Electronic Supporting Information (ESI)

All inorganic Cs_2CuX_4 (X= Cl, Br, Br/I) perovskite quantum dots with blue-green luminescence

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Chemicals. All reagents were used as received without further purification: $CuCl_2$ (>99%, Adamas), $CuBr_2$ (99.95%, Aladdin), CsCl (99.99%, Aladdin), CsBr (99.9%, Meryer), CsI (99.999%, Aladdin), n-octylamine (OLAm, 99%, Macklin), oleic acid (OA, 90%, Sigma Aldrich), N,N-dimethylformamide (DMF, AR, 99.5%, Macklin), dimethylsulfoxide (DMSO, 99%, Aladdin), n-octane(96%, Macklin), n-octane (Super dry, J&K chemical CO., Ltd, China).

Fabrication of Cs_2CuX_4 inorganic perovskite quantum dots (IPQDs). Colloidal Cs_2CuBr_4 QDs were fabricated following the improved ligand-assisted reprecipitation (LARP) technique,[1] which could be briefly described as following. In a typical synthesis of Cs_2CuBr_4 QDs, 0.1 mmol CsBr was dissolved in 1 mL DMSO, 0.2 mmol $CuBr_2$ were dissolved in 1 mL DMF, two types of solutions were mixed fully to form a precursor solution for the following synthesis. 500 μL precursor solution was quickly dropped into a mixture of 5 mL octane, 20 μL n-octylamine and 625 μL OA under vigorous stirring. As a typical LARP reaction, the reprecipitation strategy was accomplished by simply mixing a solution of perovskite precursors in good solvent (DMF or DMSO) into a vigorously stirred poor solvent (octane) with long-chain organic ligands (n-octylamine and oleic acid), which subsequently result in the controlled crystallization of precursors into colloidal nanoparticles. Moreover, n-octylamine and oleic acid was dissolved into octane to control the crystallization rate and stabilize the colloidal solution instead of adding them into the good solvent. Complete crystallization of the product was achieved in a few seconds at room temperature and a blue-green colloidal solution was observed. After the reaction, the solution was centrifuged at 4000 rpm for 5 min to discard the precipitate. Finally, a bright blue-green colloidal solution was obtained for characterization and anion exchange. For the bandgap tuning by changing the molar ratio of the precursor molecules, the solubility of $CuBr_2$ in DMF and DMSO is better than that of CsBr. The color change of precursor solution from light blue to navy blue was observed when $CuBr_2$/CsBr ratio increased, indicating the formation of higher saturation concentration of perovskite precursors. As described in the $Cs_3Bi_2Br_9$ system, the concentration of precursor solution can slightly change the NCs' size.[2] In our work, when CsBr:$CuBr_2$ ratio was 1:4, more $CuBr_2$ in the precursors resulted in the formation of larger spherical dots with average diameter of 14.2

± 0.7 nm, while the lower concentration ($CsBr:CuBr_2$ =1:3) gives size 9.1 ± 0.5 nm, as shown in Figure S7. Moreover, when the ratio of the precursor molecules changes, the corresponding PL peak position is also changing, which were consistent with those in $Cs_3Sb_2Br_9$ QDs.[3] However, the change in the position of the PL peak is larger than that of $Cs_3Sb_2Br_9$ QDs.

Cs_2CuBr_4 QDs powders were obtained by rotary evaporation to remove the residual organic solvents at 100°C, which were further washed by n-octane and dried in the vacuum oven at 60°C. The synthesis of Cs_2CuCl_4 QDs solution was the same as Cs_2CuBr_4 QDs solution except that the CsCl and $CuCl_2$ were used for the precursor preparation. Cs_2CuCl_4 QDs powders were obtained by washing with n-octane and centrifuged at 8000 rpm for 10 min, the resulting product was dried in vacuum at 60°C. The synthesis of $Cs_2Cu(Br/I)_4$ was obtained by varying the ratio of reactant sources ($CuBr_2$, CsI) in the preparation of precursor solutions.

$Cs_2CuBr_{4-X}I_X$ was fabricated by anion exchange reaction: 0.5 mmol CsI dissolved in 5 mL DMSO as the halide source for anion exchange. Then, 200 μL CsI was added into the as-prepared colloidal Cs_2CuBr_4 QDs solution.

