Supplementary Information

Interfacial Chemical Bridge Constructed by Zwitterionic Sulfamic Acid for Efficient and Stable Perovskite Solar Cells

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Experimental Section

Materials: The SnO₂ colloid precursor was purchased from Alfa Aesar (tin (IV) oxide, 15% in H₂O colloidal dispersion). The sulfamic acid, aminomethanesulfonic acid, taurine, and 3-amino-1-propanesulfonic acid were purchased from Shanghai Macklin Biochemical Co.,Ltd. dimethylformamide (DMF), dimethyl sulfoxide (DMSO), chlorobenzene, acetonitrile were achieved from Sigma-Aldrich. Spiro-OMeATD was provided by Borun New Material Technology Ltd. All the materials used without any further purification.

Device Fabrication: The ITO coated glass substrates were sequentially ultrasonic cleaned with detergent, deionized water, acetone and isopropanol for 15 min, respectively. A 15 min ultraviolet-ozone treatment carried out to remove the residual organics and improve the work function of ITO substrates. The SnO2 aqueous solution was diluted with deionized water (volume rate 1:6 and 1:10), and then was deposited by spin-coating at 3000 rpm for 30 s as the electron transport layers (First, the 1:6 solution deposited and annealed at 150 °C for 20 min. As the substrate is cooled to room temperature, the 1:10 solution deposited again and annealed at 150 °C for 10 min). The interfacial modified materials (sulfamic acid, aminomethanesulfonic acid, taurine and 3-amino-1-propanesulfonic acid) was dissolved in deionized water at an optimum concentration of 0.5 mg mL⁻¹. The pristine SnO₂ film was immersed in those solution for 5 h, and then the substrates were rinsed with deionized water and dried. Subsequently, the perovskite layer was deposited by one-step spin coating method in a glove-box. 1.2 M organic cation (FAI/MABr = 0.85/0.15) and 1.3 M mixture of metal lead salts (PbI₂/PbBr₂ = 0.85/0.15) in a mixture solvent of DMF/DMSO (4:1, by volume). Thereafter, CsI (5% volume, 1.5 M DMSO) was added to the precursor solution to attain the Cs_{0.05}(FA_{0.85}MA_{0.15})_{0.95}Pb(I_{0.85}Br_{0.15})₃ mixed cation perovskite precursor solution.¹ The precursor solution was spin-coated onto the different substrates in a twostep programme at 1000 rpm and 5000 rpm for 10 s and 30 s, respectively. During the second step, 100 μ l of chlorobenzene was dropped on the spinning substrate at 10 s before the end of the programme, and then the deposited films were annealed at 100 °C for 45 min. The thickness of perovskite films was about 470 nm, determined by a profilometer (KLA-Tencor D-120). The holetransport materials solution containing Spiro-OMeTAD (72.3 mg), 4-tert-butylpyridine (tBP, 28.8 μ L), Li-TFSI/acetonitrile solution (17.5 μ L, 520 mg mL⁻¹), FK209 (29 μ L, in acetonitrile solution, 300 mg mL⁻¹) and chlorobenzene (1 mL). The hole-transport layer was deposited by spin-coating at 4000 rpm for 30 s. Finally, 80 nm Au back electrode deposited by thermally evaporated at a pressure of 1.0×10⁻⁴ Pa.

Measurement and characterization: *J-V* characteristics of PSCs were recorded by a Keithley 2400 source measurement unit under a simulated AM1.5 (100 mW cm⁻²) spectrum provided by XES-70S1 (SANYOU Electric Co., Ltd.) and calibrated by a standard Si reference cell. The *J-V* measurements were carried out in nitrogen environment. The devices are measured both in reverse scan ($1.2V \rightarrow -0.1V$) and forward scan ($-0.1V \rightarrow 1.2V$), with a fixed voltage interval of 10 mV. The external quantum efficiency (EQE) spectra of PSCs were measured by a Solar Cell Spectral Response Measurement System QER3011 (Enli Technology Co. Ltd., Taiwan) from 300nm to 900nm. Electrochemical impedance spectroscopy (EIS) measured using CHI660D electrochemical analyzer (CH Instruments Inc.) and the data were analyzed by the ZSimdemo program.

