Supporting Information

Tuning Surface Passivating Ligand Anchoring Position Enables Phase Robustness in $CsPbI_3$ Perovskite Quantum Dot Solar Cells

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Materials

Cs_2CO_3 (99.9%), ODE (technical grade 90%), OA (technical grade 90%) and OLA (technical grade 70%) were obtained from Sigma-Aldrich. PbI2 (99%) and n-octane (98%) were obtained from Alfa Aesar. MeOAc (anhydrous 99.5%), EtOAc (anhydrous 99.8%) and n-hexane (≥ 97.5%) were obtained from J&K. Ethyl alcohol (analytical reagent, 98%), isopropanol (analytical reagent, 98%), acetone (analytical reagent, 98%) and TiCl4 (98%) were obtained from Sinopharm Chemical Reagent Co., Ltd.. PTAA (Mn=17,000g mol-1) is obtained from Xi'an Polymer Light Technology Corp.

Instruments

SEM images were obtained by a Zeiss Supra 55 with the extra high tension of 5 kV. PL spectra tested by a Monochromator/Spectrograph (Omni-λ300, Zolix) and an Oscilloscope (GDS-3354, GWINSTEK). TEM images of $CsPbI_3$ QDs were recorded by a transmission electron microscope with the type of Tecnai G2 F20 S-Twin. EIS measurements were carried out through Zahner IM6 electrochemical workstation with a frequency between 0.25 MHz and 0.05 Hz under a monochromatic LED (500 nm, 100 mW) light irradiation. XPS were obtained through a Kratos AXIS Ultra DLD ultrahigh vacuum photoemission spectroscopy system, with an Al Kα radiation source.

Preparation of $CsPbI_3$ PQDs

1 g of Cs_2CO_3, 4 mL of OA and 100 ml of 1-octadecene (ODE) were put into a 250 ml of three-necked flask and was stirred and vacuumed at 90 ℃ for 1 h. Then, N_2 was pumped into the three-necked flask and the reaction temperature went up to 120 ℃. Finally, the reaction continued for 50 min to obtain Cs-oleate.

1 g of PbI_2 and 50 mL of ODE were put into a 250 mL of three-necked flask and was stirred and vacuumed at 90 ℃ for 1 h. Then, N_2 was pumped into the three-necked flask followed by the addition of 5 mL of OA and 5 mL of OLA. The three-necked flask was vacuumed again for 1 h until N_2 was pumped into it again and heated up to 160 ℃. Next, 8 mL of preheat clear Cs-oleate was injected into the three-necked flask rapidly and after 5s, the reaction was cooled to 40 ℃ under ice bath.

Purification of $CsPbI_3$ PQDs

The $CsPbI_3$ PQDs mixture was transferred into a N_2-filled glovebox. 30 mL of MeOAc was added into 10 ml of as-prepared $CsPbI_3$ PQD solution and centrifuged at 8000 rpm for 5 min aiming at removing ODE, unreacted OA and unreacted OLA. The precipitation was re-dispersed into 3 mL of hexane. Then, 3 mL of MeOAc was added into 3 mL $CsPbI_3$ PQD hexane solution and centrifuged at 8000 rpm for 3 min aiming at removing undersized $CsPbI_3$ PQDs. Then, all the precipitation was re-dispersed into 20 mL of hexane and centrifuged at 4000 rpm for 5 min. The last precipitation was not needed aiming at removing excess PbI_2, excess Cs-oleate and oversized $CsPbI_3$ PQDs. The $CsPbI_3$ PQDs need to be stored in dark at 0 ℃ overnight and centrifuged at 4000 rpm for 5 min aiming at removing excess PbI_2, Cs-oleate and Pb-oleate to achieve $CsPbI_3$ PQD solid. The $CsPbI_3$ PQD solid was dispersed into octane for 70 mg/mL to prepare $CsPbI_3$ PQD solar cells.

