Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information

Hydrogen-Bond Enhancement Triggered Structural Evolution and Band Gap Engineering of Hybrid Perovskite $(C_6H_5CH_2NH_3)_2PbI_4$ under High Pressure

Can Tian,[a] Yongfu Liang,[a] Wuhao Chen,[a] Yanping Huang,[a] Xiaoli Huang,*[a] Fubo Tian,[a] and Xinyi Yang*[a]

[a] State Key Laboratory of Superhard Materials, College of Physics, Jilin University, Changchun 130012, China.

*Email: Xiaoli Huang: huangxiaoli@jlu.edu.cn; Xinyi Yang: yangxinyi@jlu.edu.cn

Calculated Method

Electronic band structures and DOS were calculated using the pseudopotential plane-wave methods based on First-principles density functional theory implemented in the CASTEP package. For the $(PMA)_2PbI_4$, we included the Spin-orbit coupling (SOC) effect in the calculation. The local density approximation (LDA-CAPZ) approach of exchange-correlation functional was employed with the plane-wave energy cutoff 760 eV and the k-point spacing 0.03 $Å^{-1}$ in the Brillouin zone. The self-consistent field (SCF) tolerance was set as 5.0×10^{-7} eV/atom. The convergence thresholds between optimization cycles for maximum force, maximum stress and maximum displacement are set as 0.03 eV/Å, 0.05 GPa, and 1.0×10^{-3} Å, respectively.

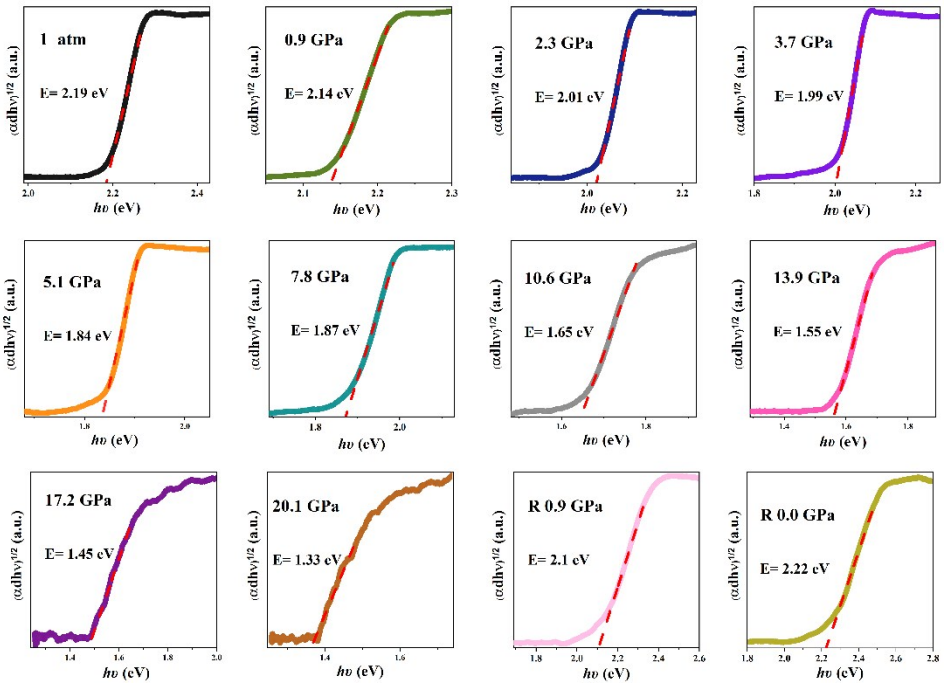

Fig. S1 The band gap of $(PMA)_2PbI_4$ was estimated at different pressures by extrapolating the linear portion of $(\alpha dh\nu)^2$ versus hν curve direct band-gap Tauc Plots, where α is the absorption coefficient, d is the sample thickness, and $h\nu$ is photon energy.

