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Supporting Information for

Triplet Sensitization by Perovskite Nanocrystals for Photon Upconversion

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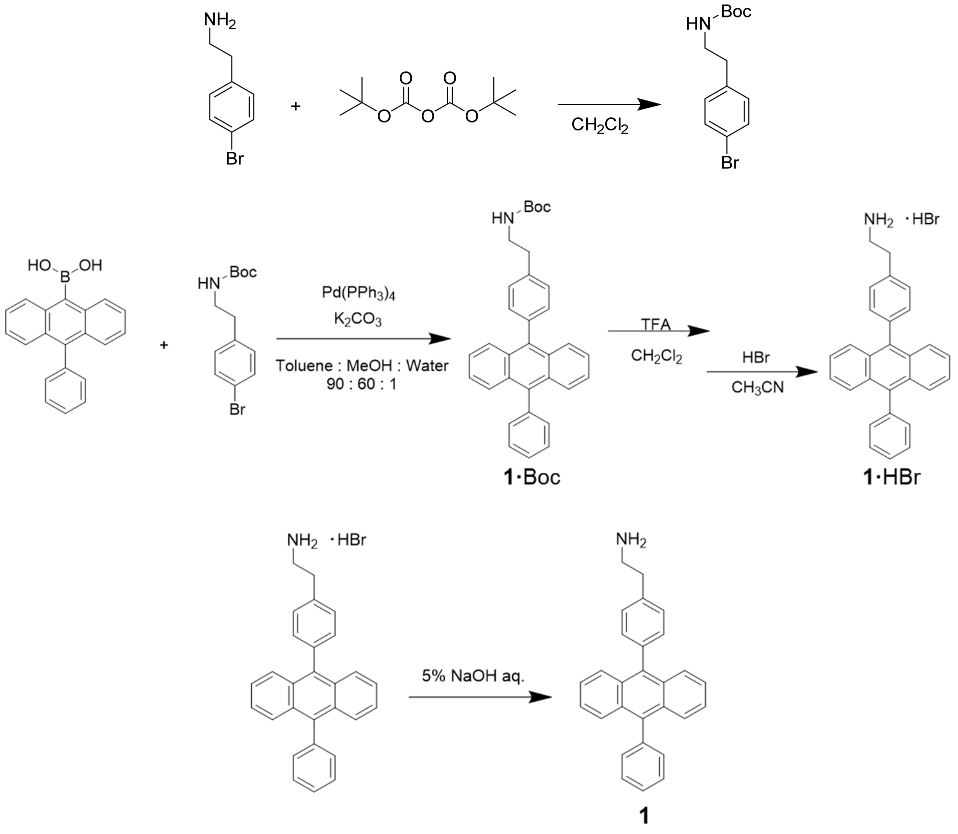
Characterizations. ^1H NMR (300 MHz) spectra were measured on a Bruker DRX-spectrometer. Elemental analysis was conducted at the Elemental Analysis Center, Kyushu University. UV/Vis absorption spectra were recorded on a JASCO V-670 spectrophotometer. Fluorescence spectra were measured by using a PerkinElmer LS 55 fluorescence spectrometer. The absolute quantum yields were measured in an integrating sphere using a Hamamatsu Photonics absolute quantum yield measurement system. Time-resolved photoluminescence lifetime measurements were carried out by using a time-correlated single photon counting lifetime spectroscopy system, HAMAMATSU Quantaurus-Tau C11567–01 (for delayed luminescence lifetime)/C11567–02 (for fluorescence lifetime).

