Electronic Supplementary Information (ESI)

Near-infrared multiphoton absorption and third harmonic generation with CsPbBr$_3$ quantum dots embedded in micro-particles of metal-organic frameworks

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1. Experiment

1.1 materials synthesis

All chemicals were purchased from commercial corporation and used without further purification. Methanol (MeOH, 99.5%), N,N-dimethylformamide (DMF, 99.5%), 2-methylimidazole(2-mim, 98%), Caesium bromide (CsBr, 99.5%) and lead bromide (PbBr$_2$, 99.9%) were purchased from Macklin. Zinc nitrate hexahydrate (Zn(NO$_3$)$_2$ • 6H$_2$O) was purchased from Alfa Aesar.

Synthesis of ZIF-8. Zn(NO$_3$)$_2$·6H$_2$O (1.78 g, 6 mmol) and 2-mim (0.49 g, 6 mmol) were dissolved in DMF (130 mL). A Teflon-lined stainless-steel autoclave (150 mL) was used as reaction vessel to load mixture. After that, we put it into a programmable oven and heated at a rate of 5 ^{o}C min^{-1} to 140 ^{o}C for 24 hours, then followed by cooling naturally to room temperature. After washing three times with DMF, the upper clear layer was washed three times with methanol, the white ZIF-8 crystallites were dried at 80 °C overnight.

Synthesis of CsPbBr$_3$@ZIF-8. ZIF-8 powder (0.50 g) and CsBr (4.24 g, 20 mmol) were dissolved in MeOH (20 mL) and transferred in the autoclave, the mixture was then stirred at 60 ^{o}C for 12 hours to ensure that CsBr was immersed into the cages of ZIF-8. The CsBr@ZIF-8 powder was obtained after washing three times with methanol and dried at 80 °C overnight. CsBr@ZIF-8 (0.50 g) and PbBr$_2$ (0.36 g, 1 mmol) were put in an agate mortar and grinded for 20 minutes and washed with DMF for three times, then the CsPbBr$_3$@ZIF-8 powders were obtained.

Synthesis of CsPbBr$_3$. With the similar method of CsPbBr$_3$@ZIF-8, CsBr (0.21 g, 1 mmol) and PbBr$_2$ (0.36 g, 1 mmol) were put in an agate mortar and grinded for 20 minutes and the CsPbBr$_3$ powders were obtained.

1.2 Characterization

SEM images, EDS and SEM mapping were obtained using a JSM-6700F. TEM, HRTEM images and HRTEM mapping were obtained using a Talos F200X. XRD patterns were obtained using a SmartLab 9KW. The thermogravimetric analysis was using a TGA5500. XPS spectra was obtained using Thermo Fisher ESCALAB XI+. The PL spectra were obtained using a FluoroMax-4. UV absorption spectra were obtained using a ChirascanV100. B&H SPC-150N TCSPC module was utilized for fluorescence lifetime measurement.

1.3 Multiphoton excitation photoluminescence.

The system consisted of a femtosecond laser (CARBIDE-CB5, Light Conversion Ltd.) and an optical parametric amplification (OPA, Orpheus and Lyra, Light Conversion Ltd.) as the laser source. The emitted laser pulses have a repetition frequency of 60 kHz, wavelength range from 300 to 2600 nm and pulse width of ~216 fs. The laser output beam was divided into two paths by a beam splitter, one path was detected by a power meter as the reference and another path directly entered the microscope (Nikon, ECLIPSE Ti2). In the microscope, the laser was reflected by a dichroic mirror (Thorlabs DMSP950R) and then focused on the sample on X-Y stage by a 20× objective lens (Nikon, NA = 0.45). The fluorescence generated by the sample was collected through the objective lens, and then passing through the dichroic mirror to the bottommost mirror. The reflected fluorescence was focused by a lens, and filtered by a suitable filter (Thorlabs

FESH0750). Finally, the fluorescence signal was collected by the optical fiber, which waveguided it to the detector of a spectrometer (QE Pro, Ocean Optics Ltd.).

