Supplementary Information (SI) for Journal of Materials Chemistry C.

Mesoporous Silica-Coated $CsPbBr_3$:$ZnBr_2$:NaBr Nanocrystals with High Photoluminescence and Tunable Wavelength for micro light-emitting diodes

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Experimental Section

Materials. Cesium bromide (CsBr, 99.5%), lead bromide ($PbBr_2$, 99%), Zinc bromide ($ZnBr_2$, AR), Hexadecyl trimethyl ammonium bromide (CTAB, 99%), Polyethylene-polypropylene glycol (F127), Sodium Hydroxide Solution (NaOH, 10N) were purchased from Macklin. Caesium carbonate (Cs_2CO_3, 99 %), oleylamine (OAm,80%-90%) were purchased from Aladdin. 1-Octadecene (ODE, 90%), Oleic acid (OA, 90%) were purchased from Alfa Aesar. Ethanol (AR) was purchased from Xilong Scientific. Tetraethyl orthosilicate (TEOS, AR), Potassium carbonate (K_2CO_3, AR), Hydrochloric acid (HCl, AR) were purchased from Sinopharm Chemical Reagent. All the chemicals were used without further purification.

Preparation of MSNs in a two-step process. Dissolve cetyltrimethylammonium bromide (CTAB, 1.00g) and F127 (100mg) in 480 mL of ultrapure water and stir in an 80 °C water bath for 20 minutes. Add ammonium fluoride (NH_4F, 0.9g) to the above solution and stir at 80 °C for 20 minutes. Then, a two-step method is used to add TEOS solution dropwise. The first step is to add 1.0 mL of TEOS and 20 mL of ethanol mixed solution, and stir in an 80 °C water bath for 8 hours. The second step is to add 4.0 mL of TEOS and 20 mL of ethanol mixed solution, and stir in an 80 °C water bath for 5 hours. Then add 3.0 mL of NaOH (2M) solution and stir in an 80 °C water bath for 1 hour. Centrifuge at 1000 rad/min for 5 minutes to remove bottom solids, then centrifuge at 11000 rad/min for 20 minutes to collect solids, and dry at 80 °C. Put the dried solid into 30mL of ultrapure water and 30mL of acidic ethanol solution, stir at room temperature for 4 hours, and dry at 80 °C. Finally, place the synthesized solid in a muffle furnace and calcine at 550 °C for 6 hours.

Preparation of MSNs in a one-step process and synthesis of colloidal $CsPbBr_3$ NCs. MSNs were synthesized in a one-step process and colloidal $CsPbBr_3$ NCs were all synthesized according to Li's work[1, 2].

Preparation of $CsPbBr_3$:$ZnBr_2$@MSNs NCs. 0.075 mmol of CsBr and 0.075 mmol of $PbBr_2$ were added to 50mL of ultrapure water, sonicated for 5 minutes, and stirred at 80 °C for 20 minutes until clear. Then add 119.3 mg of MSNs (pre-dispersed in 20 mL of ultrapure water and sonicated for 10 minutes), and stir at 80 °C for 20 minutes. Add 0.20mL, 0.25 mL, 0.30mL, 0.35mL and 0.40mL of $ZnBr_2$ (0.3M) solution and stir at 80 °C for 20 minutes. Finally, add 0.25 mL of K_2CO_3 (0.3M) solution. Stir the mixture continuously at 80 °C until dry. After grinding the collected mixture, it is placed in a muffle furnace and calcined at the set temperature (maintained at 450 °C for 300 minutes, 600 °C for 30 minutes, with a heating rate of 5 °C/min). Cool to room temperature, grind the sample and wash several times with ultrapure water. Finally, dry at 80 °C to obtain the sample.

Preparation of $CsPbBr_3$:$ZnBr_2$:NaBr@MSNs NCs. Similar to the preparation of $CsPbBr_3$:$ZnBr_2$@MSNs NCs, the difference lies in that adding the different amount of NaBr (0.3M) solution before adding the K_2CO_3 (0.3M).

Preparation of $CsPbBr_3$:$ZnBr_2$:NaBr@MSNs photoresist ink. 30 mg of $CsPbBr_3$:$ZnBr_2$:NaBr@MSNs powder was added to 5 mL of ethanol and sonicated for 1 hour. The solution was centrifuged and the supernatant was extracted to obtain a uniformly dispersed $CsPbBr_3$:$ZnBr_2$:NaBr@MSNs solution. Take 0.5 mL of the homogeneously dispersed $CsPbBr_3$:$ZnBr_2$:NaBr@MSNs solution and add 1 mL of photoresist (SU-8 2002), and magnetically stir for 1 h. The homogeneously dispersed $CsPbBr_3$:$ZnBr_2$:NaBr@MSNs ink was obtained.

Preparation of ink films. $CsPbBr_3$:$ZnBr_2$:NaBr@MSNs NCs inks were rotationally coated onto 1-inch glass substrates by a process of 1500 rpm for 20 seconds. After rotational coating, the films were baked at 90°C for 90 seconds. Then, the films were exposed to 365 nm UV radiation and immediately baked at 90°C for 90 s.