For TTA-UC emission measurements, diode lasers (532 nm, 200 mW, RGB Photonics; 635 nm, 75 mW, RGB Photonics) was used as excitation sources. The laser power was controlled by combining a software (Ltune) and a variable neutral density filter, and measured using a PD300-UV photodiode sensor (OPHIR Photonics). The laser beam was focused on a sample using a lens. The diameter of laser beam ($1/e^2$) was measured at the sample position using a CCD beam profiler SP620 (OPHIR Photonics). Typical laser size were 2.8×10^{-4} cm^2 and 5.1×10^{-4} cm^2 for 532 nm and 635 nm lasers, respectively. The emitted light was collimated by an achromatic lens, the excitation light was removed using notch and short-pass filters, and the emitted light was again focused by an achromatic lens to an optical fiber connected to a multichannel detector MCPD-9800 (Otsuka Electronics). Transmission electron microscopy (TEM) was conducted on a JEOL JEM-2010 with an accelerating voltage of 120 kV. Energy dispersive X-ray (EDX) spectroscopy was carried out using a HITACHI SU9000 SEM with an accelerating voltage of 25 kV.

Materials. All reagents and solvents for synthesis and sample preparation were used as received otherwise indicated. $PbBr_2$, oleic acid, and 48% HBr aqueous solution were purchased from Sigma-Aldrich. Oleylamine, 2-(4-bromophenyl)ethylamine, 10-phenyl-9-anthraceneboronic acid, and 9,10-diphenylanthracene (DPA) were purchased from TCI. Cs_2CO_3 and di-*tert*-butyl dicarbonate were purchased from Wako. LiI was purchased from Kishida.

A synthetic scheme of **1**.



Synthesis of *tert*-butyl(4-bromophenethyl)carbamate.[1] 2-(4-bromophenyl)ethylamine (2.0 g, 10 mmol) and di-*tert*-butyl dicarbonate (2.4 g, 11 mmol) were dissolved in CH_2Cl_2 (100 mL). The mixture was stirred at RT for 3.5 h in N_2 atmosphere. After the reaction, it was washed with saturated NH_4Cl aqueous solution (100 mL), saturated $NaHCO_3$ aqueous solution (100 mL), and water (100 mL). The organic layer was collected and dried over anhydrous Na_2SO_4 and evaporated under reduced pressure. Since the unreacted material remained, the crude product was again reacted with di-*tert*-butyl dicarbonate (3.9 g, 18 mmol) in CH_2Cl_2 (120 mL) at RT for 11 h in N_2 atmosphere. After the reaction, it was washed with a saturated NH_4Cl aqueous solution (100 mL), saturated $NaHCO_3$ aqueous solution (100 mL), and water (100 mL). The organic layer was collected and dried over anhydrous Na_2SO_4 and evaporated under reduced pressure. The crude product was purified using silica gel column chromatography ($CHCl_3$). After removing $CHCl_3$ under reduced pressure, the colorless solid was obtained. Yield: 2.6 g, 87%. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): $\delta = 1.43$ (s, 9H), 2.73-2.78 (t, 2H), 3.32-3.38 (m, 2H), 4.52 (s, 1H), 7.06-7.08 (d, 2H), 7.41-7.44 (d, 2H).

Synthesis of 1·Boc. *tert*-butyl(4-bromophenethyl)carbamate (600 mg, 2.0 mmol), 10-phenyl-9-anthraceneboronic acid (599 mg, 2.0 mmol), $Pd(PPh_3)_4$ (127 mg, 0.11 mmol), and K_2CO_3 (0.84 g, 6.1 mmol) dissolved in the mixture of toluene (9.5 mL), MeOH (6.3 mL), and water (0.11 mL). The mixture was sealed in a vial tube under N_2, and stirred at 110°C for 3 h in a microwave reactor. After the reaction, the mixture was poured into 50 mL $CHCl_3$ and washed with water (100 mL×3). The organic layer was collected and dried over anhydrous Na_2SO_4 and evaporated under reduced pressure. The crude product was purified using silica gel column chromatography ($CHCl_3$). After removing $CHCl_3$ under reduced pressure, the colorless solid was obtained. Yield: 0.80 g, 84%. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ = 1.49 (s, 9H), 2.96-3.01 (t, 2H), 3.55-3.57 (m, 2H), 4.72 (s, 1H), 7.32-7.72 (m, 17H).

