Supporting Information

Pressure-Induced Distinct Excitonic Properties of 2D Perovskites with Isomeric Organic Molecules for Spacer Cations

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Sample Preparation

Materials: Isopentylamine ($(CH_3)_2CH(CH_2)_2NH_2$, 99%), Amylamine ($CH_3(CH_2)_4NH_2$, 99%) Hypophosphorous acid (H_3PO_2, 50%wt) and Lead oxide (PbO, 99%) are purchased from Aladdin. Hydriodic acid (HI, 57%wt) is purchased from Sigma Aldrich. All the chemical materials are used as received.

Preparation of $[CH_3(CH_2)_4NH_3]_2PbI_4$: PbO(0.15 mmol) is dissolved in 1ml of 57% HI in a sample vial. Thereafter, 0.25 mmol of $CH_3(CH_2)_4NH_2$ is added and the precipitate dissolved for 2 h at 363 K. The solution is slowly cooled to room temperature.

Preparation of $[(CH_3)_2CH(CH_2)_2NH_3]_2PbI_4$: PbO(0.15 mmol) is dissolved in 1 ml of 57% HI and 0.02 ml of H_3PO_2 in a sample vial. Thereafter, 0.25 mmol of $(CH_3)_2CH(CH_2)_2NH_2$ is added and the precipitate dissolved by refluxing for 2 h at 368 K. The solution is slowly cooled to room temperature.

Optical Measurement

High Pressure: A diamond anvil cell (DAC) with 500 μm diameter culets was used to reach high pressure conditions. A T301 stainless steel gasket with a 150 μm hole and 40 μm thickness served as the sample chamber. The sample was loaded into the sample chamber along with a ruby ball to determine pressure according to the ruby fluorescence technique. In high pressure optical absorption, PL spectra and PL lifetime experiments, we used silicone oil as a pressure-transmitting medium.