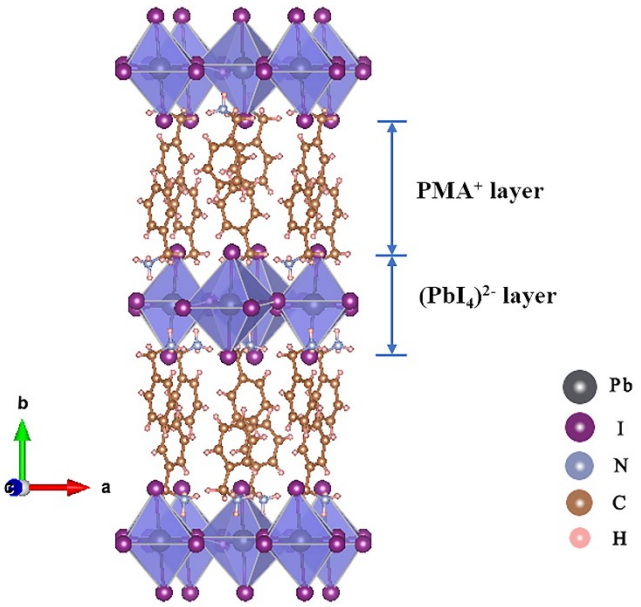

Fig. S2 Crystal structures of $(PMA)_2PbI_4$ at ambient pressure. Here, the compression along b-axis for $(PMA)_2PbI_4$ is described as layer-to-layer compression.

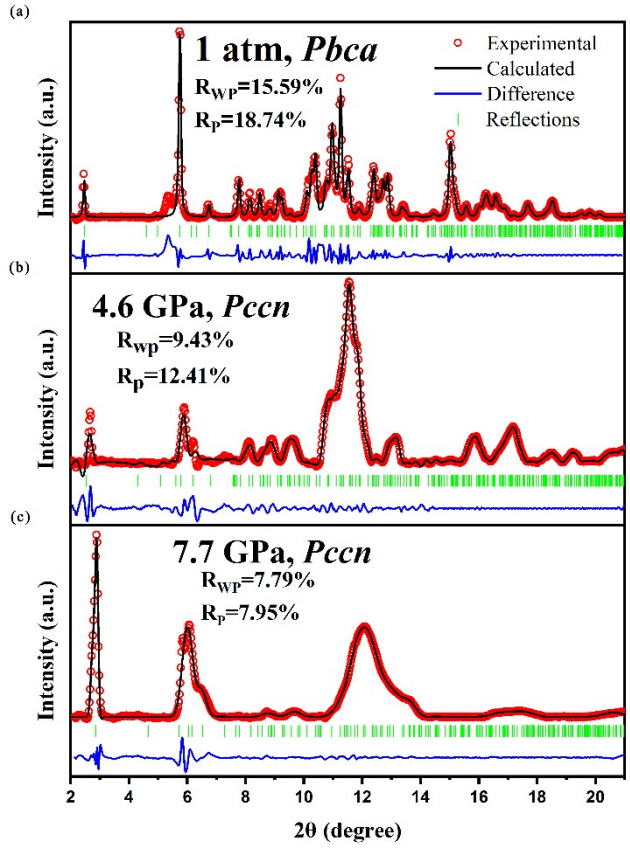

Fig. S3 The Rietveld refinement analysis of the XRD data of $(PMA)_2PbI_4$ (a) at 1 atm with the orthorhombic *Pbca* structure; (b) at 4.6 GPa with the orthorhombic *Pccn* structure; (c) at 7.7 GPa with the orthorhombic *Pccn* structure.

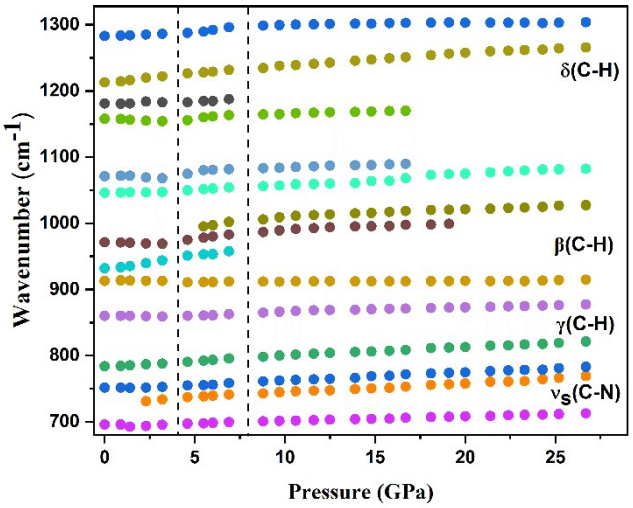

Fig. S4 The frequency shift of the PMA section at different pressure. The corresponding representative variation modes are marked: ν, stretching; δ, bending; β, benzene ring in-plane bending; γ, benzene ring out-of-plane bending.