Synthesis of 1·HBr. Under N_2 atmosphere, trifluoroacetic acid (TFA, 6.3 mL) was added to the solution of **1·Boc** (798 mg, 1.7 mmol) in CH_2Cl_2 (40 mL). The mixture was stirred at RT for 4 h. After the reaction, the solvents were removed under reduced pressure. 5% Na_2CO_3 aqueous solution (40 mL) and CH_2Cl_2 (35 mL) were added to the crude product, and it was stirred at RT for 6 h under N_2 atmosphere. The organic layer was collected and dried over anhydrous Na_2SO_4 and evaporated under reduced pressure. The obtained pale yellow solid was dissolved in hot CH_3CN (200 mL), and 48% HBr aqueous solution (0.3 mL) was added. The precipitate was collected and washed with $CHCl_3$ and ethanol. The pale yellow solid was dried under reduced pressure at 60°C. Yield: 449 mg, 58%. ^{1}H NMR (300 MHz, DMSO, TMS): δ = 3.04-3.09 (t, 2H), 3.23-3.28 (t, 2H), 7.39-7.70 (m, 17H), 7.89 (s, 3H). Elemental analysis, calculated for $C_{28}H_{24}NBr$: C, 74.01; H, 5.32; N, 3.08; found: C, 73.86 ; H, 5.37; N, 3.15.

Synthesis of 1. Under N_2 atmosphere, 5% NaOH aqueous solution (9.5 mL) was added to the solution of **1·HBr** (100 mg, 0.22 mmol) in CH_2Cl_2 (50 mL). The mixture was stirred at RT for 2 h. The organic layer was collected and dried over anhydrous Na_2SO_4 and evaporated under reduced pressure. **1** was obtained as pale yellow solid. Yield: 81 mg, 99%. ^{1}H NMR (300 MHz, DMSO, TMS): δ = 2.81-2.85 (t, 2H), 2.92-2.97 (t, 2H), 7.35-7.69 (m, 17H).

Preparation of Cs-OA solution.[2] The synthesis followed the literature method. Cs_2CO_3 (0.21 g, 0.64 mmol), 1-octadecene (10 mL) and dried oleic acid (OA, 625 μL) were added in a 3-neck flask and degassed at 120 °C for 1 h. Then the mixture was heated to 150°C under N_2 atmosphere until all Cs_2CO_3 reacted with OA. After the reaction, the solution temperature was maintained at 100°C.

Synthesis of $CsPbBr_3$ NCs. $PbBr_2$ (0.28 g, 0.76 mmol) and 1-octadecene (20 mL) were combined in a 3-neck flask and degassed for 1 h at 120 °C. Dried OA (2 mL) and dried oleylamine (2 mL) were injected at 120 °C under N_2 atmosphere. After $PbBr_2$ was completely dissolved, the temperature was raised to 160 °C. Then 1.6 mL of the Cs-OA solution was injected quickly and 10 s later, the reaction mixture was cooled by the ice-water bath. 20 mL of ethanol was added to the mixture, and the precipitate was collected by centrifugation (3000 rpm, 15 min). In an Ar-filled grove box ($[O_2]<0.1$ ppm), the obtained $CsPbBr_3$ NCs was re-dispersed in toluene (30 mL) and filtered through 0.45 µm PTFE syringe filter.

Sample preparation for energy transfer and TTA-UC. All the sample preparation was carried out in the Ar-filled glovebox. For surface-modification, 5.6 mg/mL $CsPbBr_3$ nanocrystals toluene solution (0.5 mL) and **1** (0.7 mg, 0.0019 mmol) were added to toluene (1.5 mL), and the mixture was stirred at RT for overnight. To control the bandgap of perovskite nanocrystals, 14 µL of LiI ethanol solution (0.25, 0.40, 0.55, 0.64, and 0.95 M) was added to toluene solution of **1**-modified $CsPbBr_3$. The obtained mixture was filtered through 0.45 µm PTFE syringe filter, and then DPA (10 mM) was added.