In Situ High-Pressure Optical Measurements: The in situ high-pressure PL measurements were carried out using the 405 nm pulsed laser. In situ high-pressure UV–vis absorption measurements were performed by using a deuterium-halogen light source. The fiber spectrometer used is an Ocean Optics QE65000 spectrometer. The PL micrographs of the samples upon compression were taken with a camera (CanonEos 5D mark II) installed on a microscope (Ecilipse TI-U, Nikon). In situ high-pressure Raman spectra were collected by using a Raman spectrometer (iHR550, Symphony II, Horiba Jobin Yvon) with a 785 nm and 10 mW excitation laser. The photoluminescence lifetime information is obtained by a time-correlated single-photon counting (TCSPC) system.
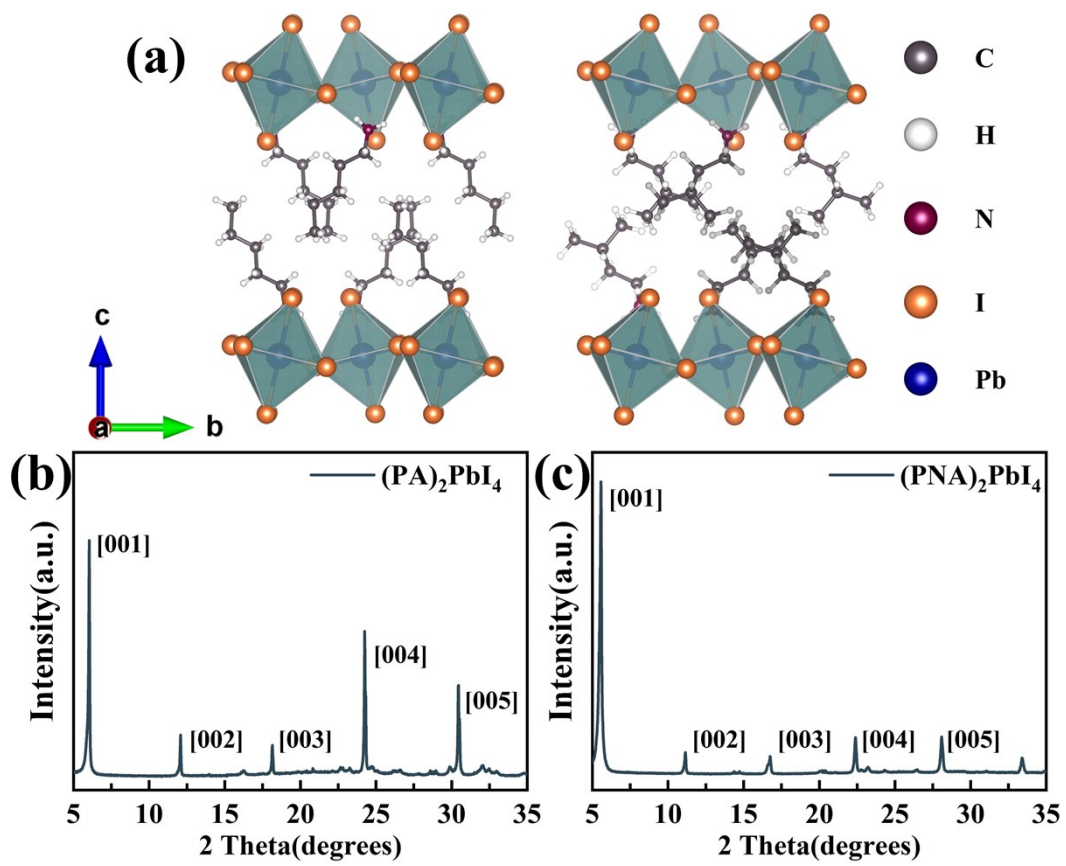
Figure S1 XRD patterns of $(PA)_2PbI_4$ and $(PNA)_2PbI_4$ at ambient condition.
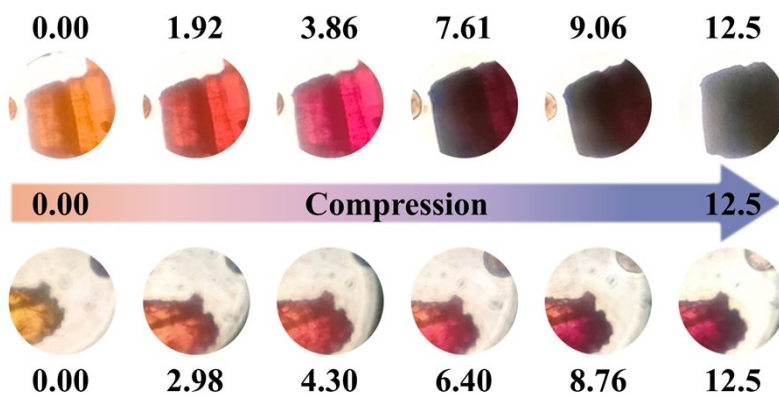
Figure S2 Piezochromic transitions of 2D crystals in DAC chamber. From top to bottom, $(PA)_2PbI_4$, $(PNA)_2PbI_4$ respectively.
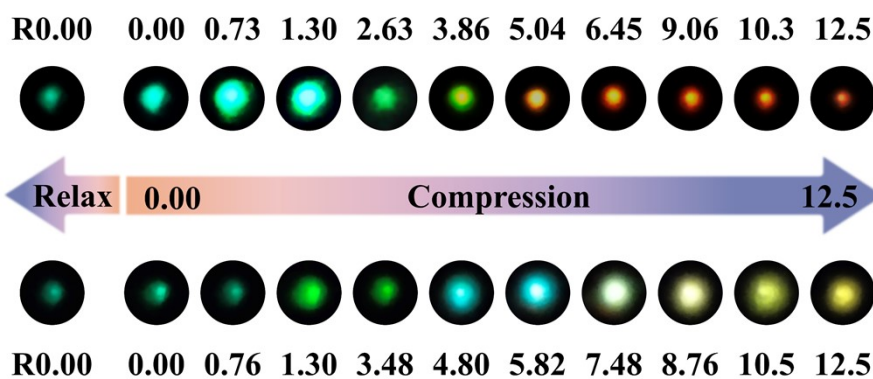

