Electronic Supplementary Materials

Title: High open-circuit voltage in lead sulfide quantum dot solar cells *via* solution-phase ligand exchange with low electron affinity cadmium halides

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Experimental section:

Materials: Oleic acid (OA; 90%), lead oxide (PbO; 99%), bis-(trimethylsilyl) sulfide (TMS), 1-octadecene (ODE; 90%), ammonium acetate (99%), lead bromide (PbBr$_2$; 99%), lead iodide PbI$_2$ (99%),Cadmium iodide (CdI$_2$; 99%), Cadmium bromide (CdBr$_2$; 98%), cadmium chloride (CdCl$_2$;99.99%), 1,2-ethanedithiol (EDT; 98%, GC), 3-chloro-1-propanethiol (CPT; 98%), zinc acetate dihydrate, butylamine (99.5%), Oleylamine (70%), tetradecylphosphonic acid (TDPA ; 97%), octane, toluene, acetone, methanol, Isopropanol (IPA), N,N-Dimethylformamide (DMF; 99.8%) and acetonitrile (ACN ; 99.8) were received from Sigma-Aldrich and used as received.

Synthesis of PbS QDs for active layer: PbS QDs with an excitonic peak at 930 nm were synthesized using the described approach.[1] In the typical synthesis procedure, 1.74 g PbO, 5.8 ml ODE, and 11.6 ml OA were placed in a three-necked round-bottomed flask and degassed at 110°C for 12 h under vacuum and constant stirring. The reaction

temperature was set to 100°C, and 18ml of ODE and 400 µl of Oleylamine were added to the reaction mixture. For the injection of the sulphur precursor, the reaction medium was changed from vacuum to argon, and the temperature was raised to 109 °C. Using a syringe, 206 µl of TMS dissolved in 9.6 ml of ODE was rapidly injected into the reaction mixture, and the temperature source was switched off. After allowing the reaction medium to reach 60°C, 1ml of 1mM $PbBr_2$ in Oleylamine was introduced. At 30°C, 10 ml of acetone was injected into the reaction mixture and stirred for another 5 min. The synthesized product was then transferred to several test tubes, and additional acetone was added to precipitate the QDs from the solution. The test tubes were centrifuged at 3000 RPM, and the supernatant was discarded to isolate the QDs. The QDs were re-dispersed using toluene and precipitated again using acetone. The QDs were separated using centrifugation and dried under a vacuum for 5 minutes. Finally, the QDs were dispersed in octane and stored in an Argon glove box for further use.

-$PbBr_2$ precursor preparation: $PbBr_2$ was dissolved in Oleylamine at the concentration of 1mM/ml and kept under vacuum for 1hr at 100°C prior to their use.

Synthesis of PbS QDs for HTL layer: PbS QDs with the excitonic peak at 880 nm were used for the HTL layer formation.[2] In the typical synthesis process, 1.74 g PbO, 5.8 ml ODE, and 11.6 ml OA were taken in a three-necked round-bottomed flask and degassed at a temperature of 110 °C for 12h under vacuum and continuous stirring. The reaction temperature was then set to 100°C, and 15 ml of ODE with 400 µl of Oleylamine was injected. The reaction medium was changed from vacuum to argon, and the temperature was set to 109 °C. At the set temperature, 206 µl of TMS dissolved in 9.6 ml ODE was injected rapidly using a syringe, and immediately the heating source was switched off. At

80°C, 1 ml of $CdCl_2$ precursor solution was injected, and the reaction mixture was allowed to cool down to 30°C. At ambient temperature, 10 ml of acetone was injected into the reaction mixture and stirred for another 5 min. The synthesized product was then transferred to test tubes, and additional acetone was added to precipitate the QDs from the solution. To isolate the QDs, the test tubes were centrifuged at 3000 RPM, and the supernatant was removed. Toluene was used to disperse the QDs once more, and acetone was used to precipitate them. After being separated by centrifugation, the QDs were dried for five minutes in a vacuum. The QDs were then dispersed in octane and kept for future use in an Argon glove box.

-$CdCl_2$ precursor preparation: 600mg (3.28 mM) $CdCl_2$ was dissolved in 10 ml Oleylamine with 66mg of tetradecylphosphonic acid. The solution was kept under vacuum for 16 hrs at 105°c. The product was kept at 80°C under Ar to avoid solidification prior to their use.

Preparation of Cadmium halide ligand solution: 150 mM CdI_2, 75 mM $CdBr_2$, 50 mM ammonium acetate and 70mM CPT were dissolved in 5 mL of DMF to form a clear transparent solution. The ligand solution is denoted as 150mM CdI_2. The molar ratio $CdBr_2$ was maintained to half of CdI_2 while keeping the concentrations for ammonium acetate (50 mM) and CPT (70mM) unchanged for the preparation of 100mM CdI_2, 120mM CdI_2 and 200mM CdI_2 ligand solutions.

Preparation of control-Pb ligand solution: Control lead halide ligand solution was prepared by dissolving 100 mM PbI_2, 25 mM $PbBr_2$, 50 mM ammonium acetate and 50mM CPT in 5 mL of DMF to form a clear yellow solution.

Solution phase ligand exchange: Both Cd-halide and control-Pb ligand exchanges were performed using the same protocol. A 5 ml of PbS QDs (15 mg/ ml) dispersed in octane was added to a 5ml ligand solution in DMF. The reaction vial was vortexed for two minutes before being left alone for a short while. The QDs were completely transferred from the non-polar octane phase to the polar DMF phase, indicating successful ligand exchange of aliphatic OA molecules by ionic metal halide ligands. The clear octane solution was then discarded from the top with the help of a pipette, and the QD solution was washed two more times using fresh octane to remove any residual oleic acid ligands. The QDs were precipitated with the addition of 13 ml of toluene and centrifuged at 3000 rpm for 5 minutes. The supernatant was then discarded, and the QDs were dried under a vacuum for 15 minutes. The QDs were finally dispersed in butylamine at a concentration of 300–350 mg/ml for spin coating.

