Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supplemental Material for "Optical properties of Ytterbium-doped and undoped $Cs_2AgInCl_6$ thin films deposited by co-evaporation of chloride salts"

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I. Cross Sectional Scanning Electron Microscope Image

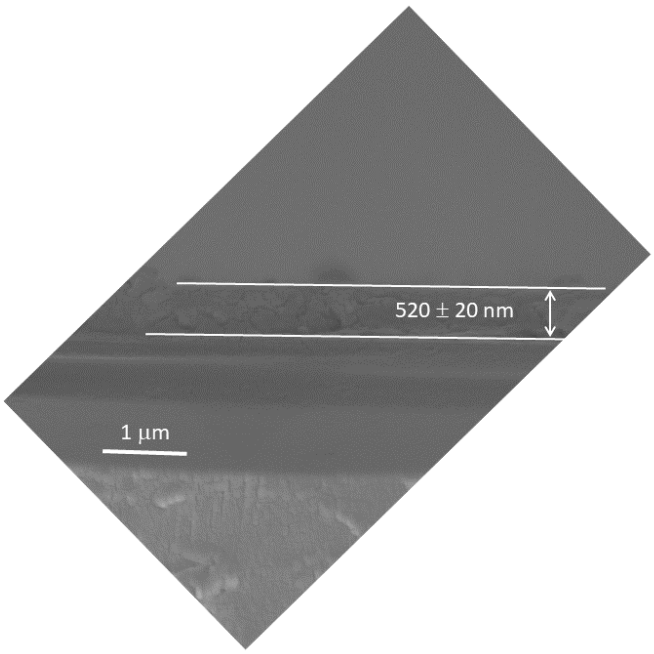

Figure S1. SEM of an as-deposited undoped $Cs_2AgInCl_6$ film showing a thickness of 520±20 nm thickness

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II. Comparison of as-deposited undoped $Cs_2AgInCl_6$ film to precursor and $Cs_3In_2Cl_9$ XRDs

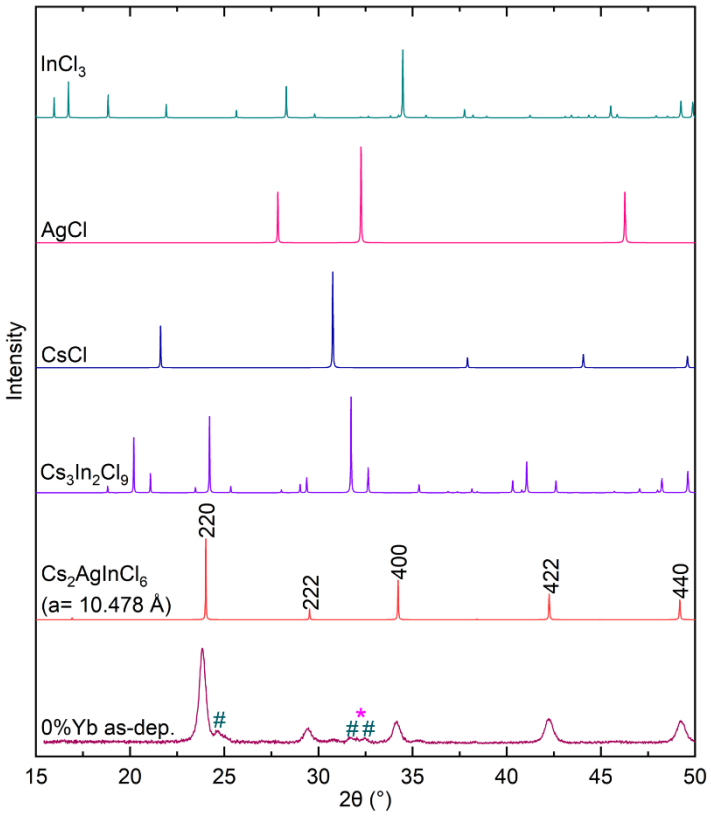

Figure S2. From bottom to top, the XRD pattern of an undoped (0%Yb) as-deposited (as-dep.) film and simulated XRD patterns (with VESTA software) of cubic $Cs_2AgInCl_6$ (a = 10.478 Å), $Cs_3In_2Cl_9$, CsCl, AgCl and $InCl_3$.[1–4] Impurity and unreacted precursor XRD peaks are labeled with # for $Cs_2In_3Cl_9$ and with * for AgCl. The XRD are offset along the intensity axis for clarity.