Figure S3 PL photographs of $(PA)_2PbI_4$ (top) and $(PNA)_2PbI_4$ (bottom) crystal upon compression up to 12.5 GPa.
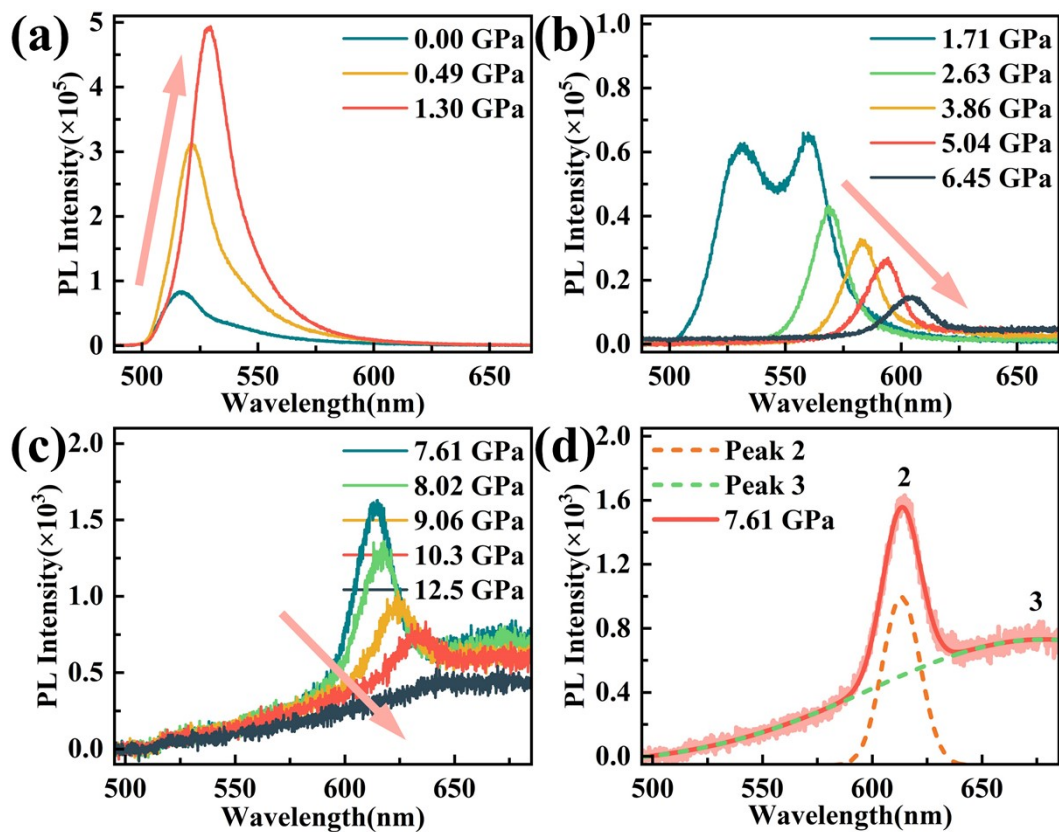
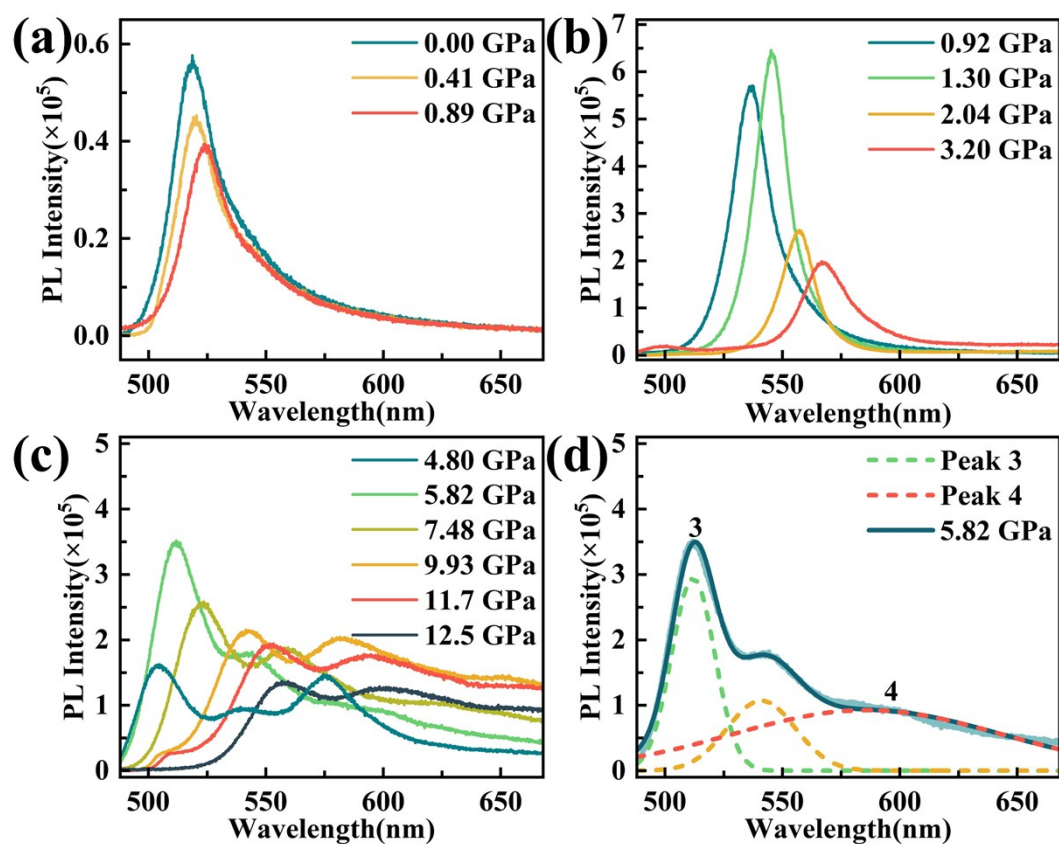**Figure S4** (a-c) PL spectra of (PA)$_2$PbI$_4$ crystal upon compression up to 12.5 GPa. (d) The fitting result at 7.61 GPa.

