

## Supporting Information

### Blue Photoluminescence Enhancement Achieved by Zero-Dimensional Organic Indium Halides and Metal Ion Doping Strategy

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## Experimental section

### Materials

Methylamine hydrochloride (MAHCl, Aladdin, 98%), Cesium chloride (CsCl, Aladdin, 99.9%), Manganese(II) chloride (MnCl<sub>2</sub>, Macklin, 99%), Antimony trichloride (SbCl<sub>3</sub>, Macklin, 99.9%), Anhydrous indium chloride (InCl<sub>3</sub>, Aladdin, 99.99%), Hydrochloric acid (HCl, Guangzhou Chemical Reagent, 36 weight % in water), N,N-Diethylformamide (DEF, Aladdin, 99%), Ethyl acetate (EA, Macklin, 99.9%), Ethanol (EtOH, Aladdin, ≅99.99%). All materials were used for synthesis in this work without further purification.

### Synthesis of (MA)<sub>4</sub>InCl<sub>7</sub> crystals

(MA)<sub>4</sub>InCl<sub>7</sub> single crystals were prepared by solvothermal reaction. a mixture of 0.5 mmol InCl<sub>3</sub> and 1 mmol MA•HCl were dissolved in DEF and EA (2/2mL) and stirred in 20mL glass bottle for 30 minutes and was sealed in a stainless steel Parr autoclave and heated to a temperature of 100°C for 24 hours, then cooled naturally to room temperature. Colorless crystals was collected through filtration, washed three times with EtOH and dried in a vacuum oven overnight. Antisolvent diffusion and microwave synthesis methods could also obtain MA<sub>4</sub>InCl<sub>7</sub> but in powder form. Solvothermal method is necessary to grow single crystals large enough for further characterizations.

To estimate the pressure inside the container, we take approximation that EA give saturated vapor pressure and DEF have negligible vapor pressure at 100°C considering their boiling point. The saturated vapor pressure of EA at 100 °C vapor could be estimated by Clausius–Clapeyron equation:

$$\ln\left(\frac{p_1}{p_2}\right) = \frac{\Delta H}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

where  $p$  is the pressure (Pa),  $\Delta H$  is the enthalpy of vaporization (J),  $T$  is the temperature (K), and  $R$  is the molar gas constant (J\*mol<sup>-1</sup>\*K<sup>-1</sup>). Given that  $\Delta H$  is 3.54\*10<sup>4</sup> J/mol, the pressure of EA at 100°C is calculated to be 2.17\*10<sup>5</sup>Pa.

Further applying Raoult's law assuming ideal solvent behavior:

$$p = p_A^*x_A + p_B^*x_B$$

where  $p^*$  stands for the "pure" vapor pressure of each component, and  $x$  stands for the mole fraction. The calculated vapor pressure of the mixed solvent of EA/DEF is 1.16\*10<sup>5</sup> Pa.

Together with the pressure provided by air sealed in, which is 1.27\*10<sup>5</sup> Pa, the total pressure inside the container is about 2.43\*10<sup>5</sup> Pa, that is 2-3 atm.

### Synthesis of (MA)<sub>4</sub>InCl<sub>7</sub>:Cs<sup>+</sup>

The syntheses of (MA)<sub>4</sub>InCl<sub>7</sub>:Cs<sup>+</sup> is similar as the that of (MA)<sub>4</sub>InCl<sub>7</sub> by solvothermal reaction. A stock solution of 10<sup>-4</sup> M CsCl in HCl was pre-made. The mixture of InCl<sub>3</sub>, MAHCl and CsCl solution according to the stoichiometric ratio was placed in a 20 mL glass bottle with the DEF and EA, which stirred for 1h and sealed in a stainless steel Parr autoclave, heating to a temperature of 100°C for 24 hours, then cooled slowly to room temperature. Crystals were collected by filtration and dried in vacuum overnight.

### Synthesis of (MA)<sub>4</sub>InCl<sub>7</sub>:Mn<sup>2+</sup>

The synthesis of (MA)<sub>4</sub>InCl<sub>7</sub>:Mn<sup>2+</sup> is similar as that of (MA)<sub>4</sub>InCl<sub>7</sub>:Cs<sup>+</sup> except using MnCl<sub>2</sub> dissolved in DEF instead of CsCl. Pure phase of crystal sample was collected by filtration after 24 h of continuous heating and was dried in vacuum overnight.

### Synthesis of (MA)<sub>4</sub>InCl<sub>7</sub>:Sb<sup>3+</sup>

The synthesis of Sb<sup>3+</sup> doped compounds are similar as that of (MA)<sub>4</sub>InCl<sub>7</sub>:Cs<sup>+</sup> except using SbCl<sub>3</sub> dissolved in DEF instead of CsCl.

### **Sb metal ion detector**

The responsivity of  $(\text{MA})_4\text{InCl}_7$  to Sb ions was tested experimentally by measuring the photoluminescence (PL) spectra. First, different concentration of antimony ions ethanol solutions ( $10^{-1}$ - $10^{-4}\text{M}$ ) were prepared which were then added to the mixture of 50mg  $(\text{MA})_4\text{InCl}_7$  and ethanol and oscillated for several minutes, then the PL spectra were measured of all above solutions. For the other metal ions,  $\text{Pb}^{2+}$  and  $\text{Bi}^{3+}$ , the procedures are the same except using N,N-Diethylformamide instead of ethanol.

