Supplementary Information (SI) for Materials Chemistry Frontiers.

Supporting Information

Mechanically Rigid 2D Lead Halide Perovskite $(PMA)_2PbCl_4$ with Pressure-Stable Broadband Emission

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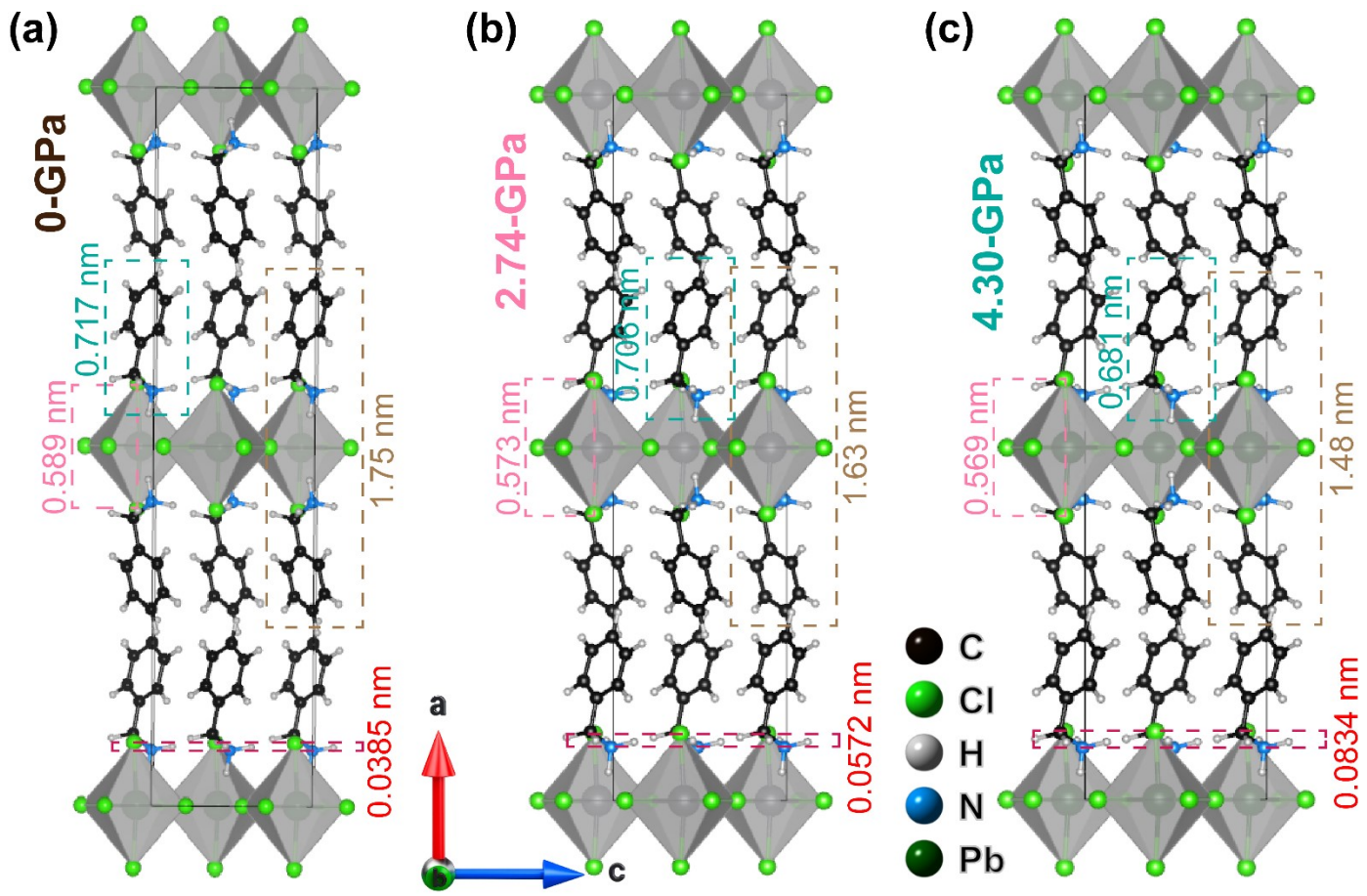

Figure S1. Optimized structure of $(PMA)_2PbCl_4$, where the inorganic $PbCl_6$ sheet is sandwiched between two organic layers, and inorganic sheet thickness, organic cation size and penetration, single layer thickness, at various pressures viewed along the *b* direction. (a) 0-GPa (b) 2.74-GPa (c) 4.30-GPa.

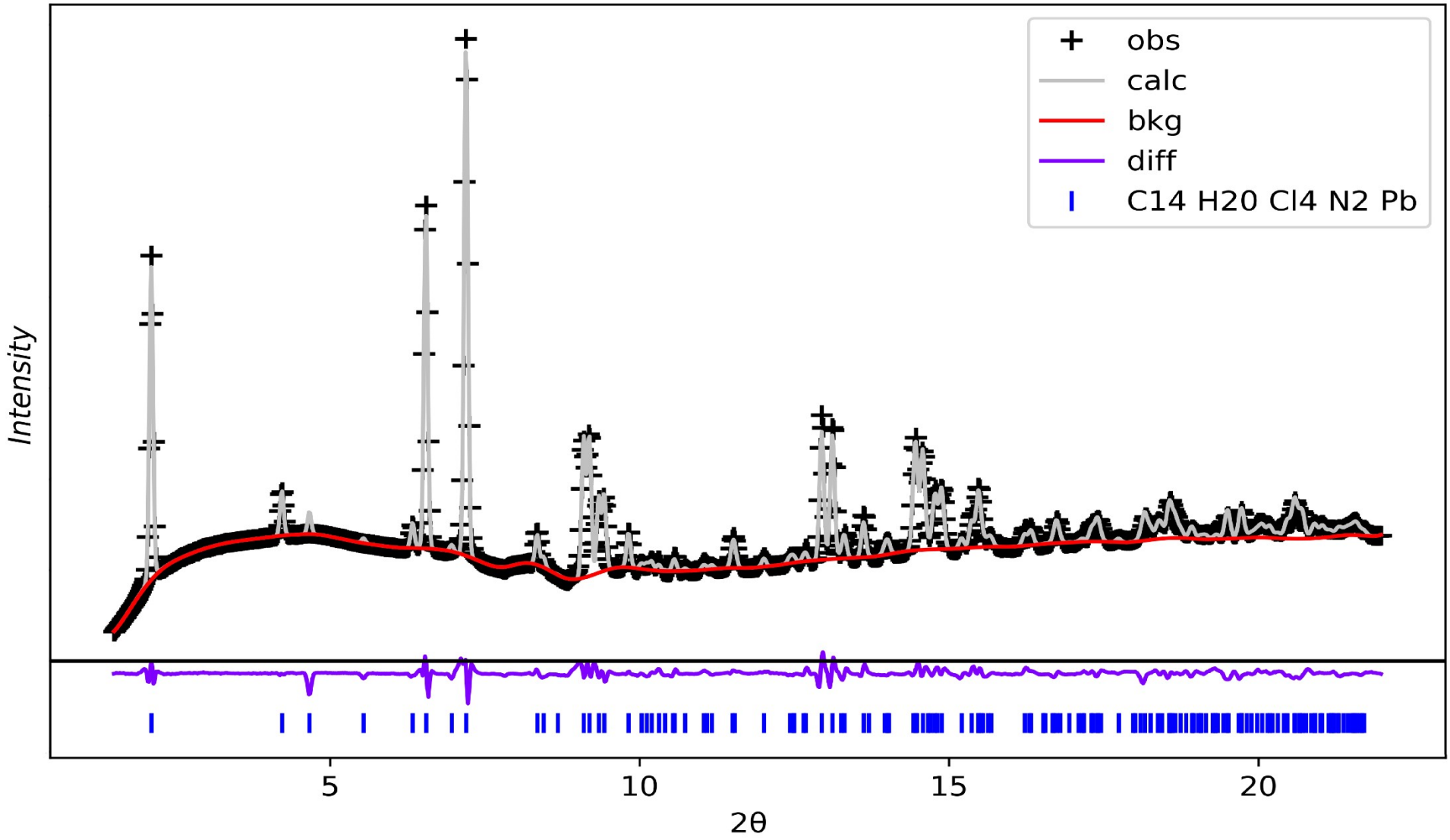

Figure S2. Le-Bail refinements of $(PMA)_2PbCl_4$ at ambient pressure in orthorhombic *Cmc2₁*.

