

Supporting Information

The Preparation and Up-Conversion Properties of Full Spectrum CsPbX₃ (X = Cl, Br, I) Quantum Dots Glasses

Huiling Zhang^a, Mengfeifei Jin^a, Xiaodong Liu^a, Yaqian Zhang^a, Yanxia Yu^a, Xiaojuan Liang^a,

Weidong Xiang^{a} and Ting Wang^{b*}*

^aCollege of Chemistry and Materials Engineering, Wenzhou University, Wenzhou 325035, People's Republic of China. E-mail: xiangweidong001@126.com

^bDepartment of Applied Physics, The Hong Kong Polytechnic University, Hong Kong 999999, People's Republic of China. E-mail: wangtkm@foxmail.com

1. Experimental

1.1 Raw materials

Particular description are listed as following: B₂O₃ (99.9%), ZnO (99%), SiO₂ (AR), Cs₂CO₃ (99%), PbBr₂ (99%), PbI₂ (98%), PbCl₂ (AR), NaCl (AR, 99.5%), NaBr (AR, 99%), NaI (AR, 99.5%). All the raw materials were sourced from Aladdin and not carried out further processing.

1.2 Detail steps for synthesizing CsPbX₃ (X = Cl, Br, I) QD glasses

For the synthesis of full spectra QDs glass samples, conventional melt-quenching technique and glass crystallization methods were employed. The matrix is borosilicate glass (B-Zn-Si), and the theoretical feed molar ratios are reference the chemical equation: Cs₂CO₃ + 2 PbX₂ + 2 NaX → 2 CsPbX₃ + CO₂ + Na₂O (X = Cl, Br, I). After weighing the material, the materials were dropped into the glass mortar and grinded. Mixing uniformly ingredients are put into the alumina crucible and placed into the muffle furnace melted at 1180 °C for 130 min. Then, the melts were poured into the preheated round mold which diameter is 2 cm. The obtained glasses were annealed at 400 ~ 430 °C for 3 h to eliminate internal stress. Then, the CsPbX₃ QDs glasses were cut into thickness of 0.8 cm. After that, the as-prepared glasses pieces were annealed at suitable temperature (470~520 °C) for further glass crystallization and diversiform characterizations. As a result, CsPbX₃ nanocrystals with fluorescence emission through the entire visible range were precipitated in the borosilicate glasses matrix.

1.3 Measurements and Characterization

A Horiba Jobin Yvon Fluoromax-4P spectrofluorometer (Edinburgh, FS5) was adopted to monitor a series of PL spectra. A series of UV-Vis absorption spectra were detected using UV-vis spectrometer (PerkinElmer Lambda 750). Operated at 40 kV and 40 mA with Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$), the structure identification for glass samples were implemented using X-ray diffraction

(XRD, D8 Advance, Bruker, Germany). The images of TEM, HTEM, SAED and Mapping were captured on the FEI Tecnai G2 F20 S-TWIN with acceleration voltage of 200 kV. The XPS spectra were collected using an AXI ULTRA DLD spectrometer with a monochromator Al K α as the X-ray source.

The UC emission data of CsPbX₃ (X = Cl, Br, I and mixed halogens systems) QDs glasses were excited by 800 nm femtosecond (fs) pulsed laser. Here, a Ti: sapphire laser (coherent Libra) and optical parametric amplifier (Coherent OperA Solo) were used as the excitation sources to generate the 800 nm fs pulses (1k Hz) lasing. The laser beam with a diameter of 8 mm was focused on the QDs glasses surface by a convex lens of 10 cm focal lens. The emitted light from the QDs glasses surface was collected by an optical fiber (600 μ m in diameter). And the optical fiber was coupled to a spectrum analyzer (Ocean Optics USB 2000+VIS-NIR). In term of the UC spectra measurement at low-temperature (i.e., varies from 77 to 300 K), the laser beam was focused on the QDs glasses surface, which was located inside a low temperature chamber (Linkam DSC 600 temperature-controlled stage) purged with N₂ gas.

