

## Supporting Information for

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## **Experimental section**

### ***Materials***

All reagents were used as received without further purification. The SnO<sub>2</sub> aqueous colloidal precursor (tin (IV) oxide 15% in H<sub>2</sub>O colloidal dispersion, Alfa Aesar). PbI<sub>2</sub> (99.999%, Advanced Election Technology Co. Ltd), FAI (99.999%, Advanced Election Technology Co., Ltd), MAI (≥99.5%, Xi'an Polymer Light Technology Corp.), Butylamine (99.5%, Xi'an Polymer Light Technology Corp), MACl (99.5%, Xi'an Polymer Light Technology Corp), 2, 2', 7, 7'-Tetrakis[N, N-di(4-methoxyphenyl)amino]-9, 9'-spirobifluorene (Spiro-OMeTAD, ≥99%, Shenzhen Feiming Science and Technology Co., Ltd), Isopropanol (IPA, 99.5%, Sigma-Aldrich), dimethylformamide (DMF, >99.9%, Sigma-Aldrich), dimethyl sulfoxide (DMSO, >99.9%, Sigma-Aldrich), Bis (trifluoromethane) sulfonimide lithium salt (Li-TFSI, ≥99%, Sigma-Aldrich), 4-tert-Butylpyridine(4-tBP, 98%, Sigma-Aldrich). ITO substrate (10 Ω, Advanced Election Technology Co. Ltd).

### ***Synthesis of butylamine bis(trifluoromethyl)sulfonylimine (BATFSI) ionic liquids***

Butylamine (0.268 g, 3.67 mmol) and HTFSI (1.03 g, 3.49 mmol) were mixed and stirred for 12 h to obtain the resulting ionic liquid (1.30 g). The ionic liquid was used after evaporation under reduced pressure using a rotary evaporator.

### ***Perovskite Solar Cells Preparation***

ITO substrates were sequentially washed with deionized water, ethyl alcohol, and then again with ethyl alcohol in an ultrasonic bath for 30 min, and which was further treated with UV/ozone (UVO) for 20 min before use. The SnO<sub>2</sub> film was spin-coated onto the ITO using a commercial SnO<sub>2</sub> colloidal solution (3% diluted with water) at 3500 rpm for 25 s, and then annealed at 150°C for 30 min in ambient air. A 30 μL PbI<sub>2</sub> solution (1.5 M mol/L PbI<sub>2</sub> in DMF:DMSO = 9:1) was spin-coated onto SnO<sub>2</sub> at 1500 rpm

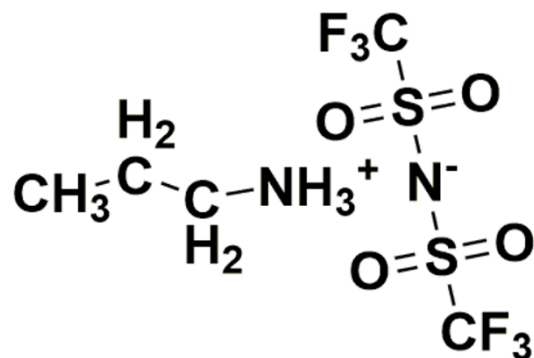
for 30 s, and then annealed at 70°C for 1 min. Subsequently, a 30  $\mu$ L organic salt solution (0.468 M mol/L FAI: 0.41 M mol/L MAI: 0.133 M mol/L MACl in IPA) was spin-coated at 2000 rpm for 30 s and then annealed with a two-step program: at 30°C for 5 min and at 150°C for 15 min, respectively. The hole transfer materials were deposited by preparing a Spiro-OMeTAD chlorobenzene solution (750 mg/mL) and mixing it with 28.8  $\mu$ L 4-tBP, 17.5  $\mu$ L Li-TFSI (520 mg/mL in acetonitrile). The BATFSI solution (10 mg/mL in IPA) was added to the hole transfer materials at volume ratios of 1%, 2%, and 3%, respectively. The Spiro-OMeTAD film was spin-coated onto the perovskite film at 1,000 rpm for 10 s and then at 3,500 rpm for 20 s. Finally, 100 nm thick silver layers were deposited using a thermal evaporator.

