Supporting Information

Diverse $CsPbI_3$ Assembly Structures: The Role of Surface Acids

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Experimental part

Materials: Lead (II) bromide (PbI_2, 99%), Cesium carbonate (Cs_2CO_3, 99.9%), oleylamine (OAm, 80-90%), oleic acid (OA, 90%), and 1,4-Dodecyl benzene sulfonic acid (1,4-DBSA, 95%) were purchased from Aladdin. 1-octadecene (ODE, 90%), Ethyl acetate (EA, AR, 97%), and Hexane (anhydrous, 99.5%) were bought from Macklin. All chemicals were used without any further purification.

Preparation of Cesium oleate precursors: Cs_2CO_3 (0.36 g, 1.1 mmoL), octadecene (15 mL), and oleic acid (1.5 mL) were added into 100 mL 3-neck flask, exhausted for half an hour at 120°C, and then heated to 150°C under Ar atmosphere until all Cs_2CO_3 reacted with OA. The solution was kept at 120°C to avoid solidification before injection.

Synthesis of Cs_4PbI_6 NCs: PbI_2 (0.54 mmoL, 0.1242 g), ODE (7.5 mL), OAm (1.5 mL), OA (1.5 mL) were loaded into a 100 mL 3-neck flask and degassed for half an hour at 120°C under Ar flow. The temperature was increased to 160°C under Ar atmosphere. The preheated Cs-oleate solution (0.75 mL, 0.033 mmoL) was swiftly injected into the transparent precursor solution. After 5 seconds, the reaction mixture was cooled down using an ice bath.

Synthesis of nanowires-like $CsPbI_3$ NCs ($CsPbI_3$-S_1 NCs): PbI_2 (0.54 mmoL, 0.1242 g), ODE (7.5 mL), the molar ratio of 4-DBSA and OAm (2.6, 2.37 moL:0.91 moL) were loaded into a 100 mL 3-neck flask and degassed for half an hour at 120°C under Ar flow. The temperature was increased to 160°C and OA (1.5 mL) was injected into the 3-neck flask, and keeps heating up to 180°C under Ar atmosphere. When the temperature remains at 180°C, OAm (3.6 moL) was added into the reaction solution. The preheated Cs-oleate solution (0.75 mL, 0.033 mmoL) was injected into the transparent precursor solution swiftly. After 5 seconds, the reaction mixture was cooled down using an ice bath.

Synthesis of nanospheres-like $CsPbI_3$ NCs ($CsPbI_3$-S_2 NCs): PbI_2 (0.54 mmoL, 0.1242 g), ODE (7.5 mL), the molar ratio of 4-DBSA and OAm (1.5, 2.37 moL:1.5 moL) were loaded into a 100 mL 3-neck flask and degassed for half an hour at 120°C under Ar flow. The temperature was increased to 160°C and OA (1.5 mL) was injected into the 3-neck flask, and keeps heating up to 180°C under Ar atmosphere. When the temperature remains at 180°C, OAm (3 moL) was added into the reaction solution. The preheated Cs-oleate solution (0.75 mL, 0.033 mmoL) was injected into the transparent precursor solution swiftly. After 5 seconds, the reaction mixture was cooled down using an ice bath.

Synthesis of four-leaf clover-like $CsPbI_3$ NCs ($CsPbI_3$-S_3 NCs): PbI_2 (0.54 mmoL, 0.1242 g), ODE (7.5 mL), the molar ratio of 4-DBSA and OAm (1, 2.37 moL: 2.3 moL) were loaded into a 100 mL 3-neck flask and degassed for half an hour at 120°C under Ar flow. The temperature was increased to 160°C and OA (1.5 mL) was injected into the 3-neck flask, and keeps heating up to 180°C under Ar atmosphere. When the temperature remains at 180°C, OAm (2.3 moL) was added into the reaction solution. The preheated Cs-oleate solution (0.75 mL, 0.033 mmoL) was injected into the transparent precursor solution swiftly. After 5 seconds, the reaction mixture was cooled down using an ice bath.

