Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting information

Above-room-temperature switching of quadratic nonlinear optical properties in a Bi-halide organic-inorganic hybrid

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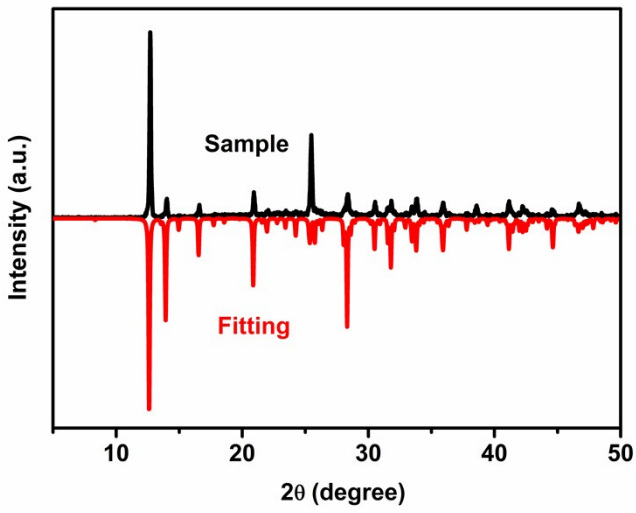

Figure S1: Powder X-ray diffraction patterns of experimental and calculated of **1**.

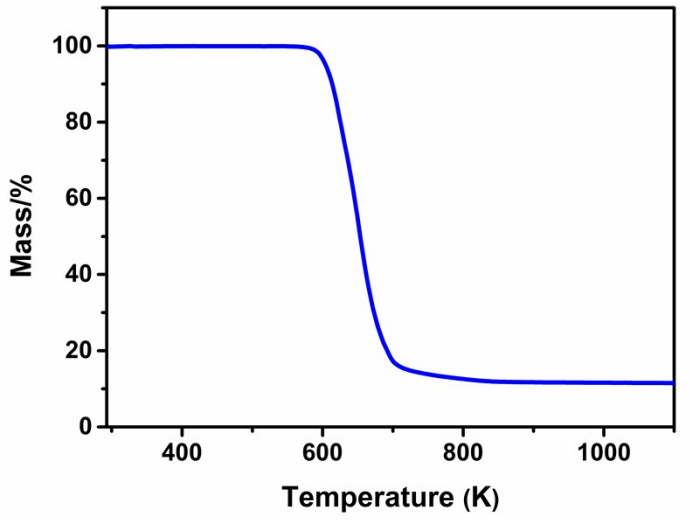

Figure S2: The TG curves of **1**. This compound can maintain the thermal stable up to 580 K.

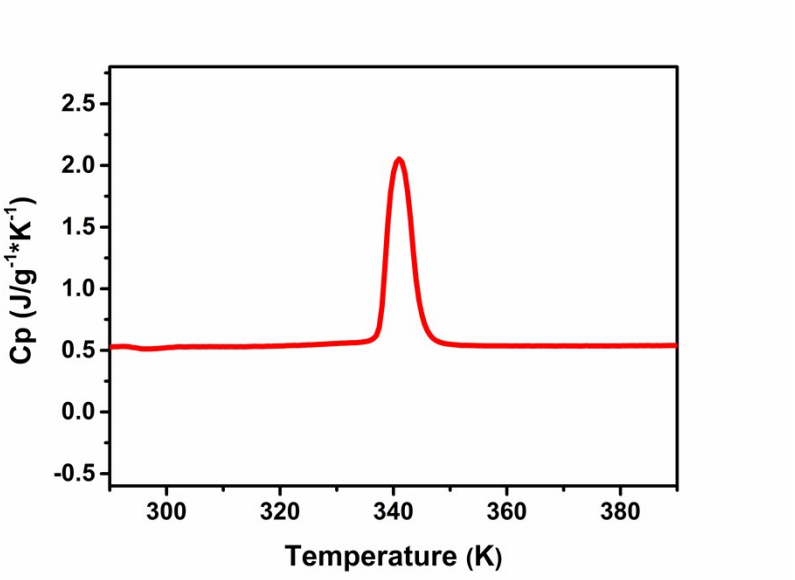

Figure S3: Temperature dependence of *Cp* curve of **1**.