### ***Characterization***

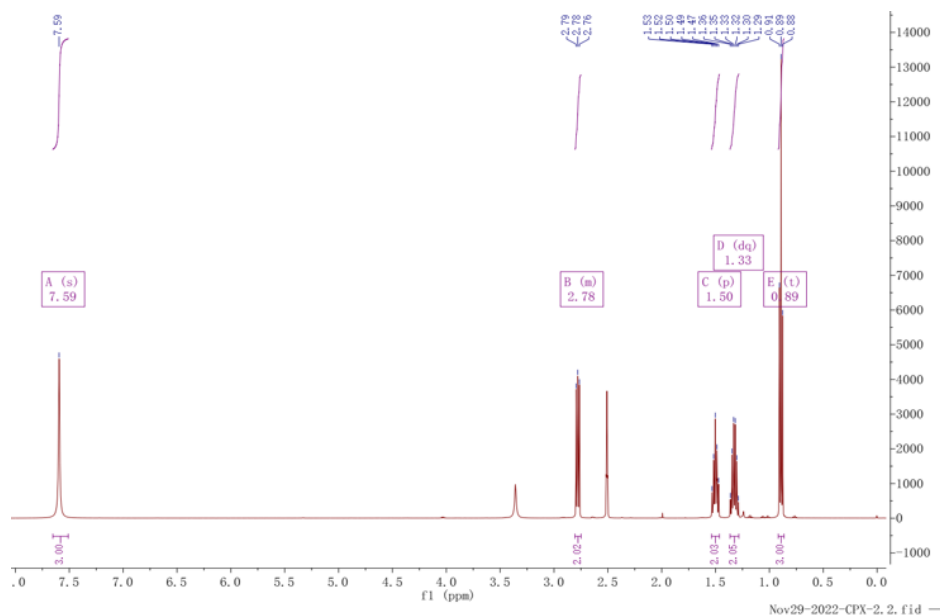
The Scan electron microscope pictures were taken with FE-SEM (JSM-7610F Plus, Japan). The surface roughness and contact potential difference of the HTL were measured using high-resolution atomic force microscopy (AFM) on a Bruker Multimode-8 system from the USA. An intelligent mode with a scan rate of 0.977 Hz was applied. X-ray photoelectron spectra (XPS) and ultraviolet photoelectron spectroscopy (UPS) were measured by X-ray photoelectron spectrometer (Thermo Fisher Scientific K-Alpha<sup>+</sup>, U.K.). UV-vis absorption spectra were measured by UV-vis spectrometer (PerkinElmer Lambda 950, USA). The ESR measurements were carried out with an X-band spectrometer (JEOL RESONANCE JES-FA200, Japan). The conductivity of the HTL was measured by the four-point probe (Tektronix 4200A-SCS, China). X-ray diffraction (XRD) spectra were tested by X-ray powder diffractometer (Smart Lab, Japan). The Time-resolved fluorescence spectroscopy (TRPL) spectra and steady-state PL were measured by Multifunctional fluorescence spectrum measurement system (OmniFluo-510HQ, China) using an excitation wavelength of 350 nm. The photocurrent density-

voltage (J–V) curves were measured with a light intensity of  $100 \text{ mW}\cdot\text{cm}^{-2}$  (AM 1.5G) which was calibrated by a silicon reference cell certificated by NREL. The Electrochemical Workstation (China) recorded impedance spectroscopy with a bias voltage of 0 V and the Z-View program calculated and analyzed the data. The EQE spectra were obtained using a quantum efficiency measurement system (RR0121013, QE-R, Eclitech, China). Long-term stability tests were measured with an RH of 35% and a temperature of 25 °C.

