

## Supporting Information

### **Fabrication of Efficient Formamidinium Tin Iodide Perovskite Solar Cells through SnF<sub>2</sub>-Pyrazine Complex**

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## Experimental section

### Chemicals

Hydriodic acid (99.95 %, 57 wt.% in H<sub>2</sub>O), formamidine acetate salt (99 %), titanium diisopropoxide bis(acetylacetonate) (75 wt.% in isopropanol), N,N-dimethylformamide (anhydrous, 99.8 %), dimethyl sulfoxide (anhydrous,  $\geq 99.9$  %), tin(II) fluoride (99 %), pyrazine ( $\geq 99$  %), toluene (anhydrous, 99.8 %), chlorobenzene (anhydrous, 99.8 %), bis(trifluoromethane) sulfonimide ( $\geq 95.0$  %), acetonitrile (anhydrous, 99.8 %), 2,6-lutidine ( $\geq 99$  %) were purchased from Aldrich. Ethanol and diethyl ether were purchased from Burdick & Jackson. 2,2',7,7'-tetrakis(N,N-bis(p-methoxyphenyl)amino)-9,9'-spirobifluorene (Spiro-MeOTAD) was purchased from Luminescence Technology Corp (Lumtec). All chemicals mentioned above were used without further purification.

### Synthesis of formamidinium iodide (CH(NH<sub>2</sub>)<sub>2</sub>I, FAI)

CH(NH<sub>2</sub>)<sub>2</sub>I (FAI) was synthesized according to the literature. 30 mL of hydriodic acid was added to 250 mL round-bottom flask which is containing 15 g of formamidine acetate and the reaction was proceeded at 0 °C for 2 h with vigorous stirring. The precipitate was recovered by evaporating the reaction mixture at 50 °C for 1h. The product was dissolved in ethanol and recrystallized by diethyl ether. The resulting FAI was collected by filtration and dried in a vacuum oven at 60 °C overnight.

### Film fabrication

Formamidinium iodide (FAI, 1 mmol), tin iodide (SnI<sub>2</sub>, 1 mmol) and tin fluoride (SnF<sub>2</sub>, 0.1 mmol) were dissolved in the following solvent (1 mL): 1. DMF, 2. DMF and DMSO, and 3. DMF and DMSO including pyrazine. The resulting solution (80  $\mu$ L) was loaded

and deposited onto the mesoporous TiO<sub>2</sub>/blocking TiO<sub>2</sub>/FTO substrate via a two-step spin-coating process, at 1,000 rpm and 5,000 rpm for 10 s and 50 s, respectively. In the case of non-solvent dripping process, 1 mL of toluene was dripped onto the substrates during the second spin-coating step. The substrate was annealed at 60 °C for 10 min.

### **Device fabrication**

A dense blocking layer of TiO<sub>2</sub> with 60 nm thickness was prepared by spray pyrolysis. 20 mM titanium diisopropoxide bis(acetylacetonate) diluted in ethanol was spread onto a F-doped SnO<sub>2</sub> (FTO, Pilkington, TEC8) substrate at 450 °C. This procedure is for preventing a direct contact between FTO and the hole-conducting layer. A mesoporous TiO<sub>2</sub> with 400 nm thickness was deposited onto the blocking TiO<sub>2</sub>/FTO substrate by spin coating at 2,000 rpm for 50 s using a diluted TiO<sub>2</sub> paste and sintered at 500 °C for 1 h. The TiO<sub>2</sub> paste was prepared by the same procedure as described in our previous report.<sup>1</sup>