Figure S5 (a-c) PL spectra of (PNA)$_2$PbI$_4$ crystal upon compression up to 12.5 GPa. (d) The fitting result at 5.82 GPa.
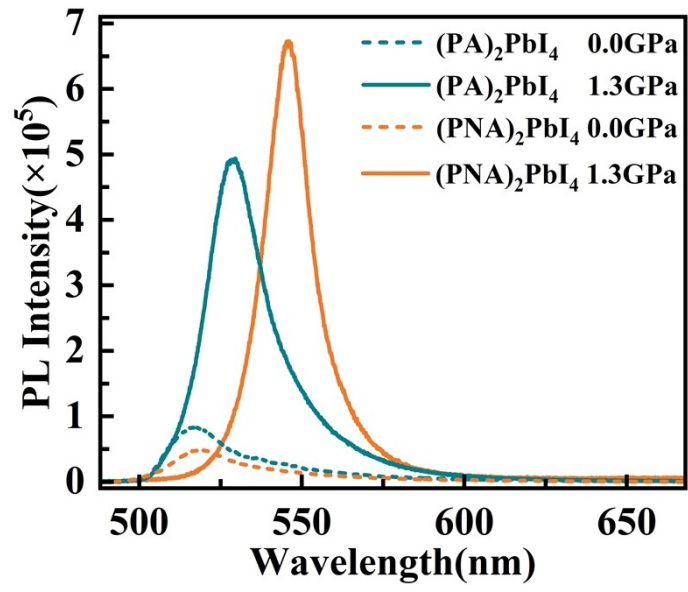
Figure S6 Comparison of the PL intensity $(PA)_2PbI_4$ and $(PNA)_2PbI_4$ at the same excitation power.
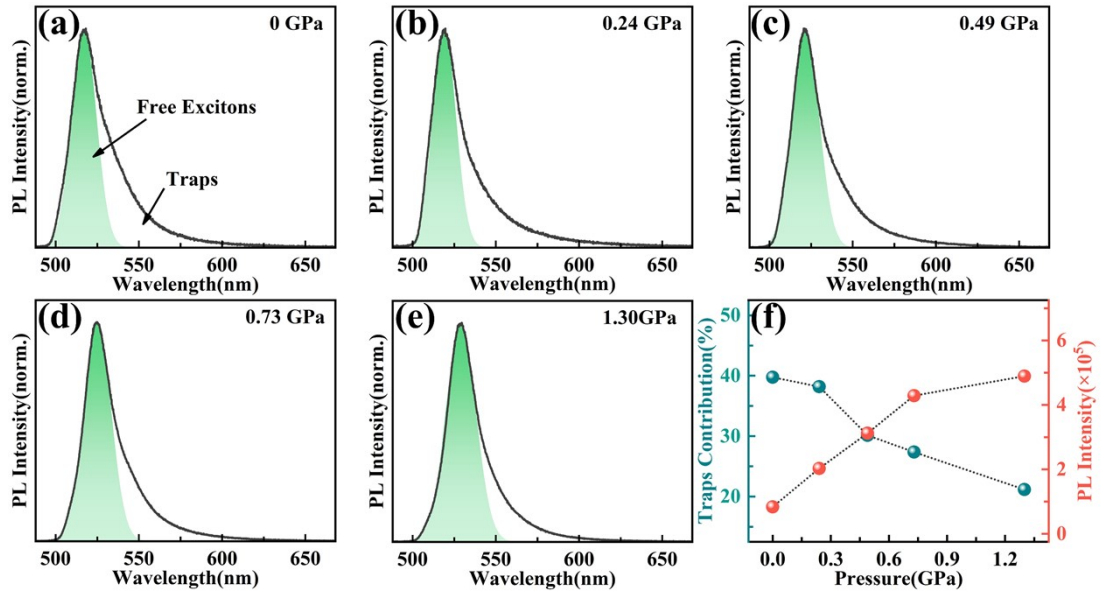
