Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Circularly polarized luminescence and nonlinear optical harmonic generation based on chiral zinc halides

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Experimental Methods

Materials. Chemicals such as zinc oxide (ZnO, TCI, 99%), antimony trichloride ($SbCl_3$, Macklin, 99.98%), hydrochloric acid (HCl, Aladdin, 36 wt%. in water), (*R*)-(-)-2-Methylpiperazine (*R*-2-MP, Aladdin, 99%), (*S*)-(+)-2-Methylpiperazine (*S*-2-MP, Aladdin, 99%) are commercially available and used without further purification.

Synthesis and crystal growth. Synthesis of ***R*/*S*-Zn** single crystals. (*R*)-(-)-2-Methylpiperazine or (*S*)-(+)-2-Methylpiperazine (5 mmol, 0.505 g), and ZnO (5 mmol, 0.410 g) was dissolved in 4 mL of hydrochloric acid in a 20 mL reaction vial. The mixture was stirred continually to form a transparent solution. Then the resultant solution was filtered and allowed to evaporate slowly at room temperature to acquire the colorless crystals.

For the synthesis of Sb^{3+}-doped ***R*/*S*-Zn** crystals, the same method was used. The amount of *R*-/*S*-2-MP, and HCl aqueous solution remain unchanged, and different molar proportions (*x*mol%) of $SbCl_3$ were added to replace the original ZnO. In this work, *x* of ***R*-Zn:*x*%Sb** only represents the feeding level of Sb^{3+} in the preparation process, rather than the actual proportion after crystallization.

Characterization. Single-crystal X-ray diffraction (SCXRD) data for all the compounds were recorded on Rigaku XtaLAB MM007 CCD diffractometer with Mo Kα radiation (λ= 0.71073 Å) at 100 K. The structures were solved by SHELXT methods with the Olex2 programs[S1] and all non-hydrogen atoms were refined anisotropically by least-squares technique on weighted F^2 using SHELXL. Powder X-ray diffraction (PXRD) spectra were recorded on a Rigaku D/Max-2500 diffractometer at 40 kV, 100 mA with a Cu-target tube and a graphite monochromator. UV–vis absorbance spectra and UV–vis–NIR spectra were collected with PerkinElmer LAMBDA 750. X-ray photoelectron spectra (XPS) were carried out on a Thermo Scientific ESCALAB 250Xi with Al Kα radiation. The binding energy was calibrated using the C 1s photoelectron peak at 284.6 eV as the reference. Thermogravimetry analyses (TGA) were performed on a standard TG-DTA analyzer under an Ar atmosphere in the temperature range 30-800 °C at a heating rate of 10 °C min^{-1}. Edinburgh FS5 fluorescence spectrometer was applied to collect the luminescence spectra, lifetimes and quantum yields. For the time-resolved spectra at nanosecond and microsecond scales, we used a pulsed laser source (365 nm, pulse width: 897.4 ps, bandwidth: 13.9 nm) and a microsecond lamp source (10 Hz) for measurement, respectively. Instrument response function (IRF) curves were obtained via collecting the decay signals only from the excitation sources. Transmission circular dichroism (CD) spectrum of the prepared films was measured and collected using a CD spectrometer (J-1700, JASCO) with the scanning rate of 50 nm/min. The circularly polarized luminescence (CPL) spectrum was recorded on JASCO CPL-200 spectrometer. Fourier transform infrared (FTIR) spectra of the ***R*-/*S*-Zn** and ***R*-Zn:*x*%Sb** were collected on FTIR spectrometer (TENSOR 37) from 4000 to 400 cm^{-1}.

Nonlinear optical measurements. The nonlinear optical (NLO) measurements were conducted using a home-built multiphoton nonlinear optical microscope system. Briefly, a commercial femotosecond pump (Mai Tai HP, <100 fs, 80 MHz, wavelength ranging from 690 to 1040 nm) in reflection geometry. A laser beam is incident on the samples with an incident angle γ (γ = 45˚) and the generated SHG signals are collected in the reflection configuration. The linearly polarized pump was altered with the λ/2 plate. The measured SHG signal is reflected from the front surface of crystal and quartz. The wavelength-dependent SHG responses were collected via switching the pumped wavelengths from 800 to 1040 nm at the same incident laser power. The azimuth-polarization-dependent SHG signals have been collected at intervals of 10˚. The power-dependent SHG measurements were collected upon excitation at the optimal wavelength with different laser power (the laser spot of ≈ 20 μm in diameter). The *Z*-cut quartz is used as a benchmark for SHG signal intensity.

DFT calculations. DFT calculations were implemented in Vienna Ab initio Simulation Package (VASP 5.4.4) adopting the projector augmented-wave method (PAW) to deal with the ion-electron interaction[S2, 3]. We selected the generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof (PBE) to approximate the exchange-correlation energy[S4]. Considering the nonbonding and long-range interaction in the hybrid organic-inorganic metal halides, the van der Waals (vdW) correction (DFT-D3) was adopted in the calculations[S5]. The plane-wave basis set was defined by the energy cut-off at 450 eV. The energy convergence criterion for electronic iteration was set to be 10-4 eV. The structural relaxation was performed until the Hellmann-Feynman forces on each atom are less than 0.001 eV/Å. A Γ-centered 4 × 4× 3 grid was adopted to simulate the k-space integrations. The DFT calculations about the Zn-Sb alloying system were based on the model, in which the three Zn^{2+} were replaced by two Sb^{3+} and one hole in a unit cell.

