Supporting Information

Pressure-Tuned Quantum Well Configuration in Two-Dimensional $PA_8Pb_5I_{18}$ Perovskites for Highly Efficient Yellow Fluorescence

*Yongfu Liang[1,2#], Min Wu[1#], Can Tian[1], Xiaoli Huang[1], Yanping Huang[1], Yulia Lekina[3,4], Ze Xiang Shen[3,4] and Xinyi Yang[1]**

[1]State Key Laboratory of Superhard Materials, College of Physics, Jilin University, Changchun, 130012, People's Republic of China.

[2]Henan Key Laboratory of Magnetoelectronic Information Functional Materials, School of Physics and Electronic Engineering, Zhengzhou University of Light Industry, Zhengzhou, 450002, People's Republic of China.

[3]Division of Physics and Applied Physics, School of Physical & Mathematical Sciences, Nanyang Technological University 637371, Singapore

[4]Centre for Disruptive Photonic Technologies, the Photonics Institute, Nanyang Technological University 637371, Singapore

*To whom correspondence should be addressed. Email: yangxinyi@jlu.edu.cn.

Methods

Diamond Anvil Cell. Two identical diamond anvils with a culet of 300 μm were employed to generate pressure. One sheet of T301 stainless steel gasket was pre-indented to 45 μm in thickness with a hole of 80 μm in diameter was drilled in the center of the indentation by laser to serve as sample chamber. The sample are microcrystalline powder with purity greater than 99.9%. It was purchased from Xi'an Polymer Light Technology Corp. The purchased $PA_8Pb_5I_{18}$ ($PA=C_3H_7NH_3$) and a small ruby ball were loaded together into the chamber. The pressure was calibrated using the pressure-dependent ruby fluorescent technique[1].

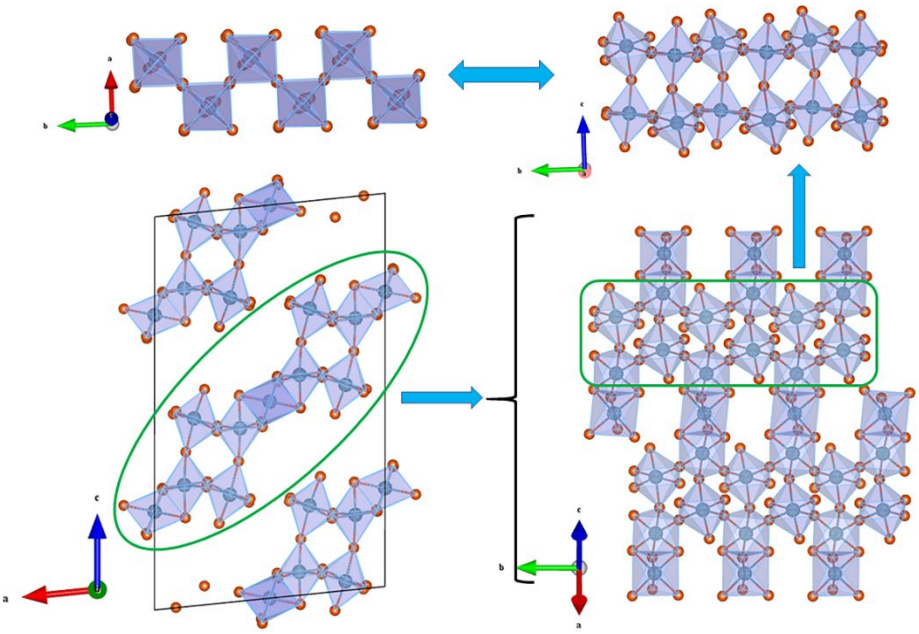

Figure S1. Structure analysis of $PA_8Pb_5I_{18}$.

