Supporting Information for

Synthesis of P-Type PbS Quantum Dot Ink via Inorganic Ligand Exchange in Solution for High-Efficiency and Stable Solar Cells

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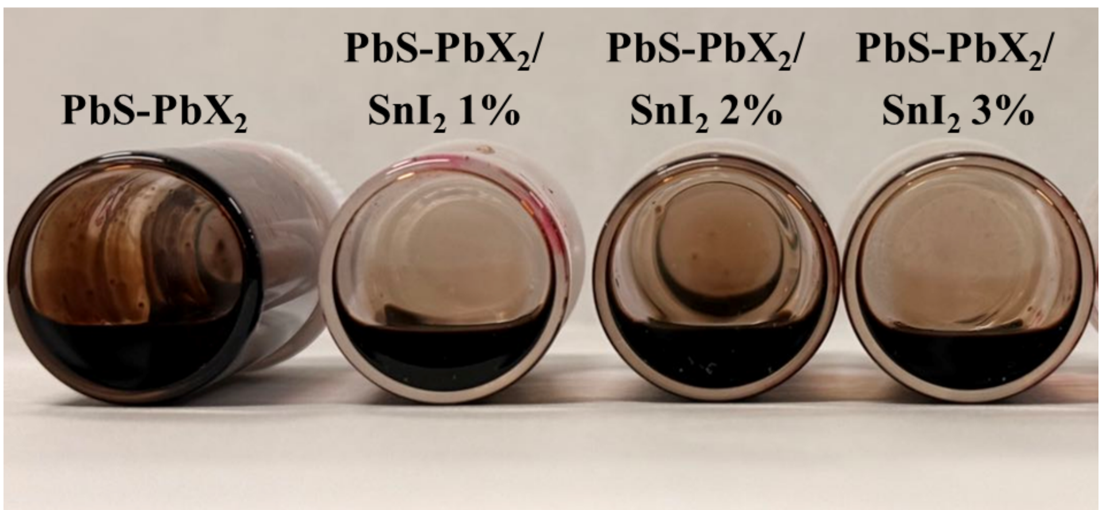

Fig. S1. $PbS-PbX_2$ ink and $PbS-PbX_2/SnI_2$ 1%–3% inks (left to right) were dispersed in mixed-amine