Supplementary Figures

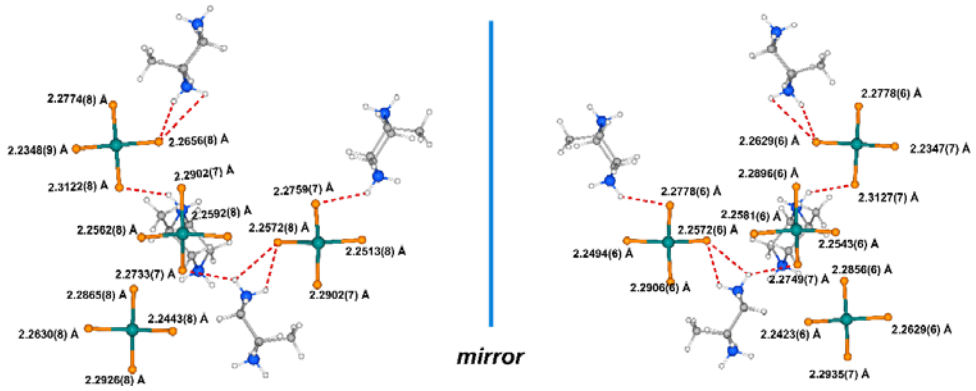

Fig S1. N−H•••Cl−Zn hydrogen bonds (red dotted lines) and inorganic $(ZnCl_4)^{2-}$ tetrahedrons in ***R*-Zn** (left) and ***S*-Zn** (right) crystals.

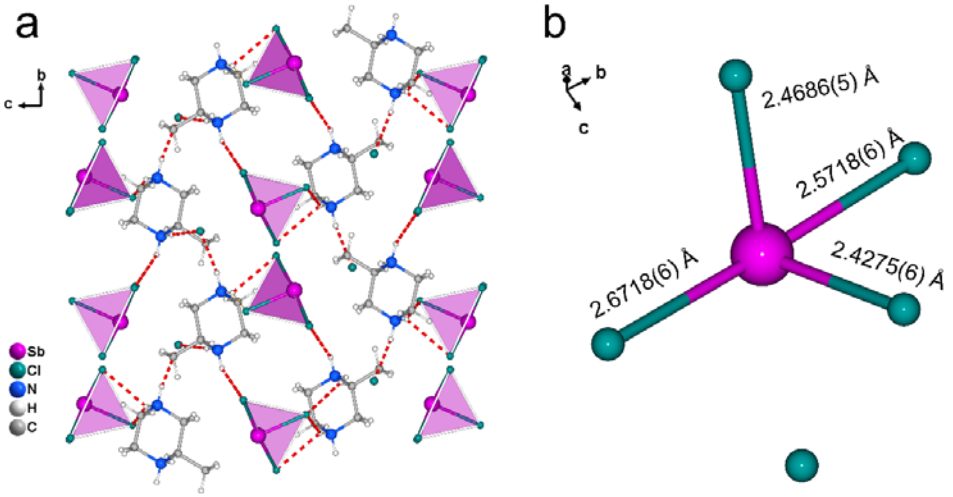

Fig S2. (a) Crystal packing diagram of ***R*-Sb** and the N−H•••Cl hydrogen bonds (red dotted lines); (b) inorganic $(SbCl_5)^{2-}$ building blocks in ***R*-Sb** crystals.

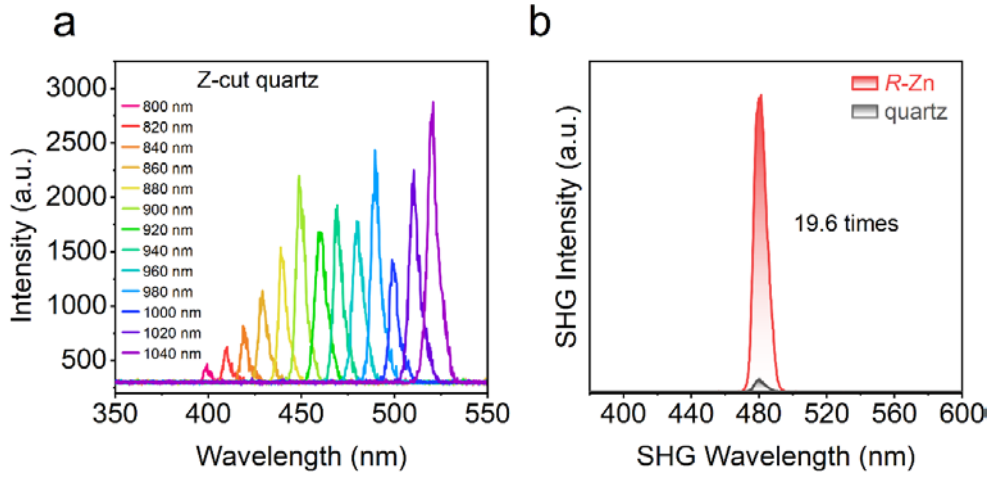

Fig S3. The SHG spectra of (a) Z-cut quartz and at different wavelengths. (b) Comparison of SHG intensities of ***R*-Zn** with that of the Z-cut quartz at 480 nm.

