

## Supplementary Information

### **Small-Molecule-Templated Nanostructure Back Electrode for Enhanced Light Absorption and Photocurrent in Perovskite Quantum Dot Photovoltaics**

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## Experimental section

**Materials:** Lead iodide (II) ( $\text{PbI}_2$ , 99.999%), 1-octadecene (technical grade 90%), oleic acid (technical grade 90%), cesium carbonate ( $\text{Cs}_2\text{CO}_3$ , 99.99%), n-hexane (anhydrous), n-octane (99%), lithium bis(trifluoromethylsulfonyl)imide (Li-TFSI, 98%), and 2-n-pentylpyridine were bought from Alfa Aesar. Oleylamine (technical grade 70%), sodium acetate (NaOAc, 99.995%), chlorobenzene (anhydrous 99.8%), and acetonitrile (99.8%) were bought from Sigma-Aldrich. Phenethylammonium iodide (PEAI) was bought from GreatcellSolar. Methyl acetate (MeOAc,  $\geq 99.5\%$ ) and ethyl acetate (EtOAc,  $\geq 99.5\%$ ) were bought from Duksan.  $\text{TiO}_2$  precursor solution (0.15 M), and  $\text{TiCl}_4$  aqueous solution (2 M) were bought from Sharechem. 2,20,7,70-Tetrakis(N,N-di-p-methoxyphenylamine)-9,90-spirobifluorene (Spiro-OMeTAD,  $\geq 99.5\%$ ) was bought from Lumtec. Silicone elastomer base and Silicone elastomer curing agent were bought from Sylgard. Diffraction gratings were bought from Edmund optics.

**Synthesis and purification of  $\text{CsPbI}_3$ -PQDs:** To prepare the Cs-oleate precursor, 0.407 g of  $\text{Cs}_2\text{CO}_3$ , 1.25 mL of oleic acid and 20 mL of 1-octadecene were put into a 250 mL of three-necked flask. The flask was degassed at 120 °C until the  $\text{Cs}_2\text{CO}_3$  was completely dissolved. After that, the flask was filled with Ar gas while reducing the temperature of the Cs-oleate precursor to 90 °C. For the synthesis of  $\text{CsPbI}_3$ -PQDs, 0.5 g of  $\text{PbI}_2$  and 25 mL of 1-octadecene were put into a 100 mL of three-necked flask. The flask was degassed for 30 min at 115 °C. After that, 2.5 mL of oleic acid and 2.5 mL of oleylamine were added into the flask. When the  $\text{PbI}_2$  was fully dissolved, the flask was heated up to 180 °C while filling with Ar gas. Finally, the pre-heated 2 mL of Cs-oleate precursor was injected rapidly into the flask and after 5 s, the flask was cooled to 40 °C under ice bath. To purify the  $\text{CsPbI}_3$ -PQD crude solution, the 60 mL of MeOAc was mixed with the 30 mL of crude solution and the mixture was centrifuged at 5000 rpm for 3 min. After the supernatant solution was removed, the precipitates were

dispersed in the 10 mL of hexane. Sequentially, the 14 mL of MeOAc was added and the mixture was centrifuged at 5000 rpm for 3 min and then the supernatant solution was removed. The precipitates were re-dispersed in the 30 mL of hexane and the solution was centrifuged at 5000 rpm for 3 min. Finally, the CsPbI<sub>3</sub>-PQDs dispersed in hexane were fully evaporated under vacuum. Lastly, CsPbI<sub>3</sub>-PQD solids were re-dispersed in octane with a concentration of 75 mg mL<sup>-1</sup>.

***Fabrication of nanostructured PDMS molds:*** The mixture of silicone elastomer base as a precursor of poly(dimethylsiloxane) (PDMS) and curing agent was evaporated for 1 h to eliminate bubbles in the mixture. After fully eliminate the bubbles, put a diffraction grating on the mixture to transfer the nanostructures, and cured at 90 °C for 4 h. After that, the cured PDMS was slowly peeled off from a diffraction grating.