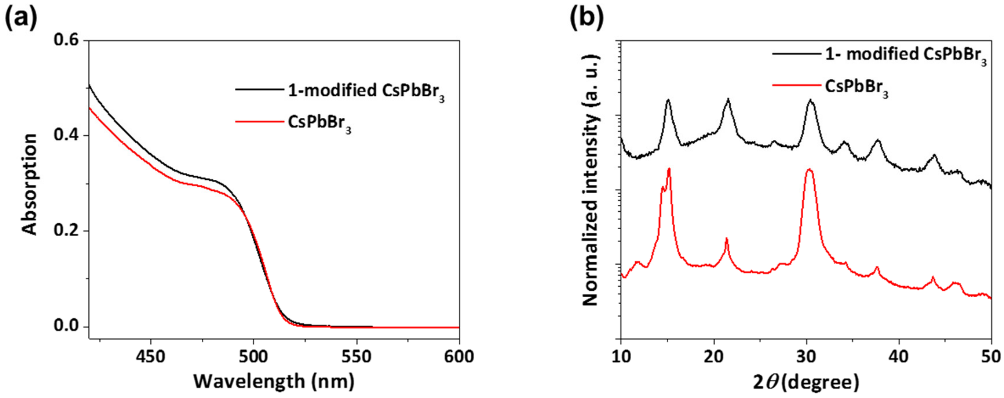


Fig. S1. (a) Absorption spectra and (b) XRPD patterns of $CsPbBr_3$ nanocrystals (red) and **1**-modified $CsPbBr_3$ nanocrystals (black).

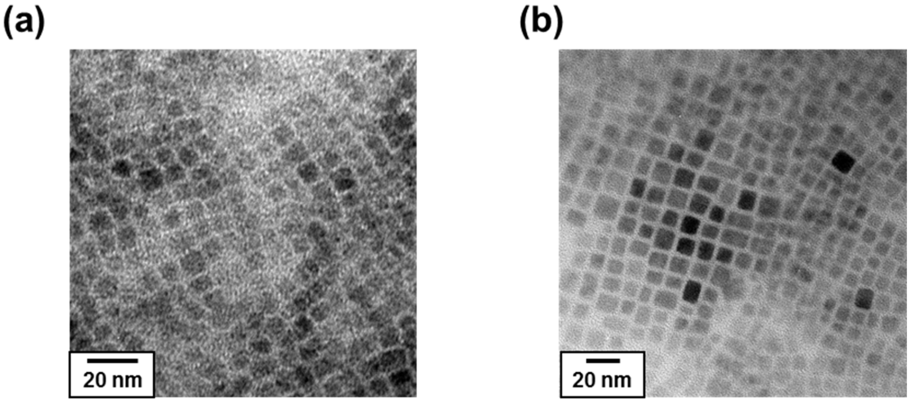


Fig. S2. TEM images of (a) $CsPbBr_3$ nanocrystals (average size = 8.1 ± 1.5 nm) and (b) **1**-modified $CsPbBr_3$ nanocrystals (average size = 8.8 ± 1.9 nm).

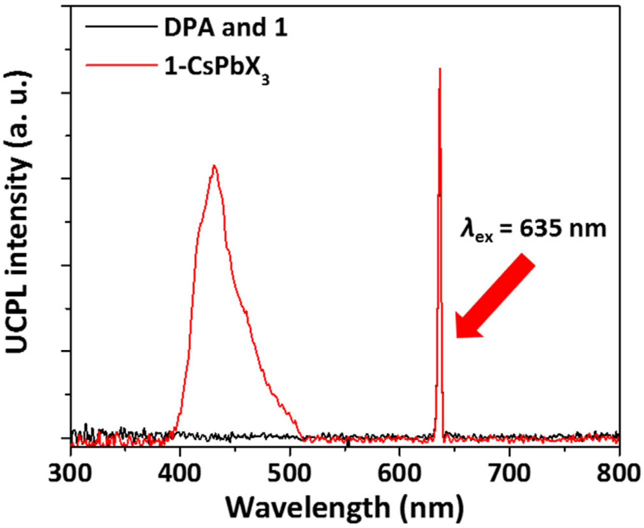


Fig. S3. UC emission spectrum of **1**-CsPbX$_3$ with 10 mM DPA (red, excitation intensity = 98 W/cm^2, perovskite emission peak at 650 nm), and 10 mM DPA and 0.94 mM **1** in the absence of CsPbX$_3$ (black, excitation intensity = 98 W/cm^2) in deaerated toluene excited by a 635 nm laser. A notch filter (λ = 635 nm) and a short pass filter (λ = 590 nm) were used to remove the scattered incident light.