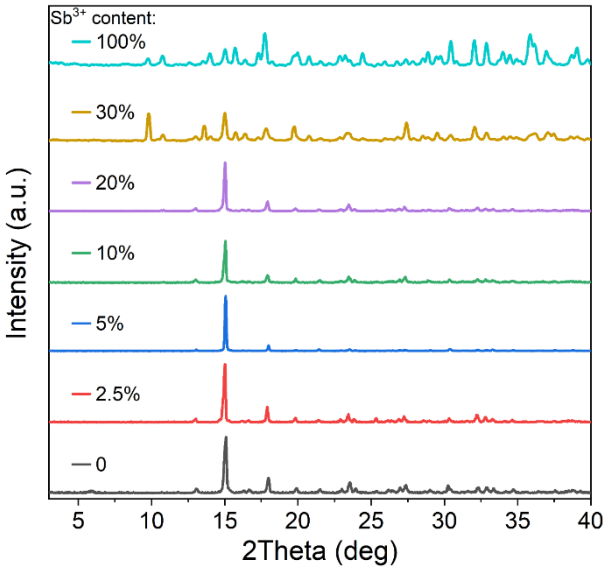

Fig S4. XRD patterns of the undoped and the representative Sb-doped ***R*-Zn** samples.

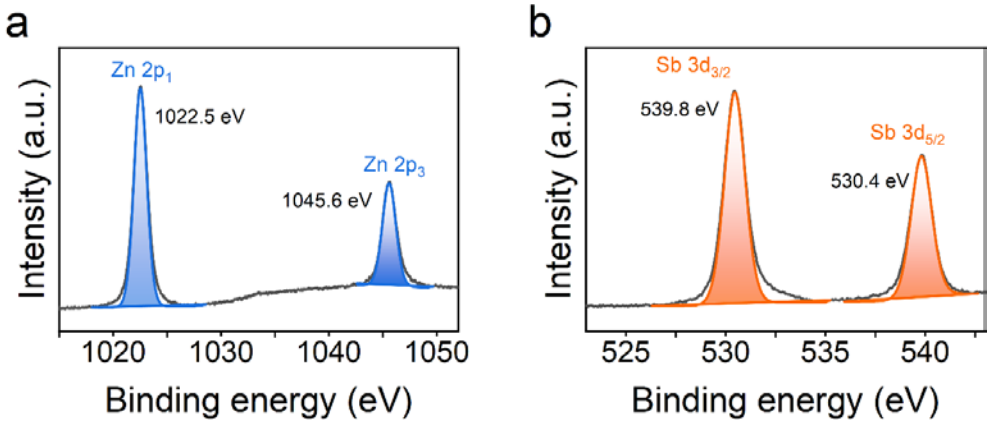

Fig S5. High-resolution XPS spectrum of Zn 2p and Sb 3d for ***R*-Zn:10%Sb^{3+}**.

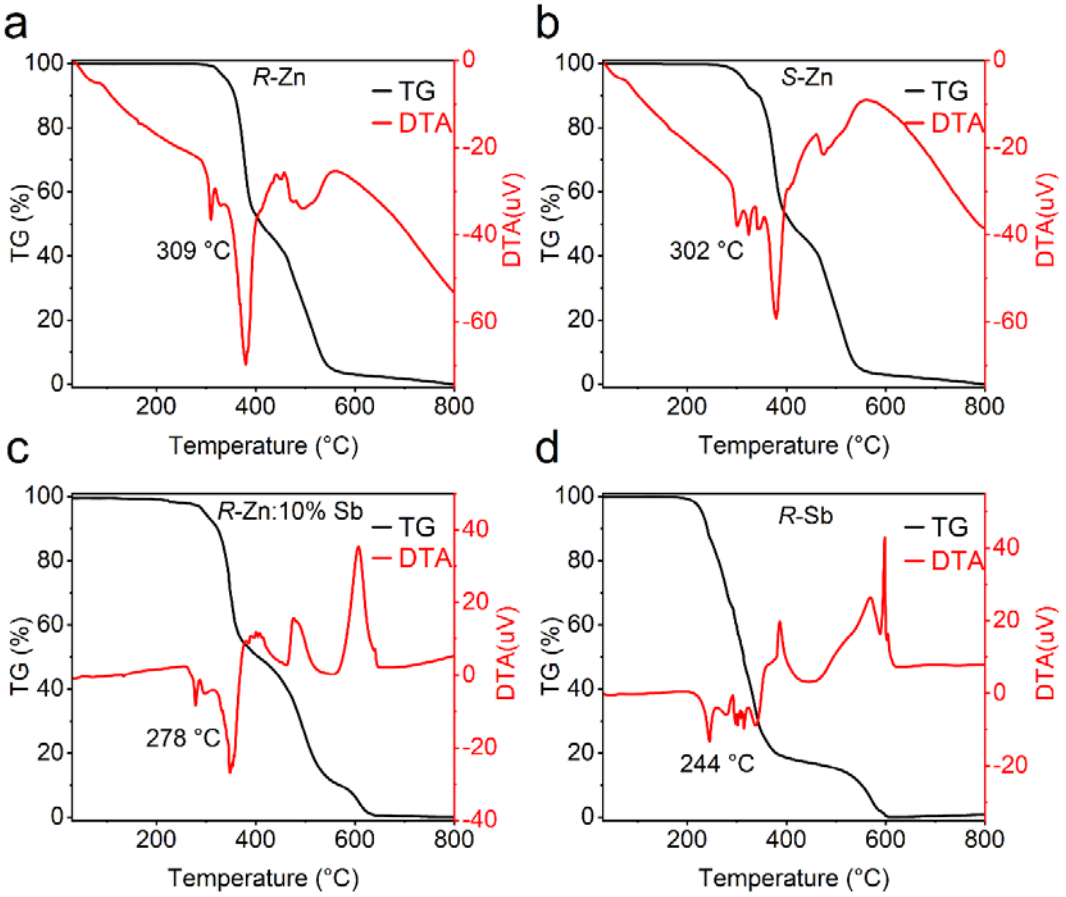

Fig S6. Thermogravimetric analyses (TGA) for ***R*-Zn**, ***S*-Zn**, ***R*-Zn:10% Sb**, and ***R*-Sb**.

