Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Supporting information

Rational design of organic-inorganic hybrid with Schiff based cation for efficient quadratic nonlinear optical switch

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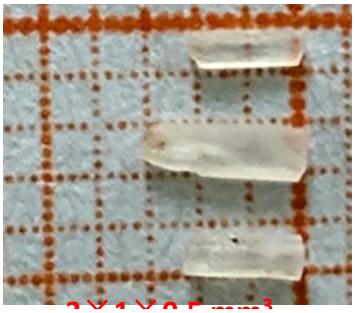

Figure S1. Crystal photograph of **1**.

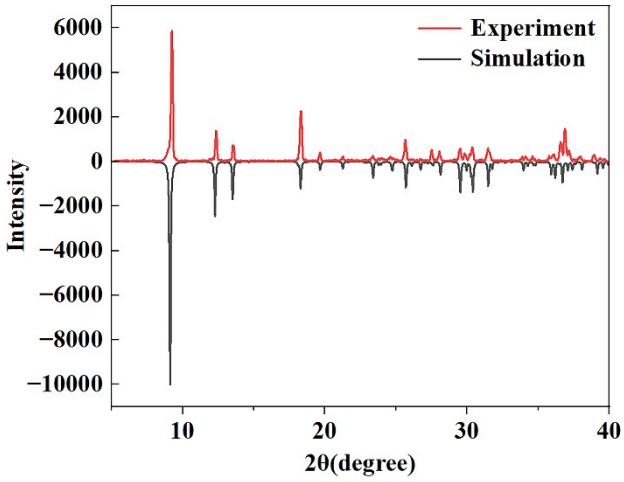

Figure S2. Experimental and simulated Powder X-ray diffraction patterns for **1**.

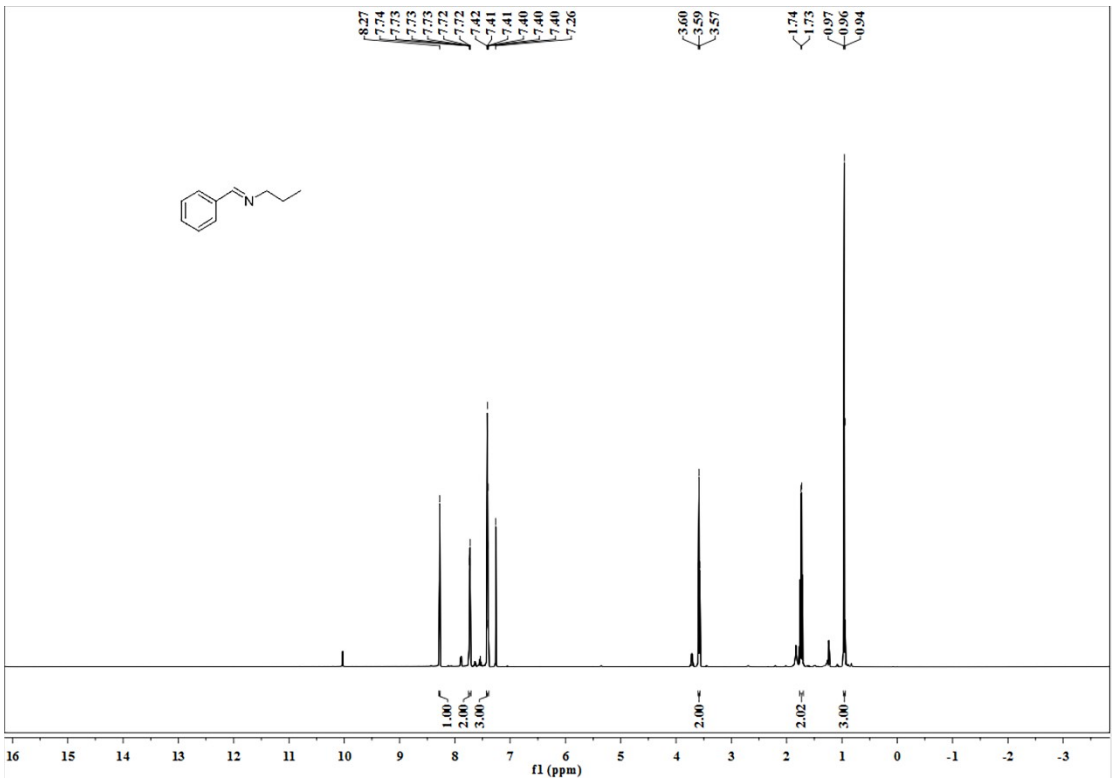

Figure S3. The ^{1}HNMR spectrum of the Schiff base.