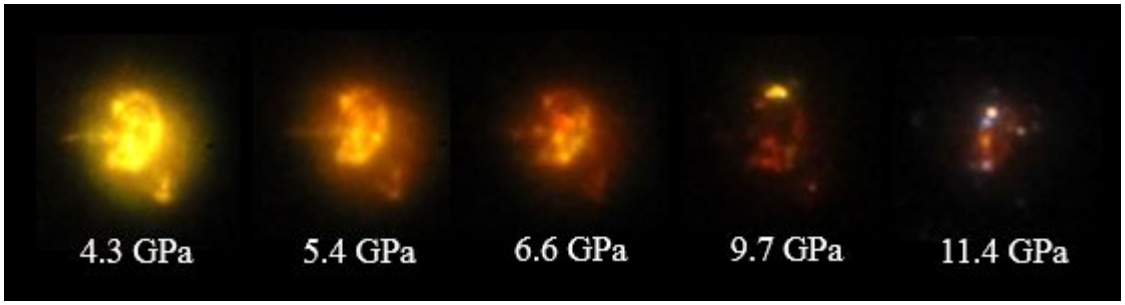

Figure S2. The PL micrographs at pressure from 4.3 to 11.4 GPa.

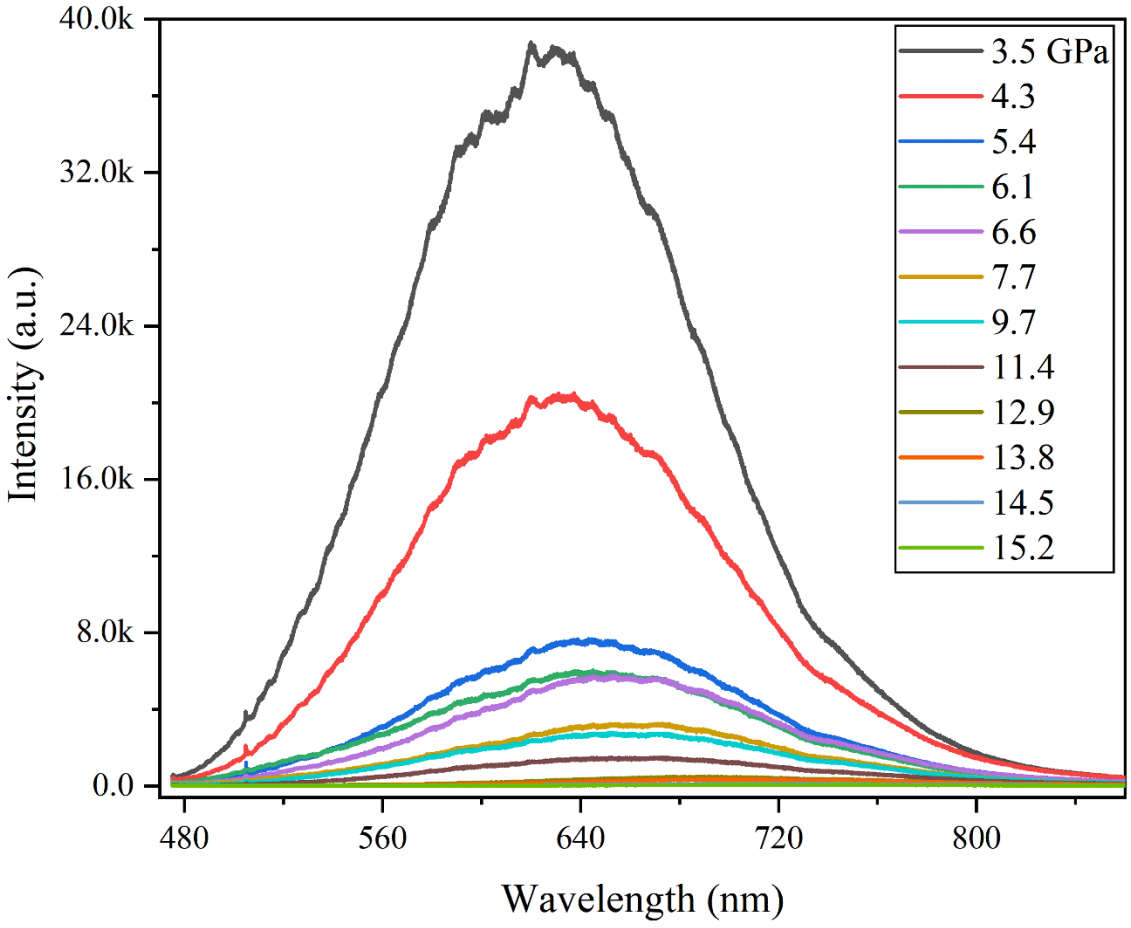

Figure S3. The PL spectra at pressure from 3.5 to 18.0 GPa.

