

## Supplementary Information

### Replacing Li<sup>+</sup> in Li-TFSI with benzene ring: Constructing non-ionic p-dopant for stable and efficient perovskite solar cells

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#### 1. Experimental procedures

##### Materials preparation

FAI (99.99%), MABr (99.99%), PbI<sub>2</sub> (99.99%), PbBr<sub>2</sub> (99.99%), PTAA, 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. **Ph-TFSI was purchased from Sigma-Aldrich.** 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 PbI<sub>2</sub>, 154.14 mg of PbBr<sub>2</sub>, 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. A 103.92 mg of CsI was dissolved in 200 μL DMSO.

After fully stirring of the two solution, 68  $\mu\text{L}$  CsI precursor was added to the perovskite precursor solution and then continue stirring. PTAA: Li-TFSI/tBP solution: dissolved 15 mg of PTAA in 1 mL of chlorobenzene, then add 7.5  $\mu\text{L}$  of 4-tert-butyl pyridine and 7.5  $\mu\text{L}$  of lithium bis(trifluoromethanesulfonyl)imide (Li-TFSI) solution (34 mg of Li-TFSI in 200  $\mu\text{L}$  of acetonitrile) and stirred constantly. PTAA: Ph-TFSI solution: dissolved 15 mg of PTAA in 1 mL of chlorobenzene, then added Ph-TFSI by desired Li-TFSI ratios of 15 mol% (mole ratios with respect to the repeat unit mass).

### **Perovskite solar cells 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/ $\text{TiO}_2$  substrates were exposed to ultraviolet light and ozone for 15 min.

The perovskite film was deposited on the treated FTO/ $\text{TiO}_2$  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  $\mu\text{L}$  chlorobenzene was dropped at the center of the substrates at the last 18 seconds, and then followed by 110  $^\circ\text{C}$  heating for 60 minutes to complete the phase transition process. Then, the HTM solution was deposited onto the perovskite layer by spin-coating at 3000 rpm for 30 s. Finally, 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  $\text{cm}^2$  for each device.

### **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  $\text{Cu K}\alpha$  radiation. Water-contact angles of PTAA: Li-TFSI/tBP and PTAA: Ph-TFSI fresh films were examined by drop shape analyzer (Krüss DSA100), and the test 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 incident photon-to-electron conversion efficiency (IPCE) was recorded by QTest Station2000 IPCE Measurement System (CROWNTECH, USA). The ion distribution of devices was measured by time of flight-second ion mass spectrometry (TOF.SIMS 5, ION-TOF GmbH, Germany). The ultraviolet photoemission spectroscopy (UPS) measurements were performed by ThermoFisher ESCALAB 250Xi. The electron spin resonance (ESR) spectroscopy of PTAA: Li-TFSI/tBP and PTAA: Ph-TFSI 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).

### **DFT calculations**

The molecular geometry optimization of Ph-TFSI was calculated by Dmol3 program and PBE-GGA base set.

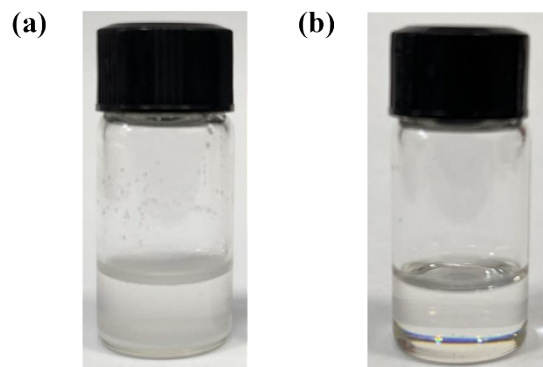


Figure S1. The dissolution of Li-TFSI (a) and Ph-TFSI (b) in chlorobenzene.

