Electronic Supplementary Information

A polar oxyhalogen-vanadate compound $(C_5NH_{13}Cl)_2VOCl_4$ with optical and two-staged dielectric switch behavior

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Single-Crystal Structure Determination. Variable-temperature X-ray single diffraction data were collected by an Agilent Supernova CCD diffractometer in a ω-scan mode with $\Delta\omega$ = 1.0°. The structure data were collected at 200 K, 300 K and 365 K respectively by using a Cu-Kα (λ = 1.5418 Å) radiation. Data collection and processing were performed by CrysAlis PRO program. The structures were solved by direct methods (ShelXT),[S1] and nonhydrogen atoms were refined by full-matrix methods based on F^2 by means of ShelXL on the OLEX2 program.[S2, S3] All H atoms were refined using a riding model. CCDC 2055429 (LTP-200 K), 2055430 (ITP-300 K) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre.

Variable-Temperature Powder X-ray Diffraction. Variable temperature Powder X-ray Diffraction (PXRD) patterns were collected by a Bruker D8 Discover X-ray Powder Diffractometer in helium atmosphere at 300 K (ITP) and 400 K (HTP)(Fig.

S1).

Thermal Properties. Thermogravimetric analysis (TGA) was performed using an SDT-Q600 thermal analyzer in nitrogen atmosphere at a heating rate of 10 $K \cdot min^{-1}$ (Fig. S5). Differential scanning calorimetry (DSC) measurements were collected using a NETZSCH DSC 200F3 instrument with heating and cooling rates of 10 $K \cdot min^{-1}$ under nitrogen atmospheres (Fig. 3).

Dielectric Measurements. The temperature-dependent dielectric permittivity ε ($\varepsilon = \varepsilon' - i\varepsilon''$) was measured using the two-probe *a.c.* impedance method in the testing temperature range from 100 to 400 K and the frequency range from 100 Hz to 1 MHz on Wayne Kerr 6500B analyzer.

Optical Second Harmonic Generation (SHG). SHG activities were recorded using powder sample with sizes of 80-100 μm. An unexpanded laser (OPOTEK, 355 Ⅱ) with a low divergence (Nd: YAG, 1064 nm, 5 ns, 10 Hz repetition rate, 1.6 MW peak power) was used.

Caution! The high-power laser is dangerous for the eyes; adequate eye protection is necessary during the SHG experiments.

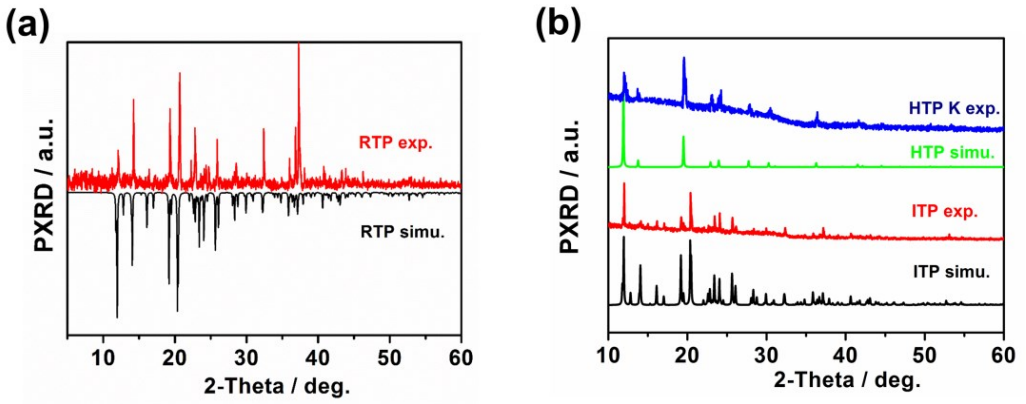

Fig. S1. (a) Simulated and experimental PXRD powder patterns for **1** at room temperature. (b) Variable temperature PXRD patterns at 300 K (ITP) and 400 K (HTP) for **1**.

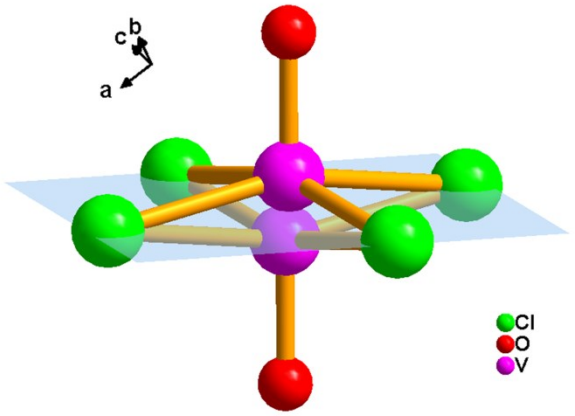

Fig. S2. The $[VCl_4O]^{2-}$ anions site disorder in **1**.

