

# Supporting Information

## A high temperature optic-electric duple switching organic ionic compound: 1,4,7-Triazoniacyclononane tetrafluoroborate dichloride †

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### Synthesis.

A solution containing 1,4,7-triazacyclononane (119.3 mg, 0.50 mmol) and tetrafluoroboric acid (40.0 %, 109.8 mg, 0.50 mmol) in water (1.0 mL) was prepared and left to slowly evaporate. After several days colourless crystals of **1**, [9-tacn-3]<sup>3+</sup>[BF<sub>4</sub>]<sup>-</sup>·2[Cl]<sup>-</sup> (9-tacn-3 = 1,4,7-Triazoniacyclononane), were obtained (yield ~ 117.4 mg, 81.0 %). Microanalysis (%) Found: C 25.2; H 6.7; N 13.9. Calc. for C<sub>6</sub>H<sub>18</sub>N<sub>3</sub>Cl<sub>2</sub>BF<sub>4</sub>: C 24.9; H 6.3; N 14.5. IR bands  $\nu$  (KBr disk, cm<sup>-1</sup>): 3455 w, 2946 s, 2823 s, 2765 s, 2617 m, 2461 w, 2374 w, 2071 w, 1812 w, 1611 m, 1587 m, 1462 m, 1450 m, 1423 m, 1404 m, 1387 m, 1298 w, 1111 s, 1084 s, 1060 s, 1032 s, 981 m, 932 m, 876 w, 785 w, 527 m, 486 m.

**Single-crystal X-ray crystallography.** Variable-temperature X-ray single-crystal diffraction data at 298 and 413 K were collected on a *Rigaku Varimax<sup>TM</sup> DW* diffractometer with *Mo-K $\alpha$*  radiation ( $\lambda = 0.71073$  Å) by using four-circle measurement method. The *Hypix-6000HE* detector and Crystalclear software package (*Rigaku OD*, 2018) was used for collection of diffraction data and data processing including empirical absorption corrections, respectively. The structures were solved by direct methods and refined by the fullmatrix method based on  $F^2$  using the SHELXLTL software package. All nonhydrogen atoms were refined anisotropically using all reflections with  $I > 2\sigma(I)$ . The positions of the hydrogen atoms were generated geometrically and refined using a "riding" model with  $U_{iso} = 1.2U_{eq}$  (C and N). The molecular structures and the packing views were drawn with *DIAMOND* (Brandenburg and Putz, 2005). Angles and distances between some atoms were carried out using *DIAMOND*, and other calculations were calculated using *SHELXLTL*. Crystallographic data and structure refinement at 298 and 413 K are list in Table S2.

**Physical measurements.** IR spectra were recorded at ambient temperature using a Shimadzu model IR-60 spectrometer with KBr pellets. DSC (Differential scanning calorimetry) was carried out on a Perkin-Elmer Diamond DSC instrument by heating and cooling the polycrystalline samples (21.5 mg) with a heating rate of 10 K min<sup>-1</sup> in aluminum crucibles under nitrogen at atmospheric pressure. VT-SHG (variable-temperature second harmonic generation) experiments were executed at a

heating/cooling rate of 10 K min<sup>-1</sup> in the temperature ranges of 210-360 K, by Kurtz-Perry powder SHG test using an unexpanded laser beam with low divergence (pulsed Nd:YAG at a wavelength of 1064 nm, 5 ns pulse duration, 1.6 MW peak power, 10 Hz repetition rate). The instrument model is Ins 1210058, INSTEC Instruments, while the laser is Vibrant 355 II, OPOTEK. The numerical values of the nonlinear optical coefficients for SHG have been determined by comparison with a KDP (KH<sub>2</sub>PO<sub>4</sub>, potassium dihydrogen phosphate) reference. The pressed-powder pellet sandwiched between two parallel (0.64 mm thick and 6.65 mm<sup>2</sup> in area) copper electrodes was used for dielectric constant measurements. Complex dielectric permittivity  $\varepsilon$  ( $\varepsilon = \varepsilon' - i\varepsilon''$ ) was measured on a Tonghui TH2828A instrument at a heating/cooling rate of 10 K min<sup>-1</sup> in the temperature range between 300 and 440 K with an applied voltage of 1 V.

**Calculation of  $\Delta S$  and  $N$  for Compound 1.** According to the Boltzmann equation,  $\Delta S = nR \ln(N)$ , where  $\Delta S$  is calculated from the measured enthalpy changes during the phase transitions at  $T_C$ ,  $n$  is the number of guest molecules per mole ( $n = 1$ , here),  $R$  is the gas constant, and  $N$  is the number of possible orientations for the disordered system. The calculations of  $\Delta S$  and  $N$  of **1** are as follows.

$$\begin{aligned} \Delta S &= \int_{T_1}^{T_2} \frac{Q}{T} dT \\ &\approx \frac{\Delta H}{T_C} \\ &= \frac{28.21 \text{ J} \cdot \text{g}^{-1} \times 289.94 \text{ g} \cdot \text{mol}^{-1}}{400.00 \text{ K}} \\ &= 20.45 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \\ \Delta S &= R \ln N \\ N &= \exp\left(\frac{\Delta S}{R}\right) = \exp\left(\frac{20.45 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}}{8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}}\right) \\ &= 11.69 \end{aligned}$$

