

Electronic Supplementary Information

An organic-inorganic hybrid double perovskite-type cage-like crystal (MA)₂KBiCl₆ (MA = methylammonium Cation) with dielectric switch behavior†

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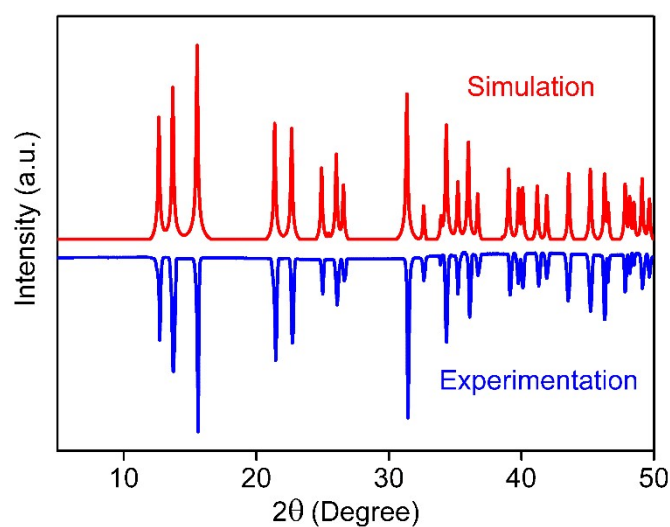


Figure S1. PXRD pattern **1** measured at room temperature.

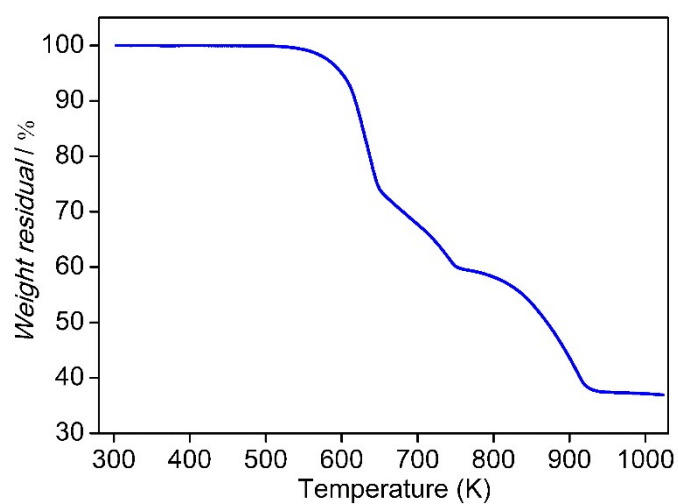


Figure S2. TGA curve of **1**.

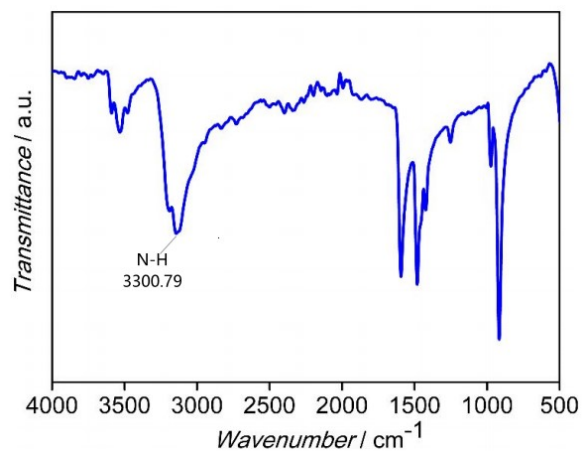


Figure S3. IR spectrum of **1** measured at room temperature.