***Fabrication of flat and back-side nanostructured CsPbI<sub>3</sub>-PQD solar cells:*** Pre-patterned fluorine-doped tin oxide (FTO) substrates were sonicated using detergent, deionized water, acetone, and isopropyl alcohol. The FTO substrates were treated by UV/O<sub>3</sub> for 20 min to make the FTO substrate hydrophilic. The c-TiO<sub>2</sub> precursor solution was spin coated on the FTO substrates for 30 s at 3000 rpm, and then the substrates were annealed at 500 °C for 1 h. The substrates were cooled to room temperature and immersed in a 120 mM TiCl<sub>4</sub> solution which diluted in deionized water at 70 °C for 1 h. The substrates were washed using deionized water and annealed at 500 °C for 1 h. The CsPbI<sub>3</sub>-PQD solution was spin-coated onto the FTO/c-TiO<sub>2</sub> for 20 s at 1000 rpm and for 5 s at 2000 rpm to fabricate as-cast CsPbI<sub>3</sub>-PQD solid. The as-cast CsPbI<sub>3</sub>-PQD solid was soaked in 1 mg mL<sup>-1</sup> of NaOAc solution in MeOAc for 3 s and spin-dried and then rinsed using neat MeOAc to remove excess salt. This procedure was repeated several times to obtain desired CsPbI<sub>3</sub>-PQD absorber thickness (~300 nm). After that, the CsPbI<sub>3</sub>-PQD absorber was soaked in 1 mg mL<sup>-1</sup> of PEAI solution in EtOAc for 10 s and

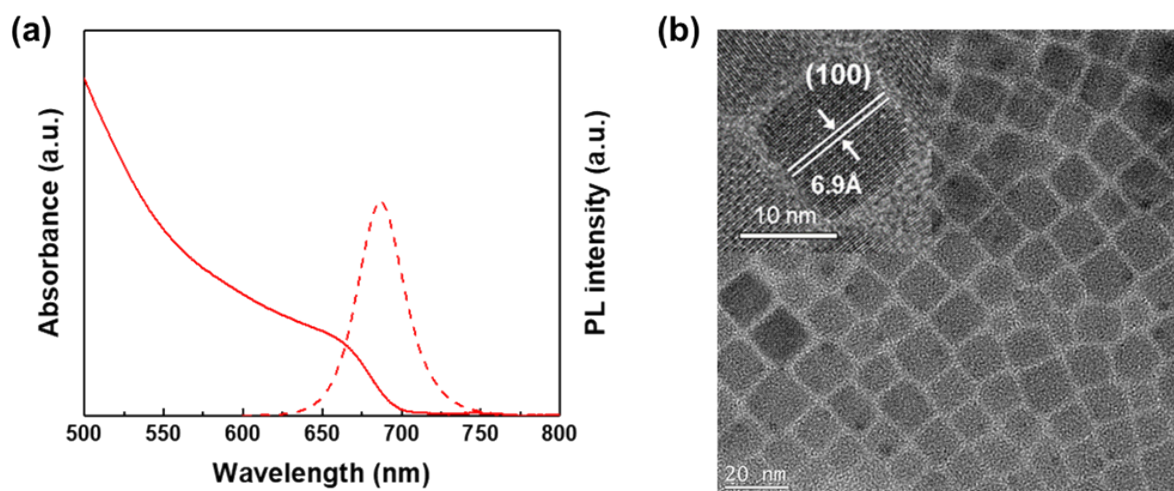
then rinsed using neat MeOAc. To prepare the spiro-OMeTAD solution, the 72.3 mg of spiro-OMeTAD was dispersed in 1 mL of chlorobenzene together with 28.8  $\mu\text{L}$  of 2-n pentylpyridine and 17.5  $\mu\text{L}$  of Li-TFSI solution in acetonitrile with a concentration 520  $\text{mg mL}^{-1}$ . For the flat CsPbI<sub>3</sub>-PQD solar cells, the prepared spiro-OMeTAD solution was spin-coated on the CsPbI<sub>3</sub>-PQD absorber for 30 and 1.2 s at 4000 rpm. For the back-side nanostructured CsPbI<sub>3</sub>-PQD solar cells, the spiro-OMeTAD solution was spin coated for 1.2 s at 4000 rpm, and immediately pressed using the PDMS mold for 2 min before the spiro-OMeTAD solution was completely solidified. Finally, 15 nm of MoO<sub>x</sub> and 120 nm of Ag electrodes were deposited using thermal evaporator.

**Solar cell measurement:** The total absorption (A) was calculated by  $A (\%) = 100 - R (\%) - T (\%)$  formula, where R is the total reflectance and T is the total transmittance. R and T were obtained using an Agilent Cary 5000 UV-Vis-NIR spectrophotometer with an integrating sphere. The current density-voltage ( $J$ - $V$ ) characteristics of solar cells were measured using a Newport Oriel Sol 3A solar simulator with a Keithley 2400 sourcemeter under air mass 1.5 (AM 1.5) and 100  $\text{mW cm}^{-2}$  (1 sun) illumination. The  $J$ - $V$  curves of the solar cells were obtained with reverse scan direction from 1.3 V to -0.05 V with active area of 0.096  $\text{cm}^2$ . External Quantum Efficiency (EQE) spectra were obtained using a Newport Oriel QuantaX-300 and Oriel Cornerstone 130 monochromator. The EQE spectra were measured from the 340 nm to 800 nm of wavelength range with 20 nm of wavelength step.