### **Measurement and characterizations**

Single crystal X-ray diffraction (SCXRD) data were collected at 225K on a Bruker D8 Venture diffractometer with graphite-monochromated Ga K $\alpha$  radiation ( $\lambda = 1.34139 \text{ \AA}$ ). Powder X-ray diffraction (PXRD). PXRD analyses were carried out on a Bruker D8 Advance automated diffraction system using Cu K $\alpha$  radiation ( $\lambda=1.5406 \text{ \AA}$ ). The data were collected at room temperature in a  $2\theta$  range of  $3\text{--}50^\circ$  with a scan speed of  $1^\circ/\text{min}$ . The operating power was 40 kV/40 mA.

X-ray photoelectron spectroscopy (XPS) was performed with Thermo Scientific K-Alpha+ equipped with monochromatic Al-K $\alpha$  source. Instrument scan pattern was CAE. The X-ray power of 72 W at 15 kV was used for all experiments.

Inductively coupled plasma optical emission spectrometry (ICP-OES) analysis was conducted using Thermo Scientific iCAP 7000.

Optical diffuse reflectance spectra were measured at room temperature on a Shimadzu UV-3600 spectrophotometer. Data were collected in the wavelength range of 200-600 nm.  $\text{BaSO}_4$  powder was used as a standard (100% reflectance). A similar procedure as previously described was used to collect and convert the data using the Kubelka-Munk function.

Thermogravimetric (TG) analysis (TGA) of the title compounds were performed on a computer-controlled TG 550 (TA Instrument). Pure powder samples were loaded into platinum pans and heated with a ramp rate of  $10 \text{ }^\circ\text{C}/\text{min}$  from room temperature to  $600 \text{ }^\circ\text{C}$ .

Steady-state photoluminescence (PL) spectra and time-resolved photoluminescence (TRPL) data were measured on a FLS1000 spectrofluorometer (Edinburgh Instruments).

Photoluminescence quantum efficiency (PLQE) measurements of samples in powder form was measured on a C9920-03 absolute quantum yield measurement system (Hamamatsu Photonics) with a 150 W xenon monochromatic light source and 3.3 inch integrating sphere.

### **Computational Methods**

All the calculations are implemented by the VASP code.<sup>1</sup> The GGA-PBE functional is selected for the exchange and correlation potential.<sup>2</sup> Weak van der Waals interaction is considered by the DFT-D3 functional.<sup>3</sup> The cut off energy for the plane-wave is 400 eV. The Gamma point in the Brillouin-zone is chosen for integration. Total energies of the systems converge to  $10^{-5} \text{ eV}$  in the iteration solution of Kohn-Sham equation. The force on each atoms reduce to  $0.05 \text{ eV/\AA}$  after geometry optimization.

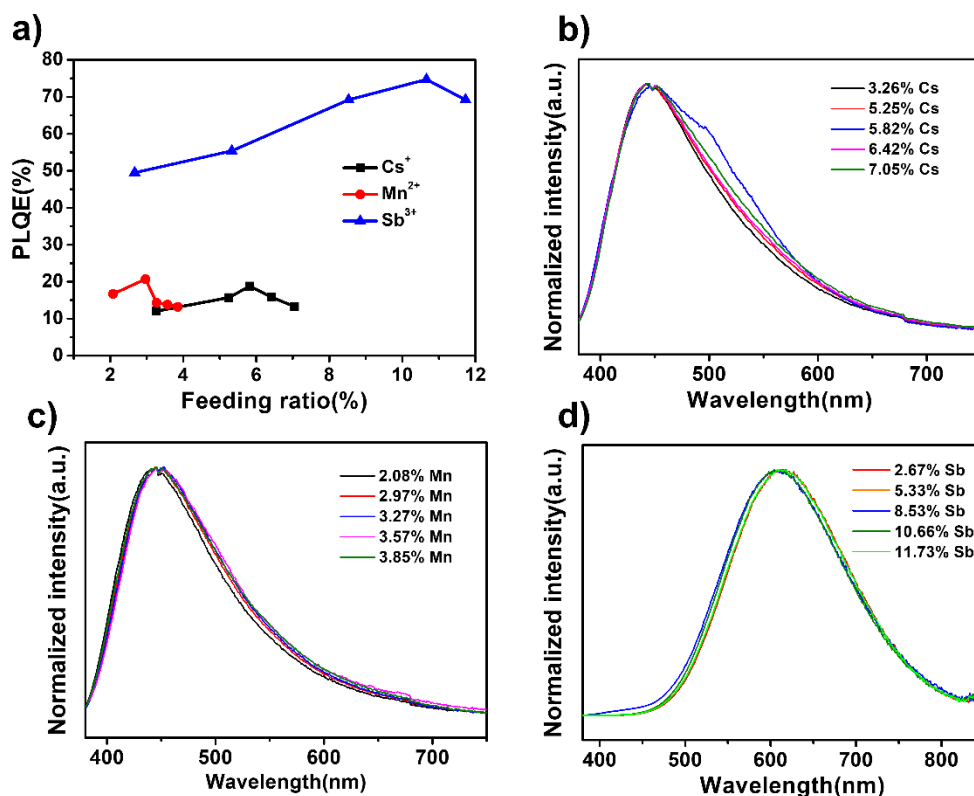
### **Average lifetime calculation**

The equation of average lifetime:

