

## Supporting Information

# Enhancing FAPbI<sub>3</sub> Perovskite Solar Cell Performance with a Methanesulfonate-Based Additive

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## Materials and Methods

### Materials

Formamidinium iodide (FAI), methylammonium chloride (MACl), and titanium dioxide paste (30 NR-D) were purchased from GreatCell Solar Limited. Lead Iodide ( $\text{PbI}_2$ ) was purchased from Tokyo Chemical Industries Co., Ltd. Formamidine acetate salt (FAAc), methanesulfonic acid ( $\text{CH}_3\text{SO}_3\text{H}$ ), dimethyl sulfoxide (DMSO), *N,N*-dimethylformamide (DMF), 4-*tert*-butyl pyridine (*t*BP), *iso*-propanol (IPA), lithium bis(trifluoromethanesulfonyl)imide (Li-TFSI), acetylacetone, titanium diisopropoxide bis(acetylacetonate) 75 wt% in IPA, chlorobenzene were purchased from Sigma Aldrich. DMF- $d_7$  and DMSO- $d_6$  were purchased from Cambridge Isotope Laboratories, Inc. Octylammonium Iodide (OAI) was synthesized following the previous procedure (Koh *et al. J. Mater. Chem. A*, 2018, **6**, 2122–2128). Titanium (IV) chloride solution was purchased from Fujifilm Wako Pure Chemical Corporation. 2,2',7,7'-Tetrakis[*N,N*-di(4-methoxyphenyl)amino]-9,9'-spirobifluorene (Spiro-OMeTAD) was purchased from Luminescence Technology Corp. Fluorine-doped tin oxide conductive substrate (FTO) was purchased from YingKuo Shangneng Photoelectric Materials.

### Synthesis of Formamidinium Methanesulfonate (FAMeSf)

Formamidinium acetate (FAAc, 99 %, Sigma Aldrich) was dissolved in ethanol and cooled in an ice bath for around 15 mins. Then, methanesulfonic acid ( $\text{CH}_3\text{SO}_3\text{H}$ ) was added dropwise into the solution at 1.2 equivalent. The solution was stirred for 2 hours and subsequently dried via rotary evaporation at 40 °C. The resulting powder was then dissolved in ethanol and recrystallized with diethyl ether 5 times.

### Perovskite Solar Cells Fabrication

*Substrate cleaning.* FTO substrates were cleaned with decon soap, deionized water, and IPA via ultra-sonication for at least 15 mins in each washing solution/solvent. The substrates were further treated with UV-ozone for 15 mins at 100°C.

*Electron transport layer (ETL).* The compact  $\text{TiO}_2$  (c- $\text{TiO}_2$ ) was deposited by spray pyrolysis using titanium diisopropoxide bis(acetylacetonate) diluted in IPA in 1:9 ratio + 4 vol% acetylacetone, followed by annealing at 450°C for 1 hour. The mesoporous  $\text{TiO}_2$  (m- $\text{TiO}_2$ ) paste was prepared using titanium dioxide paste (30 NR-D) diluted in anhydrous ethanol in 1:9 ratio and deposited by

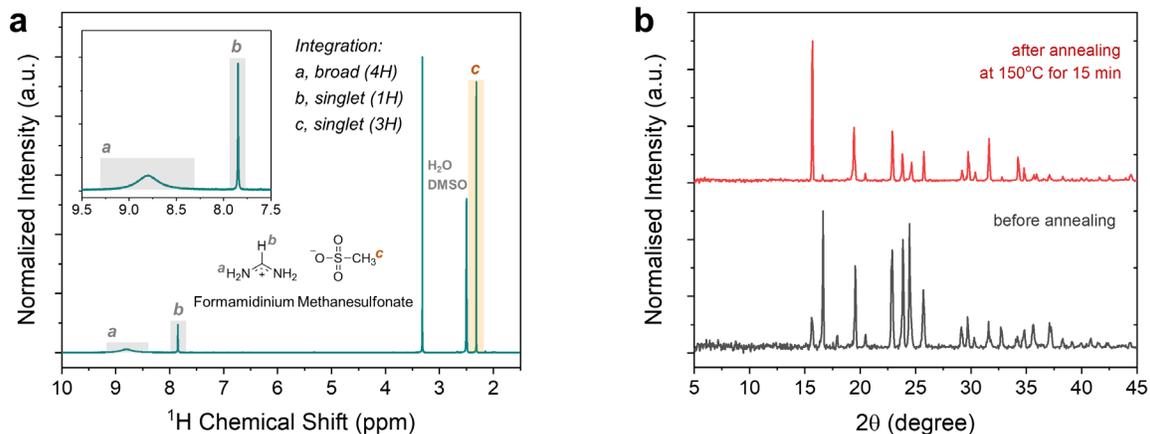
spin coating at 3000 rpm for 30 s, followed by sintering at 500 °C for 1 hour. The FTO/c-TiO<sub>2</sub>/m-TiO<sub>2</sub> substrates were then post-treated with titanium (IV) chloride (1:50 volume dilution with DI water) at 70°C for 30 mins, followed by annealing at 500°C for 1 hour.