$Cs_2CuBr_{4-X}Cl_X$ was fabricated by anion exchange reaction: 0.5 mmol CsCl dissolved in 5 mL DMSO as the halide source for anion exchange. Then, 200 μL CsCl was added into the as-prepared colloidal Cs_2CuBr_4 QDs solution.

Characterization. The optical absorption spectra of the synthesized QDs were measured on a Varian Cary 5000 UV−Vis near infrared (NIR) spectrophotometer. Samples were prepared by diluting the crude solutions in n-octane. PL measurements were performed on a Fluoromax-4 photoluminescence system. The sample preparation method was identical to that for optical absorption measurements. X-ray diffraction (XRD) data was collected on a Rigaku Smartlab (3) diffractometer, using a Cu Kα source and operating at 40 kV and 40 mA. Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) results were recorded using a JEM-2100 instrument. Time-resolved photoluminescence decays were conducted on a FluoroLog-3 TCSPC (Horiba Jobin Yvon Inc) spectrofluorometer. The light source for photo stability was a UV lamp (JIAPENG, ZF-

05, China). X-ray photoelectron spectroscopy (XPS) measurements were carried out on a Thermo ESCALAB 250XI machine (Thermo Fisher Scientific) with Al Kα as the X-ray source to analyze the chemical nature of QDs of Cs_2CuBr_4. The absolute PLQYs of diluted QDs solutions were determined using the FluoroLog-3 TCSPC (Horiba Jobin Yvon Inc) spectrofluorometer.

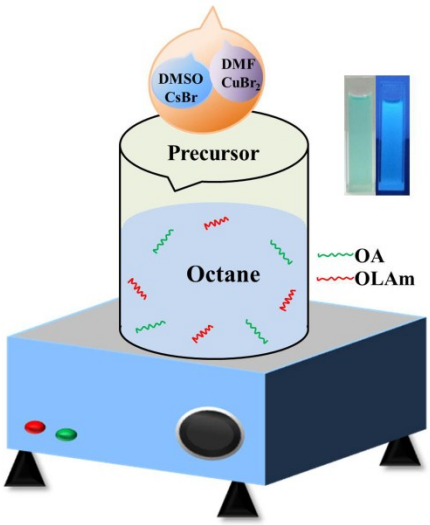

Fig. S1 Schematic illustration of the reaction system and process of synthesis Cs_2CuBr_4. Inset: Photographs of as-obtained colloidal Cs_2CuBr_4 without and with the UV lamp illumination.

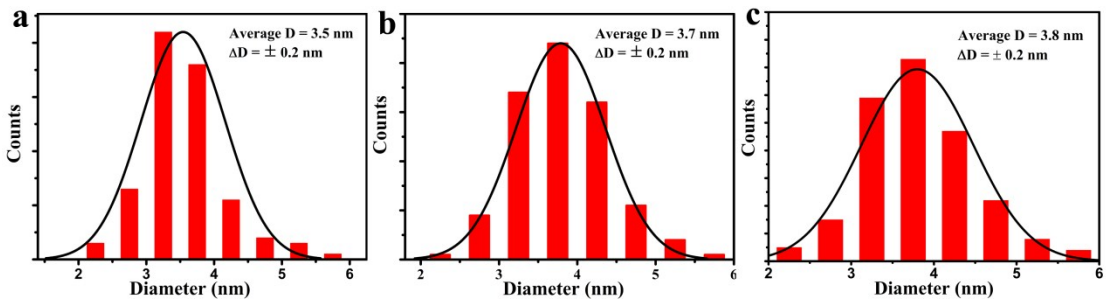

Fig. S2 The corresponding size distribution histograms of the as-synthesized Cs_2CuCl_4 QDs (a), as-synthesized Cs_2CuBr_4 QDs (b), and the as-synthesized $Cs_2Cu(Br/I)_4$ QDs.