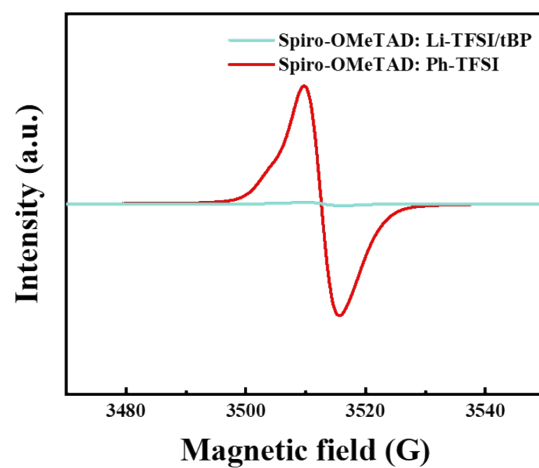


Figure S2. The ESR spectra of Li-TFSI/tBP and Ph-TFSI doped Spiro-OMeTAD solution.

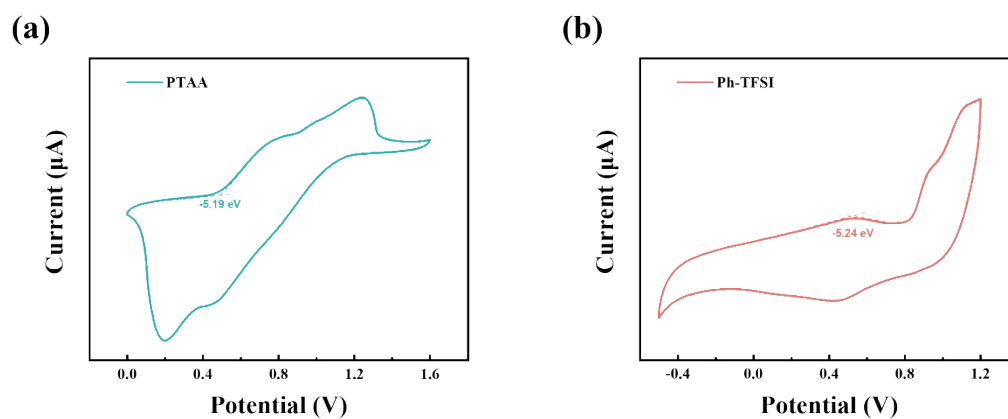


Figure S3. Cyclic voltammograms of PTAA (a) and Ph-TFSI (b).

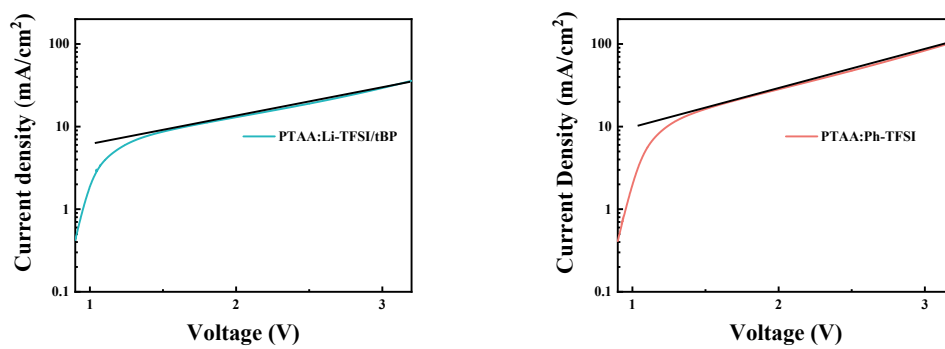


Figure S4.  $J$ - $V$  curves for the hole only devices using the SCLC method.

