

## Supporting Information

### **Increasing the Li-TFSI doping concentration in Spiro-OMeTAD enables efficient and stable perovskite solar cells**

Zhongquan Wan<sup>1,2\*</sup>, Runmin Wei<sup>2</sup>, Shaoliang Jiang<sup>1</sup>, Yuanxi Wang<sup>1</sup>, Haomiao Yin<sup>1</sup>,  
Huaibiao Zeng<sup>2</sup>, Muhammad Azam<sup>1</sup>, Junsheng Luo<sup>1,2\*</sup>, Chunyang Jia<sup>1,2\*</sup>

<sup>1</sup>National Key Laboratory of Electronic Films and Integrated Devices, School of Integrated Circuit Science and Engineering, University of Electronic Science and Technology of China, 611731 Chengdu, P. R. China

<sup>2</sup>Shenzhen Institute for Advanced Study, University of Electronic Science and Technology of China, 518110 Shenzhen, P. R. China

\*Correspondence to: [zqwan@uestc.edu.cn](mailto:zqwan@uestc.edu.cn), [luojs@uestc.edu.cn](mailto:luojs@uestc.edu.cn), [cyjia@uestc.edu.cn](mailto:cyjia@uestc.edu.cn)

## Materials preparation

FAI (99.99%), MABr (99.99%),  $\text{PbI}_2$  (99.99%),  $\text{PbBr}_2$  (99.99%), Spiro-OMeTAD, and 4-tert-butylpyridine (tBP) were purchased from Xi'an Polymer Light Technology Corp. The N,N-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), bis(trifluoromethane)sulfonimide lithium salt (Li-TFSI) and chlorobenzene (CB) were purchased from Sigma-Aldrich. 12-crown-4 was purchased from Aladdin. All chemicals and solvents were obtained from commercial sources with certified purity and used as received without further purification.

Perovskite precursor was prepared by dissolution 1097.20 mg of  $\text{PbI}_2$ , 154.14 mg of  $\text{PbBr}_2$ , 380.24 mg of FAI and 43.68 mg of MABr in 2 mL DMF and DMSO (the volume ratio of 4:1) mixing solution. 103.92 mg of CsI was dissolved in 200  $\mu\text{L}$  DMSO. After fully stirring the two solution, 68  $\mu\text{L}$  CsI precursor was added to the perovskite precursor solution and then continued stirring.

Spiro:Li-TFSI/tBP solution: Dissolved 72.3 mg of Spiro-OMeTAD in 1 mL of chlorobenzene, then add 28.8  $\mu\text{L}$  of tBP and 17.5  $\mu\text{L}$  of Li-TFSI solution (104 mg of Li-TFSI in 200  $\mu\text{L}$  of acetonitrile) and stirred constantly. Spiro:Li-TFSI/12-crown-4 solution: Dissolved 72.3 mg of Spiro-OMeTAD and 17.5  $\mu\text{L}$  of Li-TFSI solution (104 mg of Li-TFSI in 200  $\mu\text{L}$  of acetonitrile) in 1 mL of chlorobenzene, then added 12-crown-4 by desired 12-crown-4/Spiro-OMeTAD ratio of 40 mol% (mole ratios with respect to the repeat unit mass). All tests related to the Spiro-OMeTAD solution without specified test conditions in the main text, as well as the HTL used in the best-performing devices, were prepared using Spiro-OMeTAD solution that had been fully oxidized under light and oxygen for twenty days.

