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Ambient air processed mixed-ion perovskite for high efficiency solar cells

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Figure S1. Photograph of the perovskite precursor solution.

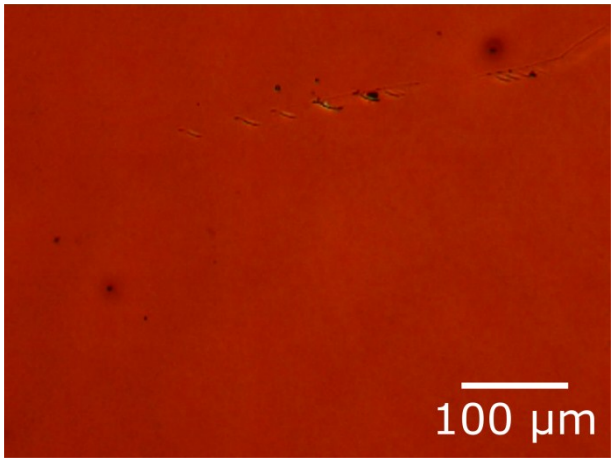


Figure S2. Optical microscope image (x255) of a methylammonium lead(II) triiodide ($MAPbI_3$) intermediate film prior to annealing.

Transmittance and reflectance measurements

The absorptance (*A*) at each wavelength (*λ*) of the measured films was calculated using the transmittance (*%T*) and reflectance (*%R*) spectra, so that:

$$A(\lambda) = 1 - \left(\frac{\%T(\lambda)}{100\%}\right) - \left(\frac{\%R(\lambda)}{100\%}\right)$$

The absorption coefficient, α, is calculated using[1]:

$$\alpha(\lambda) = \frac{1}{d}\ln\left(\frac{1 - R(\lambda)}{T(\lambda)}\right)$$

where *d* is the thickness of the perovskite film. To obtain the absorption coefficient of the perovskite thin film α_p, the absorption from the FTO glass and the TiO_2 (substrate) was subtracted from the total absorption α_{tot} according to:

$$\alpha_p d_p = \alpha_{tot} d_{tot} - \alpha_{sub} d_{sub}$$

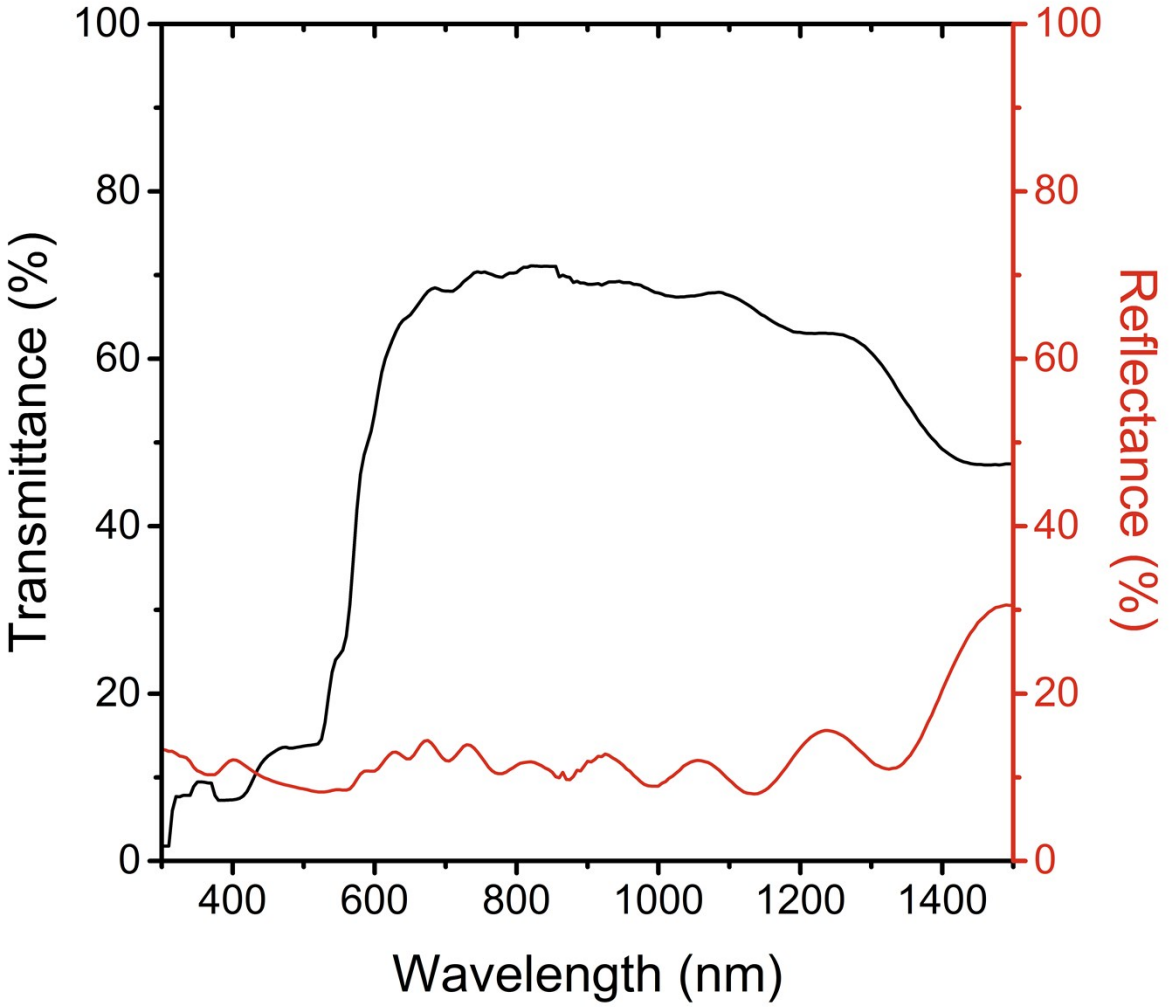


Figure S3. UV-Vis-NIR transmittance (black) and reflectance (red) spectra of the red intermediate phase. The interference fringes observed in the reflectance spectrum indicate a uniform thickness of the film.

