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Support Information

Visual Low-high Interchange in Dielectric Switch for Trimethylchloroethylamine Tetrachlozincate with Large Leap Symmetry Breaking

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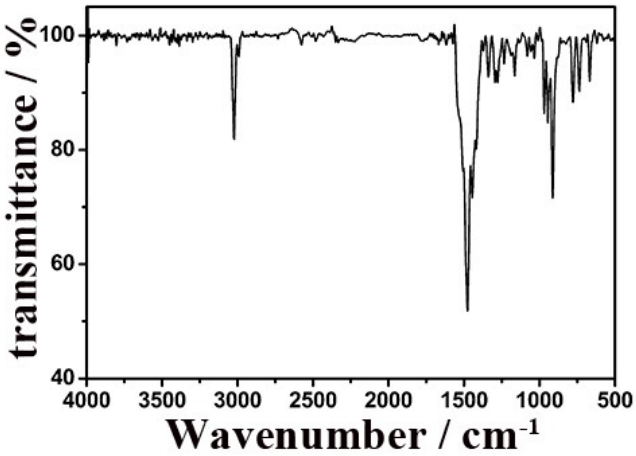

Fig S1. The IR (a) of compound **1**

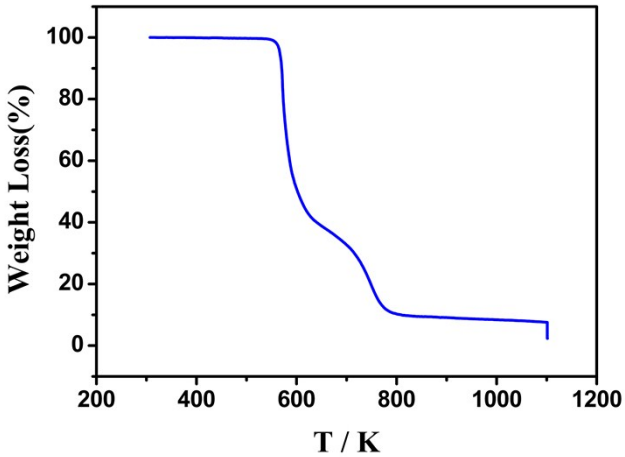

Fig S2. TG curves of compound **1**

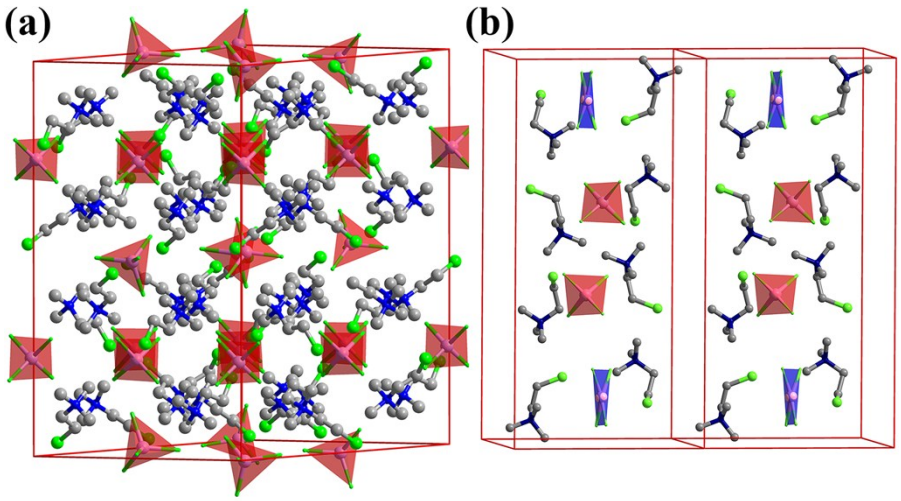

Fig S3. Packing structures view of 1 at LTP (a) and HTP (b), showing the similarities and differences of lattice framework. The ordered $ZnCl_4$ anions form the red tetrahedron and disordered $ZnCl_4$ anions form the blue tetrahedron. H atoms were omitted for clarity.