The fabrication of $CsPbI_3$ PQD solar cells

TiO_2 electron transfer layer was deposited on the FTO substrate by means of chemical bath deposition. Before depositing $CsPbI_3$ PQDs, the FTO/TiO_2 substrates were treated by UV-zone for about 10 min and transferred to a glove box which atmosphere is 70 % of N_2 and 30 % of O_2. Then, 15 uL of as-prepared octane solution of $CsPbI_3$ PQDs was spin coated on the FTO/TiO_2 substrate at 1000 rpm for 15 s and 2000 rpm for 20 s. 150 uL of MeOAc was dropped on the $CsPbI_3$ PQD layer for 5 s to remove the long chain insulated ligands at the surface of $CsPbI_3$ PQD and then spun at 2000 rpm for 20 s. This process was needed to repeat five times to obtain thick enough $CsPbI_3$ CQD film. The film was soaked into solution of ethyl acetate of Py (3 μL/mL), 2-MP (0.05 mg/mL) and 4-MP (0.05 mg/mL) and pure MeOAc for 3 s respectively and then blown dry with N_2. The as-prepared substrate was transferred to a glove box with pure N_2 to deposited hole transfer layer. 15 mg/mL of tris(pentafluorophenyl)borane-doped PTAA toluene solution was spin coated on the as-prepared $FTO/TiO_2/CsPbI_3$ PQDs substrate at 3000 rpm for 40 s. Finally, 8 nm of MoO_3 and 120 nm of Ag electrode were deposited by thermal evaporation through a shadow mask to form 0.075 cm^2 devices under a vacuum of 2×10^{-6} mbar.

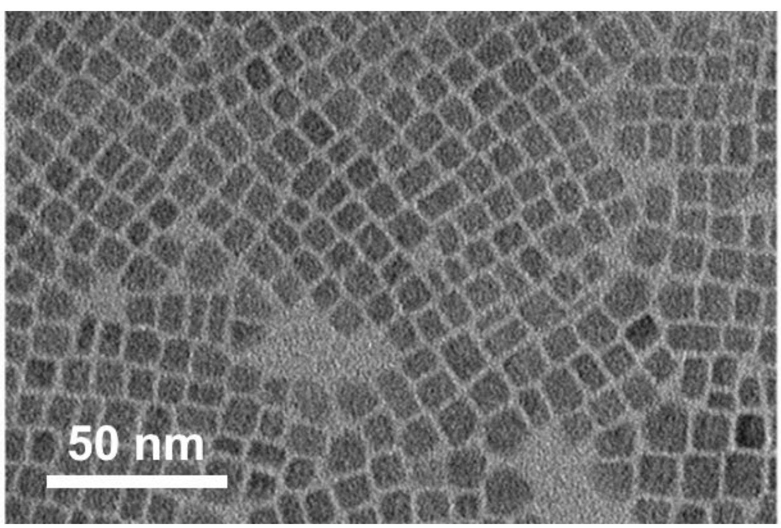

Figure S1. TEM image of purified $CsPbI_3$ PQDs with an average size around 9 nm.

