Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supplementary Information

Confinement of MACl Guest in 2D ZIF-8 Triggers Interface and Bulk Passivation for Efficient and UV-Stable Perovskite Solar Cells

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1. Materials

The zinc (II) nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$) and dimethylimidazole (2-MIM) were purchased from the Sinopharm Chemical Regent Co. Ltd. The tin (IV) oxide colloid precursor (SnO_2, 15% in H_2O colloid dispersion) was purchased from Alfa Aesar. Formamidinium iodide (FAI), and Lead (II) iodide (PbI_2) were purchased from Xi'an Polymer Light Technology Corp. Bis (trifluoromethane) sulfonimidelithium salt (Li-TFSI) was purchased from Sigma-Aldrich. And the perovskite precursor solution was prepared according to the previous work of our group. Generally, 1.4 M CsMAFA precursor solution was prepared by dissolving 18.2 mg CsI, 26.7 mg MABr, 199.8 mg FAI, 573.9 mg PbI_2, and 87.4 mg $PbBr_2$ in 1 mL mixed solvent of N, N-dimethylformamide (DMF), and dimethyl sulfoxide (DMSO) at a volume ratio of 4:1.

2. Experimental

2.1 Synthesis of 2D ZIF-8 Nanosheets and MACl@ZIF-8

The synthesis of ZIF is mainly according to a previous report with modifications.[1] Generally, 594.98 mg (2 mmol) $Zn(NO_3)_2 \cdot 6H_2O$ was dissolved in 30 mL mixed solvent of N, N-dimethylformamide (DMF), and ethanol with equal volume ratio under stirring, to obtain a solution A. Then 656.8 mg (8 mmol) 2-MIM was dissolved in the same mixed solvent as above to obtain solution B. The homogenous solutions were stirred for 15 min at room temperature, and then solution A was rapidly poured into solution B. Then 30 min of continuous stirring was required to fully combine the two solutions. The off-white precipitate was separated by centrifugation at 8000 rpm after aging for 24 h. Afterward, the precipitate was washed twice with ethanol and once with DMF,

respectively. The resultant ZIF-8 nanosheets were then continuously stirred for 24 h into a saturated MACl DMF solution. The resultant nanosheets for the MACl@ZIF-8 capsules were collected by filtration and cleaned with ethanol. For further use, the moist precipitate was redissolved in DMF.

2.2 Device Fabrication

Under continuous ultrasonic treatment, detergent, deionized water, ethanol, and acetone were used to clean the etched FTO (14 sq^{-1}) substrates. The resulting dry substrates were then treated with clean, dry air before being exposed to plasma for 15 min to increase their capacity to moisten. Tin oxide (SnO_2) colloidal precursors were created by combining deionized water in a 1:4 volume ratio with a 15% SnO_2 colloidal dispersion. By spin-coating on FTO at 3000 rpm for 30 s and subsequently annealing at 120 °C for 30 min in free air, SnO_2 layers were created. After that, the substrate was spin-coated with the MACl@ZIF-8 solution (200 mg/mL) at 5000 rpm for 30 s. The substrates were then annealed for 30 min at 100 °C. After spinning the perovskite precursor solution at 4000 rpm for 30 s on an FTO/SnO_2/MACl@ZIF-8 substrate, 200 mL of chlorobenzene (CB) was then immediately poured over the substrate.[2] All of the perovskite layers were annealed for 30 min at 105 °C. The Spiro-OMeTAD solution was made according to the following recipe for the hole transport layer: 13.125 μL Li-TFSI, and 21.6 μL TBP and 30 mg of Spiro-OMeTAD were dissolved in 825 μL of CB before being spin-coated onto the perovskite layer at 4000 rpm for 30 s. The top electrode was then thermally evaporated to a thickness of around 90 nm Au.

3. Characterization

X-ray diffraction (XRD) spectra were characterized by a Bruker apparatus (D2) using Cu Kα radiation. The scan range for 2θ was between 5° and 60°. The film morphologies were observed by a field emission-scanning electron microscope (FE-SEM) (SU8010, Hitachi, Japan). AST VCA Optima XE drops shape analyzer was applied to characterize the contact angles of different films by using a mixed-solvent (DMF:DMSO=4:1). The absorption spectra were implemented using a UV–vis spectrophotometer (Lambda 950, Perkin-Elmer Co.). The surface roughness of films was observed by atomic force microscopy (AFM) with Bruker Dimension Icon. X-ray photoelectron spectroscopy (XPS) and time-resolved photoluminescence (TRPL) spectra and steady-state photo-luminescence (PL) were performed by using a FLS920 transient optical spectrometer (Edinburgh Instruments, UK). The photocurrent density-voltage (J-V) curves were performed by a digital source meter analyzer (Keithley 2400) under AM 1.5 G with the light intensity calibrated to 100 mW cm^{-2}. Electrochemical impedance spectroscopy (EIS) was acquired with a Zahner-Elektrik (Germany) workstation under dark conditions. The UV ageing test is performed by using a 365 nm UV lamp with the intensity of 36.4 mW cm^{-2}.