2. Analysis results

2.1 Determination of molar concentrations of pure $CsPbBr_3$

The concentration of pure $CsPbBr_3$ was determined with the same way as previous reports, which is $C_{pure} = (m_{pure}/M_{pure}) (V_u/V)(1/V_s)$, [S1, S2] where C_{pure}, m_{pure} and M_{pure}, and V_s represents the molar concentration, weight, molar mass, and volume of pure $CsPbBr_3$, respectively, V_u represents the unit cell volume of $CsPbBr_3$ and V represents the particle volume. Since the substances used were the same, we approximated that the molar concentration ratio be the density ratio. We weighed 350 μL of $CsPbBr_3$ to obtain a mass of 0.77 g. Substituting the values and comparing with the data in the previous articles result in $C_{pure} = 9.3 \times 10^{-4}$ mol/L.

2.2 Determination of molar concentrations of $CsPbBr_3$ QDs in ZIF-8

The molar concentration of the $CsPbBr_3$ QDs encapsulated in ZIF-8 was determined from the results of element mapping. Because Cs^+ was added first, and then, Pb^{2+} was added during the reaction, there was inevitably an excess of unreacted Cs^+. We assumed that all Pb^{2+} were derived from the $CsPbBr_3$ QDs and all Zn^{2+} were derived from the ZIF-8. Therefore, the ration of the number of $CsPbBr_3$ QD and the numbers of ZIF-8 was n_{Pb}/n_{Zn}. According to the CIF files, we obtained the unit cell volume of ZIF-8 (V_{ZIF}) of 4.905 nm^3 and the unit cell volume of ZIF-8 ($V_{uCsPbBr3}$) of 0.805 nm^3. From the HRTEM and TEM images, the shape of $CsPbBr_3$ can be approximated as a cube and its average length was about 12 nm, and the volume ($V_{CsPbBr3}$) could

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be calculated from this. As such, the molar concentration of the CsPbBr$_3$@ZIF-8 was calculated to be $C_{CsPbBr3@ZIF-8}$ = (n_{Pb} / n_{Zn}) * ($V_{u\ CsPbBr3}$ / $V_{CsPbBr3}$) * [1 / (N_A * V_{ZIF})] = (8.51 ± 1.35) $\times$ 10^{-6} mol/L. [S1, S2]

2.3 Multiphoton excited photonluminescence (MPEPL) signal

The MEPL signal formula for 2,3,4, or 5 photon absorption (MPA) can be obtained as:

$$F_2 = \iiint \Delta f_2 = \alpha \frac{\pi^{3/2}}{8\sqrt{2}(\hbar\omega)^2} \tau\phi\eta\sigma_2\rho L_0 w_0^2 I_{00}^2$$

$$F_3 = \iiint \Delta f_3 = \alpha \frac{\pi^{3/2}}{18\sqrt{3}(\hbar\omega)^3} \tau\phi\eta\sigma_3\rho L_0 w_0^2 I_{00}^3$$

$$F_4 = \iiint \Delta f_4 = \alpha \frac{\pi^{3/2}}{64(\hbar\omega)^4} \tau\phi\eta\sigma_4\rho L_0 w_0^2 I_{00}^4$$

$$F_5 = \iiint \Delta f_5 = \alpha \frac{\pi^{3/2}}{50\sqrt{5}(\hbar\omega)^5} \tau\phi\eta\sigma_5\rho L_0 w_0^2 I_{00}^5$$

In these equations, F_n is the *MPA-PL* strength collected by spectrometer, *n* counts for the fact that *n* photons are absorbed; α is the proportion of signal propagate into the collection system; $\hbar\omega$ is the photon energy of the incident laser beam; τ is pulse duration of the Gaussian laser pulse; ϕ is the efficiency of collection system; η is the PL quantum yield; σ_n is the n-photon-absorption cross-section; the product of η and σ_n is multi-photon action cross-section; ρ is the sample molar concentration; L_0 is the effective length of sample; w_0 is the beam waist of laser beam at the focal point; I_{00} is peak intensity of the input pulse at the focus.