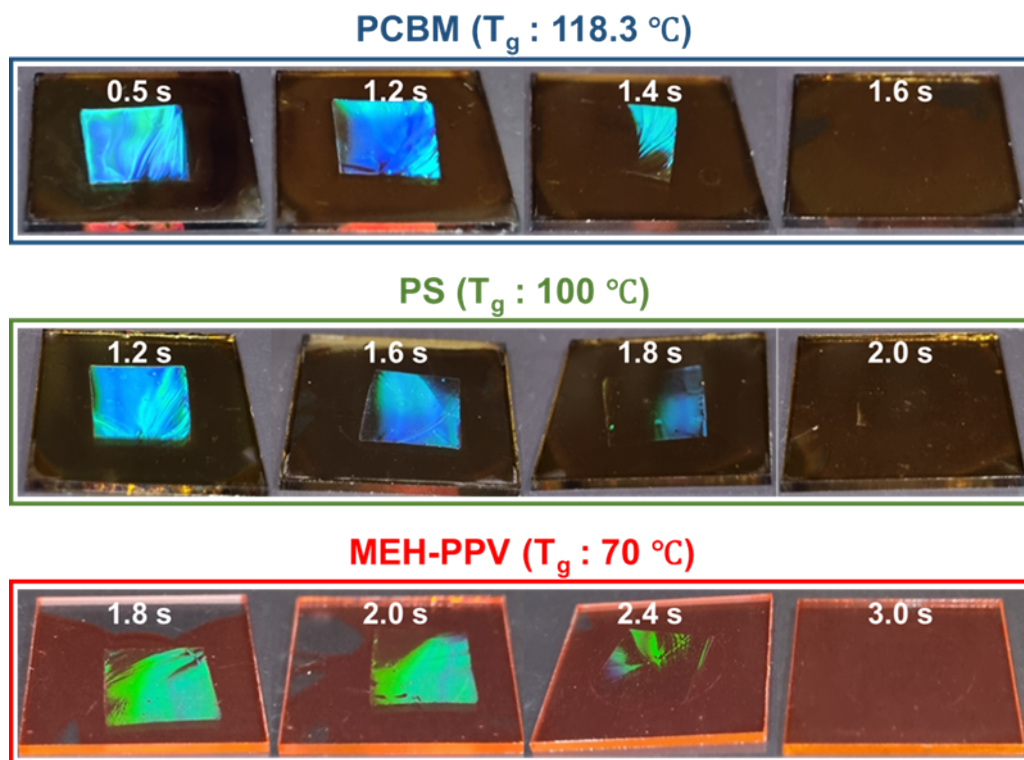
**FDTD simulations:** The optical calculations were performed using Lumerical FDTD solutions ([www.lumerical.com](http://www.lumerical.com)). For characterization, the optical parameters of all layers were extracted from previous works and ellipsometry measurements. The modelled device structure and the thickness of each layer were obtained by SEM images shown in Fig. 3. A linearly

polarized plane wave source (a wavelength ranging from 350 to 1100 nm) was irradiated to a unit structure. The modelled structure did not consider roughness and morphology of device.