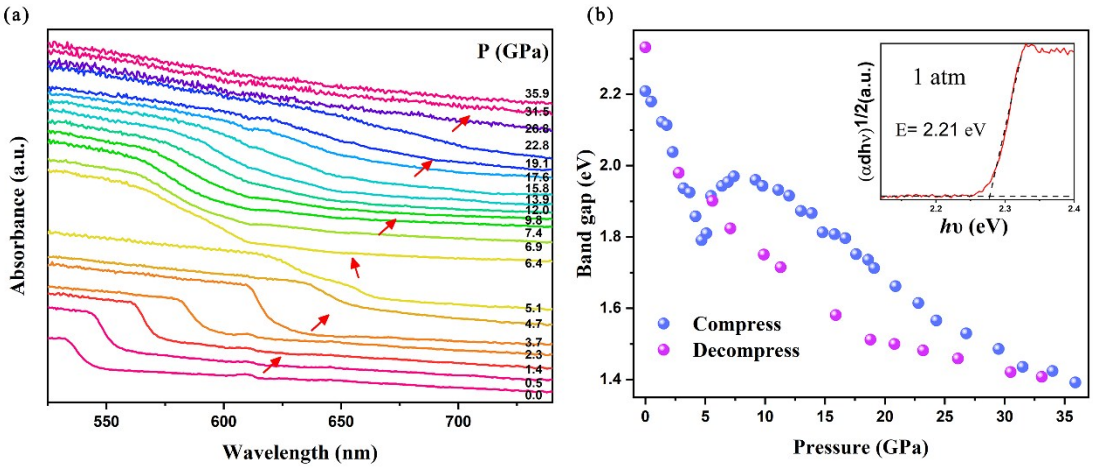

Fig. S5 The absorption spectra and band gap of $(PEA)_2PbI_4$ as a function of pressure. a) UV/Vis absorption spectra of the $(PEA)_2PbI_4$ crystal at high pressure. b) band gap evolution of $(PEA)_2PbI_4$ under high pressure. The illustration exhibits selected band gap Tauc plots for $(PEA)_2PbI_4$ at 1 atm.

