Supporting Information

An organic-inorganic hybrid ferroelastic with near-room-temperature phase transition

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Spontaneous strain tensor matrix of 2/*m*F$\bar{1}$-type phase transition:

$$\varepsilon_{ij} = \begin{bmatrix} 0 & \varepsilon_{12} & 0 \\ 0 & 0 & \varepsilon_{23} \\ 0 & 0 & 0 \end{bmatrix}$$

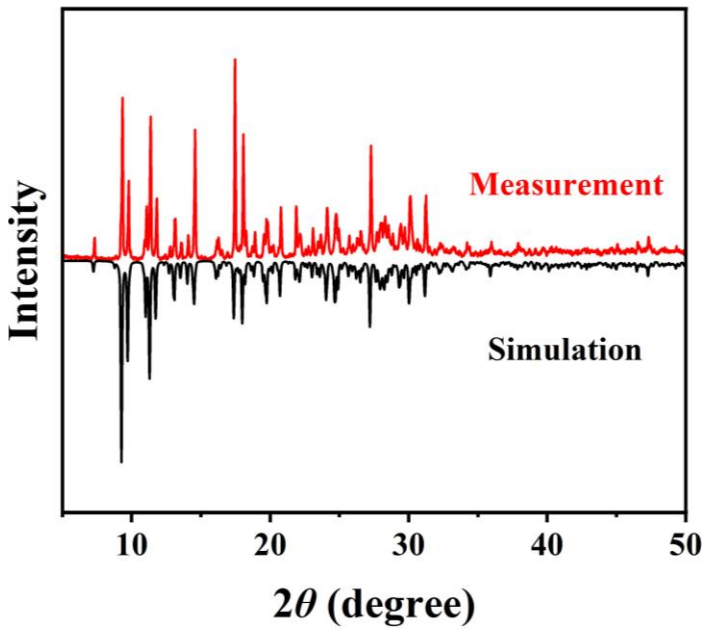

Fig. S1 The PXRD patterns of (*E*, *E*)-[BPHD]$ZnBr_4$ at 298 K.

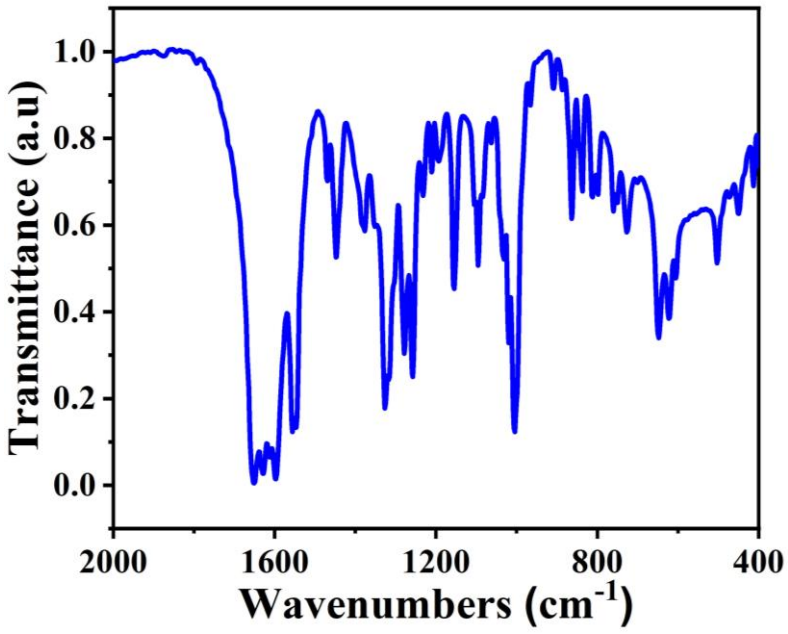

Fig. S2 The Infrared spectrums of (*E*, *E*)-[BPHD]$ZnBr_4$ at room temperature.