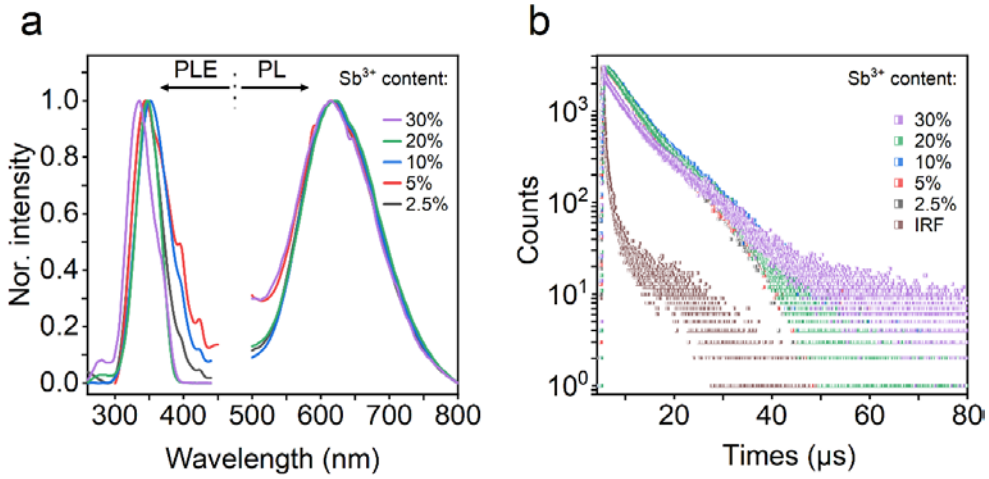

Fig S7. (a) Photoluminescence excitation (PLE), photoluminescence (PL) and the corresponding (b) time-resolved spectra for ***R*-Zn** with different Sb^{3+} doping content.

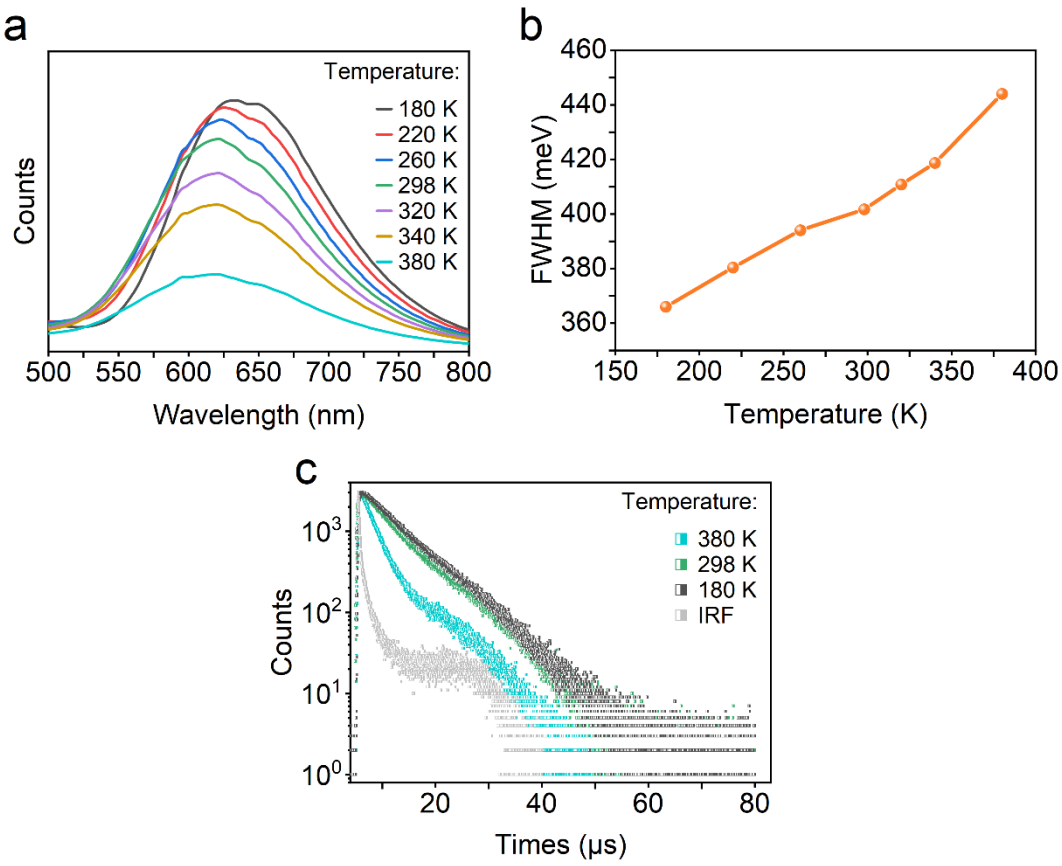

Fig S8. (a) Varied-temperature PL spectra of ***R*-Zn:10%Sb** and (b) corresponding full width at half-maximum (FWHM) at the excitation of 351 nm. (c) Time-solved PL spectra of ***R*-Zn:10%Sb** at varied temperatures.