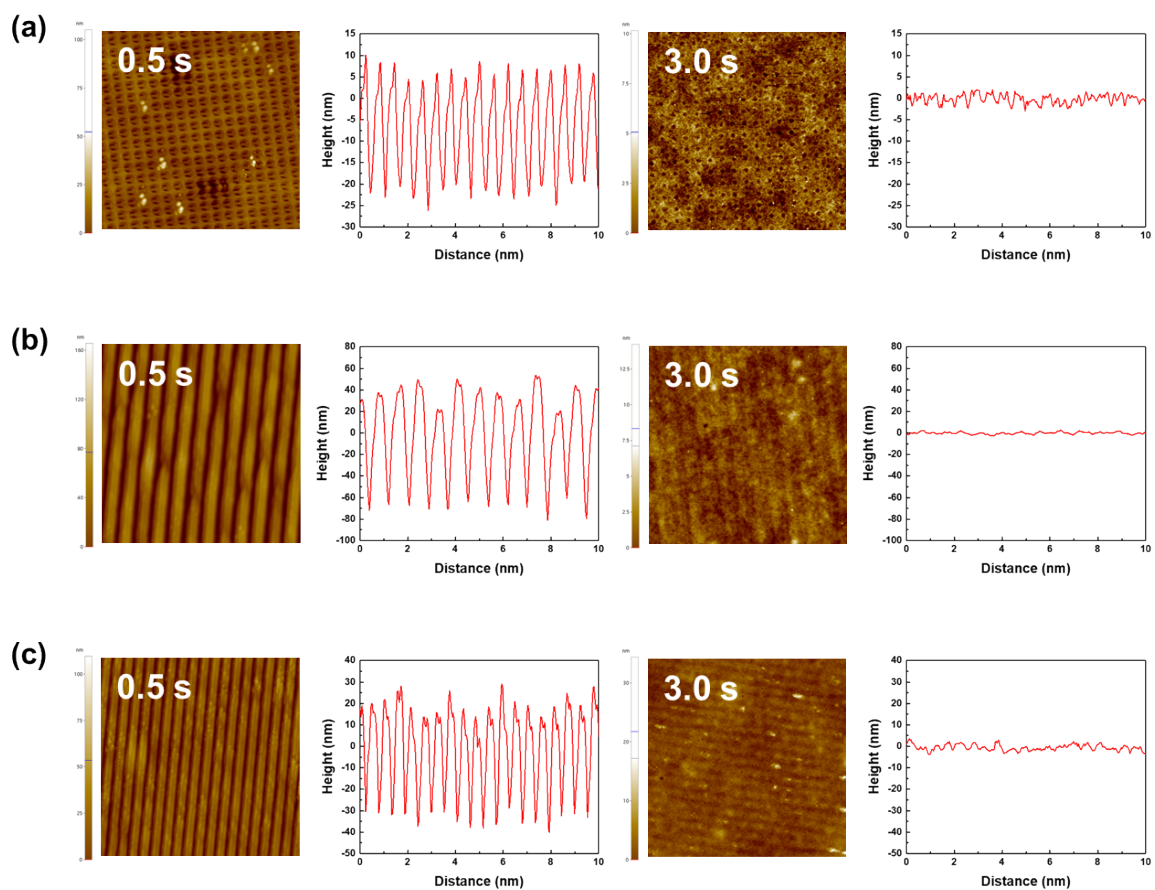
***Other characterization:*** Absorption and transmittance spectra were obtained using an Agilent Technologies/Cary 5000 UV-Vis-NIR spectrophotometer. Cross-sectional SEM images were acquired using Hitachi SU8230 ultra-high-resolution FE-SEM. AFM images and line profiles were measured using Park system XE-150 large sample microscope.



**Fig. S1.** (a) Solution-phase UV-Vis absorbance and PL spectra of CsPbI<sub>3</sub>-PQDs. (b) HR-TEM image of CsPbI<sub>3</sub>-PQDs.

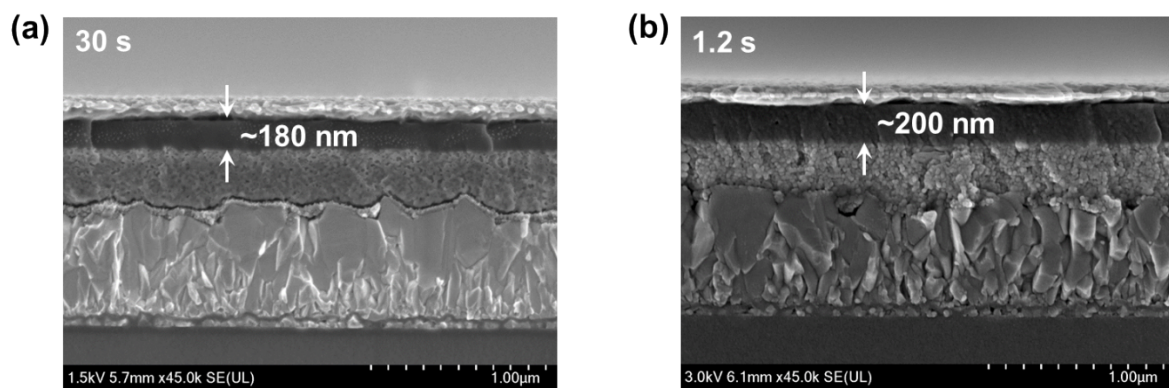


**Fig. S2.** Photographic images of PCBM, PS, and MEH-PPV thin films, performed nanoimprint soft lithography using P4 PDMS mold after spin-coating with different spin-coating time.

