Electronic Supporting Information

Lead-Free Hybrid Indium Perovskites with Near-Unity PLQY and White-Light Emission by Sb^{3+} Doping Strategy

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Contents

Part 1. Experimental section

1.1 Materials

All reagents were purchased commercially and used without further purification. Indium powder (99.99%, Jiangsu Aikon), Sb_2O_3 (99.5%, Macklin), diethylenetriamine (DETA) (99%, Macklin), deionized water, hydrochloric acid (HCl, 36-38 wt% aqueous solution, Sinopharm Chemical Reagent Co., Ltd.).

1.2 Synthesis

3 mmol diethylenetriamine and 1 mmol indium powder were placed in a 25 mL glass bottle. Then, 5 mL HCl and 8 mL water was added to the mixture. A clear solution was obtained with continuous magnetic stirring at room temperature. After 12 hours of volatilization, bulk crystals crystallized from the solution, yield, 0.285 g, 66.3% based on In. The synthetic route for Sb-doped samples was similar to that of the pure (DETA)$InCl_6$ with the Sb_2O_3 added for the targeted compositions. The element analysis for (DETA)$InCl_6$:10%Sb^{3+}. Anal. (%) calc.: C 11.15, H 3.04, N 9.76. Found (%): C 11.19, H 3.70, N 9.74. Yield, 0.243 g, 56.66% based on In. And for the (DETA)$InCl_6$:15%Sb^{3+}. Anal. (%) calc.: C 11.15, H 3.04, N 9.76. Found (%): C 11.28, H 3.51, N 9.84. Yield, 0.279 g, 65.0% based on In.

1.3 Characterization

Single-crystal X-ray diffraction data of (DETA)$InCl_6$ and (DETA)$InCl_6$:15%Sb^{3+} at 301 K and 297 K were collected on a Rigaku synergistic diffractometer with Mo-Kα (λ = 0.71073 Å) radiation from a graphite monochromator. The crystal structure of (DETA)$InCl_6$ was solved using the direct method and refined using the full matrix method from the F^2 data of the Olex2 software package.[1] Powder X-ray diffraction

patterns were recorded on a Rigaku DMax 2500 powder diffractometer. Solid-state optical diffuse reflectance spectroscopy was measured on a Shimadzu 2600 UV/Vis spectrometer with a test range of 800-200 nm using a $BaSO_4$ plate as a standard. Raman spectral recordings were performed on an nVia RM2000. XPS measurements were performed on ESCALAB 250Xi. Surface morphology and elemental analysis were observed using a field emission scanning electron microscope (FEI Nova NanoSEM 450) equipped with an energy dispersive X-ray spectrometer (Inca Energy X-Max20). TG analyses were recorded on a NETZSCH STA 449F3 instrument with a heating rate of 10 $K \cdot min^{-1}$ under a dry N_2 atmosphere. Steady-state PL emission and PL excitation (PLE) spectra were measured using a PL spectrometer (FLS980; Edinburgh Instruments). Temperature-dependent steady-state and TRPL spectra were recorded by using a FLS980 spectrometer (Edinburgh) equipped with a continuous xenon lamp (450 W), a pulsed flash lamp, a 375 nm picosecond pulsed laser as well as a temperature control instrument (Linkam THMS600). The absolute PLQY of single crystals were measured by using a standard $BaSO_4$-coated integrating sphere (150 mm diameter, Edinburgh) as the sample chamber mounted on a FLS980 spectrometer. Inductively coupled plasma mass spectrometry (ICP-MS) testing was performed on the XSerise II. Chromaticity coordinate, CCT and CRI of PiG-based WLEDs were measured in an integrated sphere of 50 cm diameter, which was connected to a CCD detector with an optical fiber from Everfine (HAAS-2000, Everfine Photo-E-Info Co. LTD.).

1.4 Theoretical Band Calculation

Calculations were performed by using the Dmol3 module in the Materials Studio

package.[2, 3] The exchange–correlation inter-actions were described by using Perdew–Burke–Ernzerhof (PBE) general gradient approximation (GGA) method with the double numerical basis sets plus polarization function (DNP).[4] The SCF tolerance was set as 10^{-6} eV per atom. The Fermi smearing of 0.005 Hartree was selected to accelerate convergence. Monkhorst–Pack grid of 3×3×3 for (DETA)$InCl_6$ and (DETA)$InCl_6$:15%Sb^{3+} were utilized in the Brillouin-zone integrations, respectively.

