Electronic Supplementary Information (ESI)

A Lead-Free Perovskite-like Hybrid with Above-room-temperature Switching of Quadratic Nonlinear Optical Properties

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Experimental section

Synthesis

All reagents and solvents used in experiment were commercial products without further purification. Compound **1** was easily synthesized by the reaction of hexamethyleneimine and antimony pentachloride with the molar ratio 2:1. Powder X-ray diffraction (PXRD) was performed on Miniflex 600 powder X-ray diffractometer.

Thermal measurements

The differential scanning calorimetry (DSC) (10 K/min, 5 K/min and 2 K/min) data was recorded by Netzsch DSC 200 F3 calorimeter. And a Mettler Toledo TGA/SDTA 851e was used to thermogravimetric analysis data.

Dielectric measurements

The complex permittivity of powder was performed on a Tonghui TH2828A analyzer in the temperature range of 310−349 K. The complex dielectric permittivity ε and ε'' ($\varepsilon = \varepsilon' - i\varepsilon''$) were measured in different frequency (500 kHz and 1000 kHz).

Linear and NLO properties

The UV/vis diffuse reflection spectrum of **1** was measured on Lambda 950 spectrometer with the range of 800−250 nm at 298 K. The FLS 920, Edinburgh Instruments was used to measure the variable-temperature NLO properties in the temperature range of 306 K to 348 K, by using an unexpanded laser beam with low divergence (pulsed by Nd:YAG laser at a wavelength of 1064 nm).

Single-crystal X-ray diffraction

Single-crystal X-ray were collected on a SuperNova diffractometer with Mo-*Kα* radiation (λ = 0.71073Å) at different temperatures (290 K and 350 K). All of crystal data were performed by the Crystalclear software package (Rigaku, 2005). The crystal structures were processed by the direct method and then refined by the full-matrix least-squares refinements on F^2, which use the

SHELXLTL software package. Non-H atoms were refined anisotropically according to all reflections with $I > 2\sigma(I)$ and all of hydrogen atoms were obtained geometrically. The supplementary crystallographic data for this paper were contained in CCDC (1588041, LTP) and CCDC (1588042, HTP).

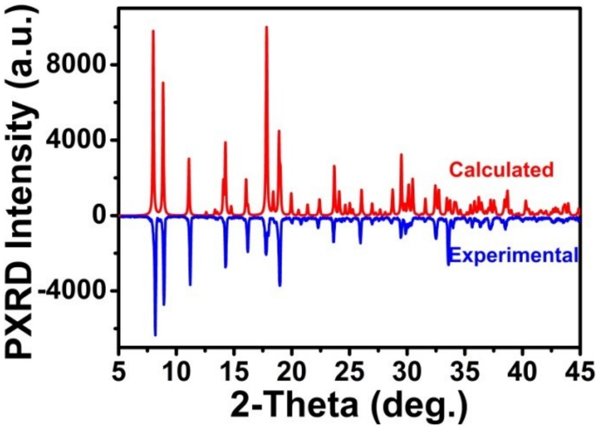

Figure S1. Experimental and calculated powder X-ray diffraction patterns of **1.**

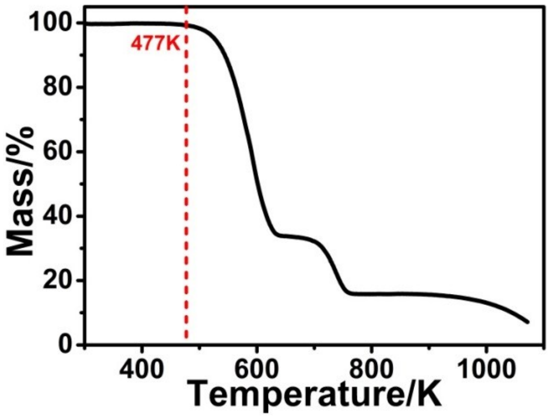

Figure S2. The TG curves of **1** with heating rate 10 K/min.

