

Supporting Information

3D Metal-free Molecular Perovskite with Thermally Induced Switchable Dielectric Response

Lu-Lu Chu^{‡,†}, Tie Zhang^{‡,†}, Wan-Ying Zhang[§], Ping-Ping Shi[†], Ji-Xing Gao[§], Qiong

Ye^{},[†], Da-Wei Fu^{*,[†],[§]}*

(Ordered Matter Science Research Center, Jiangsu Key Laboratory for Science and Applications of Molecular Ferroelectrics, Southeast University, Nanjing, 211189, P.R. China)

Experimental methods

Synthesis

All starting chemicals came from commercial sources and were not further purified. As previously reported, the H₂dabco(NH₄)(BF₄)₃(**1**) was synthesized by using the hydrothermal method.¹ Colorless bulk crystals were shown in figure 1b. Moreover, the H₂dabcoRb(BF₄)₃(**2**) was obtained as cubic crystal by slow evaporation of mixture of H₂dabco(BF₄)₂ solution and RbBF₄ solution at room temperature (Figure 1c). The specific procedure as follows: The solution H₂dabco(BF₄)₃ was prepared as a solution containing stoichiometric the 1,4-diazabicyclo[2.2.2]octane and the HBF₄ (40%) at room temperature. The solution RbBF₄ was prepared by adding 1.097g HBF₄(40%) (5mmol) to an aqueous solution with 2.5 mmol Rb₂CO₃, then stirred under heating for 20 minutes to remove carbon dioxide gas.

Single-crystal X-ray crystallography

The X-ray single-crystal diffraction data of compounds **1** and **2** at room temperature were collected on the Rigaku XtaLAB mini II diffractometer with Mo Ka radiation($\lambda = 0.71073 \text{ \AA}$), while the data of high temperature were obtained by a *Rigaku VarimaxTM DW* diffractometer with Mo Ka radiation ($\lambda = 0.71073 \text{ \AA}$) using the ω scan technique. The crystallographic data were processed through direct

methods and refined by full-matrix least-squares methods using the SHLXTL-2014 procedure. The non-H atoms were refined anisotropically limiting all reflections with $I > 2\sigma(I)$; meanwhile, the rational positions of the H atoms were generated geometrically and refined with a “riding” model($U_{iso}(H)=1.2 U_{eq}(C \text{ or } N)$).

Thermal and Phase Stabilities

In the differential scanning calorimetry (DSC) experiments, the dry powders of **1** (8.5 mg), **2** (11.0 mg) were put in aluminum crucibles respectively, and then put them into the PerkinElmer Diamond DSC instrument. The measurement was carried out under nitrogen at atmospheric pressure with heating and cooling rate of 20 K min^{-1} . The stability of **1** and **2** was tested through thermogravimetric analysis (TGA). The powder X-ray diffraction (PXRD) patterns were recorded on Rigaku D/MAX 2000 PC X-ray diffractometer, which matches well with the simulated patterning (Figure S2 and S3).

Dielectric Responses

Dielectric response of **1** and **2** both was measured by Tonghui TH2828A Precision LCR Meter with the measuring AC voltage fixed at 1 V. The pressed-powder pellets with carbon glue painted and cubic crystals with silver glue painted were used as electrodes for testing the dielectric constants.

Infrared (IR) spectroscopy

The functional groups of both compounds were tested by Nicolet 4700 FTIR Spectrometer (Thermo, USA) at room temperature. (Figure S4).

