Supporting information for the article: "*In situ* roll-to-roll X-ray scattering studies of slot-die coated perovskite solar cell active layers on flexible substrates"

IN SITU ROLL-TO-ROLL X-RAY SCATTERING STUDIES OF SLOT-DIE COATED PEROVSKITE SOLAR CELL ACTIVE LAYERS ON FLEXIBLE SUBSTRATES

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SUPPORTING INFORMATION

BEAM DAMAGE CHARACTERIZATION:

Using time-of-flight secondary ion mass spectroscopy (TOFSIMS), we studied a beam damaged sample, coated on PET-ITO-P4083 to try and determine what direct effect the X-ray beam has had on the sample(from a region of 5×2.5 mm^2 in the irradiated area).

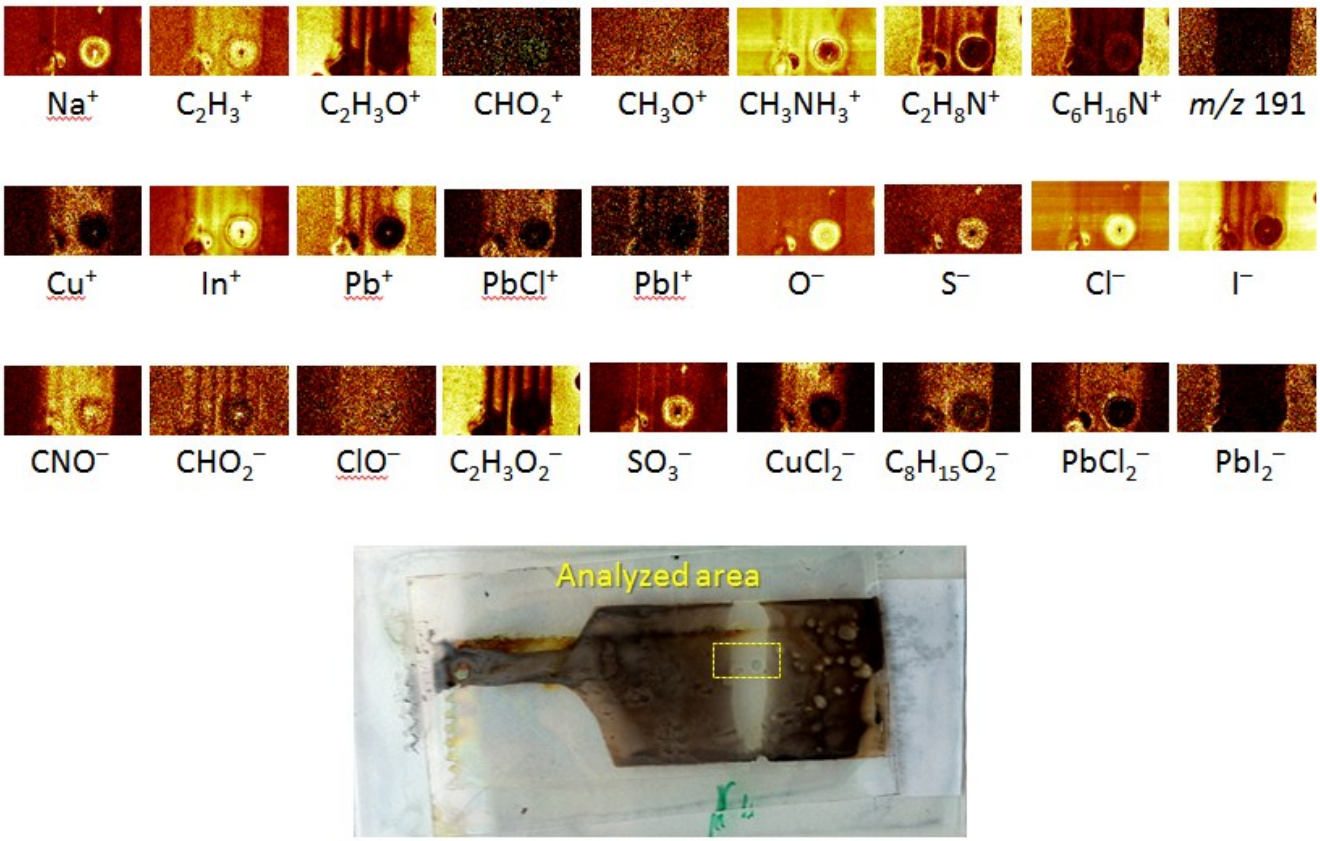

FIGURE S1: Maps of positive and negative ions extracted by TOFSIMS on an area showing clear visual signs of sample degradation due to beam exposure.

