

# Supporting Information

## High Temperature Switchable Dielectric Properties in Molecular Crystal Material: 1,4,7-Triazacyclononane Trihydrochloride

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### Recrystallization / Synthesis.

Crystallized samples 1,4,7-Triazacyclononane trihydrochloride, [9-tacn-3]·3Cl (9-tacn-3 = 1,4,7-Triazoniacyclononane), **1**, can be obtained by recrystallization of powder samples from commercial sources.

Crystallized samples **1**, were grown by slow evaporation of an aqueous solution containing 1:3 molar amounts of 1,4,7-triazacyclononane and hydrochloric acid. The colourless crystals of **1** were obtained (yield ~ 78.6 %). Microanalysis (%) Found: C 30.3; H 7.8; N 17.5. Calc. for C<sub>6</sub>H<sub>18</sub>N<sub>3</sub>Cl<sub>3</sub>: C 30.2; H 7.6; N 17.6. IR bands  $\nu$  (KBr disk, cm<sup>-1</sup>): 3502 w, 3380 w, 2960 s, 2767 s, 2518 w, 2434 m, 2361 w, 2298 w, 2067 w, 1928 w, 1589 s, 1441 s, 1266 m, 1230 m, 1120 m, 1027 m, 982 s, 932 m, 882 s, 766 m, 705 w, 481 s, 452 m.

### Single-crystal X-ray crystallography.

Variable-temperature X-ray single-crystal diffraction data at 298 and 403 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 403 K are list in Table S2.

### Physical measurements:

(1) IR spectra were recorded at ambient temperature using a Shimadzu model IR-60 spectrometer with KBr pellets.

(2) TGA (Thermogravimetric Analysis) was tested in the temperature range of 300 to 1000 K to verify the thermal stability of the polycrystalline samples **1** (3.8711 mg) on a NETZSCH TG 209F3 TG instrument with rate of 10 K·min<sup>-1</sup> under the protection of nitrogen at atmospheric pressure in Al<sub>2</sub>O<sub>3</sub> crucibles.

(3) DSC (Differential scanning calorimetry) was carried out on a Perkin–Elmer Diamond DSC instrument by heating and cooling the polycrystalline samples (18.1 mg) with a heating/cooling rate of 20 K·min<sup>-1</sup> under nitrogen at atmospheric pressure in aluminum crucibles.

(4) The collection of PXRD (Powder X-Ray Diffraction) data was performed by Cu-K $\alpha$  radiation ( $\lambda = 1.54184 \text{ \AA}$ ) in the temperature range of 298 to 423 K on a PANalytical X'Pert PRO X-ray diffractometer with the  $2\theta$  from 5 to 55 degree, with a step size of 0.02°.

(5) The pressed-powder pellet sandwiched between two parallel (0.60 mm thick and 9.50 mm<sup>2</sup> in area) copper electrodes were used for dielectric constant measurements. Complex dielectric permittivity  $\varepsilon$  ( $\varepsilon = \varepsilon' - i\varepsilon''$ ) was measured on a Tonghui TH2828A instrument over the frequency range of 500 Hz to 1 MHz and in the temperature range between 310 K and 410 K, with a heating/cooling rate of 20 K·min<sup>-1</sup>. The applied electric field was 2 V mm<sup>-1</sup>.

### Calculation of $\Delta S$ and $N$ for **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  $T_{H2}$  and  $T_{C1}$ ,  $n$  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.

Heating process	Cooling process
$\Delta S = \int_{T_1}^{T_2} \frac{Q}{T} dT \approx \frac{\Delta H}{T_2}$ $= \frac{21.49 \text{ J} \cdot \text{g}^{-1} \times 238.58 \text{ g} \cdot \text{mol}^{-1}}{379.7 \text{ K}}$ $= 13.503 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$	$\Delta S = \int_{T_1}^{T_2} \frac{Q}{T} dT \approx \frac{\Delta H}{T_C}$ $= \frac{20.45 \text{ J} \cdot \text{g}^{-1} \times 238.58 \text{ g} \cdot \text{mol}^{-1}}{363.5 \text{ K}}$ $= 13.422 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$
$\Delta S = R \ln N$	$\Delta S = R \ln N$
$N = \exp\left(\frac{\Delta S}{R}\right)$	$N = \exp\left(\frac{\Delta S}{R}\right)$

$$= \exp\left(\frac{13.503 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}}{8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}}\right) = 5.1$$

$$= \exp\left(\frac{13.422 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}}{8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}}\right) = 5.0$$