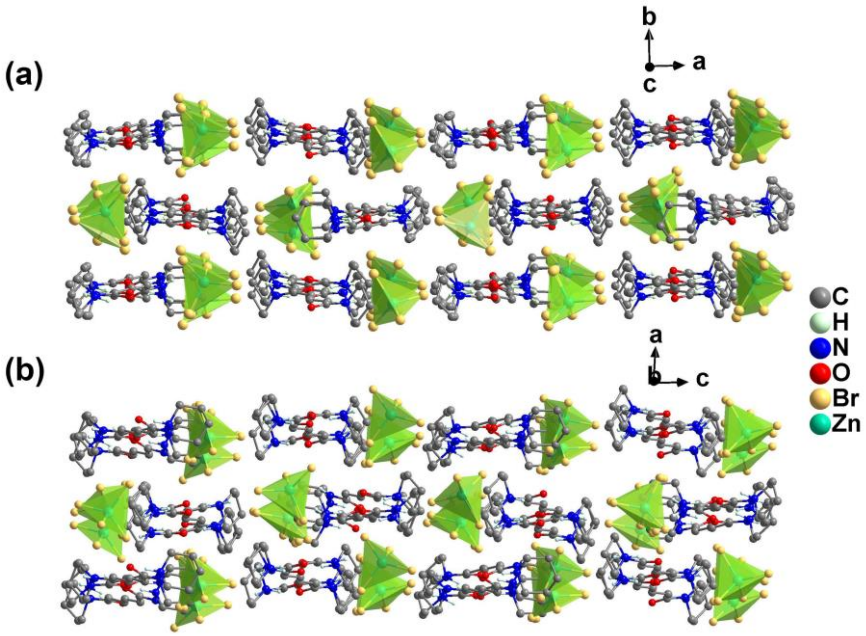

Fig. S3 Packing view of (*E*, *E*)-[BPHD]$ZnBr_4$ in RTP (a) and LTP (b). Some hydrogen atoms are omitted for clarity.

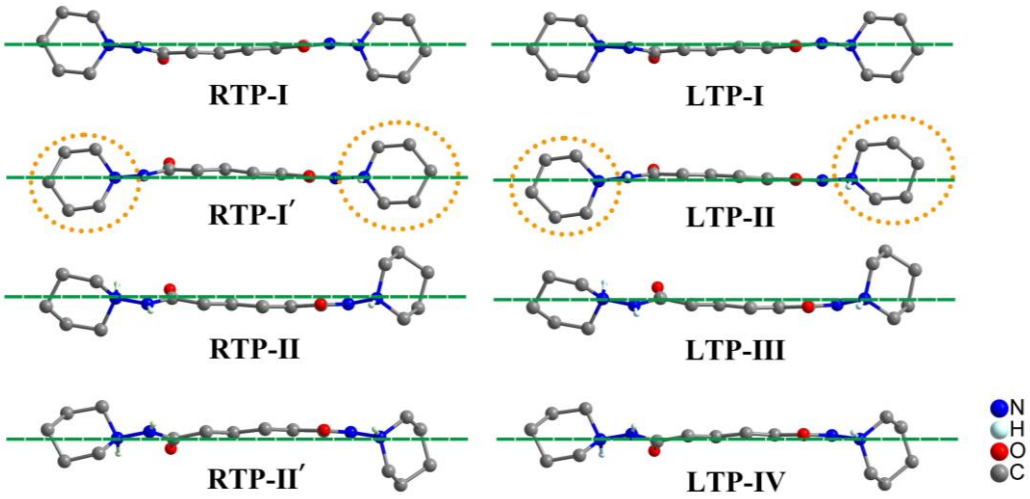

Fig. S4 The cation structures of (*E*, *E*)-[BPHD]$ZnBr_4$ at 298 K and 233 K.

