Electronic Supplementary Material (ESI) for Nanoscale.

Supplementary Information: Spatially resolved studies of the phases and morphology of methylammonium and formamidinium lead tri-halide perovskites

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Fig. 1 of the supplementary information presents macro-transmission (transmission of white light averaged over 1 mm^2 spot) measured as a function of the temperature for MAPbI$_3$. Panel (a) contains the transmission spectra taken at different temperatures, and panel (b) shows resulting absorbtion energies plotted as a function of the temperature. At temperatures around the phase transition (150-170 K) the spectra reveal presence of both orthorhombic (orthorhombic phase, OP) and tetragonal (tetragonal phase, TP) phases. The phase transition from tetragonal to orthorombic phase causes an abrupt rise of around 100 meV in the energy of the absorption edge. The temperature dependence of the TP peak reveals a turning point at 168 K (b). No trace of the OP is found above 170 K in transmission and in both temperature dependent and spatially resolved μ-PL studies, suggesting that above 168 K the material is entirely in the tetragonal phase.

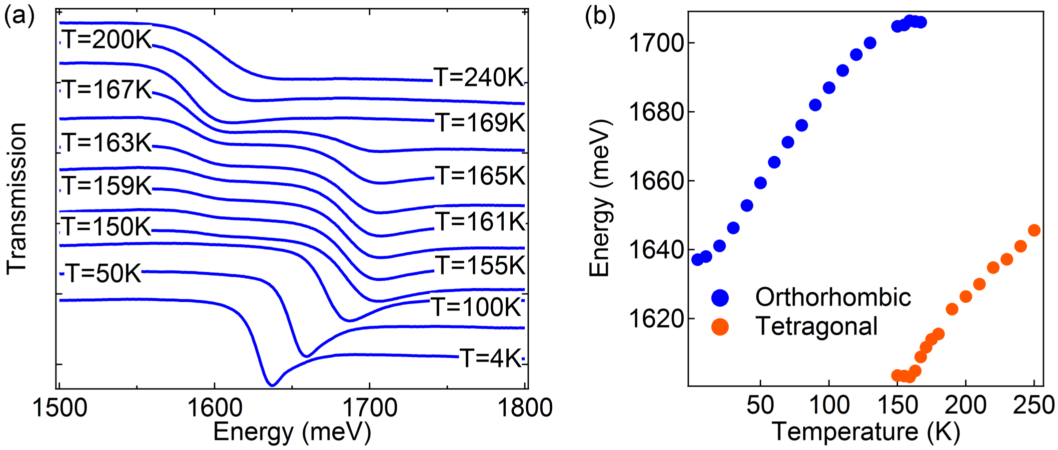

Figure 1. (a) Transmission spectra and (b) energy of the absorption edge as a function of temperature.

Fig. 2 shows a low-temperature (5 K) μ-PL map of a selected region of a MAPbCl$_x$I$_{3-x}$ sample. This demonstrates an obvious positive/negative correlation between the peaks at 1535 meV and 1565/1600 meV. As stated in the main article, we attribute the 1535 meV emission (panel a) to high temperature, tetragonal phase and the 1565 (panel b)/1600 meV(panel c) peaks respectively to bound and free exciton of the low temperature, orthorhombic phase. The positive/negative correlation of the OP and TP peaks is particularly clear for the narrow-strip regions with well-defined borders (compare panels (a) and (b)). This may suggest an enhanced presence of the of high temperature phase in strained or cracked areas. There is also significantly more variation in the intensity of the bound exciton when compared to the free exciton for the OP phase, which is found to be most strongly quenched in the regions close to the tetragonal phase inclusions (c).