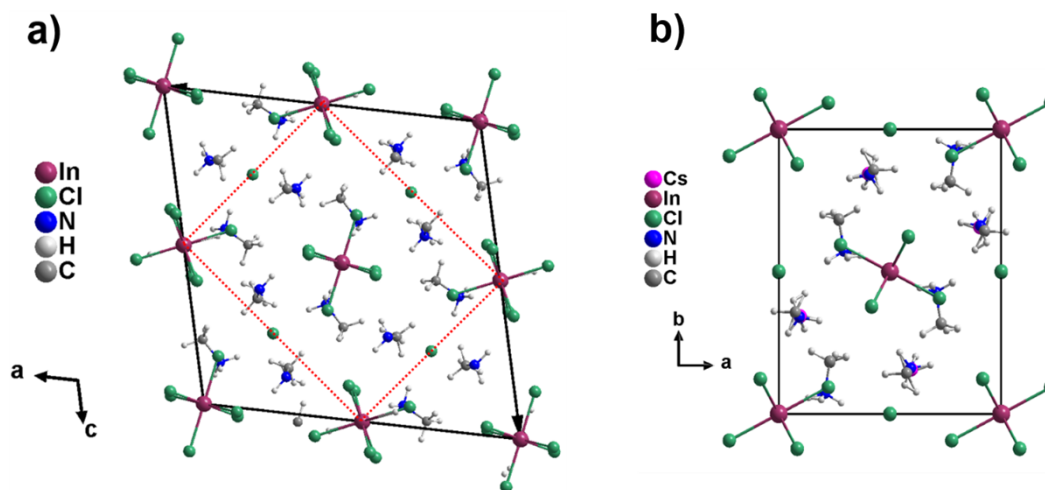
$$\tau_{\text{ave}} = \frac{A_1\tau_1^2 + A_2\tau_2^2 + A_3\tau_3^2}{A_1\tau_1 + A_2\tau_2 + A_3\tau_3}$$

where  $A_1, A_2, A_3$  are the pre-exponential factor, and,  $\tau_1, \tau_2$  and  $\tau_3$  are the lifetimes components, if necessary.

## Results and Discussion



**Figure S1.** a) PLQE of  $(\text{MA})_4\text{InCl}_7$  and the doped compounds with different feeding ratios. b-d) PL spectra at different doping ratios of  $(\text{MA})_4\text{InCl}_7:\text{Cs}^+$ ,  $(\text{MA})_4\text{InCl}_7:\text{Mn}^{2+}$  and  $(\text{MA})_4\text{InCl}_7:\text{Sb}^{3+}$ , respectively.



**Figure S2.** Unit cells of  $(\text{MA})_4\text{InCl}_7$  and  $(\text{MA})_4\text{InCl}_7:\text{Cs}^+$ . The size of the former one is about twice of the latter one and the area in red dash line is very similar to the latter, suggesting the high similarity of the two crystals.

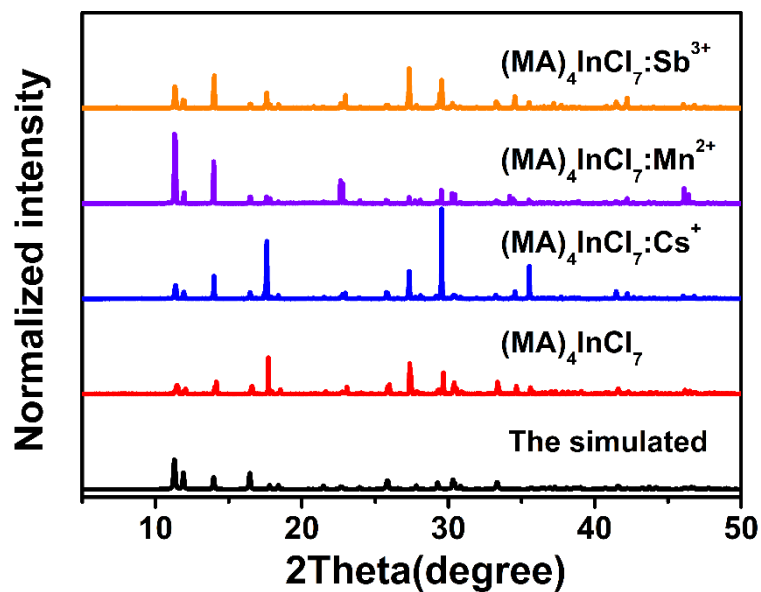


Figure S3. PXRD patterns of all compounds (red:  $(\text{MA})_4\text{InCl}_7$ ; blue:  $(\text{MA})_4\text{InCl}_7:\text{Cs}^+$ ; purple:  $(\text{MA})_4\text{InCl}_7:\text{Mn}^{2+}$ ; orange:  $(\text{MA})_4\text{InCl}_7:\text{Sb}^{3+}$ ;) and simulated pattern of  $(\text{MA})_4\text{InCl}_7$  (black).

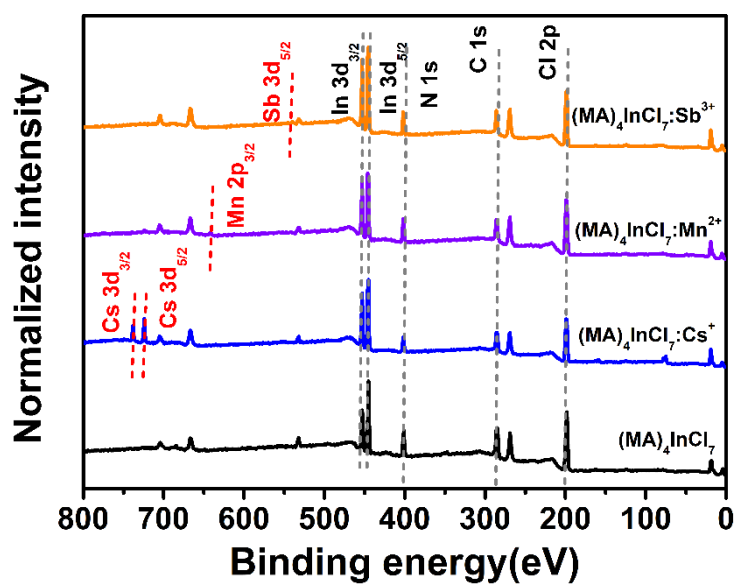


Figure S4. XPS spectra of all compounds.