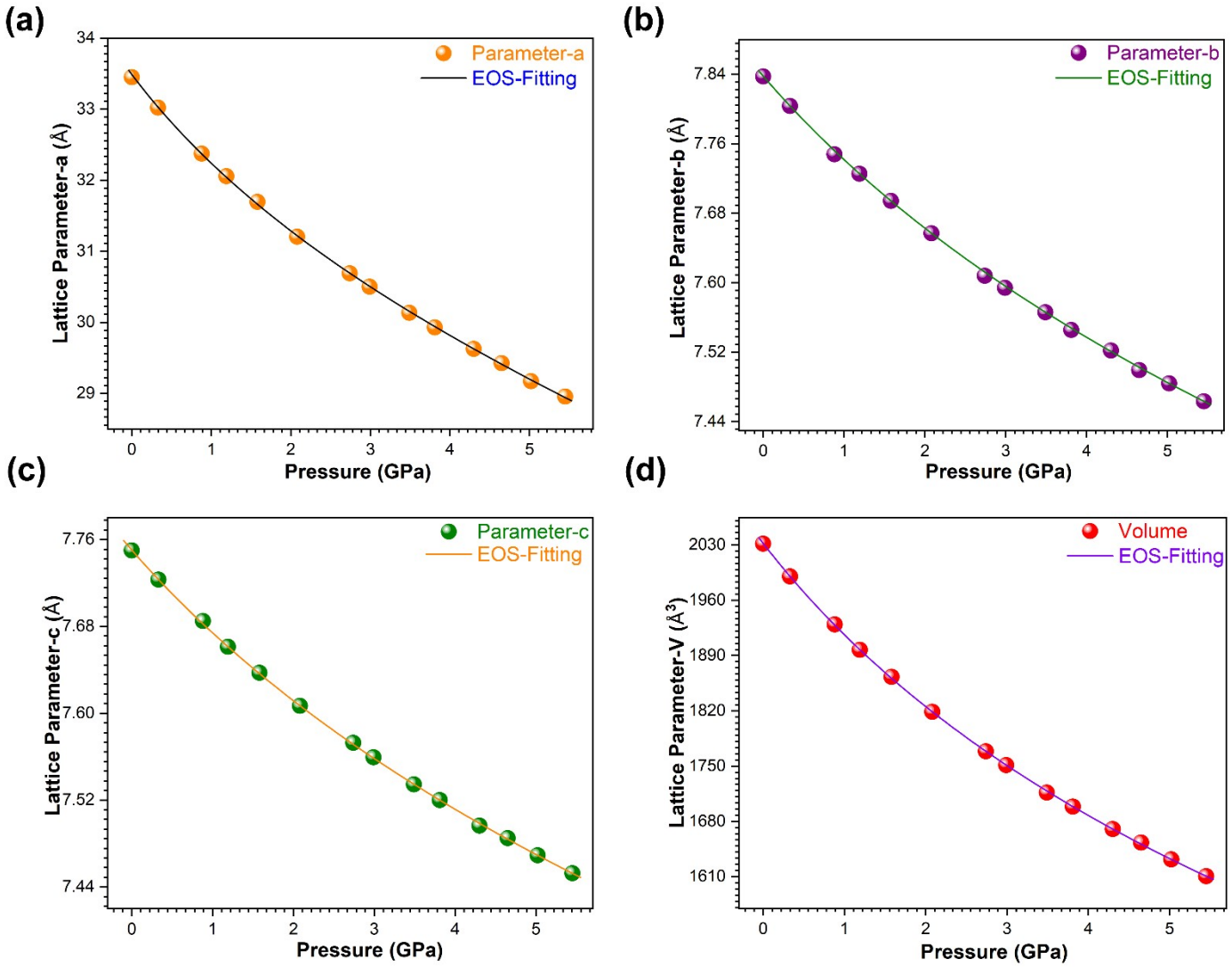

Figure S3. Lattice parameters (*a, b, c, V*) extracted from the Le-Bail refinement of HP-PXRD data and their fitting by third-order BM-EOS in EosFit7-GUI.

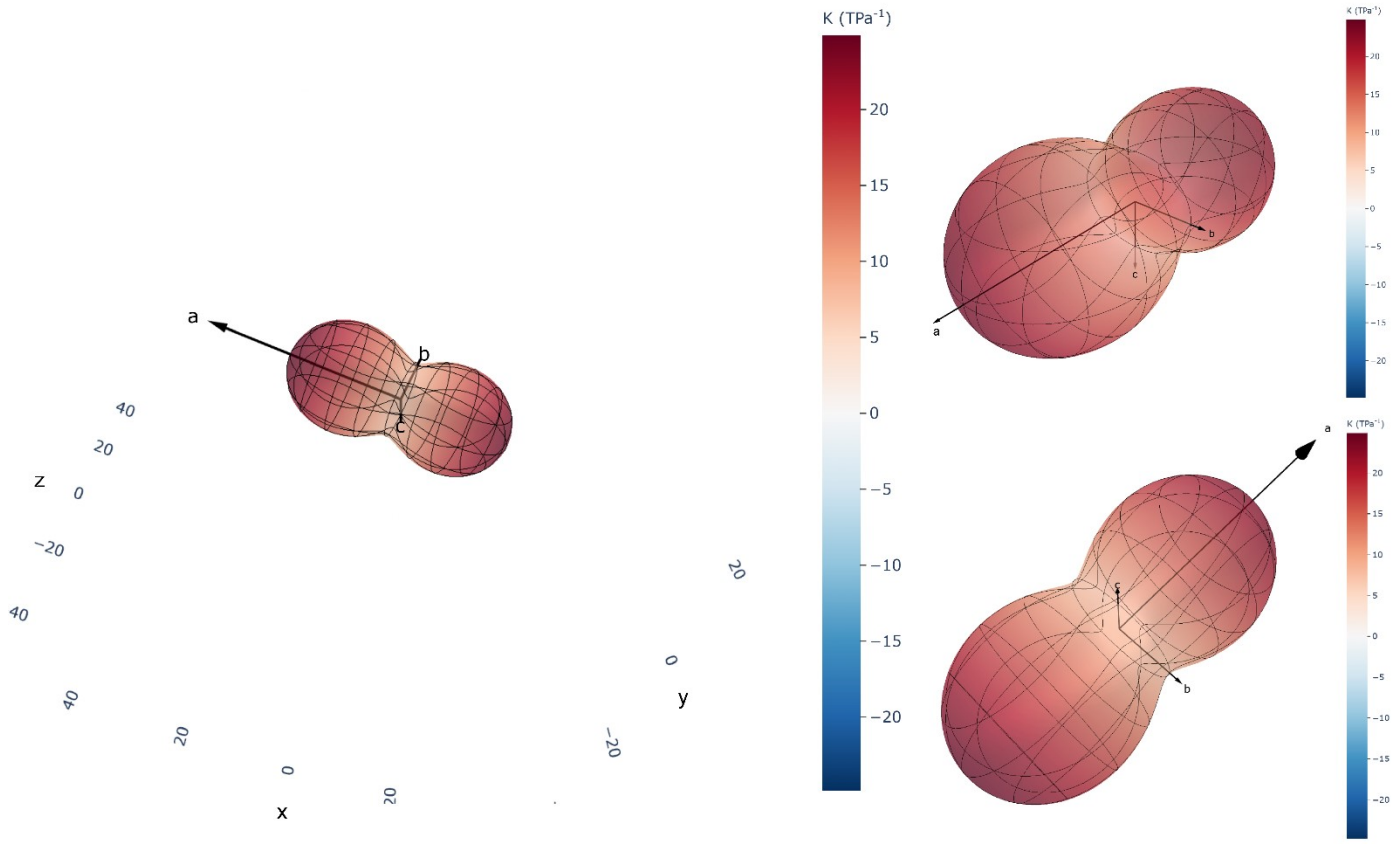

Figure S4. Compressibility indicatrix along three principal axes viewed in different directions.

