Supporting Information

Symmetry breaking through molecular engineering to achieve "on-off-on" nonlinear optical switch in a $[SnCl_6]^{2-}$ framework

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Fig. S1 ^{1}H-NMR of. *N*, *N*, *N*, *O*-tetramethylhydroxylammonium.

Fig. S2 Simulated and measured PXRD patterns of **1** (a) and **2** (b).

Fig. S3 TG measurements of **1** (a) and **2** (b).

Fig. S4 IR test of **1** (a) and **2** (b).

Fig. S5 (a) Dielectric constant of **1** at different frequencies. (b) Dielectric constant of **1** at 1 MHz (Red line is heating while black line is cooling).

Fig. S6 Maximal subgroups and minimal supergroups of the three-dimensional crystallographic point groups. The change of crystal system of **1** and **2** during the phase transition.

Table S1 Crystal data and structure refinement of **1**.

Table S2 Crystal data and structure refinement of **2**.

Synthesis

12 mL trimethylamine (33% in ethanol solution) was added into the flask and stirred in ice water batch. 15 mL 30 % H_2O_2 solution was is dropped into the solution and the mixture was left standing overnight. The mixture was then stirred at 350 K for 4 hours. The solvent was removed to afford the trimethylamine oxide as white solid (5.14 g, yielded 99.9 %).

5.14 g trimethylamine oxide and 100 mL acetonitrile were mixed and stirred in ice water batch. 6 mL dimethyl sulfate was added slowly into the solvent and the mixture was then heated to 340 K for 3 hours. The reaction mixture was quenched by the addition of 10 mL water. The solvent was removed to obtain *N*,*N*,*N*,*O*-tetramethylhydroxylammonium sulfate (7.12 g, yielded 98.0 %). The structure was confirmed by ^{1}H NMR (600 MHz, Deuterium Oxide) δ 3.78 – 3.72 (m, 3H), 3.42 – 3.37 (m, 9H) as shown in **Fig. S1**.

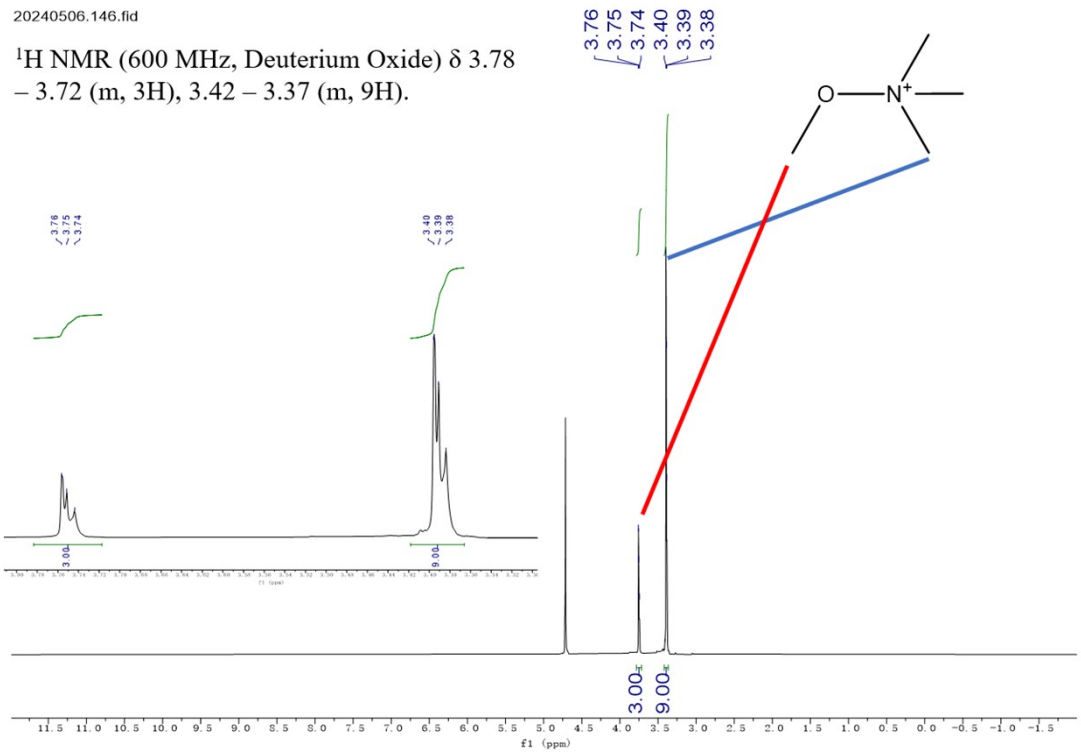

Fig. S1 [1]H-NMR of *N*, *N*, *N*, *O*-tetramethylhydroxylammonium.