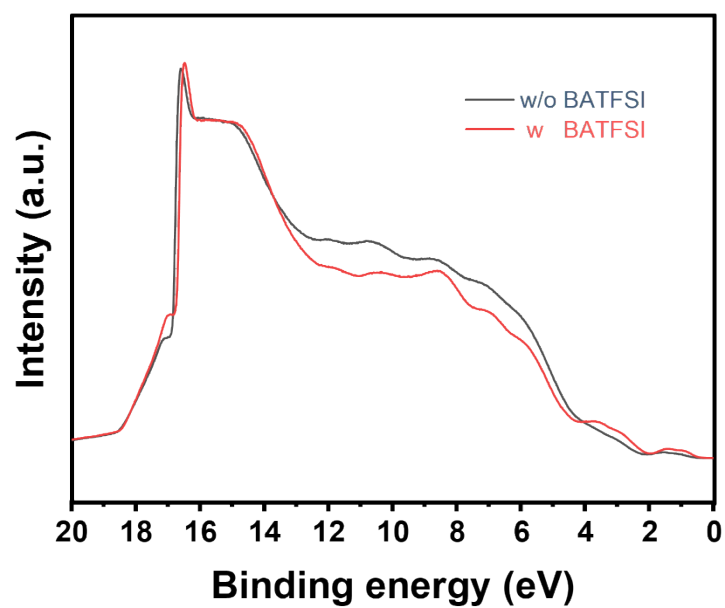
## Figure S1~S12



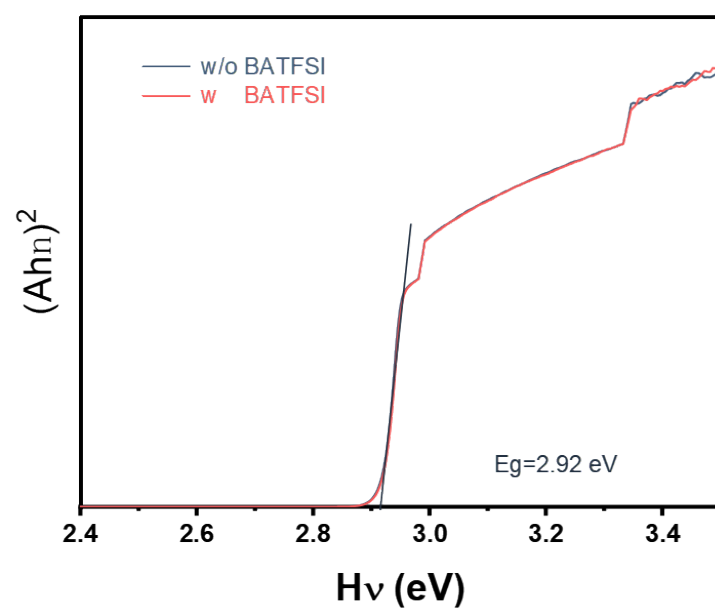
**Figure S1.** Chemical structure of butylamine bis(trifluoromethyl)sulfonylimine (BATFSI)



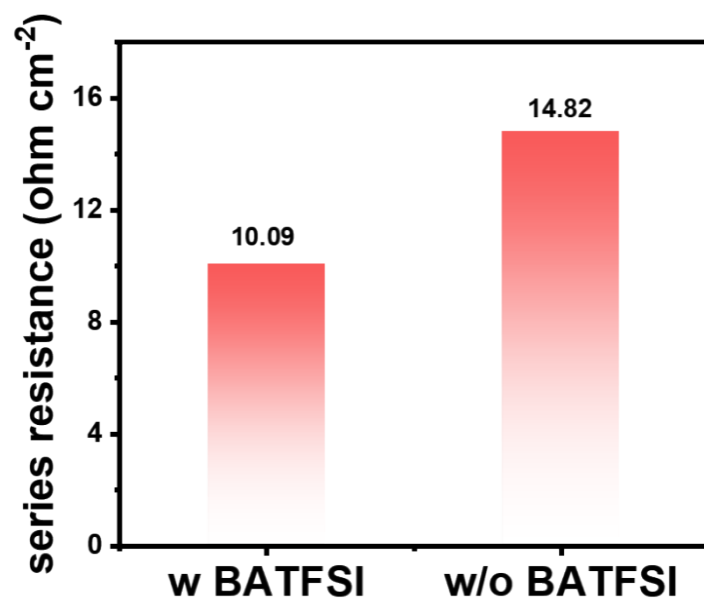
**Figure S2.**  $^1\text{H}$  NMR (500 MHz,  $\text{DMSO-}d_6$ )  $\delta$  7.59 (s, 3H), 2.81 – 2.75 (m, 2H), 1.50 (p,  $J = 7.5$  Hz, 2H), 1.33 (dq,  $J = 14.6, 7.3$  Hz, 2H), 0.89 (t,  $J = 7.4$  Hz, 3H) of BATFSI.