Figures:

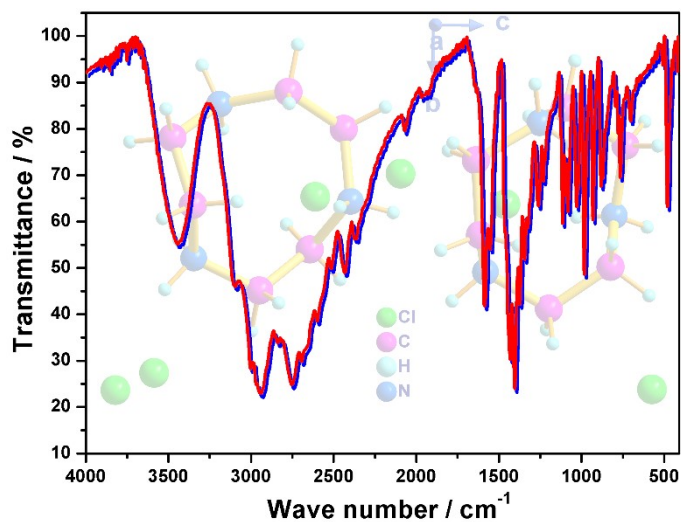


Fig. S1 IR spectrum of **1** at room temperature.

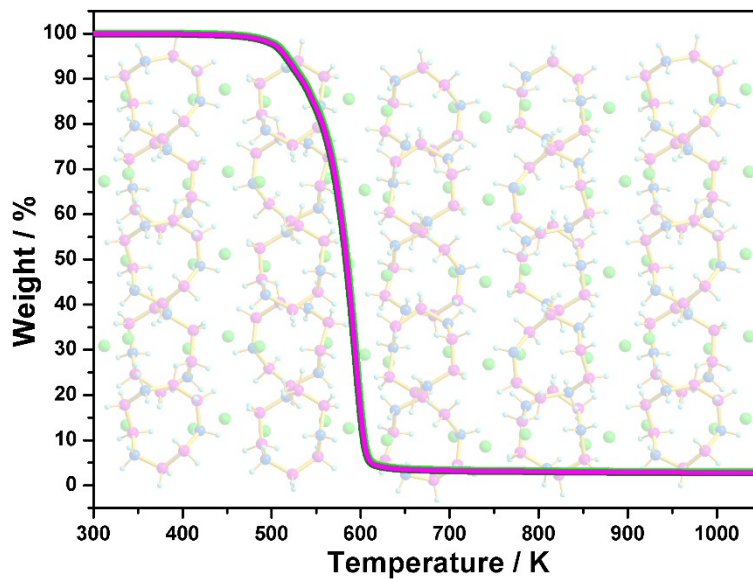


Fig. S2 TGA spectrum of **1**.

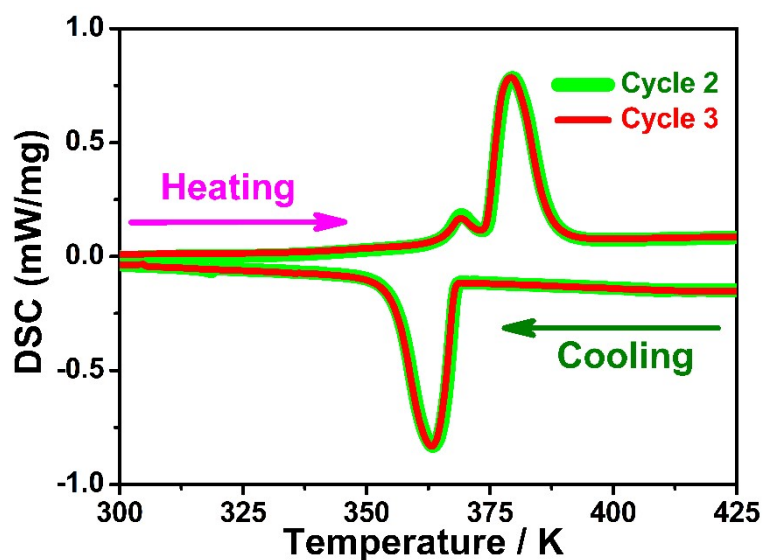


Fig. S3 DSC curve cycles of **1**.