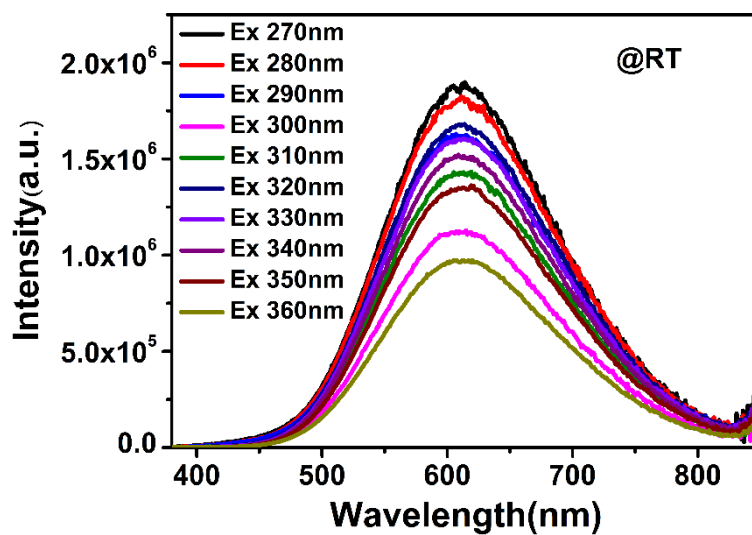


Figure S5. Excitation-dependent PL spectra of  $(\text{MA})_4\text{InCl}_7:\text{Sb}^{3+}$  at room temperature.

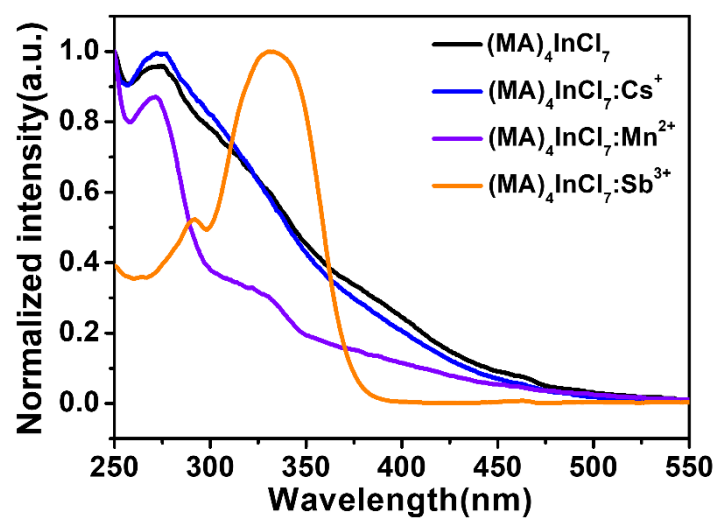
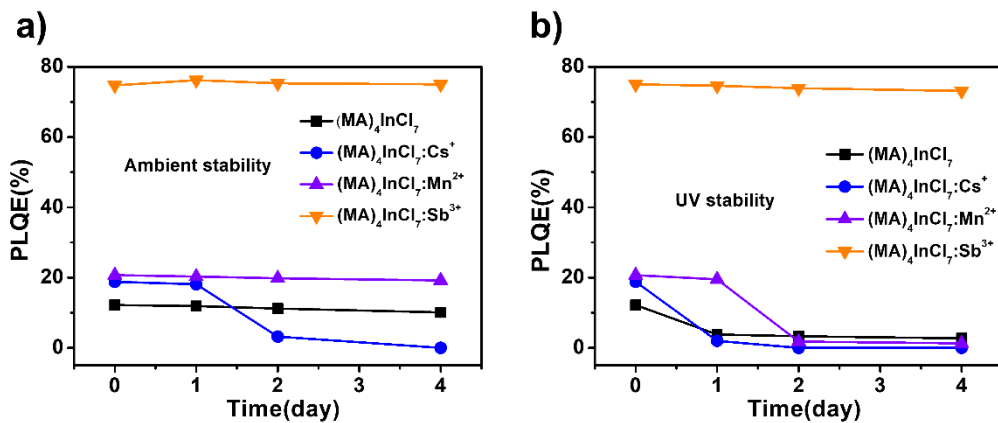
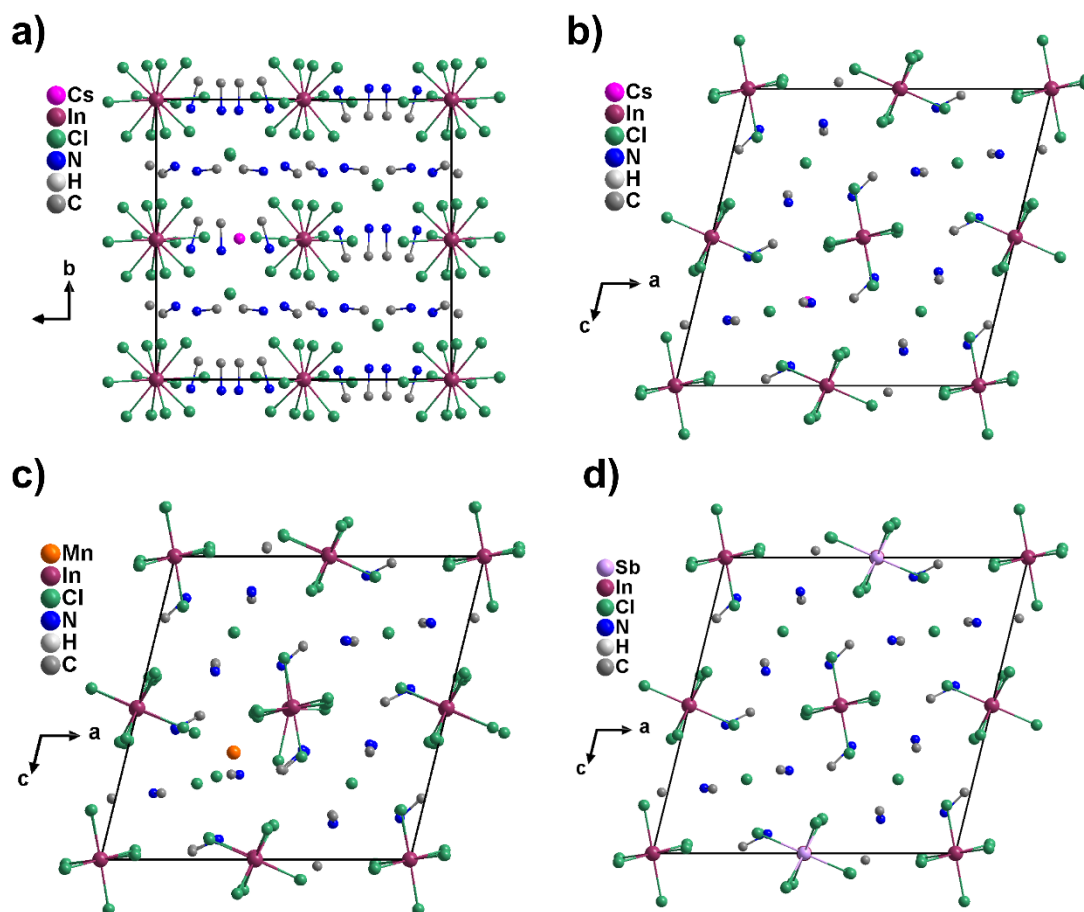


