Electronic Supplementary Information

A Photoluminescent Chiral Lead-free Hybrid Ferroelastic Semiconductor with Switchable Second-Harmonic Generation

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Experimental details

Sample preparation. All reagents and solvents in this experiment were of reagent grade and used without further purification. *R*-3-hydroxyl piperidine and antimony chloride were dissolved in concentrated hydrochloric acid by a stoichiometric ratio of 2:1. Colorless crystals of $[R\text{-HP}]_2SbCl_5$ were finally obtained after a slow evaporation of the solvent at 313 K.

Thin film preparation. For the preparation of a thin film sample of $[R\text{-HP}]_2SbCl_5$, the precursor solution was prepared by dissolving 15 mg of the as-grown crystals of $[R\text{-HP}]_2SbCl_5$ in 300 μL concentrated HCl aqueous solution. Spreading 20 μL of the precursor solution on the clean ITO (indium tin oxide) glass substrate, The thin films were prepared by heat treatment and then annealing the substrate at 343 K.

Characterization methods. Single-crystal X-ray diffraction data were performed on a Rigaku Oxford Diffraction 2019 diffractometer in the scan mode with Mo-Kα radiation (λ = 0.71073). We used the CrystalClear software package to process the data. We utilized the Olex2 software to solve the structure by direct methods and refined the structure by the full-matrix method based on F^2 by means of the SHELXLTL software package. Non-H atoms were refined anisotropically. All H atoms were generated geometrically. Differential scanning calorimetry (DSC) measurements were carried out on a NETZSCH DSC 214 instrument under a dinitrogen atmosphere in aluminum crucibles. The dielectric

measurements were carried on a TH2828A impedance analyzer. Thermogravimetric analysis (TGA) were carried out on a PerkinElmer TGA 8000 instrument by heating crystalline samples under a nitrogen atmosphere. We used the Rigaku D/MAX 2000 PC X-ray diffraction instrument in the 2θ between 7.5° and 40° with a step size of 0.02° to record PXRD patterns. The SHG measurements were carried on an INSTEC Instrument (pulsed Nd: YAG laser with a wavelength of 1081 nm, 1.6 MW peak power, 5 ns pulse duration). The numerical values of the nonlinear optical coefficients for SHG were determined by comparison with a KDP reference. Band structure and Partial Density of states (PDOS) were performed with Vienna Ab initio Simulation Package (VASP)[1-2] using the Perdew-Burke-Ernzerhof (PBE) functional[3] with the generalized gradient approximation (GGA). Electron−ion interactions were described using the projector augmented wave (PAW) method. The initial model was based on the single-crystal structure of 293 K and optimized before calculation with cell parameters of a = 10.06 Å, b = 9.99 Å, c = 18.16 Å, and $\alpha = \beta = \gamma = 90°$. The Monkhorst−Pack grid was 3 × 3 × 2 for works, and the plane-wave cutoff energy was 500 eV. The energy and force tolerances for optimization were 10−5 eV and 0.01 eV/Å, respectively. All calculations were performed using the Grimme's DFT-D3 method to deal with Van der Waals effects.

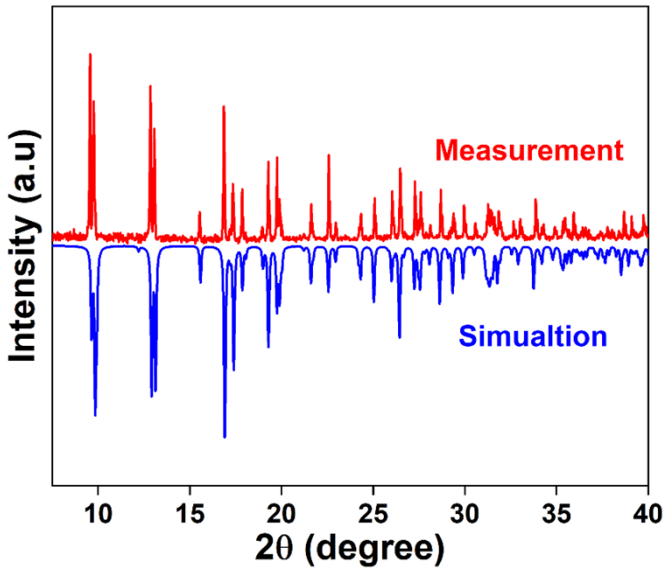

Fig. S1. Experimental PXRD patterns and simulated ones from crystal structure of [*R*-HP]$_2$SnCl$_5$ at room temperature.

