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Pressure-Engineered Structural and Optical Properties of Two-Dimensional $(\text{C}_4\text{H}_9\text{NH}_3)_2\text{PbI}_4$ Perovskite Exfoliated nm-Thin FlakesTingting Yin,[‡] Bo Liu,^{§,||} Jiaxu Yan,^{*,†,||} Yanan Fang,^{⊥,||} Minghua Chen,[▽] Wee Kiang Chong,^{#,||} Shaojie Jiang,[○] Jer-Lai Kuo,[◆] Jiye Fang,[○] Pei Liang,[¶] Shuhuai Wei,[□] Kian Ping Loh,^{§,||} Tze Chien Sum,^{*,||} Timothy J. White,^{*,⊥} and Ze Xiang Shen^{*,‡,||}[†]Key Laboratory of Flexible Electronics (KLOFE) & Institute of Advanced Materials (IAM), Jiangsu National Synergistic Innovation Center for Advanced Materials (SICAM), Nanjing Tech University (Nanjing Tech), 30 South Puzhu Road, Nanjing 211816, P. R. China[‡]Centre for Disruptive Photonic Technologies, School of Physical and Mathematical Sciences, Nanyang Technological University 637371, Singapore[§]Department of Chemistry and Centre for Advanced 2D Materials (CA2DM), 3 Science Drive 3 117543, Singapore^{||}Division of Physics and Applied Physics, School of Physical and Mathematical Sciences (SPMS), NTU, 21 Nanyang Link 637371, Singapore[⊥]ERI@N, Research Techno Plaza, X-Frontier Block, Level 5, 50 Nanyang Drive 637553, Singapore[#]Energy Research Institute @ NTU, ERI@N, Interdisciplinary Graduate School, Nanyang Technological University 639798, Singapore[▽]Key Laboratory of Engineering Dielectric and Applications (Ministry of Education), Harbin University of Science and Technology, Harbin 150080, P. R. China[○]Materials Science and Engineering Program, State University of New York at Binghamton Binghamton, New York 13902, United States[◆]Institute of Atomic and Molecular Sciences, Academia Sinica, Taipei 10617, Taiwan[¶]College of Optical and Electronic Technology, China Jiliang University, 310018 Hangzhou, China[□]Beijing Computational Science Research Center, 100094 Beijing, China

Supporting Information

ABSTRACT: Resolving the structure–property relationships of two-dimensional (2D) organic–inorganic hybrid perovskites is essential for the development of photovoltaic and photoelectronic devices. Here, pressure (0–10 GPa) was applied to 2D hybrid perovskite flakes mechanically exfoliated from butylammonium lead halide single crystals, $(\text{C}_4\text{H}_9\text{NH}_3)_2\text{PbI}_4$, from which we observed a series of changes of the strong excitonic emissions in the photoluminescence spectra. By correlating with in situ high-pressure X-ray diffraction results, we examine successfully the relationship between structural modifications in the inorganic PbI_4^{2-} layer and their excitonic properties. During the transition between $Pbca$ (1b) phase and $Pbca$ (1a) phase at around 0.1 GPa, the decrease in $\langle\text{Pb}-\text{I}-\text{Pb}\rangle$ bond angle and increase in $\text{Pb}-\text{I}$ bond length lead to an abrupt blue shift of the excitonic bandgap. The presence of the $P2_1/a$ phase above 1.4 GPa increases the $\langle\text{Pb}-\text{I}-\text{Pb}\rangle$ bond angle and decreases the $\text{Pb}-\text{I}$ bond length, leading to a deep red shift of the excitonic bandgap. The total band gap narrowing of ~ 350 meV to 2.03 eV at 5.3 GPa before amorphization, facilitates $(\text{C}_4\text{H}_9\text{NH}_3)_2\text{PbI}_4$ as a much better solar absorber. Moreover, phase transitions inevitably modify the carrier lifetime of $(\text{C}_4\text{H}_9\text{NH}_3)_2\text{PbI}_4$, where an initial 150 ps at ambient phase is prolonged to 190 ps in the $Pbca$ (1a) phase along with enhanced photoluminescence (PL), originating from pressure-induced strong radiative recombination of trapped excitons. The onset of $P2_1/a$ phase shortens significantly the carrier lifetime to 53 ps along with a weak PL emission due to pressure-induced severe lattice distortion and amorphization. High-pressure study on $(\text{C}_4\text{H}_9\text{NH}_3)_2\text{PbI}_4$ nm-thin flakes may provide insights into the mechanisms for synthetically designing novel 2D hybrid perovskite based photoelectronic devices and solar cells.

