

Electronic Supplementary Information

Size-tunable CsPbBr₃ Perovskite Rings Array for Lasing

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Experimental Section

Materials: Monodisperse polystyrene spheres (2.5wt%, Aladdin), PbBr₂ (lead (II) bromide 99%, Aladdin), PbCl₂ (lead (II) chloride 99.99%, Aladdin), PbI₂ (lead (II) iodine 99.99%, Aladdin), CsBr (cesium bromide 99.5%, Macklin), Dimethyl sulfoxide (DMSO) (>99.5%, Sinopharm Chemical Reagent Co., Ltd), Toluene (99.5%, Sinopharm Chemical Reagent Co., Ltd), Rhodamine 6G (95%, Aladdin).

Preparation of 2D colloidal crystals template: Ordinary glass or silicon substrates were first ultrasonically cleaned in turn with acetone, ethanol, 3:1 98% H₂SO₄/H₂O₂, and distilled water, each step for 1h. A drop (~20μL) of the polystyrene (PS) spheres suspension was pipetted onto a glass or silicon substrates (1.5cm × 1.5cm) in a spin coater. Then a large area (more than 1 cm²) of 2D colloidal crystals was synthesized with the spin-coating method. The pinning speed was 60rpm for 8μm spheres, 50rpm for 15μm and 40rpm for 25μm spheres.

Preparation of perovskite ring arrays: PS spheres 2D colloidal crystals was chosen as the original template. As the first step, the as-prepared 2D colloidal crystals on substrate were put on hot stage and kept at a certain temperature for a certain time. The 2D colloidal crystals bounded to the substrate, and plane contacts were formed between the spheres and the substrate. A perovskite precursor solution (0.2mol/L), which was prepared by dissolving CsBr

and PbBr_2 with a molar ratio of 1:1 in DMSO, was spin-coated onto the annealed substrate at 5000rpm for 30s, which was then dried at room temperature for 4h by placing horizontally in a vacuum oven. Afterward, the sample was immersed into toluene for 5min to remove the PS spheres. Finally, the substrate was annealed at 150°C for another 1h to ensure complete crystallization of the CsPbBr_3 perovskite, resulting in highly crystalline and uniform CsPbBr_3 ring arrays. The ring size could be easily tuned by the annealing time and annealing temperature of the 2D colloidal crystals.

Characterization: Photoluminescence (PL) spectra were recorded with a Shimadzu RF-5301 PC spectrofluorometer. The excitation wavelength was set as 350 nm. Micrographs were recorded by three-dimensional digital microscope (HIROX Co., Ltd. Made in Japan). Atomic force microscope (AFM) was performed with Bruker bioscope. Environmental scanning electron microscope (ESEM) was recorded by FEI Quanta200 with an acceleration voltage of 7kV equipped with an energy dispersive X-ray analysis (EDS) analyzer. X-ray powder diffraction (XRD) investigation was carried out by using the Bruker d8 advance. The ultrafast pump pulses were from a femtosecond laser (Legend-F-1k, Coherent, 1 kHz, 100 fs). The optical wavelength of 400 nm was obtained by doubling the fundamental wavelength in a β -barium borate (BBO) crystal. For the biexciton dynamics measurements, emission was detected and analyzed by a streak camera (C5680, Hamamatsu) with optimized temporal resolution of ~ 10 ps.

Figure S1: Top view micrographs of 2D colloidal crystals. The diameter of PS spheres are $8\mu\text{m}$ (a) and $25\mu\text{m}$ (b).