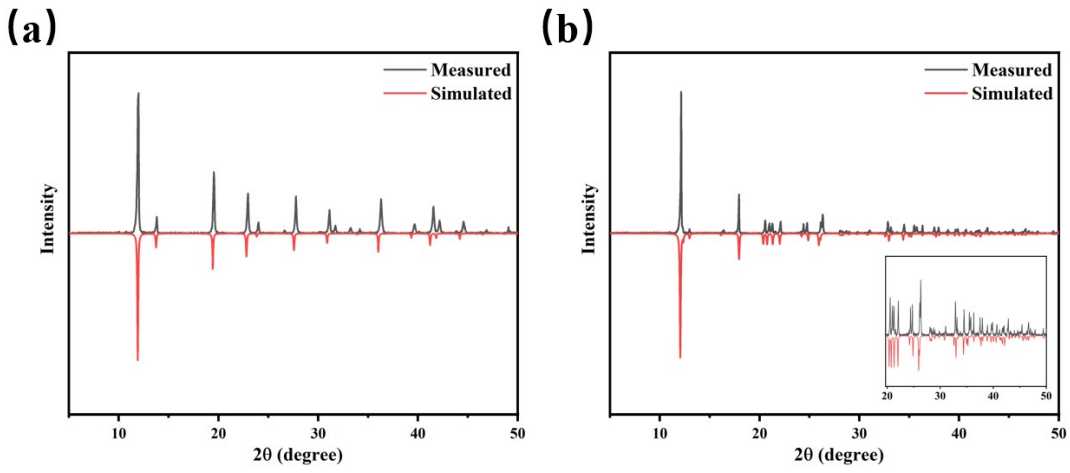

Fig. S2 Simulated and measured PXRD patterns of **1** (a) and **2** (b).

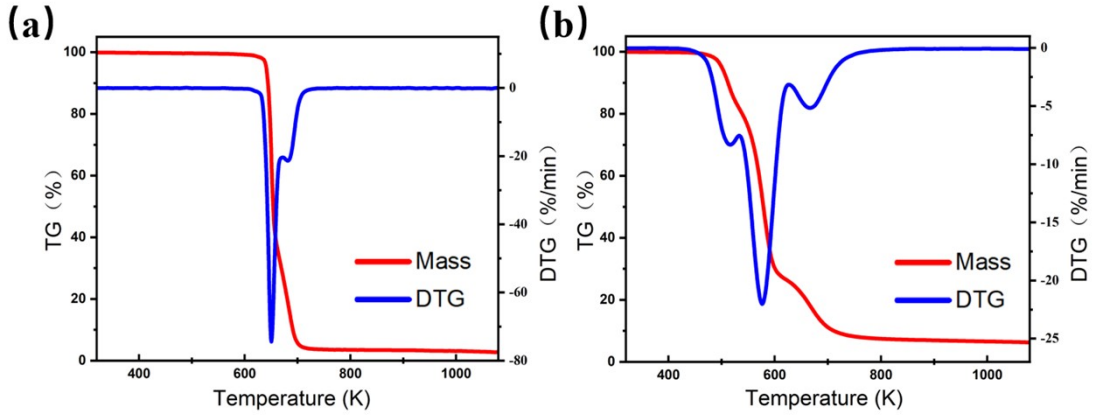

Fig. S3 TG measurements of **1** (a) and **2** (b).

