

Supporting Information

Yellow Phosphor Based on Zero-dimensional Antimony Halide for White Light-emitting Diodes

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1. Experiment sections

Materials: SbCl_3 (99.9%), 2,4,6-trimethylbenzenamine ($\text{C}_9\text{H}_{13}\text{N}$, 98%), hydrochloric acid (HCl, AR, 36-38%), N, N-dimethylformamide (DMF, AR, $\geq 99.5\%$), acetone (AR, 99.5%) and ethyl ether (AR, $\geq 99.5\%$) were purchased for use without further processing.

Synthesis of 2,4,6-trimethylbenzenamine chloride: The salt was synthesized using a rotary evaporator. We added excess hydrochloric acid (15 mL) to 2,4,6-trimethylbenzenamine (5 mL), then set condensate temperature to minus 15°C , with the water bath heating temperature to 75°C and the rotation speed to 60r/min. Distillation was continued under reduced pressure until the corresponding salt was obtained. Finally, the salt (2,4,6-trimethylbenzenamine chloride) was obtained after being dried for about 2 days in vacuum drying oven.

Synthesis of $(\text{NII})_2\text{SbCl}_5$ single crystal: The $(\text{NII})_2\text{SbCl}_5$ single crystal was prepared by antisolvent way. 186 mg (0.81 mmol) SbCl_3 and 277 mg (1.62 mmol) 2,4,6-trimethylbenzenamine chloride were dissolved into 3 mL DMF in a 5 mL glass bottle and stirred for about 10 minutes to form the clear precursor solutions. Then, the glass bottle containing 1 mL of precursor solution was placed in a large test tube containing 3 mL acetone and sealed in the refrigerator for 3-4 days. Finally, the glass bottle was placed in a large test tube containing 3 mL anhydrous diethyl ether and sealed in the refrigerator for 2 days to obtain transparent single crystal. The in-situ synthesis reaction of Schiff's base is verified by hydrogen nuclear magnetic resonance (H-NMR) and carbon nuclear magnetic resonance (C-NMR). ^1H NMR (600 MHz, DMSO-d_6) δ/ppm : 7.08 (s, 2H), 2.80 (s, 3H), 2.29 (s, 3H), 2.20 (s, 3H), 2.13 (s, 6H). ^{13}C NMR (151 MHz, DMSO-d_6) δ/ppm : 194.12, 138.97, 132.24, 131.42, 129.30, 24.91, 22.03, 20.50, 17.23.

Measurements and Instruments: The structure data of single crystal was collected by the direct method using SHELXS-97 and refined using software of VESTA. PXRD data were recorded using a Bruker D8 Advance XRD using $\text{Cu K}\alpha$ radiation (1.54 \AA). A UV-vis spectrophotometer (LAMBDA 950, PerkinElmer) was used to collect the absorption spectra. The PL spectra, the temperature-dependent PL spectra, the time-resolved photoluminescence (TRPL) spectra and PLQY were measured for the powder sample using FLS980, Edinburgh Instruments. The thermogravimetric analysis (TGA) was recorded from R.T. to 800°C using a TA Instruments TGAQ500 with nitrogen atmosphere. ^1H

NMR spectra and ^{13}C NMR were recorded at 298 K on a Bruker AVANCE III 600MHz NMR Spectrometer in designated deuterated solvent.

UV pumped LEDs based on $(\text{NII})_2\text{SbCl}_5$: First, the $(\text{NII})_2\text{SbCl}_5$ phosphors were obtained by grinding $(\text{NII})_2\text{SbCl}_5$ single crystals. Then, blue phosphor ($\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}^{2+}$), green phosphor ($\text{Ba}_2\text{SiO}_4:\text{Eu}^{2+}$) and $(\text{NII})_2\text{SbCl}_5$ phosphors were mixed in ratio of 6:1.3:18, and were blended with Sylgard 184 polydimethylsiloxane (PDMS) encapsulant. Finally, the phosphors doped PDMS were coated on a commercial UV-LED (365 nm) lamp and then the whole mold was heated at 100°C for 1 hour in an oven to cure PDMS. This is the entire process about fabrication UV pumped LEDs based on $(\text{NII})_2\text{SbCl}_5$.