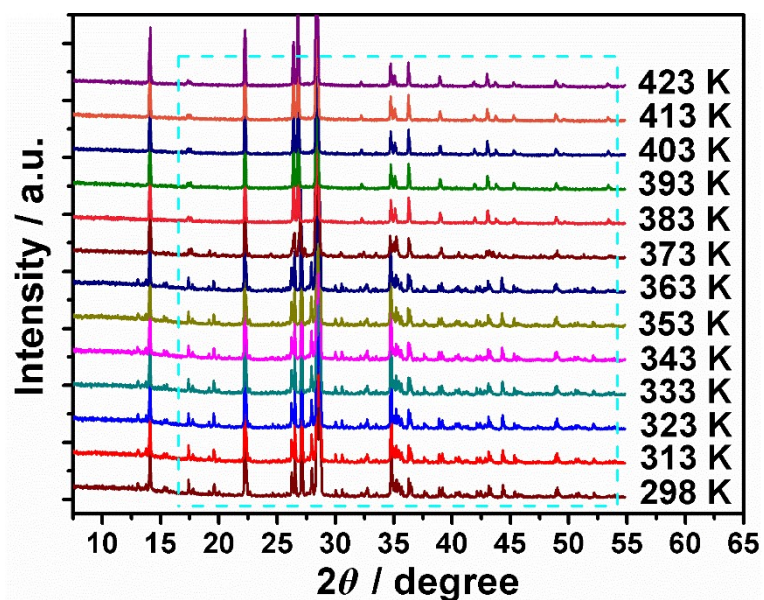


Fig. S4 VT-PXRD (variable-temperature PXRD) spectra at different temperature.

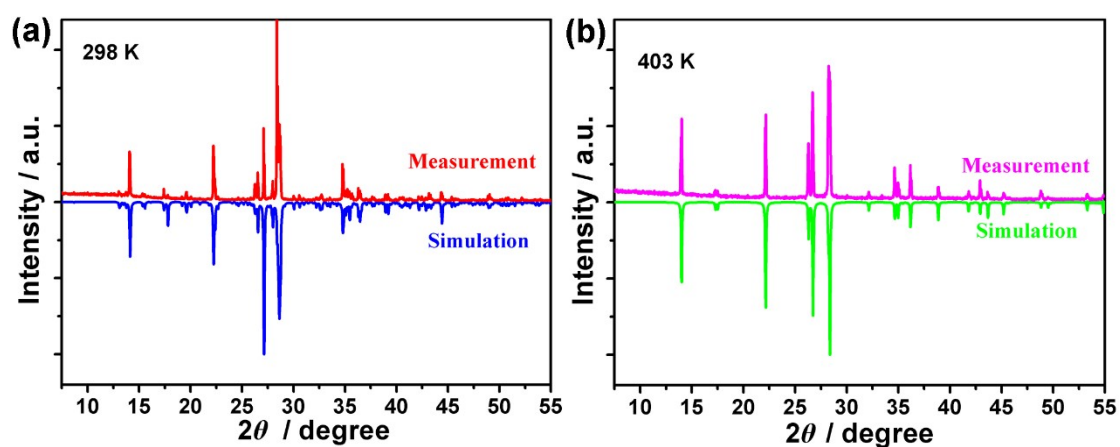


Fig. S5 PXRD (Powder X-Ray Diffraction) spectra of **1** at 298 K (a) and 403 K (b).