Preparation of the μ-LED conversion pattern. $CsPbBr_3$:$ZnBr_2$:NaBr@MSNs NCs inks were rotationally coated onto 1-inch glass substrates by a process of 1500 rpm for 20 seconds. After rotational coating, the films were baked at 90°C for 90 seconds. The films were then exposed to 365 nm UV radiation under a customized mask for 30 s , and immediately baked again at 95°C for 90 s. The films were then developed for 2 min (immersed in MicroChem's SU-8 developer) and rinsed with an isopropyl alcohol solution.

Characterizations. XRD patterns of NCs were recorded by a powder diffractometer (Smart Lab 3KW) using Cu-K_a radiation (λ=0.154 nm). Microstructures of all the prepared samples were studied using a scanning electron microscope (SEM, J ZEISS Sigma 500). The sizes and morphologies of $CsPbBr_{3:}ZnBr_2$@MSNs samples were investigated via a transmission electron microscope (TEM, FEI Talos F200s). The high-angle annual dark-field scanning transmission electron microscopy (HAADF-STEM) observations were carried out on a FEI aberration-corrected Titan Cubed S-Twin transmission electron microscope equipped with an energy dispersive X-ray spectroscope (EDS) operated at 200 kV. TEM and STEM specimens were prepared by directly dropping a water dispersion solution of $CsPbBr_3$:$ZnBr_2$@MSNs on a carbon coated copper grid. PL spectra and time-resolved spectra were recorded on an Edinburgh Instruments FLS1000 spectrofluor ometer equipped with a 450 W xenon lamp and a 375 nm picosecond laser. PLQY, defined as the ratio of emitted photons to absorbed ones, was determined with a spectrofluorometer (FLS1000) equipped with a xenon lamp as the excitation source and a 15 cm integrating sphere.

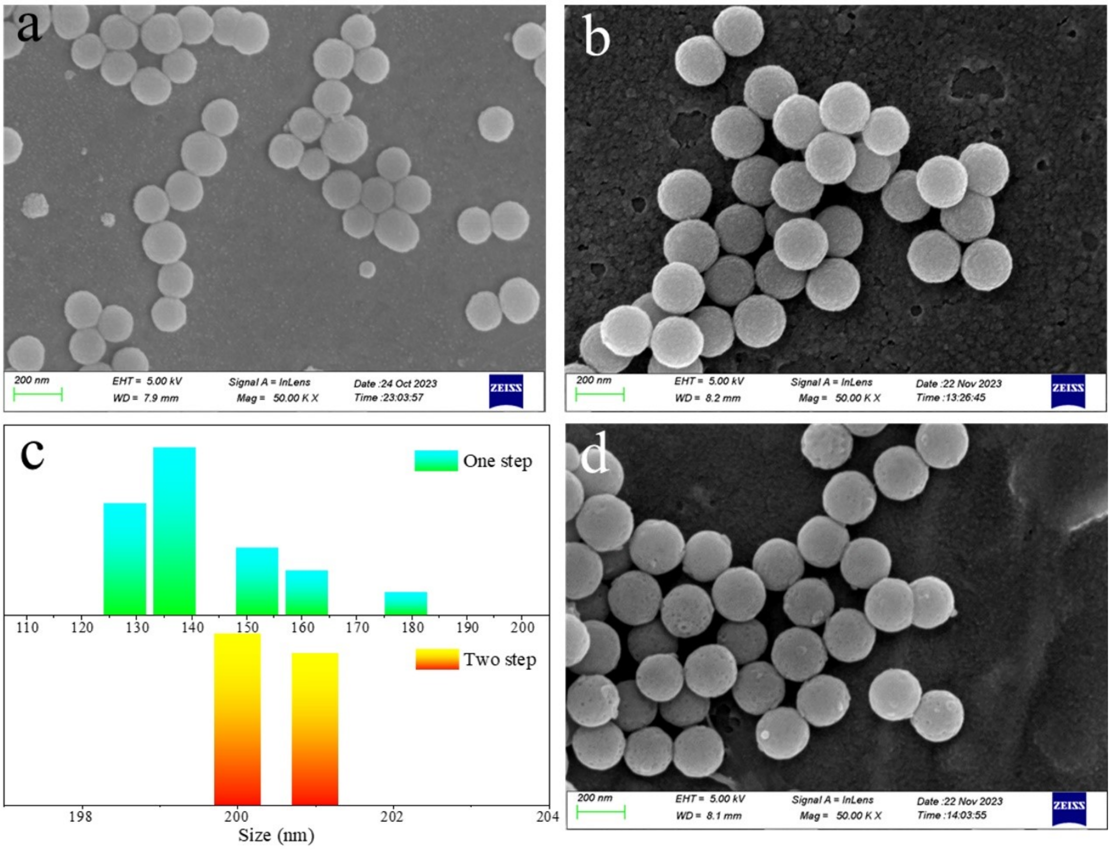

Figure S1. SEM image of MSNs prepared (a) by one-step method and (b) two-step method. (c) A comparison of the sizes of MSNs produced by the two approaches. (d) SEM picture of $CsPbBr_3$@MSNs.