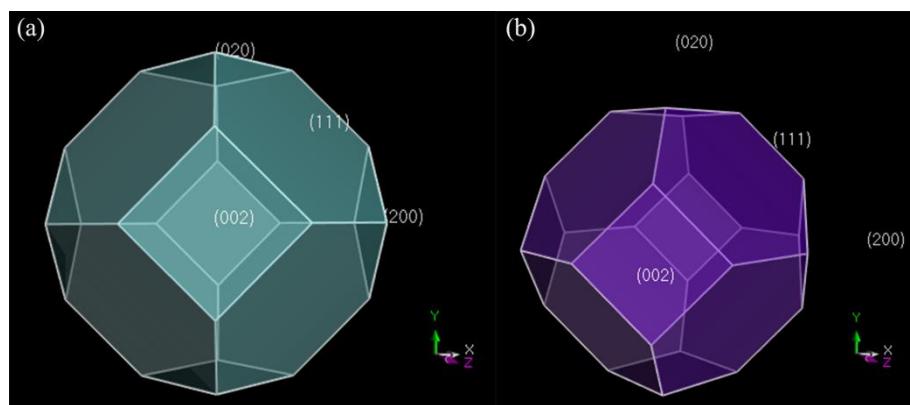


Figure S1 The simulative single crystal shape of compound **1** (a) and **2** (b).

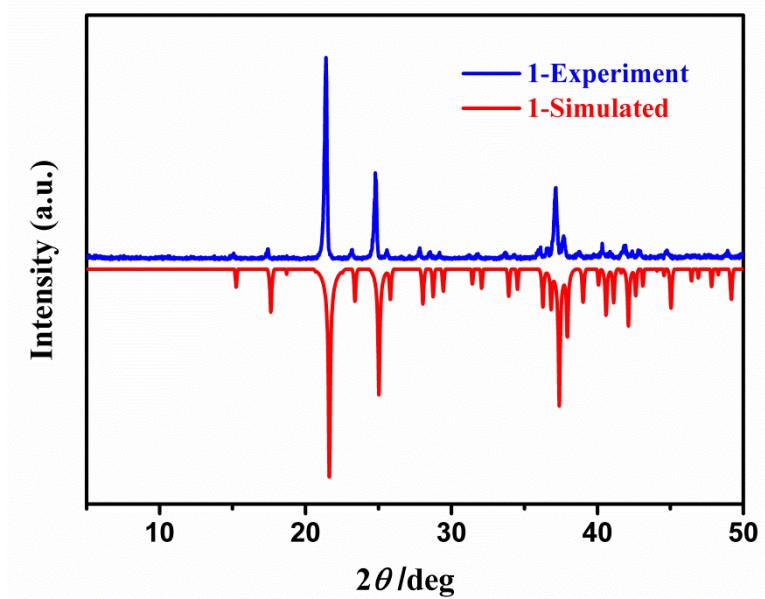


Fig. S2 PXRD pattern of compound **1**.

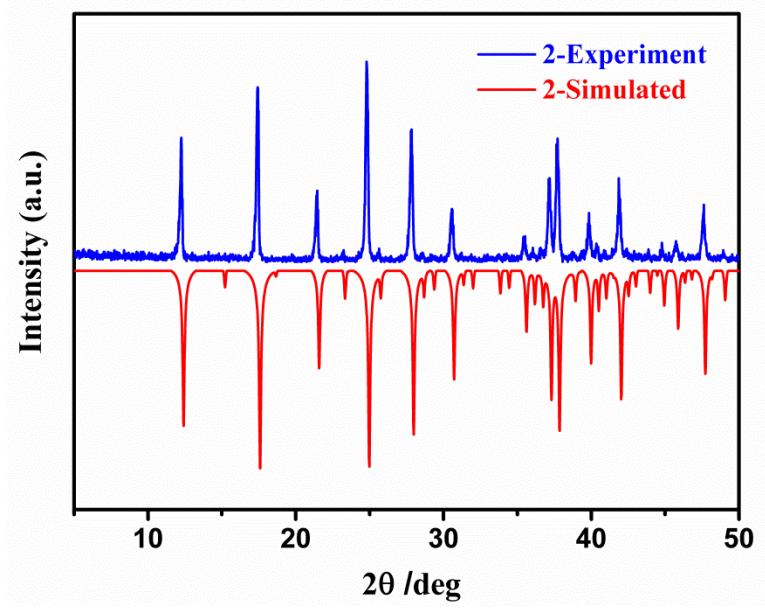


Fig. S3 PXRD pattern of compound **2**.