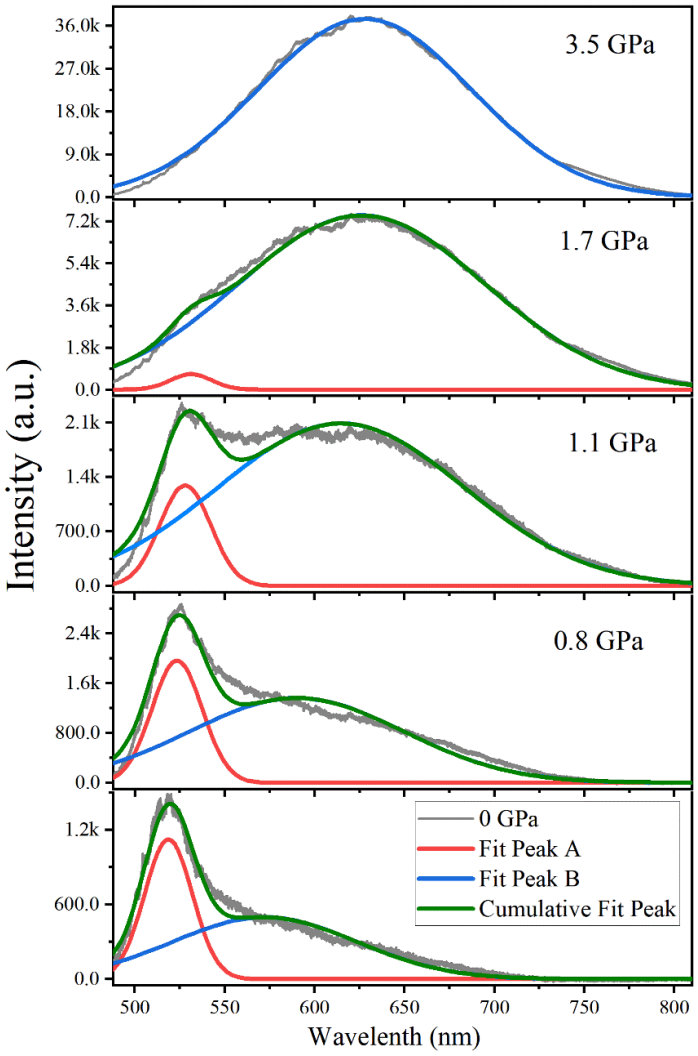

Figure S4. The selected PL spectra fitting with multi-Gaussian function into two peaks.

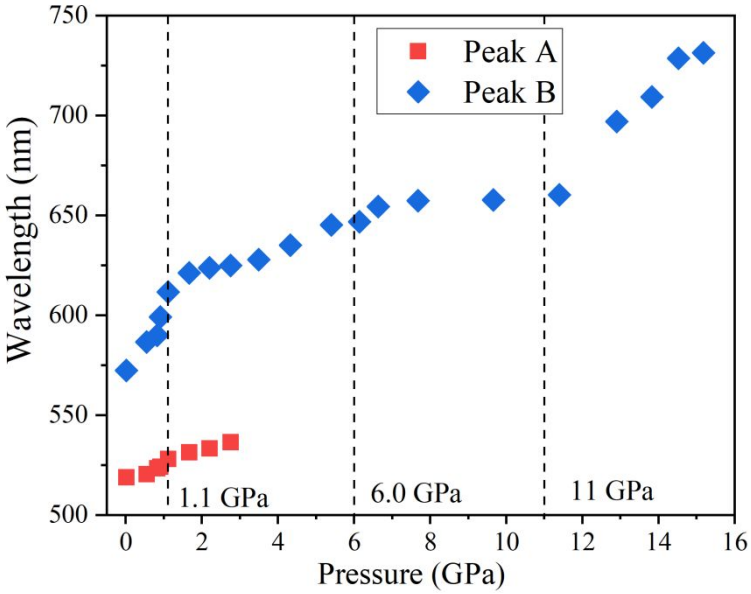

Figure S5. Pressure-induced peak position evolution of $PA_8Pb_5I_{18}$.

Table S1. The values of the peak intensity and full width at half maxima (FWHM) at different pressures.