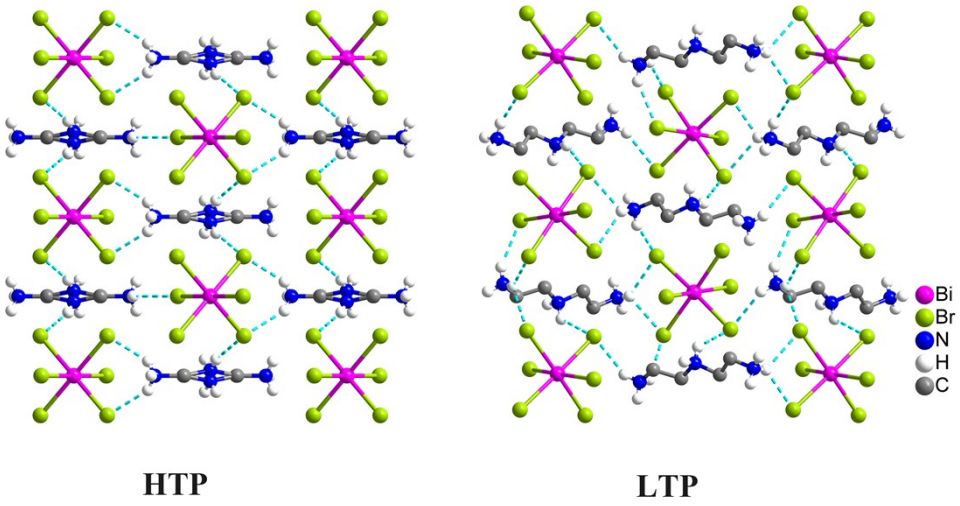

Figure S4: Comparison of the crystal structures of **1** at HTP and LTP. The The N-H···Br hydrogen-bonding interactions between organic cations and inorganic framework in compound **1** were showed. Some hydrogen bonds were omitted for clarity.

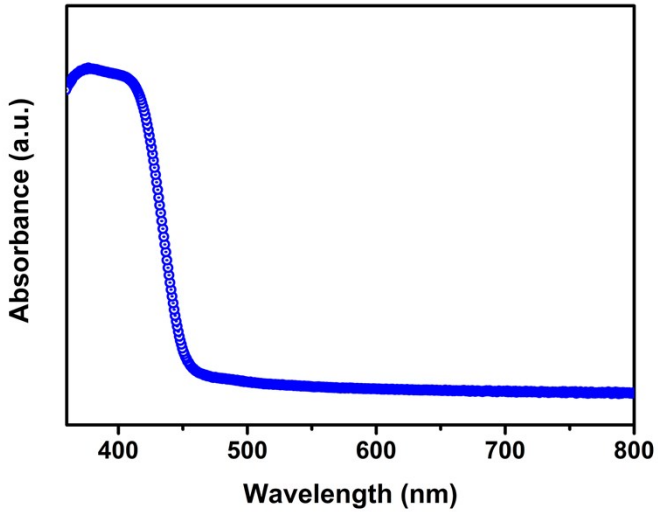

Figure S5: The UV/vis absorption spectrum of **1**, the absorption edge of this compound is estimated to be 455 nm.

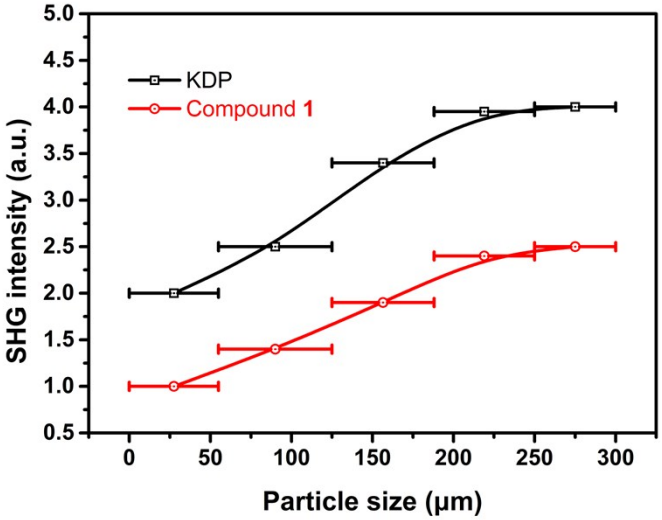

Figure S6: SHG intensity vs. particle size curves for **1**. KDP samples serve as the references.