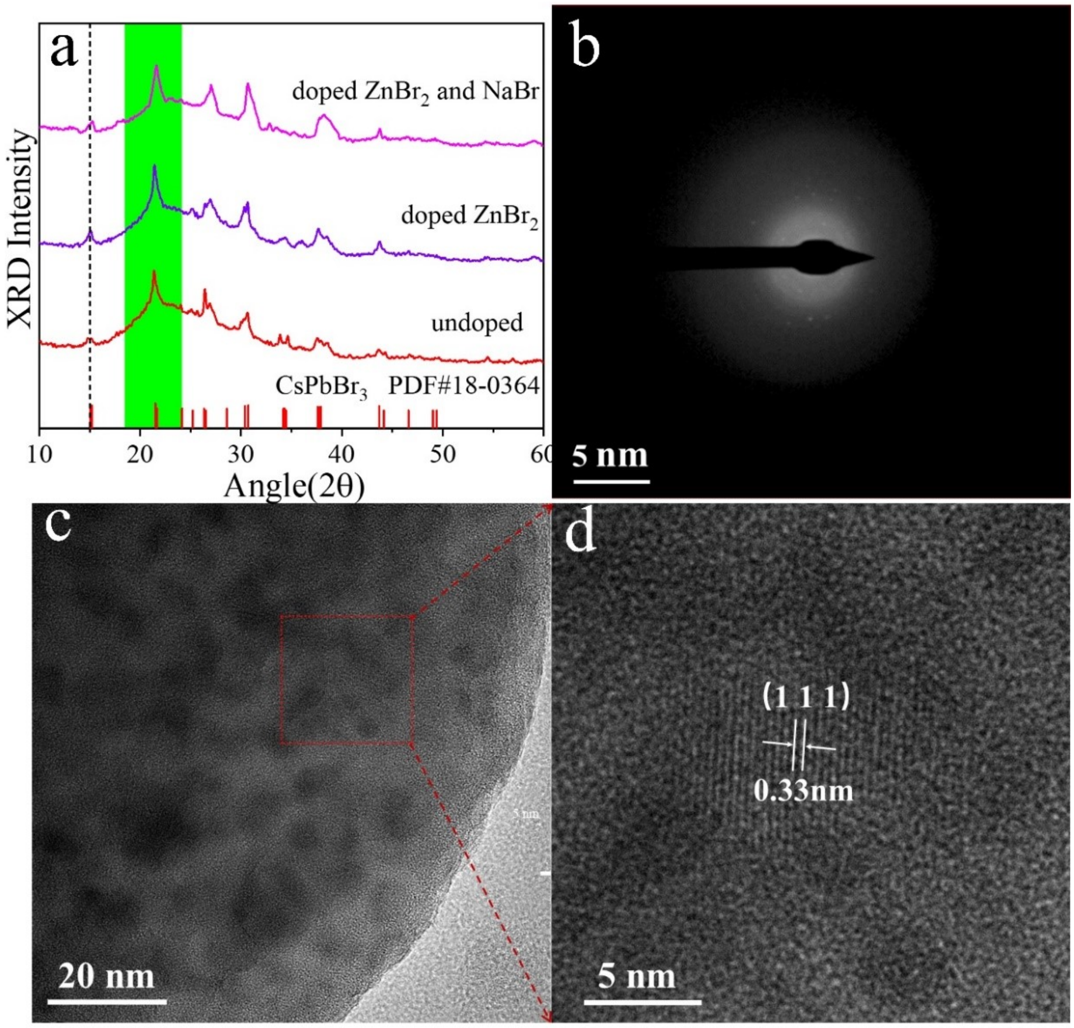

Figure S2. (a) XRD diffraction pattern, (b) The SAED pattern and (c-d) the HRTEM micrographs of NCs.

