Electronic Supplementary Material (ESI) for Nanoscale.

Analysing the effect of crystal size and structure in highly efficient $CH_3NH_3PbI_3$ perovskite solar cells by spatially resolved photo- and electroluminescence imaging

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V_{OC} – EQE_{EL} relation

$$Voc = \frac{k_B T}{q} ln\left(EQE_{EL}\frac{J_{sc}}{J_{em,0}} + 1\right)$$ Equation 1

where:

$$J_0 = \frac{J_{em,0}}{EQE_{EL}}$$ Equation 2

and $J_{em,0}$ defined by:

$$J_{em,0} = q\int_0^\infty EQE_{PV}(E)\Phi_{bb}(E)dE$$ Equation 3

where q is the absolute value of electron charge, ϕ_{bb} the black body photon flux of the environment, k_B the Boltzmann's constant, J_0 the dark saturation current and $J_{em,0}$ the same quantity in the radiative limit (equilibrium injection current)[1]. It follows that, at a given J_{SC}, the V_{OC} maximization can occur both by lowering $J_{em,0}$ [2] and by EQE_{EL} increase. Hence, the EQE_{EL} values shown in Figure 4b (highest for 0.044M and lowest for 0.032 M) are well in accordance with the measured V_{OC} of the three cell typologies and their discrepancy.

V_{OC} – light intensity and I-V curves under dark

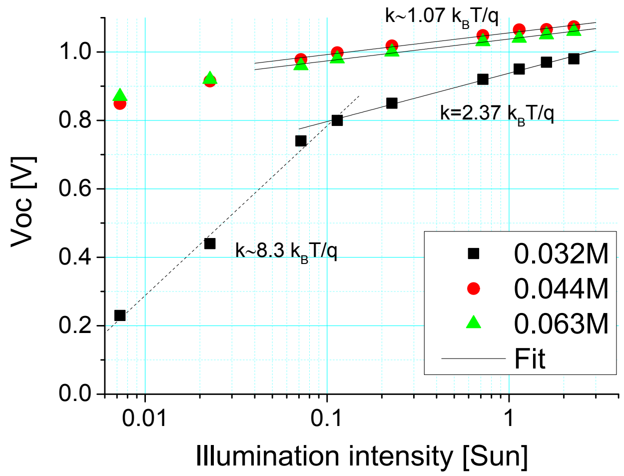

Figure S1. Light intensity dependence of the open circuit voltage for cells with the MAI concentration used (0.032 M, 0.044 M and 0.063 M). 1 sun is equivalent to 100 mW/cm^2. Cell 0.032 M clearly shows steeper slopes and lower V_{OC} values at low light intensity with respect to the other cell typologies. Slopes were obtained by linearly fitting V_{OC} vs the illumination intensity expressed in the log scale as done in ref [3].

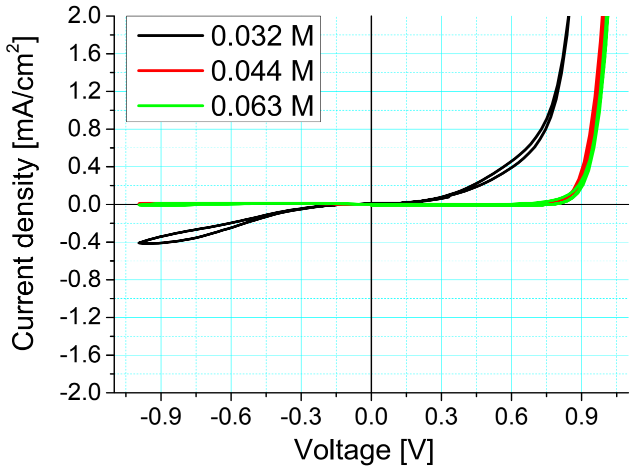

Figure S2. Current density-voltage curves (limited for the range ± 2 mA/cm^2) measured under dark for the perovskite solar cells with the MAI concentration used (0.032 M, 0.044 M and 0.063 M). Note that cell 0.032 M shows current flowing under reverse bias and under forward bias already at low applied voltages

PL – EL mapping

PL images for cell 0.044 M for voltages from 0 V to V_{OC}. The rectangular active area (~0.5 cm^2) and the external inactive area (where there is no evaporated gold) can be clearly recognized. A slight increase in PL intensity can be observed in the active area in the range 0 V – V_{MPP}, which then sharply increases approaching the cell´s V_{OC}. No voltage dependency of the inactive area appears since no charge can be extracted from there.