III. Additional SEMs of an annealed undoped $Cs_2AgInCl_6$ films after 9 months

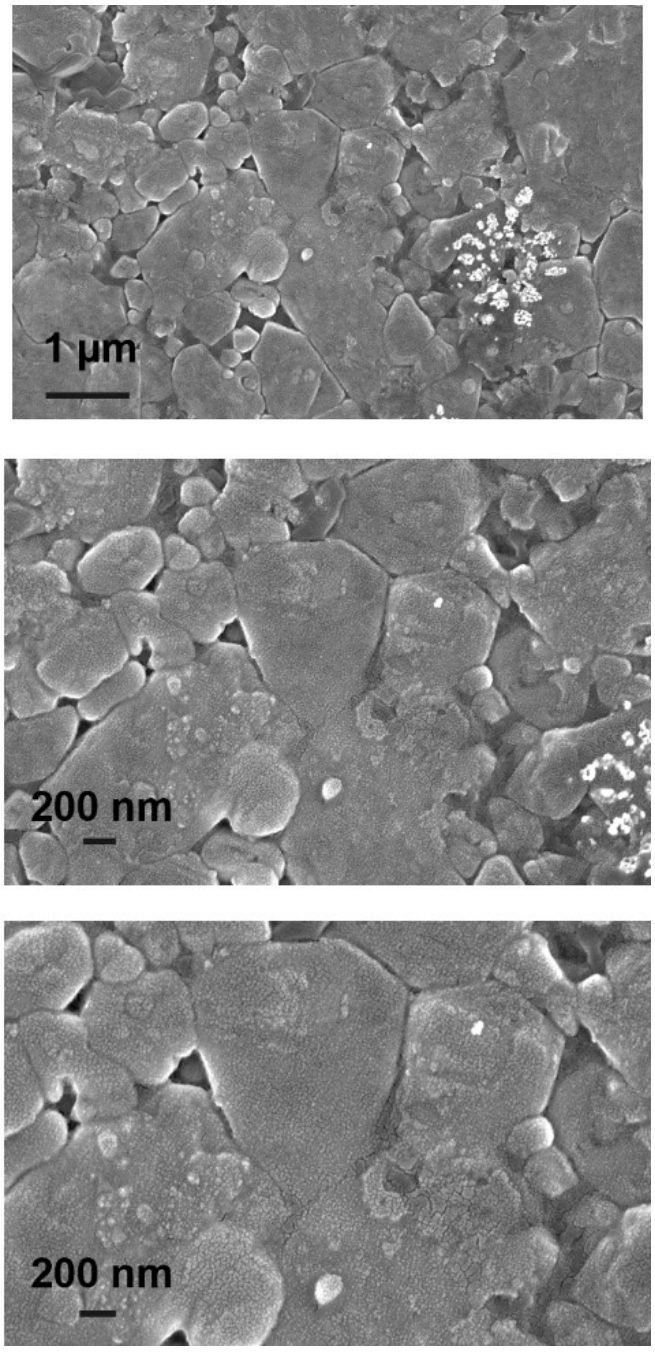

Figure S3. SEM images of an undoped (0% Yb) film annealed at 350 °C for one hour and stored under ambient conditions for nine months at three different magnifications.

IV. Unnormalized emission spectra of $Cs_2AgInCl_6$, $Cs_2AgBiCl_6$, and $Cs_2AgBiBr_6$ thin films when excited at 370 nm, 370 nm, and 420 nm, respectively