## Device fabrication

Glass/FTO substrates were cleaned with isopropyl alcohol, ethyl alcohol and deionized water in an ultrasonic bath for 30 min, respectively, and then dried by flowing nitrogen gas.  $\text{TiO}_2$  electron transport layers of about 60 nm thickness were deposited

on FTO substrates using a chemical bath. And then the FTO/TiO<sub>2</sub> substrates were exposed to ultraviolet light and ozone for 15 min. The perovskite film was deposited on the treated FTO/c-TiO<sub>2</sub>/m-TiO<sub>2</sub> substrates by spin-coating filtered perovskite precursor at the speed of 1300 rpm for 10 seconds and 5000 rpm for 45 seconds. During the process of spin-coating, 200  $\mu$ L CB was dropped at the center of the substrates at the last 15 seconds, and then followed by 110 °C heating for 60 minutes. The HTL was spin-coated on the surface of perovskite films with the speed of 3000 rpm for 30 seconds. All of these aforementioned steps were operated in the nitrogen-filled glove box. In the end, the Au electrode was deposited by vacuum thermal evaporation, and the active area is 0.09 cm<sup>2</sup> for each PSC.

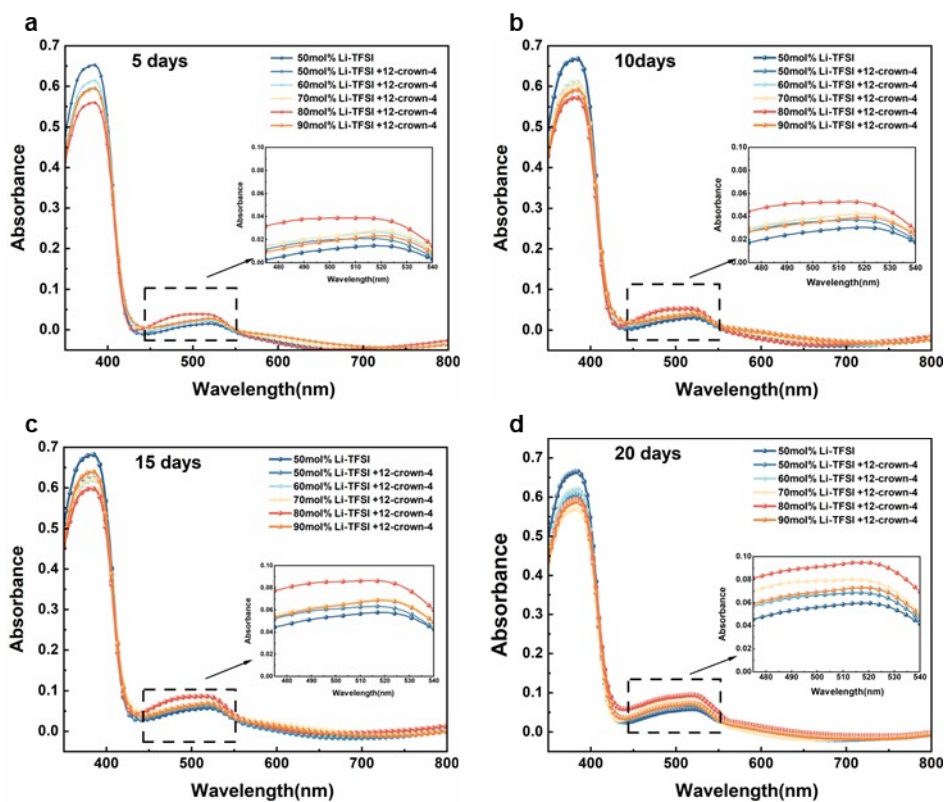
## Characterizations

The surface and cross-sectional morphologies of perovskite films were observed by scanning electron microscope (SEM) analysis (JEOL JSM-7600F). The X-ray diffraction measurement (XRD) was performed by Panalytical X' Pert PRO with Cu K $\alpha$  radiation. Water-contact angles of Spiro:Li-TFSI/tBP and Spiro:Li-TFSI/12-crown-4 fresh films were examined by drop shape analyzer (Krüss DSA100), and the testing time of the two contact angles is the same. The photovoltaic and EIS analysis were performed by using electrochemical workstation (CHI 760E, Shanghai Chenhua) and solar simulator (Sirius-SS150A-D, Zolix Instruments Co. Ltd., Beijing, China) in ambient air condition. The voltage sweep range of current-voltage characteristics is 0~1.2 V, the sweep speed is 0.2 V/s, and the dwell time is 2 s. Before analysis, the light source was precisely calibrated by standard Si solar cell. The EIS data was fitted by Z-View equivalent circuit. The external quantum efficiency (EQE) spectra were recorded by QTest Station2000 IPCE Measurement System (CROWNTECH, USA). The ultraviolet photoemission spectroscopy (UPS) measurements were performed by ThermoFisher ESCALAB 250Xi. The electron spin resonance (ESR) spectroscopy of Spiro:Li-TFSI/tBP and Spiro:Li-TFSI/12-crown-4 solutions were performed by Brooke A300. The atomic force microscope (AFM) measurements were performed by Bruker