Apparently, substantial amounts of material are sublimated, as evidenced by the relative increase in the signal from the underlying ITO (In^+).

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SUBSTRATE SURFACE CHEMISTRY

The different substrate surfaces were characterized using time-of-flight secondary ion mass spectroscopy (TOFSIMS), with depth sensitivity.

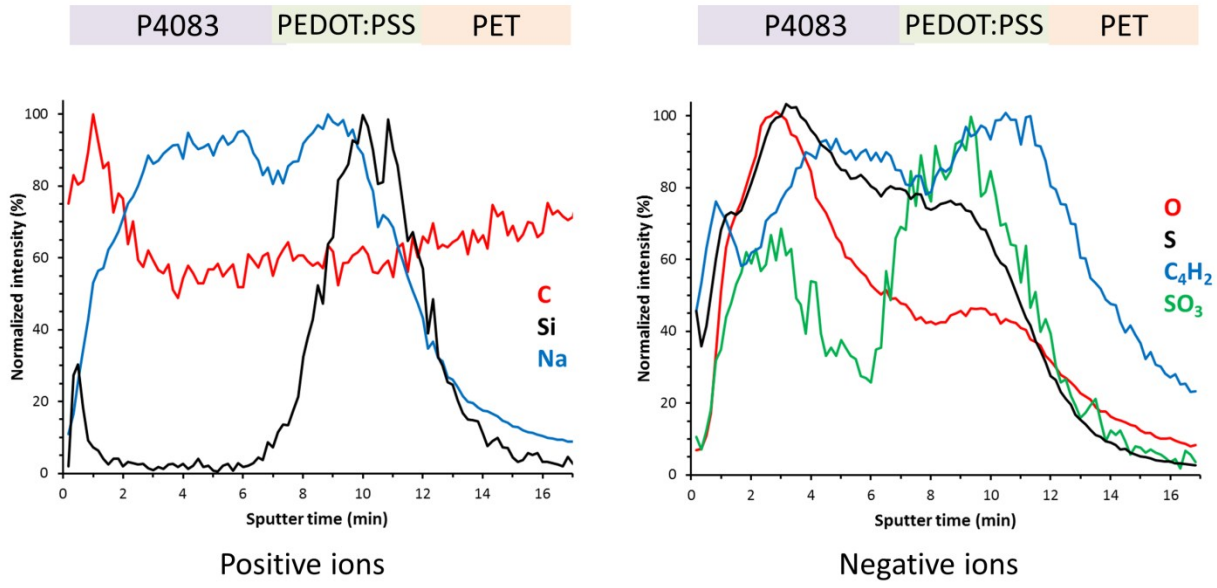

FIGURE S2 Depth profiles of PET/PEDOT:PSS/P4083. The two layers on top of PET can be clearly distinguished.

