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Supporting Information

Bi-functional Additive Engineering for High-performance Perovskite Solar Cells with Reduced Trap Density

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Experimental section

S1. Materials and Solar Cell Fabrication

Materials: ABS (>97%) was purchased from Ark Pharm. Lead (II) Bromine (purity, 99.99%) (for Perovskite precursor) and Lead (II) Iodide (99.99%, trace metals basis) was purchased from TCI (Japan), Methylammonium iodide (MAI), methylammonium bromide (MABr), and formamidinium Iodide (FAI) from Dyesol (Australia). Chlorobenzene, DMF, and DMSO were obtained from Aldrich (U.S.). Lithium bis(trifluoromethylsulfonyl)amine (Li-TFSI), 4-tert-butylpyridine (tBP), Tris(2-(1Hpyrazol-1-yl)-4-tert-butylpyridine)cobalt(III) tris(bis(trifluoromethylsulfonyl)-imide) (FK209-cobalt(III)-TFSI) and spiro-MeOTAD were purchased from Xi'an Polymer Light Technology (China). All reagents were used as received.

Device Preparation: The solar cell was fabricated on FTO substrates washed sequentially with detergent, deionized water and ethanol in an ultrasonic bath. The TiO_2 blocking layer was deposited onto the substrates by spray pyrolysis of 20-mM isopropanol solution of titanium diisopropoxide bis(acetylacetonate) using O_2 as carrying gas at 500°C. The substrates were then annealed at 500°C for 20 min. A 200 nm mesoporous TiO_2 from 30 nm particle paste (Dyesol 30 NR-D) diluted in ethanol was spin-coated onto the blocking TiO_2/FTO substrate at 5000 rpm for 20 s with a ramp of 2500 $rpm \cdot s^{-1}$. The films were then dried at 100 °C for 10 min and sintered at 500°C for 30 min in air. The perovskite precursor solution was prepared by dissolving 553.2 mg PbI_2 and 187 mg MAI into 0.2 mL DMF and 0.8 mL DMSO. The solution was stirred for 30 min at room temperature. The perovskite layers were spin coated onto the substrates at a speed of 1,000 rpm for 10 s, then 4000 rpm for 30 s in an air glovebox. At 10s before the end of the procedure, 0.1 mL chlorobenzene was quickly dripped onto the spinning film. Thereafter, the substrates were put onto a hotplate for 15 min at 100°C. The $FA_{0.85}MA_{0.15}PbI_{2.55}Br_{0.45}$-based perovskite layers were deposited by spin-coating 1.45 mol/mL Pb^{2+} perovskite precursor solution (DMF: DMSO = 4:1) in an air glovebox first 1,000 rpm for 10 s, second 5,000 rpm for 30 s. 0.1 mL chlorobenzene was dropped on the spinning substrate 20 s before the end of the procedure. The substrate was then heated on a hotplate at 100°C for 60 min. For ABS incorporated process, corresponding amount of ABS was added into the precursor solution and all other steps in device preparation were completely the same with the reference ones. The hole-transporting material spiro-OMeTAD was dissolved in chlorobenzene at a concentration of 72.3 mg/mL, with the addition of 17.5 μL Li-TFSI stock solution in acetonitrile (520 mg/mL), 28.8 μL tBP and 8μL FK209-cobalt(III)-TFSI stock solution in acetonitrile (300 mg/mL). Finally, 70 nm of gold was deposited under high vacuum by thermal evaporation as a speed of 0.2 nm/s.

S2. Characterizations

The PCE and *J–V* curves were measured with a Keithley 2400 source-meter together with a sunlight simulator (XES-300T1, SAN-EI Electric, AM 1.5), which was calibrated using a standard silicon reference cell. The solar cells were masked with a black aperture to define an active area of 0.09 cm^2. Scanning electron microscopy (SEM) images were taken with a SU8010 (Hitachi). The crystal structure of the $MAPbI_3$ films were examined by XRD (Bruker X-ray diffractometer) with Cu Kα radiation source. X-ray photoelectron spectroscopy (XPS) was obtained with a Thermo Scientific ESCALAB 250Xi spectrometer. Absorption spectra were measured with a UV-2450 spectrophotometer (Shimadzu) from 300 nm to 800 nm. The PL mapping signals were carried out with a laser confocal Raman spectrometer (Princeton Instruments, Acton Standard Series SP-2558), a digital CCD (PIXIS:100B_eXcelon) and a 485 nm laser (PicoQuant LDH-P-C-485, 0.4 mW with a 1% optical density filter), using a home-built confocal microscope on a 5 × 5 μm2 sample area. The thermal admittance spectroscopy analysis for devices were measured at a frequency (f) range of 1 Hz to 1 MHz at different temperatures (T) from 178 K to 300 K. The light intensity dependence measurements and transient photovoltage decay measurements were performed on an electrochemical workstation (Zahner) combined with modules for controlled IMPS and fast intensity transients. A white LED with an intensity of 1000W m^{-2} was used as the light source in the experiments, devices were soaked in light for 2s before the LED light was turned off.