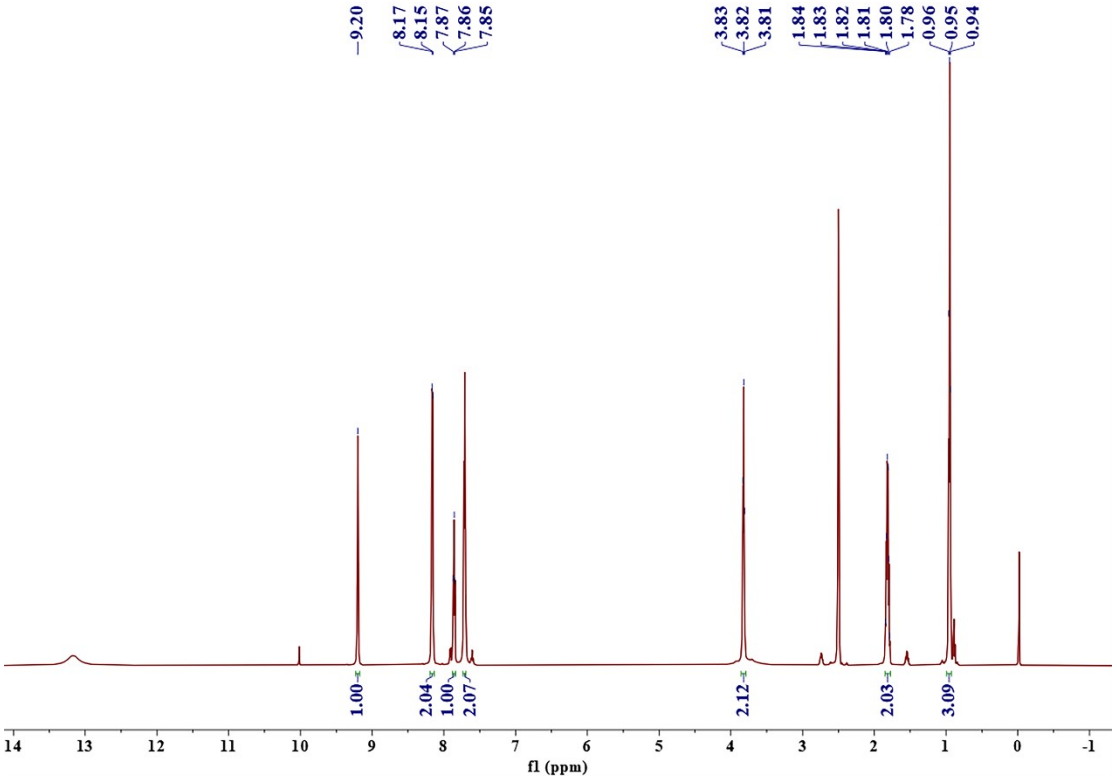

Figure S4. The ^{1}HNMR spectrum of 1.