*Perovskite deposition.* Perovskite precursor solutions were prepared by dissolving 0.348 g FAI, 0.934 Pbl<sub>2</sub>, and 35 mol% MACl (for better crystallization) in 1.5 ml DMF/DMSO solvent mixture of 4:1 ratio, respectively. Different concentrations of FAMEsf ranging from 0-5 mol% were added accordingly. The perovskite layer was deposited onto the FTO/c-TiO<sub>2</sub>/m-TiO<sub>2</sub> substrate by spin coating at 6000 rpm for 50 s, and using chlorobenzene as antisolvent, followed by annealing at 150°C for 10 mins. Octylammonium iodide (0.01 g OAI dissolved in 3 ml IPA) was deposited as surface passivation by spin coating at 6000 rpm for 50 s without any post-annealing.

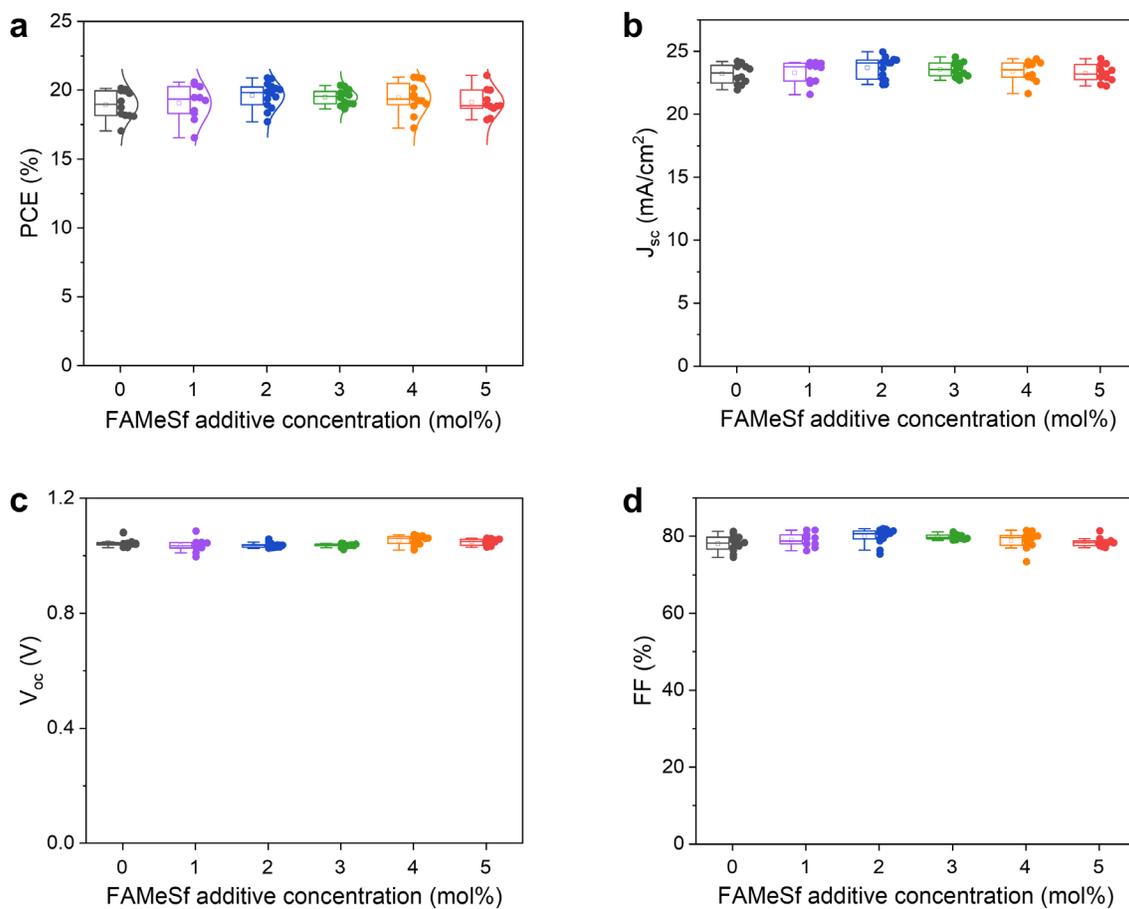
*Hole transport layer (HTL) and Au deposition.* 72.3 mg of Spiro-OMeTAD was dissolved in 1 ml chlorobenzene with the addition of 28.5 μL TBP and 17.5 μL Li-TFSI (520 mg/ml in acetonitrile) as dopants. The Spiro-OMeTAD was deposited by dynamic spin-coating at 4000 rpm for 30 s. The 100-nm gold electrode layer was deposited by thermal evaporation as a back contact.

