Tunable Phase Transition Temperature and Nonlinear Optical Property of Organic-Inorganic Hybrid Perovskites Enabled by Dimensional Engineering

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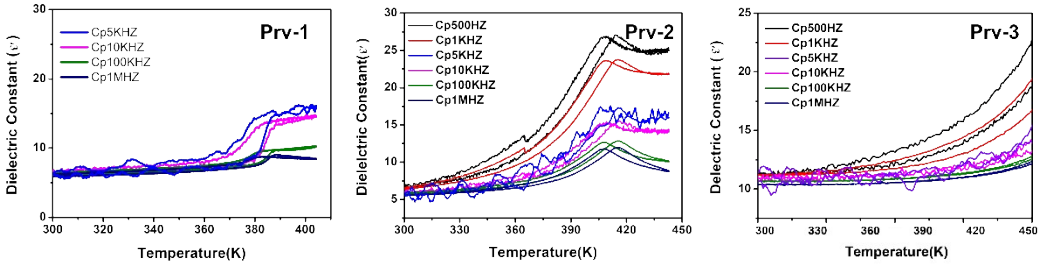

Figure S1. The dielectric constants of three perovskite materials in different frequencies.

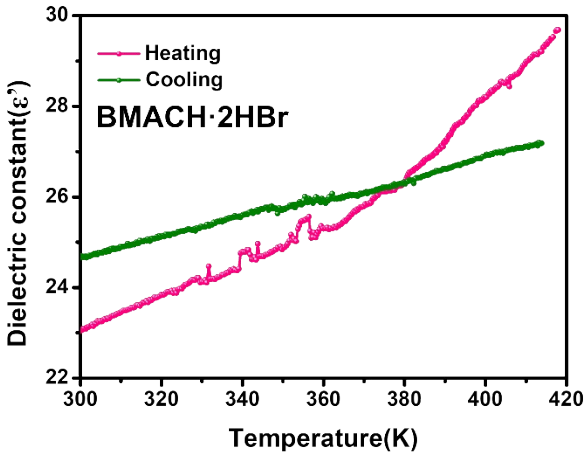

Figure S2. The temperature dependent dielectric constant of BMACH·2HBr at 1 MHz.

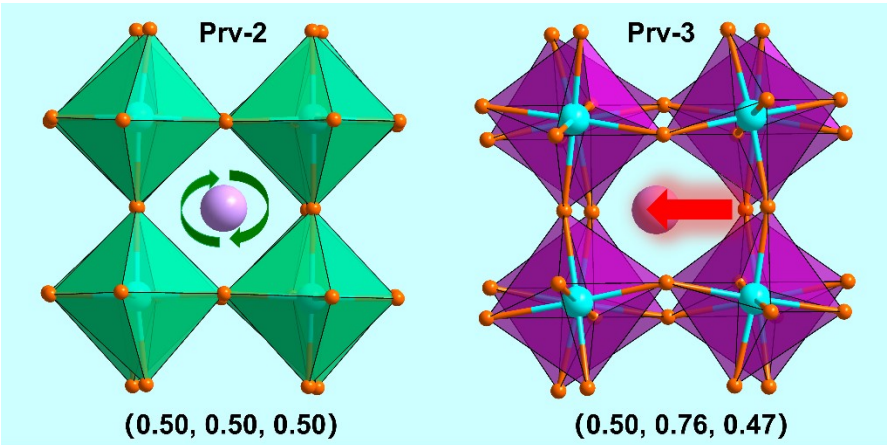

Figure S3. Structural changes of inorganic frameworks and mineralizers in Prv-2 and Prv-3.