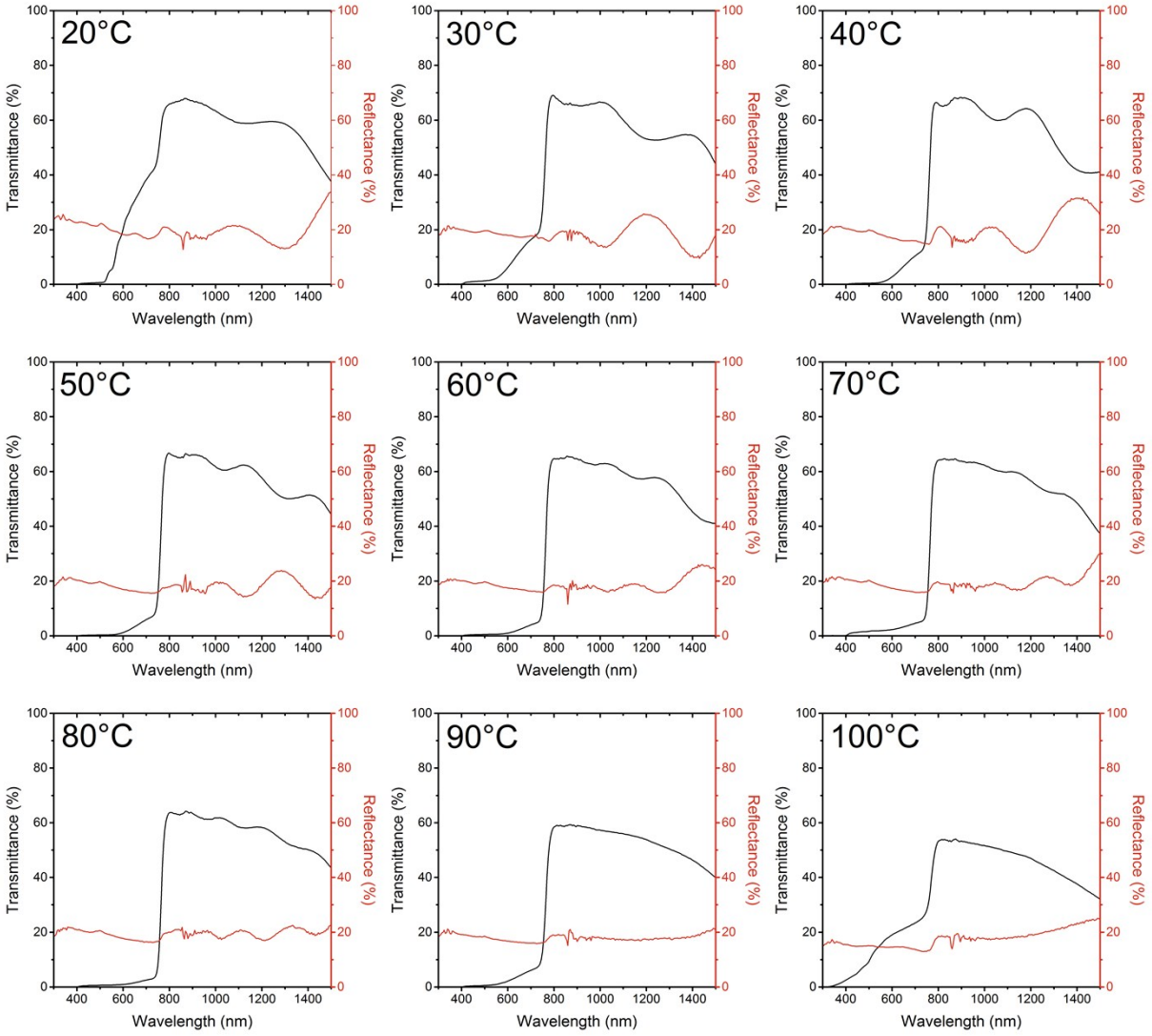


Figure S4. UV-Vis-NIR transmittance (black) and reflectance (red) spectra of the perovskite films prepared with different substrate temperatures.

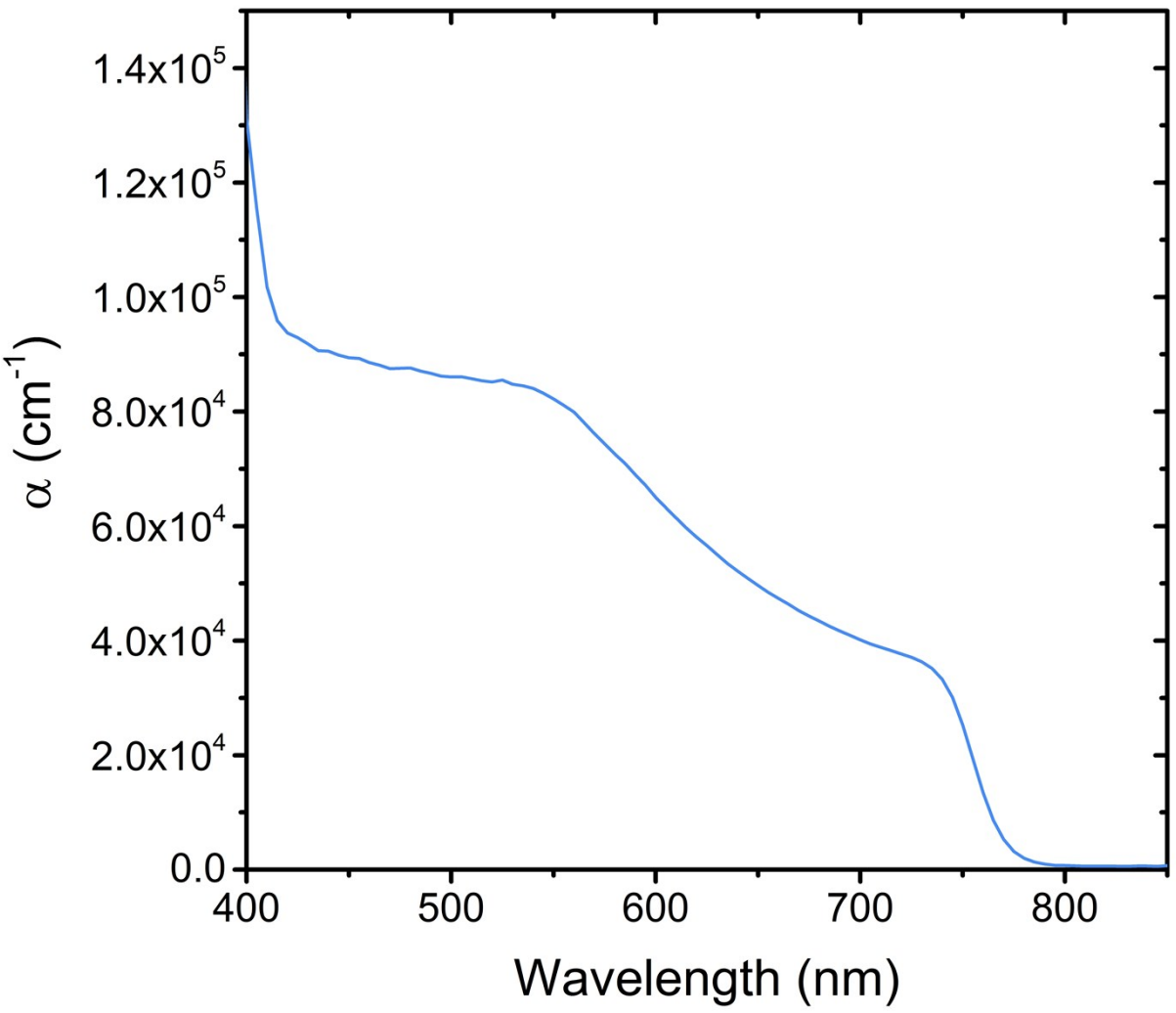


Figure S5. Absorption coefficient (α) of the $(FAPbI_3)_{0.85}(MAPbBr_3)_{0.15}$ perovskite film prepared with substrate temperatures of 50 °C. Values are calculated from the equations described above using the data from Figure S4.

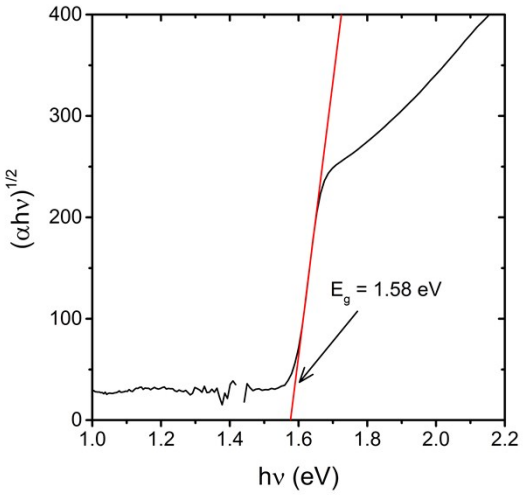


Figure S6. Tauc plot for optical band-gap determination the perovskite film prepared at 50°C. Values are calculated from the absorption coefficient in Figure S5.