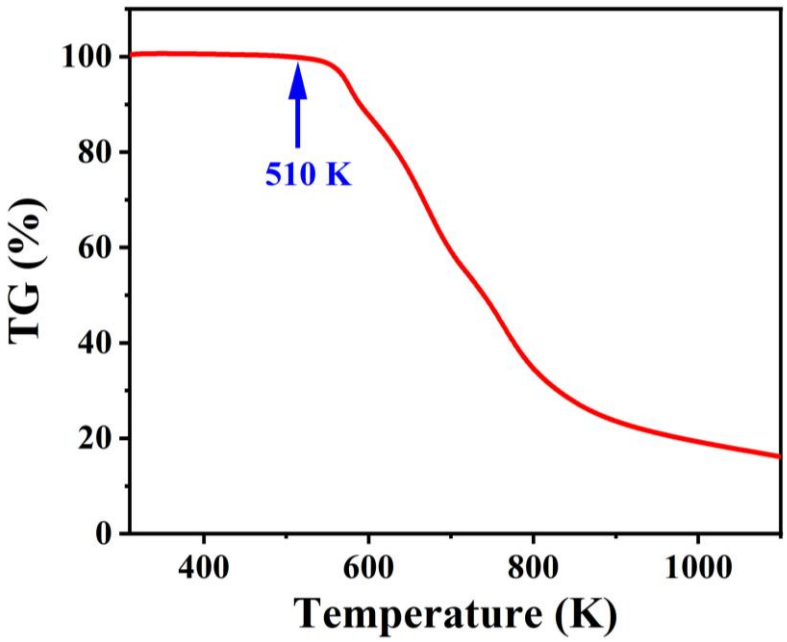

Fig. S5 The TGA curves of (*E*, *E*)-[BPHD]$ZnBr_4$.

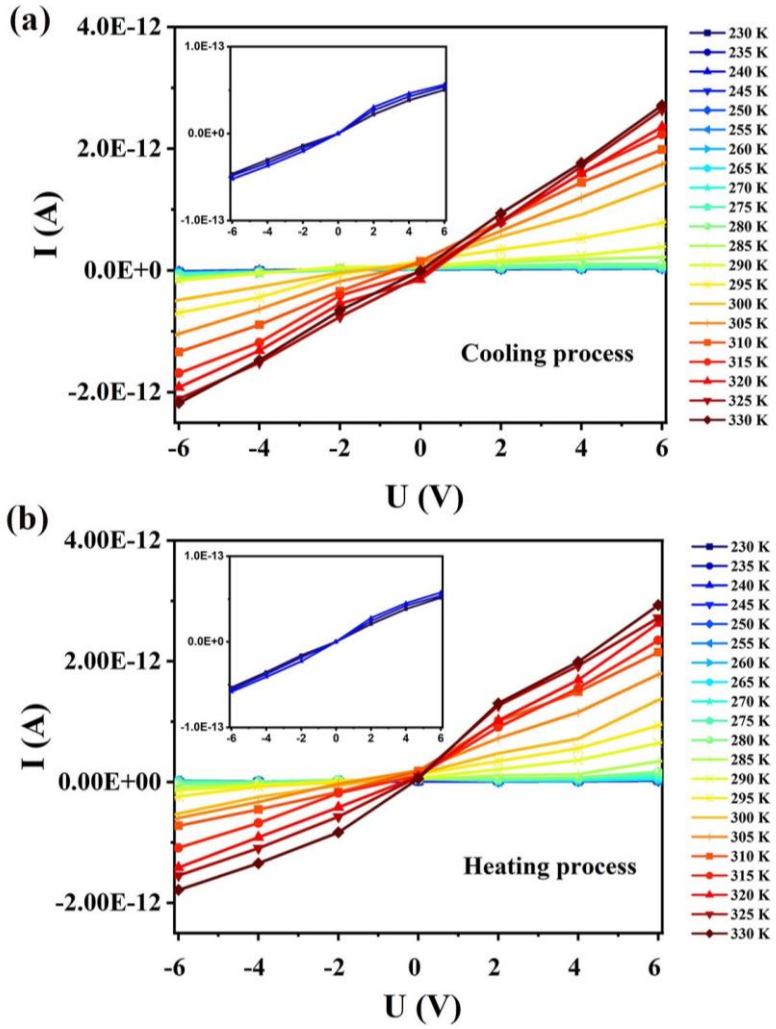

Fig. S6 I-V curves of (*E*, *E*)-[BPHD]$ZnBr_4$ in cooling (a) and heating (b) process. Inset: I-V curves at 230, 235 and 240 K.