Device Fabrication: The ITO substrates were cleaned sequentially by sonicating with soap water, deionized water, acetone, and boiling IPA. ITO substrates were further cleaned by UV-Ozone treatment for 20 minutes before film deposition. For the ETL layer deposition, ZnO nanocrystals dispersed in chloroform at a concentration of 65 mg/mL were spin-coated on ITO substrates for 30 seconds at 3000 RPM. The ZnO-coated substrates were then annealed at 250°C for 1 hour in ambient conditions. To deposit the active QD layer, the following steps were followed sequentially: the ZnO substrates were preheated at 60 °C, quickly transferred to the spin coater, the rotation speed was set, and a drop of QD solution was added during the rotating condition. The rotation speed and concentration of the QD solution were adjusted to vary the thickness of the active QD layer. The spin-coated films were then transferred to an argon glove box and annealed at

70 °C for 10 minutes inside the glove box. EDT solution (0.02%) in acetonitrile was used as a ligand to deposit two layers of PbS QD (excitonic peak at 880 nm) film using solid-state layer-by layer ligand-exchange to grow 50nm thick HTL layer. The top electrode was formed by depositing 100 nm of Au using a thermal evaporator (HHV BC-300) at a base pressure of 1×10^{-6} Torr. The active device area, defined by the top electrode, is 9mm^2.

J-V Characterization: A Keithley 2634B source meter and a solar simulator (Peccell, PEC-L01) were used to record the current-voltage data. Using a Thorlabs thermocouple detector (S302C), the solar intensity was adjusted to 100 mW/cm^2 (AM 1.5 G). Different neutral density filters were applied for the light intensity-dependent J-V measurements. Temperature-dependent J-V measurements were carried out using liquid nitrogen-cooled cryostat equipment (Janis, Model no.VPF-100) controlled by a Lakeshore temperature controller 325 module.

 EQE Measurement: The monochromatic illuminations were produced with the help of a monochromator (SLS-M266) coupled with a 100W Quartz halogen light source. The response of the solar cells was recorded by a Keithley 2634B source meter. Thorlabs detectors S120VC (for the wavelength range of 300 -1100 nm) and S122C (700- 1800 nm) were used for optical power measurements.

Carrier lifetime from transient photovoltage (TPV) decay: - A diode laser of 658 nm (Newport LQA658- 30C) modulated through a function generator (Tektronics, AFG 3021C) was used to generate short light pulses. A solar simulator (Peccell, PEC-L01) was used to provide light bias to the solar cells. Different V_{oc} values were attained by varying the intensity of the light bias. For TPV measurement, the device was connected

to the oscilloscope (Tektronics, MDO 3104) through 1 MΩ resistance. Laser pulse intensities were modulated to keep the perturbation voltage below 10 % of V_{oc}.

Carrier mobility from transient photocurrent (TPC) measurement: We employed bias-dependent transient photocurrent measurement to assess the photogenerated carriers' mobility under solar illumination. The device under test was continuously illuminated at 1.5 AM (using the solar simulator PEC-L01). At the same time, it was excited by a brief light pulse of 2μs (wavelength 658 nm) using the Newport LQA658- 30C diode laser. Varied DC biases across the solar cells were applied using the oscilloscope's (Tektronics, MDO 3104) built-in function generator. The transient signal from the device was monitored across a 50Ω resistance using the oscilloscope.

Material Characterisation:

Absorbance measurements were conducted using an integrating sphere (ISR-603) and a Shimadzu UV-VIS-IR (UV-3600 Plus) spectrometer. Using a spectrofluorometer, emission spectra were captured (FS5, Edinburgh Instrument). The SEM images were taken with a field emission scanning electron microscope (FESEM NNS 450). With a Thermo Scientific K-Alpha spectrometer, XPS spectra were recorded at ultrahigh vacuum (109 mbar). The XPS spectra were obtained using a monochromatic Al Kα X-ray source (1486.6 eV) with a 50 eV pass energy. Peak fitting was carried out using Casa-XPS software after the XPS spectra were calibrated to the C_{1s} peak (284.8 eV). The UPS tests, which employed a He-Iα light source with an energy of 21.22 eV, were conducted using the same apparatus. An X'Pert Pro model PANalytical diffractometer (Philips PANalytical) was used to record XRD profiles while being operated at a voltage of 40 kV and a current

of 30 mA with Cu K (1.5418 Å) radiation. The QDs samples were scanned at a rate of 1° per minute for the 2θ range of 10°–60°.

Additional discussion:

1. **Determination of QD diameter from excitonic peak energy.**

   The empirical equation that correlates excitonic peak energy with QD diameter is

   $$E_{ex} = 0.41 + \frac{1}{0.0392d^2 + 0.114d}$$ ---S1

Where E_{ex} is the excitonic peak energy in eV, and d is the QD diameter in nm.

2. **Determination Size distribution of QDs**

   The size dispersity of the QDs form their excitonic peak is determined by the model developed by Weidman et al.

   $$HWHM\ (d,\sigma) = \frac{\sigma(a\gamma^2 d\sigma + 2a\gamma d + b\gamma)}{(\gamma\sigma + 1)(ad + b)(a\gamma d\sigma + ad + b)d}$$ ----------S2

a=0.0398, b =0.114, d – is diameter in nm, γ=0.118, $HWHM$ – in meV and σ is the size dispersion in percent normalized with respect to diameter.