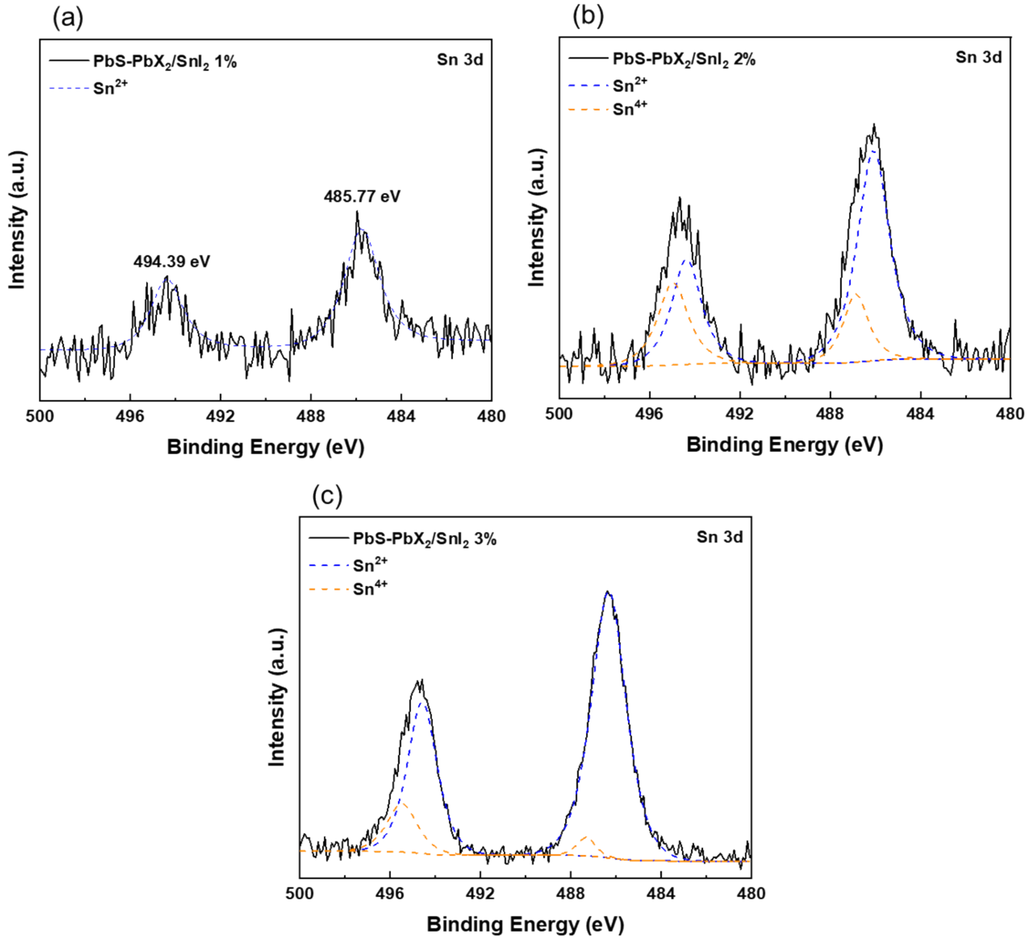

Fig. S2. XPS spectra of Sn 3d region of (a) PbS-PbX_2/SnI_2 1%, (b) PbS-PbX_2/SnI_2 2%, and (c) PbS-PbX_2/SnI_2 3% with two components of Sn^{2+} (blue dash line) and Sn^{4+} (orange dash line)

Table S1. The area ratio of Sn^{2+} and Sn^{4+} components in PbS-PbX_2/SnI_2 samples (mixing SnI_2 1%–3%)

Samples	**Oxidation state**	**Centre (eV)**	**Intensity (eV)**	**Area (cps*eV)**	**Ratio* (%)**
PbS-PbX_2/SnI_2 1%	Sn^{2+}	485.8	159.1	306.6	
		494.4	96.0	169.3	100
PbS-PbX_2/SnI_2 2%	Sn^{2+}	486.1	291.6	525.2	
		494.4	146.3	241.3	55.28
	Sn^{4+}	486.9	94.4	132.6	
		495.3	114.1	195.2	44.72
PbS-PbX_2/SnI_2 3%	Sn^{2+}	486.3	738.7	1451.1	
		494.6	419.9	704.9	75.42
	Sn^{4+}	487.3	52.4	52.9	
		495.5	134.8	229.8	24.58

*The area ratio of Sn^{2+} and Sn^{4+} component of Sn $3d_{3/2}$ peak, denoted as X, was determined using the formula:

$$Ratio\ (\%) = \left(\frac{X}{\mathrm{Sn}^{2+} + \mathrm{Sn}^{4+}}\right)\times 100$$

Where X is the area of Sn^{2+} or Sn^{4+}.

