

## **Supporting Information**

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Electroluminescent Solar Cells Based on CsPbl<sub>3</sub> Perovskite Quantum Dots

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#### Materials

The following materials were purchased from Sigma-Aldrich: Cs<sub>2</sub>CO<sub>3</sub> (99.9%), octadecene (technical grade 90%), oleic acid (technical grade 90%), oleylamine (technical grade 70%) and triphenyl phosphite (97%). The following materials were purchased from Alfa Aesar: PbI<sub>2</sub> (99%) and n-octane (98%). The following materials were purchased from J&K: methyl acetate (anhydrous 99.5%), ethyl acetate (anhydrous 99.8%) and n-hexane ( $\geq$  97.5%). The following materials were purchased from J&K: methyl acetate (anhydrous 99.5%), ethyl acetate (anhydrous 99.8%) and n-hexane ( $\geq$  97.5%). The following materials were purchased from Sinopharm Chemical Reagent Co., Ltd.: ethanol (analytical reagent, 98%), isopropanol (analytical reagent, 98%), acetone (analytical reagent, 98%) and TiCl<sub>4</sub> (98%). The following materials were purchased from Xi'an Polymer Light Technology Corp: PTAA (Mn=17,000 g/mol) and FAI (99.99%). Tris(pentafluorophenyl)borane (95%) was purchased from Acros Organics.

#### Characterizations

The UV-vis absorption spectra measurements were performed using a Perkin Elmer model Lambda 750 spectrophotometer. The PL spectra were obtained by using a FluoroMax-4 spectrofluorometer (HORIBA Scientific). Time-resolved PL spectra were measured using a Hamamatsu streak camera. FTIR spectra were analyzed on a Bruker HYPERION FTIR spectrometer and cumulated 32 scans at a resolution of 4 cm<sup>-1</sup>. XPS measurements were performed on a Kratos AXIS Ultra DLD ultrahigh vacuum photoemission spectroscopy system equipped with an Al-K (1486.6 eV) and He-I UV- light source (21.22 eV) radiation source and a hemispherical electron energy analyzer (Scienta R3000). SEM measurements were obtained from a Zeiss 500 with the extra high tension of 10 kV. TEM measurements were performed by a Tecnai G2 F20 S-Twin system operated at 200 kV. GIWAXS (Shanghai Synchrotron Radiation Facility Laboratory on Beamline BL14B1 using X-rays with a wavelength of  $\lambda \sim 1.24$  Å). AFM images were obtained using a Bruker Dimension Icon SPM system. The fs-TA measurements were performed on a Helios pump-probe system (150 fs, 1

kHz) combined with an amplified femtosecond laser system (excitation wavelength at 400 nm and laser energy of 7  $\mu$ J/cm<sup>2</sup>/pulse, the sample was on glass substrate).

#### Synthesis of Cs-oleate

2 g of  $Cs_2CO_3$ , 8 mL of OA and 100 mL of octadecene (ODE) were added to a 250 mL of three-necked flask. The system was vacuumed and heated to 90 °C under vigorous stirring conditions, then continuing to vacuum for another hour. N<sub>2</sub> was charged into the system, then the system was heated to 120 °C and kept at this temperature for another hour to achieve Cs-oleate.

#### Synthesis of CsPbI<sub>3</sub> QDs

1 g of PbI<sub>2</sub>, 50 mL of ODE were added to a 250 mL of three-necked flask. The system was vacuumed and heated to 90 °C under vigorous stirring conditions, then continuing to vacuum for another hour. N<sub>2</sub> was charged into the system. 5 mL of OA and 5mL of OLA were added to the system aiming at completely dissolve lead iodide in the octadecene, then the system was vacuumed again for an hour. N<sub>2</sub> was charged into the system again, then the system was heated to 160 °C. Finally, 4 mL of preheat Cs-oleate was quickly injected into the system to react for 5 s and temperature of the system was cooled to room temperature under ice bath.

#### Purification of CsPbI<sub>3</sub> QDs

The as-prepared pristine CsPbI<sub>3</sub> QDs solution was transferred into the glovebox with pure nitrogen atmosphere. 180 mL of MeOAc was added into 60 mL of as-prepared CsPbI<sub>3</sub> QD solution and then the system was centrifugated at 8000 rpm for 5 min to eliminate ODE as well as unreacted OA and OLA. The as-prepared precipitates were redistributed in 18 mL of n-hexane, then 18 mL of MeOAc was added into the system and centrifugated at 8000 rpm for 3 min to eliminate undersized CsPbI<sub>3</sub> QDs. The as-prepared precipitates were redistributed in 20

mL of n-hexane and centrifugated at 4000 rpm for 5 min to eliminate oversized CsPbI<sub>3</sub> PQDs. The purified CsPbI<sub>3</sub> QD solution was stored in dark with a temperature of -4 °C to remove excess PbI<sub>2</sub>, Cs-oleate and Pb-oleate to achieve CsPbI<sub>3</sub> QD solid. Finally, the as-prepared CsPbI<sub>3</sub> QD solid was redistributed in n-octane to obtain n-octane dispersion of CsPbI<sub>3</sub> QDs with a concentration of 70 mg/mL.