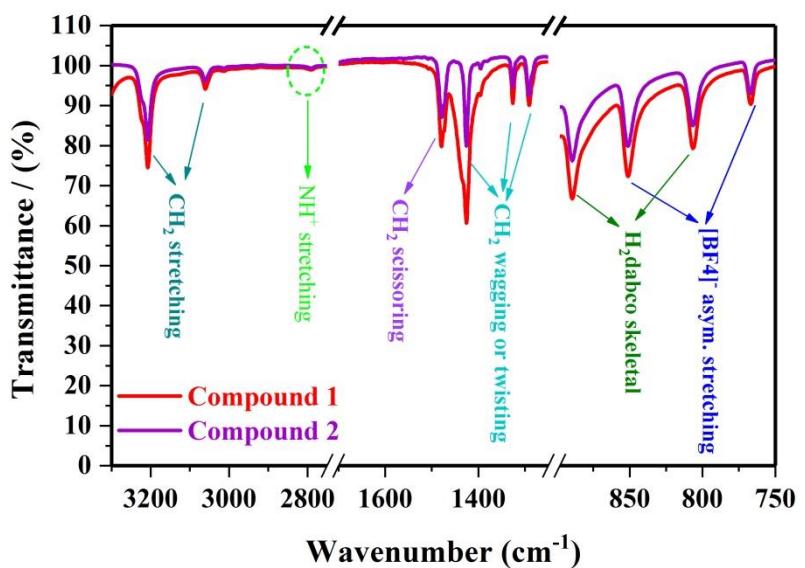


Fig. S4 The IR spectrum for compound **1, 2** display the characteristics peaks

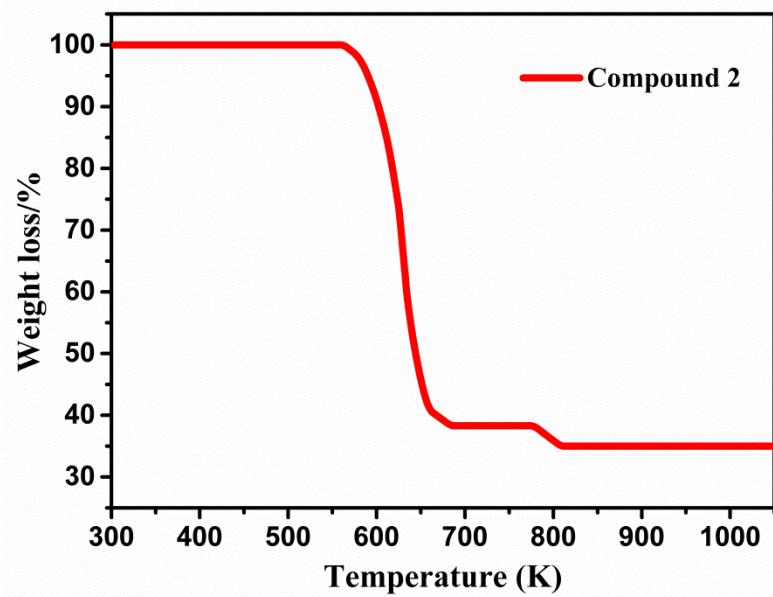


Fig. S5. TGA curves of compound **2**.