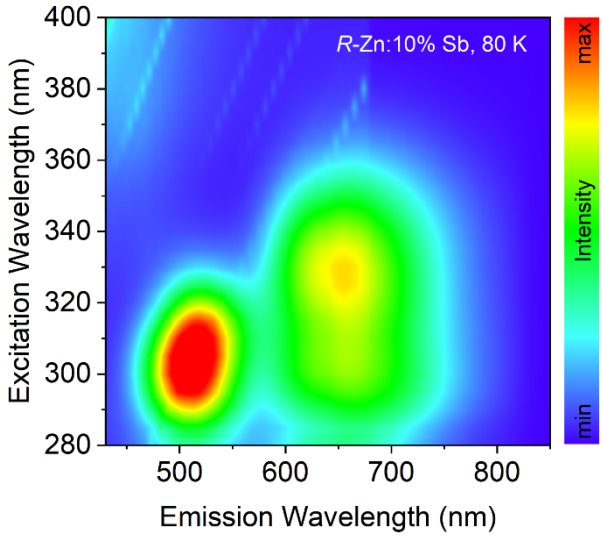

Fig S9. Excitation-emission mapping pattern of ***R*-Zn:10%Sb** at 80 K.

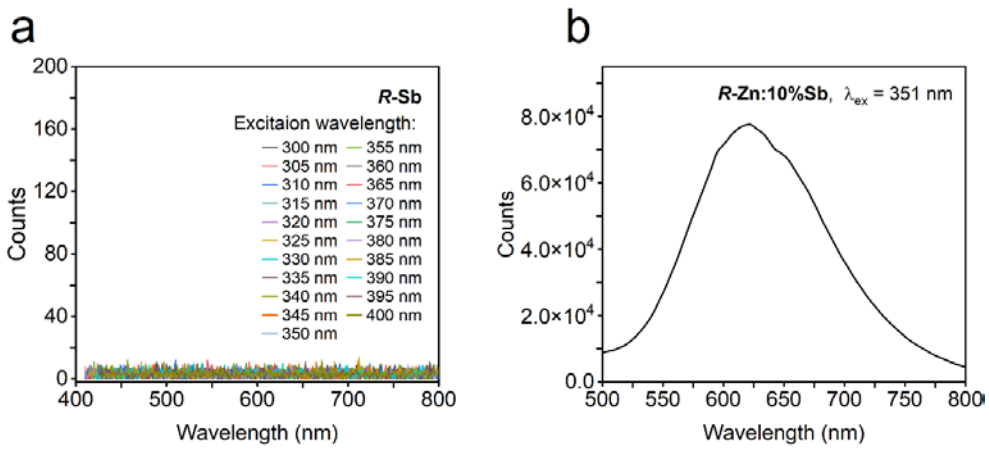

Fig S10. (a) Excitation-emission mapping pattern of ***R*-Sb** and (b) PL spectra of ***R*-Zn:10%Sb** at the excitation of 351 nm.

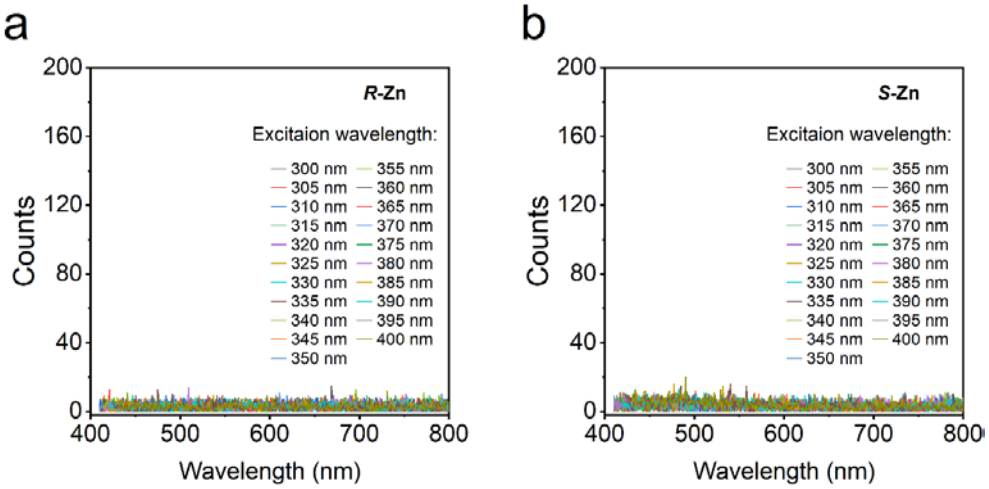

Fig S11. Excitation-emission mapping pattern of (a) ***R*-Zn** and (b) ***S*-Zn**.

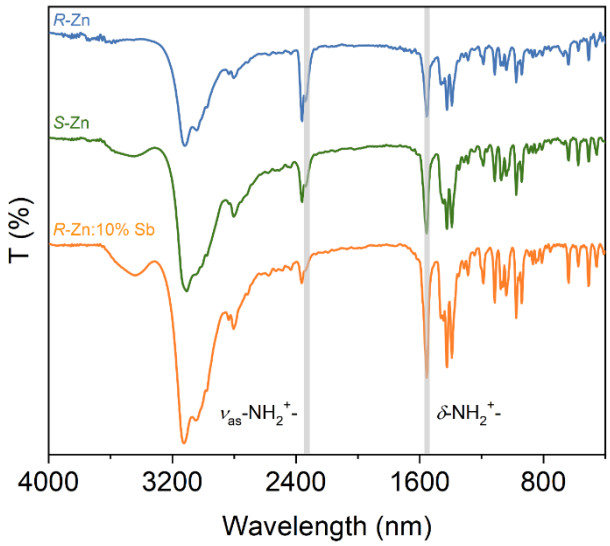

Fig S12. Fourier transform infrared (FTIR) spectra for ***R*-/*S*-Zn** and ***R*-Zn:10%Sb**.