#### **Calculations and fitting**

The test results of TRPL were fitted by a biexponential function as follows:

$$f(t) = A_1 e^{\left(-\frac{t}{\tau_1}\right)} + A_2 e^{\left(-\frac{t}{\tau_2}\right)} + A_0$$

 $A_0$  is a constant, t is the time,  $A_1$  and  $A_2$  are the decay amplitudes,  $\tau_1$  and  $\tau_2$  is the decay times.

Therefore, the average PL lifetime ( $\tau_{ave}$ ) can be obtained by the equation as follows:

$$\tau_{ave} = \frac{A_1 \tau_1^2 + A_2 \tau_2^2}{A_1 \tau_1 + A_2 \tau_2}$$

The electronic trap density  $(n_e)$  can be obtained by the equation as follow:

$$n_e = \frac{2\varepsilon_0 \varepsilon V_{TFL}}{eL^2}$$

Thereinto, *e* is the elementary charge,  $\varepsilon$ ,  $\varepsilon_0$  and *L* are the relative dielectric constant, the vacuum permittivity and the thickness of the CsPbI<sub>3</sub> QD films, respectively. The electronic carrier mobility ( $\mu_e$ ) can be obtained by the equation as follows:

$$J_D = \frac{9}{8}\varepsilon_0\varepsilon\mu_e\frac{V^2}{L^3}$$

where V is the bias voltage.

For fs-TA, the change of excitation intensity with respect to time at near band edge can be fitted by a tri-exponential equation as follows:

$$f(t) = A_1 e^{(-\frac{t}{\tau_1})} + A_2 e^{(-\frac{t}{\tau_2})} + A_3 e^{(-\frac{t}{\tau_3})} + A_0$$

Thereinto,  $\tau_1$  is the decay time related to hot carrier cooling.<sup>1-2</sup> In addition, our samples for fs-TA testing have no charge extraction layer, indicating that the decay process is mainly due to the production of recombination. Moreover, the decay time related to electron transfer between QDs has been confirmed to be in the range of 10 ns and 100 ns.<sup>3</sup> Therefore,  $\tau_2$  and  $\tau_3$  are the decay times related to Auger recombination and defect trap states, respectively.

Figure 5g was derived from Figure 3b. In the reverse bias region, the as-achieved values of -dJ/dV can be defined as shunt conductance (*G*),<sup>4</sup> which is associated with leakage current.

Figure 5h was derived from Figure 3b according to on the formula:

$$-\frac{\mathrm{d}V}{\mathrm{d}J} = \frac{nkT}{q}(J_{\mathrm{sc}} - J)^{-1} + R_{\mathrm{s}}$$

where *n*, *k*, *T*, *q* and  $R_s$  are defined as ideality factor, Boltzmann contant, thermodynamic temperature, elementary charge and series resistance respectively, the slopes and intercepts of the linear fitting results can be applied to calculate the values of *n* and  $R_s$  respectively.<sup>4-5</sup> **Figure 5i** was derived from **Figure 3b** according to the aquation:

$$\ln(J_{\rm sc} - J) = \frac{q}{nkT}(V + R_{\rm s}J) + \ln J_0$$

where  $J_0$  is defined as saturated recombination current density, the values of  $J_0$  can be obtained by the intercepts derived from the fitting results of the linear regions.

# The computational method of first-principles calculations based on density functional theory (DFT)

First-principles calculations based on density functional theory (DFT)<sup>6</sup> were carried out to investigate the mechanism of CsPbI<sub>3</sub> surface passivation induced by OA, OAm and TPPI. The generalised gradient approximation (GGA)<sup>7</sup> with Perdew-Burke-Ernzerhof (PBE) was used to describe the effects of electronic exchange and correlation. The projector-augmented wave method (PAW)<sup>8</sup> was employed to represent the ionic cores and the following electronic

state were considered as valence: Cs 5s 5p and 6s; Pb 6p and 5d; I 4d 5s and 5p; C 2s and 2P; O 2s and 2p; H 1s. The energy cutoff was set to 400 eV. A 5-atom unit cell of CsPbI<sub>3</sub> was first relaxed with a Monkhorst-Pack k-point mesh of  $10 \times 10 \times 10$ . Then, a  $2 \times 2 \times 5$  slab system reproducing the surface Miller index <001> of CsPbI<sub>3</sub> was generated by adding a vacuum region of 40 Å height, in which the Pb and Br ions were exposed. A k-point grid of  $3 \times 3 \times 1$  was employed for the slab calculations. The geometry optimizations were halted when the forces in the atoms were all below 0.05 eV/Å.

