Supporting Information

Simultaneous Passivation of Perovskite Interfaces at Multiple Active Sites Improves Device Performance: Combining Theory and Experiment

Li Liu,*[a] Huan Bi,*[b] Yongheng Chen,[a] Xifang Chen,[a] Pengyu Su,[c] Gongfa Li,[d] Hanjun Zou,[e] and Zao Yi*[a]

[a] *Joint Laboratory for Extreme Conditions Matter Properties, School of Mathematics and Physics, Southwest University of Science and Technology, Mianyang, P. R. China, 621010. E-mail: liuli_phy@swust.edu.cn, yizaomy@swust.edu.cn.*

[b] *Graduate School of Informatics and Engineering, The University of Electro-Communications, 1-5-1 Chofugaoka, Chofu, Tokyo, Japan, 182-8585. E-mail: hbi.trans.sci@gmail.com*

[c] *School of Electronic Information Engineering, Yangtze Normal University, No. 16, Juxian Avenue, Fuling District, Chongqing, P. R. China, 408100.*

[d] *Hubei Key Laboratory of Mechanical Transmission and Manufacturing Engineering, Wuhan University of Science and Technology, Wuhan, P. R. China, 430081.*

[e] *Analytical and Testing Center, Chongqing University, Chongqing, P. R. China. 401331*

Materials: The SnO_2 precursor was procured from Thermo Scientific (tin (IV) oxide, 15 % in H_2O colloidal dispersion). 2-Mercapto-4-methyl-5-thiazoleacetic acid (MMTA) and rubidium iodide (RbI, 99.9 %) were obtained from Aladdin Scientific. Lead(II) chloride ($PbCl_2$, 99.99 %), and methylamine hydrochloride (MACl, 99.5 %) were sourced from Xi'an Polymer Light Technology Corp. Lead (II) iodide (PbI_2, 99.99 %), Formamidine hydroiodide (FAI), Lead (II) bromide ($PbBr_2$, 99.999 %), and Spiro-OMeTAD (>99 %) were acquired from Advanced Election Technology Co., Ltd. N,N-dimethylformamide (DMF, 99.8 %), dimethyl sulfoxide (DMSO, 99.9 %), and chlorobenzene (CB, 99.8 %) were purchased from Sigma Aldrich.

Device Fabrication: FTO glasses were subjected to ultrasonic cleaning for 15 min using detergent water and ethanol. After nitrogen blow-drying, the FTO underwent a 25-minute treatment with ultraviolet ozone (UV-O_3). The SnO_2 solution was prepared by mixing the SnO_2 with deionized water at a volume ratio of 1:3. The diluted SnO_2 solution was spin-coated onto FTO substrates for 30 s at a speed of 3000 rpm, and the SnO_2 film was annealed at 150 °C for 30 min. Then, it underwent a 20-minute UV-O_3 treatment. Subsequently, the substrates were transferred into an N2-filled glovebox for the next step. The perovskite ($Rb_{0.02}(FA_{0.95}Cs_{0.05})_{0.98}PbI_{2.91}Br_{0.03}Cl_{0.06}$) solution was made by dissolving 682.7 mg of PbI_2 , 8.5 mg of $PbBr_2$, 6.6 mg of RbI , 12.7 mg of $PbCl_2$, 19.7 mg of CsI, 248.2 mg of FAI , and 35 mg of MACl (additive) into the 200 μL of DMSO and 800 μL of DMF. The perovskite film was formed through a sequential spin-coating method at 4000 rpm for 30 s. During the last 15 s of the spin-coating program, 100 μL of CB antisolvent was dripped over the perovskite films. Subsequently, the film underwent annealing at 130 °C for 30 min. The MMTA solution was prepared by dissolving MMTA in an isopropanol solvent. For the modified perovskite films, the filtered MMTA solution, obtained through a PTFE filter, was spin-coated on the as-prepared perovskite films at 5000 rpm for 30 s. A Spiro-OMeTAD solution was created by combining 72.3 mg of Spiro-OMeTAD, 28.8 μL of 4-tert-butyl pyridine (*t*BP), and 17.5 μL of lithium bis(trifluoromethane sulfonyl)imide (Li-TFSI) (520 mg of Li-TSFI in 1 mL acetonitrile) in 1 mL CB. Subsequently, the HTL was created by spin-coating 40 μL of Spiro-OMeTAD solution onto the perovskite films at 4000 rpm for 30 s. Finally, employing a shadow mask, a 100 nm

