Manipulating Emission Enhancement and Piezochromism in Two-Dimensional Organic–Inorganic Halide Perovskite \([(\text{HO})(\text{CH}_2)_2\text{NH}_3)]_2\text{PbI}_4\) by High Pressure

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Two-dimensional (2D) organic–inorganic halide perovskites present remarkable stability and diversity and are promising alternatives to their three-dimensional (3D) counterparts. The 2D halide perovskite \([(\text{HO})(\text{CH}_2)_2\text{NH}_3)]_2\text{PbI}_4\) (ETA2PbI4) is regarded as a superior moisture-stable “smooth” perovskite because of distinct hydrogen-bond networks that connect adjacent organic–inorganic layers. However, effectively engineering the optical properties of ETA2PbI4 for practical applications still represents considerable challenges. Herein, we studied the effect of pressure on the optical characteristics and crystalline structure of ETA2PbI4 through a diamond anvil cell. The emission was enhanced four times at 1.5 GPa and was accompanied by a photoluminescence (PL) peak that became more symmetric, which was attributed to pressure-suppression nonradiative recombination and an increase in exciton binding energy. Moreover, the red shift of the PL peak from 542 to 674 nm was continuous at a rate of 14.4 nm/GPa with pressure up to 9.2 GPa. Meanwhile, the optical micrographs showed visualized piezochromism. High-pressure in situ synchrotron X-ray diffraction (XRD), Raman measurements, and first-principles calculations indicated a distortion of the \([\text{PbI}_6]^{4-}\) inorganic octahedron with a decrease of the Pb–I–Pb bond angle and the Pb–I bond length leading to this series of transformations. Our findings demonstrate that 2D halide ETA2PbI4 is a prospective candidate for pressure sensors.

Keywords: two-dimensional perovskite, emission enhancement, piezochromism, high pressure, band gap red shift
Introduction

The reduced-dimensionality perovskites, especially the two-dimensional (2D) organic–inorganic halide perovskites, have become the “next big thing” in emerging hybrid halide perovskites owing to their excellent tunability and photophysical properties.1-4 In strictly 2D organic–inorganic perovskite (A)$_2$BX$_4$, where the large (A)$^+$ cations divide the infinite inorganic layers, the most common B-site cations are Pb$^{2+}$, and the X-site cations typically are Cl$^-$, Br$^-$, or I$^-$ anions.5 In this case, each of the active layers is an infinite 2D sheet of the corner-sharing PbX$_6$ octahedra.6 Through their unique crystal structures, quantum confinement leads to strong excitonic effects, therefore, strong photoluminescence (PL) was observed at room temperature.7 The uniform and stable emission spectra perovskite is the ideal material for making perovskite light-emitting diodes (LEDs).8 Moreover, 2D perovskites possess significant light absorption in the visible region which makes them a likely light absorber for photovoltaic applications.9 ETA$_2$PbI$_4$ (ETA = ([HO](CH$_2$)$_2$NH$_3$)$^+$) is a unique organic–inorganic hybrid perovskite because it consists of alcohol-based bifunctional ammonium ions.10 The strong Coulomb interactions within the ETA organic layer are attributed to the extremely smooth crystal surface of ETA$_2$PbI$_4$. Therefore, ETA$_2$PbI$_4$ is considered a “smooth” 2D halide perovskite, which is less sensitive to ambient moisture and exhibits a considerably low dark current.11 However, it is essential to adjust the band gap in a wide range to realize PL tunability in this 2D hybrid perovskite.

