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Supplementary Information for:

The hysteresis-free behavior of perovskite solar cells from the perspective of the measurement conditions

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Contents:

- 1. Simulated dynamic J-V characteristics.
- 2. Temporary degradation induced by bias stress.
- 3. Inverted hysteresis: low vs. high scan rates.

1. Simulated dynamic J-V characteristics

Simulations corresponding to the reference and aged samples are performed using DEM. For the reference PSC, the equivalent circuit model parameters are: the series resistance $R_{\rm s} = 120 \ \Omega$, the shunt resistance $R_{\rm sh} = 2 \ \mathrm{k\Omega}$, the ideality factor n = 1.55, the diode saturation current $J_{\rm s} = 1.1 \ \mathrm{pA/cm^2}$, the photogenerated current $J_{\rm ph} = 14.4 \ \mathrm{mA/cm^2}$ and steady-state polarization at open circuit $P_{\infty} = 12 \ \mathrm{mC/cm^2}$. As suggested by the experimental data in Fig. 1, aged samples differ significantly by the photogenerated currents, $J_{\rm ph} = 8.9 \ \mathrm{mA/cm^2}$ (after 1 week) and $J_{\rm ph} = 7.4 \ \mathrm{mA/cm^2}$ (after 3 weeks). Also, the series resistance increases after one week to 200 Ω for the aged PSCs and more ions are accumulating at the interface as the initial polarization increases.



Figure S1: Simulated reverse-forward J-V characteristics using DEM, with the parameters indicated in the main text: (a) Reference PSC: $J_{\rm ph} = 14.4 \text{ mA/cm}^2$, $R_{\rm s} = 120 \Omega$, $P_0 = 2P_{\infty}$; (b) Aged for 1 week: $J_{\rm ph} = 8.9 \text{ mA/cm}^2$, $R_{\rm s} = 200 \Omega$, $P_0 = 4P_{\infty}$; (c) Aged for 3 weeks: $J_{\rm ph} = 7.4 \text{ mA/cm}^2$, $R_{\rm s} = 200 \Omega$, $P_0 = 4P_{\infty}$. The aged samples exhibit increased series resistance and a larger initial polarization. Temporary degradation effects were not accounted for.

2. Temporary degradation induced by bias stress



Figure S2: J-V characteristics performed at 20 mV/s showing the temporary degradation induced by performing a sequence of seven J-V scans with the scan rates $\alpha = 10^5, 10^4, 10^3, 10^2, 20, 10, 5 \text{ mV/s}$, performed in this order. Typically, the PSCs recover from the bias-stress induced degradation as opposed to irreversible degradation [1].

3. Inverted hysteresis: low vs. high scan rate



Figure S3: The inverted hysteresis was also observed by pre-conditioning at large positive biases, e.g. using $V_{\rm pol} = 1.4$ V in Figs. 2 and 3 in the main text. We obtain this behavior using DEM [2, 3], by including in the simulated J-V characteristics an additional recombination term, i.e. the collected current in the reverse-forward scan becomes $\tilde{J} = J - J_{\rm ph} \exp(-t/\tau_{\rm r})$, where $\tau_{\rm r} = 0.5$ s corresponds to additional recombinations induced by ionic displacement and accumulation at the interfaces, leading to a potential spike in the conduction band [4]. The current \tilde{J} is represented by solid (red/blue) lines, while J, the current in the standard DEM model, is represented by black dotted lines. At a scan rate of 100 mV/s (a), IH appears only near open-circuit, while for a faster scan rate of 1000 mV/s (b), IH becomes dominant for the entire measurement interval. The vertical dashed line in (a) marks the crossing point between the forward and reverse characteristics, separating NH and IH for the scan rate of 100 mV/s. The position of the crossing point depends on both τ_r and α .

4. PSCs with modified (a) ETL structure and (b) perovskite absorber:
(a) FTO/TiO₂-c/TiO₂-m/PCBM/CH₃NH₃PbI_{2.6}Cl_{0.4}/Spiro/Au
(b) FTO/TiO₂-c/TiO₂-m/[(CH₃NH₃)_{0.95}(C₃N₂H₄)_{0.05}]PbI_{2.6}Cl_{0.4}/Spiro/Au



Figure S4: Scan rate dependence of the reverse-forward J-V characteristics of modi-fied PSCs with (a) PCBM additional layer and (b) mixed organic cation perovskite $[(CH_3NH_3)_{0.95}(C_3N_2H_4)_{0.05}]PbI_{2.6}Cl_{0.4}$. Both types of structures exhibit a similar behav-ior by varying the bias scan rate: a maximum hysteresis occurs for the intermediate scan rates, the short circuit current increases with the bias scan rate and a current 'bump' is typically visible in reverse characteristics at low to medium scan rates. The hysteresis is minimized for small scan rates (5 mV/s) and for very high ones (100 V/s).



Figure S5: Poling effects at a scan rate of 100 mV/s of modified PSCs with (a) PCBM additional layer and (b) mixed organic cation perovskite $[(CH_3NH_3)_{0.95}(C_3N_2H_4)_{0.05}]PbI_{2.6}Cl_{0.4}$. The bias pre-poling voltage V_{pol} is indicated in each sub-plot, in the range from 1.4 V to -5 V. For large positive poling voltage (e.g. 1 - 1.4 V) the reverse-forward characteristics typically display a large hysteresis, which is reduced as the poling voltage is lowered, yielding almost hysteresis free behavior. For low negative poling voltage (e.g. -5 V) a small inverted hysteresis (a) or a mixed hysteresis, denoted by MH, in (b) is observed.



Figure S6: Poling effects at a larger scan rate of 1000 mV/s of modified PSCs with (a) PCBM additional layer and (b) mixed organic cation perovskite $[(CH_3NH_3)_{0.95}(C_3N_2H_4)_{0.05}]PbI_{2.6}Cl_{0.4}$. As shown in Fig. S3 and Fig. 3 in the manuscript, a large positive poling bias may temporarily enhance the recombinations with a typically shorter time scale τ_r . At the high scan rate of 1000 mV/s the effect is present over the entire measurement interval, which, for $V_{\rm pol} = 1.4$ V, is translated into an IH in (a) and a reduced NH, as e.g. compared to $V_{\rm pol} = 1.2$ V or 1 V in (b). For both types of PSCs, as the poling voltage decreases, the NH is first recovered/enhanced, subsequently turned into a mixed hysteresis and, lastly, into IH.

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