Electronic Supplementary Material (ESI) for New Journal of Chemistry.

1D Chiral Infinite Chain Organic Metal Halide Hybrid with Excellent SHG Switch and Moderate Spontaneous Polarization

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EXPERIMENTAL SECTIONS

Synthesis

All chemical reagents are purchased directly. For the chemical synthesis of **1**, stoichiometric Sb_2O_3 (1 mmol) and (S)-3-hydroxypyrrolidine hydrochloride (3 mmol) were slowly dissolved together in 5 mL of acetonitrile and hydrochloric acid (pH = 2), and then, the mixture was stirred for half an hour and filtrated. The colorless lamellar crystals of **1** were obtained after one week of slow evaporation. the yield (1.243 g) is 72.3% based on (S)-3-hydroxypyrrolidine hydrochloride. Elemental analysis for ($(C_4H_{10}NO)_2SbCl_5$), Calc. (%), C, 20.218; H, 4.240; N, 5.890; O, 6.730; Sb, 25.618; Cl, 37.298. Found (%), C, 20.268; H, 4.238; N, 5.891; O, 6.742; Sb, 25.623; Cl, 37.238. The powder X-ray diffraction (PXRD) (**Figure S1**) and Infrared absorption (IR) spectroscopy (**Figure S2**) results confirm the phase purity of the obtained crystals. As shown in **Figure S2**, 3490 cm^{-1} is the characteristic peak of -OH. The absorption peak near 3300-2800 cm^{-1} was derived from the stretching vibration of C-H, and near 3500-3400 cm^{-1} was derived from the stretching vibration of N-H. Near 1350-1000 cm^{-1} is the absorption peak of C-N stretching vibration.

Single Crystal X-Ray Diffraction.

The crystal structures of **1** were determined at 300 K by single crystal X-ray diffraction analyses. The data were corrected for L_p and absorption effects. Their crystal structures were solved by direct methods with the Olex 2 program. The crystal data and structure refinement for **1** are shown in **Table S1**. Their selected intra-atomic distances and bond

angles are given in **Tables S2** and **S3**. Their hydrogen bonds parameters are given in **Table S4**.

Measurements. Powder X-ray diffraction (PXRD) patterns were carried out on a Rigaku D/MAX 2000 PC X-ray diffraction instrument with Cu radiation ($K_{\alpha 1}$=1.54060 Å, $K_{\alpha 2}$=1.54443 Å). The data were collected during the heating process in the temperature range of 230-300 K for a θ in the range of 5-50°. DSC measurements were performed by heating / cooling the powder sample at a rate of 15 K / min on a PerkinElmer Diamond DSC instrument. Thermogravimetric analysis (TGA) measurement was performed on a TA-Instruments STD2960 system from room temperature to 1050 K at a rate of 10 K / min under a nitrogen atmosphere. The dielectric constant of compounds **1** is measured by Agilent or TH2828A impedance analyzer. During heating and cooling, the powder particle sample is measured at a rate of 5 K / min. The SHG signals were measured through an FLS 920 Edinburgh instrument on a laser with low divergence (Nd: YAG, 1064 nm, 5 ns, 1.6 MW peak power, 10 Hz repetition rate). The laser is a Vibrant 355 II, OPOTEK. The ferroelectric hysteresis loop was measured on a standard RT 6000 ferroelectric tester (Albuquerque, USA). UV−vis absorption spectra were obtained using a Shimadzu (Tokyo, Japan) UV-2550 spectrophotometer in the range of 200−800 nm. The band structure and PDOS were performed by the DFT method within the total-energy code CASTEP.