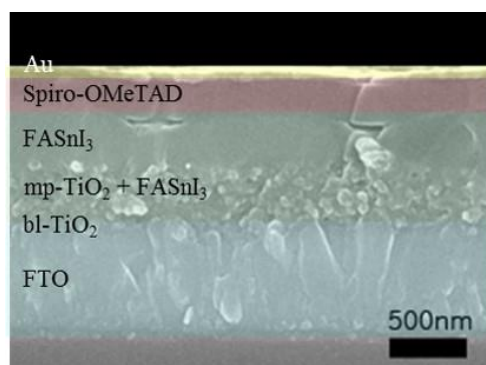
The CH(NH<sub>2</sub>)<sub>2</sub>SnI<sub>3</sub> (FASnI<sub>3</sub>) perovskite absorbing layer was prepared in glove box. FAI (1 mmol) and SnI<sub>2</sub> (1 mmol) were dissolved in 1 mL of DMF and DMSO mixed solvent (4:1 volume ratio) and then SnF<sub>2</sub> and pyrazine were sequentially added. The resulting solution was coated onto the mesoporous TiO<sub>2</sub>/blocking TiO<sub>2</sub>/FTO substrate via a two-step spin-coating process, at 1,000 rpm and 5,000 rpm for 10 s and 50 s, respectively. During the second spin-coating step, 1 mL of toluene was dripped onto the substrates. The substrate was annealed at 60 °C for 1 h. A solution of spiro-MeOTAD/chlorobenzene (72.3 mg/mL) containing 17.5 µL of bis(trifluoromethane)sulfonimide/acetonitrile (509 mg/mL) and 30 µL of 2,6-lutidine was spin-coated on the perovskite layer at 3,000 rpm for 30 s. Finally, 60 nm thick gold electrode was deposited onto the devices using a thermal evaporator while maintaining N<sub>2</sub> condition. The effec-

tive active area was fixed at  $0.16\text{ cm}^2$ . The devices were thermally encapsulated with cover glass ( $2.5\text{ cm} \times 1.5\text{ cm}$ ) using a polymer and an epoxy resin under nitrogen atmosphere.

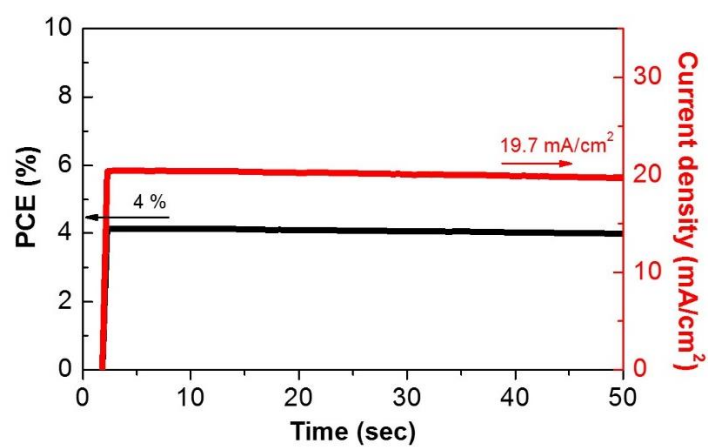
### **Characterization**

The morphology of  $\text{FASnI}_3$  films and full device were investigated using field emission scanning electron microscopy (Mira 3 LMU, Tescan) operated at 20 kV. X-ray diffraction (XRD) patterns of the prepared films were measured on a Rigaku SmartLab X-ray diffractometer. The Fourier transform infrared (FT-IR) spectra were recorded with a Bruker ALPHA-P spectrophotometer. X-ray photoelectron spectroscopy (XPS) studies were carried out using a Thermo VG Scientific K-Alpha. The absorption spectra were collected on a Shimadzu UV 2550 spectrophotometer using the encapsulated films. The external quantum efficiency (EQE) was measured using a power source (Newport 300 W Xenon lamp, 66920) with a monochromator (Newport Cornerstone 260) and a multimeter (Keithley 2001). Transient photovoltage decay measurements were performed using a nanosecond laser (10 Hz, NT342A-10, EKSPLA) as a small perturbation light source and a Xe lamp (150 W, Zolix) as a bias light source. The device was directly connected to a digital oscilloscope (500 MHz, DSO-X 3054A, Agilent) and the input impedance of the oscilloscope was set to  $1\text{ M}\Omega$  for an open circuit condition. The bias light intensity was controlled by neutral density filters for various open circuit voltages ( $V_{oc}$ ) and a strongly attenuated laser pulse of 550 nm, which generated a voltage transient ( $\Delta V$ ) that did not exceed 20 mV. The  $J$ - $V$  curves were measured using a solar simulator (Newport, Oriel Class A, 91195A) under standard air-mass 1.5 global (AM 1.5G) illumination with an irradiation intensity of  $100\text{ mW cm}^{-2}$  (Keithley 2420) and a calibrated Si-reference cell certified by the National

