Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information: Microseconds, milliseconds and seconds: deconvoluting the complex response of planar perovskite solar cells.

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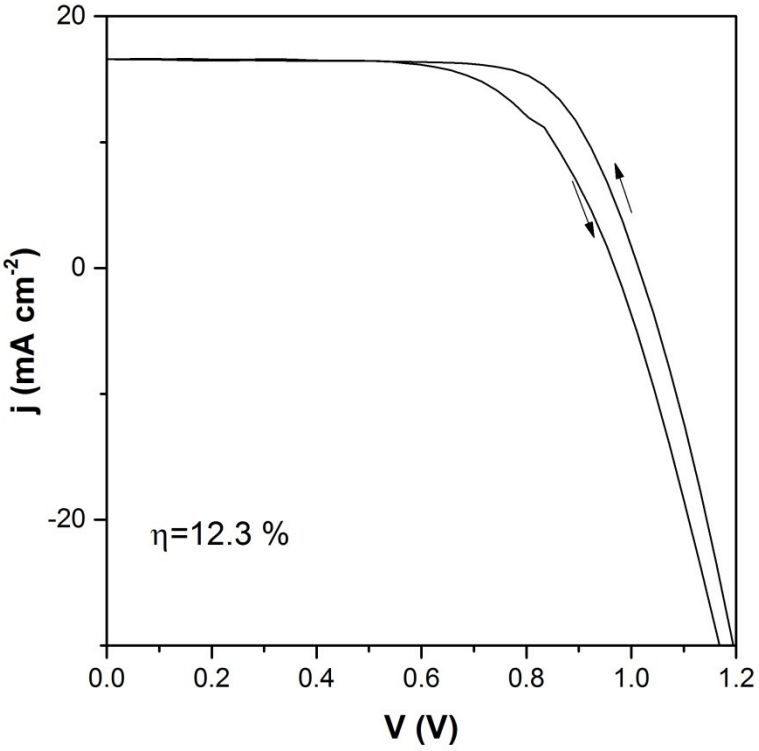

Figure S1. jV curve of typical planar perovskite cells (CT-3) used for EIS, IMVS and OCVD measurements.

Calculation of double layer capacitance in the PSC:

ε = 24[1]

V_{bi} = 1eV [2]

Distance of closest approach of ions = 0.5 x 10^{-7} cm

$$C = \frac{\varepsilon\varepsilon_0 A}{d} = \frac{8.854 \times 10^{-14} F cm^{-1} \times 24 \times 1\ cm^2}{0.5 \times 10^{-7} cm} = 4.2 \times 10^{-5} F\ cm^{-2}$$

Q=C x V = 4.2 x 10^{-5}F x 0.5 V = 2.1 C cm^{-2}= 1.3 x 10^{14} ions cm^{-2} in each double layer

In a ~500 nm perovskite film you would therefore need a total of 2.6 x 10^{14} mobile vacancies to create fully collapsed double layers. This corresponds to a defect density of roughly 5 x 10^{18} cm^{-3}. Given that the computed defect density is frequently given in the range of 10^{17} - 10^{19} cm^{-3} [3]it suggests that it should be possible to create full collapsed double layers at the perovskite interfaces and there will not be a field in the bulk perovskite.