Part 2. Supporting figures

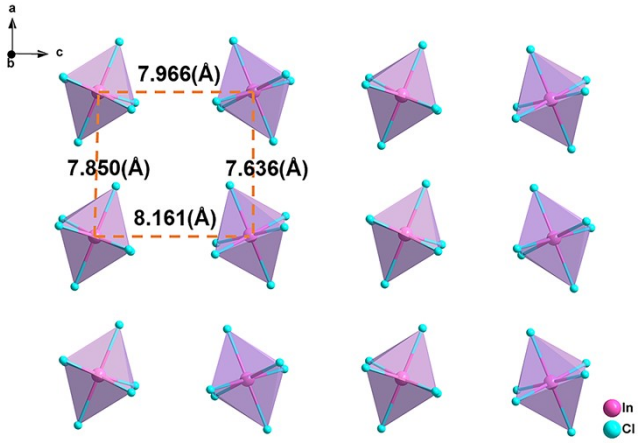

Figure S1. Detailed view of adjacent $[InCl_6]^{3-}$ in compound $(DETA)InCl_6$.

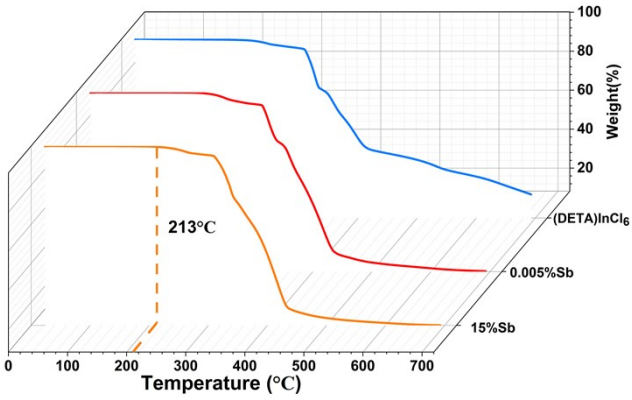

Figure S2. TG curves of $(DETA)InCl_6$:x%Sb^{3+} (x = 0, 0.005, 15) in the temperature range of 20 – 700℃.

Table S1 ICP-MS for·$(DETA)InCl_6$:x%Sb^{3+}

$(DETA)InCl_6$:x%Sb^{3+}	Sb nominal / mol%	Sb actual / mol%
0.005%	0.005%	0.0043%
0.01%	0.01%	0.0086%
10%	10%	8.56%
15%	15%	15.42%

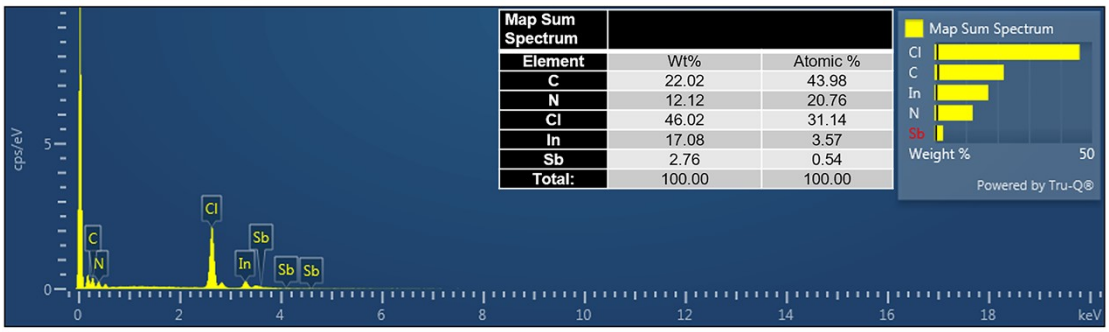

Figure S3. EDX spectrum of (DETA)$InCl_6$:15%Sb^{3+}, showing the elements of C, N, Cl, In, and Sb in the (DETA)$InCl_6$:15%Sb^{3+}, the inset shows the atomic percentage of each element in the chemical composition of the (DETA)$InCl_6$:15%Sb^{3+}.