To calculate the $\eta\sigma_n$ from the experimental data, we need to firstly obtain the other parameters in the above equations. Here, we set the effective length of sample $L_0 = 2Z_0$, in which Z_0 is the Raleigh length of the objective lens. As above mentioned, the molar concentration of the CsPbBr$_3$@ZIF-8 can be expressed to be (8.51 ± 1.35) × 10^{-6} mol/L and the molar concentration of the CsPbBr$_3$ can be expressed to be 9.3 × 10^{-4} mol/L. The multiphoton excitation fluorescence ratio method was used to determine the multiphoton absorption cross-section of the sample. Firstly, the two-photon absorption coefficient of pure chalcogenide in the 1000 nm band can be found from the literature as 5 cm/GW. [S3] Then, according to the equation: $\sigma_n = (hw)^{n-1}a_n / (2nN_0d_0)$. [S4] In the equation, $\hbar\omega$ is the photon energy of the incident laser beam; a_n is the multiphoton absorption coefficient; $N_0\ and\ d_0$ represent the Avogadro constant and the molar concentration of the sample, respectively. We calculate the two-photon action cross-section $\eta\sigma_2$ of CsPbBr$_3$ wo be 2.7 × 10^4 GM. In the calculation process, the fluorescence quantum yield was taken as 60%. The beam waist radius w_0 is proportional to the incident wavelength with $w_0 \approx 0.61\lambda / NA$. The actual beam waist radius w_0 can be measured as 3 μm, 3.9 μm, 5.4 μm and 6.6 μm for the lease beam spots at 1000 nm, 1300 nm, 1800 nm and 2200 nm, respectively.

By selection of CsPbBr$_3$ as reference material, according to the equation: $$\eta\sigma_{2MOF} = \frac{F_{2MOF} \cdot \eta\sigma_2\left(\rho I_{00}^2\right)Pure}{F_2 \cdot \left(\rho I_{00}^2\right)MOF}$$, we calculated the two-photon action cross-section $\eta\sigma_2$ of CsPbBr$_3$@ZIF-8 to be (14 ± 3) × 10^6 GM. As for the determination of multiphoton action cross-sections corresponding to the 1300, 1800, and 2200 nm bands, we compared their MPA-PL signals to the 2MPA-PL signal and employed the above equations to infer the MPA action cross-sections.

2.4 Third harmonic generation (THG) signal

We observed the THG of CsPbBr$_3$ and CsPbBr$_3$@ZIF-8 at 1800 nm and 2200 nm, respectively. We found that their THG signals are almost the same at the same incident intensity, regardless of 1800 nm or 2200 nm. A filter was used in the spectrometer collection to filter out the fluorescence signal. The THG signals from CsPbBr$_3$, CsPbBr$_3$@ZIF-8, or, α-quartz powders were measured under the same experimental conditions. We used α-quartz powders as a standard sample, since its $\chi^{(3)}$ values are documented in the literature.

The intensity of the THG signal intensity is approximated as: $F_3 \propto |\chi^{(3)}|^2 I_\omega^3 L^2 \dfrac{sin^2(\Delta k_q L_q/2)}{(\Delta k_q L_q/2)^2}$, where $\chi^{(3)}$ is the third-order polarizability of the sample, Δk_q is the wavenumber difference between the THG of the sample and the excitation light, and L_q represents the thickness of the sample. By comparing the THG signal from CsPbBr$_3$, or, CsPbBr$_3$@ZIF-8 to α-quartz, their $\chi^{(3)}$ were determined.