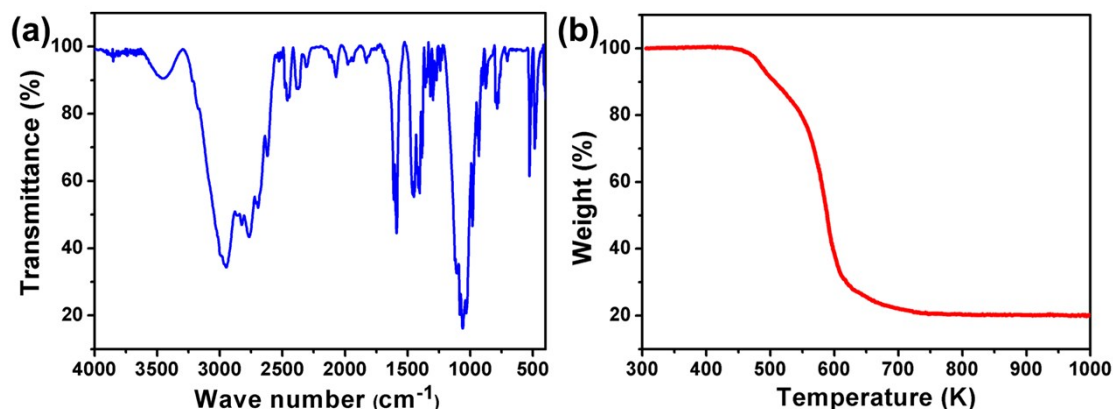


Fig. S1 (a) IR (Infrared spectrum) of **1** at room temperature and (b) TGA (Thermogravimetric Analysis) curve of **1**.

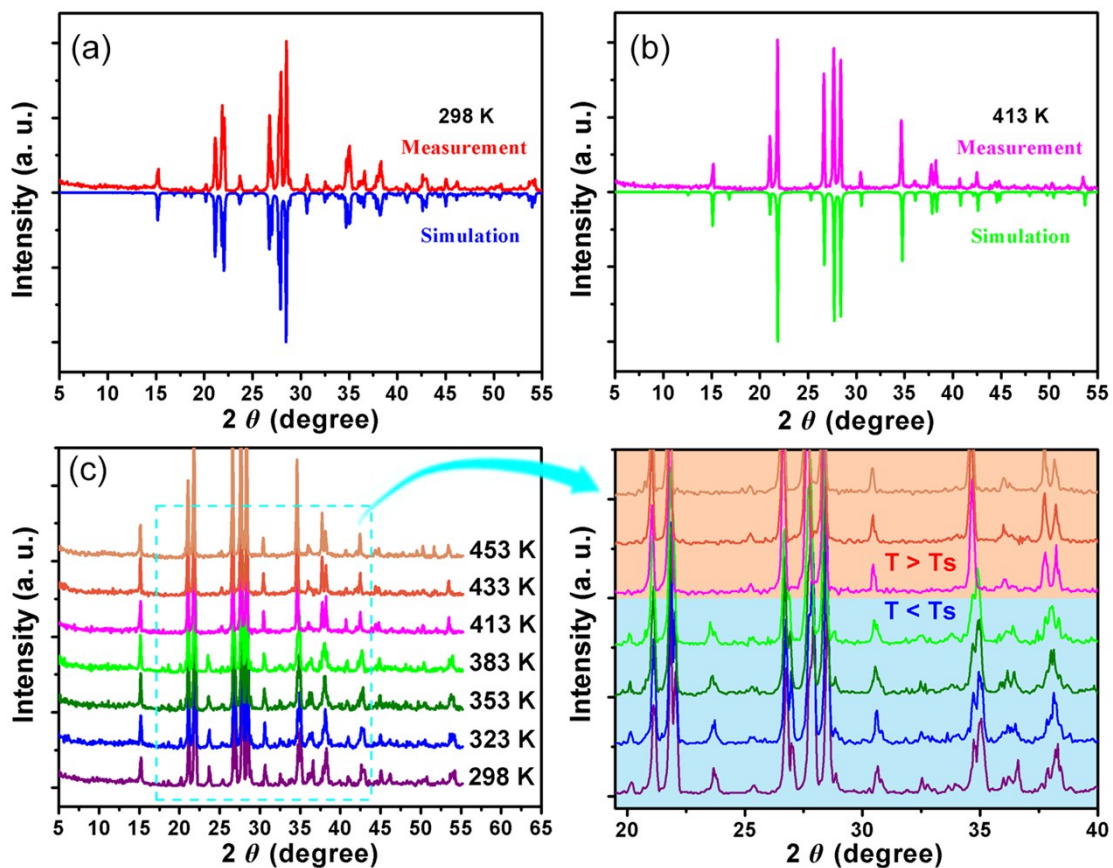


Fig. S2. PXRD (Powder X-Ray Diffraction) spectra of **1** at 298 K (a) and 413 K (b) and VT-PXRD (variable-temperature PXRD) spectra (c) at different temperature.