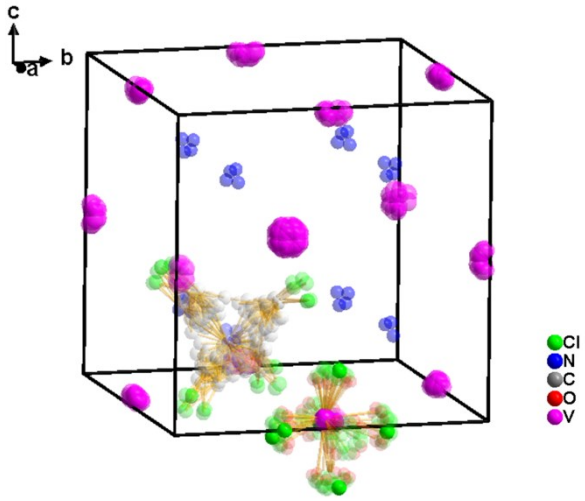

Fig. S3. The structure of **1** at 365 K. Hydrogen atoms, part of chlorine, oxygen, and carbon atoms were omitted for clarity.

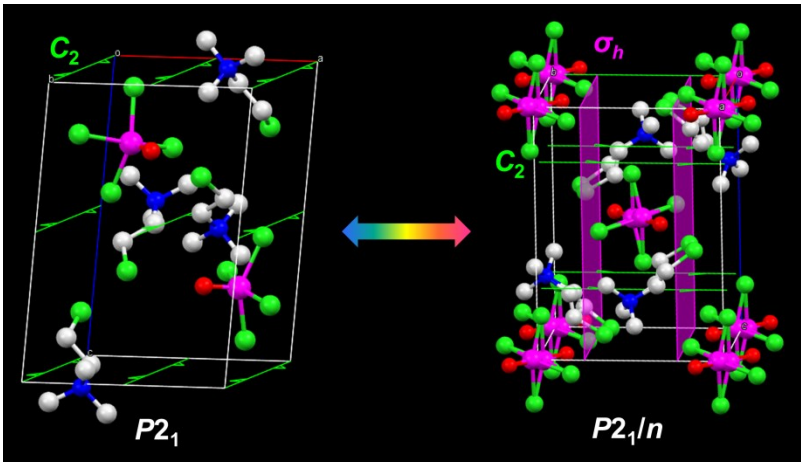

Fig. S4. Comparison of crystal structures at LTP and ITP for **1**.

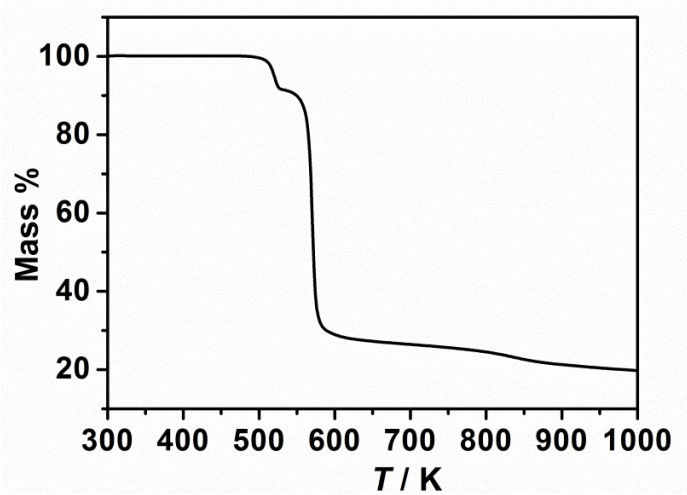

Fig. S5. TGA curve for **1**.

