Electronic Supporting Information(ESI)

Enhanced three-photon absorption excited at near-infrared laser pulses and stability of $MAPbBr_3$ quantum dots encapsulated in mesoporous single MOF-5 crystal

Wenqing Wang, [#a] Renhua Liu, [#b] Shaowen Zhu, [a] Minjie Zhou, [c] Bing Jin, [d] Shunbin Lu, *[b] Min Liu, *[a] Xuantao Su *[a] and Wei Ji [b, e]

[a.] *School of Integrated Circuits, Shandong University, Jinan 250100, China. E-mail: liumin@sdu.edu.cn, xtsu@sdu.edu.cn*

[b.] *International Collaborative Laboratory of 2D Materials for Optoelectronic Science & Technology of Ministry of Education, Institute of Microscale Optoelectronics (IMO), Shenzhen University, Shenzhen 518060, China. E-mail: shunbin_lu@szu.edu.cn*

[c.] *Center for Optics and Research Engineer, Key Laboratory of Laser and Infrared System, Ministry of Education, Shandong University, Qingdao 266237, China.*

[d.] *Institute of Frontier Chemistry, School of Chemistry and Chemical Engineering, Shandong University, Qingdao 266237, China.*

[e.] *Department of Physics, National University of Singapore, Singapore 117551, Singapore.*

Experiment

materials synthesis

All chemicals were purchased from commercial corporation and used without further purification. 1,4-dicarboxybenzene (PTA, 99%), Lead bromide ($PbBr_2$, 99%), Methylammonium bromide (MABr, 99.5%), Ethanol (EtOH, 99.5%), Isopropyl alcohol (IPA, 99.5%) and N,N-dimethylformamide (DMF, 99.5%) were purchased from Macklin. Zinc nitrate hexahydrate ($Zn(NO_3)_2{\cdot}6H_2O$, 99.9%) was purchased from Alfa Aesar. Cetyltrimethylammonium bromide (CTAB, 99%) was purchased from damas-beta. Mesitylene(TMB, 98%) was purchased from Energy Chemical.

Synthesis of mesoporous MOF-5 Microcrystals

1.1899 g (4 mmol) of $Zn(NO_3)_2{\cdot}6H_2O$ and 0.3323 g (2 mmol) of PTA are dissolved in 50 mL of DMF. CTAB and TMB are then added to the solution under stirring. The mixture is heated in a 100 mL Teflon autoclave liner to

135°C for 24 hours. The resulting powder is washed with DMF and Methanol, and the collected MOF-5 crystals are dried under vacuum at 80°C for 2 h. In order to investigate the effect of Zn^{2+}/PTA/CTAB/TMB molar ratio on the products, the Zn^{2+}/PTA/CTAB/TMB molar ratios were adjusted to 1:0.5:0:0, 1:0.5:0.3:0.3, 1:0.5:0.3:0.6, 1:0.5:0.3:0.9, and 1:0.5:0.3:1.2, respectively.

Synthesis of $MAPbBr_3$@MOF-5

1 mmol of $PbBr_2$ is dissolved in 20 mL of DMF and stirred until completely dissolved. 100 mg of MOF-5 is added to the $PbBr_2$ solution, and the mixture is heated at 60°C for 12 h. The resulting powder is washed with DMF. Finally, Pb^{2+}@MOF-5 is dried under vacuum at 60°C for 6 h. 30 mg of MABr are dissolved in 20 mL of IPA (1.5 mg/mL) and stirred until completely dissolved. Pb^{2+}@MOF-5 is added to the MABr solution, and the mixture is heated at 40 °C for 12 h. The resulting powder is washed with IPA. Finally, $MAPbBr_3$@MOF-5 is dried under vacuum at 40 °C for 6 h.

Synthesis of $MAPbBr_3$

$MAPbBr_3$ is synthesized through a mechanical grinding method. MABr and $PbBr_2$ powders are placed in a dry and clean agate mortar and ground for 30 min, then the resulting powder is washed with IPA. The washed product is dried in a vacuum drying oven at 40°C for 6 h to obtain $MAPbBr_3$ powder.