DFT methods: Density functional theory (DFT) calculations were performed using the projector-augmented wave (PAW) method implemented in the VASP code.^[1, 2] The generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional and a uniform $3\times 4\times 2$ k -mesh grid in the Brillouin zone were employed to optimize the crystal structure of $(\text{NII})_2\text{SbCl}_5$. The atomic positions of $(\text{NII})_2\text{SbCl}_5$ were fully relaxed until the forces on each atom less than $0.01\text{ eV}/\text{\AA}$. The Heyd-Scuseria-Ernzerhof hybrid functional (HSE06, $\alpha = 0.2$) was used to calculate the electronic bands, projected density of states (PDOS), and charge densities for $(\text{NII})_2\text{SbCl}_5$. The plane-wave basis set cutoff of the wave functions was set at 450 eV for the structural optimization at GGA/PBE level and 350 eV for the electronic bands and PDOS calculations at HSE06 level.

2. Figure sections

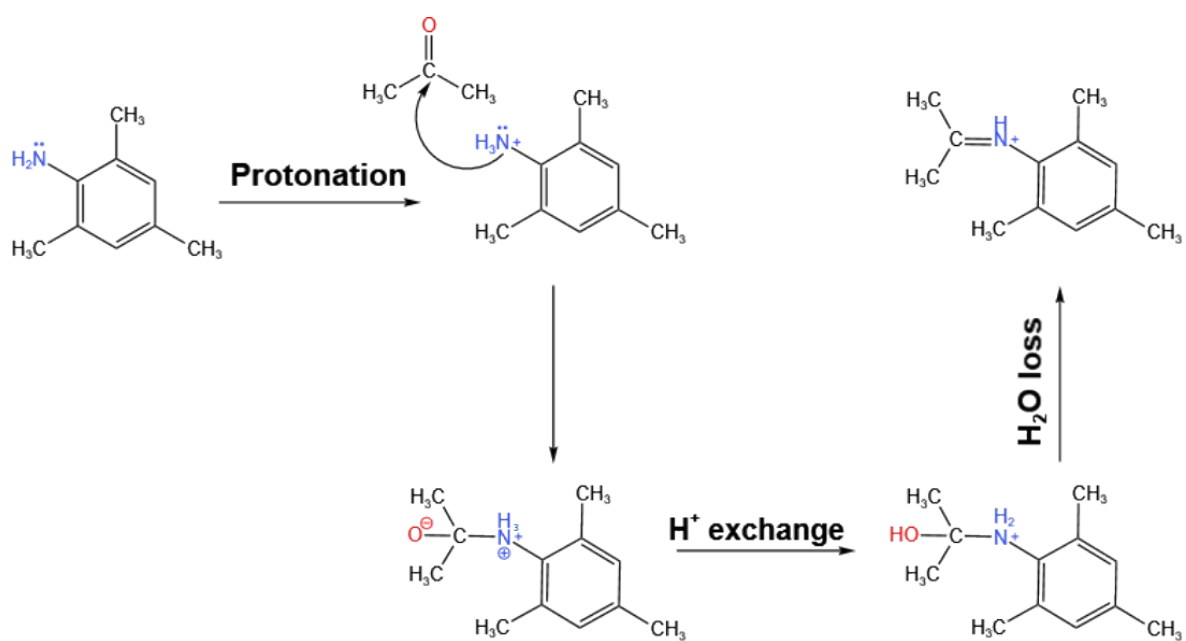


Figure S1 The synthetic route about NII⁺ cation.