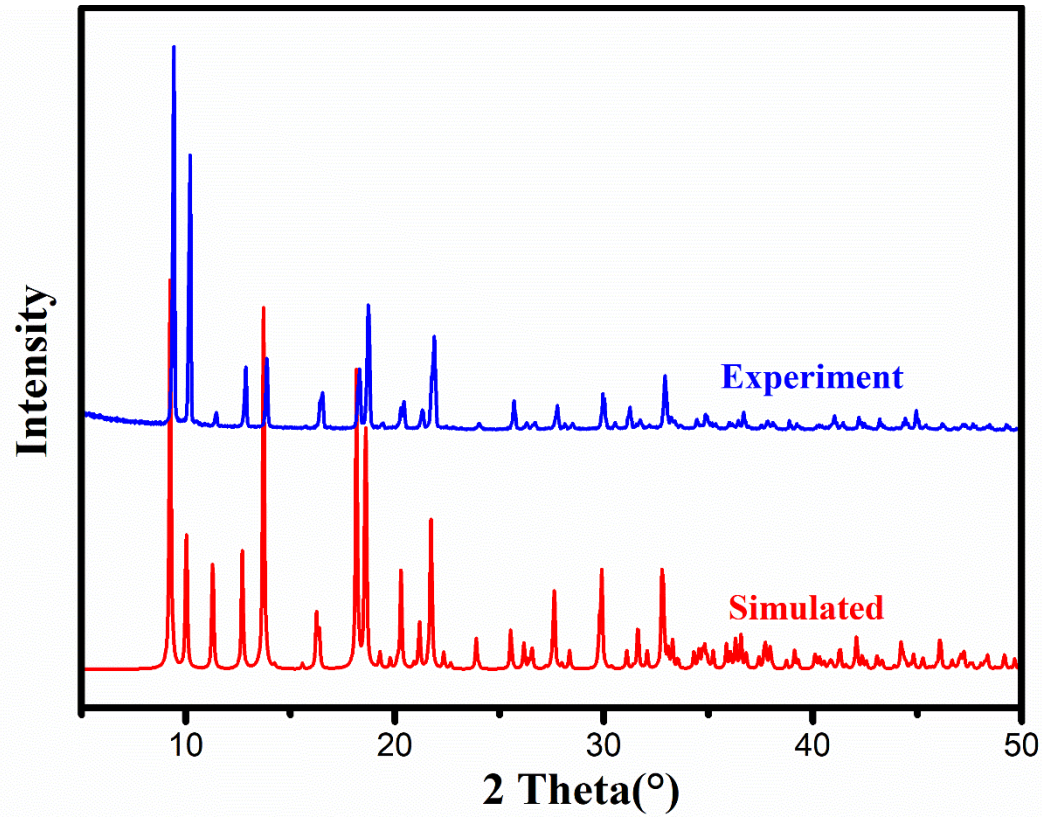

Figure S1. Simulation and measurement PXRD patterns of **1** at room temperature.