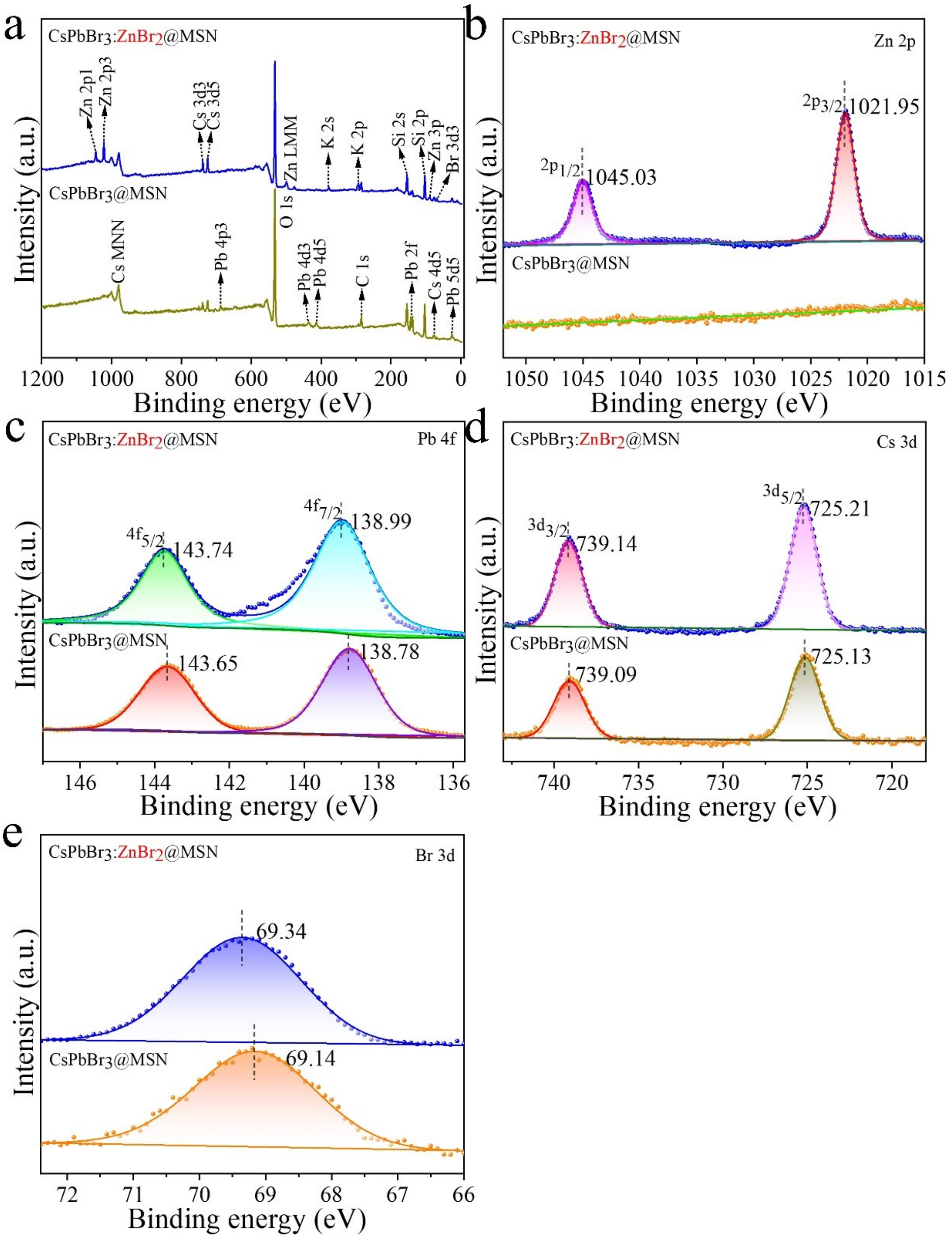

Figure S3. (a) Wide and (b)–(d) narrow-scan XPS profiles of Zn ($^2p_{1/2}$, $^2p_{3/2}$), Cs (3d), Pb ($^4f_{5/2}$, $^4f_{7/2}$), and Br(3d) energy states of pristine $CsPbBr_3$@MSNs and $ZnBr_2$-doped $CsPbBr_3$:@MSNs.