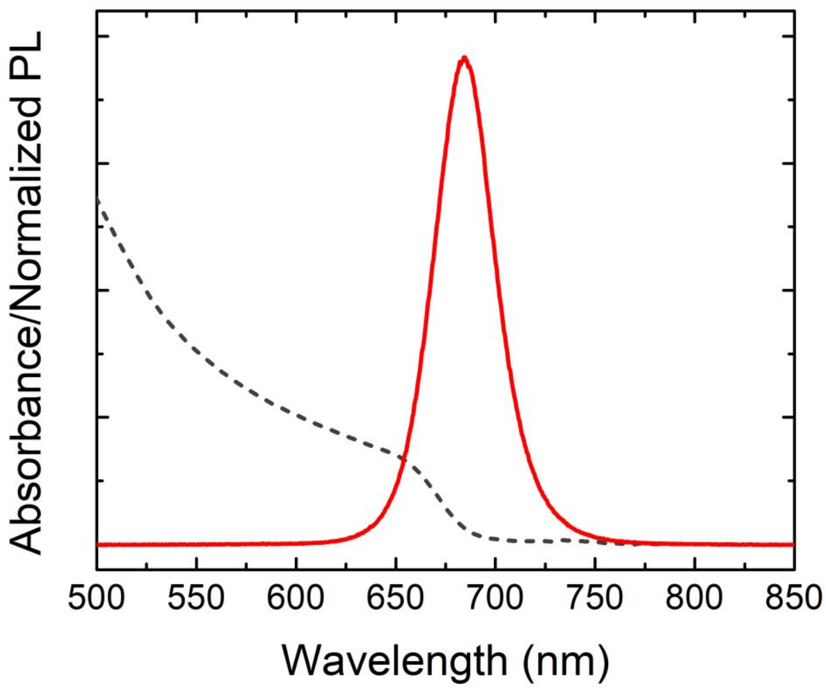

Figure S2. UV-vis absorption and PL spectra of $CsPbI_3$ PQD solution in hexane.

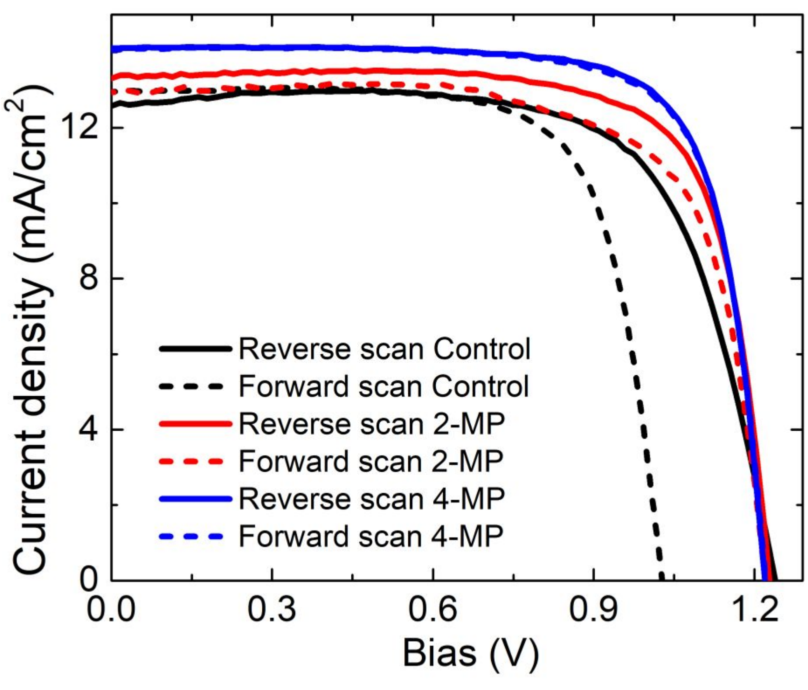

Figure S3. The J-V curves of control, 2-MP and 4-MP post-treated devices under reverse and forward scanning.

