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Aromatic amine-assisted pseudo-solution-phase ligand exchange in $CsPbI_3$ perovskite quantum dot solar cells

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Materials

Cesium carbonate (Cs_2CO_3, 99.9%, Sigma), lead iodide (PbI_2, 99.9%, Sigma), 1-octandecene (ODE, 90%, J&k), oleic acid (OA, 90%, Alfa), oleylamine (OAm, 90%, Alfa), PEA (≥ 98%, TCI), FPEA (≥ 98%, TCI), n-hexane (97.5%, J&K), n-octane (anhydrous, ≥ 98%, Alfa), MeOAc (anhydrous, 99.5%, Sigma); PTAA and formamidinium iodide (FAI, 99.9%) are purchased from Xi'an Polymer Light Technology Corp. (China). All the materials were used directly without further purification. Glass/FTO were purchased from Advanced Election Technology Co., Ltd (China).

$CsPbI_3$ QD synthesis

1 g of Cs_2CO_3, 4 mL of OA and 50 mL of ODE were added into 250 mL three-neck flask and under vacuum at 90 ^oC for 60 min to degas. Then the flask was filled with N_2 and heated up to 120 ^oC until the Cs_2CO_3 and OA completely reacted to form the clear Cs-oleate (CsOA) solution. The CsOA was stored in N_2 glove box and kept at 80 ^oC for QDs synthesis. Meanwhile, 1 g of PbI_2 and 50 mL of ODE were added into 250 mL three-neck flask and under vacuum at 90 ^oC for 60 min. The stable N_2 flow then was purged into the flask, followed by the injection with 5 mL of OA and 5 mL of OAm. Until the PbI_2 was completely dissolved, the mixture solution was heated up to 160 ^oC under N_2 protection. Afterward, 4 mL of preheated CsOA was rapidly injected into the flask, and after 5 s the reaction was quenched by an ice bath.

$CsPbI_3$ QD purification

The crude solution was loaded equally into six centrifuge tubes. Subsequently,

each $CsPbI_3$ QD solution was added into 32-mL MeOAc (QD solution: MeOAc is 1:3), then centrifuged at 8000 rpm for 5 min. The precipitate in each centrifuge tube was re-dispersed in 3 mL hexane. For control $CsPbI_3$ QDs, each QD solution was added into 3-mL MeOAc (QD solution: MeOAc is 1:1) and centrifuged at 8000 rpm for 3 min; For p-SPLE $CsPbI_3$ QDs, each QD solution was added into 3-mL mixed anti-solvent, that prepared by MeOAc and PEA or FPEA with different volume ratios, and centrifuged at 8000 rpm for 3 min. Finally, the obtained QD precipitate was re-dispersed in 20 mL hexane total and centrifuged at 4000 rpm for 5 min to remove excess PbI_2 and CsOA. Then, the $CsPbI_3$ QD solution was storage at 4 ^oC for 12 h to precipitate excess CsOA and PbOA.

$CsPbI_3$ QD film and solar cell fabrication

The FTO/glass substrates were cleaned by industrial acetone, deionized water, isopropanol and acetone for 15 min, respectively. The ~40-nm-thickness compact TiO_2 was sequentially deposited on the FTO substrates by chemical bath deposition, and then annealed at 200 ^oC for 30 min. Before depositing the $CsPbI_3$ QD film, the TiO_2 film was treated with UV-ozone for 15 min. Subsequently, the QD solution (70 mg/mL in octane) was deposited by spin coating at 1000 rpm for 15 s and 2000 rpm for 20 s. Then, 150 μL MeOAc was dropped on the QD array and stayed for 5 s following by spinning at 2000 rpm for 20 s to remove the exchanged ligands. To build up optimal thickness of QD film, this procedure was repeated 5 times. Subsequently, the as-cast QD film was dipped into FAI solution (saturated solution in ethyl acetate) and then

rinsed in neat anhydrous MeOAc. The above processes were performed in air glove box with relative humidity of 15% and room temperature. PTAA solution (15 mg/mL in toluene, doped by TPB) was spin coated on resultant film as the HTL layer. Finally, the electrode of MoO_3 (8 nm) and Ag (120 nm) was deposited by thermal evaporator.