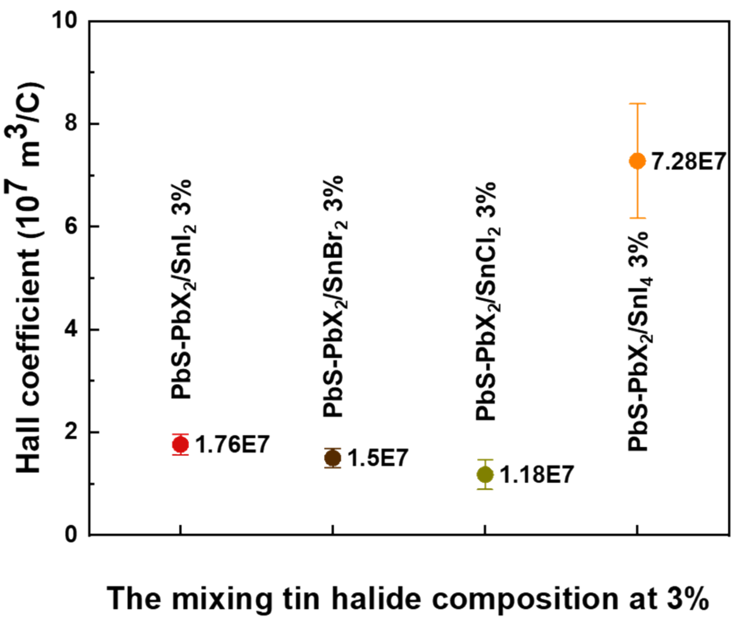

Fig. S3. The hall coefficient of mixing SnX_2 (X = I, Br, Cl) and SnI_4 at 3% (The dots show average values, and the error bars represent the top and lower margins of the 95% confidence interval.)

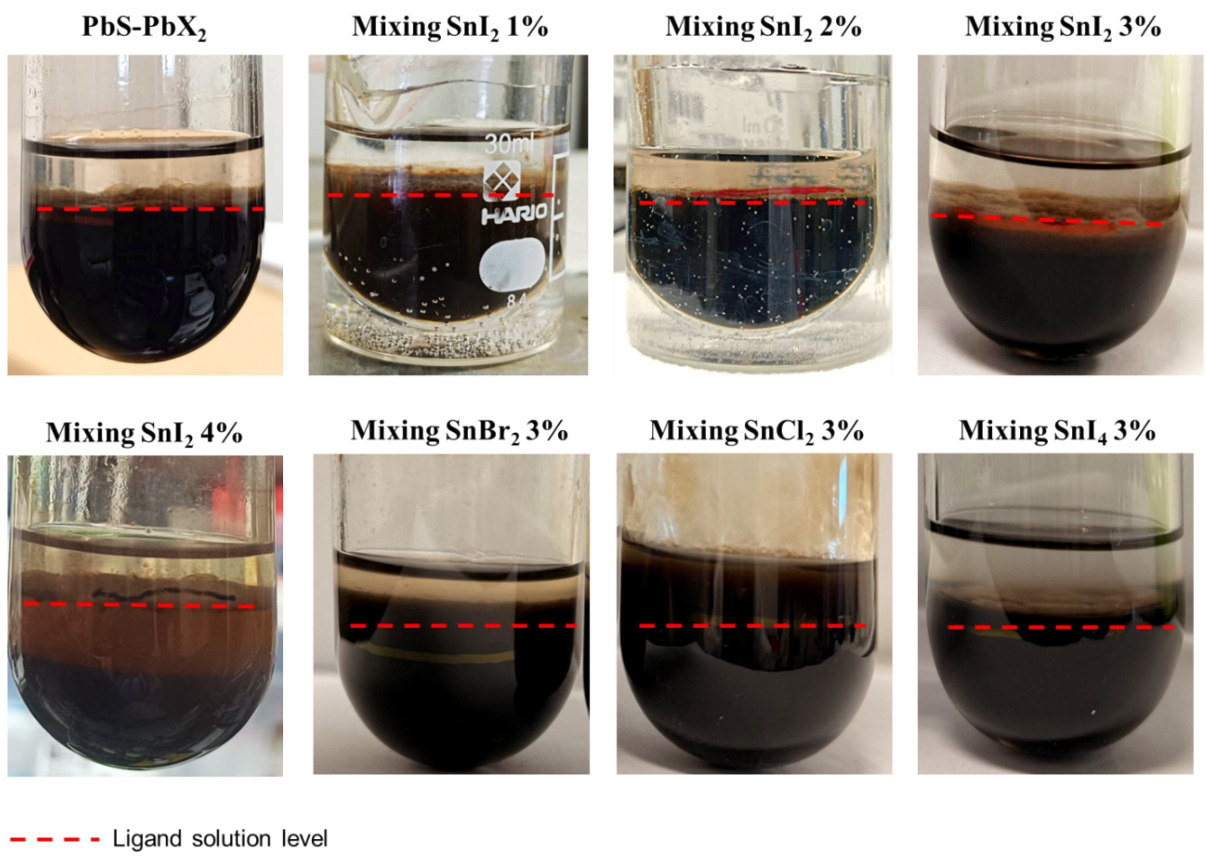

Fig. S4. Photographs of the SPLE technique of PbS CQD in PbX_2, mixing SnI_2 1%–4%, mixing $SnBr_2$ 3%, mixing $SnCl_2$ 3%, and mixing SnI_4 3% ligand solutions