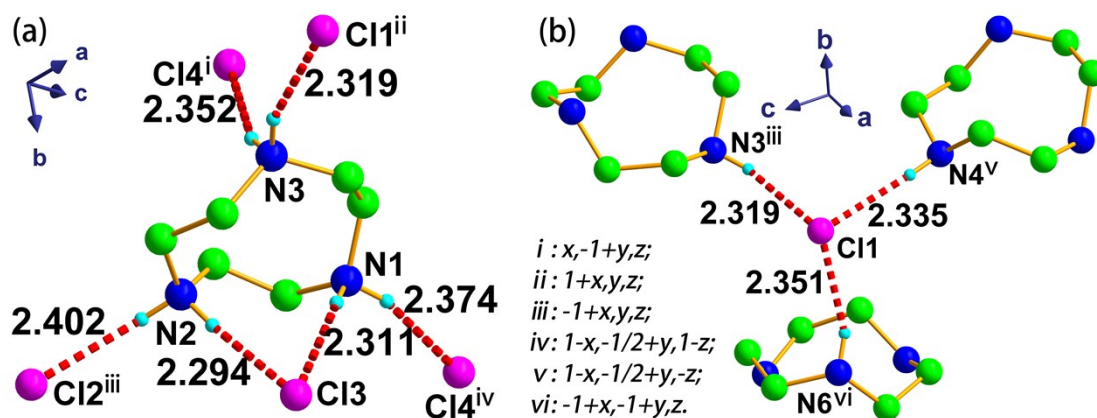


Fig. S3 Hydrogen bonds environment of the cation (a) and anion (b) of **1** at 298K.

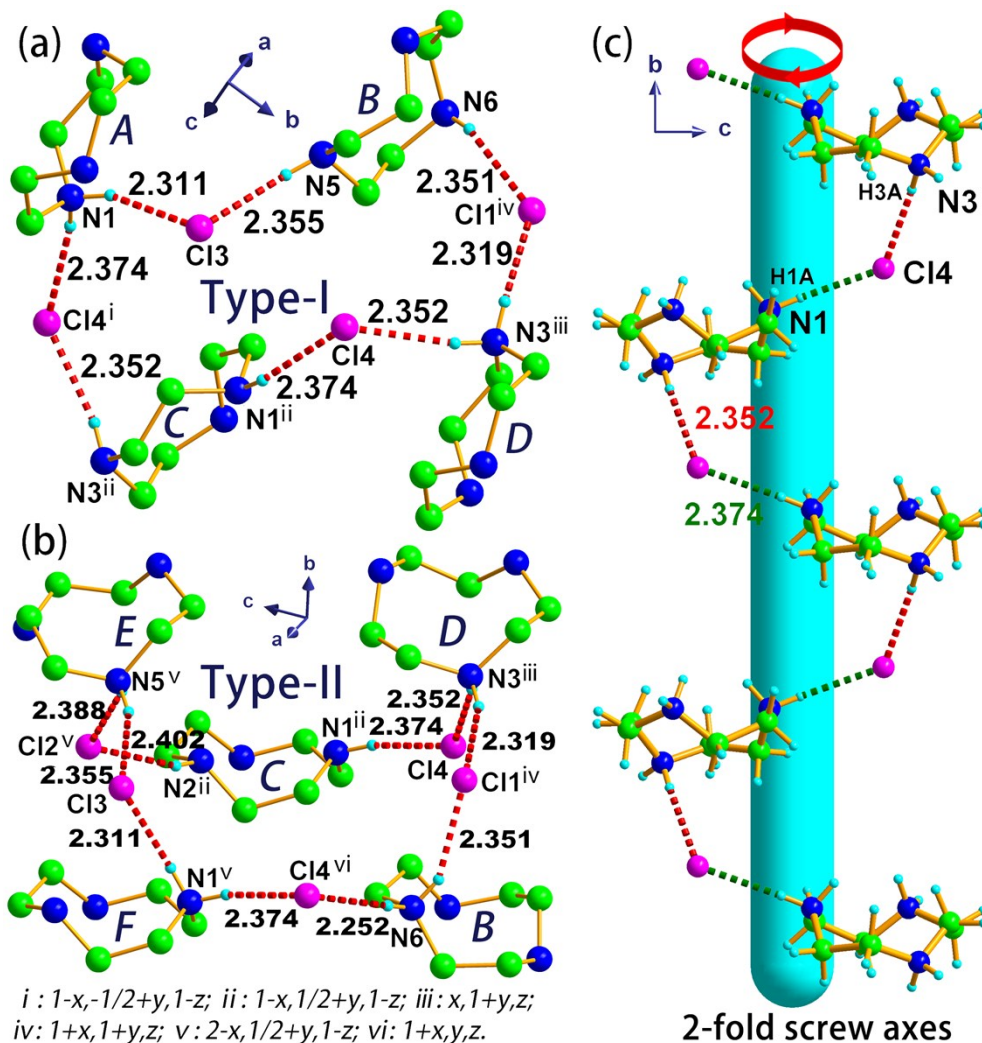


Fig. S4 Hydrogen-bonding interactions (red and green dashed lines) between the cation and anion moieties of **1** at 298K. Formed type-I (a) and type-II (b) cyclic structures and spiral chains (c).