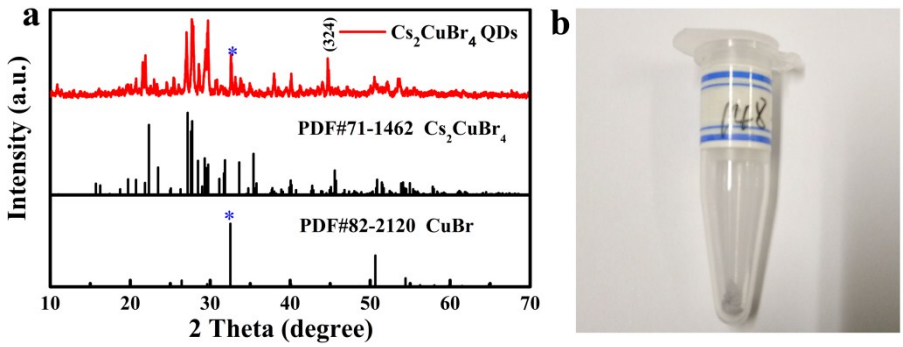

Fig. S3 (a) XRD patterns of Cs_2CuBr_4 QDs. (b) Powders of Cs_2CuBr_4 QDs prepared by rotary evaporation.

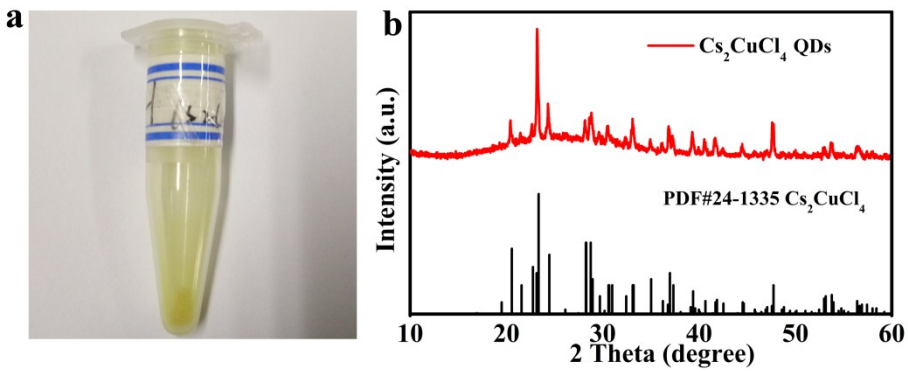

Fig. S4 (a) Powders of Cs_2CuCl_4 QDs prepared by centrifugation. (b) XRD patterns of Cs_2CuCl_4 QDs.

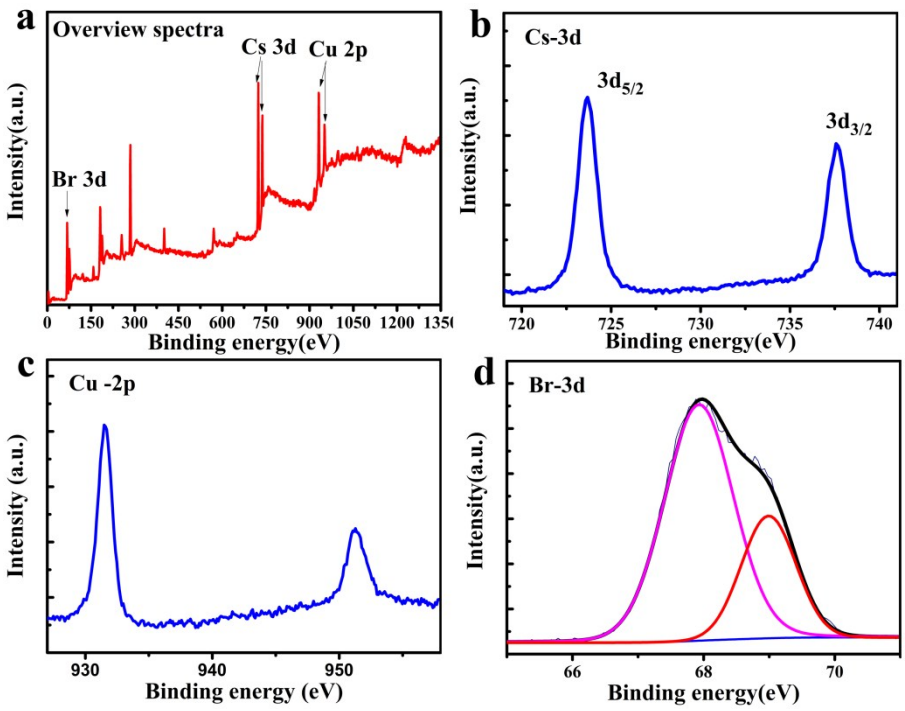

Fig. S5 Characterization of Cs_2CuBr_4 QDs. (a) Overview X-ray photoelectron spectroscopy (XPS) scans of the Cs_2CuBr_4 QDs powder. (b) XPS Cs 3d spectra for Cs_2CuBr_4. (c) XPS Cu 2p spectra for Cs_2CuBr_4. (d) XPS Br 3d spectra for Cs_2CuBr_4.