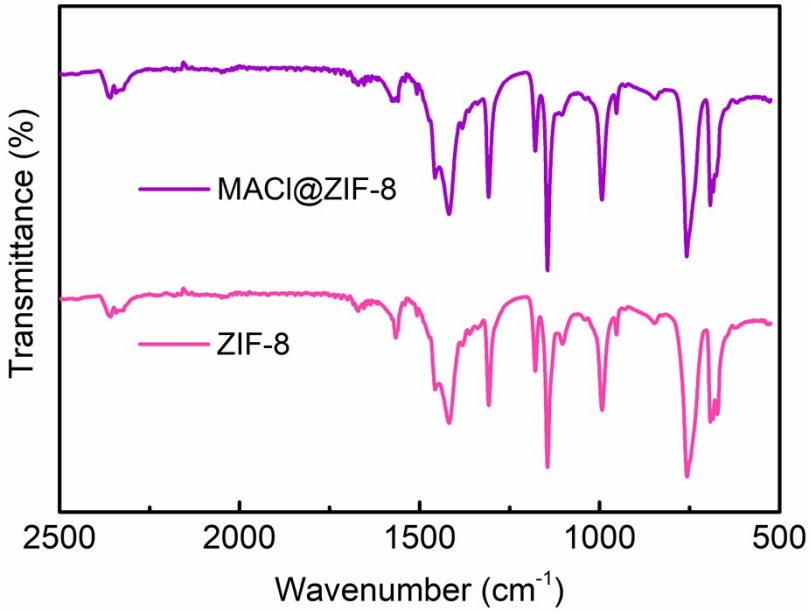

Fig. S1 FTIR spectra of ZIF-8 and MACl@ZIF-8.

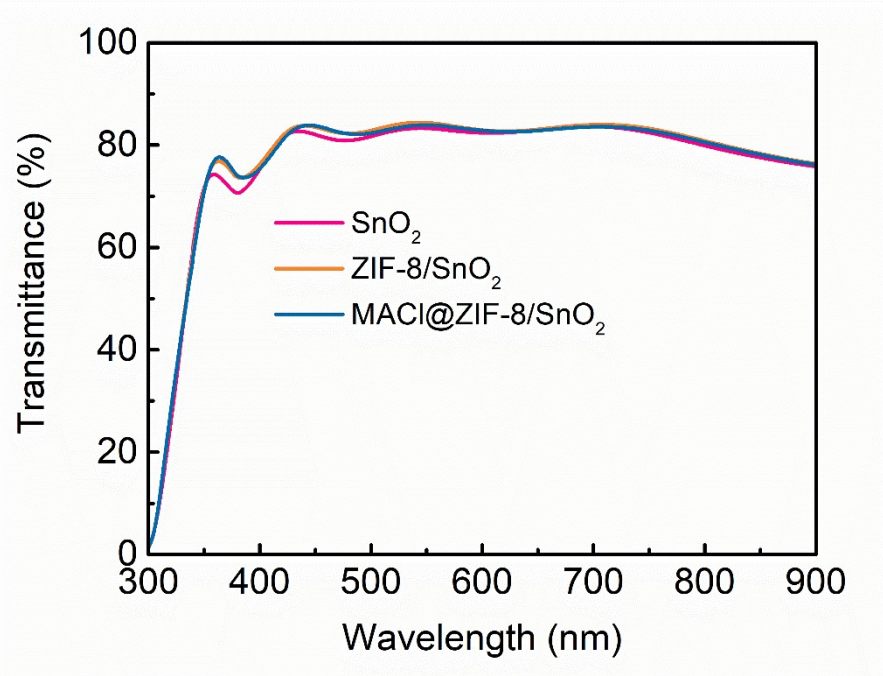

Fig. S2 UV-vis transmittance spectra of the different ETLs.