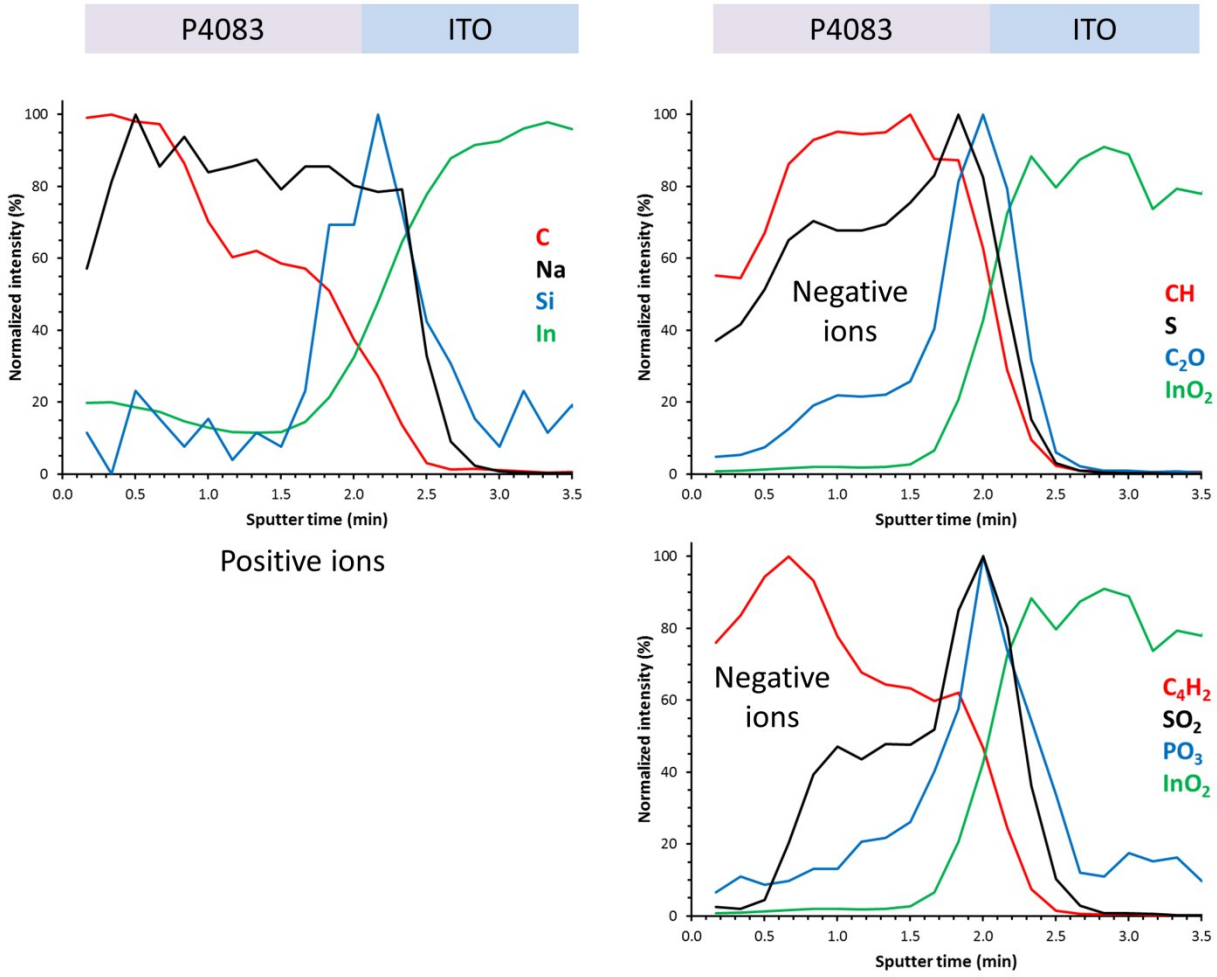

FIGURE S3 Depth profiles of PIP (PET/ITO/P4083). Indium diffusion is observed throughout the P4083 layer, and there are impurities detected in the P4083/ITO interface.