Synthesis of NPLs-like $CsPbI_3$ NCs ($CsPbI_3$-S_4 NCs): PbI_2 (0.54 mmoL, 0.1242 g), ODE (7.5 mL), the molar ratio of 4-DBSA and OAm (0.79, 2.37 moL: 3 moL) were loaded into a 100 mL 3-neck flask and degassed for half an hour at 120°C under Ar flow. The temperature was increased to 160°C and OA (1.5 mL) was

injected into the 3-neck flask, and keeps heating up to 180^{o}C under Ar atmosphere. When the temperature remains at 180^{o}C, OAm (1.5 moL) was added into the reaction solution. The preheated Cs-oleate solution (0.75 mL, 0.033 mmoL) was injected into the transparent precursor solution swiftly. After 5 seconds, the reaction mixture was cooled down using an ice bath.

Synthesis of $CsPbI_3$ NCs nanorods ($CsPbI_3$-S_6 NCs): PbI_2 (0.54 mmoL, 0.1242 g), ODE (7.5 mL), the molar ratio of 4-DBSA and OAm (0.5, 2.37 moL: 4.6 moL) were loaded into a 100 mL 3-neck flask and degassed for half an hour at 120^{o}C under Ar flow. The temperature was increased to 160^{o}C and OA (1.5 mL) was injected into the 3-neck flask, and keeps heating up to 180^{o}C under Ar atmosphere. The preheated Cs-oleate solution (0.75 mL, 0.033 mmoL) was injected into the transparent precursor solution swiftly. After 5 seconds, the reaction mixture was cooled down using an ice bath.

Characterizations: X-ray diffraction data of powder was recorded on Bruker D8 Advance using Ni-filtered Cu Kα radiation (λ = 1.542 Å). Fluorescence and absorption spectra were measured on Varian Cary Eclipse instrument and Shimadzu UV-3600, respectively. TEM measurements were carried out on a FEI Tecnai G20 with a Cu grid. X-ray photoelectron spectroscopy (XPS) measurements were performed using an achromatic Al Kα source (1486.6 eV) and a double pass cylindrical mirror analyzer (ULVAC-PHI 5000 VersaProbe). FTIR results were measured with a Tensor-27 spectrometer. The absolute PLQY of NCs solution was determined using a Quantaurus-QY absolute photoluminescence quantum yield spectrometer (C11347-11, Hamamatsu Photonics, Japan).

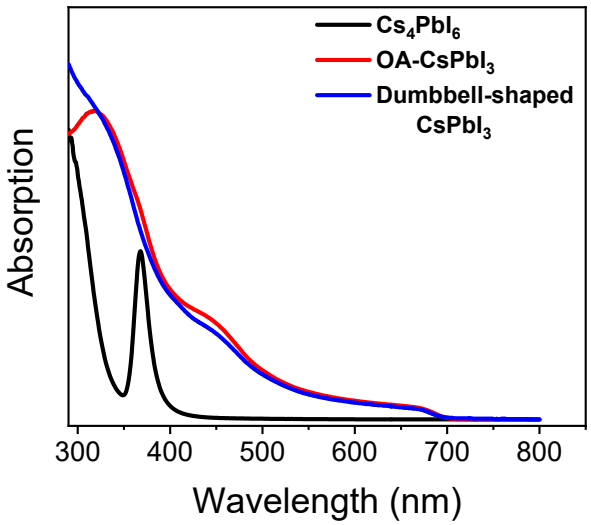

Figure S1. The absorption data of Cs_4PbI_6 NCs, OA-$CsPbI_3$ and Dumbbell-shaped $CsPbI_3$ NCs.

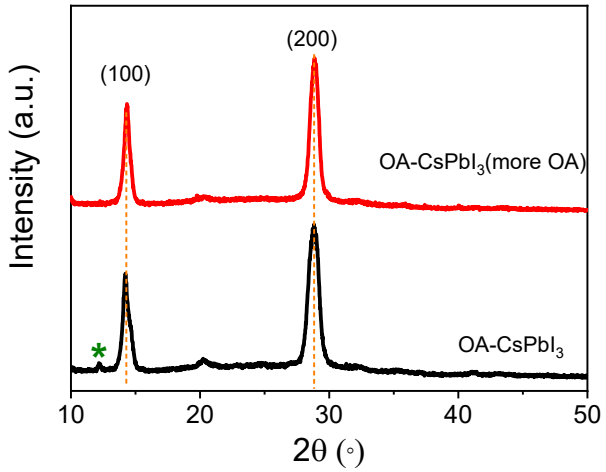

Figure S2. The XRD patterns of OA-$CsPbI_3$ and OA-$CsPbI_3$ (more OA) NCs.