Figure S6. UV absorption of all four compounds.



**Figure S7.** Ambient stability test (at 29°C with relative humidity of ~ 50%) and UV stability test (under continuous UV illumination of 7.96mW/cm<sup>2</sup>) of all four compounds.



**Figure S8.** a-b) Simulated model of (MA)<sub>4</sub>InCl<sub>7</sub>:Cs<sup>+</sup>, c) Simulated model of (MA)<sub>4</sub>InCl<sub>7</sub>:Mn<sup>2+</sup>. d) Simulated model of (MA)<sub>4</sub>InCl<sub>7</sub>:Sb<sup>3+</sup>. In these models, one Cs<sup>+</sup> replaces one MA<sup>+</sup> in the unit cell of (MA)<sub>4</sub>InCl<sub>7</sub>:Cs<sup>+</sup>, one Mn<sup>2+</sup> replaces two MA<sup>+</sup> in the unit cell of (MA)<sub>4</sub>InCl<sub>7</sub>:Mn<sup>2+</sup> and two Sb<sup>3+</sup> substitute two In<sup>3+</sup> in the unit cell of (MA)<sub>4</sub>InCl<sub>7</sub>:Sb<sup>3+</sup>.



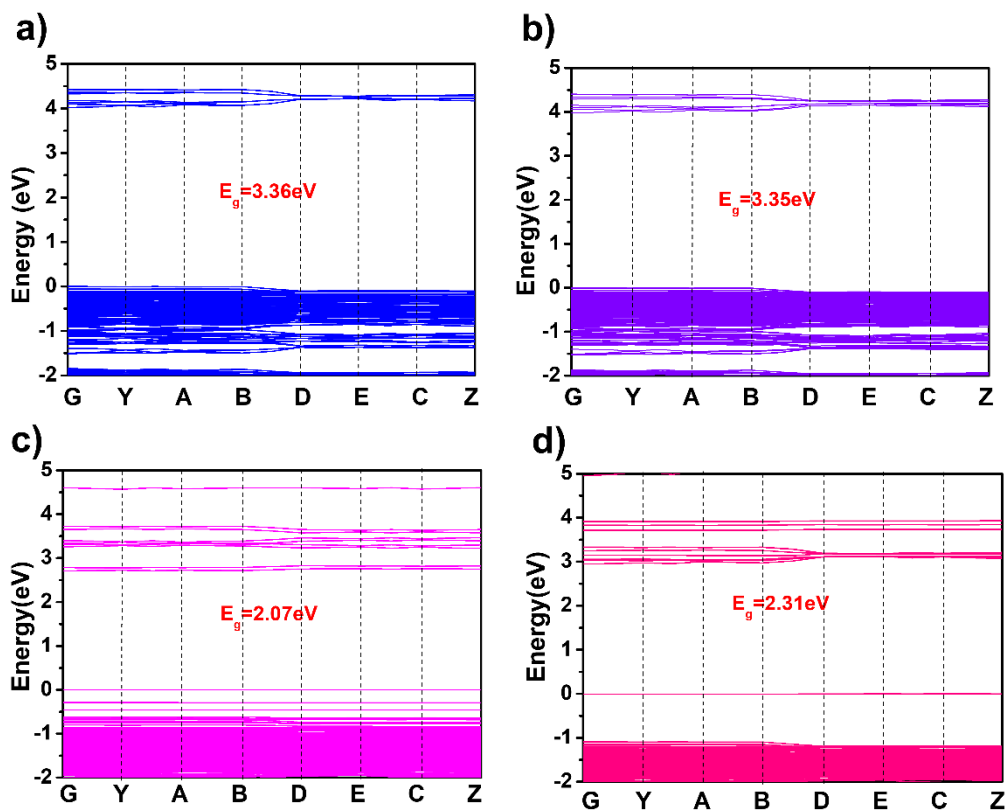


Figure S9. a-d) Electronic band structures of  $(\text{MA})_4\text{InCl}_7$ ,  $(\text{MA})_4\text{InCl}_7:\text{Cs}^+$ ,  $(\text{MA})_4\text{InCl}_7:\text{Mn}^{2+}$  and  $(\text{MA})_4\text{InCl}_7:\text{Sb}^{3+}$ , respectively.