### Characterizations

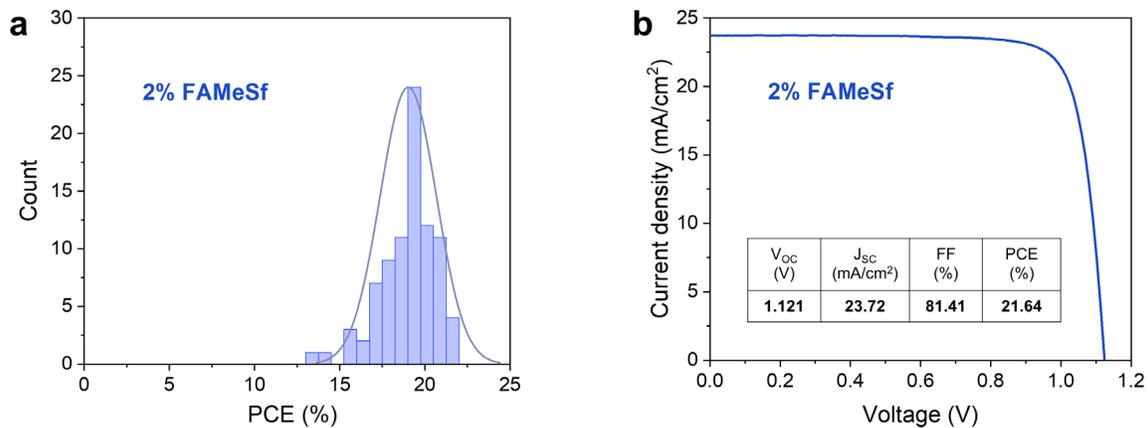
Morphological characterization was done using a Field Emission Scanning Electron Microscope (FESEM, JEOL JSM-7600F, 5 kV, and 10 mA). The steady-state absorbance spectra were recorded using UV-Vis-NIR Spectrophotometer (UV3600, Shimadzu). Time-resolved photoluminescence (TRPL) measurements were carried out on a Picoquant PicoHarp 300 time-correlated single-photon counting (TCSPC) setup using a 405 nm laser excitation. The X-ray diffraction (XRD) patterns were collected on a Bruker D8 Advance diffractometer with Cu K $\alpha$  radiation. The proton nuclear magnetic resonance (<sup>1</sup>H-NMR) spectra were recorded on a Bruker Advance II (400 MHz) spectrometer. The NMR samples were prepared by dissolving the solid material in DMF-*d*<sub>7</sub> and DMSO-*d*<sub>6</sub>. The ultraviolet photoelectron spectroscopy (UPS) and the X-ray photoelectron spectroscopy (XPS) measurements were performed using an AXIS Supra spectrometer (Kratos Analytical Inc., UK). The etching was done using an Ar Gas Cluster Ion Source (GCIS, Kratos Analytical Inc., Minibeam) operated at 10 keV, Ar<sub>1000</sub><sup>+</sup> with a raster size of 2×2 mm<sup>2</sup>. The current density-voltage (*J*-*V*) curves were measured using AM 1.5 sunlight (Newport Oriel Sol3ATM) and a 450-Watt Xenon lamp calibrated using standard Si solar cell. The incident photon-to-current conversion efficiency (IPCE) was measured with PVE300 (Bentham).