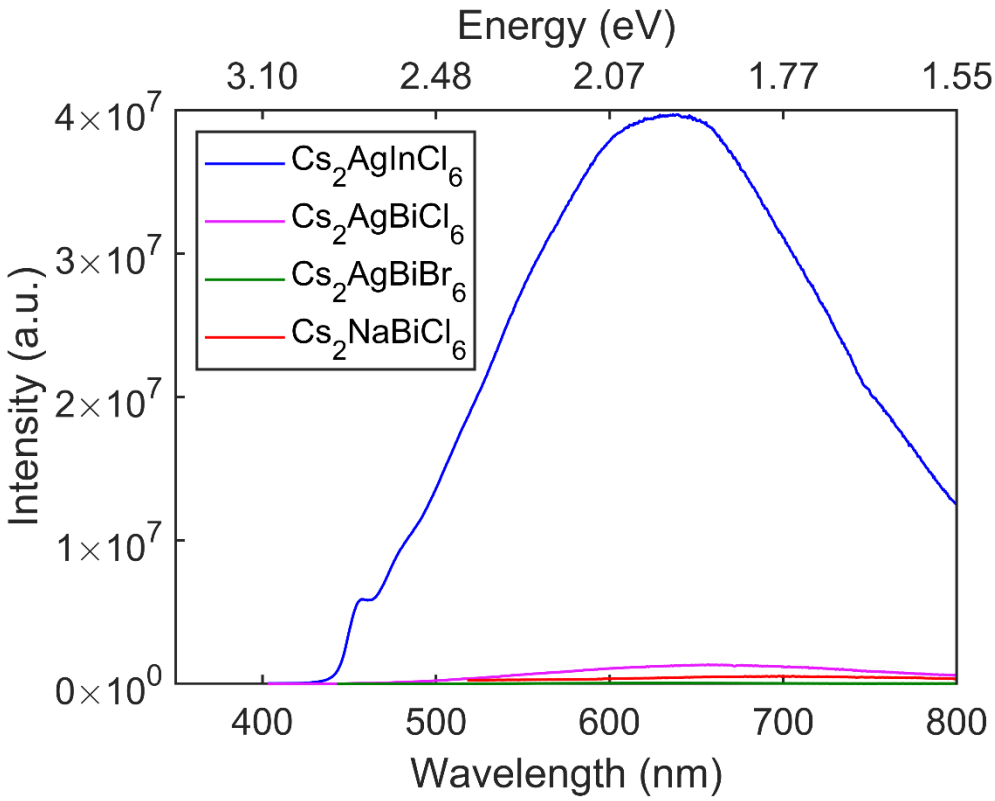

Figure S4. Unnormalized emission spectra of $Cs_2AgInCl_6$, $Cs_2AgBiCl_6$, $Cs_2AgBiBr_6$, and $Cs_2NaBiCl_6$ thin films when excited at 370 nm, 370 nm, 420 nm, and 360 nm, respectively. The ratio of the magnitudes of the peak heights is approximately 4×10^8:1.5×10^6:5×10^5:6×10^4 $Cs_2AgInCl_6$:$Cs_2AgBiCl_6$:$Cs_2NaBiCl_6$:$Cs_2AgBiBr_6$.