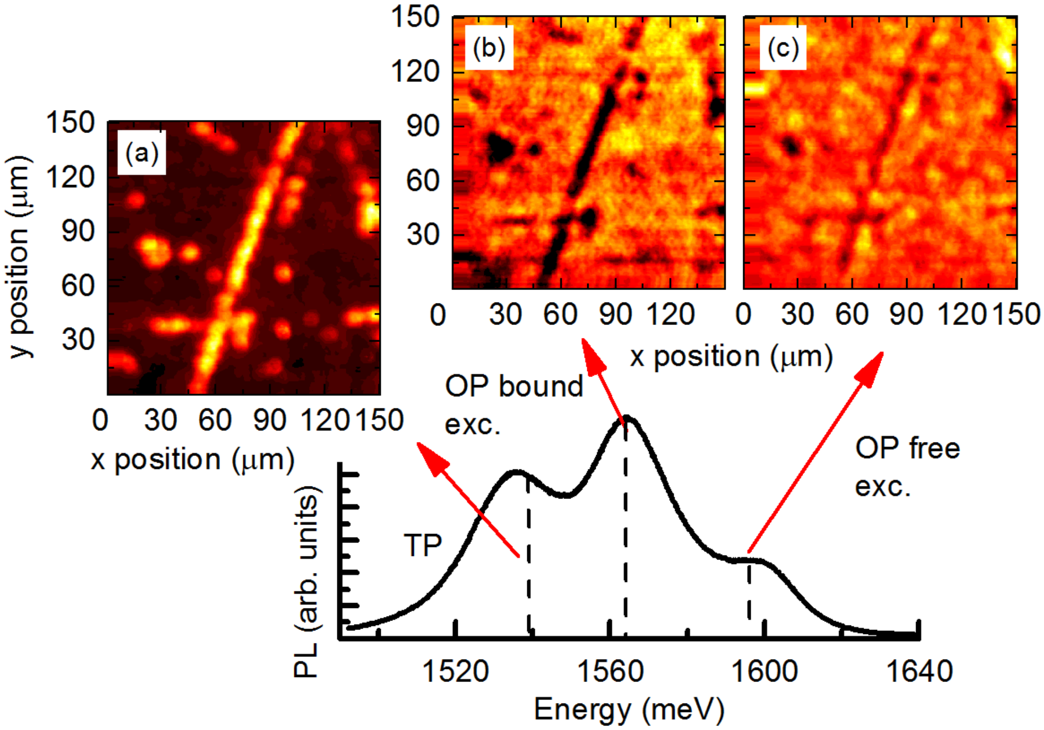

Figure 2. Photoluminescence spectrum and integrated intensity maps of the sample corresponding to: (a) high temperature, TP peak and bound (b) and free (c) exciton peaks of the low temperature OP.

Further conclusions about the nature of observed inhomogenities come from an investigation of regions exposed to a focused laser spot. It has been reported recently[1], that photo - annealing induces the migration of halide ions away from the point of exposure, influencing the PL properties of the material. Fig. 3 presents low temperature spatially resolved microphotoluminescence for a $MAPbCl_xI_{3-x}$ sample illuminated for several minutes with a 532 nm laser spot of 10^9 W/m^2 power density at room temperature. As a result of photo annealing, regions of decreased and enhanced halide content are formed Fig. 3 (a), leading to emissions characteristic of both the tetragonal phase and both excitons of the orthorhombic phase (e). The center of the laser spot is a dark core (upper right corner of the maps). Moving away from the dark core (with a probably increasing iodine content), we find regions of TP emission (b). Sequentially, we observe rings of emission from OP bound excitons, OP free excitons (d) and then again OP bound excitons which are dominant in the unaffected areas. This picture is consistent with the emission being controlled by an iodine content as shown in panel (a), where OP free excitons are only dominant at low temperatures in regions of enhanced iodine content.