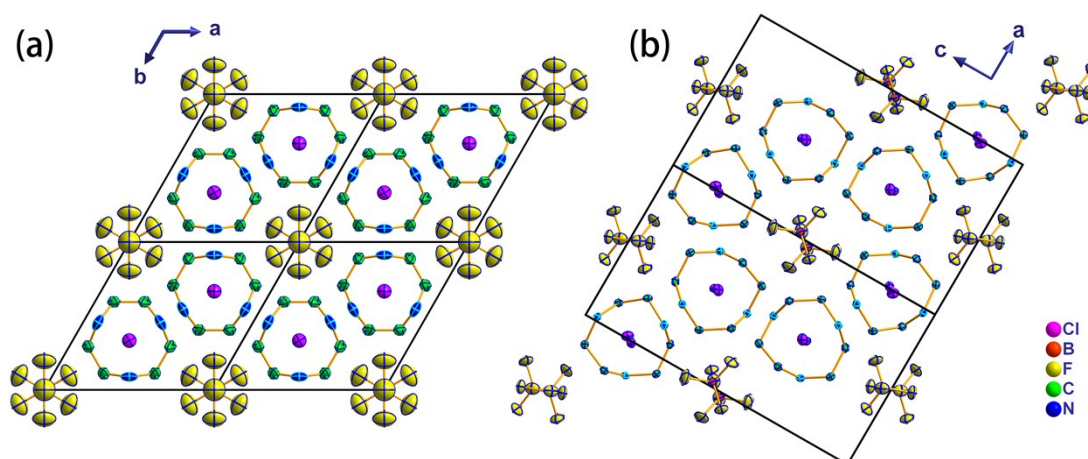


Fig. S5 View of the packing structure of **1** obtained at 298 K (a) and 413 K (b) showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. H atoms of cations are labeled for clearly.



