# Supplemental Information for

## Synergistic Effect of Fluorinated Passivator and Hole Transport Dopant Enables Stable Perovskite Solar Cells with Efficiency Near 24%

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#### Materials and methods.

## Materials

Cesium iodide (CsI) was purchased from TCI Co. Ltd. Lead iodide (PbI<sub>2</sub>) was purchased from Alfa Co. Ltd. Formamidinium iodide (FAI), Mthylammonium bromide (MABr) and 2,2',7,7'-Tetrakis[*N*,*N*-di(4-methoxyphenyl)amino]-9,9'-spirobifluorene (spiro-OMeTAD) were purchased from Dyesol. Ultradry dimethylformamide (DMF), ultradry dimethyl sulfoxide (DMSO), ethanol (EtOH) and ultradry chlorobenzene (CB) were purchased from Acros. Dry isopropanol (IPA), diethyl ether (DEE), lithium bistrifluorosulfonyl imide (Li-TFSI), 4-(Trifluoromethyl)pyridine, 4trifluoromethyl-benzylamine and titanium diisopropoxide bis(acetylacetonate), 75 weight % in IPA were purchased from Sigma-Aldrich. All the chemicals were used as received without further purification. Conductive glass, FTO (10 ohms/sq), was purchased from Nippon Sheet Glass, and titanium dioxide paste (30 NR-D) was purchased from GreatCell Solar.

## Synthesis of 4-trifluoromethyl-benzylammonium iodide (TFMBAI)

In a round bottle flask, 4-trifluoromethylbenzylamine (1.0 g, 5.7 mmol) was dissolved in ethanol (EtOH) (10 mL) and stirred at room temperature for 10 min. Hydroiodide acid (HI, *aq*, 57%, 1.2 mL, 8.7 mmol) was added into 4-*tert*-butylbenzylamine solution dropwise within a period of 30 min. The resulting mixture was stirred for 1 h at room temperature and was then concentrated under vacuum and re-dissolved into 3 mL of EtOH. The solution was then poured into diethyl ether (DEE), and the obtained precipitate was filtered and washed with DEE and dried under vacuum to afford TFMBAI as a crystalline light yellow solid (1.59 g, 5.26 mmol, 92.3%).

#### Substrate preparation

The substrate preparation processes follow the previously reported approaches<sup>1</sup>. The fluorine doped tin oxide (FTO) glass is etched by 4 mM hydrochloric acid solution and zinc powder, then the etched FTO glass was consecutively cleaned using Hellmanex (2%, deionized water), acetone and ethanol by sonicating for 10–15 min for each solvent. After drying with compressed air, the glass was further cleaned by UV-ozone for 15 min. A compact TiO<sub>2</sub> (c-TiO<sub>2</sub>)layer was deposited on top of FTO glass using the spray pyrolysis method (O<sub>2</sub> as the carrier gas): The substrate was preheated to 450 °C; a precursor solution was diluted 0.6 mL titaniumdiisopropoxide bis(acetylacetonate), 75 wt % in IPA

and 0.4 mL acetyl acetone with 9 mL dry ethanol. After spray pyrolysis, the FTO/c-TiO<sub>2</sub> substrate was heated at 450 °C for 5 min before cooling down to ambient temperature. Next, mesoporous TiO<sub>2</sub> (m-TiO<sub>2</sub>) layer was coated on the c-TiO<sub>2</sub> substrate by spin-coating for 20 s at 4000 rpm with a ramp rate of 2000 rpm s<sup>-1</sup>, using the commercial TiO<sub>2</sub> paste (30NRD, GreatCell Solar) diluted with anhydrous ethanol at a weight ratio of 1:6. After drying at 80 °C, the as-prepared FTO/c-TiO<sub>2</sub>/m-TiO<sub>2</sub> paste was sinter at 450 °C for 30 min under dry air flow, yielding FTO/c-TiO<sub>2</sub>/ m-TiO<sub>2</sub>, which was then deposited with perovskite freshly.