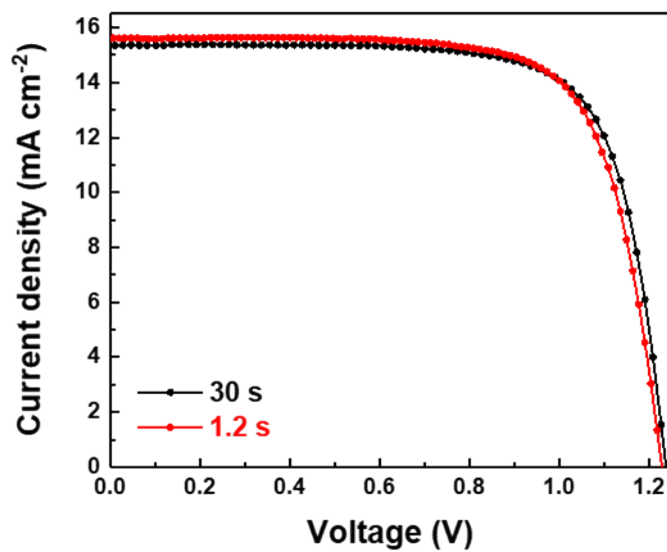


**Fig. S3.** AFM height images and line profiles of spiro-OMeTAD oligomer thin films performed nanoimprint soft lithography using (a) P1, (b) P2, and (c) P3 molds after spin-coating with the spin-coating time of 0.5 and 3.0 s, respectively.