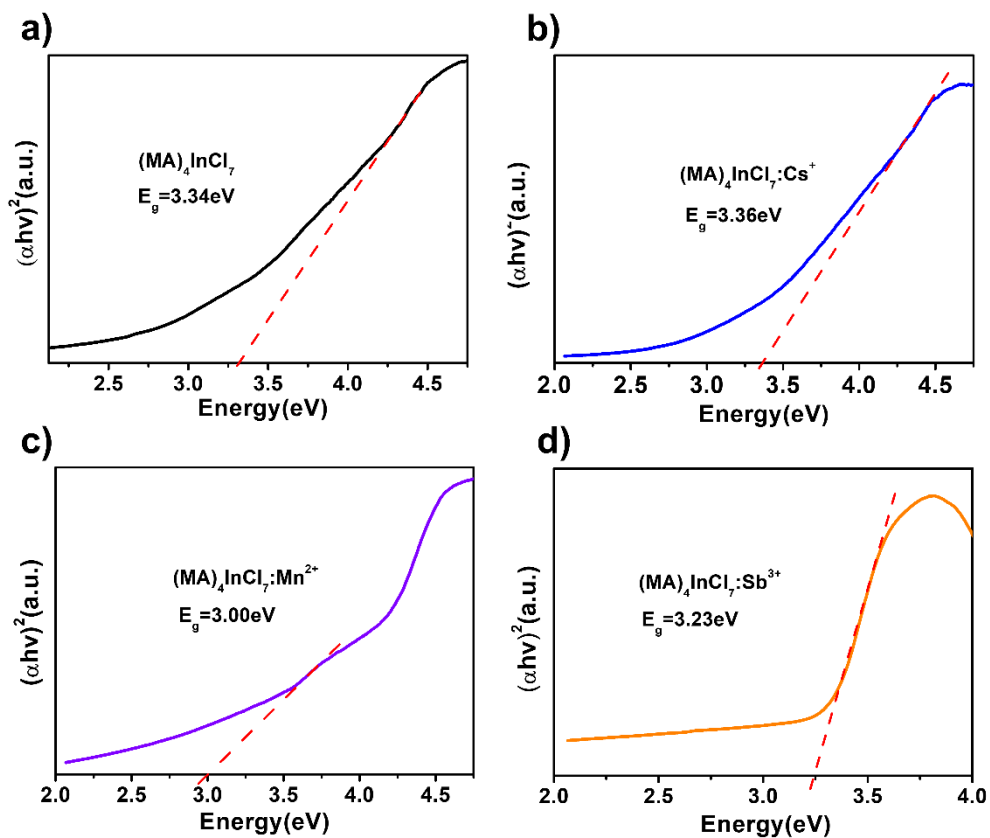


Figure S10. Experimental optical bandgap of  $(\text{MA})_4\text{InCl}_7$  and doped compounds.

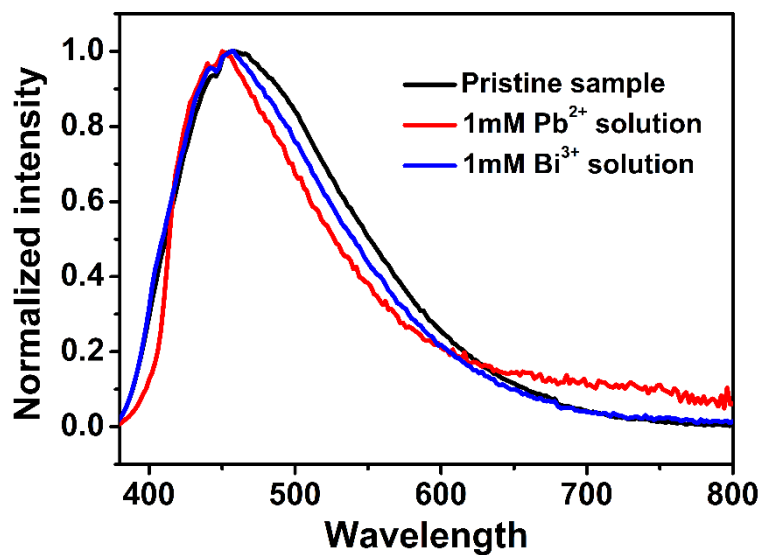


Figure S11. Emission spectra of  $(\text{MA})_4\text{InCl}_7$  when added with different metal ions.