Table S2. The element ratio-to-S of PbS CQD film without and with mixing SnI_2 1%–3%

Samples	Pb/S	Sn/S	I/S	Br/S
PbS-PbX_2	1.963	0	0.686	0.217
PbS-PbX_2/SnI_2 1%	2.062	0.054	0.714	0.233
PbS-PbX_2/SnI_2 2%	2.121	0.156	0.720	0.251
PbS-PbX_2/SnI_2 3%	2.164	0.297	0.763	0.269

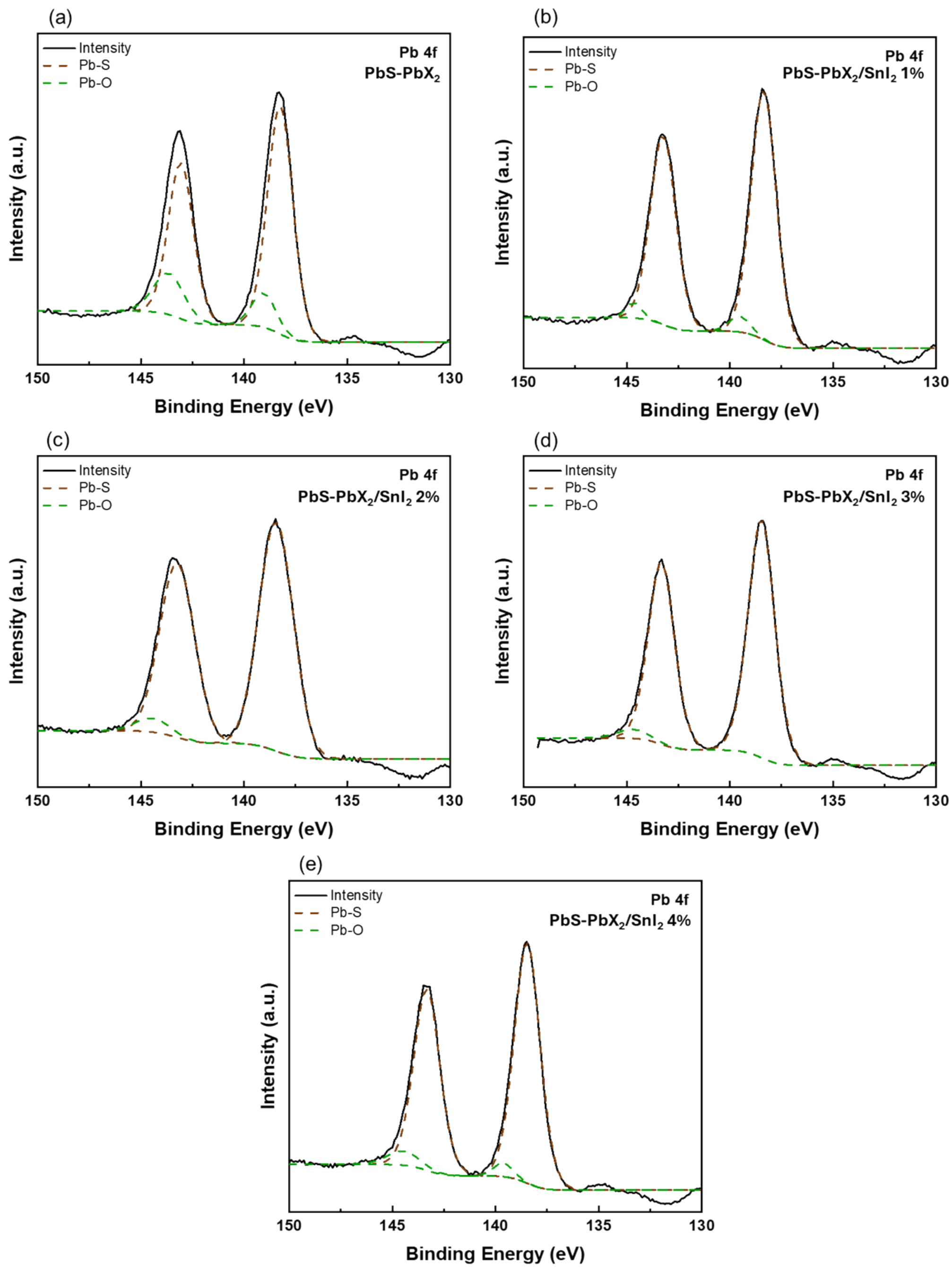