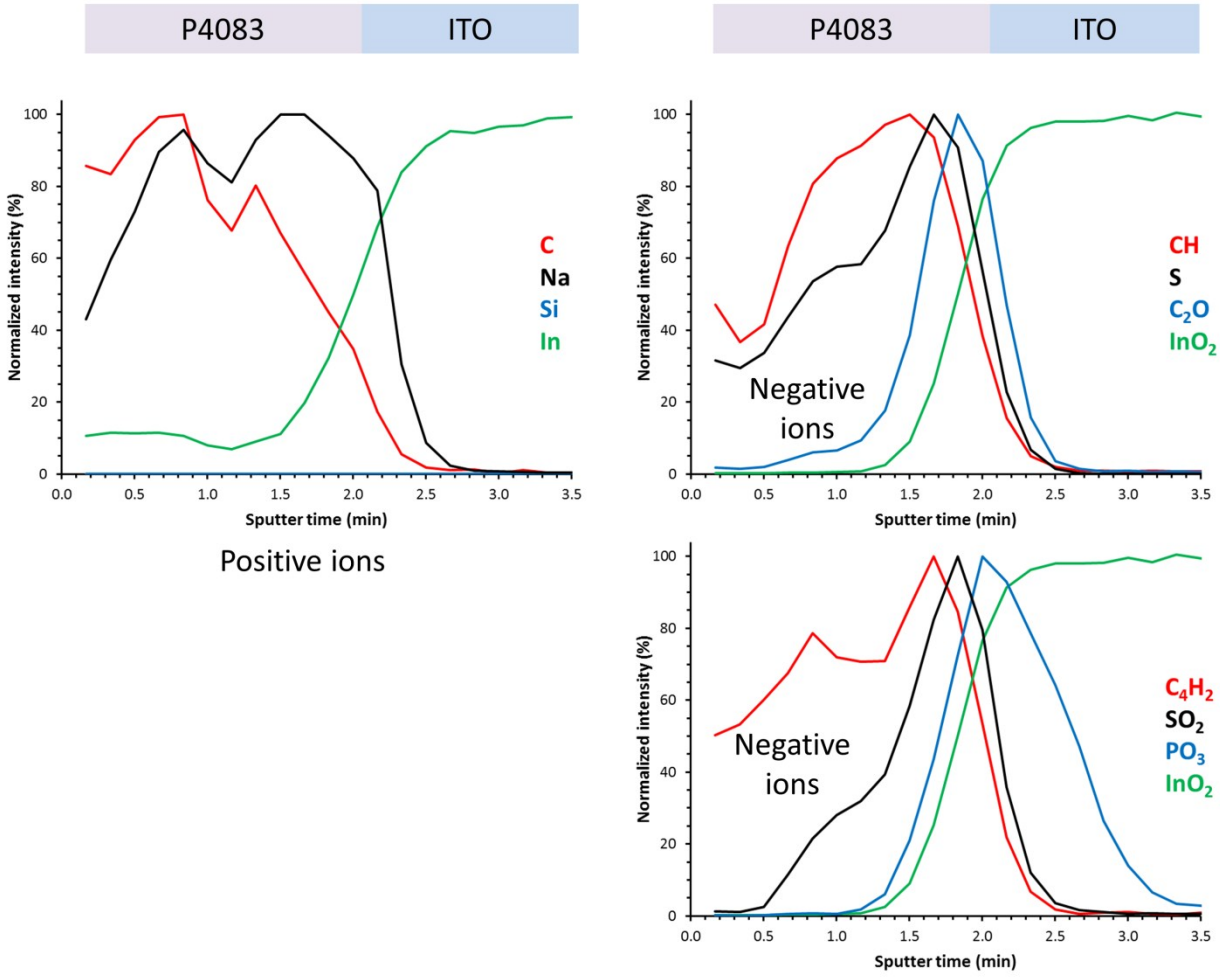

FIGURE S4 Depth profiles of GLASS/ITO/P4083. Indium diffusion is observed throughout the P4083 layer, and there are impurities detected in the P4083/ITO interface.

The relative surface chemistry between samples PET/PEDOT:PSS/P4083, PET/ITO/P4083, and glass/ITO/P4083 was rather complex, but we found no differences in surface chemistry that could account for substantial differences in the dynamics of perovskite formation.

UV-VIS:

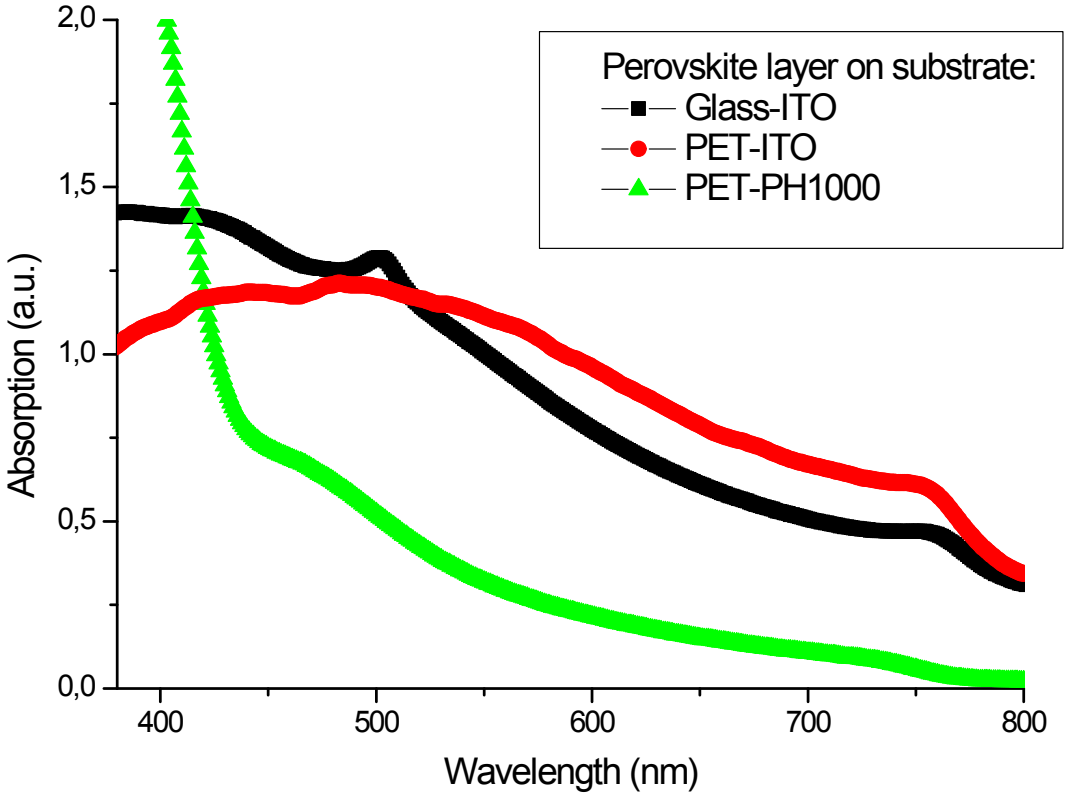

FIGURE S5: UV-VIS of the P4084/perovskite stack as formed by spin coating on the various substrates. The substrate absorption has been subtracted. The PET-PH1000 signal is seen to have changed significantly compared to the other perovskite samples.