Figure S7 (a-e) The fitting curves of the $(PA)_2PbI_4$ spectra under selected pressures, where the green and white regions are the emission of the free excitons (FEs) and trapped states (Traps), respectively. (f) Contribution of trapped states emission and the PL intensity as function of pressure.
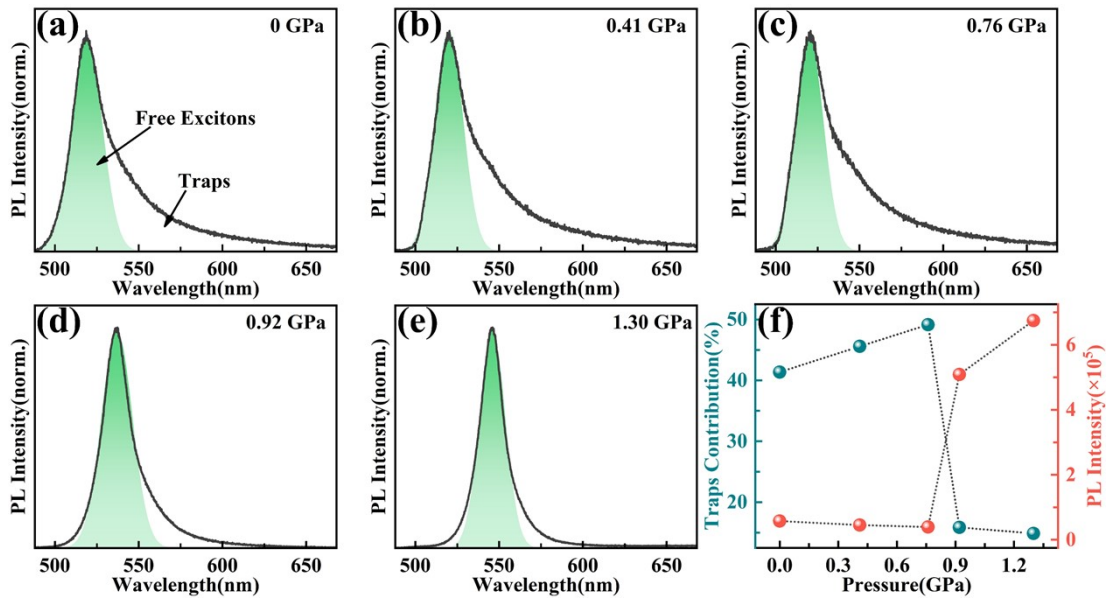