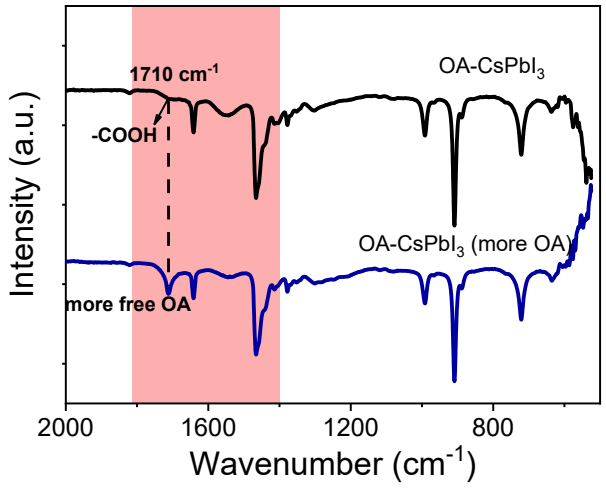

Figure S3. The FTIR curves of OA-$CsPbI_3$ and OA-$CsPbI_3$ (more OA) NCs.

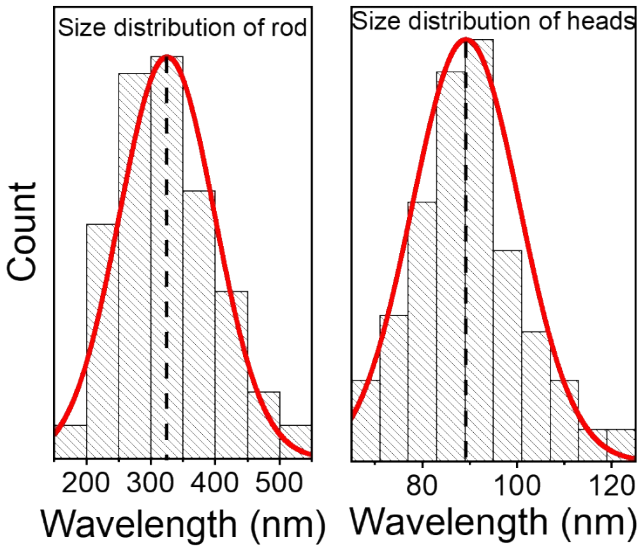

Figure S4. The size distribution of rod and heads of dumbbell-shaped $CsPbI_3$ NCs.

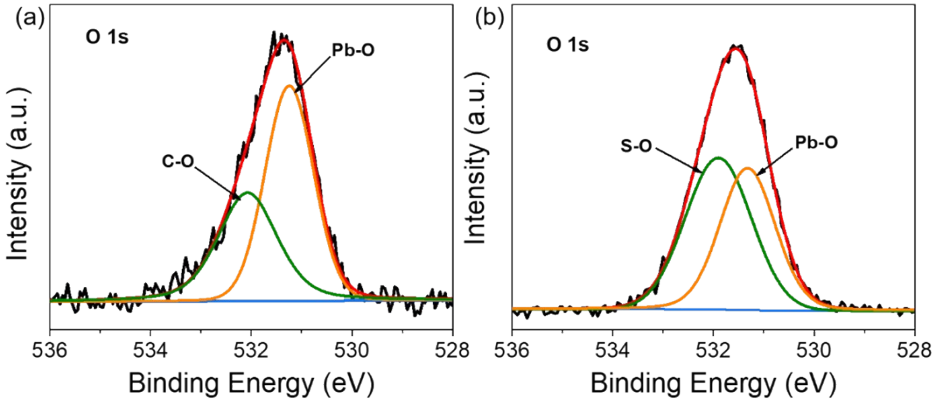

Figure S5. XPS refined curves of (a) O 1s of OA-$CsPbI_3$ and (b) dumbbell-shaped $CsPbI_3$ NCs.