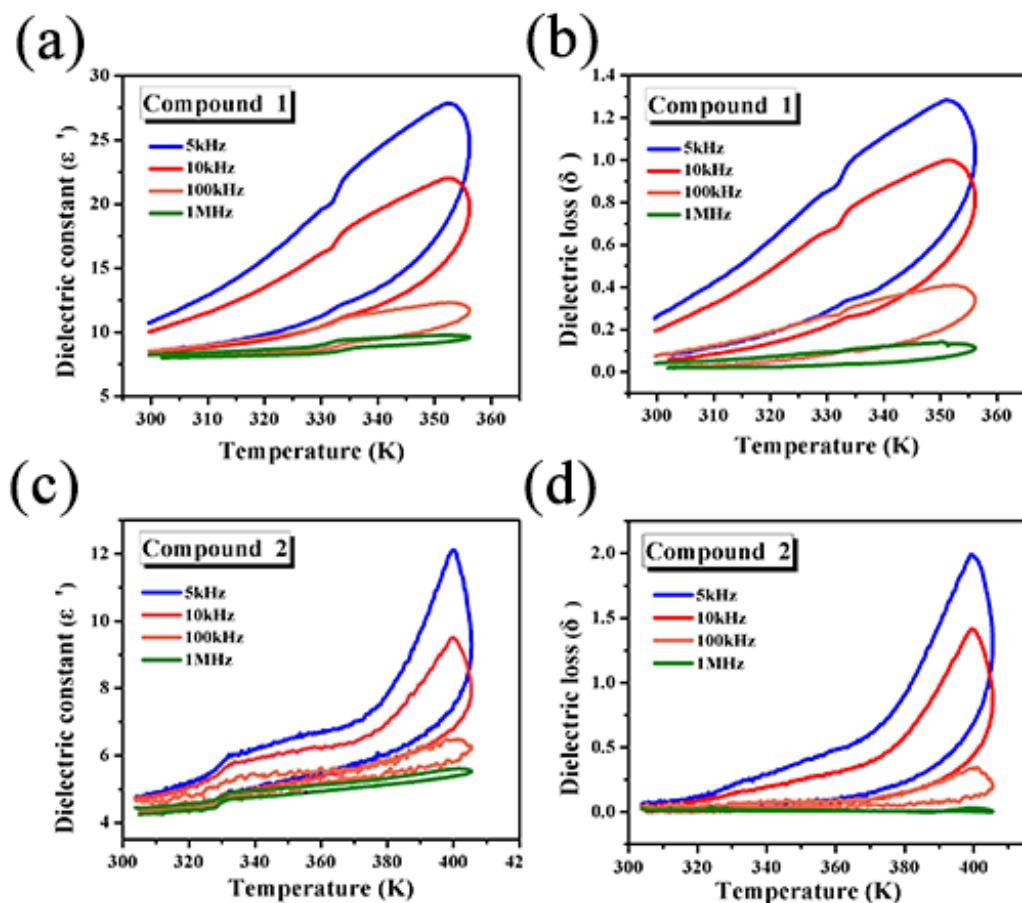


Fig. S6. Dielectric constant [(a),(c)] and loss [(b),(d)] of powder samples **1,2** measured at selected frequencies in a heating/cooling mode.

Table S1 Selected bond lengths [\AA] and angles [°] for **1** and **2**

	Bond lengths (\AA)		Bond angles (°)	
1 (273 K)	F1—B1	1.3911 (16)	F2—B1—F4	110.18 (12)
	F2—B1	1.3844 (16)	F2—B1—F1	109.34 (11)
	F3—B1	1.4001 (16)	F4—B1—F1	109.75 (11)
	F4—B1	1.3881 (16)	F2—B1—F3	109.39 (11)
	N5—C1	1.4949 (15)	F4—B1—F3	109.52 (11)
	N4—C2	1.4977 (14)	F1—B1—F3	108.63 (11)
	C1—C2	1.528 (2)		
1 (358 K)	B1—F1 ⁱ	1.367 (3)	F1 ⁱ —B1—F1	110.67 (13)
	B1—F1 ⁱⁱ	1.367 (3)	F1 ⁱⁱ —B1—F1	107.1 (3)
	B1—F1 ⁱⁱⁱ	1.367 (3)	F1 ⁱⁱⁱ —B1—F1	110.67 (13)
	B1—F1	1.367 (3)		

Symmetry codes: (i) $y, x, -z+1/2$; (ii) $-x, -y, z$; (iii) $-y, -x, -z+1/2$;

