Electronic Supplementary Information for

Plastic Phase Transitions in Tris(hydroxymethyl)aminomethane Perchlorate

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Experimental

Materials. Perchloric acid and Tris(hydroxymethyl)aminomethane were purchased from Aladdin and used as received. Methyl alcohol was purchased from Merck and used as the solvent.Crystallography.

Crystal growth. A stoichiometric mixture of tris(hydroxymethyl)aminomethane and perchloric acid was allowed to slowly evaporate for crystal growth. Colorless block-shaped crystals were obtained after one week at ambient conditions.

Single-crystal diffraction. The variable temperature single crystal X-ray diffraction (XRD) data was carried out by using a Rigaku Oxford diffractometer with Cu$K\alpha$ radiation ($\lambda = 0.71073$ Å). The direct method was used to solve the crystal structure and the SHELXTL-2014 program package was used to correct it by the full-matrix least-squares method. For all non-hydrogen atoms, their anisotropy is refined. All hydrogen atoms are generated geometrically and at the same time in proper positions. CCDC 2321879 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, by emailing

data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

Powder X-ray diffraction (PXRD). Variable-temperature powder X-ray diffraction measurements were performed on a Rigaku D/MAX 2000 PC X-ray diffractometer. The measurement condition is in a 2θ range of 5°-50°, the step size is 0.02°, and the corresponding PXRD pattern is obtained.

Differential scanning calorimetry (DSC) The DSC measurement is performed by using a PerkinElmer Diamond DSC instrument. Added the power sample to an alumina crucible and cover it. Then the powder sample was studied in by heating and cooling with a rate of 5 $K \cdot min^{-1}$ at nitrogen atmosphere.

Hirshfeld surface analysis The Hirshfeld surfaces and their associated 2D-fingerprint plots was conducted using the Crystal Explorer software, utilizing CIF format structure files as input.[1,2] The morphology of these surfaces is contingent on the interactions both between molecules within the crystal and between atoms within the molecule. All Hirshfeld surfaces were generated at a standard high surface resolution. The intensity of molecular interactions is visually represented on the Hirshfeld surface through a color scheme comprising red, blue, and white regions. Specifically, white regions correspond precisely to van der Waals contact distances, blue regions indicate longer contacts, and red regions signify closer contacts.

The normalized contact distance, denoted as d_{norm}, is derived from the parameters de, di, and the van der Waals (vdW) radii of the two atoms, one external (r_e^{vdW}) and one internal (r_i^{vdW}) to the surface. Mathematically, d_{norm} is defined as:

$$d_{\text{norm}} = \frac{d_i - r^{vdW}}{r^{vdW}_i} + \frac{d_e - r}{r^{vdW}_e}$$

The d_{norm} value is a valuable metric for identifying close intermolecular interactions. A smaller d_{norm} value indicates stronger intermolecular interactions within the system.

Dielectric properties measurements. The complex dielectric permittivity curves were measured on an automatic impedance Tonghui 2828 analyzer. Dielectric studies were performed on pressed-powder pellets samples, and conductive silver glue was deposited on the surface of electrode to simulate parallel plate capacitors.

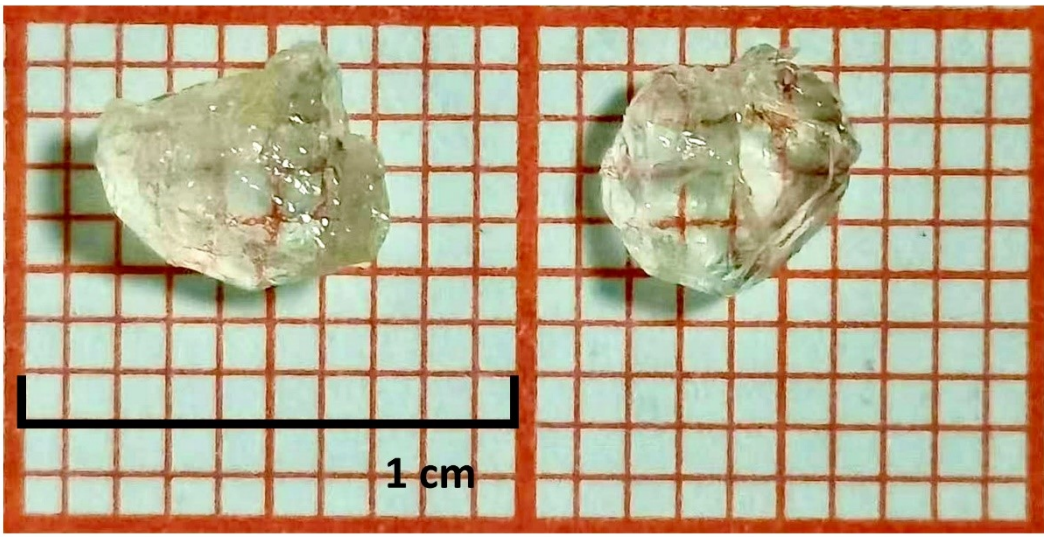

Figure S1. Crystal picture of Tris-$HClO_4$.