Table S1. The optically determined band-gap of the perovskite films prepared with different substrate temperatures. The absorption coefficient was estimated for all films and the band-gap determined from Tauc plots.

Substrate Temperature (°C)	Optically determined band-gap (eV)
20	1.566
30	1.574
40	1.578
50	1.576
60	1.571
70	1.575
80	1.575
90	1.576
100	1.554

Steady-state photoluminescence

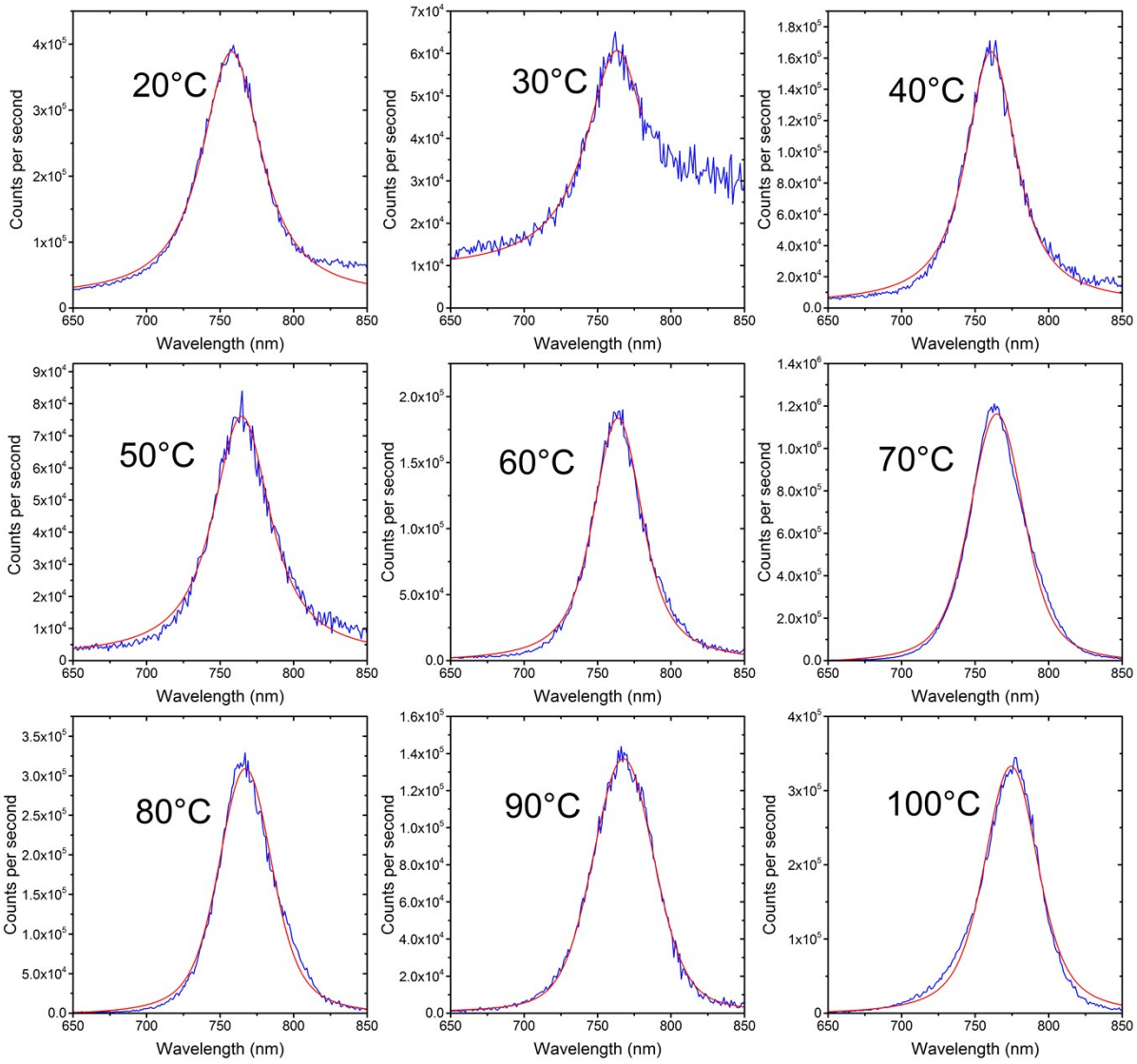


Figure S7. Raw-data (blue) from steady-state photoluminescence measurements of the perovskite films prepared with different substrate temperatures. The data was fitted using a Voigt profile probability density function (red) in Origin 2015. An excitation wavelength of 500 nm was used.

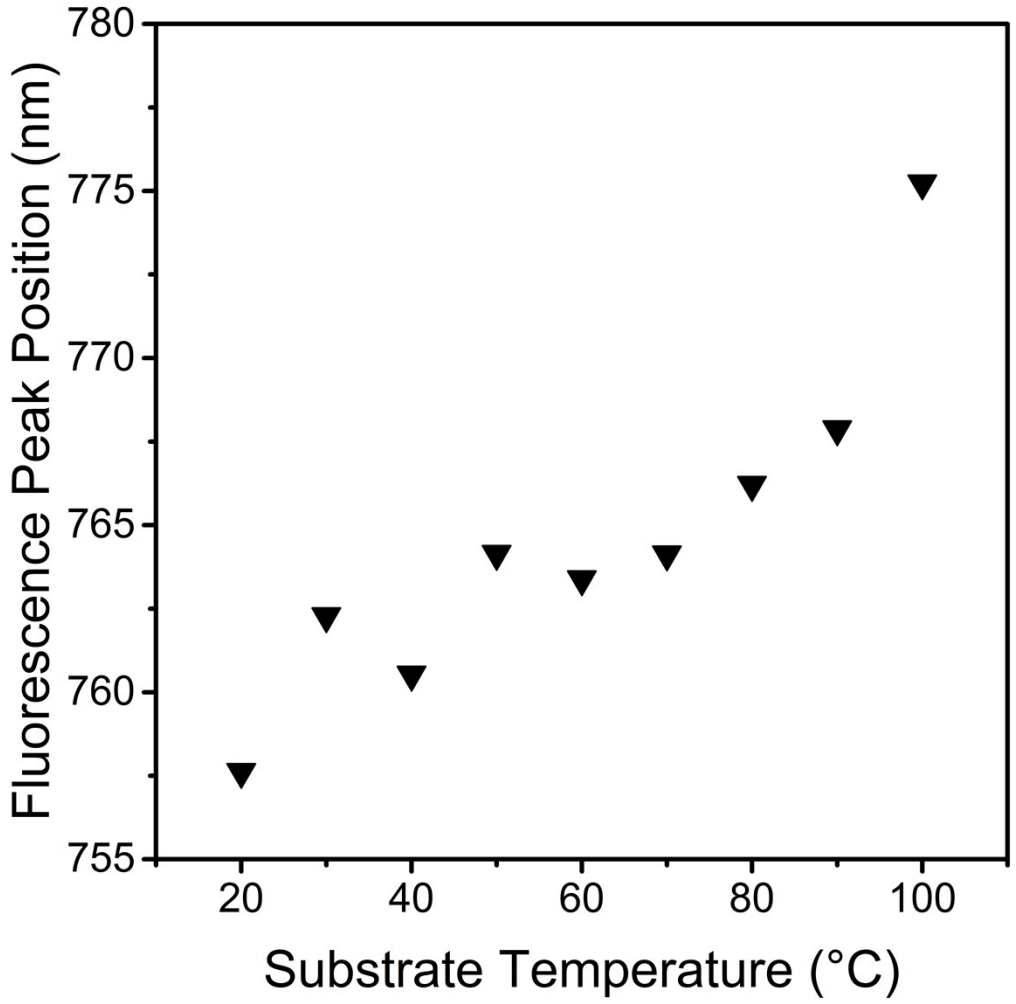


Figure S8. Steady-state photoluminescence peak positions of the perovskite films as a function of substrate temperature.