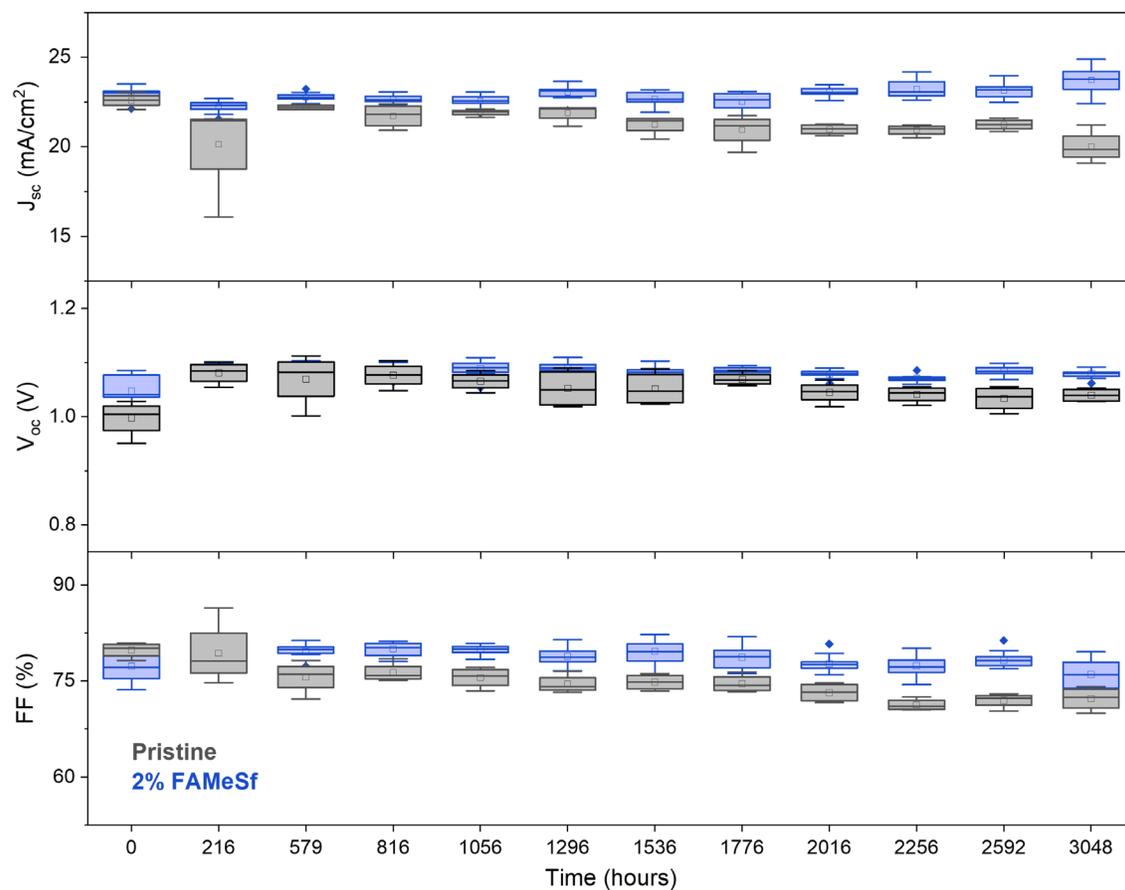
**Figure S1.** (a)  $^1\text{H}$ -NMR spectrum of FAMEsF in  $\text{DMSO-}d_6$ , confirming the purity of the material. (b) Powder XRD patterns of FAMEsF before (black) and after (red) its annealing at  $150^\circ\text{C}$  for 15 mins, showing no degradation of the material at high temperatures.