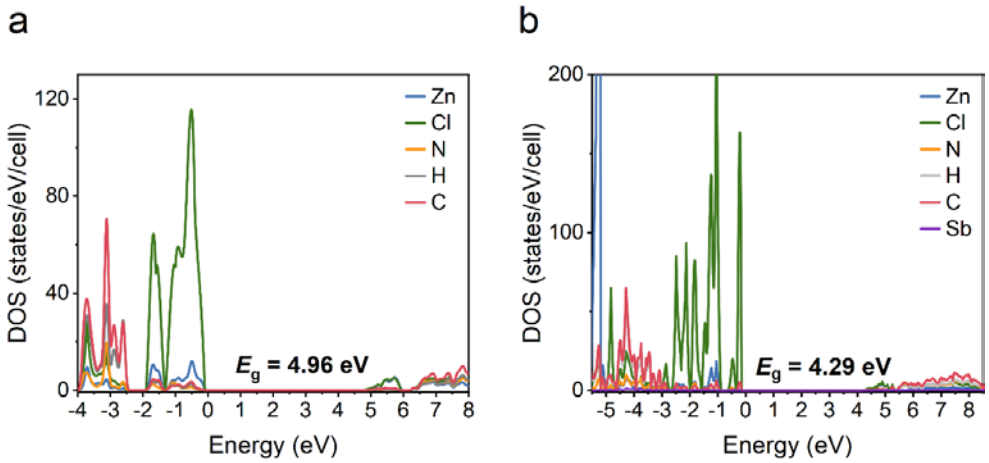

Fig S13. Calculated DOS plots of (a) ***R*-Zn** and (b) doped ***R*-Zn**.

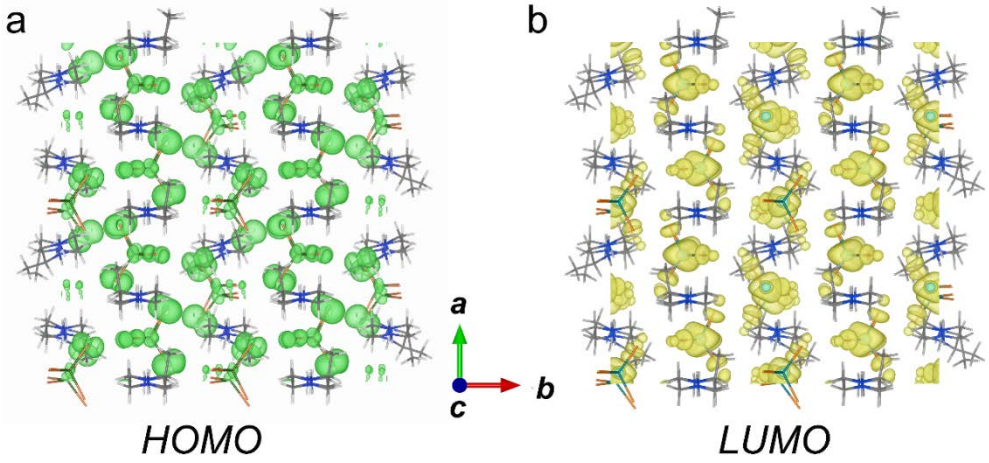

Fig S14. Calculated orbital nature for ***R*-Zn**.

Supplementary Tables

Table S1. Crystallographic data and structure refinement details for ***R*-Zn**, ***S*-Zn** and ***R*-Sb**.

Identification code	***R*-Zn**	***S*-Zn**	***R*-Sb**
Empirical formula	$C_{10}H_{28}Cl_8N_4Zn_2$	$C_{20}H_{56}Cl_{16}N_8Zn_4$	$C_5H_{14}Cl_5N_2Sb$
Formula weight	618.70	1237.545	401.18
Temperature/K	100	100	100
Crystal system	monoclinic	monoclinic	orthorhombic
Space group	$P2_1$	$P2_1$	$P2_12_12_1$
a/Å	11.6505(4)	11.6567(4)	7.6221(2)
b/Å	12.1341(4)	12.1248(4)	10.6784(2)
c/Å	16.4837(6)	16.4859(5)	16.3487(3)
α/°	90	90	90
β/°	90.02(3)	90	90
γ/°	90	90	90
Volume/Å^3	2330.27(14)	2330.04(13)	1330.65(5)
Z	4	2	4
ρ_{calc}g/cm^3	1.764	1.764	2.003
μ/mm^{-1}	2.979	2.980	3.041
F(000)	1248.0	1255.8	776.0
Reflections collected	28131	25218	17010
Data/restraints/parameters	12085/1/437	11317/1/438	3823/0/119
Goodness-of-fit on F^2	0.972	1.024	1.102
Final R indexes [I>=2σ (I)]	R_1 = 0.0236, wR_2 = 0.0472	R_1 = 0.0258, wR_2 = 0.0567	R_1 = 0.0139, wR_2 = 0.0308
Final R indexes [all data]	R_1 = 0.0271, wR_2 = 0.0479	R_1 = 0.0286, wR_2 = 0.0573	R_1 = 0.0142, wR_2 = 0.0310
Flack parameter	0.015(5)	-0.001(6)	-0.013(8)
CCDC	2241401	2241402	803026[S6]

