

## Supporting Information

### Reversible ON/OFF switching of photoluminescence from CsPbX<sub>3</sub> quantum dots coated with silica using photochromic diarylethene

Yuji Akaishi,<sup>a</sup> Azzah Dyah Pramata,<sup>a</sup> Shuhei Tominaga,<sup>a</sup> Shimpei Kawashima,<sup>a</sup> Tuyoshi Fukaminato<sup>\*b</sup>  
and Tetsuya Kida<sup>\*b</sup>

- Department of Applied Chemistry and Biochemistry, Graduate School of Science and Technology, Kumamoto University, Kumamoto 860-8555, Japan
- Faculty of Advanced Science and Technology, Kumamoto University, Kumamoto 860-8555, Japan  
<sup>\*</sup>E-mail: [tetsuya@kumamoto-u.ac.jp](mailto:tetsuya@kumamoto-u.ac.jp) (T.K.), [tuyoshi@kumamoto-u.ac.jp](mailto:tuyoshi@kumamoto-u.ac.jp) (T.F.)

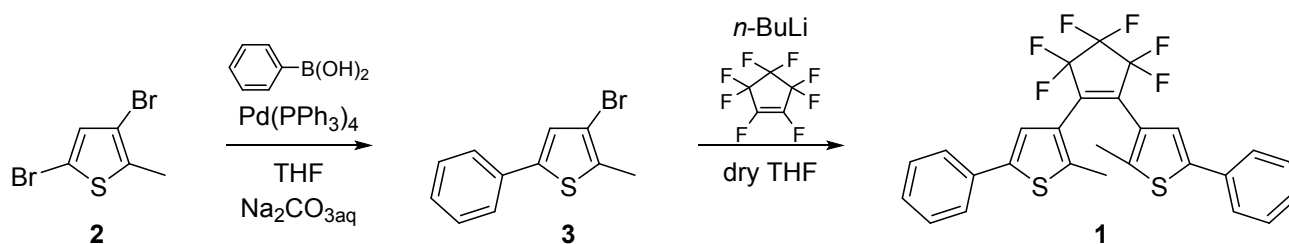
#### Materials Synthesis, characterization, and PL control

**Chemical.** CsBr (98.0%), PbCl<sub>2</sub> (99.0%), PbI<sub>2</sub> (99.9%), 3-aminopropyltrimethoxysilane (APTMS, 97.0%), oleic acid (60.0%), octylamine (98.0%), N,N-dimethylformamide (DMF, 99.5%), toluene (99.5%), hexane (96.0%), and acetone (99.5%) were purchased from Wako Pure Chemical Industries. PbBr<sub>2</sub> (99.999%) was purchased from Sigma-Aldrich. These chemicals were used as received without any further treatment and purification.

**Synthesis of CsPbBr<sub>3</sub> Quantum Dots (QDs).** CsPbBr<sub>3</sub> QDs were synthesized by an emulsion method reported by Huang et al.<sup>1)</sup> In a typical synthesis, CsBr (0.3 mmol) was dissolved in distilled water (0.3 mL) to form a precursor solution A. PbBr<sub>2</sub> (0.3 mmol) was dissolved in DMF (0.35 mL) to form a precursor solution B. Hexane (10 mL) was mixed with oleic acid (2 mL) and *n*-octylamine (0.25 mL) to form a precursor solution C. The solutions B and A were added dropwise into the solution C under vigorous stirring. After that, a designated amount of acetone (8 mL) was added as a demulsifier to the mixed solution, forming CsPbBr<sub>3</sub> QDs. The mixture was centrifugated at 7000 rpm for 10 min to obtain precipitates that contain colloidal QDs and aggregates of by-products. The precipitates were redissolved in toluene (10 mL) to extract the colloidal QDs. After another centrifugation at 7000 rpm for 10 min, a bright yellow-green colloidal solution was finally obtained. To avoid the degradation of QDs under atmospheric air, the synthesis was carried out in a glovebox.

