Electronic Supplementary Information

Roll-to-Roll Slot-Die Coated P-I-N Perovskite Solar Cells Using Acetonitrile Based Single Step Perovskite Solvent System

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1 Experimental Methods

1.1 Perovskite Ink Preparation.

Perovskite inks were prepared using the method given in[1], that were adapted from[2]. Briefly, methylammonium iodide (GreatCell Solar) and lead iodide (TCI) were weighed out in a glovebox with nitrogen atmosphere in a 1:1.06 ratio and acetonitrille added to give a 1.5M mixture. Methylamine gas was bubbled through the mixture and a solution formed, the solution was stored in a refrigerator at 5°C and used over the course of several weeks. Directly before use this was then further diluted with acetonitrille to form a 1M solution and concentrated hydrochloric acid added at $20\mu\text{lml}^{-1}$ and the solution filtered using a $0.45\mu\text{m}$ PTFE filter.

1.2 Device Fabrication Methods.

1.2.1 Spin Coated Device Standard Fabrication Method

Spin coating was carried out in a humidity controlled cleanroom (class 7, 30% relatively humidity). ITO (indium tin oxide) coated glass (15Ω/sq) or ITO coated PET (50Ω/sq) were cleaned sequentially with acetone, water, 2-propanol from wash bottles and dried using a nitrogen jet. Poly(2,3-dihydrothieno-1,4-dioxin)-poly(styrenesulfonate) (PEDOT:PSS) (Clevios P VP AI 4083 - Heraeus) was diluted with 2-propanol in a 1:3vol/vol ratio and spin coated on the substrates at 1000RPM for 5s with an acceleration of 1000RPMs^{-1} and then at 5000RPM for a further 10s, then directly moved onto a hot-plate at 120°C and dried for 10 minutes. Once cooled to room temperature perovskite solution in ACN/methylamine solvent system, with the addition of $20\mu\text{lml}^{-1}$ $\text{HCl}_{(aq)}$, was spin coated on the PEDOT:PSS films at 2000RPM for 60s with an acceleration of 2000RPMs^{-1} then moved directly onto a hot-plate at 100°C and dried for 60 minutes, then cooled to room temperature. [6,6]-phenyl-C_{61}-butyric acid methyl ester (PCBM) (Solenne) in chlorobenzene (40mgml^{-1}) was spin coated on the perovskite films at 3000RPM for 45s with an acceleration of 3000RPMs^{-1}. Then bathcuproine (BCP) (Sigma-Aldrich) in ethanol (0.5mgml^{-1}) was spin coated on the PCBM films at 7000RPM for 10s with an acceleration of 7000RPMs^{-1}. Finally silver top contacts were thermally evaporated under vacuum, using a shadow mask to define pixel areas.

1.2.2 Roll-to-Roll and Sheet-to-Sheet Slot-Die Coating

Roll-to-roll (R2R) coating was performed using a Coatema Smartcoater (SC08) machine, with inbuilt corona unit and two stage oven (total length approx. 1m), the machine was housed in a humidity controlled cleanroom environment, a web guide system (BST ekr 500 Plus) was used to improve registration of the web with the coating head. Sheet-to-Sheet (S2S) coating was performed using a bench-top coating system, the same coating heads used with the R2R coater were used with the S2S coater, substrates were mounted on a metal platen that sat on a conveyor belt and carried the platen under the coating head then on to the machines inline ovens. Both slot-die systems used syringe pumps to control the flow of ink to the coating head (WPI Aladdin AL-1000), ink was delivered to the coating head using fluoropolymer tubing (RS). For small area devices pre-patterned ITO coated PET substrate (Mekoprint OC50, 50Ω/sq) with 100mm web width was used as received. For slot-die coating PEDOT:PSS diluted with IPA (1:3vol/vol) was deposited over a 90mm coating width with a pump rate of 0.9mlmin^{-1} and web speed of 1mmin^{-1} to give an approximately 10μm wet film thickness, a gap between the meniscus guide lower edge and web of approximately 250-350μm was set using dial indicators and feeler gauges, the films were dried in the machines inline oven units with set-point temperatures of 120 and 140°C, both with air flow set-points of 50% (45m^{3}hr^{-1}).

For the perovskite layer the same ink as for spin coating was deposited over a 90mm coating width with a pump rate of 0.45mlmin^{-1} and web speed of 1mmin^{-1} to give an approximately 5μm wet film thickness, a 1000μm tab length meniscus guide was used as part of the coating head, the gap between meniscus guide and web was set to approximately 150-250μm. The wet films were then initially dried with a stream of nitrogen from an air knife (Exair Standard Air Knife), with a flow rate of 50lmin^{-1}, positioned just after the coating head, before traveling into the machines inline ovens, both with air flow set-points of 50% and at the temperature set-points discussed in the main text, with the optimized conditions using a set point temperature of 150°C (approximately 120-130°C measured by thermocouple placed in oven unit).