Pressure (GPa)	Intensity (a.u.)		FWHM (nm)	
	Peak A	Peak B	Peak A	Peak B
0	1122.6	495.2	31.6	120.3
0.6	919.2	522.1	35.9	141.7
0.8	1259.7	1355.9	33	140.2
0.9	1529.3	1398.6	33.1	151.4
1.1	1294.1	2094.6	33.5	161.5
1.7	672	7465.1	68.8	153.6
2.2	390.1	11921.9	52.9	146.3
2.8	87	19815.7	60.8	138.3
3.5		37459		134.5
4.3		18927.6		137.9
5.4		7192.7		145.8
6.1		5610.8		150.1
6.6		5432.4		151
7.7		3154.5		151.8
9.7		2695		153.3
11.4		1437.2		158.8
12.9		462.6		158.3
13.8		362.6		174.3
14.5		119.2		217.3

Table S2. The rates of peak shift with pressure.

Pressure (GPa)	0-1.1	1.1-6.1	6.1-11.4	11.4-15.2
Peak B (nm/GPa)	32.9	6.0	1.0	19.3
Peak A (nm/GPa)	13.6			

Table S3. Pressure dependence of PLQY and recombination rate.

Pressure (GPa)	PL integral intensity I/I_0	Cell volume V/V0	Average lifetime (ns)	Refractive index square n^2	PLQY	Radiative recombination rate(ns^{-1})	Non-radiative recombination rate(ns^{-1})
0.02	1.0	1.000	0.62	3.24	0.008	8.051E-6	0.0016
0.55	1.2	0.987	0.65	3.29	0.010	9.790E-6	0.00154
0.83	3.2	0.981	0.80	3.32	0.026	2.044E-5	0.00123
0.91	3.5	0.979	1.04	3.32	0.029	1.756E-5	9.468E-4
1.11	5.7	0.973	1.65	3.35	0.047	1.781E-5	5.883E-4
1.67	18.9	0.965	5.74	3.39	0.158	1.724E-5	1.569E-4
2.2	30.3	0.955	10.82	3.43	0.257	1.484E-5	7.757E-5
2.76	48.0	0.948	11.82	3.46	0.410	2.166E-5	6.291E-5
3.49	88.5	0.936	13.53	3.52	0.770	3.556E-5	3.836E-5
4.33	47.7	0.925	10.22	3.58	0.423	2.587E-5	7.199E-5
5.4	18.0	0.912	9.18	3.65	0.162	1.1058E-5	9.784E-5
6.14	14.7	0.903	8.02	3.70	0.135	1.049E-5	1.142E-4
6.63	14.1	0.898	7.35	3.72	0.130	1.104E-5	1.249E-4
7.68	7.8	0.889	6.15	3.78	0.073	7.377E-6	1.552E-4
9.66	6.9	0.871	2.06	3.89	0.066	2.011E-5	4.665E-4
11.4	3.7	0.850	0.95	4.04	0.037	2.459E-5	0.00103

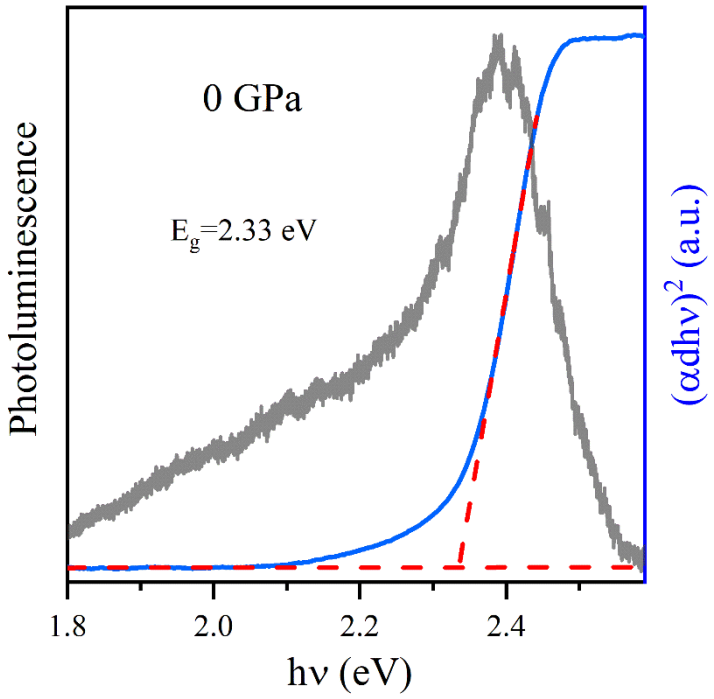

Figure S6. The bandgap Tauc plots and photoluminescence at 0 GPa.