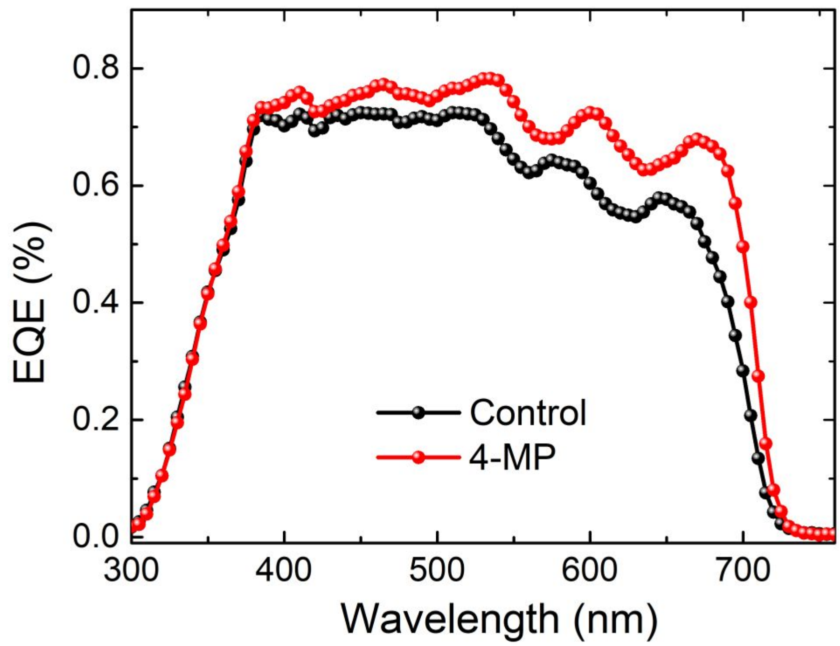

Figure S4. EQE curves of control and optimal 4-MP post-treated devices

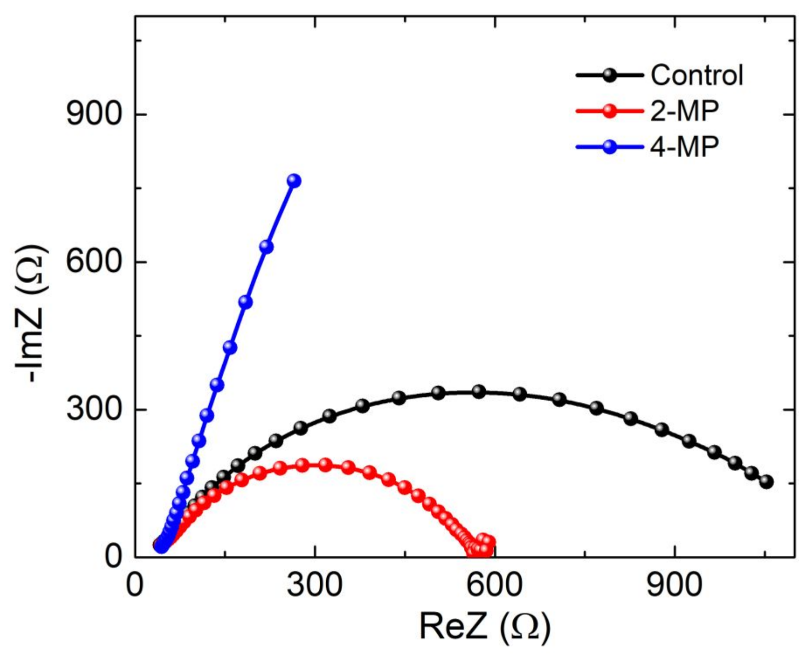

Figure S5. EIS curves of control, 2-MP and 4-MP treated devices under illumination.

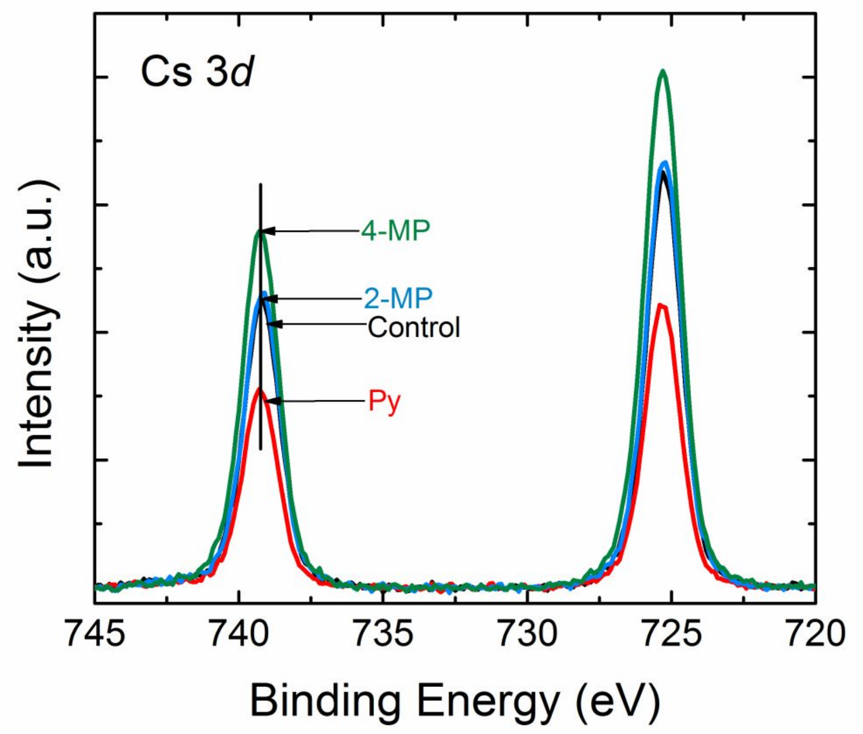

Figure S6. XPS signals of Cs 3*d* in control, Py, 2-MP and 4-MP post-treated $CsPbI_3$ PQD films.