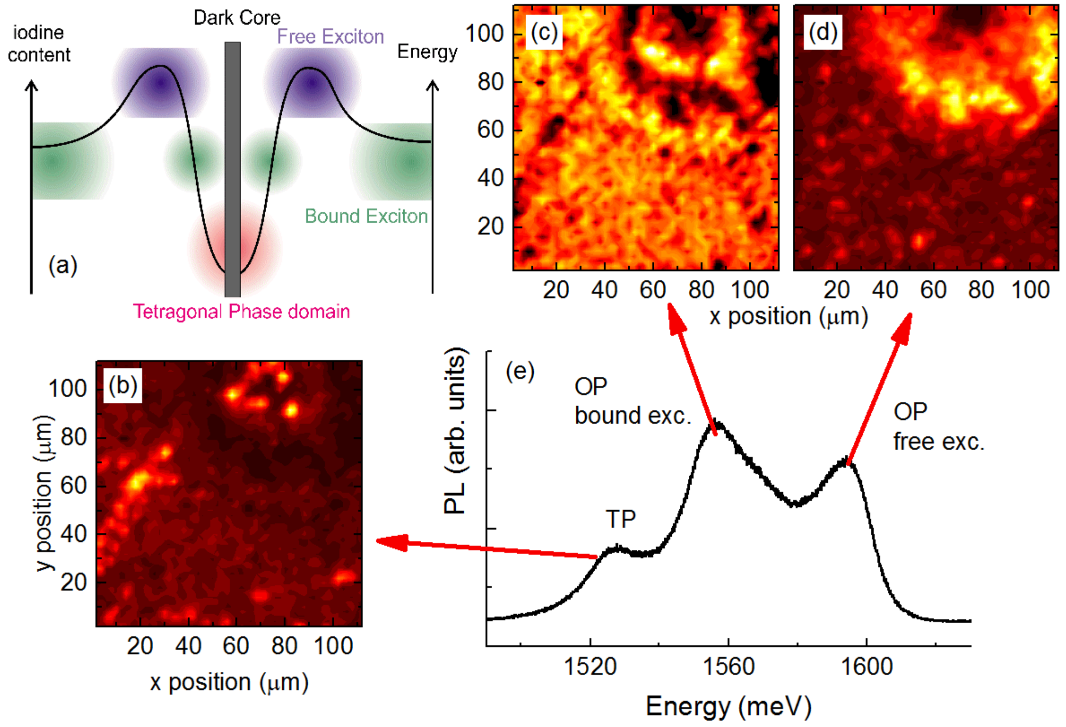

Figure 3. (a) the distribution of iodine ions as a function of distance from the point of exposure. (b)-(d)integrated intensity maps of the sample corresponding to: (b) high temperature, TP peak and bound (c) and free (d) exciton peaks of the low temperature OP. (e) Photoluminescence spectrum showing all observed transitions.

We supplement the spatially resolved μ-PL obtained for $MAPbI_3$ with measurements performed on compounds based on the Formamidinium cation,$FAPbI_3$ (Fig.4). We show a predominantly uniform region (panels a- d) and an area in proximity of a dark ribbon, being probably a crack or fissure (panels (d)-(h)). Similarly to $MAPbI_3$, at low temperatures we observe the anti correlation of the OP and TP emission peaks, with TP phase grains up to 10 μm in size (panels (a) and (b)). Both bound and free excitons of OP occur simultaneously in the investigated region (c). The regions close to the dark ribbon (panels (d)-(e)) show a 1D analogy of the photo-annealing results. Close to the ribbon, we observe enhanced emission from the TP peak, with additional narrow emission lines probably from localized states (g). In addition the TP/OP anticorrelation is significantly stronger than in the case of the region shown in (a) (compare panels (d) and (h)). This gives further evidence to link the existence of the tetragonal phase inclusions with the presence of strained or defected areas.

