Supporting Information

Pressure response to the structure and optical properties in two-dimensional perovskite-like CsPb₂Br₅ microplates

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1 Experimental Section

Materials: PbBr₂ (Aladdin, 99.9%), Cs₂CO₃ (Sigma-Aldrich, 99.9%), oleylamine (OLA Aladdin, 80-90%),
oleic acid (OA, Sigma-Aldrich, 90%), octadecylene (ODE, Aladdin, 90%) and toluene (99.9%,
Sinopharm Chemical Reagent Co., Ltd., China). All regents were used directly without further
purification.

6 **Preparation of Cs-oleate (Cs-OA):** In a typical experiment, Cs_2CO_3 (0.1 g), OA (0.4 mL) and ODE 7 (3.75 mL) were added into a 50 mL 3-neck flask, degassed at room temperature for 30 min and then 8 dried for 1 h at 120 °C under N₂ until all Cs_2CO_3 reacted with OA.

Preparation of CsPb₂Br₅ Microplates: CsPb₂Br₅ MPs were synthesized according to a modified 9 synthetic approach.¹ In the typical synthesis of CsPb₂Br₅ MPs, ODE (5 mL) and PbBr₂ (0.138 g) were 10 11 added into a 50 mL 3-neck flask. The mixture was degassed and heated to 120 °C. OLA (0.5 ml) and OA (0.8 mL) were added into the flask and then the mixture was heated to 140 °C under N₂ until all 12 PbBr₂ dissolved. Cs-OA (0.4 mL) was injected into the flask under 140 °C. The reaction was 13 terminated at 4 h and the crude solution was guenched by toluene. The as-synthesized MPs were 14 precipitated by centrifugation at 5000 rpm and redispersed in toluene. After three to four 15 centrifugations, the supernatant was discarded and the precipitate was dispersed in toluene for 16 further characterization. 17

18 **Characterization and High Pressure Generation**: SEM images were observed by JSM-6700F, JAPAN. 19 A symmetrical diamond anvil cell (DAC) was employed to generate high pressure. A stainless steel 20 gasket was preindented to 40 μm in thickness followed by laser-drilling the central part to form a 21 150 μm diameter hole to serve as the sample compartment. The CsPb₂Br₅ MPs and a small ruby ball 22 were loaded together in the sample compartment. In high pressure optical absorption, PL and XRD 23 experiments, we used silicone oil as pressure-transmitting medium the pressures were determined 24 by the ruby fluorescence method. All of the measurements were performed at room temperature.

In Situ High-Pressure Optical Experiments: The excitation source, a 355 nm line of a UV DPSS laser with the power of 5.0 mW, was used for PL measurements. The high-pressure evolution of steadystate PL spectra of $CsPb_2Br_5$ MPs was collected by a modified spectrophotometer (Ocean Optics, QE65000) with the data-collection time of 5 s. The laser beam passed through tunable filter and was focused onto the sample with 20 μ m spot 20× UV Plan apochromatic objective. Each new

acquisition was carried out several minutes later after elevation of the pressure, aiming to restrain 1 any kinetic factor during the measurements. PL micrographs of the samples were obtained using a 2 camera (Canon Eos 5D mark II) equipped on a microscope (Ecilipse TI-U, Nikon). The camera can 3 record the photographs under the same conditions including exposure time and intensity. 4 Absorption spectra were measured in the exciton absorption band region using a Deuterium-5 Halogen light source. High-pressure absorption and PL spectra of CsPb₂Br₅ MPs were recorded with 6 7 an optical fiber spectrometer (Ocean Optics, QE65000). The in situ high pressure angle-dispersive XRD experiments were carried out at the 4W2 High Pressure Station in Beijing Synchrotron 8 Radiation Facility. A focused monochromatic X-ray beam with about 5 µm in diameter and 9 wavelengths of 0.6199 Å was used for the diffraction experiments. CeO₂ was used as the standard 10 11 sample to do the calibration. The diffraction pattern were recorded by a two-dimensional area Mar-165 CCD detector and integrated into one-dimensional profile with the Fit2D program. All the high-12 13 pressure experiments were conducted at room temperature.

14 **Computation:** Geometry optimization was calculated using the plane-wave pseudopotential 15 method with the generalized gradient approximation (GGA) based on density functional theory 16 with CASTEP package. The starting structure was obtained from the Cambridge Structure Database. 17 The kinetic energy cutoff of 910 eV and the Brillouin zone sampling for geometry optimizations was 18 performed using a 6×6×3 Monkhorst-Pack k-point mesh. The convergence thresholds were set at 19 values of 1.0 e-6 eV/atom for energy and 0.03 eVÅ⁻¹ for force.

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Figure S1. EDS of the CsPb₂Br₅ MPs





Figure S2. DFT calculated total and partial DOS projected onto Cs, Pb, and Br atoms.



laser.