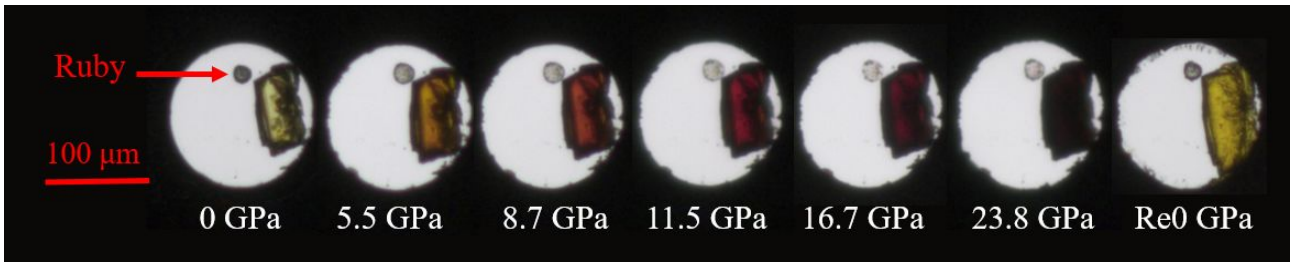

Figure S7. Piezochromic transitions of a $PA_8Pb_5I_{18}$ crystal in the diamond anvil cell (DAC) chamber in the pressure range 0.0-23.8 GPa, the last microscopic image is released from 23.8 GPa to 0 GPa.

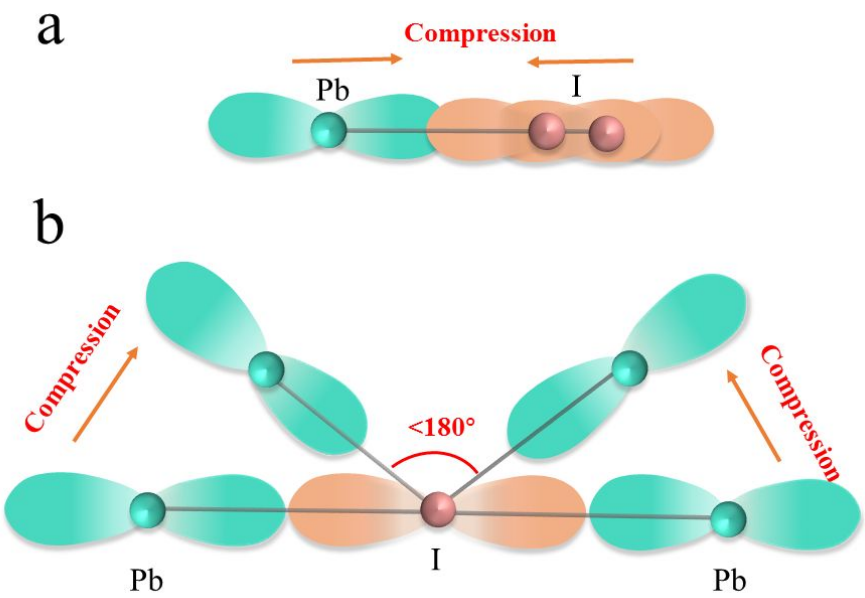

Figure S8. Schematic illustration of Pb-I bond length (a) and Pb-I-Pb bond angle under compression. As the pressure increases, the Pb-I bond contraction, the electron wave function overlapped more. However, the Pb-I-Pb bond angle decrease, the electron wave function overlapped less.