Ag counter electrode was thermally evaporated on top of Spiro-OMeTAD under a 1*10^{-4} Pa vacuum.

Characterization: UV-vis absorption spectra were recorded using a UV-vis spectrometer (Shimadzu UV-1800, Japan). Fourier-transform infrared spectroscopy (FTIR) was conducted using a Nicolet iS50 Infrared Fourier-transform microscope from Thermo Fisher Scientific (America). TRPL spectra were measured using Edinburgh FLS1000 (UK). X-ray photoelectron spectra (XPS) measurements were performed using a Thermo-Fisher ESCALAB 250Xi system. *J–V* curves were obtained utilizing solar simulator equipment equipped with a 150 W Xenon lamp and a Keithley 2400 source meter. The effective active area of the device was set at 0.1 cm^2 using a black metal mask. Incident photon-to-current conversion efficiency (IPCE) spectra were recorded employing a monochromatic Xenon lamp. Impedance spectroscopy was measured by the Electrochemical Workstation (China). All calculations were performed utilizing the CP2K package. The grid cutoff was 450 Ry. Multiwfn 3.8(dev) was used in this work.

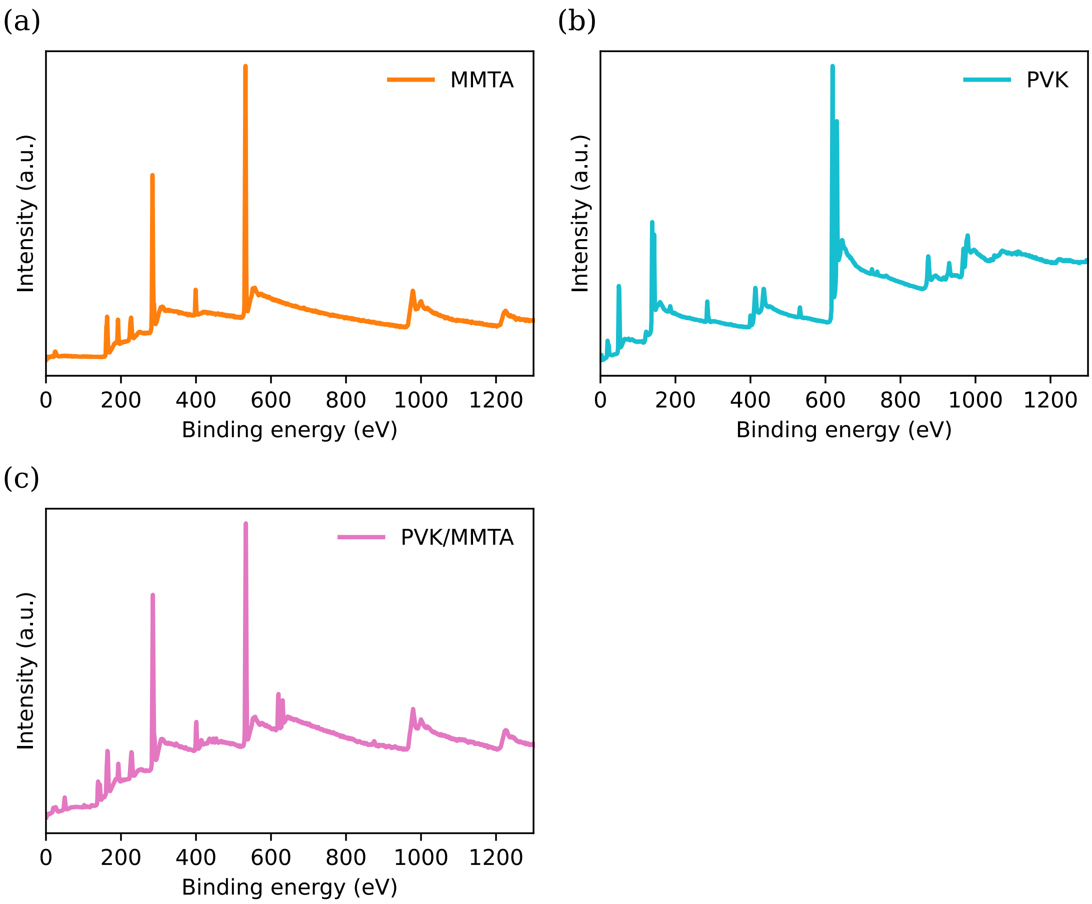

Fig. S1. XPS full spectra of (a) MMTA, (b) PVK, and (c) PVK/MMTA.

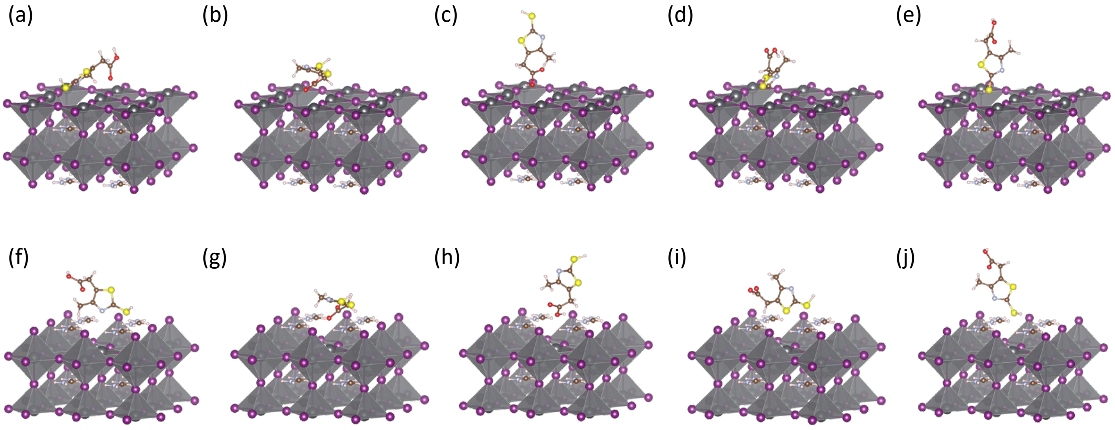

Fig. S2. Initial structure of the interfaces for the inorganic PbI_2 plane and FAI plane with the iodine defect in contact with the different sites of MMTA. PbI_2 interface with (a) N1, (b) O1, (c) O2, (d) S1, and (e) S2 of MMTA. FAI interface with (a) N1, (b) O1, (c) O2, (d) S1 and (e) S2 of MMTA.

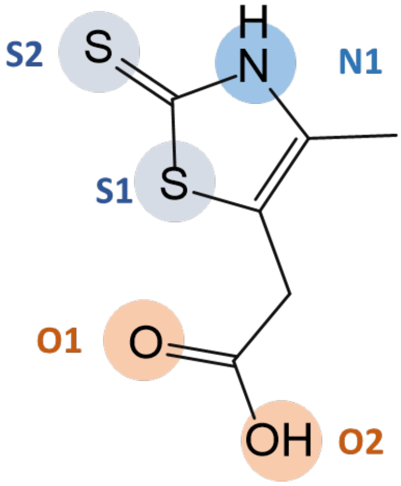

Fig. S3. MMTA molecular structure and naming of multiple active sites.