Table S1. Crystal data and structure refinements for 1 at LTP and HTP.

	LTP	HTP
T / K	288(2)	370(2)
Formula weight	452.42	904.84
Crystal system	monoclinic	tetragonal
Space group	$P2_1/c$	$I4_1/a$
a / Å	24.5577(7)	12.7985(3)
b / Å	18.3997(4)	12.7985(3)
c / Å	18.1621(4)	25.8884(6)
α/ °	90.00	90.00
β / °	92.376(2)	90.00
γ/ °	90.00	90.00
V / Å^3	8199.6(3)	4240.6(3)

Z	16	4
D_{calc}/ g·cm^{-3}	1.466	1.417
μ / mm^{-1}	1.97	1.91
F(000)	3712.0	1856
ϑ range / °	2.5 - 31.9	2.8 - 21.6
Reflns Collected(R_{int})	61763(0.0374)	7976(0.0299)
Independent reflns	14440	1868
No. of parameters	697	75
R_1[a] [$I > 2\sigma(I)$]	0.047	0.201
wR_2[b][$I > 2\sigma(I)$]	0.126	0.607
GOF	1.12	1.14
$\Delta\rho$[C] / e·Å^{-3}	0.79, -0.81	1.53, -1.24

Table S2 Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2) at 288 K (No hydrogen atoms)

	x	y	z	U_{iso}*/U_{eq}
Zn1	0.250168 (17)	0.50486 (2)	0.00952 (2)	0.04040 (12)
Cl2	0.20002 (4)	0.40232 (5)	0.01513 (6)	0.0605 (3)
Cl4	0.29883 (5)	0.50697 (6)	−0.09352 (6)	0.0627 (3)
Cl3	0.19446 (5)	0.60243 (6)	0.00625 (7)	0.0696 (3)
Zn2	0.248584 (17)	0.50366 (2)	0.50815 (2)	0.04112 (12)
Cl7	0.29853 (5)	0.40074 (5)	0.51646 (7)	0.0642 (3)
Cl6	0.19500 (5)	0.50733 (6)	0.40428 (6)	0.0632 (3)
Zn3	0.48639 (2)	0.25174 (2)	0.27403 (2)	0.04941 (13)
Cl10	0.49981 (5)	0.15034 (6)	0.34451 (7)	0.0697 (3)
Zn4	0.014617 (19)	0.27020 (2)	0.74545 (2)	0.04668 (12)
Cl14	0.00484 (5)	0.34115 (7)	0.64347 (6)	0.0699 (3)
Cl9	0.40043 (5)	0.24726 (6)	0.22577 (7)	0.0731 (3)
Cl1	0.30761 (5)	0.51092 (7)	0.10888 (6)	0.0747 (3)
Cl15	0.10028 (5)	0.22524 (7)	0.75226 (7)	0.0738 (3)
Cl8	0.30436 (5)	0.60092 (6)	0.50951 (7)	0.0723 (3)