Pressure is a powerful and convenient strategy to alter the crystalline structure and electronic properties of 2D perovskite materials that are sometimes inaccessible by nonconfinement effects. Meanwhile, pressure-induced emission was ascribed to the radiative recombination of trap states.12 Intriguingly, ETA$_2$PbI$_4$ PL intensity was enhanced by four times from 1 atm to 1.5 GPa (Figure 1a), which was accompanied by a more symmetrical PL emission peak (Supporting Information Figure S2). Upon further compression, the PL intensity gradually decreased until it completely disappeared at 10.3 GPa (Figure 1a). Upon decompression, the PL spectra returned to its original shape and position, but the PL intensity was slightly weaker than its atmospheric pressure state (Supporting Information Figure S4). The emission spectra showed a wide range of pressure-induced peak shift throughout the compression process (Figure 1b). A series of optical photographs clearly reveal the varying trend of the ETA$_2$PbI$_4$, and the following sequence could be easily visualized by the naked eyes: green → yellow → orange → red (Figure 1b). The PL emission peak of the ETA$_2$PbI$_4$ crystal can be tuned at a rate of 14.4 nm/GPa upon compression (Figure 1c). Furthermore, the chromaticity coordinates of PL upon compression from 1 atm to 9.2 GPa are shown in Figure 1d. The emission at 1 atm belongs to the green component (0.34, 0.64). At 9.2 GPa, the emission moved toward the monochromatic red light (0.70, 0.29). Compression resulted in high color purity and colorful PL modulation, which are favorable conditions for the development of pressure sensors.15,16 Consequently, we also used pressure to tune the chromaticity of emission, which facilitates the use of ETA$_2$PbI$_4$ as a gas sensor with ultrasensitivity to pressure in the low-pressure regime (<8 GPa).

The evolution process of the ETA$_2$PbI$_4$ band gap was obtained by UV–Vis absorption spectroscopy. At ambient conditions, a steep absorption edge was observed at approximately 553 nm and showed remarkable red shifts.
when the pressure reached 8.0 GPa (Figure 2a). The extraordinary piezochromism transition of ETA$_2$PbI$_4$ is evident in optical micrographs (Figure 2b). The band gap of the material was estimated by extrapolating the linear portion of $\alpha d h \nu$ versus the $h \nu$ curve, where $\alpha$ is the absorption coefficient, $d$ is the sample thickness, and $h \nu$ is the photon energy (Figure 2c). ETA$_2$PbI$_4$ exhibited a direct gap of 2.24 eV at ambient conditions consistent with a previous report. With increasing pressure, the band gap of ETA$_2$PbI$_4$ obviously narrowed by 0.39 eV at 8.0 GPa, suggesting that the band gap of the 2D organic–inorganic halide perovskite is significantly modified by high pressure.

We obtained the in situ high-pressure angle-dispersive X-ray diffraction (ADXRD) patterns of ETA$_2$PbI$_4$ to investigate the correlation between the optical properties and structural variations of ETA$_2$PbI$_4$ (Figure 3a). Rietveld refinement results of the XRD data at ambient conditions showed that ETA$_2$PbI$_4$ possessed a monoclinic system with the P2$_1$/c space group; the lattice parameters were $a = 10.22(1)$ Å, $b = 8.04(1)$ Å, and $c = 8.93(2)$ Å, $\beta = 100.27(3)^\circ$ (Supporting Information Figure S6). Figure 3b shows the layered crystalline structure of ETA$_2$PbI$_4$ along the crystallographic $b$ axis. It was formed by alternating sheets of the corner-sharing PbI$_6$ octahedra and the organic (ETA) cation layers. Two continuous inorganic octahedral layers move slightly along the $a$ axis, and the interlayer I–I bond was very short approximately along the $c$ axis. Within the [PbI$_6$]$^{4-}$ cluster, Pb–I bonds could be divided into two groups: four

Figure 1 | (a) Pressure-dependent PL spectra of ETA$_2$PbI$_4$ under increasing pressure. (b) The microphotographs in the sample chamber at selected pressures measured by a 355 nm laser. (c) The PL location of ETA$_2$PbI$_4$ as a function of pressure (red square) and PL intensity as a function of pressure (green pentagon). (d) Pressure-dependent chromaticity coordinates of the emissions from 1 atm to 9.2 GPa. PL, photoluminescence.
We also investigated the evolution of the cell parameters and volume (Supporting Information Figure S9) to further analyze the structural evolution of ETA\(_2\)PbI\(_4\). Crystal lattice parameters and volumes of ETA\(_2\)PbI\(_4\) were stably and continuously compressed before occurrence of the severely disordered crystallinity. It was found that the deformation \(\Delta a\) (~1.13 Å) was bigger than \(\Delta b\) (~0.75 Å) and \(\Delta c\) (~0.87 Å) under quasi-hydrostatic pressure at 13.0 GPa. Moreover, the deformation percentage along the a axis (11.1%) was greater than the b axis (8.3%) and the c axis (9.7%), with an average 24% decrease. As such, clear anisotropic compression may correspond to the sandwich structure made up of alternately connected organic and inorganic layers. Moreover, the experimental pressure–volume (P–V) data (Supporting Information Figure S9b) obtained from atmospheric conditions to 13.0 GPa were fitted by utilizing the third-order Birch-Murnaghan equation of state. The fitting bulk modulus \((K_0)\) of ETA\(_2\)PbI\(_4\) was 22.3 GPa, comparable to that of other 2D halide perovskites.\(^{39}\) The compressibility of a material is inversely proportional to \(K_0\). The compressibility of ETA\(_2\)PbI\(_4\) is obviously smaller than that of its analog 3D perovskites (13.6 GPa of MAPb\(_3\)).\(^{40}\) Therefore, 2D perovskite ETA\(_2\)PbI\(_4\) is harder and more resistant to pressure than 3D perovskites.