#### Perovskite active layer deposition

Perovskite precursor solution was prepared by dissolving a mixture of PbI<sub>2</sub> (1.60 mmol, 735.3 mg), FAI (1.31 mmol, 224.4 mg), MABr (0.15 mmol, 16.2 mg), and CsI (0.08 mmol, 19.8 mg) Cs<sub>0.05</sub>FA<sub>0.85</sub>MA<sub>0.10</sub>Pb(I<sub>0.97</sub>Br<sub>0.03</sub>)<sub>3</sub> with 5% excess of PbI<sub>2</sub> in 1 mL of mixed solution of DMF and DMSO [DMF (v):DMSO (v) = 4:1] under mild heating condition at ~70 °C to assist dissolving. The perovskite active layer was deposited using an antisolvent method, with CB as the antisolvent. The perovskite precursor solution was deposited on the freshly prepared FTO/c-TiO<sub>2</sub>/m-TiO<sub>2</sub> substrate, and a two-step spin-coating method was applied. The first step was carried out at 2000 rpm with an acceleration rate of 200 rpm/s for 10 s. The second step followed at 6000 rpm with an acceleration rate of 2000 rpm/s for 30 s. CB (100  $\mu$ L) was slowly dripped at the 15 s before the second step end. After this, the substrate was annealed at 120 °C for 20 min. For TFMBAI treatment, 9 mg/ml TFMBAI is dissolved in IPA and spin-coated on the surface of the perovskite at 2000 r.p.m for 20 s without additional annealing procedure. The preparation of the perovskite layer was carried out in a dry air-filled glove box with the relative humidity about 2%.

#### Hole-transporting layer deposition

spiro-OMeTAD was dissolved in CB with a concentration of 77.6 mM, 1 mL spiro-OMeTAD solution was doped by 20.6  $\mu$ L Li-TFSI (520 mg/mL in Acetonitrile) and 35.5  $\mu$ L *t*BP. The mixed spiro-OMeTAD solution was spin coated on the surface of the perovskite at 4000 rpm for 20 s with an acceleration rate of 2000 rpm/s.

spiro-OMeTAD HTL solution with different volume ratio of *t*BP substituted by TFP is denoted by TFPx (x = 0.1-0.6). For instance, TFP<sub>0.5</sub> refers to 1 mL corresponding HTL solution is doped with

17.75  $\mu$ L tBP and 17.75  $\mu$ L TFP. Other components including Li-TFSI and spiro-OMeTAD concentrations remain unchanged compared to the standard (control) HTL solution.

#### Gold electrode deposition

The gold electrode was thermally evaporated on the surface of the spiro-OMeTAD with the shadow mask with an aperture area of 5 mm by 5 mm. The thickness of the gold electrode was adjusted to 80 nm, and the evaporation speed was adjusted to  $0.01 \text{ nm s}^{-1}$  at the first 10 nm,  $0.02 \text{ nm s}^{-1}$  for the thickness between 10 nm and 20 nm and  $0.08 \text{ nm s}^{-1}$  for the rest 60 nm.

#### Photovoltaic performance measurements

Current–voltage characteristics were recorded under ambient temperature and air conditions. The PSCs were measured using a 300-W Xenon light source from Oriel. The spectral mismatch between AM 1.5G and the solar simulator was calibrated by a Schott K113 Tempax filter (Prazosopms Glas & Optik GmbH). A silicon photodiode was used as light intensity calibrator for each measurement. Keithley 2400 was used for the current-voltage scan by applying an external voltage bias and measuring the response current with a scan rate of 50 mV/s. The cells were masked with a black metal mask with an area of 0.16 cm<sup>2</sup>. IPCE was recorded with a commercial apparatus (Aekeo-Ariadne, Cicci Research s.r.l.) based on a 300-W Xenon lamp.

The humidity stability data were acquired from the tracking of a unencapsulated device exposed to open air. The relative humidity of the ambient atmosphere varies from 60–70%. Relative humidity was monitored by Sigma-Aldrich Humidity/Temperature Pen 445580.

The MPPT stability of the cells was measured under a white light-emitting diode lamp with biologic MPG2 potentiostat and was performed under  $N_2$  gas flow. The device area was masked to around 0.16 cm<sup>2</sup>. The spectral mismatch between AM 1.5G and the solar simulator was calibrated by a Schott K113 Tempax filter, whose light intensity was calibrated with a silicon diode. The light intensity was around 83 mW cm<sup>-2</sup>, and the actual current was adjusted according to in-time calibration result from the silicon diode.

#### Contact angle measurement

The hydrophilicity of surfaces as a function of time was assessed by contact angle measurement

using a drop shape analyzer (KRÜSS, DSA100) at ambient temperature.

## TRPL, and UV-vis measurements

UV-vis absorptions were measured using a Varian Cary 500 spectrometer (Varian, USA). The photoluminescence lifetime was measured via time-correlated single photon counting (TCSPC) using a LifeSpec II (Edinburgh Instruments) fluorescence spectrometer with a picosecond pulsed diode laser (EPL-510, Edinburgh Instruments) at 510 nm wavelength and 85 ps pulse width. The laser fluence used was 5 nJ/cm<sup>2</sup>.

