

Supporting Information

Experimental Section

Chemicals and Materials: Antimony trichloride (SbCl_3 , 99%) were purchased from Aladdin Reagent Co. Ltd (Shanghai, China). Indium chloride were purchased from Heowns Biochem Technologies, LLC, Tianjin. (*R/S*)-3-hydroxypyrrolidine dihydrochloride (*R/S*-BLOH, 98%) were purchased from Adamas Reagent Co., Ltd. hydrochloric acid (HCl, 38% in water) were purchased from Tianjin Feng chuan Chemical Reagent Technology Co., Ltd. Ethylether (Et_2O , AR) were purchased from Tianjin Bohua Chemical Reagent Co., Ltd, China. All chemicals were used without any further purification.

Synthesis of (*R/S*-3AP) $_2$ InCl $_7$ single crystals: 2 mmol of InCl_3 and 4 mmol of *R/S*-BLOH were dissolved in 1 mL of concentrated HCl. Then, the solution was heated to 100°C to form a clear solution under continuous stirring. *R/S*-MgInCl single crystals can be obtained by naturally cooling the aqueous solution to room temperature. The crystals were washed with ethylether and dried at room temperature.

Synthesis of (*R/S*-3AP) $_2$ InCl $_7$:x%Sb $^{3+}$ single crystals: The synthesis of (*R/S*-3AP) $_2$ InCl $_7$:x%Sb $^{3+}$ ($x = 1 \sim 100$) single crystals are similar to that of pristine (*R/S*-3AP) $_2$ InCl $_7$, except that the different amounts of SbCl_3 are added. Taking (*R/S*-3AP) $_2$ InCl $_7$:5%Sb $^{3+}$ as an example, 1.9 mmol of InCl_3 , 0.1 mmol of SbCl_3 and 4 mmol of *R/S*-BLOH were dissolved in 1 mL of concentrated HCl by heating the solution to 100 °C. Single crystals can be obtained by naturally cooling the solution to room temperature.

Characterization: Single-crystal X-ray diffractions (SCXRD) measurements were conducted on D8-Focuse diffractometer. The crystal was kept at 100 K during data collection. Using Olex2, the structure was solved with the SHELXT structure solution program using Intrinsic Phasing and refined with the SHELXL refinement package using Least Squares minimisation. Powder XRD (PXRD) data were collected by Bruker Advance D8 with $\text{Cu K}\alpha$ ($\lambda = 1.5406\text{\AA}$) radiation source. Scanning electron microscope (SEM) and energy dispersive spectrometry (EDS) were conducted on Apreo S LoVac. The photoluminescence (PL), photoluminescence excitation (PLE), and time-resolved PL spectra, as well as the photoluminescence quantum yield (PLQY), were measured using an Edinburgh FLS1000 fluorescence spectrometer equipped with an integrating sphere, with instrument response correction, and each sample was measured at least three times to ensure reproducibility. Circular Dichroism (CD) Measurements

CD spectra were recorded using KBr pellets prepared by thoroughly mixing the sample powder with KBr at a mass ratio of approximately 1:100, followed by pressing into transparent discs. The measurements were carried out on a commercial circular dichroism spectrometer over a wavelength range of 250–420 nm, with a scan rate of 500 nm min $^{-1}$, a bandwidth of 4 nm, and a data interval of 1 nm. Each sample was measured at least three times to ensure the reliability and reproducibility of the data. The circular dichroism (CD) spectra were measured by a Jasco J-1700 CD spectrometer.

Circularly Polarized Luminescence (CPL) Measurements

CPL spectra were collected using a commercial CPL spectrometer. The sample powder was evenly spread in a sample holder for measurement. The excitation wavelength was set at 350 nm, and the emission spectra were recorded over the range of 450–850 nm with a scan rate of 500 nm min $^{-1}$. To improve the signal-to-noise ratio, all spectra were averaged over multiple scans. Circularly polarized luminescence (CPL) spectra were recorded by a JASCO CPL-300 instrument.