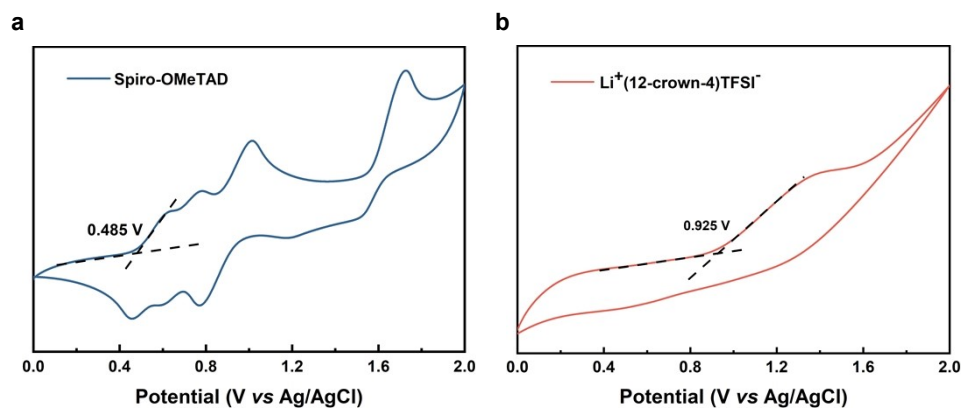
Dimension Icon. The steady-state photoluminescence (PL) spectra were measured by HITACHI (model F-4600) spectrophotometer with the excitation wavelength of 460 nm. The time-resolved PL (TRPL) spectra were measured at room temperature using of time-correlated single photon counting (TCSPC) technique with an excitation wavelength of 474 nm and an emission wavelength of 785 nm. The instrument for TRPL measurement was FluoroLog-3 Modular spectrofluorometer (HORIBA Jobin Yvon).



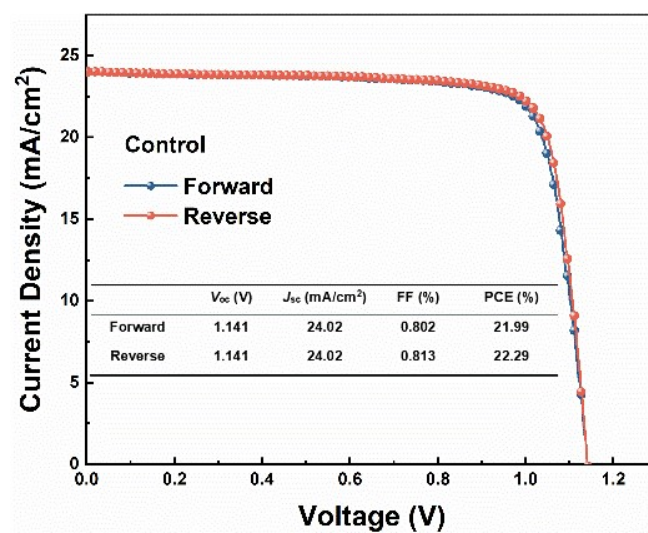
**Figure S1.** The color changes of the Spiro solutions doped with different concentrations of Li-TFSI.