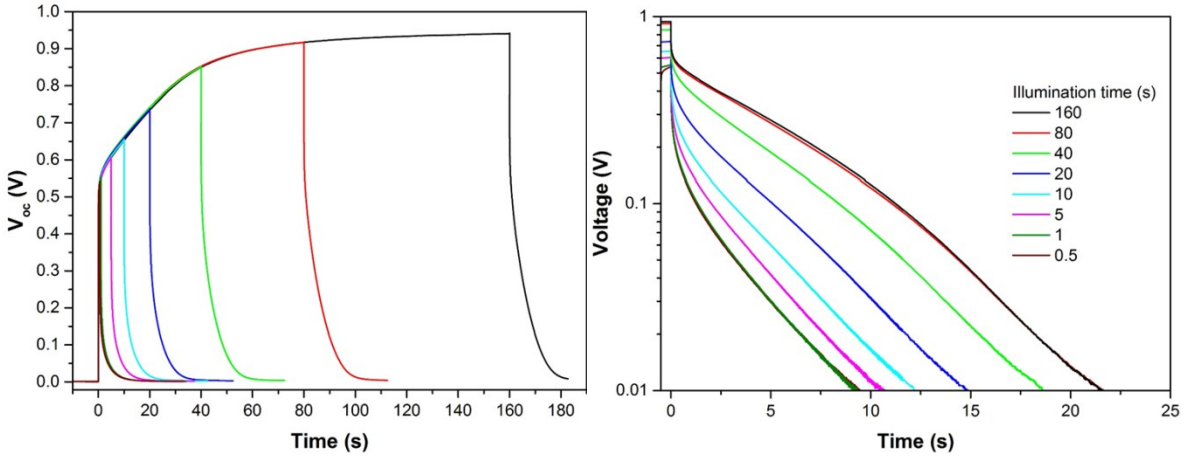

Figure S2. Reproducibility of the large amplitude photovoltage rise measurements and comfirmation that for this cell (CT-3)the illumination time had to be > 80 s to get a reproducible decay curve. The shape of the curves is clearly highly dependent on the condition the cell is in before the measurement and whether a true photostationary state has been achieved.

One of the benefits of large transient measurements is that we can start from a condition (i.e. equilibrium in the dark or a photostationary state under illumination) where the band alignment in the device is well understood. One of the problems when measuring perovskite solar cells is that their characteristics can change depending on pre-conditioning such as light soaking or the application of external bias. Figure S5 shows the reproducibility of the large amplitude technique. If the cell was allowed to relax fully in the dark before the light was switched on we found that photovoltage rise curves overlaid perfectly (e.g. this can be seen for the 8 experiments overlaid in Figure S5(a)). In order to get such close reproducibility we had to wait until the V_{oc} of the cell in the dark fell **below 1mV**. It is important to note that if **even a few mV** of V_{oc} remained when the light was switched on then the curves did not overlay and the shape of the transient was affected. The measurement underlies how important it is to have a defined protocol for measuring OCVD if results are to be compared. OCVD papers often do not report the rise time and pre-treatment steps carried out, instead the assumption is made that the device has reached steady state after a fixed illumination time. It is clear from our measurements that a 5 second difference in illumination time leads to different OCVD curves for the same cell. A second problem is the lack of knowledge about the state the cell was in before the measurement started – any remaining voltage will change the rise time of the device and could affect the decay curve. The time taken to reach steady state can also vary greatly between devices and measurement conditions – in the cell shown in Figure A(a) illumination times of >80s were required to reach the photostationary state. At lower light intensities and at lower temperatures the time taken was considerably longer. This finding has wider implications for measurements which involve stepping between different

voltages or illumination intensities. Unless the cell is allowed to relax fully between measurements the results will be strongly influenced by the previous pre-conditioning.

Ionic distribution in the dark

Figure S3 illustrates conceptually the formation of the planar MAPI solar cell from its constituent components. When the junctions with the n^+-TiO_2 and the spiro redox system are formed initially, the transfer of electrons from the TiO_2 to the spiro occurs, allowing the Fermi levels to equilibrate. This leads to the formation of the so-called 'built in voltage', V_{bi}. The condition for electron/hole equilibrium is the gradient of the electron Fermi level (equivalent to the electrochemical potential of electrons) is zero through the junction. However, this equilibrium only applies to electrons and holes and not to mobile ion vacancies. The generation of an electric field ($E = V_{bi}/d$) that occurs when the junction is formed perturbs the initial ionic equilibrium, and ions and electrons/holes will move until the gradients of the electrochemical potentials of *all* species (ions and electronic charges) become zero. The initial electric field for an open circuit voltage of 0.6 V and a MAPI layer thickness of 300 nm is 2×10^4 V cm^{-1}. The ionic vacancies are expected to have diffusion coefficient of the order of 10^{-12} cm^2 s^{-1}, corresponding to mobilities of the order of 4×10^{-11} cm^2 V^{-1} s^{-1}, so that ions will initially move with a velocity of around 10 nm s^{-1}. This corresponds to a relaxation time of the order of some tens of seconds. If the concentration of defects is high enough, then compact double layers will from at the contacts as shown in Figure S1.