**Synthesis of silica-coated CsPbX<sub>3</sub> QDs.** SiO<sub>2</sub>/CsPbX<sub>3</sub> (X = Cl, Br, I) QDs were synthesized by a ligand-assisted reprecipitation method (LARP method) reported by Yanga et al.<sup>2)</sup> In a typical synthesis, CsBr (0.2 mmol) and PbBr<sub>2</sub> (0.2 mmol) were dissolved in DMF (1 mL) to form a precursor solution. A supernatant of the precursor solution (0.5 mL) was injected into a solution containing toluene (10 mL), oleic acid (40 μL), and APTMS (40 μL) under vigorous stirring. After further stirring for 4 h, precipitates were formed and collected by centrifugation at 4000 rpm for 10 min. Then, the precipitates were redissolved into 20 mL toluene, producing a bright yellow-green colloidal solution. SiO<sub>2</sub>/CsPbBr<sub>3-x</sub>Cl<sub>x</sub> and SiO<sub>2</sub>/CsPbBr<sub>3-x</sub>I<sub>x</sub> QDs were synthesized by a similar method to the above according to the LARP strategy. The partial substitution of halide was performed by mixing PbCl<sub>2</sub>, PbBr<sub>2</sub>, and PbI<sub>2</sub> in a designated ratio in precursor solutions. All of the synthesis was carried out in a glovebox.

**Synthesis of 1,2-bis(2-methyl-5-phenyl-3-thienyl)perfluorocyclopentene (1).** The synthetic route to **1** is illustrated in Scheme S1. Detailed synthetic procedures of **1** were described below.



**Scheme S1** Synthetic scheme of 1,2-bis(2-methyl-5-phenyl-3-thienyl)perfluorocyclopentene (**1**).

1,2-Bis(2-methyl-5-phenyl-3-thienyl)perfluorocyclopentene (**1**) was synthesized according to the modified method reported by Irie.<sup>3)</sup> **3** was prepared by reacting 3,5-bromo-2-methylthiophene (**2**) (5.0 g; 19.5 mmol) with phenylboronic acid (2.38 g; 19.5 mmol) in the presence of Pd(PPh<sub>3</sub>)<sub>4</sub> (208 mg; 0.18 mmol) in 20 wt% Na<sub>2</sub>CO<sub>3</sub> aqueous solution (100 mL) and tetrahydrofuran (THF) (150 mL) for 10 h at 70 °C. **3** was purified by column chromatography on SiO<sub>2</sub> using hexane as the eluent and 3.6 g obtained as colorless crystals in 73% yield. The obtained compound **3** (2.02 g, 8.0 mmol) was dissolved in dry THF (40 mL) and then 1.6 M n-BuLi/hexane solution (2.6 mL; 4.3 mmol) was added dropwise at -78 °C under argon atmosphere. After stirring for 30 min at the temperature, octafluorocyclopentene (0.84 g; 4.0 mmol) was slowly added to the reaction mixture at -78 °C, and the mixture was stirred for 2 h at that temperature. The reaction was stopped by the addition of water. The product was extracted with ether. The organic layer was washed with 1 N HCl aqueous solution and water. The organic layer was dried over MgSO<sub>4</sub>, filtrated, and evaporated. The crude product was purified by column chromatography on SiO<sub>2</sub> using hexane as the eluent to give 1.6 g of **1** in 77% yield as white powder.

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  1.96 (s, 6H), 7.29 (s, 2H), 7.2-7.6 (m, 10H), MS (MALDI)  $m/z = 521.21$   $[\text{M}+1]^+$  (Exact Mass: 520.55); Elemental analysis: Found: C, 62.37; H, 3.48. Anal. Calcd. for  $\text{C}_{27}\text{H}_{18}\text{F}_6\text{S}_2$ : C, 62.30; H, 3.49.

**Characterization.** The colloidal size of QDs was examined with a DLS spectrophotometer (Zetasizer Nano ZS, Malvern Instruments). The crystal phase was determined by XRD with  $\text{CuK}\alpha$  radiation (RINT2100, Rigaku). The morphology was observed by TEM (JEM-2000FX, JEOL). High resolution TEM (HR-TEM) and high angle annular dark-field scanning transmission electron microscopy (HAADF) images were obtained using Tecnai F20 (FEI). Steady-state PL spectra were measured with a spectrometer (FP-6000, JASCO Co). The light absorption properties of QDs were studied with a spectrometer (V-650, JASCO Co.). Quantum yields were determined with a spectrometer (FP-8000, JASCO Co) equipped with an integrating sphere unit (ILF-835). The long-term photostability of QDs was examined by irradiating QD solutions with visible and UV light using a Xe lamp (USHIO) equipped with and without an optical cut-off filter ( $\lambda > 420$  nm) and measuring changes in the emission intensity. The powers of the Xe lamp with and without an optical cut-off filter were 160 and 196 mW, respectively.