Characterizations

The current density-voltage (*J-V*) characteristics of the $CsPbI_3$ QD solar cells were measured by a Keithley 2400 Digital Source Meter under N_2 glovebox and simulated AM 1.5G spectrum at 100 mW cm^{-2} with a solar simulator (Class AAA, 94023A-U, Newport). Before test, the light intensity of the Xenon lamp was calibrated with a standard silicon solar cell (91150V, Newport Oriel). The active area of 7.25 mm^2 was defined by a shadow mask. The external quantum efficiency (EQE) measurement of the solar cells was characterized on a Solar Cell Scan 100 system (Zolix Instruments Co. Ltd.).

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) with excitation wavelength at 470 nm. Time-resolved PL spectra were measured using a Hamamatsu streak camera. FTIR spectra (the zoon region of FTIR spectra) were analyzed on a Bruker HYPERION FTIR spectrometer. TEM measurements were performed by a Tecnai G2 F20 S-Twin system. XRD patterns were recorded by using a Rigaku D/Max-Ra X-ray diffractometer.

XPS measurements were performed on a Kratos AXIS Ultra DLD ultrahigh vacuum photoemission spectroscopy system equipped with an Al-Kα (1486.6 eV) radiation source.

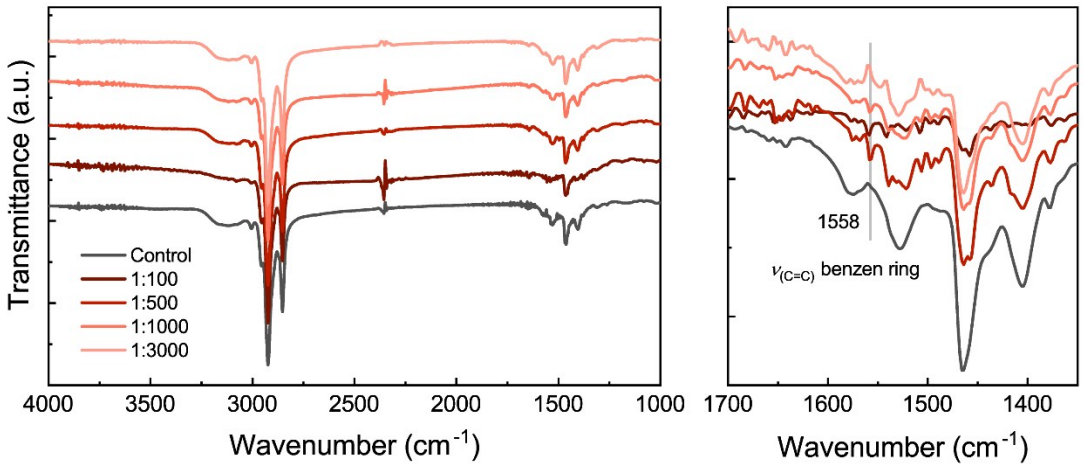

Fig. S1 FTIR spectra of $CsPbI_3$ QD arrays with different mixed-ratio PEA p-SPLE.

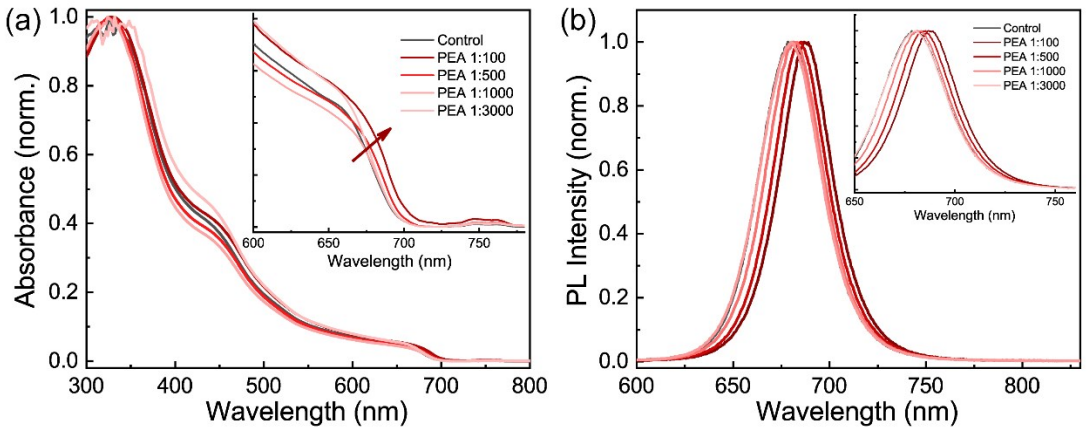

Fig. S2 (a) UV-vis absorption and (b) PL spectra of $CsPbI_3$ QD solution with different mixed-ratio PEA p-SPLE.