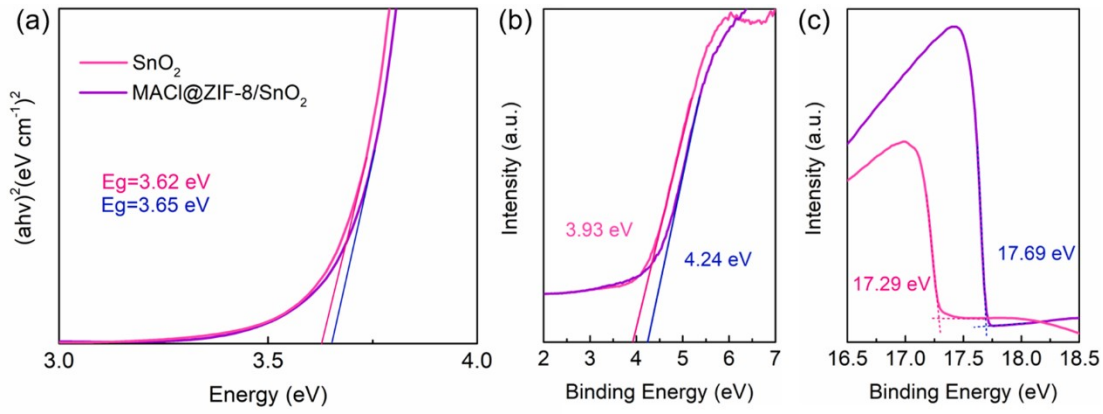

Fig. S3 (a) Tauc plots calculated from UV–vis spectra. (c) Valence regions in UPS survey and (b) secondary-electron cutoff spectra.

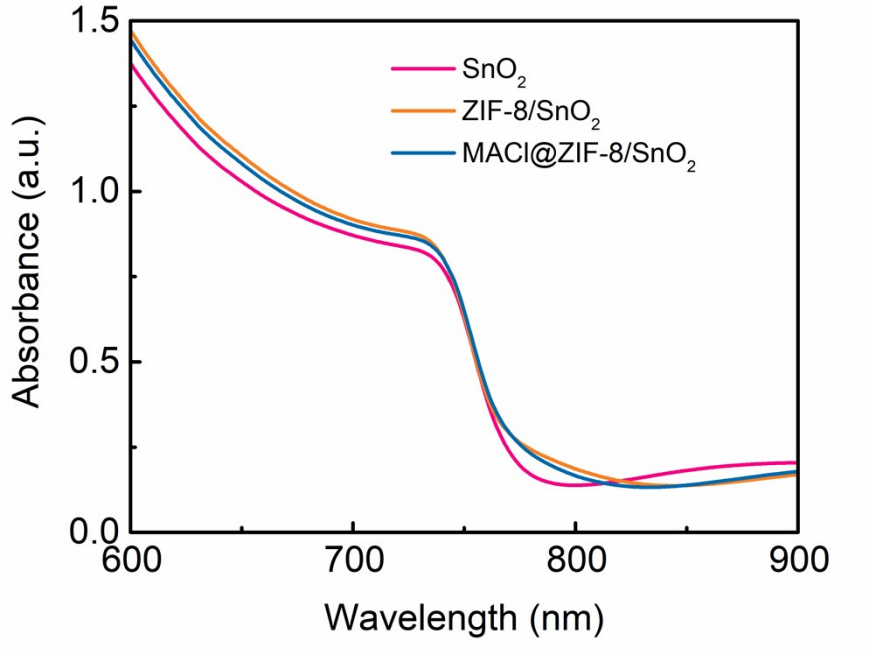

Fig. S4 UV-vis absorbance spectra of the perovskite films based on different ETLs.

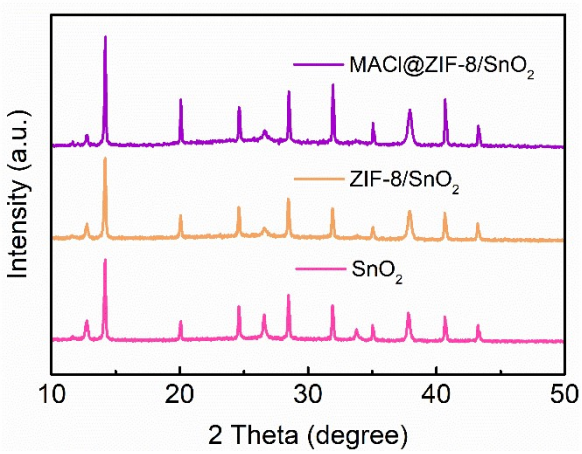

Fig. S5 XRD patterns of perovskite films based on different ETLs.