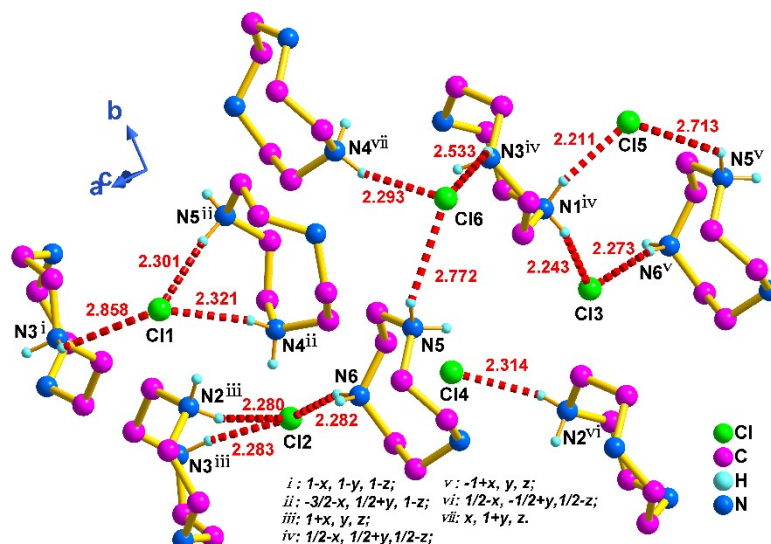


Fig. S6 Hydrogen bonds environment of anions (Cl) of **1** at 298 K. The H atoms on C of cations are labeled for clearly.

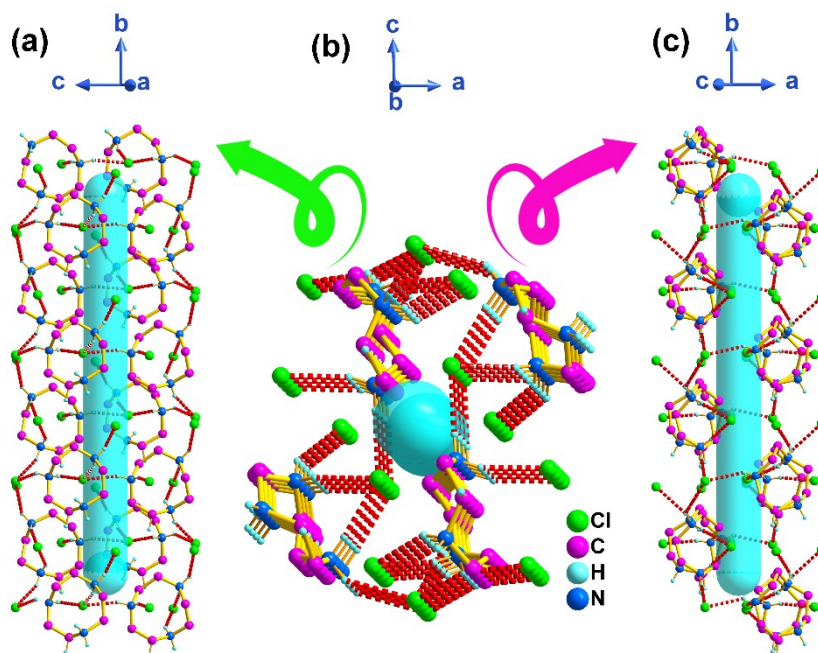


Fig. S7 The helical structure of **1** at 298 K formed by hydrogen bonding of ions near the 2-fold axis almost along a-axis (a), b-axis (b) and c-axis (c). Hydrogen-bonding interactions (red dashed lines) between the cation and anion moieties of **1** at 298K. The H atoms on C of cations are labeled for clearly.