SOLAR CELL IV-DATA:

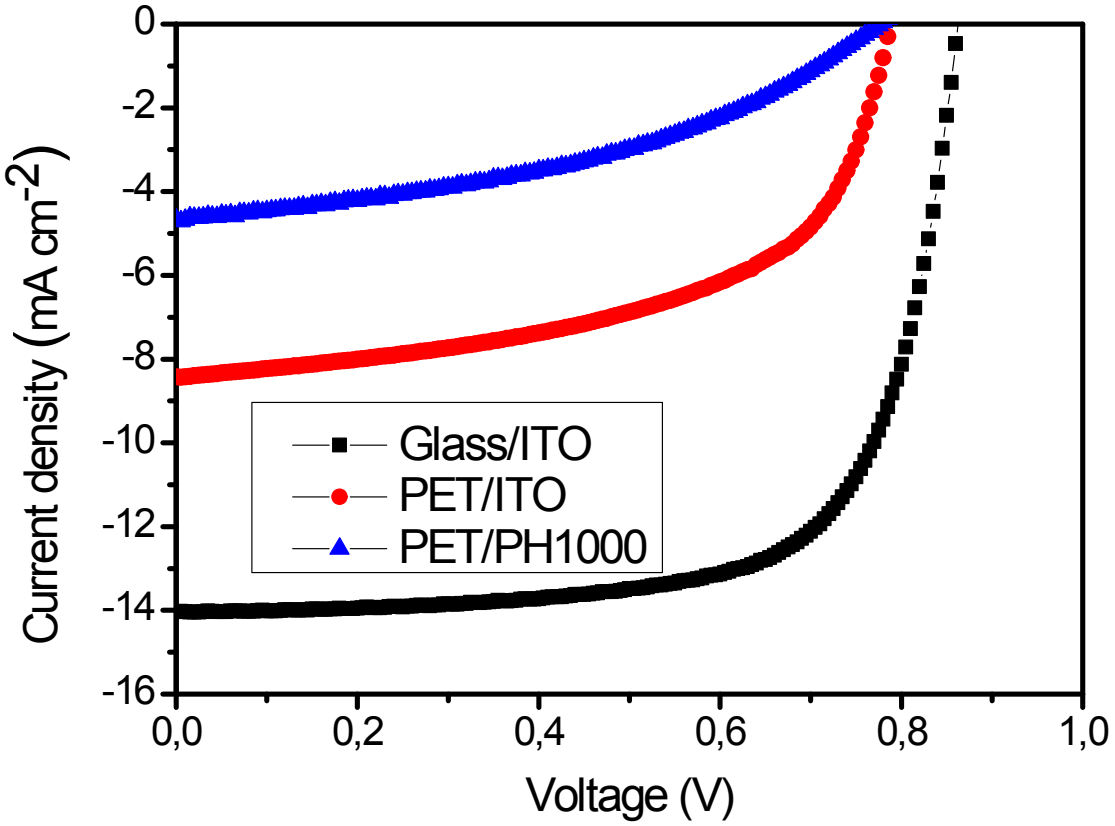

FIGURE S6 IV-curves of the best devices prepared by spin coating on the different substrates, as indicated by the legend.

Table S1: Photovoltaic parameters extracted from IV-curves in Figure S1.

Substrate	PCE (%)	Voc (V)	Jsc (mA/cm)	FF (%)
Glass/ITO	8.5	0.86	-14.0	70
PET/ITO	3.7	0.79	-8.4	56
PET/PH1000	1.5	0.78	-4.7	42

The IV-characterization was performed under simulated sun light (AM1.5G @ 1000 W/m), using a Keithley sourcemeter and custom made software. IV-curves were recorded using a forward voltage sweep from −0.1 to 1.0 V and voltage steps of 5 mV, giving a sweep rate of 0.05 V/s, a setting we found gave close to steady-state values.

