Supporting Information

Mitigating Sn Loss via Anion Substitution in the Cu^{2+}-Sn^{2+} Precursor System for $Cu_2ZnSn(S, Se)_4$ Solar Cells

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Table S1: ICP-MS results of *Cl-only* solution before and after filtration.

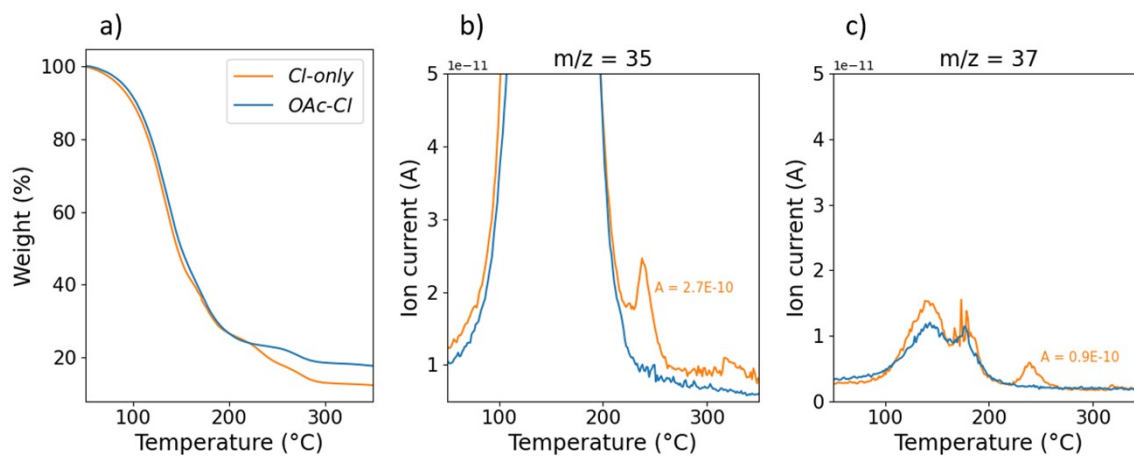|	Solution before filtration	Solution after filtration
Target Cu/Sn	1.12	1.12
Cu (mg/L)	28700	29000
Zn (mg/L)	23000	23500
Sn (mg/L)	48800	48900
Calculated Cu/Sn	1.10	1.11

Figure S1: (a) TGA of *Cl-only* and *OAc-Cl* solution under artificial air. (c) and (d) MS signal for mass 35 and 37. A coupled mass spectrometer (NETZSCH QMS 403C Aeolos) was used to analyze volatile decomposition products of TGA. The legend applies to all subplots. The values for A correspond to the area below the peak assigned to Sn loss.
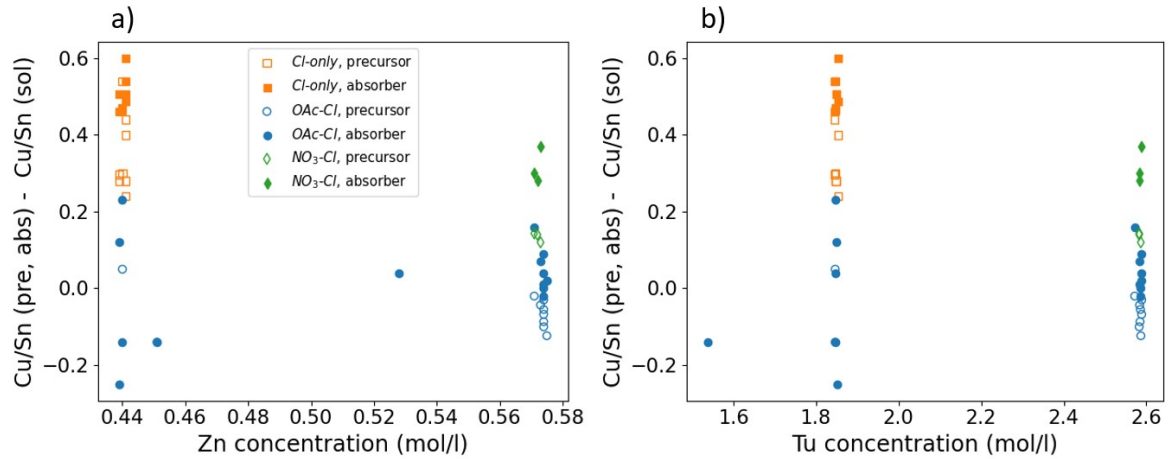
Figure S2: The difference between Cu/Sn of the precursor or absorber and the Cu/Sn ratio of the solution is shown with respect to the Zn concentration (a) and the Tu concentration (b). There is no trend for Sn loss in either figure, ruling out the influence of total metal salt concentration (here Zn) and thiourea concentration on Sn loss.