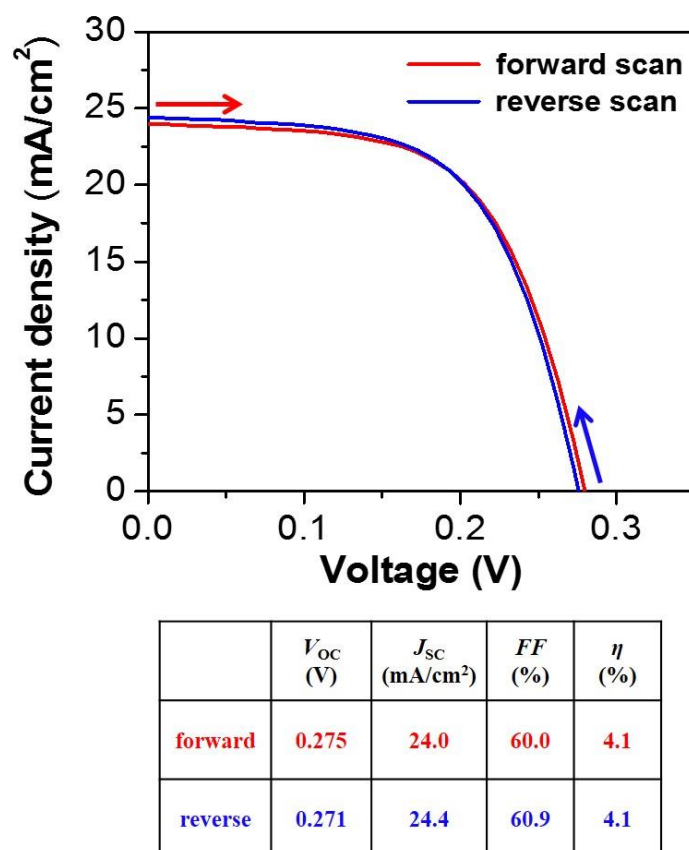
Renewable Energy Laboratory, USA. The  $J$ - $V$  curves were measured by reverse scan (forward bias (1.2 V)  $\rightarrow$  short circuit (0 V)) or forward scan (short circuit (0 V)  $\rightarrow$  forward bias (1.2 V)). The step voltage and the delay time, which is a delay set at each voltage step before measuring each current, were set to 10 mV and 10 ms, respectively. The  $J$ - $V$  curves for all devices were measured by masking the active area using a metal mask with an area of 0.096 cm<sup>2</sup>. Time-dependent current was measured with a potentiostat (PGSTAT302N, Autolab) under one sun illumination.



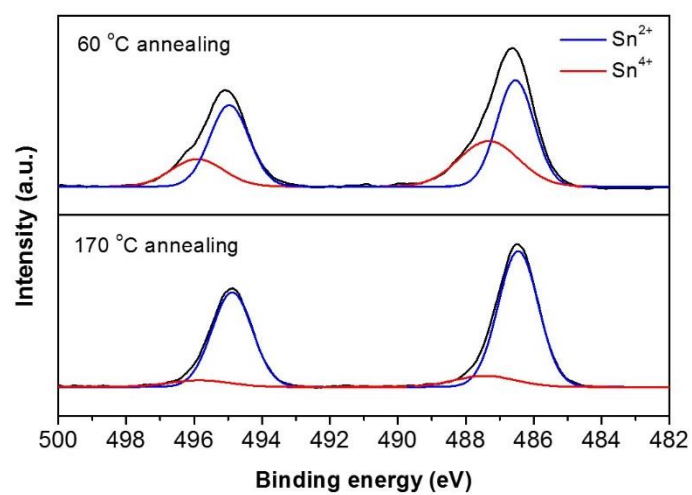
**Figure S1.** Cross-sectional SEM image of the full device in this work.



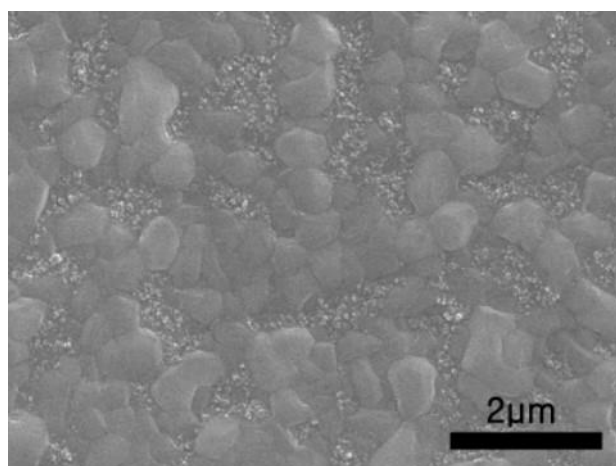
**Figure S2.** Stabilized power conversion efficiency and photocurrent density of FASnI<sub>3</sub> PSC measured at maximum power voltage of 0.202 V for 50 seconds.