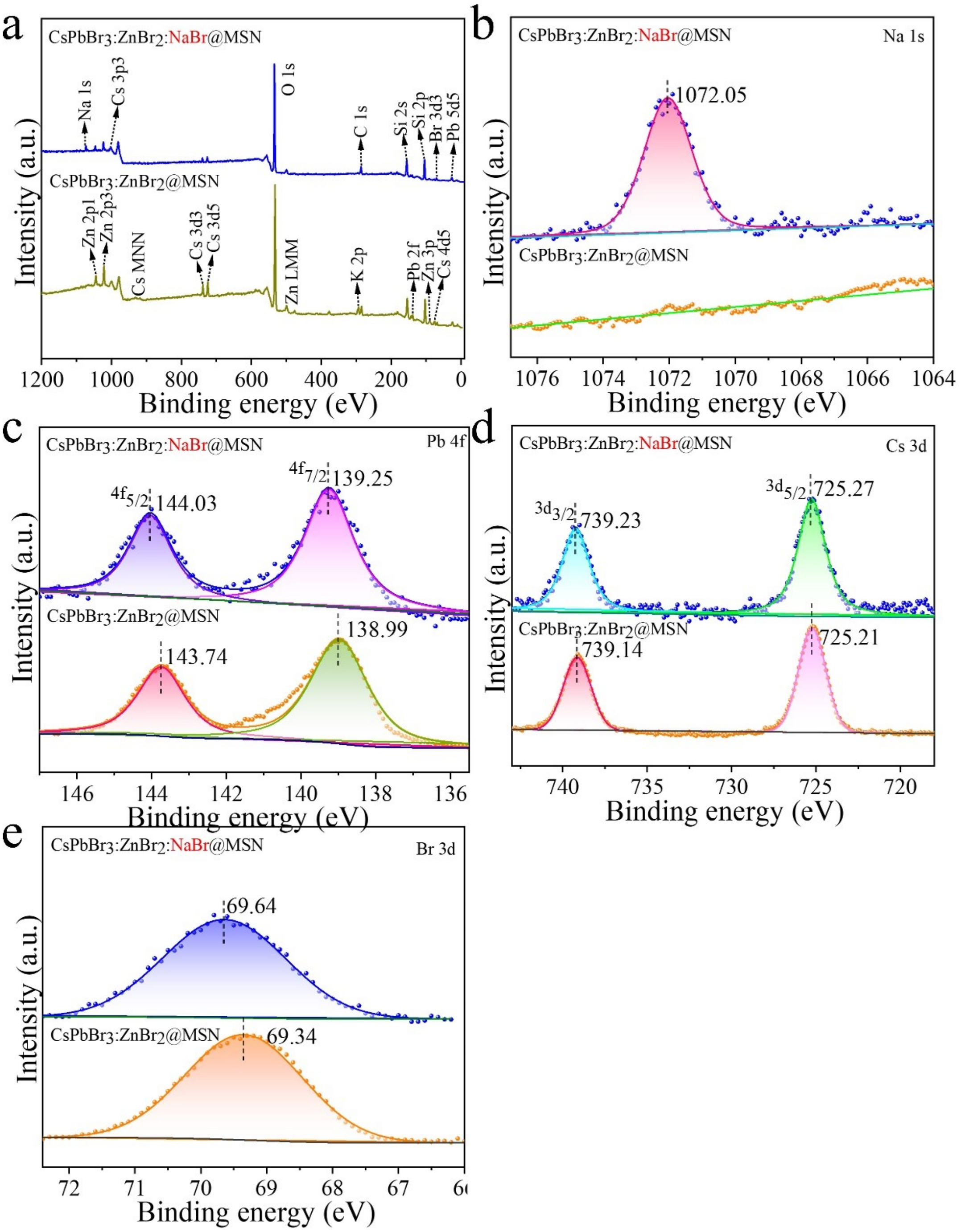

Figure S4. (a) Wide and (b)–(f) narrow-scan XPS profiles of Na (1s), Cs ($^3d_{3/2}$, $^3d_{5/2}$), Pb ($^4f_{5/2}$, $^4f_{7/2}$), and Br(3d) energy states of pristine $CsPbBr_3$:$ZnBr_2$@MSNs and NaBr-doped $CsPbBr_3$:$ZnBr_2$@MSNs.

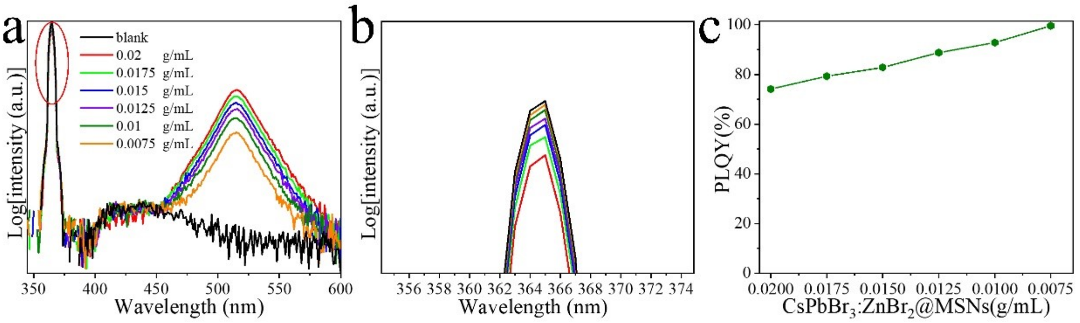

Figure S5 (a, c) PLQY of solution diluted with different concentrations, (b) An enlarged view of the part inside the red circle in (a).

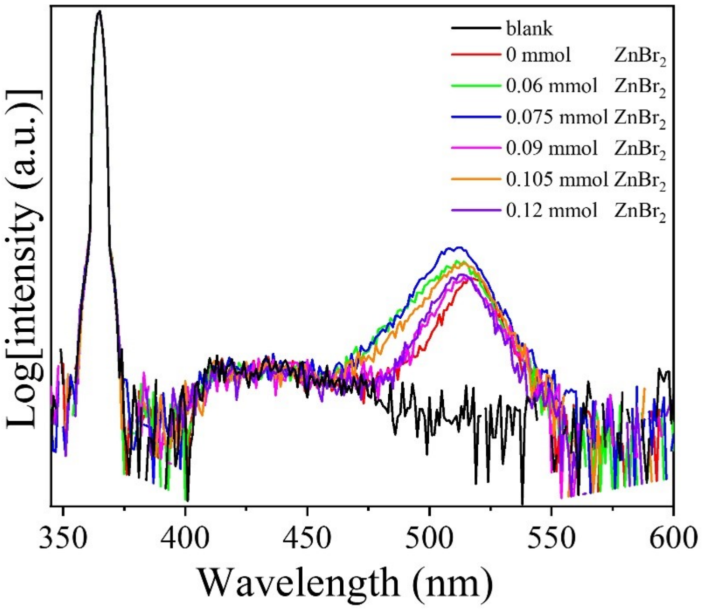

Figure S6. PLQY of $CsPbBr_3$@MSNs doped with varying amounts of $ZnBr_2$.