**ON/OFF switching of photoluminescence of  $\text{CsPbBr}_3$  QDs.** QDs (1.5 mg) were dispersed in a toluene solution (3 mL) containing diarylethene (0.4  $\mu\text{M}$ ). This solution was alternately irradiated with UV light ( $\lambda = 365$  nm) using a handy UV lamp (LUV-4, AS ONE) for 5 min and with visible light ( $\lambda > 530$  nm) using a Xe lamp (USHIO) equipped with an optical cut-off filter for 5 min. The powers of the handy UV lamp and the Xe lamp were 0.5 and 150 mW, respectively. Changes in the PL intensity were monitored with a spectrometer. The above modulation procedures were repeated for 3 cycles. All of the experiments were performed under ambient conditions in air.

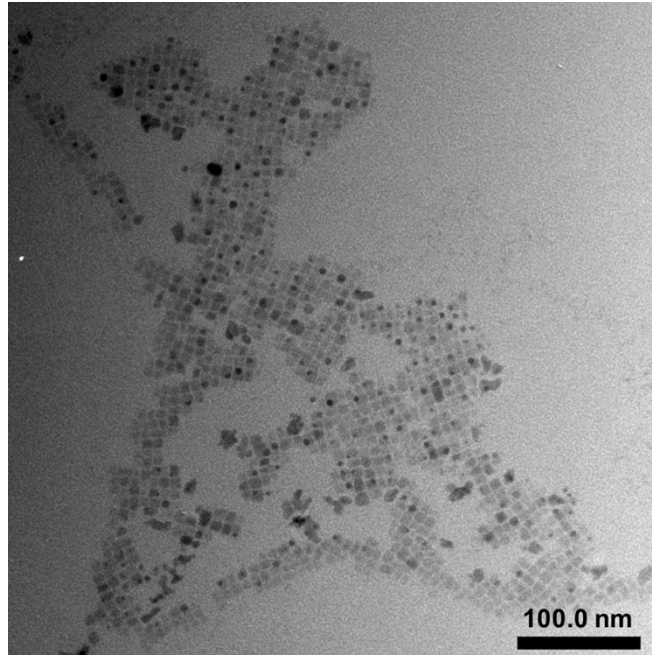


Fig. S1 Low-magnification TEM image of native CsPbBr<sub>3</sub> QDs.