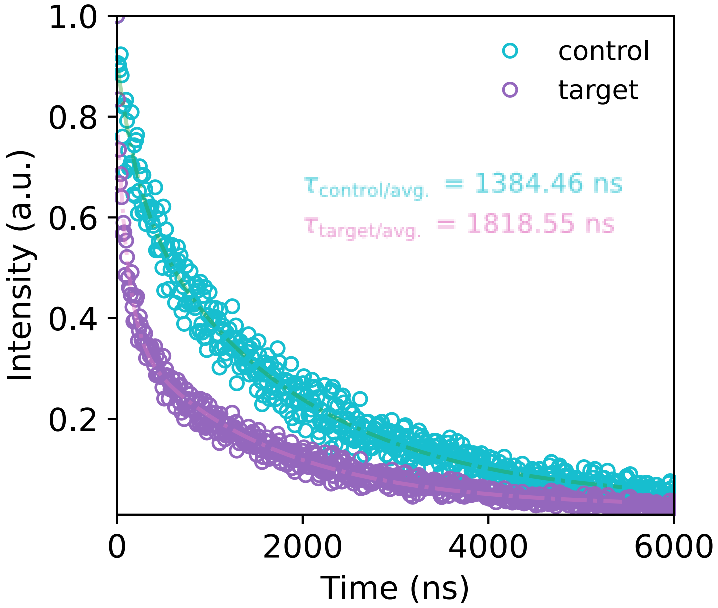

Fig. S4. TRPL curves of the perovskite film with the structure of glass/perovskite with or without MMTA modification.

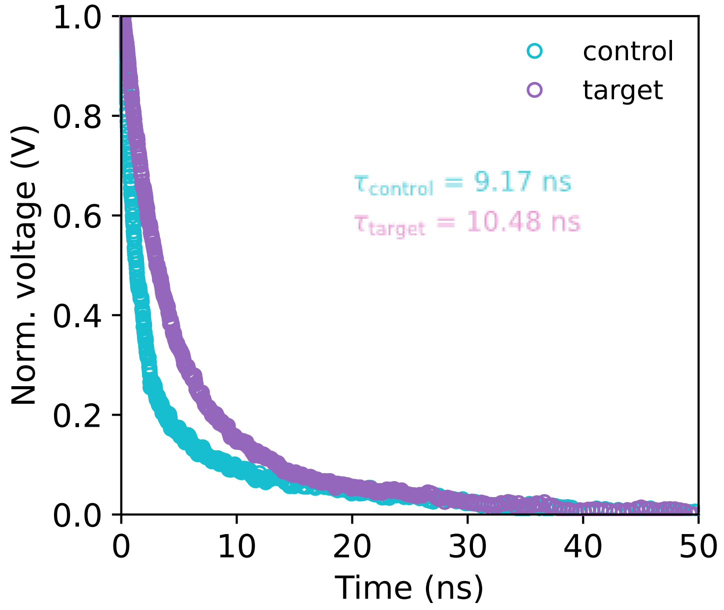

Fig. S5. TPV curves of the device with or without MMTA modification.

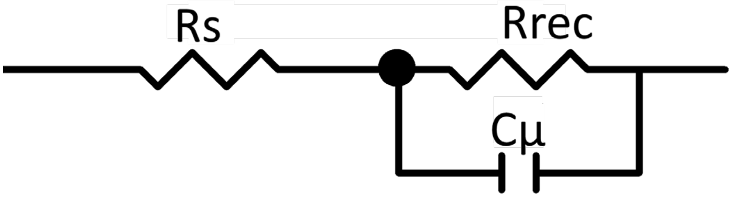

Fig. S6. The equivalent circuit model for EIS.

