## **Supporting Information**

## Lead Selenide Colloidal Quantum Dot Solar Cells Achieving High Open-Circuit Voltage with One-Step Deposition Strategy

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## EXPERIMENTAL

**Materials**. Oleic acid (OA, 90%), 1-octadecene (ODE, 90%), tetradecylphosphonic acid (TDPA, 97%), oleylamine (OLA, 70%), 3-mercaptopropionic acid (MPA, 99%) were purchased from Sigma-Aldrich. Bis(trimethylsilyl) selenide ((TMS)<sub>2</sub>Se) was purchased from Gelest. Lead iodide (PbI<sub>2</sub>, 99%) was purchased from Kanto Chemical. Lead(II) oxide (PbO, 99.5%), cadmium chloride (CdCl<sub>2</sub>, 95%), ammonium acetate (NH<sub>4</sub>Ac, 95%), tetrabutylammonium iodide (TBAI, 98%), *N*,*N*-dimethylformamide (DMF, 99.7%), octane (99%), butylamine (99%), 1-butanol (99.7%), methanol (99.7%), ethanol (99.7%), acetone (99.7%), hexane (96%), and toluene (99%) were purchased from Wako. All chemicals were used without any purification.

**Synthesis of PbSe-OA CQDs**. PbSe CQDs were synthesized following a modified our previous method.<sup>1</sup> Briefly, 6 mmol PbO and 15 mmol OA were mixed with 50 mL ODE in a 100 mL three-neck flask. The mixture was stirred and degassed at room temperature for 0.5 h and then at 100 °C for 2 h. The solution was then heated to 135 °C under nitrogen for another 0.5 h, followed by the injection of (TMS)<sub>2</sub>Se solution (2 mmol (TMS)<sub>2</sub>Se mixed with 5 mL pre-degassed ODE) at 125 °C. After injection, the heater was removed while stirring of the solution was maintained. When the solution was cooled to 75 °C, a CdCl<sub>2</sub>/TDPA/OLA solution was added into the colloidal PbSe solution. The PbSe CQDs were isolated from the reaction solution by using acetone/1-butanol/methanol/hexane solvent system in air, and this purification process was repeated for three times. After purification, the obtained PbSe-OA CQDs

precipitate was then dried by an  $N_2$  flow and dispersed in octane at a concentration of 50 mg/mL.

**Preparation of PbSe-PbI<sub>2</sub> CQD inks**. The PbSe-PbI<sub>2</sub> CQD inks were prepared by a solution-phase ligand-exchange process. Briefly, 0.08 M PbI<sub>2</sub> and 0.03 M NH<sub>4</sub>Ac were pre-dissolved in DMF. 5 mL PbSe-OA CQDs octane solution (10 mg/mL) was dropwise added to 5 mL DMF precursor solution with vigorous stirring. This mixture was continued to stir for 5 minutes after PbSe-OA CQDs octane solution dropping out. The upper octane phase was removed and the DMF phase was washed for three times with 5 mL octane. Then PbSe-PbI<sub>2</sub> CQDs were precipitated by adding 2.5 mL of toluene and were collected by centrifugation. The obtained PbSe-PbI<sub>2</sub> CQDs precipitate was then dried in a vacuum oven at room temperature for 20 min and dispersed in butylamine at a concentration of 160 mg/mL.

**Photovoltaic Device Fabrication**. The FTO/TiO<sub>2</sub> substrate was prepared following a published method.<sup>1</sup> The substrate was annealed again and further treated with oxygen plasma for 5 min before use. For PbSe-PbI<sub>2</sub> architecture device, the PbSe-PbI<sub>2</sub> CQDs layer was deposited onto FTO/TiO<sub>2</sub> substrate by one step spinning 120  $\mu$ L PbSe-PbI<sub>2</sub> CQD inks at 3000 r.p.m. for 30 s to achieve 200 nm thickness film. For PbSe-TBAI architecture device, PbSe-TBAI CQDs layer was deposited by a typical LBL spin-coating method using a fully automatic spincoater. Each cycle was consisted of three steps. Generally, 120  $\mu$ L PbSe-OA octane solution was dropped onto FTO/TiO<sub>2</sub> substrate and spun-cast at 2500 rpm for 15 s. Then, 400  $\mu$ L TBAI ligand solution (30 mM TBAI in ethanol) was dropped onto the substrate and spun dry after a 60s wait.