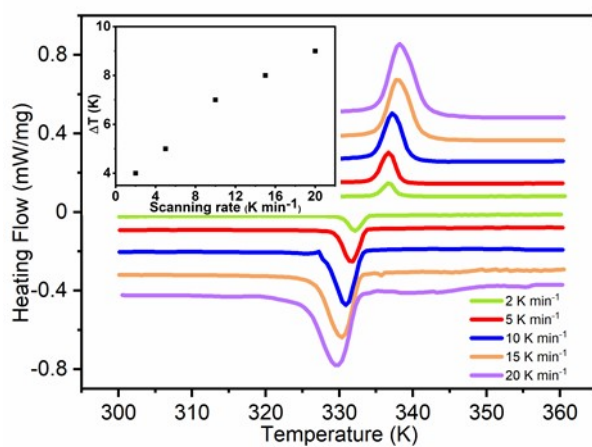
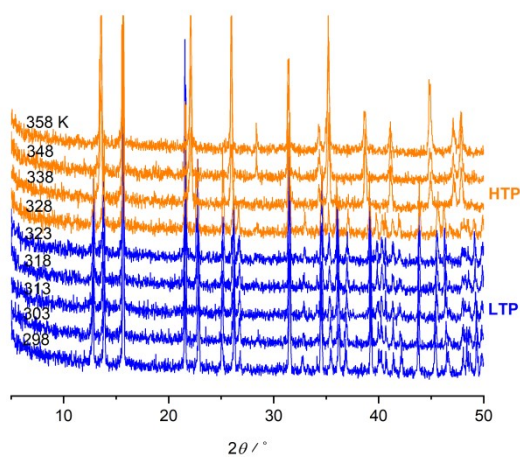


Figure S4. The scanning rate dependence of the DSC measurements on compound **1**.



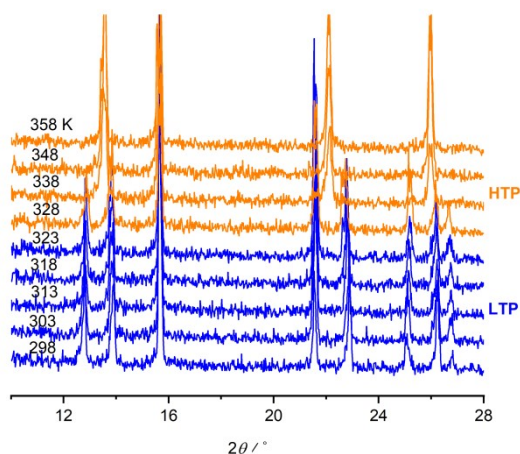


Fig S5. The variable-temperature powder XRD patterns of **1**.

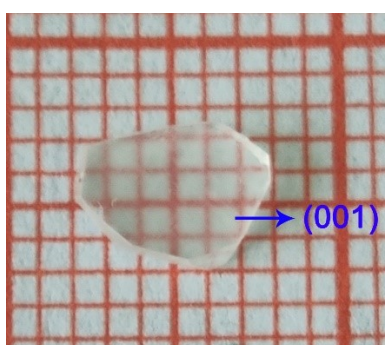


Figure S6. Crystal morphology of **1**.

Table S1. Selected bond lengths [Å] and angles [°] for **1** (293 K, 373 K).

1 (293 K)			
Bi1–C11 ⁱ	2.6791 (13)	C11 ⁱ –Bi1–C11 ⁱⁱ	91.74 (6)
Bi1–C11 ⁱⁱ	2.6791 (13)	C11 ⁱ –Bi1–C11 ⁱⁱⁱ	91.74 (6)
Bi1–C11 ⁱⁱⁱ	2.6791 (13)	C11 ⁱⁱ –Bi1–C11 ⁱⁱⁱ	91.74 (6)
Bi1–C11 ^{iv}	2.6791 (13)	C11 ⁱ –Bi1–C11 ^{iv}	88.26 (6)
Bi1–C11 ^v	2.6791 (13)	C11 ⁱⁱ –Bi1–C11 ^{iv}	180.0
Bi1–C11	2.6792 (13)	C11 ⁱⁱⁱ –Bi1–C11 ^{iv}	88.26 (6)
C11–K1	3.0469 (13)	C11 ⁱ –Bi1–C11 ^v	88.26 (6)
N1–C1	1.287 (16)	C11 ⁱⁱ –Bi1–C11 ^v	88.26 (6)
N1–H1A	0.8900	C11 ⁱⁱⁱ –Bi1–C11 ^v	180.0
N1–H1B	0.8900	C11 ^{iv} –Bi1–C11 ^v	91.74 (6)
N1–H1C	0.8900	C11 ⁱ –Bi1–C11	180.0
N1–H1A ^{vi}	0.89 (5)	C11 ⁱⁱ –Bi1–C11	88.26 (6)
N1–H1A ^{vii}	0.89 (18)	C11 ⁱⁱⁱ –Bi1–C11	88.26 (6)
N1–H1A ^{viii}	0.89 (13)	C11 ^{iv} –Bi1–C11	91.74 (6)
C1–H1D	0.9600	C11 ^v –Bi1–C11	91.74 (6)
C1–H1E	0.9600	Bi1–C11–K1	173.07 (8)