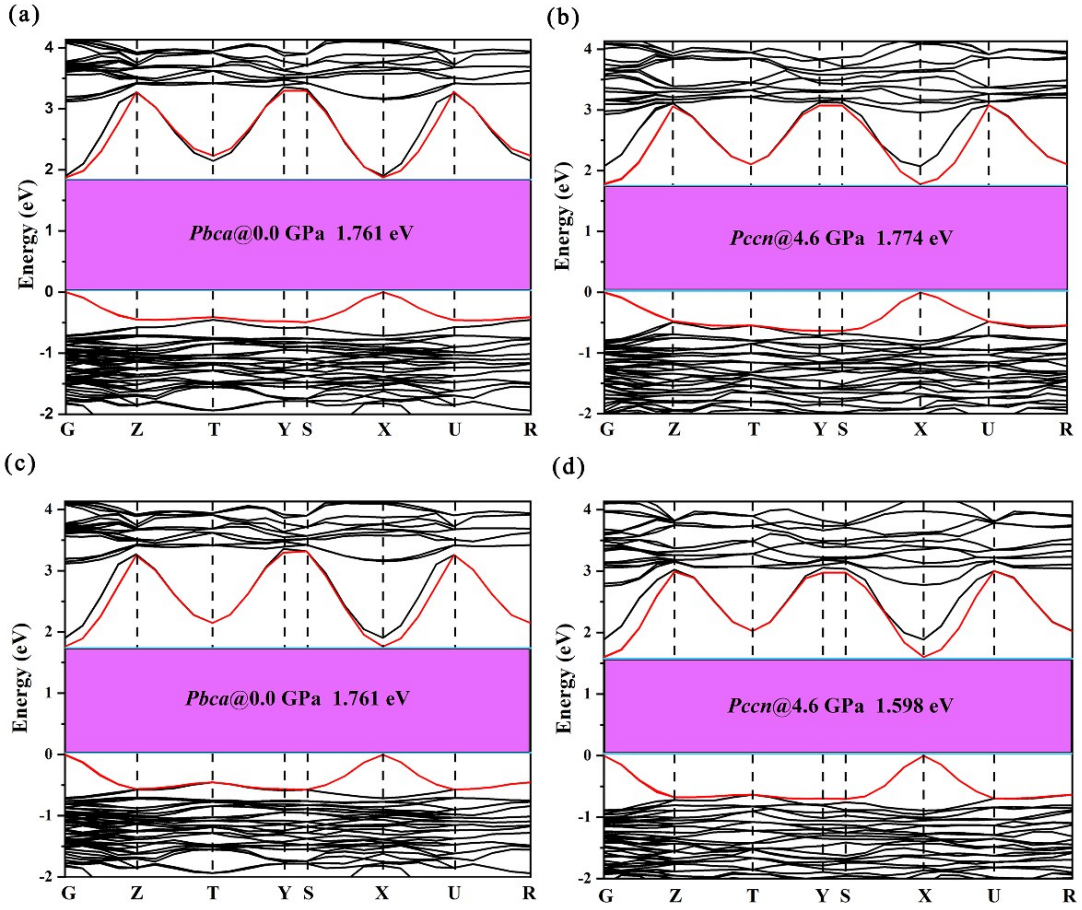

Fig. S6 Calculated electronic band structure of $(PMA)_2PbI_4$ at 1 atm (a), 4.6 GPa (b) and the electronic band structure of considering the spin-orbit coupling at 1atm (c), 4.6 GPa (d).

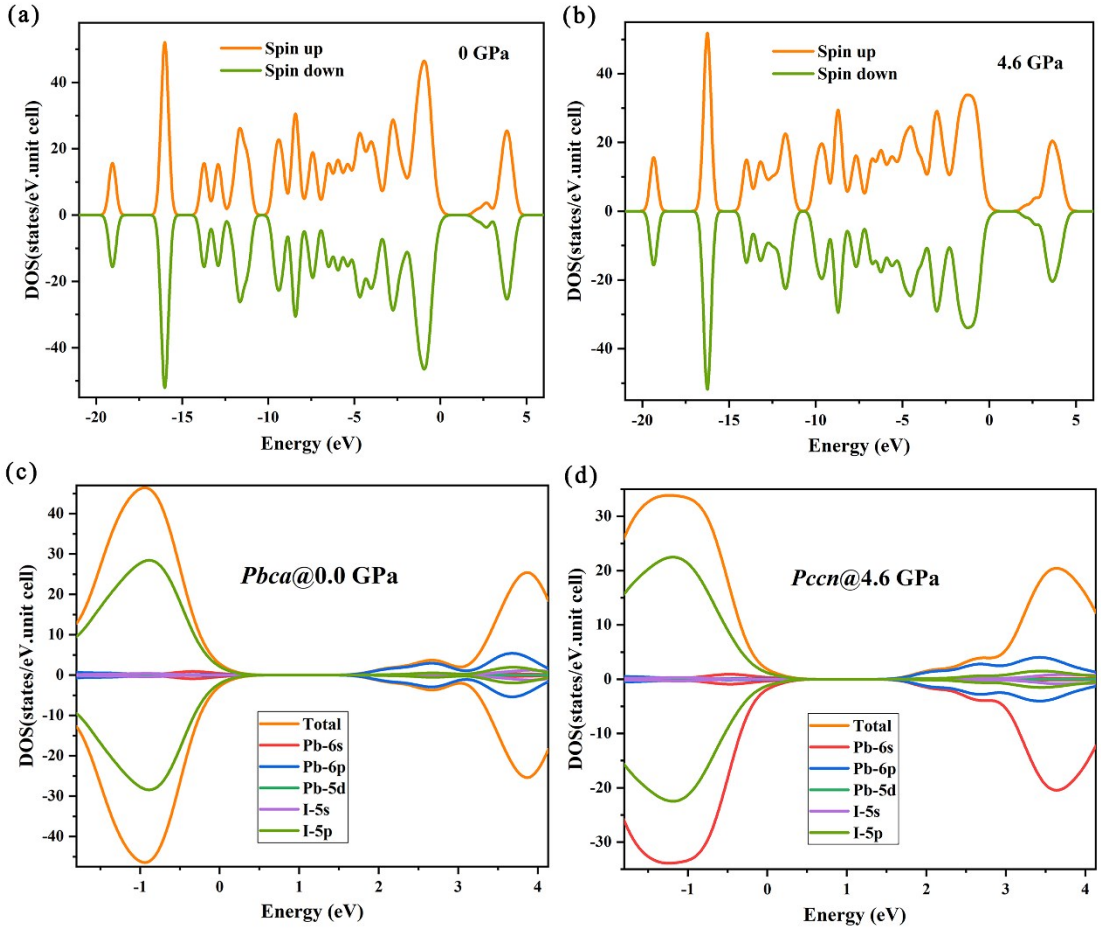

Fig. S7 Calculated density of states (DOSs) of $(PMA)_2PbI_4$ with considering the spin-orbit coupling at 1 atm (a), 4.6 GPa (b), 1atm (c), 4.6 GPa (d).