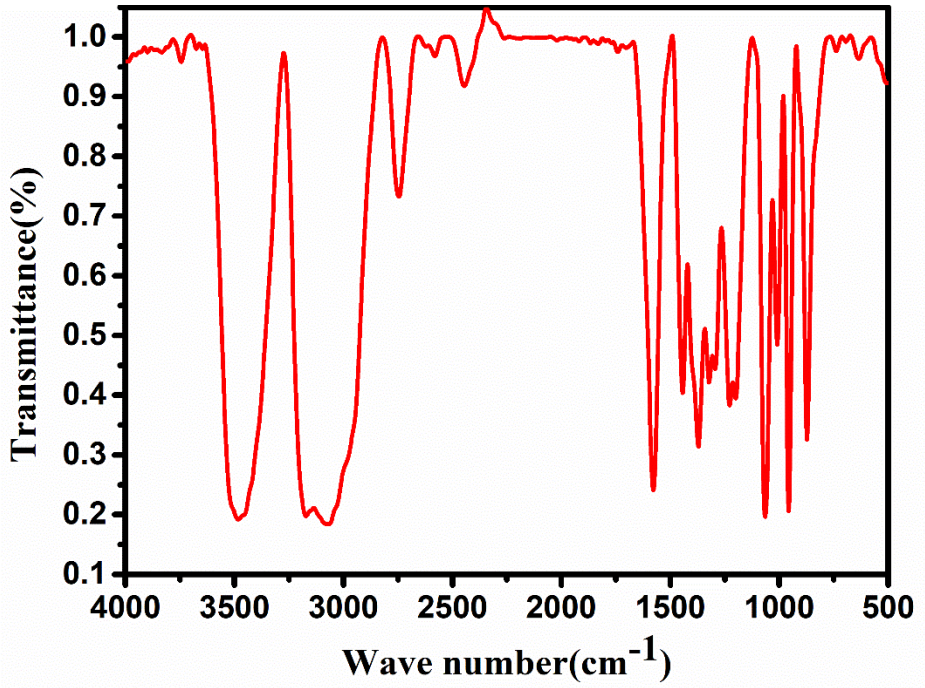

Figure S2. Infrared absorption (IR) spectroscopy of **1.**

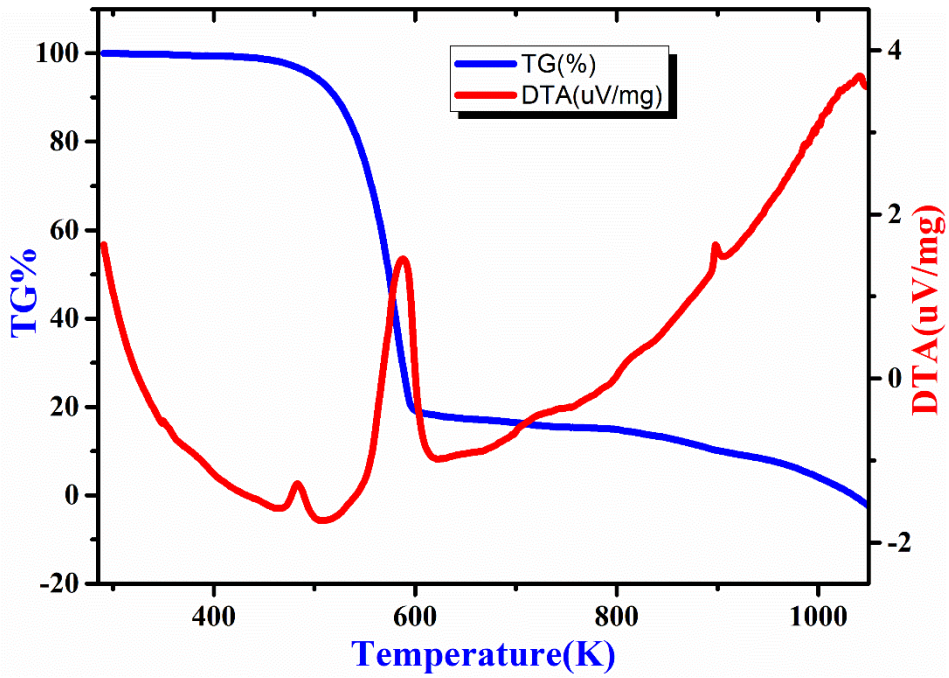

Figure S3. The TG-DTA (thermo gravimetric analysis and differential thermal analysis) curves of **1**.