C1-H1F	0.9600	C11 ^{ix} -K1-C11 ^x	81.69 (5)
C1-H1D ^{vi}	0.96 (12)	C11 ^{ix} -K1-C11 ^{xi}	180.0
C1-H1D ^{vii}	0.96 (3)	C11 ^x -K1-C11 ^{xi}	98.31 (5)
C1-H1D ^{viii}	0.96 (16)	C11 ^{ix} -K1-C11 ^{xii}	98.31 (5)
Bi1-K1	5.716	C11 ^x -K1-C11 ^{xii}	180.0
		C11 ^{xi} -K1-C11 ^{xii}	81.69 (5)
		C11 ^{ix} -K1-C11	98.31 (5)
		C11 ^x -K1-C11	98.31 (5)
		C11 ^{xi} -K1-C11	81.69 (5)
		C11 ^{xii} -K1-C11	81.69 (5)
		C11 ^{ix} -K1-C11 ^{xiii}	81.69 (5)
		C11 ^x -K1-C11 ^{xiii}	81.69 (5)
		C11 ^{xi} -K1-C11 ^{xiii}	98.31 (5)
		C11 ^{xii} -K1-C11 ^{xiii}	98.31 (5)
		C11-K1-C11 ^{xiii}	180.0
		C1-N1-H1A	109.5
		C1-N1-H1B	109.5
		H1A-N1-H1B	109.5
		C1-N1-H1C	109.5
		H1A-N1-H1C	109.5
		H1B-N1-H1C	109.5
		C1-N1-H1A ^{vi}	109.5 (12)
		H1A-N1-H1A ^{vi}	138.1
		H1B-N1-H1A ^{vi}	70.8
		H1C-N1-H1A ^{vi}	41.6
		C1-N1-H1A ^{vii}	109 (4)
		H1A-N1-H1A ^{vii}	70.8
		H1B-N1-H1A ^{vii}	41.6
		H1C-N1-H1A ^{vii}	138.1
		H1A ^{vi} -N1-H1A ^{vii}	109.5
		C1-N1-H1A ^{viii}	109 (3)
		H1A-N1-H1A ^{viii}	41.6
		H1B-N1-H1A ^{viii}	138.1
		H1C-N1-H1A ^{viii}	70.8
		H1A ^{vi} -N1-H1A ^{viii}	109.5
		H1A ^{vii} -N1-H1A ^{viii}	109.5
		N1-C1-H1D	109.5
		N1-C1-H1E	109.5
		H1D-C1-H1E	109.5
		N1-C1-H1F	109.5
		H1D-C1-H1F	109.5
		H1E-C1-H1F	109.5
		N1-C1-H1D ^{vi}	109 (3)
		H1D-C1-H1D ^{vi}	46.6

H1E–C1–H1D ^{vi}	65.8
H1F–C1–H1D ^{vi}	139.7
N1–C1–H1D ^{vii}	109.5 (6)
H1D–C1–H1D ^{vii}	139.7
H1E–C1–H1D ^{vii}	46.6
H1F–C1–H1D ^{vii}	65.8
H1D ^{vi} –C1–H1D ^{vii}	109.5
N1–C1–H1D ^{viii}	109 (3)
H1D–C1–H1D ^{viii}	65.8
H1E–C1–H1D ^{viii}	139.7
H1F–C1–H1D ^{viii}	46.6
H1D ^{vi} –C1–H1D ^{viii}	109.5
H1D ^{vii} –C1–H1D ^{viii}	109.5

