Electronic Supplementary Information (ESI)

Correlation of Annealing Time with Crystal Structure, Composition, and Electronic Properties of $CH_3NH_3PbI_{3-x}Cl_x$ Mixed-Halide Perovskite Films

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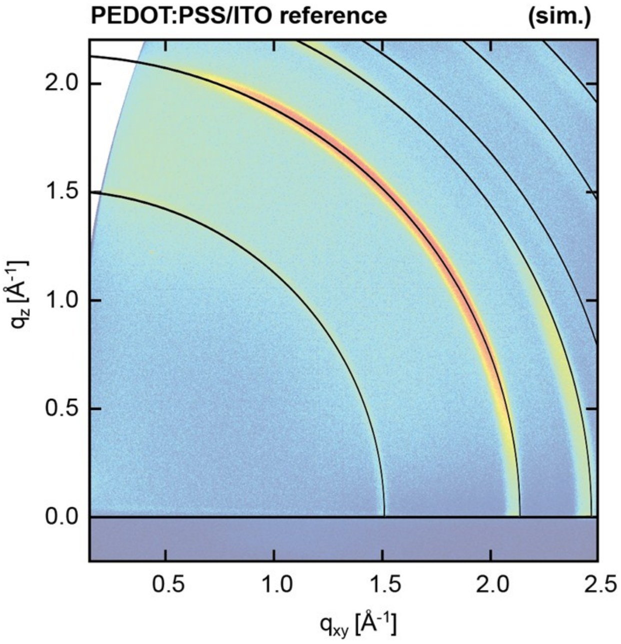

Fig. S1 GIXRD data for a PEDOT:PSS/ITO reference sample, as used as substrate for the perovskite films in the whole study; rings indicate simulated diffraction features of non-textured ITO.

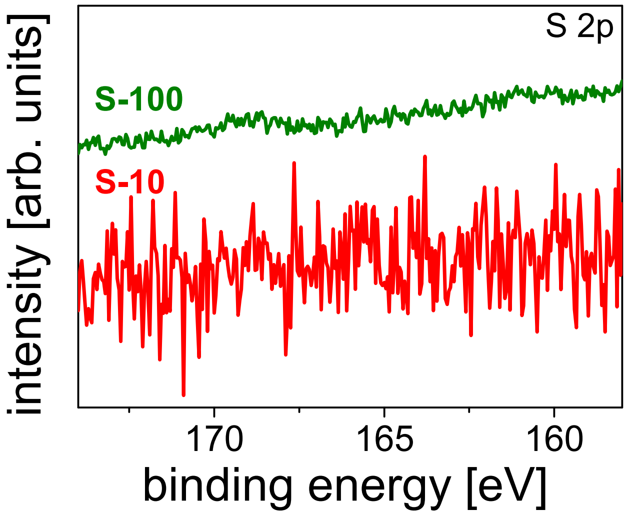

Fig. S2 XPS core level spectra of S 2p for S-10 (red curve) and S-100 (green curve) annealed at 100 °C for 10 min and 100 min, respectively.