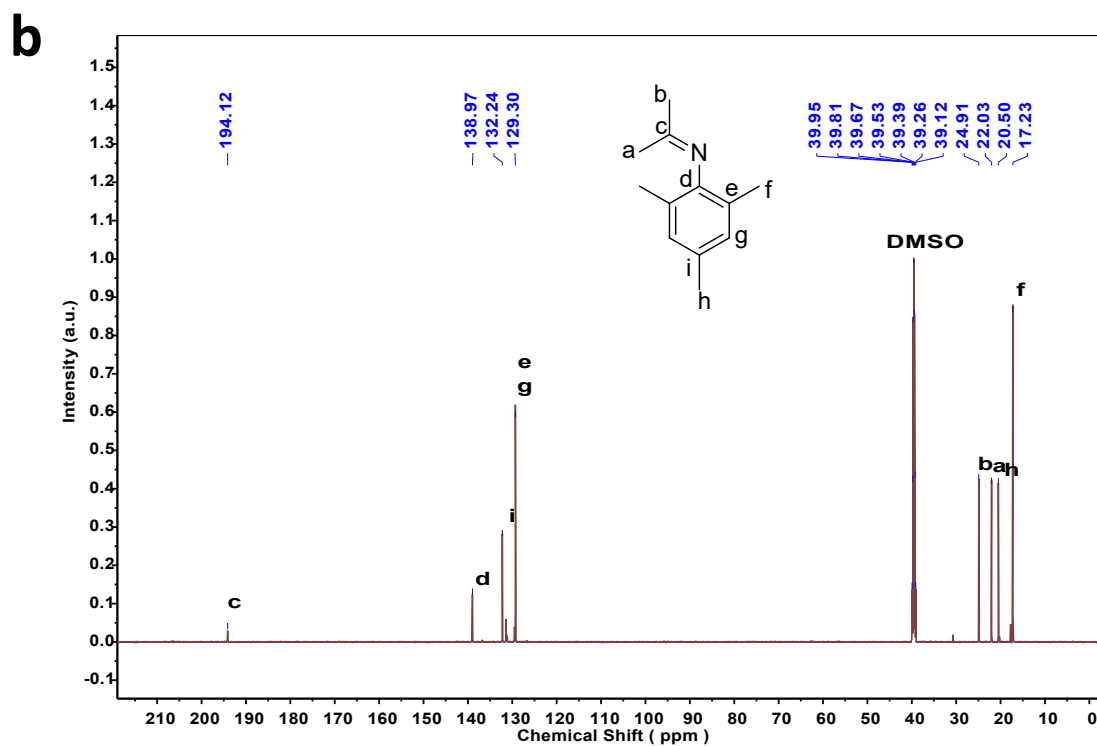
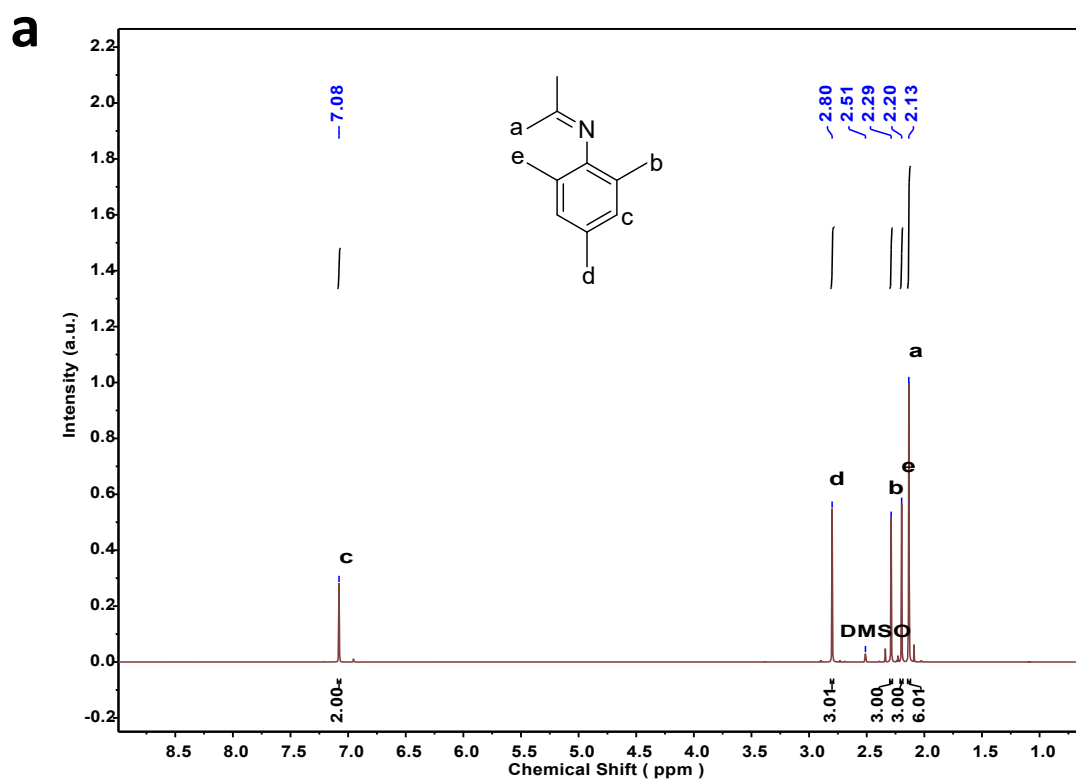