Symmetry codes: (i) $-x+4/3, -y+2/3, -z+2/3$; (ii) $y+1/3, -x+y+2/3, -z+2/3$; (iii) $x-y+1/3, x-1/3, -z+2/3$; (iv) $-y+1, x-y, z$; (v) $-x+y+1, -x+1, z$; (vi) $-y+1, -x+1, z$; (vii) $-x+y, y, z$; (viii) $x, x-y+1, z$; (ix) $y-1/3, -x+y+1/3, -z+1/3$; (x) $x-y+2/3, x+1/3, -z+1/3$; (xi) $-y+1, x-y+1, z$; (xii) $-x+y, -x+1, z$; (xiii) $-x+2/3, -y+4/3, -z+1/3$.

1 (373 K)

Bi1–C11 ⁱ	2.686 (2)	C11 ⁱ –Bi1–C11	90.0
Bi1–C11	2.686 (2)	C11 ⁱ –Bi1–C11 ⁱⁱ	90.0
Bi1–C11 ⁱⁱ	2.686 (2)	C11–Bi1–C11 ⁱⁱ	90.0
Bi1–C11 ⁱⁱⁱ	2.686 (2)	C11 ⁱ –Bi1–C11 ⁱⁱⁱ	90.0
Bi1–C11 ^{iv}	2.686 (2)	C11–Bi1–C11 ⁱⁱⁱ	180.0
Bi1–C11 ^v	2.686 (2)	C11 ⁱⁱ –Bi1–C11 ⁱⁱⁱ	90.0
C11–K1	3.040 (2)	C11 ⁱ –Bi1–C11 ^{iv}	180.0
N1–C1	1.35 (3)	C11–Bi1–C11 ^{iv}	90.0
Bi1–K1	5.726	C11 ⁱⁱ –Bi1–C11 ^{iv}	90.0
		C11 ⁱⁱⁱ –Bi1–C11 ^{iv}	90.0
		C11 ⁱ –Bi1–C11 ^v	90.0
		C11–Bi1–C11 ^v	90.0
		C11 ⁱⁱ –Bi1–C11 ^v	180.0
		C11 ⁱⁱⁱ –Bi1–C11 ^v	90.0
		C11 ^{iv} –Bi1–C11 ^v	90.0
		Bi1–C11–K1	180.0
		C11 ^{vi} –K1–C11 ^{vii}	180.0
		C11 ^{vi} –K1–C11 ^{viii}	90.0
		C11 ^{vii} –K1–C11 ^{viii}	90.0
		C11 ^{vi} –K1–C11 ^{ix}	90.0
		C11 ^{vii} –K1–C11 ^{ix}	90.0
		C11 ^{viii} –K1–C11 ^{ix}	90.0
		C11 ^{vi} –K1–C11 ^x	90.0
		C11 ^{vii} –K1–C11 ^x	90.0
		C11 ^{viii} –K1–C11 ^x	90.0

C11 ^{ix} -K1-C11 ^x	180.0
C11 ^{vi} -K1-C11	90.0
C11 ^{vii} -K1-C11	90.0
C11 ^{viii} -K1-C11	180.0
C11 ^{ix} -K1-C11	90.0
C11 ^x -K1-C11	90.0

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

Table S2. Hydrogen bonds (Å, °) for **1** (293 K).

	D-H	H···A	D···A	D-H···A
D-H···A				
N1-H1A···C11 ^{xi}	0.89	2.83	3.429(7)	126
N1-H1B···C11 ^{xii}	0.89	2.83	3.429(7)	126
N1-H1C···C11	0.89	2.83	3.429(7)	126

Symmetry codes: (xi) $-y+1, x-y+1, z$; (xii) $-x+y, -x+1, z$.