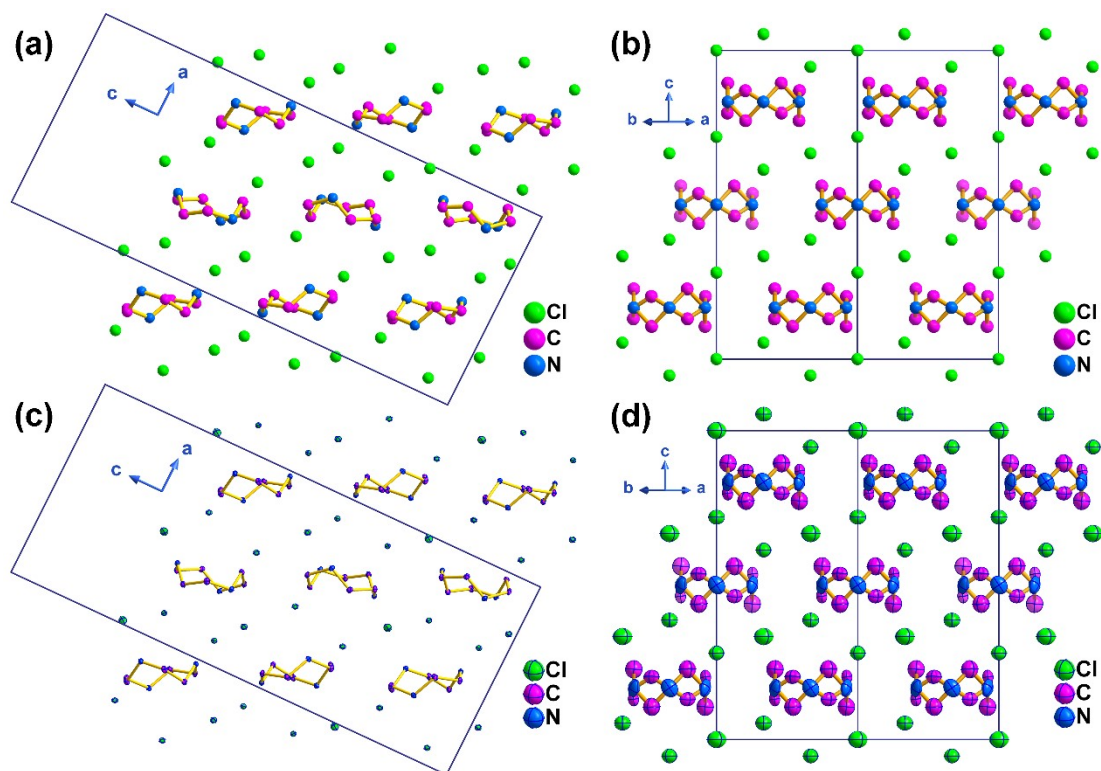


Fig. S8 View of the packing structure of **1** obtained at 298 K (a, c) and 403 K (b, d) showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level in (c) and (d) (in (d) for C1 is drawn at the 15% probability level). All H atoms of cations are labeled for clearly.

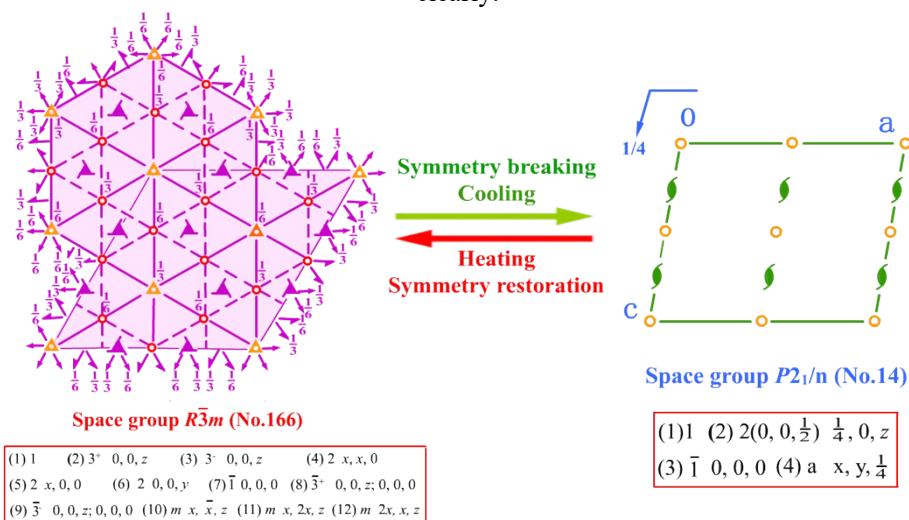


Fig. S9 Spatial symmetry operation change of **1** from the HTP ( $R\bar{3}m$ ) to the LTP ( $P2_1/n$ ).