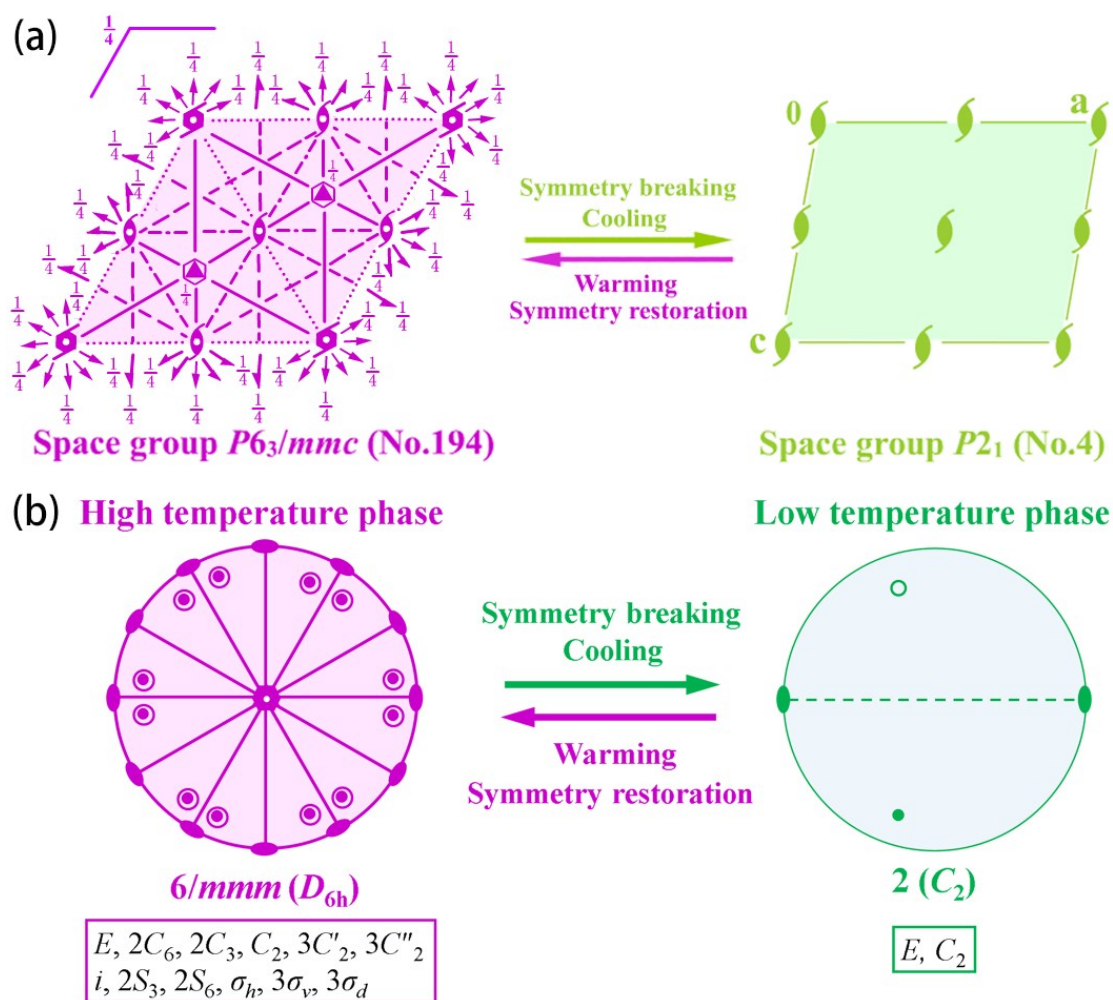


Fig. S6 (a) Spatial symmetry operation change of **1** from the HTP ( $P6_3/mmc$ ) to the LTP ( $P2_1$ ). (b) Equatorial plane projection of point groups  $6/mmm (D_{6h})$  in the HTP and  $2 (C_2)$  in the LTP.

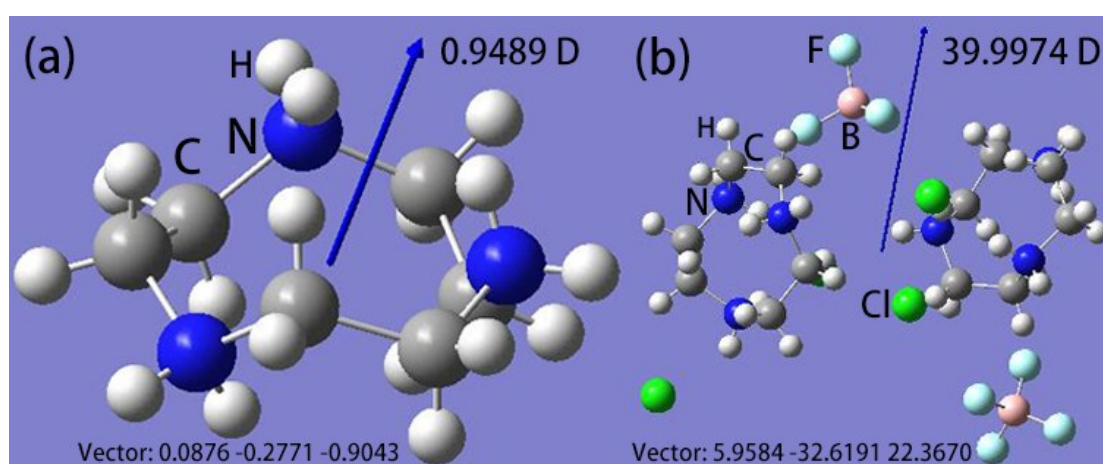


Fig. S7 Dipole moment direction and magnitude of  $[9\text{-tacn-3}]^{3+}$  (a) and **1** (b) at 298 K was calculated through GaussView 5.0.9 software.

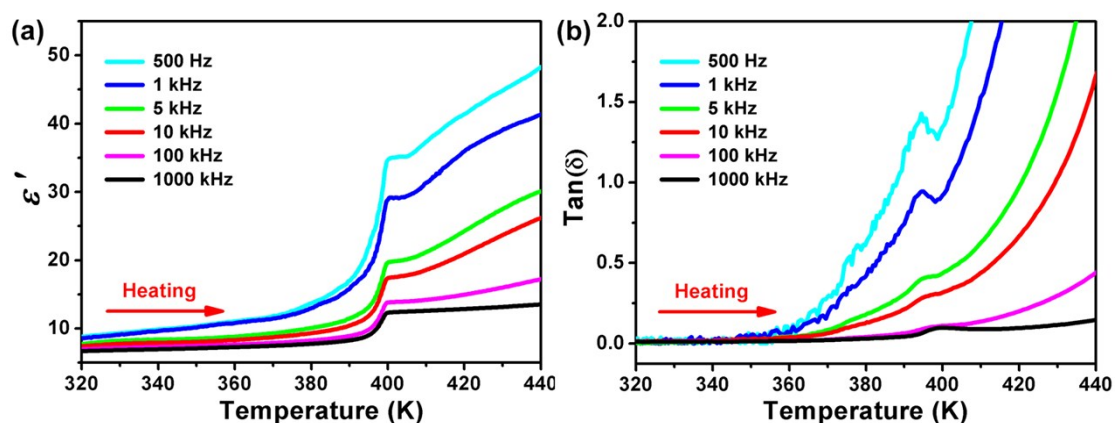


Fig. S8 Temperature-dependence of the real part ( $\epsilon'$ ) (a) and dielectric loss ( $\tan(\delta)$ ) (b) of the polycrystalline sample of **1** at different frequency.

Table S1 List of some classical phase transition materials.