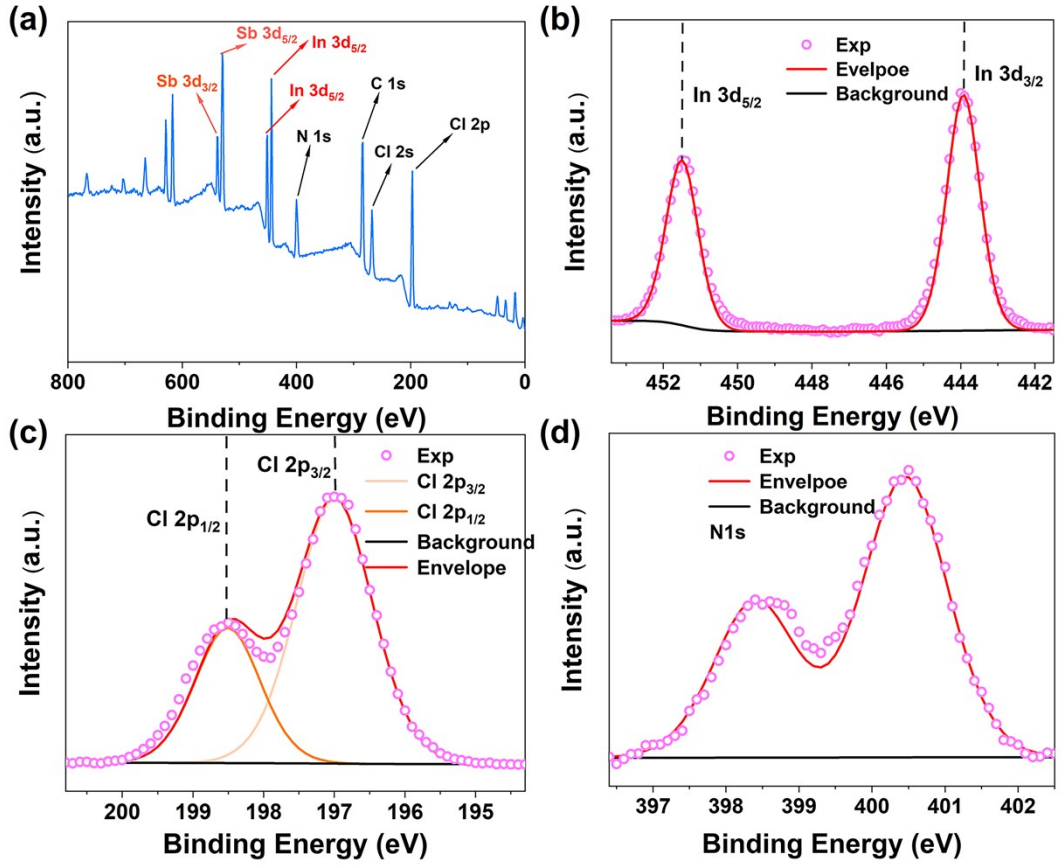

Figure S4. XPS characterization of 15%Sb^{3+}:(DETA)$InCl_6$ single crystal.

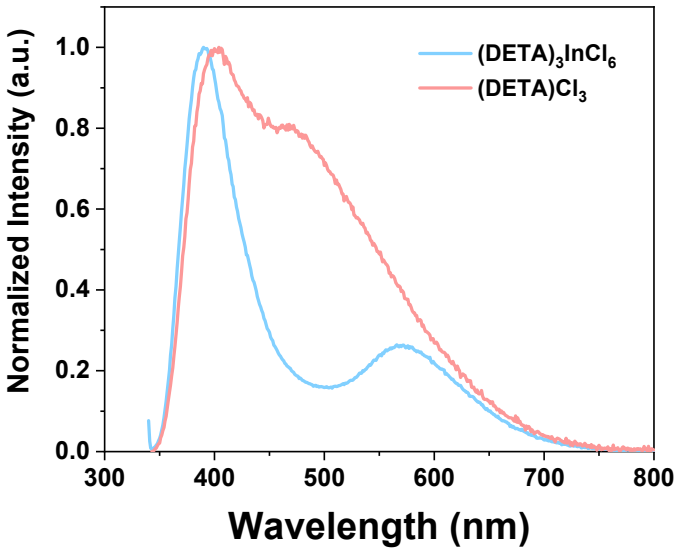

Figure S5. PL emission spectra of $(DETA)_3InCl_6$ and $(DETA)Cl_3$ under excited at 325 nm.

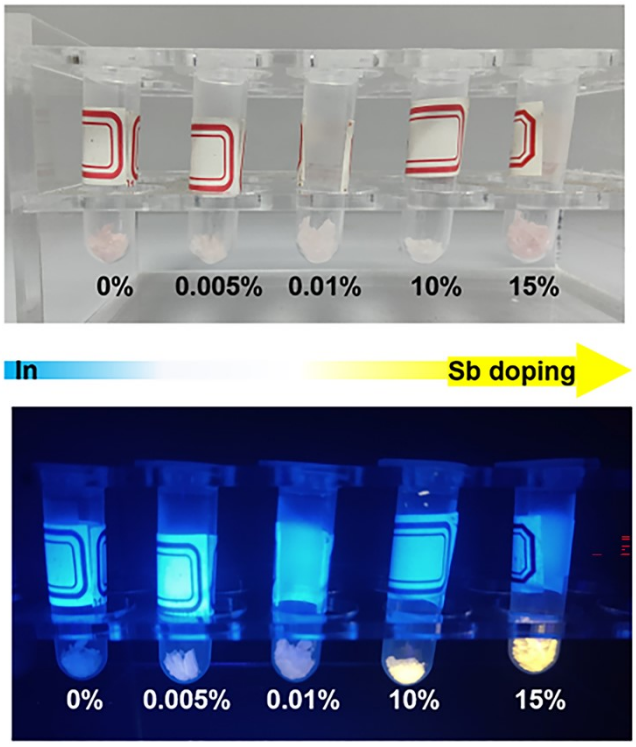

Figure S6. Images of crystal $(DETA)InCl_6$:xSb^{3+} doped with various Sb contents under sunlight (top) and UV light (bottom).