**Figure S3.** Photocurrent density–voltage ( $J$ – $V$ ) curves of FASnI<sub>3</sub> perovskite solar cell with pyrazine measured by forward ( $J_{sc} \rightarrow V_{oc}$ ) and reverse ( $V_{oc} \rightarrow J_{sc}$ ) scans.

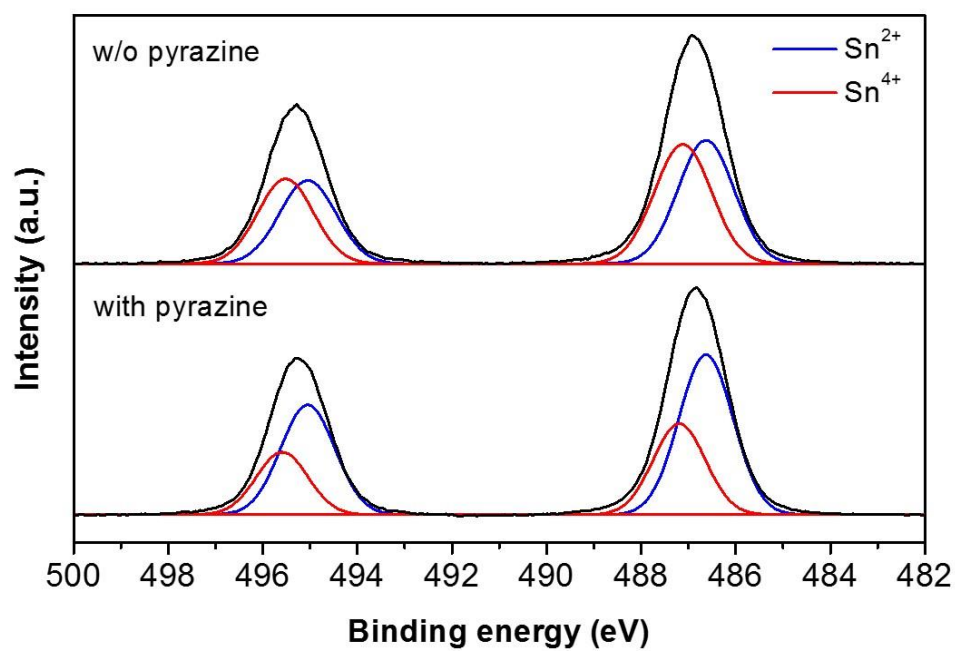


**Figure S4.** XPS spectra of the Sn (3s) bands of FASnI<sub>3</sub> films prepared in the absence of SnF<sub>2</sub> with different annealing temperature (60 °C and 170 °C).



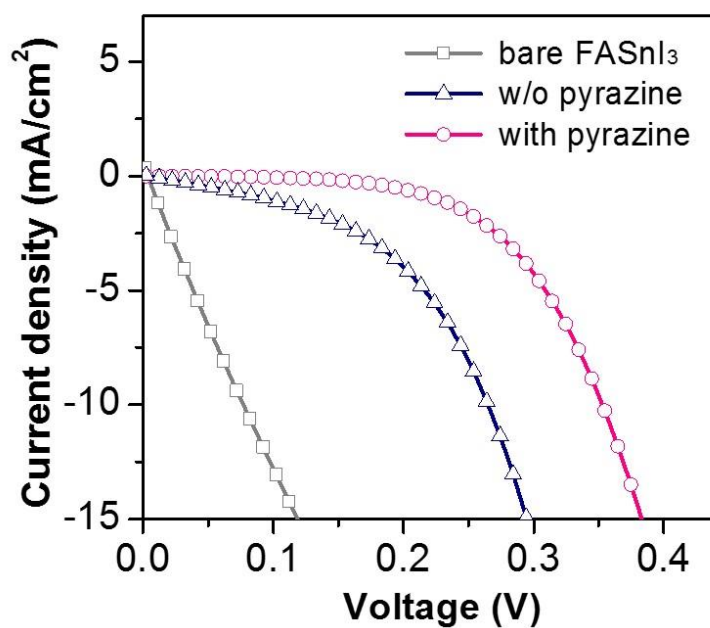
**Figure S5.** SEM plane image of FASnI<sub>3</sub> perovskite film prepared in the absence of SnF<sub>2</sub> and annealed at 170 °C.