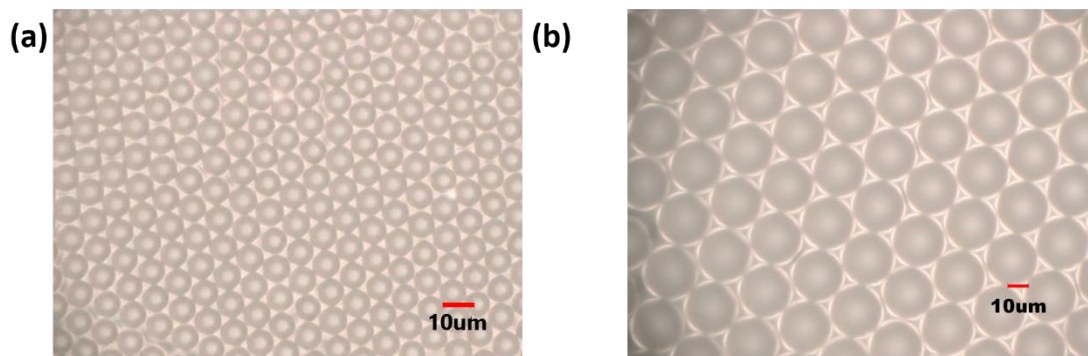
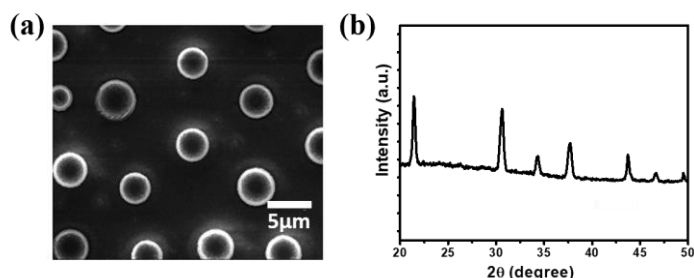


Figure S2. ESEM image (a) and the corresponding XRD patterns (b) of CsPbBr₃ perovskite ring prepared by a new precursor solution (0.2mol/L) according to ref 3. The detail process including the following steps: First the PbBr₂ powder was dissolved in a HBr to form a pale yellow solution. Then, the CsBr aqueous solution was added dropwise to PbBr₂-HBr solution leading to CsPbBr₃ precipitates. After centrifuging, washing and drying, as-prepared CsPbBr₃ was redissolved into DMSO as the new precursor solution, which is used for preparing rings array.



According to the reference viewpoint,^[3] when the mixture of CsBr and PbBr₂ is used as the precursor, the limited solubility of CsBr in DMSO will affect the formation of perovskites. Similarly, the evaporation of DMSO in our work can also lead to the precipitation of CsBr first before the final formation of perovskites. A proof is the appearance of diffraction peak at 29.3° in XRD patterns (Figure 2h), which is assigned to (110) for CsBr crystal (PDF#05-0588). In the case of small PS template, the larger strain for small rings makes it more difficult to form uniform annular CsBr. This should be the reason for the larger roughness and obvious grain boundaries of perovskite rings at small size. To overcome this problem, we have tried to improve the precursor composition before DMSO evaporation. Following the reference method,^[3] we first prepared CsPbBr₃ by equal moles of CsBr and PbBr₂ in solution, then as-prepared CsPbBr₃ were redissolved into DMSO to obtain a new precursor solution. According to reference viewpoint,^[4] the actual present state in this case is highly soluble Cs⁺ and PbX₆⁴⁻ ions. As a result, the problem of preferential precipitation of CsBr can be avoided

in the new precursor solution (as confirmed by no CsBr diffraction peaks at 29.3° in XRD pattern in Figure S2b). By using this new precursor, as-prepared small rings are smooth in Figure S2a.

XRD pattern of the small rings with much smoother surface (Figure S2b) show similar diffraction patterns to that in Figure 2h except less obvious diffraction peaks between 20 to 30 degrees. Interesting, this phenomenon is also observed in the case of large rings which have much smoother surface (Figure 2h). It indicates that the less obvious diffraction peaks between 20 to 30 degrees are more likely induced by the disappeared grains boundaries rather than by the increased ring size. Note that the diffraction peaks at 21.4° , 24.1° , 25.2° , 26.5° , and 28.5° in XRD pattern of Figure 2h can good match to the standard XRD line of monoclinic CsPbBr_3 (PDF#18-0364). The diffraction peak at 29.3° is assigned to (110) for CsBr crystal (PDF#05-0588).

Figure S3: EDAX of the CsPbBr₃ ring prepared on glass substrate. The inset is the ESEM image of ring and the percentage of corresponding elements, of which Cs, Pb and Br were from the ring, Au from the gold plating and others from the glass substrate and residual polystyrene.

