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Synergistic improvements in stability and performance of inverted planar $MAPbI_3$ based perovskite solar cells incorporating benzylammonium halide salt additives

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Experimental detail and Characterization:

The synthesis of benzylammonium halide salts were followed the literature reported method.[1,2] The UV-Vis absorption spectra were measured on a Thermo Scientific Evolution 60S UV-vis spectrophotometer. Steady-state photo-luminescence (PL) was measured on FLS980 (Edinburgh Instrument, UK) with excitation wavelength of 470 nm. The time-resolved photoluminescence decay was measured by a time-correlated single photon counting spectrometer (WELLS-001 FX, DongWoo Optron). The pulse laser had a 440-nm wavelength and an average power of 1 mW; it was operated with a duration of excitation of 2 μs. The maximum emission was collected at a wavelength of 770 nm on a single-photon counter.

X-ray photoelectron spectroscopy (XPS) of perovskite film was measured in the ultrahigh vacuum environment using a ULVACPHI PHI 5000 Versaprobe II spectrometer and a monochromatic Al Kα source. The morphologies of the perovskite films were characterized by the field-emission scanning electron microscope (JEOL JSM 6701F). X-ray diffraction (XRD) patterns (2θ scans) were carried out using by X-ray diffractometer (D2 PHASER, Bruker, Germany). The time-of-flight secondary ion mass spectra (ToF-SIMS) were conducted on a TOF-SIMS V instrument (Ion-TOF, GmbH). The water contact angle values were measured by Rame-Hart goiniometer in sessile drop mode.

The electrochemical impedance spectra (EIS) of all devices were measured with an electrochemical workstation (IM 6, Zahner, Germany). The frequency ranges of EIS measurement

went from 1 MHz to 1 Hz with ac amplitude 20 mV under illumination, which calibrated to same light intensity as AM1.5G. The EIS curves were fitted with Z-view software (version 3.4e) based on the electronic circuit model.

Photovoltaic characterization of perovskite solar cells

The photocurrent density–voltage (J–V) performance of the devices were measured on a computer-controlled Keithley 2400 source measurement unit (SMU) and a Enlitech simulator (AAA Class Solar Simulators) under AM 1.5 illumination (1000 Wm^{-2}). The illumination intensity was calibrated using a standard Si reference cell and a KG-5 filter. EQEs were measured using an Enlitech QE-R spectral response measurement system to calibrate the current densities of the devices. The PSCs were kept in a humidity-controlled cabinet (RH = 45 ± 5%. EDRY, FD-50EA) for humidity-stability measurement.

Table S1. Photovoltaic performance parameters of perovskite solar cells with various benzylammonium halide salt additives and related concentrations in the $MAPbI_3$ precursor solution.

Additive	Conc. (mg/ml)	Jsc (mA/cm^2)	Voc (V)	FF (%)	PCE (%)
w/o		19.49	1.04	75.9	15.9
BAZCl	0.1	20.81	1.06	75.1	16.5
	0.5	22.37	1.09	76.8	18.7
	1.0	18.28	1.08	68.6	13.5
BAZBr	0.1	20.96	1.11	76.0	17.7
	0.5	19.00	1.09	77.5	16.0
	1.0	15.05	1.09	71.6	11.7
BAZI	0.1	20.34	1.11	74.0	16.7
	0.5	21.25	1.06	72.2	16.2
	1.0	17.3	1.09	67.2	12.7

Table S2. EIS parameters of PSCs w/o and with various BZA halide salt additives			
Device	R_s/Ω	R_{ct}/Ω	C_{dl}/Fcm^{-2}
Pristine	22.9	587.2	1.3E-08
BZACl	20.8	205.0	1.0E-08
BZAI	18.7	511.8	1.2E-08
BZABr	16.1	487.5	1.1E-08