Figure S2 The information of (a) $^1\text{H-NMR}$ spectroscopy and (b) $^{13}\text{C-NMR}$ spectroscopy about $(\text{NII})_2\text{SbCl}_5$ in DMSO-d_6 .

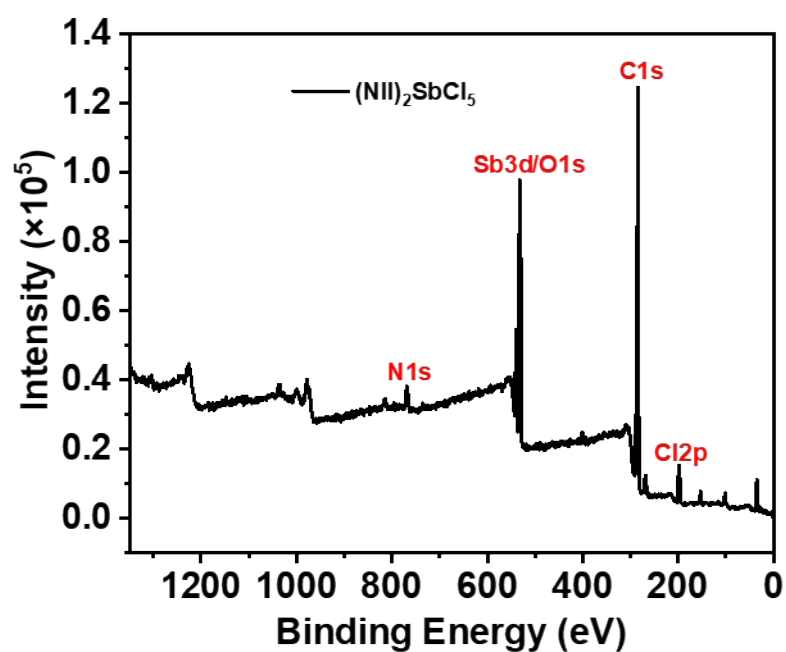


Figure S3 X-ray photoelectron spectroscopic (XPS) analysis of $(\text{NII})_2\text{SbCl}_5$ powders.