Results and Discussion

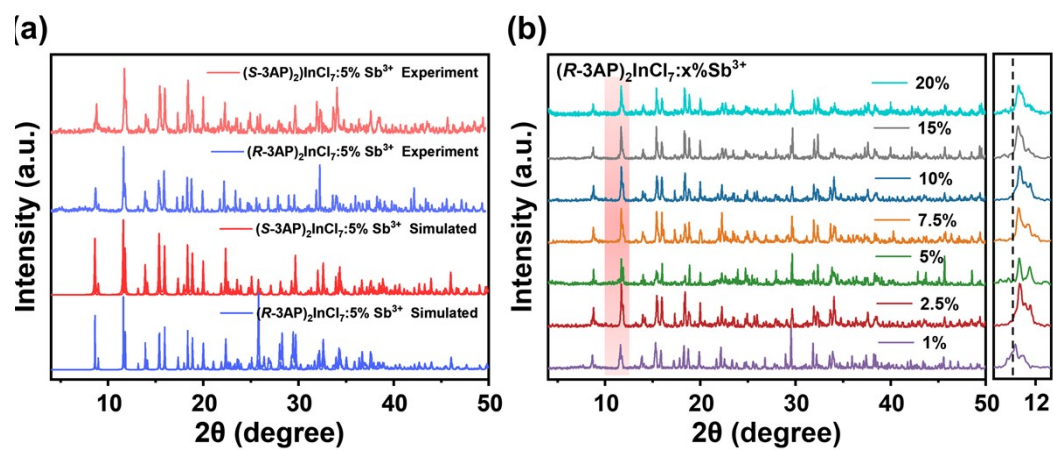


Figure S1. (a) Experimental and calculated XRD patterns of $(R/S-3AP)_2InCl_7:5\%Sb^{3+}$. (b) PXRD of $(R-3AP)_2InCl_7:x\%Sb^{3+}$ with various doping ratios of Sb^{3+}

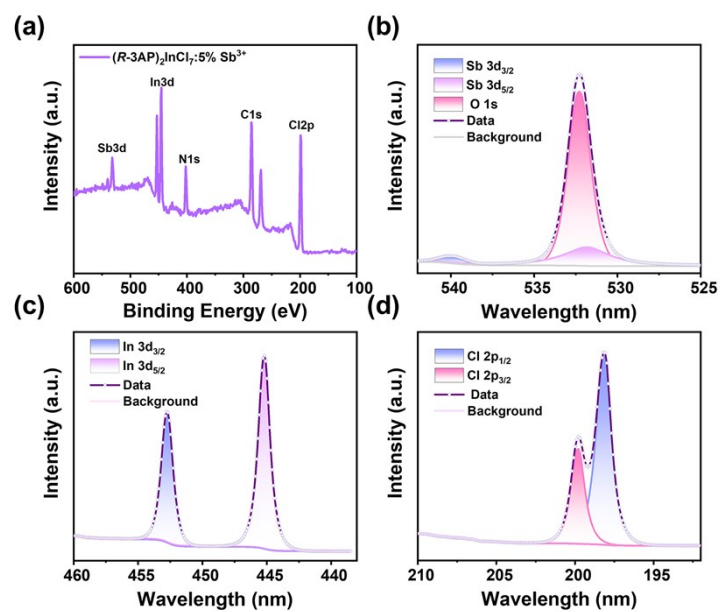


Figure S2. (a) XPS of $(R-3AP)_2InCl_7:5\%Sb^{3+}$ powder, (b-d) XPS of Sb 3d, In 3d, Cl 2p in $(R-3AP)_2InCl_7:5\%Sb^{3+}$ powder