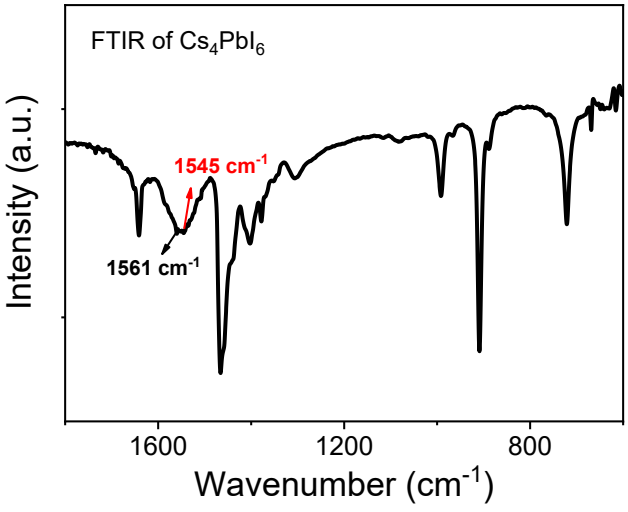

Figure S6. FTIR curve of Cs_4PbI_6 NCs.

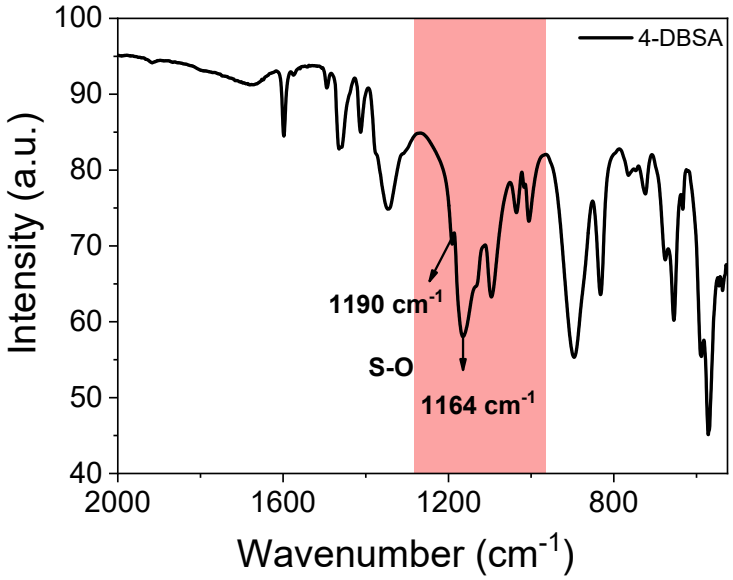

Figure S7. FTIR curve of 4-DBSA.

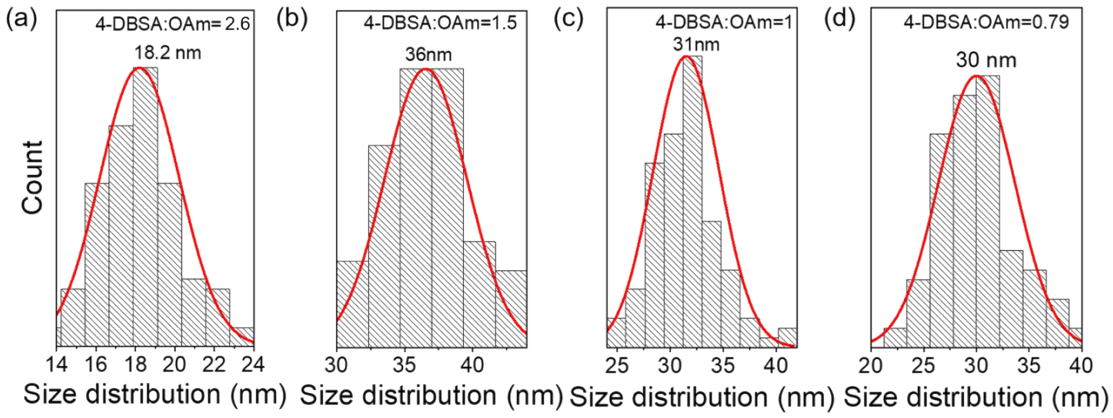

Figure S8. Size distribution of (a) $CsPbI_3$-S_1, (b) $CsPbI_3$-S_2, (c) $CsPbI_3$-S_3, and (d) $CsPbI_3$-S_4 NCs by changing the molar ratio of 4-DBSA and OAm.