V. Optical Extinction of Yb-doped $Cs_2AgInCl_6$ films

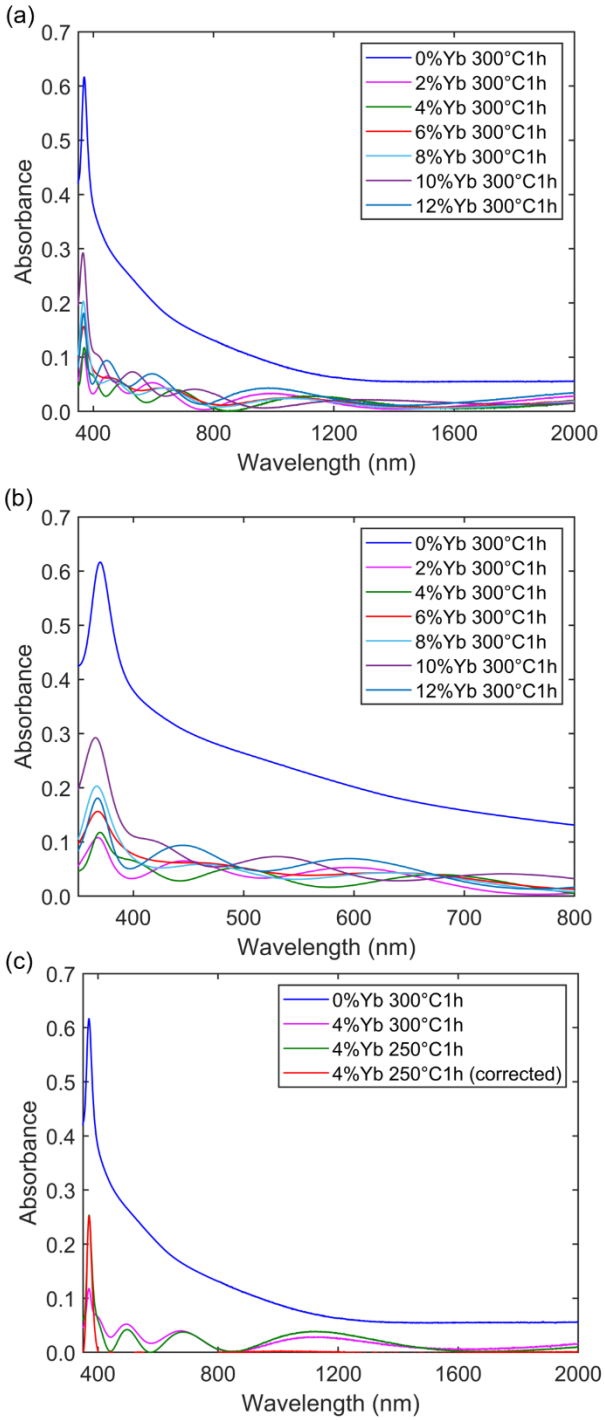

Figure S5. (a) Optical extinction of $Cs_2AgInCl_6$ thin films doped with 0, 2, 4, 6, 8, 10, 12% of Yb. All films were annealed at 300 °C for 1 hour. (b) is same as (a) but zoomed in scale to the visible region near the absorption edge ~400 nm. (c) Figure 6 of the text expanded to 200 nm to show all the fringes.