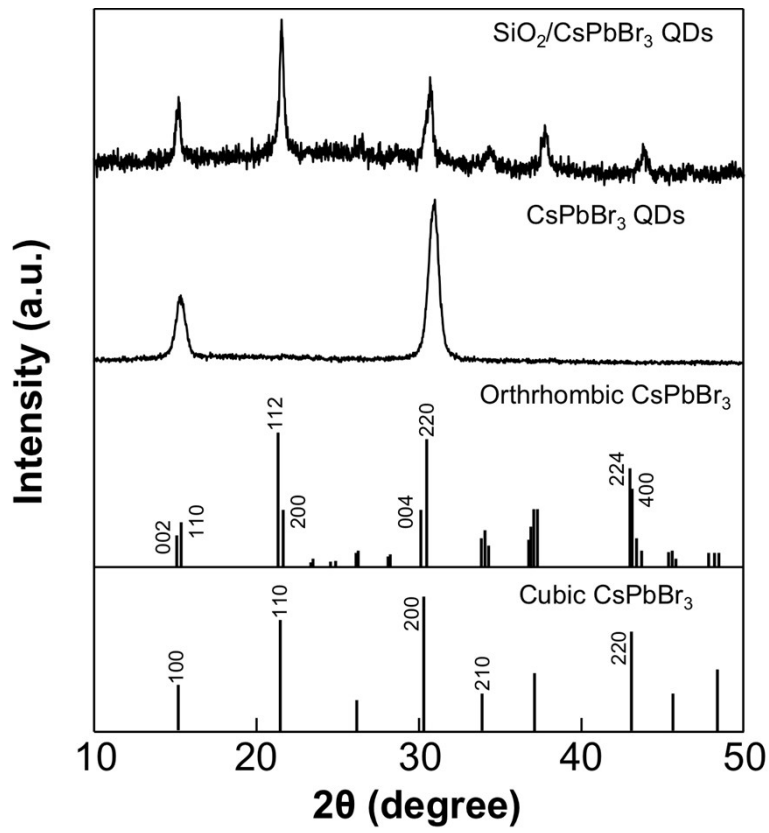
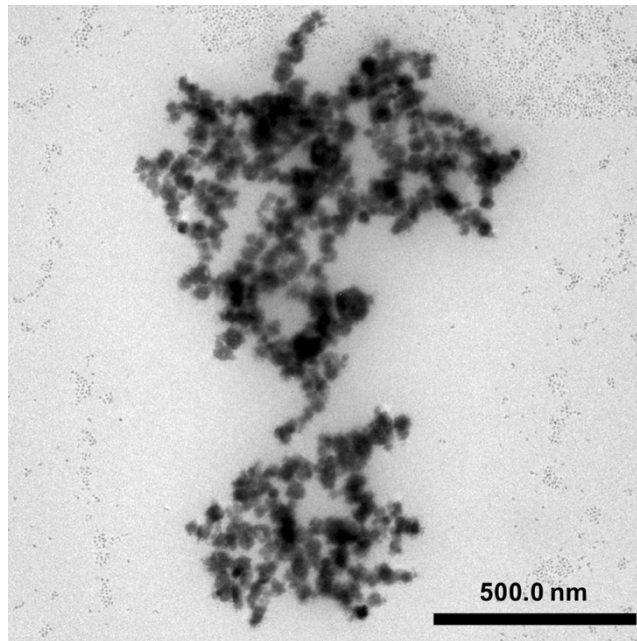
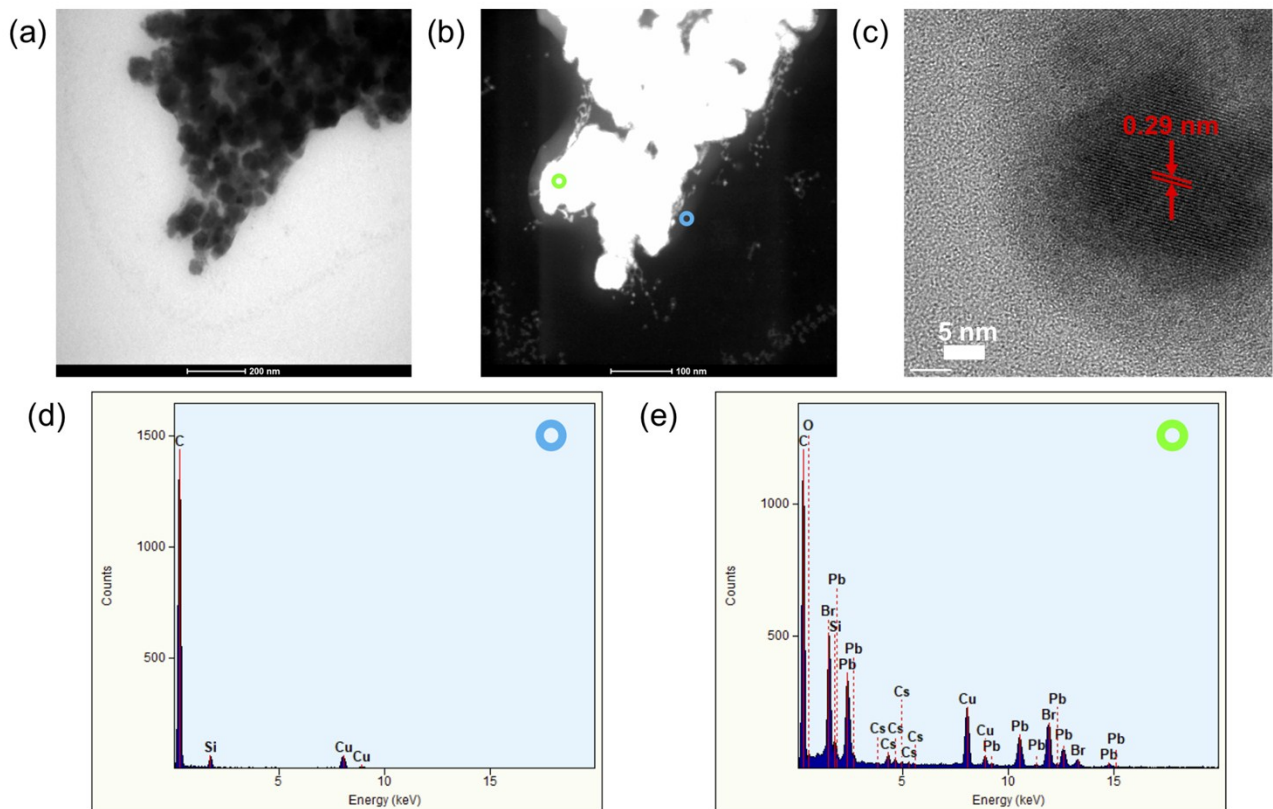