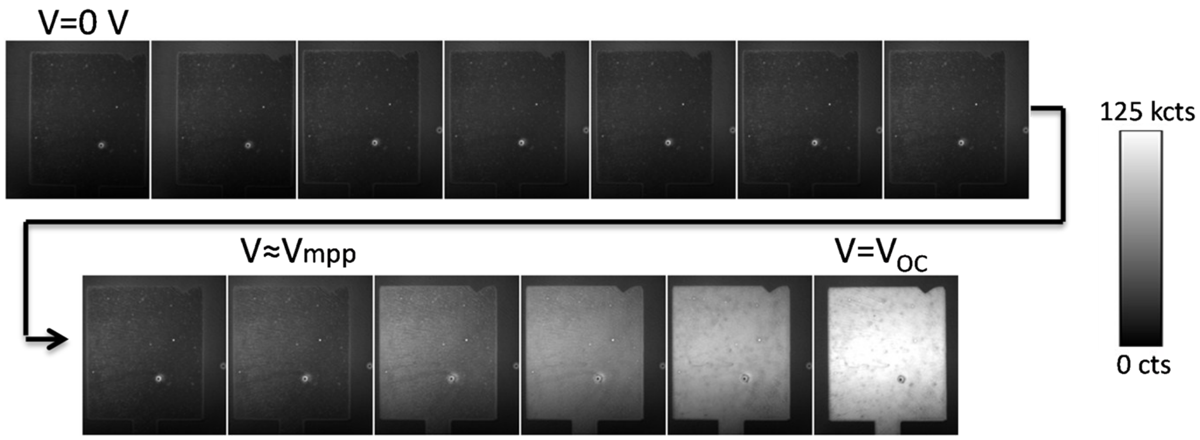

Figure S3. Voltage dependent photoluminescence emission imaging for cell 0.044 M measured from I_{SC} (V=0 V) to V_{OC} with voltage step of 100 mV until the cell´s maximum power point (V_{MPP}) and 50 mV onwards till the cell´s V_{OC}. The rectangular cell active area (ca. 0.5 cm^2) and the external area can be seen (see fig. 2c). Low PL intensities can be observed in the active area at V=0 V, which become high with exponential behaviour reaching V_{OC}. The voltage dependent PL intensity averaged over the cell active area gives the PL trends vs V shown in Figure 3.

Figure S4 reports the EL images for cell 0.044 M at forward bias voltages in the range 0.8 – 1.3 V with a 50 mV voltage step. Different features and increasing contrast can be observed while increasing the applied voltage. The EL signal is given by the radiative recombination of electrons and holes which are injected into the perovskite through the external contacts. Hence, materials and interfaces which transport and transfer the charges significantly influence the EL intensity. This behavior clearly emerges as the voltage approaches high values because of localized series resistance variations[4, 5], shunts and due to the presence of non-radiative recombination sites.