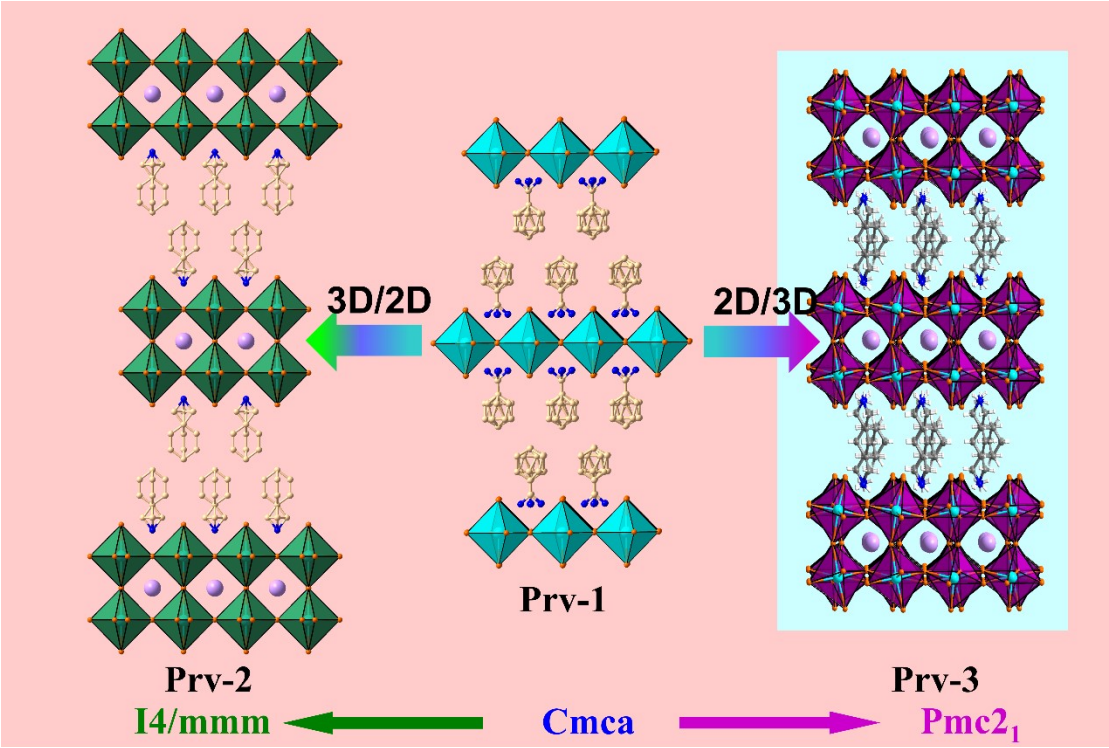

Figure S4. High temperature phase (HTP) structures of three compounds.

Hirshfeld surface analysis

Hirshfeld surface was generated by the CIF document of crystallographic data based on CrystalExplorer software with HF functional. The standard resolution is used for the all Hirshfeld surface generation (The intensity of molecular interaction is mapped onto the Hirshfeld surface by using the respective red-blue-white scheme: where the white or green regions exactly correspond to the distance of Van der Waals contacts, the blue regions correspond to longer contacts, and the red regions represent closer contacts. Besides, each coordinate in 2D fingerprint is calculated by the distance between the inner (d_i) and outer (d_e) nearest atoms of the Hirshfeld d_{norm} surface. Notably, the Hirshfeld surface and 2D fingerprint corresponding to each structure are unique. The normalized contact distance d_{norm} is calculated by the *van der Waals* (vdW) radii based on two atoms external (r_e^{vdW}) and internal (r_i^{vdW}) to the surface:

$$d_{\text{norm}} = \frac{d_i - r^{vdW}}{r^{vdW}_i} + \frac{d_e - r}{r^{vdW}_e}$$

d_{norm} surface is used for the identification of close intermolecular interactions.

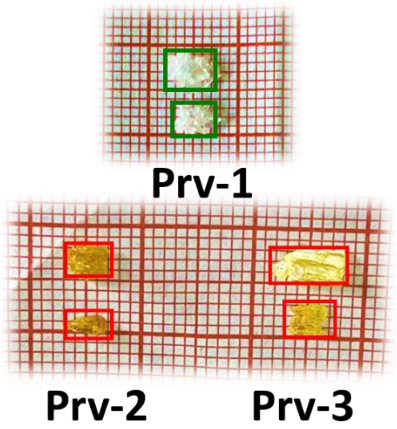

Figure S5. Large size single crystal images.