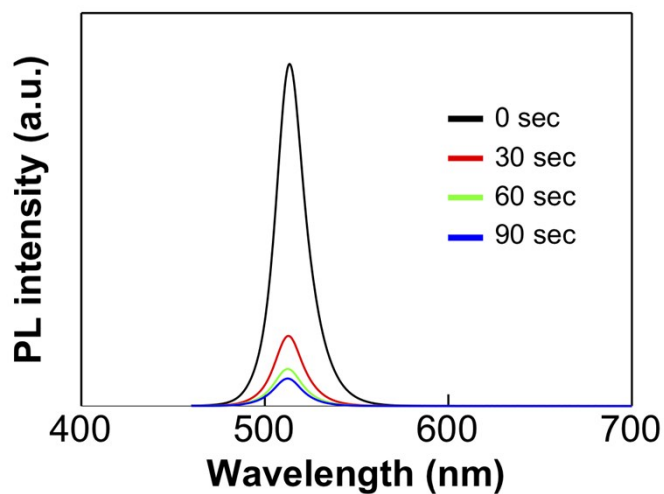
Fig. S2 XRD patterns of CsPbBr<sub>3</sub> and SiO<sub>2</sub>/CsPbBr<sub>3</sub> QDs.



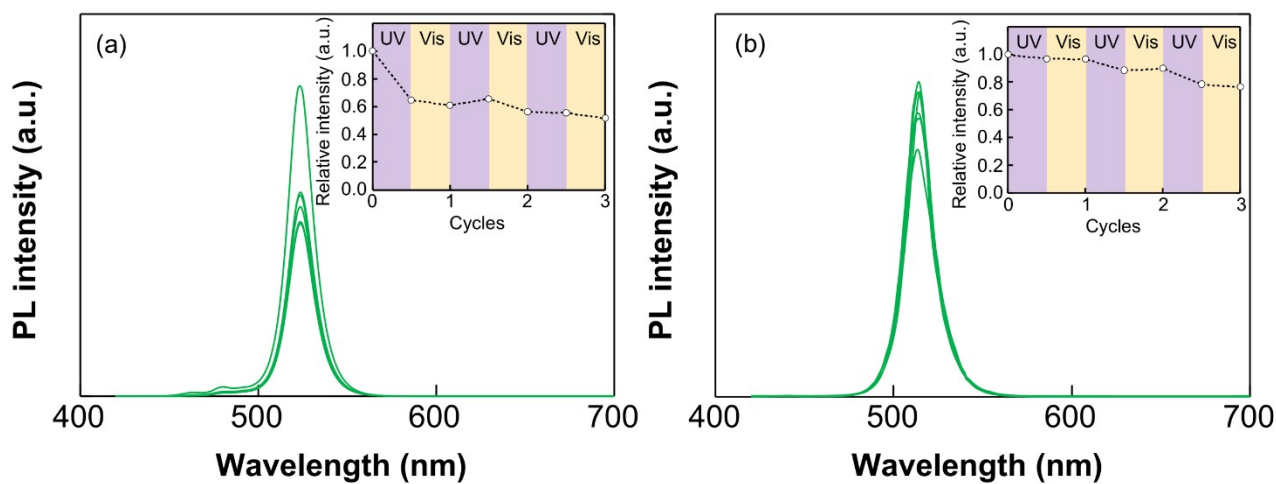
**Fig. S3** Low-magnification TEM image of SiO<sub>2</sub>/CsPbBr<sub>3</sub> QDs.