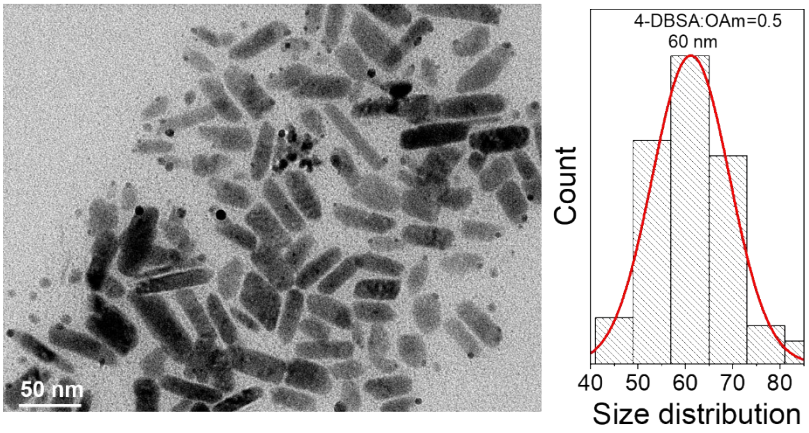

Figure S9. TEM image (left) and size distribution (right) of $CsPbI_3$ -S_6 NCs.

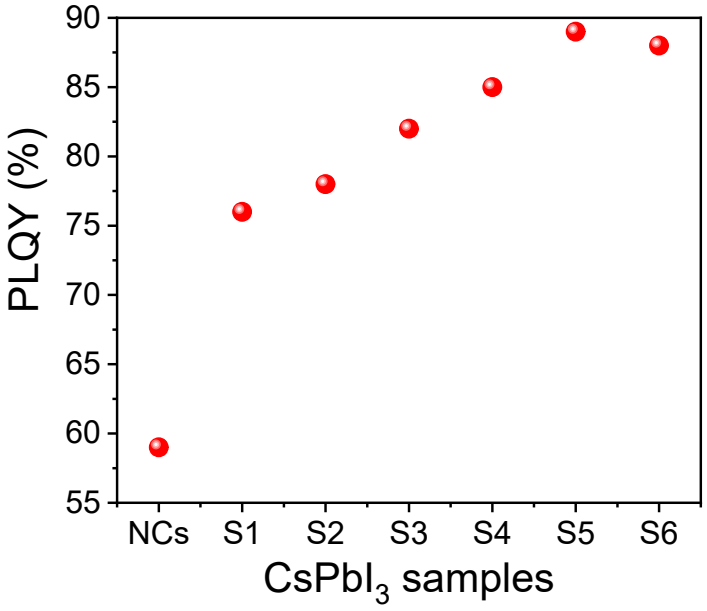

Figure S10. PLQY data of OA-$CsPbI_3$ and $CsPbI_3$-S_n NCs.

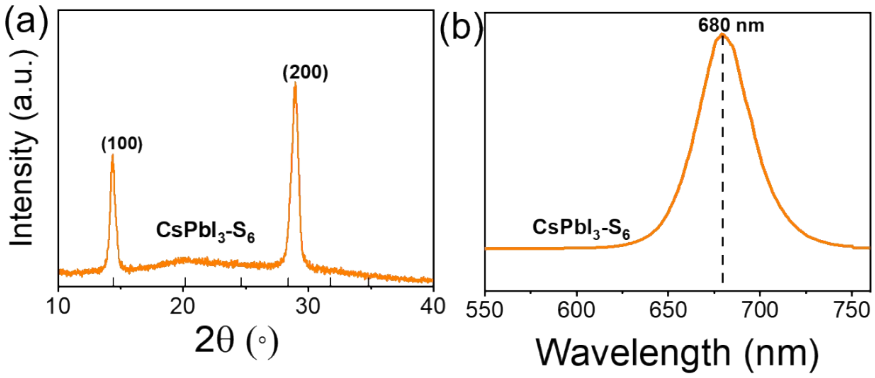

Figure S11. (a) XRD pattern and (b) PL spectrum of $CsPbI_3$-S_6 NCs.