3. **Determination the number of Pb atoms per QD and ligand mediated change of Pb atoms per QD.**

The volume of each QD is $V_{QD} = \frac{4}{3}\pi\left(\frac{d}{2}\right)^3$ nm³

Volume of one unit cell of PbS= (0.594 × 0.594 × 0.594) nm³

Numbers of Pb atoms per QD = $\dfrac{V_{QD}}{(0.594 \times 0.594 \times 0.594)} \times 4$

4 is the number of Pb atoms per unit cell in PbS crystal.

To determine the change of Pb atoms per QD; total number of Pb atoms per QD for a certain ligand is subtracted by the total number of Pb atoms per QD for OA ligand.

4. Urbach energy determination from absorbance

The Urbach energy E_u can be described as

$$\alpha = \alpha_0\, exp\left(\frac{E - E_0}{E_u}\right)$$ ---

S4

Where α is absorption coefficient.

According to Beer-Lambert law

$$\alpha = \frac{2.303 \times A}{t}$$ --

S5

where A is absorbance, t-thickness.

Substituting value of α from the equation S5, equation S4 can be written as

$$A = \frac{\alpha_0\, t}{2.303}\, exp\left(\frac{E - E_0}{E_u}\right)$$

and,

$$\ln A = lnA_0 + \frac{E - E_0}{E_u} \; ;$$

where $A_0 = \dfrac{\alpha_0 \, t}{2.303}$

Fig. S1. Image of ligand solution and ligand exchanged QD ink in DMF

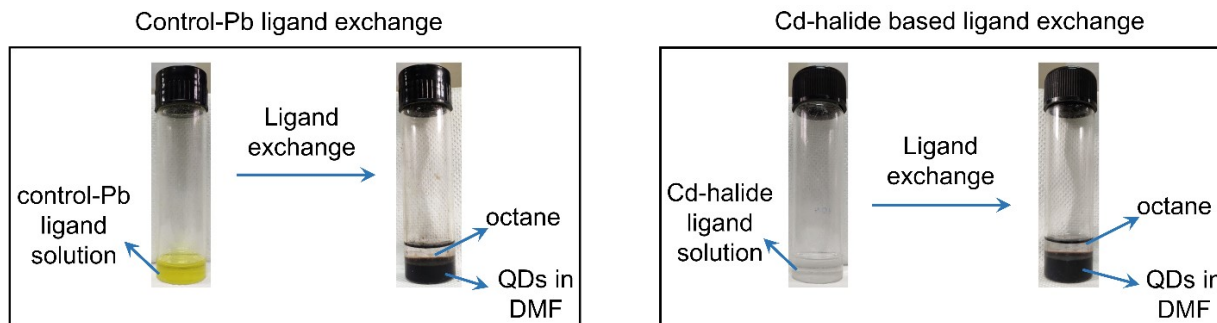Control-Pb ligand exchange

Cd-halide based ligand exchange

Fig. S1 Pictorial depiction of ligand treatment process. Images of ligand solution and ligand exchanged QDs for (a) control-Pb and (b) Cd-halide ligand exchange.
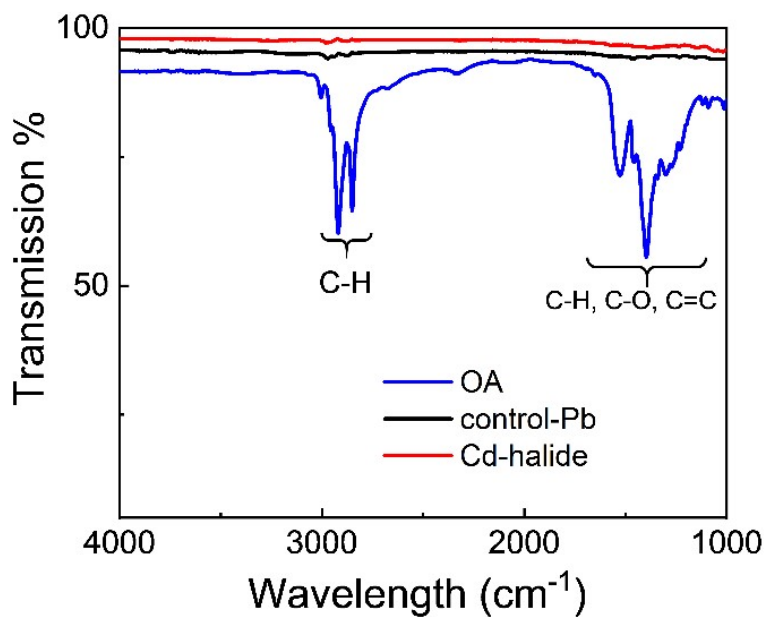
Fig. S2. FTIR characterization

Fig. S2 ATR-FTIR spectra of as synthesized OA capped QD film and ligand exchanged QD films treated with control-Pb and Cd-halide ligands. The characteristics peaks of OA: C−H stretching modes (2800-3000 cm^{-1}), and C−H bending vibrations, C-O (carboxylic) and vinyl C=C stretching modes (1000-1500 cm^{-1}) are absent in control-Pb and Cd-halide treated samples. This absence of OA stretching modes confirms the successful ligand exchange of

PbS QDs.