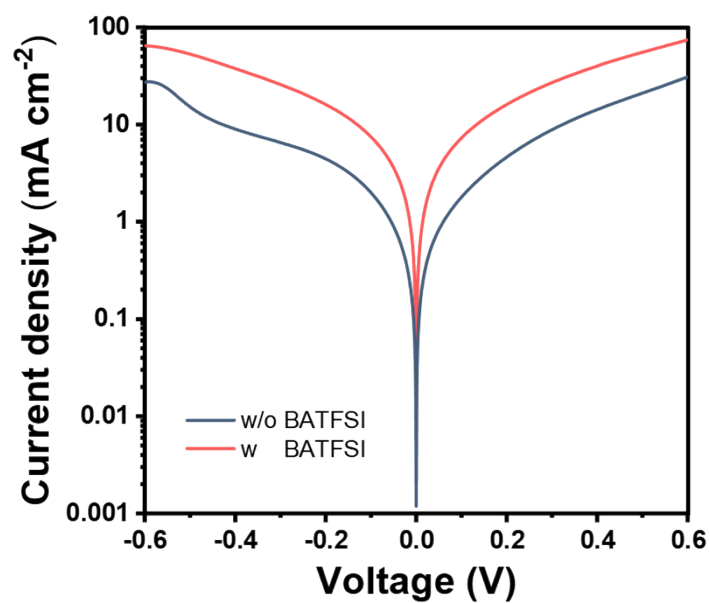
**Figure. S3** The UPS broad spectra of PVK films.



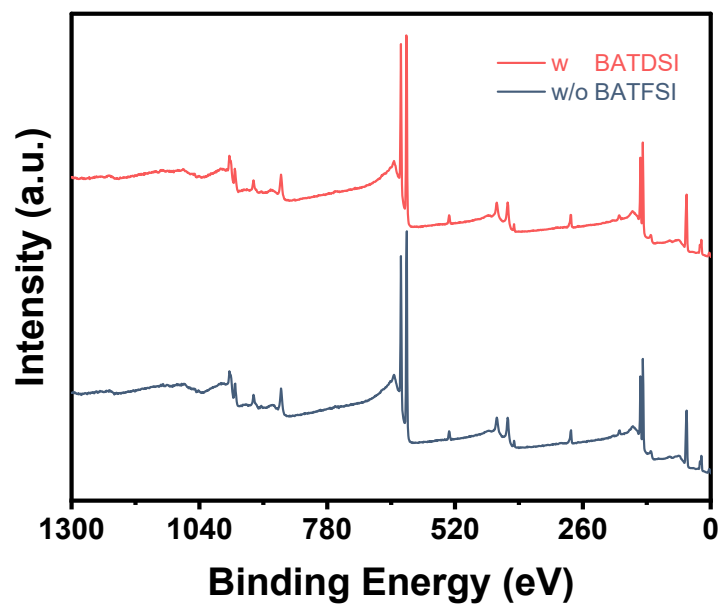
**Figure S4.** Tauc plots were used to estimate the optical bandgap ( $E_g$ ) of the spiro-OMeTAD with and without BATFSI from absorption spectra.



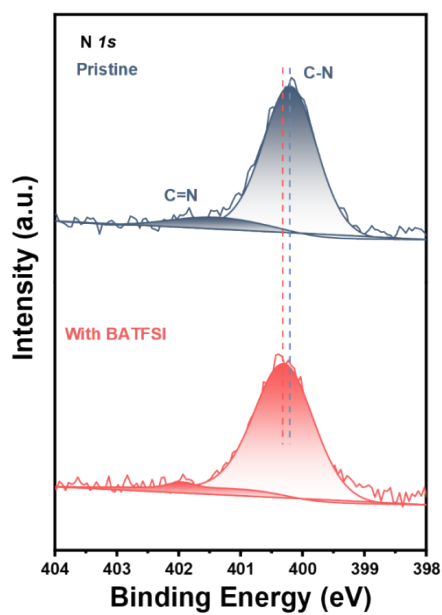
**Figure S5.** Four-point probe conductivity measurements with structures of ITO/HTL (with LiTFSI doped or BATFSI and LiTFSI co-doped)/Ag.



