

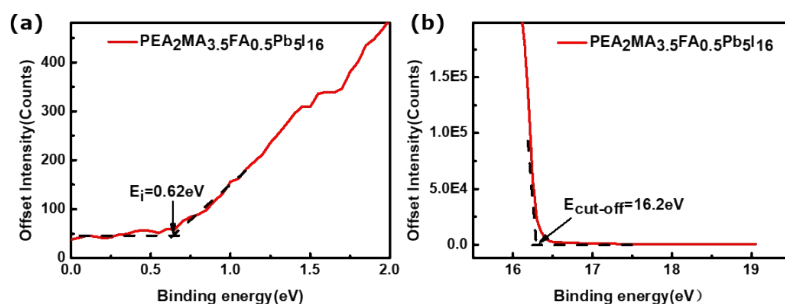
## Supporting Information

### Engineering the underlying surface to manipulate the growth of 2D perovskites for highly efficient solar cells

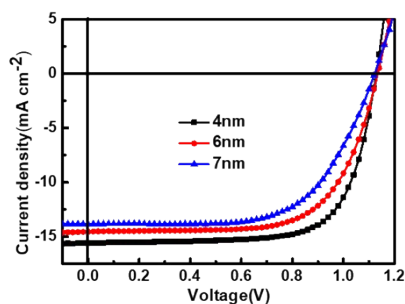
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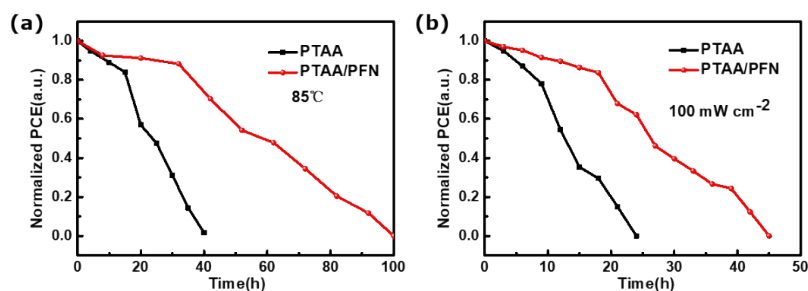
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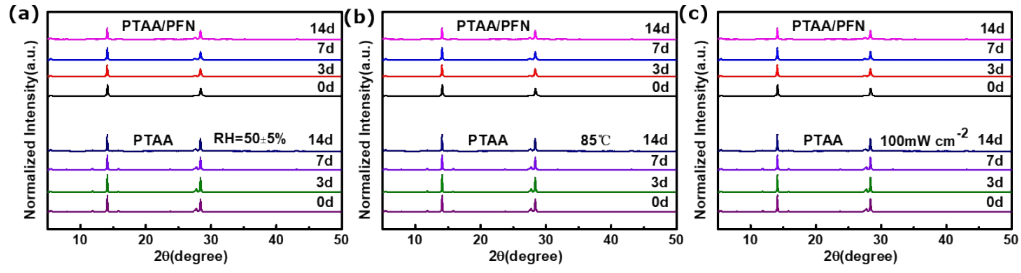
**Fig. S1** UPS in the onset ( $E_i$ ) (a) and the cutoff ( $E_{\text{cut-off}}$ ) (b) energy regions of the surface measurement for  $\text{PEA}_2\text{MA}_{3.5}\text{FA}_{0.5}\text{Pb}_5\text{I}_{16}$  perovskite films.



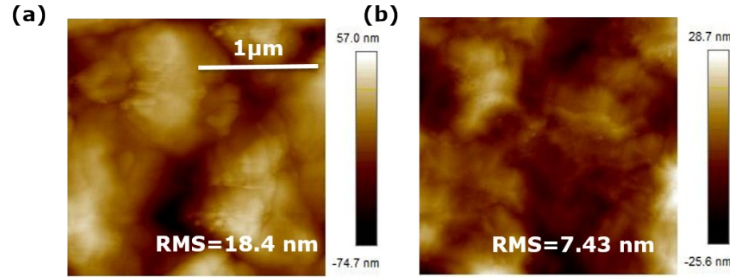
**Fig. S2**  $J$ - $V$  curves of the PVSCs with different thicknesses of PFN layer.



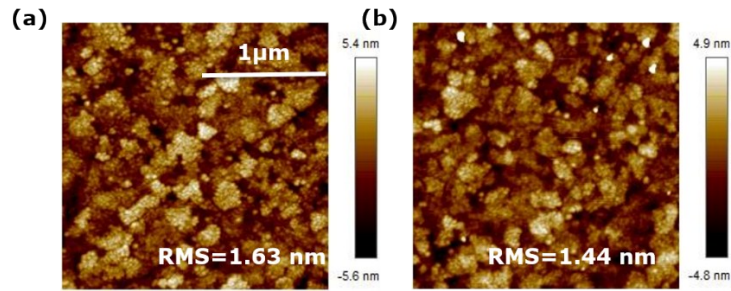
**Fig. S3** Thermal stability (a) and light stability (b) curves of the devices with and without PFN.



**Fig. S4** The XRD patterns of perovskite films before and after humidity (a), heat (b) and light (c) aging test.



**Fig. S5** Atomic force microscopy (AFM) images of perovskite films based on PTAA (a) and PTAA/PFN (b). The root-mean-square roughness (RMS) of perovskite films on the PTAA and PTAA/PFN are 18.4 nm and 7.43 nm, respectively, indicating the film on PTAA/PFN has a smoother surface, which is agreed well with the SEM images (**Fig. 3a** and **Fig. 3b**).



**Fig. S6** Atomic force microscopy (AFM) images of PTAA and PTAA/PFN substrates.

**Table S1** XRD pattern parameters of the perovskite films on PTAA and PTAA/PFN substrates.

Peak	(111)		(222)	
	Intensity (cps)	FWHM (°)	Intensity (cps)	FWHM (°)
PTAA	$1.75 \times 10^7$	0.24	$1.38 \times 10^7$	0.29
PTAA/PFN	$9.89 \times 10^6$	0.25	$5.25 \times 10^6$	0.31