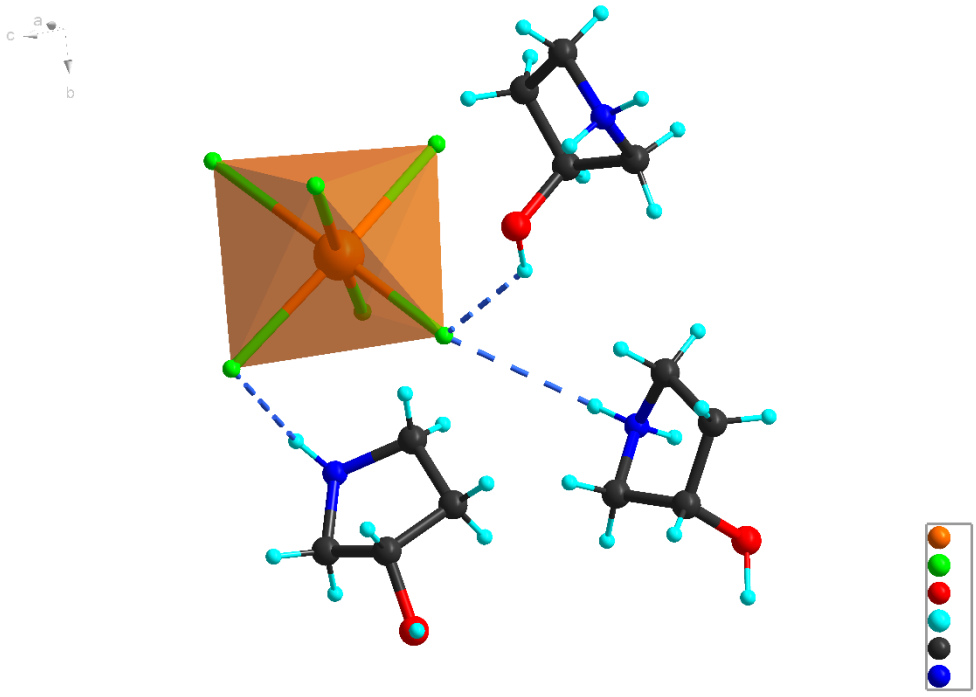

Figure S4. The H-bonds in the crystal structure of **1**.

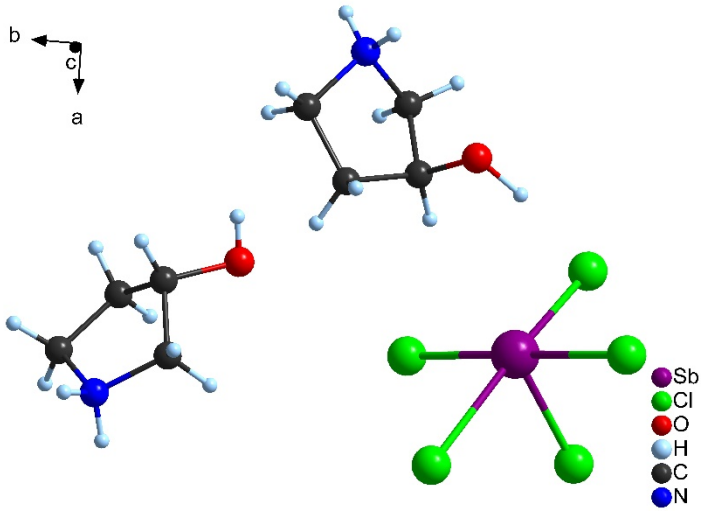

Figure S5. Asymmetric unit of **1** at room temperature.