Photoluminescence self-absorption modeling

In order to confirm whether the photoluminescence (PL) self-absorption, or the so called inner filter effect, of the perovskite material can result in a PL-peak shift we modelled a situation where a defined emission from the perovskite is subjected to different optical density filtering from the perovskite material.

To study this, the data for the perovskite sample made at 20 °C was used. A theoretical, and arbitrary, absorptance spectrum was constructed by taking the 20 °C absorptance spectrum and normalizing it from 0 to 1 between the wavelengths 580 - 850 nm, which is the range where the PL was measured. For simplicity we call the obtained spectrum *Abs* and the original normalized 20 °C PL spectrum PL_{init}. The spectrum was then multiplied by four different factors to obtain *0.25*Abs*, *0.5*Abs*, *0.75*Abs* and *1.5*Abs*. In this case, PL_{init} is assumed to be the pure unfiltered emission from the $(FAPbI_3)_{0.85}(MAPbBr_3)_{0.15}$ perovskite. This emission is then subjected to different amounts of filtering from the different *Abs* spectra, which simulates perovskite films of different thickness, by calculating $PL_{init} * (1 - Abs)$. In Figure S9, the results have been compiled to show the apparent red shift of the PL-peak, from 757 nm to 766 nm, as PL_{init} is subjected to different amounts of filtering. In the inset of Figure S9 the resulting PL spectra have been normalized for comparison.

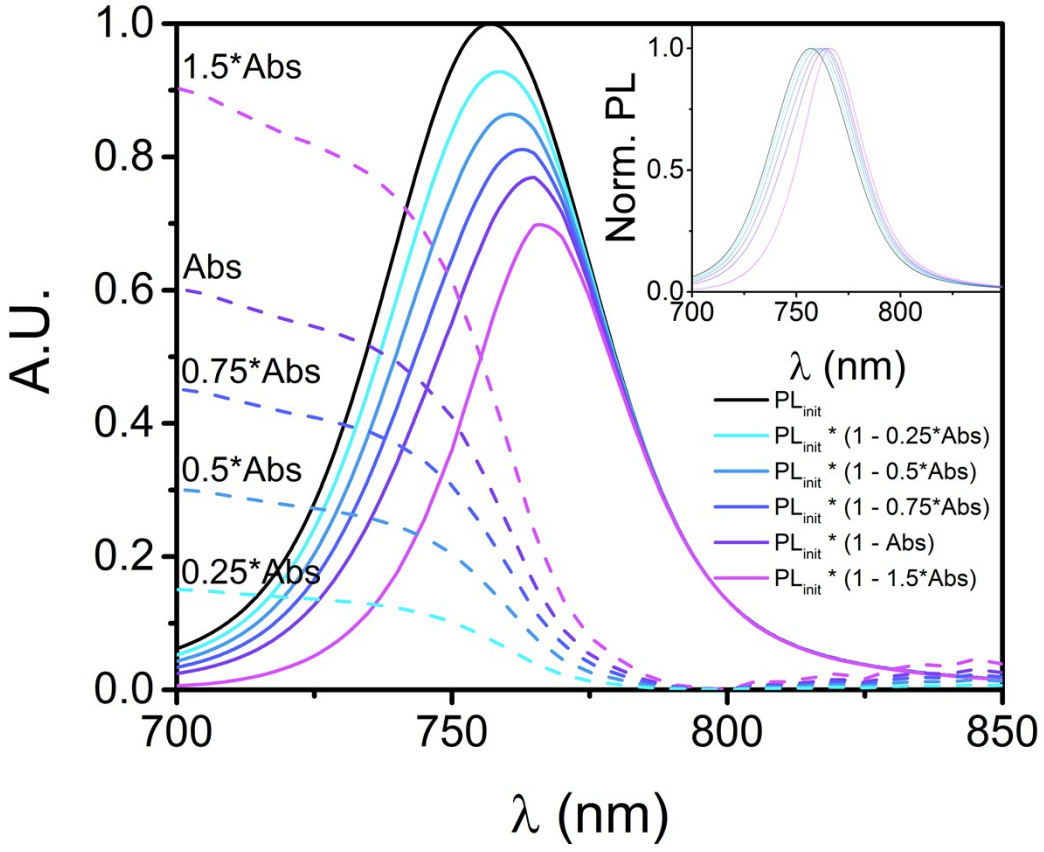
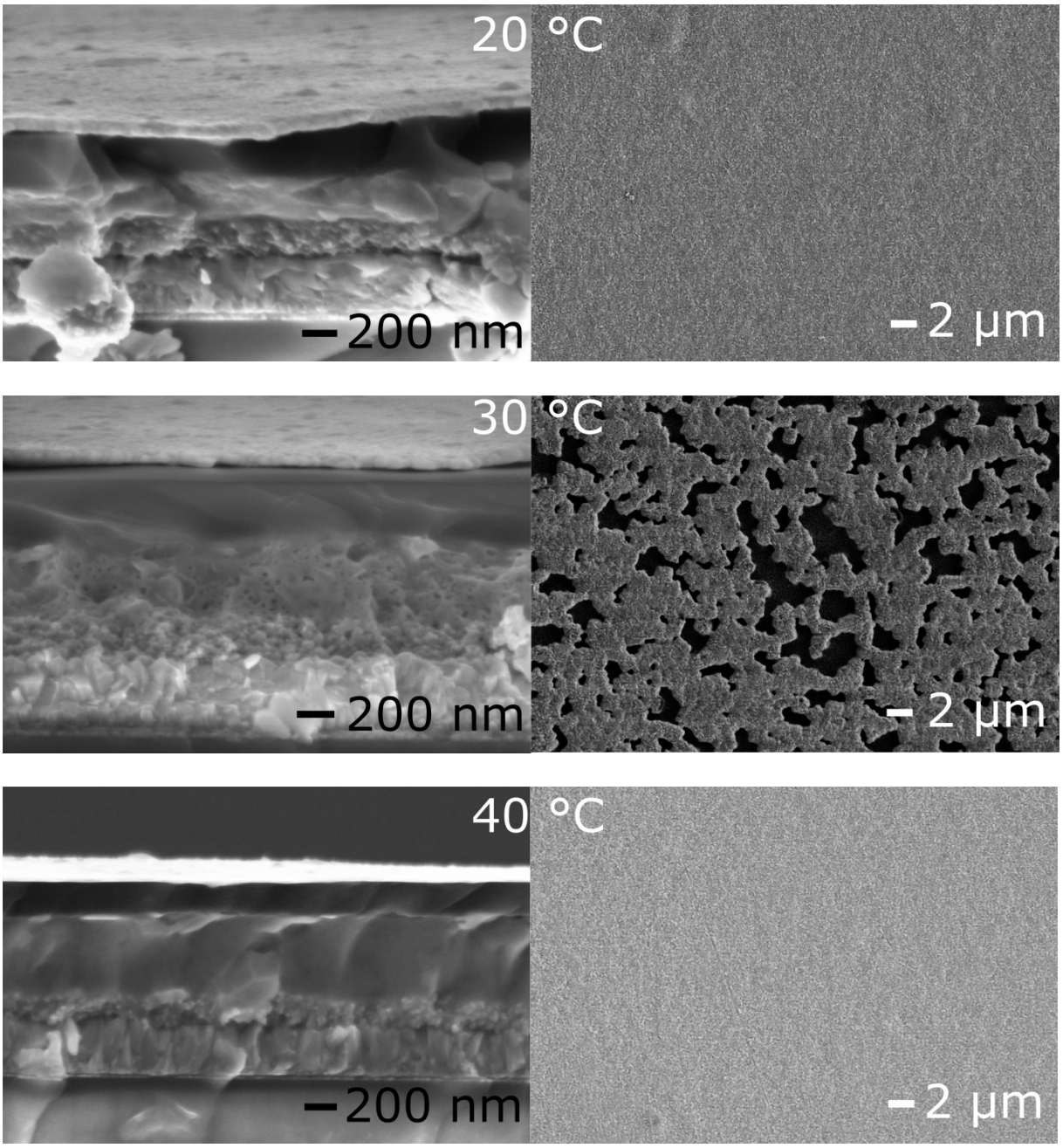
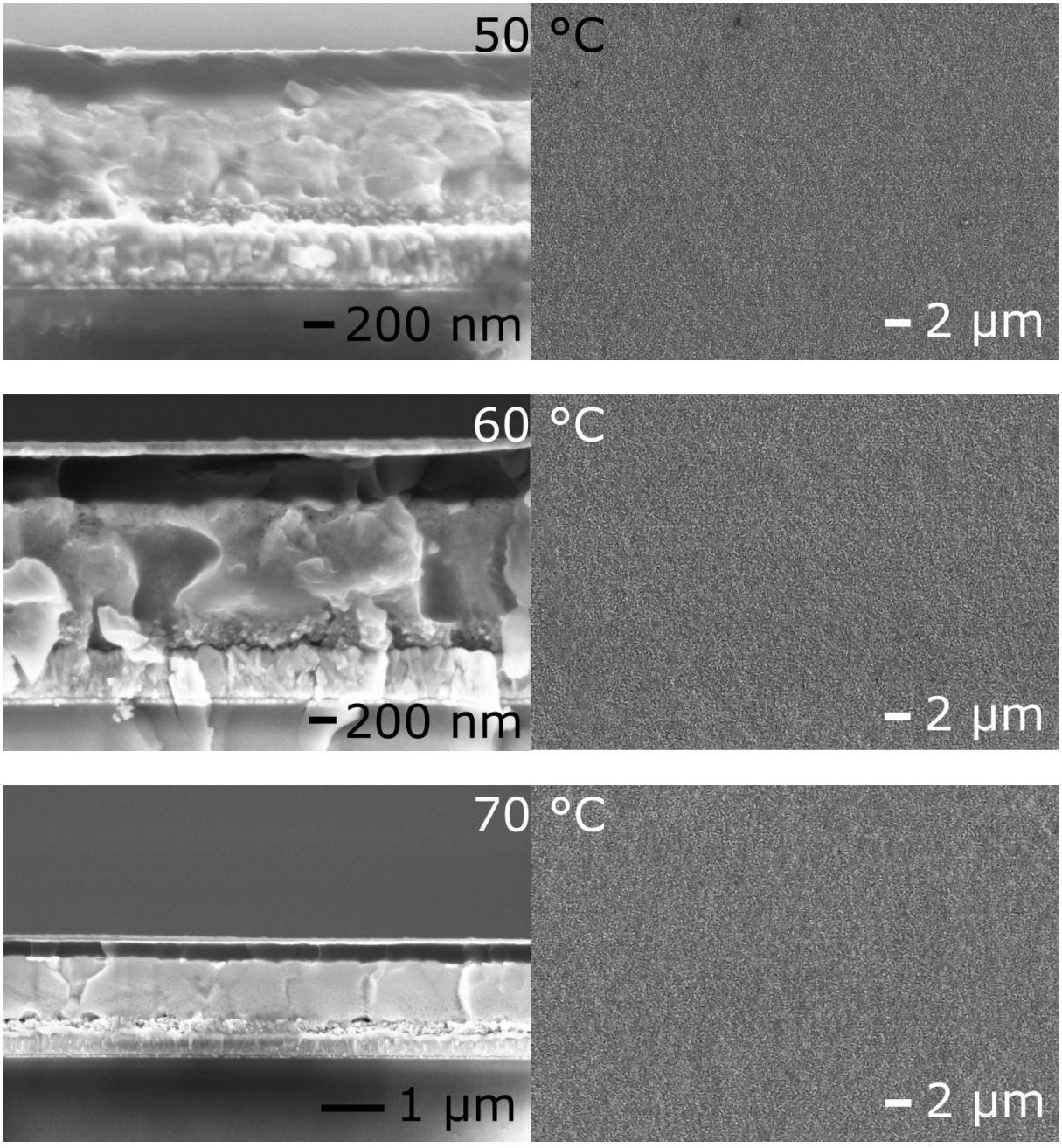