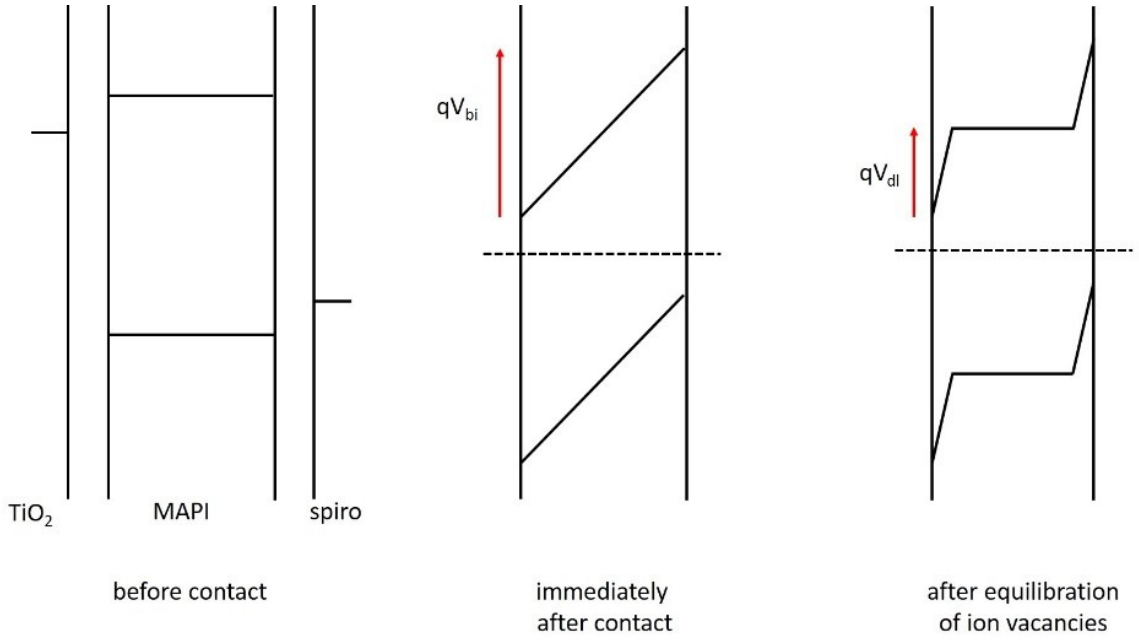

Figure S3. Formation of the junction with equilibration of electrons and holes followed on a much slower time scale by equilibration of ionic vacancies to form double layers at the contacts.

If, as shown here, the double layers absorb all of the built in voltage (usually assumed to be around 1 V), then in this simple picture the voltage drop in each double layer would be ca. 0.5 V. The plane of closest approach of the ion vacancies is not known, but if we assume it is

of the order of δ_H = 0.5 nm, then taking the relative permittivity of MAPI as 30, the Helmholtz capacitance $C_H = \varepsilon\varepsilon_0/\delta_H$ would be ca. 50 μF cm^{-2}. So for a voltage drop V_{dl} = 0.5V, the accumulated ionic charge would be 2.5 × 10^{-5} C, corresponding to a total vacancy number 1.6 × 10^{14}. It follows that in order for compact double layers to form, the vacancy concentration must be greater than 1.6 × 10^{14}/d_{MAPI} = 1.6 × 10^{14}/ 3 ×10^{-5}, i.e. $C_{vacancy}$ > 5 ×10^{18} cm^{-3}. This is consistent with reported values, so we conclude that compensation of the built in field by the formation of compact double layers is likely.

Ionic distribution under illumination at open circuit.

If we begin from the situation in which both electronic and ionic charges are in equilibrium as shown on the right hand side of Figure S1, illumination will quickly establish a steady state profile of electron and hole concentrations that correspond to a splitting of the quasi Fermi levels equal to qV_{oc}. Since in the initial state, the electrical field in the bulk is close to zero due to the formation of double layers, the appearance of a photovoltage creates an electrical field V_{oc}/d_{MAPI} in the film that is opposite in sign to the original built in voltage and will cause ions in the double layers to move towards the bulk, effectively discharging the double layer capitance until a new equilibrium for ionic species is established (gradient of electrochemical potential zero at all points). Again, the time scale for this ionic discharge process is expected to be tens of seconds. The sequence of events is illustrated in Figure S4, and the direction of vacancy movement is shown in Figure S5. When the light is switched off, the double layers need to recharge to re-establish the initial dark equilibrium shown on the left hand side of Figure S4. This involves vacancies moving back form the bulk towards the contacts.