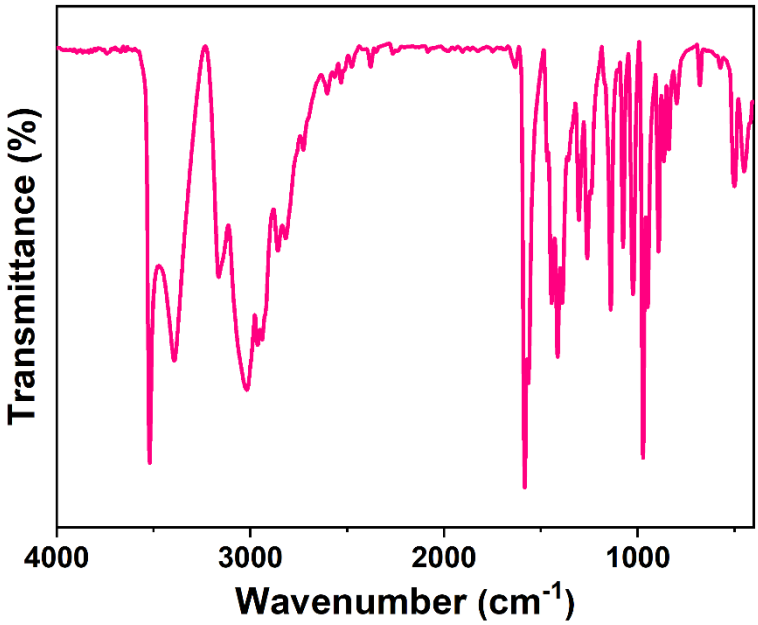

Fig. S2. Infrared (IR) spectrum of [*R*-HP]$_2$SbCl$_5$ recorded on a Bruker NVENIO spectrometer at room temperature.

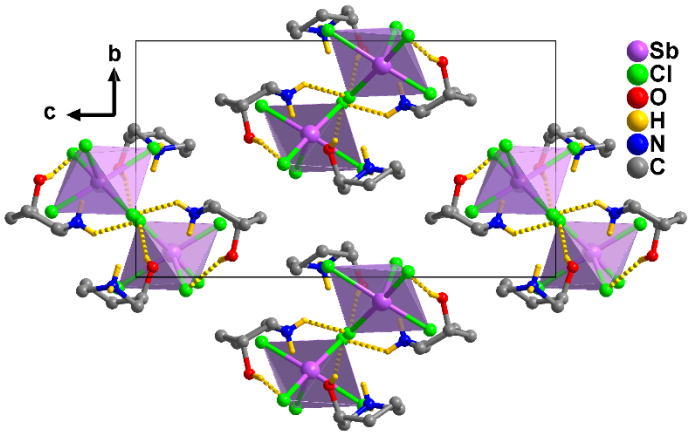

Fig. S3. Packing views of the structures of $[R\text{-HP}]_2SbCl_5$. The yellow dashed line denotes hydrogen bonds.

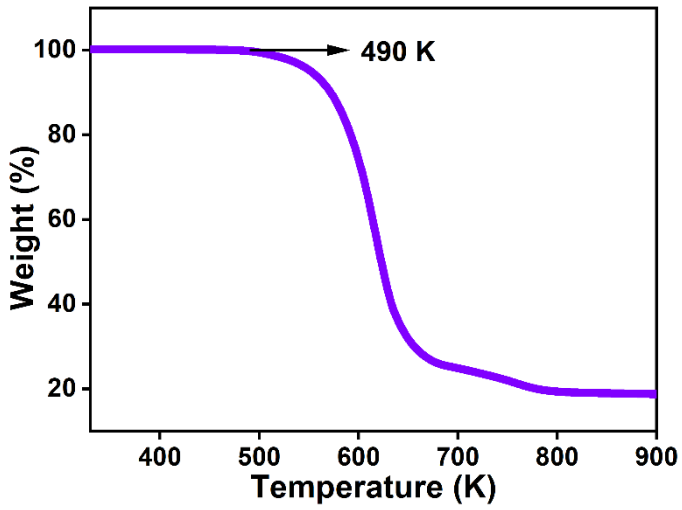

Fig. S4. TGA curve of $[R\text{-HP}]_2SnCl_5$ in the temperature range of 303 K-900 K, showing thermal stability up to about 490 K.