**Table S1.** Single-crystal X-ray diffraction data of all compounds at 200K.

	(MA) <sub>4</sub> InCl <sub>7</sub>	(MA) <sub>4</sub> InCl <sub>7</sub> :Cs <sup>+</sup>	(MA) <sub>4</sub> InCl <sub>7</sub> :Mn <sup>2+</sup>	(MA) <sub>4</sub> InCl <sub>7</sub> :Sb <sup>3+</sup>
empirical formula	C <sub>4</sub> H <sub>24</sub> N <sub>4</sub> InCl <sub>7</sub>	C <sub>3.92</sub> H <sub>35.04</sub> N <sub>3.92</sub> Cs <sub>0.08</sub> InCl <sub>7</sub>	C <sub>4</sub> H <sub>24</sub> N <sub>4</sub> InCl <sub>7</sub>	C <sub>4</sub> H <sub>24</sub> N <sub>4</sub> InCl <sub>7</sub>
formula mass	491.24	491.24	491.24	491.24
space group	P2/n	Pbam	P2/n	P2/n
a/Å	16.0816(4)	9.9548(3)	16.0605(3)	16.0580(4)
b/Å	7.4280(2)	12.7187(5)	7.4193(1)	7.4278(2)
c/Å	16.1475(4)	7.4452(3)	16.1327(4)	16.1429(4)
α/°	90	90	90	90
β/°	103.638(1)	90	103.600(1)	103.633(1)
γ/°	90	90	90	90
V/Å <sup>3</sup>	1874.50(8)	942.65(6)	1868.43(6)	1871.21(8)
Z	4	2	4	4
λ	0.71073	0.71073	0.71073	0.71073
T/K	200	200	200	200
R <sup>1</sup> [a]	0.0638	0.0233	0.0321	0.0269
wR <sup>2</sup>	0.1279	0.0622	0.0706	0.0536

[a] Acetonitrile molecule was removed for the formulation consistency.

**Table S2.** Selected bond lengths for all compounds.

Bonds	(MA) <sub>4</sub> InCl <sub>7</sub>	(MA) <sub>4</sub> InCl <sub>7</sub> :Cs <sup>+</sup>	(MA) <sub>4</sub> InCl <sub>7</sub> :Mn <sup>2+</sup>	(MA) <sub>4</sub> InCl <sub>7</sub> :Sb <sup>3+</sup>
In1—Cl1	2.5216(13)	2.5118(7)	2.5088(6)	2.5120(4)
In1—Cl1 <sup>[i]</sup>	2.5216(13)	2.5118(7)	2.5088(6)	2.5081(4)
In1—Cl2	2.5059(13)	2.5050(5)	2.5215(6)	2.5081(4)
In1—Cl2 <sup>[i]</sup>	2.5059(13)	2.5050(5)	2.5215(6)	2.5270(4)
In1—Cl3	2.5095(12)	2.5050(5)	2.5040(6)	2.5270(4)
In1—Cl3 <sup>[i]</sup>	2.5095(12)	2.5050(5)	2.5040(6)	2.5130(4)
In2—Cl4 <sup>[ii]</sup>	2.5083(12)	2.5050(5)	2.5061(6)	2.5130(4)
In2—Cl4	2.5084(12)	2.5050(5)	2.5061(6)	2.5115(4)
In2—Cl5 <sup>[ii]</sup>	2.5120(14)		2.5099(6)	2.5115(4)
In2—Cl5	2.5120(14)		2.5098(6)	2.5114(4)
In2—Cl6 <sup>[ii]</sup>	2.5073(14)		2.5088(6)	2.5114(4)
In2—Cl6	2.5072(14)		2.5088(6)	2.5120(4)

Symmetry transformations used to generate equivalent atoms: [i] 1-x, 2-y, -z; [ii] 1-x, -y, 1-z.

**Table S3.** Selected bond angles for all compounds.

	(MA) <sub>4</sub> InCl <sub>7</sub>	(MA) <sub>4</sub> InCl <sub>7</sub> :Cs <sup>+</sup>	(MA) <sub>4</sub> InCl <sub>7</sub> :Mn <sup>2+</sup>	(MA) <sub>4</sub> InCl <sub>7</sub> :Sb <sup>3+</sup>
Cl1—In1—Cl3 <sup>[i]</sup>	89.745(19)	89.61(5)	89.37(2)	89.586(15)
Cl1—In1—Cl3	90.255(19)	90.39(5)	90.63(2)	90.414(15)
Cl1 <sup>[ii]</sup> —In1—Cl3	89.745(19)	89.61(5)	89.37(2)	89.586(15)
Cl1 <sup>i</sup> —In1—Cl3 <sup>[ii]</sup>	90.254(19)	90.39(5)	90.63(2)	90.414(15)
Cl2—In1—Cl1 <sup>[i]</sup>	89.745(19)	89.62(5)	89.62(2)	89.325(15)
Cl2—In1—Cl1	90.255(19)	90.38(5)	90.38(2)	90.676(15)
Cl2 <sup>[ii]</sup> —In1—Cl1	89.745(19)	89.62(5)	89.62(2)	89.325(15)
Cl2 <sup>[ii]</sup> —In1—Cl1 <sup>[ii]</sup>	90.255(19)	90.38(5)	90.38(2)	90.674(15)
Cl2—In1—Cl3	90.47(3)	90.67(5)	90.34(2)	90.317(16)
Cl2—In1—Cl3 <sup>[i]</sup>	89.53(3)	89.33(5)	89.66(2)	89.683(16)
Cl2 <sup>i</sup> —In1—Cl3 <sup>[ii]</sup>	90.47(3)	90.37(5)	90.34(2)	90.317(16)
Cl2 <sup>i</sup> —In1—Cl3	89.53(3)	89.99(5)	89.66(2)	89.683(16)
Cl5—In2—Cl4		89.99(5)	89.43(2)	90.634(17)
Cl5 <sup>[iii]</sup> —In2—Cl4		90.01(5)	90.57(2)	89.366(17)
Cl5 <sup>[iii]</sup> —In2—Cl4 <sup>[iii]</sup>		89.99(5)	89.43(2)	90.634(17)
Cl5—In2—Cl4 <sup>[iii]</sup>		90.01(5)	90.57(2)	89.366(17)
Cl6—In2—Cl4		90.55(1)	90.47(2)	90.518(15)
Cl6 <sup>[iii]</sup> —In2—Cl4		89.45(5)	89.53(2)	89.482(15)
Cl6 <sup>[iii]</sup> —In2—Cl4 <sup>[iii]</sup>		90.55(5)	90.47(2)	90.518(15)
Cl6—In2—Cl4 <sup>ii</sup>		89.45(5)	89.53(2)	89.483(15)
Cl6—In2—Cl5		89.35(5)	89.85(2)	90.143(16)
Cl6 <sup>ii</sup> —In2—Cl5 <sup>[iii]</sup>		89.35(1)	89.86(2)	90.142(16)
Cl6—In2—Cl5 <sup>[ii]</sup>		90.65(5)	90.15(2)	89.857(16)
Cl6 <sup>[iii]</sup> —In2—Cl5		90.65(5)	90.15(2)	89.858(16)