The $\chi^{(3)}$ of α-quartz reported in many literatures with an average value of $\chi^{(3)}$ = 2.6 × 10^{-14} esu. [S5] At 1800 nm, the third-order nonlinear polarizability $\chi^{(3)}$ of CsPbBr$_3$ and CsPbBr$_3$@ZIF-8 was then determined to be 5.14 × 10^{-12} esu and 8.08 × 10^{-12} esu, respectively, while, at 2200 nm, the $\chi^{(3)}$ value of CsPbBr$_3$ and CsPbBr$_3$ @ ZIF-8 was 7.43 × 10^{-12} esu and 2.02 × 10^{-11} esu, respectively, see Fig. S5.
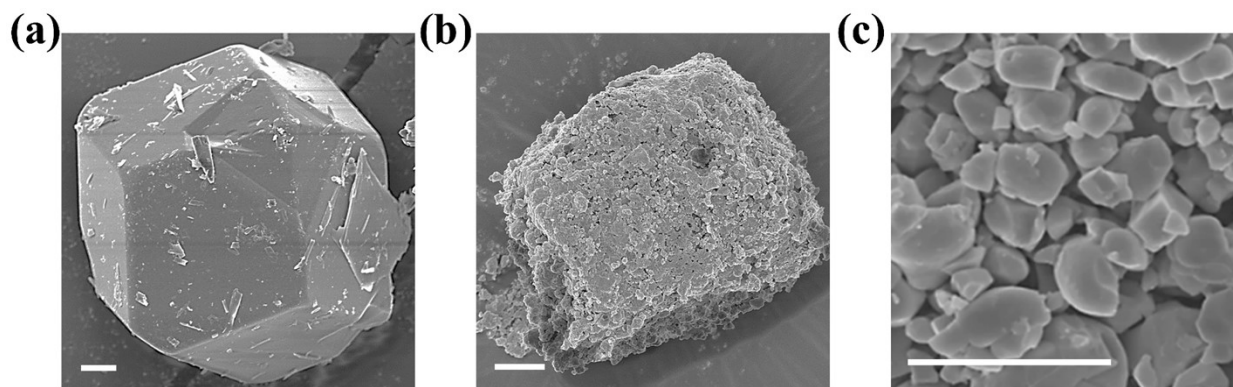
Fig. S1 The SEM of (a) ZIF-8 with scale bar of 2 μm,

(b) CsPbBr$_3$@ZIF-8 and (c) CsPbBr$_3$ with scale bar of 5 μm.
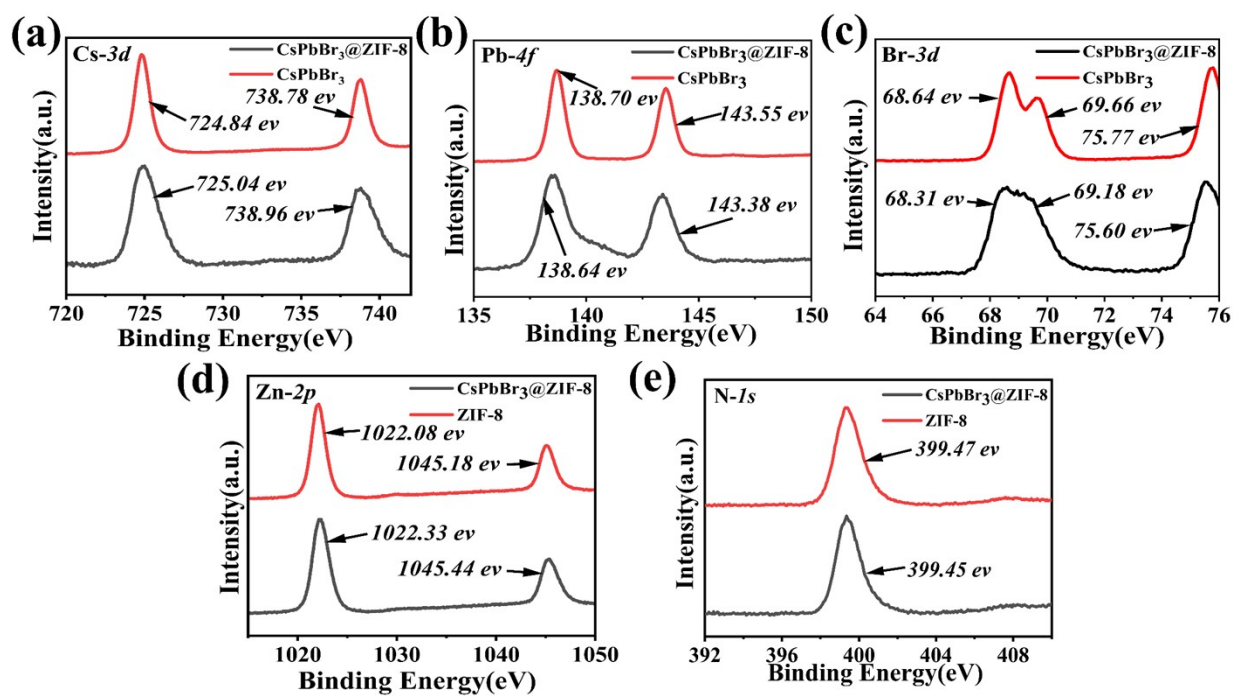
Fig. S2 The high resolution X-ray photoelectron spectra (XPS) of