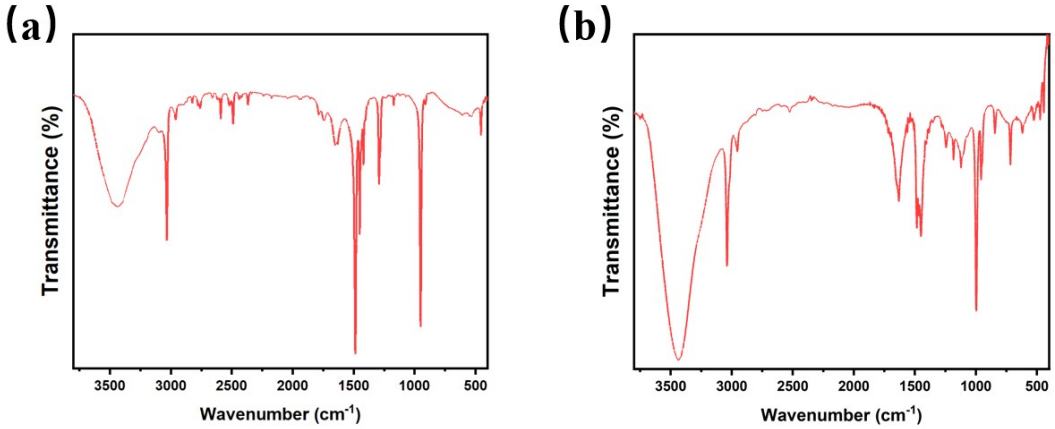

Fig. S4 IR test of **1** (a) and **2** (b).

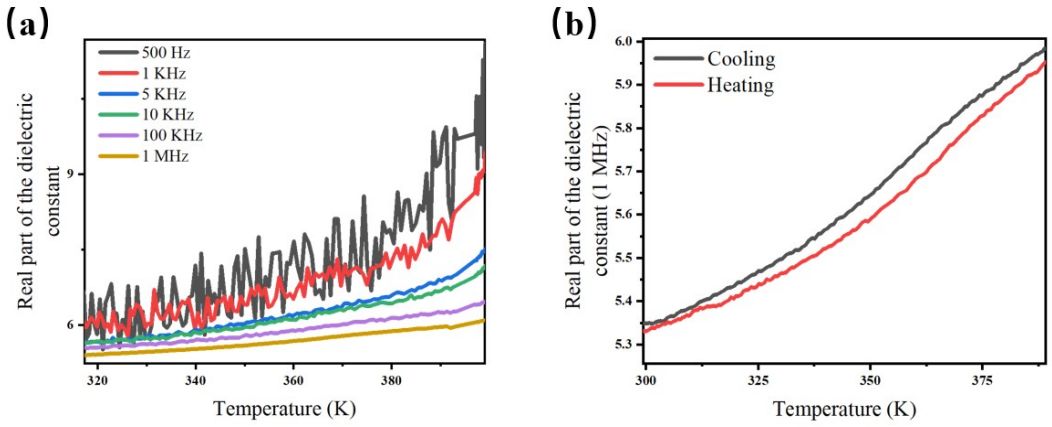

Fig. S5 (a) Dielectric constant of **1** at different frequencies. (b) Dielectric constant of **1** at 1 MHz (Red line is

heating while black line is cooling).