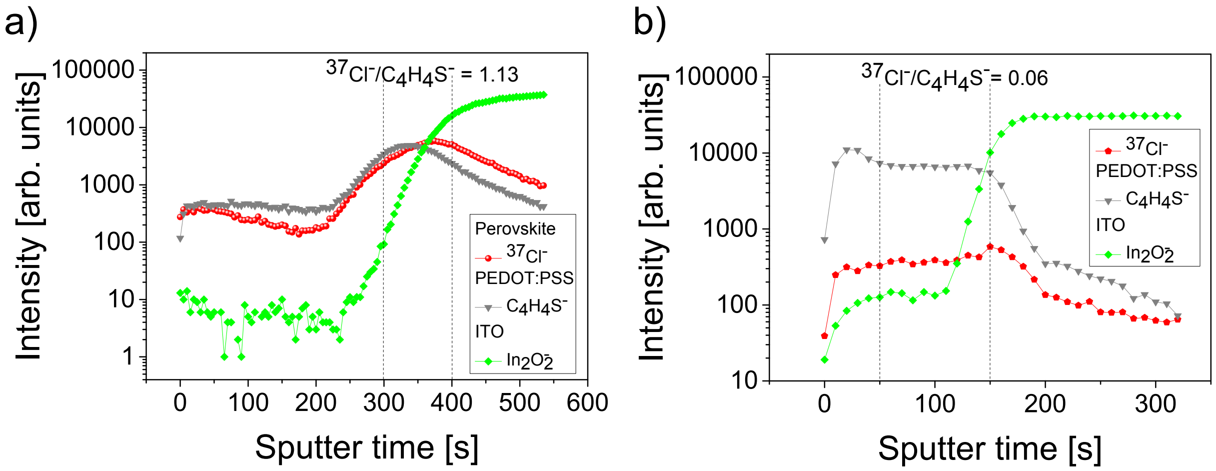

Fig. S3 ToF-SIMS depth profiles of a) S-100 min (cf. Figure 3a in the main text) and b) of a pristine PEDOT:PSS film on ITO substrate. The intensity ratio of the secondary ions ^{37}Cl$^-$/C$_4$H$_4$S$^-$ in the PEDOT:PSS layer (delimited by dotted vertical lines) is 18 times higher in S-100 (a), this excludes that ^{37}Cl$^-$ signal in S-100 would simply come from contaminations due to air.

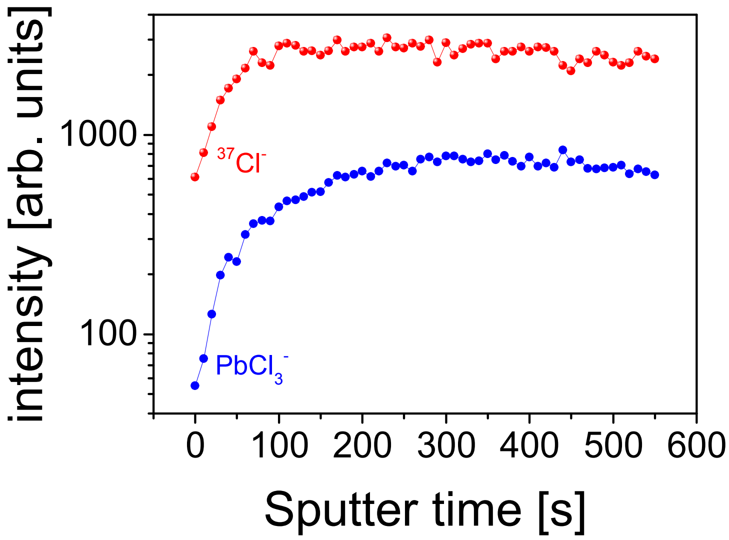

Fig. S4 ToF-SIMS depth profiles of $^{37}Cl^-$ and $PbCl_3^-$ obtained in S-10; the similar curve shapes suggest that both ions arise from the fragmentation of the same lead chloride-based species.

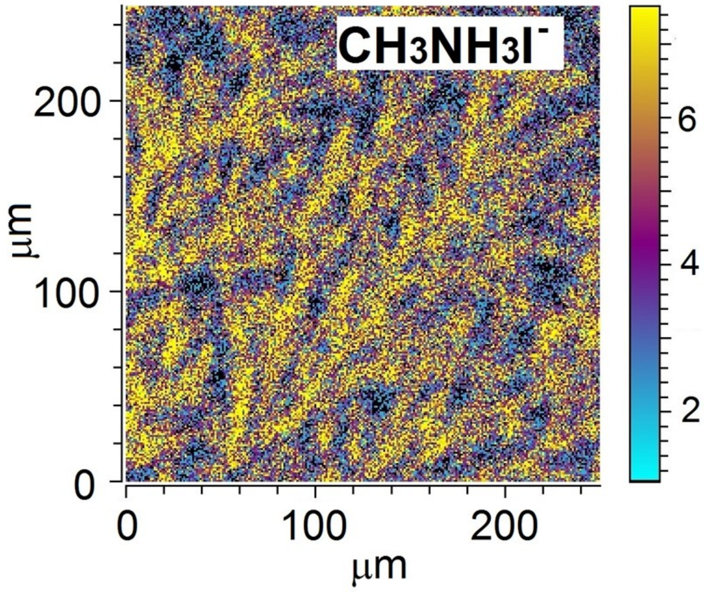

Fig. S5 ToF-SIMS XY map of S-10, displaying the depth-integrated intensity of $CH_3NH_3I^-$ ($MAI\text{-}H^+$) for MAI.