Figure S8 (a-e) The fitting curves of the $(PNA)_2PbI_4$ spectra under selected pressures, where the green and white regions are the emission of the free excitons (FEs) and trapped states (Traps), respectively. (f) Contribution of trapped states emission and the PL intensity as function of pressure.
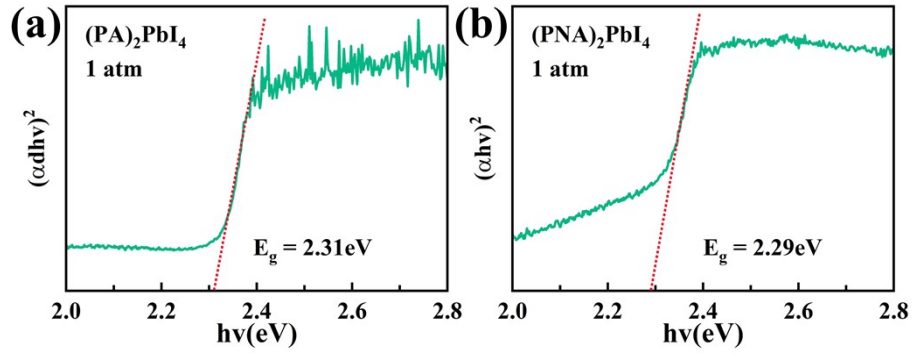
Figure S9 The band-gap Tauc plots at 1 atm. (a) $(PA)_2PbI_4$. (b) $(PNA)_2PbI_4$.