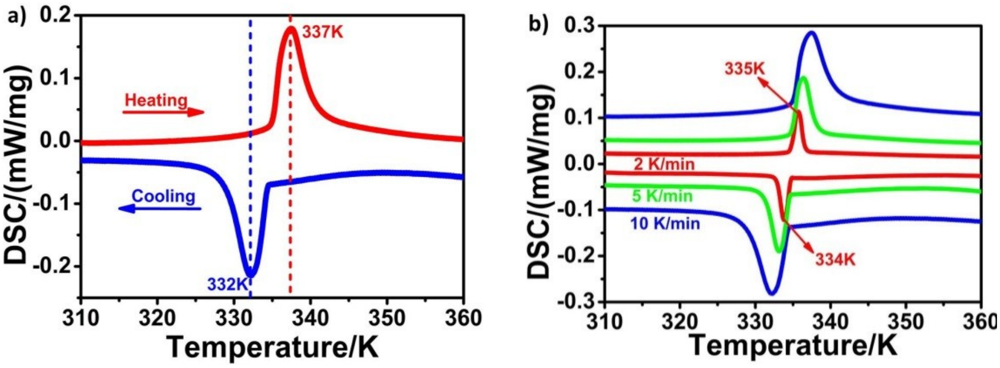

Figure S3. a) DSC curves of **1** measured at 10 K/min; b) DSC traces measured with the different heating/cooling rates (10, 5 and 2 K/min).

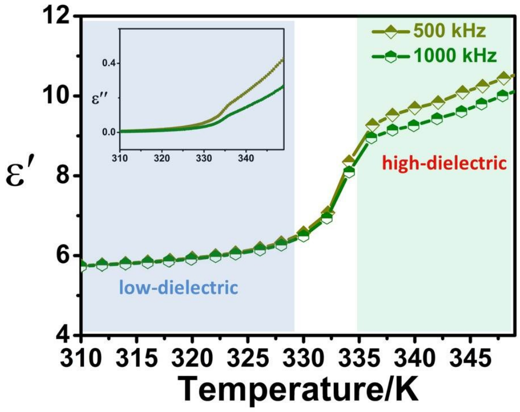

Figure S4 The real part of the dielectric constant of **1** measured on 500 kHz and 1000 kHz. Inset: The corresponding imaginary part (ε″).

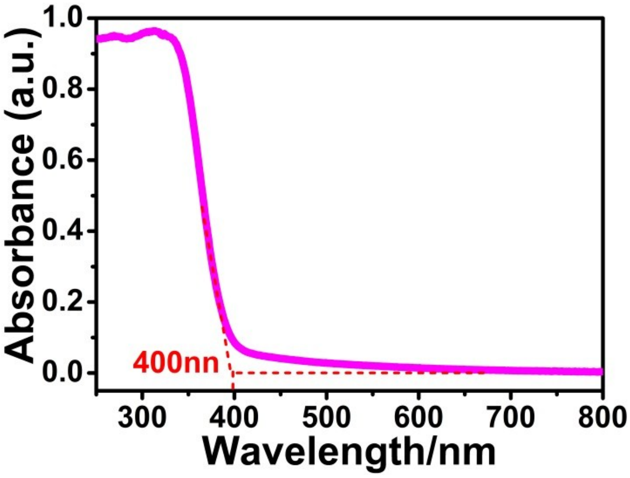

Figure S5. UV-vis diffuse reflection spectrum of **1**.

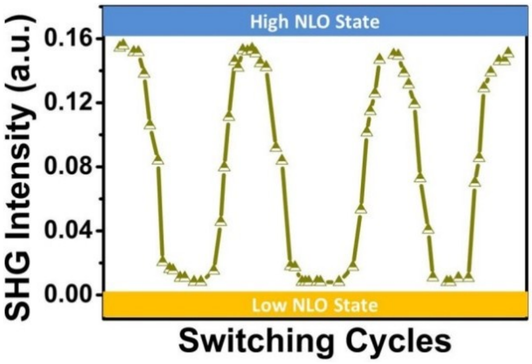

Figure S6 Completely reversible and recoverable switching of NLO effects.