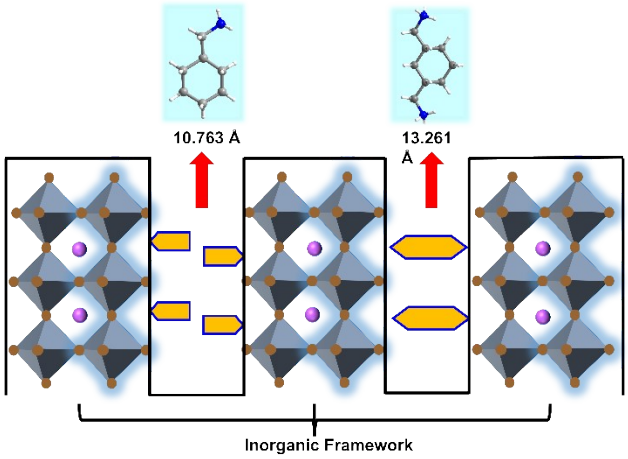

Figure S6. A diagrammatic sketch of organic barriers and inorganic wells.

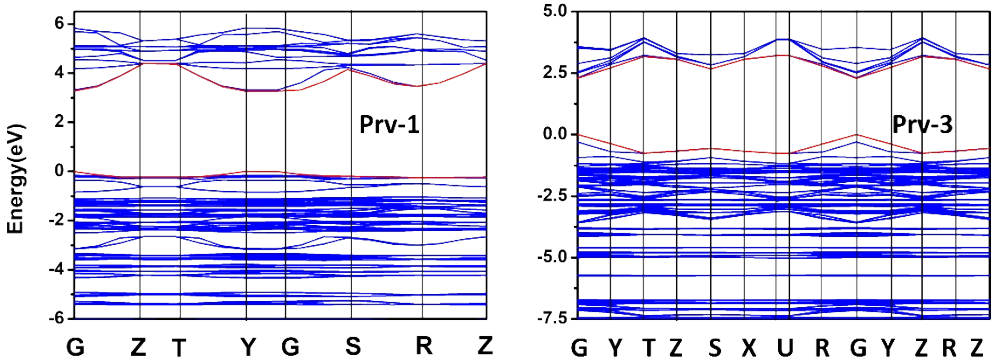

Figure S7. The band structures of Prv-1 and Prv-3.

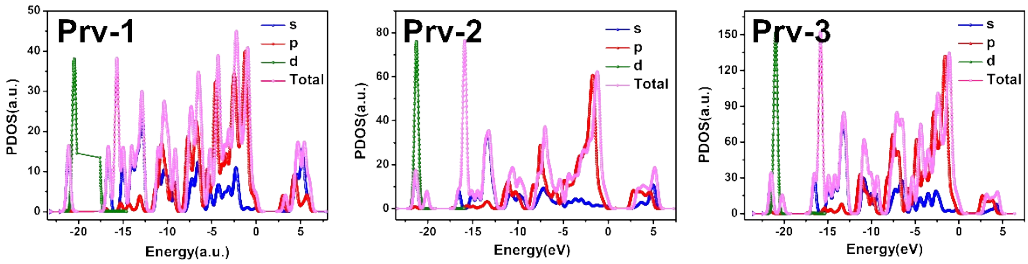

Figure S8. Partial density of states (PDOS) of three compounds.

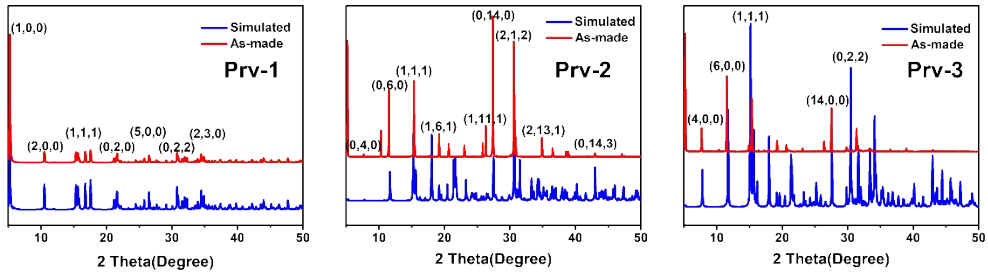

Figure S9. Powder X-Ray diffraction (PXRD) patterns of three perovskite materials.

