Two Metal-Free Perovskite Molecules with Different 3D Frameworks Show Reversible Phase Transition, Dielectric Anomaly and SHG Effect

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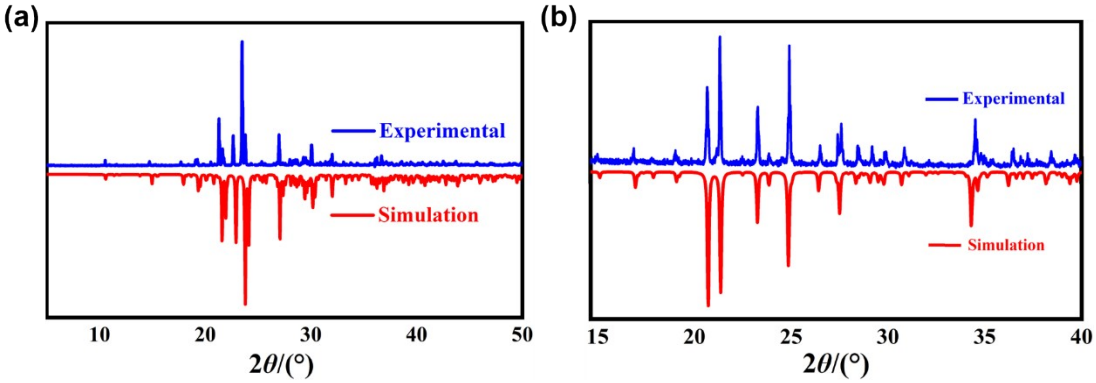

Fig. S1. The powder XRD of **1** (a) and **2** (b) with the simulated one in red and the measured one in blue.

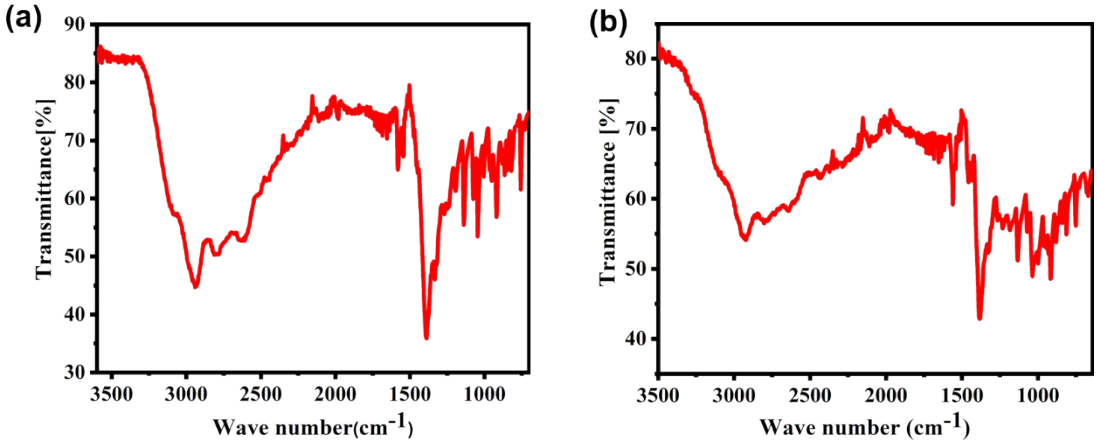

Fig. S2. The infrared spectra of **1** (a) and **2** (b).