Cl5	0.19625 (6)	0.51102 (8)	0.60645 (7)	0.0811 (4)
Cl13	0.00190 (5)	0.34157 (6)	0.84598 (6)	0.0689 (3)
Cl19	0.46567 (5)	0.42474 (7)	0.54765 (6)	0.0734 (3)
Cl17	0.02520 (5)	0.41345 (6)	0.03471 (6)	0.0711 (3)
Cl21	0.52913 (5)	0.96428 (7)	0.41437 (7)	0.0804 (4)
Cl12	0.49784 (6)	0.35067 (6)	0.34789 (7)	0.0779 (4)
Cl20	0.30081 (8)	0.76854 (9)	0.69489 (9)	0.1128 (6)
Cl24	0.23037 (6)	0.32733 (7)	0.78626 (10)	0.1002 (5)
Cl23	0.20000 (8)	0.77863 (11)	0.82680 (10)	0.1210 (6)
Cl18	0.27365 (7)	0.34198 (8)	0.29264 (12)	0.1135 (6)
Cl16	−0.04489 (7)	0.17823 (9)	0.74559 (12)	0.1272 (7)
Cl11	0.54614 (9)	0.25368 (14)	0.18454 (11)	0.1566 (10)
N3	0.37724 (14)	0.50311 (17)	0.71434 (17)	0.0506 (8)
N4	0.37161 (13)	0.79449 (17)	0.49971 (18)	0.0507 (8)
N6	0.86683 (13)	0.69961 (17)	0.50158 (18)	0.0516 (8)
N5	0.62557 (14)	0.80608 (16)	0.50473 (18)	0.0511 (8)
N8	0.12611 (14)	0.49497 (19)	0.80486 (19)	0.0568 (9)
N7	0.12159 (14)	0.79519 (18)	1.01713 (19)	0.0565 (9)
N1	0.11935 (14)	0.50698 (17)	0.19734 (17)	0.0512 (8)
C17	0.41308 (18)	0.7350 (2)	0.5046 (3)	0.0617 (11)
N2	0.37399 (16)	0.5135 (2)	0.31512 (19)	0.0661 (8)
C14	0.40488 (18)	0.4953 (2)	0.6418 (2)	0.0549 (10)
C4	0.08852 (17)	0.4938 (2)	0.1252 (2)	0.0517 (10)
C22	0.66942 (18)	0.7985 (2)	0.4502 (3)	0.0680 (12)
C37	0.08732 (18)	0.4882 (3)	0.7407 (2)	0.0643 (12)
C11	0.4175 (2)	0.5052 (3)	0.7772 (3)	0.0776 (15)
C16	0.4002 (2)	0.8661 (2)	0.5001 (3)	0.0709 (13)
C24	0.59387 (18)	0.8757 (2)	0.4926 (2)	0.0586 (11)
C3	0.16491 (18)	0.4533 (3)	0.2101 (2)	0.0679 (12)
C26	0.82613 (18)	0.7058 (3)	0.5591 (2)	0.0640 (11)

C27	0.9053 (2)	0.7620 (2)	0.5058 (3)	0.0775 (15)
C18	0.3377 (2)	0.7871 (3)	0.4298 (3)	0.0740 (13)
C19	0.3311 (2)	0.7869 (3)	0.5598 (3)	0.0738 (13)
C36	0.16076 (19)	0.5600 (3)	0.7972 (3)	0.0735 (13)
C28	0.8375 (2)	0.7013 (3)	0.4282 (3)	0.0825 (15)
C32	0.0935 (2)	0.8672 (2)	1.0155 (3)	0.0795 (15)
C6	0.40213 (19)	0.5089 (3)	0.3882 (2)	0.0661 (8)
C34	0.1657 (2)	0.7897 (3)	0.9611 (3)	0.0736 (13)
C12	0.3372 (2)	0.4438 (3)	0.7241 (3)	0.0767 (14)
C25	0.5664 (2)	0.8817 (3)	0.4190 (3)	0.0773 (14)
C33	0.0810 (2)	0.7357 (2)	1.0068 (3)	0.0788 (15)
C13	0.3476 (2)	0.5742 (3)	0.7125 (3)	0.0889 (17)
C31	0.1516 (3)	0.7866 (3)	1.0899 (3)	0.0983 (19)
C5	0.0624 (2)	0.4203 (2)	0.1202 (2)	0.0669 (12)
C2	0.1432 (2)	0.5817 (3)	0.1955 (3)	0.0882 (16)
C15	0.4334 (2)	0.4243 (2)	0.6334 (2)	0.0692 (13)
C23	0.6513 (3)	0.8087 (3)	0.5800 (3)	0.101 (2)
C20	0.3553 (3)	0.7860 (4)	0.6345 (3)	0.0992 (18)
C8	0.4133 (2)	0.5091 (3)	0.2570 (3)	0.0880 (17)
C38	0.0951 (2)	0.5036 (3)	0.8726 (3)	0.0859 (16)
C21	0.5892 (2)	0.7415 (2)	0.4980 (3)	0.0738 (14)
C35	0.1447 (3)	0.7945 (4)	0.8845 (3)	0.1045 (19)
C39	0.1584 (3)	0.4254 (4)	0.8211 (4)	0.142 (2)
C1	0.08225 (19)	0.5033 (3)	0.2602 (2)	0.0643 (12)
C7	0.3440 (3)	0.5835 (4)	0.3076 (3)	0.115 (2)
C9	0.3262 (3)	0.4653 (4)	0.3067 (4)	0.151 (3)
C40	0.1849 (3)	0.3961 (4)	0.7614 (4)	0.142 (2)
C10	0.3330 (4)	0.3913 (4)	0.3093 (6)	0.176 (4)
Cl25	0.96787 (6)	0.53827 (7)	0.57513 (8)	0.0843 (4)
C41	0.89839 (19)	0.6287 (2)	0.5071 (2)	0.0620 (11)