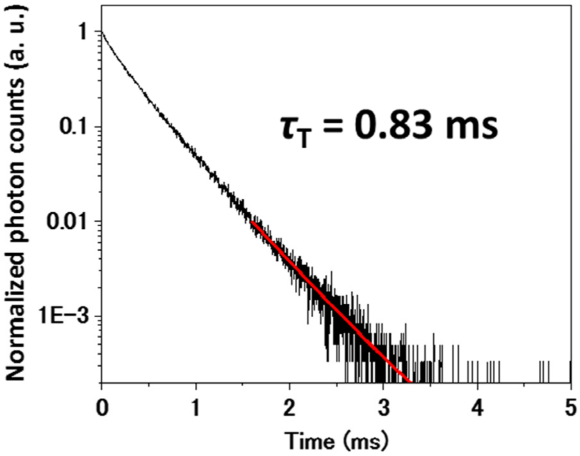


Fig. S4. UC emission decay at 430 nm of **1**-CsPbX$_3$ in deaerated toluene under pulsed excitation at 531 nm. The red fitting curve was obtained by considering the known relationship of $I_{UC}(t) \propto \exp(-2t/\tau_T)$, where τ_T is acceptor triplet lifetime (0.83 ms).

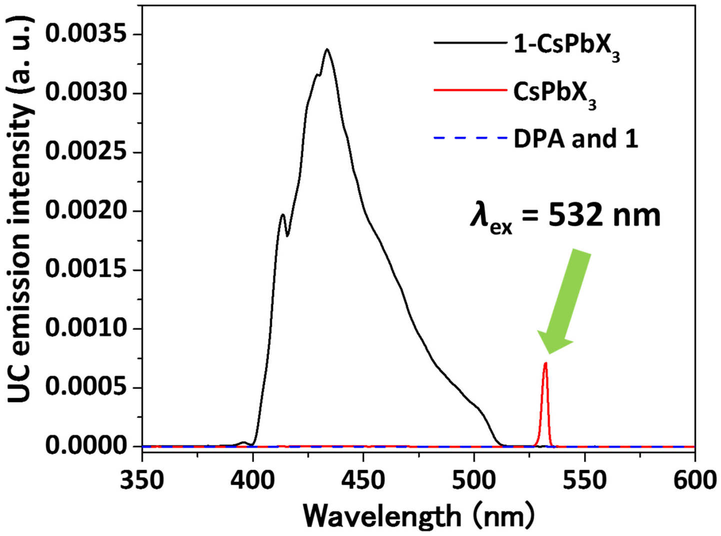


Fig. S5. UC emission spectrum of **1**-$CsPbX_3$ with 10 mM DPA (black, excitation intensity = 1.1 W/cm^2, perovskite emission peak at 618 nm), $CsPbX_3$ with 10 mM DPA in the absence of **1** (red, excitation intensity = 722 W/cm^2, perovskite emission peak at 630 nm), and 10 mM DPA and 0.94 mM **1** in the absence of $CsPbX_3$ (blue, excitation intensity = 3.9 W/cm^2) in deaerated toluene excited by a 532 nm laser. A notch filter (λ = 532 nm) was used to remove the scattered incident light.