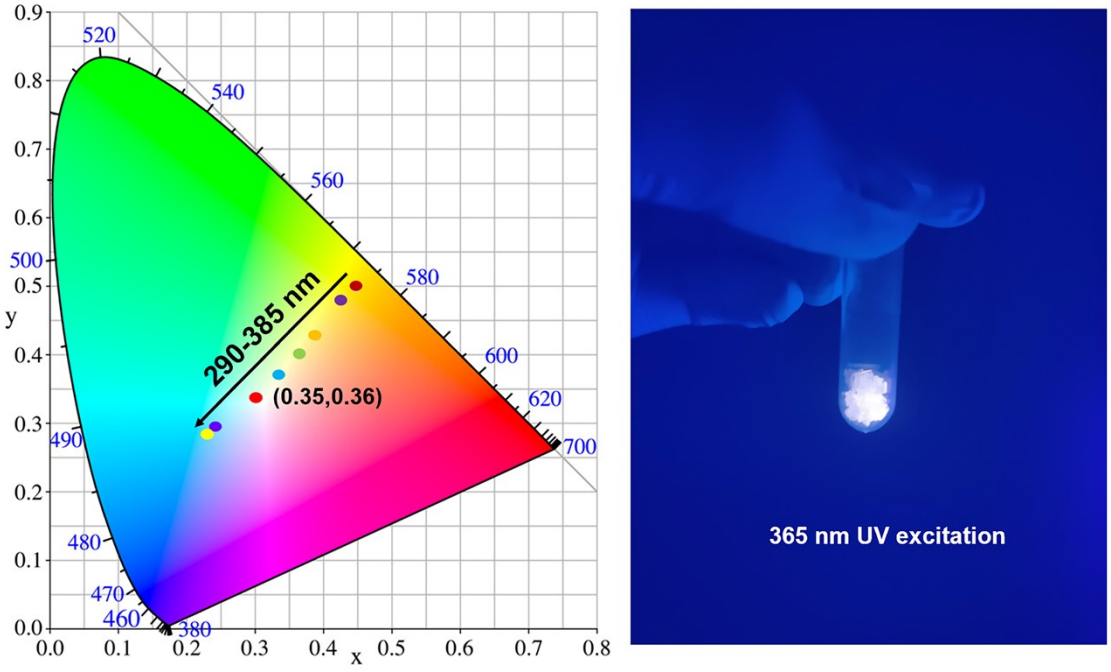

Figure S7. The CIE diagram of (DETA)$InCl_6$:0.005%Sb^{3+} under the excitation band of 290 nm-385 nm and the picture of sample under 365 nm UV excitation.

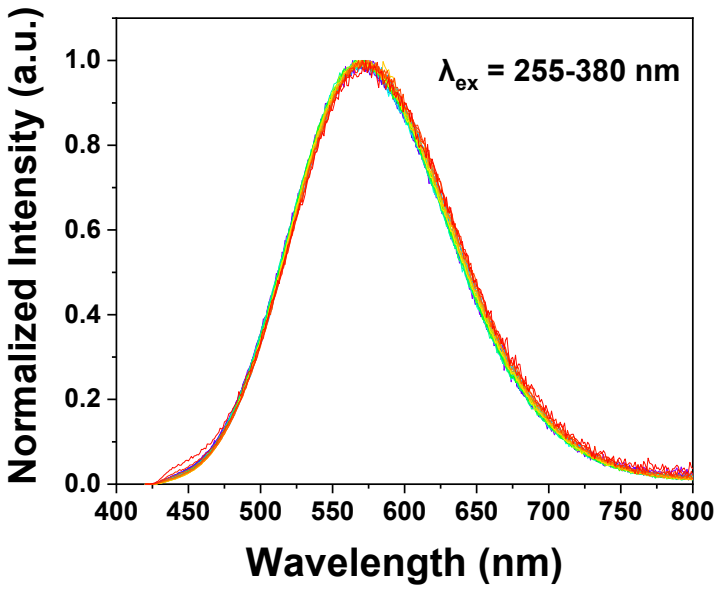

Figure S8. Normalized PL spectra of (DETA)$InCl_6$:10%Sb^{3+} measured at different excitation wavelengths.