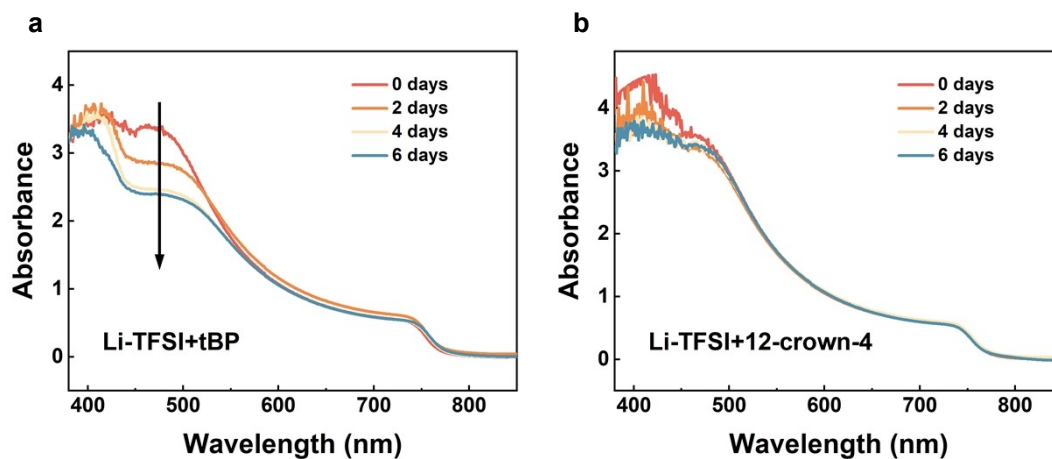
**Figure S2.** UV-vis absorption spectra of the Spiro films doped with Li-TFSI/tBP and Li-TFSI/12-crown-4 at different time periods.