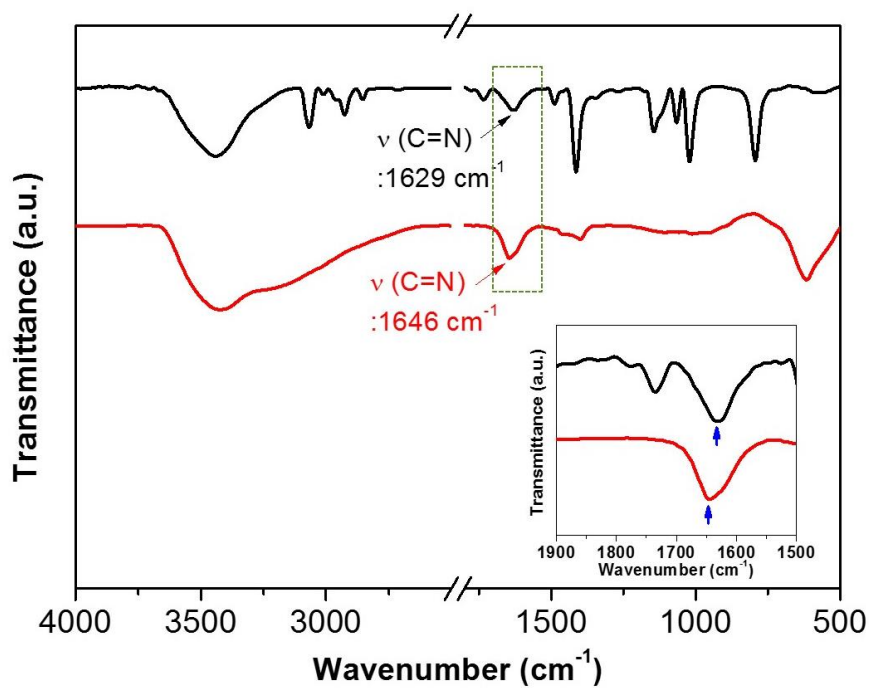


	Sn <sup>4+</sup> contents (%)
w/o pyrazine	49.8
with pyrazine	35.3

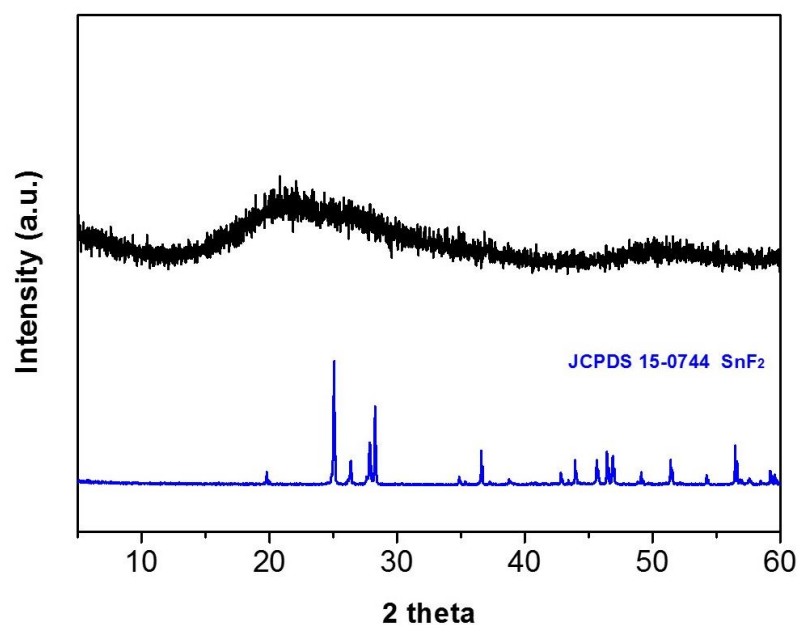
**Figure S6.** XPS spectra of the Sn (3s) bands of FASnI<sub>3</sub> films when the etching time is 60 seconds.