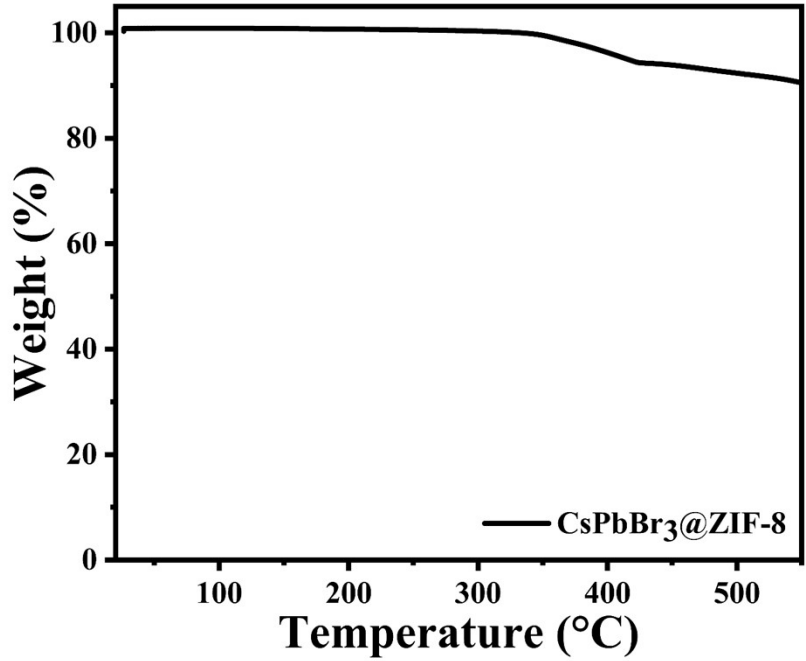(a) Cs-*3d*, (b) Pb-*4f*, (c) Br-*3d*, (d) Zn-*2p* and (e) N-*1s*.