**Figure S6.** Tafel plots with structures of ITO/HTL (with LiTFSI doped or BATFSI and LiTFSI co-doped)/Ag.

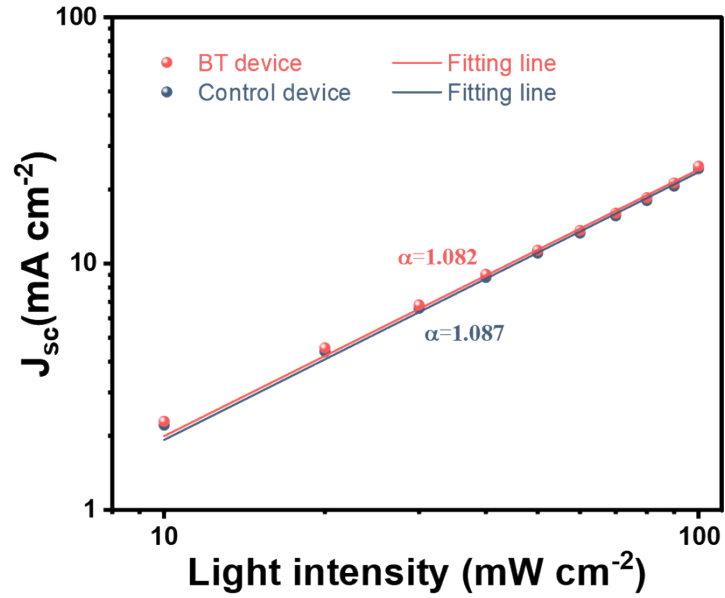


**Figure S7.** The XPS broad spectra of the PVK/HTL samples were rinsed with chlorobenzene.

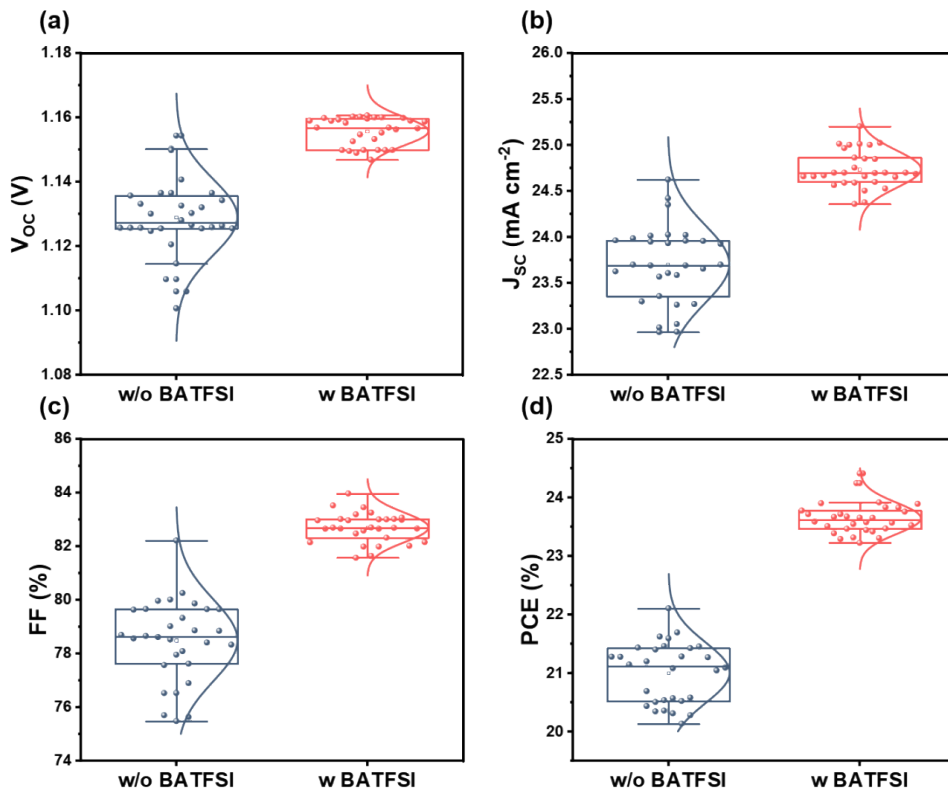


**Figure S8.** XPS measurements of the feature peak of N 1s for perovskites after removing the HTLs with and without BATFSI.