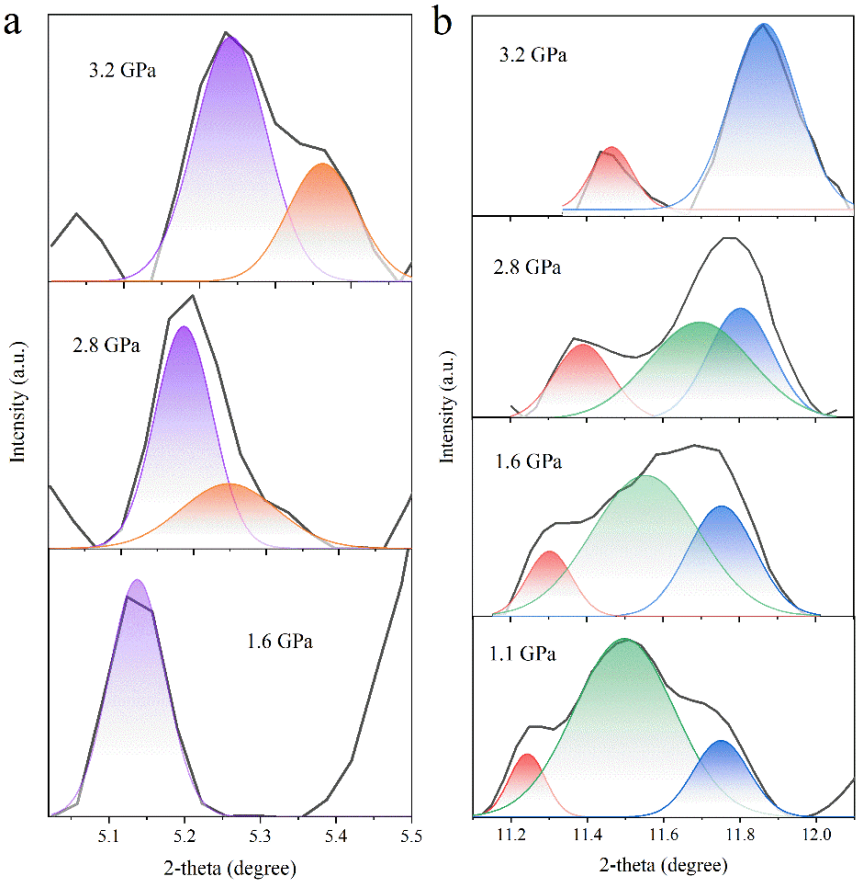

Figure S9. Peak fittings of (020) and (4 1 -10) diffraction peaks (at around 5.14° and 11.48°) through the phase transition.

Table S4. The statistics of length, angle of hydrogen bond, and the Effect of hydrogen bonding on carbon nitrogen bond.

0 GPa	A (N-H···I)	L(C-N) (Å)	E	2.3 GPa, After distortion	A′((N-H···I)	H···I change	E′
N'_2-H···I_5	135.0°	1.44	compression		130.7°	shorten	compression
N_3-H···I_5	168.9°	1.44	stretch		164.1°	shorten	stretch
N'_1-H_A···I_3	166.2°	1.47	stretch		<166.2°	shorten	compression
N_1-H_A···I_1	158.6°	1.47	stretch		>158.6°	shorten	stretch
N_1-H_B···I_2	147.4°	1.47	stretch		<147.4°	shorten	stretch
N'_1-H_B···I_2	126.7°	1.47	stretch		<126.7°	shorten	stretch
N'_4-H···I_6	144.4°	1.52	compression		>144.4°	shorten	--
N_4-H···I_3	153.9°	1.52	stretch		>153.9°	shorten	stretch
N_5-H···I_6	167.8°	1.50	--		>167.8°	shorten	stretch

"E": Effect of hydrogen bonding on carbon nitrogen bond.

"A": Angle

"L": length

Table S5. The fit quality of all curves in our work.

Figure 1g	R-Square (Linear fit)					
	0-3.5 GPa		3.5-12.0 GPa		12.0-16.5 GPa	
	0.97558		0.99738		0.99626	
Figure S4		0 GPa	0.8 GPa	1.1 GPa	1.7 GPa	3.5 GPa
	R-Square	0.97133	0.99755	0.9971	0.99633	0.99503
	Reduced Chi-Sqr	66.18345	29.93325	79.4105	77.20727	57.98144
Figure 2c		0-3.7 GPa			3.7-22.7 GPa	
	R-Square	0.98963			0.99575	
	Reduced Chi-Sqr	0.01985			0.15029	
Figure 4a		0 GPa	1.0 GPa	1.6 GPa	2.7 GPa	3.3 GPa
	R-Square	0.99191	0.98932	0.97806	0.98793	0.98869
	Reduced Chi-Sqr	1.1278E-5	3.68665E-5	1.21124E-4	1.72567E-4	2.24771E-4