C44	0.9295 (2)	0.6198 (3)	0.5785 (3)	0.0870 (16)

Table S3 Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2) at 370 K (No hydrogen atoms)

	x	*y*	*z*	U_{iso}*/U_{eq}
Zn1	0.0000	−0.2500	0.8750	0.0734 (5)
N1	0.1928 (3)	−0.0011 (4)	0.80010 (17)	0.689 (2)
C4	0.0972 (3)	−0.0128 (6)	0.83306 (17)	0.674 (5)
C5	0.120 (2)	0.0175 (5)	0.8879 (3)	0.688 (15)
Cl1	0.0946 (3)	−0.1432 (3)	0.92583 (13)	0.1585 (14)
C2	0.2286 (5)	−0.1043 (3)	0.7793 (2)	0.682 (6)
C1	0.2818 (3)	0.0450 (5)	0.8300 (2)	0.689 (2)
C3	0.1725 (6)	0.0690 (4)	0.75481 (17)	0.690 (5)
Cl2	0.103 (3)	0.1474 (11)	0.9125 (6)	0.689 (2)
Zn2	0.5000	0.2500	0.8750	0.1640 (16)
Cl3	0.4588 (8)	0.2179 (11)	0.8036 (3)	0.532 (6)

Table S4 Selected structural data for 1 at 288K and 370K

	288 K		370 K	
Bond lengths (Å)	Zn1-Cl1	2.2468 (11)	Zn1-Cl1	2.250 (3)
	Zn1-Cl3	2.2565 (11)	Zn1-Cl1^{i}	2.250 (3)
	Zn1-Cl2	2.2577 (10)	Zn1-Cl1^{ii}	2.250 (3)
	Zn1-Cl4	2.2622 (11)	Zn1-Cl1^{iii}	2.250 (3)
	Zn2-Cl5	2.2467 (12)	Zn2-Cl3	1.965 (7)
	Zn2-Cl8	2.2531 (11)	Zn2-Cl3^{iv}	1.965 (7)
	Zn2-Cl6	2.2559 (11)	Zn2-Cl3^{v}	1.965 (7)
	Zn2-Cl7	2.2578 (11)	Zn2-Cl3^{vi}	1.965 (7)
	Zn3-Cl11	2.2347 (16)	N1-C2	1.498 (5)