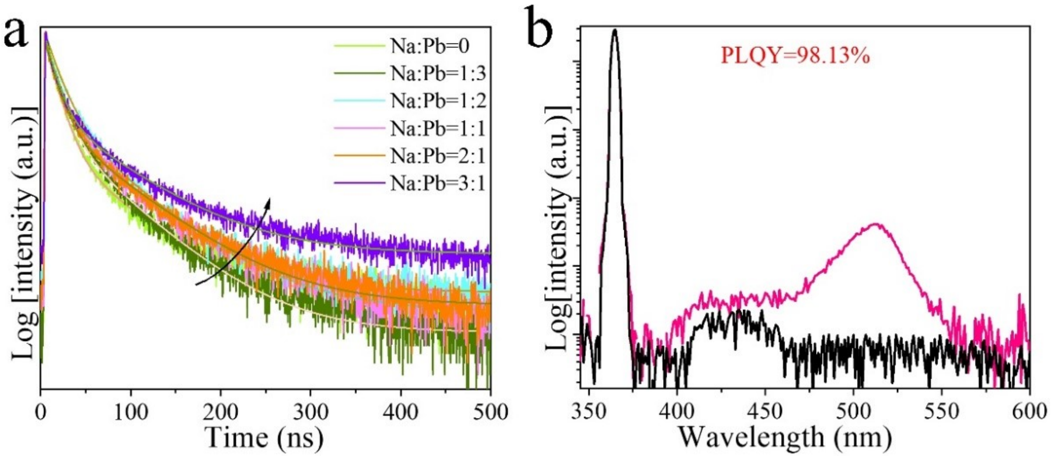

Figure S7 (a) Time-resolved PL decay spectra of $CsPbBr_3$:$ZnBr_2$:NaBr@MSNs NCs,(b)PLQY of $CsPbBr_3$:$ZnBr_2$:NaBr@MSNs (Na:Pb = 2:1).

Table S1 Emission wavelength, lifetime, FWHM and color coordinates of NaBr-doped $CsPbBr_3$:$ZnBr_2$@MSNs NCs.

Na:Pb	Wavelength (nm)	Lifetime (ns)	FWHM (nm)	Color coordinates
0	518	37.45	23.4	（0.093,0.721）
1:3	523	39.37	25.1	（0.141,0.765）
1:2	526	42.00	18.7	（0.149,0.774）
1:1	528	45.86	20.9	（0.165,0.773）
2:1	530	48.64	20.1	（0.176,0.772）
3:1	532	53.62	19.9	（0.185,0.767）

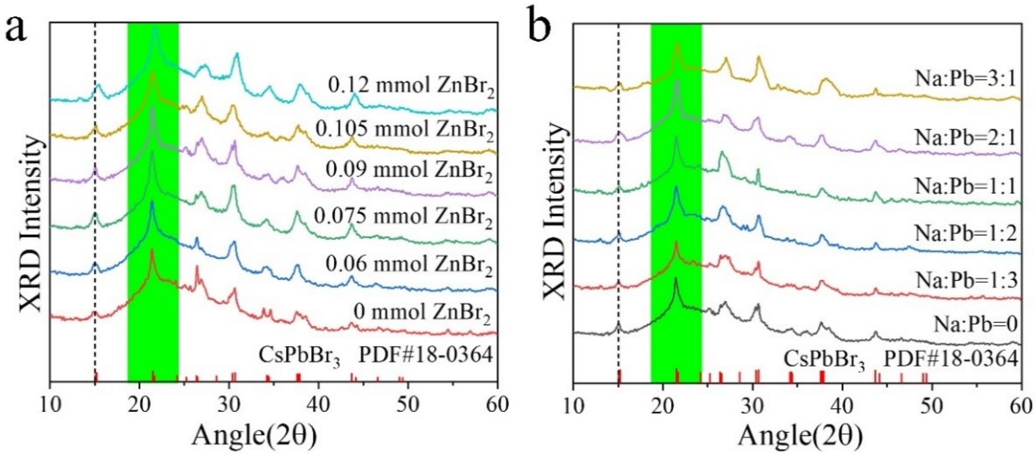

Figure S8. XRD diffraction patterns of $CsPbBr_3$@MSNs NCs prepared at different concentrations of $ZnBr_2$ (a) and NaBr (b).