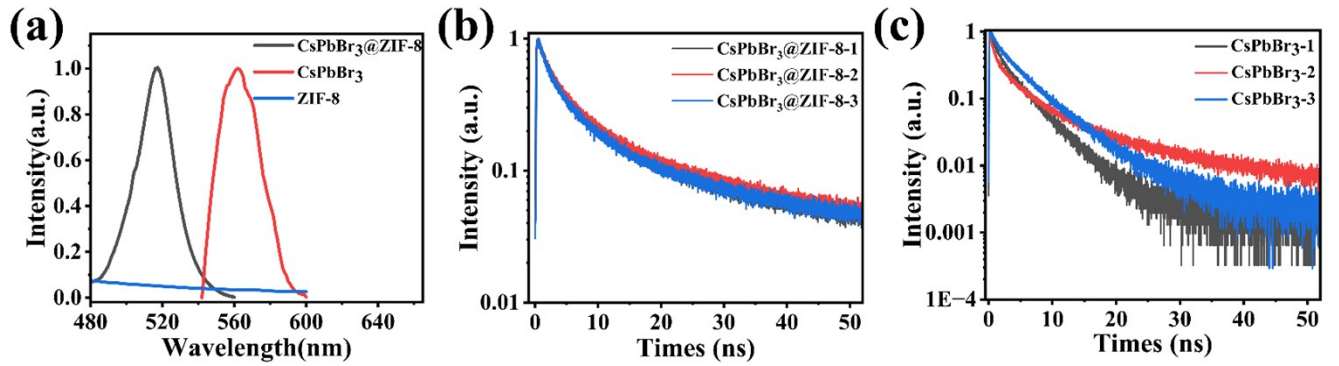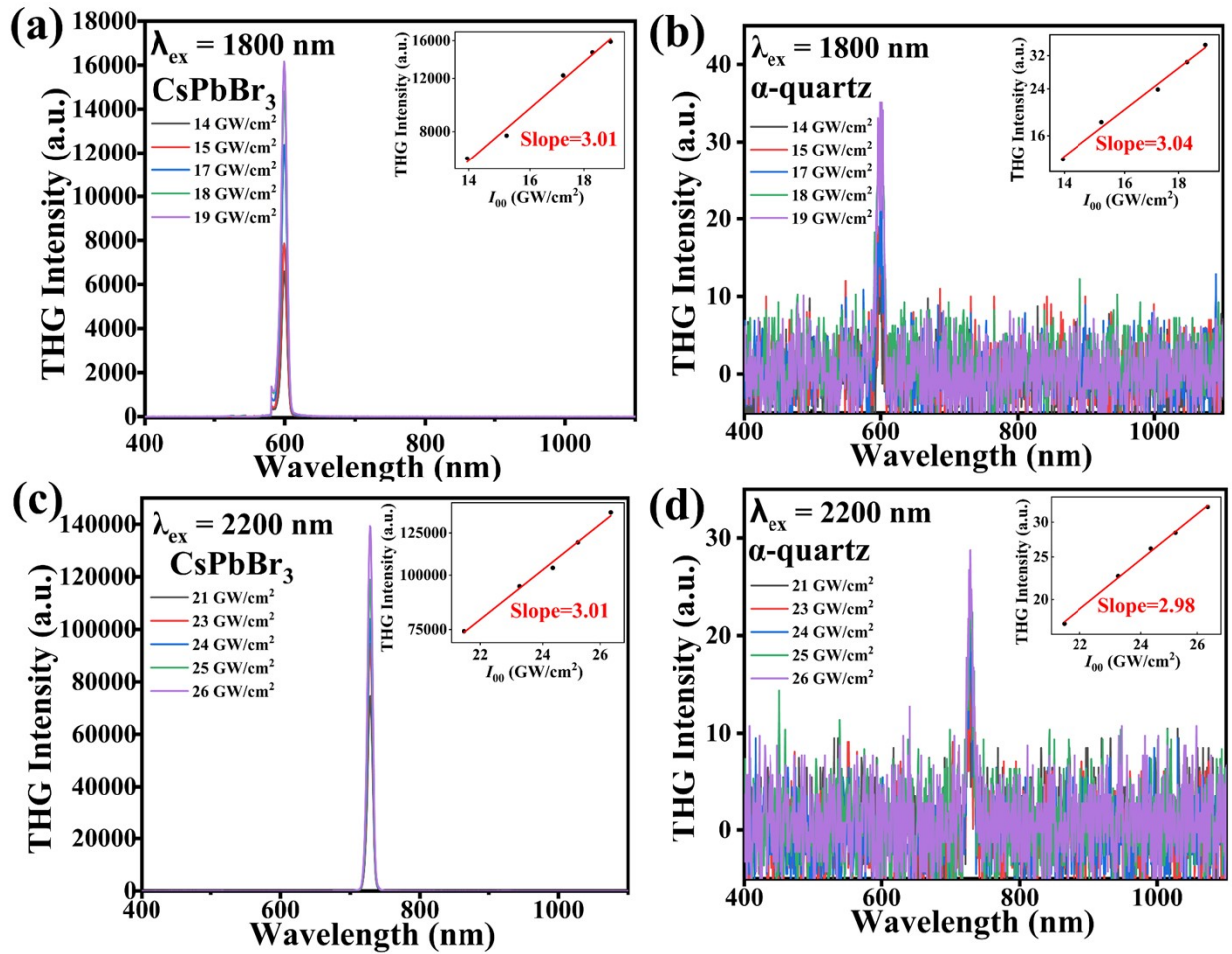**Fig. S3** The thermogravimetric analysis of CsPbBr$_3$@ZIF-8.

Fig. S4 (a)The photoluminescence (PL) spectra of CsPbBr$_3$@ZIF-8, CsPbBr$_3$, and ZIF-8. The PL decay

plots of (b) CsPbBr$_3$@ZIF-8 and (c) CsPbBr$_3$ at 405 nm.

Fig. S5 Comparison of THG of CsPbBr$_3$ (a. At 1800nm, c. At 2200nm) and α-quartz (b. At 1800nm, d. At 2200nm).

References

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