#### XRD measurement

X-ray diffraction (XRD) spectra were recorded on an X'Pert MPD PRO (PANanalytical) equipped with a ceramic tube providing Ni-filtered (Cu anode,  $\lambda = 1.54060$  Å) radiation and a RTMS X'Celerator (PANalytical). The measurements were done in BRAGG-BRENTANO geometry from  $2\theta = 5-80^{\circ}$ .

#### PLQY

Absolute photoluminescence measurements were done using an integrating sphere (from Fluorolog, Horiba JobinYvon). The samples were excited with a 660 nm CW laser (Obis) with a beam diameter of 1.1 mm (FWHM) and 0.64 mW intensity. This results in a photon flux similar to the above bandgap photon flux at 1 sun  $(1.66 \cdot 10^{21} \text{ s}^{-1}\text{m}^{-2})$ . The output of the integrating sphere was measured with a fiber connected with an Andor Kymera 193i spectrometer using a silicon CCD camera (iDus DU240A-OE). We calibrated the system with a halogen calibration lamp (HL-3 plus CAL from Ocean Optics).

#### Conductivity

Conductivities were measured on samples with the architecture glass/spiro-OMeTAD with or without TFP/Au (see **Figure S8**). *I-V* sweeps from -8 to 8V were recorded using a Keithley 2400 source meter to determine the resistance R.

The conductivities are calculated as  $\sigma = \frac{L}{w t R}$ , where L is the channel length 200 µm, w is the

channel width 10 mm and t is the film thickness ~140 nm.

## <u>FTIR</u>

Fourier transfer infrared spectra (FTIR) was recorded on Portmann FTS 7000 series spectrometer.

## SUPPLEMENTARY NOTES

#### Note 1. Numerical simulations to model TRPL data

Since for a single TRPL trace we can't distinguish between surface and bulk recombination, here we considered two extreme cases. In the first case we assumed the non-radiative monomolecular bulk recombination constant is  $k_1 = 0$  for both films, which means that the decays are due to recombination at the perovskite surface only. In the second case we assumed that the FBAI treatment eliminates the surface recombination completely so that for this film the PL decay is dominated by bulk recombination with  $k_1$  calculated to be  $2.5 \cdot 10^6$  s<sup>-1</sup>. We take the same  $k_1$  for the untreated film and calculated S. To avoid the more complex fitting of the first 30 ns where initial fast carrier trapping is dominant as has been recently shown by Trimpl et al.,<sup>2</sup> we fitted the TRPL traces for t > 30 ns, the results of which can be seen in **Figure 3b** and **Table S1**. Note that for the low laser fluences used here bimolecular and Auger recombination is negligible. For both scenarios we obtain the same fit curves. FBAI passivation leads to a significant reduction of the surface recombination velocity of  $125 \pm 20$  cm s<sup>-1</sup>.



Figure S1. Images of water droplets between water and  $\operatorname{BAI}/\operatorname{TFMBAI}$  on glass.

 Table S1. Calculated surface recombination velocities according to the two scenarios described in

 Note 1.

	Case 1: $k_1 = 0$ S (cm s <sup>-1</sup> )	Case 2: $k_1 = 2.5 \cdot 10^6 \text{ s}^{-1}$ S (cm s <sup>-1</sup> )
Perovskite	231	108
Perovskite/TFMBAI	90	0
$\Delta S (cm s^{-1})$	141	108



**Figure S2.** UPS spectra measured with photon energy of 21.22 eV on the perovskite and perovskite/TFMBAI surface are reported in the left of (a) and right of (b) showing secondary electron cut-off and valence band region, respectively. a.u., arbitrary units.



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Figure S3. PLQY for the layer structure glass/ $FTO/c-TiO_2/mp-TiO_2/perovskite/interface$  layer with HTL.



**Figure S4.** Effect of TFP*x* addition on the contact angle of spiro-OMeTAD films. spiro-OMeTAD HTL solution with different volume ratio of *t*BP substituted by TFP is denoted by TFP*x* (x = 0-0.6, see Supporting Information, Materials and Methods, Hole-transporting layer deposition). The contact angles with different *x* values, and corresponding contact angles are denoted in the figures.