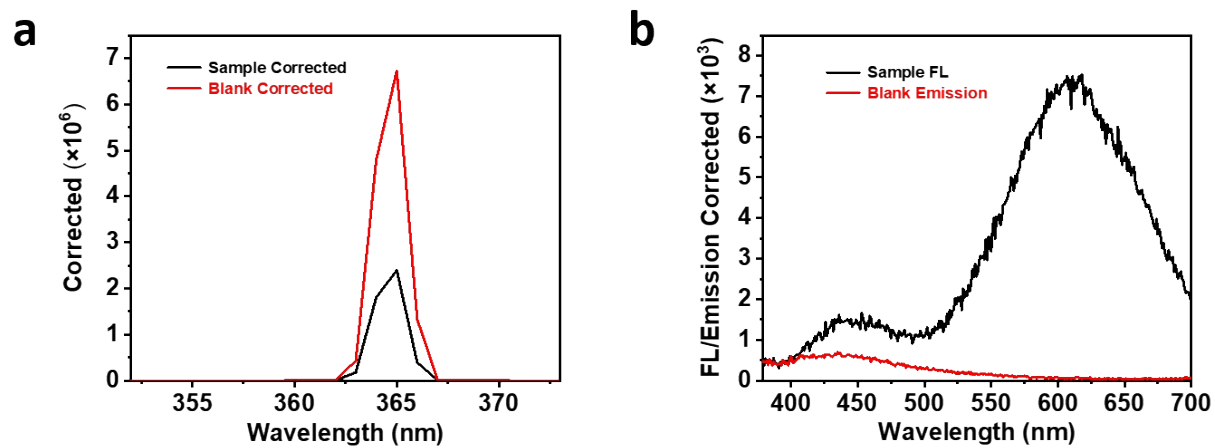


Figure S4 PLQY spectrum of $(\text{NII})_2\text{SbCl}_5$ crystal under excitation of 365 nm

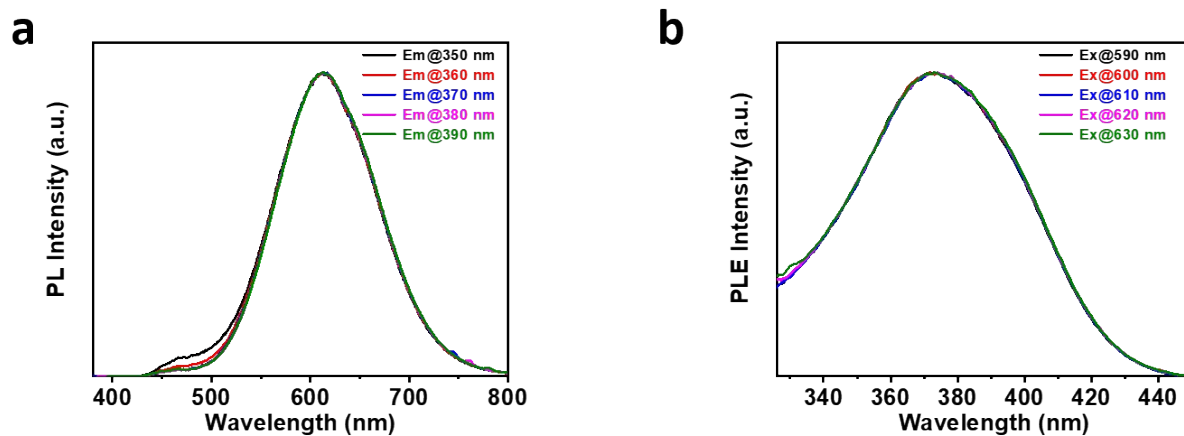


Figure S5 (a) Excitation-wavelength-dependent photoluminescence (PL) spectra of $(\text{NII})_2\text{SbCl}_5$. (b) Emission-wavelength-dependent photoluminescence excitation (PLE) spectra of $(\text{NII})_2\text{SbCl}_5$.