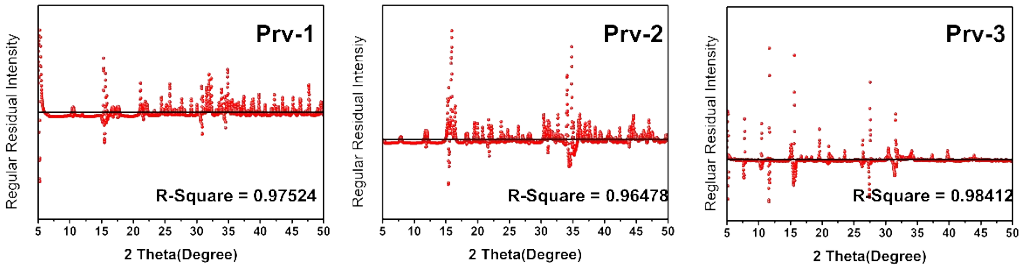

Figure S10. Calculation of three compounds lattice distances from powder X-Ray diffraction data according to *Scherrer* equation.

Calculation details of lattice distances for three compounds.

Compounds								
	Prv-1			Prv-2			Prv-3	
2θ	width	Distance	2θ	width	Distance	2θ	width	Distance
5.19122	0.0826	112.539	7.88072	0.10518	108.328	5.2547	0.11909	76.6564
7.7116	0.18219	57.7074	11.89388	0.1156	72.83588	10.52049	0.10928	139.6417
10.42006	0.25734	64.67064	15.42902	0.17363	329.2962	15.52729	0.57318	153.7132
11.66144	0.14455	61.10793	18.30335	0.11285	73.1434	16.77627	0.11105	140.586
15.61129	0.33498	490.8275	21.80274	0.2473	3410.683	17.58675	0.11134	88.4388
19.59875	0.00427	1999	25.69534	0.11092	74.58983	21.62207	0.18375	235.737
20.9906	0.36768	45	28.13892	0.1131	1038.751	26.49988	0.10569	96.99704
26.36991	0.29492	33.06	31.07925	0.13656	59.0384	30.81623	0.25241	32.9604
27.49843	0.21665	96.9321	34.70802	1.08113	97.7909	34.49352	0.22292	1114.44
31.52351	0.42126	18.8857	32.26007	0.13413	64.959	44.00683	0.13179	60.315
			40.9944	0.1139	908.967	42.13675		
			43.87532	0.13172	60.429	39.68966		

	45.38074	0.12802	81.1224
378.7763		427.78	213.9486

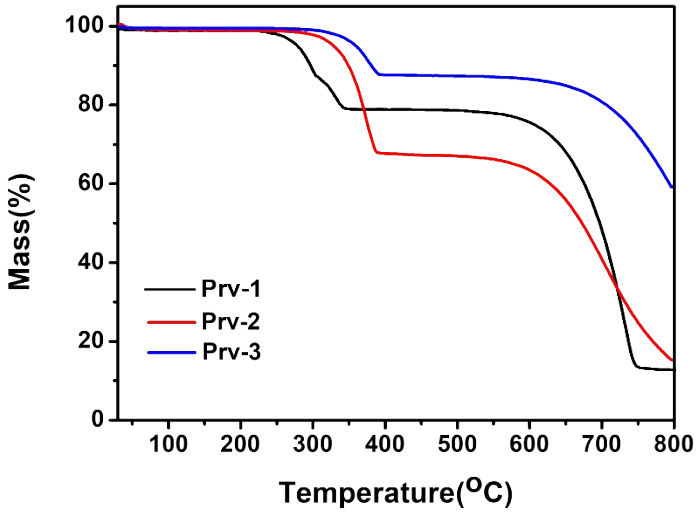

Figure S11. Thermal stability analysis of chemical structures of three compounds.

Table S1 Crystallographic data and structural refinement details of compounds

Compounds	Prv-2	Prv-2	Prv-3
CCDC Code	2193783	2193781	2193782
Formula	$2(C_7H_{16}N)\cdot CsPb_2Br_7$	$2(C_7N)\cdot CsPb_2Br_7$	$C_8H_{20}N_2\cdot CsPb_2Br_7$
Fw	1335.07	1329.31	1250.92
Temp(K)	300	413	200
Crystal Syst	Orthorhombic	Tetragonal	Orthorhombic
Space group	*Pnma*	*I4/mmm*	$Pmc2_1$
a(Å)	8.2272 (17)	5.8488 (4)	17.920 (3)
b(Å)	45.395 (10)	5.8488 (4)	7.9645 (12)
c(Å)	8.290 (2)	46.264 (4)	8.4836 (14)
α	90	90	90
β	90	90	100.611
γ	90	90	90
V(Å^3)	3096.1 (12)	1582.6 (3)	1210.8 (3)
Z	4	2	2
μ(mm-1)	21.06	20.60	26.91
GOF on F^2	1.003	1.144	1.069
R_1[[I > 2σ(I)][a]	0.0392	0.0396	0.0252
wR_2 (all data)[b]	0.0878	0.1228	0.0574