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Figure 1. Optical characterizations of BAPI (BA = $\text{C}_4\text{H}_9\text{NH}_3^+$) 2D layered perovskite single crystal under high pressure. (a,b) The optical image of the original BAPI exfoliated flakes inside the DAC. (c) Optical micrographs at selected pressures showing piezochromism in BAPI. (d,e) In situ high-pressure absorption and PL spectra of the BAPI exfoliated flakes.

INTRODUCTION

Three-dimensional (3D) hybrid perovskites have been extensively studied as light-harvesting materials with power conversion efficiencies (PCE) of up to 23.3% certified,¹ but suffer compromised performance due to hygroscopic decomposition,^{2,3} ready oxidization,⁴ heat sensitivity,⁵ and light degradation.⁶ These limitations are less severe in butylammonium (BA)–methylammonium (MA) two-dimensional (2D) lead iodide perovskites with general formula, $(\text{C}_4\text{H}_9\text{NH}_3)_2(\text{CH}_3\text{NH}_3)_{n-1}\text{Pb}_n\text{I}_{3n+1}$, or more simply, $((\text{BA})_2(\text{MA})_{n-1}\text{Pb}_n\text{I}_{3n+1})$, where n is the inorganic layer number with $1 \leq n \leq \infty$.⁷ The BA^+ groups intercalate with $((\text{MA})_{n-1}\text{Pb}_n\text{I}_{3n+1})^{2-}$ blocks to produce lamellar structures that are stable for at least two months in air^{8,9} and achieve PCE of 12.52%.^{9,10} In addition, the direct band gap can be tailored to cover the visible region by adjusting the inorganic layer number n .¹¹ These features render 2D hybrid perovskites superior to their 3D counterparts as tunable and highly efficient light absorbers for optoelectronic^{12–15} and photovoltaic applications.^{10,16–18} Thus, from the point of view of improved photovoltaic operation, it is essential to satisfy a wide-range bandgap tunability in 2D layered hybrid perovskites.

The electronic band structure is intimately linked with chemical bonding character that is pressure sensitive, and can be modified by “internal” stress through the modification of relative ionic sizes¹⁹ or “externally” through application of strain²⁰ and hydrostatic pressure. The latter approach proves particularly useful to develop a fundamental understanding of electronic structures since the influence of compositional variation is avoided. Moreover, in hybrid perovskites, relatively modest pressures of a few gigapascals (up to 10 GPa), can elicit polymorphic conversions sometimes inaccessible by chemical

tuning.²¹ For 3D perovskites, pressure-induced phase transformations,^{13,22–24} amorphization,²⁵ bandgap shifts,^{13,23,26} increased electronic conductivity,²⁷ and carrier-lifetime prolongation^{23,28} have been observed. As for 2D hybrid perovskites, only one preliminary high-pressure study on $(\text{C}_4\text{H}_9\text{NH}_3)_2\text{PbI}_4$ (BAPI) bulk crystals in 2004,²⁹ reported the pressure-driven change of the excitonic band edge in the absorption spectra without any structural analysis and physical explanation. Recently, pressure-induced two-step red shift in photoluminescence (PL) of $(\text{BA})_2(\text{MA})\text{Pb}_2\text{I}_7$ ($n = 2$) bulk crystals was reported and explained by the layer-to-layer and the interlayer compression under high pressure, without paying close attentions to phase transitions.³⁰ Most recently, one paper reported that an enduring bandgap narrowing (8.2% decrease) was achieved in $(\text{BA})_2(\text{MA})_2\text{Pb}_3\text{I}_{10}$ ($n = 3$) bulk crystals after compression–decompression cycles.³¹ Until now, complete crystal structures under high pressure fail to be resolved and the pressure-dependent evolution of the direct excitonic transitions cannot be obtained by using thick samples. Therefore, a full assessment of the crystal structures of 2D hybrid perovskites under high pressure will shed light on the structure–excitonic property correlation and deepen the fundamental understanding of the crystallochemical drivers of excitonic properties for their potential applications.