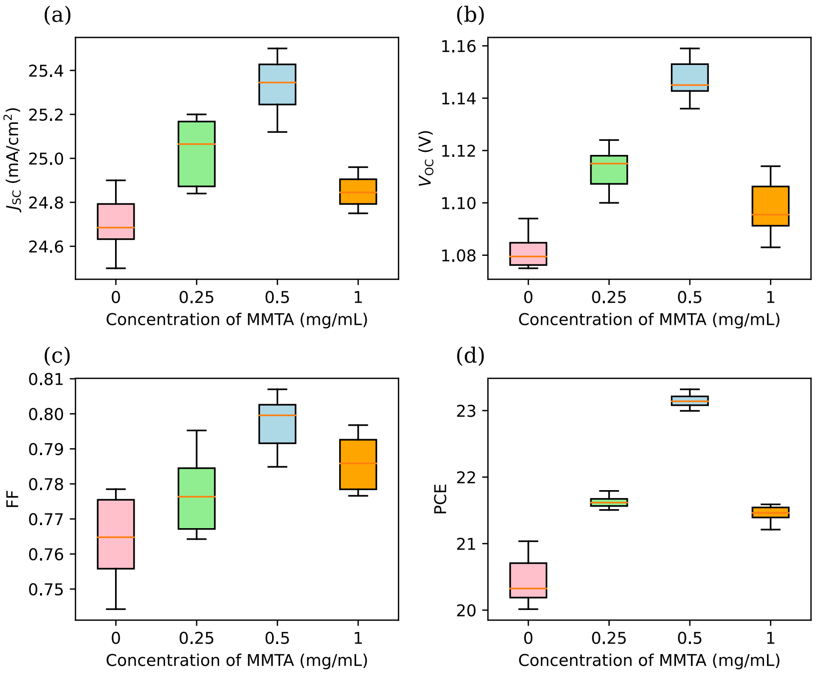

Fig. S7 . a) J_{SC}, b) V_{OC}, c) FF, and d) PCE statistical diagrams of the devices with different concentrations of MMTA.

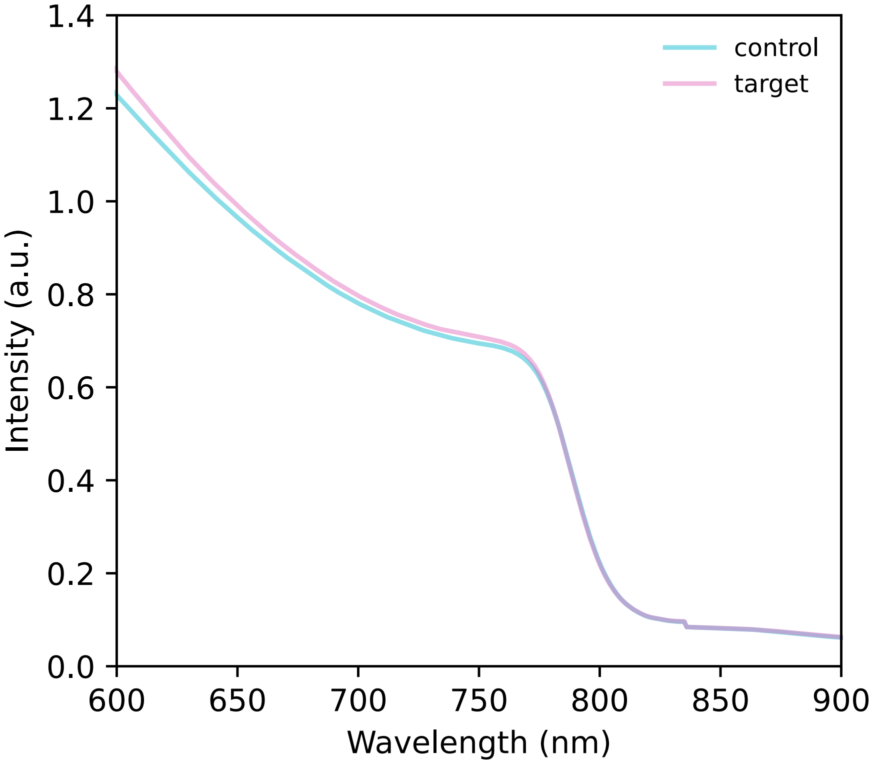

Fig. S8. UV-Vis absorption spectra of the perovskite films with or without modifiers.