First-principles calculations were performed to investigate the variations of the electronic band structure upon compression, calculated electronic band structure is essential to fully understand the interaction between crystal structure and excitonic bands under high pressure. The results indicate that ETA\(_2\)PbI\(_4\) possesses a direct band gap of 1.78 eV at ambient conditions, and the band gap shrinks continuously with increasing pressure up to 8.0 GPa (Figure 4c), which is consistent with the results of our experiments. The valence band maximum (VBM) is mainly comprised of Pb 6s states with contribution of I 5p states. Simultaneously, the conduction band minimum (CBM) is mainly formed by Pb 6p orbitals with contribution of I 5s states (Supporting Information Figure S10). Upon compression, all the Pb–I–Pb angles showed a slight compression (Figure 4a and Supporting Information Table S1) because of the tilting and rotation of \([\text{PbI}_6]^{4-}\) inorganic octahedra relative to its adjacent octahedra along the a axis. Meanwhile, the bridging Pb–I bonds and terminal Pb–I bonds were gradually reduced (Figure 4b and Supporting Information Table S2). As such, an increasing electronic band dispersion accompanied rising VBM and falling CBM (Figures 4d and 4e).\(^{22,22}\) Therefore, the band gap exhibits a remarkable decrease under 8.0 GPa.\(^{41}\)

Under lower pressure, the well thickness (L) showed obvious decrease (Supporting Information Figure S11)
caused by the increase of dielectric confinement due to the negative correlation between L and dielectric confinement. Given that the exciton binding energy is positively correlated with the dielectric confinement, the exciton binding energy increase led to the PL enhancement of ETA$_2$PbI$_4$ under mild pressure. In addition, the more symmetrical PL peak ascribed to pressure-suppressed carrier trapping caused the decrease of the

**Figure 3** | (a) Representative ADXRD of ETA$_2$PbI$_4$ upon compression up to 20.2 GPa. (b) Crystal structure of ETA$_2$PbI$_4$ at ambient conditions, viewed along the b axis. Gray, violet, brown, silver, red, and pink spheres represent Pb, I, C, N, O, and H atoms, respectively. (c) Distorted Pb–I inorganic framework layer at ambient condition, viewed along the a axis. ADXRD, angle-dispersive X-ray diffraction.

**Figure 4** | (a) Schematic illustrations of Pb–I–Pb bond angle within inorganic octahedral framework upon compression. (b) Schematic illustrations of Pb–I bond length within PbI$_6$ octahedral framework upon compression. (c) First-principles calculated band gap for ETA$_2$PbI$_4$ at different pressures. (d and e) Electronic band structure for ETA$_2$PbI$_4$ under ambient conditions and 8.0 GPa, respectively.
nonradiative recombination, which also triggers the enhanced emission. As a result, there was a four times PL enhancement of ETA₂PbI₄ observed under 1.5 GPa. Above 1.5 GPa, although L still decreased, the pressure-induced suppression effect on the PL began to dominate the emission process, which was mainly caused by the structural disorder and which resulted in slow and nonlinear PL weakening.