Figures and Comments

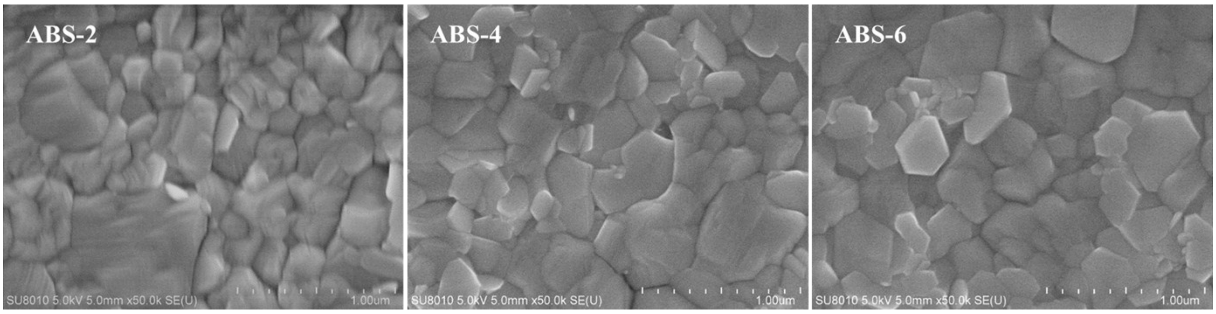

Figure S1. SEM top-view images of $MAPbI_3$-based perovskite films with excessive ABS addition.

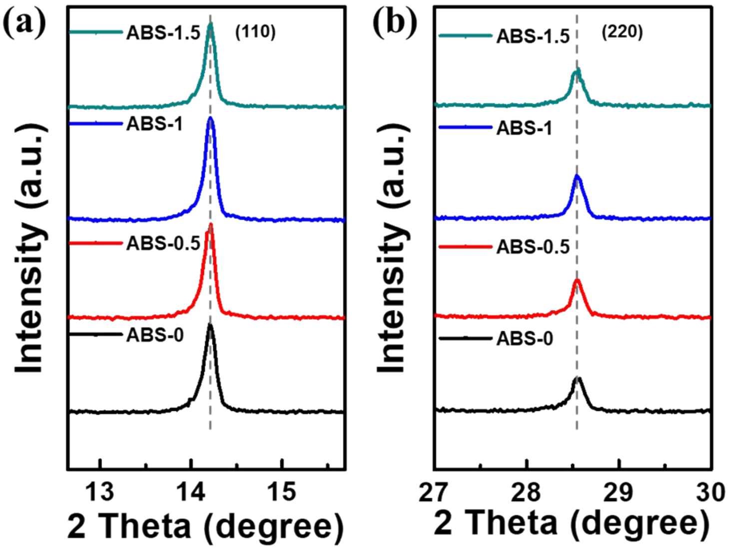

Figure S2. Magnified XRD patterns of $MAPbI_3$-based perovskite films with different ABS contents.

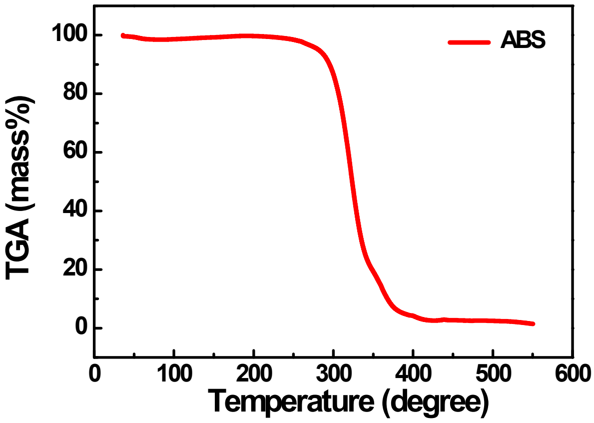

Figure S3. TGA data of ABS powders.