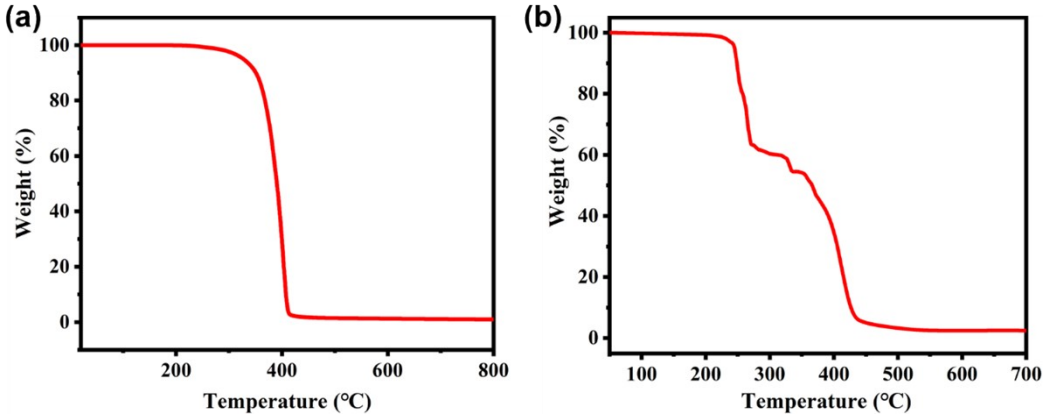

Fig. S3. TGA curves of compounds **1**(a) and **2** (b).

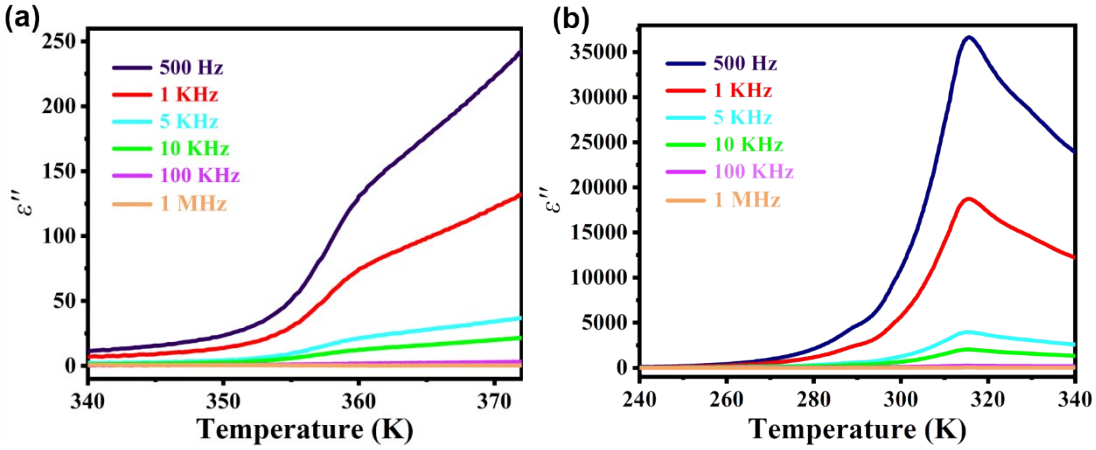

Fig. S4. The ε'' of compound **1** (a) and **2** (b) varies with temperature at the different frequencies.

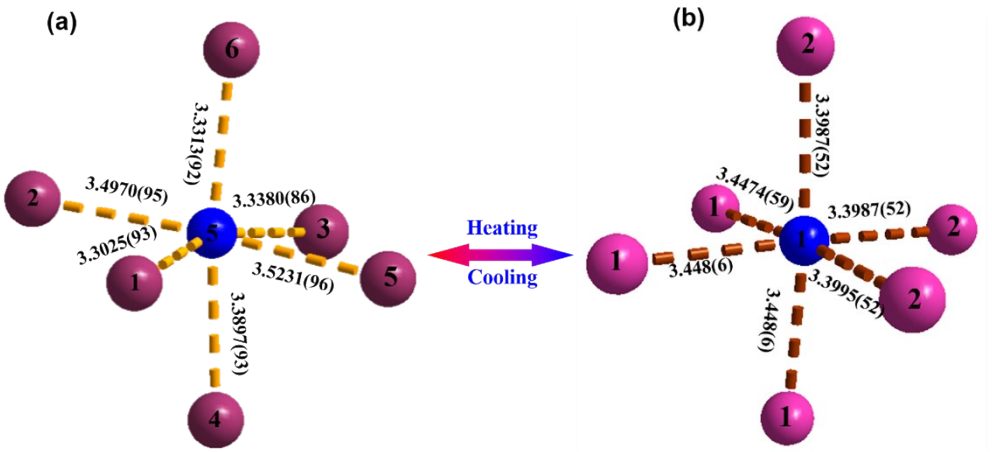

Fig. S5. The N···Br distances in **1** at LTP (a) and at HTP (b)