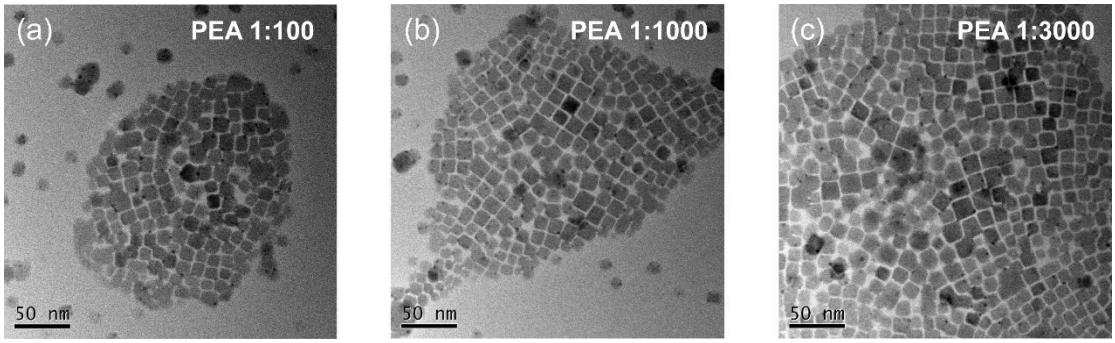

Fig. S3 TEM images of $CsPbI_3$ QDs with different volume-ratio (v:v) PEA p-SPLE. (a) v:v=1:100, (b) v:v=1:1000 and (c) v:v=1:3000.

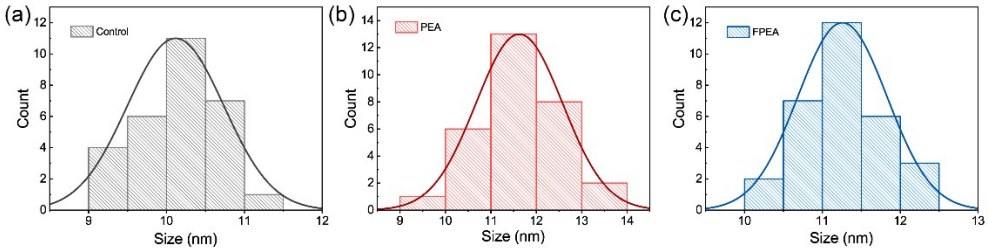

Fig. S4 The size distributions of $CsPbI_3$ QDs w/wo p-SPLE.

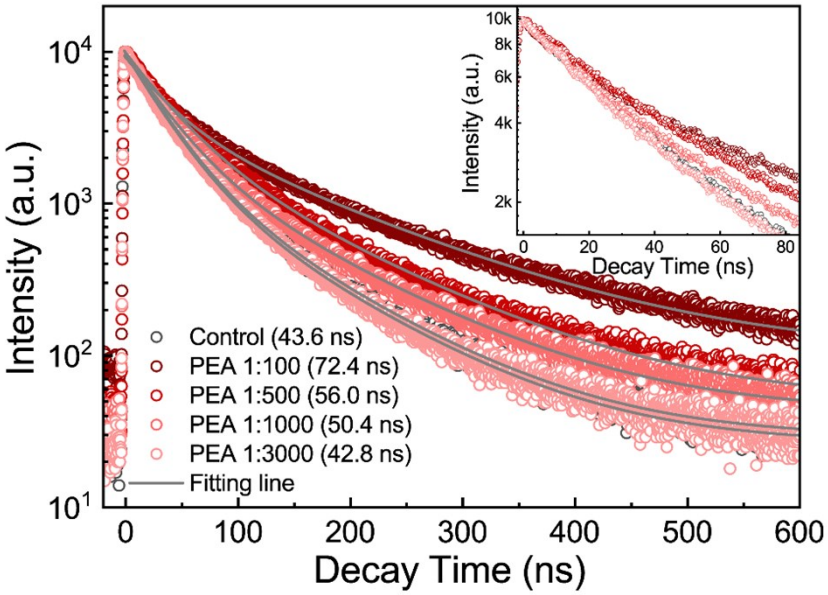

Fig. S5 TRPL spectra of $CsPbI_3$ QD solution with different mixed-ratio PEA p-SPLE.