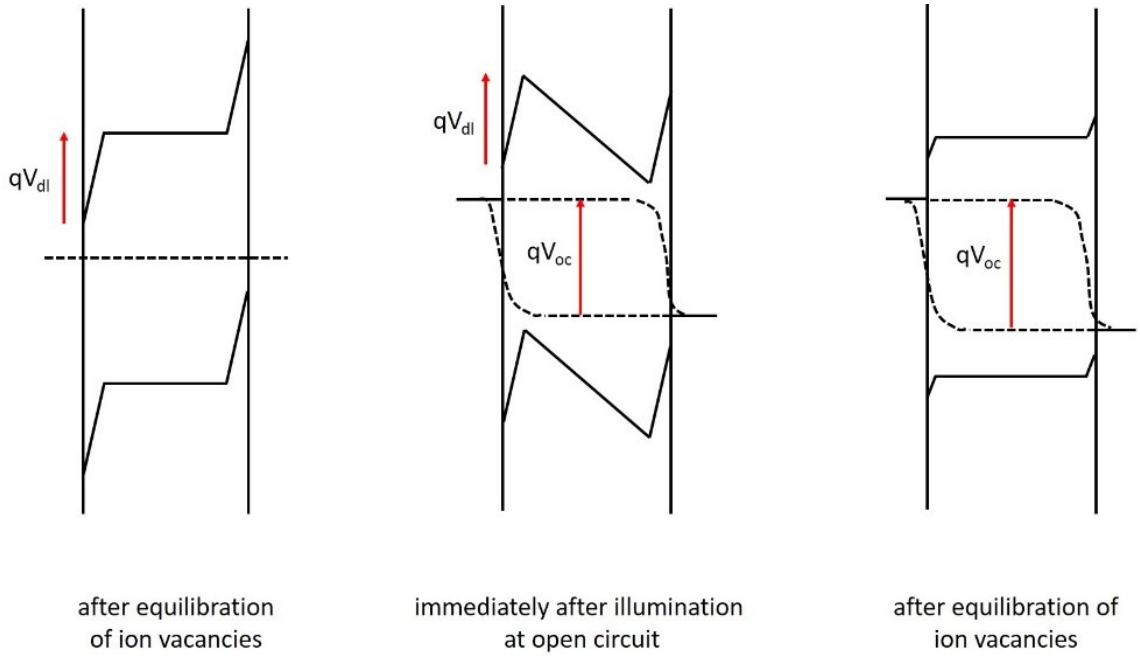

Figure S4. Changes in band bending induced by illumination of a cell that in which ion vacancies as wells as electrons and holes are in equilibrium. The photo-induced field leads to discharge of the double layers as ions return to the bulk form the near surface regions. The

Figure is reproduced from Figure 5 in the main text to aid the clarity of the discussion in the ESI.

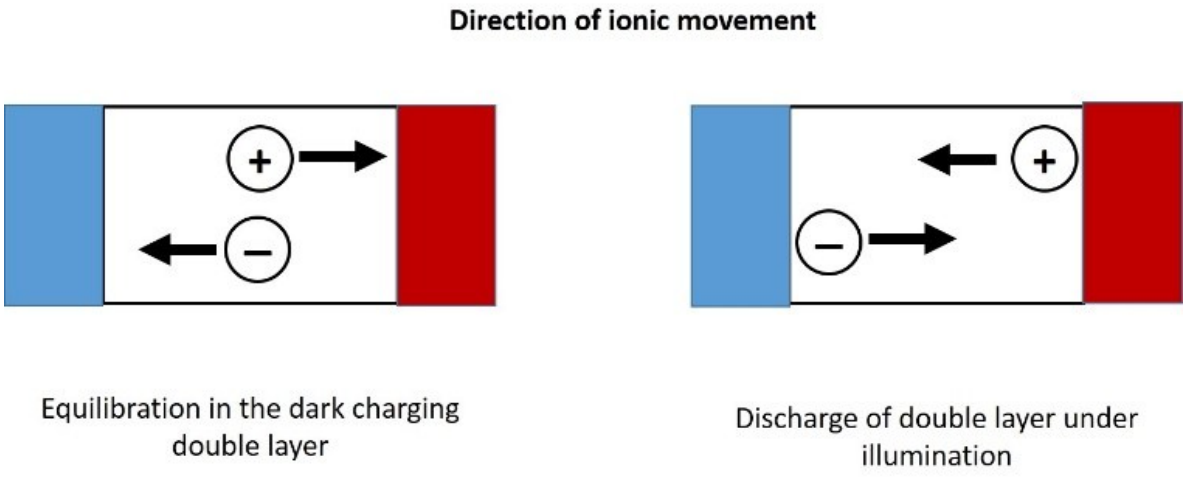

Figure S5. Directions of ionic movement corresponding to formation of ionic double layers at the contacts in the dark and their subsequent discharge under illumination at open circuit. During open circuit voltage decay the double layers charge up again to re-establish the dark equilibrium condition.