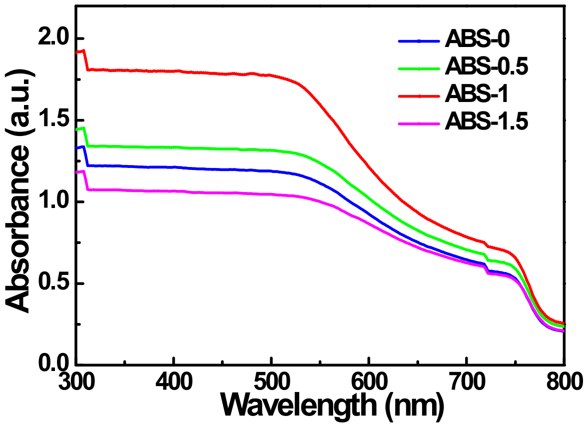

Figure S4. UV-vis spectra of $MAPbI_3$ films with different ABS contents.

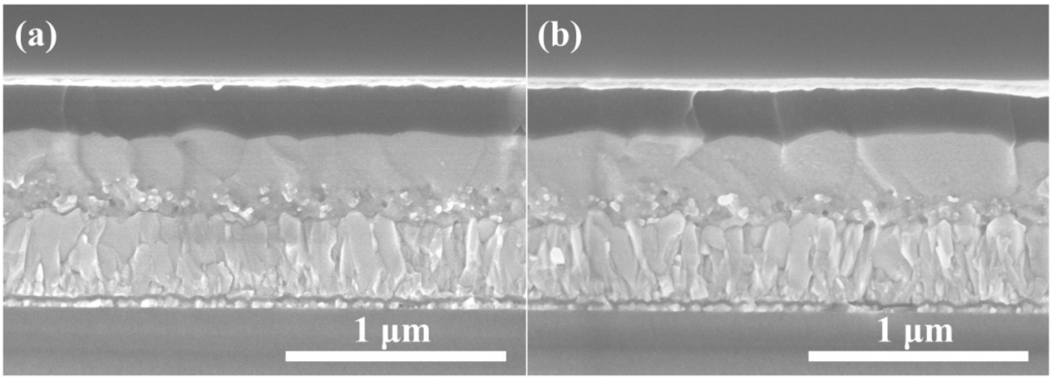

Figure S5. Cross-sectional SEM images of a) MAPbI$_3$-based devices without ABS and b) target device with ABS.

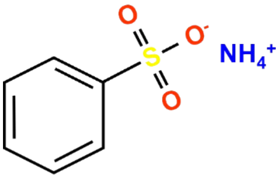

Figure S6. Structural formula of ammonium benzenesulfonate (ABS).

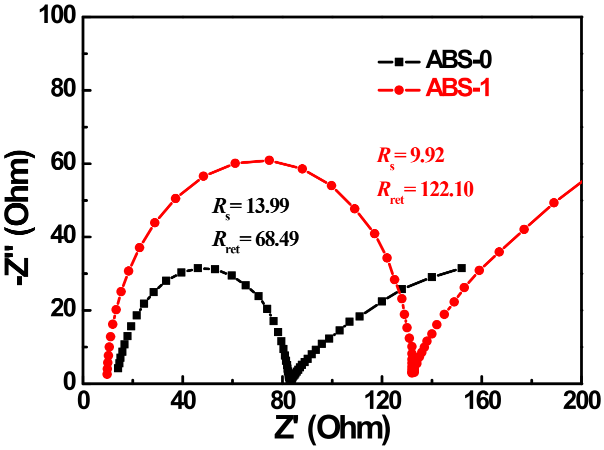

Figure S7. EIS spectra for MAPbI$_3$-based devices with and without ABS.

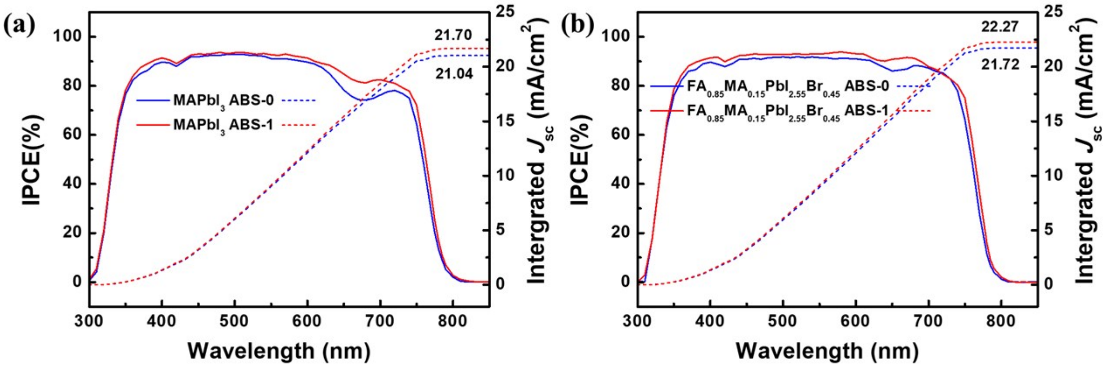

Figure S8. IPCE spectra for a) $MAPbI_3$-based devices with and without ABS and b) $FA_{0.85}MA_{0.15}PbI_{2.55}Br_{0.45}$-based devices with and without ABS.