Zn3-Cl9	2.2535 (13)	N1-C3	1.499 (5)
Zn3-Cl12	2.2716 (12)	N1-C4	1.499 (5)
Zn3-Cl10	2.2788 (11)	N1-C1	1.499 (6)
Zn4-Cl16	2.2358 (13)	C4-C5	1.501 (2)
Zn4-Cl15	2.2590 (13)	C5-Cl2	1.794(2)
Zn4-Cl14	2.2706 (11)		
Zn4-Cl13	2.2810 (11)		
Cl19-C15	1.777 (4)		
Cl17-C5	1.773 (4)		
Cl21-C25	1.774 (4)		
Cl20-C20	1.795 (6)		
Cl24-C40	1.735 (6)		
Cl23-C35	1.773 (6)		
Cl18-C10	1.733 (8)		
N3-C11	1.479 (5)		
N3-C12	1.484 (5)		
N3-C13	1.496 (6)		
N3-C14	1.515 (5)		
N4-C16	1.494 (5)		
N4-C18	1.495 (5)		
N4-C17	1.495 (5)		
N4-C19	1.512 (6)		
N6-C26	1.479 (5)		
N7-C31	1.495 (6)		
N7-C34	1.520 (6)		
N1-C1	1.491 (5)		
N1-C2	1.496 (5)		
N1-C3	1.503 (5)		
N1-C4	1.505 (5)		
N2-C8	1.462 (6)		

	N2-C9	1.475 (7)		
	N2-C6	1.473 (5)		
	N2-C7	1.486 (7)		
	C14-C15	1.492 (6)		
	C4-C5	1.498 (6)		
	C24-C25	1.477 (6)		
	C19-C20	1.459 (7)		
	C34-C35	1.467 (7)		
	C39-C40	1.397 (7)		
	C9-C10	1.373 (7)		
	Cl25-C44	1.774 (5)		
	C41-C44	1.488 (7)		
	N6-C27	1.486 (5)		
	N6-C28	1.487 (6)		
	N6-C41	1.518 (5)		
	N5-C23	1.483 (6)		
	N5-C21	1.488 (5)		
	N5-C22	1.499 (6)		
	N5-C24	1.510 (5)		
	N8-C37	1.480 (5)		
	N8-C36	1.478 (6)		
	N8-C38	1.483 (6)		
	N8-C39	1.529 (7)		
	N7-C33	1.488 (6)		
	N7-C32	1.494 (5)		
Bond angles (°)	Cl1-Zn1-Cl3	109.97 (5)	Cl1-Zn1-Cl1^{i}	110.00 (9)
	Cl1-Zn1-Cl2	109.31 (5)	Cl1-Zn1-Cl1^{ii}	108.43 (18)
	Cl3-Zn1-Cl2	109.56 (5)	Cl1^{i}-Zn1-Cl1^{ii}	110.00 (9)
	Cl1-Zn1-Cl4	109.15 (5)	Cl1-Zn1-Cl1^{iii}	110.00 (9)

Cl3-Zn1-Cl4	107.76 (5)	Cl1^{i}-Zn1-Cl1^{iii}	108.43 (18)
Cl2-Zn1-Cl4	111.07 (4)	Cl1^{ii}-Zn1-Cl1^{iii}	110.00 (9)
Cl5-Zn2-Cl8	108.11 (5)	Cl3-Zn2-Cl3^{iv}	152.2 (5)
Cl5-Zn2-Cl6	109.25 (5)	Cl3-Zn2-Cl3^{v}	152.2 (5)
Cl8-Zn2-Cl6	108.58 (5)	Cl3^{iv}-Zn2-Cl3^{v}	39.7 (7)
Cl5-Zn2-Cl7	108.94 (5)	Cl3-Zn2-Cl3^{vi}	39.7 (7)
Cl8-Zn2-Cl7	109.70 (5)	Cl3^{iv}-Zn2-Cl3^{vi}	152.2 (5)
Cl6-Zn2-Cl7	112.17 (4)	Cl3^{v}-Zn2-Cl3^{vi}	152.2 (5)
Cl11-Zn3-Cl9	110.51 (7)		
Cl11-Zn3-Cl12	110.35 (8)		
Cl9-Zn3-Cl12	110.49 (5)		
Cl11-Zn3-Cl10	109.73 (7)		
Cl9-Zn3-Cl10	107.45 (5)		
Cl12-Zn3-Cl10	108.23 (5)		
Cl16-Zn4-Cl15	109.27 (6)		
Cl16-Zn4-Cl14	112.89 (7)		
Cl15-Zn4-Cl14	108.78 (5)		
Cl16-Zn4-Cl13	108.89 (7)		
Cl15-Zn4-Cl13	108.97 (5)		
Cl14-Zn4-Cl13	107.97 (5)		
C11-N3-C12	110.6 (4)	C2-N1-C3	107.5 (4)
C11-N3-C13	107.6 (4)	C2-N1-C4	111.4 (4)
C12-N3-C13	108.7 (4)	C3-N1-C4	111.4 (4)
C11-N3-C14	111.4 (3)	C2-N1-C1	107.5 (4)
C12-N3-C14	110.9 (3)	C3-N1-C1	107.4 (4)
C13-N3-C14	107.4 (3)	C4-N1-C1	111.5 (4)
C16-N4-C18	109.2 (3)	N1-C4-C5	110.9 (11)
C16-N4-C17	109.1 (3)	Cl2-C5-C4	123.5(2)
C18-N4-C17	109.7 (3)		
C16-N4-C19	113.6 (3)		

