## **Supporting Information**

## Interfacial defect passivation and stress release by multifunctional KPF<sub>6</sub> modification for planar perovskite solar cells with enhanced efficiency and stability

Huan Bi, Baibai Liu, Dongmei He, Le Bai, Wenqi Wang, Zhigang Zang\*, Jiangzhao Chen\* Key Laboratory of Optoelectronic Technology & Systems (Ministry of Education), College of Optoelectronic Engineering, Chongqing University, Chongqing 400044, China

Corresponding authors E-mail: zangzg@cqu.edu.cn E-mail: jiangzhaochen@cqu.edu.cn



Fig. S1. XPS survey spectra of the pristine  $SnO_2$  and the KPF<sub>6</sub>-modified  $SnO_2$ .



Fig. S2. UV–vis absorption spectra of the perovskite films spin-coated on the  $SnO_2$  without and with KPF<sub>6</sub> modification.



**Fig. S3.** AFM images of the perovskite films spin-coated on (a) SnO<sub>2</sub> and (b) SnO<sub>2</sub> modified by KPF<sub>6</sub>.



Fig. S4. Schematically illustrated diagram of the GIXRD measurement.



**Fig. S5.** GIXRD spectra of the perovskite deposited on  $SnO_2$  with  $\omega = 1.3^{\circ}$  and  $1.5^{\circ}$  to ensure penetration depth.



**Fig. S6.** FWHM statistics of the diffraction peaks corresponding to (211) crystal plane of the perovskite films without or with KPF<sub>6</sub>. FWHM stands for full width at half maxima.



**Fig. S7.** Mott–Schottky analysis at 1000 Hz of the devices based on SnO<sub>2</sub> and SnO<sub>2</sub> modified by KPF<sub>6</sub>.



**Fig. S8.** The equivalent circuit used for electrical impedance spectroscopy (EIS) analysis. The equivalent circuit is composed of series resistance ( $R_s$ ), transport resistance ( $R_{ct}$ ), recombination resistance ( $R_{rec}$ ), and constant phase element (*CPE*).



Fig. S9. *J-V* curves of the (a) control and (b) target devices measured in the reverse scan (RS) and forward scan (FS) at a scan rate of 100 mV/s under simulated AM 1.5G one sun illumination of 100 mW/cm<sup>2</sup>.



**Fig. S10.** Normalized (a)  $J_{SC}$ , (b)  $V_{OC}$ , and (c) FF as a function of time for the unencapsulated devices based on SnO<sub>2</sub> without and with KPF<sub>6</sub> modification exposed to the humidity of 15-20 RH% at room temperature in the dark.



**Fig. S11.** Normalized (a)  $J_{SC}$ , (b)  $V_{OC}$ , and (c) FF as a function of time for the unencapsulated devices based on SnO<sub>2</sub> without and with KPF<sub>6</sub> modification aged at 60 °C in the dark where the devices were located in the glove box filled with nitrogen.



**Fig. S12.** Normalized (a)  $J_{SC}$ , (b)  $V_{OC}$ , and (c) **FF** as a function of time for the unencapsulated devices based on SnO<sub>2</sub> without and with KPF<sub>6</sub> modification aged under one sun illumination at room temperature in the nitrogen-filled glove box.

Commiss	Direction	Glass side		PVSK side	
Samples		$ au_1$	$ au_2$	$ au_1$	$ au_2$
Glass/PVSK	$\tau$ (ns)	475.9	1519.2	488.7	1616.0
	%	38.58	61.42	19.36	80.64
	$\tau_{\rm ave}  ({\rm ns})$	1347.6		1539.7	
Class/VDE /DUCV	$\tau$ (ns)	513.4	2653.6	495.3	2288.9
Glass/KPF6/PVSK	%	21.24	78.76	27.12	72.88
	$\tau_{\rm ave} ({\rm ns})$	2547.5		2155.2	

Table S1. TRPL decay parameters of PSCs without or with KPF<sub>6</sub>.

	Glass/SnO <sub>2</sub> /PVSK	Glass/SnO <sub>2</sub> /KPF <sub>6</sub> /PVSK
$\tau_1$ (ns)	388.3	315.8
%	36.42	32.63
$\tau_2$ (ns)	1519.9	1053.9
%	63.58	67.37
$\tau_{ave}$ (ns)	1384.4	960.3

**Table S2.** Fitted results of TRPL curves of the perovskite films deposited on the  $SnO_2$  without or with KPF<sub>6</sub>.

 ETL
  $R_{\rm s}$  (Ω)
  $R_{\rm ct}$  (Ω)
  $R_{\rm rec}$  (Ω)

 SnO<sub>2</sub>
 6.00
 550
 530

 SnO<sub>2</sub>/KPF<sub>6</sub>
 4.43
 502
 843

Table S3. The fitted EIS parameters of the devices based on SnO<sub>2</sub> and SnO<sub>2</sub>+KPF<sub>6</sub> ETLs.

KPF <sub>6</sub> (mg/mL)		$J_{\rm SC}$ (mA/cm <sup>2</sup> )	$V_{\rm OC}\left({ m V} ight)$	FF	PCE (%)
0	Champion	22.38	1.100	0.798	19.66
	Average	22.43±0.07	1.093±0.005	0.797±0.004	19.58±0.12
0.05	Champion	22.73	1.121	0.803	20.49
	Average	22.57±0.05	1.112±0.004	0.803±0.002	20.15±0.14
0.1	Champion	22.83	1.145	0.818	21.39
	Average	22.92±0.09	1.128±0.006	0.812±0.002	21.05±0.15
0.15	Champion	22.86	1.120	0.805	20.57
	Average	22.61±0.10	1.120±0.003	0.804±0.002	20.17±0.15
0.2	Champion	22.34	1.111	0.804	19.96
	Average	22.12±0.11	1.109±0.004	0.801±0.002	19.81±0.10

**Table S4.** Photovoltaic parameters of the PSCs based on  $SnO_2$  modified with different concentrations of KPF<sub>6</sub> from 0 to 0.2 mg/mL. The statistical data were obtained from 20 individual cells for each kind of device.