Supplementary Information

Dynamic interface charge governing the current-voltage hysteresis in perovskite solar cells

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1. The measuring process of the interface charge, the photocurrent and the J–V curves.

The Source-Measure Unit (Agilent B2902A) that we used is a programmable and flexible power supply. We can put the pre-biasing and the following measurement (of interface charge, the photocurrent or the J–V curves) into one process.

• The measurement of the interface charge. For example, a bias of 1.0 V was applied on the device for 10 s to reach the quasi-steady state at 1.0 V, the device is then kept at zero bias to measure the non-zero ion current. Firstly, we set the measure delay time at 0.1s, then set the voltage sweep from 1V to 1V for 100 points, and from 0V to 0V for 200 points. Figure S1 shows the setting and the measuring process. After the relaxation ion current is obtained, the time integral of the current density gives the change of the density of the interface charge between the initial quasi-steady-state and 0 V state. The measurement of the interface charge is under dark condition. The interface charge under other voltage can be measured in the similar way.

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Figure S1. Measuring the dynamics of interface charge with the programmable power supply. After the pre-biasing, the device is kept at zero bias to measure the short-circuit current (Isc) under dark condition.

- The measurement of dynamic change of the photocurrent at zero bias (Isc). The setting and measuring process of the Source-Measure Unit (SMU) is the same (Figure S1). The only difference is that the measurement of photocurrent is under light illumination.
- The measurement of the J–V curves with different scan routs. As shown in Figure 3 of the main text we designed several scan routes. The setting and measuring processes of the J–V scans are illustrated in Figure S2.



Figure S2. Measuring process of the J–V curves with specially designed scan routs. **Scan 0** is a slow scan with the delay time of 10 s. **Scan 1, 2 and 3** are fast scans with a scan rate of 0.5 V/s. **Scan 1** is from 1.0 V to 0 V, and the initial state is the quasi-steady state of 1.0 V. **Scan 2** is from 0 V to 1.0 V, and the initial state is the quasi-steady state of 0 V. **Scan 3** is from 0 V to 1.0 V, and the initial state of 1.0 V. **The** measurement is under one Sun illumination.

• The measurement of the interface charge density in the different scan routs. As shown in Figure 3 inset we designed several scan routes. The measuring processes of the charge density of the different points are illustrated in Figure S3.



Figure S3. Measuring processes of the interface charge on the curve **Scan 0** (1.0 V as an example), and **after Scan 1** (point C Figure 3 inset), **Scan 2** (point D)and **Scan 3** (point H) in Figure 3 inset. The measurement is under dark.

2. The possible mechanism of ion migration in the organic-inorganic halide perovskites

There are more and more results¹⁻⁴ showing ion behavior in the organic-inorganic halide perorskites. In fact, migration of ion is a well-accepted property of halide perovskites to the solid state ionics community. For example, ionic conduction was demonstrated in the halide perovskites, CsPbCl3, CsPbCl3, KMnCl3⁵, CsCdCl3 and CsSnBr3⁶, The ionic conductivities of CsPbCl3 and CsPbBr3 are close to those of the well-known halide-ion conductors, PbCl2 and PbBr2. The conduction is caused by the migration of halide-ion vacancies⁵. Importantly, ionic conduction was also demonstrated in the organic-inorganic halide perovskite CH₃NH₃GeCl₃. The mobile ion is also the halide ion⁷.

Figure S4 shows the possible mechanism of ion migration if halide-ion vacancies exist in the material.



Figure S4. Schematic showing the vacancy mechanism of ion migration. There are vacant atom sites in which an adjacent ions can move (or hop) into vacancies (to leave their own site vacant) when the sample is under bias.

3. The influence of illumination on the dynamics of the interface charge.

Figure S5 shows the influence of illumination on the dynamics of the interface charge. The black line (in dark) and the red line (under one Sun illumination) are almost identical, suggesting that the influence of illumination on the dynamics of the interface charge is limited. We also confirmed that the charge density against voltage under dark and under one Sun illumination has the same trend as shown in Figure 1 d. However, it should be note that because the ion current

can only be measured under dark condition, the illumination is only applied in the pre-biasing period of the measurement.



Figure S5. The influence of illumination on the dynamics of the interface charge. **In dark** a bias of 1.0 V was applied on the device for 10 s, and the device was then kept at short-circuit condition to observe the non-zero current (black line). **Under one Sun illumination** a bias of 1.0 V was applied on the device for 10 s, and the device was then kept in dark and at short-circuit condition to observe the non-zero ion current (red line).

4. The mobile-ion model can consistently explain the experiments, but the trap model cannot.

Snaith et al.⁸ proposed an insightful mechanism about trap effects. They proposed that perovskite absorbers may have a very large defect density within or near the surface of the material. These defects could act as traps for electrons and holes and fill under forward bias working conditions, resulting in good p- and n-type contacts at the interfaces. Under short-circuit conditions, the traps may empty due to charge transfer directly to the p- and n-type contacts, resulting in poor operation until the traps are filled once more. They further elucidated that this trapping-and-detrapping mechanism can explain many hysteresis behaviors.