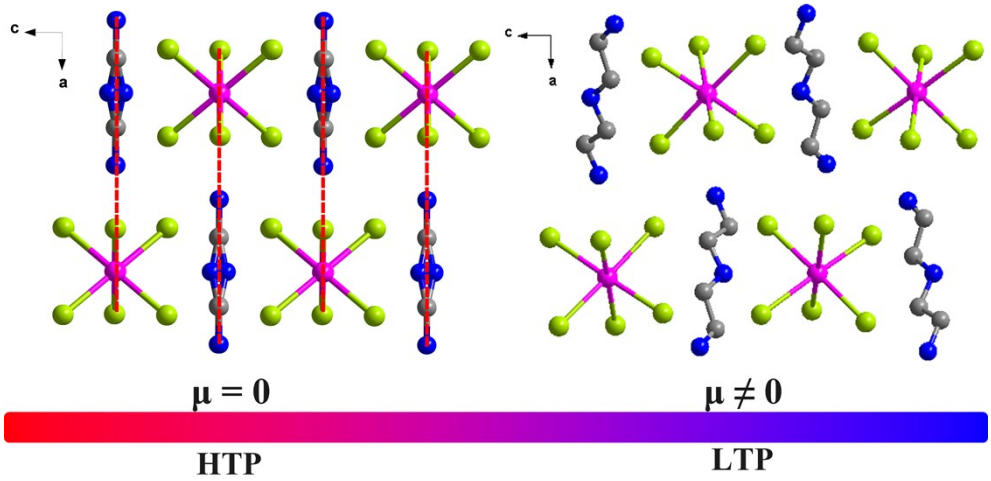

Figure S7: Schematic diagram for molecular dipole moments in **1** during its NLO-switching process.

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

Empirical formula	$C_4H_{16}N_3BiBr_6$	$C_4H_{16}N_3BiBr_6$
Formula weight	794.64	794.64
Temperature, K	300(2)	345(2)
Crystal system, space group	orthorhombic, $P2_12_12_1$	orthorhombic, *Pnnm*
a, Å	14.0146(2)	13.8796(9)
b, Å	7.15630(10)	7.3670(5)
c, Å	16.2662(2)	8.0696(6)
α, deg	90	90
β, deg	90	90
γ, deg	90	90
V, Å^3	1631.38(4)	825.12(10)
Z, Calculated density	4, 3.235	2, 3.198
Absorption coefficient	25.479	25.188
F(000)	1416	708
Theta range, deg	2.50 to 27.49	2.92 to 27.47
Limiting indices	-17<=h<=18	-18<=h<=17
	-9<=k<=9	-9<=k<=9
	-21<=l<=19	-10<=l<=10
Reflections collected / unique	11842 / 3730	4982 / 1018
Completeness	99.7 %	99.7 %
Data / restraints / parameters	3730 / 0 / 129	1018 / 8 / 45
Goodness-of-fit on F^2	1.028	1.081
Final *R* indices [*I*>2sigma(*I*)]	$R_1 = 0.0396$, $wR_2 = 0.1077$	$R_1 = 0.0694$, $wR_2 = 0.2051$
R indices (all data)	$R_1 = 0.0459$, $wR_2 = 0.1121$	$R_1 = 0.0857$, $wR_2 = 0.2241$

[a] $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$, $wR_2 = \{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma w[(F_o)^2]^2\}^{1/2}$

Table 2: Selected bond lengths [Å] and angles [deg] of **1** in HTP and LTP.