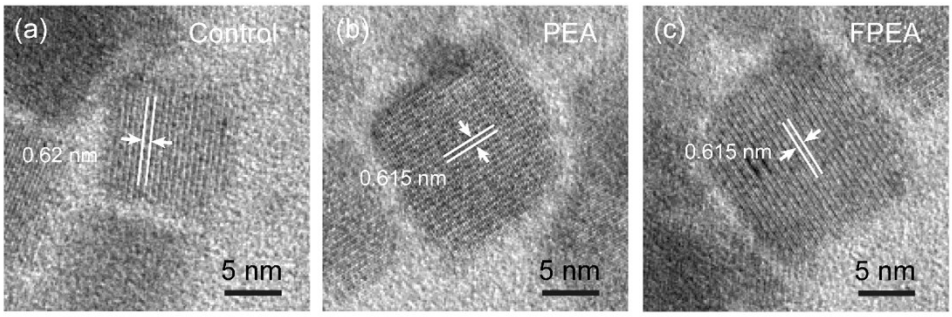

Fig. S6 The lattice distance of the $CsPbI_3$ QD w/wo p-SPLE treatment.

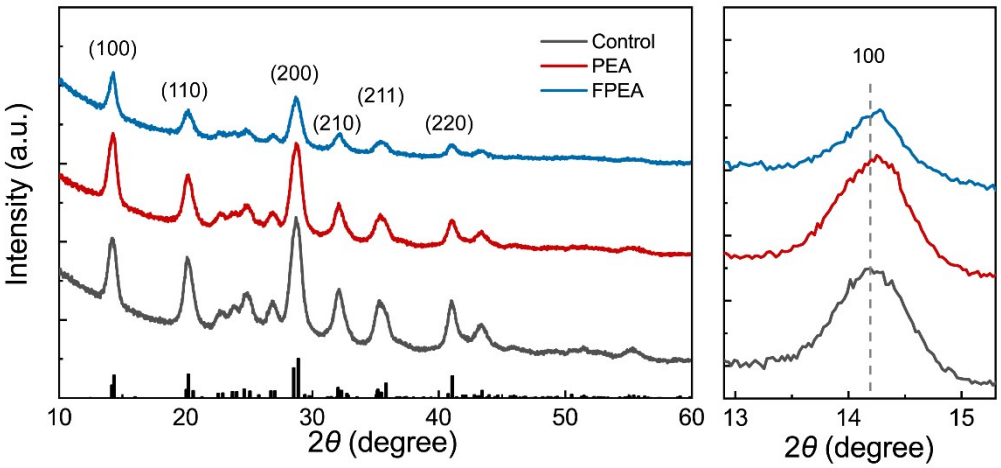

Fig. S7 XRD spectra of w/wo p-SPLE $CsPbI_3$ QD films.