VI. SEMs of Yb-doped films

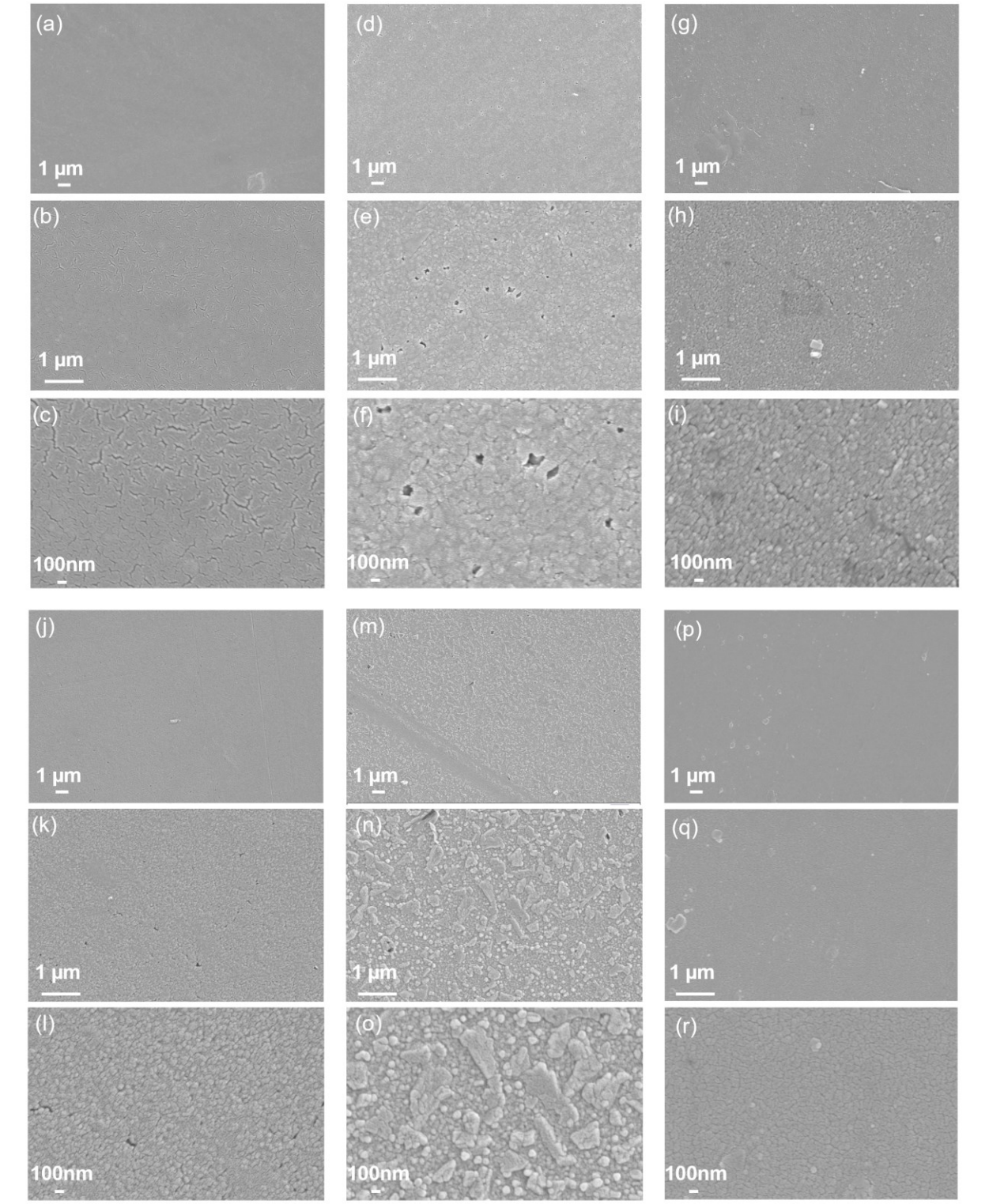

Figure S6. SEM images of $Cs_2AgInCl_6$ thin films doped with (a, b, c) 2% Yb, (d, e, f) 4% Yb, (g, h, i) 6% Yb, (j, k, l) 8% Yb, (m, n, o) 10% Yb and (p, q, r) 12% Yb at three different magnifications. All films were annealed at 300 °C for 1 h.

VII. Optical extinction of Yb-doped films annealed under different conditions

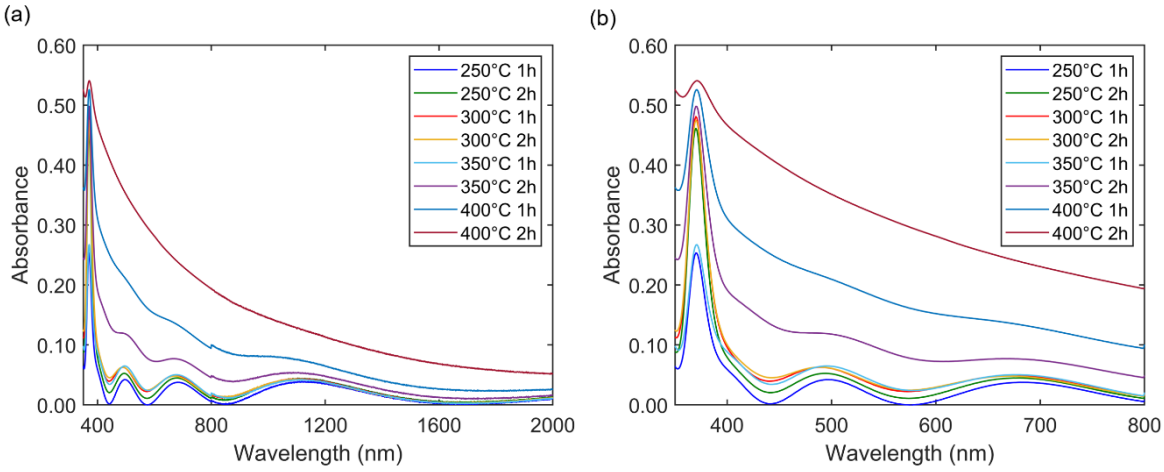

Figure S7. Optical Extinction of $Cs_2AgInCl_6$ thin films doped with 4% Yb and annealed at 250 °C, 300 °C, 350 °C, and 400 °C for 1 h or 2 h (a) over 350 nm to 2000 nm and (b) over 350 nm to 800 nm. All films were annealed in nitrogen-filled glove box and measured at ambient conditions.

VIII. Table of $^2F_{5/2}$ and $^2F_{7/2}$ levels splittings by the crystal field

Table S1. Measured emission peaks determined using a nonlinear least squares fitting of the spectrum between 900-1050 nm, the corresponding energy in cm^{-1}, the assigned transition (see Figure 8 of the text), and the predicted energy of the transitions from the energy level diagram in Figure 8 of the text.