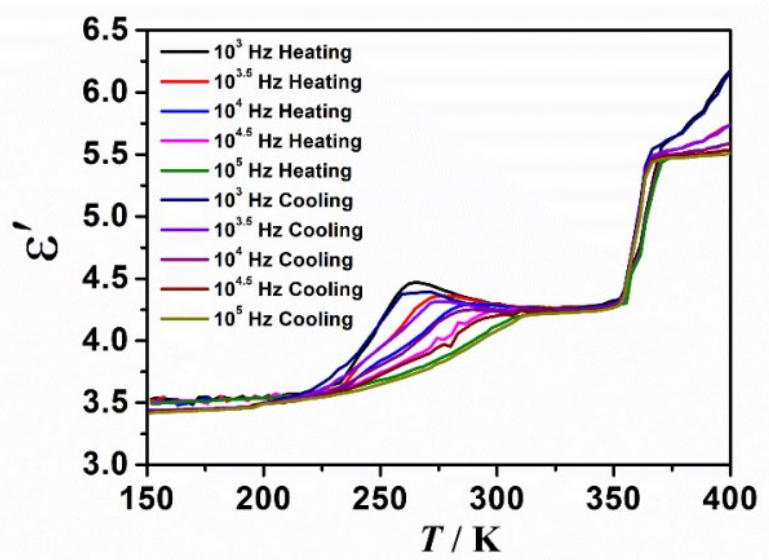

Fig. S6. Dielectric constant versus temperature at different frequencies with heating and cooling.

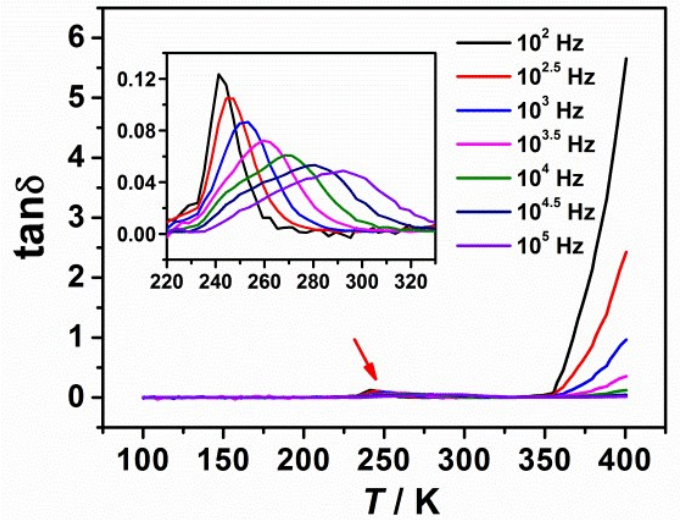

Fig. S7. The dielectric loss varied with frequencies and temperatures for **1**.

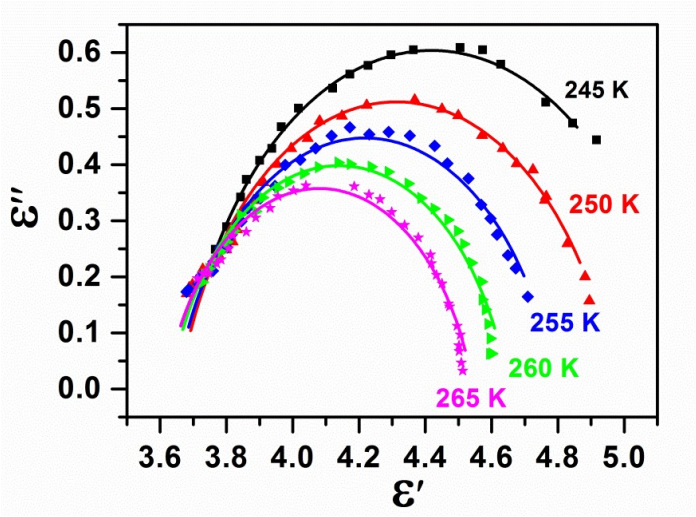

Fig. S8. Cole-Cole plot of **1** at temperatures 245 K, 250 K, 255 K, 260 K and 265 K.

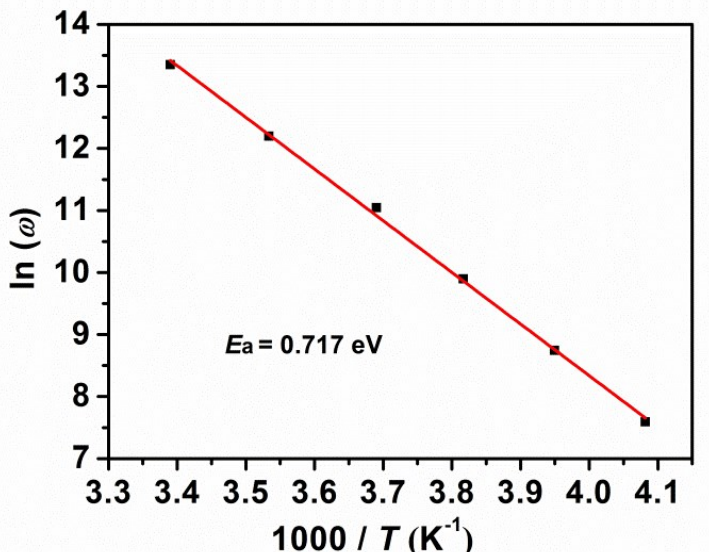

Fig. S9. Linear fitting of ln (ω) versus 1000 / T for **1**.