Characterization

The X-ray diffraction (XRD) patterns were obtained using a SmartLab 9KW. The thermogravimetric analysis was using a TGA5500. The Scanning Electron Microscopy (SEM) images were obtained using a JSM-6700F. The Transmission Electron Microscope (TEM) and the High-Resolution Transmission Electron Microscopy (HRTEM) images were obtained using a Talos F200X. The PL spectra were obtained using a FluoroMax-4. UV-visible absorption spectra were recorded using a Shimadzu UV-2600i spectrophotometer to evaluate the optical properties and bandgap of the material. We measured the absorption spectrum of the powder sample with 0-degree incidence diffuse reflection based on a standard whiteboard as the reference. Firstly, place the standard whiteboard at the exit window parts of both the sample side and the reference side of the integrating sphere for baseline correction. Then, after baseline correction, replace the standard whiteboard on the sample side with the sample and proceed with the measurement. FLS 1000 was utilized for fluorescence lifetime measurement.

Multi-photon excited photoluminescence

The light source of this system consists of a femtosecond laser (CARBIDE-CB5, Light Conversion Ltd.) and an optical parametric amplifier (OPA, Orpheus and lyra, Light Conversion Ltd.). The excitation light has a wavelength range of 300-2600 nm, a repetition frequency of 60 kHz and a pulse width of 225 fs. After passing through filters

and attenuators, the beam is divided into two paths by a beam splitter. One path is detected by a power meter as a reference light, the other path enters the microscope (Nikon, ECLIPSE Ti2). In the microscope, the laser is reflected by a dichroic mirror (Edmund, 700nmSP) and then focused on the sample by an objective lens (Nikon, 20x, NA=0.45). The sample is excited to fluoresce, and the fluorescence collected by the objective lens passes downward through the dichroic mirror to the bottommost mirror. After being filtered by a suitable filter, the reflected fluorescence is focused by a lens. Eventually, the fluorescence signal is collected by the optical fiber and passed to the spectrometer (QE Pro, Ocean Optics Ltd.).

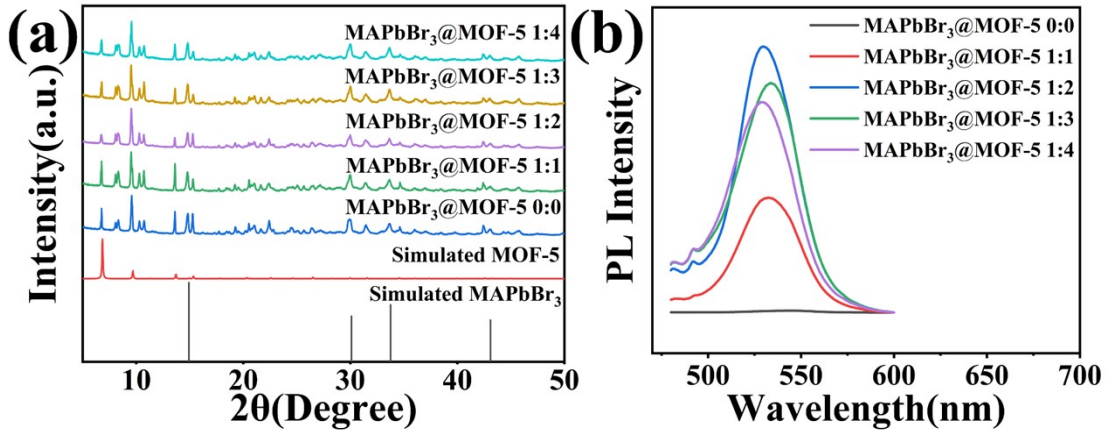

Fig. S1 X-ray diffraction (XRD) analysis (a) and PL spectra (b) of $MAPbBr_3$@MOF-5 in different CTAB to TMB mole ratios.