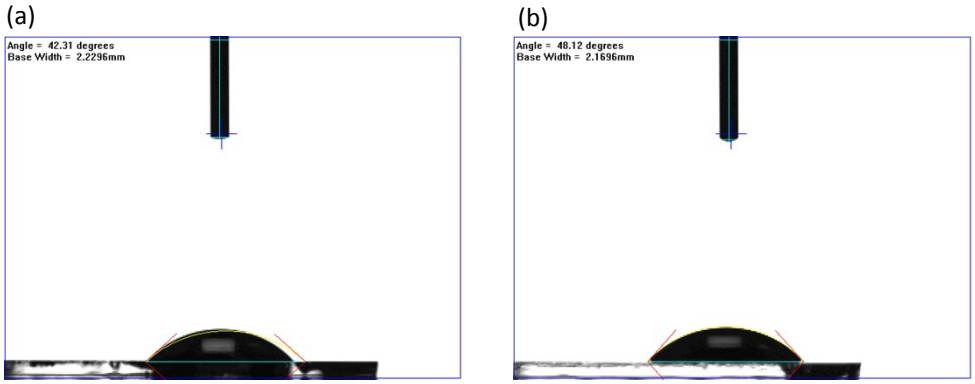

Figure S1. The contact angle measurements performed on the (a) pristine and (b) BZACl doped perovskite substrate. The contact angles are 42.31° and 48.12° in (a) and (b), respectively.

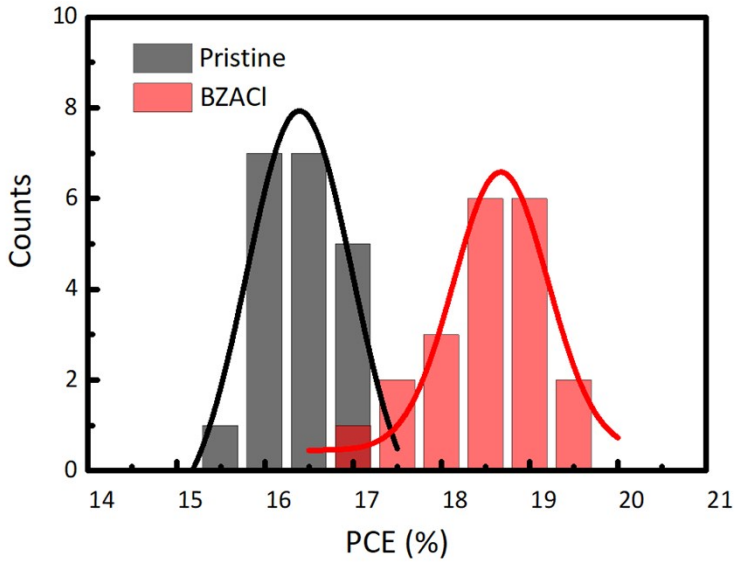

Figure S2. Statistical PCE distribution histogram of 20 devices based on pristine and BZACl doped perovskite, respectively.

Table S3. The reported photovoltaic performances and stability of inverted planar $MAPbI_3$ or $MAPbI_{3-x}Cl_x$ based PSC devices with additives