Formula	$T_C$ (K)	Symmetry Changes	Year	Ref
Rochelle salt	297	$2 \leftrightarrow 222$	1920	1
Tri-glycine sulfate (TGS)	322	$2 \leftrightarrow 2/m$	1957	2
Triglycine fluoberyllate (TGFB)	352	$2 \leftrightarrow 2/m$	1962, 1976	3
Pyridinium perrhenate	333	$mm2 \leftrightarrow \text{---}$	1997	4
Hdabco perchlorate	377	$mm2 \leftrightarrow 4/mmm$	1999, 2016	5
Hdabco tetrafluoroborate	374	$mm2 \leftrightarrow 4/mmm$	1999, 2017	6
Hdabco perrhenate	377, 500	$m \leftrightarrow 4mm \leftrightarrow m-3m$	2017	7
Guanidinium perchlorate	454	$3m \leftrightarrow m-3m$	2011, 2017	8
Tetraethylammonium perchlorate	378	$m \leftrightarrow m-3m$	2016	9
Quinuclidinium periodate	322	$mm2 \leftrightarrow m-3m$	2017	10
Quinuclidinium perrhenate	345, 367	$mm2 \leftrightarrow 3m \leftrightarrow m-3m$	2017	11
[D-55DMBP][Hia]	268	$1 \leftrightarrow -1$	2007	12
[D-55DMBP][Dia]	335	$1 \leftrightarrow -1$	2007	12
Bis(imidazolium) L-Tartrate	351	$2 \leftrightarrow 222$	2012	13
[H-dppz][Hca]	402	$m \leftrightarrow 2/m$	2013	14
Diisopropylammonium Chloride	440	$2 \leftrightarrow 2/m$	2011	15
Diisopropylammonium Bromide	426	$2 \leftrightarrow 2/m$	2013	16
[Me-dabco]- $\text{NH}_4\text{I}_3$	448	$3 \leftrightarrow 432$	2018	17
Cyclohexylammonium-(18-crown-6)- perchlorate	390	$mm2 \leftrightarrow mmm$	2015	18
Cyclohexylammonium-(18-crown-6)-tetrafluoroborate	397	$mm2 \leftrightarrow mmm$	2015	18
(R)-(-)-3 hydroxyquinuclidinium Chloride	340	$4 \leftrightarrow 432$	2016	19
Pyridinium periodate	321	$mm2 \leftrightarrow mmm$	2001	20
Imidazolium periodate	310	$2 \leftrightarrow 2/m$	2014	21
Acetamidinium perchlorate	320	$2 \leftrightarrow m-3m$	2018	22

Bromocholine bromide	329	$2 \leftrightarrow 2/m$	2018	23
$[\text{C}(\text{NH}_2)_3]_4\text{Cl}_2\text{SO}_4$	356	$mm2 \leftrightarrow -42m$	2005	24
$[\text{C}(\text{NH}_2)_3]_4\text{Br}_2\text{SO}_4$	365.5	$mm2 \leftrightarrow -42m$	2006	25
$\alpha$ -[H-6,6'-dmbp][Hca]	380	$2 \leftrightarrow \text{---}$	2014	26
Imidazolium perchlorate	373	$3m \leftrightarrow -3m$	2014	27
<b>[9-tacn-3]Cl<sub>2</sub>[BF<sub>4</sub>]</b>	<b>400</b>	<b><math>2 \leftrightarrow 6/mmm</math></b>	<b>2019</b>	<b>This work</b>
$[\text{CN}_4\text{H}_8]\text{ZrF}_6$	383	$mm2 \leftrightarrow mmm$	2001	28
$[\text{Et}_3\text{MeN}][\text{FeBr}_4]$	171, 360	$6 \leftrightarrow 6mm \leftrightarrow 6/mmm$	2012	29
$[\text{MeNH}_3]_5\text{Bi}_2\text{Cl}_{11}$	250, 307	$2 \leftrightarrow mm2 \leftrightarrow mmm$	1989	30
$[\text{MeNH}_3]_5\text{Bi}_2\text{Br}_{11}$	312	$mm2 \leftrightarrow mmm$	1989	31
$[\text{Me}_2\text{NH}]_3\text{Sb}_2\text{Cl}_9$	242	$\text{---} \leftrightarrow 2/m$	1986	32
TMCM-MnCl <sub>3</sub>	406	$m \leftrightarrow 6/mmm$	2017	33
[Cyclopentylaminium][CdCl <sub>3</sub> ]	300	$m \leftrightarrow mmm$	2014	34
[3-Pyrrolinium][CdCl <sub>3</sub> ]	316	$mm2 \leftrightarrow mmm$	2014	35
(Cyclohexylammonium) <sub>2</sub> PbBr <sub>4</sub>	363	$mm2 \leftrightarrow mmm$	2016	36
[3-Pyrrolinium][MnCl <sub>3</sub> ]	376	$mm2 \leftrightarrow mmm$	2015	37
$[(\text{CH}_3)_3\text{NCH}_2\text{Br}]_2\text{-ZnBr}_4$	387	$2/m \leftrightarrow mmm$	2018	38
<i>Conventional ferroelectrics</i>				
HCl	98	$mm2 \leftrightarrow$ (cubic)	1967	39
KH <sub>2</sub> PO <sub>4</sub> (KDP)	123	$mm2 \leftrightarrow -42m$	1935	40
(NH <sub>4</sub> )HSO <sub>4</sub>	270, 154	$1 \leftrightarrow m \leftrightarrow 2/m$	1958	41
PVDF	—	$mm2 \leftrightarrow \text{---}$	1974	42
SbSI	295	$mm2 \leftrightarrow mmm$	1962	43
BaTiO <sub>3</sub>	393	$4mm \leftrightarrow m-3m$	1944	44
NaNO <sub>2</sub>	436	$mm2 \leftrightarrow mmm$	1958	45
KNbO <sub>3</sub>	708	$4mm \leftrightarrow m-3m$	1951	46
SrTeO <sub>3</sub>	585, 758	$m \leftrightarrow \text{---}$	1967, 1973	47
PbTiO <sub>3</sub>	763	$4mm \leftrightarrow m-3m$	1950	48
LiTaO <sub>3</sub>	938	$3m \leftrightarrow -3m$	1949	49
BiFeO <sub>3</sub>	1123	$3m \leftrightarrow m-3m$	1969	50
LiNbO <sub>3</sub>	1483	$3m \leftrightarrow -3m$	1949	49

