

Supplementary Information

Voltage Output of Efficient Perovskite Solar Cells with high Open-Circuit Voltage and Fill Factor

Seungchan Ryu[‡], Jun Hong Noh[‡], Nam Joong Jeon, Young Chan Kim, Woon Seok Yang, Jang Won Seo and Sang Il Seok*

Experimental Section

Solar cell fabrication.

A compact TiO₂ blocking layer was first deposited onto the surface of a pre-cleaned F-doped SnO₂ (FTO, Pilkington, TEC15) substrate by spray pyrolysis, on a hotplate kept at 450 °C, using an airbrush at a distance of 5 cm. The thickness was controlled by the number of spray cycles. The solution used in the spray pyrolysis was 0.2 M Ti-isopropoxide and 2 M acetylacetonate in isopropanol. Ten spray cycles were set as the standard. Mesoporous TiO₂ (mp-TiO₂) films with a thickness of 250 nm were spin-coated onto the bl-TiO₂/FTO substrate using the home-made paste (average particle size of TiO₂ nanoparticles is ca. 40 nm, crystalline phase = anatase). The films were calcined at 500 °C for 1 h to remove the organic part used as the binder. CH₃NH₃I (=MAI) and CH₃NH₃Br (=MABr) were first synthesized by reacting 27.86 ml CH₃NH₂ (40% in methanol, Junsei Chemical Co.) and 30 ml HI (57 wt% in water, Aldrich) and 44 ml HBr (48 wt% in water, Aldrich) in a 250 ml round-bottom flask at 0 °C for 4 h with stirring, respectively. The precipitate was recovered by evaporation at 55 °C for 1 h. MAI and MABr were dissolved in ethanol, recrystallized from diethyl ether, and dried at 60 °C in a vacuum oven for 24 h. The synthesized MABr powders were mixed with PbBr₂ (Aldrich) in the mixture solvent of γ -butyrolactone:dimethyl sulfoxide (7:3, v/v) for 1.2 M MAPbBr₃ solution and the synthesized MAI powders were mixed with PbI₂ (Aldrich) in the mixture solvent for 0.8 M MAPbI₃ solution. The perovskite solutions were spin-coated onto the mp-TiO₂/bl-TiO₂/FTO substrate at 500 r.p.m. for 5 s, 1000 r.p.m. for 40 s, and 5,000 r.p.m. for 50 s and the toluene in final spin-stage was dripped onto the substrate during spin coating. After that, the substrates were dried on a hot plate at 100 °C for 10 min. A PTAA (EM index, Mn 17,500 gmol⁻¹)/toluene (20 mg/1 ml) solution with added 15 ml Libis(trifluoromethanesulfonyl) imide (Li-TFSI)/acetonitrile (170 mg/1 ml) and 15 ml TBP:acetonitrile (1:1, v/v) was spin-coated on MAPbBr₃ (or MAPbI₃)/mp-TiO₂/bl-TiO₂/FTO substrate at 3,000 r.p.m. for 30 s. In cases of PF8-TAA (EM index, Mn 48,200 gmol⁻¹)/toluene (10 mg/1 ml) and PIF8-TAA (EM index, Mn 58,200 gmol⁻¹)/toluene (10 mg/1 ml) solution with added 7.5 ml Li-TFSI/acetonitrile and 7.5 ml TBP:acetonitrile was used to deposit a same thickness with P-TAA. Finally, a gold counter electrode was deposited by thermal evaporation. The active area was fixed at 0.16 cm².

Characterization

The ionization energy for MAPbBr₃, MAPbI₃, PTAA, PF8-TAA, and PIF8-TAA films on fused silica was measured using photoelectron spectroscopy (Riken Keiki AC-2). EQE was measured using a power source (Newport 300 W xenon lamp, 66920) with a monochromator (Newport Cornerstone 260) and a multimeter (Keithley 2001). The current density–voltage (J – V) curves were measured using a solar simulator (Newport, Oriel Class A, 91195A) with a source meter (Keithley 2420) under 100 mAc⁻² illumination (AM 1.5G) and a

calibrated Si-reference cell certificated by NREL. The $J-V$ curves of all devices were measured by masking the active area with a metal mask of area 0.096 cm^2 .