It is evident from the slow increase in voltage after switching on the illumination corresponds to a decrease in recombination rate. Typically, an open circuit voltage of around 600 mV is established rapidly after illumination. This is followed by a slow increase towards 900 mV. Such a large increase in the Fermi level splitting must reflect a decrease in bulk or surface recombination by many orders of magnitude. This effect could be due to shielding of electrons and holes by vacancies of opposite sign, reducing the capture cross section. It seems unlikely that this effect alone can explain the reduction in recombination rate, so that it is necessary also to consider the effect of the changes in local band bending of the electron and holes concentration profiles illustrated in Figure S4 (centre).

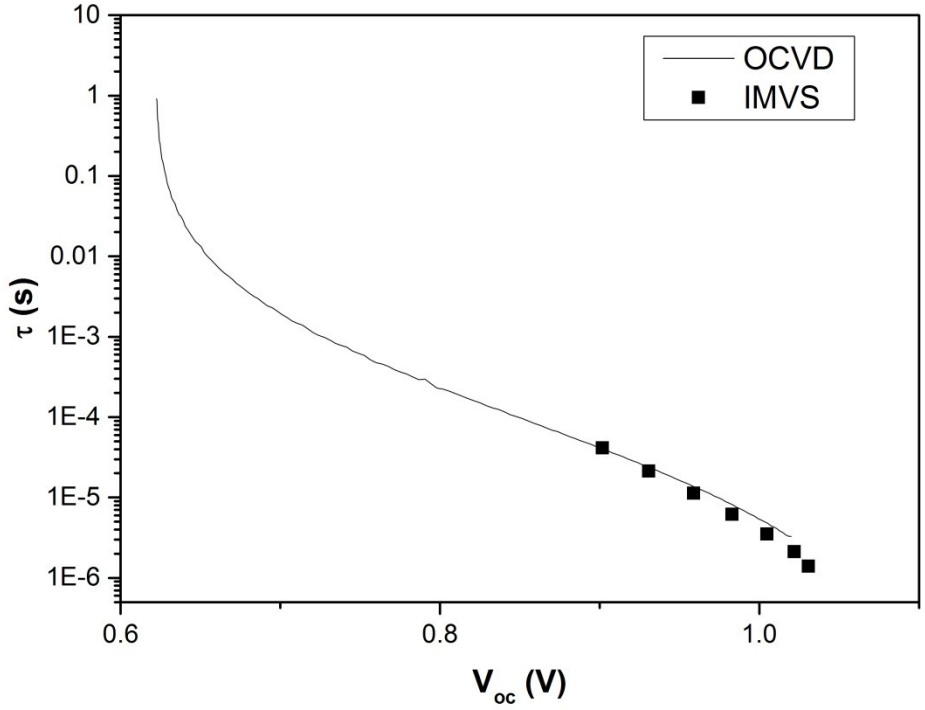

Figure S6. A comparison of $\tau_{OCVD,fast}$ (calculated using equation 1 in the main text) with τ_{HF} from the OCVD.

Modelling the open circuit voltage decay in the absence of effects due to vacancies

In our previous work, we established that the high frequency impedance response of planar MAPI cells under illumination can be represented by the equivalent circuit in Figure S7. Here the recombination resistance corresponds to dV/dI at V_{oc} and the shunt resistance is due to imperfections in the films and other leakage paths. The geometric capacitance is determined by the thickness of the MAPI film. We note that the effects of ionic vacancy movement are not accounted for in this circuit.

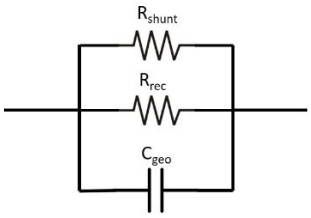

Figure S7. Equivalent circuit describing the high frequency response of a planar MAPI cell (excluding effects due to movement of vacancies).