The substrate was then rinsed three times with ethanol. The absorption spectra of PbSe-TBAI CQDs layer was measured after each deposition cycle finish, in order to obtain similar thickness with PbSe-PbI<sub>2</sub> samples. Then two PbSe-MPA layers (about 30 nm) were deposited onto PbSe-PbI<sub>2</sub> and PbSe-TBAI layers by a similar LBL method with PbSe-TBAI. In this step, a 10 vol% MPA ethanol solution was used as MPA ligands source. Finally, Au top electrode was deposited onto the CQDs layer by thermal evaporation through a shadow mask to create four identical cells on each substrate, each solar cell with an active area of  $0.35 \text{ cm}^2$ .

**Characterization**. The UV-vis-NIR absorption spectra of PbSe CQDs solution and the ligands treated PbSe CQD films were recorded using a spectrophotometer (JASCO, V-670). The fourier transform infrared absorption (FT-IR) spectra (Thermo Scientific, Nicolet 6700) of the PbSe CQD films were measured to verify that the as-synthesized ligand (OA) on PbSe CQDs were successfully exchanged. *X*-ray photoelectron spectroscopy (XPS) measurement was conducted to identify the presence of I within the samples. The measurement was carried on JEOL JPS-9200. The phase identification of sample was carried out using a powder X-ray diffraction (XRD, TTR-III, Rigaku Corp., Japan). Ultra-fast transient absorption (TA) spectra were examined by using a fs-TA system. The laser source was a Ti/sapphire laser (CPA-2010, Clark-MXR Inc.) with a wavelength of 775 nm, a pulse width of 150 fs, and a repetition rate of 1 kHz, all samples are pumped by 470 nm. The morphology of solar cell was examined using a scanning electron microscope (SEM, JEOL, JSM-6340). The sizes and distance between ligand treated PbSe CQDs was determined by transmission electron microscope (TEM, JEOL, JEM-2100F). The current density–voltage (J–V) measurements were performed using a Keithley 2400 source meter under AM 1.5 G irradiation (100 mW cm<sup>-2</sup>), with a Peccell solar simulator PEC-L10. The incident photon to current conversion efficiency (IPCE) spectra were recorded under illumination using a Nikon G250 monochromator equipped with a 300 W Xe arc lamp. The impedance spectroscopy measurements were obtained by applying a bias from 0 to 0.6 V (amplitude 0.01V) with a frequency ranging from 1 MHz to 1 Hz on a SP-300 (BioLogic) impedance analyzer under dark.



Figure S1. XRD patterns of PbSe-OA, PbSe-TBAI and PbSe-PbI<sub>2</sub> films.



**Figure S2**. Power dependent TA decay spectra of the PbSe-PbI<sub>2</sub> CQD solid films. The sample is pumped by 470 nm (2.64 eV) and probed at 940 nm (1.32 eV). When the pump fluence reduced to 6  $\mu$ J/cm<sup>2</sup>, the signal of Auger recombination disappeared and the TA spectra can be well fitted by single exponential decay.

**Table S1.** Fitted proportionality constants and time constants obtained from the TAdecay curves of PbSe-TBAI and PbSe-PbI2 CQD solid films as shown in Figure 2a.

COD Films	$A_1$	<b>7</b> ( <b>2</b> 5)	<i>y</i> 0	
CQDTIIIIs	$(A_1/(y_0+A_1))$	$\iota_{\rm ct}$ (ps)	$(y_0/(y_0+A_1))$	
	$-0.849 \pm 0.005$	1027.24	-0.144±0.004	
PbSe-TBAI	(85.5%)	183.7±3.4	(14.5%)	
PbSe-PbI <sub>2</sub>	-0.782±0.006	161 2 4 4	-0.133±0.005	
	(85.4%)	101.3±4.4	(14.6%)	

The TA decay curves of both PbSe-TBAI and PbSe-PbI<sub>2</sub> CQD solid films can be well fitted by using single exponential decay according to the following equation:

$$y = y_0 + A_1 * \exp(-x/\tau_1)$$

where  $y_0$  is constant (weight of charge carriers which lifetime are more longer than 1 ns),  $A_1$  is proportionality constant and  $\tau_1$  is time constant. The fast decay process ( $\tau_1$ ) reflects the charge transfer behavior ( $\tau_{ct}$ ) between CQDs-CQDs, and the  $y_0$ corresponds to the weight of charge recombination process (time more longer than 1 ns) in the solid film. According to the fitting data, the values of  $\tau_{ct}$  in PbSe-TBAI and PbSe-PbI<sub>2</sub> CQD solid films are about 183.7 ps and 161.3 ps, respectively. It means that charge transfer of PbSe-PbI<sub>2</sub> CQD solid film is slightly faster than that of PbSe-TBAI CQD solid film. The weights of charge transfer process ( $A_1$ ) in both PbSe-TBAI and PbSe-PbI<sub>2</sub> CQD solid films are about 85.5%, respectively. It means that charge transfer efficiency for two type films are similar, and about 85.5% photoexcited charges are transferred out from CQD before recombination.