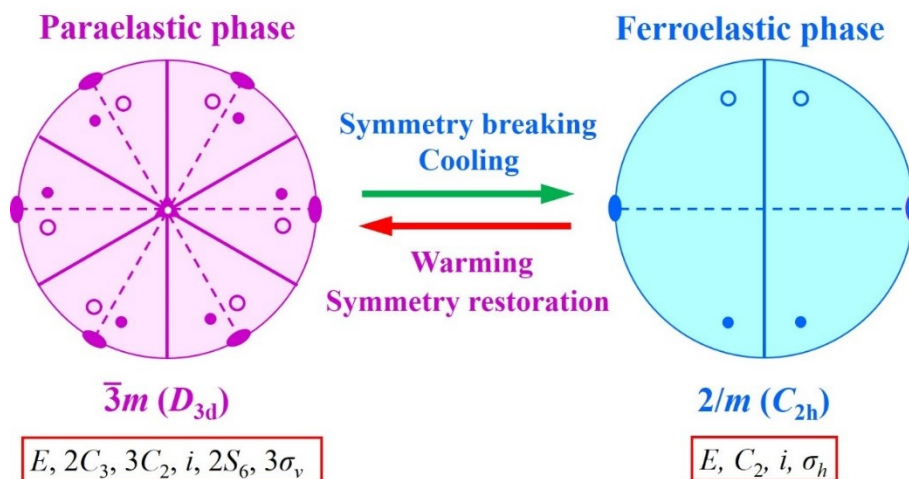


Fig. S10 Equatorial plane projection of point groups  $\bar{3}m (D_{3d})$  in HTP and  $2/m (C_{2h})$  in LTP.

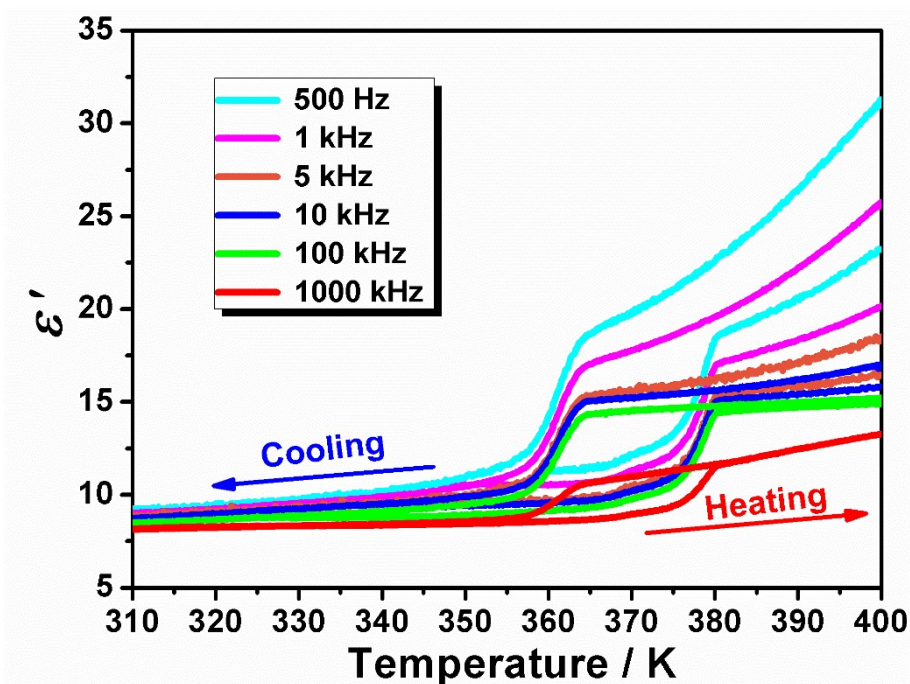


Fig. S11 Temperature dependence of the real part ( $\epsilon'$ ) of the polycrystalline sample of **1** at different frequencies.

**Tables:**

Table S1 Crystal data and structure refinement for **1** at 298 K and 403 K.