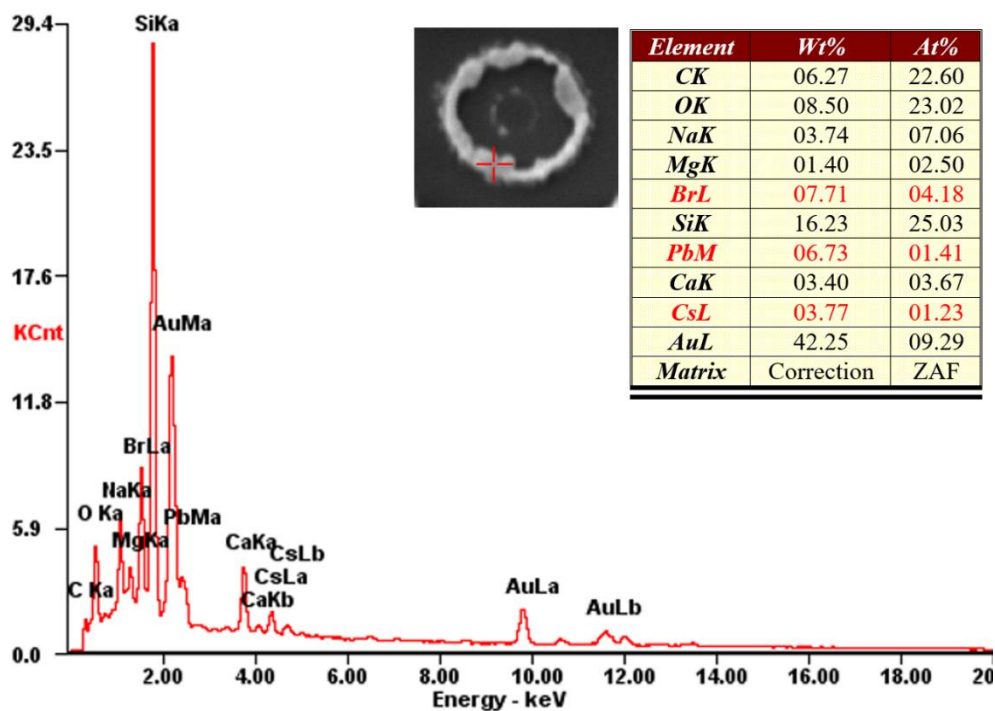


Figure S4. (a) Environmental scanning electron microscope (ESEM) image and (b-f) mapping results of CsPbBr₃ perovskite ring (2.6μm).