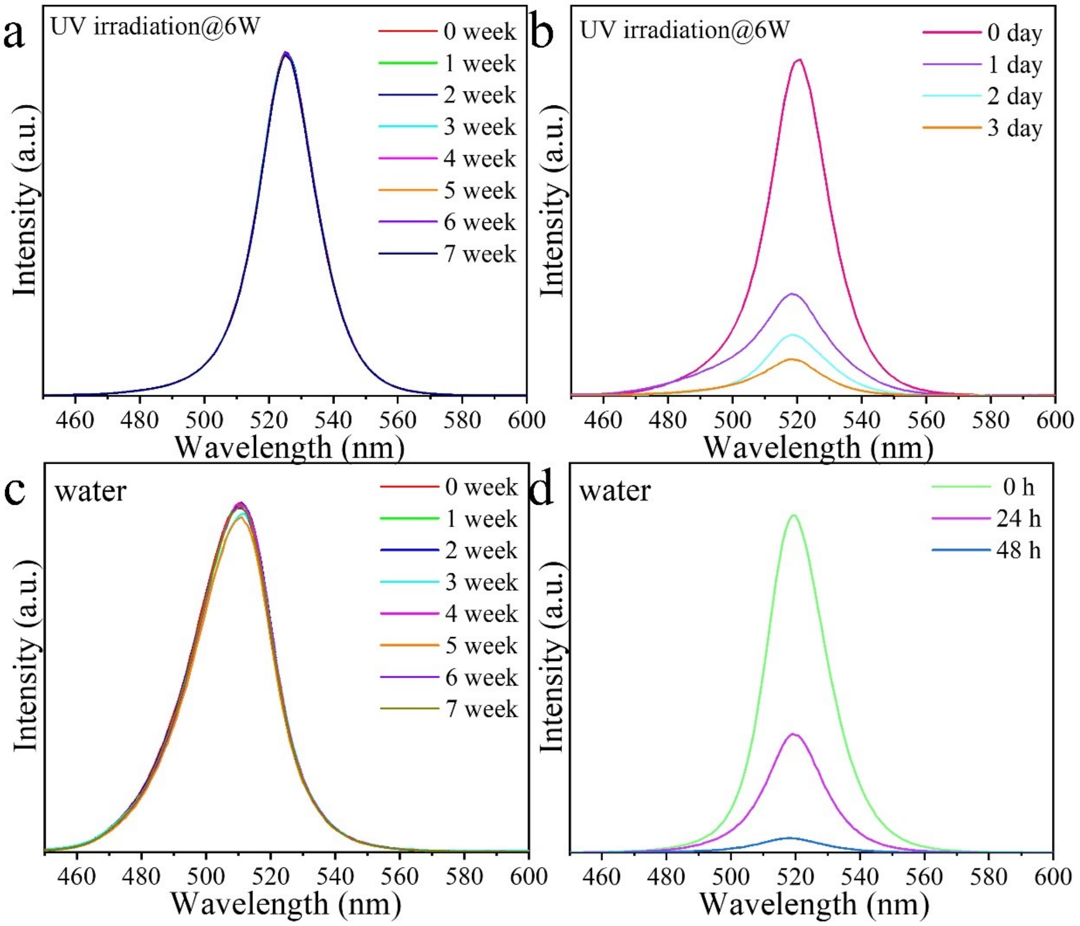

Figure S9. Comparison of stability between $CsPbBr_3$:$ZnBr_2$:NaBr@MSNs and colloidal oil-based quantum dots: (a-b) 6 W UV irradiation, (c-d) immersion in water.

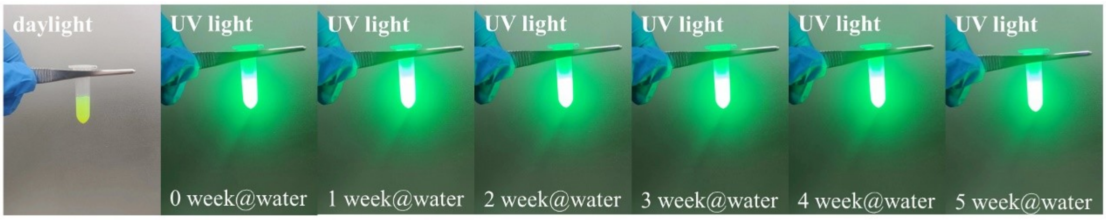

Figure S10. Luminescence of powder samples in water at different times.