Table S2. Selected bond lengths (Å) for ***R*-Zn**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Zn1	Cl4	2.2572(8)	N8	C15	1.487(4)
Zn1	Cl1	2.2902(7)	N8	C12	1.489(4)
Zn1	Cl2	2.2513(8)	N1	C012	1.494(4)
Zn1	Cl3	2.2759(7)	N1	C2	1.507(4)
Zn4	Cl16	2.2630(8)	N2	C3	1.495(4)
Zn4	Cl13	2.2926(8)	N2	C4	1.485(4)

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Zn4	Cl14	2.2443(8)	N5	C17	1.498(4)
Zn4	Cl15	2.2865(8)	N5	C18	1.488(4)
Zn2	Cl8	2.2562(8)	N7	C14	1.496(4)
Zn2	Cl6	2.2592(8)	N7	C13	1.498(4)
Zn2	Cl7	2.2895(7)	C14	C15	1.514(4)
Zn2	Cl5	2.2733(7)	C20	C17	1.526(4)
Zn3	Cl10	2.2656(8)	C20	C16	1.514(4)
Zn3	Cl11	2.2774(8)	C7	C6	1.518(4)
Zn3	Cl9	2.3122(8)	C7	C8	1.517(4)
Zn3	Cl12	2.2348(9)	C18	C19	1.512(4)
N3	C8	1.492(4)	C10	C9	1.504(4)
N3	C9	1.501(4)	C12	C4	1.520(4)
N6	C20	1.515(4)	C3	C2	1.518(5)
N6	C19	1.496(4)	C12	C13	1.516(4)
N6	C19	1.496(4)	C12	C13	1.516(4)
N4	C7	1.510(3)	C2	C1	1.516(4)
N4	C10	1.494(4)	C13	C11	1.514(4)

Table S3. Selected bond angles (°) for ***R*-Zn**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
Cl4	Zn1	Cl1	108.24(3)	C12	N1	C2	114.9(2)
Cl4	Zn1	Cl3	107.93(3)	C4	N2	C3	111.0(2)
Cl2	Zn1	Cl4	116.34(3)	C18	N5	C17	112.0(2)
Cl2	Zn1	Cl1	109.50(3)	C14	N7	C13	111.1(2)
Cl2	Zn1	Cl3	107.45(3)	N7	C14	C15	110.7(3)

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
Cl3	Zn1	Cl1	107.01(3)	N8	C15	C14	111.2(2)
Cl16	Zn4	Cl13	107.87(3)	N6	C20	C17	108.5(2)
Cl16	Zn4	Cl15	106.09(3)	C16	C20	N6	111.2(2)
Cl14	Zn4	Cl16	117.05(3)	C16	C20	C17	114.2(3)
Cl14	Zn4	Cl13	109.41(3)	N4	C7	C6	111.9(2)
Cl14	Zn4	Cl15	109.95(3)	N4	C7	C8	109.1(2)
Cl15	Zn4	Cl13	105.87(3)	C8	C7	C6	113.0(3)
Cl8	Zn2	Cl6	120.70(3)	N5	C17	C20	111.9(2)
Cl8	Zn2	Cl7	106.11(3)	N5	C18	C19	110.4(2)
Cl8	Zn2	Cl5	108.21(3)	N6	C19	C18	110.9(2)
Cl6	Zn2	Cl7	105.16(3)	N4	C10	C9	110.3(2)
Cl6	Zn2	Cl5	104.99(3)	N1	C12	C4	110.8(3)
Cl5	Zn2	Cl7	111.67(3)	N2	C3	C2	112.3(3)
Cl10	Zn3	Cl11	107.77(3)	N8	C12	C13	110.2(2)
Cl10	Zn3	Cl9	106.32(3)	N3	C8	C7	111.5(2)
Cl11	Zn3	Cl9	109.99(3)	N2	C4	C12	109.8(2)
Cl12	Zn3	Cl10	114.04(3)	N3	C9	C10	110.6(2)
Cl12	Zn3	Cl11	110.68(3)	N1	C2	C3	109.1(3)
Cl12	Zn3	Cl9	107.92(3)	N1	C2	C1	111.8(3)
C8	N3	C9	111.6(2)	C1	C2	C3	113.6(3)
C19	N6	C20	114.1(2)	N7	C13	C12	109.1(2)
C10	N4	C7	114.1(2)	N7	C13	C11	110.6(3)
C15	N8	C12	111.7(2)	C11	C13	C12	111.7(3)

Table S4. Selected bond lengths (Å) for ***S*-Zn**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Zn2	Cl5	2.2581(6)	N3	C19	1.493(3)
Zn2	Cl7	2.2543(6)	N3	C18	1.503(4)
Zn2	Cl6	2.2749(7)	N1	C5	1.496(4)
Zn2	Cl8	2.2906(6)	N1	C2	1.511(4)
Zn3	Cl9	2.2423(6)	N5	C15	1.499(3)
Zn3	Cl13	2.2856(6)	N5	C12	1.499(3)
Zn3	Cl12	2.2629(6)	N6	C14	1.488(3)
Zn3	Cl10	2.2935(7)	N6	C13	1.485(3)
Zn1	Cl11	2.2896(6)	N7	C9	1.502(3)
Zn1	Cl1	2.2494(6)	N7	C8	1.494(3)
Zn1	Cl4	2.2778(6)	C15	C14	1.511(4)
Zn1	Cl3	2.2572(6)	C5	C4	1.518(4)
Zn4	Cl14	2.2628(6)	C7	C6	1.518(4)
Zn4	Cl17	2.2784(7)	C7	C8	1.521(3)
Zn4	Cl15	2.3127(7)	C10	C9	1.508(4)
Zn4	Cl16	2.2347(7)	C19	C20	1.514(3)
N8	C7	1.509(3)	C13	C12	1.526(4)
N8	C10	1.497(3)	C17	C16	1.516(4)
N4	C17	1.519(3)	C17	C18	1.526(4)
N4	C20	1.497(4)	C2	C3	1.518(4)
N2	C4	1.493(3)	C2	C1	1.510(4)
N2	C3	1.490(4)	C12	C11	1.510(4)