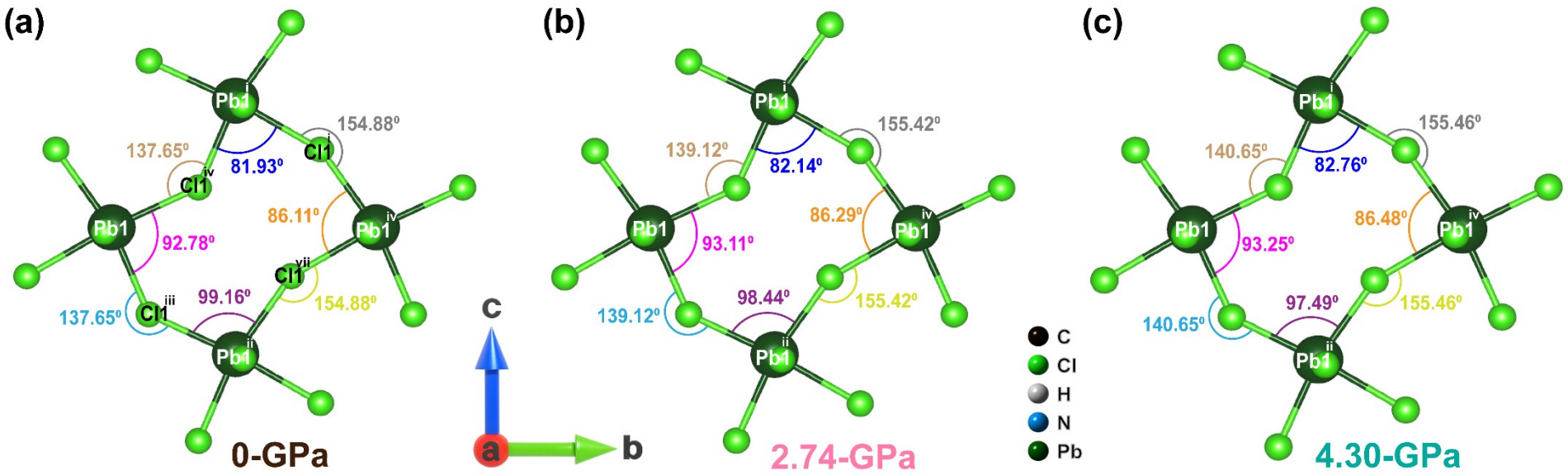

Figure S5. Pressure-dependent evolution of angular distortions among four interconnected $PbCl_6$ octahedra through bridging atoms ($Cl1^{i}$ and $Cl1^{iv}$) and between adjacent Cl atoms at each Pb center. (a) 0 GPa, (b) 2.74 GPa, (c) 4.30 GPa.

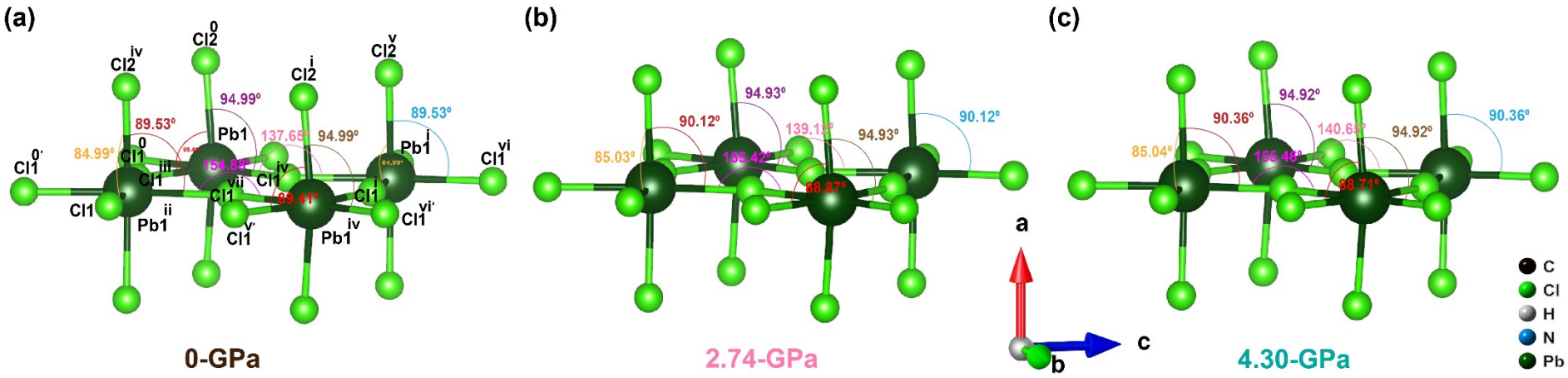

Figure S6. Pressure-dependent changes of bridging bond angles among four $PbCl_6$ octahedra connected via chlorine bridges, along with Pb-centered angles between bridging and terminal chlorine atoms at: (a) 0 GPa, (b) 2.74 GPa, (c) 4.30 GPa.

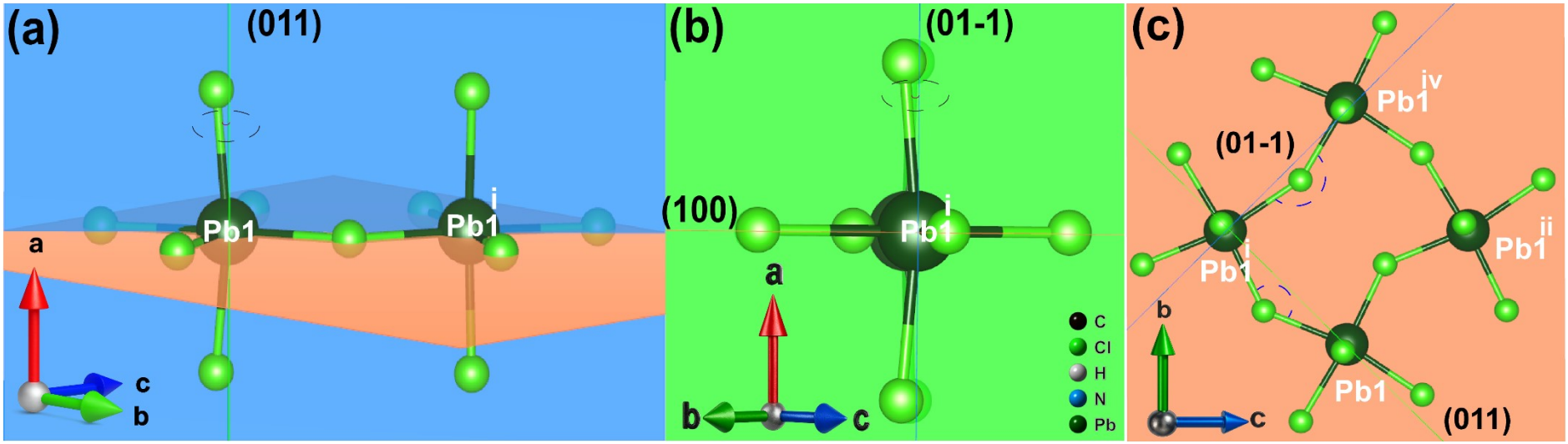

Figure S7. In-plane-distortion and out-of-plane distortion (a) Angle between terminal Cl atom and (01-1) plane viewed along [011] direction. (b) Angle between the terminal Cl atom and the (011) plane viewed along the [01-1] direction. (c) Supplementary angles at bridging Cl atoms for in-plane-distortion viewed along the [100] direction.

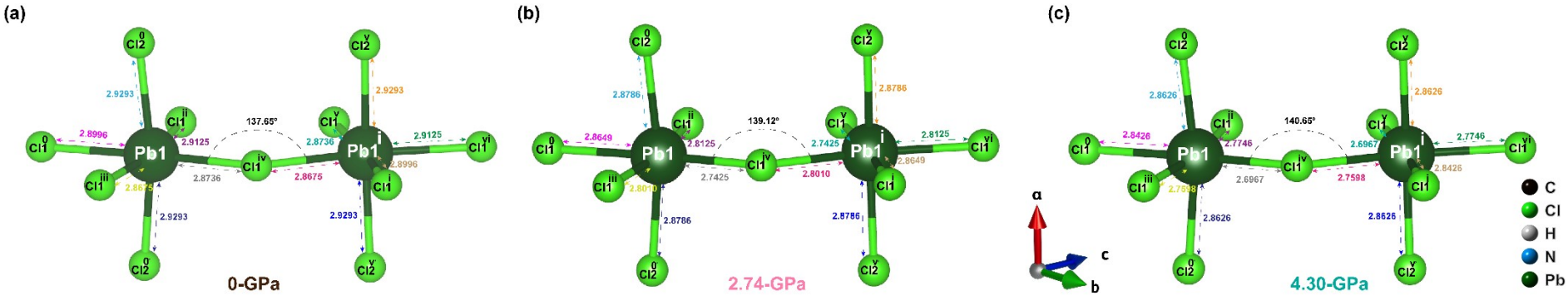

Figure S8. Evolution of bond lengths (Pb-Cl) between two $PbCl_6$ octahedra connected through a bridging Cl atom and Pb-Cl for the terminal Cl atom at different pressures. (a) 0-GPa (b) 2.74-GPa (c) 4.30-GPa.