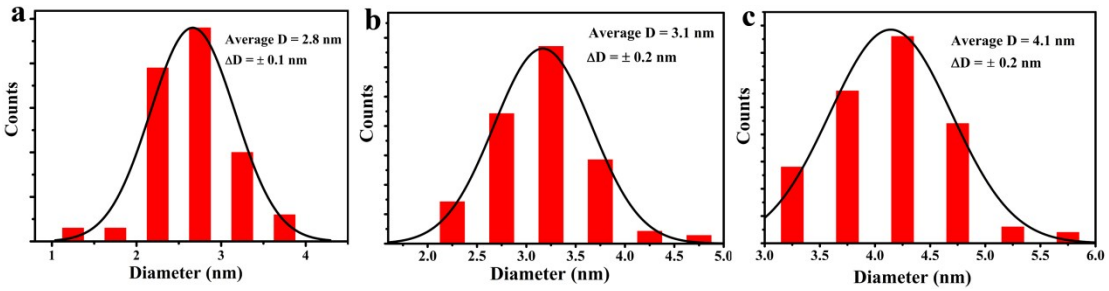

Fig. S6 The corresponding size distribution histograms for mixed halide perovskite QDs obtained by anion-exchange reactions (From a to c, $Cs_2CuCl_xBr_{4-x}$, Cs_2CuBr_4, $Cs_2CuBr_{4-x}I_x$).

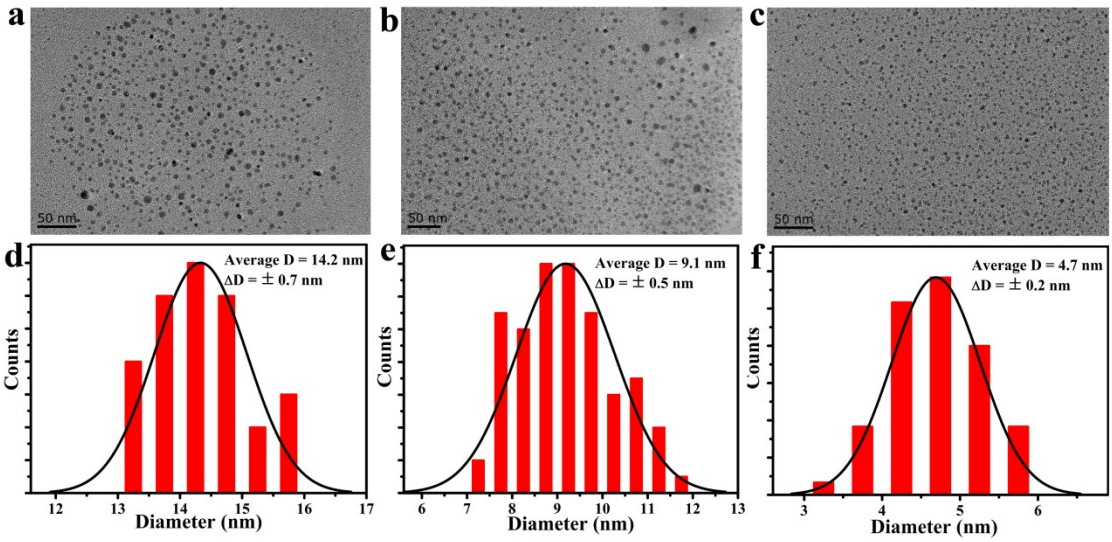

Fig. S7 TEM images and Size distribution analysis of Cs_2CuBr_4 QDs by altering the stoichiometric ratio of the precursors. (a) CsBr:$CuBr_2$ =1:4. (b) CsBr:$CuBr_2$ =1:3. (c) CsBr:$CuBr_2$ =1:2. (d)-(f) Corresponding size distribution analyses for the sample in (a)-(c), respectively.