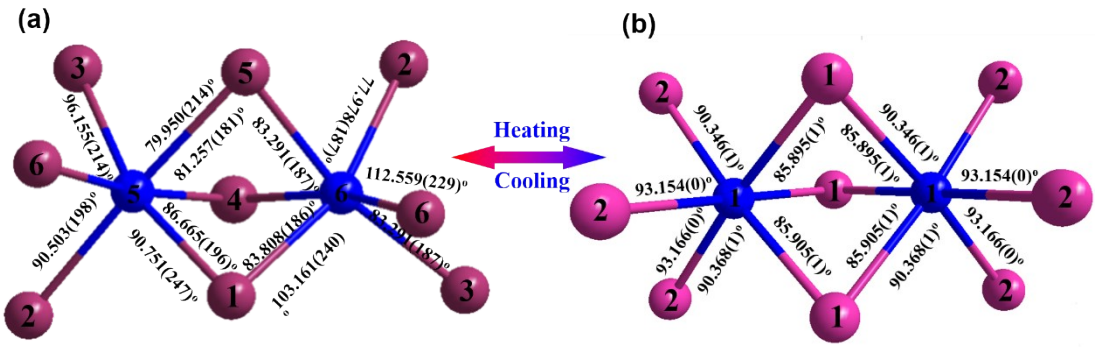

Fig. S6. The Br···N···Br bond angles (°) of **1** at LTP (a) and at HTP (b).

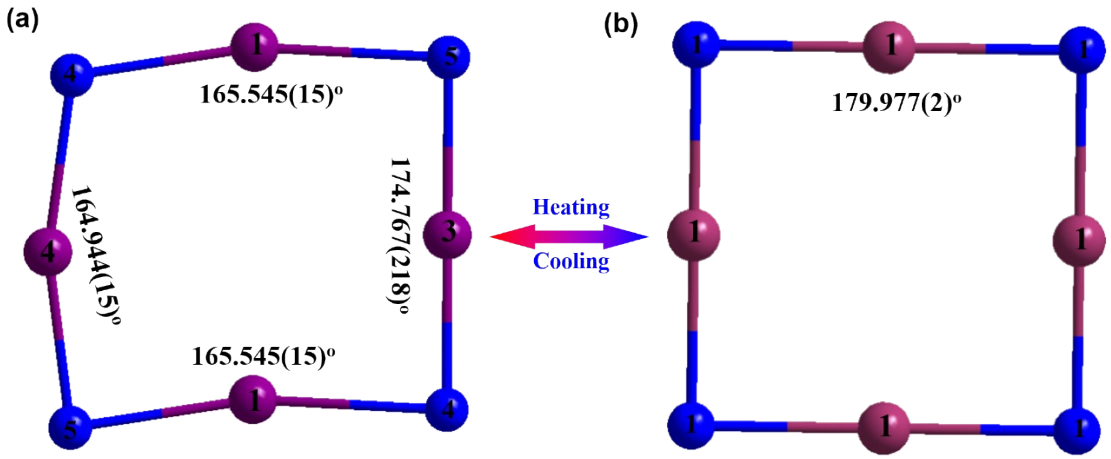

Fig. S7. The I···N···I bond angles (°) of **2** at LTP (a) and HTP (b).