In this work, correlations between pressure-mediated crystal structural adjustments and excitonic properties were examined for the first time in the BAPI ($n = 1$) 2D perovskite exfoliated flakes using in situ synchrotron powder X-ray diffraction (XRD), Raman spectroscopy and PL spectroscopy supported with *ab initio* calculations. As for the excitonic absorption spectra, we have chosen the thinner exfoliated BAPI flakes with thickness of 50 nm. We found that bandgap shifts under pressure are controlled by Pb and I orbital interactions reflected both in the

Figure 2. Structural characterizations of BAPI under high pressure. (a) Integrated in situ high-pressure synchrotron powder XRD patterns of BAPI at three representative 2 theta ranges. (b) Schematic illustrations of three crystal structures of BAPI under high pressure: organic-inorganic packing diagrams with interdigitating bilayers of BA spacer cations being inserted between PbI₄²⁻ inorganic sheets. (c) Representative vibrational modes of inorganic PbI₆ octahedra and BA organic molecules under pressure. Black, purple, brown, blue, and light pink spheres represent Pb, I, C, N, and H atoms, respectively. H atoms are omitted in packing diagram of the crystal structure for clarity.

Pb–I bond length within a PbI₆ octahedron and the ⟨Pb–I–Pb⟩ bond angle between two PbI₆ octahedra, where the decrease of Pb–I bond length and ⟨Pb–I–Pb⟩ bond angle modifies the bandgap in an opposite sense. In addition, the ⟨Pb–I–Pb⟩ bond angle (octahedral tilting) is the dominant structural factor impacting the band gap across polymorphic transitions, while

the Pb–I bond length (contraction) is the major influence on the excitonic structure within each single phase. The structure–property relationship established here provides general guidance for engineering the excitonic character of 2D hybrid perovskites. By choosing proper M/X element combinations that deliver less distorted MX₄²⁻ lattices and shorter M–X bond lengths, 2D

Figure 3. Correlation of structure-excitonic property of BAPI under high pressure. (a–c) Calculated band structures and the isosurfaces of partial electron densities for VBM and CBM of BAPI under representative pressures (0 GPa, 0.4 and 3.0 GPa). (d) Exciton evolution as a function of pressure: experiment (spheres) and calculation (circles), respectively. The colorful shadows represent phase evolution with increasing pressure. Derived structural parameters of $\langle \text{Pb–I–Pb} \rangle$ bond angle (e) and the averaged value of two equatorial Pb–I bond lengths (f) from the structural models used for bandgap calculations in (d). (g) Band gaps calculated by purely changing the bond angle (diamonds) or changing the bond length (pentagons). For LT and HP phases, we adopted the optimized atomic structure at 0 and 1.5 GPa as the initial model, respectively.

layered hybrid perovskites with smaller band gaps are produced especially for solar cell applications.

RESULTS AND DISCUSSION

Solution grown BAPI ($n = 1$) perovskites appear as orange yellow bulk polycrystals, which limit the optical characterizations of intrinsic excitonic properties. So thin flakes of BAPI (Figure 1a) were exfoliated by following the method developed for graphene exfoliation,³² and transferred onto a culet of 500 μm of the diamond anvil cell (DAC) (Figure 1b) for in situ high-pressure optical analyses. Since the thin flakes of BAPI sample is air sensitive, the hexagonal boron nitride (hBN) thin layer was also transferred onto the culet to cover the BAPI thin flakes to prevent direct air contact.³³ Alignment of the transferred BAPI flakes and hBN layer was performed under a microscope in the glovebox, a controlled argon environment. The sample thickness determination is shown in Figure S1 of the Supporting Information (SI). Upon compression from 0 to 10 GPa, the BAPI displays piezochromic transitions (Figure 1c), indicating pressure-driven shifts of absorption edge in BAPI (Figure 1d). The strong absorption peaks confirm the intense direct excitonic transitions. More important, we observed a series of changes of the strong excitonic emissions in the PL spectra, where the initial PL peak I of BAPI at ambient condition is 524 nm (2.37 eV), then red shifts a little bit to 527 nm (2.35 eV) with an additional peak II at 503 nm (2.47 eV) at ~ 0.14 GPa, suggesting the appearance of the second phase. With increasing pressure, peak II keeps a consistent red shift until another new emission peak III grows up at ~ 540 nm (2.30 eV) at 1.4 GPa, indicating the third phase. With further compression, the peak III becomes dominant and exhibits a consistent red

shift with a pronounced band gap narrowing down to 611 nm (2.03 eV) at 5.3 GPa. At 10 GPa, both the absorption and PL spectra become very broad, which is obvious that BAPI crystals transform into the amorphous phase at very high pressure. After pressure released back to 0 GPa, the PL emission was reversible (the blue line in Figure S2b), as demonstrated by the diffraction pattern (the top black line in Figure 2a) and the Raman spectra (the top lines in Figure 2c) measured in the pressure-released BAPI sample.