Conclusion

The pressure-engineered crystalline structure and optical properties of ETA₂PbI₄ were systematically studied with a symmetric diamond anvil cell (DAC) apparatus. The perovskite crystal exhibited distinct enhancement of PL intensity and narrowing of band gap when pressure was applied. High-pressure PL micrographs and UV–Vis absorption micrographs indicated the distinct piezochromism of ETA₂PbI₄ crystal. Synthetic experiments containing in situ high-pressure ADXRD and Raman measurements indicated that ETA₂PbI₄ crystal experienced remarkable distortion of the [PbI₆]⁴⁻ octahedral. Our work provides supplementary information on the intrinsic characteristics of 2D organometal halide perovskites. The pressure-induced distinct PL color change allows the possible use of ETA₂PbI₄ in pressure fiber optic sensors and photovoltaic applications.

Supporting Information

Supporting Information is available.

Conflict of Interest

The authors declare no competing financial interests.

Acknowledgments

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References

1. Zhang, Q.; Zhao, J.; Xiao, Z.; Zhou, J.; Hong, B.; Luo, Z.; Bao, J.; Gao, C. Improved Moisture Stability of 2D Hybrid Perovskite (HOCO–CH₂–NH₃)₂PbI₄ by Dehydration Condensation Between Organic Components. ACS Appl. Energy Mater. 2018, 1, 2502–2511.
2. Chen, S.; Shi, G. Two-Dimensional Materials for Halide Perovskite-Based Optoelectronic Devices. Adv. Mater. 2017, 29, 1605448.
3. Cao, D. H.; Stoumpos, C. C.; Farha, O. K.; Hupp, J. T.; Kanatzidis, M. G. 2D Homologous Perovskites as Light-Absorbing Materials for Solar Cell Applications. J. Am. Chem. Soc. 2015, 137, 7843–7850.
4. Lan, C.; Zhou, Z.; Wei, R.; Ho, J. C. Two-Dimensional Perovskite Materials: From Synthesis to Energy-Related Applications. Mater. Today Energy 2019, 17, 61–82.
5. Hu, J.; Yan, L.; You, W. Two-Dimensional Organic-Inorganic Hybrid Perovskites: A New Platform for Optoelectronic Applications. Adv. Mater. 2018, 30, 1802041.
6. Mao, L.; Stoumpos, C. C.; Kanatzidis, M. G. Two-Dimensional Hybrid Halide Perovskites: Principles and Promises. J. Am. Chem. Soc. 2019, 141, 1171–1190.
7. Cheng, Z.; Lin, J. Layered Organic-Inorganic Hybrid Perovskites: Structure, Optical Properties, Film Preparation, Patterning and Templating Engineering. Cryst. Eng. Comm. 2010, 12, 2646–2662.
8. Zhou, N.; Shen, Y.; Li, L.; Tan, S.; Liu, N.; Zheng, G.; Chen, Q.; Zhou, H. Exploration of Crystallization Kinetics in Quasi Two-Dimensional Perovskite and High-Performance Solar Cells. J. Am. Chem. Soc. 2018, 140, 459–465.
9. Sheikh, T.; Shinde, A.; Mahamuni, S.; Nag, A. Possible Dual Bandgap in (C₂H₅C₂H₄NH₃)₂PbI₄ 2D Layered Perovskite: Single-Crystal and Exfoliated Few-Layer. ACS Energy Lett. 2018, 3, 2940–2946.
10. Smith, M. D.; Connor, B. A.; Karunadasa, H. I. Tuning the Luminescence of Layered Halide Perovskites. Chem. Rev. 2019, 119, 3104–3139.
11. Quarti, C.; Marchal, N.; Beljonne, D. Tuning the Optoelectronic Properties of Two-Dimensional Hybrid Perovskite Semi-Conductors with Alkyl Chain Spacers. J. Phys. Chem. Lett. 2018, 9, 3416–3424.
12. Safdari, M.; Svensson, P. H.; Hoang, M. T.; Oh, I.; Kloo, L.; Gardner, J. M. Layered 2D Alkylammonium Lead Iodide Perovskites: Synthesis, Characterization, and Use in Solar Cells. J. Mater. Chem. A 2016, 4, 15638–15646.
13. Nicolas Mercier, S. P.; Amédée, R.; Patrick, B. Unique Hydrogen Bonding Correlating with a Reduced Band Gap and Phase Transition in the Hybrid Perovskites (HO(CH₂)₃NH₂)₂PbX₄ (X=F, Cl, Br). Inorg. Chem. 2004, 43, 8361–8366.
14. Ho, K. T.; Leung, S. F.; Li, T. Y.; Maity, P.; Cheng, B.; Fu, H. C.; Mohammed, O. F.; He, J. H. Surface Effect on 2D Hybrid Perovskite Crystals: Perovskites Using an Ethanolamine Organic Layer as an Example. Adv. Mater. 2018, 30, 1804372.
15. Li, Q.; Wang, Y.; Pan, W.; Yang, W.; Zou, B.; Tang, J.; Quan, Z. High-Pressure Band-Gap Engineering in Lead-Free Cs₂AgBiBr₆ Double Perovskite. Angew. Chem. Int. Ed. 2017, 56, 15969–15973.
16. Zhang, L.; Wu, L.; Wang, K.; Zou, B. Pressure-Induced Broadband Emission of 2D Organic-Inorganic Hybrid Perovskite (Cs₂H₅C₂H₄NH₃)₂PbBr₄. Adv. Sci. 2018, 5, 1801628.
17. Zhang, L.; Liu, C.; Lin, Y.; Wang, K.; Ke, F.; Liu, C.; Mao, W. L.; Zou, B. Tuning Optical and Electronic Properties in Low-Toxicity Organic-Inorganic Hybrid (CH₃NH₃)₂Bi₂I₉ Under High Pressure. J. Phys. Chem. Lett. 2019, 10, 1676–1682.
18. Gu, Y.; Wang, K.; Dai, Y.; Xiao, G.; Ma, Y.; Qiao, Y.; Zou, B. Pressure-Induced Emission Enhancement of Carbazole: The...
Restiction of Intramolecular Vibration. *J. Phys. Chem. Lett.* 2017, 8, 4191–4196.