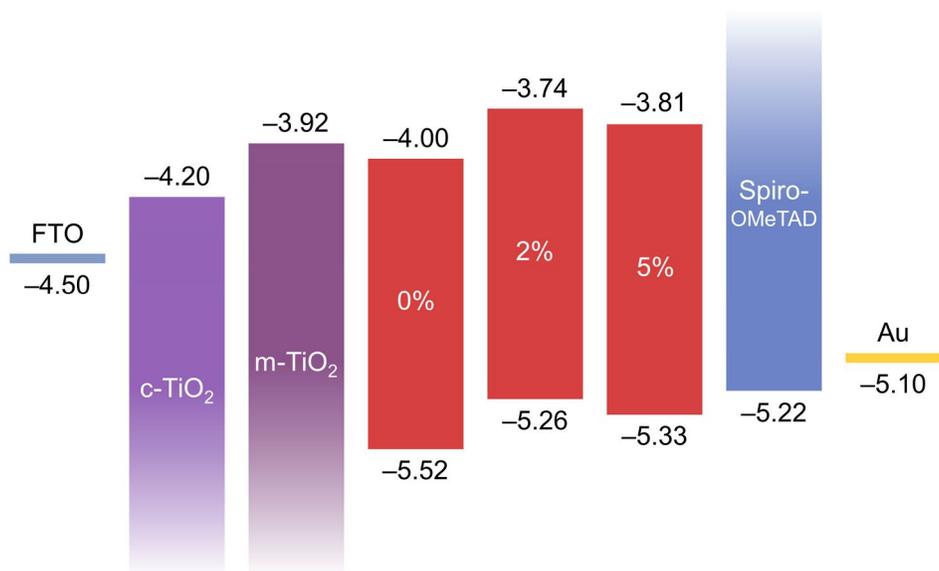
**Figure S2.** Photovoltaic parameters of  $\text{FAPbI}_3$  PSCs fabricated using different FAMEsF additive concentrations: (a) PCE, (b)  $J_{\text{sc}}$ , (c)  $V_{\text{oc}}$ , and (d) FF.



**Figure S3.** (a) Histogram showing the reproducibility of 2 mol% FAMEsF-added PSCs with an average PCE of 19.0% for more than 80 devices from different batches. (b) J-V curve of the champion device fabricated using 2 mol% FAMEsF additive.



**Figure S4.** Long-term stabilities of the pristine (black) and 2 mol% FAMEsF-added (blue) unencapsulated PSCs showing the evolution of their photovoltaic parameters ( $J_{sc}$ ,  $V_{oc}$ , and FF) with time upon prolonged storage in dark, at room temperature and 30% relative humidity (RH).



**Figure S5.** Band energy alignment between 0, 2, and 5 mol% FAMEsf-added FAPbI<sub>3</sub> perovskite and the charge-transporting layers.

**Table S1.** The bi-exponential fitting parameters of the TRPL curves for 0, 2, and 5 mol% FAMEsf-added FAPbI<sub>3</sub> perovskite thin films.

FAMEsf additive concentration	fast component: $\tau_1$ , ns	slow component: $\tau_2$ , ns	average: $\tau_{ave}$ , ns
0 mol%	32.6 ± 0.2 (70.3%)	451.7 ± 4.5 (29.7%)	157.1 ± 1.5
2 mol%	48.3 ± 0.5 (46.5%)	763.2 ± 8.3 (53.5%)	430.8 ± 4.7
5 mol%	27.4 ± 0.2 (61.5%)	1049 ± 11 (38.5%)	420.9 ± 4.4

**Table S2.** The <sup>1</sup>H-NMR quantitative analysis of the 0, 2, and 5 mol% FAMEsf-added FAPbI<sub>3</sub> perovskite thin films. The values are relative to the FA amount.

FAMEsf additive concentration	CH(NH <sub>2</sub> ) <sub>2</sub> <sup>+</sup> or FA	CH <sub>3</sub> NH <sub>3</sub> <sup>+</sup> or MA	CH <sub>3</sub> SO <sub>3</sub> <sup>-</sup> or MeSf
0 mol%	1.000	0.075	0.000
2 mol%	1.000	0.050	0.010
5 mol%	1.000	0.046	0.037