Table S2 Crystal data and structure refinement for **1** at 298 K and 413 K.

	298 K	413 K
Empirical formula	C <sub>6</sub> H <sub>18</sub> N <sub>3</sub> F <sub>4</sub> BCl <sub>2</sub>	C <sub>6</sub> H <sub>18</sub> N <sub>3</sub> F <sub>4</sub> BCl <sub>2</sub>
Formula weight	289.94	289.94
Crystal system	Monoclinic	Hexagonal
Space group	$P2_1$	$P6_3/mmc$
$a$ (Å)	8.0679(2)	8.1276(7)
$b$ (Å)	10.5006(3)	8.1276(7)
$c$ (Å)	14.0399(4)	10.5327(13)
$\alpha$ (deg)	90	90
$\beta$ (deg)	90.802(2)	90
$\gamma$ (deg)	90	120
Volume (Å <sup>3</sup> )	1189.31(6)	602.55(13)

$Z, D_{\text{calcd}} / \text{g cm}^{-3}$	4, 1.619	2, 1.598
$\mu$ (mm <sup>-1</sup> )	0.574	0.567
$F(000)$	600	300
Goodness-of-fit on $F^2$	1.000	1.959
$T_{\text{min}}/T_{\text{max}}$	0.861 / 0.856	0.863 / 0.858
Flack parameter	0.06(2)	-
$R_1^a$ ( $> 2\sigma$ )	0.0324	0.1161
$wR_2^b$ ( $> 2\sigma$ )	0.0800	0.3897

$$^a R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|, \quad ^b wR_2 = [\sum (|F_o|^2 - |F_c|^2) / \sum |F_o|^2]^{1/2}$$

Table S3 Bond lengths [Å] and angles [°] for **1** at 298 K.

B(1)-F(3)	1.370(5)	B(2)-F(5)	1.373(4)
B(1)-F(2)	1.372(4)	B(2)-F(8)	1.374(5)
B(1)-F(4)	1.381(5)	B(2)-F(7)	1.388(5)
B(1)-F(1)	1.397(4)	B(2)-F(6)	1.393(4)
C(1)-N(1)	1.491(4)	C(7)-C(8)	1.502(5)
C(1)-C(2)	1.507(5)	C(7)-N(4)	1.507(4)
C(2)-N(2)	1.499(4)	C(8)-N(5)	1.495(4)
C(3)-N(2)	1.497(4)	C(9)-N(5)	1.506(4)
C(3)-C(4)	1.513(4)	C(9)-C(10)	1.513(4)
C(4)-N(3)	1.514(4)	C(10)-N(6)	1.501(4)
C(5)-N(3)	1.499(4)	C(11)-N(6)	1.502(4)
C(5)-C(6)	1.511(5)	C(11)-C(12)	1.516(4)
C(6)-N(1)	1.502(4)	C(12)-N(4)	1.494(4)
F(3)-B(1)-F(2)	110.0(3)	F(5)-B(2)-F(8)	112.0(3)
F(3)-B(1)-F(4)	112.3(3)	F(5)-B(2)-F(7)	109.5(3)
F(2)-B(1)-F(4)	109.3(3)	F(8)-B(2)-F(7)	109.5(3)
F(3)-B(1)-F(1)	109.3(3)	F(5)-B(2)-F(6)	110.0(3)
F(2)-B(1)-F(1)	106.4(3)	F(8)-B(2)-F(6)	109.1(3)
F(4)-B(1)-F(1)	109.4(3)	F(7)-B(2)-F(6)	106.7(3)
N(1)-C(1)-C(2)	115.8(3)	N(5)-C(8)-C(7)	115.7(2)
N(2)-C(2)-C(1)	114.9(3)	N(5)-C(9)-C(10)	115.7(2)
N(2)-C(3)-C(4)	115.4(3)	N(6)-C(10)-C(9)	116.4(3)
N(3)-C(5)-C(6)	117.3(3)	N(6)-C(11)-C(12)	116.7(2)
N(1)-C(6)-C(5)	116.1(3)	N(4)-C(12)-C(11)	114.7(3)
C(3)-C(4)-N(3)	116.8(3)	C(8)-C(7)-N(4)	114.4(3)
C(1)-N(1)-C(6)	116.8(3)	C(12)-N(4)-C(7)	115.7(2)
C(3)-N(2)-C(2)	114.8(2)	C(8)-N(5)-C(9)	115.0(2)
C(5)-N(3)-C(4)	117.2(2)	C(10)-N(6)-C(11)	116.3(2)

Table S4 Hydrogen bonds parameters for **1** at 298 K.