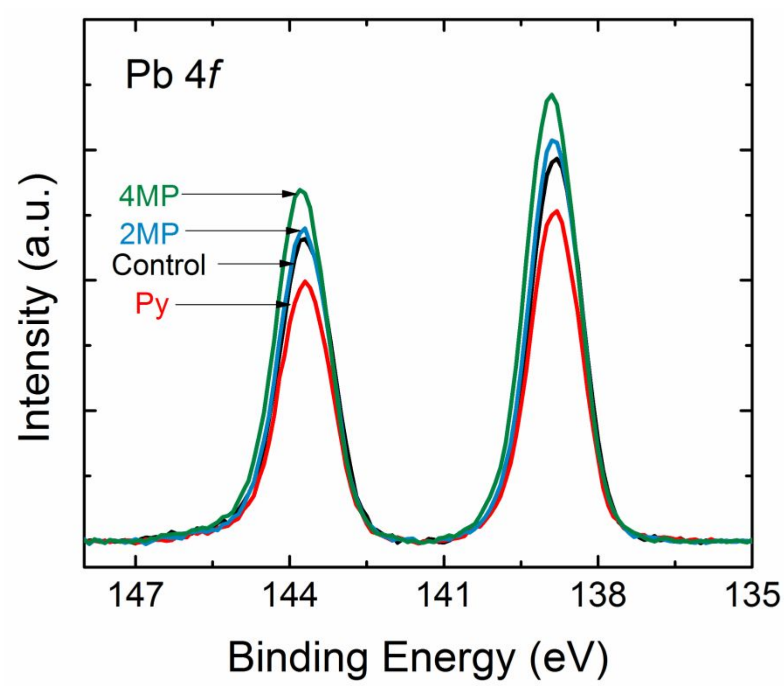

Figure S7. XPS signals of Pb 4*f* in control, Py, 2-MP and 4-MP post-treated $CsPbI_3$ PQD films.