2. Support images

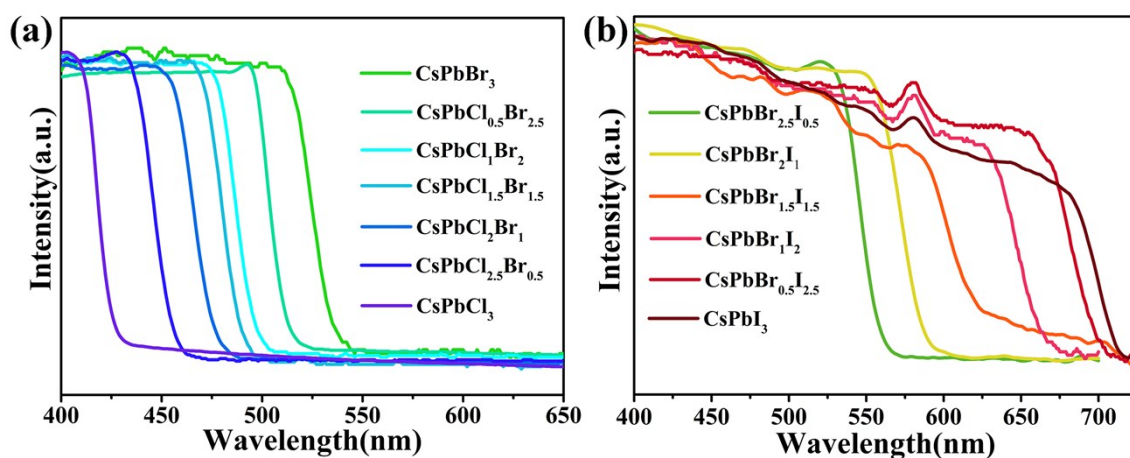


Fig. S1 Absorption spectra of (a) CsPbCl_{3-x}Br_x (x = 0, 0.5, 1, 1.5, 2, 2.5, 3) QDs glasses, and (b) CsPbBr_{3-y}I_y (y = 0.5, 1, 1.5, 2, 2.5, 3) QDs glasses.

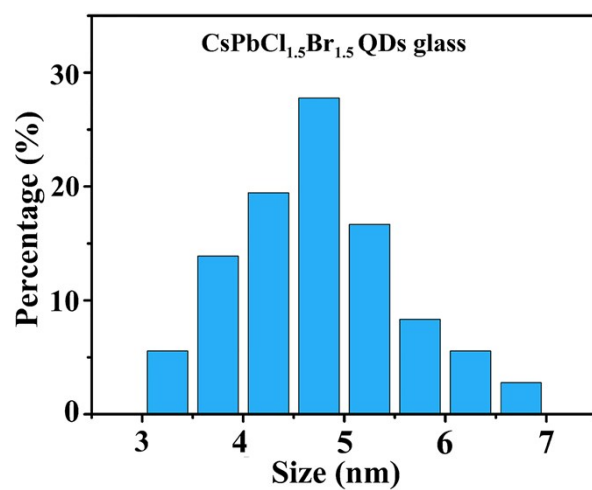


Fig. S2 The size distribution of the CsPbCl_{1.5}Br_{1.5} QDs glass.

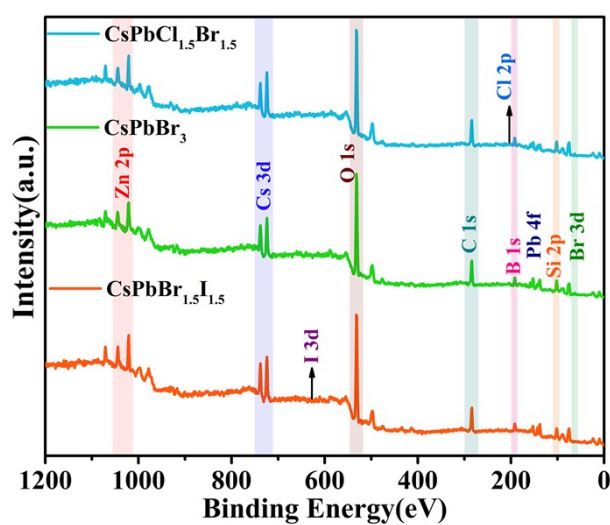


Fig. S3 Full XPS scan spectra of CsPbCl_{1.5}Br_{1.5}, CsPbBr₃ and CsPbBr_{1.5}I_{1.5} QDs glasses.