Table S5. Selected bond angles (°) for ***S*-Zn**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
Cl7	Zn2	Cl5	120.69(3)	C2	N1	C5	114.4(2)
Cl6	Zn2	Cl5	105.00(2)	C12	N5	C15	111.1(2)
Cl6	Zn2	Cl7	108.20(2)	C13	N6	C14	112.0(2)
Cl8	Zn2	Cl5	105.17(2)	C8	N7	C9	111.55(19)
Cl8	Zn2	Cl7	106.15(2)	C14	C15	N5	110.5(2)
Cl8	Zn2	Cl6	111.64(3)	C4	C5	N1	110.8(2)
Cl13	Zn3	Cl9	109.97(2)	C15	C14	N6	110.9(2)
Cl12	Zn3	Cl9	116.98(3)	C6	C7	N8	111.7(2)
Cl12	Zn3	Cl13	106.15(2)	C8	C7	N8	109.1(2)
Cl10	Zn3	Cl9	109.41(2)	C8	C7	C6	113.4(2)
Cl10	Zn3	Cl13	105.83(3)	C9	C10	N8	109.8(2)
Cl10	Zn3	Cl12	107.92(2)	C20	C19	N3	110.4(2)
Cl1	Zn1	Cl11	109.51(2)	C12	C13	N6	110.0(2)
Cl4	Zn1	Cl11	106.98(3)	C16	C17	N4	111.2(2)
Cl4	Zn1	Cl1	107.54(3)	C18	C17	N4	108.5(2)
Cl3	Zn1	Cl11	108.24(2)	C18	C17	C16	114.3(2)
Cl3	Zn1	Cl1	116.23(3)	C5	C4	N2	109.6(2)
Cl3	Zn1	Cl4	107.96(2)	C10	C9	N7	110.6(2)
Cl17	Zn4	Cl14	107.73(2)	C3	C2	N1	109.5(2)
Cl15	Zn4	Cl14	106.35(2)	C1	C2	N1	111.6(2)
Cl15	Zn4	Cl17	110.00(3)	C1	C2	C3	114.3(2)
Cl16	Zn4	Cl14	113.99(3)	C19	C20	N4	110.6(2)
Cl16	Zn4	Cl17	110.67(3)	C2	C3	N2	111.5(2)
Cl16	Zn4	Cl15	107.98(3)	C7	C8	N7	111.0(2)

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C10	N8	C7	114.41(19)	C17	C18	N3	111.8(2)
C20	N4	C17	114.1(2)	C13	C12	N5	108.6(2)
C3	N2	C4	111.3(2)	C11	C12	N5	110.7(2)
C18	N3	C19	111.9(2)	C11	C12	C13	111.2(2)

Table S6. Crystal data and structure refinement for CCDC 803026 and ***R*-Sb**.

Identification	Reported	This work (***R*-Sb**)
Empirical formula	$C_5H_{14}Cl_5N_2Sb$	$C_5H_{14}Cl_5N_2Sb$
CCDC	803026	
Formula weight	401.18	401.18
Temperature (K)	293(2)	100
Crystal system	orthorhombic	orthorhombic
Space group	$P2_12_12_1$	$P2_12_12_1$
a (Å)	7.745(5)	7.6221(2)
b (Å)	10.773(7)	10.6784(2)
c (Å)	16.318(9)	16.3487(3)
α (°)	90.00	90
β (°)	90.00	90
γ (°)	90.00	90
V (Å^3)	1361.6(14)	1330.65(5)
Z	4	4
ρ (calculated) (g/cm^3)	1.957	2.003
F(000)	776.0	776.0
Final R indexes [I>=2σ (I)]	R_1 = 0.0190, wR_2 = 0.0414	R_1 = 0.0139, wR_2 = 0.0308
Final R indexes [all data]	R_1 = 0.0198, wR_2 = 0.0417	R_1 = 0.0142, wR_2 = 0.0310
Goodness-of-fit on F^2	1.081	1.102
Flack parameter	-0.037(17)	-0.013(8)

Table S7. The comparison of Sb-Cl bond lengths and Cl-Sb-Cl angles of CCDC 803026 and ***R*-Sb**.

Identification	Reported	This work (***R*-Sb**)
Bond lengths (Å)		
Sb1-Cl1	2.5667(13)	2.5718(6)
Sb1-Cl2	2.4351(12)	2.4275(6)
Sb1-Cl3	2.4702(14)	2.4686(5)
Sb1-Cl4	2.6932(13)	2.6718(6)
Bond angles (°)		
Cl1-Sb1-Cl4	176.26(3)	175.865(18)
Cl2-Sb1-Cl1	89.95(5)	89.777(17)
Cl2-Sb1-Cl3	89.51(4)	89.619(19)
Cl2-Sb1-Cl4	88.38(5)	88.062(18)
Cl3-Sb1-Cl1	89.02(4)	88.819(18)
Cl3-Sb1-Cl4	87.62(4)	87.642(18)

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