

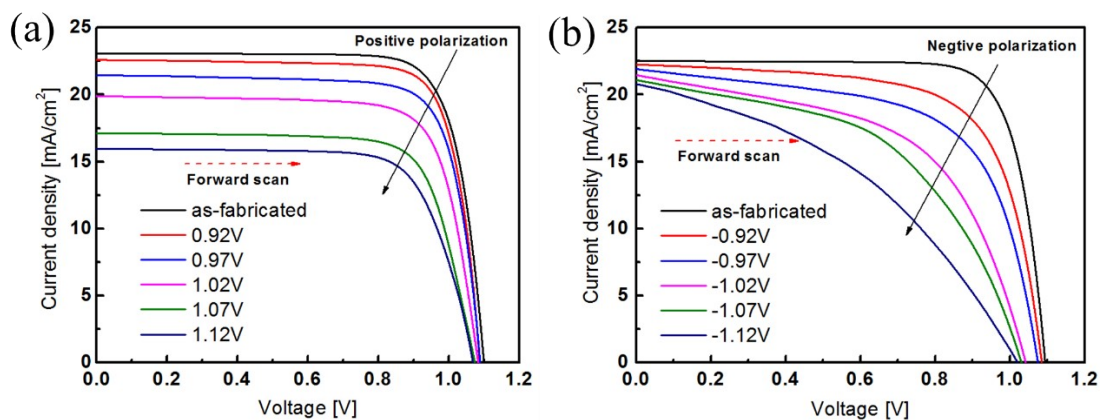
## Supplementary materials

**Table S1.** Photovoltaic electrical parameters of PSCs under positive polarizations, calculated from reverse scan.

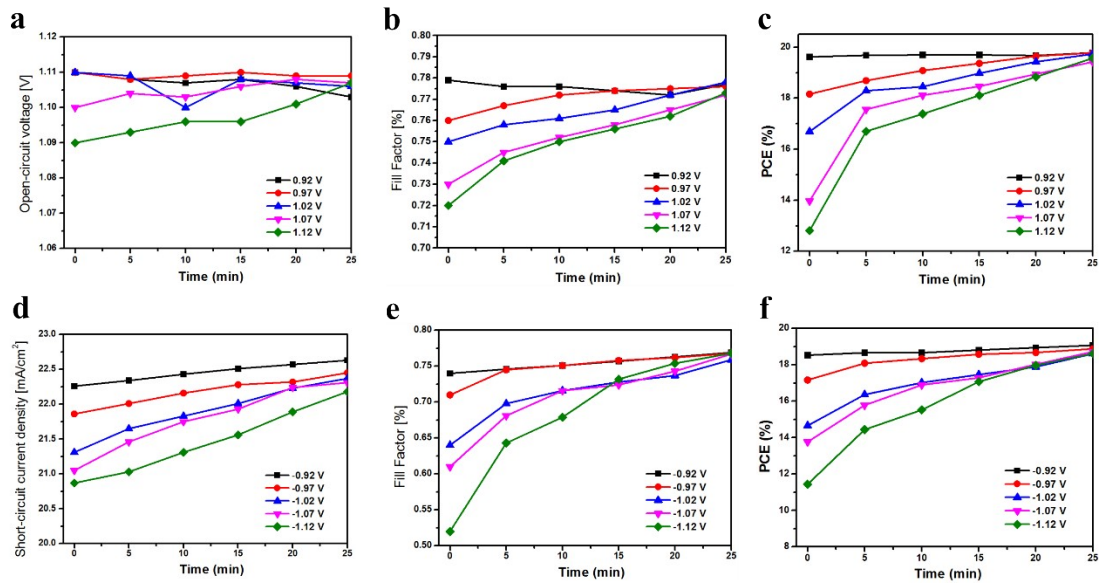
Poling conditions	$V_{oc}$ [V]	$J_{sc}$ [mA/cm <sup>2</sup> ]	FF [%]	PCE [%]
As-fabricated	1.11	23.15	77.3	19.86
+0.92V	1.11	22.69	78.0	19.64
+0.97V	1.11	21.53	76.8	18.52
+1.02V	1.11	20.05	74.8	16.65
+1.07V	1.10	17.41	72.7	13.93
+1.12V	1.09	16.32	71.6	12.85

**Table S2.** Photovoltaic electrical parameters of PSCs under negative polarizations, calculated from reverse scan.

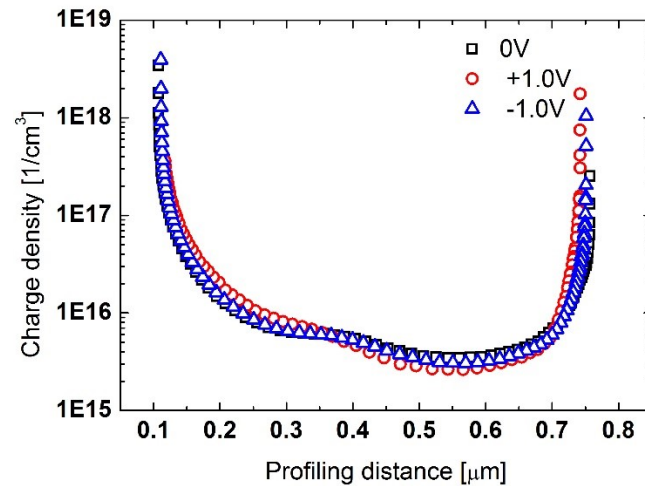
Poling conditions	$V_{oc}$ [V]	$J_{sc}$ [mA/cm <sup>2</sup> ]	FF [%]	PCE [%]
As-fabricated	1.10	22.70	77.2	19.28
-0.92V	1.13	22.27	73.7	18.55
-0.97V	1.11	21.86	70.5	17.11
-1.02V	1.08	21.31	63.8	14.68
-1.07V	1.08	21.05	60.5	13.92
-1.12V	1.05	20.87	52.0	11.39