The absorbance spectra of perovskite films were obtained by using a UV-vis spectrometer (PE Lambda 650/850/950 UV-vis spectrophotometer). The AFM/KPFM images scanned by a Bruker multimode 8 microscope in the tapping mode. Top-view and cross-section SEM images of perovskite were captured by a Hitachi S4800 electron microscope. XRD spectra of perovskite were

measured using a Rigaku D/MAX-TTRIII (CBO) X-ray diffractometer equipped with a push-plug gobel mirror and a monochromatic CuK α (λ = 1.5405 Å) radiation source. Steady-state PL excitation and emission spectra were recorded by a HORIBA Fluorolog-III spectrofluoroemeter housed with a Janis cryostat. PL decay kinetics were measured by a HORIBA Jobin-Yvon Fluorolog-III fluorimeter in the transient mode with the excitation provided by a 509 nm diode laser. The PL decay was acquired with a peak preset of 3000 counts and the data were analyzed using the Data Analysis Software. TPC and TPV measurements were performed by a customized transient measurement systems (Physike Technology Co., Ltd) with using a pulsed semiconductor laser (Coherent, Inc.).

Gaussian Calculation: Geometry optimizations were carried out on the molecules in the gas phase, using the software Avogadro² to enter the starting geometry. The molecules were distorted to form a variety of conformers which were then allowed to optimize, in order to find the global minimum on the potential energy surface. Frequency calculations were performed on all the optimized geometries to distinguish whether they were minima or transition states on the potential energy surfaces. All calculations were carried out using the Gaussian 09 program³ with the B3LYP functional⁴ and the standard 6-31G(d) basis set.

Supplementary Tables

Table S1. The bi-exponential fitted parameters of perovskite deposited on SnO_2 and SnO_2 -SA ETMs from TRPL spectra.

ETM	$\tau_1^{(ns)}$	A ₁ (%)	$\tau_2^{}(ns)$	A ₂ (%)
SnO ₂	3.4	4.91	228.5	95.09
SnO ₂ -SA	3.2	6.18	100.7	93.82

Table S2. EIS Parameters for the PSCs based on SnO₂ and SnO₂-SA ETMs.

ETM	$R_{s}\left(\Omega ight)$	$R_{rec}\left(\Omega ight)$	C (F)
SnO_2	36.24	93.02	2.02×10 ⁻⁸
SnO ₂ -SA	41.74	179.0	1.50×10 ⁻⁸

Table S3. The best photovoltaic performances of the PSCs with various modifiers-based SnO_2 ETMs obtained from the *J-V* reverse scan.

Modifier	$V_{\rm oc}({ m V})$	$J_{\rm sc}$ (mA/cm ²)	FF (%)	PCE (%)
Aminomethylsulfonic acid	1.12	22.78	76.86	19.62
2-aminoethanesulfonic acid	1.12	22.82	76.04	19.22
3-amino-1-propanesulfonic acid	1.11	22.83	74.35	18.84

Table S4. The bi-exponential fitted parameters from TRPL spectra of perovskite deposited on modified-SnO₂ with the three modifiers (aminomethylsulfonic acid, 2-aminoethanesulfonic acid and 3-amino-1-propanesulfonic acid, respectively).

Sample	$\tau_1^{}(ns)$	A ₁ (%)	$\tau_2^{}(ns)$	A ₂ (%)	
Aminomethylsulfonic acid	3.8	6.07	110.8	93.93	
2-aminoethanesulfonic acid	4.3	9.39	140.2	90.61	
3-amino-1-propanesulfonic acid	8.4	12.69	153.3	87.31	

Supplementary Figures



Figure S1. Distribution of the PSCs efficiencies based on different SA concentrations (at least 30 devices were studied).



Figure S2. UV-vis absorption spectra for the perovskite films deposited on SnO₂ and SnO₂-SA.



Figure S3. The steady-state photocurrent densities near the maximum power point of the devices based on SnO_2 and SnO_2 -SA ETMs.



Figure S4. Surface potential images of different films. The surface potential are measured with KPFM by probing the difference surface potential (SP) between Pt/Ir-coated tip and the samples.⁵ The Fermi level of Au is -5.1 eV. The Fermi level of samples can be calculated as follows: $FL = -5.1 + e(SP_{Au} - SP_{sample})$, the measured SP_{Au} is 0.836 V.



Figure S5. The electrostatic potential map of the sulfamic acid (SA) used in this study.



Figure S6. The equivalent circuit model for EIS. The equivalent circuit composed of the series resistance (R_s) and recombination resistance (R_{rec}).



Figure S7. Chemical structures of three modifiers (aminomethylsulfonic acid, 2-aminoethanesulfonic acid and 3-amino-1-propanesulfonic acid).



Figure S8. Time-resolved PL decays of perovskite films deposited on modified-SnO₂ with the three modifiers (aminomethylsulfonic acid, 2-aminoethanesulfonic acid and 3-amino-1-propanesulfonic acid, respectively).

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