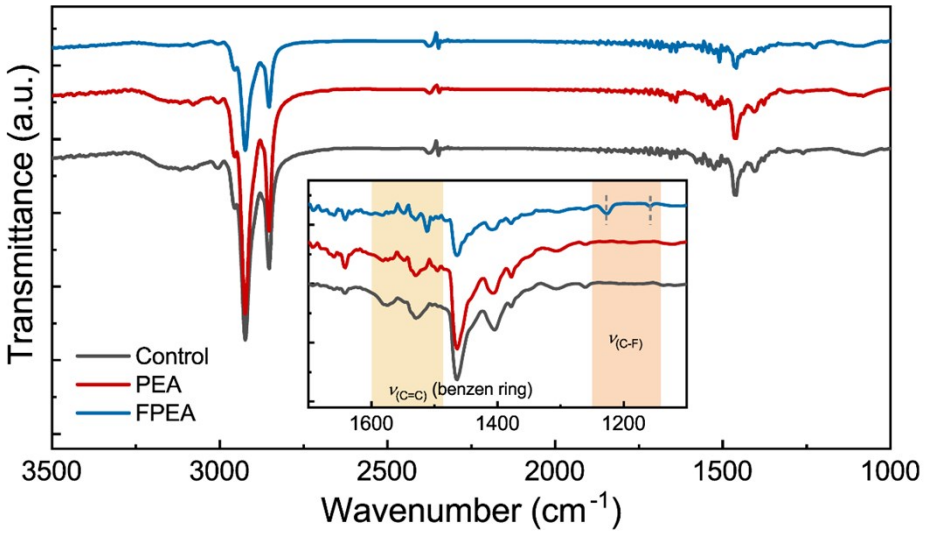

Fig. S8 FTIR spectra of w/wo p-SPLE $CsPbI_3$ QD films.

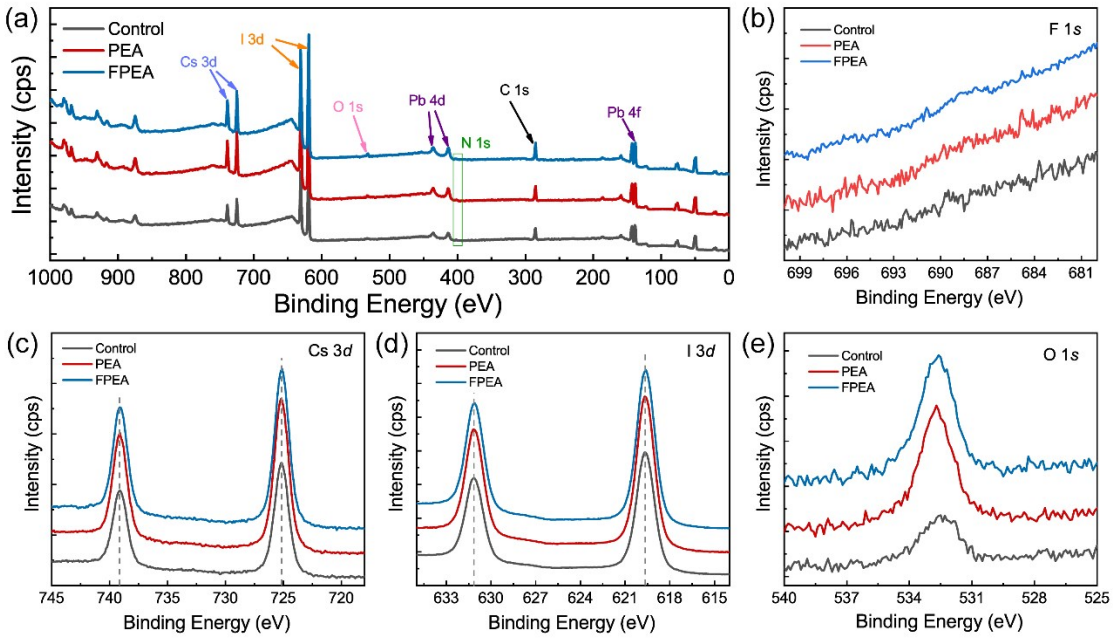

Fig. S9 XPS spectra (a) full region, (b) F 1*s* core-level, (c) Cs 3*d* core-level, (d) I 3*d* core-level and (e) O 1*s* core-level of w/wo p-SPLE $CsPbI_3$ QD films.