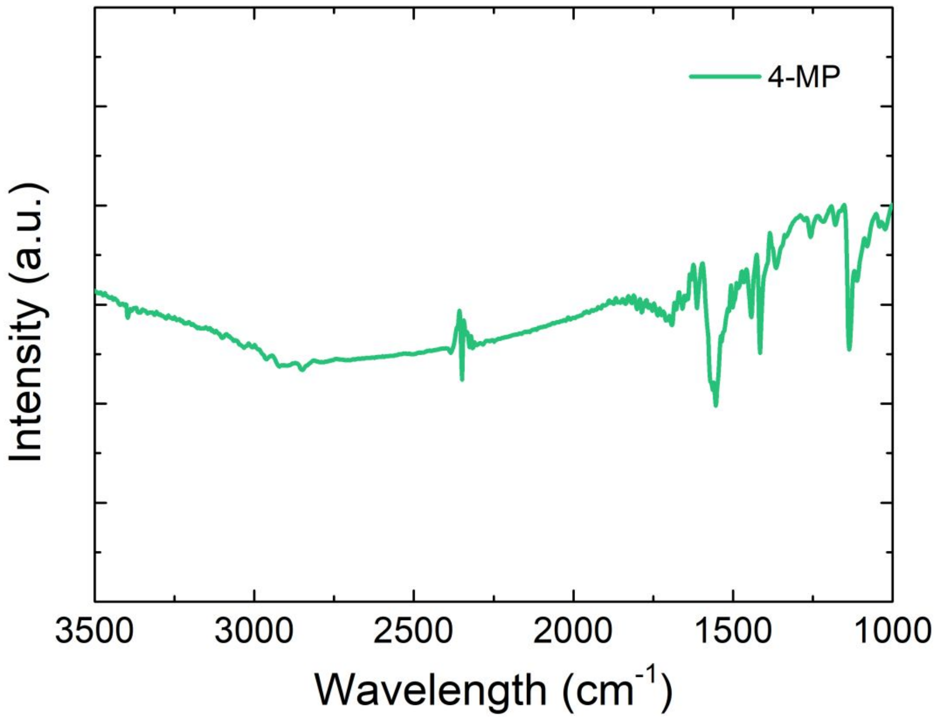

Figure S8. FTIR spectra of neat 4-MP, the stretching vibration of C=N appearing at the region of 1660 to 1430 cm^{-1}.

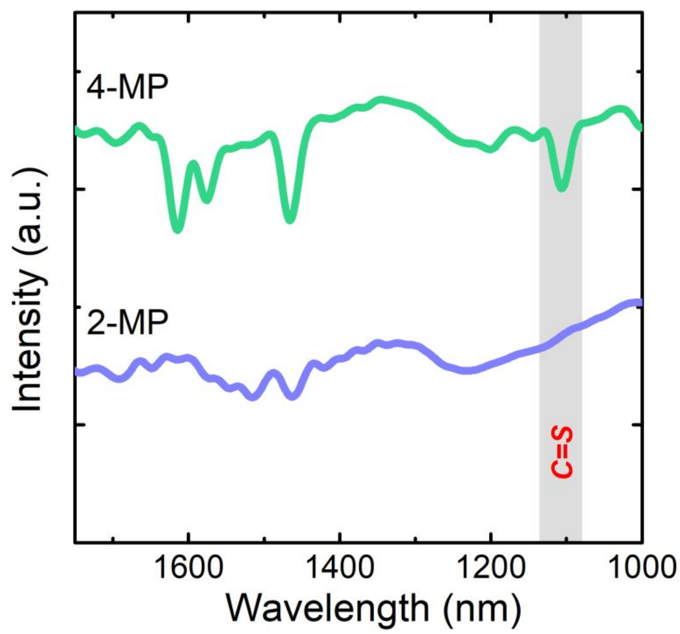

Figure S9. The enlarged FTIR areas of 2-MP and 4-MP tretaed $CsPbI_3$ QD films.