Cu/Sn estimation in precursor

Assumptions:

- Nominal Cu^{2+} concentration: 0.56 M
- Nominal Sn^{2+} concentration: 0.49 M
- Sn^{4+} is completely lost via complex decomposition
- Cu^{2+} completely reacts to Cu^+, because the precursor solution is colorless. Cu^{2+} would color the solution bluish.

Using Equation (1) from the main manuscript, the resulting concentrations in the solution are:

$$c(Cu^{2+}) = 0\ M$$

$$c(Sn^{2+}) = 0.49 - \frac{0.56}{2} = 0.21\ M$$

$$c(Cu^+) = 0.56\ M$$

$$c(Sn^{4+}) = \frac{0.56}{2} = 0.28\ M$$

If Sn4+ were lost completely during precursor fabrication, the Cu/Sn ratio would be:

$$\left(Cu/Sn\right)_{pre} = \frac{c(Cu^{2+}) + c(Cu^+)}{c(Sn^{2+}) + c(Sn^{4+})} = \frac{0 + 0.56}{0.21 + 0} \approx 2.67$$
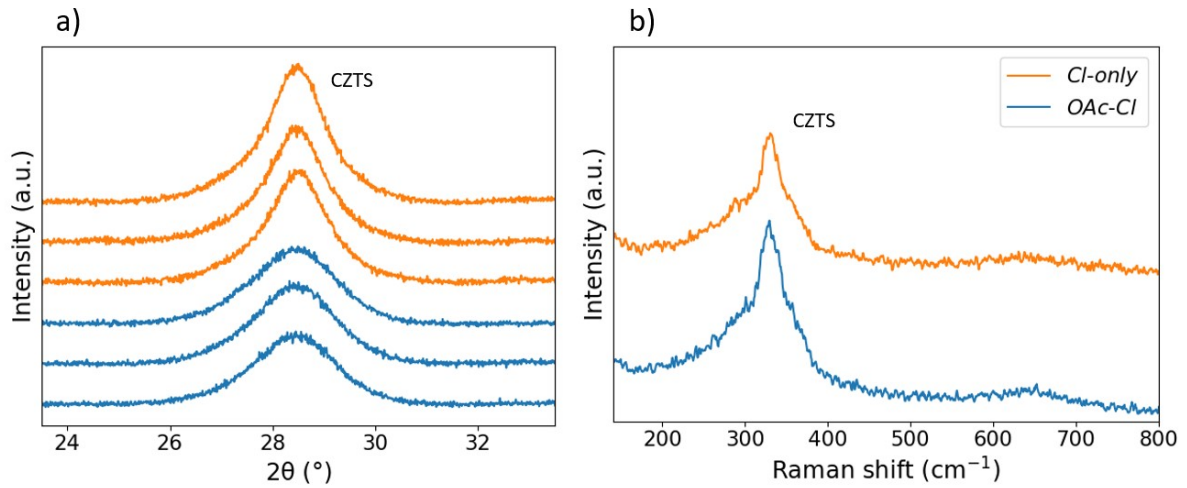
Figure S3: (a) XRD 20-35 precursor measurement to demonstrate reproducibility of a-CZTS peak for *Cl-only* (orange) and *OAc-Cl* (blue) recipe. The measurement parameters differed from the description in the main manuscript, a step size of 0.01° and a scan rate of 0.2 s/step were used. (b) Raman measurements of the same precursors as shown in Figure 4 of the main manuscript. Raman spectroscopy was conducted using a 532 nm laser with a power density of ~120 W/cm2.
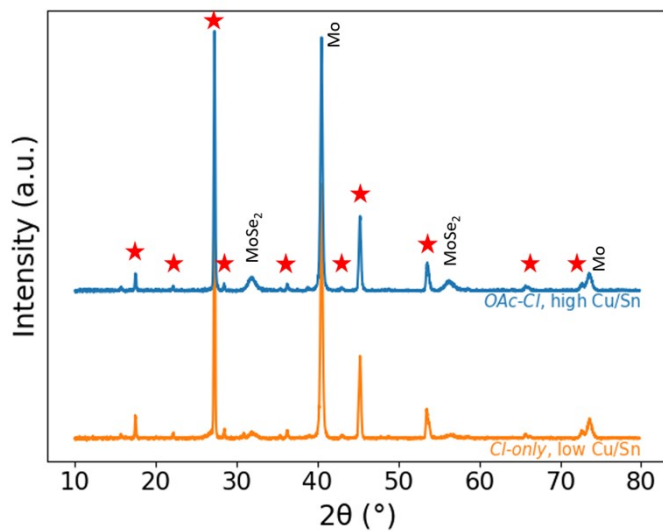