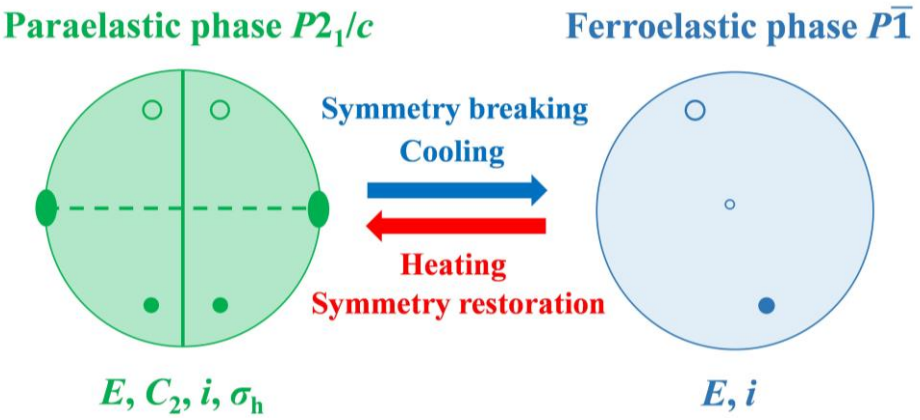

Fig. S7 Symmetry breaking of (*E*, *E*)-[BPHD]ZnBr$_4$ from paraelastic phase $P2_1/c$ to ferroelastic phase $P\bar{1}$.

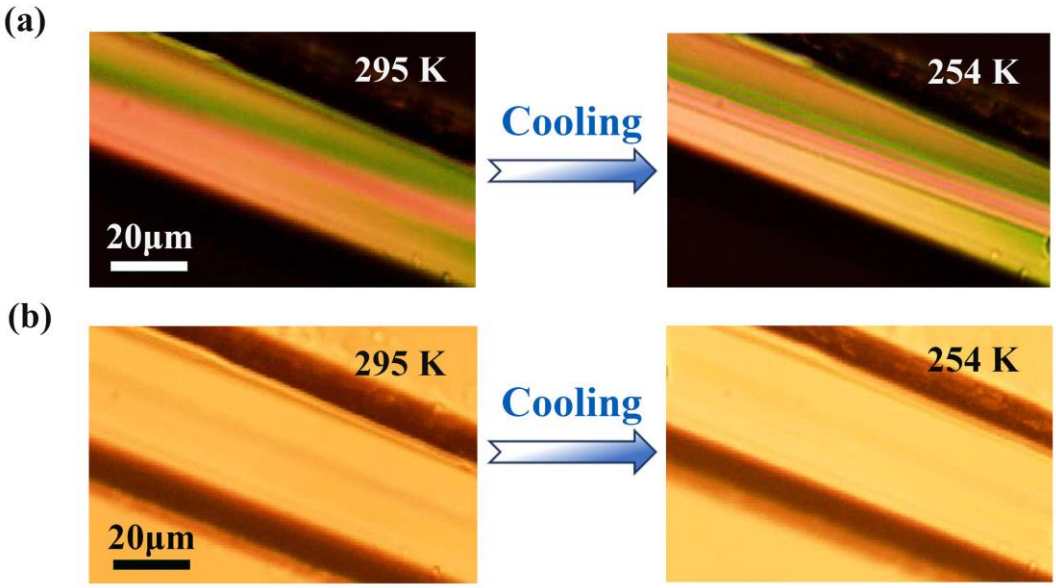

Fig. S8 The domain patterns of (*E*, *E*)-[BPHD]ZnBr$_4$ under polarized light (a) and morphologies of (*E*, *E*)-[BPHD]ZnBr$_4$ under unpolarized light (b).