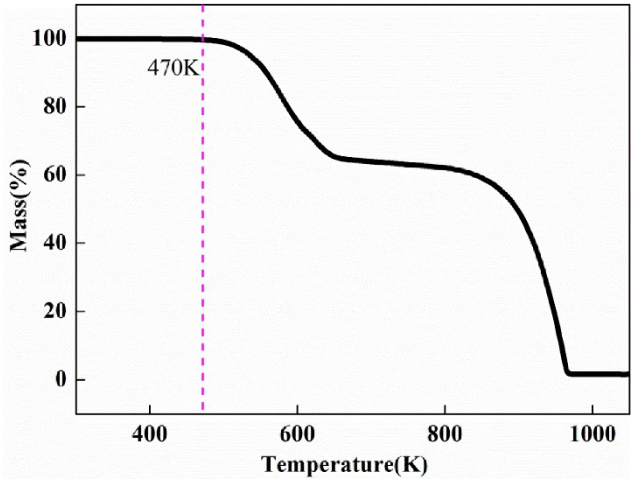

Figure S5. The TG curves of **1**. This compound can maintain the thermal stable up to 470 K.

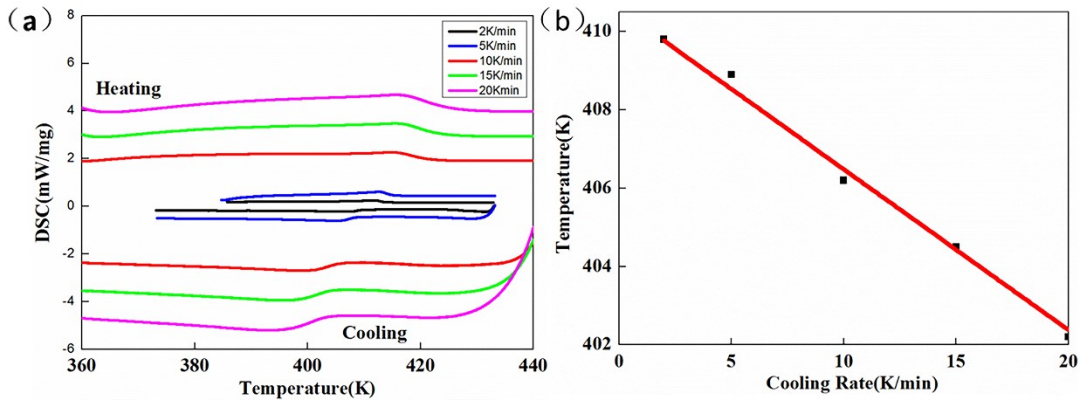

Figure S6. a) Differential scanning calorimetry of **1** at different heating/cooling rate. b) The actual phase transition point confirmed by extrapolating intercept of the plot of peak points at different heating/cooling rates and is finally measured to be 411 K.

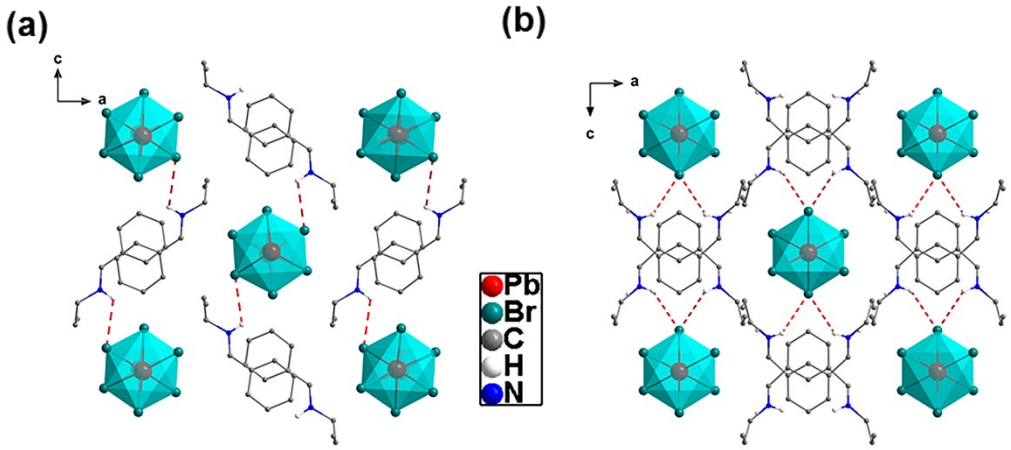

Figure S7. The N- H…Br hydrogen-bonding interactions between organic cations and inorganic framework in compound **1** were showed at a) LTP and b) HTP. Some hydrogen bonds were omitted for clarity.