Figure S9. Modeling of the inner-filter effect. A normalized emission spectrum, $PL_{init,}$ is subjected to different amounts of filtering from the absorptance spectrum, *Abs*, of the perovskite. This filtering serves to shift the emission peak towards longer wavelengths.

Scanning electron microscopy




50 °C
200 nm
2 µm
60 °C
200 nm
2 µm
70 °C
1 µm
2 µm

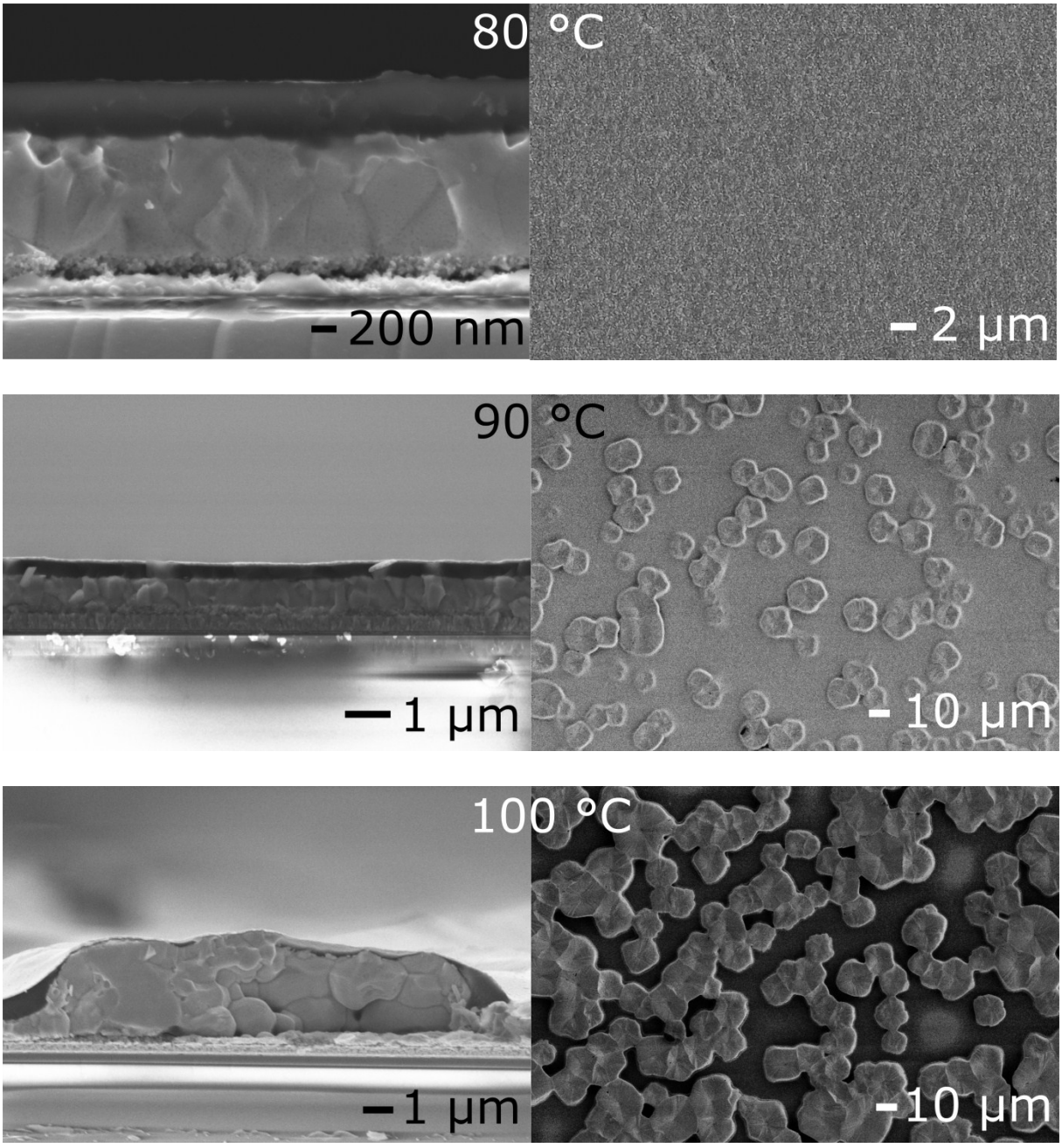
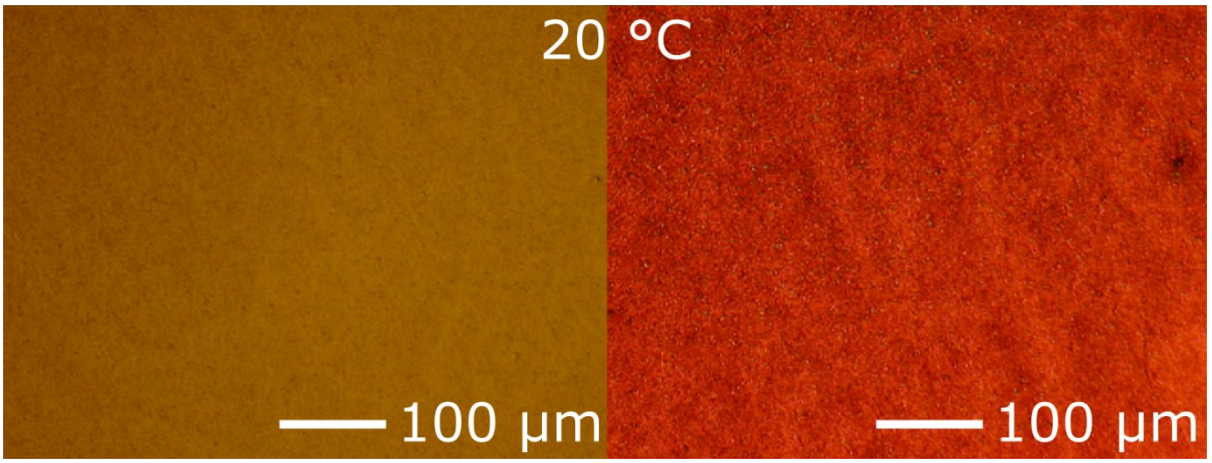
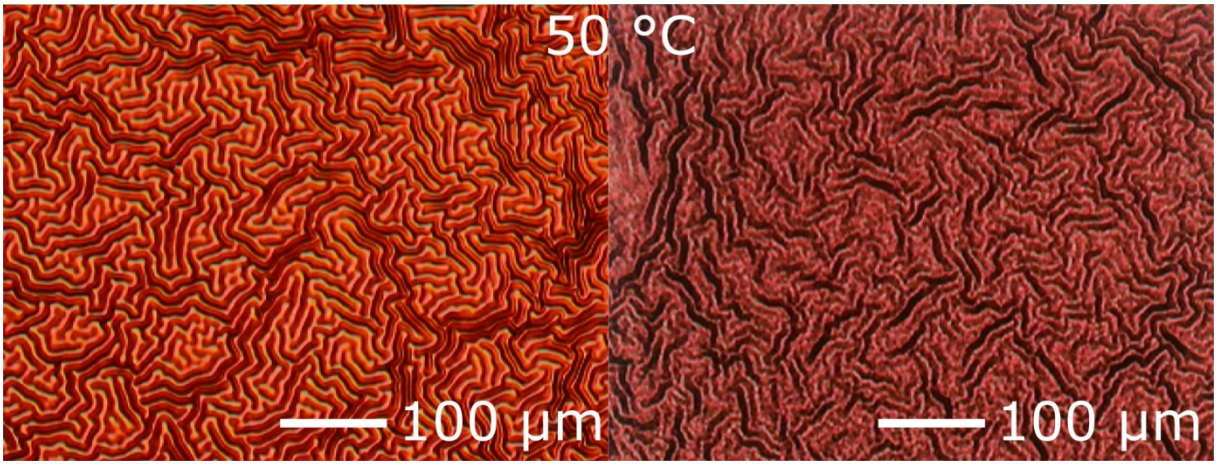
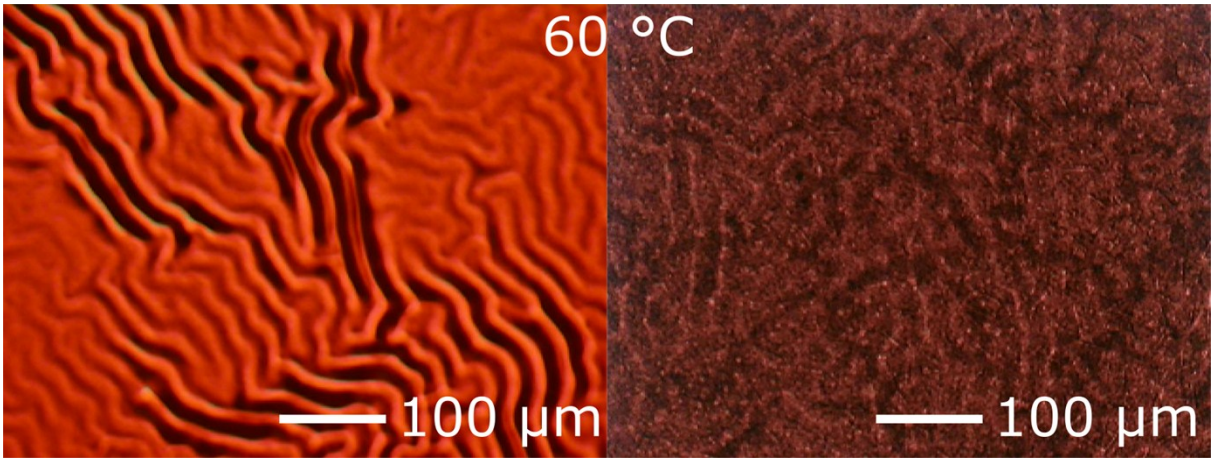