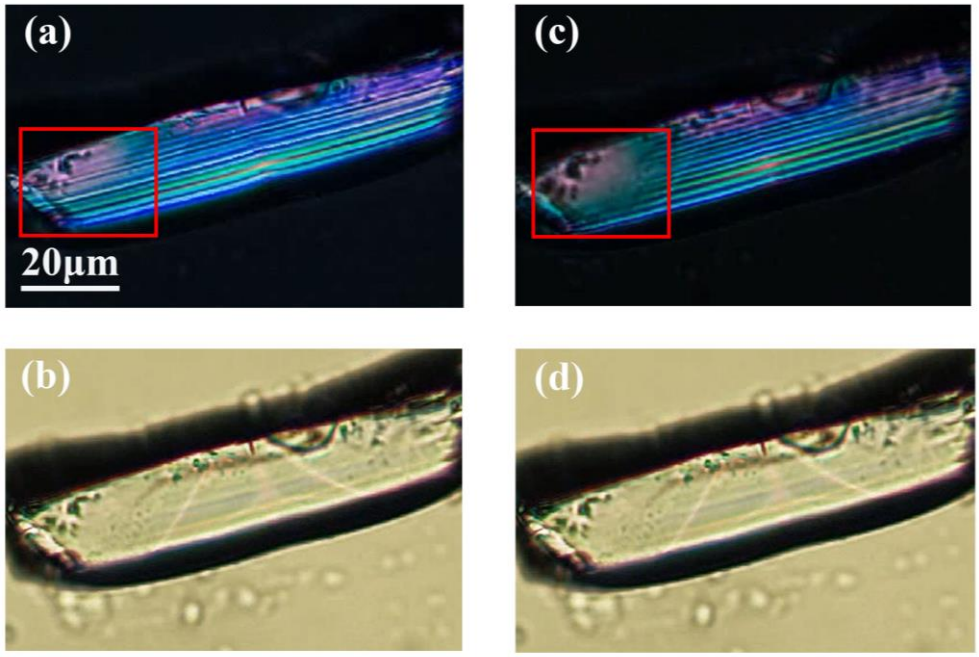

Fig. S9 The domain pattern (a) and morphology (b) of (*E*, *E*)-[BPHD]$ZnBr_4$ before applying stress at 278 K; the domain pattern (c) and morphology (d) after applying stress on the left side.

Table S1. Crystal data and structure refinement of (*E*, *E*)-[BPHD]$ZnBr_4$ at 298 K and 233 K.

Compound	**(*E*, *E*)-[BPHD]$ZnBr_4$**	
Temperature	298 K	233 K
Formula	$C_{16}H_{28}N_4O_2ZnBr_4$	$C_{16}H_{28}N_4O_2ZnBr_4$
Formula weight	693.43	693.43
Crystal system	monoclinic	triclinic
Space group	$P2_1/c$	$P\bar{1}$
a/Å	25.8689(5)	10.1213(2)
b/Å	10.2058(2)	20.2424(3)
c/Å	20.2127(4)	25.7250(5)
α/°	90	70.636(2)
β/°	109.232(2)	86.5060(10)
γ/°	90	89.6140(10)
Volume/Å^3	5038.60(18)	4962.63(17)
Z	8	8
R_1	0.0826	0.0670
wR_2	0.1724	0.1980
GOF	1.089	1.011

Table S2. Selected bond lengths/Å and bond angles/° for compound (*E*, *E*)-[BPHD]$ZnBr_4$ at 298 K.

Temperature	**Bond lengths**		**Bond angles**	
298K	Zn1—Br1A	2.423（5）	Br1A—Zn1—Br2	98.0（4）
	Zn1—Br1B	2.363（4）	Br1A—Zn1—Br3	118.4（2）
	Zn1—Br2	2.413（2）	Br1A—Zn1—Br4	112.37（12）
	Zn1—Br3	2.3941（19）	Br1B—Zn1—Br2	120.6（4）
	Zn1—Br4	2.4332（17）	Br1B—Zn1—Br3	103.4（3）
	Zn2—Br5	2.4026（19）	Br1B—Zn1—Br4	105.38（18）
	Zn2—Br6	2.411（2）	Br2—Zn1—Br4	110.33（7）
	Zn2—Br7	2.3987（16）	Br3—Zn1—Br2	106.34（7）
	Zn2—Br8	2.3990（18）	Br3—Zn1—Br4	110.41（7）
			Br5—Zn2—Br6	108.69（7）
			Br5—Zn2—Br7	110.83（7）
			Br5—Zn2—Br8	106.78（7）
			Br6—Zn2—Br7	110.18（7）
			Br6—Zn2—Br8	109.13（7）
			Br7—Zn2—Br8	111.14（7）

Table S3. Selected bond lengths/Å and bond angles/° of hydrogen bonding for (*E*, *E*)-[BPHD]$ZnBr_4$ at 298 K.

D—H···A	D—H	H···A	D···A	D—H···A
N4—H4···O1^{i}	0.98	1.92	2.857(9)	159.1
N7—H7···Br7^{ii}	0.86	2.54	3.392(8)	171.2
N5—H5···O4^{iii}	0.98	1.82	2.704(9)	148.5
N2—H2···Br6^{iii}	0.86	2.61	3.314(8)	139.6
N1—H1···O2^{iv}	0.98	1.91	2.856(9)	161.7
N3—H3···Br4^{v}	0.86	2.45	3.298(8)	168.6
N8—H8···O3^{vi}	0.98	2.19	3.058(10)	147.5

Symmetry codes: ^{i}+X,-1/2-Y,-1/2+Z; ^{ii}1-X,-1/2+Y,1/2-Z; ^{iii}+X,1/2-Y,1/2+Z; ^{iv}+X,-1/2-Y,1/2+Z; ^{v}-X,-1/2+Y,1/2-Z; ^{vi}+X,1/2-Y,-1/2+Z

Table S4. Selected bond lengths/Å and bond angles/° for compound (*E*, *E*)-[BPHD]$ZnBr_4$ at 233 K.