2 (293 K)	Rb1—F2	2.964 (2)	F3—B1—F1	110.7 (4)
	Rb1—F2 ⁱ	2.964 (2)	F3—B1—F5	109.8 (4)
	Rb1—F2 ⁱⁱ	2.964 (2)	F1—B1—F5	109.5 (4)
	Rb1—F2 ⁱⁱⁱ	2.964 (2)	F3—B1—F2	109.7 (4)
	Rb1—F2 ^{iv}	2.964 (2)	F1—B1—F2	109.3 (4)
	Rb1—F2 ^v	2.964 (2)	F5—B1—F2	107.8 (4)
	Rb1—F1 ^v	2.986 (2)	F2—Rb1—F2 ⁱ	115.87 (7)
	Rb1—F1 ^{iv}	2.986 (2)	F2—Rb1—F2 ⁱⁱ	64.13 (7)
	Rb1—F1 ⁱⁱⁱ	2.986 (2)	F2—Rb1—F2 ⁱ	115.87 (7)
	Rb1—F1 ⁱⁱ	2.986 (2)	F2—Rb1—F2 ⁱⁱ	64.13 (7)
	Rb1—F1 ⁱ	2.986 (2)	F2—Rb1—F2 ⁱⁱⁱ	180.0
	Rb1—F1	2.986 (2)	F5—Rb2—F3 ^{vii}	102.11 (7)
	Rb2—F5 ^{vi}	2.835 (3)	F3—Rb2—F3 ^{vii}	59.01 (8)
	Rb2—F5 ^{vii}	2.835 (3)	F2—Rb1—F2 ^{iv}	115.87 (7)
	Rb2—F5 ^{viii}	2.835 (3)	F2—Rb1—F2 ^v	64.13 (7)
	Rb2—F5 ^{ix}	2.835 (3)	F5—Rb2—F3 ^{vi}	77.89 (7)
	Rb2—F5 ^x	2.835 (3)	F3—Rb2—F3 ^{vi}	120.99 (8)
	Rb2—F5	2.835 (3)	F2—Rb1—F1 ^v	79.14 (8)
	Rb2—F3	3.181 (3)	F5—Rb2—F3 ^{ix}	74.00 (7)
	Rb2—F3 ^{vii}	3.181 (3)	F3—Rb2—F3 ^{ix}	59.01 (8)
	Rb2—F3 ^{vi}	3.181 (3)	F2—Rb1—F1 ^{iv}	100.86 (8)
	Rb2—F3 ^{ix}	3.181 (3)	F2—Rb1—F1 ⁱⁱⁱ	135.14 (8)
	Rb2—F3 ^x	3.181 (3)	F5—Rb2—F3 ^x	136.33 (7)
	Rb2—F3 ^{viii}	3.181 (3)	F3—Rb2—F3 ^x	180.0
	F1—B1	1.374 (5)	F2—Rb1—F1 ⁱⁱ	108.73 (6)
	F2—B1	1.409 (5)	F5—Rb2—F3 ^{viii}	106.00 (7)
	F3—B1	1.372 (5)	F3—Rb2—F3 ^{viii}	120.99 (8)
	F5—B1	1.391 (5)	F2—Rb1—F1 <i>i</i>	71.27 (6)
	N2—C1	1.485 (5)	F2—Rb1—F1	44.86 (8)
	C1—C2	1.513 (6)	F2 ⁱ —Rb1—F1	100.86 (8)
	C2—N1	1.484 (5)	F2 ^{iv} —Rb1—F1	71.27 (6)
			F2 ^v —Rb1—F1	108.73 (6)
			F1 ^v —Rb1—F1	114.29 (4)
			F1 ^{iv} —Rb1—F1	65.71 (4)
			F1 ⁱⁱⁱ —Rb1—F1	180.0
			F1 ⁱⁱ —Rb1—F1	114.29 (4)
			F1 ⁱ —Rb1—F1	65.71 (4)
			F5 ^{vi} —Rb2—F5	69.72 (4)
			F5 ^{vii} —Rb2—F5	110.28 (4)
			F5 ^{viii} —Rb2—F5	69.72 (4)
			F5 ^{ix} —Rb2—F5	110.28 (4)
			F5 ^x —Rb2—F5	180.0