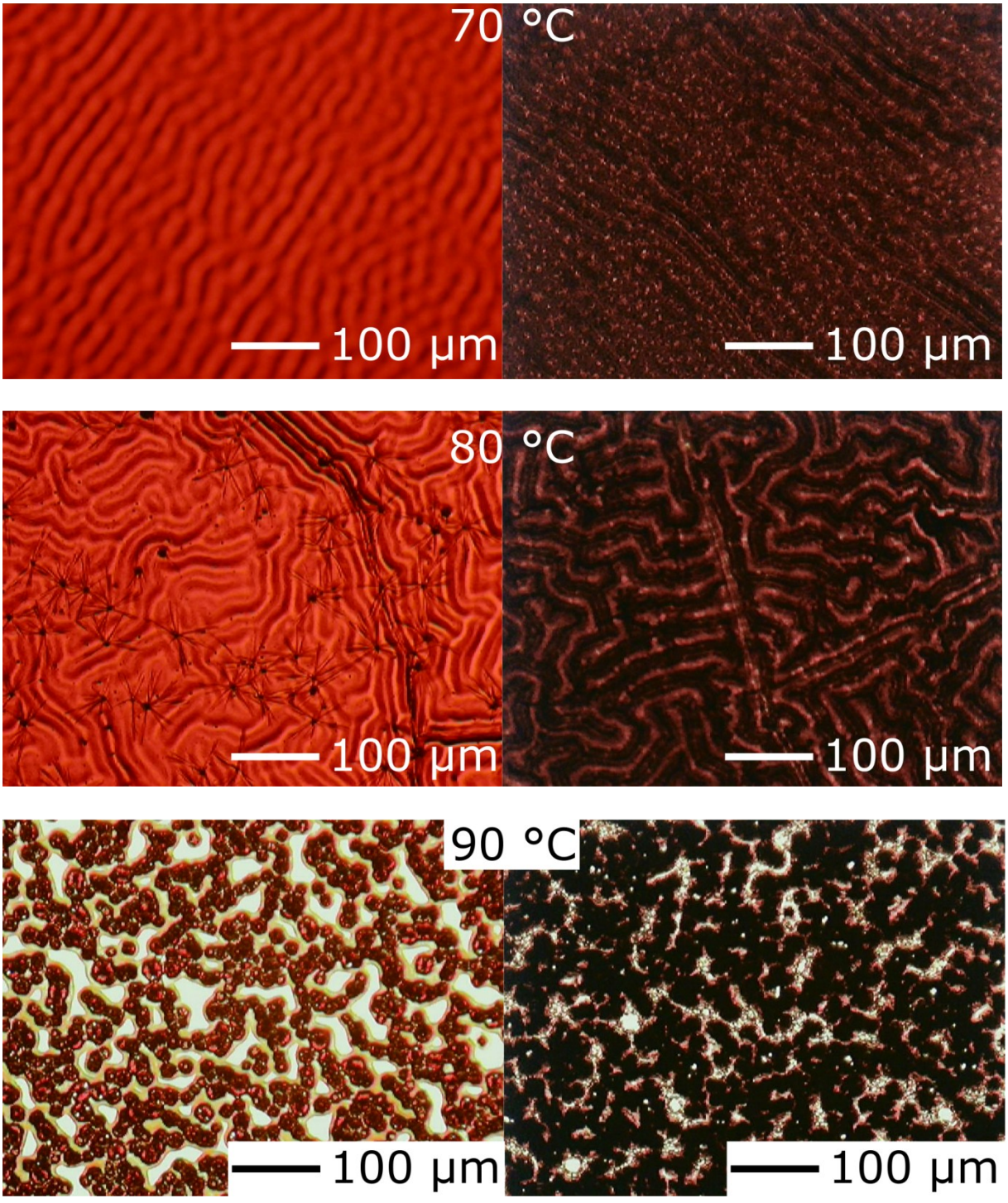
Figure S10. Scanning electron microscope images of perovskite solar cell cross-sections (left) and of the surface morpholgy for perovskite films (right) prepared with different substrate temperatures.

Optical microscopy








70 °C
100 µm
100 µm
80 °C
100 µm
100 µm
90 °C
100 µm
100 µm

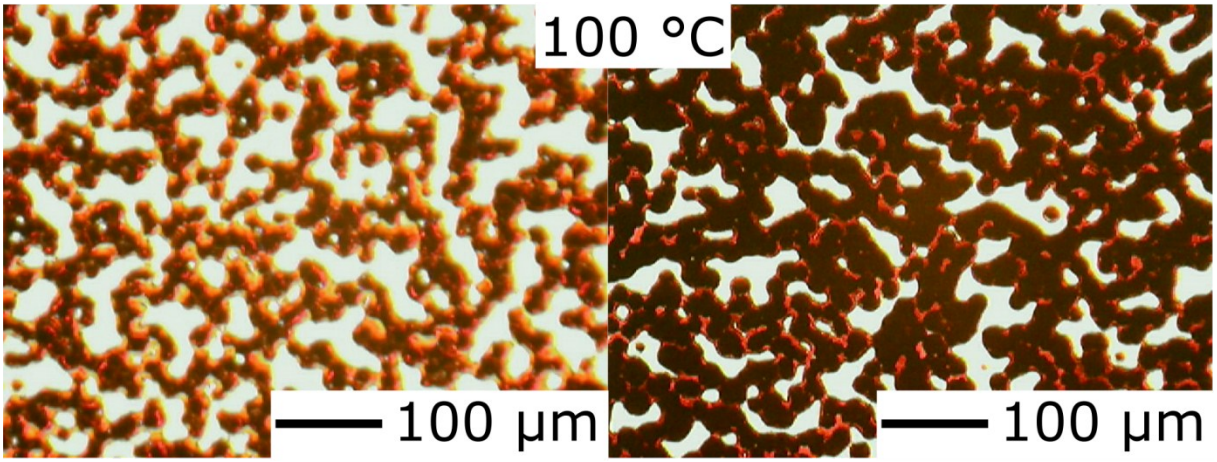


Figure S11. Optical microscope images (x255 magnification) of the intermediate films obtained with different substrate temperatures (left) and of the resulting perovskite films after annealing at 100 °C (right).