Figure S4: XRD patterns of *OAc-Cl* with high nominal Cu/Sn (blue) and *Cl-only* with low nominal Cu/Sn (orange) in the solution shown over a broader 2θ range of 10-80°. The red stars mark peaks assigned to CZTSSe.
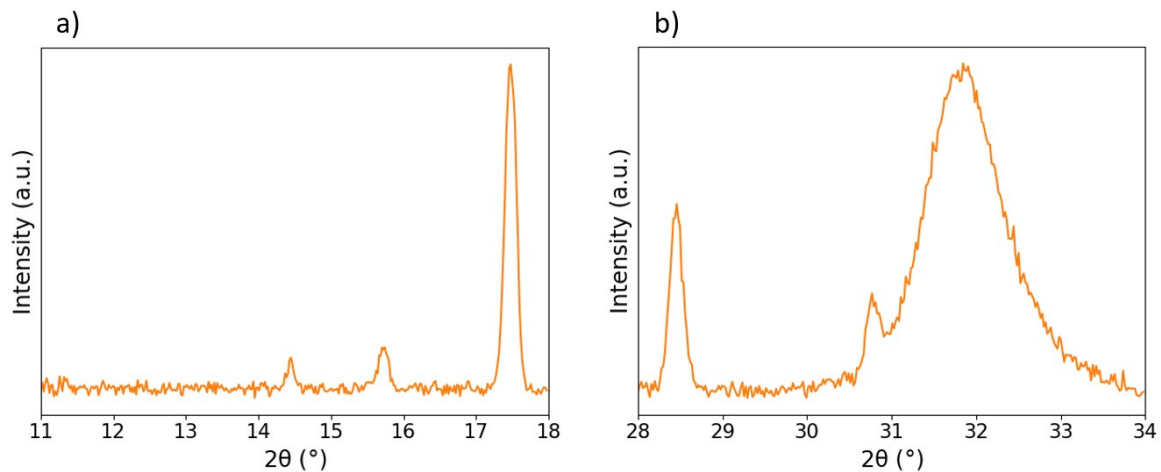
Figure S5: XRD patterns of an additional *Cl-only* absorber fabricated from a solution with low Cu/Sn ratio reveals peaks corresponding to SnSe$_2$.
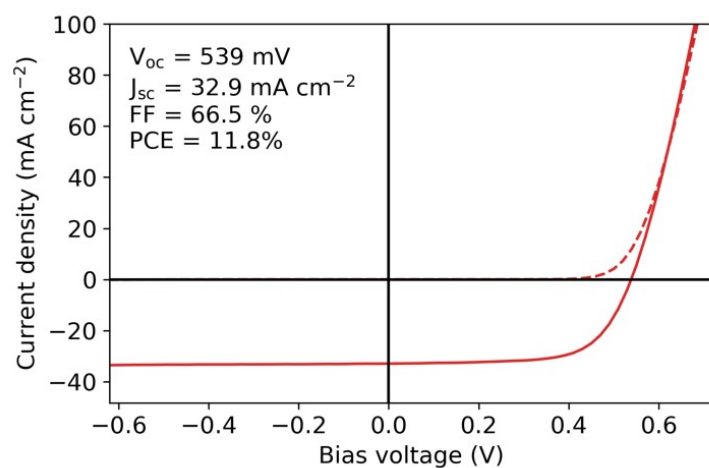