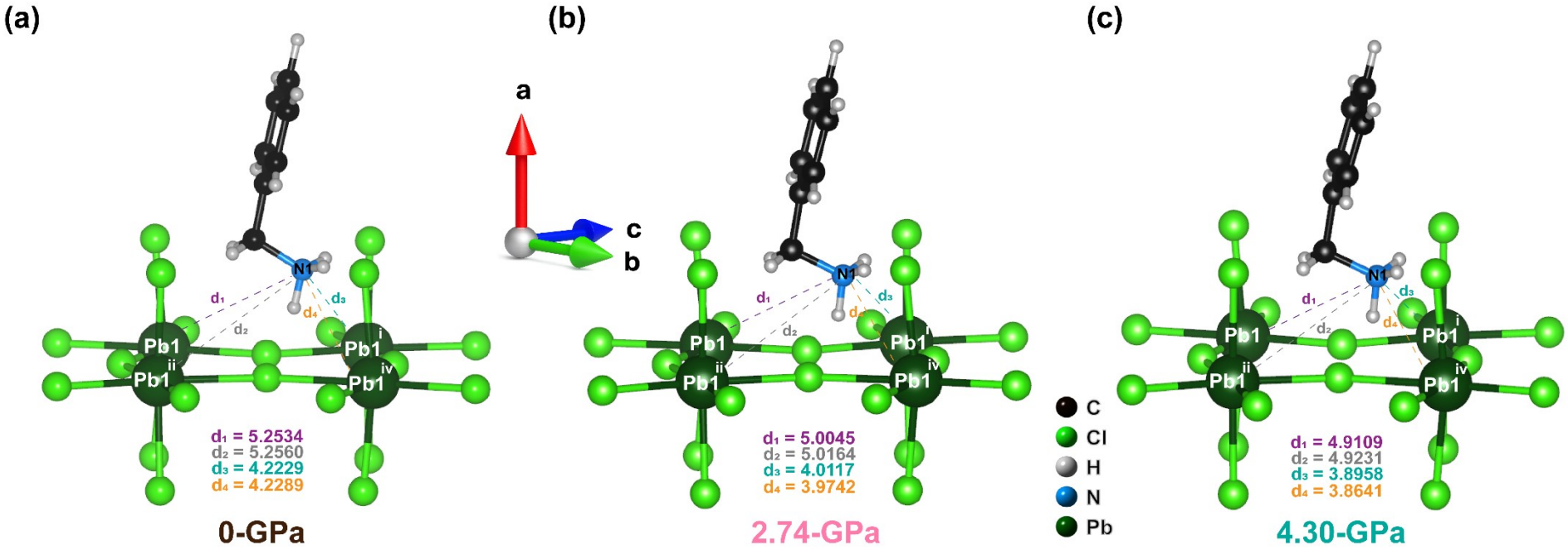

Figure S9. Pressure-induced contraction of distances between terminal N atoms of PMA^+ cations and Pb centers. (a) 0-GPa (b) 2.74-GPa (c) 4.30-GPa.

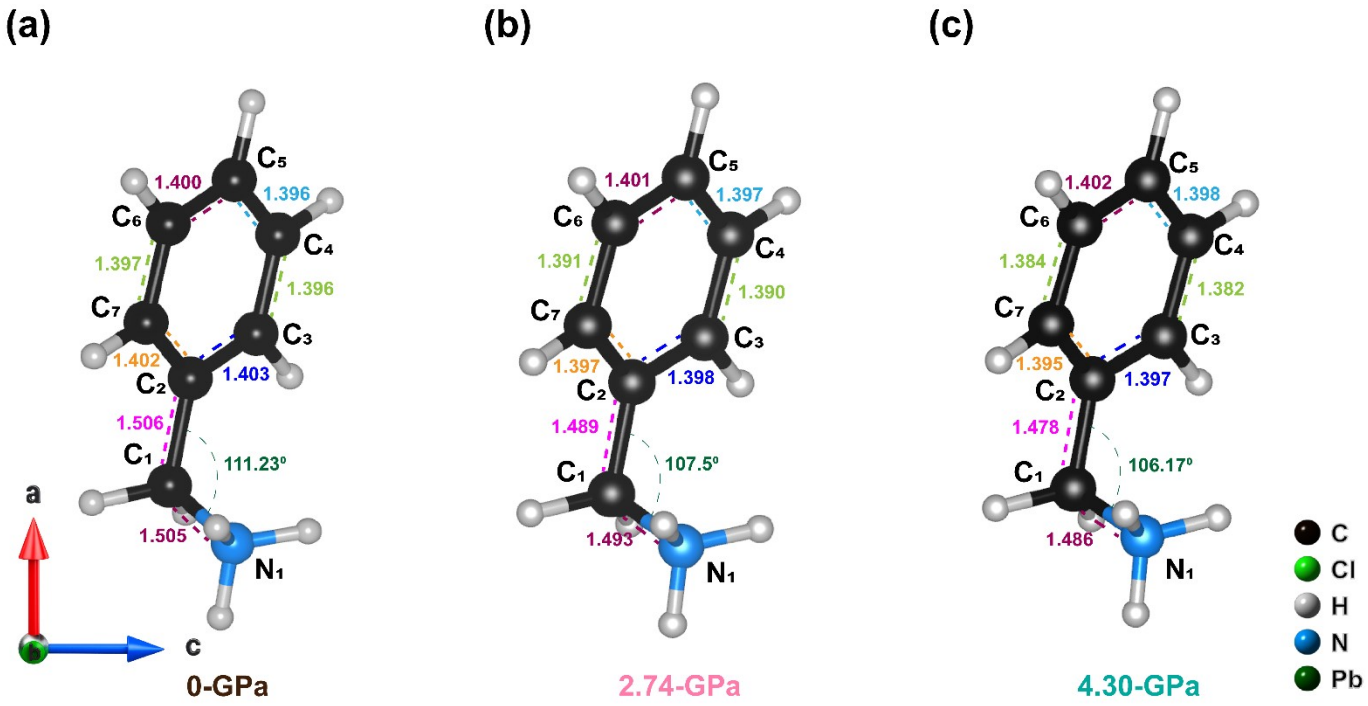

Figure S10. Pressure-dependent changes of bonds and angles within the organic cation PMA^{+}. (a) 0-GPa (b) 2.74-GPa (c) 4.30-GPa.