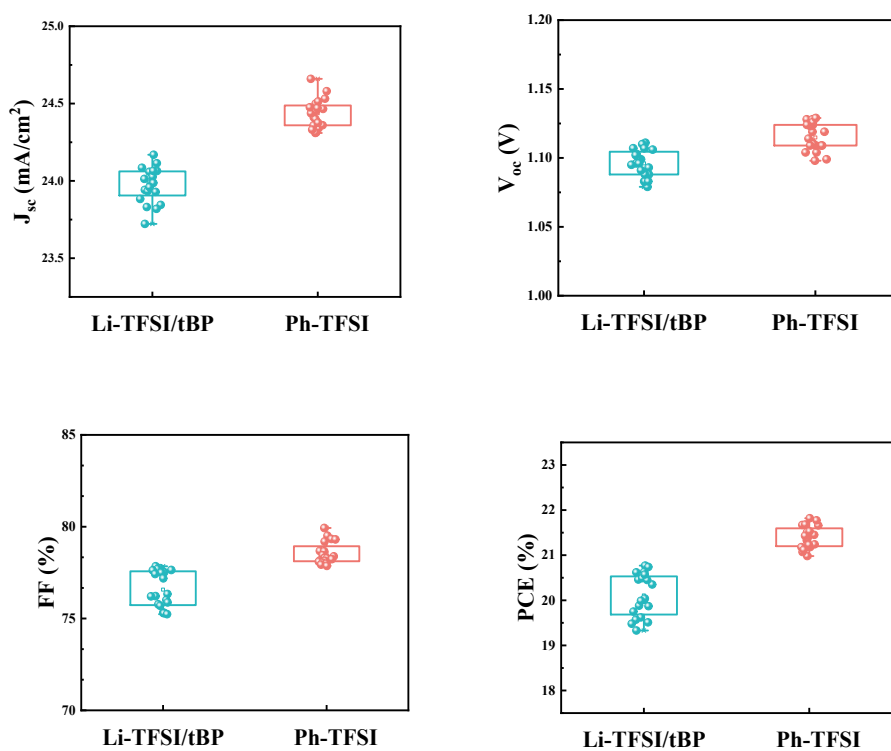


Figure S5. The  $J_{sc}$ ,  $V_{oc}$ , FF and PCE of 20 PSCs with PTAA:Li-TFSI/tBP and PTAA:Ph-TFSI.

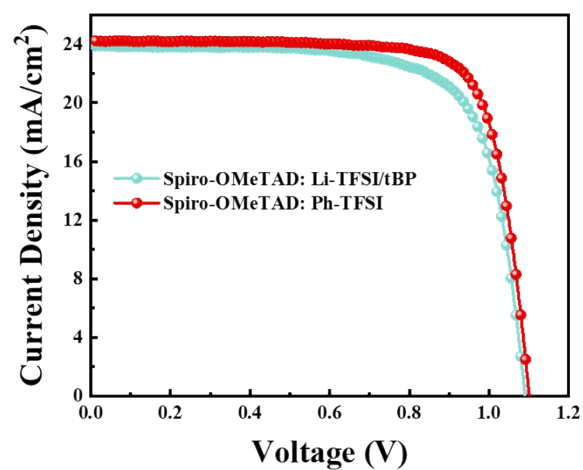


Figure S6. The  $J$ - $V$  curves of champion efficiencies of PSCs based on Spiro-OMeTAD:Ph-TFSI and Spiro-OMeTAD:Li-TFSI/tBP.