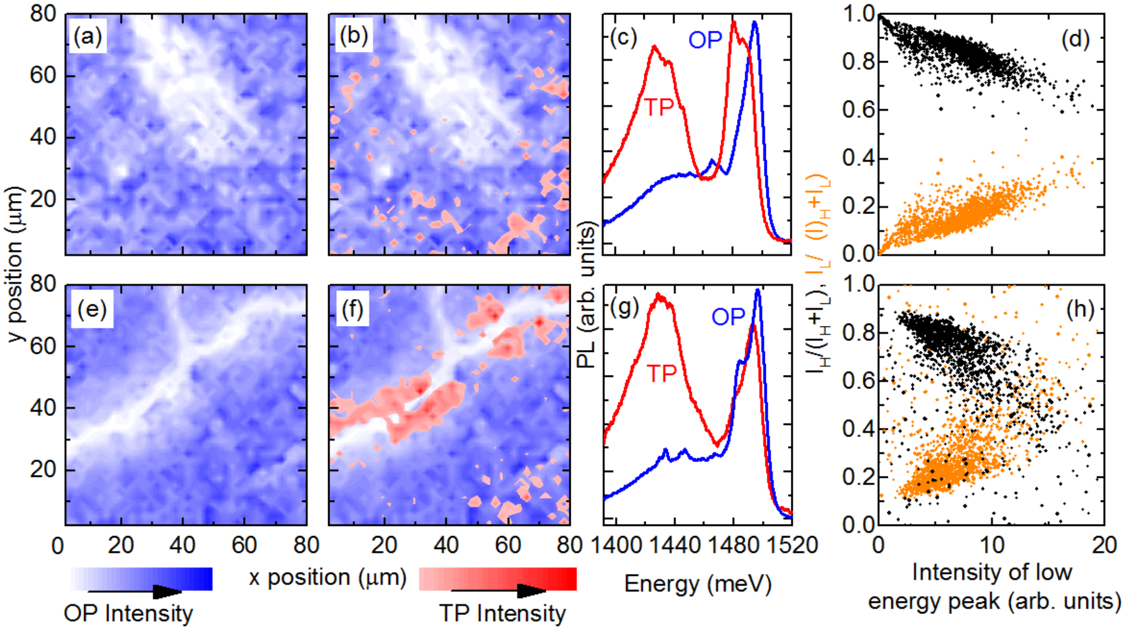

Figure 4. The images present a homogenous area (a)-(d) and a region around dark ribbon (e)-(h). (a),(e): Integrated intensity of the OP peak across the sample. The intensity increases from white to dark blue. (b),(f): Two maps of the integrated intensity of the OP and TP peaks. The intensity of the OP (TP) is marked in blue (red) respectively. (c),(g): Typical photoluminescence spectra with dominance of OP (blue) and TP (red) peaks. (d),(h): Correlation of the integrated intensity of the TP (orange) and OP (black) peaks versus intensity of the TP peak.

In order to demonstrate the batch to batch and measurement to measurement reproducibility we compare examples of the same batch mapped with two different mapping systems in different laboratories Fig.5 and of two separate batches made approximately one year apart mapped with the same system Fig.6.

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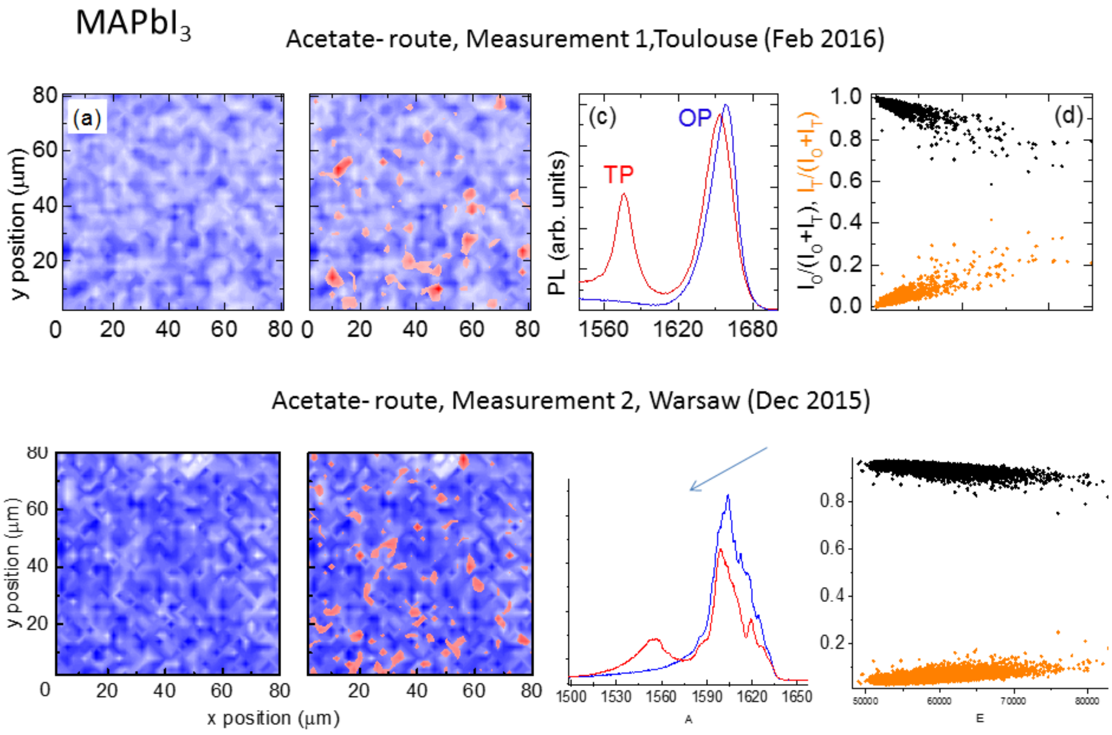