Symmetry transformations used to generate equivalent atoms: [i] 1-x, 2-y, -z; [ii] 1-x, -y, 1-z.

**Table 4.** The extent of distortion of  $\text{InCl}_6^{3-}$  for all compounds.

		$D_{\text{avg}}$	$\Delta_{\text{oct}}$	$\lambda_{\text{oct}}$	$\sigma_{\text{oct}}^2$
$(\text{MA})_4\text{InCl}_7$	In1	2.512	$7.21 \times 10^{-6}$	1.0000072	0.2711
	In2	2.509	$6.82 \times 10^{-7}$	1.0000007	0.2637
$(\text{MA})_4\text{InCl}_7:\text{Cs}^+$	In1	2.507	$1.63 \times 10^{-6}$	1.0000016	0.1276
$(\text{MA})_4\text{InCl}_7:\text{Mn}^{2+}$	In1	2.511	$8.64 \times 10^{-6}$	1.0000086	0.2389
	In2	2.508	$3.91 \times 10^{-7}$	1.0000004	0.2064
$(\text{MA})_4\text{InCl}_7:\text{Sb}^{3+}$	In1	2.519	$1.05 \times 10^{-5}$	1.0000100	0.2645
	In2	2.512	$5.23 \times 10^{-8}$	1.0000000	0.2510

$[D_{\text{avg}}]$  Average bond length,  $[\Delta_{\text{oct}}]$  bond length distortion,  $[\lambda_{\text{oct}}]$  octahedral elongation,  $[\sigma_{\text{oct}}^2]$  octahedral angle variance.

**Table S5.** Elemental analysis of doped compounds via ICP-OES and XPS.

Metal ions	Feeding ratio <sup>[a]</sup> (%)	Experimental ratio of ICP-OES (%)	Experimental ratio of XPS (%)
$(\text{MA})_4\text{InCl}_7:\text{Cs}^+$	5.82	2.52	3.57
$(\text{MA})_4\text{InCl}_7:\text{Mn}^{2+}$	2.97	0.20	0.37
$(\text{MA})_4\text{InCl}_7:\text{Sb}^{3+}$	10.6	9.37	8.97

**Table S6.** PL decay dynamics for all compounds at room temperature and 77K.

		$\tau_{\text{ave}}^{[a]}(\text{ns})$	$A_1$	$\tau_1$ (ns)	$A_2$	$\tau_2$ (ns)	$A_3$	$\tau_3$ (ns)
MACl	RT							
	77K	7.57	0.92	3.60	0.07	14.0	0.01	55.0
(MA) <sub>4</sub> InCl <sub>7</sub>	RT	6.72	0.81	3.45	0.19	11.4		
	77K	8.14	0.65	3.33	0.33	7.51	0.02	16.8
(MA) <sub>4</sub> InCl <sub>7</sub> :Cs <sup>+</sup>	RT	6.53	0.92	2.75	0.08	11.5		
	77K	10.1	0.73	2.75	0.26	7.38	0.01	20.8
(MA) <sub>4</sub> InCl <sub>7</sub> :Mn <sup>2+</sup>	RT	7.94	0.82	2.41	951	0.18		
	77K	6.72	0.65	2.78	0.32	8.30	0.03	19.5
(MA) <sub>4</sub> InCl <sub>7</sub> :Sb <sup>3+</sup>	RT	5454	-0.22	3.18	1.22	5232		
	77K	6113	-0.22	1782	1.22	5903		

$$[a] \tau_{\text{ave}} = A_1\tau_1^2 + A_2\tau_2^2 + A_3\tau_3^2 / A_1\tau_1 + A_2\tau_2 + A_3\tau_3$$

where  $A_1, A_2, A_3$  are the pre-exponential factors, and  $\tau_1, \tau_2, \tau_3$  are the lifetimes components.

## References

- 1 G. Kresse and J. Furthmüller, Efficient Iterative Schemes for Ab Initio Total-Energy Calculations Using a Plane-Wave Basis Set, *Phys. Rev. B*, 1996, **16**, 11169–11186.
- 2 J. P. Perdew, K. Burke and M. Ernzerhof, Generalized Gradient Approximation Made Simple. , *Phys. Rev. Lett.*, 1996, **77**, 3865.
- 3 S. Grimme, J. Antony, S. Ehrlich and J. Krieg, A Consistent and Accurate ab Initio Parametrization of Density Functional Dispersion Correction (DFT-D) for the 94 Elements, *J. Chem. Phys.*, 2010, **132**, 154104.