298 K	403 K
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Empirical formula	C <sub>6</sub> H <sub>18</sub> N <sub>3</sub> Cl <sub>3</sub>	C <sub>6</sub> H <sub>18</sub> N <sub>3</sub> Cl <sub>3</sub>
Formula weight	238.58	238.58
Crystal system	Monoclinic	Trigonal
Space group	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>R</i> <sup>3</sup> <i>m</i>
<i>a</i> (Å)	11.0022(2)	8.0176(6)
<i>b</i> (Å)	7.9484(2)	8.0176(6)
<i>c</i> (Å)	25.1766(7)	15.1832(12)
$\alpha$ (deg)	90	90
$\beta$ (deg)	91.703(2)	90
$\gamma$ (deg)	90	120
Volume (Å <sup>3</sup> ), <i>Z</i>	2200.72(9), 8	845.24(14), 3
<i>D</i> <sub>calcd</sub> / g cm <sup>-3</sup>	1.440	1.406
$\mu$ (mm <sup>-1</sup> )	0.790	0.771
<i>F</i> (000)	1008	378
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.000	1.002
<i>T</i> <sub>min</sub> / <i>T</i> <sub>max</sub>	0.840 / 0.834	0.844 / 0.838
<i>R</i> <sub>1</sub> <sup>a</sup> (> 2 $\sigma$ )	0.0440	0.1164
<i>wR</i> <sub>2</sub> <sup>b</sup> (> 2 $\sigma$ )	0.1045	0.3415

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

Table S2 Bond lengths [Å] and angles [°] for **1** at 298 K.

C(1)-N(1)	1.503(3)	C(7)-N(4)	1.489(3)
C(1)-C(2)	1.511(4)	C(7)-C(8)	1.508(3)
C(2)-N(2)	1.501(3)	C(8)-N(5)	1.504(3)
C(3)-N(2)	1.492(3)	C(9)-N(5)	1.494(3)
C(3)-C(4)	1.502(4)	C(9)-C(10)	1.510(4)
C(4)-N(3)	1.508(3)	C(10)-N(6)	1.507(3)
C(5)-N(3)	1.499(3)	C(11)-N(6)	1.503(3)
C(5)-C(6)	1.511(4)	C(11)-C(12)	1.511(3)
C(6)-N(1)	1.505(3)	C(12)-N(4)	1.505(3)
N(1)-C(1)-C(2)	117.7(2)	N(6)-C(10)-C(9)	116.6(2)
N(2)-C(2)-C(1)	115.0(2)	N(6)-C(11)-C(12)	116.4(2)
N(2)-C(3)-C(4)	114.9(2)	N(4)-C(12)-C(11)	116.1(2)
C(3)-C(4)-N(3)	114.1(2)	C(1)-N(1)-C(6)	118.8(2)
N(3)-C(5)-C(6)	116.4(2)	C(3)-N(2)-C(2)	116.4(2)
N(1)-C(6)-C(5)	117.4(2)	C(5)-N(3)-C(4)	116.00(19)
N(4)-C(7)-C(8)	116.0(2)	C(7)-N(4)-C(12)	116.3(2)
C(7)-C(8)-N(5)	114.3(2)	C(9)-N(5)-C(8)	116.2(2)
N(5)-C(9)-C(10)	116.6(2)	C(11)-N(6)-C(10)	117.5(2)

Table S3 Anisotropic displacement parameters (Å<sup>2</sup> × 10<sup>3</sup>) for **1** at 298 K and 403 K. The anisotropic displacement factor exponent takes the form: -2 pi<sup>2</sup> [h<sup>2</sup> a\*<sup>2</sup> U11 + ... + 2 h k a\* b\* U12].