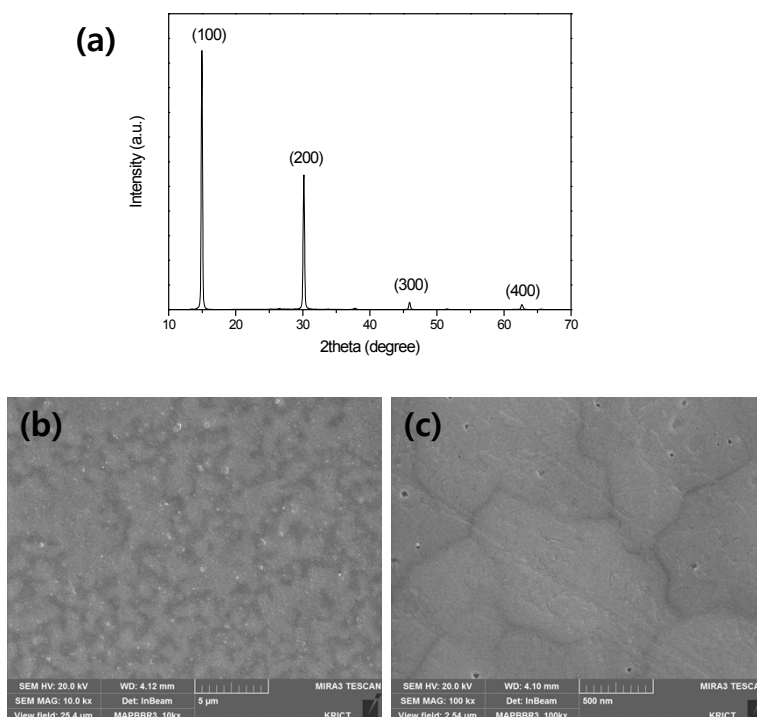


Fig. S1. X-ray diffraction spectrum (a) and plain-view scanning electron microscope (SEM) images (b,c) of FTO/bl-TiO₂/mp-TiO₂/MAPbBr₃ specimen. The high crystalline MAPbBr₃ film is formed on mp-TiO₂ and the film completely covers on surface of mp-TiO₂ layer.