19. Jiang, S.; Fang, Y.; Li, R.; Xiao, H.; Crowley, J.; Wang, C.; White, T. J.; Goddard, W. A.; Wang, Z.; Baikie, T.; Fang, J. Pressure-Dependent Polymorphism and Band-Gap Tuning of Methylammonium Lead Iodide Perovskite. *Anorg. Chem. Int. Ed.* 2016, 55, 6540–6544.

20. Wang, L.; Wang, K.; Zou, B. Pressure-Induced Structural and Optical Properties of Organometal Halide Perovskite-Based Formamidinium Lead Bromide. *J. Phys. Chem. Lett.* 2016, 7, 2556–2562.

21. Liu, S.; Sun, S.; Gan, C. K.; Del Aguila, A. G.; Fang, Y.; Xing, J.; Do, T. T. H.; White, T. J.; Li, H.; Huang, W.; Xiong, Q. Manipulating Efficient Light Emission in Two-Dimensional Perovskite Crystals by Pressure-Induced Anisotropic Deformation. *Sci. Adv.* 2019, 5, eaav9445.

22. Liu, G.; Gong, J.; Kong, L.; Schaller, R. D.; Hu, Q.; Liu, Z.; Yan, S.; Yang, W.; Stoumpos, C. C.; Kanatzidis, M. G.; Mao, H. K.; Xu, T. Isothermal Pressure-Derived Metastable States in 2D Hybrid Perovskites Showing Enduring Bandgap Narrowing. *Proc. Natl. Acad. Sci. U. S. A.* 2018, 115, 8076–8081.

23. Yin, T.; Liu, B.; Yan, J.; Fang, Y.; Chen, M.; Chong, W. K.; Jiang, S.; Kuo, J. L.; Fang, J.; Liang, P.; Wei, S. H.; Loh, K. P.; Sum, T. C.; White, T. J.; Shen, Z. X. Pressure-Engineered Structural and Optical Properties of Two-Dimensional (CH$_3$NH$_3$)$_2$PbI$_4$ Perovskite Exfoliated nm-Thin Flakes. *J. Am. Chem. Soc.* 2019, 141, 1235–1241.

24. Jaffe, A.; Lin, Y.; Mao, W. L.; Karunadasa, H. I. Pressure-Induced Conductivity and Yellow-to-Black Piezochromism in a Layered Cu–Cl Hybrid Perovskite. *J. Am. Chem. Soc.* 2015, 137, 1673–1678.

25. Liu, G.; Kong, L.; Yang, W.; Mao, H. K. Pressure Engineering of Photovoltaic Perovskites. *Mater. Today* 2019, 27, 91–106.