SURFACE MORPHOLOGY

Optical

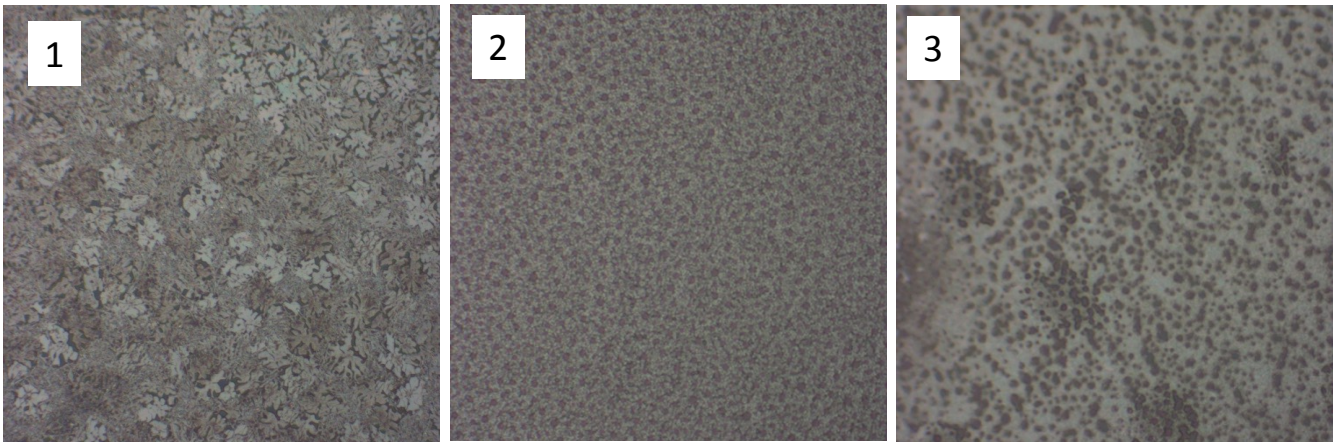

FIGURE S7 195 X 195 µm optical micrographs of perovskite surfaces as formed on the different substrates by spin coating +45 min annealing @110°C: (1) GLASS/ITO/P4083, (2) PET/ITO/P4083 AND (3) PET/PH1000/P4083.

AFM

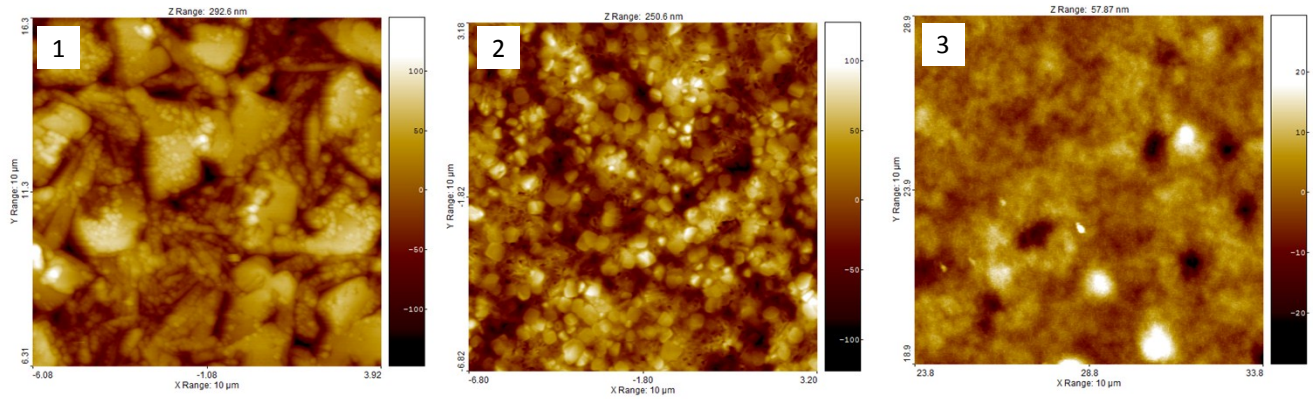

FIGURE S8 Atomic force microscopy (10 x 10 µm) of perovskite surfaces as formed on the different substrates by spin coating +45 min annealing @110°C: (1) GLASS/ITO/P4083, (2) PET/ITO/P4083 AND (3) PET/PH1000/P4083.

AFM was performed on an N8 NEOS (Bruker Nano GmbH) operating in an intermittent contact mode using PPP-NCLR cantilevers (NANOSENSORS). Images were recorded at a scan speed of one line per minute. The images were analyzed using the SPIP 6.3.4 (Image Metrology A/S) software.