	U11	U22	U33	U23	U13	U12
<b>298 K</b>						
Cl(1)	24(1)	39(1)	32(1)	-5(1)	1(1)	-1(1)
Cl(2)	28(1)	38(1)	29(1)	4(1)	-2(1)	-5(1)
Cl(3)	26(1)	26(1)	34(1)	4(1)	-1(1)	-3(1)
Cl(4)	53(1)	78(1)	63(1)	-38(1)	8(1)	-25(1)
Cl(5)	30(1)	35(1)	36(1)	9(1)	-4(1)	-4(1)
Cl(6)	32(1)	34(1)	41(1)	-8(1)	0(1)	-3(1)
C(1)	39(2)	26(1)	28(2)	-1(1)	5(1)	2(1)
C(2)	25(1)	26(1)	30(2)	0(1)	7(1)	2(1)
C(3)	31(1)	20(1)	37(2)	-1(1)	10(1)	3(1)
C(4)	28(1)	25(1)	26(1)	-4(1)	4(1)	-2(1)
C(5)	37(1)	23(1)	29(2)	4(1)	6(1)	-2(1)
C(6)	32(1)	24(1)	36(2)	-5(1)	6(1)	-6(1)
C(7)	36(1)	26(1)	24(1)	-3(1)	4(1)	4(1)
C(8)	21(1)	32(2)	25(1)	3(1)	4(1)	0(1)
C(9)	37(1)	21(1)	31(2)	-2(1)	5(1)	1(1)
C(10)	30(1)	32(2)	30(2)	-1(1)	5(1)	6(1)
C(11)	36(1)	27(1)	27(2)	5(1)	6(1)	-3(1)
C(12)	32(1)	22(1)	28(2)	3(1)	1(1)	3(1)
N(1)	26(1)	20(1)	30(1)	-3(1)	1(1)	4(1)
N(2)	26(1)	27(1)	26(1)	8(1)	4(1)	3(1)
N(3)	26(1)	29(1)	25(1)	2(1)	5(1)	2(1)
N(4)	29(1)	23(1)	28(1)	-3(1)	-2(1)	-1(1)
N(5)	33(1)	24(1)	26(1)	5(1)	0(1)	0(1)
N(6)	27(1)	31(1)	20(1)	-2(1)	1(1)	-1(1)
<b>403 K</b>						
Cl(1)	105(2)	105(2)	82(3)	0	0	52(1)
Cl(2)	160(5)	160(5)	115(5)	0	0	80(2)
N(1)	60(4)	112(7)	129(8)	-21(7)	-11(3)	56(4)
C(1)	226(14)	226(14)	229(17)	-1(7)	1(7)	123(10)
C(2)	105(6)	105(6)	76(6)	2(3)	-2(3)	82(6)

Table S4 Hydrogen bonds parameters for **1** at 298 K. D: Donor, A: acceptor.

D-H...A	D-H	H...A	D...A	∠D-H...A
N(1)-H(1C)...Cl(5)#1	0.89	2.21	3.062(2)	160.8
N(1)-H(1D)...Cl(3)#1	0.89	2.24	3.075(2)	156.2
N(2)-H(2C)...Cl(4)#3	0.89	2.31	3.088(2)	145.8
N(2)-H(2D)...Cl(2)#2	0.89	2.28	3.121(2)	158.4
N(3)-H(3C)...Cl(1)#4	0.89	2.86	3.324(2)	114.0
N(3)-H(3C)...Cl(6)#1	0.89	2.53	3.209(2)	134.3
N(3)-H(3D)...Cl(2)#2	0.89	2.28	3.164(2)	169.9
N(4)-H(4C)...Cl(6)#7	0.89	2.29	3.120(2)	155.4
N(4)-H(4D)...Cl(1)#6	0.89	2.32	3.100(2)	147.1
N(5)-H(5C)...Cl(5)#5	0.89	2.71	3.285(2)	123.9
N(5)-H(5C)...Cl(6)	0.89	2.77	3.380(2)	127.0
N(5)-H(5D)...Cl(1)#6	0.89	2.30	3.170(2)	166.6
N(6)-H(6C)...Cl(3)#5	0.89	2.27	3.120(2)	159.7
N(6)-H(6D)...Cl(2)	0.89	2.28	3.132(2)	161.3

Symmetry transformations used to generate equivalent atoms : #1  $-x+1/2, y-1/2, -z+1/2$ ; #2  $x-1, y, z$ ;  
#3  $-x+1/2, y+1/2, -z+1/2$ ; #4  $-x+1, -y+1, -z+1$ ; #5  $x+1, y, z$ ; #6  $-x+3/2, y-1/2, -z+1/2$ ; #7  $x, y-1, z$ .