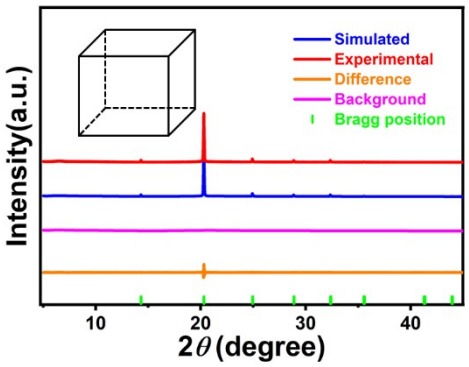

Figure S2. The final Rietveld refinement plot of Tris-$HClO_4$ structure at 403K in HTP. : experimental pattern (red line), calculated pattern (blue line), difference profile (yellow line) and background profile (green dot).

	A	B	C	D	E	F	G	H	I	J	K	L	M	N
	#	F O M	Rwp	Space Group	I T #	Option	System	a	b	c	alpha	beta	gamma	Volume
1	1	0.00000000	7.85157846	PM-3M	221	Origin-1	Cubic	6.17843400	6.17843400	6.17843400	90.00000000	90.00000000	90.00000000	235.84964957
2	2	0.00000000	7.85157846	PM-3	200	Origin-1	Cubic	6.17843400	6.17843400	6.17843400	90.00000000	90.00000000	90.00000000	235.84964957
3	3	0.00000000	7.85157846	P-43M	215	Origin-1	Cubic	6.17843400	6.17843400	6.17843400	90.00000000	90.00000000	90.00000000	235.84964957
4	4	0.00000000	7.85157846	P23	195	Origin-1	Cubic	6.17843400	6.17843400	6.17843400	90.00000000	90.00000000	90.00000000	235.84964957
5	5	0.00000000	7.85157846	P432	207	Origin-1	Cubic	6.17843400	6.17843400	6.17843400	90.00000000	90.00000000	90.00000000	235.84964957
6	6	-182.65700526	9.54915566	P213	198	Origin-1	Cubic	6.17843400	6.17843400	6.17843400	90.00000000	90.00000000	90.00000000	235.84964957
7	7	-182.65700526	9.54915566	P4232	208	Origin-1	Cubic	6.17843400	6.17843400	6.17843400	90.00000000	90.00000000	90.00000000	235.84964957
8	8	-335.40071388	10.77571345	P4332	212	Origin-1	Cubic	6.17843400	6.17843400	6.17843400	90.00000000	90.00000000	90.00000000	235.84964957
9	9	-335.40071388	10.77571345	P4132	213	Origin-1	Cubic	6.17843400	6.17843400	6.17843400	90.00000000	90.00000000	90.00000000	235.84964957
10	10	-383.11449023	11.12035521	PN-3M	224	Origin-1	Cubic	6.17843400	6.17843400	6.17843400	90.00000000	90.00000000	90.00000000	235.84964957
11	11	-383.11449023	11.12035521	PN-3	201	Origin-1	Cubic	6.17843400	6.17843400	6.17843400	90.00000000	90.00000000	90.00000000	235.84964957
12	12	-383.11449023	11.12035521	PN-3	201	Origin-2	Cubic	6.17843400	6.17843400	6.17843400	90.00000000	90.00000000	90.00000000	235.84964957
13	13	-383.11449023	11.12035521	PN-3M	224	Origin-2	Cubic	6.17843400	6.17843400	6.17843400	90.00000000	90.00000000	90.00000000	235.84964957
14	14	-573.70830546	12.43177435	P-43N	218	Origin-1	Cubic	6.17843400	6.17843400	6.17843400	90.00000000	90.00000000	90.00000000	235.84964957
15	15	-573.70830546	12.43177435	PM-3N	223	Origin-1	Cubic	6.17843400	6.17843400	6.17843400	90.00000000	90.00000000	90.00000000	235.84964957

Figure S3. The simulated high-temperature structure of Tris-$HClO_4$ at 403 K. Through the Pawley refinements of the PXRD data, we obtained the cubic point group *m*-3*m*, among which the most possible space group is *Pm*-3*m*.