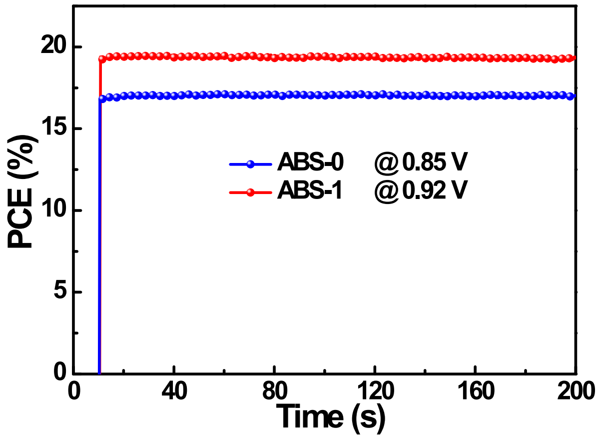

Figure S9. Time corresponding power output of the $MAPbI_3$-based PSCs measured under the bias at 0.85 and 0.92 V, respectively.

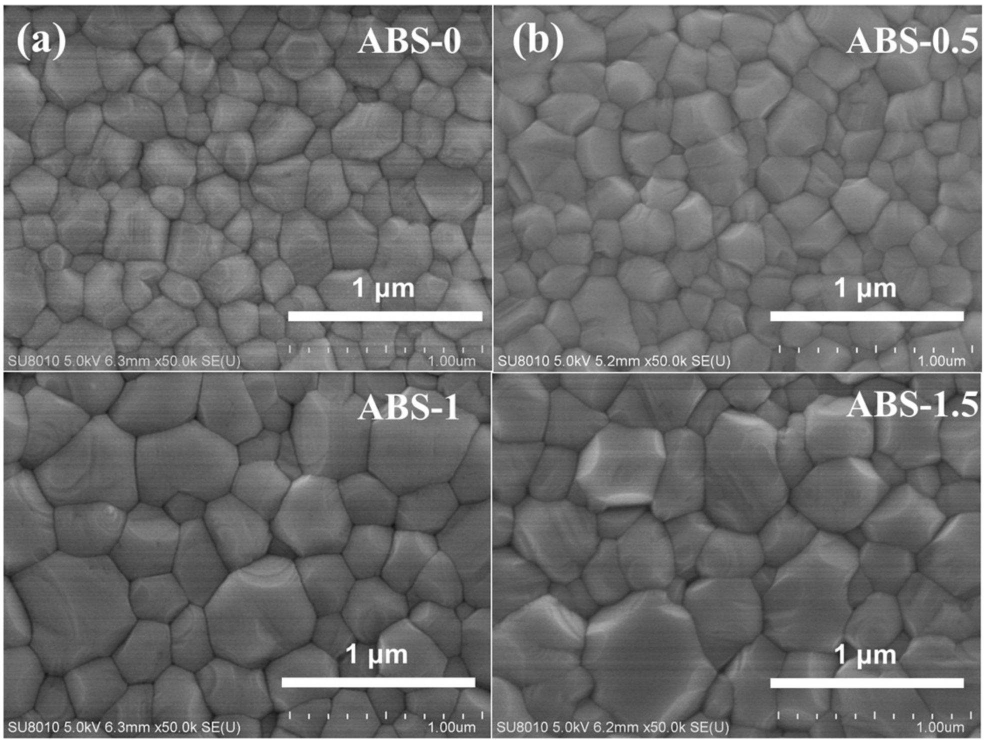

Figure S10. SEM top-view images of $FA_{0.85}MA_{0.15}PbI_{2.55}Br_{0.45}$-based perovskite films with different ABS contents.