**Fig. S4** (a) TEM, (b) HAADF, and (c) HR-TEM images of SiO<sub>2</sub>-coated CsPbBr<sub>3</sub> QDs, together with (d, e) EDS spectra taken at the selected points.



**Fig. S5** Time dependence of the PL emission intensity of  $\text{SiO}_2/\text{CsPbBr}_3$  QDs coupled with diarylethene in toluene during 365 nm UV light irradiation with a high intensity (300 mW).



**Fig. S6** PL emission spectra of (a) native  $\text{CsPbBr}_3$  QDs and (b)  $\text{SiO}_2/\text{CsPbBr}_3$  QDs in toluene upon alternating the irradiation with UV (365 nm, 0.5 mW) and visible light ( $\lambda > 530$  nm, 150 mW). The excitation wavelength is 390 nm.

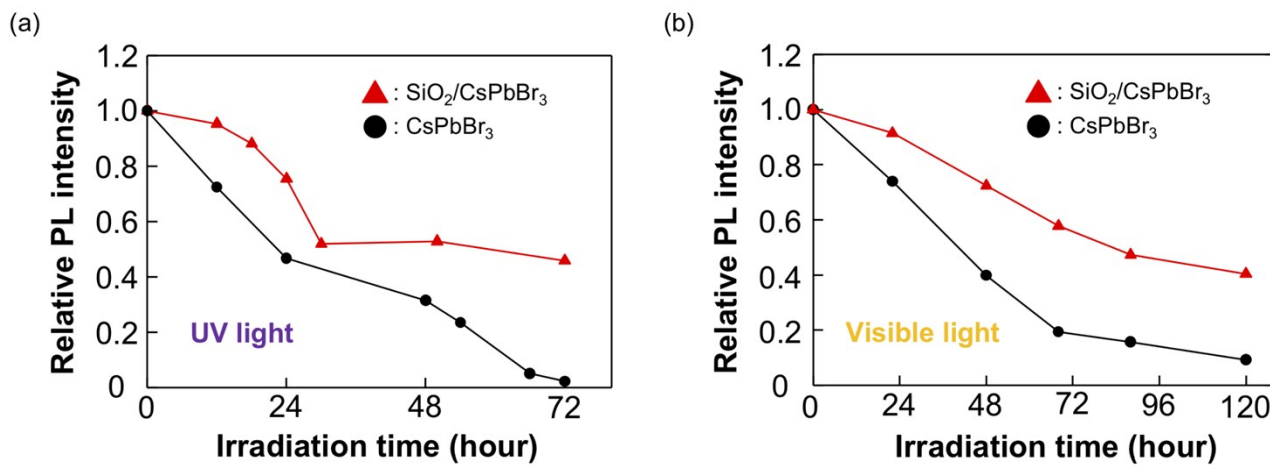


Fig. S7 Time dependence of the relative PL emission intensity under (a) UV (196 mW) and (b) visible light (160 mW) irradiation for native CsPbBr<sub>3</sub> QDs and SiO<sub>2</sub>/CsPbBr<sub>3</sub> QDs in toluene.