Pressure-Mediated Crystal Structures. Structural variation is the main origin for the intriguing excitonic band change under high pressure. Figure 2a shows the in situ high-pressure powder X-ray diffraction patterns obtained from BAPI powder sample. At ambient conditions, the BAPI polymorph is orthorhombic $Pbca$ (1b), i.e., room-temperature (RT) phase,^{34,35} with $a = 8.851(2)$ Å; $b = 8.654(3)$ Å; $c = 27.735(3)$ Å (Figure S3a and Table S1), where the PbI_4^{2-} sheets are separated by interdigitated bilayers of butylammonium (BA) cations (Figure 2b).³⁴

The inorganic–organic layers communicate through hydrogen-bonding between the NH_3^+ groups and the I^- ions.^{36,37} From the structural top view, the NH_3^+ group faces to the obtuse angle of the parallelogram defined by the four bridging I (Figure S4a). The first phase transition starts from ~ 0.1 GPa (Figure S5), the pure new structure shows abrupt displacements for Bragg (002) and (111) reflections and the interchange of Bragg (200) and (020) reflections (Figure 2a). On the basis of the structural refinement, we identify that this new phase still maintains $Pbca$ (1b) space symmetry but swapping a and b axis, with $a = 8.484(1)$ Å; $b = 9.111(1)$ Å; $c = 27.128(4)$ Å (Figure S3b and Table S1), i.e., $Pbca$ (1a). This space group is consistent

with that low-temperature (LT) phase reported in previous temperature-dependent differential scanning calorimetry (DSC) and XRD measurements on the BAPI single crystals.³⁵ Since cooling and compression have the similar effects on the structural symmetry of crystals, we name this high-pressure induced new phase, *Pbca* (1a), as “LT” phase in this paper. In the *Pbca* (1b) RT phase, PbI_6 octahedral tilting is entirely in the *a*-*b* plane, while the out-of-plane tilting leads to a large change in the *a* and *b*,³⁸ and the NH_3^+ group faces to the acute angle of the parallelogram defined by the four bridging I (Figure S4b). At ~ 1.6 GPa, the emergence of Bragg (002), (111) and (020) reflections appear at $\sim 2.15^\circ$, 4.45° and 6.09° , indicates a lower symmetry. The diffraction pattern can be fitted well by the monoclinic $P2_1/a$ space group with $a = 8.500(3)$ Å; $b = 9.298(6)$ Å; $c = 12.673(5)$ Å; $\beta = 103.48(1)^\circ$ that coexists with the *Pbca* (1a) polymorph (Figure S3c and Table S1). Above 5.0 GPa, the transformation to the high-pressure (HP) $P2_1/a$ phase has completed (Figure S3d), and is characterized by the monoclinic angle (β) (Table S1) due to the movement of every second layer of the LT phase by $b/2$ to realize an eclipsed arrangement of the adjacent inorganic layers (Figure 2b), that efficiently halves the *c* parameter (Table S1).

These two phase transitions are confirmed from the Raman spectra in the low-frequency region (Figure 2c), due to the inorganic octahedral in-phase (W1) and out-of-phase bending (W3) modes becoming remarkably sharp in the *Pbca* (1a) LT phase with an additional octahedral out-of-phase rotation (W2) mode appearing in the $P2_1/a$ HP phase.^{39,40} During octahedral tilting, the BA molecule (Figure S4), reorients from almost parallel to the long diagonal of the parallelogram formed by the adjacent four bridging I atoms in *Pbca* (1b) RT phase, to the short diagonal in *Pbca* (1a) LT and $P2_1/a$ HP phase. The orientation of the BA molecule is directly revealed by the representative Raman modes in high-frequency region (Figure 2c),^{40,41} where the BA rocking mode is sharp in *Pbca* (1a) LT phase, while the BA breathing and C–N stretching modes are active only in $P2_1/a$ HP phase. All the Raman shifts are reversible upon decompression (the top lines in Figure 2c), demonstrating that $[\text{C}_4\text{H}_9\text{NH}_3]^+$ chains act as the spring cushion to protect the PbI_4^{2-} layers and the whole structure.^{24,42}