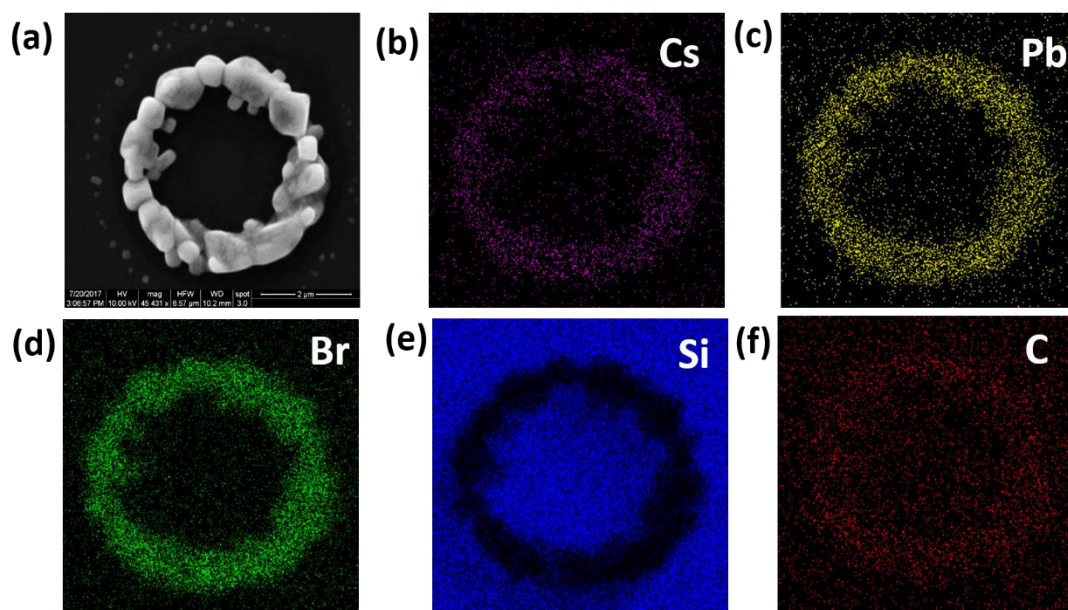
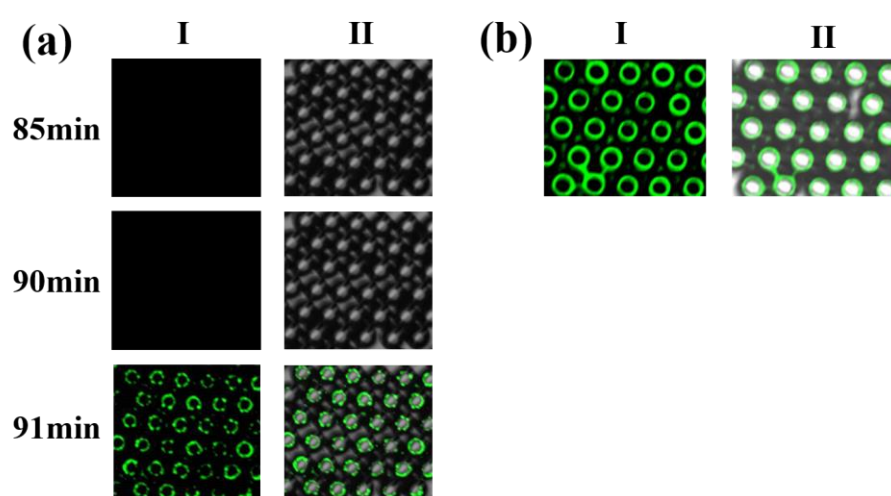


Figure S5. The CLSM images at different drying time after spin-coating the perovskite precursor solution on 2D PS spheres colloidal crystals template. The excitation laser was 488nm and photons with wavelengths ranging from 500-550nm were collected. (a) The drying process of solvent was carried out at 25 °C in the open air and (b) vacuum environment. The images in the column I is the emission of perovskites (500-550nm). Column II show the integrating images of both template spheres under bright field and the emission of perovskites under dark field with 488nm excitation and 500-550nm collection..



From CLSM result, we cannot see the evaporation of DMSO due to no emission of the precursor for perovskite. Once the emission of perovskite appears, the ring like structure is formed. We found the emission of perovskite appears quite quickly (just few second from no emission to bright emission). It is hardly to capture the intermediate states. Thus, the dynamic process of nucleation and growth of perovskite cannot be observed from CLSM. However, according to the integrating the image of template spheres and the emission of perovskites in Figure S5, it is no doubt the formation of perovskite around the template spheres.

The reason why perovskite emission appears so suddenly can be easily comprehended. The evaporation of DMSO occurs first in the void space of template spheres, and then the residue DMSO around template spheres will finally be evaporated (as confirmed by dewetting process of rhodamine 6G in DMSO in Figure 4). As for perovskite, the CLSM results suggest

that the emission of perovskite appears only at the second state (namely the evaporation of residue DMSO around template spheres). This can explain why perovskite emission appears suddenly with a ring-like structure.

Figure S6: Micrographs of CsPbBr₃ rings prepared at different crystallization temperature.