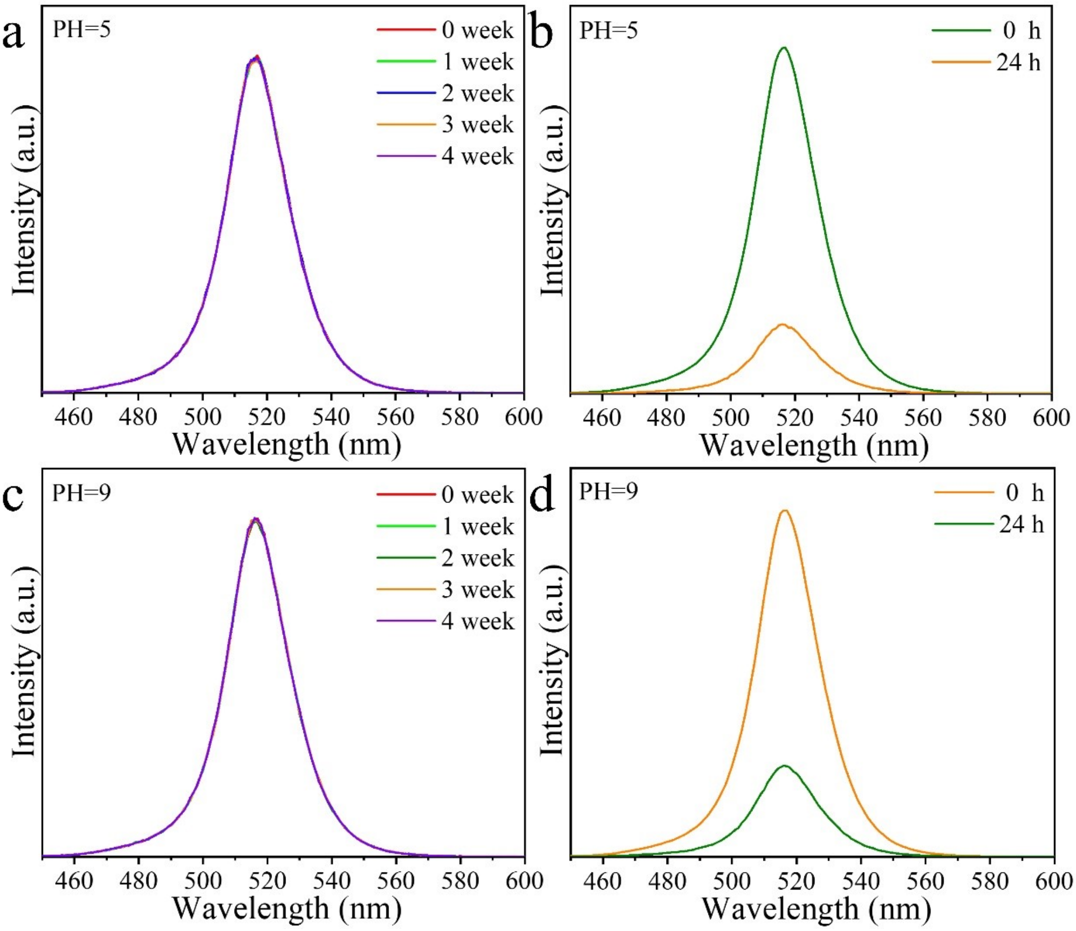

Figure S11. Comparison of the stability of CsPbBr$_3$:ZnBr$_2$:NaBr@MSNs and colloidal quantum dots in acid-base solutions: (a-b) acid (PH=5), (c-d) base (PH=9).

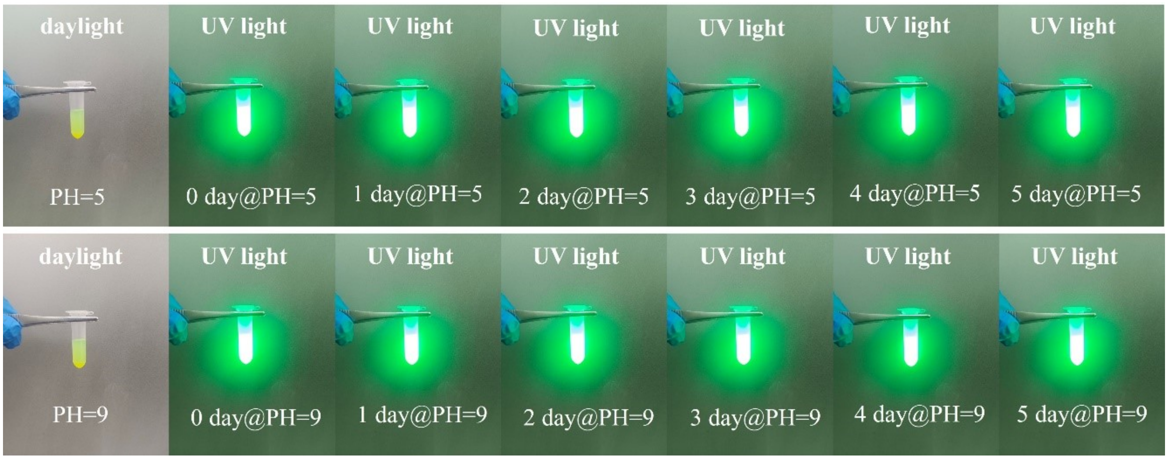

Figure S12. The luminescent photographs for the CsPbBr$_3$:ZnBr$_2$:NaBr@MSNs dispersed in acid-base solutions: acid (PH=5), base (PH=9).

Reference

[1] M. D. He, Q. G. Zhang, F. Carulli, A. Erroi, W. Y. Wei, L. Kong, C. W. Yuan, Q. Wan, M. M. Liu, X. R. Liao, W. J. Zhan, L. Han, X. J, Guo, S. Brovelli and L. Li, Ultra-stable, Solution-Processable $CsPbBr_3$-SiO_2 Nanospheres for Highly Efficient Color Conversion in Micro Light-Emitting Diodes, *ACS Energy Lett.*, 2022, **8,** 151-158.

[2] Z. Li, L. Kong, S. Huang and L. Li, Highly Luminescent and Ultrastable $CsPbBr_3$ Perovskite Quantum Dots Incorporated into a Silica/Alumina Monolith, Angew. *Chem. Int. Ed.*, 2017, **56,** 8134-8138.