C18-N4-C19	104.1 (4)
C17-N4-C19	110.9 (3)
C26-N6-C27	110.5 (3)
C26-N6-C28	108.3 (4)
C27-N6-C28	108.2 (4)
C26-N6-C41	112.2 (3)
C27-N6-C41	109.8 (3)
C28-N6-C41	107.6 (3)
C23-N5-C21	109.5 (4)
C23-N5-C22	108.7 (4)
C21-N5-C22	108.5 (3)
C23-N5-C24	107.7 (4)
C21-N5-C24	111.2 (3)
C22-N5-C24	111.3 (3)
C37-N8-C36	110.3 (4)
C37-N8-C38	109.0 (4)
C36-N8-C38	108.1 (4)
C37-N8-C39	113.2 (4)
C36-N8-C39	113.6 (5)
C38-N8-C39	102.1 (4)
C33-N7-C32	110.0 (4)
C33-N7-C31	109.7 (4)
C32-N7-C31	108.8 (4)
C33-N7-C34	111.1 (4)
C32-N7-C34	112.8 (4)
C31-N7-C34	104.2 (4)
C1-N1-C2	108.1 (3)
C1-N1-C3	109.1 (3)
C2-N1-C3	108.5 (4)
C1-N1-C4	111.0 (3)

C2-N1-C4	108.2 (3)
C3-N1-C4	111.9 (3)
C8-N2-C9	116.0 (5)
C8-N2-C6	110.4 (4)
C9-N2-C6	113.7 (4)
C8-N2-C7	108.7 (4)
C9-N2-C7	97.1 (5)
C6-N2-C7	110.1 (4)
C15-C14-N3	113.6 (3)
C5-C4-N1	113.4 (3)
C25-C24-N5	114.2 (3)
C20-C19-N4	114.6 (4)
C35-C34-N7	113.5 (4)
C24-C25-Cl21	108.9 (3)
C4-C5-Cl17	108.8 (3)
C14-C15-Cl19	108.3 (3)
C19-C20-Cl20	106.6 (4)
C34-C35-Cl23	107.7 (4)
C40-C39-N8	115.3 (6)
C10-C9-N2	119.8 (8)
C39-C40-Cl24	113.2 (5)
C9-C10-Cl18	114.3 (7)
C44-C41-N6	113.2 (3)
C41-C44-Cl25	108.5 (3)

Symmetry Codes (370K): (i) −*y*−1/4, *x*−1/4, −*z*+7/4; (ii) −*x*, −*y*−1/2, *z*; (iii) *y*+1/4, −*x*−1/4, −*z*+7/4; (iv) −*y*+3/4, *x*−1/4, −*z*+7/4; (v) *y*+1/4, −*x*+3/4, −*z*+7/4; (vi) −*x*+1, −*y*+1/2, *z*.