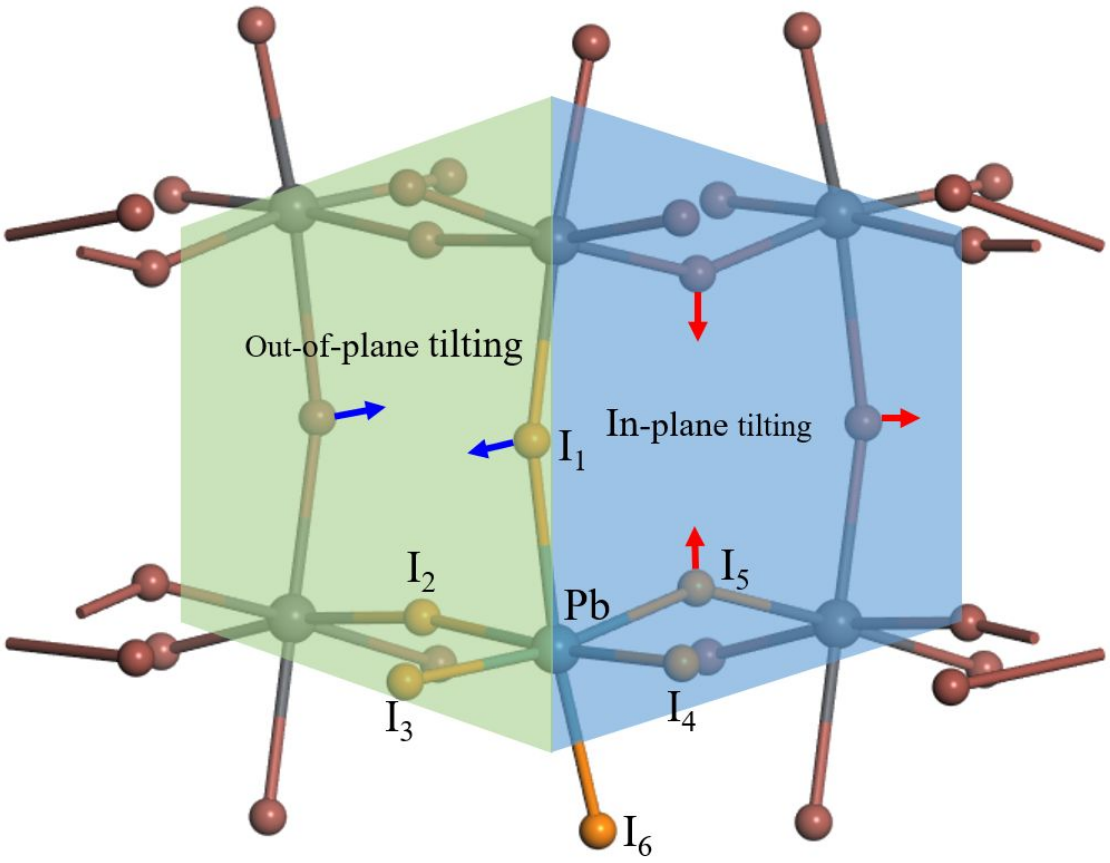

Figure S10. Out-of-plane tilting and in-plane tilting in Pb-I in inorganic skeleton. The red arrow is parallel to the blue plane, and the blue arrow is perpendicular to the green plane.