Pressure-Mediated Excitonic Structures. To fully understand the interplay between crystal structures and excitonic bands under high pressure, a series of theoretical calculations are performed. First, we compared the excitonic band structures at 0 GPa, 0.4 and 3.0 GPa, three key pressure points corresponding to *Pbca* (1b) RT, *Pbca* (1a) LT and $P2_1/a$ HP pure phases (Figure 3a–c). It is clear that the band gap is increased up to 2.16 eV at 0.4 GPa compared to the value of 1.97 eV at 0 GPa while is decreased to 1.96 eV at 3.0 GPa, which correlates to the blue shift for the first phase transition and a red shift for the second phase transition observed in both measured absorption and PL spectra. Then, we calculated a series of bandgap energies (the circles in Figure 3d) and plotted them as a function of pressure to compare with the experimental excitonic peak positions (the spheres in Figure 3d). The pressure dependency of the band gaps for LT and HP phases was evaluated with respect to two distinct structural effects: $\langle \text{Pb–I–Pb} \rangle$ bond angle (Figure 3e) and Pb–I bond length (Figure 3f). At 0.4 GPa, the $\langle \text{Pb–I–Pb} \rangle$ bond angle undergoes a sudden drop from 150.2° to 144.9° and the elongated averaged equatorial Pb–I bond length enlongates dramatically from 3.09 Å to ~ 3.14 Å (Table S2), corresponding to a transition from *Pbca* (1b) RT – *Pbca* (1a) LT phase. The more acute $\langle \text{Pb–I–Pb} \rangle$ bond angle and

longer Pb–I bond length diminish Pb–I orbital overlap, weakening antibonding interactions of the Pb 6s and the I 5p_x/p_y orbitals and reducing the valence band maximum (VBM). Simultaneously, the conduction band minimum (CBM) mainly formed by Pb 6p orbitals keeps almost no shift (Figure 3a and Figure 3b). Overall, the band gap becomes broad and a blue shift is observed at 0.4 GPa in both absorption and PL spectra (Figure 1d and Figure 1e). The anomalous increase of the bond length under compression is due to structural symmetry change in *Pbca* (1a) LT phase, where the reorientation of long-chain BA molecules and the out-of-plane bended distortion of inorganic PbI_6 octahedra may make Pb–I bond more space to release (Figure 2b). The onset of the $P2_1/a$ HP phase at ~ 1.5 GPa, the $\langle \text{Pb–I–Pb} \rangle$ bond angle increases to 150.5° and the averaged Pb–I bond length further decreases to 3.09 Å (Table S2), both contributing a more narrowed band gap and a second peak in both absorption and PL spectra (Figure 1d and Figure 1e). Such an increase of the $\langle \text{Pb–I–Pb} \rangle$ bond angle originates from the more intersected long-chain BA molecules under higher pressure and the in-plane twisted inorganic PbI_6 octahedra (Figure 2b).

To determine quantitatively the effect of two structural factors on the excitonic band gap in each single phase. The calculated bandgap energy as a function of the $\langle \text{Pb–I–Pb} \rangle$ bond angle (the wine red diamonds) and Pb–I bond length (the ink blue diamonds) is plotted in Figure 3g. Within the *Pbca* (1a) LT phase from 0.4 to 3.0 GPa, the decrease in bond angle ($\Delta = -1.21^\circ$) and bond length ($\Delta = -0.071$ Å) modifies the bandgap in an opposite sense, as the bond length narrows the energy bandgap $\Delta = -0.23$ eV and the bond angle widens the bandgap only $\Delta = 0.08$ eV (the ink blue diamonds in Figure 3g), resulting in an overall red shift in the spectroscopic data in Figure 3d. Within the $P2_1/a$ HP phase from 1.4 to 5.3 GPa, the increase of bond angle ($\Delta = 3.75^\circ$) and further decreased bond length ($\Delta = -0.087$ Å) contribute a consistent action in bandgap narrowing (the wine red pentagons in Figure 3g), resulting in a more pronounced red shift in the observed excitonic peaks compared to the *Pbca* (1a) LT phase. Our comprehensive calculations fully resolve the structural origin for the observed blue jump and red drop during phase transitions and two-regime red-shift behavior of the excitonic emission peaks in two distinct phases, providing a synthetic method for fine-tuning the energy band structure.