Fig. S3. Elemental data from EDX

a) control-Pb

Element	Wt%	At%
CK	20.59	59.45
NK	03.26	08.08
OK	03.92	08.50
BrL	03.35	01.45
SK	10.03	10.85
PbM	44.19	07.40
ClK	00.39	00.38
IL	14.27	03.90
Matrix	Correction	ZAF

b) Cd-halide passivated

Element	Wt%	At%
CK	17.41	52.49
NK	03.48	09.00
OK	04.58	10.36
BrL	08.67	03.93
SK	09.37	10.58
PbM	39.13	06.84
ClK	02.31	02.36
CdL	03.92	01.26
IL	11.13	03.18
Matrix	Correction	ZAF
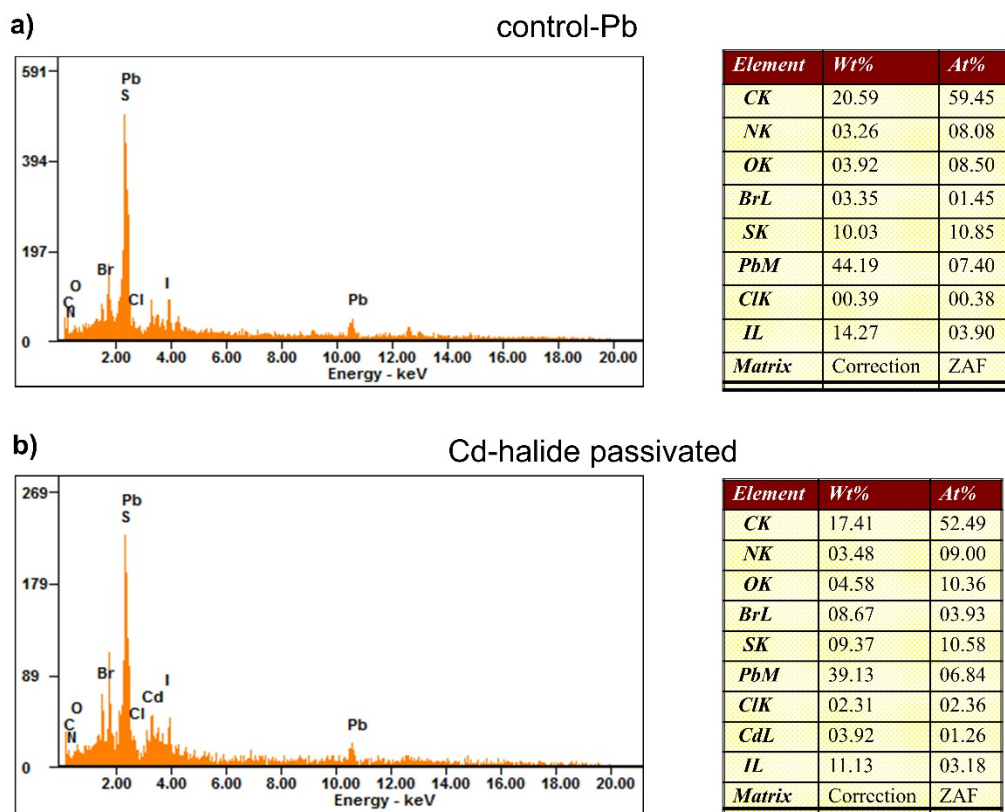
Fig. S3 EDX data for (a) control-Pb treated QD film and (b) Cd-halide passivated QD film.
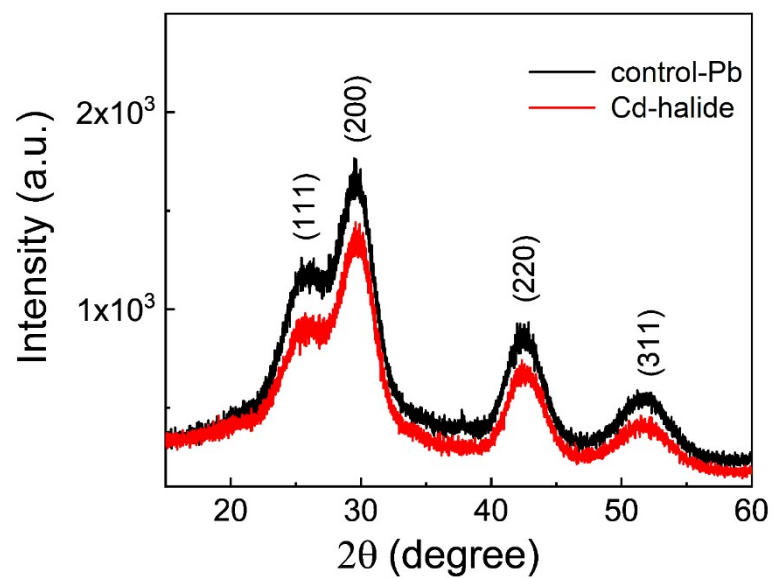
Fig. S4 XRD spectrum of control-Pb and Cd-halide ligand passivated PbS QDs.

Fig. S4. XRD pattern of ligand exchanged QDs

Fig. S5. Atomic ratio from XPS analysis.
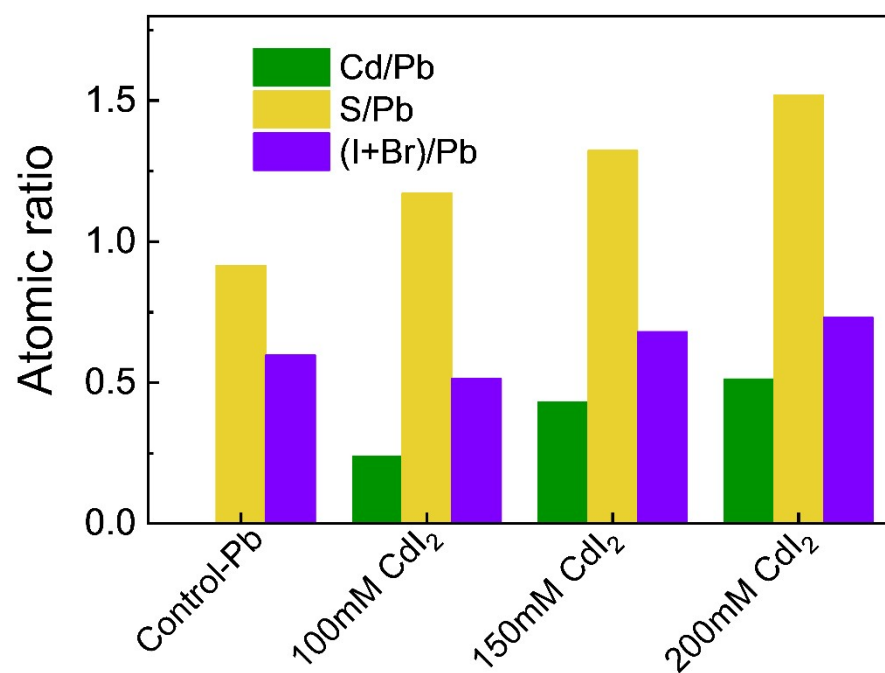
Fig. S5 Atomic ratio of Cd, S and halides (I+Br) with respect to Pb for different ligand conditions, determined by XPS analysis.