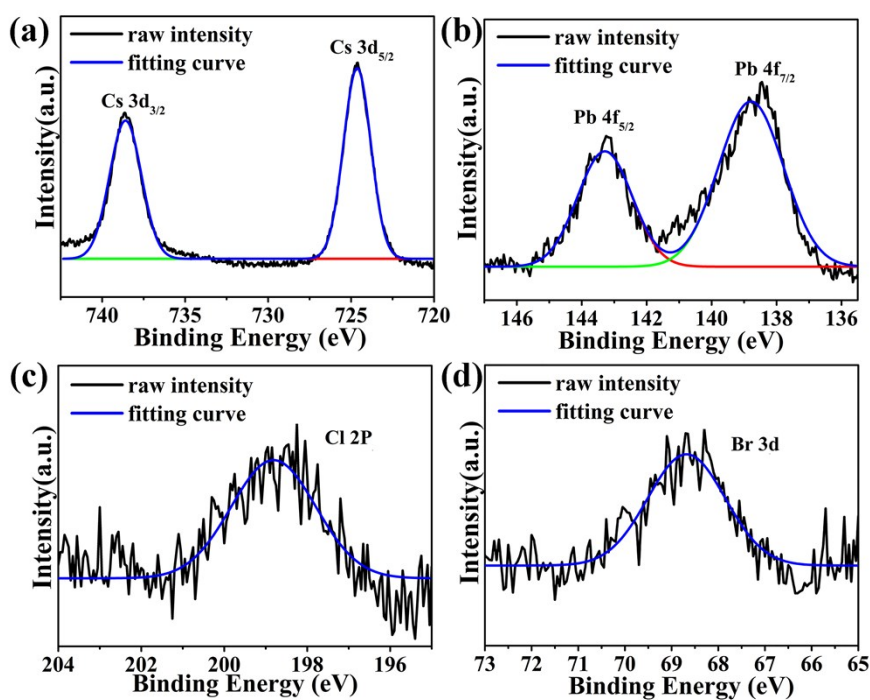


Fig. S4 High-resolution XPS spectra of (a) Cs 3d, (b) Pb 4f, (c) Cl 2P and (d) Br 3d for CsPbCl_{1.5}Br_{1.5} QDs glass.

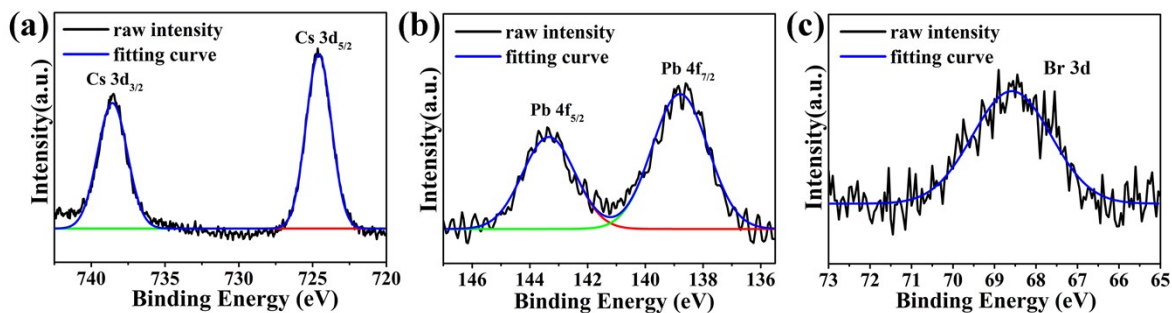


Fig. S5 High-resolution XPS spectra of (a) Cs 3d, (b) Pb 4f and (c) Br 3d for CsPbBr₃ QDs glass.