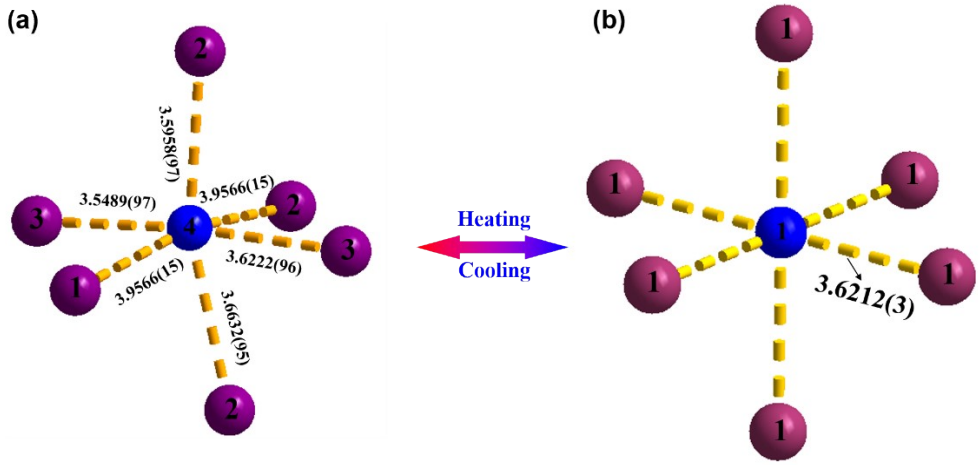

Fig. S8. The N···I bond lengths (Å) of **2** at LTP (a) and HTP (b).

Tab. S1 Crystal data and structure refinements for **1** at LTP and HTP.

Formula	**1**

Temperature	296 K	373 K
Formula Mass	381.93	381.93
Crystal system	orthorhombic	hexagonal
Space group	*Pna2₁*	*P63/mmc*
a (Å)	16.767(8)	9.8750(2)
b (Å)	9.909(4)	9.8750(2)
c (Å)	15.520(7)	15.9170(6)
V (Å)^3	2579(2)	1344.21(6)
Z	8	1
D_{calc} (g·cm^{-3})	1.967	1.699
F (000)	1472.0	628.0
θ_{max}	24.990	75.610
μ(Mo Ka,mm^{-1})	9.352	10.786
Total no. of reflns.	12617	4469
No. of unique reflns.	4529 [R_{int} = 0.0625]	573 [Rint = 0.0159]
No. of variables	236	44
R_1, wR_2 (obsd data)	0.0461, 0.1006	0.1283, 0.4144
R_1, wR_2 (all data)	0.0638, 0.1080	0.1327, 0.4233
GOF, *S*	1.052	3.772
Max./min. peak (e. Å^{-3})	0.77, -0.79	1.20, -1.15

Tab. S2 Crystal data and structure refinements for **2** at LTP and HTP.

Formula	**2**	
Temperature	293 K	330 K
Formula Mass	1063.87	502.8
Crystal system	orthorhombic	trigonal
Space group	*Ama2*	*Rm*
a (Å)	30.562(6)	10.2423(12)
b (Å)	10.349(2)	10.2423(12)

c (Å)	9.908(2)	12.5442(14)
V (Å)^3	3133.9(11)	1139.6(2)
Z	4	3
D_{calc} (g·cm^{-3})	2.255	2.799
F (000)	1944.0	866.0
θ_{max}	27.600	75.870
μ(Mo Ka,mm^{-1})	5.962	48.482
Total no. of reflns.	9204	1532
No. of unique reflns.	3709[R_{int} =0.0453]	295[R_{int} =0.1551]
No. of variables	132	16
R_1, wR_2 (obsd data)	0.0293, 0.0613	0.1211, 0.2973
R_1, wR_2 (all data)	0.0323, 0.0629	0.1414, 0.3265
GOF, S	0.967	1.006
Max./min.peak(e.Å^{-3})	0.65, -0.82	0.81, -2.27

Tab. S3 Hydrogen bond lengths [Å] and angles [°] of **1** at 293 K.

D-H…A	D-H [Å]	H…A[Å]	D…A[Å]	D-H…A[°]
N1-H1C…Br1	0.91	2.41	3.246(7)	153
N2-H2A…Br6	0.90	2.70	3.550(11)	157
N2-H2B…Br4	0.90	2.64	3.427(11)	147
N3-H3…Br6	0.91	2.27	3.187(12)	175
N4-H4C…Br2	0.90	2.62	3.453(12)	154
N4-H4D…Br5	0.90	2.46	3.318(12)	159

Tab. S4 Hydrogen bond lengths [Å] and angles [°] of **2** at 293 K.

D-H…A	D-H [Å]	H…A[Å]	D…A[Å]	D-H…A[°]
N1-H1…I2	0.98	2.61	3.527(6)	156
O1-H1C…I4	0.85	2.64	3.475(5)	167
O1-H1D…I4	0.85	2.90	3.475(5)	127

N2-H2A…O1	0.89	2.00	2.829(7)	155
N2-H2B…I1	0.89	2.81	3.647(6)	158