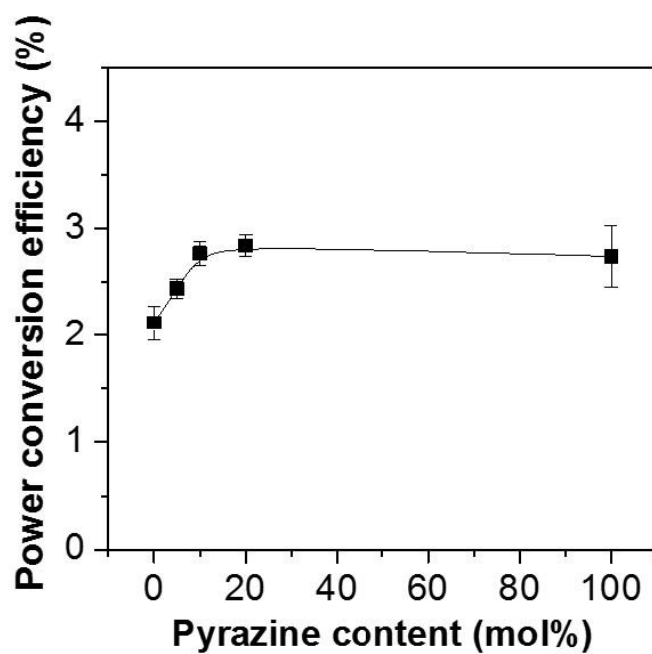
**Figure S7.** Dark  $J$ - $V$  curves of bare FASnI<sub>3</sub> PSC PSC with and without pyrazine in the presence of SnF<sub>2</sub> (10 mol%).



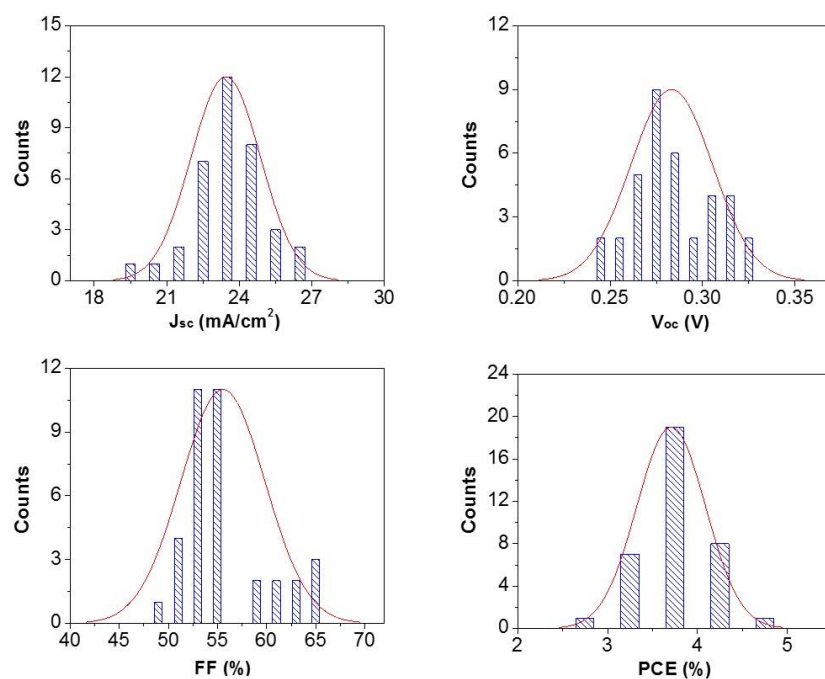
**Figure S8.** IR spectra of the free pyrazine (black) and SnF<sub>2</sub>-pyrazine complex (red). The inset shows the magnified view from 1900 nm to 1500 nm.



**Figure S9.** X-ray diffraction (XRD) pattern of the SnF<sub>2</sub>-pyrazine complex.



**Figure S10.** Power conversion efficiency of devices as a function of pyrazine content.



**Figure S11.** Histograms of photovoltaic parameters measured for 36 devices.

## References

- (1) Jeon, N. J.; Noh, J. H.; Yang, W. S.; Kim, Y. C.; Ryu, S.; Seo, J.; Seok, S. I. *Nature* **2015**, *517*, 476-480.