Figure S6: Dark and illuminated JV curve of the champion device fabricated from *Cl-only* solution.
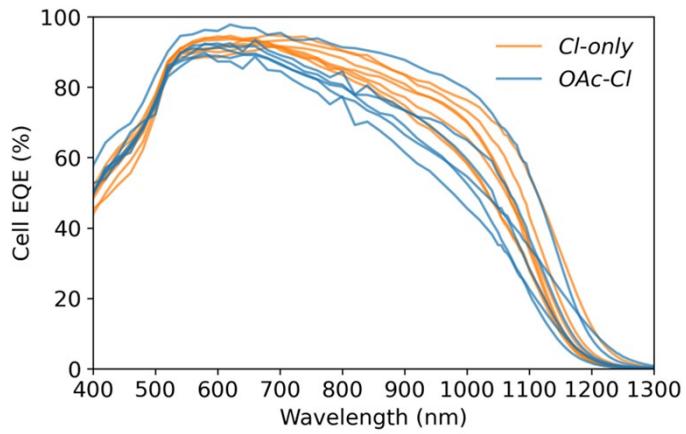
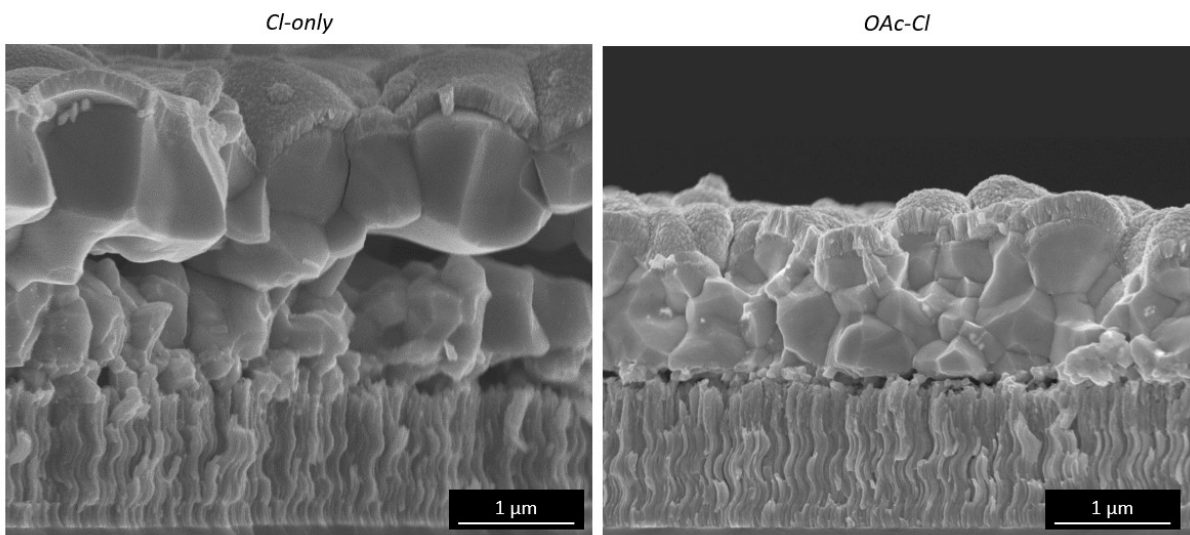Figure S7: EQE curves of best cells for each *Cl-only* (orange) and *OAc-Cl* (blue) sample.