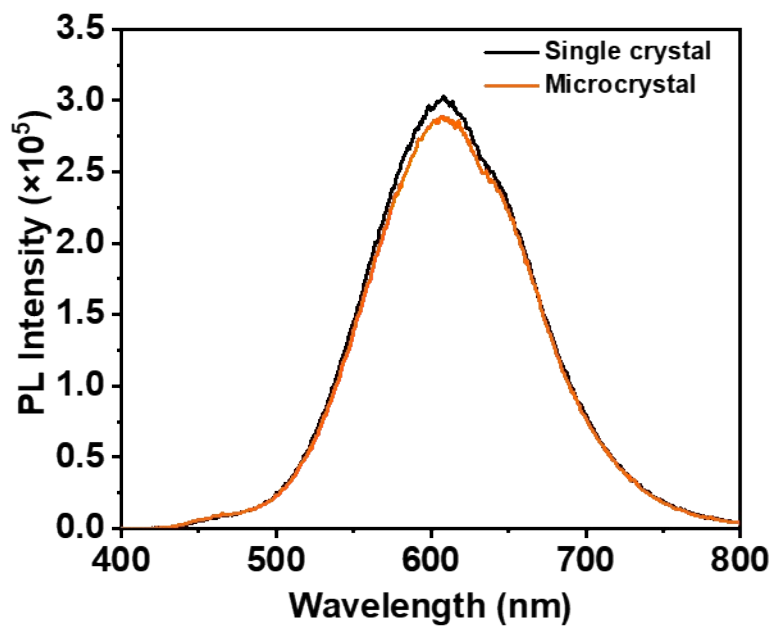


Figure S6 PL spectrum of bulk and powder crystals.

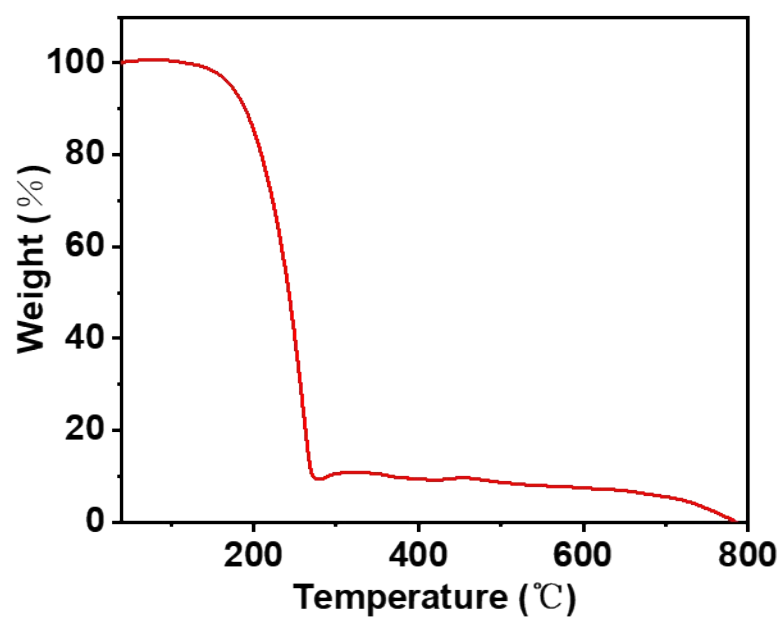


Figure S7 The thermogravimetric analysis (TGA) of $(\text{NII})_2\text{SbCl}_5$.

3. Table section

Table S1 Summary of the optical properties of the Sb-based organic-inorganic hybrid metal halides.

Compounds	λ_{em} (nm)	Lifetime (μ s)	PLQY (%)	Ref
(Bzmim) ₃ SbCl ₆	525	2.4	87.5	[3]
(Bzmim) ₂ SbCl ₅	600	2.6	22.3	[3]
(TTA) ₂ SbCl ₅	625	7.49	86	[4]
(TEBA) ₂ SbCl ₅	590	7.73	98	[4]
(TMA) ₂ SbCl ₅ ·DMF	630	6.62	67	[5]
(TPA) ₂ SbCl ₅	610	5.3	95	[6]
(C ₁₃ H ₂₂ N) ₂ Sb ₂ Cl ₈	865	1.87	5	[7]
(C ₁₀ H ₁₆ N) ₂ Sb ₂ Cl ₈	990	1.58	3	[7]
(C ₁₆ H ₃₆ P)SbCl ₄	1070	1.34	1	[7]
(C ₁₆ H ₂₈ N) ₂ SbCl ₅	633	4.71	98	[8]
(2cepyH)SbCl ₄	570	6.85	5	[9]

Table S2 Crystal data for (NII)₂SbCl₅ single crystal.