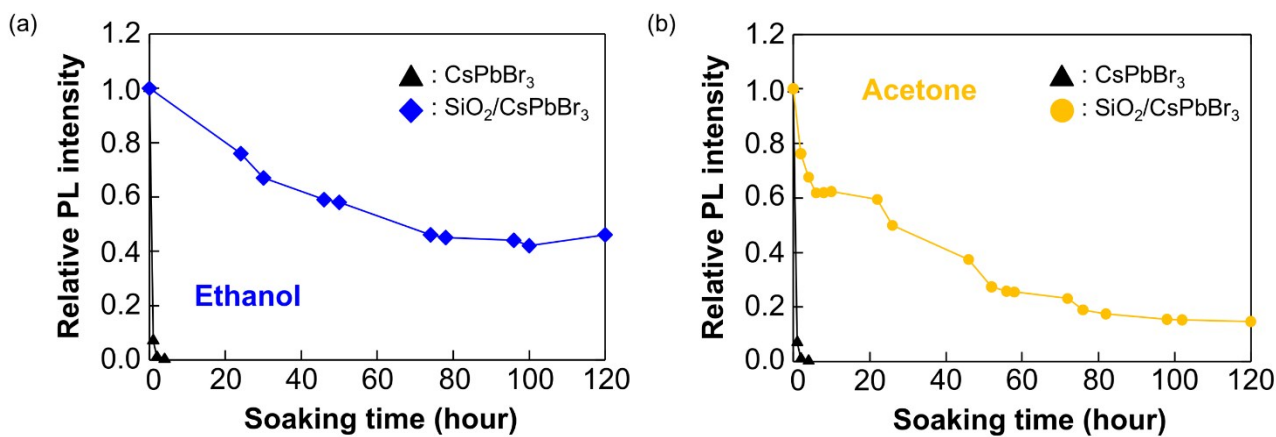
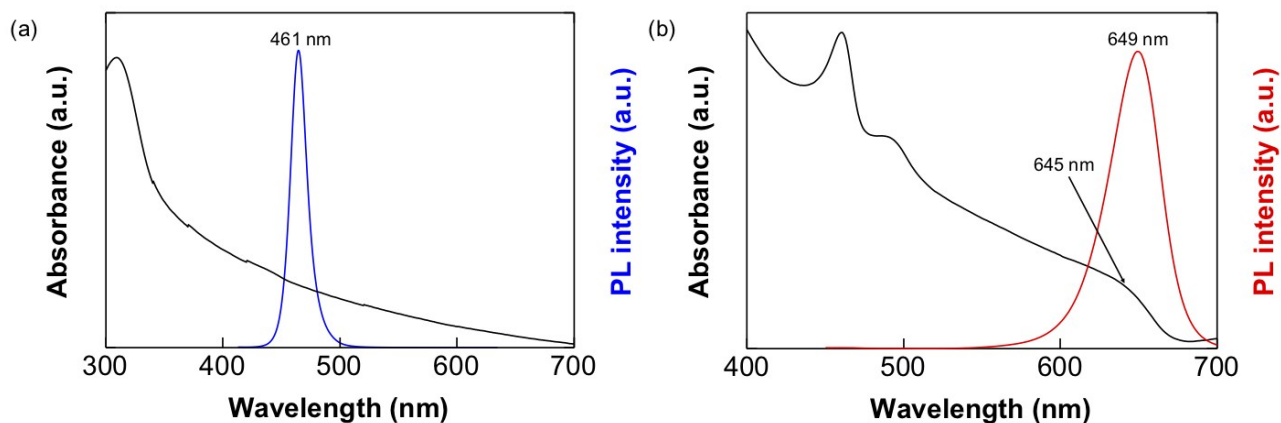


Fig. S8 PL intensity at 390 nm of native CsPbBr<sub>3</sub> and SiO<sub>2</sub>/CsPbBr<sub>3</sub> QDs in (a) ethanol and (b) acetone as a function of soaking time.



**Fig. S9** UV-Vis absorption and PL emission spectra of (a) SiO<sub>2</sub>/CsPbBr<sub>2</sub>Cl and (b) SiO<sub>2</sub>/CsPbBrI<sub>2</sub> QDs.

The excitation wavelengths are 390 and 460 nm for SiO<sub>2</sub>/CsPbBr<sub>2</sub>Cl and SiO<sub>2</sub>/CsPbBrI<sub>2</sub> QDs, respectively.

## References

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- 3 M. Irie, T. Lifka, S. Kobatake, N. Kato, *J. Am. Chem. Soc.*, 2000, **122**, 4871-4876.