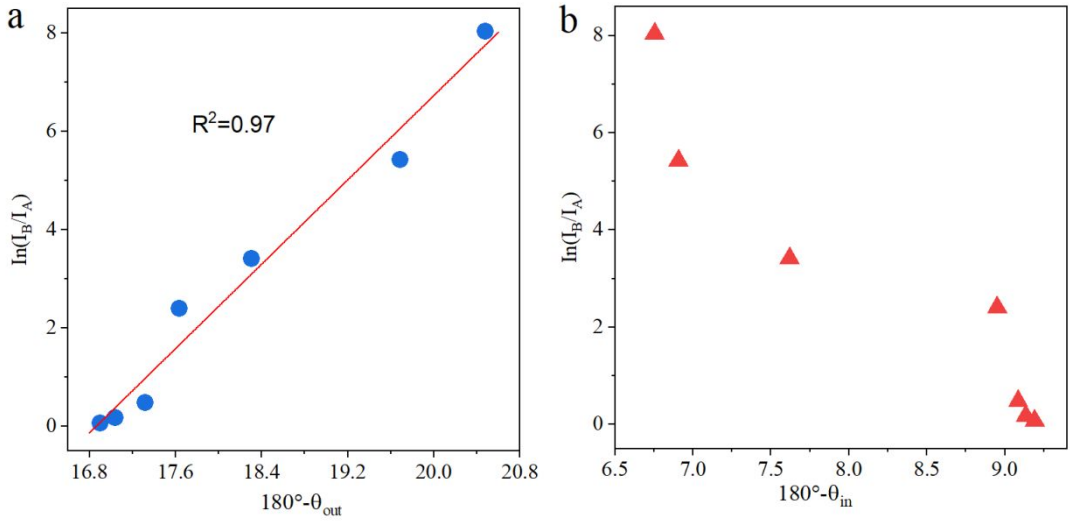

Figure S11. Values of $\ln(I_B/I_A)$ for $PA_8Pb_5I_{18}$ at series of pressure plotted as a function of (a) 180°-θ_{out} and (b) 180°-θ_{in} value obtained from Rietveld refined XRD spectrum. I_B and I_A are integrated intensities of peak B and peak A.

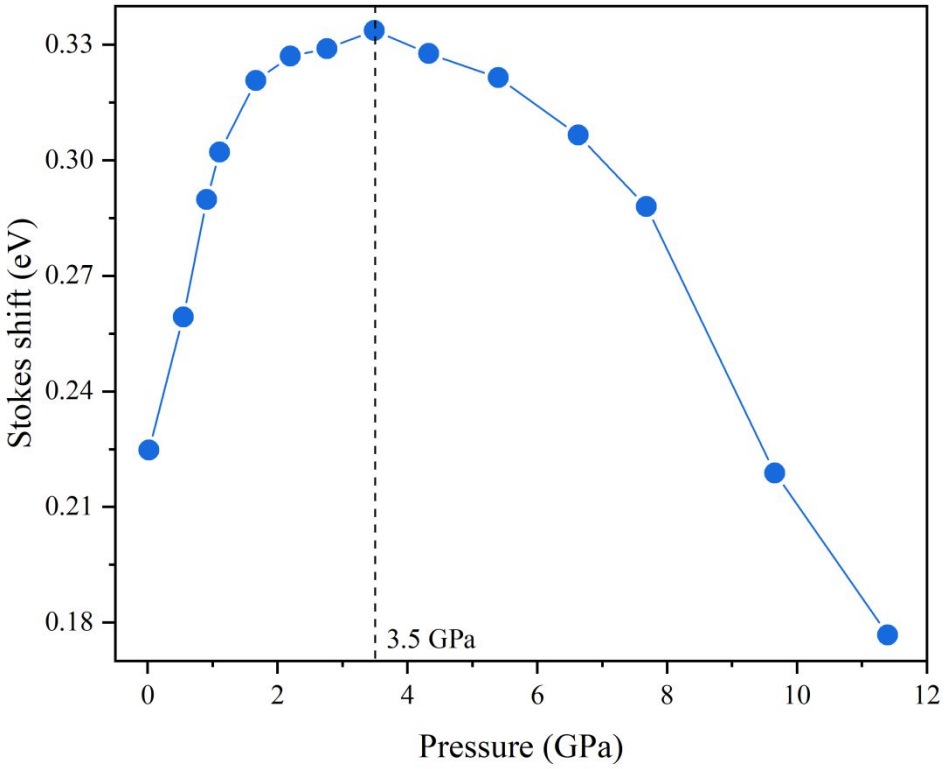

Figure S12. Stokes shift of $PA_8Pb_5I_{18}$ under high pressure.

REFERENCE

1. Mao, HK, Xu, J, Bell, PM. Calibration of the ruby pressure gauge to 800 kbar under quasi-hydrostatic conditions. 1986; **91**(B5): 4673-6.