SOLAR CELL DEVICES AND UV-VIS/OPTICAL MICROSCOPY/AFM SAMPLE PREPARATION

Substrates, being either Glass/ITO, PET/ITO or PET/PH1000, were spin coated with PEDOT:PSS 4083 (in 2:1 v/v mix with isopropanol) at 2000 rpm followed by subsequent annealing at 120°C for 10 min. After the substrates have cooled to room temperature, the perovskite layer was spin coated at 2000 rpm, by on-the-fly-application of 60µL of precursor solution, consisting of 110 mg $PbCl_2$ and 190 mg Methyl ammonium iodide (MAI) mixed in 1 mL. The slide was left spinning for 10 sec and subsequently put on a

hotplate at 110 °C for 45 min. Samples for UV-vis, AFM and optical microscopy were removed, and in the case of PET-based substrates for AFM, finalized by fastening to a microscope glass slide with epoxy.

Solar cell devices were completed by spin coating of a layer of PCBM (40 mg/mL in chlorobenzene @ 1000 rpm) followed by spin coating of a layer of ZnO nanoparticles (56 mg/mL in acetone) at 2000 rpm. Devices were finalized by evaporation of an Ag electrode, through a shadow mask at a pressure <1.0 × 10 −5 mbar. All the above, apart from the electrode deposition, was done under ambient conditions.

ADDITIONAL SMALL ANGLE SCATTERING RESULTS

Two measurements were performed in the small angle scattering geometry, and while the first experiment showed some changes during drying, the second dataset as shown in fig. S9

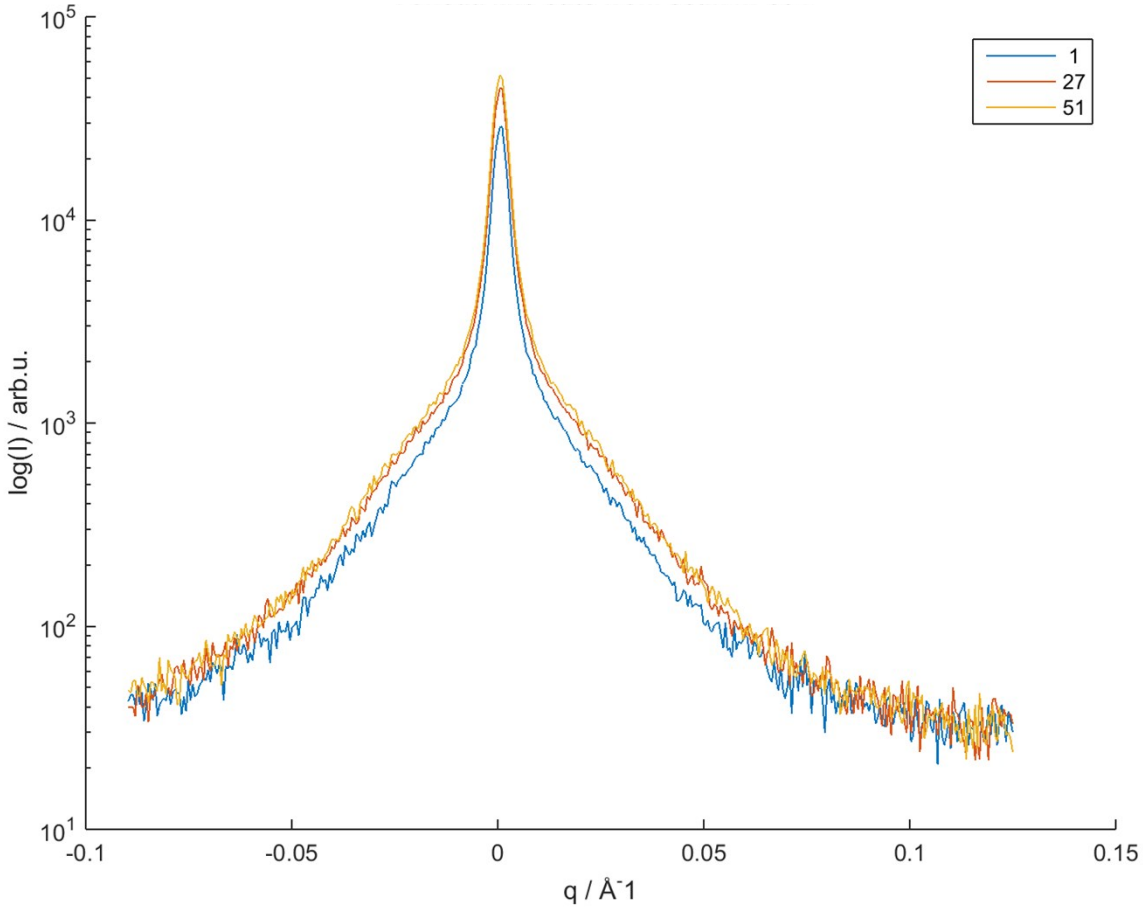

FIGURE S9 Line cuts around the Yoneda line from the second set of small angle scattering data. The sample was moved twice(signal #27 and #51), and although a change is observed is appears from the initial measurement #1 to disappear as the sample is moved and fresh material is observed.