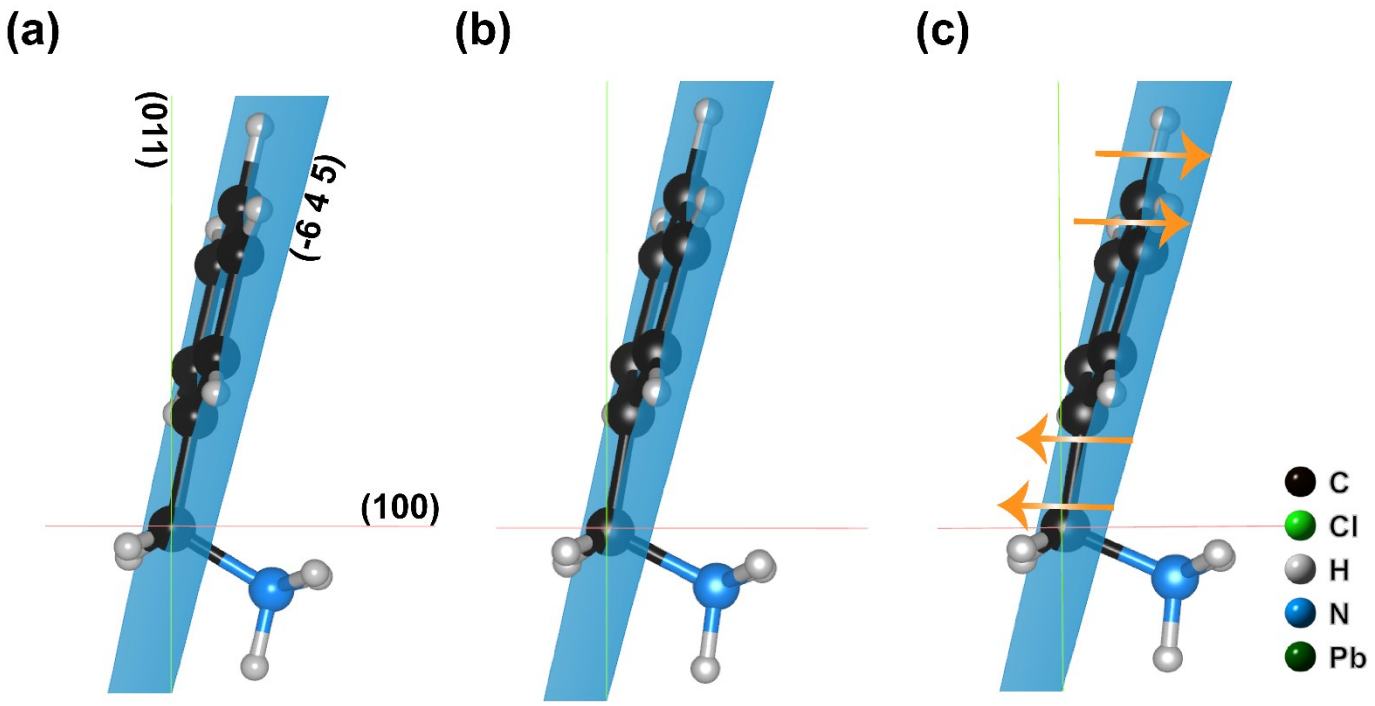

Figure S11. Pressure-dependent movement of C atoms from the benzene ring through the (-6 4 5) plane. (a) 0-GPa (b) 2.74-GPa (c) 4.30-GPa.

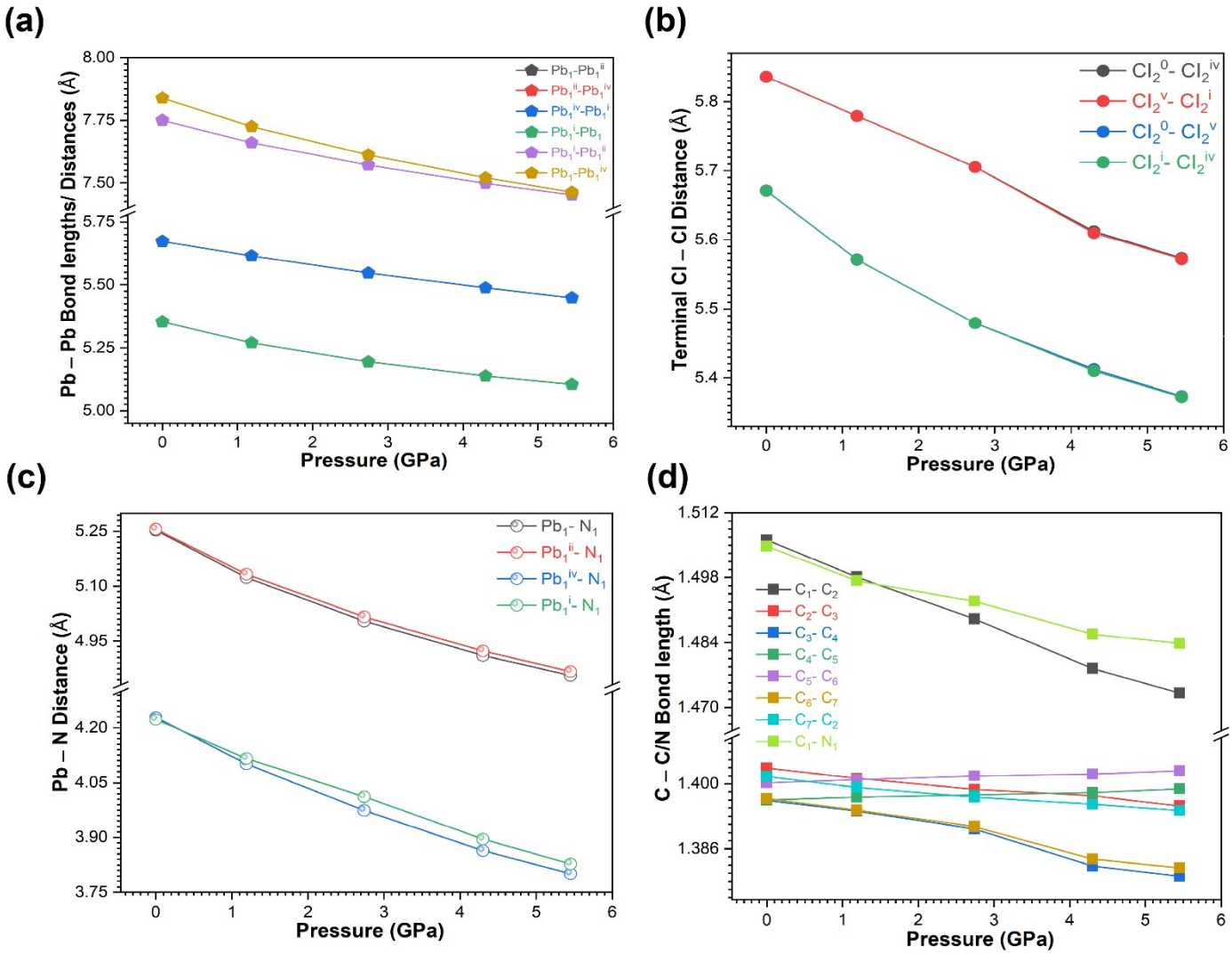

Figure 12. Structural changes in $(PMA)_2PbCl_4$ under varying pressure conditions: Pressure-dependent changes in the interatomic distances between (a) Pb-Pb, (b) Cl-Cl, (c) Pb-N, and (d) C-C and C-N.