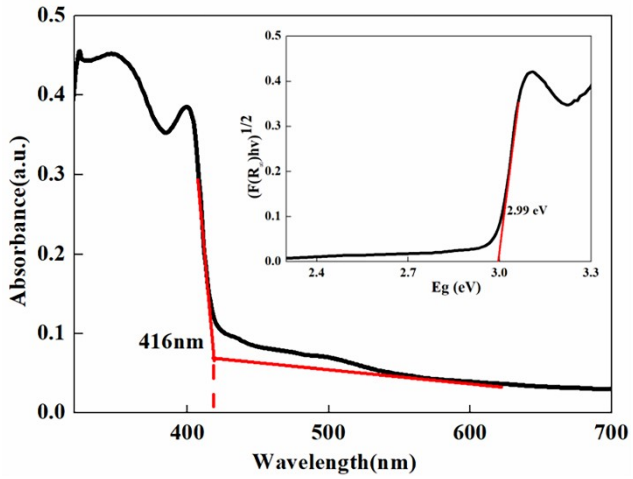

Figure S8. The UV/vis absorption spectrum of **1**, the absorption edge of this compound is estimated to be 420 nm.

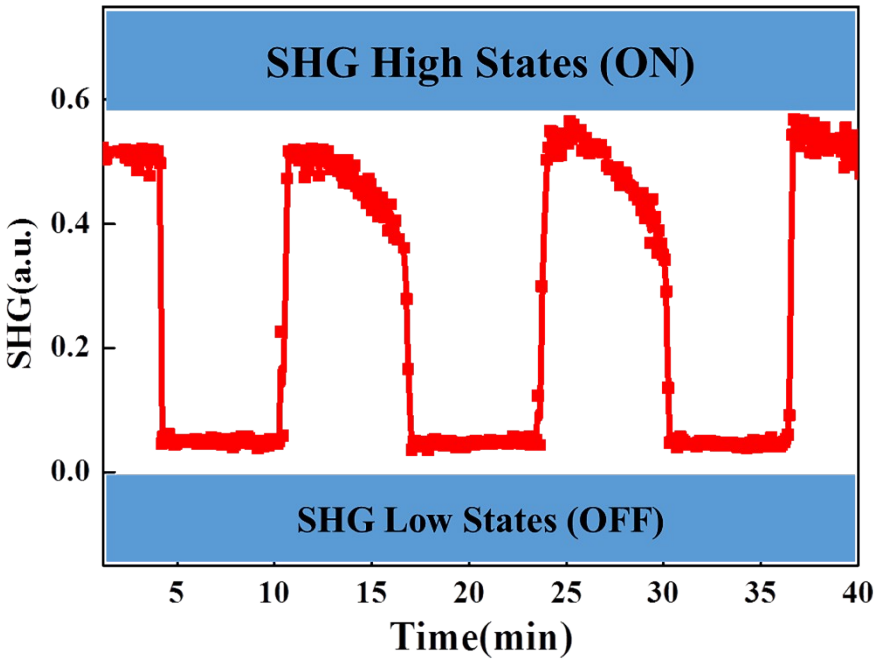

Figure S9. Completely reversible and recoverable switching of SHG effects.