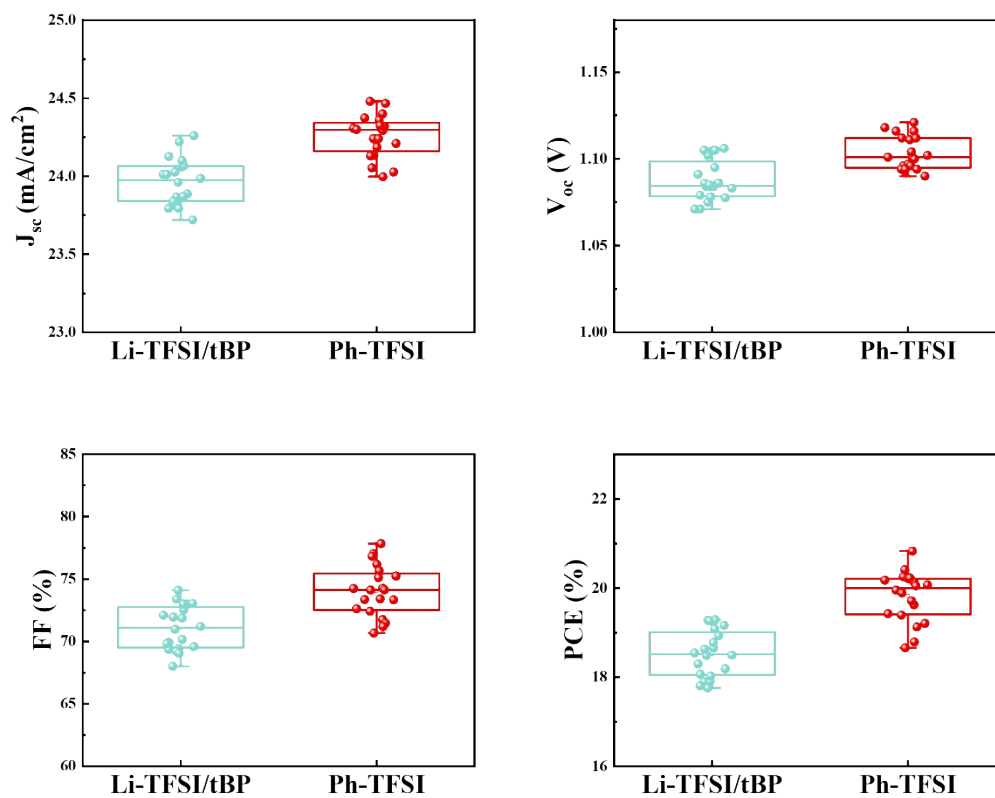


Figure S7. The  $J_{sc}$ ,  $V_{oc}$ , FF and PCE of 20 PSCs with Spiro-OMeTAD:Li-TFSI/tBP and Spiro-OMeTAD:Ph-TFSI.

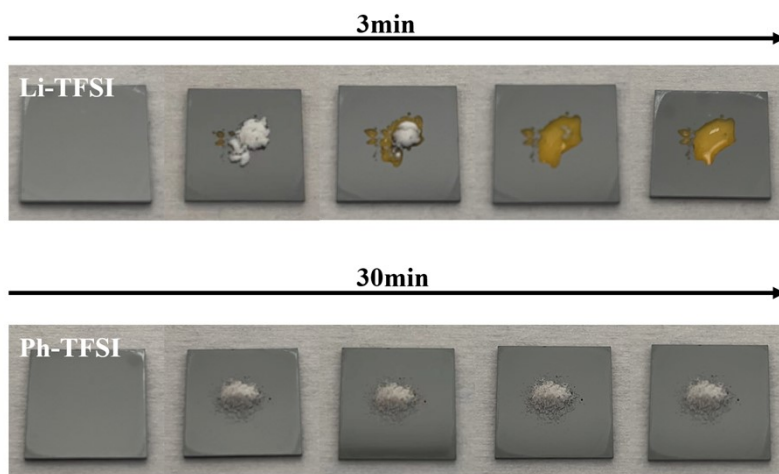


Figure S8. The water absorption test of Li-TFSI and Ph-TFSI molecules.

Table S1. The fitting parameters of TRPL.

	$A_1$	$t_1$ (ns)	$A_2$	$t_2$ (ns)	$A_3$	$t_3$ (ns)	$\tau_{ave}$ (ns)
PVK	0.223	22.77986	3.20373	1.62142	0.03382	302.67042	157.1
PVK/PTAA: Li-TFSI/tBP	2.24898	1.89853	0.30261	12.82301	0.05873	122.11574	76.2
PVK/PTAA: Ph-TFSI	0.61229	5.4885	12.14755	0.77244	0.089	89.19186	27.4

$\tau_{ave}$  (ns) was is calculated according to the equation:

$$\tau_{ave} = \frac{A_1 t_1^2 + A_2 t_2^2 + A_3 t_3^3}{A_1 t_1 + A_2 t_2 + A_3 t_3}$$

Table S2. The  $J-V$  detailed data of PSCs based on PTAA doped with Ph-TFSI.

	$V_{oc}$ (V)	$J_{sc}$ (mA cm <sup>-2</sup> )	FF (%)	PCE (%)
ref	1.099	24.16	0.777	20.64
10 mol%Ph-TFSI	1.103	24.00	0.778	20.61
15 mol%Ph-TFSI	1.124	24.51	0.792	21.82
20 mol%Ph-TFSI	1.109	24.29	0.783	21.09
25 mol%Ph-TFSI	1.083	24.06	0.753	19.62