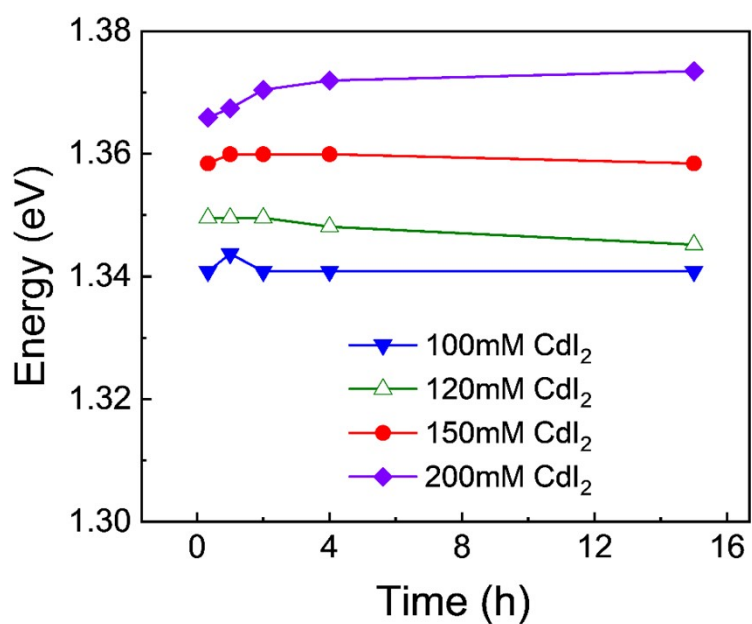**Fig. S6. Evolution of the excitonic peak with reaction time in ligand solution**

Fig. S6 Evolution of excitonic peak energy with time for PbS QD in different concentrations of Cd-halide ligand solutions.

**Fig. S7. Photovoltaic parameters for ten batches of solar cells**
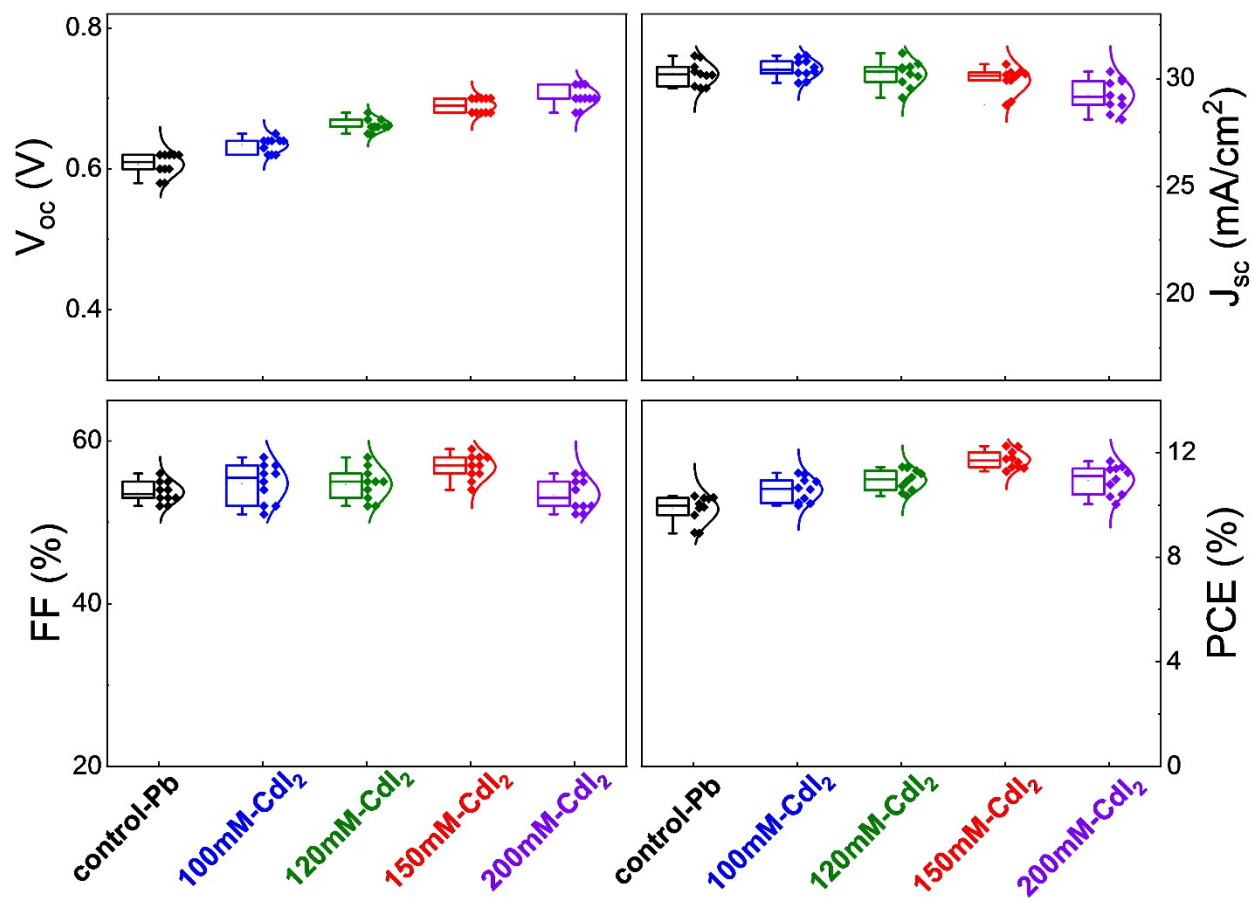
Fig. S7 Batch-to-batch variation in photovoltaic parameters (V_{oc}, J_{sc}, FF and PCE) for 10 batches of devices. V_{oc} increases steadily with increase in Cd-halide ligand concentration. The

peak PCE is obtained for 150mM-CdI$_2$ concentration due to optimum J$_{sc}$ and FF.