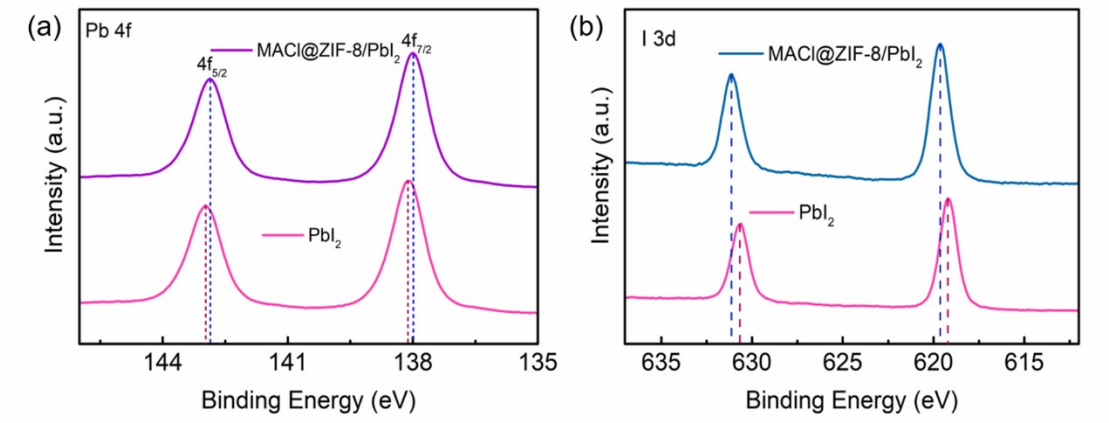

Fig. S6 XPS spectra of (a) Pb 4f and (b) I 3d.

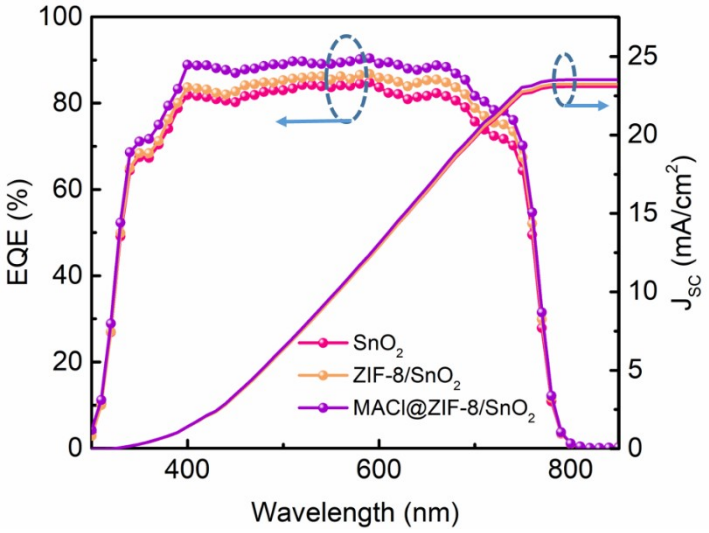

Fig. S7 EQE curves of devices based on SnO_2, ZIF-8/SnO_2, and MACl@ZIF-8/SnO_2, respectively.

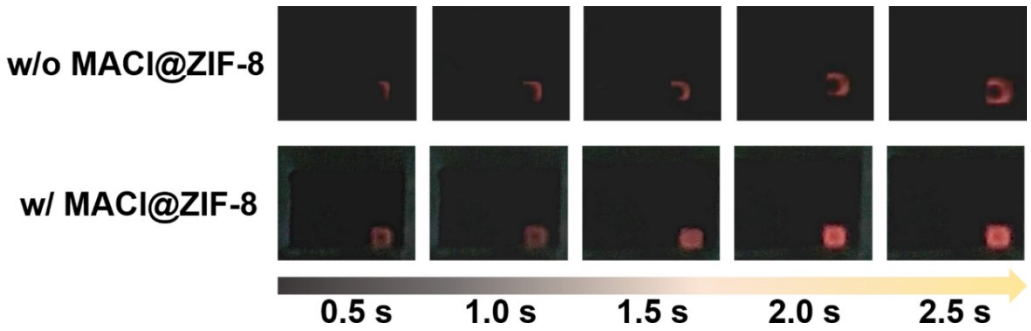

Fig. S8 Digital photographs of the electroluminescence of two devices.

Table S1 The fractions of oxygen vacancy and Sn-O.

Sample	Oxygen vacancy (%)	Sn-O (%)
SnO_2	54	46
MACl@ZIF-8/SnO_2	38	62

Table S2 TRPL fitting parameters.

Sample	A_1	τ_1	A_2	τ_2	τ_{ave}
SnO_2	0.23	4.13	0.77	52.45	51.38
MACl@ZIF-8/SnO_2	0.33	1.90	0.67	150.95	150.03

References

1. G.J. Wei; Z. Zhou; X.X. Zhao; W.Q. Zhang; C.H. An, Ultrathin Metal-Organic Framework Nanosheet-Derived Ultrathin Co_3O_4 Nanomeshes with Robust Oxygen-Evolving Performance and Asymmetric Supercapacitors. *ACS Applied Materials & Interfaces* **2018,** *10* (28), 23721-23730.

2. J. Shi; B. Li; Q. Zhang; Y. Rui, Electrodeposited Ternary $AgCuO_2$ Nanocrystalline Films as Hole

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