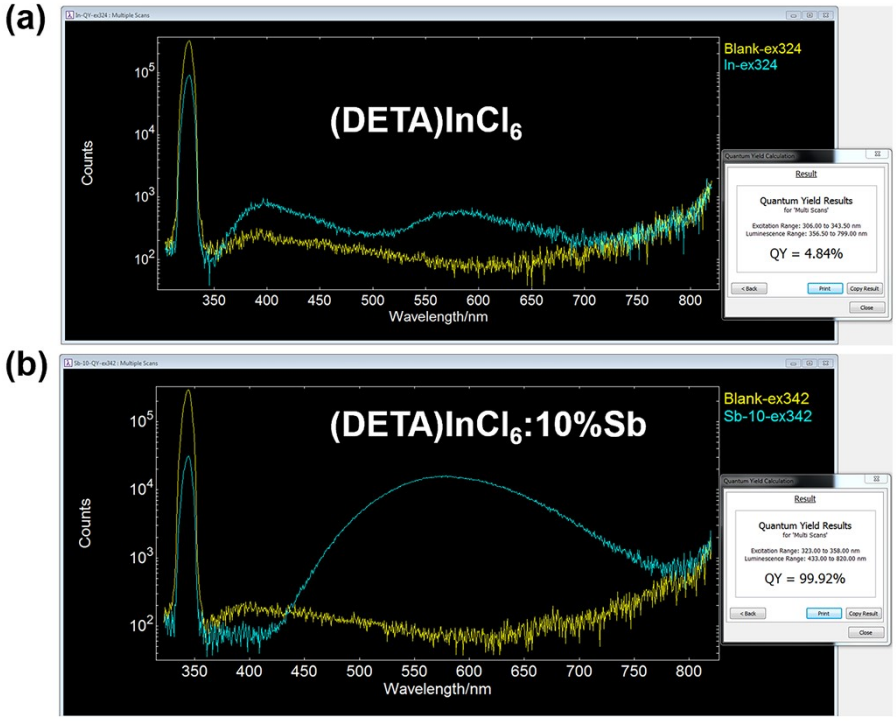

Figure S9. (a) Excitation line of reference (324 nm) and emission spectrum of: (DETA)$InCl_6$ collected by an integrating sphere. (b) Excitation line of reference (342 nm) and emission spectrum of 10% Sb^{3+}: (DETA)$InCl_6$ collected by an integrating sphere.

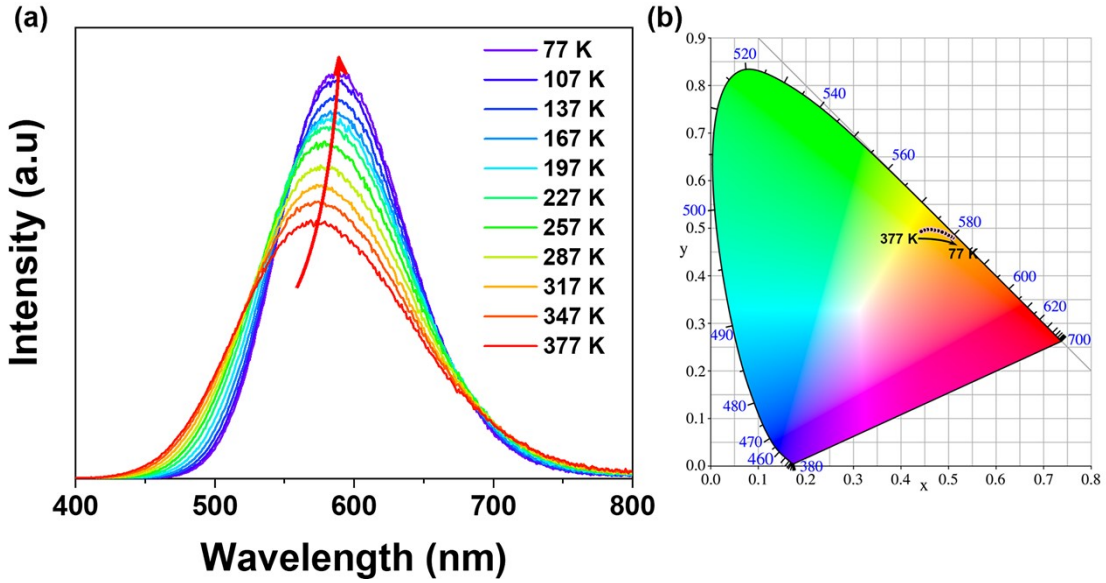

Figure S10. (a) Temperature-dependent PL spectra of (DETA)$InCl_6$:10%Sb^{3+} excited by 342 nm (77−377 K). (b) The CIE chromaticity coordinates of 77−377 K for (DETA)$InCl_6$:10%Sb^{3+}.