Fig. S8. Scan direction dependent hysteresis effect in J-V characteristics
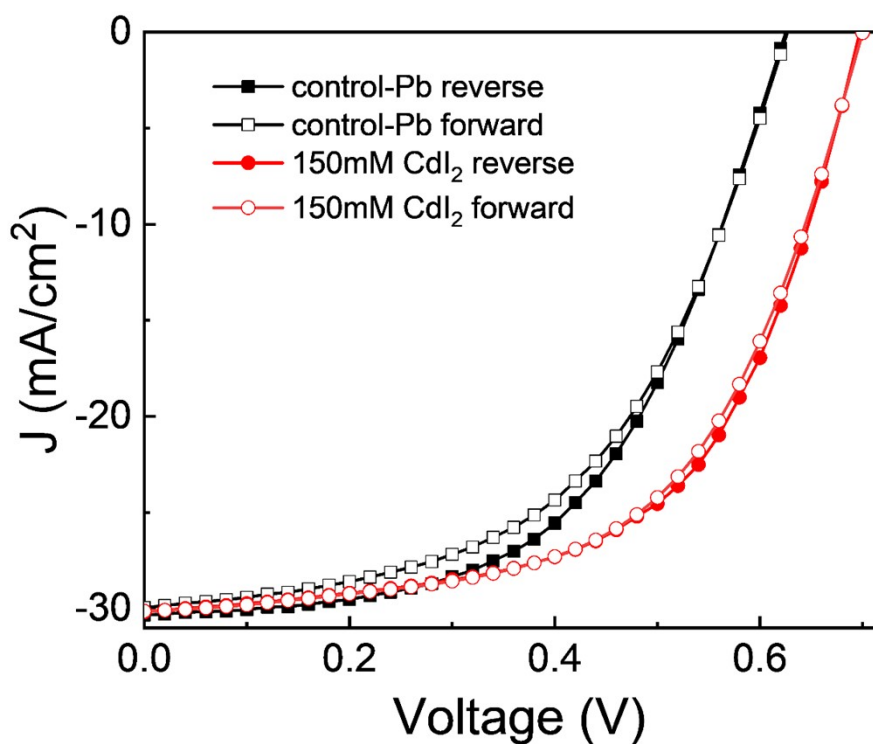
Ligand type	Scan direction	V$_{oc}$ (V)	J$_{sc}$ (mA/cm^2)	FF (%)	PCE (%)
control-Pb	reverse	0.62	30.33	55	10.4
	forward	0.62	29.94	53	9.9
150mM CdI$_2$	reverse	0.7	30.18	58	12.3

	forward	0.7	30.13	57	12.1

Fig. S8 Scan direction dependent photovoltaic parameters for control-Pb and 150mM CdI$_2$ treated QD solar cells. Table shows the photovoltaic parameters for opposite scan directions for control-Pb and 150mM CdI$_2$ solar cells.

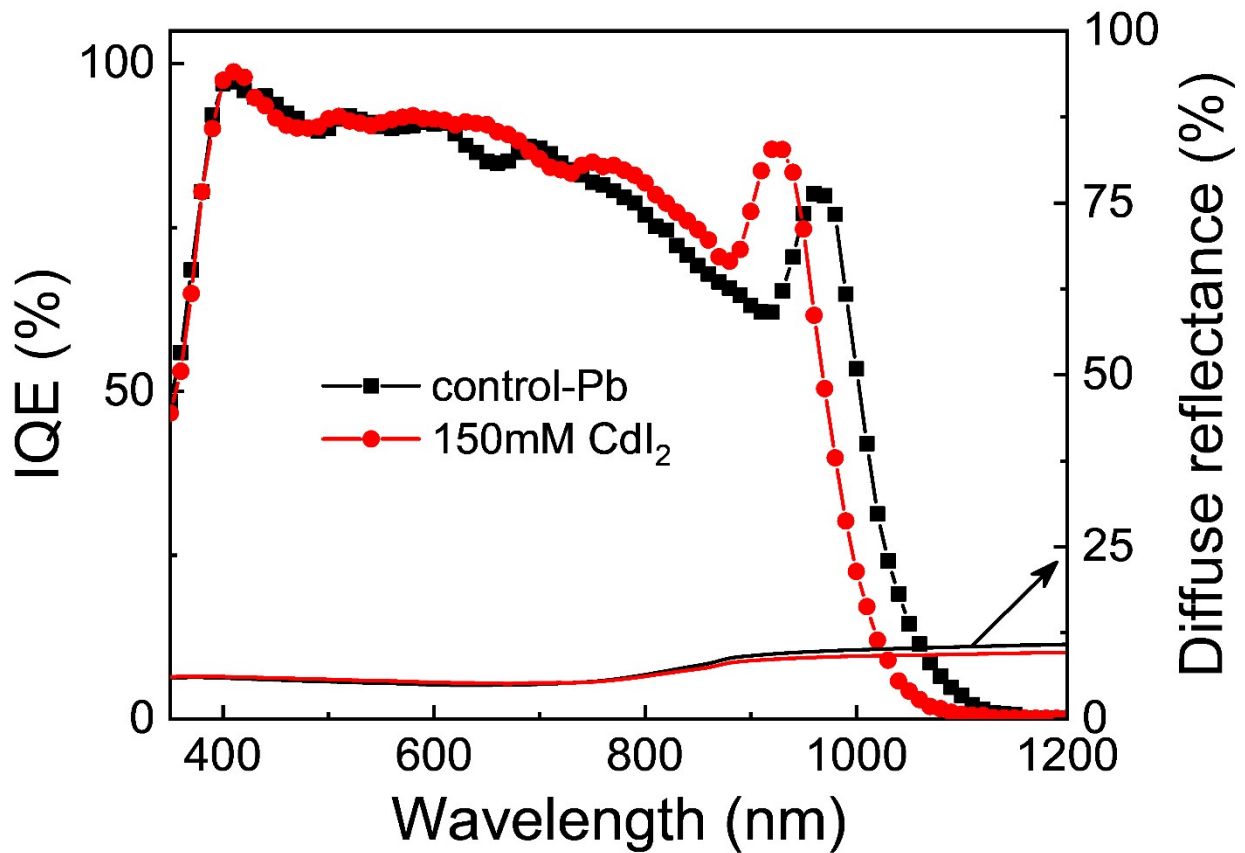**Fig. S9. Internal quantum efficiency and diffuse reflectance**