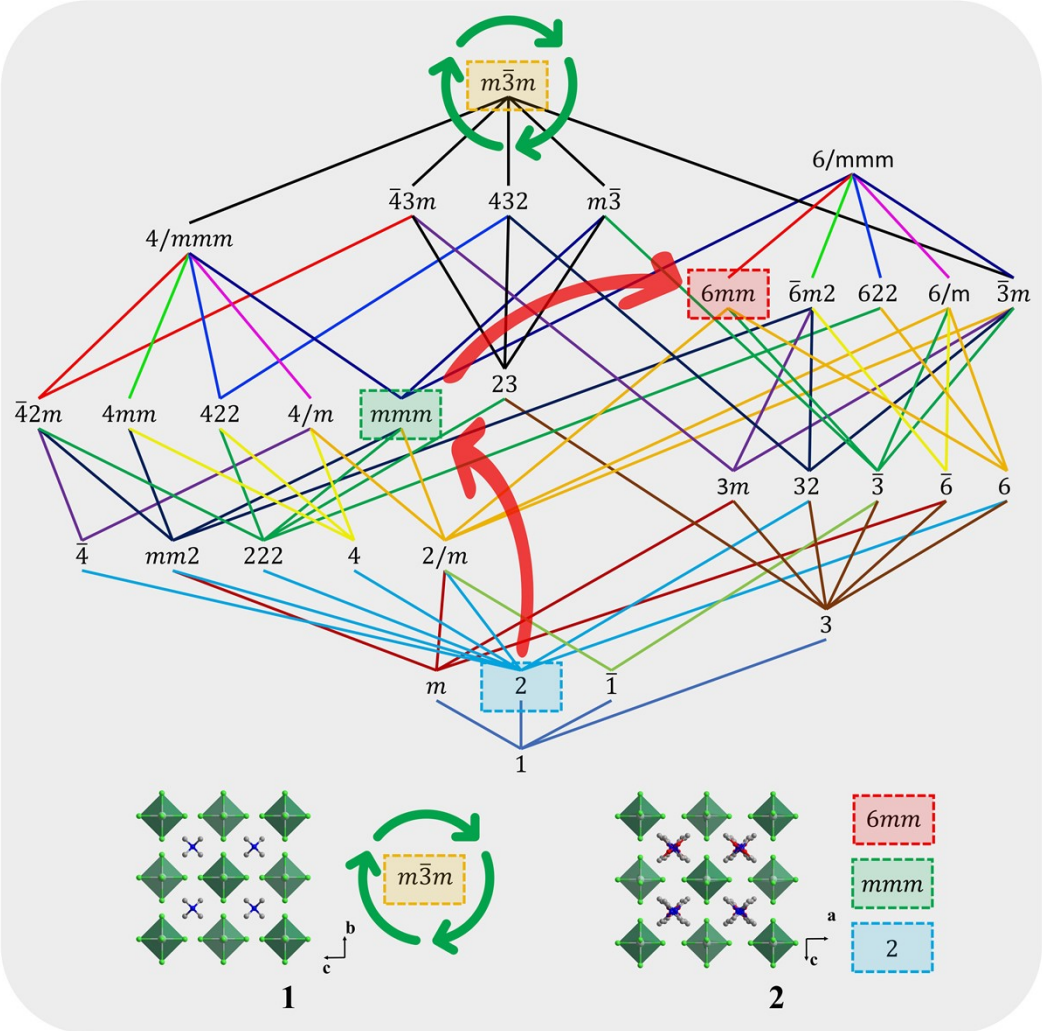

Fig. S6 Maximal subgroups and minimal supergroups of the three-dimensional crystallographic point groups. The change of crystal system of **1** and **2** during the phase transition.

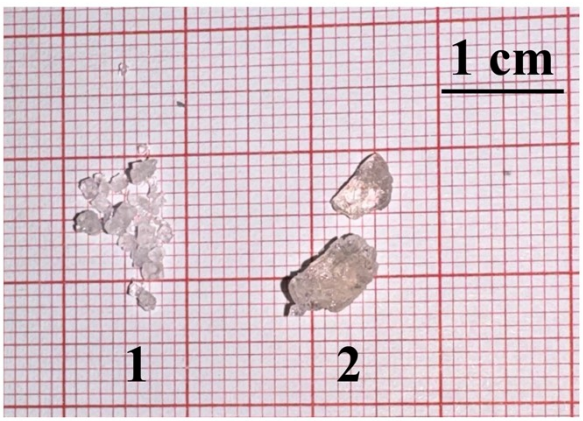

Fig. S7 Crystal sample of **1** and **2**.

Table S1 Crystal data and structure refinement of **1** at LTP.