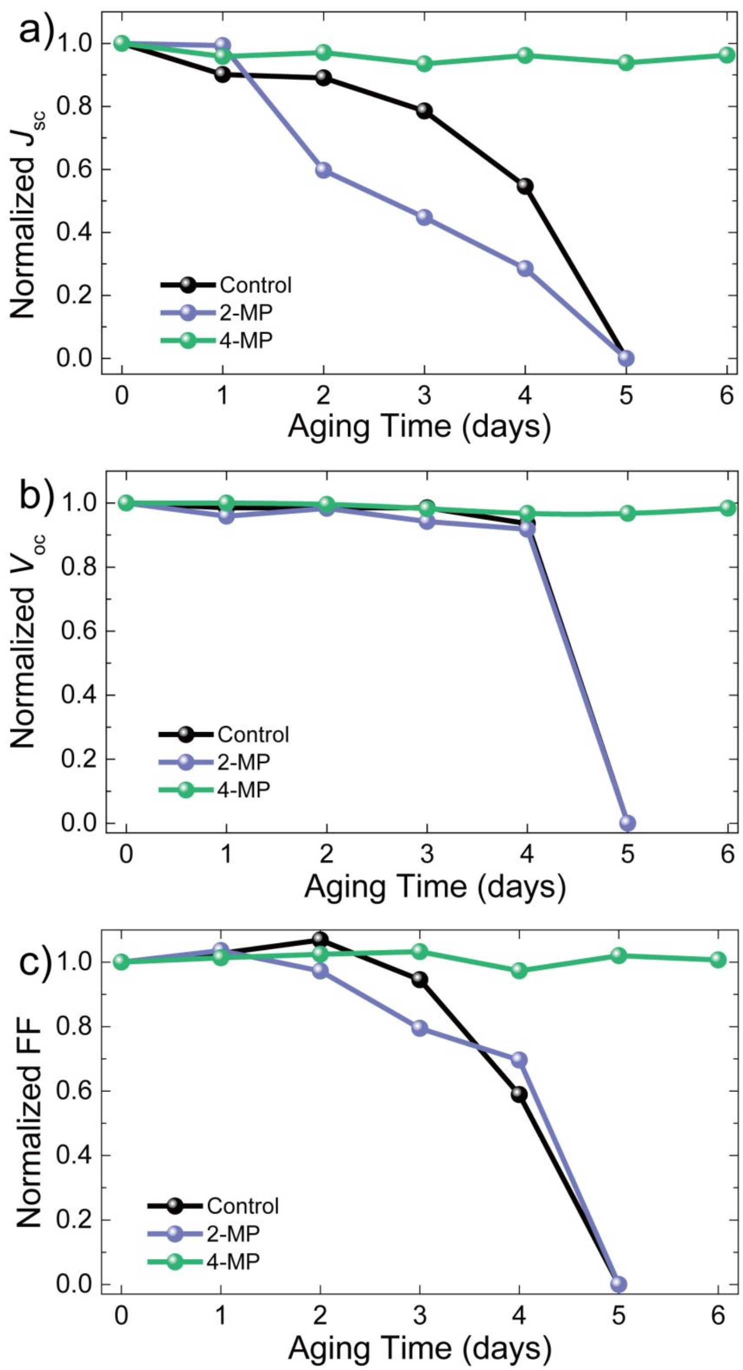

Figure 10. J_{sc}, V_{oc} and FF of control, 2-MP and 4-MP treated $CsPbI_3$ PQD solar cells as a function of aging under RH of 20-30% at 20-30 ^oC condition.