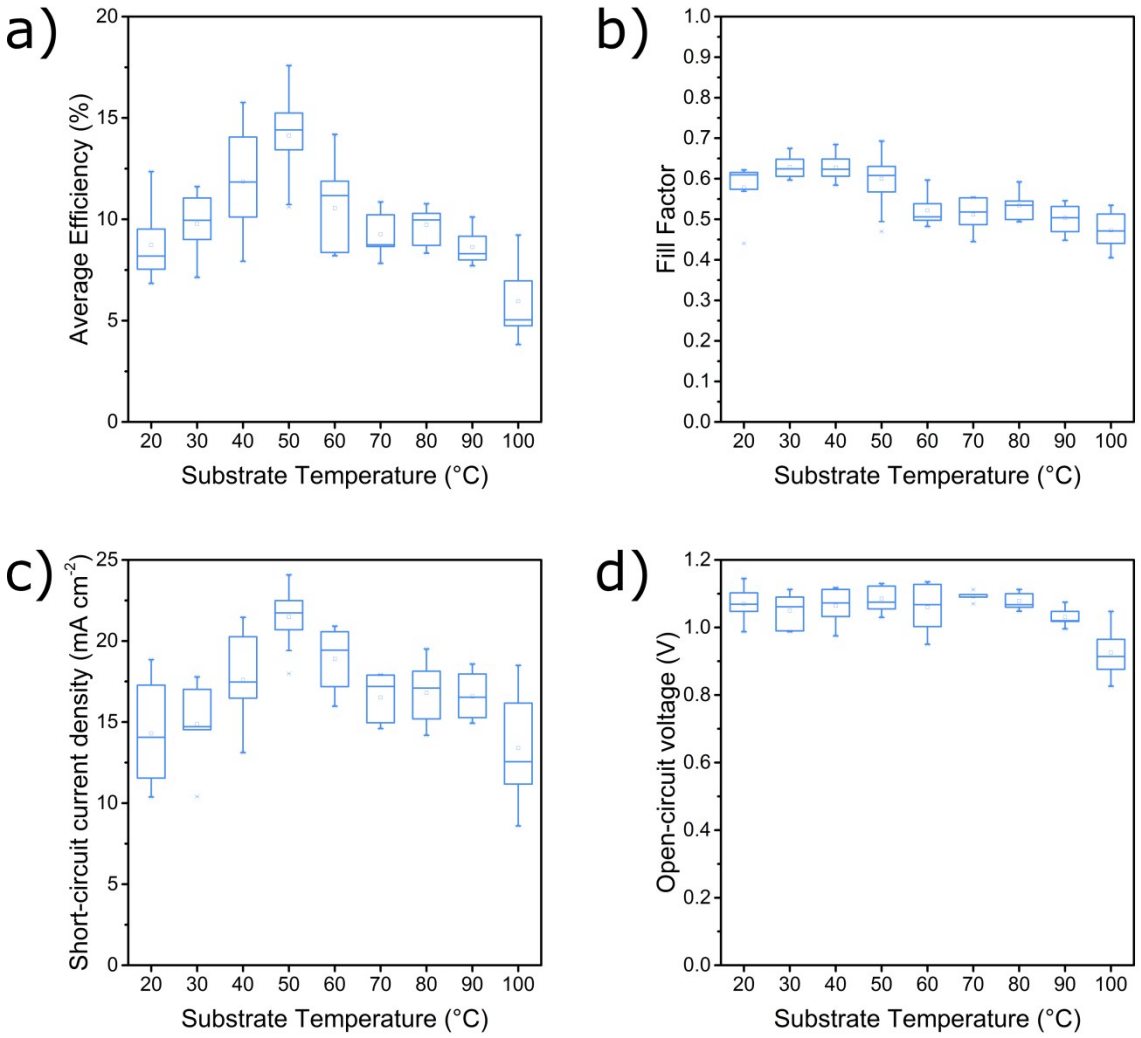


Figure S12. Boxplot statistics of; a) photovoltaic performances, b) fill factors, c) short-circuit current densities and d) open circuit voltages of solar cells prepared with different substrate temperatures. The parameters are derived from the average of the backward (open-circuit to short-circuit) and forward (short-circuit to open-circuit) *I-V* scans. The scan rate was 10 mV/s.

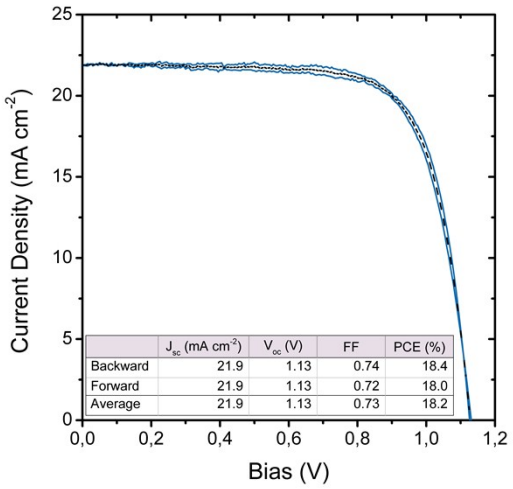


Figure S13. Current-voltage (*I*-*V*) scan of a standard mixed-ion perovskite device prepared in a dry nitrogen glovebox under 1 sun illumination intensity. Both backward and forward scans are depicted (blue) along with the average of the two (dashed). Parameters presented in the inset table are: short circuit current density (J_{sc}), open circuit voltage (V_{oc}), fill factor (*FF*), and power conversion efficiency (PCE). The scan rate was 10 mV/s.

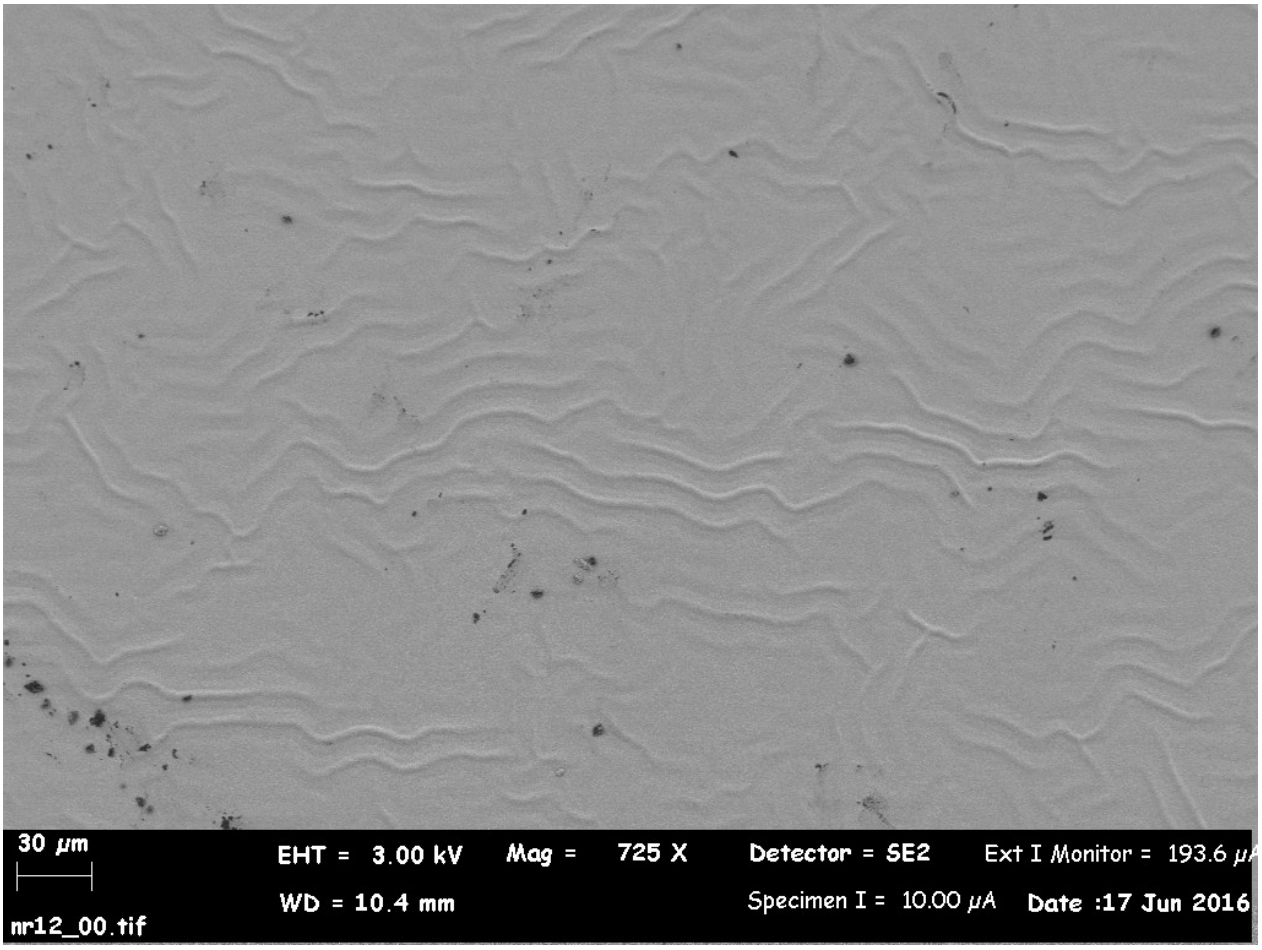


Figure S14. Scanning electron microscope image of the surface morphology for a mixed-ion perovskite film prepared at 50 °C. Similar wrinkle features are observed as for the optical microscope with approximately the same wavelength distance (~15 µm) between each wrinkle.

1 W. Q. Hong, *J. Phys. D. Appl. Phys.*, 1989, **22**, 1384–1385.