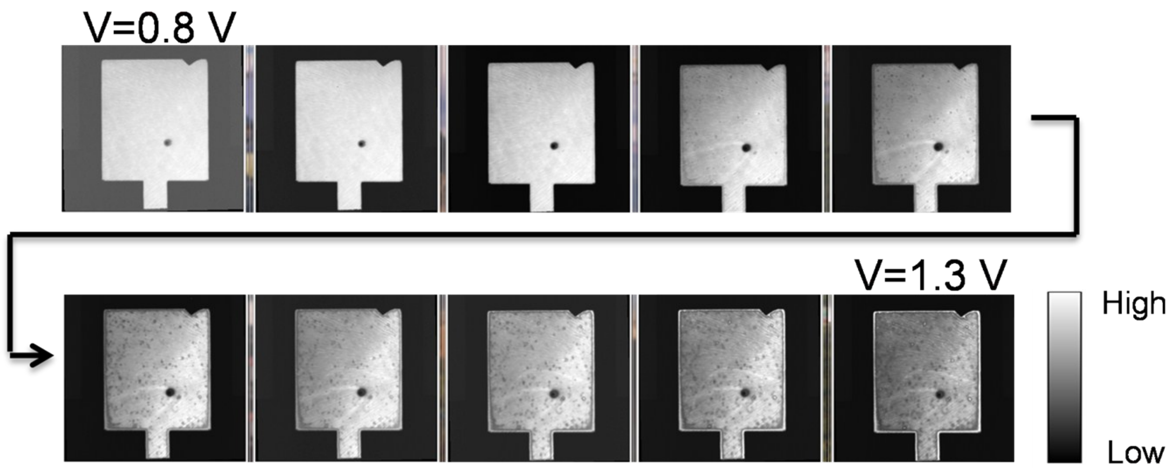

Figure S4. Voltage dependent electroluminescence images measured on cell 0.044 M (applied voltage in the range 0.8 - 1.3 V with 50 mV voltage step). The scale is optimized for each image. EL intensity is in the 10-30 CCD cts/s range at 0.8 V and 0.6 M CCD cts at 1.3 V. Only the rectangular cell active area, where charges can be injected giving radiative recombination (ca. 0.5 cm^2), can be seen (see fig. 2c). The voltage dependent EL intensity averaged over the cell active area gives the EL trends shown in Figure 4.

SEM images

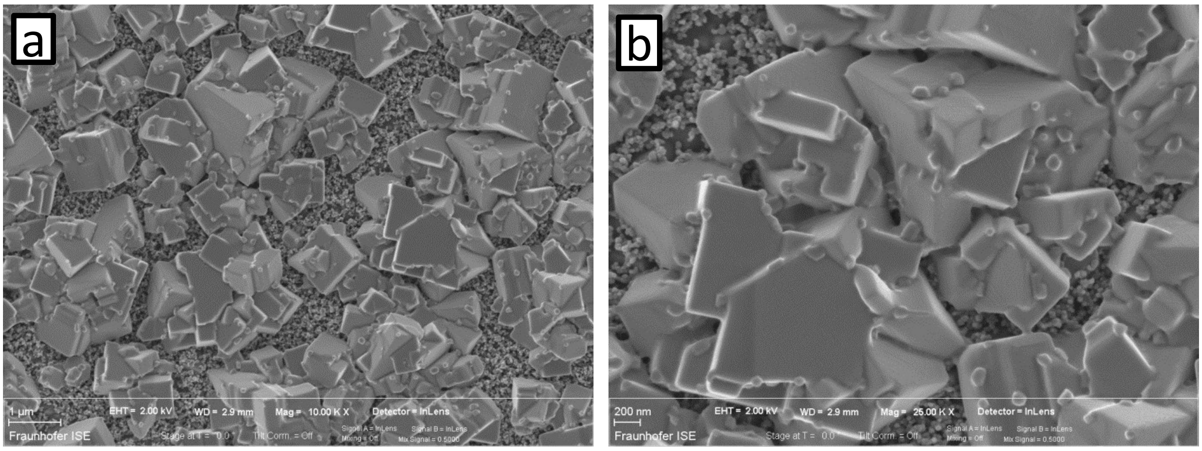

Figure S5. Surface SEM image of a perovskite film with 0.032 M MAI concentration. Perovskite agglomerations and poly-crystalline structures with dimension > 2 µm with not-well defined facets can be observed. Scale bar is 1 µm (a) and 200 nm (b).

References

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