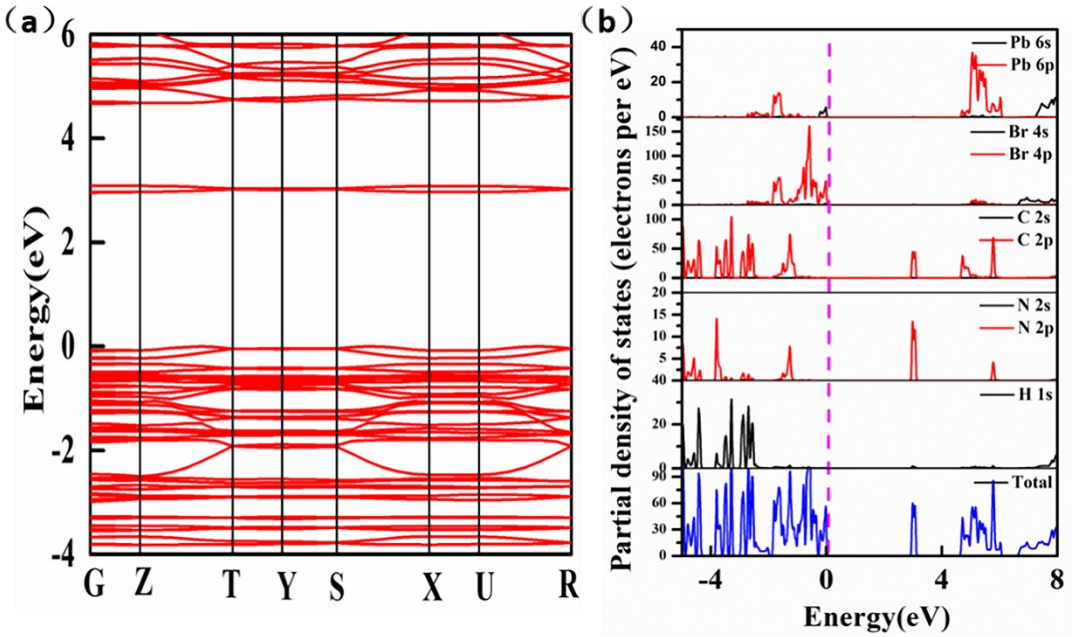

Figure S10. a) Electronic band structure and b) partial density of states for **1**.

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

Empirical formula	$C_{10}H_{14}Br_3NPb$	$C_{10}H_{14}Br_3NPb$
Formula weight	595.14	595.14
Temperature/K	100.01	419.98
Crystal system	orthorhombic	orthorhombic
Space group	$P2_12_12_1$	*Imma*
a/Å	7.7413(4)	14.8489(16)
b/Å	13.0896(7)	7.7744(7)
c/Å	14.4126(7)	13.5892(14)
α/°	90	90
β/°	90	90
γ/°	90	90
Volume/Å^3	1460.44(13)	1568.8(3)
Z	4	4
ρ_{calc}g/cm^3	2.707	2.520
μ/mm^{-1}	19.732	18.370
F(000)	1072.0	1072.0
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2θ range for data collection/°	6.114 to 50.174	6.038 to 55.084
Index ranges	-9≤*h*≤9, -15≤*k*≤12, -17≤*l*≤17	-19≤*h*≤18,-9≤*k*≤10, -17≤*l*≤17
Reflections collected	8643	6460
Independent reflections	2591 [R_{int} = 0.0521, R_{sigma} = 0.0494]	1002 [R_{int} = 0.0359, R_{sigma} = 0.0221]
Data/restraints/parameters	2591/0/137	1002/67/85
Goodness-of-fit on F^2	0.945	1.040
Final R indexes [I>=2σ (I)]	R_1 = 0.0252, wR_2 = 0.0578	R_1 = 0.0272, wR_2 = 0.0591
Final R indexes [all data]	R_1 = 0.0267, wR_2 = 0.0591	R_1 = 0.0481, wR_2 = 0.0694

Table S2. Bond lengths of **1** at different temperatures.

LTP				HTP			
Pb1-Br2	2.9209(10)	C5-C6	1.408(13)	Pb1-Br1^1	3.0508(5)	C2-C3	1.343(6)
Pb1-Br2^1	3.1662(10)	N1-C8	1.466(11)	Pb1-Br1	3.0508(5)	C4-C3^3	1.348(6)
Pb1-Br1^2	3.0820(10)	C5-C4	1.375(14)	Pb1-Br2	3.0279(4)	C4-C3	1.348(6)
Pb1-Br1	2.9593(10)	C8-C9	1.527(15)	Pb1-Br2^2	3.0279(4)	C3-C5	1.508(9)
Pb1-Br3	2.9476(10)	C2-C3	1.404(13)	Pb1-Br2^3	3.0279(4)	C7-C8	1.520(10)
Pb1-Br3^2	3.0910(10)	C2-C1	1.371(14)	Pb1-Br2^1	3.0279(4)	C7-C6	1.502(10)
C6-C1	1.405(14)	C6-C7	1.443(13)	C1-C2^3	1.366(6)	N1-C5	1.349(9)
C3-C4	1.379(15)	C10-C9	1.512(14)	C1-C2	1.366(6)	N1-C6	1.469(10)
C7-N1	1.270(13)						
^{1}1/2+X,1/2-Y,1-Z;^{2}-1/2+X,1/2-Y,1-Z				^{1}-X,1-Y,2-Z;^{2}+X,1/2+Y,2-Z;^{3}-X,1/2-Y,+Z			