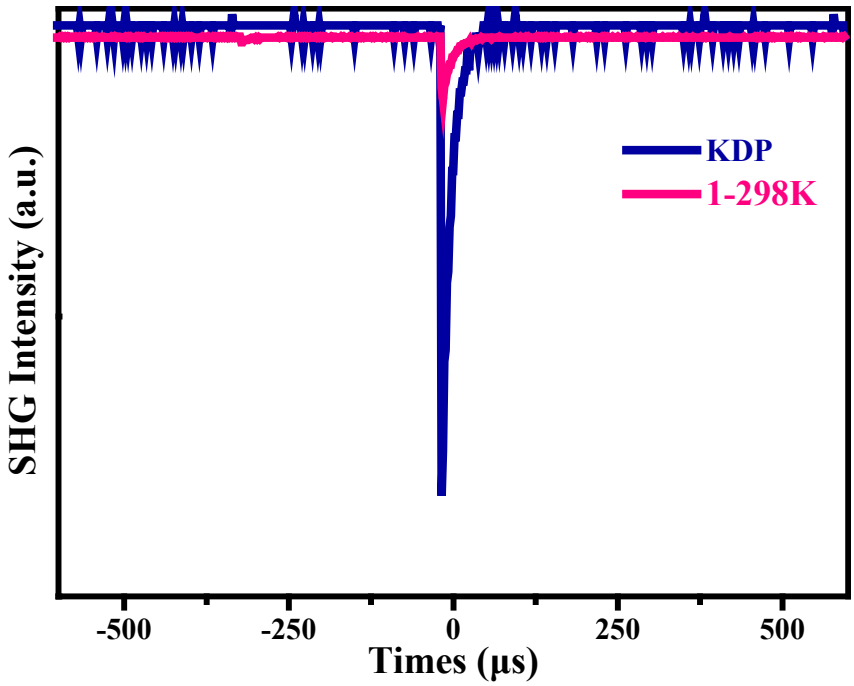

Figure S6. Oscilloscope traces of SHG signals for **1** at room temperature.

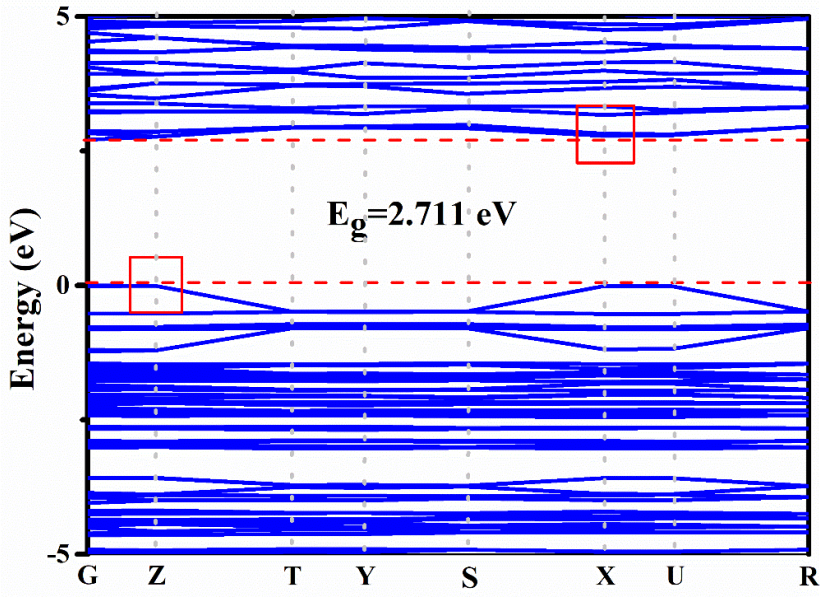

Figure S7. Calculated band structure of **1**.

Table S1. The crystallographic data of **1**.

Empirical formula	$C_8H_{20}Cl_5N_2O_2Sb$
Formula weight	475.26
Temperature (K)	300 K
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a (Å)	8.7467(4)
b (Å)	11.3654(5)
c (Å)	17.6409(9)
V (Å^3)	1753.68(14)
Z	4
Density (g/cm^3)	1.800
m (mm^{-1})	2.331
F(000)	936.0
Date/restraints/parameters	3074/179/137

GOF	1.153
R_1, wR_2[$I > 2\sigma(I)$]	R_1 = 0.0877, wR_2 = 0.2589
R_1, wR_2 (all data)	R_1 = 0.1032, wR_2 = 0.2891
$\triangle\rho_{max}$ /$\triangle\rho_{min}$ (eÅ^{-3})	1.61/-0.98

Table S2. Bond lengths (Å) for **1**.