HTP		LTP	
Bi(1)-Br(1)	2.841(3)	Bi(1)-Br(5)	2.7809(13)
Bi(1)-Br(1)#1	2.841(3)	Bi(1)-Br(1)	2.7996(10)
Bi(1)-Br(2)	2.8599(14)	Bi(1)-Br(4)	2.8588(12)
Bi(1)-Br(2)#2	2.8599(14)	Bi(1)-Br(2)	2.8761(11)
Bi(1)-Br(2)#3	2.8599(14)	Bi(1)-Br(6)	2.9048(12)
Bi(1)-Br(2)#1	2.8599(14)	Bi(1)-Br(3)	2.9454(11)
Br(1)-Bi(1)-Br(2)	91.65(7)	Br(5)-Bi(1)-Br(1)	88.70(4)
Br(1)#1-Bi(1)-Br(2)	88.35(7)	Br(5)-Bi(1)-Br(4)	90.94(5)
Br(1)-Bi(1)-Br(2)#2	91.65(7)	Br(1)-Bi(1)-Br(4)	89.90(3)
Br(1)#1-Bi(1)-Br(2)#2	88.35(7)	Br(5)-Bi(1)-Br(2)	87.44(4)
Br(2)-Bi(1)-Br(2)#2	89.63(7)	Br(1)-Bi(1)-Br(2)	91.25(3)
Br(1)-Bi(1)-Br(2)#3	88.35(7)	Br(1)-Bi(1)-Br(6)	84.92(3)
Br(1)#1-Bi(1)-Br(2)#3	91.65(7)	Br(4)-Bi(1)-Br(6)	95.50(4)
Br(2)-Bi(1)-Br(2)#3	90.37(7)	Br(2)-Bi(1)-Br(6)	86.24(4)
Br(1)-Bi(1)-Br(2)#1	88.35(7)	Br(5)-Bi(1)-Br(3)	89.96(4)
Br(1)#1-Bi(1)-Br(2)#1	91.65(7)	Br(4)-Bi(1)-Br(3)	88.99(4)
Br(2)#2-Bi(1)-Br(2)#1	90.37(7)	Br(2)-Bi(1)-Br(3)	89.82(3)
Br(2)#3-Bi(1)-Br(2)#1	89.63(7)	Br(6)-Bi(1)-Br(3)	96.54(3)
Symmetry transformations used to generate equivalent atoms: #1 -x,-y,-z #2 x,y,-z #3 -x,-y,z #4 -x,-y+1,-z+1			

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, Bi 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 ($\bar{a}$) and total intrinsic first hyperpolarizability (β_{tot}) can be estimated according to the following equations:

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

and

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

where

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

Table S3 Calculated dipole moment (in D), linear polarizability (in 10^{-24} esu) and first hyperpolarizability (in 10^{-30} esu) values.

	$BiBr_6$	$C_4N_3H_{16}$	$(C_4N_3H_{16})BiBr_6$
μ_x	-4.125	0.080	-29.148
μ_y	1.105	-0.060	9.653
μ_z	1.443	0.345	22.925
u_g	4.508	0.360	38.319
α_{xx}	88.197	7.538	84.979
α_{xy}	0.428	-1.707	-2.557
α_{yy}	89.878	8.511	79.710
α_{xz}	1.453	-0.418	-10.455
α_{yz}	-0.930	0.133	-0.357
α_{zz}	91.451	6.343	87.038
α_{tot}	89.842	7.464	83.909
β_{xxx}	16.387	0.022	3.464
β_{xxy}	-1.584	0.015	-4.672
β_{xyy}	3.158	-0.005	-0.102
β_{yyy}	7.426	0.013	-3.944
β_{zxx}	4.667	0.009	-6.759
β_{xyz}	-1.171	-0.001	3.453
β_{zyy}	0.386	0.022	-2.055
β_{xzz}	2.240	-0.025	4.890
β_{yzz}	4.544	-0.006	-0.153
β_{zzz}	-7.369	0.011	-0.222
β_{total}	24.244	0.048	15.056

1. Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, et al. Gaussian 09. Revision A. 02 ed. Wallingford, CT: Gaussian, Inc.; 2009. p. 271.