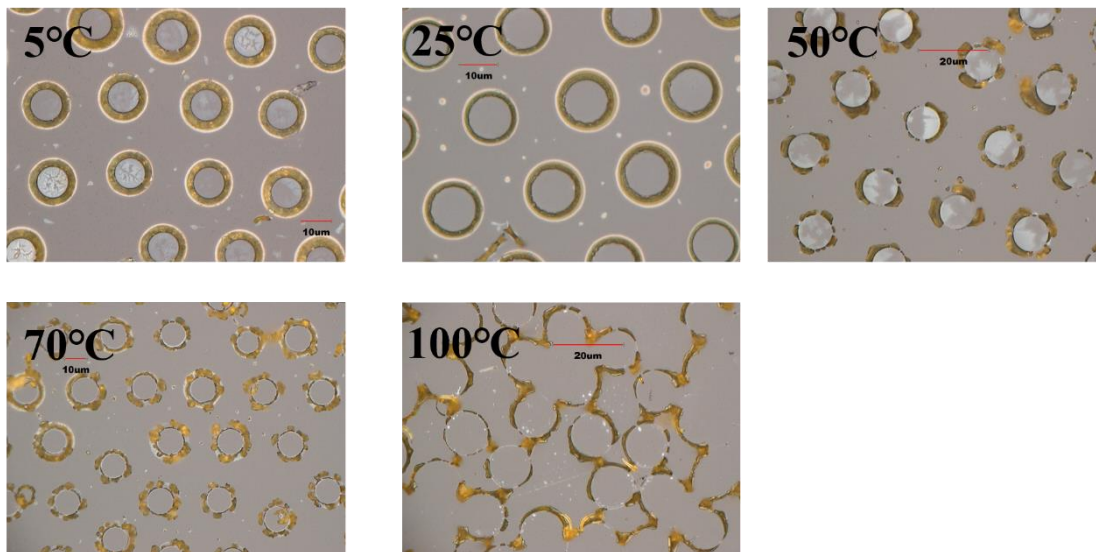


Figure S7: CsPbBr₃ rings inner diameter statistics (black, red, blue line) based on 8 μ m PS spheres template with different annealing temperature (100 $^{\circ}$ C, 105 $^{\circ}$ C, 110 $^{\circ}$ C) and annealing time (0-10min, 0-3h, 0-21h).

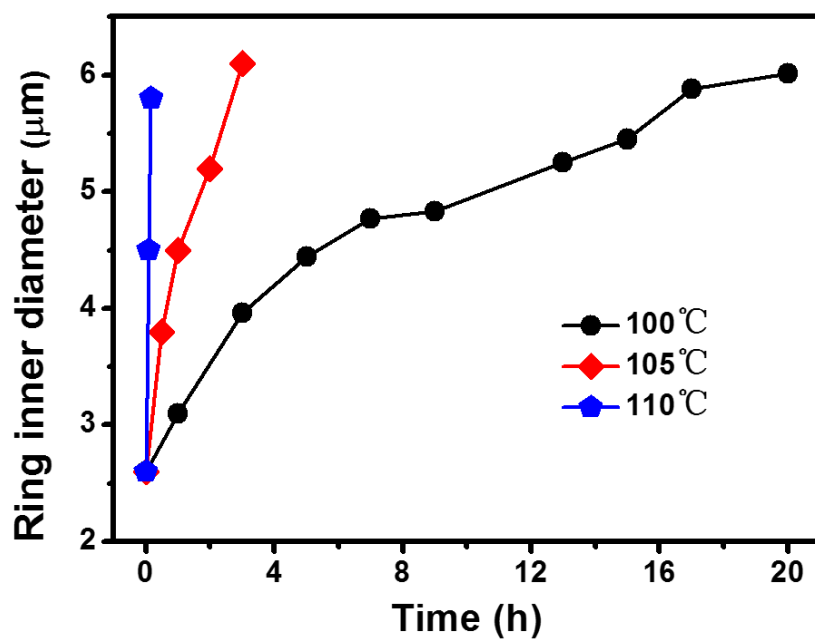
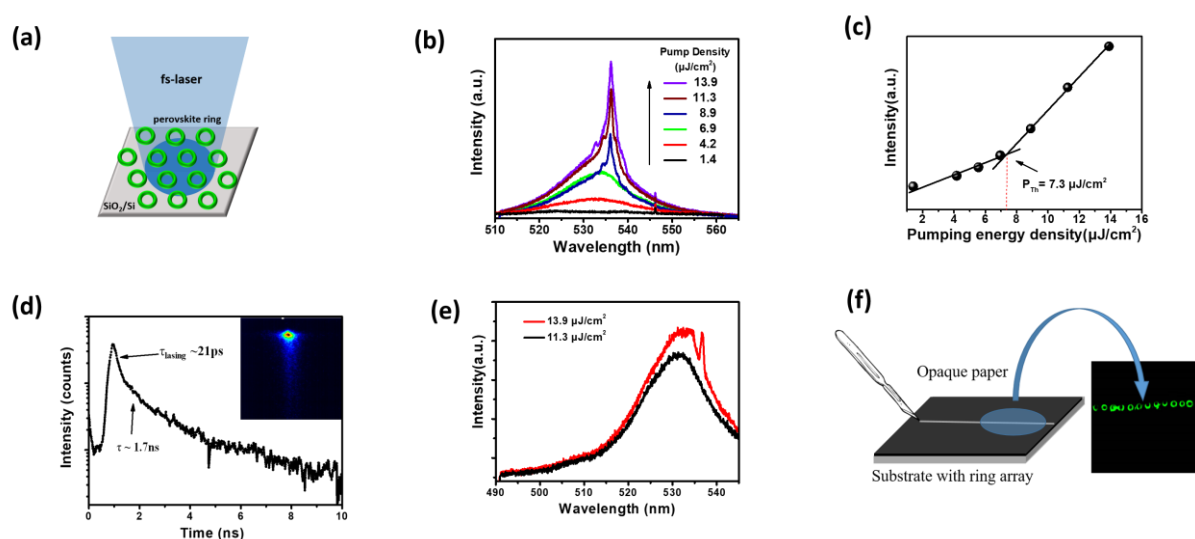