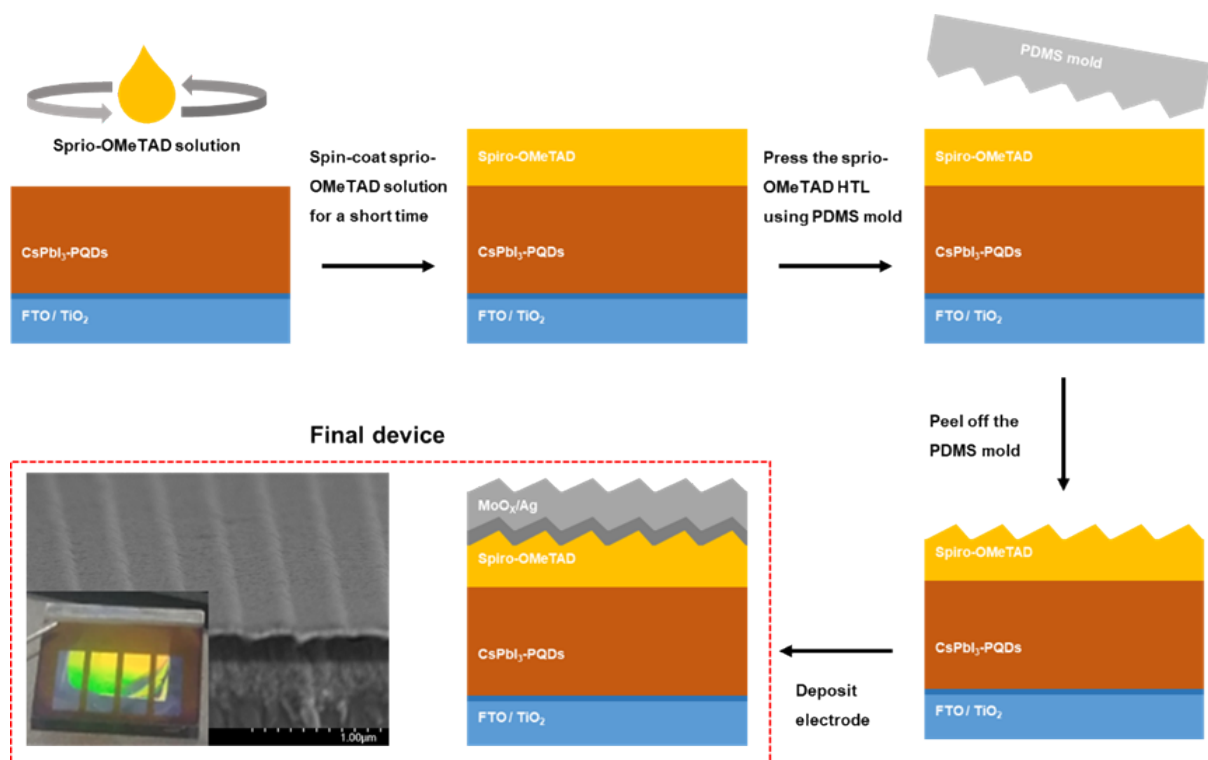




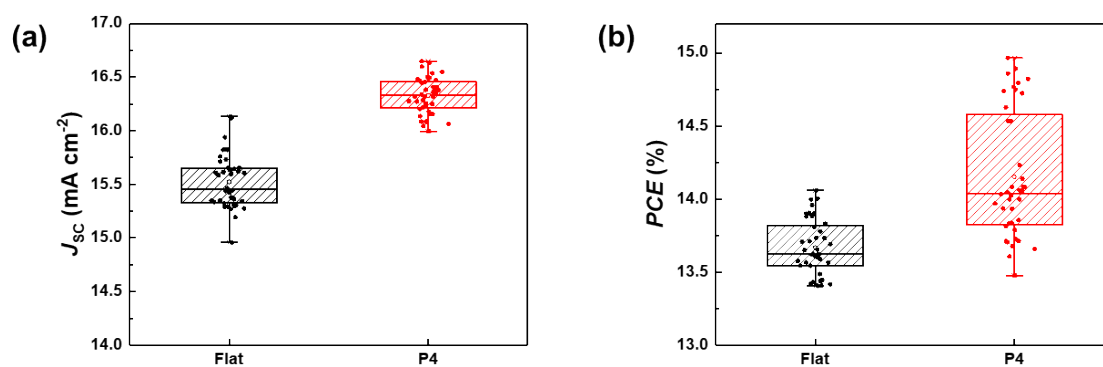
**Fig. S4.** Cross-sectional SEM images of the flat CsPbI<sub>3</sub>-PQD solar cells composed of spiro-OMeTAD HTLs, fabricated via spin-coating with different spin-coating time of (a) 30 and (b) 1.2 s.



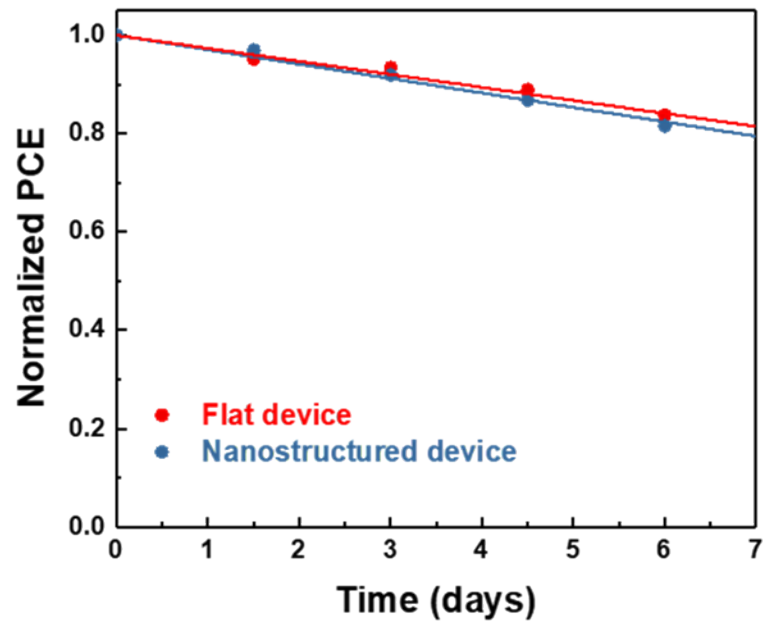
**Fig. S5.**  $J$ - $V$  curves of the flat CsPbI<sub>3</sub>-PQD solar cells composed of spiro-OMeTAD HTLs, fabricated via spin-coating with the spin-coating time of 30 and 1.2 s, respectively.