1 Refinements methods and procedures

Pawley and Rietveld refinements of XRD patterns were accomplished using the Reflex module combined in Materials Studio 8.0 program.²⁻⁴ All Pawley and Rietveld refinements were performed using four refinement cycles fine convergence criteria. First, the pattern was indexed by means of the peak picking option of the software package. Potential solutions for cell parameters were found using the TREOR 90 and DICVOL 91 methods. Then, a Pawley profile-fitting procedure was applied to refine cell parameters and search space group. The final Rietveld refinement (including Pawley refined parameters, Pb and halide atomic positions, preferred orientations and overall isotropic factor) were performed to obtain the crystal structural parameters. The quality of the fitting between the experimental and calculated profile is assessed by the various R parameters like R_p (profile factor) and R_{wp} (weighted profile factor).⁴

$$R_p = \left\{ \frac{\sum_i \left| I_i^{obs} - I_i^{cal} \right|}{\sum_i I_i^{obs}} \right\}$$

$$R_{wp} = \left\{ \frac{\sum_{i} w_{i} (I^{obs}_{i} - I^{cal}_{i})^{2}}{\sum_{i} w_{i} (I^{obs}_{i})^{2}} \right\}^{\frac{1}{2}}$$

15 Where I_{i}^{obs} , I_{i}^{cal} and "*i*" indicates the experimental, calculated and total number of points 16 respectively. And the " W_{i} " is the reciprocal of the variance of observation I_{i}^{obs} .



4 Figure S4. Pressure dependence of angle dispersive synchrotron X-ray diffraction peak positions for
5 CsPb₂Br₅ MPs in the range (a) from 16° to 19° and (b) from 8° to 15°.





Figure S5. (a) SEM image of the obtained CsPb₂Br₅ MPs when the pressure was completely released to ambient conditions. (b) Element mapping images for Cs, Pb, and Br, respectively. Elemental mapping indicates that the elements of Cs, Pb and Br are homogeneously distributed throughout the whole sample, which suggests high purity of the final products. (c) The PL spectra of the obtained CsPb₂Br₅ MPs at ambient condition and quenched phase upon completely releasing the pressure to ambient conditions

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- 2 Table S1. Refinement cell parameters and refinement statistics at ambient pressure and 2.45 GPa
- 3 for $CsPb_2Br_5$ MPs.

	1 atm	2.45 GPa
Temperature (K)	293 (3)	293 (3)
Crystal system	Tetragonal	Tetragonal
Space group	I4/mcm	I4/mcm
<i>a=b</i> (Å)	8.46	8.32
<i>c</i> (Å)	15.14	14.39
<i>α=θ=γ</i> (°)	90	90
Volume (ų)	1083.76	997.26
Z	32	32
θ range (°)	5-20	5-20
Wavelength (Å)	0.6199	0.6199
Number of refined peaks	12	12
R _{wp} (%)	3.05	2.02
R _p (%)	2.00	2.85

Table S2. The lattice parameters and unit cell volume for structures of $CsPb_2Br_5$ MPs at different

3 pressures.

	Pressure (GPa)	<i>a=b</i> (Å)	<i>c</i> (Å)	<i>V</i> (ų)
	0	8.46	15.14	1083.76
I4/mcm	0.43	8.42	15.08	1070.11
	0.83	8.39	14.95	1054.75
	1.24	8.37	14.92	1045.89
	1.65	8.37	14.49	1014.34
	2.06	8.35	14.44	1007.15
	2.45	8.32	14.39	997.26
I4/mcm	3.02	8.3	14.34	988.34
	3.51	8.27	14.27	976.92
	4.01	8.24	14.22	966.04
	5.05	8.2	14.13	950.01

- 2 Table S3. The three Pb-Br bonds and two Br-Pb-Br angles within lead-bromide pentahedra for

Pressure (GPa)	Pb-Br bonds L ₁ (Å)	Pb-Br bonds L ₂ (Å)	Br-Pb-Br angles A ₁ (degrees)	Br-Pb-Br angles A ₂ (degrees)
0	3.141	2.788	144.482	85.693
0.43	3.128	2.781	144.296	84.923
0.83	3.122	2.776	144.015	83.848
1.24	3.115	2.766	143.832	83.567
1.65	3.114	2.758	143.342	78.63
2.05	3.108	2.76	143.117	77.76
2.45	3.104	2.764	143.004	77.69
3.01	3.098	2.766	142.628	77.532
3.51	3.09	2.768	142.315	76.658
4.03	3.086	2.774	141.655	76.142
5.05	3.071	2.792	140.89	75.641

3 CsPb₂Br₅ MPs as function of pressure.

	Initial bandgap (eV)	Slope of change in band gaps dE(gap)/dP (eV/GPa)	Phase transition pressure (GPa)
$CsPb_2Br_5$	2.37	0.019	~1.6
CsPbBr ₃	2.52	0.092	~1.2

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