub>3</sub> NCs with nanocube morphology after reaction for 180 min in presence of TI-Ti.

	Cs	Pb	Br	Ti
Weight %	49.52	15.36	34.98	0.13
Atomic %	15.36	8.35	49.33	0.31

 Table S2 Percentage of element content for CsPbBr3 NCs with nanocube morphology

after reaction for 180 min in presence of TI-Ti.



Scheme S1. Schematic diagram of the organic titanates coupling machanism.

There are some of hydroxyls on the surface of hydrophilic inorganic reactants (PbBr<sub>2</sub> and Cs<sub>2</sub>CO<sub>3</sub>). During the formation process, some parts of hydroxyls present on the surface of hydrophilic inorganic reactants (PbBr<sub>2</sub> and Cs<sub>2</sub>CO<sub>3</sub>) may react with short alkoxy groups (especially those bond with organic titanate molecules) to form an organic active monolayer on the surfaces of inorganic reactants. Once the inorganic reactants are covered by organic titanate active monolayer, the inorganicorganic units thus formed would become hydrophobic, and can be dissolved in the organic solutions (e.g., octadecylene, oleic acid, and oleamine). Therefore, the structural units of PbBr<sub>2</sub> could steadily react with those of Cs<sub>2</sub>CO<sub>3</sub> to form CsPbBr<sub>3</sub> NCs. In the whole reaction process, organic titanates act as a coupling agent to activate the formation of CsPbBr<sub>3</sub> NCs. On the other hand, accompanying the formation of organic active monolayer on the surfaces of inorganic reactants, alkoxy anions (R-O<sup>-</sup>) could be produced. These R-O<sup>-</sup> anions together with the other organic species in the reaction solution can be preferentially adsorbed on the surface of CsPbBr<sub>3</sub> NCs to affect the growth rates of different crystal facets and shapes of the obtained nanocrystals. Besides, the presence of different organic titanates could also change the rate of the reaction, and further affect the size of CsPbBr<sub>3</sub> NCs.



**Fig. S11.** (a) TEM image of  $CsPbBr_xCl_{3-x}$  nanocubes. (b) TEM image of  $CsPbBr_xI_{3-x}$  nanocubes. Both of samples are the intermediates of anion exchange for  $CsPbBr_3$  NCs shown in Fig. 4.