Fig. S5. XPS spectra Pb 4f region of (a) PbS-PbX_2, (b) PbS-PbX_2/SnI_2 1%, (c) PbS-PbX_2/SnI_2 2%, (d) PbS-PbX_2/SnI_2 3%, and (e) PbS-PbX_2/SnI_2 4%

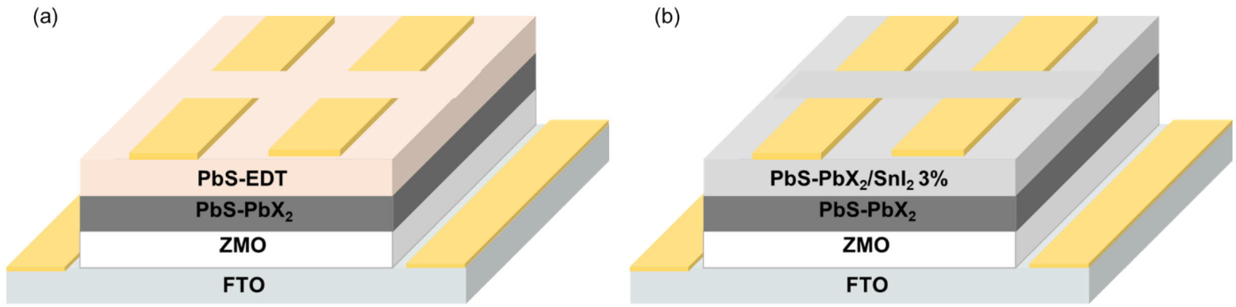

Fig. S6. The schematic structure of the (a) control device (PbS-EDT HTL), (b) target device (p-type PbS ink HTL)