Table S2. The important band lengths and band angles.

Prv-2			
LTP		HTP	
Pb01—Br03	2.9760 (13)	Pb1—Br4	3.0136 (9)
Pb01—Br04	2.9990 (12)	Pb1—Br3	2.9863 (9)
Pb01—Br04^{i}	3.0056 (12)	Pb1—Br3^{ii}	2.9863 (9)
Pb01—Br05	2.9761 (12)	Pb1—Br3^{iv}	2.9863 (9)
Pb01—Br05^{ii}	2.9787 (12)	Pb1—Br3^{v}	2.9863 (9)
Pb01—Br2	3.0169 (8)	Pb1—Br3^{vi}	2.9863 (9)
N008—C00B	1.473 (13)	Pb1—Br3^{vii}	2.9863 (9)
C00A—C00B	1.502 (15)	Pb1—Br2	2.935 (3)
C00A—C6	1.539 (14)	C1—C1^{vi}	1.26 (4)
C6—C13	1.499 (17)	C1—C1^{xii}	1.78 (6)
C8—C10	1.476 (16)	C4—C4^{xiv}	1.698 (10)
C10—C12	1.476 (17)	C5—C4^{xiv}	1.494 (10)
C12—C13	1.49 (2)	C5—C4	1.494 (10)
Br03—Pb01—Br04	92.40 (3)	C3—C4	1.495 (10)
Br03—Pb01—Br04^{i}	85.59 (3)	N1—C1	1.48 (2)
Br03—Pb01—Br05	90.33 (3)	C2—C3	1.487 (9)
Br03—Pb01—Br05^{ii}	97.50 (3)	Br3^{vii}—Pb1—Br4	89.07 (6)
Br03—Pb01—Br2	173.90 (4)	Br3—Pb1—Br4	89.07 (6)
Br04—Pb01—Br04^{i}	88.63 (2)	Br3—Pb1—Br3^{ii}	113.27 (15)
Br04^{i}—Pb01—Br2	88.35 (4)	Br3^{i}—Pb1—Br3^{iv}	66.70 (15)
Br04—Pb01—Br2	88.11 (4)	Br3—Pb1—Br3^{iv}	156.64 (16)
Br05^{ii}—Pb01—Br04^{i}	176.70 (3)	Br3^{v}—Pb1—Br3^{vi}	113.27 (15)
Br05—Pb01—Br04	175.76 (3)	Br3^{vii}—Pb1—Br3^{iv}	113.27 (16)

Table S3. The important band lengths and band angles.

Prv-3	
LTP	
Pb01—Br03	2.9784 (13)
Pb01—Br03^{ii}	2.9991 (14)
Pb01—Br04	3.0126 (14)
Pb01—Br04^{iii}	3.0266 (13)
Pb01—Br05	2.9058 (13)
Pb01—Br06	3.0320 (7)
N008—C4	1.457 (16)
C1—C2	1.508 (16)
C007—C1	1.547 (19)
C007—C4	1.501 (16)
C007—C009	1.521 (14)
C1—C2	1.508 (16)
Br03—Pb01—Br04^{iii}	177.93 (4)
Br03^{ii}—Pb01—Br06	86.67 (5)
Br03—Pb01—Br06	87.38 (4)
Br04—Pb01—Br04^{iii}	91.159 (18)
Br04—Pb01—Br06	91.30 (5)
Br05—Pb01—Br03^{ii}	88.48 (4)
Br05—Pb01—Br03	93.53 (3)
Br05—Pb01—Br04^{iii}	88.53 (4)
Br05—Pb01—Br04	93.53 (4)
Br05—Pb01—Br06	175.11 (6)