Measured Emission (nm)	Energy (cm^{-1})	Transition	Predicted Transition Energy (cm^{-1})
927.0	10787	2'⟶ 0	10787
941.4	10622	1'⟶ 0	10622
954.3	10479	0'⟶ 0	10479
967.1	10340	2'⟶ 1	10350
972.8	10280	2'⟶ 2	10270
980.9	10195	1'⟶ 1	10185
987.7	10125	1'⟶ 2	10105
995.9	10041	0'⟶ 1	10042
1005.8	9942	0'⟶ 2	9962
1017.1	9832	2'⟶ 3	9834
1034.0	9671	1'⟶ 3	9669
1049.8	9526	0'⟶ 3	9526

IX. Comparison of orange luminescence between Yb-doped and undoped films

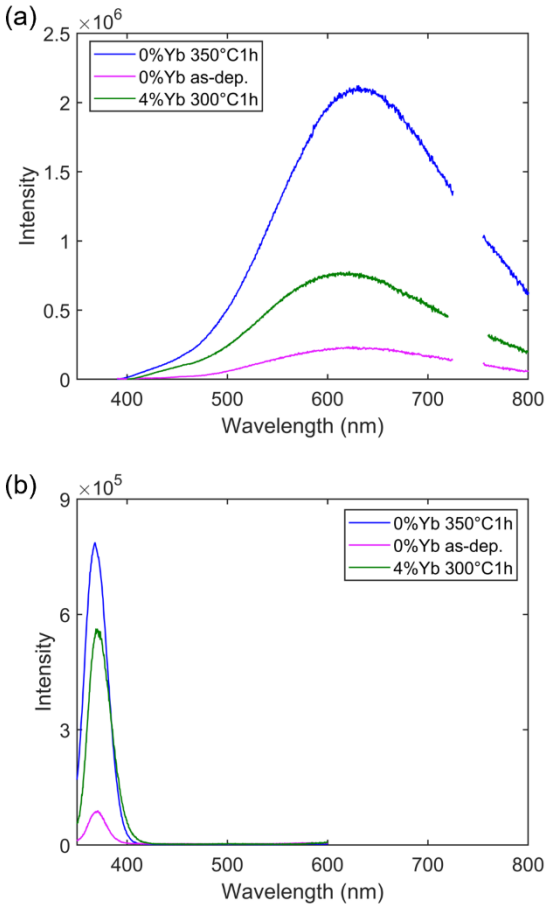

Figure S8. (a) Photoluminescence upon excitation at 370 nm from an undoped as-deposited $Cs_2AgInCl_6$ film, an undoped $Cs_2AgInCl_6$ film after annealing in the nitrogen-filled glove box at 350°C for one hour, and a $Cs_2AgInCl_6$ film dope with 4% Yb after annealing in the nitrogen-filled glove box at 300°C for one hour. (b) Excitation spectrum of the emission at 630 nm for the films in (a).