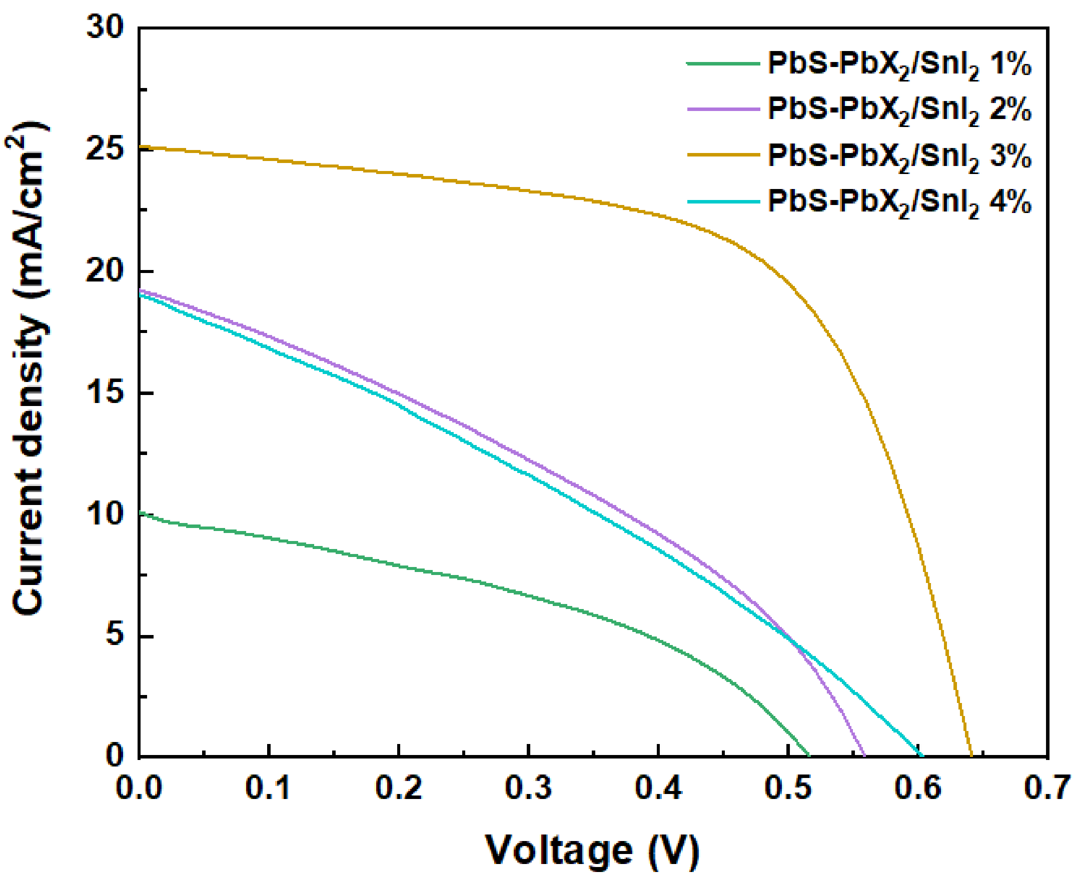

Fig. S7. The comparison J-V characteristics of champion device based on PbS-PbX$_2$/SnI$_2$ (1%–4%) HTLs at the fresh state

Table S3. Statistics for device performance of PbS CQD solar cells and champion device

	Device	J_{sc} **[mA/cm²]**	V_{oc} **[V]**	**FF**	**PCE [%]**
Fresh state	Control	26.22±1.26 (29.44)	0.63±0.01 (0.63)	0.54±0.01 (0.53)	9.31±0.33 (10.54)
	Target	25.39±0.49 (25.15)	0.63±0.01 (0.64)	0.57±0.01 (0.61)	9.60±0.27 (10.37)
1 week storage	Control	26.74±0.55 (29.58)	0.61±0.01 (0.63)	0.57±0.02 (0.52)	9.69±0.14 (10.42)
	Target	26.79±0.60 (28.20)	0.62±0.01 (0.60)	0.57±0.01 (0.60)	9.95±0.13 (10.81)
4 weeks storage	Control	27.28±0.85 (30.18)	0.61±0.01 (0.61)	0.51±0.02 (0.50)	8.93±0.36 (9.83)
	Target	26.91±0.75 (29.57)	0.62±0.01 (0.61)	0.59±0.01 (0.58)	10.33±0.12 (10.93)
6 weeks storage	Control	28.58±0.24 (29.11)	0.61±0.01 (0.61)	0.45±0.03 (0.55)	7.87±0.63 9.78
	Target	26.92±0.66 (28.83)	0.61±0.01 (0.61)	0.54±0.01 (0.58)	8.98±0.35 (10.30)
8 weeks storage	Control	26.69±0.85 (27.60)	0.59±0.01 (0.59)	0.47±0.01 (0.51)	7.37±0.37 (8.24)
	Target	25.73±0.47 (27.70)	0.60±0.01 (0.60)	0.53±0.01 (0.57)	8.12±0.29 (9.38)

* Results of J_{sc}, V_{oc}, FF, and PCE for the champion devices are shown in parentheses. The statistics are based on 8 cells for each condition.