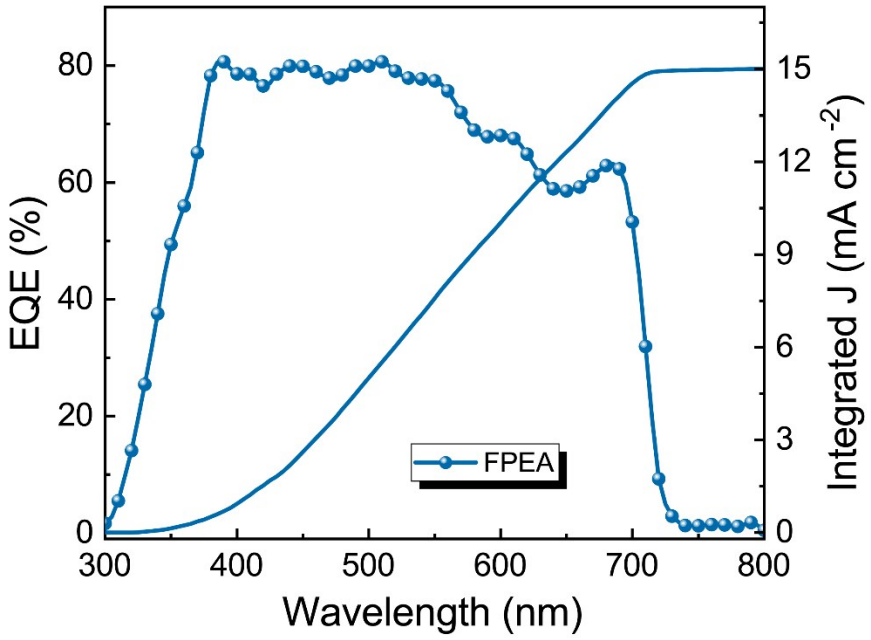

Fig. S10 EQE spectra of w/wo p-SPLE $CsPbI_3$ QD solar cells.

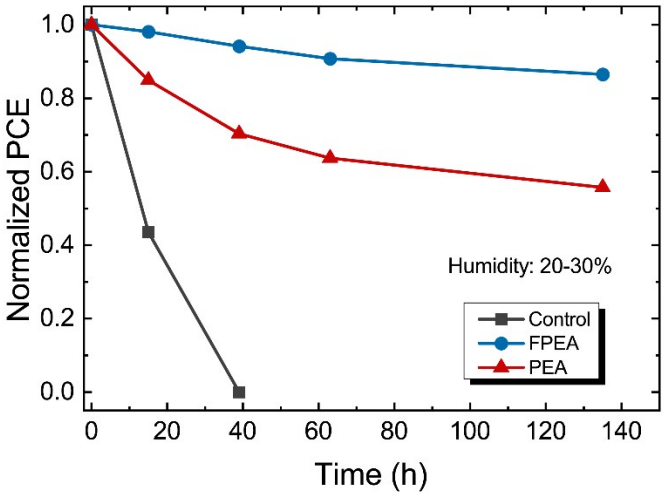

Fig. S11 The air stability of w/wo p-SPLE $CsPbI_3$ QD solar cells.

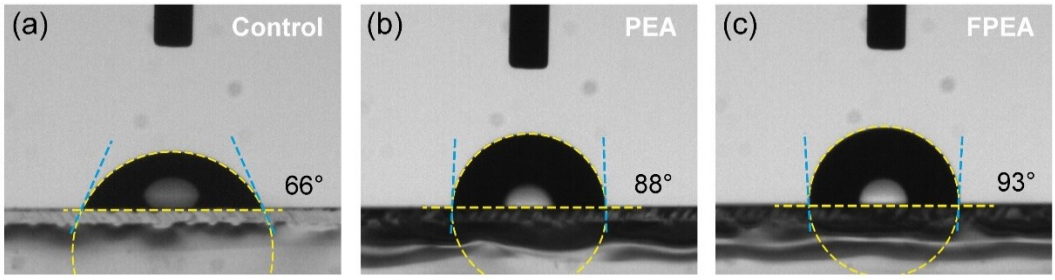

Fig. S12 The deionized water contact angles of w/wo p-SPLE $CsPbI_3$ QD films after MeOAc treatment.

Table S1. The FWHM of the PEA p-SPLE QDs PL spectra.

Sample	Control	1:3000	1:1000	1:500	1:100
FWHM (nm)	37.6	37.5	35.2	33.2	32.6

Table S1. The FWHM of the p-SPLE QDs PL spectra.

Sample	Control	PEA	FPEA
FWHM (nm)	37.8	33.1	32.8

Table S3. The detailed parameters of the best devices

Sample	V_{OC} (V)	J_{SC} (mA cm^{-2})	FF	PCE (%)
Control	1.255	14.52	0.733	13.36
PEA	1.255	15.23	0.742	14.18
FPEA	1.275	15.38	0.747	14.65