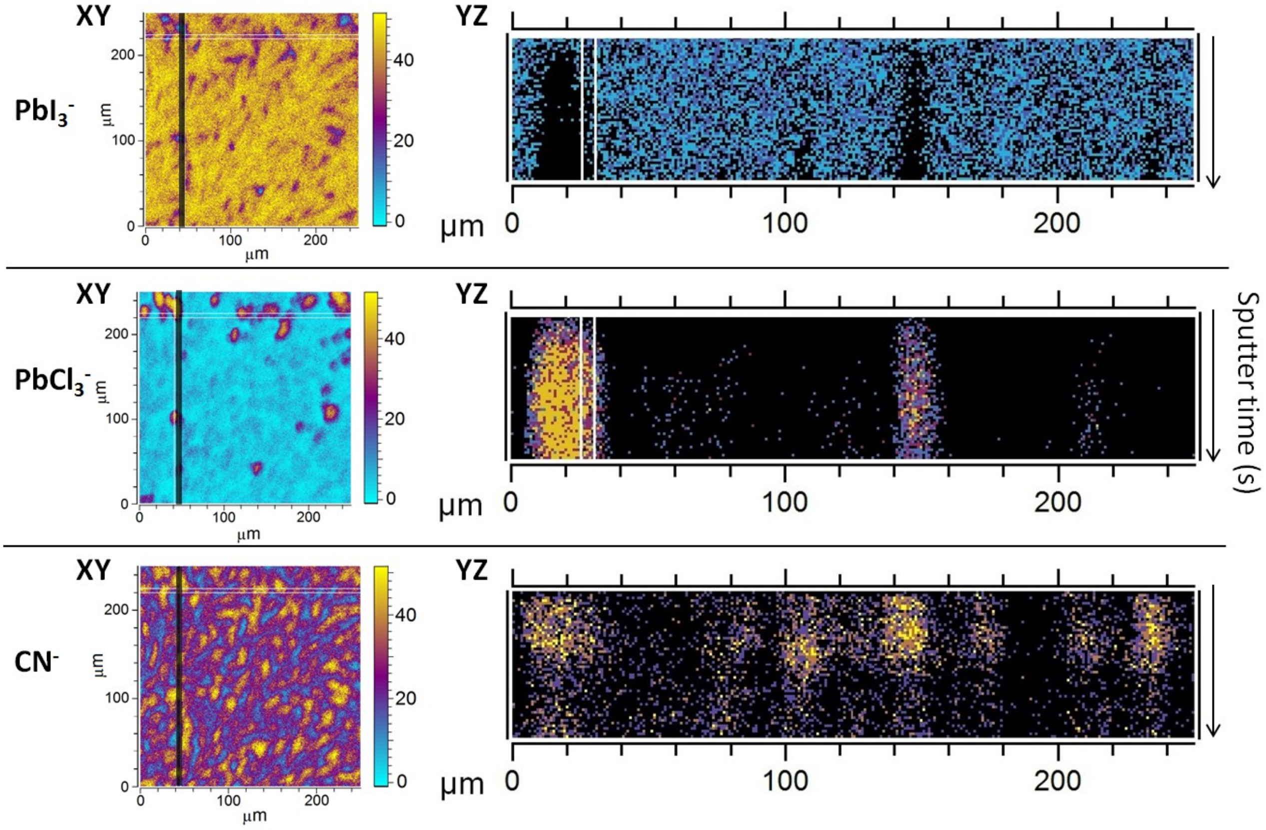

Fig. S6 ToF-SIMS XY maps and cross section reconstructions along YZ sections (shown by the black line in XY maps) for selected ions from S-10 sample. The YZ maps indicate the phase separation extends throughout the whole film depth.