CCDC number	2361546	2361547
Empirical formula	$C_8H_{24}Cl_6N_2Sn$	$C_8H_{24}Cl_6N_2Sn$
Formula weight	479.68	479.68
Temperature [K]	300.00	400.00
Crystal system	cubic	cubic
Space group (number)	$Fd\bar{3}c$ (228)	$Fm\bar{3}m$ (225)
a [Å]	25.724(4)	13.017(6)
b [Å]	25.724(4)	13.017(6)
c [Å]	25.724(4)	13.017(6)
α [°]	90	90
β [°]	90	90
γ [°]	90	90
Volume [Å^3]	17023(8)	2205(3)
Z	32	4
ρ_{calc} [gcm^{-3}]	1.497	1.445
μ [mm^{-1}]	1.941	1.873
F(000)	7616	952
Crystal size [mm^3]	0.15×0.14×0.12	
Crystal colour	clear light colourless	
Crystal shape	block	
Radiation	MoK_α (λ=0.71073 Å)	MoK_α (λ=0.71073 Å)
2θ range [°]	4.48 to 52.80 (0.80 Å)	10.39 to 54.68 (0.77 Å)
Index ranges	−28 ≤ h ≤ 32 −28 ≤ k ≤ 31 −32 ≤ l ≤ 32	−16 ≤ h ≤ 15 −14 ≤ k ≤ 16 −16 ≤ l ≤ 16
Reflections collected	22802	4152
Independent reflections	732 R_{int} = 0.0906 R_{sigma} = 0.0248	161 R_{int} = 0.0668 R_{sigma} = 0.0360
Completeness to θ = 25.242°	98.5 %	97.0 %
Goodness-of-fit on F^2	1.101	1.225
Final R indexes [I≥2σ(I)]	R_1 = 0.0316 wR_2 = 0.0742	R_1 = 0.0429 wR_2 = 0.1422
Final R indexes [all data]	R_1 = 0.0503 wR_2 = 0.0897	R_1 = 0.0437 wR_2 = 0.1445
Largest peak/hole [eÅ^{-3}]	0.37/−0.62	0.24/−0.48

Table S2 Crystal data and structure refinement of **2** at LTP.

CCDC number	2357973	2357974	2357975
Empirical formula	$C_8H_{24}Cl_6N_2O_2Sn$	$C_8H_{24}Cl_6N_2O_2Sn$	$C_8H_{24}Cl_6N_2O_2Sn$
Formula weight	511.68	511.68	511.68
Temperature [K]	260.00	363.00	400.00
Crystal system	monoclinic	orthorhombic	hexagonal
Space group (number)	$P2_1$ (4)	*Cmca* (64)	*P*63*mc* (186)
a [Å]	9.2612(17)	14.3092(14)	9.6998(9)
b [Å]	12.665(3)	10.9809(14)	9.6998(9)
c [Å]	9.3535(18)	13.6510(14)	12.6019(18)
α [°]	90	90	90
β [°]	114.940(7)	90	90
γ [°]	90	90	120
Volume [Å^3]	994.8(3)	2145.0(4)	1026.8(2)
Z	2	4	2
ρ_{calc} [gcm^{-3}]	1.708	1.584	1.655
μ [mm^{-1}]	2.089	1.937	2.024
F(000)	508	1016	508
Crystal size [mm^3]		0.11×0.09×0.07	
Crystal colour		clear light colourless	
Crystal shape		block	
Radiation		MoK_α (λ=0.71073 Å)	
2θ range [°]	4.85 to 52.65 (0.80 Å)	7.42 to 52.76 (0.80 Å)	9.71 to 50.05 (0.84 Å)
Index ranges	−11 ≤ h ≤ 11 −15 ≤ k ≤ 15 −11 ≤ l ≤ 11	−16 ≤ h ≤ 17 −13 ≤ k ≤ 13 −15 ≤ l ≤ 17	−11 ≤ h ≤ 10 −11 ≤ k ≤ 11 −15 ≤ l ≤ 12
Reflections collected	8615	7797	6536
Independent reflections	3942 R_{int} = 0.0430 R_{sigma} = 0.0573	1136 R_{int} = 0.0517 R_{sigma} = 0.0320	691 R_{int} = 0.0567 R_{sigma} = 0.0304
Completeness to θ = 25.242°	98.9 %	98.9 %	97.9 %
Goodness-of-fit on F^2	1.034	1.028	1.014
Final *R* indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0315 wR_2 = 0.0718	R_1 = 0.0422 wR_2 = 0.1263	R_1 = 0.0481 wR_2 = 0.1329
Final *R* indexes [all data]	R_1 = 0.0344 wR_2 = 0.0737	R_1 = 0.0600 wR_2 = 0.1442	R_1 = 0.0559 wR_2 = 0.1453
Largest peak/hole [eÅ^{-3}]	0.45/−0.45	0.61/−0.26	0.14/−0.08
Flack X parameter	0.03(2)	-	0.04(5)