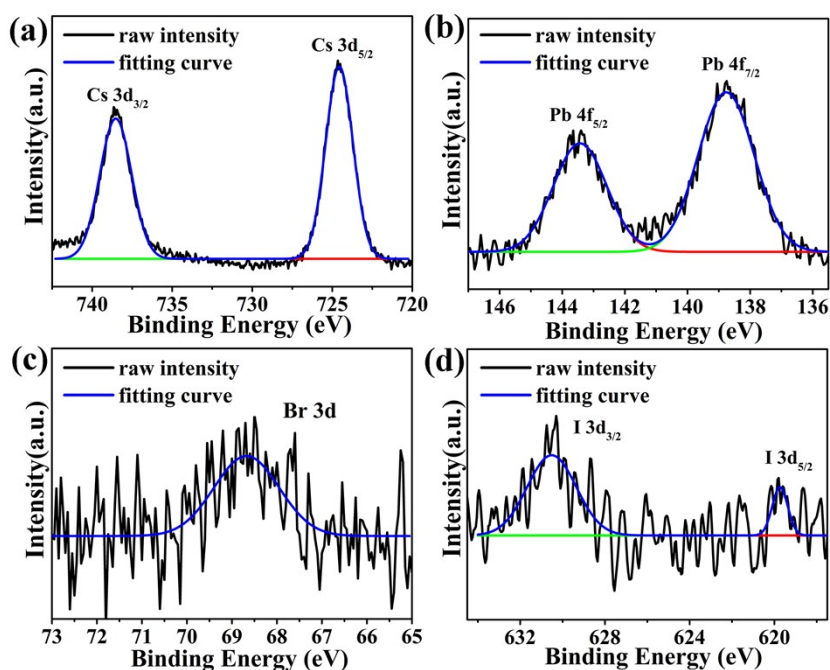


Fig. S6 High-resolution XPS spectra of (a) Cs 3d, (b) Pb 4f, (c) Br 3d and (d) I 3d for CsPbBr_{1.5}I_{1.5} QDs glass.

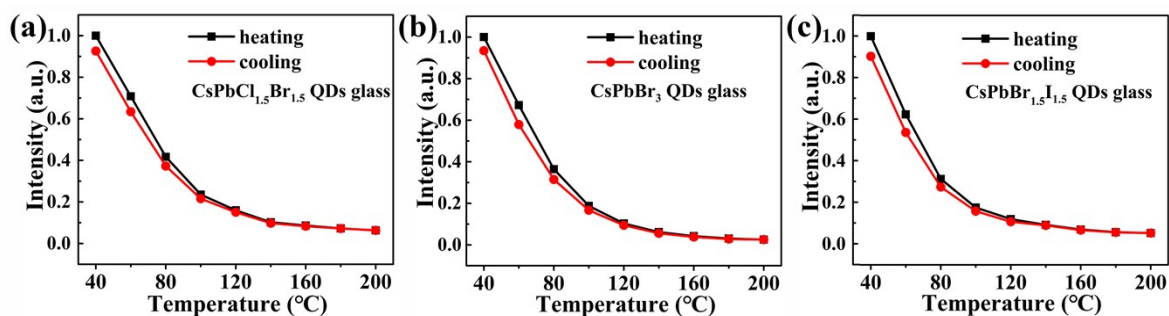


Fig. S7 The spectra of integral emission intensities of (a) CsPbCl_{1.5}Br_{1.5}, (b) CsPbBr₃, and (c) CsPbBr_{1.5}I_{1.5} QDs glasses recorded from the heating and cooling cycles. The excitation wavelengths are consistent with the PL spectra in Fig. 1e-f. Although the CsPbCl_{1.5}Br_{1.5}, CsPbBr₃, and CsPbBr_{1.5}I_{1.5} QDs glasses have experienced a 40 ~ 200 °C heating and cooling cycles process, the emission intensity of all the QDs glasses maintain nearly 90% of the original intensity.