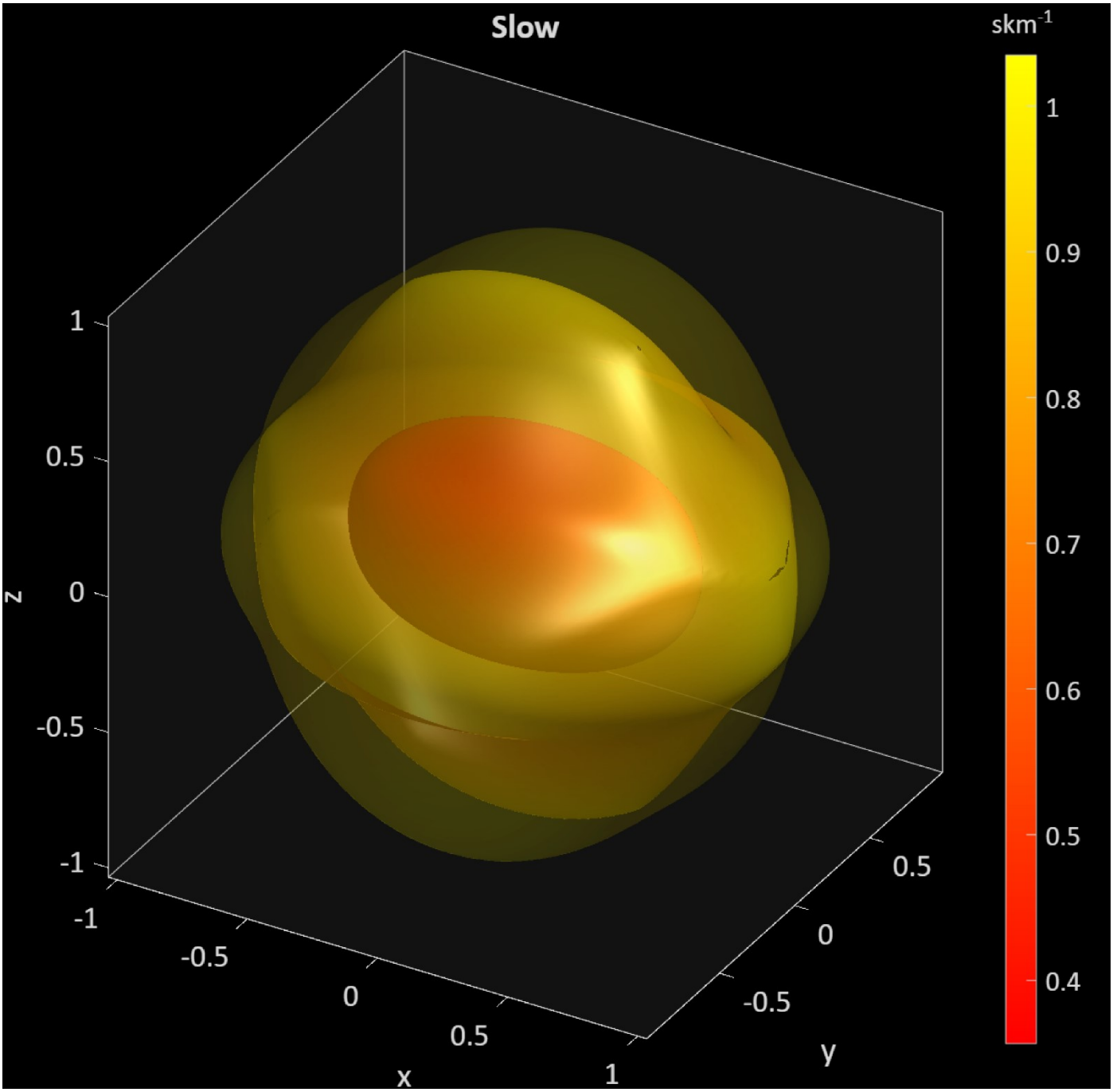

Figure S13. Three-dimensional counterplot of the slowness surface for $(PMA)_2PbCl_4$, generated using elastic stiffness tensors obtained from density functional theory (DFT) calculations.

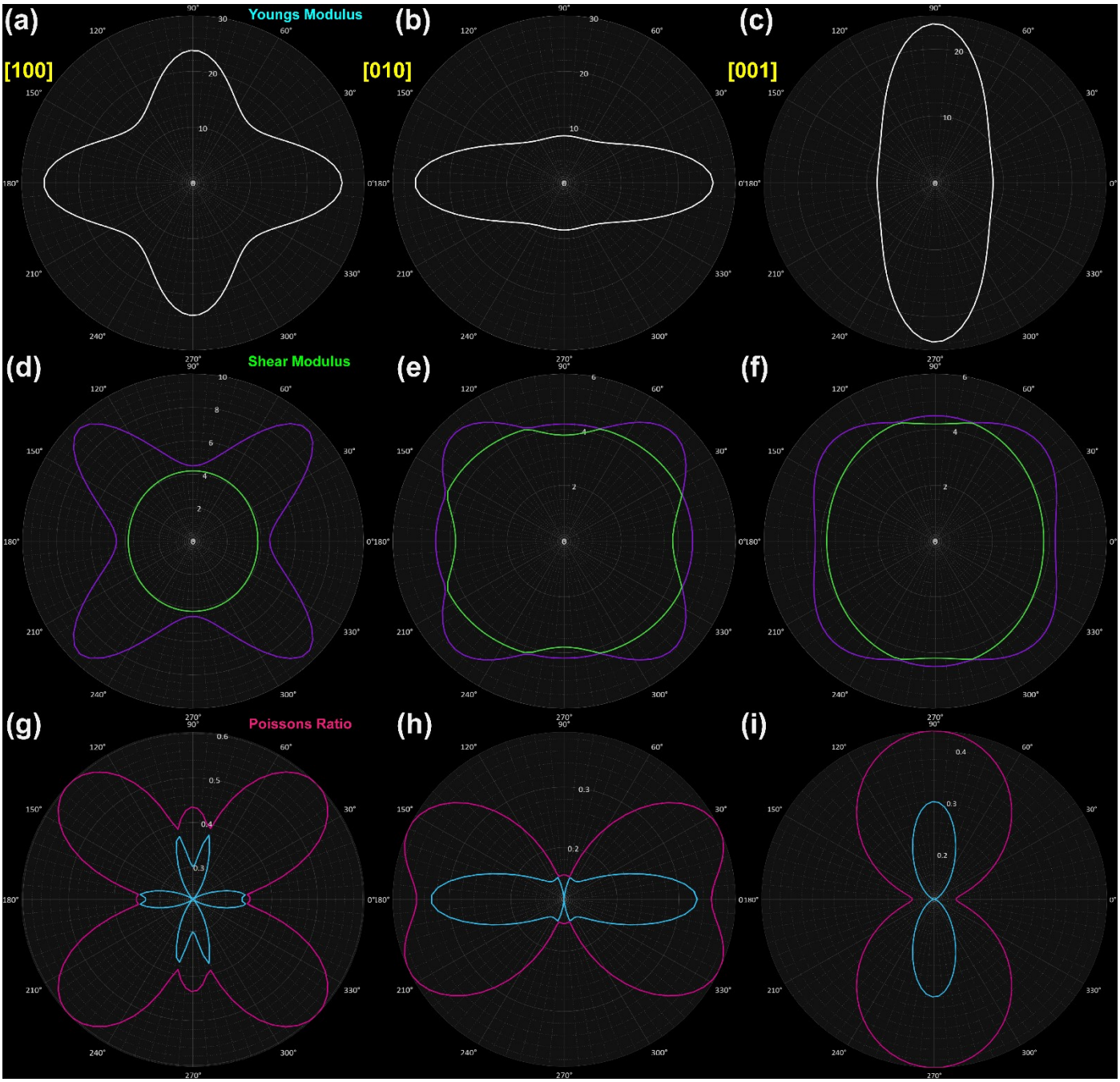

Figure S14. Two-dimensional maps along three [100], [010], and [001] directions for (a-c) Young's modulus, (d-f) Shear Modulus, (g-i) Poisson's ratio, generated using elastic stiffness tensors obtained from density functional theory (DFT) calculations.