Figure S8. (a) Scheme of CsPbBr₃ rings on Si/SiO₂ substrate pumped by 400nm pulsed laser. (b) Emission spectra of the CsPbBr₃ rings (9.8μm) at different pump densities. (c) The emission intensity versus pump density, showing the lasing threshold at 7.3μJ/cm². CsPbBr₃ rings with rings inner diameter of 9.8μm were used. (d) PL decay traces of perovskite rings. The inset is the corresponding streak-camera images monitored at an excitation wavelength of 400nm. (e) Emission spectra of the CsPbBr₃ rings (2.6μm) at different pump densities. (f) Scheme the demonstration experiment (left); CLSM image of the CsPbBr₃ ring arrays observed from the slit, here showing the symbol “—” (right).



A beam of 400nm femtosecond pulsed laser served as the uniform pump source to excite perovskite ring(Figure S8a). (The laser source used to excite perovskite rings was a Ti: sapphire oscillator/amplifier and a SHG system (model Mira900-F and Legend from Coherent), which produced ~150fs duration, 400nm wavelength laser output with a repetition rate of 1kHz.) The typical emission spectra from CsPbBr₃ rings with inner diameter of 9.8μm at different excitation powers are shown in Figure S8b. The CsPbBr₃ rings exhibit a broad spontaneous emission with a peak centered at 534nm and a full-width at half-maximum (FWHM) of ~15nm below the threshold pump density of 7.3μJ/cm² (Figure S8c). With the increase of input power, the cavity modes at 536nm emerge and grow rapidly. In particular,

the peak shows narrower FWHM of 2nm than that of spontaneous emission, validating the lasing oscillation behavior of perovskite rings. Compare to 9.8 μm perovskite rings, CsPbBr₃ rings with inner diameter of 2.6 μm show higher threshold (Figure S8e) and lower PL intensity due to the relatively rough and irregular boundary. The lifetime τ can be obtained through the decay curves. For excitation intensity of far below the threshold ($\sim 2\mu\text{J}/\text{cm}^2$), the PL decay trace follows the single exponential decay ($\sim 1.8\text{ns}$)(Figure S10). Above the threshold ($\sim 15\mu\text{J}/\text{cm}^2$), the PL decay time of CsPbBr₃ rings collapses to $\sim 21\text{ps}$ (Figure S8e), which further demonstrates the transition from spontaneous emission to stimulated emission. Notably, the number of resonance mode can be tuned by controlling the diameter of CsPbBr₃ rings. As the inner diameter of the ring increases, the laser changes from single mode to multimode, while the mode spacing decreases. The mode spacing in the WGM oscillation cavity is predicted by the relationship $\Delta\lambda = \lambda^2/2\pi Rn$, where R is the outer radius of ring, $\Delta\lambda$ is the mode spacing and n is effective refractive index at wavelength of λ .^[1] Therefore, for a fixed λ , $\Delta\lambda$ should scale proportionally to 1/R. This behavior is illustrated in Figure S9. The fit line between $\Delta\lambda$ and 1/R, suggests WGM mode lasing in these perovskite ring cavities.