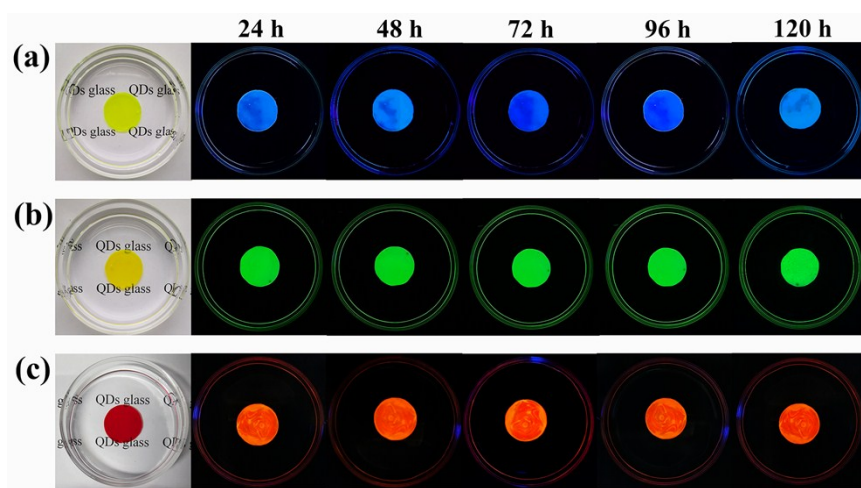


Fig. S8 The luminescent photographs of (a) CsPbCl_{1.5}Br_{1.5}, (b) CsPbBr₃, and (c) CsPbBr_{1.5}I_{1.5} QDs glasses immersed in the water under the UV lamps excitation ($\lambda_{\text{ex}} = 365 \text{ nm}$). The left photographs are the corresponding QDs glasses under the sunlight. This can demonstrate that the CsPbCl_{1.5}Br_{1.5}, CsPbBr₃, and CsPbBr_{1.5}I_{1.5} QDs glasses can maintain high brightness color for 120 h.

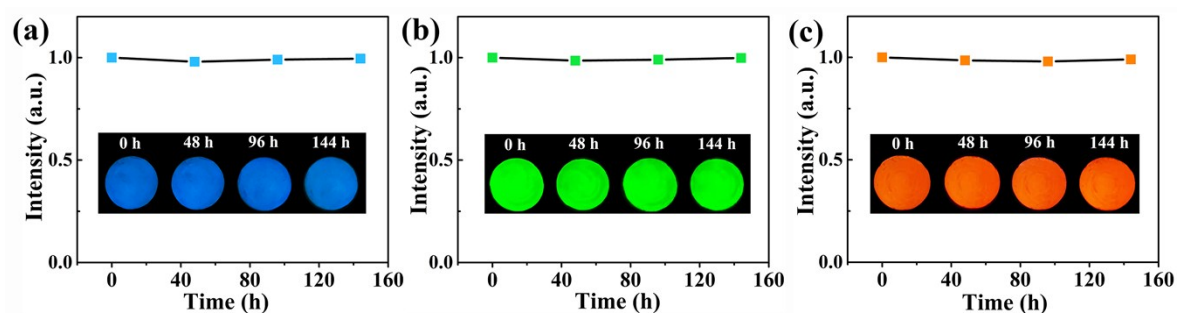


Fig. S9 The luminescent photographs of (a) CsPbCl_{1.5}Br_{1.5}, (b) CsPbBr₃, and (c) CsPbBr_{1.5}I_{1.5} QDs glasses exposed under the UV lamps excitation ($\lambda_{\text{ex}} = 365 \text{ nm}$). The left photographs are the corresponding QDs glasses under the sunlight. By prolonging the irradiation time, there are no obvious changes for their brightness.

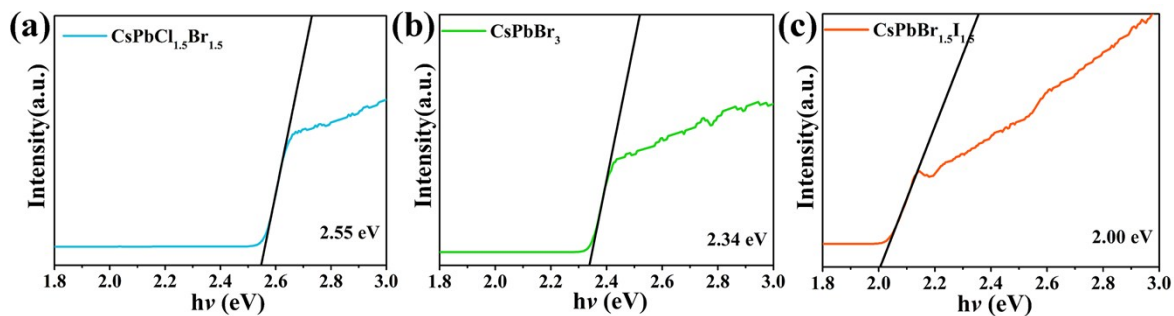


Fig. S10 Band gap spectra of (a) CsPbCl_{1.5}Br_{1.5}, (b) CsPbBr₃, and (c) CsPbBr_{1.5}I_{1.5} QDs glasses.