D-H...A	D-H	H...A	D...A	$\angle$ D-H...A
N(1)-H(1A)...Cl(4)#1	0.89	2.37	3.216(3)	157.7
N(1)-H(1B)...Cl(3)	0.89	2.31	3.148(3)	156.6
N(2)-H(2A)...Cl(2)#2	0.89	2.40	3.234(3)	155.6



N(2)-H(2B)...Cl(3)	0.89	2.29	3.179(3)	173.4
N(3)-H(3A)...Cl(4)#3	0.89	2.35	3.205(3)	160.6
N(3)-H(3B)...Cl(1)#4	0.89	2.32	3.165(3)	158.8
N(4)-H(4C)...Cl(2)	0.89	2.25	3.135(3)	171.4
N(4)-H(4D)...Cl(1)#5	0.89	2.34	3.180(3)	158.5
N(5)-H(5C)...Cl(2)	0.89	2.39	3.187(3)	149.6
N(5)-H(5D)...Cl(3)	0.89	2.35	3.202(3)	159.1
N(6)-H(6C)...Cl(4)#4	0.89	2.25	3.116(2)	163.2
N(6)-H(6D)...Cl(1)#6	0.89	2.35	3.161(3)	151.3

Symmetry transformations used to generate equivalent atoms : #1 -x+1,y-1/2,-z+1; #2 x-1,y,z;

#3 x,y-1,z; #4 x+1,y,z; #5 -x+1,y+1/2,-z; #6 x+1,y+1,z.

Table S5 Weak Hydrogen bonds parameters for **1** at 298 K.

D-H...A	D-H	H...A	D...A	∠D-H...A
C(1)-H(1C)...F(2)#1	0.97	2.34	3.242(4)	153.9
C(1)-H(1C)...F(4)#1	0.97	2.63	3.384(5)	134.8
C(1)-H(1D)...F(1)#2	0.97	2.52	3.098(4)	118.2
C(2)-H(2D)...F(1)#2	0.97	2.51	3.188(4)	127.2
C(3)-H(3C)...F(7)#3	0.97	2.53	3.233(4)	128.8
C(3)-H(3D)...F(8)#4	0.97	2.61	3.341(4)	132.0
C(4)-H(4B)...F(6)#3	0.97	2.55	3.330(4)	137.0
C(5)-H(5B)...F(2)#5	0.97	2.52	3.240(4)	131.1
C(6)-H(6B)...F(1)#5	0.97	2.59	3.367(4)	137.6
C(7)-H(7B)...F(6)	0.97	2.46	3.144(4)	127.0
C(8)-H(8A)...F(6)	0.97	2.49	3.078(4)	118.9
C(8)-H(8B)...F(7)#3	0.97	2.38	3.263(4)	150.8
C(8)-H(8B)...F(8)#3	0.97	2.51	3.259(4)	134.2
C(9)-H(9A)...F(1)	0.97	2.46	3.035(4)	117.3
C(9)-H(9A)...F(2)#6	0.97	2.42	3.031(4)	120.7
C(10)-H(10A)...F(3)#6	0.97	2.51	3.475(4)	170.9
C(11)-H(11B)...F(6)#7	0.97	2.47	3.031(4)	116.9
C(11)-H(11B)...F(7)#8	0.97	2.44	3.015(4)	118.0
C(12)-H(12B)...F(5)#8	0.97	2.55	3.513(5)	171.3
C(2)-H(2C)...Cl(4)#4	0.97	2.72	3.681(3)	170.5
C(4)-H(4A)...Cl(3)	0.97	2.78	3.639(3)	147.4
C(6)-H(6A)...Cl(4)#4	0.97	2.80	3.651(3)	146.6
C(7)-H(7A)...Cl(1)#9	0.97	2.88	3.838(3)	171.8
C(9)-H(9B)...Cl(1)#9	0.97	2.75	3.574(3)	142.7
C(11)-H(11A)...Cl(2)	0.97	2.74	3.592(3)	147.6

Symmetry transformations used to generate equivalent atoms : #1 x-1,y,z; #2 -x+1,y-1/2,-z+1; #4 x,y-1,z;

#3 -x+1,y-1/2,-z; #5 -x+2,y-1/2,-z+1; #6 -x+2,y+1/2,-z+1; #7 x+1,y,z; #8 -x+2,y-1/2,-z; #9 x+1,y+1,z.

## References and Notes

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