**Figure S5.** *J*–*V* curves of PSCs based on spiro-OMeTAD with TFPx (x = 0-0.6).

	Voc (V)	$J_{\rm sc}$ (mA cm <sup>-2</sup> )	FF	PCE (%)
control	1.078	24.7	0.771	20.53
<i>x</i> = 0.1	1.072	24.33	0.780	20.34
<i>x</i> = 0.2	1.079	24.79	0.760	20.33
<i>x</i> = 0.3	1.081	24.71	0.771	20.58
<i>x</i> = 0.4	1.073	24.36	0.761	19.89
<i>x</i> = 0.5	1.068	24.41	0.760	19.81
<i>x</i> = 0.6	1.069	24.3	0.703	18.26

**Table S2.** Photovoltaic parameters of PSCs based on spiro-OMeTAD with TFPx (x = 0-0.6)measured under simulated AM 1.5G irradiance



Figure S6. SEM images of spiro-OMeTAD and (b) spiro-OMeTAD/TFP spin-coated on the perovskite film.



**Figure S7.** (a) TRPL for the layer structure glass/FTO/mesoscopic-Al<sub>2</sub>O<sub>3</sub>/perovskite/spiro-OMeTAD with and without TFP. (b) Absolute PL photon flux spectra for the layer structure glass/FTO/mesoscopic-Al<sub>2</sub>O<sub>3</sub>/perovskite/spiro-OMeTAD with and without TFP.



Figure S8. Sketch of device for conductivity measurements, in which L is the channel length 200  $\mu$ m, w is the channel width 10 mm and t is the film thickness ~140 nm. See Materials and Methods, Conductivity part.



**Figure S9**. Fourier-transform infrared spectroscopy (FTIR) technique is conducted to probe the interaction between TFMBAI/TFP. From FTIR results, the interaction between TFMBAI and TFP is slightly stronger as compared to that between TFMBAI and TBP. We infer such interactions can be related to a better interface between the molecular passivator and HTL, and thus leading to an improved FF and PCE. Figures: FTIR spectra of (a) TFMBAI, TFMBAI/tBP and TFMBAI/TFP, (b) spiro-OMeTAD, spiro-OMeTAD/TFP and spiro-OMeTAD/tBP. The amounts of dopants are controlled at the same level to that applied for fabrication PSCs.



**Figure S10**. *J*–*V* curves of perovskite/TFMBAI devices (a) based on different TFMBAI concentration in isopropanol and (b) the best performing PSC with TFMBAI concentration at 9 mg/ml.

Concentration	V <sub>oc</sub> (V)	$J_{\rm sc} ({\rm mA/cm}^{-2})$	FF	PCE (%)
5 mg/ml	1.142	25.05	0.798	22.83
8 mg/ml	1.155	24.97	0.801	23.10
9 mg/ml	1.159	24.95	0.805	23.28
10 mg/ml	1.156	24.72	0.738	21.10
13 mg/ml	1.152	23.71	0.677	18.49
Control	1.099	24.78	0.768	20.9

**Table S3**. Photovoltaic parameters of PSCs based on perovskite passivation by different TFMBAI

 concentrations measured under simulated AM 1.5G irradiance.



**Figure S11**. Statistic data showing  $J_{sc}$ ,  $V_{oc}$  and FF distributions of 20 devices obtained from control and perovskite/TFMBAI/TFP device.



**Figure S12**. MPP ageing tests in inert atmosphere ( $N_2$ ) under continuous 1 sun light soaking of pristine, perovskite/TFMBAI and perovskite/TFMBAI/TFP devices. The error bars represent the standard deviation of 4 devices in one batch.



**Figure S13**. Contact angle measurement (a), between water droplet and bare perovskite, (b), between water droplet and perovskite passivated with TFMBAI (c), between water droplet and control perovskite passivated with TFMBAI, coated with spiro-OMeTAD based hole transporting layer without TFP, and (d), between water droplet and perovskite passivated with TFMBAI, and then coated with TFP –doped spiro-OMeTAD based hole transporting layer.



**Figure S14**. Environmental stability of pristine, perovskite/TFMBAI and perovskite/TFMBAI/TFP device under a *r.h.* of 60–70%. The error bars represent the standard deviation of 4 devices in one batch.

## REFERENCES

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(2) Trimpl, M. J.; Wright, A. D.; Schutt, K.; Buizza, L. R. V.; Wang, Z.; Johnston, M. B.; Snaith, H. J.; Mueller-Buschbaum, P.; Herz, L. M., Charge-Carrier Trapping and Radiative Recombination in Metal Halide Perovskite Semiconductors. *Adv. Funct. Mater.* **2020**, *30*, 2004312.