Figure S8: SEM cross section of a *Cl-only* device (left) and a *OAc-Cl* device (right). A Hitachi S-4800 electron microscope was used to obtain the images.
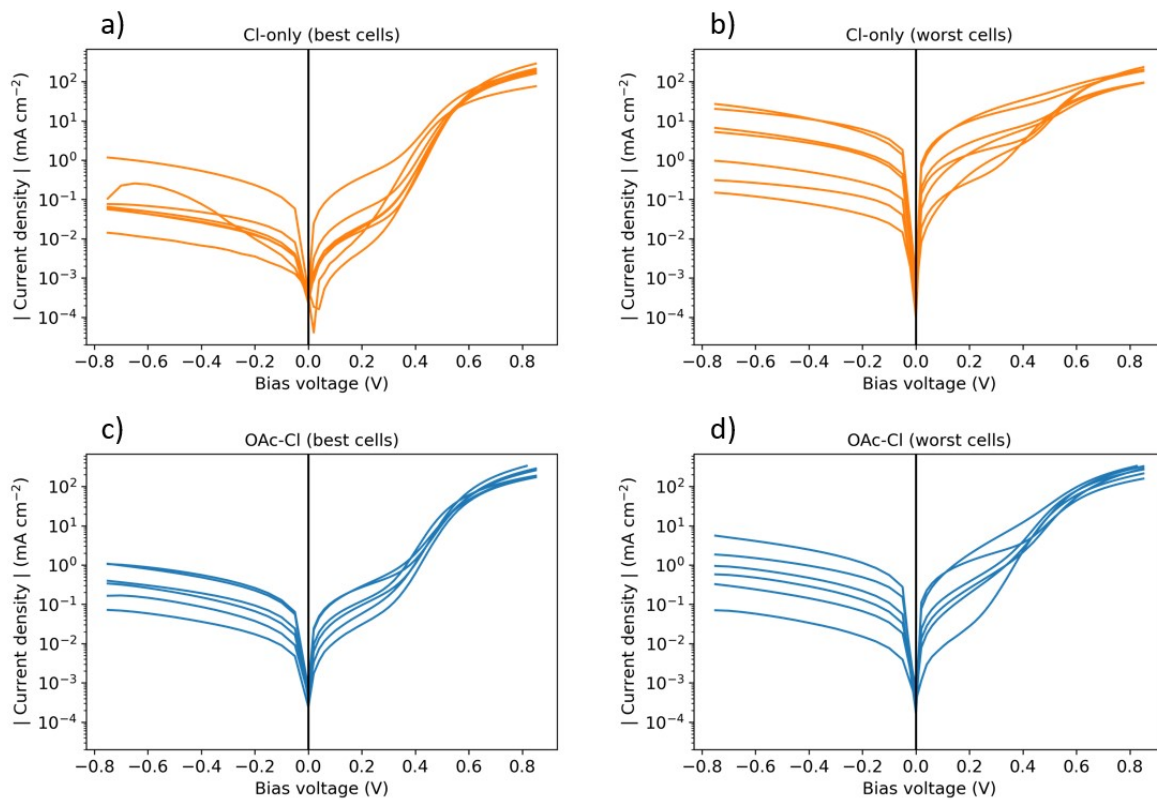
Figure S9: JV curves of best cells (left) and worst cells (right) for each *Cl-only* (top) and *OAc-Cl* (bottom) sample.