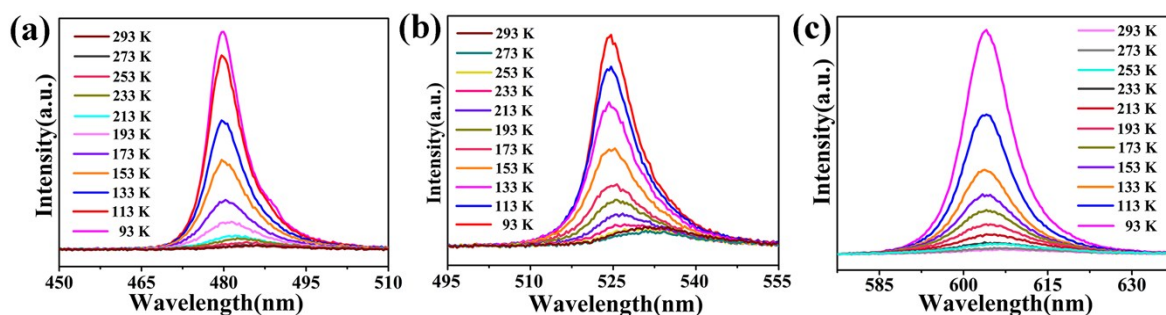


Fig. S11 Emission spectra of (a) CsPbCl_{1.5}Br_{1.5}, (b) CsPbBr₃ and (c) CsPbBr_{1.5}I_{1.5} QDs glasses recorded at various temperature under the excitation of 800 nm laser pump. The pump density is 0.398 mJ/cm².

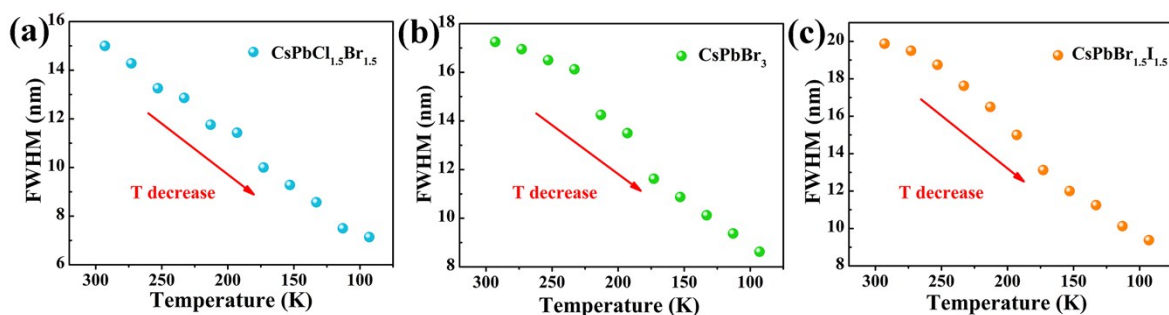


Fig. S12 Temperature dependent FWHM spectra for (a) CsPbCl_{1.5}Br_{1.5}, (b) CsPbBr₃ and (c) CsPbBr_{1.5}I_{1.5} QDs glasses. The FWHM turn to narrow with the temperature decrease for all the samples.

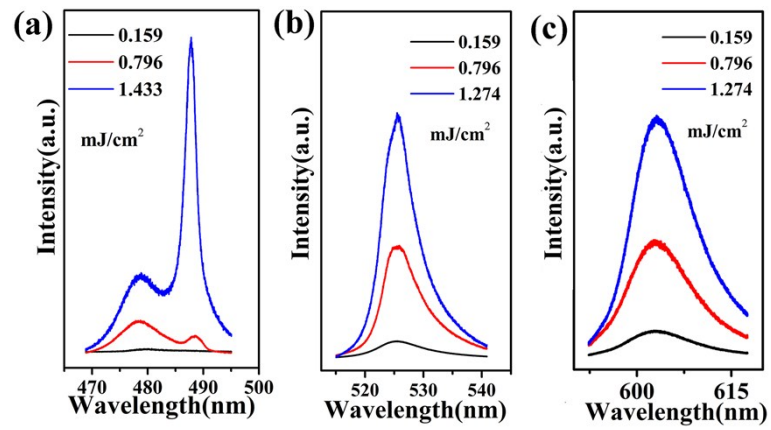


Fig. S13 UC Emission spectra of **(a)** CsPbCl_{1.5}Br_{1.5}, **(b)** CsPbBr₃ and **(c)** CsPbBr_{1.5}I_{1.5} QDs glasses under the excitation of 800 nm fs laser versus pump intensity. The spectra are all measured at 93 K. Compared to the other samples, CsPbCl_{1.5}Br_{1.5} QDs glass emerges ASE more easily.