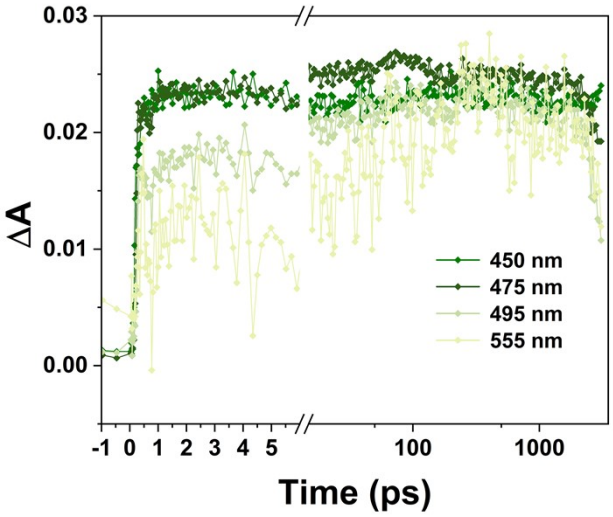

Figure S11. PIA decay curves of the (DETA)$InCl_6$:10%Sb^{3+} by monitoring at 450, 475, 495, and 555 nm, respectively.

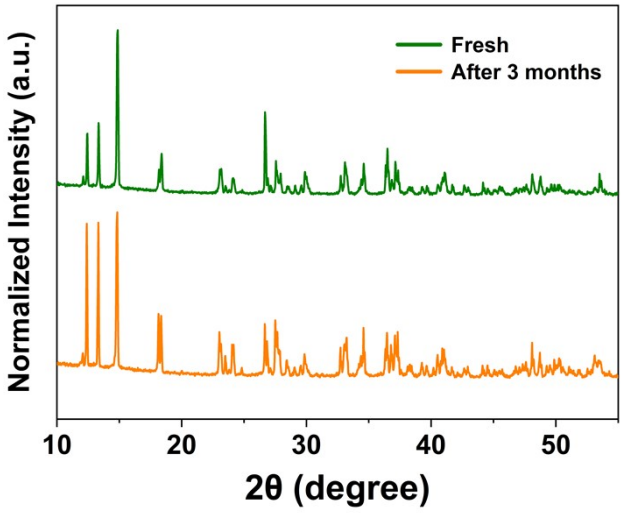

Figure S12. PXRD patterns of fresh 10%Sb^{3+}: (DETA)$InCl_6$ after being exposed to air for three months.

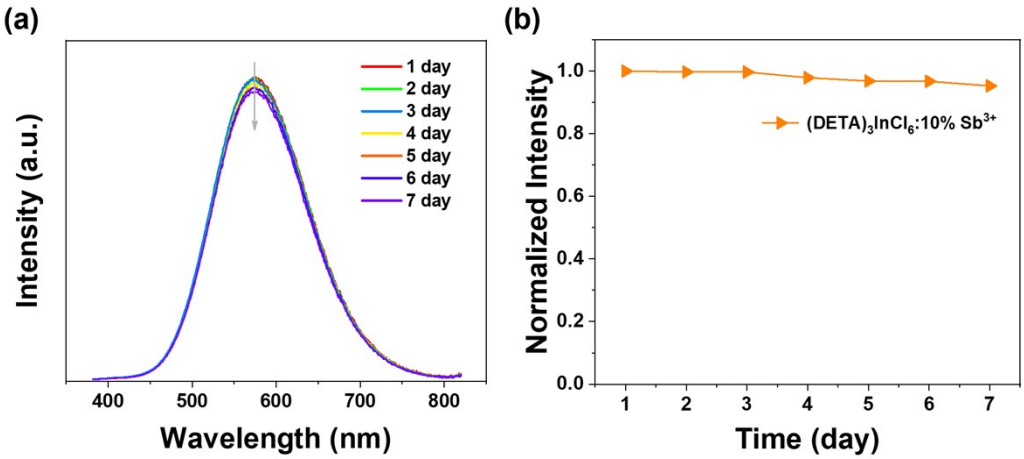

Figure 13. Photostability of (DETA)$InCl_6$:10%Sb^{3+} exposed to environmental conditions for 7 days.

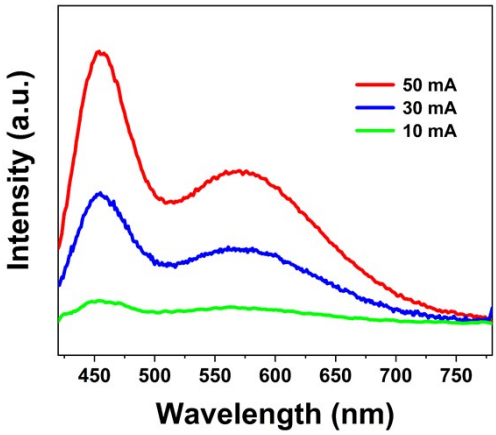

Figure S14. Drive-current-dependent EL emission spectra.