Addtive	Device configuration	V_{oc} (V)	J_{sc} (mA/cm^2)	FF (%)	PCE (%)	stability test (the retainment of its initial PCE)*	Reference
benzylammonium chloride (BZACl)	ITO/NiO_X/$MAPbI_3$+**BZACl**/PCBM/BCP/Ag	1.10	22.7	79.3	19.8	unencapsulated, 90% after 30 days (~45 % RH, RT)	this work
oxalic acid (OA)	FTO/PEDOT:PSS/$MAPbI_3$+**OA**/PCBM/rhodamine 101/Ag	0.95	23.8	75.0	17.1	unencapsulated, 90% after 9h (glove box, 100 °C)	[3]*ACS Appl. Energy Mater.* **2020,** 3, 2432
IT-4F	ITO/NiO_X/$MAPbI_3$+**IT-4F**/PCBM/PFN-Br/Ag	1.13	23.7	76.0	20.3	unencapsulated , 74% after 1hr (~90 % RH, RT)	[4]*ACS Appl. Mater. Interfaces* **2020**, 12, 39063
chelidamic acid (CA)	ITO/NiO_X/$MAPbI_3$+**CA**/PCBM/rhodamine 101/Ag	1.10	23.5	74.0	19.1	unencapsulated , 80% after 1000h (30~40 % RH, RT)	[5]*Adv. Sustainable Syst.* **2020**, 4, 2000078
phenylhydrazinium iodide (PHAI)	FTO/PEDOT:PSS/$MAPbI_3$+**PHAI**/PCBM/rhodamine /Ag	1.02	23.1	74.0	17.5	unencapsulated , 90% after 20 days (~30 % RH, RT)	[6]*Adv. Funct. Mater.* **2020,** 30, 2000778
Ammonium chloride (NH_4Cl)	ITO/PTAA/$MAPbI_3$+**NH_4Cl**/C_{60}/BCP/Cu	1.09	22.8	79.1	19.7	n/a	[7]*Adv. Energy Mater.* **2020**, 10, 1903108
1-butyl-3-methylimidazolium tetrafluoroborate (BMIMBF4)	FTO/NiO_X/$MAPbI_3$+**$BMIMBF_4$**/PCBM/BCP/Au	1.08	23.8	80.0	19.8	unencapsulated, 86% after 100h (40~50% RH, 60–65 °C)	[8]*Nature* **2019,** 571, 245
trimethylammonium chloride, (TACl)	ITO/polyTPD/$MAPbI_3$+**TACl**/PCBM/ZrAcac/Ag	1.01	22.2	78.1	17.6	n/a	[9]*ACS Appl. Mater. Interfaces* **2019**, 11, 37833
Poly(amic acid), (PAA)	ITO/NiO_X/$MAPbI_3$+**PAA**/PCBM/BCP/Ag	1.06	20.6	76.5	17.9	unencapsulated , 95% after 500h (Ar-filled glovebox)	[10]*J. Phys. Chem. C* **2019**, 123, 23826
2,5-di(thiophen-2-yl)terephthalic acid (DTA)	ITO/PTAA/$MAPbI_{3-x}Cl_x$+**DTA**/C_{60}/BCP/Ag	1.17	22.5	81.4	21.5	unencapsulated , 87% after 40 days (15~20 % RH, RT)	[11]*J. Mater. Chem. A*, **2019**, 7, 21140
π-conjugated Lewis base ITIC	ITO/NiO_X/$MAPbI_{3-x}Cl_x$+**ITIC**/C_{60}/BCP/Ag	1.06	22.7	79.0	19.0	n/a	[12]*J. Mater. Chem. A,* **2018**, 6, 23865
3-(decyldimethylammonio)-propane-sulfonate inner salt (DPSI)	ITO/PTAA/$MAPbI_{3-x}Cl_x$+**DPSI**/PCBM/C_{60}/BCP/Ag	1.12	22.8	79.0	22.0	n/a	[13]*Adv. Mater.* **2018**, 30, 1803428

2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F4TCNQ)	ITO/NiO_X/$MAPbI_3$+**F4TCNQ**/PCBM/BCP/Ag	1.06	19.6	80.0	16.6	unencapsulated, 75% after 21 days (Ar-filled glovebox)	[14]*ACS Appl. Mater. Interfaces* **2018**, 10, 1909
Carbon Nanodot/urea (CND/urea)	ITO/NiO_X/$MAPbI_3$+**CND/urea** /PCBM/BCP/Ag	1.07	22.7	76.9	18.7	unencapsulated , ~100% after 500h (40 % RH, RT)	[15]*Adv. Energy Mater.* **2018**, 8, 1802323
Thiazole	FTO/NiO_X/$MAPbI_3$+**Thiazole**/PCBM/Ag	1.04	21.0	82.0	18.0	n/a	[16]*ACS Appl. Mater. Interfaces* **2018**, 10, 42436
hydrazinium chloride (N_2H_5Cl)	ITO/PEDOT:PSS/$MAPbI_3$+**N_2H_5Cl**/PCBM/C_{60}/BCP /Ag	0.92	19.4	71.0	12.7	n/a	[17]*ACS Appl. Mater. Interfaces* **2017**, 9, 36810
benzoquinone (BQ)	ITO/PEDOT:PSS/$MAPbI_3$+**BQ** /C60/BCP/Au	1.02	21.3	72.0	15.7	80% after 950h (continuous one sun solar irradiation)	[18]*Adv. Mater.* **2017**, 29, 1603808
methylammonium acetate (MAAc) and thio-semicarbazide (TSC)	FTO/NiOX/$MAPbI_3$+**MAAc+TSC**/PCBM/Ag	1.11	22.8	77.1	19.5	90% after 1000h (continuous one sun solar irradiation)	[19]*Adv. Mater.* **2017**, 29, 1701073
PCBM	ITO/PEDOT:PSS/$MAPbI_3$+ **PCBM**/PCBM/Ca/Al	0.97	20.2	82.0	16.0	n/a	[20]*Nature Photonics* **2016**, 10, 196.
KCl	ITO/PEDOT:PSS/$MAPbI_3$+ **KCl/**PCBM/C_{60}/Al	1.04	18.3	75.6	15.1	unencapsulated , 83.5% after 50 days (glove box, RT)	[21]*J. Mater. Chem. A,* **2016**, 4, 1591

* relative humidity = RH, room temperature =RT, 20~25°C

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