The voltage dependence of R_{rec} can be obtained from the fact that it depends inversely on light intensity and V_{oc} depends on the natural log of the light intensity with a slope equivalent to mk_BT/q. For the cells studied here, the ideality factor m was found to be 1.4, and the

recombination resistance at the highest intensity (ca 80 mW cm^{-2}) is around 3 ohms cm^2 for V_{oc} = 1.02 V.

In the absence of complications due to the movement of vacancies, the open circuit voltage decay would correspond to the discharge of the geometric capitance through the parallel combination of R_{rec} (voltage dependent) and R_{shunt} (constant). Figure S8 shows that the decay should give a linear plot of voltage vs. the logarithm of time until a point is reached when R_{rec} becomes larger than R_{shunt}, after which the decay will be exponential. Typically, shunt resistances are found to be less than 10^5 ohm cm^2, and as Figure S8 shows, the decay should therefore be completed in less than 100 ms.

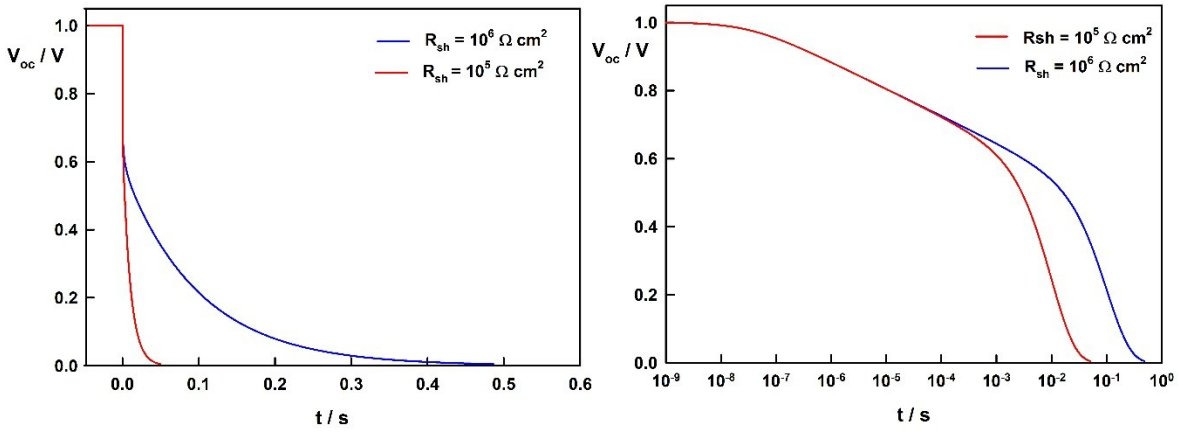

Figure S8. Simulated decay plots on linear and logarithmic time scales for the circuit shown in Figure S4. Non -ideality factor m = 1.4. C_{geo} = 100 nF cm^{-2}, R_{rec} = 10 Ω cm^2 at V_{oc} = 1 V. Shunt resistance as shown. Note that the decay is expected to be complete in less than a one second for realistic values of the shunt resistance.

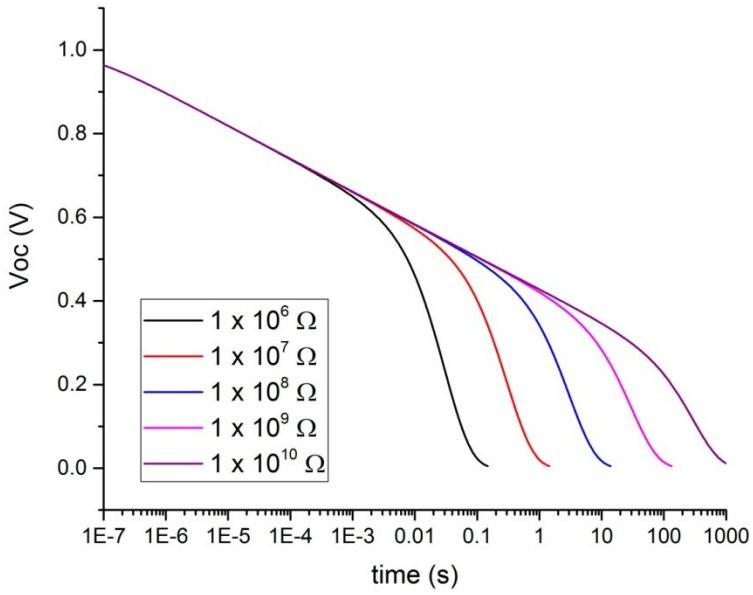

Figure S9. Modelled V_{oc} decay for a simulated system with a recombination resistance of 50Ω in parallel with a shunt resistance (10^6-10^9 Ω), a V_{oc} of 1V, an ideality factor of 1.4 and a geometric capacitance of 30 nF.