Figure 5. The two sets of images and spectra were taken using similar mapping systems located in Toulouse and Warsaw, approximately 3 months apart, using samples fabricated at the same time.

[1] deQuilettes, D. W. *et al.* Photo-induced halide redistribution in organic-inorganic perovskite films. *Nature Communications* **7**, 11683 (2016).

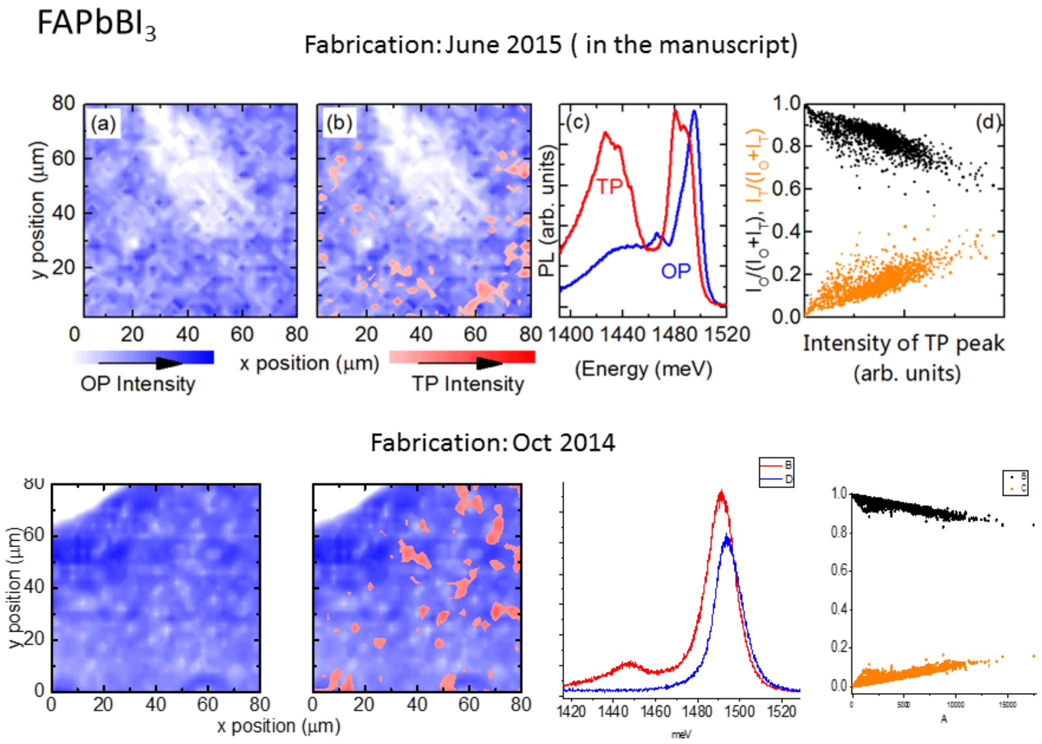

Figure 6. The two sets of images and spectra were taken from samples fabricated approximately one year apart.