X. Dependence of PLQY on annealing temperature and time

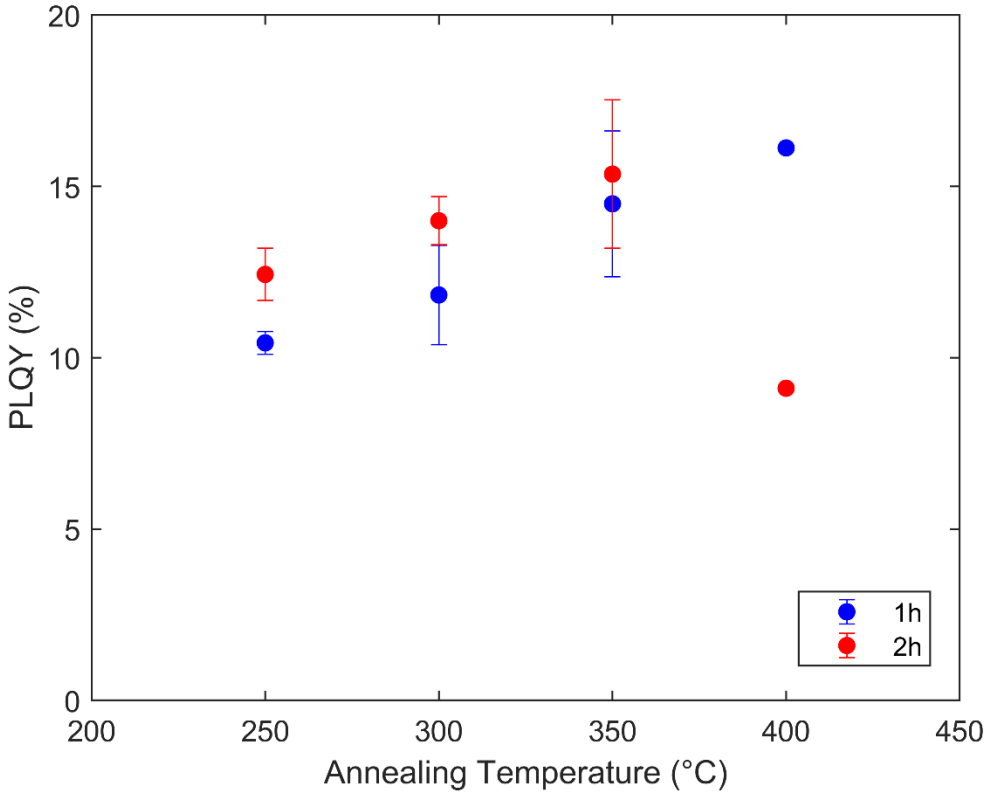

Figure S9. PLQY of $Cs_2AgInCl_6$ films doped with 4% Yb as a function of annealing temperature and annealing time. All films were annealed under nitrogen environment and measured at ambient conditions.

XI. Additional TRPL data

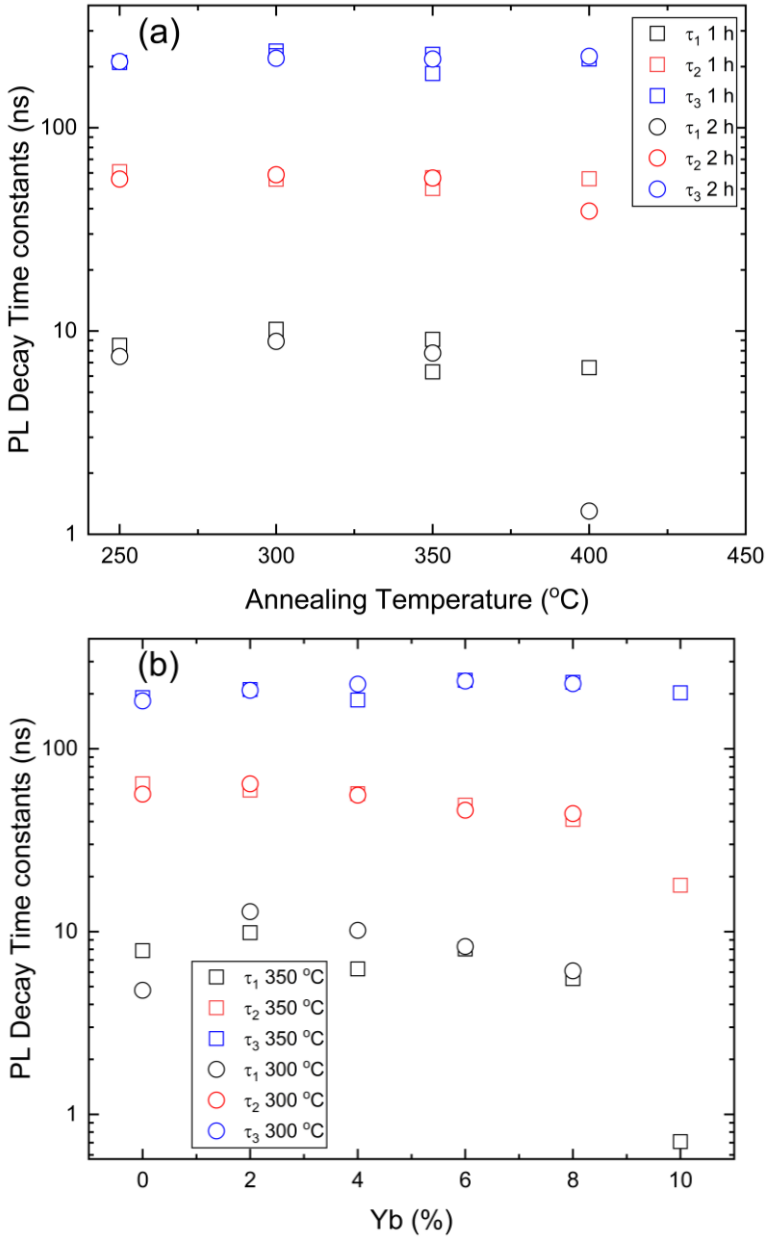

Figure S10 (a) TRPL triexponential decay time constants as a function of annealing temperature for a $Cs_2AgInCl_6$ film doped with 4% Yb and annealed for 1 or 2 h. (b) TRPL triexponential decay time constants as a function of Yb concentration for a $Cs_2AgInCl_6$ film and annealed at 300 or 350 °C for 1 h.