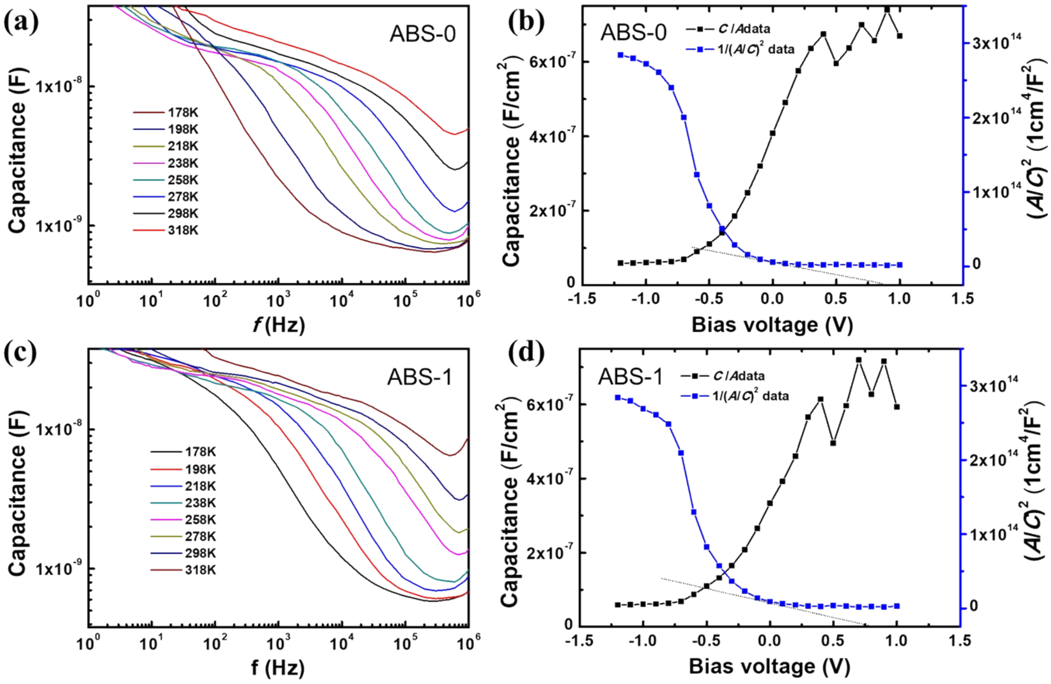

Figure S11. Temperature dependence of capacitance for a) device without ABS and c) device with ABS. Mott-Schottky plots for b) devices without ABS and d) with ABS addition were measured at a frequency (f) of 10 kHz at a temperature (T) of 298 K, where A is the area of the measured pixel. The dash lines are extrapolations to determine the built-in voltage.

Table S1. *J-V* parameters of the $MAPbI_3$-based devices under different conditions

Conditions		J_{sc} (mA·cm^{-2})	V_{oc} (V)	FF (%)	PCE (%)
ABS-0	reverse	22.23	1.03	75.68	17.29
	forward	21.66	1.02	74.39	16.36
ABS-1	reverse	22.92	1.09	78.62	19.64
	forward	22.67	1.09	77.37	19.07

Table S2. TAS parameters for determining the tDOS of different devices.

Devices	V_{bi} (V)	N_d (cm^{-3})	W (cm)
ABS-0	0.87	$1.7*10^{17}$	$13.1*10^{-6}$
ABS-1	0.78	$3.7*10^{16}$	$15.2*10^{-6}$

From extrapolating the $(A/C)^2$ graphs to $(A/C)^2 = 0$ in Mott-Schottky plots, the built-in voltage (V_{bi}) can be obtained. Then the slope of the extrapolation can be used to determine the doping density N_d and the depletion width W (Table S2) at $V_{bias} = 0$ V:

$$N_d = -\frac{2}{q\varepsilon}\left(\frac{d(C/A)^{-2}}{dV}\right)^{-1}$$

$$W = \sqrt{\frac{2\varepsilon(V_{bi} - V_{bias})}{qN_d}}$$

where ε is the dielectric constant (ε_r for this perovskite is 30).[1]

Assuming that the occupancy of the states is in thermal equilibrium, which is determined by the Fermi–Dirac distribution, the thermal emission depth of the defect

E_a and the characteristic transition frequencies ω_0 can be expressed in the equation:

$$\omega_0 = 2CT^2 exp(-\frac{E_a}{kT})$$

Where C is a constant related to the effective density of states in the conduction band, the thermal velocity and the carrier capture cross-section.[1]

References

1. D. Hsin-Sheng, Z. Huanping, C. Qi, S. Pengyu, L. Song, S. Tze-Bin, B. Brion and Y. Yang, *Physical Chemistry Chemical Physics Pccp*, 2014, **17**, 112-116.