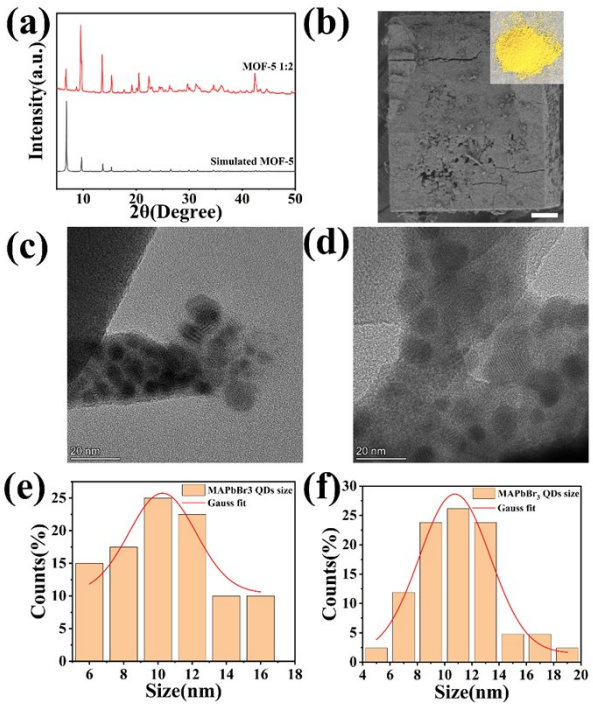

Fig. S2 X-ray diffraction (XRD) analysis (a) and the SEM image (b) of MOF-5 synthesized with a molar ratio of CTAB to TMB of 1:2 (Scale bar, 10 μm). Insets: Photographs of the $MAPbBr_3$@MOF-5 sample. (c, d) HRTEM (Scale bar: 20 nm) and (e, f) Histogram of $MAPbBr_3$ particle size distribution with Gauss fitting.

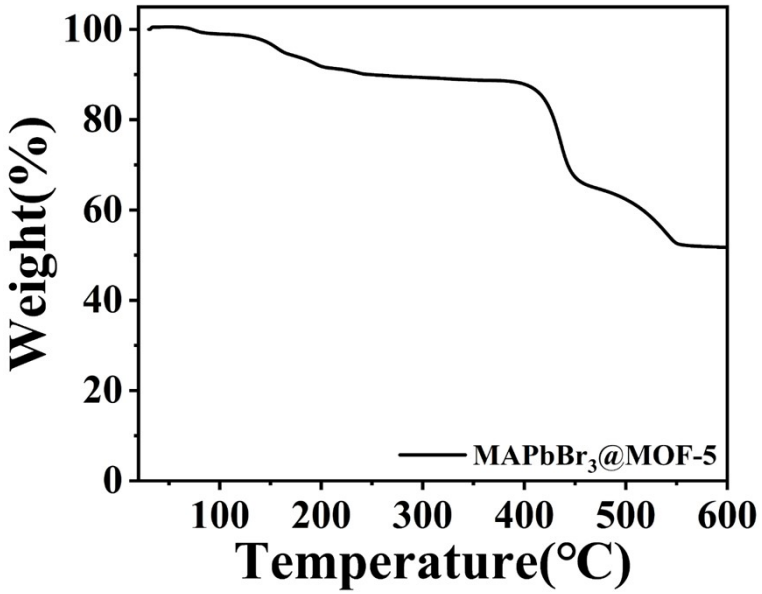

Fig. S3 The thermogravimetric analysis of $MAPbBr_3$@MOF-5.

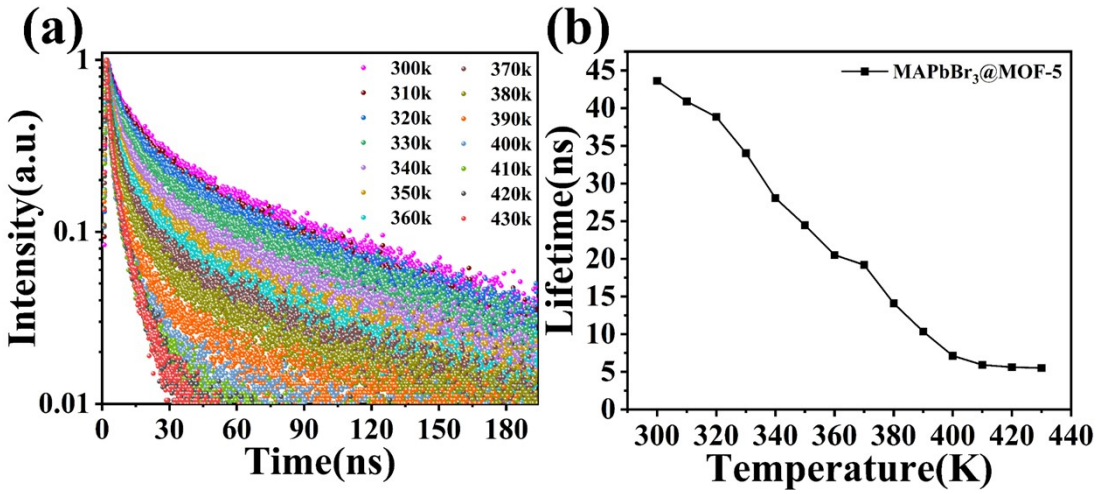

Fig. S4 (a) PL decay curves in the temperature range 300–430 K under 400 nm excitation, (b) Variation tendency of the fitted decay lifetimes with temperature.