Pressure-Mediated Exciton Dynamics. Changes in crystal structures may further engineer carrier properties, as explored by high-pressure time-resolved photoluminescence (TRPL) (Figure 4a–c). At ambient pressure, the mean exciton lifetime is $\sim 150 \pm 20$ ps, consistent with the reported time scale for $n = 1$ BAPI single crystals,^{12,43} where the fast decay channel ($\tau_1 = 51 \pm 1$ ps) refers to the recombination of free excitons and the slow decay channel ($\tau_2 = 320 \pm 10$ ps) refers to the recombination of localized trapped excitons. It can also be demonstrated by the asymmetric line-shape of PL spectra (Figure 1e), the long tail comes from radiative recombination of excitonic trap states.⁴⁴ A longer exciton lifetime of $\sim 190 \pm 10$ ps is observed at 0.4 GPa *Pbca* (1a) LT phase, where the lifetime of trapped excitons is prolonged to 440 ± 20 ps, indicating that more excitons are trapped by the distorted PbI_4^{2-} lattices and localized at the organic–inorganic interfaces of BAPI.²³ This trap-assisted excitonic radiative emission process contributes to enhanced PL emission in *Pbca* (1a) LT phase with a maximum value of 2.3 (Figure 4d). The presence of the $P2_1/a$ HP phase leads to a significant shortening in carrier lifetime, indicating a strong nonradiative recombination process due to more and

Figure 4. Carrier lifetime in high pressure-induced three phases. (a–c) TRPL spectra of BAPI single crystal at 0 GPa (RT phase), 0.4 GPa (LT phase), and 2.3 GPa (LT+HP phase). All the TRPL spectra were obtained from the peak I in static PL spectra. A biexponential treatment ($I_{PL}(t) = I_{int} [A_{slow} \exp(-t/\tau_{slow}) + A_{fast} \exp(-t/\tau_{fast}) + I_0]$) used to extract the mean carrier time ($\langle\tau\rangle = [A_{slow} \tau_{slow}^2 / (A_{slow} \tau_{slow} + A_{fast} \tau_{fast})] + [A_{fast} \tau_{fast}^2 / (A_{slow} \tau_{slow} + A_{fast} \tau_{fast})]$), where τ_{slow} and τ_{fast} are assigned to the trapped and free exciton recombination, respectively. (d) Pressure dependence of integrated PL intensities for the corresponding peaks from 0 to 5.3 GPa. PL emission is enhanced in *Pbca* (1a) LT phase with a maximum enhancement of 2.3 times at 0.4 GPa.

more defects introduced by pressure-induced mixed phase and the onset of amorphization. For example, the carrier lifetime becomes $\sim 36 \pm 5$ ps at 2.3 GPa, where the lifetime of both free and trapped excitons shortens significantly to 16 ± 1 ps and 153 ± 6 ps, respectively. The second PL peak is dominated from these self-trapped excitations, as demonstrated by the relative fat and symmetric PL spectra under higher pressure (Figure 1e). The PL emission intensity in *P2₁/a* HP phase (the wine red cubes in Figure 4d) becomes even lower than the initial PL intensity (the black cube in Figure 4d) just due to the nonradiative decay of self-trapped excitations. Further high-pressure time-resolved characterizations assist the physical understanding of the high-pressure effect on photoelectric properties.

CONCLUSIONS

The straightforward relationship between crystallographic polymorphism and excitonic behaviors has been resolved for 2D hybrid perovskites via the comprehensive high-pressure characterizations, by optically monitoring the evolution of strong excitonic peaks in exfoliated flakes and carefully refining the structural variation supported by a series of *ab initio* calculations. Smaller $\langle\text{Pb—I—Pb}\rangle$ bond angles widen the band gap, while shorter Pb—I bond lengths have the opposite effect. The two-step redshift behavior in excitonic bandgap of BAPI 2D perovskite will lead to superior solar absorbers. High pressure is an effective tool to provide deeper insights into structure–property correlations from the atomic level, to inform the optimization of functional properties (e.g., high-level bandgap narrowing and carrier lifetime prolongation/short-

ening) through the synthetic design of hybrid perovskite materials for photovoltaic and photoelectric applications.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.8b07765.

Synthesis process of thin layer $(\text{C}_4\text{H}_9\text{NH}_3)_2\text{PbI}_4$; in situ high-pressure experimental details of XRD measurements, static absorption/PL/Raman measurements and time-resolved PL measurements; *ab initio* calculations; crystallographic information; and additional results and references (PDF)

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Notes

The authors declare no competing financial interest.

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