XII. Long-term stability and robustness of the PLQY measurements

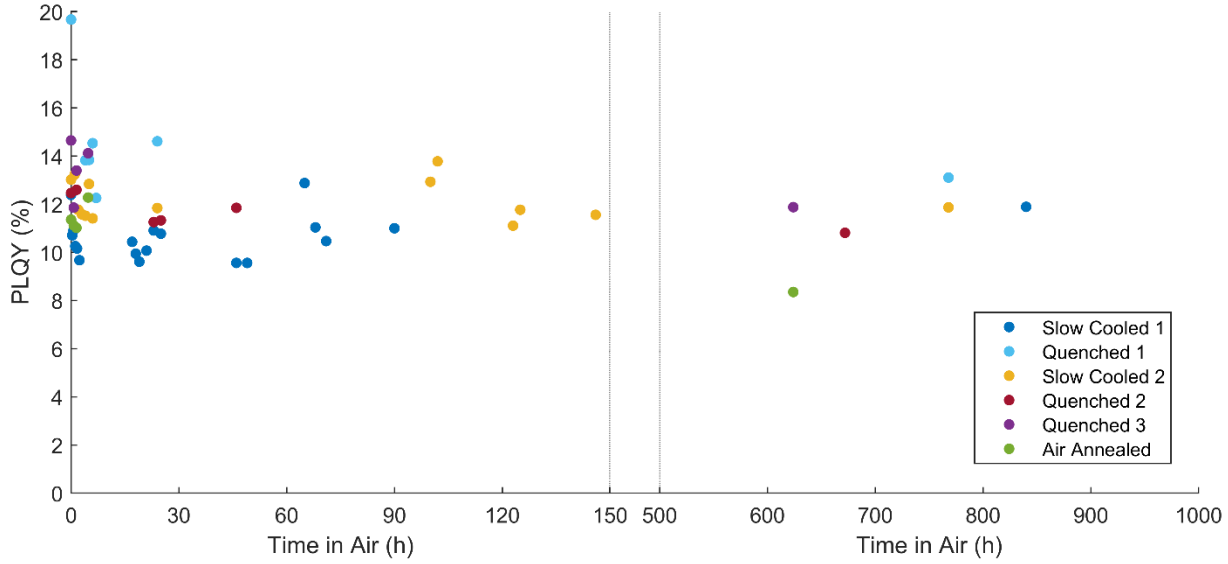

Figure S11. PLQY measurements of six different $Cs_2AgInCl_6$ thin films over time exposed to air after annealing. All films were doped with 4% Yb and were annealed at 300 °C for one hour. All films were annealed under nitrogen-filled glove box except the film marked air-annealed which was annealed at the same temperature and duration as others but in air. Films were either cooled naturally by leaving them on the hot plate but turning off heating (labeled slow cooling) or by taking them off the hot plate and setting them on a surface at room temperature (labeled quenched). The time zero is the first measurement. The average value and standard deviation of this data set is shown as the PLQY of the 4% Yb film data point in Figure 7 (c).

Figure S11 shows the temporal stability of the PLQY value as well as the robustness of the measurement with subtle changes in the annealing protocol for a film doped with 4% Yb and annealed at 300 ºC for one hour. Specifically, films were cooled naturally to room temperature on the hot plate after turning off the hot plate ("slow cooling"), taken off the hot plate, and cooled by placing on a room temperature surface ("quenched"). We also annealed one film in the air at the same temperature and duration (air-annealed). The film PLQY remained in a range of around ~12% after exposure to air for nearly a month. While there is scatter in the measurements, no significant difference was observed in PLQY. The average PLQY of all the above measurements was 11.8%, with a standard deviation of 1.4%.

We observed outliers during experiments and suspect that there are hidden variables that affect the PLQY. By hidden variables, we mean those experimental variables that may affect the PLQY but are not expected to affect it and, therefore, are not normally controlled (or mentioned in articles). Examples include chemical lots and batches of precursors, differences in hot plates used for annealing despite efforts to reproduce the temperature, environmental humidity, substrate cleaning protocols, etc. For instance, a notable high initial PLQY (19.7%) was observed on a quenched film that decayed rapidly to the ~12% range in a few hours, but we could never reproduce this value. Efforts to identify such hidden variables continue. The film annealed in air behaved the same as

films annealed in a nitrogen-filled glove box and then taken out to air, though the long-term stability of this film appears somewhat worse than the film annealed in the glove box.

References

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