26. Zhang, L.; Fang, Y.; Sui, L.; Yan, J.; Wang, K.; Yuan, K.; Mao, W. L.; Zou, B. Tuning Emission and Electron-Phonon Coupling in Lead-Free Halide Double Perovskite Cs$_2$AgBiCl$_6$ Under Pressure. *ACS Energy Lett.* 2019, 4, 2975–2982.

27. Zhu, H.; Cai, T.; Que, M.; Song, J.; Rubenstein, B.; Wang, Z.; Chen, O. Pressure-Induced Phase Transformation and Band-Gap Engineering of Formamidinium Lead Iodide Perovskite Nanocrystals. *J. Phys. Chem. Lett.* 2018, 9, 4199–4205.

28. Nagaoka, Y.; Hills-Kimball, K.; Tan, R.; Li, R.; Wang, Z.; Chen, O. Nanocube Superlattices of Cs$_2$PbI$_4$ as a Template to Control the Crystal Structure of Lead Iodide Perovskites and Pressure-Induced Phase Transformations at Atomic and Mesoscale Levels. *Adv. Mater.* 2017, 29, 1606666.

29. Qi, G.; Wang, K.; Xiao, G.; Zou, B. High Pressure, a Protocol to Identify the Weak Dihydrogen Bonds: Experimental Evidence of C–H...H–B Interaction. *Sci. Chin. Chem.* 2017, 61, 276–280.

30. Ma, Z.; Li, F.; Zhao, D.; Xiao, G.; Zou, B. Whether or Not Emission of Cs$_4$PbBr$_6$ Nanocrystals: High-Pressure Experimental Evidence. *CCS Chem.* 2020, 2, 71–80.

31. Yu, D.; Cao, F.; Shen, Y.; Liu, X.; Zhu, Y.; Zeng, H. Dimensionality and Interface Engineering of 2D Homologous Perovskites for Boosted Charge-Carrier Transport and Photodetection Performances. *J. Phys. Chem. Lett.* 2017, 8, 2565–2572.

32. Wang, Y.; Guo, S.; Luo, H.; Zhou, C.; Lin, H.; Ma, X.; Hu, Q.; Du, M. H.; Ma, B.; Yang, W.; Lu, X. Reaching 90% Photoluminescence Quantum Yield in One-Dimensional Metal Halide Ca$_2$Na$_2$H$_2$PbBr$_6$ by Pressure-Suppressed Nonradiative Loss. *J. Am. Chem. Soc.* 2020, 142, 16001–16006.

33. Wang, Y.; Lu, X.; Yang, W.; Wen, T.; Yang, L.; Ren, X.; Wang, L.; Lin, Z.; Zhao, Y. Pressure-Induced Phase Transformation, Reversible Amorphization, and Anomalous Visible Light Response in Organolead Bromide Perovskite. *J. Am. Chem. Soc.* 2015, 137, 11144–11149.

34. Lu, X.; Wang, Y.; Stoumpos, C. C.; Hu, Q.; Guo, X.; Chen, H.; Yang, L.; Smith, J. S.; Yang, W.; Zhao, Y.; Xu, H.; Kanatzidis, M. G.; Jia, Q. Enhanced Structural Stability and Photo Responsiveness of CH$_3$NH$_3$SnI$_3$ Perovskite via Pressure-Induced Amorphization and Recrystallization. *Adv. Mater.* 2016, 28, 8663–8668.

35. Umeyama, D.; Lin, Y.; Karunadasa, H. I. Red-to-Black Piezochromism in a Compressible PbI$_2$–SCN Layered Perovskite. *Chem. Mater.* 2018, 26, 3241–3244.

36. Shi, Y.; Ma, Z.; Zhao, D.; Chen, Y.; Cao, Y.; Wang, K.; Xiao, G.; Zou, B. Pressure-Induced Emission (PIE) of One-Dimensional Organic Tin Bromide Perovskites. *J. Am. Chem. Soc.* 2019, 141, 6504–6508.

37. Ma, Z.; Liu, Z.; Lu, S.; Wang, L.; Feng, X.; Yang, D.; Wang, K.; Xiao, G.; Zhang, L.; Redfern, S. A. T.; Zou, B. Pressure-Induced Emission of Cesium Lead Halide Perovskite Nanocrystals. *Nat. Commun.* 2018, 9, 4506.