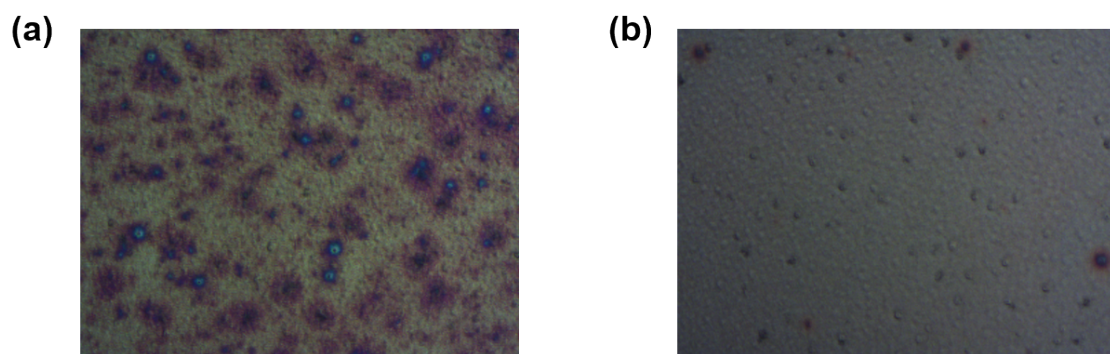




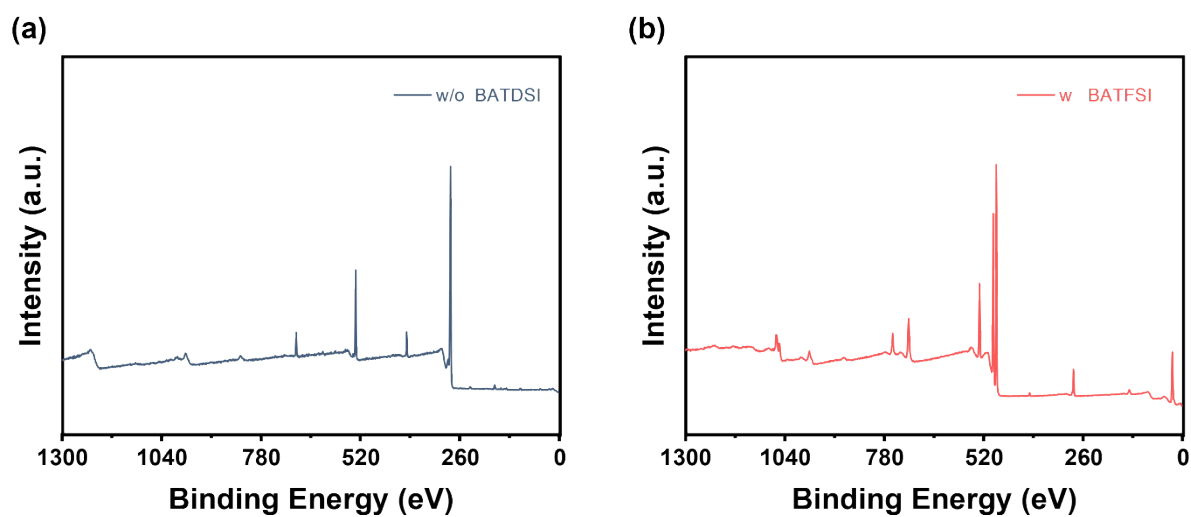
**Figure S9.** Light-dependent  $J_{SC}$  measurements of the device with and without BATFSI.



**Figure S10.** The statistics of (a)  $V_{OC}$ , (b)  $J_{SC}$ , (c) FF and (d) PCE distribution for devices without and with BATFSI.



**Figure S11.** Optical micrographs of the PVK/HTL films of (a) LiTFSI doped and (b) BATFSI and LiTFSI co-doped.



**Figure S12.** The XPS broad spectra of the PVK/HTL samples were rinsed with chlorobenzene, after one month.

## Tables S1~S3

**Table S1.** Comparison of some optoelectronic parameters between spiro-OMeTAD with and without BATFSI.

spiro-OMeTAD	$E_{\text{cutoff}}$ (eV)	$E_{\text{onset}}$ (eV)	$E_{\text{F}}$ (eV)	$E_{\text{VB}}$ (eV)	$E_{\text{CB}}$ (eV)	$E_{\text{g}}$ (eV)
w/o BATFSI	16.93	0.55	-4.29	-4.84	-1.92	2.92
w BATFSI	16.77	0.45	-4.45	-4.90	-1.98	2.92

**Table S2.** Photovoltaic data of PSCs based on HTLs doped with different concentrations of BATFSI.

Sample	$V_{\text{OC}}$ (V)	$J_{\text{SC}}$ (mA cm <sup>-2</sup> )	FF (%)	PCE (%)
0%	1.101	24.42	82.22	22.11
1.0%	1.150	25.00	83.19	23.92
2.0%	1.161	25.26	83.45	24.47
3.0%	1.160	25.02	83.52	24.24

**Table S3.** Photovoltaic performance of the solar cells using different HTLs.

Sample	$V_{\text{OC}}$ (V)	$J_{\text{SC}}$ (mA cm <sup>-2</sup> )	FF (%)	PCE (%)	
w/o BATFSI	Statistics	1.129±0.005	23.68±0.23	78.49±0.28	20.98±0.28
	Champion	1.101	24.42	82.22	22.11
w/ BATFSI	Statistics	1.156±0.005	24.74±0.18	82.70±0.83	23.64±0.30
	Champion	1.161	25.26	83.45	24.47