Empirical formula	C₂₄H₃₆Cl₅N₂Sb
Formula weight	651.55
Temperature (K)	296(2)
Crystal system	monoclinic
Space group	P2 ₁ /n
a/Å	13.916
b/Å	8.620
c/Å	26.092
α/°	90
β/°	102.084
γ/°	90
Volume/Å ³	3060.5(13)
Z	4
Density _(calc) g/cm ³	1.414
μ(mm ⁻¹)	1.352
F(000)	1320
Crystal size/mm ³	0.200×0.200×0.200
Radiation	MoKα(λ=0.71073)
Theta range for data collection/°	2.494 to 24.995
Index ranges	-16≤h≤16, -10≤k≤9, -30≤l≤30
Reflections collected	45617
Independent reflections	5358 [R _{int} = 0.0686]
Data / restraints / parameters	5358 / 0 / 299
Goodness-of-fit on F ²	1.072
Final R indices [I>2σ(I)]	R ₁ = 0.0512, wR ₂ = 0.1372
R indices [all data]	R ₁ = 0.0816, wR ₂ = 0.1531
Largest diff. peak and hole/ e Å ⁻³	1.284 and -0.523
The CCDC number	2210581

Table S3 Band angle and length for (NII)₂SbCl₅

Bonds	Angle/°	Bond	Length/Å
Cl1-Sb1-Cl2	92.26	Sb1-Cl3	2.3781
Cl1-Sb1-Cl5	85.52	Sb1-Cl2	2.7668
Cl5-Sb1-Cl4	90.17	Sb1-Cl1	2.6671
Cl4-Sb1-Cl2	92.04	Sb1-Cl5	2.536
Cl1-Sb1-Cl3	89.53	Sb1-Cl4	2.5323
Cl5-Sb1-Cl3	89.31		
Cl4-Sb1-Cl3	90.59		
Cl2-Sb1-Cl3	84.24		
Cl4-Sb1-Cl1	175.69		
Cl5-Sb1-Cl2	173.20		

Reference

- [1] G. Kresse and J. Hafner, *Phys. Rev. B* **1993**, 48, 13115-13118.
- [2] G. Kresse and J. Furthmuller, *Phys. Rev. B* **1996**, 54, 11169-11186.
- [3] Z. Wang, Z. Zhang, L. Tao, N. Shen, B. Hu, L. Gong, J. Li, X. Chen and X. Huang, *Angew. Chem. Int. Ed* **2019**, 58, 9974-9978.
- [4] Z. Li, Y. Li, P. Liang, T. Zhou, L. Wang and R.-J. Xie, *Chem. Mater.* **2019**, 31, 9363-9371.
- [5] Q. Wei, T. Chang, R. Zeng, S. Cao, J. Zhao, X. Han, L. Wang and B. Zou, *J. Phys. Chem. Lett.* **2021**, 12, 7091-7099.
- [6] H. Peng, Y. Tian, X. Wang, T. Huang, Y. Xiao, T. Dong, J. Hu, J. Wang and B. Zou, *J. Mater. Chem. C* **2021**, 9, 12184-12190.
- [7] B. Su, S. Geng, Z. Xiao and Z. Xia, *Angew. Chem. Int. Ed* **2022**, 61, e202208881.
- [8] H. Peng, Y. Tian, Z. Yu, X. Wang, B. Ke, Y. Zhao, T. Dong, J. Wang and B. Zou, *Sci. China Mater* **2022**, 65, 1594-1600.
- [9] Z. Qi, Y. Chen, H. Gao, F.-Q. Zhang, S.-L. Li and X.-M. Zhang, *Sci China Chem* **2021**, 64, 2111-2117.