**Figure S3.** Cyclic voltammetry measurements of Spiro and the Li<sup>+</sup>(12-crown-4)TFSI<sup>-</sup> complex

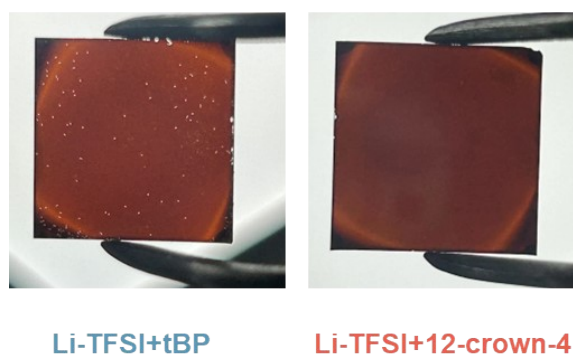


**Figure S4.** *J-V* curves of control PSC based on Spiro:50mol% Li-TFSI/tBP under forward and reverse scans.

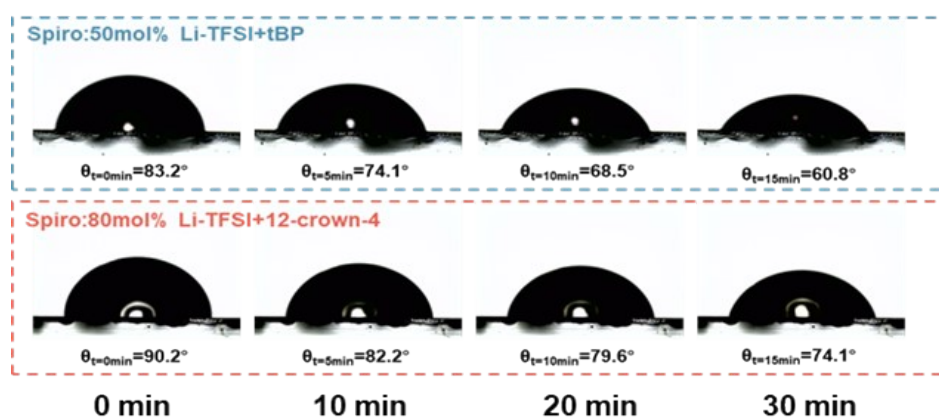


**Figure S5.** Time-dependent UV-vis measurements for PVK/HTL films under the irradiation and aerobic environment.

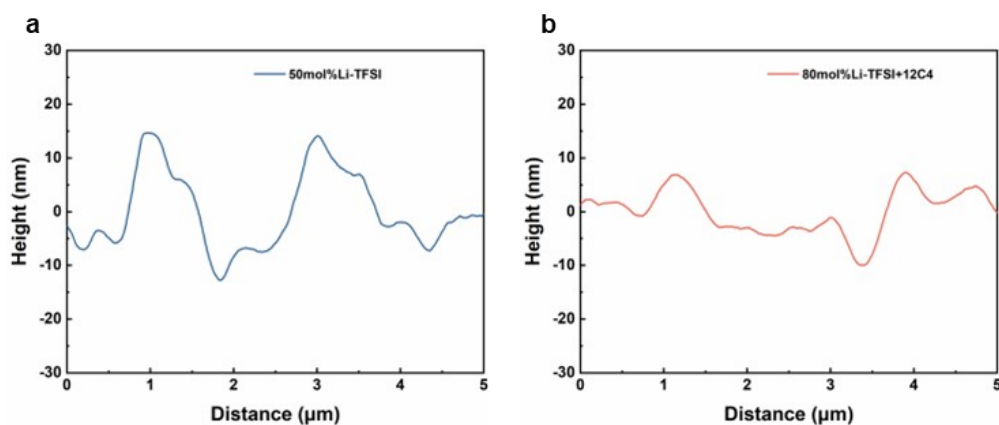
**Room temperature RH=25%±5**



**Figure S6.** Optical photographs of the perovskite films covered with Spiro:50mol% Li-TFSI/tBP and Spiro:80mol% Li-TFSI/12-crown-4 after 30 days of aging at room temperature and RH=25±5%.

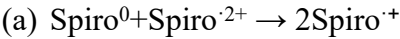


**Figure S7.** Water contact angles of Spiro:50mol% Li-TFSI/tBP and Spiro:80mol% Li-TFSI/12-crown-4 films.



**Figure S8.** Cross-section statistics for the same location of AFM images of the perovskite films covered with (a) Spiro:50mol% Li-TFSI/tBP and (b) Spiro:80mol% Li-TFSI/12-crown-4.





$$(b) \text{Standardized absorption ratio of Li-TFSI (SAR}_{\text{Li-TFSI}}) = \frac{A_{524\text{nm}}}{A_{407\text{nm}}}$$

**Scheme S1.** (a) Single step disproportionation reaction of doped Spiro. (b) Calculation formula of standardized absorption ratio of Li-TFSI.

$$J = \frac{4}{8} \frac{\epsilon_0 \epsilon_r u V^2}{L^3}$$

**Scheme S2.** Calculation formula of hole mobility.

**Table S1.** The fitting parameters of TRPL.

Simple	A <sub>1</sub>	τ <sub>1</sub> (ns)	A <sub>2</sub>	τ <sub>2</sub> (ns)	τ <sub>ave</sub> (ns)
PVK	0.003	5.691	0.445	84.208	84.17
PVK+Spiro+50mol% Li-TFSI	1.295	4.800	0.171	50.434	31.32
PVK+Spiro+80mol% Li-TFSI+12-crown-4	1.311	4.383	0.223	31.342	19.09

$$\tau_{ave} \text{ (ns) was calculated according to the formula : } \tau_{ave} = \frac{A_1 \tau_1^2 + A_2 \tau_2^2}{A_1 \tau_1 + A_2 \tau_2}$$

**Table S2.** The photovoltaic parameters of the PSCs.

	$V_{oc}$ (V)	$J_{sc}$ (mA/cm <sup>2</sup> )	FF (%)	PCE (%)
Control	1.141	24.02	0.813	22.29
50mol% Li-TFSI +12-crown-4	1.144	24.30	0.820	22.83
60mol% Li-TFSI +12-crown-4	1.152	24.33	0.823	23.10
70mol% Li-TFSI +12-crown-4	1.154	24.34	0.837	23.51
80mol% Li-TFSI +12-crown-4	1.167	24.49	0.839	23.99
90mol% Li-TFSI +12-crown-4	1.145	24.22	0.760	21.10