Tauc plot is mainly based on the formula proposed by Tauc [1]: $(\alpha h v)^{1/n} = B(h v - E_g)$, where α is absorption coefficient, h is Planck-constant, v is frequency, B is constant, E_g is bandgap width of semiconductor, exponential n is directly related to the type of semiconductor, direct bandgap $n = 1/2$, indirect bandgap $n = 2$. Based on the above formula, we know that $(\alpha h v)^{1/n}$ is only linear with hv, which can be used to estimate E_g. When calculating E_g by Tauc plot method, either 'Abs' or 'α' has no effect on E_g value (only the coefficient B is different). For simplicity, the absorbance value 'Abs' can be directly used to replace the absorption coefficient 'α'. Under ambient conditions, both $(PA)_2PbI_4$ and $(PNA)_2PbI_4$ are direct bandgap with bandgaps of 2.31 eV and 2.29 eV，respectively.

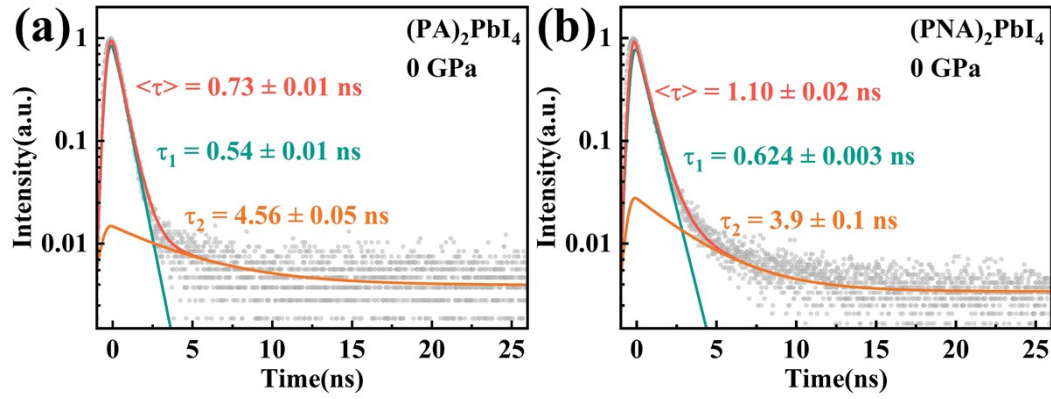**Figure S10** TRPL spectra is fitted by the biexponential function. A biexponential function $I(t) = I_0[A_1\exp\left(-{}^t\!/\tau_1\right) + A_2\exp\left(-{}^t\!/\tau_2\right)]$, and average PL lifetime are calculated by $\langle\tau\rangle = (A_1\tau_1^2 + A_2\tau_2^2)/(A_1\tau_1 + A_2\tau_2)$, where τ_1 and τ_2 refer to the recombination of free excitons and localized trapped excitons, respectively.
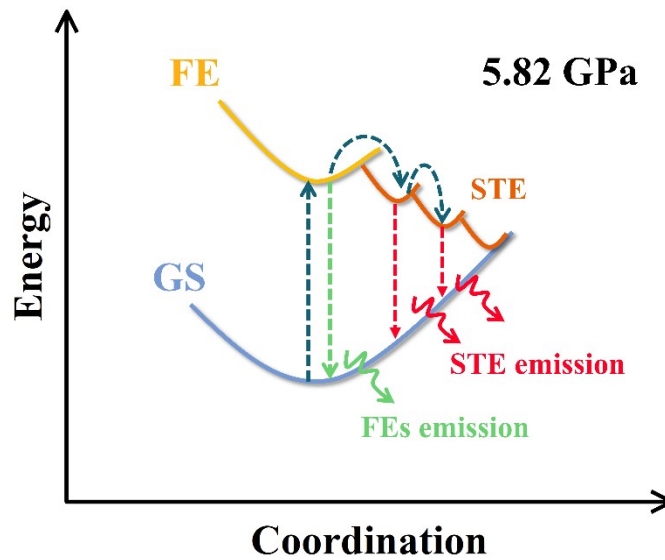

Figure S11 Illustrations of exciton dynamics in $(PNA)_2PbI_4$ at 5.82 GPa (FE, free exciton state; GS, ground state; STE, self-trapped exciton state)
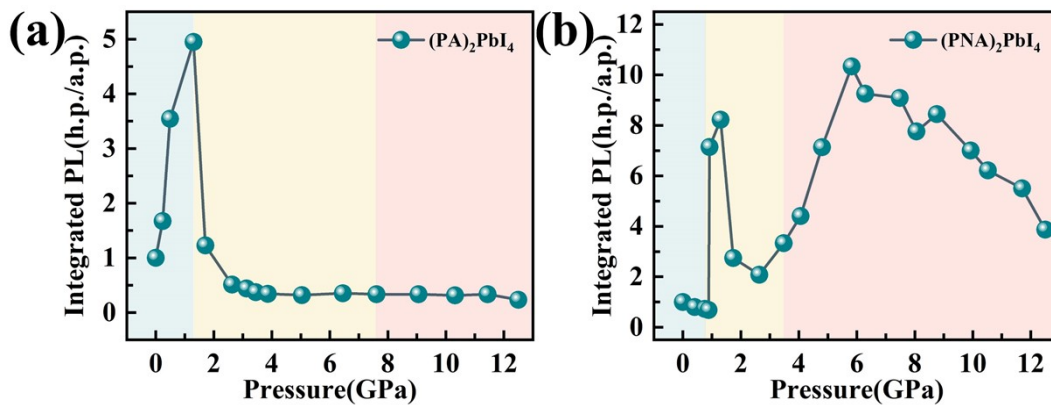
Figure S12 Variations of the relative integrated PL intensity of (PA)$_2$PbI$_4$ and (PNA)$_2$PbI$_4$ as a function of pressure.