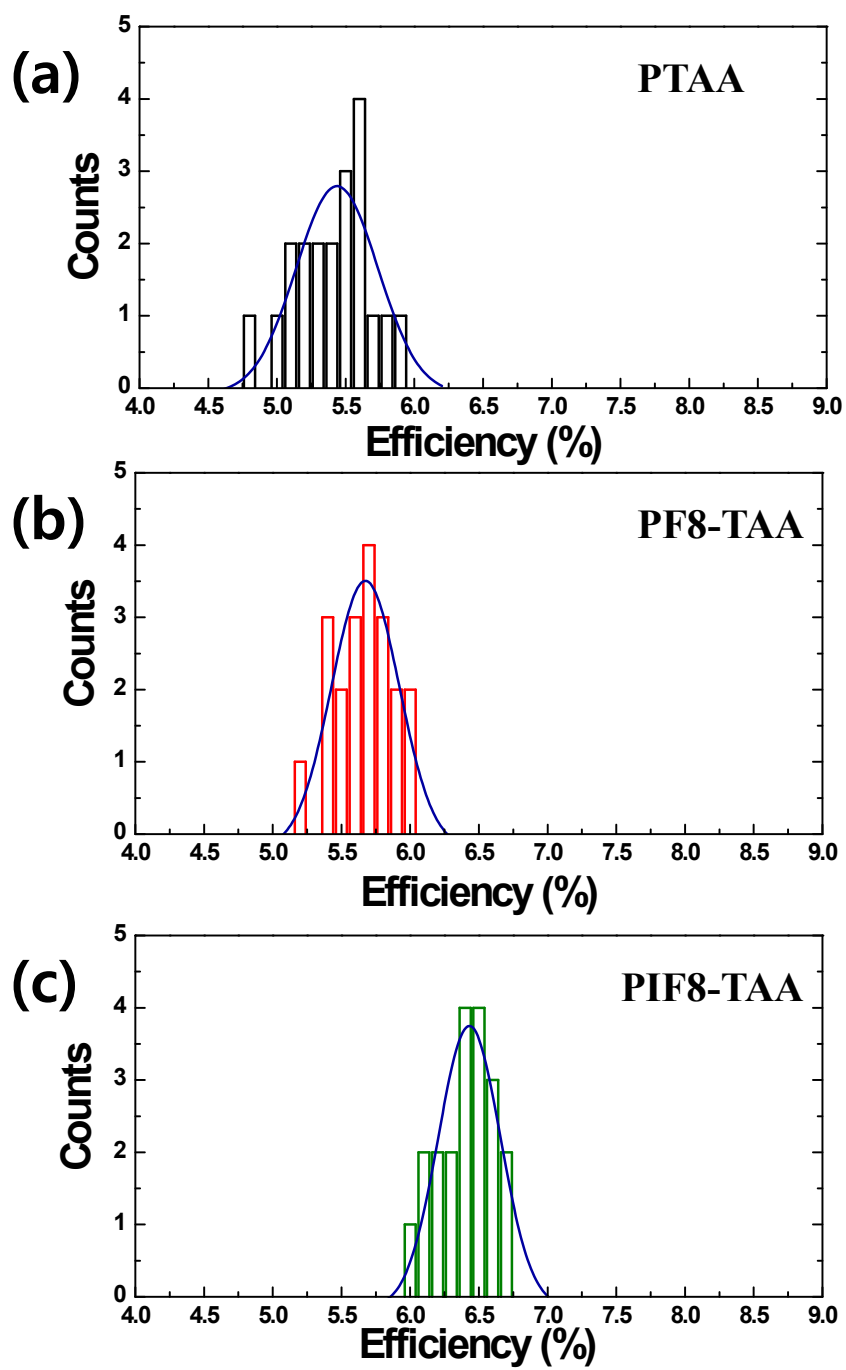


Fig. S2. Histograms for cell efficiencies of PTAA (a), PF8-TAA (b), PIF8-TAA(c)-based MAPbBr₃ solar cells.

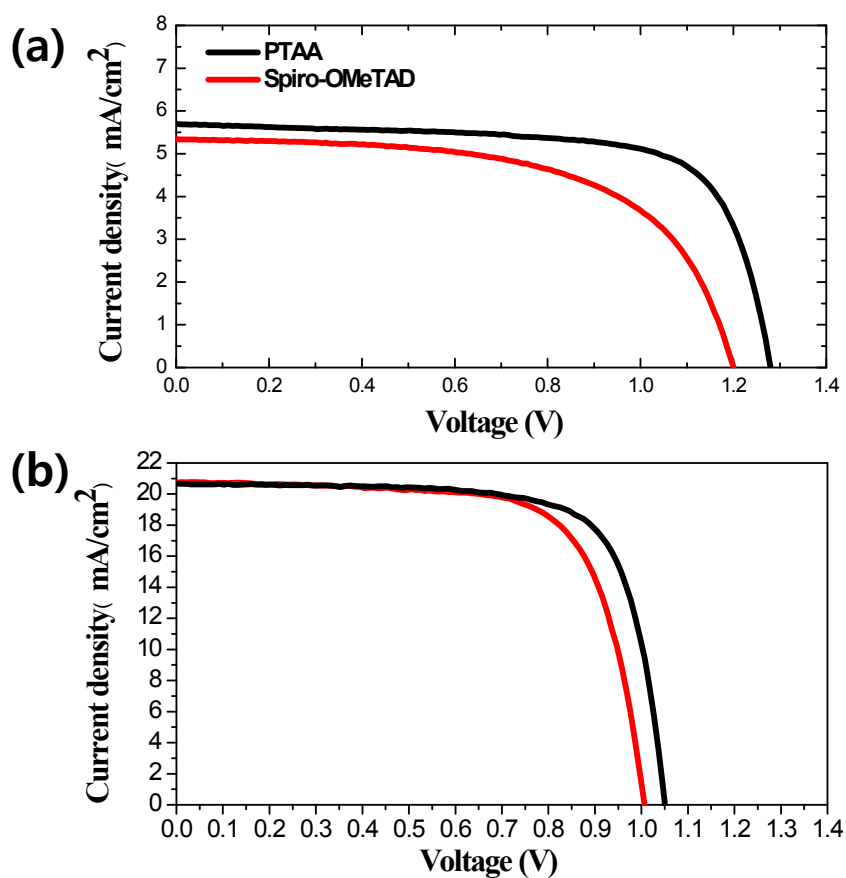


Fig. S3. J-V curves for MAPbBr₃ (a)-device and MAPbI₃ (b)-device using PTAA and spiro-OMeTAD. The photovoltaic parameters are summarized in table below.

Table S1. Photovoltaic parameters for MAPbI₃ and MAPbBr₃ perovskite solar cells using spiro-OMeTAD as HTM

Perovskite	HTMs	J _{sc} (mA/cm ²)	V _{oc} (V)	FF	PCE (%)
MAPbBr ₃	Spiro-MeOTAD	5.3	1.20	0.60	3.8
	PTAA	5.7	1.28	0.72	5.2
MAPbI ₃	Spiro-MeOTAD	20.7	1.01	0.71	14.9
	PTAA	20.7	1.05	0.74	16.1