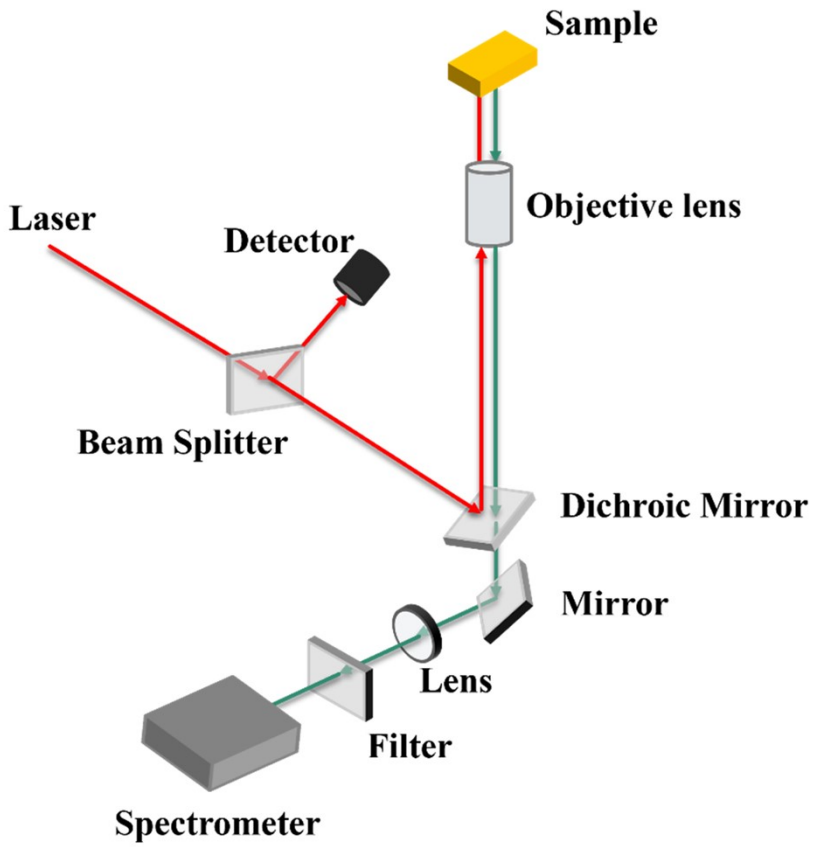

Fig. S5 Schematic diagram of multiphoton-excited photoluminescence measurement.

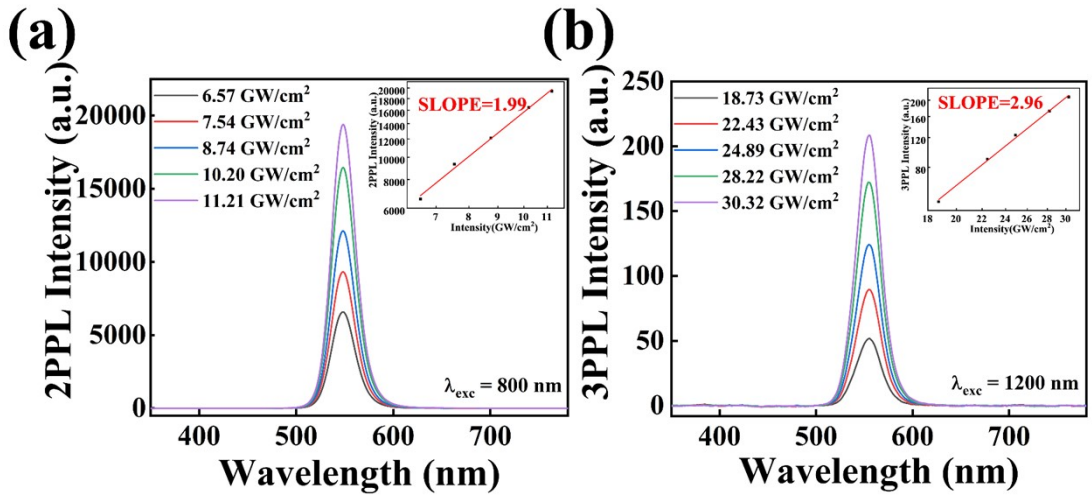

Fig. S6 Multiphoton-excited photoluminescence (MPEPL) of $MAPbBr_3$. (**a**) 2PPL spectra at 800 nm; (**b**)3PPL spectra at 1200 nm.