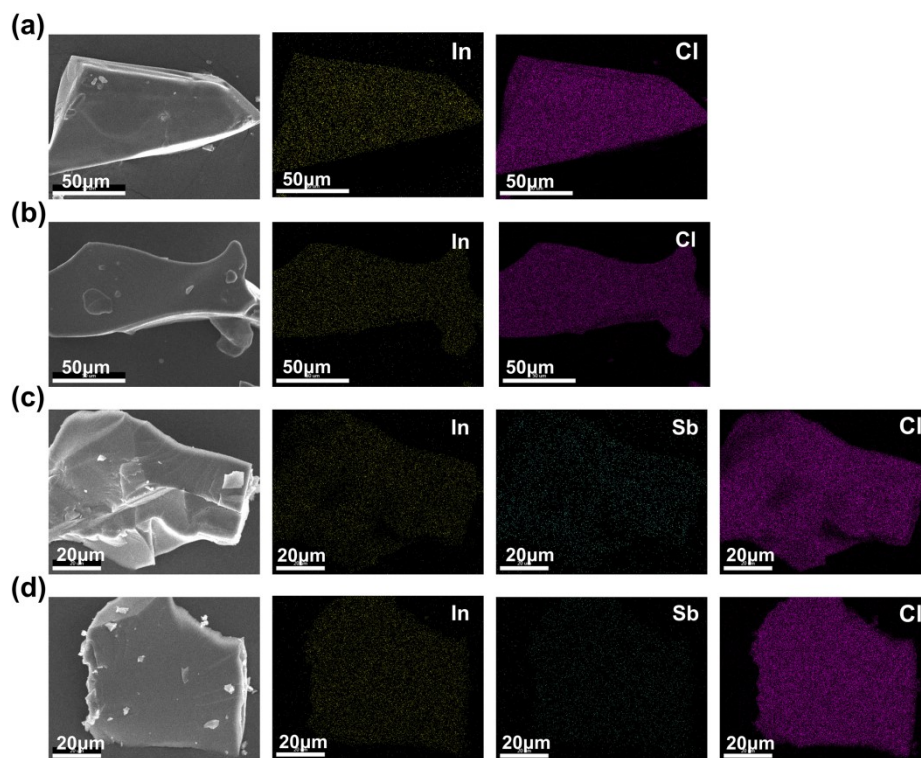


Figure S3. The SEM images and EDS of (a) $(R-3AP)_2InCl_7$, (b) $(S-3AP)_2InCl_7$, (c) $(R-3AP)_2InCl_7:5\%Sb^{3+}$ and (d) $(S-3AP)_2InCl_7:5\%Sb^{3+}$

Figure S4.

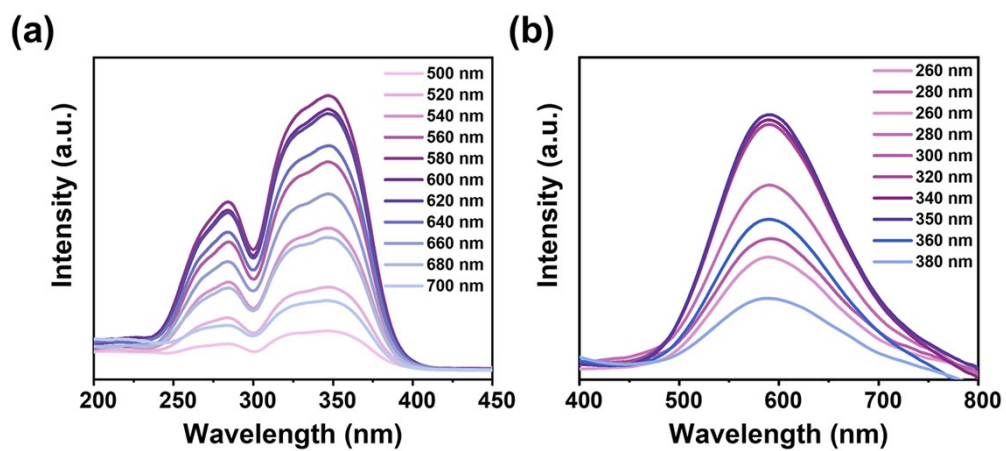


Figure S4. (a) PL spectra of $(R-3AP)_2InCl_7:5\%Sb^{3+}$ under different excitation wavelengths. (b) PLE spectra of $(R-3AP)_2InCl_7:5\%Sb^{3+}$ under different excitation wavelengths

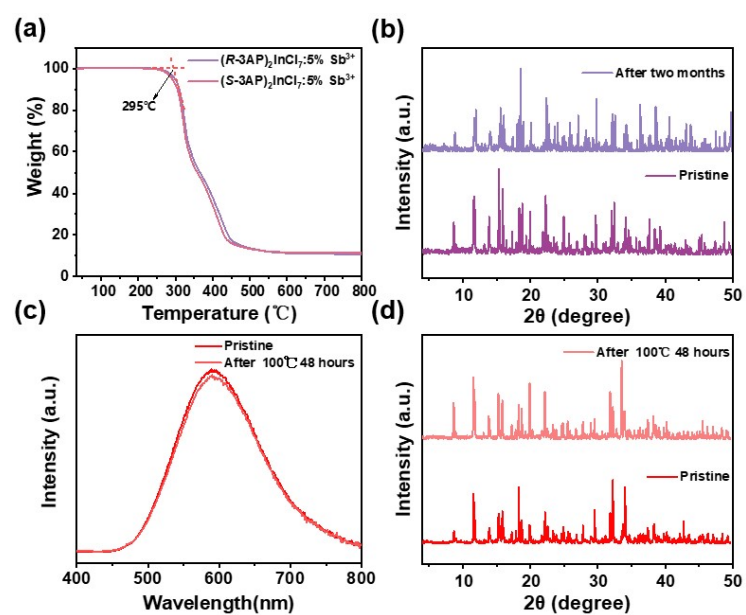


Figure S5. (a) TGA curve of $(R/S-3AP)_2InCl_7:5\%Sb^{3+}$, (b) XRD pattern of $(R-3AP)_2InCl_7:5\%Sb^{3+}$ pristine sample and after two months of storage in air. (c) PL spectra of $(R-3AP)_2InCl_7:5\%Sb^{3+}$ before and after heating at 100°C for 48 hours, (d) XRD patterns before and after heating

Table S1. Single crystal X-ray diffraction data of $(R/S\text{-}3\text{AP})_2\text{InCl}_7\cdot 5\%\text{Sb}^{3+}$.