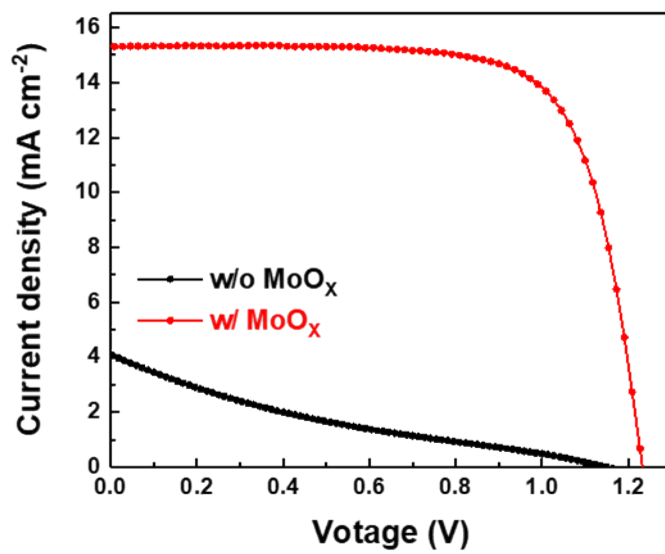
**Fig. S6.** Schematic diagram showing the nanostructure fabrication process of spiro-OMeTAD HTL using a nanoimprint soft lithography and their device completion.



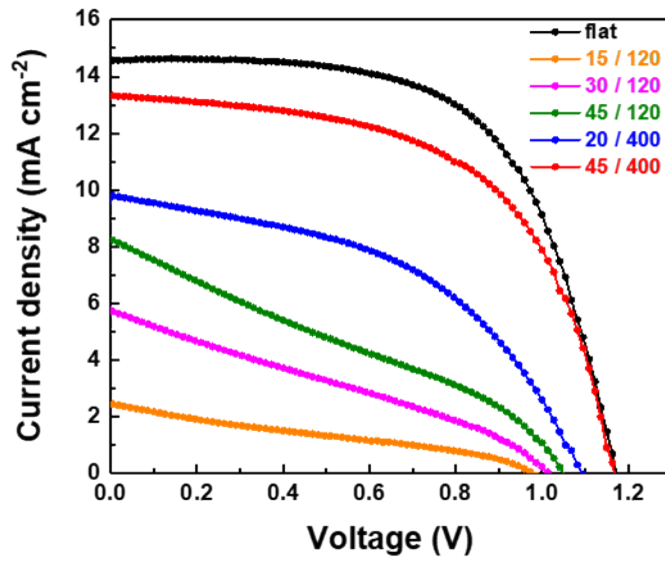
**Fig. S7.** Device histograms of each of 40 flat (black) and P4 nanostructured (red) CsPbI<sub>3</sub>-PQD solar cells, respectively: (a)  $J_{sc}$  and (b)  $PCE$ .



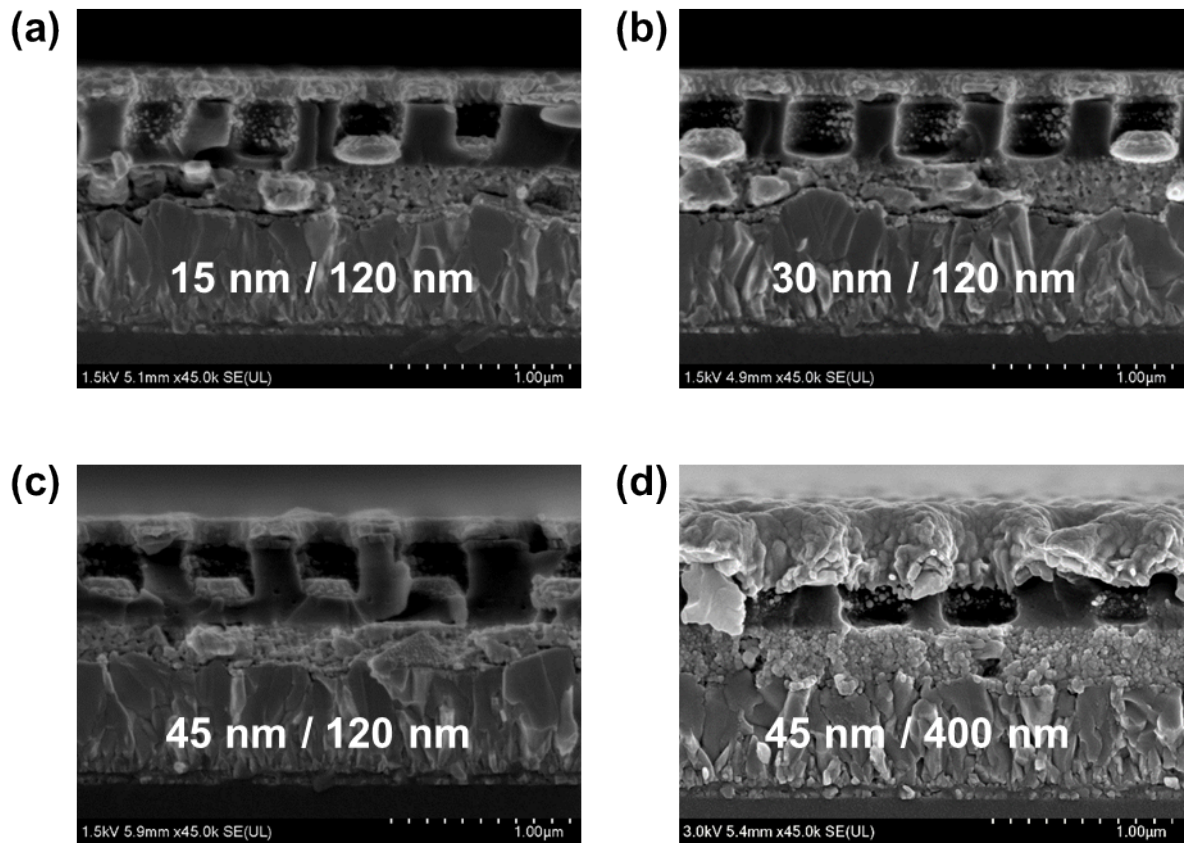
**Fig. S8.** Device stability of flat and P4 nanostructured CsPbI<sub>3</sub>-PQD solar cells stored under ambient condition with relative humidity ~20% for 7 days.