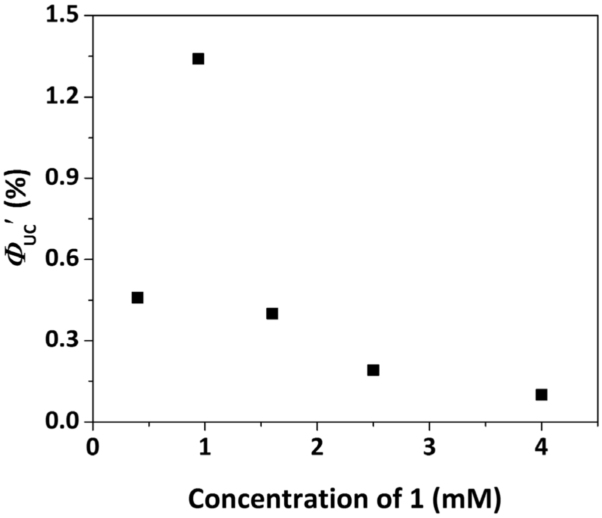


Fig. S6. Dependence of Φ_{UC}' of **1**-modified perovskite nanocrystals and DPA on the concentration of **1** in deaerated toluene. These samples were excited with 532 nm laser at sufficiently high intensity (200~1000 mW/cm^2), where the Φ_{UC}' values were saturated. The DPA concentration was fixed at 10 mM for all samples. All samples were treated by 0.64 M LiI ethanol solution.

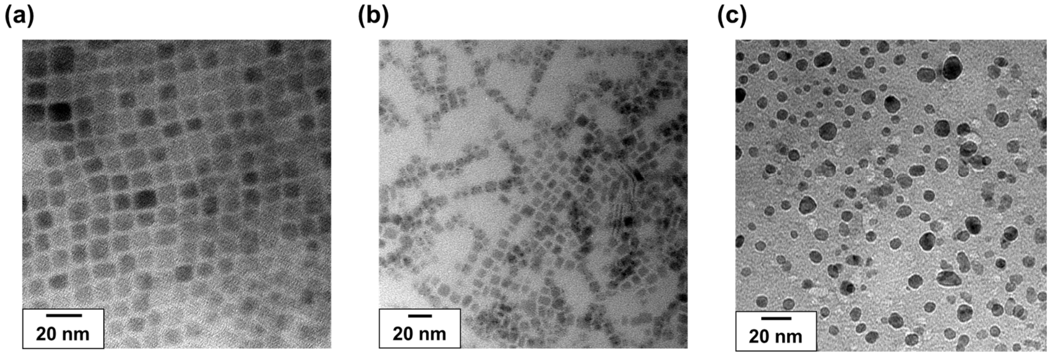


Fig. S7. TEM images of (a) $CsPbX_3$ (average size = 9.3 ± 1.7 nm), (b) $CsPbX_3$ modified with 0.94 mM **1** (average size = 7.5 ± 1.7 nm), and (c) $CsPbX_3$ modified with 4.0 mM **1** (average size = 7.5 ± 2.2 nm). All samples were treated by 0.64 M LiI ethanol solution.

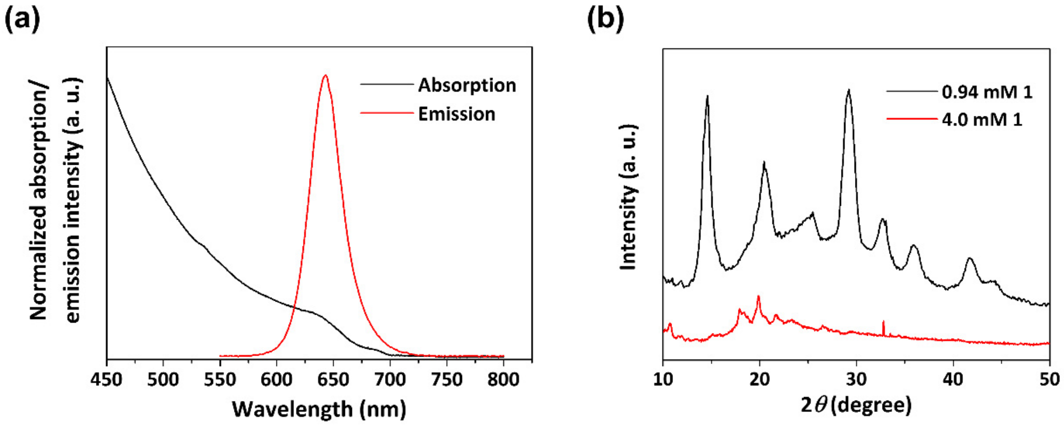


Fig. S8. (a) Absorption (black line) and emission (red line) spectra of $CsPbX_3$ nanocrystals modified with 4.0 mM of **1**. (b) XRPD patterns of $CsPbX_3$ nanocrystals modified with 0.94 mM (black line) and 4.0 mM (red line) of **1**.