Empirical formula	$(R\text{-}3\text{AP})_2\text{InCl}_7\cdot 5\%\text{Sb}^{3+}$	$(S\text{-}3\text{AP})_2\text{InCl}_7\cdot 5\%\text{Sb}^{3+}$
Temperature/K	100.00	100.00
Crystal system	orthorhombic	orthorhombic
Space group	$P2_12_12_1$	$P2_12_12_1$
a/Å	8.11233(11)	8.10900(10)
b/Å	12.01960(15)	12.0174(2)
c/Å	19.7303(2)	19.7198(3)
α°	90	90
β°	90	90
γ°	90	90
Volume/Å ³	1923.84(4)	1921.68(5)
Z	4	4
$\rho_{\text{calc}} \text{ g/cm}^3$	1.865	1.864
μ/mm^{-1}	18.941	2.198
F(000)	1073.0	1072.0
Radiation	Cu K α ($\lambda = 1.54184$)	Mo K α ($\lambda = 0.71073$)
2 θ range for data collection/ $^\circ$	8.614 to 152.468	5.344 to 52.736
	$-9 \leq h \leq 10$	$-10 \leq h \leq 10$
Index ranges	$-15 \leq k \leq 13$	$-15 \leq k \leq 14$
	$-24 \leq l \leq 22$	$-24 \leq l \leq 24$
Reflections collected	19789	17166
Independent reflections	3992 [$R_{\text{int}} = 0.0259$, $R_{\text{sigma}} = 0.0156$]	3925 [$R_{\text{int}} = 0.0259$, $R_{\text{sigma}} = 0.0206$]
Data/restraints/parameters	3992/0/185	3925/0/183
Goodness-of-fit on F ²	0.990	1.043
Final R indexes [$l > 2\sigma(l)$]	$R_1 = 0.0150$, $wR_2 = 0.0408$	$R_1 = 0.0145$, $wR_2 = 0.0328$
Final R indexes [all data]	$R_1 = 0.0151$, $wR_2 = 0.0409$	$R_1 = 0.0150$, $wR_2 = 0.0330$
Largest diff. peak/hole/e Å ⁻³	0.45/-0.54	0.24/-0.31
Flack parameter	-0.006(2)	-0.034(9)

Table S2. Selected bond lengths and bond angles for $(R/S\text{-3AP})_2\text{InCl}_7\cdot 5\%\text{Sb}^{3+}$.

$(R\text{-3AP})_2\text{InCl}_7\cdot 5\%\text{Sb}^{3+}$		$(S\text{-3AP})_2\text{InCl}_7\cdot 5\%\text{Sb}^{3+}$	
Bond	Length (Å)	Bond	Length (Å)
In1-Cl1	2.6038(6)	In1-Cl1	2.5018(6)
In1-Cl2	2.5048(6)	In1-Cl2	2.5026(7)
In1-Cl3	2.4663(6)	In1-Cl3	2.6035(6)
In1-Cl4	2.5010(6)	In1-Cl4	2.5055(6)
In1-Cl5	2.4902(6)	In1-Cl5	2.4904(6)
In1-Cl6	2.5010(6)	In1-Cl6	2.4663(6)
Bond angle	Angle (°)	Bond angle	Angle (°)
Cl2-In1-Cl1	89.87(2)	Cl1-In1-Cl2	89.59(2)
Cl3-In1-Cl1	87.22(2)	Cl1-In1-Cl4	91.09(2)
Cl3-In1-Cl2	90.78(2)	Cl2-In1-Cl3	89.34(2)
Cl3-In1-Cl4	88.86(2)	Cl4-In1-Cl3	90.00(2)
Cl3-In1-Cl6	96.12(2)	Cl5-In1-Cl1	90.73(2)
Cl4-In1-Cl1	89.30(2)	Cl5-In1-Cl2	89.51(2)
Cl5-In1-Cl1	85.88(2)	Cl5-In1-Cl3	85.86(2)
Cl5-In1-Cl2	90.77(2)	Cl5-In1-Cl4	90.77(2)
Cl5-In1-Cl4	89.50(2)	Cl6-In1-Cl1	96.17(2)
Cl5-In1-Cl6	90.74(2)	Cl6-In1-Cl2	88.89(2)
Cl6-In1-Cl2	91.16(2)	Cl6-In1-Cl3	87.20(2)
Cl6-In1-Cl4	89.59(2)	Cl6-In1-Cl4	90.75(2)