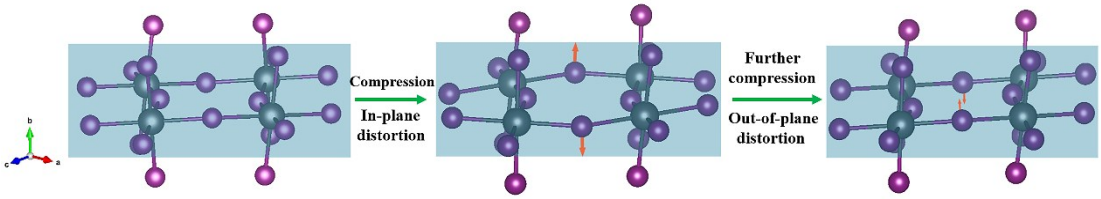

Fig. S8 Schematic diagram of Pb-I inorganic layer distortion in $(PMA)_2PbI_4$ upon compression. Gray ball: Pb, purple ball: I.

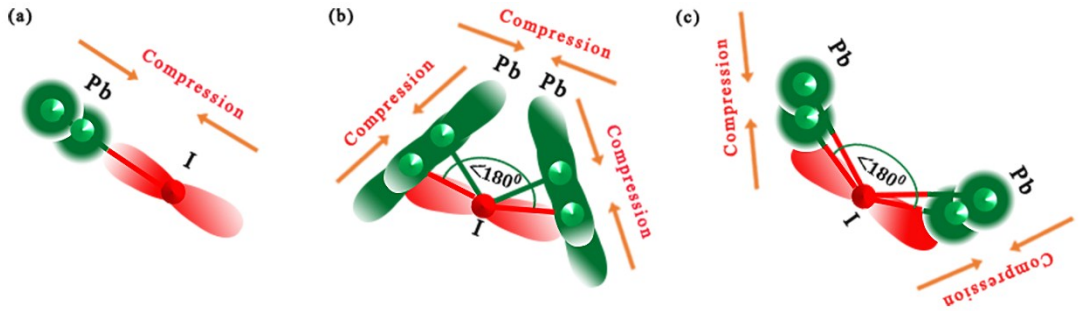

Fig. S9 Schematic illustration of Pb-I bond lengths (a) and Pb-I-Pb bond angles in $(PMA)_2PbI_4$ under compression (b) and (c).

Table S1 The band gap of $(PMA)_2PbI_4$ was estimated at representative pressure levels by extrapolating the linear portion of $(\alpha dh\nu)^2$ versus hν curve indirect band-gap Tauc plots.

Pressure (GPa)	Band gap (eV)
0.0	2.19
0.9	2.06
2.3	1.96
3.7	1.89
5.1	1.79
7.8	1.80
10.6	1.62
13.9	1.53
17.2	1.31
20.1	1.26

Table S2 The refined lattice parameters of *Pbca* and *Pccn* structure in $(PMA)_2PbI_4$ at 0.0 GPa, 4.6 GPa and 7.7 GPa, respectively.

Pressure	0.0 GPa	4.6 GPa	7.7 GPa
Crystal system	Orthorhombic *Pbca*	Orthorhombic *Pccn*	Orthorhombic *Pccn*
Cell parameter	a=8.765 (5) Å b=28.593 (2) Å c=9.138 (1) Å	a=8.547 (2) Å b=27.068 (1) Å c=9.037 (3) Å	a=8.403 (9) Å b=25.390 (5) Å c=8.881 (1) Å

Table S3 The statistics $(PMA)_2PbI_4$ sample of N···I, and C···I, H···I bond lengths and N–H···I, C–H···I and Pb–I–Pb bond angles.

Bond type	This work	Angle type	This work
$N\cdots I_5$	3.69 Å	$N\text{-}H_N\cdots I_5$	161.62°
$N\cdots I_4$	3.14 Å	$N\text{-}H_N\cdots I_4$	129.79°
$C\cdots I_5$	4.69 Å	$C\text{-}H_C\cdots I_5$	147.51°
$C\cdots I_4$	4.11 Å	$C\text{-}H_C\cdots I_4$	109.61°
$H_N\cdots I_5$	2.83 Å	$Pb\text{-}I_5\text{-}Pb$	158.45°
$H_C\cdots I_5$	5.54 Å	$Pb\text{-}I_4\text{-}Pb$	158.45°