Part 3. Crystallographic data

Table S2 Crystal structure and refinement detail of (DETA)$InCl_6$ and **(**DETA)$InCl_6$:15%Sb

	(DETA)$InCl_6$	(DETA)$InCl_6$:15%Sb
T / K	301	297
Formula weight	433.72	433.72
Crystal system	monoclinic	monoclinic
Space group	*I2/a*	*I2/a*
a / Å	13.2661(4)	13.2587(4)
b / Å	7.5660(2)	7.5658(2)
c / Å	28.4784(8)	28.4560(8)
α / °	90.00	90.00
β / °	90.496(3)	90.603(3)
γ / °	90.00	90.00
V / Å^3	2858.31(14)	2854.34(14)
Z	8	8
D_{calc} / g·cm^{-3}	2.016	2.019
μ / mm^{-1}	2.747	2.750
F(000)	1697.9	1696.0
2θ *range* / °	5.58−61.78	5.572−61.862
Reflns collected	11993	12162
Independent reflns (R_{int})	3553 (0.0287)	3546 (0.0282)
No. of parameters	131	131
R_1[a], wR_2[b] [I>2σ(I)]	0.0649, 0.1450	0.0367, 0.0918
R_1, wR_2 [all data]	0.0679, 0.1462	0.0425, 0.0945
GOF	1.004	1.021
$\Delta\rho$[c] / e·Å^{-3}	1.92, -1.78	0.69, -0.88
CCDC	2243632	2243633

[a] $R_1 = \Sigma||F_o|-|F_c||/|F_o|$; [b] $wR_2 = [\Sigma w(F_o^2-F_c^2)^2]/\Sigma w(F_o^2)^2]^{1/2}$; [c] maximum and minimum residual electron density.

Table S3 Table of selected bond lengths (Å) and bond angles (°) for compounds of (DETA)$InCl_6$ and (DETA)$InCl_6$:15%Sb

(DETA)$InCl_6$			
In(1)-Cl(1)	2.517(2)	In(2)-Cl(6)	2.472(2)
In(1)-Cl(1)^1	2.517(2)	In(2)-Cl(6)^2	2.472(2)
In(1)-Cl(2)^1	2.542(2)	Cl(1)^1-In(1)-Cl(1)	86.58(11)
In(1)-Cl(2)	2.542(2)	Cl(2)^1-In(1)-Cl(1)	92.34(8)
In(1)-Cl(3)	2.485(2)	Cl(2)-In(1)-Cl(1)	87.33(8)
In(1)-Cl(3)^1	2.485(2)	Cl(2)-In(1)-Cl(1)^1	92.34(8)
In(2)-Cl(5)^2	2.544(2)	Cl(2)^1-In(1)-Cl(2)	179.55(13)
In(2)-Cl(5)	2.544(2)	Cl(3)-In(1)-Cl(1)^1	91.50(8)
In(2)-Cl(4)^2	2.524(2)	Cl(3)^1-In(1)-Cl(1)^1	174.90(8)
In(2)-Cl(4)	2.524(2)	Cl(3)-In(1)-Cl(1)	174.90(8)
Cl(3)^1-In(1)-Cl(1)	91.50(8)	Cl(4)^2-In(2)-Cl(4)	180.0
Cl(3)^1-In(1)-Cl(2)	92.29(9)	Cl(6)-In(2)-Cl(5)^2	90.24(8)
Cl(3)-In(1)-Cl(2)	88.02(8)	Cl(6)^2-In(2)-Cl(5)^2	89.76(8)
Cl(3)^1-In(1)-Cl(2)^1	88.02(8)	Cl(6)-In(2)-Cl(5)	89.76(8)
Cl(3)-In(1)-Cl(2)^1	92.29(9)	Cl(6)^2-In(2)-Cl(5)	90.24(8)
Cl(3)-In(1)-Cl(3)^1	90.80(12)	Cl(6)^2-In(2)-Cl(4)^2	88.62(8)
Cl(5)^2-In(2)-Cl(5)	180.0	Cl(6)-In(2)-Cl(4)	88.62(8)
Cl(4)-In(2)-Cl(5)	90.31(7)	Cl(6)-In(2)-Cl(4)^2	91.38(8)
Cl(4)-In(2)-Cl(5)^2	89.69(7)	Cl(6)^2-In(2)-Cl(4)	91.38(8)
Cl(4)^2-In(2)-Cl(5)^2	90.31(7)	Cl(6)-In(2)-Cl(6)^2	180.0
Cl(4)^2-In(2)-Cl(5)	89.69(7)		

Symmetry transformations used to generate equivalent atoms: ^{1}3/2-*x*, +*y*, 1-*z*； ^{2}3/2-*x*, 5/2-*y*, 1/2-*z*.