STRUCTURE FITTING

The crystallographic patterns obtained from the wide angle scattering measurements were analysed with the structure fitting software Crystallographica-Search Match, and found that one of the pattern that emerges in the beam damaged region fits well with $PbCl_2$ as shown in figure S10.

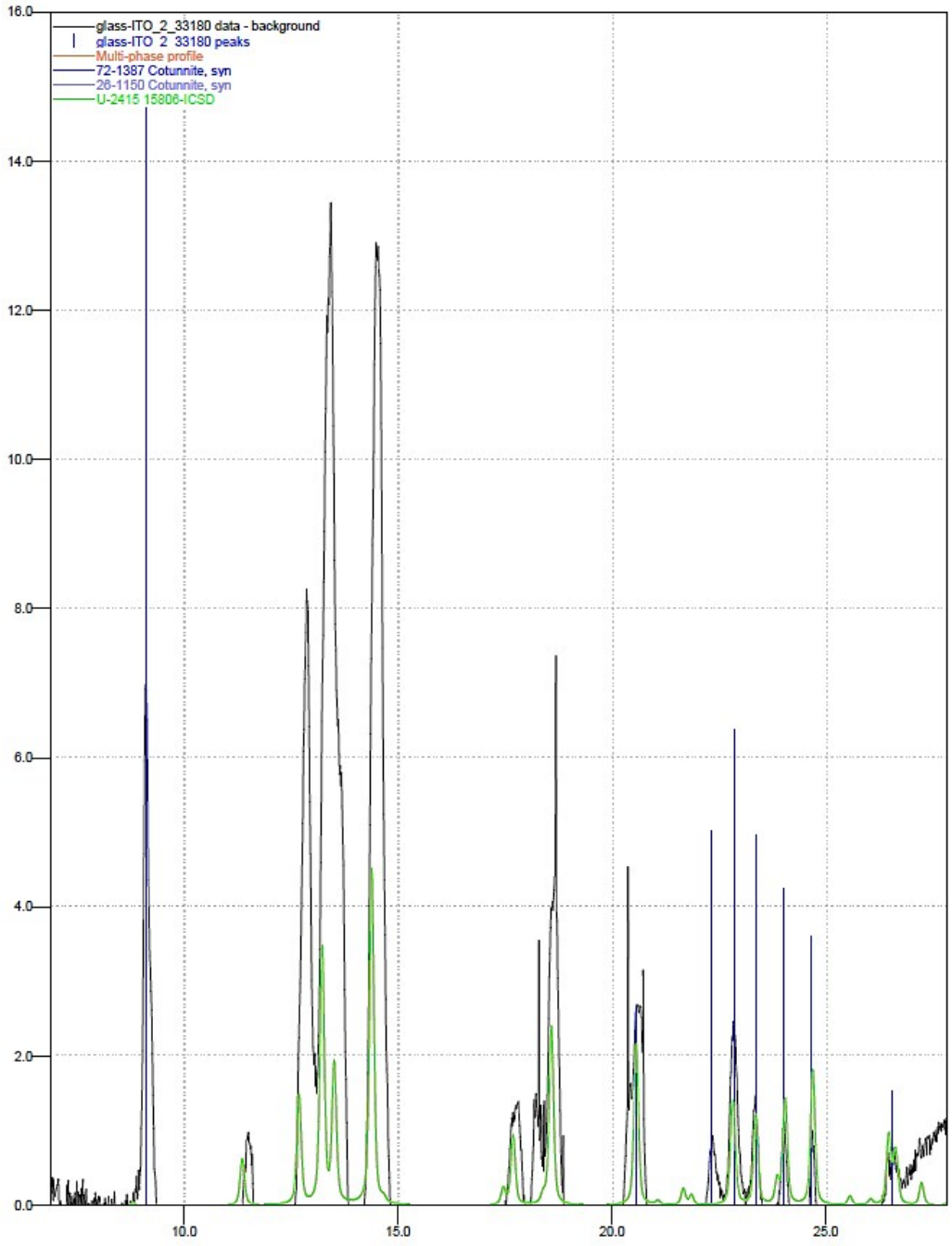

FIGURE S10 One of the few successful structure determinations – here shown for the measured pattern from perovskite on Glass-ITO-P4083(black) with the fittet pattern for $PbCl_2$ shown in green. This structure appeared after approximately 3300 seconds. The x-axis is 2Θ in degrees and the y-axis is intensity.