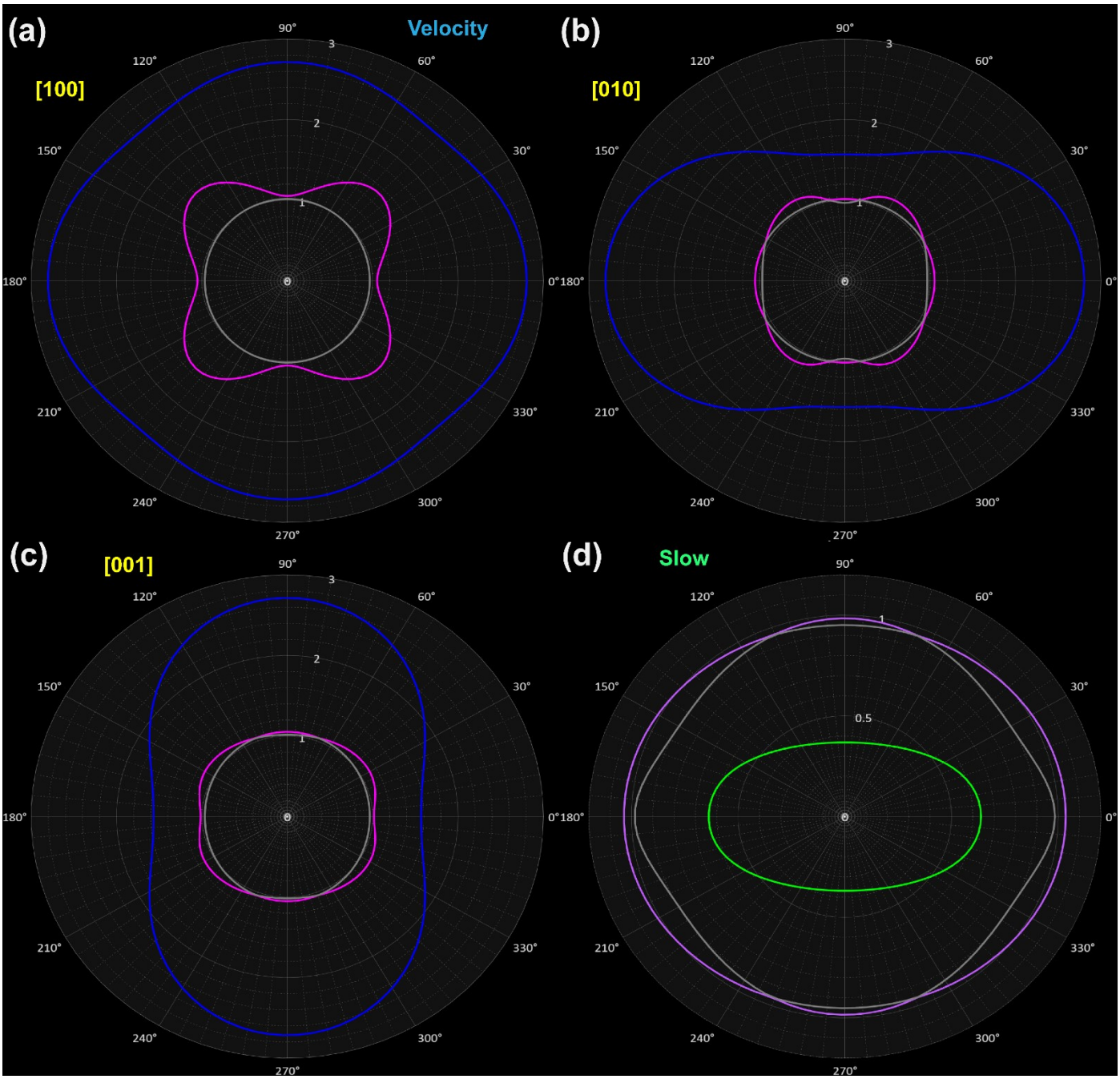

Figure S15. (a-c) Two-dimensional maps along three [100], [010], and [001] directions for sound wave velocity, (d) Two-dimensional plots for surface slowness, generated using elastic stiffness tensors obtained from density functional theory (DFT) calculations.

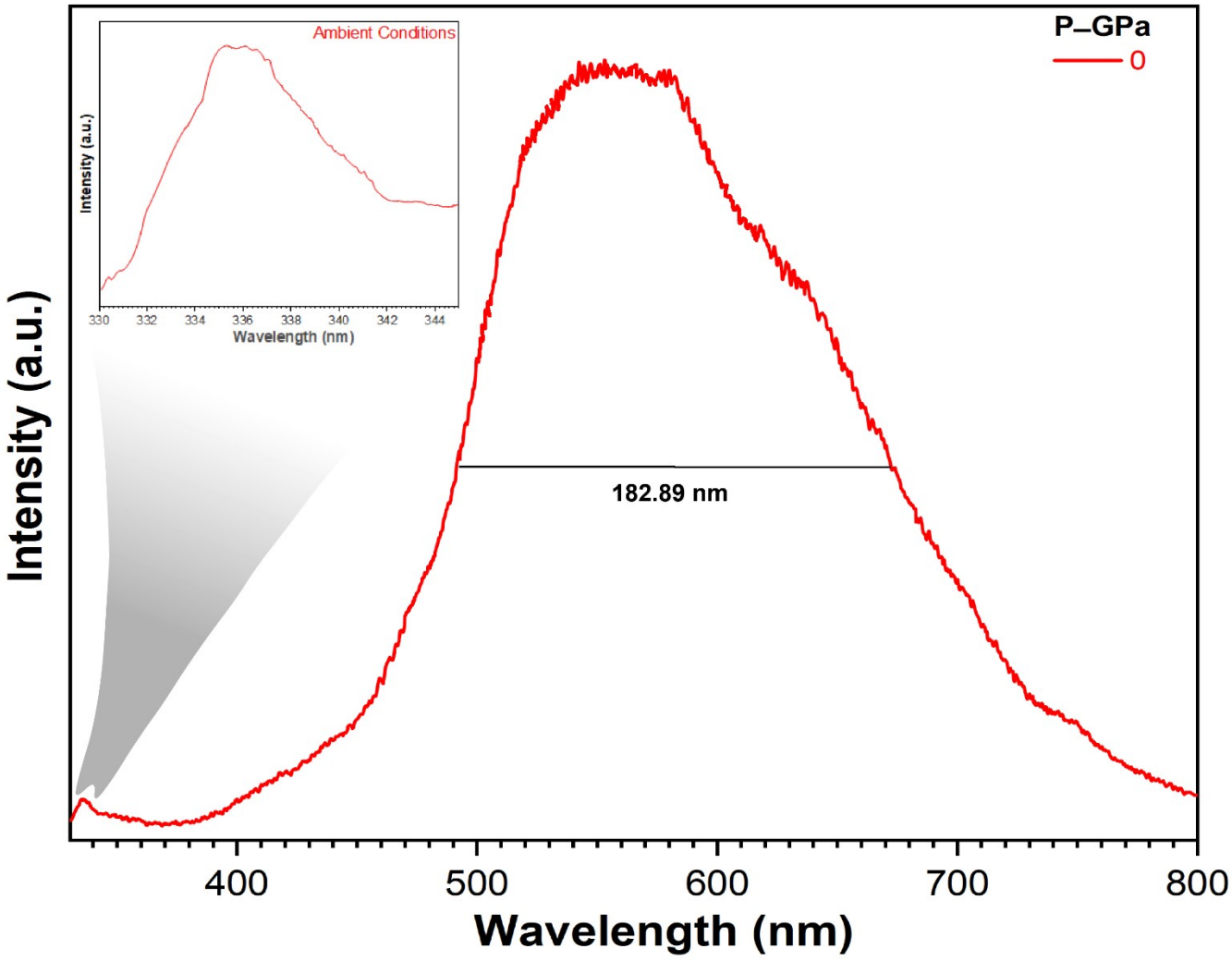

Figure S16. The PL spectrum is collected at ambient pressure after release, and the inset shows free exciton emission.

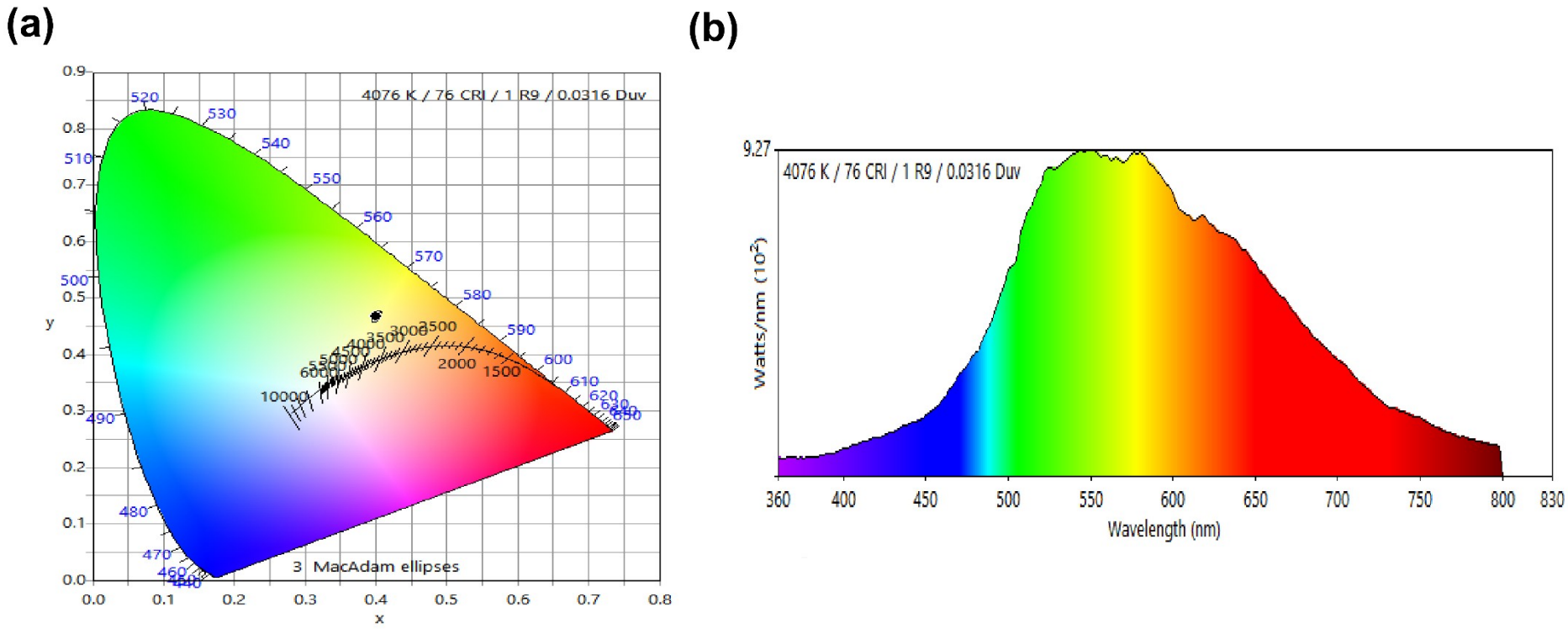

Figure S17. Chromaticity and emission characteristics of $(PMA)_2PbCl_4$. (a) CIE 1931 chromaticity diagram showing the emission coordinates under pressure, with a correlated color temperature (CCT) of 4076 K, CRI of 76, and Duv of 0.0316. (b) Corresponding emission spectrum spanning 360–800 nm, highlighting broadband luminescence across the visible range.