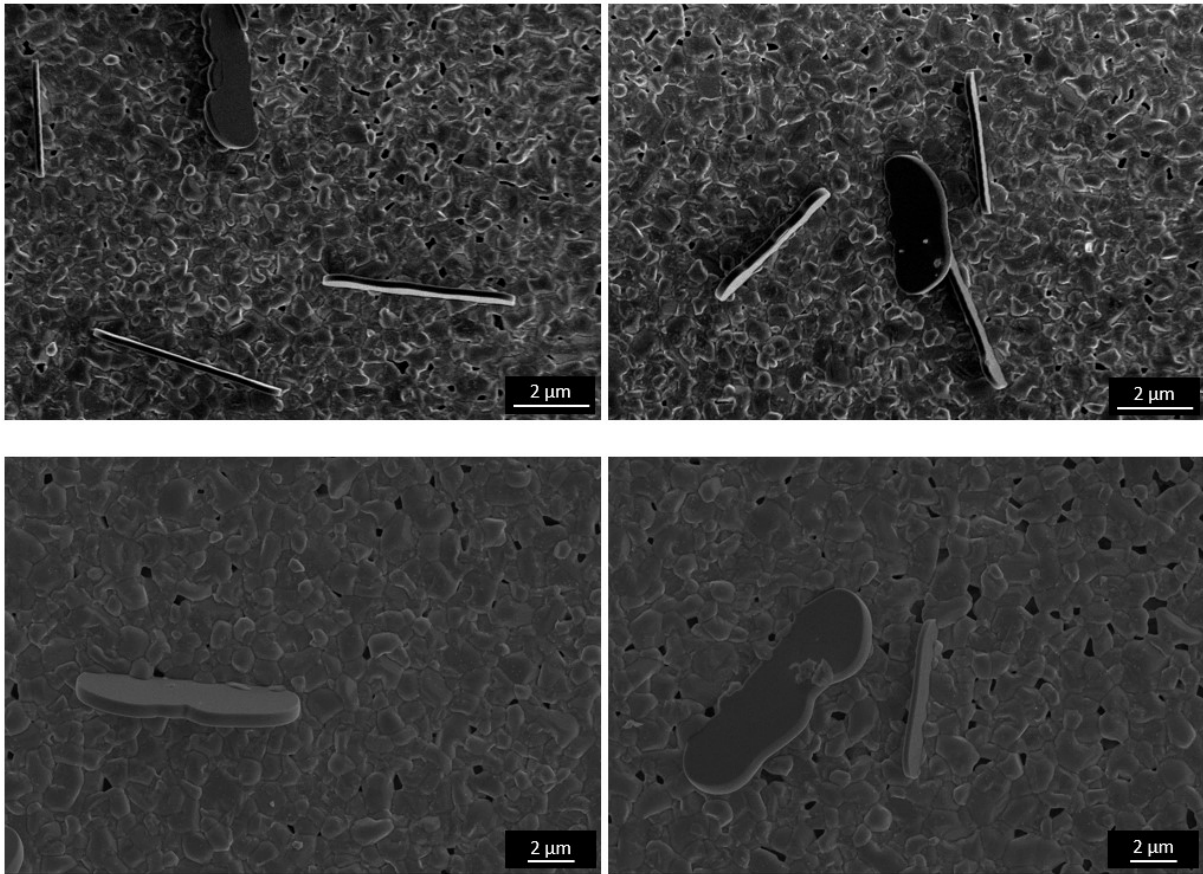
Figure S10: Additional top-view SEM images of SnSe$_2$ secondary phases of same absorber as shown in Figure 7 of the main manuscript. A Hitachi S-4800 electron microscope was used to obtain the images.