	F5^{vi} — Rb2 — F3	106.00 (7)		
	F5^{vii} — Rb2 — F3	74.00 (7)		
	F5^{viii} — Rb2 — F3	77.89 (7)		
	F5^{ix} — Rb2 — F3	102.11 (7)		
	F5^{x} — Rb2 — F3	136.33 (7)		
	F5 — Rb2 — F3	43.67 (7)		
Symmetry codes: (i) $y-1/2, z, -x+1/2$; (ii) $-y+1/2, -z+1, x+1/2$; (iii) $-x, -y+1, -z+1$; (iv) $-z+1/2, x+1/2, y$; (v) $z-1/2, -x+1/2, -y+1$; (vi) $-y+1, -z+1, -x+1$; (vii) y, z, x ; (viii) $-z+1, -x+1, -y+1$; (ix) z, x, y ; (x) $-x+1, -y+1, -z+1$; (xi) $-z+1, x+1/2, -y+3/2$; (xii) $y-1/2, -z+3/2, -x+1$.				
2 (348 K)	Rb1 — F1^{i}	2.992 (2)	F1^{i} — Rb1 — F1	180.00 (8)
	Rb1 — F1^{ii}	2.992 (2)	F1^{ii} — Rb1 — F1	110.10 (3)
	Rb1 — F1^{iii}	2.992 (2)	F1^{iii} — Rb1 — F1	69.90 (3)
	Rb1 — F1^{iv}	2.992 (2)	F1^{iv} — Rb1 — F1	110.10 (3)
	Rb1 — F1^{v}	2.992 (2)	F1^{v} — Rb1 — F1	69.90 (3)
	Rb1 — F1^{vi}	2.992 (2)	F1^{vi} — Rb1 — F1	69.90 (3)
	Rb1 — F1^{vii}	2.992 (2)	F1^{vii} — Rb1 — F1	43.42 (8)
	Rb1 — F1^{viii}	2.992 (2)	F1^{viii} — Rb1 — F1	136.58 (8)
	Rb1 — F1^{ix}	2.992 (2)	F1^{ix} — Rb1 — F	169.90 (3)
	Rb1 — F1^{x}	2.992 (2)	F1^{x} — Rb1 — F1	110.10 (3)
	Rb1 — F1^{xi}	2.992 (2)	F1^{xi} — Rb1 — F1	110.10 (3)
	Rb1 — F1	2.992 (2)	F1 — B1 — F1^{xii}	110.28 (9)
	F1 — B1	1.369 (2)	F1 — B1 — F1^{vii}	107.87 (17)
	B1 — F1^{xii}	1.369 (2)	F1 — B1 — F1^{xiii}	110.28 (9)
	B1 — F1^{vii}	1.369 (2)		
	B1 — F1^{xiii}	1.369 (2)		
Symmetry codes: (i) $-x, -y, -z$; (ii) $-y, -z, -x$; (iii) y, z, x ; (iv) $-z, -x, -y$; (v) z, x, y ; (vi) $-y, z, x$; (vii) $x, y, -z$; (viii) $-x, -y, z$; (ix) $-z, -x, y$; (x) $z, x, -y$; (xi) $y, -z, -x$; (xii) $z, -y+1/2, -x$; (xiii) $-z, -y+1/2, -x$.				

Table S2 The selected hydrogen bonds (\AA , $^\circ$) for **1** and **2**.