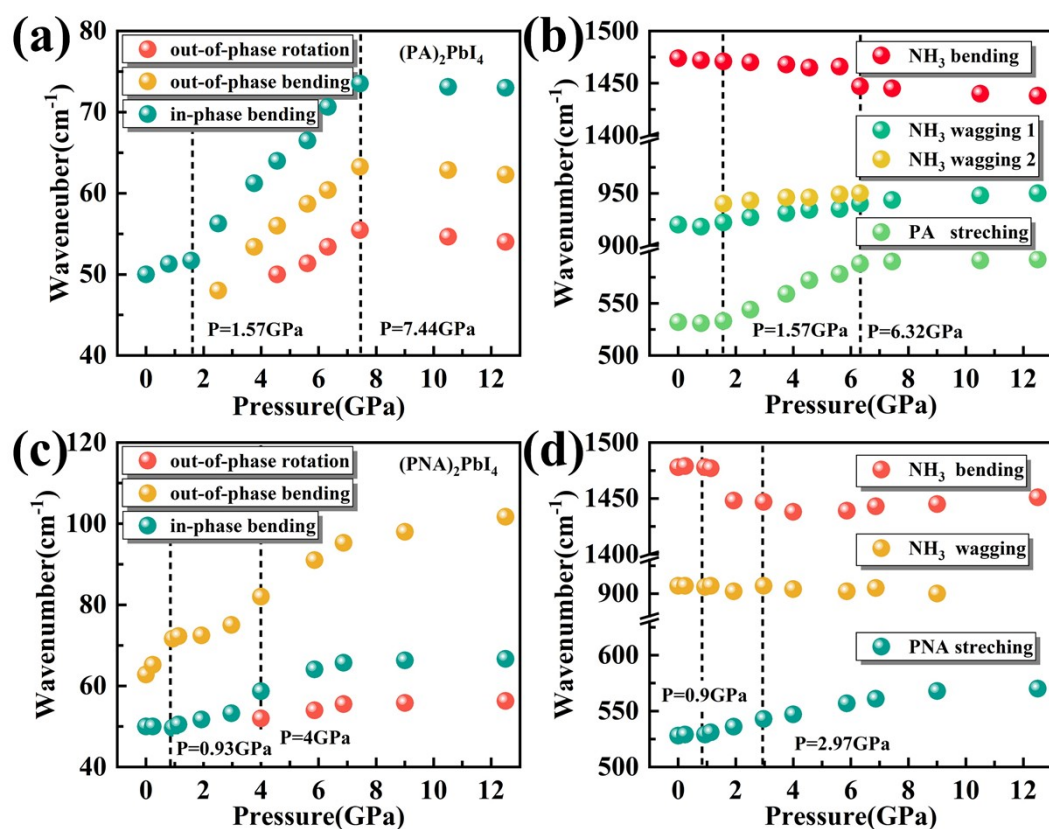**Figure S13** Pressure-induced Raman modes evolution of (PA)$_2$PbI$_4$ and (PNA)$_2$PbI$_4$. (a) Raman mode for in-phase bending, out-of-phase bending and out-of-phase rotation of [PbI$_6$]$^{4-}$ octahedron of (PA)$_2$PbI$_4$. (b) Raman mode for in-phase bending, out-of-phase bending and out-of-phase rotation of [PbI$_6$]$^{4-}$ octahedron of (PNA)$_2$PbI$_4$. (c) Raman modes for PA stretching, NH$_3$ wagging and NH$_3$ bending. (d) Raman modes for PNA stretching, NH$_3$ wagging and NH$_3$ bending.