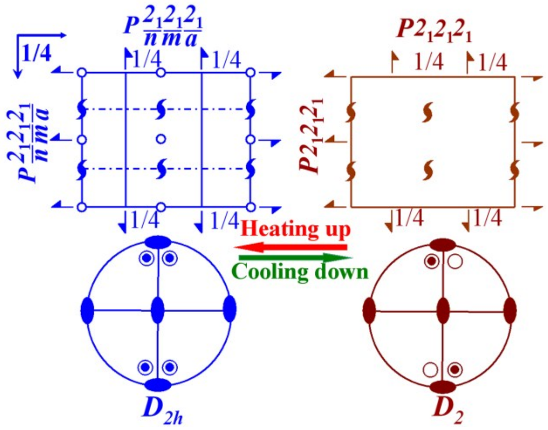

Figure S7. Symmetry transformation of **1** during the phase transition.

Table S1 Crystal structure and refinement detail of **1** at different temperatures.

Empirical formula	$(C_6H_{14}N)_2SbCl_5$	$(C_6H_{14}N)_2SbCl_5$
Formula weight	499.36	499.36
Temperature/K	350.00(10)	290.00(10)
Crystal system	orthorhombic	orthorhombic
Space group	*Pnma*	$P2_12_12_1$
Unit cell dimensions(Å)	13.0708(7)	7.5861(3)
	7.9573(5)	13.2521(5)
	20.1605(10)	20.2623(8)
V(Å^3)	2096.9(2)	2037.00(14)
Z, ρ_{cal}.(gcm^{-3})	4, 1.582	4, 1.628
F(000)	1000.0	1000.0
Theta range(°)	6.818 to 58.986	6.772 to 58.8
Limiting indices	$-9 \le h \le 17$	$-10 \le h \le 10$
	$-8 \le k \le 11$	$-17 \le k \le 13$
	$-22 \le l \le 26$	$-19 \le l \le 25$
Reflections collected/unique	7734/2718 (R_{int} = 0.0303)	8223/4546 (R_{int} = 0.0238)
Completeness (%)	99.1	98.9
Data/restraints/parameters	2718/20/118	4546/0/181
Goodness	1.029	1.031
Final R indexes [I>=2σ (I)]	R_1 = 0.0623, wR_2 = 0.1652	R_1 = 0.0349, wR_2 = 0.0647

Table S2 Bond Lengths for **1** at 290 K.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Sb_1	Cl_2	2.5298(15)	C_7	C_8	1.486(10)
Sb_1	Cl_5	2.7712(16)	C_2	C_3	1.479(12)
Sb_1	Cl_4	2.3845(15)	C_2	C_1	1.468(11)
Sb_1	$Cl_1{}^1$	3.3523(16)	C_3	C_4	1.484(11)
Sb_1	Cl_1	2.6800(16)	C_6	C_5	1.456(10)
Sb_1	Cl_3	2.5884(16)	C_8	C_9	1.435(11)
N_2	C_7	1.483(8)	C_4	C_5	1.473(10)
N_2	C_{12}	1.495(8)	C_9	C_{10}	1.442(13)
N_1	C_6	1.472(10)	C_{10}	C_{11}	1.335(13)
N_1	C_1	1.419(9)	C_{11}	C_{12}	1.382(13)