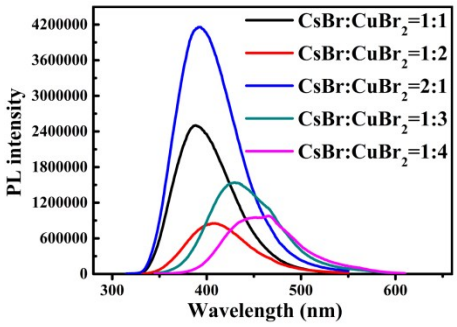

Fig. S8 PL spectra of Cs_2CuBr_4 QDs by altering the stoichiometric ratio of the CsBr and $CuBr_2$.

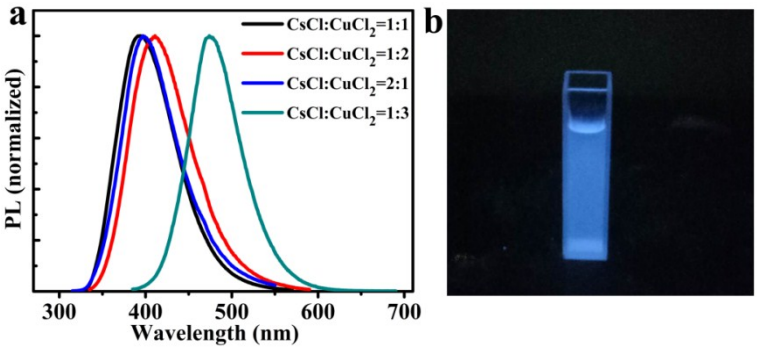

Fig. S9. (a) PL spectra of Cs_2CuCl_4 QDs by altering the stoichiometric ratio of the CsCl and $CuCl_2$. (b) Optical images of a Cs_2CuCl_4 QDs solution (CsCl/$CuCl_2$=1:3) with 365 nm UV light excitation.

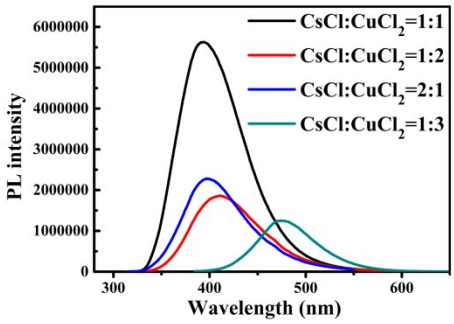

Fig. S10 PL spectra of Cs_2CuCl_4 QDs by altering the stoichiometric ratio of the CsCl and $CuCl_2$.

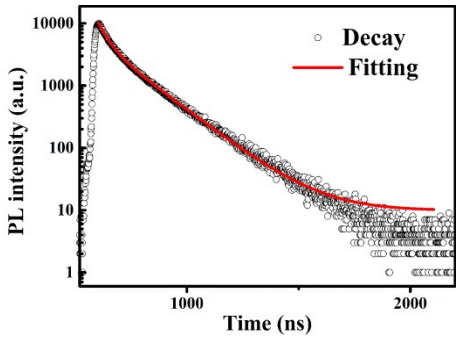

Fig. S11 Time–resolved PL decay and fitting curve of typical sample of Cs_2CuCl_4 QDs.

Table S1. Optical Parameter Comparisons of Halide Perovskite QDs.

	Emission peak(nm)	PLQY (%)	Fwhm (nm)	Temperature (°C)	Air stability	Photo stability	reference
Cs_2CuBr_4	393	37.5	74	RT	30 days (92%)	5000 min (34.2%)	This work
Cs_2CuCl_4	388	51.82	68	RT	30 days (85%)	5000 min (48%)	This work
$MA_3Bi_2Br_9$	430	12	62	RT			4
$Cs_3Bi_2Br_9$	410	19.4	48	80		78 h (80%)	5
$Cs_3Sb_2Br_9$	410	46	41	RT	35 days (70%)	108 h (50%)	3
$CsPb_xMn_{1-x}Cl_3$	579	54		170	3 months	60 min (47%)	6
$CsPbCl_3$	408	10	12	150	30 days (95%)	60 min (38%)	7
$CsSnX_3$		0.14			5 min (0.05%)		8

Reference:

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