However this trapping-and-detrapping mechanism cannot explain the recently reported switchable photovoltaics^{2, 3} in the device of ITO/PEDOT:PSS/MAPbl₃/MoO₃/Al or ITO/PEDOT:PSS/MAPbl₃/Au because of the following reasons.

Firstly, switchable polarity are well-known phenomenon in ion-related light-emitting electrochemical cells (LECs)^{9, 10} or ferroelectric-related diodes¹¹ and photovoltaics¹². No report on switchable diode or photovoltaic due to trap effects is confirmed in literatures.

Secondly, as indicated in our previous work², the switchable photovoltaic can be well explained by the existence of mobile ions. Figure S6 shows the change in band bending near the interface due to interface charge. Specifically, positive interface charge leads to downward band bending near the interface and negative interface charge leads to upward band bending (See Supplementary Information of the paper for detailed explanation). We note that in Figure S6 the interface charge can be not only the accumulated ions, but also ferroelectric polarization or trapped electrons/holes. In Figure S7 a, we show that an important consequence of mobile ions (and ferroelectrics) is that under constant bias negative interface charge always forms at the interface of the positive electrode, thus the upward bending leads to the Ohmic contact for the positive electrode. Similarly, positive interface charge always forms at the interface of the negative electrode, thus the downward bending leads to the Ohmic contact for the negative electrode. This analysis perfectly explains the observed switchable photovoltaics.

Thirdly, Figure S7 b shows that the consequence of trap effect is totally different. If the interface charge is the trapped charge, under constant bias negative interface charge always forms at the interface of the negative electrode (because the trapped charge is injected from this electrode), thus the upward bending leads to even higher barrier for the negative electrode. Similarly, positive interface charge always forms at the interface of the positive electrode, thus the downward bending leads to higher barrier for the positive electrode. Therefore the trap effect cannot explain switchable photovoltaics and we believe this is the reason why no switchable diode or photovoltaic due to trap effect has been reported so far.

Finally, the switchable photovoltaic is actually a very severe hysteresis. Therefore the result of the switchable photovoltaics actually indicates that the hysteresis originates from the mobile ions. In the present study, we observed that the insertion of the carrier selective layer PCBM greatly influences the magnitude of the interface charge and thus significantly affects the degree of the hysteresis. The use of thicker PCBM layer (90 nm) leads to very low charge density and thus eliminates the hysteresis. Therefor all these experimental results can be consistently explained with the concept of mobile ions.



Figure S6. Schematic showing the change in band bending near the interface due to interface charge. **a**, No change in band bending due to zero charge; **b**, Downward bending due to positive charges near the interface; **c**, Upward bending due to negative charges near the interface. The Interface charge and screen charges are represented in red and black, respectively.



Figure S7. Under the same bias the band diagrams are different due to different type of interface charge. **a**, the interface charge is the accumulated ions or ferroelectric polarization. **b**, the interface charge is the trapped charge. The dot lines represent the band diagram without interface charge. Interface charge is represented in red. The black + and - represent the positive and negative electrode, respectively.

5. The influence of PEDOT:PSS thickness on the interface charge and the J–V hysteresis

Figure S8 shows the influence of PEDOT:PSS thickness on the interface charge and the J–V hysteresis. No significant change of the charge density is observed with the different thickness of PEDOT:PSS layer. Thicker PEDOT:PSS layer does not remove the hysteresis. A possible reason may be that the PEDOT:PSS layer is functioning as an electrode layer rather than carrier selective layer due to the high conductivity of the material. Indeed PEDOT:PSS layer alone can serve as the electrode layer in solar cells¹³ and OLEDs¹⁴.



Figure S8. The influence of PEDOT:PSS thickness on the interface charge and the J–V hysteresis. The scan rate is 0.5 V/s. No obvious trend of charge density is found with the different thickness of PEDOT:PSS layer.

6. The overall performance of our devices

Figure S9 shows the dark and light I-V curves of one PSCs. The average power conversion efficiency in this article is ~7% (Figures S10). The highest is 10.2 %. Indeed, the performance of the devices are not high compared with the high-performance PSCs. Our devices generally suffer from low short-circuit current (Isc) and low fill factor (FF). Figure S11 shows that the Isc become apparently lower with the insertion of PCBM layer. Figure S12 shows that the Isc are significantly

lower in the device with the thicker PCBM layer. These results suggest that the electron-transport property of the PCBM that we used is not high enough, and thus hinders the photocurrent. Using the PCBM with a higher electron mobility, we should be able to improve our device. Considering this situation we believe that our results could be used to address the hysteresis of the typically high-performance PSCs.



Figure S9. The dark and light J-V curves of one PSC.



Figure S10. The PCE distribution of the PSCs.



Figure S11. The J-V curves of two devices:ITO/PEDOT:PSS/ MAPbI_xCl_{3-x} /PC₆₁BM/Au and ITO/PEDOT:PSS/ MAPbI_xCl_{3-x} / Au.



Figure S12.The J-V curves of the devices ITO/PEDOT:PSS/ $MAPbI_xCI_{3-x}/PC_{61}BM/AI$ with different PCBM thickness.

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