^{1} = 1/2+X,1/2-Y,1-Z

Computational methods

The dipole moments of constituent groups in the crystal were calculated with density functional theory (DFT) and the B3LYP extended ex-change functions employing the finite field (FF) method with the GAUSSIAN 09 electronic structure package.[1] In order to take into account the relativistic effect, Sb atoms adopted the effective core potential (ECP) double-ζ (DZ) basic set of LanL2DZ, while the nonmetal elements took standard 6-311+g (d) all-electron basis set. Average polarizability ($\overline{a}$) and total intrinsic first hyperpolarizability (β_{tot}) can be estimated according to the following equations:

$$\overline{\alpha}=(\alpha_{xx}+\alpha_{yy}+\alpha_{zz})/3$$

and

$$\beta_{tot}=[\beta_x{}^2+\beta_y{}^2+\beta_z{}^2]^{1/2}$$

where

$$\beta_i=\frac{1}{3}\sum_j[\beta_{ijj}+\beta_{jij}+\beta_{jji}] \quad i=x,y,z$$

The electronic structure and optical properties calculations were performed by the plane-wave pseudopotential method implemented in the CASTEP software package.[2, 3] The exchange-correlation potential was calculated using Perdew−Burke−Ernzerhof for solids (PBEsol)[4] functional within the generalized gradient approximation (GGA) with the scheme. To achieve energy convergence, the kinetic energy cutoff of 600 eV within normal-conserving pseudopotential (NCP)[5] was adopted. The following orbital electrons were treated as valence electrons: Sn $5s^2$ $5p^3$; Cl $3s^2$ $3p^5$; C $2s^2$ $2p^2$; N $2s^2 2p^3$ and H $1s^1$. To achieve the accurate density of the electronic states, the *k*-space integrations were done with Monkhorst-Pack grids with a 5 × 3 × 3, including more than 50 empty bands in the optical properties calculations. The so-called length-gauge formalism[6, 7] derived by Aversa and Sipe was adopted to calculate NLO coefficients, which has been proved to be successful in calculating second-order susceptibility for NLO crystal.

Table S3 Calculated dipole moment (u_g, Debye), linear polarizability (α_{tot}, $\times 10^{-24}$ esu) and first hyperpolarizability (β_{total},$\times 10^{-30}$ esu) values.

	$C_6H_{14}N$ cation 1	$C_6H_{14}N$ cation 2	$SbCl_5$	$(C_6H_{14}N)_2SbCl_5$
μ_x	-1.196	0.655	14.284	2.798
μ_y	-2.277	-2.425	15.536	3.941
μ_z	-3.929	3.953	13.002	-28.669
u_g	4.696	4.683	24.788	29.074
α_{xx}	7.546	7.792	59.626	78.641
α_{xy}	0.051	-0.220	-1.315	4.001
α_{yy}	9.159	9.101	61.549	72.642
α_{xz}	0.269	0.382	-2.707	-5.856
α_{yz}	0.004	0.134	-4.724	-4.483
α_{zz}	9.063	9.189	59.515	85.642
α_{tot}	8.590	8.694	60.230	78.975
β_{xxx}	-0.017	-0.033	14.439	-0.607
β_{xxy}	-0.025	-0.005	17.048	-9.711
β_{xyy}	0.051	-0.017	22.458	-5.608
β_{yyy}	0.273	0.207	20.472	11.687
β_{zxx}	0.081	-0.136	16.137	14.645
β_{xyz}	-0.013	-0.015	10.705	-1.999
β_{zyy}	0.147	-0.087	21.000	9.239
β_{xzz}	0.033	-0.023	24.689	9.412
β_{yzz}	0.120	0.088	1.765	12.614
β_{zzz}	0.427	-0.371	54.620	84.592
β_{total}	0.754	0.665	117.285	109.499

Table S4 Theoretical calculated SHG coefficients matrix for **1**.

Phase	HTP	LTP
Point group	*mmm*	222
SHG coefficients matrix	--	$\begin{bmatrix} 0 & 0 & 0 & 0.145 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0.145 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0.145 \end{bmatrix}$ $d_{14}=d_{25}=d_{36}=0.145$ pm/V

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