The adsorption energy corresponding to the binding of a ligand molecule to the CsPbI<sub>3</sub> slab surface is defined as:

$$E_{ad} = E_{ligand@CsPbI_3} - E_{ligand} - E_{CsPbI_3}$$

where  $E_{ligand@CsPbI_3}$  is the total energy of the system composed by the ligand molecule adsorbed on the halide perovskite surface, and  $E_{CsPbI_3}$  and  $E_{ligand}$  are the energy of the isolated halide perovskite slab and ligand, respectively.

The vacancy formation energy,  $E_{vac}$ , is defined as:

$$E_{vac} = E_{defective} - E_{total} + E_I$$

where  $E_{defective}$  is the energy of the system containing one I vacancy,  $E_{total}$  the energy of perfectly stoichiometric system, and  $E_I$  the energy of one I atom.



Figure S1. (a) The used CsPbI<sub>3</sub> QDs and their TEM image; (b) The histogram of CsPbI<sub>3</sub> QD size distribution in TEM image.













Figure S4. The XPS spectra of (a) O *Is*, (b) C *Is*, and (c) I *3d* for the control and target CsPbI<sub>3</sub> QD films; (d) The histogram of the molar ratio with respect to I element for the other atoms in the control and target CsPbI<sub>3</sub> QD films.



Figure S5. Different views of the adsorption of molecular TPPI ligands on the surface of the CsPbI<sub>3</sub> QD. Bonds are spontaneously formed between the Pb atoms in the QD surface and P atoms in the TPPI ligands. Pb, I and Cs atoms in the QD are represented with grey, lilac and green spheres, respectively. P, O, C and H atoms in the TPPI ligands are represented with violet, red, brown and pink spheres, respectively.



Figure S6. The forward scan and reverse scan *J-V* curves of the control and target devices obtained from 1 Sun illumination (AM 1.5G).





Figure S8. The relationship of EQE<sub>EL</sub> with respect to current density.



Figure S9. The curves of radiance with respect to driving voltage for the control and target CsPbI<sub>3</sub> QD electroluminescent solar cells.



Figure S11. The UV-vis absorption spectra of control and pristine CsPbI<sub>3</sub> QD films.



Figure S12. The Illustration of electron-only devices.



Figure S13. Curves of photocurrent density  $(J_{ph})$  along with effective voltage  $(V_{eff})$  for the control and target CsPbI<sub>3</sub> QD electroluminescent solar cells.



Figure S14. The relationship of  $J_{sc}$  with respect to light intensity for the control and target CsPbI<sub>3</sub> QD electroluminescent solar cells.

Table S1. The optimal PV performance of  $CsPbI_3$  PQD electroluminescent solar cells with different concentrations of TPPI in MeOAc.

Concentrations	$V_{\rm oc}({ m V})$	$J_{\rm sc}({\rm mA/cm}^2)$	FF(%)	PCE(%)
0 mg/mL	1.20	15.15	74.49	13.55
0.08 mg/mL	1.20	15.22	75.62	13.81
0.16 mg/mL	1.22	15.39	77.45	14.54
0.32 mg/mL	1.23	15.52	79.42	15.16
0.64 mg/mL	1.20	15.35	77.19	14.22

Table S2	. The values of de	ecay amplitude	constants an	d decay time	s obtained from	n fs-TA as
shown in	Figure S10.					

	$A_1$	$\tau_1(ps)$	$A_2$	$\tau_2$ (ps)	$A_3$	$\tau_3$ (ps)
MeOAc	0.32	77.96	0.31	316.67	0.33	1359.33
MeOAc (TPPI)	0.33	73.47	0.38	383.55	0.26	1822.11

Table S3. The values of decay amplitude constants and decay times obtained from TRPL as shown in Figure 5b.

	$A_1$	$\tau_1(ns)$	$A_2$	$\tau_2(ns)$	$\tau_{\rm ave}({\rm ns})$
Control	0.86	1.28	0.14	6.42	1.98
MeOAc	0.92	0.90	0.08	7.25	1.40
MeOAc (TPPI)	0.77	3.05	0.23	16.90	6.28

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