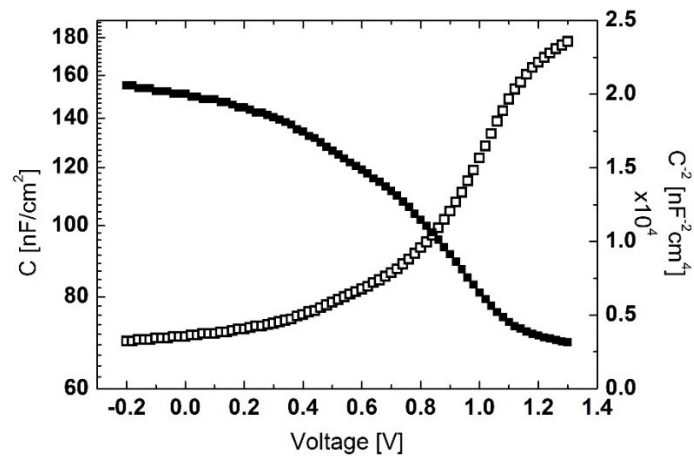
**Figure S1.** J-V curves during forward scan for positively-polarized devices (a) and negatively-polarized devices (b).



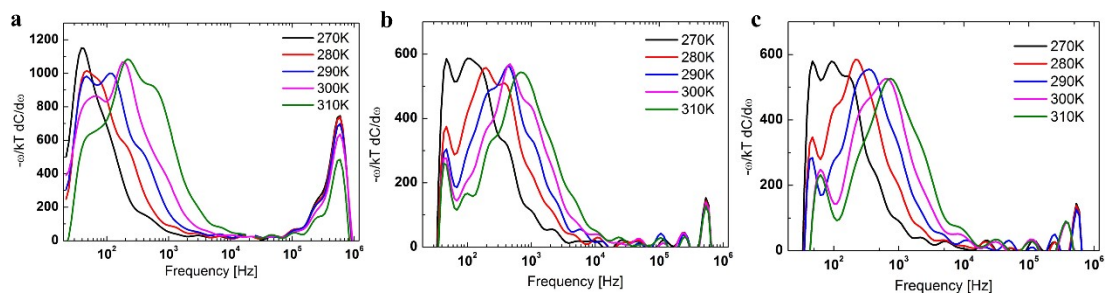
**Figure S2.** Performance recovery of positively-polarized PSCs (a-c); and negatively-polarized PSCs (d-f), calculated from reverse scan.



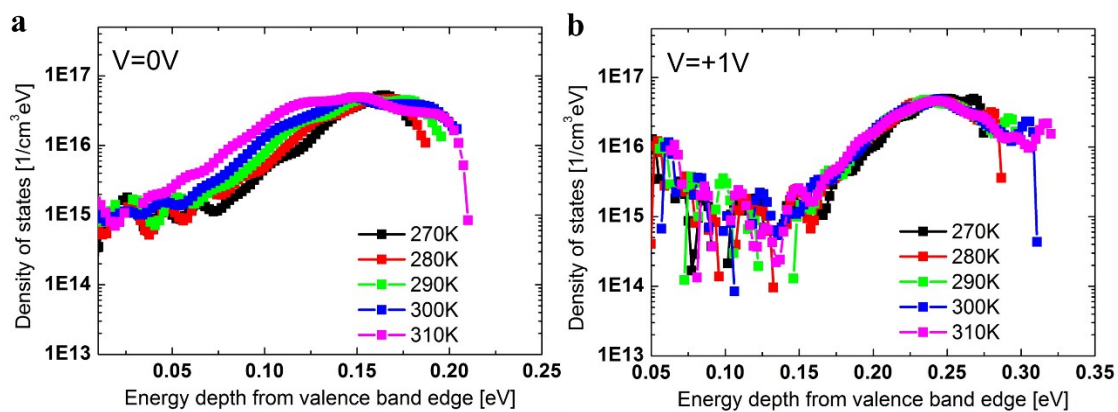
**Figure S3.** Charge density profile for PSCs under various polarizations.



**Figure S4.** Capacitance-voltage characteristics for PSCs measuring from -0.2V to 1.3V, showing full depletion conditions when  $C_{\text{dl}}$  equalizes  $C_{\text{g}}$  at forward bias. The full-depletion condition is achieved under short-circuit conditions.



**Figure S5.** Scaled derivate plot ( $-\omega/kT dC/d\omega$ ) as a function of a.c. signal frequency for PSCs under zero, +1.0V and -1.0V bias conditions.



**Figure S6.** Defect density of state profile for PSCs under zero bias a) and positive polarizations b).