38. Fang, Y.; Zhang, L.; Wu, L.; Yan, J.; Lin, Y.; Wang, K.; Mao, W. L.; Zou, B. Pressure-Induced Emission (PIE) and Phase Transition of a Two-Dimensional Halide Double Perovskite (BA)$_2$AgBiBr$_6$ (BA = CH$_3$(CH$_2$)$_3$NH$_3$). *Angew. Chem. Int. Ed.* 2019, 58, 15249–15253.

39. Li, Q.; Yin, L.; Chen, Z.; Deng, K.; Luo, S.; Zou, B.; Wang, Z.; Tang, J.; Quan, Z. High Pressure Structural and Optical Properties of Two-Dimensional Hybrid Halide Perovskite (CH$_3$NH$_3$)$_2$Bi$_2$Br$_7$. *Inorg. Chem.* 2019, 58, 1621–1626.

40. Capitani, F.; Marini, C.; Caramazza, S.; Postorino, P.; Garbarino, G.; Hanfland, M.; Pisanu, A.; Quadrelli, P.; Malavasi, L. High-Pressure Behavior of Methylammonium Lead Iodide (MAPb$_3$) Hybrid Perovskite. *J. Appl. Phys.* 2016, 119, 185901.

41. Liu, G.; Kong, L.; Guo, P.; Stoumpos, C. C.; Hu, Q.; Liu, Z.; Cai, Z.; Gosztoła, D. J.; Mao, H.-k.; Kanatzidis, M. G.; Schaller, R. D. Two Regimes of Bandgap Red Shift and Partial Ambient Retention in Pressure-Treated Two-Dimensional Perovskites. *ACS Energy Lett.* 2017, 2, 2518–2524.

42. Hong, X.; Ishihara, T.; Nurmiokko, A. V. Dielectric Confinement Effect on Excitons in PbI$_4$-Based Layered Semiconductors. *Phys. Rev. B* 1992, 45, 6961–6964.

43. Blanc, J. C.; Stier, A. V.; Tsai, H.; Nie, W.; Stoumpos, C. C.; Traore, B.; Pedesseau, L.; Kepenekian, M.; Katsunani, F.; Noe, G. T.; Kono, J.; Tretiak, S.; Crooker, S. A.; Katan, C.; Kanatzidis, M. G.; Crochet, J. J.; Even, J.; Mohite, A. D. Scaling Law for Excitons in 2D Perovskite Quantum Wells. *Nat. Commun.* 2018, 9, 2254.
44. Young-Hoon Kima, H. C.; Tae-Woo, L. Metal Halide Perovskite Light Emitters. Proc. Natl. Acad. Sci. U. S. A. 2016, 113, 11694–11702.
45. Capitani, F.; Marini, C.; Caramazza, S.; Dore, P.; Pisano, A.; Malavasi, L.; Nataf, L.; Baudelet, F.; Brubach, J. B.; Roy, P.; Postorino, P. Locking of Methylammonium by Pressure-Enhanced H-Bonding in (CH$_3$NH$_3$)$_2$PbBr$_3$ Hybrid Perovskite. J. Phys. Chem. C 2017, 121, 28125–28131.
46. Chen, Y.; Fu, R.; Wang, L.; Ma, Z.; Xiao, G.; Wang, K.; Zou, B. Emission Enhancement and Bandgap Retention of a Two-Dimensional Mixed Cation Lead Halide Perovskite Under High Pressure. J. Mater. Chem. A 2019, 7, 6357–6362.
47. Guo, S.; Zhao, Y.; Bu, K.; Fu, Y.; Luo, H.; Chen, M.; Hautzinger, M. P.; Wang, Y.; Jin, S.; Yang, W.; Lu, X. Pressure-Suppressed Carrier Trapping Leads to Enhanced Emission in Two-Dimensional Perovskite (HA)$_2$ (GA)Pb$_2$I$_7$. Angew. Chem. Int. Ed. 2020, 132, 2–9.
48. Zhang, L.; Liu, C.; Wang, L.; Liu, C.; Wang, K.; Zou, B. Pressure-Induced Emission Enhancement, Band-Gap Narrowing, and Metallization of Halide Perovskite Cs$_3$Bi$_2$I$_9$. Angew. Chem. Int. Ed. 2018, 57, 11213–11217.