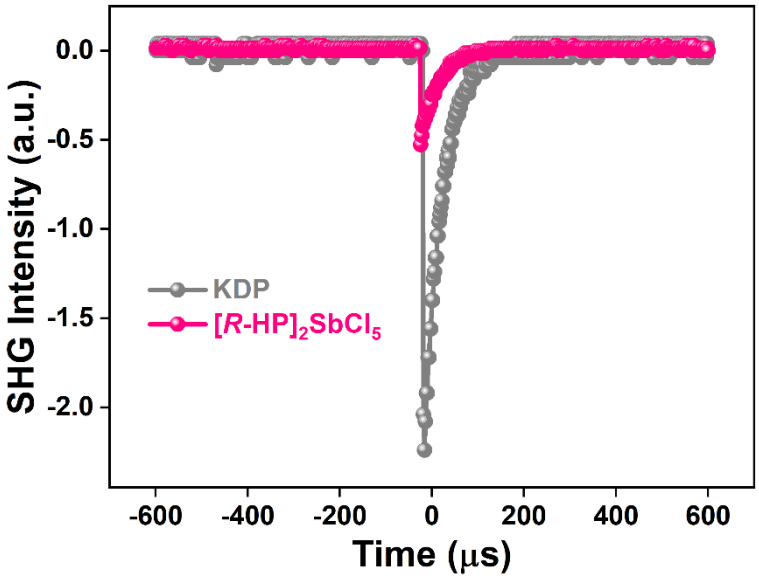

Fig. S5. SHG signals of KDP and $[R\text{-HP}]_2SbCl_5$ at room temperature.

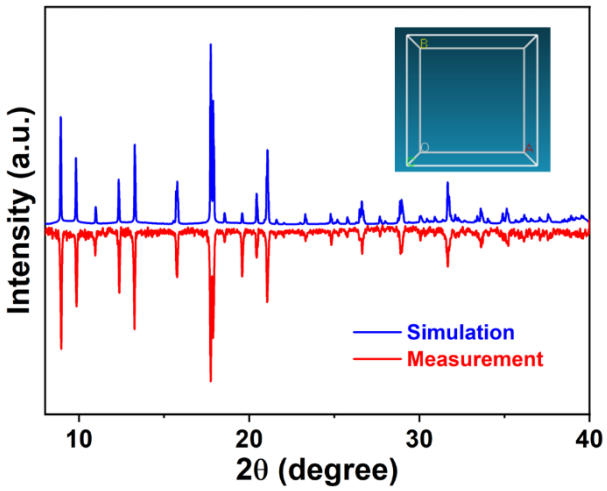

Fig. S6. Pawley refinement of PXRD data of $[R\text{-HP}]_2SbCl_5$ collected at 363 K with tetragonal crystal system.

Table S1. Crystal data and structure refinement details for [*R*-HP]$_2$SbCl$_5$ at 293 K.

Compound	[*R*-HP]$_2$SbCl$_5$
Temperature	293 K
Formula	$C_{10}H_{24}Cl_5N_2O_2Sb$
Formula weight	503.31
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a, *b*, *c* (Å)	10.1868(5) 10.3053(4) 18.3253(8)
α, *β*, *γ* (°)	90 90 90
Volume /Å^3	1923.75(15)
Z	4
R_1 [$I>2\sigma(I)$]	0.0366
wR_2 [$I>2\sigma(I)$]	0.0708
GOF	0.965
Flack parameter	-0.033(19)

Table S2. Selected Cl−Sb bond lengths [Å] and Cl−Sb−Cl bond angles [°] for $[R\text{-HP}]_2SbCl_6$ at 293K

bond lengths [Å]		bond angles [°]	
Sb1-Cl1	2.5001(15)	Cl1-Sb1-Cl3	174.73(5)
Sb1-Cl2	2.4500(16)	Cl1-Sb1-Cl5	91.12(5)
Sb1-Cl3	2.8066(14)	Cl2-Sb1-Cl1	90.52(6)
Sb1-Cl4	2.4024(15)	Cl2-Sb1-Cl3	91.43(5)
Sb1-Cl5	2.9943(16)	Cl2-Sb1-Cl5	176.21(5)
		Cl3-Sb1-Cl5	86.64(4)
		Cl4-Sb1-Cl1	89.19(6)
		Cl4-Sb1-Cl2	90.72(6)
		Cl4-Sb1-Cl3	85.89(5)
		Cl4-Sb1-Cl5	85.88(5)

Table S3. Hydrogen bond lengths [Å] and angles [°] for $[R\text{-HP}]_2SbCl_6$ at 293K

D—H···A	D—H [Å]	H···A[Å]	D···A[Å]	D—H···A[°]
O2-H2···Cl5^{I}	0.820	2.403	3.191(4)	161.47
N2-H2A···Cl3^{II}	0.890	2.355	3.204(4)	159.46
O1-H1···Cl4^{I}	0.820	2.656	3.441(6)	160.68
N1-H1B···Cl5	0.890	2.721	3.298(4)	123.61

Symmetry code(s): (I) [x-1/2, -y+1/2, -z+2], (II) [x+1/2, -y+1/2, -z+2]

References

1 G. Kresse and J. Furthmüller, *Phys. Rev. B*, 1996, **54**, 11169.

2 G. Kresse and J. Furthmüller, *Comput. Mater. Sci.*, 1996, **6**, 15-50.

3 J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865-3868.