Fig. S9 Internal quantum efficiency (IQE) (left axis) and diffuse reflectance (R$_{diffuse}$) of solar cell devices. IQE is determined using the formula IQE=EQE/(1-R$_{diffuse}$).

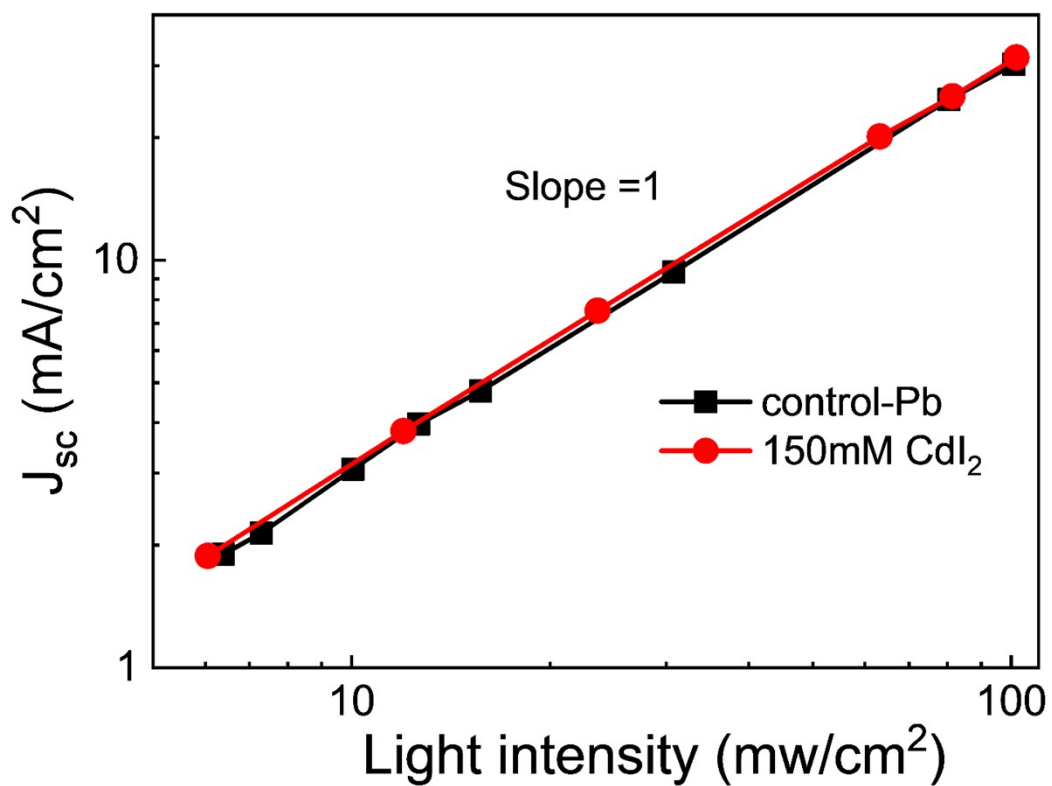**Fig. S10. Evolution of J_{sc} with light intensity in solar cells**

Fig. S10 Logarithmic plot of J_{sc} vs light intensity (I) of solar cells. Unit power dependence (slope= 1) is observed for both control-Pb and 150mM CdI_2 solar cells.

Fig. S11. Determination of carrier mobility determination from bias dependent transient photocurrent measurement.
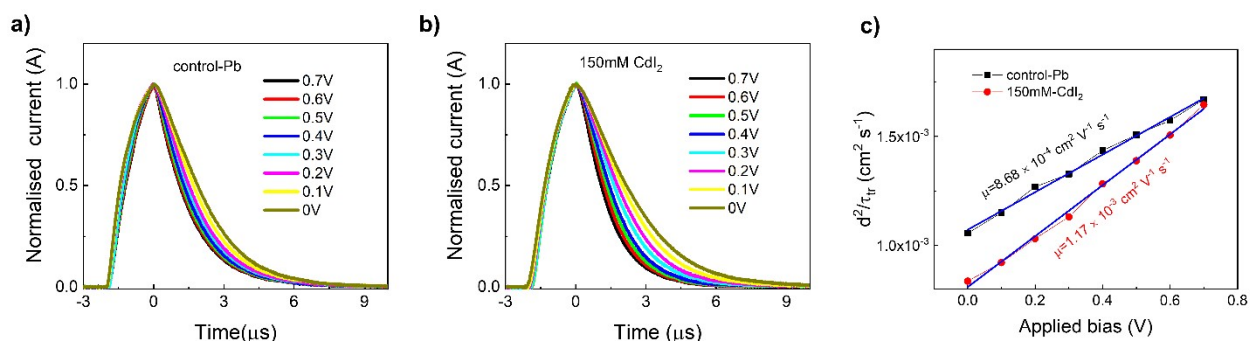

Fig. S11 Mobility determination using transient photocurrent measurement. (a) and (b) shows normalized decay of photocurrent at different applied biases. (c) shows carrier mobility for control-Pb and 150mM CdI$_2$ solar cells.