**Fig. S9.**  $J$ - $V$  curves of the flat CsPbI<sub>3</sub>-PQD solar cells with and without MoO<sub>x</sub> layer.



**Fig. S10.**  $J$ - $V$  curves of the P1 nanostructured CsPbI<sub>3</sub>-PQD solar cells with the different thickness of MoO<sub>x</sub> and Ag electrodes.



**Fig. S11.** Cross-sectional SEM images of the P1 nanostructured CsPbI<sub>3</sub>-PQD solar cells with the different thickness of MoO<sub>x</sub> and Ag electrodes: (a) 15 nm / 120 nm, (b) 30 nm / 120 nm, (c) 45 nm / 120 nm, and (d) 45 nm / 400 nm, respectively.



**Table S1.** PV performance parameters of the flat CsPbI<sub>3</sub>-PQD solar cells composed of spiro-OMeTAD, fabricated via spin-coating with spin-coating time of 30 and 1.2 s, respectively.

Spin-coating time (s)	$V_{OC}$ (V)	$J_{SC}$ (mA cm <sup>-2</sup> )	$FF$ (%)	$PCE$ (%)
30	1.24	15.3	74.3	14.1
1.2	1.23	15.6	73.3	14.1

**Table S2.** PV performance parameters and average values of each of 40 flat and P4 nanostructured CsPbI<sub>3</sub>-PQD solar cells.

		$V_{OC}$ (V)	$J_{SC}$ (mA cm <sup>-2</sup> )	$FF$ (%)	$PCE$ (%)
Flat	Champion	1.23	15.6	73.3	14.1
	Average	1.21 ± 0.02	15.5 ± 0.6	72.6 ± 3.3	13.7 ± 0.4
P4	Champion	1.22	16.5	74.7	15.0
	Average	1.21 ± 0.02	16.3 ± 0.3	71.4 ± 4.8	14.2 ± 0.8

**Table S3.** PV performance parameters of the flat CsPbI<sub>3</sub>-PQD solar cells with and without MoO<sub>x</sub> layer.

	$V_{OC}$ (V)	$J_{SC}$ (mA cm <sup>-2</sup> )	$FF$ (%)	$PCE$ (%)
w/o MoO <sub>x</sub>	1.14	4.1	17.8	0.8
w/ MoO <sub>x</sub>	1.23	15.3	72.9	13.8

**Table S4.** PV performance parameters of the P1 nanostructured CsPbI<sub>3</sub>-PQD solar cells with different thickness of MoO<sub>x</sub> and Ag electrodes.

Thickensses of MoO <sub>x</sub> (nm) / Ag (nm)	<i>V</i> <sub>OC</sub> (V)	<i>J</i> <sub>SC</sub> (mA cm <sup>-2</sup> )	<i>FF</i> (%)	<i>PCE</i> (%)
15 / 20 (P1)	0.97	2.5	29.2	0.7
30 / 120 (P1)	1.01	5.8	29.0	1.7
45 / 120 (P1)	1.04	8.3	29.8	2.6
20 / 400 (P1)	1.09	9.8	47.3	5.1
45 / 400 (P1)	1.17	13.3	57.8	9.0
45 / 400 (flat)	1.17	14.6	61.8	10.6