Temperature	Bond lengths		Bond angles	
233K	Br1—Zn1	2.4441(13)	Br2—Zn1—Br1	109.70(6)
	Br2—Zn1	2.4052(15)	Br2—Zn1—Br3A	120.54(9)
	Zn1—Br3A	2.433(2)	Br2—Zn1—Br4	105.39(5)
	Zn1—Br4	2.4237(16)	Br3A—Zn1—Br1	110.75(7)
	Zn1—Br3B	2.368(3)	Br4—Zn1—Br1	111.89(5)
	Br9—Zn3	2.4034(13)	Br4—Zn1—Br3A	97.76(11)
	Br10—Zn3	2.4092(14)	Br3B—Zn1—Br1	102.90(11)
	Br11—Zn3	2.3980(12)	Br3B—Zn1—Br2	101.85(18)
	Br12—Zn3	2.4083(14)	Br3B—Zn1—Br4	124.3(2)
	Br5—Zn2	2.406(4)	Br9—Zn3—Br10	106.15(5)
	Br6—Zn2	2.4111(13)	Br9—Zn3—Br12	108.58(5)
	Br7—Zn2	2.4207(12)	Br11—Zn3—Br9	111.27(5)
	Br8—Zn2	2.4218(13)	Br11—Zn3—Br10	110.38(5)
	Zn2—Br5A	2.355(6)	Br11—Zn3—Br12	111.87(5)
	Br13—Zn4	2.4175(14)	Br12—Zn3—Br10	108.39(6)
	Br14—Zn4	2.4024(13)	Br5—Zn2—Br6	116.3(2)
	Br15—Zn4	2.4005(12)	Br5—Zn2—Br7	110.91(15)
	Br16—Zn4	2.4040(14)	Br5—Zn2—Br8	102.4(4)
			Br6—Zn2—Br7	110.63(5)
			Br6—Zn2—Br8	105.83(5)
			Br7—Zn2—Br8	110.18(5)
			Br5A—Zn2—Br6	107.1(5)
			Br5A—Zn2—Br7	106.0(3)
			Br5A—Zn2—Br8	117.0(8)
			Br14—Zn4—Br13	109.86(5)
			Br14—Zn4—Br16	107.27(5)
			Br15—Zn4—Br13	109.59(5)

	Br15—Zn4—Br14	110.76(5)
	Br15—Zn4—Br16	110.88(5)

Table S5. Selected bond lengths/Å and bond angles/° of hydrogen bonding for (*E*, *E*)-[BPHD]$ZnBr_4$ at 233 K.

D—H···A	**D—H**	**H···A**	**D···A**	**D—H···A**
N5—H5···O4	0.99	1.89	2.838(7)	159.0
N6—H6···Br1	0.87	2.46	3.334(6)	177.4
N8—H8A···O3[1]	0.99	1.92	2.871(8)	160.1
N13—H13···O8[1]	0.99	2.16	3.041(8)	147.8
N14—H14···Br15	0.87	2.53	3.395(6)	171.5
N16—H16···O7	0.99	1.84	2.726(7)	147.7
N9—H9A···O6	0.99	2.27	3.131(8)	145.4
N10—H10A···Br11[3]	0.87	2.54	3.406(6)	171.4
N12—H12···O5[3]	0.99	1.83	2.738(7)	150.7
N1—H1···O1	0.99	1.90	2.857(7)	161.2
N2—H2···Br13	0.87	2.53	3.289(6)	145.8
N3—H3···Br7	0.87	2.55	3.324(6)	148.9
N4—H4···O2[3]	0.99	1.89	2.834(7)	158.4

Symmetry codes: [1]+X, -1+Y, +Z; [2]1-X, -Y, -Z; [3]+X,1+Y, +Z