The emission peak of $CsPbX_3$ showed a slight red shift from 630 nm to 643 nm by the addition of 4.0 mM **1**, which might be originated from aggregation of perovskite nanoparticles as observed in TEM images (Fig. S7c). The XRPD pattern became weaker in intensity and unassignable, indicating the reduced structural order of perovskite nanocrystals by the addition of excess **1**. This result agrees with the observed irregular morphology (Fig. S7c).

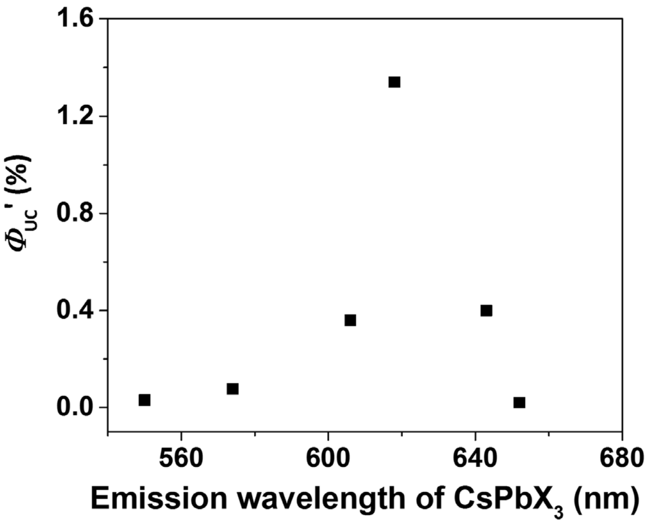


Fig. S9. Dependence of Φ_{UC}' on the energy bandgap of $CsPbX_3$ in deaerated toluene. These samples were excited with the 532 nm laser at a sufficiently high intensity (200~2000 mW/cm^2), where the Φ_{UC}' values were saturated. **1** and DPA concentrations were fixed at 0.94 mM and 10 mM for all samples.

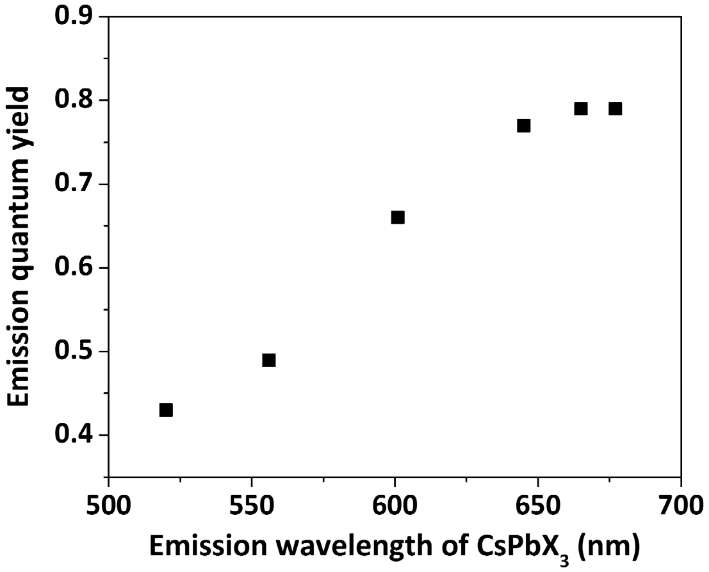


Fig. S10. Dependence of emission quantum yield of $CsPbX_3$ in deaerated toluene on its emission wavelength.

Supplementary references

1 M. B. S. Kirketerp, T. Ryhding, K. Stochkel, M. B. Nielsen and S. B. Nielsen, *J. Phys. Chem. A*, 2011, **115**, 1222-1227.

2 P. Ramasamy, D. H. Lim, B. Kim, S. H. Lee, M. S. Lee and J. S. Lee, *Chem. Commun.*, 2016, **52**, 2067-2070.