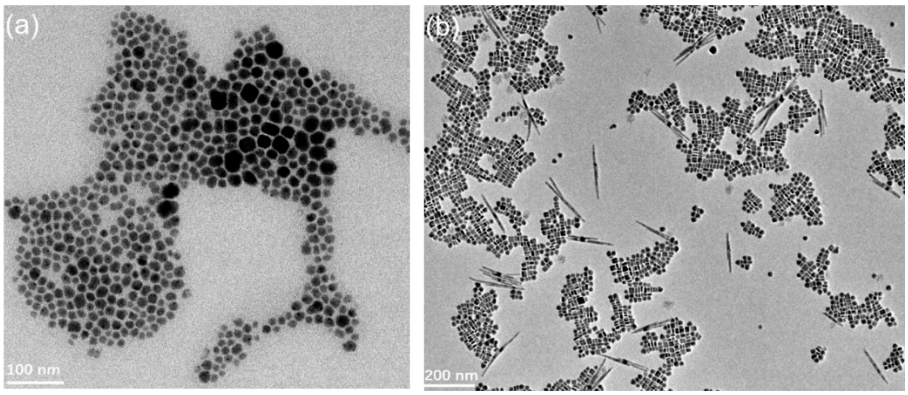

Figure S12. TEM images of $CsPbI_3$ NCs by adding 4-DBSA ligands in the second nucleation stage (a) and only adding 4-DBSA in the first nucleation (b).

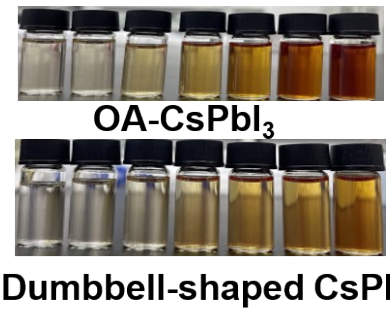

Figure S13. The photos of OA-$CsPbI_3$ and dumbbell-shaped $CsPbI_3$ NCs in natural light.

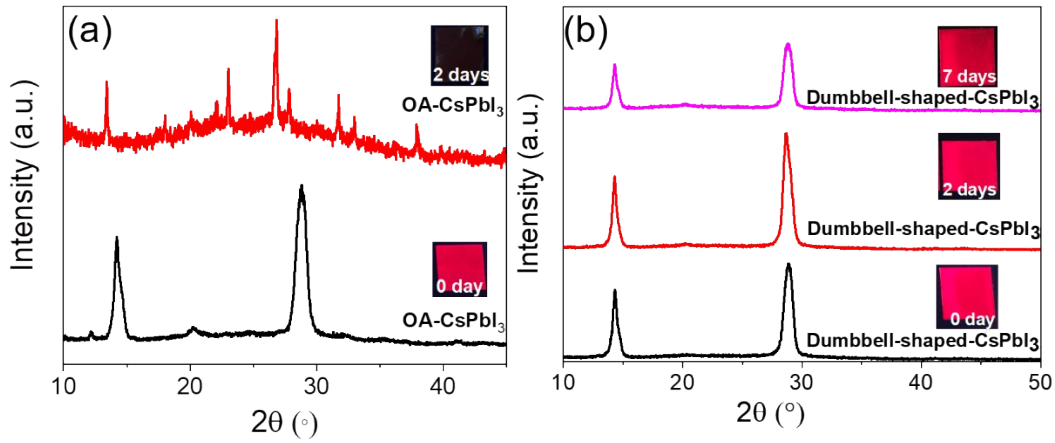

Figure S14 Time-dependent XRD patterns of (a) OA-$CsPbI_3$ NCs and (b) Dumbbell-shaped-$CsPbI_3$.