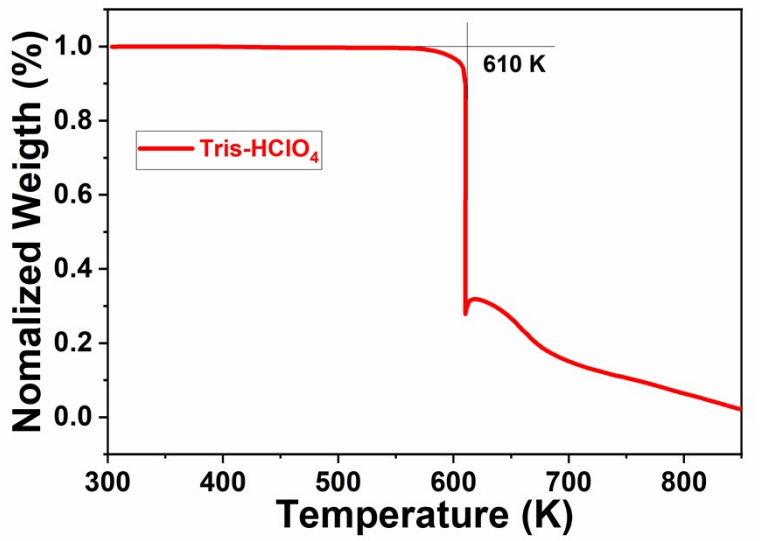

Figure S4. Thermogravimetric analysis curves of Tris-$HClO_4$.

Summary of crystal data

Table S1. Crystal data for Tris-$HClO_4$

Compound	**Tris-$HClO_4$**
Temperature	300 K
Formula	$C_4H_{12}ClNO_7$
weight	221.6
Crystal system	trigonal
Space group	*R*-3
a (Å)	8.0483(2)
b (Å)	8.0483(2)
c (Å)	23.8037(5)
α (°)	90
β (°)	90
γ (°)	120
Volume /Å^3	1335.31(7)
Z	6
Density/g cm^{-3}	1.653
μ/mm^{-1}	4.003
F(000)	696.0
Crystal size/mm^3	0.3 × 0.2 × 0.1
Radiation	Cu Kα (λ = 1.54184)
2θ range for data collection/°	11.152 to 148.66
Index ranges	-9 ≤ h ≤ 9, -9 ≤ k ≤ 9, -28 ≤ l ≤ 28
Reflections collected	1186
Independent reflections	584 [Rint = 0.0105, Rsigma = 0.0085]
Data/restraints/parameters	584/0/43

R_1	0.0547
wR_2	0.1439
GOF	1.065

Table S2. Bond lengths [Å] and angles [°] for Tris-$HClO_4$.

Temperature	300 K		
Atoms	Distances	Atoms	Angles
Cl01-O4	1.409(3)	O4-Cl01-O4[1]	110.35(17)
Cl01-O4[1]	1.409(3)	O4[1]-Cl01-O4[2]	110.35(17)
Cl01-O4[2]	1.409(3)	O4-Cl01-O4[2]	110.35(17)
Cl01-O5	1.399(5)	O5-Cl01-O4[2]	108.57(17)
O002-C005	1.427(3)	O5-Cl01-O4	108.58(17)
N1-C004	1.510(5)	O5-Cl01-O4[1]	108.57(17)
C004-C005[1]	1.528(3)	N1-C004-C005	108.01(17)
C004-C005[2]	1.528(3)	N1-C004-C005[2]	108.01(17)
C004-C005	1.528(3)	N1-C004-C005[1]	108.01(17)
		C005[2]-C004-C005[1]	110.90(16)
		C005[1]-C004-C005	110.90(16)
		C005[2]-C004-C005	110.90(16)
		O002-C005-C004	111.8(2)

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

Table S3. Hydrogen Bonds for Tris-$HClO_4$.

D	H	A	d(*D*-H)/Å	d(H-*A*)/Å	d(D-*A*)/Å	*D*-H-*A*/°
N1	H1A	O1[1]	0.89	2.02	2.893	166.9
N1	H1B	O1[2]	0.89	2.02	2.893	166.9
N1	H1C	O1[3]	0.89	2.02	2.893	166.9

Symmetry codes: (i) 2/3-Y+X ,1/3+X,4/3-Z , (ii) 2/3-X,1/3-Y,4/3-Z; (iii) 2/3+Y,1/3-X+Y,4/3-Z.

REFERENCES

1. Collins, A., Wilson, C. C. & Gilmore, C. J.， Comparing entire crystal structures using cluster analysis and fingerprint plots. *Cryst. Eng. Comm.* **2009**, *12* (3), 801-809.

2. Spackman, P. R. *et al.* CrystalExplorer: a program for Hirshfeld surface analysis, visualization and quantitative analysis of molecular crystals. *J. Appl. Crystallogr.* **2021**, *54* (3), 1006-1011.