In practice the decay of open circuit voltage exhibits a much slower component that is exponential. i.e. it corresponds to a fixed RC time constant of some tens of seconds. This component clearly cannot be due to discharge of the geometric capitance through the recombination and shunt resistances. Instead, the charge on the double layers needed to restore the equilibrium dark condition requires ions to move in response to the electrical field in the perovskite layer that is generated as recombination reduces the Fermi level splitting. In the simplest approximation, the time constant for this process would be determined by the double layer capacitances in series with a ionic resistance. E.g. for a given value of the Helmholtz double layer capacitance (for example C= 25μF cm^{-2}), the RC time corresponding to the time constant (measured at 20° C) of around 5 s gives an ionic resistance of 2×10^5 Ω cm^2. Using the order of magnitude ion mobility above, this resistance would indicate a defect concentration of the order of 10^{19} cm^{-3}. The strong temperature dependence of the time constant is consistent with the resistance being associated with ionic conductivity.

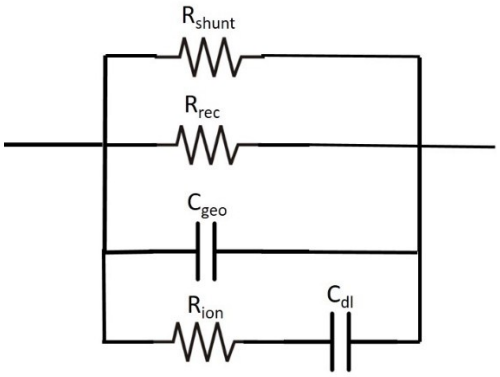

Figure 10. Full equivalent circuit which describes the behaviour in the OCVD measurements.

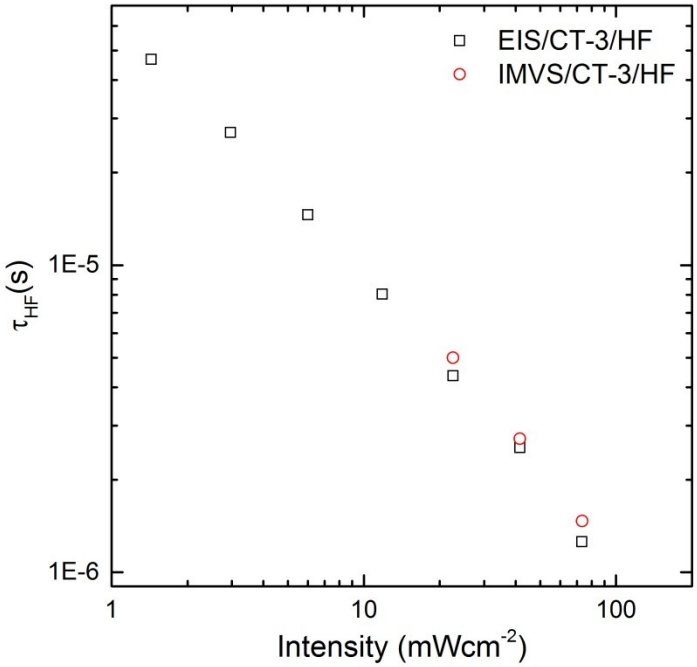

Figure S11. Comparison of high frequency time constants measured by IMVS and EIS for the same cell (CT-3)