$D\text{—H}\cdots A$	$D\text{—H}$	$H\cdots A$	$D\cdots A$	$D\text{—H}\cdots A$
1 (273 K)				
$\text{N5—H5}\cdots\text{F3}^{\text{iii}}$	0.92 (3)	2.35 (2)	3.0260 (16)	129.7 (6)
$\text{N5—H5}\cdots\text{F3}^{\text{iv}}$	0.92 (3)	2.35 (2)	3.0260 (16)	129.7 (6)
$\text{N5—H5}\cdots\text{F3}^{\text{v}}$	0.92 (3)	2.35 (2)	3.0260 (16)	129.7 (6)
$\text{N4—H4}\cdots\text{F4}^{\text{i}}$	0.90	2.35	3.0137 (17)	130
$\text{N4—H4}\cdots\text{F4}^{\text{ii}}$	0.90	2.35	3.0137 (17)	130
$\text{N4—H4}\cdots\text{F4}$	0.90	2.35	3.0137 (17)	130

N2—F1(D ..A)	—	—	2.8165	—
N2—F4(D ..A)	—	—	3.1966	—
N1—F3(D ..A)	—	—	2.9546	—
N1—F2(D ..A)	—	—	2.9732	—

Symmetry codes: (iii) $-y+1/2, z-1/2, x$; (iv) $-z+3/2, x-1/2, y+1$; (v) $-x+3/2, y+1/2, z$; (vi) $x-1/2, y, -z+3/2$; (vii) $z, x-1, y+1$; (i) $-y+1, z-1/2, -x+3/2$; (ii) $-z+3/2, -x+1, y+1/2$.

2 (293 K)

N1—H1C ..F2 ^{xvi}	0.90	2.39	3.053 (5)	131
N1—H1C ..F2 ^{vi}	0.90	2.39	3.053 (5)	131
N1—H1C ..F2 ^{xv}	0.90	2.39	3.053 (5)	131
N2—H2C ..F3 ^{xiv}	0.96 (13)	2.33 (8)	3.038 (5)	129 (2)
N2—H2C ..F3 ^{xiii}	0.96 (13)	2.33 (8)	3.038 (5)	129 (2)
N2—H2C ..F3 ^v	0.96 (13)	2.33 (8)	3.038 (5)	129 (2)
N2—H2C ..F3 ^v	0.96 (13)	2.33 (8)	3.038 (5)	129 (2)
N2—H2C ..F3 ^{xiii}	0.96 (13)	2.33 (8)	3.038 (5)	129 (2)
N2—H2C ..F3 ^{xiv}	0.96 (13)	2.33 (8)	3.038 (5)	129 (2)
N1—H1C ..F2 ^{xv}	0.90	2.39	3.053 (5)	131
N1—H1C ..F2 ^{vi}	0.90	2.39	3.053 (5)	131
N1—H1C ..F2 ^{xvi}	0.90	2.39	3.053 (5)	131

Symmetry codes: (v) $-y+1/2, -z+1, x+1/2$; (xiii) $-z+1/2, -x+1, y+1/2$; (xiv) $-x+1/2, -y+1, z+1/2$; (xv) $y, -z+3/2, x+1/2$; (vi) $-z+1, -x+1, -y+1$; (xvi) $-x+1/2, y+1/2, z$.

Table S3. Effective crystal radii for A, B and X of perovskites with the formula ABX₃. All the value came from reported crystallographic data.

A	r _{mass} (Å)	r _{Natom} (Å)	r _A (Å)
H ₂ dabco ²⁺	1.25(3)	1.32	2.57(3)
B	coordinate number or charge		r _B (Å)
NH ₄ ⁺	-3		1.46
Rb ₊	XII		1.86
X	r _{F/Oatom} (Å)	r _X (Å)	r _X (Å)
BF4 ⁻	1.15	2.28	3.95(1)

Reference

- (1) Liu, G.-Z., J. Zhang, and L.-Y. Wang, A Novel Molecular Cubic Perovskite Built From Charge-Assisted Hydrogen Bond Linkages. *Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry*. **2011**, *41*, 1091-1094.