Bond	Lengths(Å)	Bond	Lengths(Å)
Sb1-Cl2	2.964(9)	C3-C4	1.4857(14)
Sb1-Cl5	2.544(7)	C4-N1A	1.4852(14)
Sb1-Cl4	2.421(6)	O2-C6	1.4311(14)
Sb1-Cl3	2.431(7)	C8-C7	1.5013(14)
Sb1-Cl1	2.696(8)	C8-N2	1.4851(14)
O1-C3	1.4309(14)	C7-C6	1.4852(14)
C1-C2	1.5011(14)	C6-C5	1.4852(14)
C1-N1A	1.4849(14)	C5-N2	1.4851(14)
C2-C3	1.4850(14)		

Table S3. Bond angles (˚) for **1**.

Bond	Angles (˚)	Bond	Angles (˚)
Cl5-Sb1-Cl2	89.6(3)	O1-C3-C2	106.99(14)
Cl5-Sb1-Cl1	177.9(3)	O1-C3-C4	106.98(14)
Cl4-Sb1-Cl2	176.0(3)	C2-C3-C4	103.96(13)
Cl4-Sb1-Cl5	90.4(2)	C3-C4-N1A	104.71(13)
Cl4-Sb1-Cl1	91.6(3)	C1-N1A-C4	108.0(5)
Cl3-Sb1-Cl2	86.2(3)	N2-C8-C7	107.31(13)
Cl3-Sb1-Cl5	91.2(3)	C6-C7-C8	103.91(12)
Cl3-Sb1-Cl4	89.7(3)	O2-C6-C7	106.97(14)
Cl3-Sb1-Cl1	89.1(4)	O2-C6-C5	106.97(14)

Cl1-Sb1-Cl2	88.4(3)	C7-C6-C5	103.94(13)
N1A-C1-C2	105.0(8)	C6-C5-N2	104.71(13)
C3-C2-C1	103.93(13)	C5-N2-C8	96.7(3)

Table S4. Hydrogen bonds of **1** at 300 K.

D-H…A	D(D-H)	D(H…A)	< DHA	d(D…A)
O1-H1…Cl1	0.82	2.30	157	3.068
N2-H2…Cl4	1.07	2.04	130	2.853
N1A-H1Ab…Cl1	0.89	2.64	144	3.40
N2-H2C…Cl4	0.89	2.82	151	3.625

Calculation of the *ΔS* and *N* value for compounds in the heating and cooling cycles

Calculation of ΔS_1 and N in the heating cycle

$$\Delta S_1 = \int_{T^1}^{T^2} \frac{Q}{T} dT$$

$$\approx \frac{\Delta H}{T^c}$$

$$= \frac{10.2468\, J \cdot g^{-1} \times 469.21\, g \cdot mol^{-1}}{266.6\, K}$$

$$= 18.03\, J \cdot mol^{-1} \cdot K^{-1}$$

$$\Delta S_1 = R\ \ln N_1$$

$$N_1 = \exp(\frac{\Delta S_1}{R}) = \exp\left(\frac{18.03\, J \cdot mol^{-1} \cdot K^{-1}}{8.314\, J \cdot mol^{-1} \cdot K^{-1}}\right)$$

$$= 2.17$$

Calculation of ΔS_2 and N in the cooling cycle

$$\Delta S_2 = \int_{T^1}^{T^2} \frac{Q}{T} dT$$

$$\approx \frac{\Delta H}{T^c}$$

$$= \frac{7.9318\, J \cdot g^{-1} \times 469.21\, g \cdot mol^{-1}}{263\, K}$$

$$= 14.15\, J \cdot mol^{-1} \cdot K^{-1}$$

$$\Delta S_2 = R\ \ln N_2$$

$$N_2 = \exp(\frac{\Delta S_2}{R}) = \exp\left(\frac{14.15\, J \cdot mol^{-1} \cdot K^{-1}}{8.314\, J \cdot mol^{-1} \cdot K^{-1}}\right)$$

$$= 1.70$$