Figure S3. Cross-section SEM images of FTO/TiO<sub>2</sub>/PbSe-TBAI/PbSe-MPA/Au

device (a), FTO/TiO<sub>2</sub>/PbSe-PbI<sub>2</sub>/PbSe-MPA/Au device (b) and photograph of device (c).



Figure S4. J-V curves of a FTO/TiO<sub>2</sub>/PbSe-PbI<sub>2</sub>/PbSe-MPA/Au device measured by forward (short circuit  $\rightarrow$  open circuit) and reverse (open circuit  $\rightarrow$  short circuit) scans with 0.01 V voltage steps and 200 ms delay times under AM 1.5G illumination.

**Table S2**. Performance details of a FTO/TiO<sub>2</sub>/PbSe-PbI<sub>2</sub>/PbSe-MPA/Au device as shown in Figure S4.

	$J_{\rm sc}$ (mA/cm <sup>2</sup> )	$V_{ m oc}$ (V)	FF (%)	PCE (%)
Forward Scan	21.17	0.610	0.434	5.60
Reverse Scan	21.43	0.610	0.428	5.59

Average	21.30	0.610	0.431	5.60
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Figure S5.  $V_{oc}$  plotted against the logarithm of  $J_{sc}$  in the PbSe-TBAI and PbSe-PbI<sub>2</sub> CQDs based devices.

The ideality factor *n* was separately evaluated from a slope in  $V_{oc}$  plotted against the logarithm of  $J_{sc}$  based on the following equation: <sup>2, 3</sup>

$$V_{oc} = \frac{nk_BT}{q} ln\left(\frac{J_{sc}}{J_0}\right)$$

where *n* is the ideality factor,  $k_{\rm B}$  is the Boltzmann constant, *T* is temperature, *q* is the elementary charge, and  $J_0$  is the saturation current density at reverse bias. Thus, the ideality factor is estimated from a slope in plots of  $V_{\rm oc}$  against the logarithm of  $J_{\rm sc}$ .



Figure S6. Absorbance spectra of PbSe-TBAI and PbSe-PbI<sub>2</sub> CQDs based devices.



Figure S7. (a) Nyquist plots of PbSe-TBAI based CQDSCs in dark with different applied bias. (b) Nyquist plots of PbSe-PbI<sub>2</sub> based CQDSCs in dark with different applied bias. Depending on the applied voltage two arc features are observed in the S12

impedance spectra, the equivalent circuit plotted in (c). (d) Nyquist plots of PbSe-TBAI and PbSe-PbI<sub>2</sub> based CQDSCs in dark with 0.5 V applied bias, the solid curves are fitting results by using the equivalent circuit plotted in (c).



**Figure S8**. *J-V* curves of FTO/TiO<sub>2</sub>/PbSe-PbI<sub>2</sub>/PbSe-MPA/Au device which measured under AM 1.5G continuous illumination for 240 min (in air, room temperature: 20°C, humidity: 48%).

 Table S3.
 Performance details of FTO/TiO2/PbSe-PbI2/PbSe-MPA/Au device as

Illumination					
time		$J_{\rm sc}$ (mA/cm )	$V_{\rm oc}$ (V)	FF (%)	PCE (%)
0 min	Forward	18.4	0.607	0.522	5.83
	Reverse	18.3	0.607	0.523	5.81

shown in Figure S8.

20 min 40 min 60 min	Forward	17.9	0.608	0.522	5.70
	Reverse	17.9	0.609	0.520	5.68
	Forward	18.7	0.608	0.520	5.92
	Reverse	18.6	0.609	0.520	5.90
	Forward	18.6	0.608	0.519	5.85
	Reverse	18.6	0.609	0.518	5.85
90 min	Forward	18.6	0.608	0.517	5.84
	Reverse	18.5	0.609	0.516	5.83
120	Forward	18.6	0.608	0.513	5.83
min	Reverse	18.6	0.609	0.512	5.80
180	Forward	18.7	0.608	0.510	5.80
min	Reverse	18.6	0.609	0.510	5.79
240	Forward	197	0 609	0.508	5 70
min	FOIWAIU	10./	0.008	0.308	5.19
	Reverse	18.7	0.609	0.506	5.76

## References

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