Laser pulse (655nm) of 2µs width is used to induce photocurrent pulse in the solar cells. The carrier transient time (τ_{tr}) is defined as the time taken to decay 1/e times of the peak current value. Carrier mobility (µ) is determined using the equation $\mu = \dfrac{d^2}{\tau_{tr} \times V}$; where d is film thickness and V is applied bias. The slope of $\dfrac{d^2}{\tau_{tr}}$ vs. applied bias is used to determine mobility.

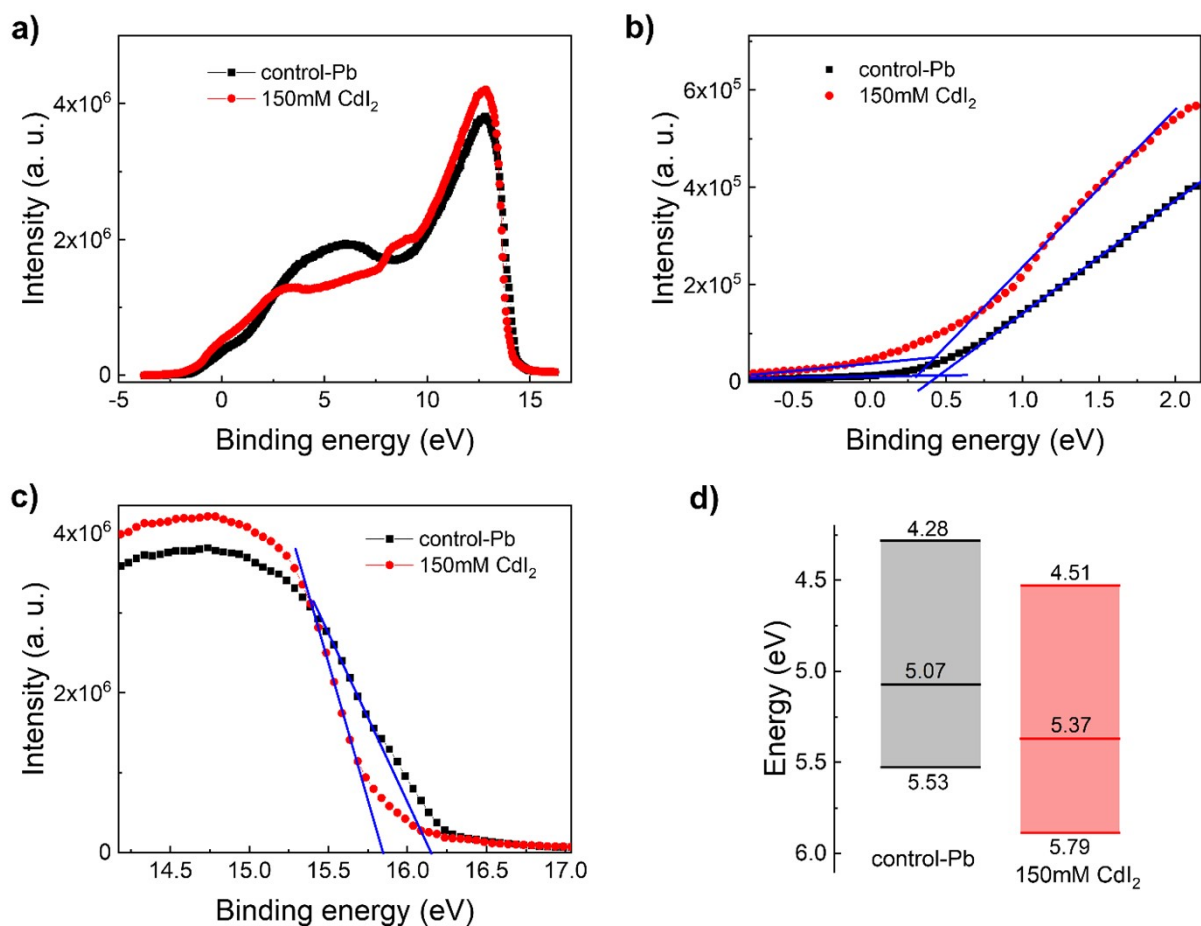**Fig. S12. Determination of energy band positions from UPS data**

Fig. S12 Energy levels determination from UPS. QD films deposited on gold-coated Si

substrates for UPS measurement. (a) Full range UPS spectra, (b) magnified view of the onset region, and (c) shows the zoomed view of the high binding energy cut-off region of the UPS spectrum. He-Iα radiation of 21.22 eV is used for UPS measurement. (d) band energy diagram for control-Pb and 150mM CdI_2 QDs.

Table S1. Photovoltaic parameters of best performing solar cells for varied ligand conditions.

Ligand name	V_{oc} (V)	J_{sc} (mA/cm^2)	FF (%)	PCE (%)
control-Pb	0.62	30.33	55	10.4
100mM CdI_2	0.64	30.76	57	11.2
120mM CdI_2	0.67	30.51	56	11.5
150mM CdI_2	0.70	30.18	58	12.3
200mM CdI_2	0.70	29.78	56	11.7

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2.   O. Voznyy, L. Levina, J. Z. Fan, M. Askerka, A. Jain, M. J. Choi, O. Ouellette, P. Todorovic, L. K. Sagar and E. H. Sargent, *Acs Nano*, 2019, **13**, 11122-11128.