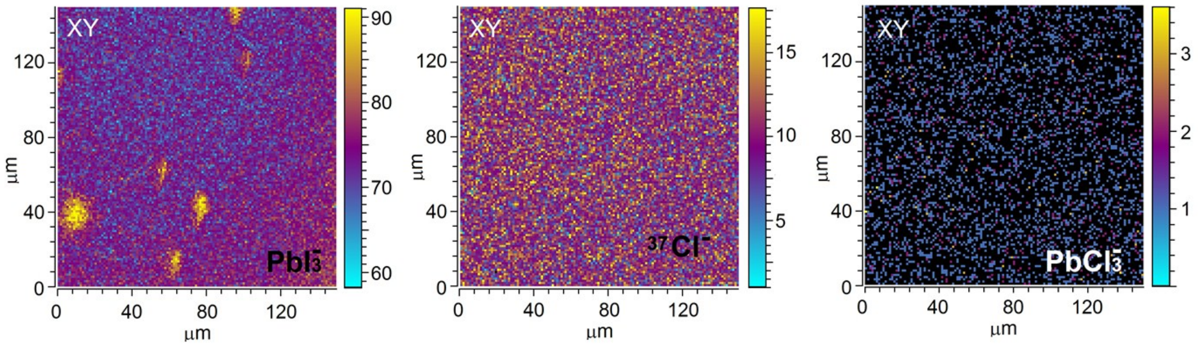

Fig. S7 ToF-SIMS XY maps from S-100. In contrast to sample S-10 (Figure 4 in the main text), no phase separation is observed here. Observed spots in PbI_3^- are due to diffusion into defects in the underlying PEDOT:PSS layer.

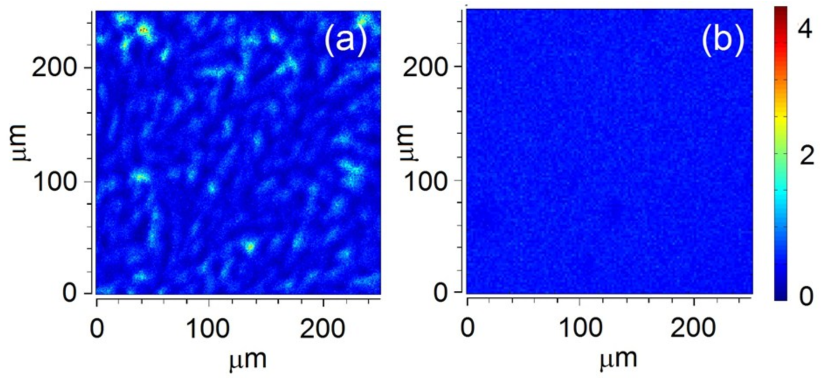

Fig. S8 ToF-SIMS XY maps showing the CN^-/PbI_3^- intensity ratio obtained for (a) S-10 and (b) S-100. In contrast to the homogeneous distribution in S-100, S-10 is characterized by regions with distinctly higher intensity ratio, thus, indicating a higher concentration of organic MA compound.

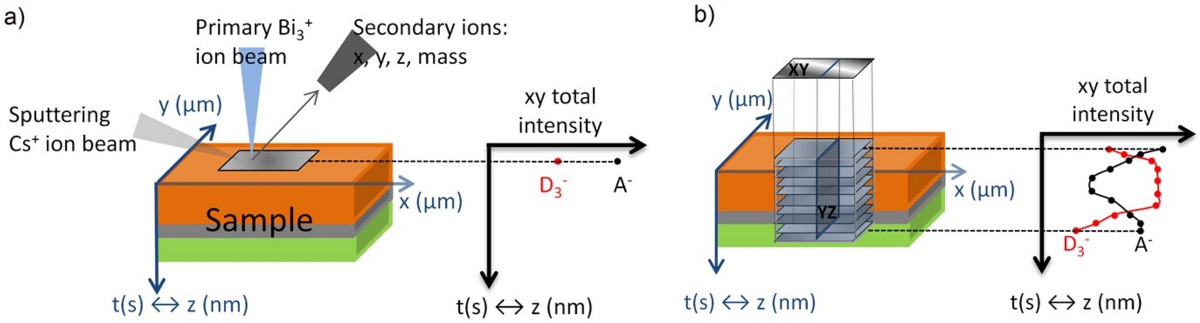

Fig. S9 Simplified illustration of the ToF-SIMS measurement process: a) The full mass spectrum is acquired at each analysis step performed with Bi_3^+ primary ion beam. Consecutively, material sputtering is performed with low energy Cs^+ ion beam for a specific sputter time. b) By alternating analysis and sputtering steps, depth profiles (after successive XY intensity integrations) are built. Specific ions can be selected in the mass spectrum to build depth-integrated maps and cross-sectional maps (XZ or YZ).