In addition, the recent reference work has demonstrated that the pixelated array of perovskites can be used as multielement emitter array in the field of high brightness displays.^[2] When a MEMS mirror is equipped on the pump laser, the pixelated perovskite array shows specific patterns or images. In order to demonstrate the possibility of CsPbBr₃ ring arrays applied in displays, a demonstration test was carried. As shown in Figure S6f, CLSM image of the CsPbBr₃ ring arrays observed from the slit show the symbol “—”. It suggests that the perovskite arrays have the potential to be applied to high brightness displays. We also look forward to the current perovskite ring arrays in similar projection display applications in future.

Figure S9. (a) The emission spectra of the CsPbBr₃ rings with different outer radius and (b) the changing trend of mode spacing.

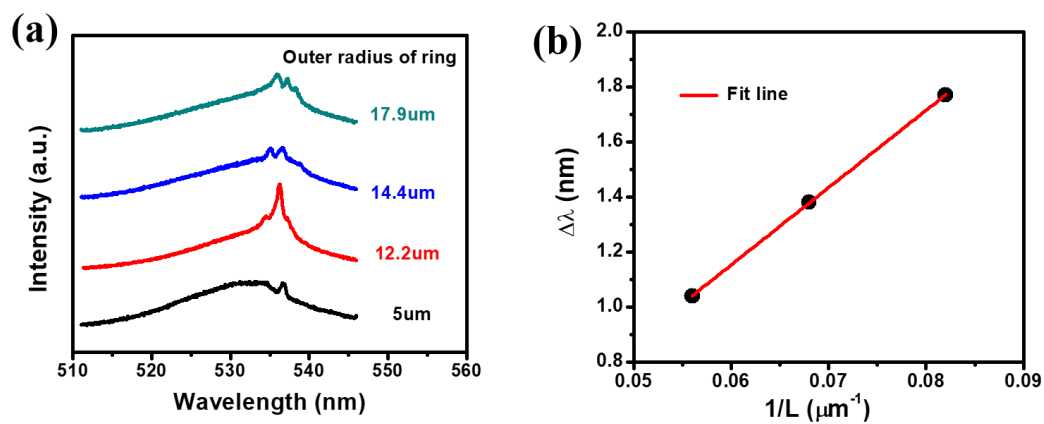
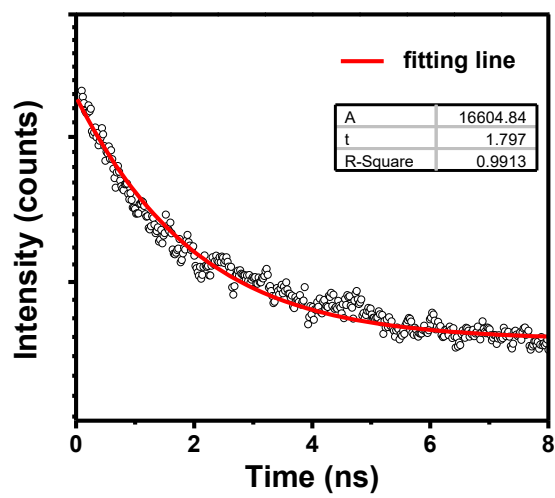


Figure S10. The PL decay traces of perovskite rings at low excitation ($\sim 2\mu\text{J}/\text{cm}^2$).



References

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