(DETA)$InCl_6$:15%Sb			
In(1)-Cl(1)^1	2.5269(11)	Cl(1)^1-In(1)-Cl(2)^1	87.34(4)
In(1)-Cl(1)	2.5269(11)	Cl(1)-In(1)-Cl(2)	87.34(4)
In(1)-Cl(2)	2.5455(12)	Cl(1)-In(1)-Cl(2)^1	92.38(4)
In(1)-Cl(2)^1	2.5455(12)	Cl(1)^1-In(1)-Cl(2)	92.38(4)
In(1)-Cl(3)^1	2.4790(12)	Cl(2)-In(1)-Cl(2)^1	179.62(7)
In(1)-Cl(3)	2.4791(12)	Cl(3)-In(1)-Cl(1)^1	91.58(4)
In(2)-Cl(4)^2	2.4706(12)	Cl(3)^1-In(1)-Cl(1)^1	174.81(4)
In(2)-Cl(4)	2.4707(12)	Cl(3)^1-In(1)-Cl(1)	91.57(4)
In(2)-Cl(5)^2	2.5461(12)	Cl(3)-In(1)-Cl(1)	174.81(4)
In(2)-Cl(5)	2.5460(11)	Cl(3)-In(1)-Cl(2)^1	92.29(5)
In(2)-Cl(6)^2	2.5240(11)	Cl(3)^1-In(1)-Cl(2)	92.29(5)
In(2)-Cl(6)	2.5240(11)	Cl(3)^1-In(1)-Cl(2)^1	87.98(4)

Cl(1)[1]-In(1)-Cl(1)	86.38(6)	Cl(3)-In(1)-Cl(2)	87.98(4)
Cl(3)[1]-In(1)-Cl(3)	90.85(6)	Cl(5)-In(2)-Cl(5)[2]	180.0
Cl(4)[2]-In(2)-Cl(4)	180.0	Cl(6)-In(2)-Cl(5)[2]	89.79(4)
Cl(4)[2]-In(2)-Cl(5)	90.32(4)	Cl(6)-In(2)-Cl(5)	90.21(4)
Cl(4)-In(2)-Cl(5)[2]	90.32(4)	Cl(6)[2]-In(2)-Cl(5)[2]	90.21(4)
Cl(4)[2]-In(2)-Cl(5)[2]	89.68(4)	Cl(6)[2]-In(2)-Cl(5)	89.79(4)
Cl(4)-In(2)-Cl(5)	89.68(4)	Cl(6)[2]-In(2)-Cl(6)	180.00(5)
Cl(4)[2]-In(2)-Cl(6)[2]	88.67(5)	C(3)-N(2)-C(2)	111.0(4)
Cl(4)[2]-In(2)-Cl(6)	91.33(5)	N(1)-C(1)-C(2)	113.2(4)
Cl(4)-In(2)-Cl(6)	88.67(5)	N(2)-C(2)-C(1)	113.6(4)
Cl(4)-In(2)-Cl(6)[2]	91.33(5)	N(2)-C(3)-C(4)	114.4(4)

Symmetry transformations used to generate equivalent atoms: [1]3/2-*x*, +*y*, 1-*z*； [2]3/2-*x*, 1/2-*y*, 1/2-*z*.

Table S4 Hydrogen bonds for·(DETA)$InCl_6$ at 301 K

D-H···A	d(D-H)	d(H···A)	d(D···A)	<(DHA)
N(2)-H(2a)···Cl(5)[1]	0.90	2.633(8)	3.279(8)	129.45(15)
N(2)-H(2b)···Cl(2)	0.90	2.552(8)	3.203(8)	129.78(16)
N(1)-H(1a)···Cl(1)	0.89	2.313(17)	3.172(8)	162(4)
N(1)-H(1b)···Cl(2)[2]	0.89	2.326(12)	3.210(8)	172(6)
N(3)-H(3a)···Cl(5)[3]	0.89	2.38(3)	3.225(9)	158(6)
N(3)-H(3c)···Cl(4)[4]	0.89	2.39(5)	3.109(9)	138(6)

Symmetry transformations used to generate equivalent atoms: [1]3/2-*x*, 3/2-*y*, 1/2-*z*； [2]1-*x*, 1-*y*, 1-*z*； [3]-1/2+*x*, 2-*y*, +*z*； [4]+*x*, -1+*y*, +*z*.

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3. Delley, B., From molecules to solids with the DMol3 approach. *J. Chem. Phys.* **2000**, *113* (18), 7756-7764.

4. Perdew, J. P., Burke, K., & Ernzerhof, M., Generalized gradient approximationmade simple. *Phys. Rev. Lett.* **1996**, *77* (18), 3865–3868.