Table S3. Bond angles of **1** at different temperatures.

LTP

Br2-Pb1-Br2[1]	171.17(3)	Pb1-Br2-Pb1[2]	78.98(2)
Br2-Pb1-Br1	93.71(3)	Pb1-Br1-Pb1[1]	79.79(2)
Br2-Pb1-Br1[2]	-84.46(3)	Pb1-Br3-Pb1[1]	79.82(2)
Br2-Pb1-Br3	89.87(3)	C4-C5-C6	120.0(9)
Br2-Pb1-Br3[2]	83.74(3)	C1-C2-C3	120.0(10)
Br1[2]-Pb1-Br2[1]	99.08(3)	C5-C6-C7	123.2(10)
Br1-Pb1-Br2[1]	82.36(3)	C1-C6-C5	119.6(9)
Br1-Pb1-Br1[2]	176.810(14)	C1-C6-C7	117.2(9)
Br1-Pb1-Br3[2]	100.54(3)	C4-C3-C2	120.5(10)
Br1[2]-Pb1-Br3[2]	81.89(3)	C2-C1-C6	119.7(9)
Br3-Pb1-Br2[1]	82.01(3)	C5-C4-C3	120.0(9)
Br3[2]-Pb1-Br2[1]	104.72(3)	N1-C7-C6	128.4(10)
Br3-Pb1-Br1	86.45(3)	C7-N1-C8	123.9(9)
Br3-Pb1-Br1[2]	90.93(3)	N1-C8-C9	112.6(8)
Br3-Pb1-Br3[2]	170.80(3)	C10-C9-C8	113.0(9)

[1]-X,1-Y,2-Z;[2]+X,1/2+Y,2-Z;[3]-X,1/2-Y,+Z

HTP

Br1-Pb1-Br1[1]	180.0	Br2-Pb1-Br2[2]	94.550(15)
Br2-Pb1-Br11	82.3(10)	Pb1[4]-Br1-Pb1	79.150(15)
Br2-Pb1-Br1	97.677(10)	Pb1[3]-Br2-Pb1	79.86 (12)
Br2[2]-Pb1-Br1	82.323(10)	C2[3]-C1-C2	116.9(7)
Br2[2]-Pb1-Br1[1]	97.677(10)	C3-C2-C1	122.0(6)
Br2[3]-Pb1-Br1[1]	82.323(10)	C3-C4-C3[3]	121.0(7)
Br2[3]-Pb1-Br1	97.677(10)	C2-C3-C4	119.1(5)
Br2[1]-Pb1-Br1	82.323(10)	C2-C3-C5	134.2(5)
Br2[1]-Pb1-Br1[1]	97.677(10)	C4-C3-C5	106.7(5)
Br2-Pb1-Br2[1]	179.999(11)	C6-C7-C8	99.6(8)
Br2-Pb1-Br2[3]	85.450(15)	C5-N1-C6	127.3(8)
Br2[2]-Pb1-Br2[3]	180.0	N1-C5-C3	123.7(7)
Br2[2]-Pb1-Br2[1]	85.450(15)	N1-C6-C7	123.1(8)
Br2[3]-Pb1-Br2[1]	94.550(15)		

[1]-X,1-Y,2-Z;[2]+X,1/2+Y,2-Z;[3]-X,1/2-Y,+Z;[4]-X,3/2-Y,+Z