The activation energy for relaxation was estimated based on the Arrhenius equation from the plot of 1 / T peak versus ln(ω)

$$\varepsilon''(T) = \frac{\omega\tau(T)}{1+\omega^2\tau^2(T)} \qquad \textbf{\textit{Eq}}.\ \text{S1}$$

$$\frac{1}{\tau} = \omega_0 \exp(-\frac{E_a}{k_B T}) \qquad \textbf{\textit{Eq}}.\ \text{S2}$$

where f is the characteristic relaxation frequency, ω is angular frequency, $\tau(T)$ is the relaxation time, E_a is the activation energy for the phase transition, T_p is the temperature of an ε'' peak, and k_B is the Boltzmann constant, ω_0 is a pre-exponential factor.

Table S1. Fitting data of Cole-Cole semicircles of **1** at different temperatures.

T (K)	ε_0	ε_∞	τ (s)	α
245	5.17	3.66	6.12×10^{-4}	0.140
250	4.96	3.65	2.38×10^{-4}	0.157
255	4.79	3.64	1.20×10^{-4}	0.155
260	4.65	3.63	6.09×10^{-5}	0.156
265	4.54	3.62	3.27×10^{-5}	0.164

Table S2. Crystal data collection and structure refinement of **1** at different temperatures

Compound		**$(C_5NClH_{13})_2VOCl_4$ (1)**	
temperature (K)	200	300	365
phase	LTP	ITP	HTP
formula weight	453.97	453.97	453.97
crystal system	monoclinic	monoclinic	cubic
space group	$P2_1$	$P2_1/n$	$Fm\bar{3}m$
a (Å)	8.75140(10)	8.7533(4)	12.8565(11)
b (Å)	9.04080(10)	9.0953(4)	12.8565(11)
c (Å)	12.5409(2)	12.7626(6)	12.8565(11)
β (deg)	95.9650(10)	95.135(4)	90
volume (Å^3)	986.86(2)	1012.00(8)	2125.0(5)
Z	2	2	4
Scan mode	ω-scan	ω-scan	ω-scan
crystal size (mm^3)	0.1× 0.2 × 0.15	0.1× 0.2 × 0.15	0.1× 0.2 × 0.15
μ (mm^{-1})	11.654	11.365	10.824
F(000)	466.0	466.0	932.0
radiation	Cu Kα	Cu Kα	Cu Kα

2θ range for data collection (deg)	7.088-151.23	11.784-148.122	11.922-125.092
index ranges	$-10 \leq h \leq 10$, $-11 \leq k \leq 11$, $-15 \leq l \leq 15$	$-7 \leq h \leq 10$, $-11 \leq k \leq 11$, $-15 \leq l \leq 15$	$-10 \leq h \leq 11$, $-13 \leq k \leq 10$, $-12 \leq l \leq 14$
density (calcd) (g cm^{-3})	1.528	1.490	1.419
reflections collected	13844	10601	495
R_{int}	0.0476	0.0556	0.0338
Refinement method	full-matrix least-squares on F^2		
data/restraints/parameters	4026/1/188	2013/0/131	121/21/40
Goodness-of-fit on F^2	1.054	1.131	1.155
R_1, ωR_2 [$I > 2\sigma(I)$]	0.0423, 0.1108	0.0758, 0.2182	0.0554, 0.1461
R_1, ωR_2 [all data]	0.0444, 0.1124	0.0878, 0.2326	0.0918, 0.2003
ρ_{max}, ρ_{min} (e $Å^{-3}$)	0.90, -0.43	1.08, -0.89	0.16, -0.19

References

S1. G. Sheldrick, *Acta Crystallogr., Sect. A*, 2015, **71**, 3-8.

S2. G. Sheldrick, Acta Crystallogr., Sect. C, 2015, **71**, 3-8.

S3. O.V. Dolomanov, L.J. Bourhis, R.J. Gildea, J.A.K. Howard, H. Puschmann, *J. Appl. Crystallogr.*, 2009, **42**, 339-341.