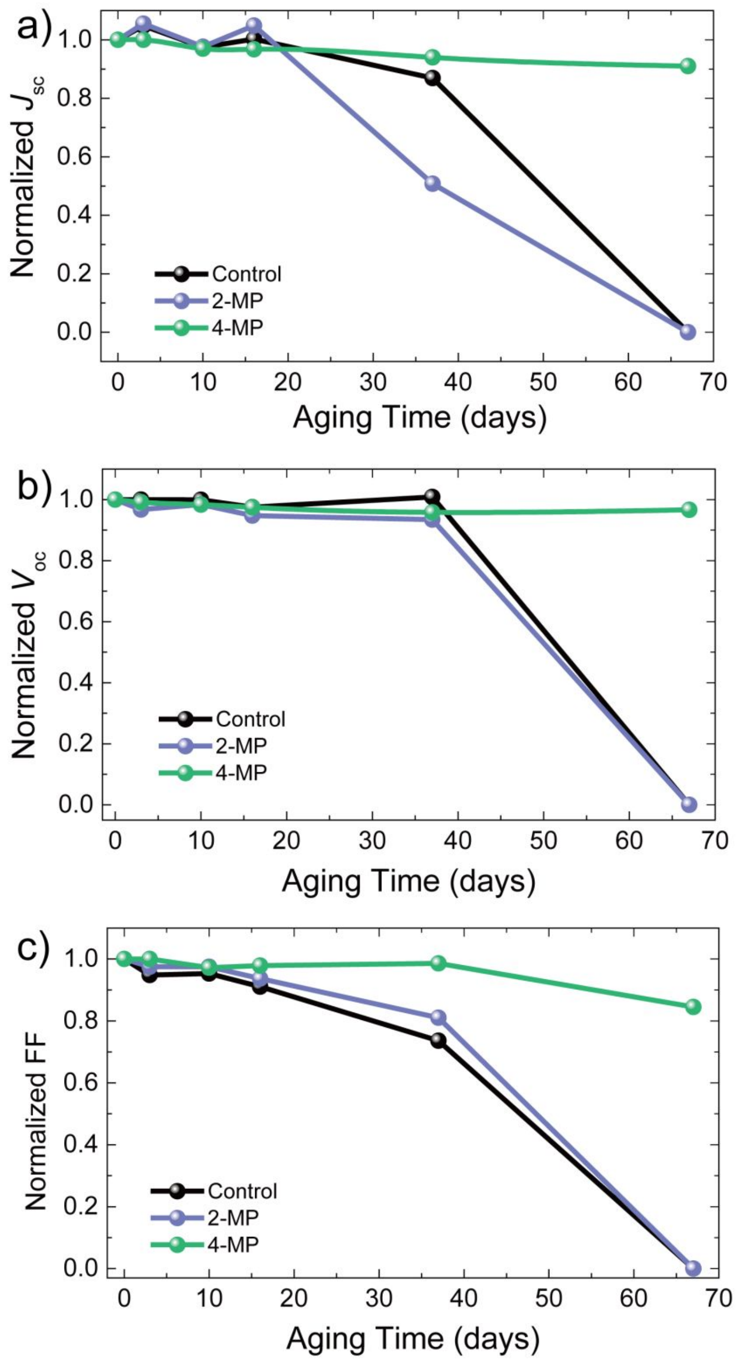

Figure 11. J_{sc}, V_{oc} and FF of control, 2-MP and 4-MP treated $CsPbI_3$ PQD solar cells as a function of aging under RH 0-5% at 20-30 ^{o}C condition.

Table S1. Summary of ambient stability of $CsPbI_3$-QD solar cells reported so far

Device architecture	**PCE**	**Ambient storage device stability**	**Reference**
FTO/TiO_2/QDs/PTB7/MoO_3/Ag	12.55%	- RH 20~30%, 25°C - 80% retention for 35 hour	Joule 2 (2018) 2450.
FTO/TiO_2/QDs/PTAA/Au	11.64%	- RH 60%, 25°C - 60% retention for 10 hour	Adv. Energy Mater. 8 (2018) 1800007.
FTO/TiO_2 /QDs/PTAA /MoO_x/Ag	12.30%	- RH 20~30%, 25°C - 20% retention for 50 hour	ACS Energy Lett. 4 (2019) 2571.
FTO/TiO_2/QDs/spiro-OMeTAD/MoO_x/Ag	12.40%	- RH 20%, 25°C - 90% retention for 22 day	Nano Energy 66 (2019) 104130.
FTO/TiO_2 /QDs/PTAA/MoO_3/Ag	14.1%	- RH 40%, 25°C - 70% retention for 50 hour	Adv. Energy Mater. 9 (2019) 1900721.
FTO/TiO_2 /QDs/PTB7 /MoO_3/Ag	12.27%	- RH 20~30%, 25°C - 70% retention for 150 hour	J. Mater. Chem. A 7 (2019) 20936.
ITO/SnO_2/QDs/spiro-OMeTAD/Au	9.6%	- RH 50~70%, 25°C - 40% retention for 4 day	Nat. Energy 5 (2020) 79.
FTO/TiO_2/QDs/spiro-OMeTAD/Ag	14.8%	- RH 20~30%, 25°C - 62% retention for 350 hour	Chem. Mater. 32 (2020) 6105.
FTO/TiO_2 /QDs/QD:Polymer/PTAA/MoO_3/Ag	13.8%	- RH 20~30%, 25°C - 88% retention for 50 hour	J. Mater. Chem. A 8 (2020) 8104.
FTO/c-TiO_2 /QDs/spiro-OMeTAD/MoO_x/Ag	14.10	- RH 20~25%, 25°C - 90% retention for 15 day	Nano Energy 75 (2020) 104985
Glass/FTO/TiO_2/QDs/PTAA/MoO_3/Ag	14.9%	- RH 30~40%, 20-30°C - 70% retention for 130 hour	Adv. Mater. 32 (2020) 2000449
Glass/FTO/TiO_2/QDs/PTAA/MoO_3/Ag	**14.25%**	**- RH 20~25%, 20-30°C** **- 60% retention for 30 day** **- RH 0~5%, 20-30°C** **- 75% retention for 67 day**	**This Work**