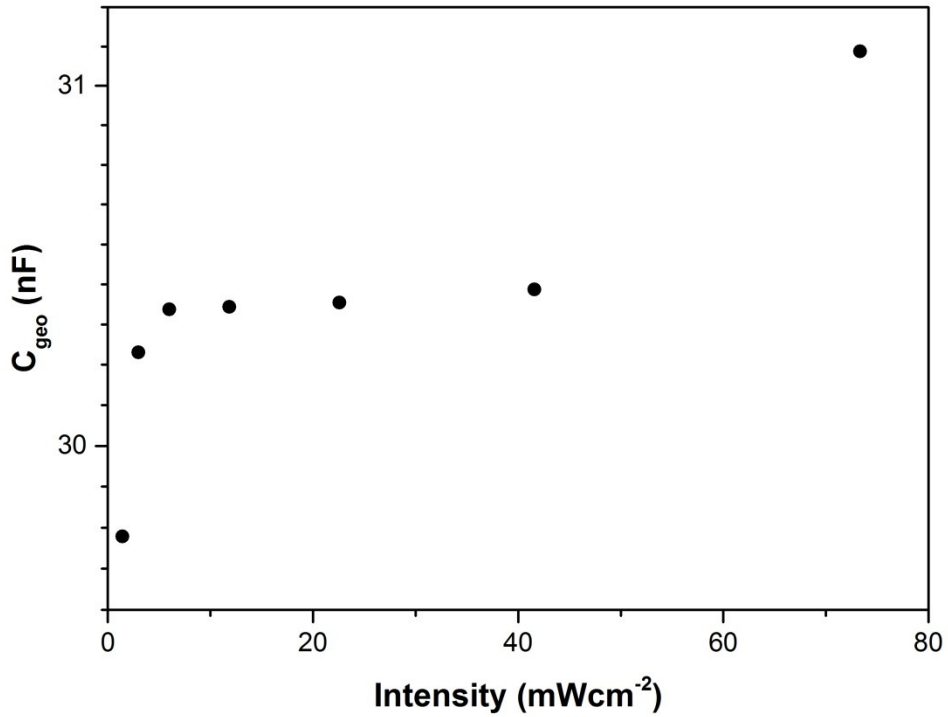

Figure S12. The geometric capacitance as a function of light intensity – showing that the capacitance is almost constant over the entire range measured. Cell EY-4.

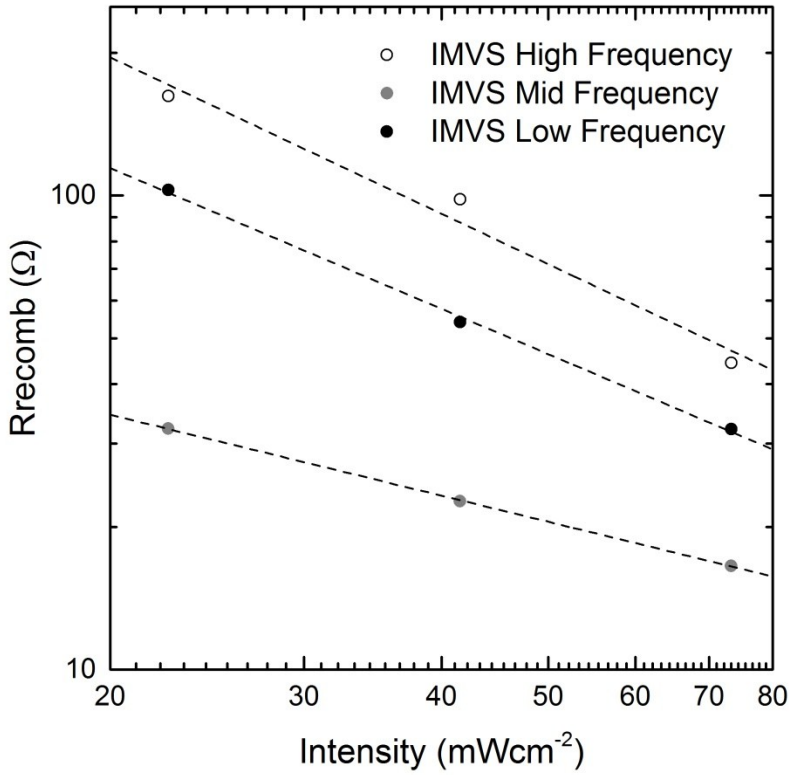

Figure S13. Intensity dependence of the resistances extracted from the high and mid frequency semi-circles measured by IMVS.for cell EY-4.

(1) Brivio, F.; Walker, A. B.; Walsh, A. *APL Materials* **2013**, *1*, 042111.

(2) Rossiter, C.; Suni, II *Surf. Sci.* **1999**, *430*, L553.
(3) Frost, J. M.; Walsh, A. *Acc. Chem. Res.* **2016**, *49*, 528.