Table S1. Le-Bail refinement extracted lattice parameters at different pressures.

Sr	P	V	a	b	c
1	0	2031.8(1)	33.4497(1)	7.8376(2)	7.7501(1)
2	0.33	1990.2(1)	33.0233(1)	7.8036(2)	7.7232(2)
3	0.87	1929.6(2)	32.3951(2)	7.7529(1)	7.6830(3)
4	1.19	1897.4(1)	32.0579(2)	7.7255(3)	7.6613(1)
5	1.58	1861.1(2)	31.6763(2)	7.6942(2)	7.6364(3)
6	2.08	1818.8(3)	31.2271(4)	7.6570(1)	7.6069(4)
7	2.74	1768.8(4)	30.6912(5)	7.6122(3)	7.5713(2)
8	2.99	1751.3(4)	30.5027(2)	7.5963(1)	7.5586(3)
9	3.49	1718.5(5)	30.1462(4)	7.5661(3)	7.5346(2)
10	3.81	1698.8(4)	29.9310(4)	7.5478(1)	7.5200(5)
11	4.3	1670.4(5)	29.6189(5)	7.5210(4)	7.4986(2)
12	4.65	1651.2(3)	29.4077(3)	7.5028(1)	7.4841(2)
13	5.02	1632.0(4)	29.1939(2)	7.4843(3)	7.4693(4)
14	5.45	1610.7(5)	28.9567(4)	7.4636(4)	7.4528(5)

Table S2. Bond length and bond angles at different pressures.

Distances and Angles in the Inorganic Part							
Pb-Cl Distances (error ~ ±0.0023–0.0042 Å)							
Atom1	**Atom2**		**0GPa**	**1.19GPa**	**2.74GPa**	**4.30GPa**	**5.45GPa**
Pb1	CI10		2.8996	2.8868	2.8649	2.8426	2.8242
Pb1	CI1ii		2.9125	2.8612	2.8125	2.7746	2.7508
Pb1	CI1iii		2.8675	2.8416	2.801	2.7598	2.7313
Pb1	CI1iv		2.8736	2.8055	2.7425	2.6967	2.6703
Pb1	CI20		2.9293	2.9007	2.8786	2.8626	2.8511
Pb1	CI2iv		2.9293	2.9007	2.8786	2.8626	2.8511
Pb1i	CI1i		2.8996	2.8868	2.8649	2.8426	2.8242
Pb1i	CI1iv		2.8675	2.8416	2.801	2.7598	2.7313
Pb1i	CI1v		2.8736	2.8055	2.7425	2.6967	2.6703
Pb1i	CI1vi		2.9125	2.8612	2.8125	2.7746	2.7508
Pb1i	CI2i		2.9293	2.9007	2.8786	2.8626	2.8511
Pb1i	CI2v		2.9293	2.9007	2.8786	2.8626	2.8511
Pb-Pb Distances (error ~ ±0.002–0.003 Å)							
Atom1	**Atom2**		**0GPa**	**1.19GPa**	**2.74GPa**	**4.30GPa**	**5.45GPa**
Pb1	Pb1ii		5.3536	5.2699	5.1946	5.138	5.1049
Pb1ii	Pb1iv		5.6732	5.6156	5.5474	5.4881	5.4481
Pb1iv	Pb1i		5.6732	5.6156	5.5474	5.4881	5.4481
Pb1i	Pb1		5.3536	5.2699	5.1946	5.1381	5.1049
Pb1i	Pb1ii		7.7501	7.6613	7.5713	7.4986	7.4528
Pb1	Pb1iv		7.8376	7.7255	7.6122	7.5211	7.4636
Cl-Cl Distances (error ~ ±0.003–0.004 Å)							
Atom1	**Atom2**		**0GPa**	**1.19GPa**	**2.74GPa**	**4.30GPa**	**5.45GPa**
CI20	CI2iv		5.8363	5.7794	5.7055	5.6124	5.5733
CI2v	CI2i		5.8363	5.7794	5.7055	5.6099	5.5721
CI20	CI2v		5.6712	5.5713	5.4793	5.4124	5.3733
CI2i	CI2iv		5.6712	5.5713	5.4793	5.4099	5.3721
Pb-Cl-Pb Angles (error ~ ±0.15–0.20 deg.)							
Atom1	**Atom2**	**Atom3**	**0GPa**	**1.19GPa**	**2.74GPa**	**4.30GPa**	**5.45GPa**
Pb1i	CI1iv	Pb1	137.65	137.87	139.12	140.65	141.84
Pb1	CI1iii	Pb1ii	137.65	137.87	139.12	140.65	141.84
Pb1ii	CI1vii	Pb1iv	154.88	155.34	155.42	155.46	155.48
Pb1iv	CI1i	Pb1i	154.88	155.34	155.42	155.46	155.48
Cl-Pb-Cl Angles (error ~ ±0.20 deg.)							
Atom1	**Atom2**	**Atom3**	**0GPa**	**1.19GPa**	**2.74GPa**	**4.30GPa**	**5.45GPa**
CI1iv	Pb1	CI20	94.99	94.96	94.93	94.92	94.91
CI1iv	Pb1i	CI2v	89.41	89.11	88.87	88.71	88.61
CI1i	Pb1i	CI2v	84.99	85.01	85.03	85.04	85.06
CI1iii	Pb1	CI20	89.41	89.11	88.87	88.71	88.61
CI1iv	Pb1	CI1iii	92.78	92.96	93.11	93.25	93.31

CI1iii	Pb1ii	CI1vii	99.16	98.76	98.44	97.49	96.84
CI1vii	Pb1iv	CI1i	86.11	86.21	86.29	86.48	86.63
CI1i	Pb1i	CI1iv	81.93	82.05	82.14	82.76	83.19
Distances and Angles in the Organic Part							
Distances in Organic Cation (error ~ ±0.0035-0.0038 Å)							
Atom1	**Atom2**		**0GPa**	**1.19GPa**	**2.74GPa**	**4.30GPa**	**5.45GPa**
C1	C2		1.5062	1.4981	1.4891	1.4784	1.4731
C2	C3		1.4034	1.4012	1.3988	1.3974	1.3952
C3	C4		1.3964	1.3941	1.3903	1.3823	1.3801
C4	C5		1.3965	1.3971	1.3976	1.3981	1.3989
C5	C6		1.4002	1.4009	1.4017	1.4021	1.4028
C6	C7		1.3968	1.3943	1.3908	1.3838	1.3819
C7	C2		1.4016	1.3992	1.3971	1.3956	1.3942
C1	N1		1.5048	1.4973	1.4929	1.4858	1.4838
N-C-C Angles (error ~ ±0.30 deg.)							
Atom1	**Atom2**	**Atom3**	**0GPa**	**1.19GPa**	**2.74GPa**	**4.30GPa**	**5.45GPa**
N1	C1	C2	111.23	109.39	107.5	106.17	105.18
Angle of in-plane distortion (error ~ ±0.15-0.20 deg.)							
Angle	at atom		**0GPa**	**1.19GPa**	**2.74GPa**	**4.30GPa**	**5.45GPa**
∠2	CI1iv		42.35	42.13	40.88	39.35	38.16
∠2	CI1iii		42.35	42.13	40.88	39.35	38.16
∠3	CI1vii		25.12	24.66	24.58	24.54	24.52
∠3	CI1i		25.12	24.66	24.58	24.54	24.52
Angle of out-of-plane distortion (error ~ ±0.15-0.20 deg.)							
Angle	at atom		**0GPa**	**1.19GPa**	**2.74GPa**	**4.30GPa**	**5.45GPa**
∠1	CI20		4.99	4.96	4.93	4.92	4.91
∠1	CI2i		4.99	4.96	4.93	4.92	4.91

C_{ij}	C_{11}	C_{12}	C_{13}	C_{22}	C_{23}	C_{33}	C_{44}	C_{55}	C_{66}
Values	10	6	5.5	30	12	32	4.5	3.8	4.2

Table S3. Elastic stiffness constants calculated by DFT.