For slot-die coating of PCBM layers inks with concentrations of 10mgml^{-1} were used, for S2S coatings a 90mm coating width was used with a pump rate of 0.45mlmin^{-1} and conveyor speed of 1mmin^{-1} to give an approximately 5μm wet film thickness, a 1000μm tab length meniscus guide was used as part of the coating head, the conveyor speed was slowed to 0.3mmin^{-1} in the oven unit to give a similar oven residence time (approximately 1 minute) to that of the R2R coated films.

For R2R coating of PCBM a 90mm coating width was used and a coating speed of 1mmin^{-1} and the ink flow rate adjusted to give the different wet film thicknesses discussed in the main text, a 1000μm tab length meniscus guide was used as part of the coating head, films were dried in the machines inline ovens with air flow rate set-points of 50% and temperature set-points of 90°C (approximately 80-90°C measured by thermocouple placed in the oven unit).

BCP in ethanol (0.5mgml^{-1}) was coated over 90mm coating width with a web speed of 1mmin^{-1} and the ink flow rate adjusted to give the wet film thicknesses discussed in the main text, a 2000μm tab length meniscus guide was used as part of the coating head, the films were dried with air flow rate set-points of 50% and temperature set-points of 60°C (approximately 50-60°C measured by thermocouple placed in oven unit).

1.3 Characterization Methods.

1.3.1 Photovoltaic Device Testing

Current-Voltage (IV) curves were recorded using a custom built system with a National Instruments source measure unit performing IV scans, an Arduino and relay board was used to provide automated pixel selection and the system was controlled using a graphical user interface written in Labview, the light source was provided by a class AAA solar simulator (Newport) calibrated with a reference photodiode fitted with a KG5 filter. A scan rate of approximately 0.15Vs^{-1} was used and cells tested in both the forwards and reverse scan directions, no pre-biasing of devices was used, cells were masked to an illumiated area of 0.09cm^2 using photo-etched opaque black anodized aluminum masks (Photofab).

1.3.2 Time Lapse Image Analysis

Time lapse imaging was performed and analyzed adapting a previously reported method[3], using a Ortery Photosmile 200 light box and Canon EOS digital camera, the illumination level of the light box was approximately 3580 lux, images were taken every 30 minutes. Analysis of image RGB color channel levels was performed with scripts written in the Python[4] programming language and developed using the Pillow, Skimage[5], Matplotlib and Numpy[6] package libraries.

1.3.3 White Light Interferometry

White light interferometry was performed using a WYKO NT:9300 with measurements taken using vertical scanning interferometry mode. Measurements were taken in three random positions on the sample and analysed using vision 32 software.

1.3.4 X-ray Photoelectron Spectroscopy

X-ray Photoelectron Spectroscopy (XPS) was performed on a Kratos Axis Supra instrument using 15mA 20kV Al Kα x-rays and a monochromator. In all cases samples were electrically floated and the integral charge neutralised used to eliminate differential charging. For perovskite films, all UHV procedures were carried out in the dark. Typical XPS experiments included a wide scan at 160eV pass energy and 1eV step size, used to identify the elements present in the surface volume. The analysis area is 300 x 700μm and typically samples less than 10nm deep into the surface. Quantification and fitting is based on high resolution scans collected at a pass energy of 20eV, step size of 0.1eV, with dwell times and sweeps extended to limit signal to noise. Elements that might change due to exposure to UHV and/or X-rays, such as N(1s) and Pb(4f), were examined prior to more stable elements. Spectra were analysed using CasaXPS version 2.3.17dev6.4k, using Shirley backgrounds and the default GL(30) lineshape. All spectra were charge reference to the CxHy component of the modelled C(1s) envelope and quantified using the Kratos RSF library.

1.3.5 Transient Photoluminescence

Transient Photoluminescence decays were acquired using a Time-Correlated Single Photon set-up, Life-Spec II (Edinburgh Instruments Ltd.). The excitation was an Edinburgh Instruments laser diode with a 635 nm central wavelength and pulse duration of 60 ps.

1.3.6 Simultaneous Thermal Analysis

Simultaneous thermal analysis (STA) experiments were performed using a PerkinElmer STA6000. Samples of approximately 20μL of the PCBM formulations in neat and blended solvent systems were dispensed into the ceramic crucible within the instrument furnace. Thermal equilibrium between sample and crucible was ensured at the beginning of the experiment by a one-minute isothermal hold at 30°C. After this period the samples were heated to 800°C at 10°Cmin^{-1} whilst the sample weight was logged at 0.12 second intervals. A baseline experiment was performed under identical conditions using an empty crucible, these data were subtracted from the sample data to improve resolution by removing the inherent noise and curvature of the instrument baseline. The STA data plots show the sample weight (%) and heatflow (mW) as a function of sample temperature over the region of interest, 30-120°C for this study. The temperature corresponding to the total evaporation of the solvent content was mathematically determined as the point at which the weight derivative with respect to time reaches zero, these points are annotated in main text Figure 5c. The annotated heatflow peaks indicate when the sample is removing heat from the instrument at the greatest rate, as these appear before the weight derivative equals zero they are due to evaporation of the solvent.

Table S1: Contact angle of water on corona treated ITO coated PET substrate with various treatment powers.

Power Setting (kW)	Contact Angle ($^{\circ}$)
0	70
0.25	20
0.50	18
0.74	22
1.00	21

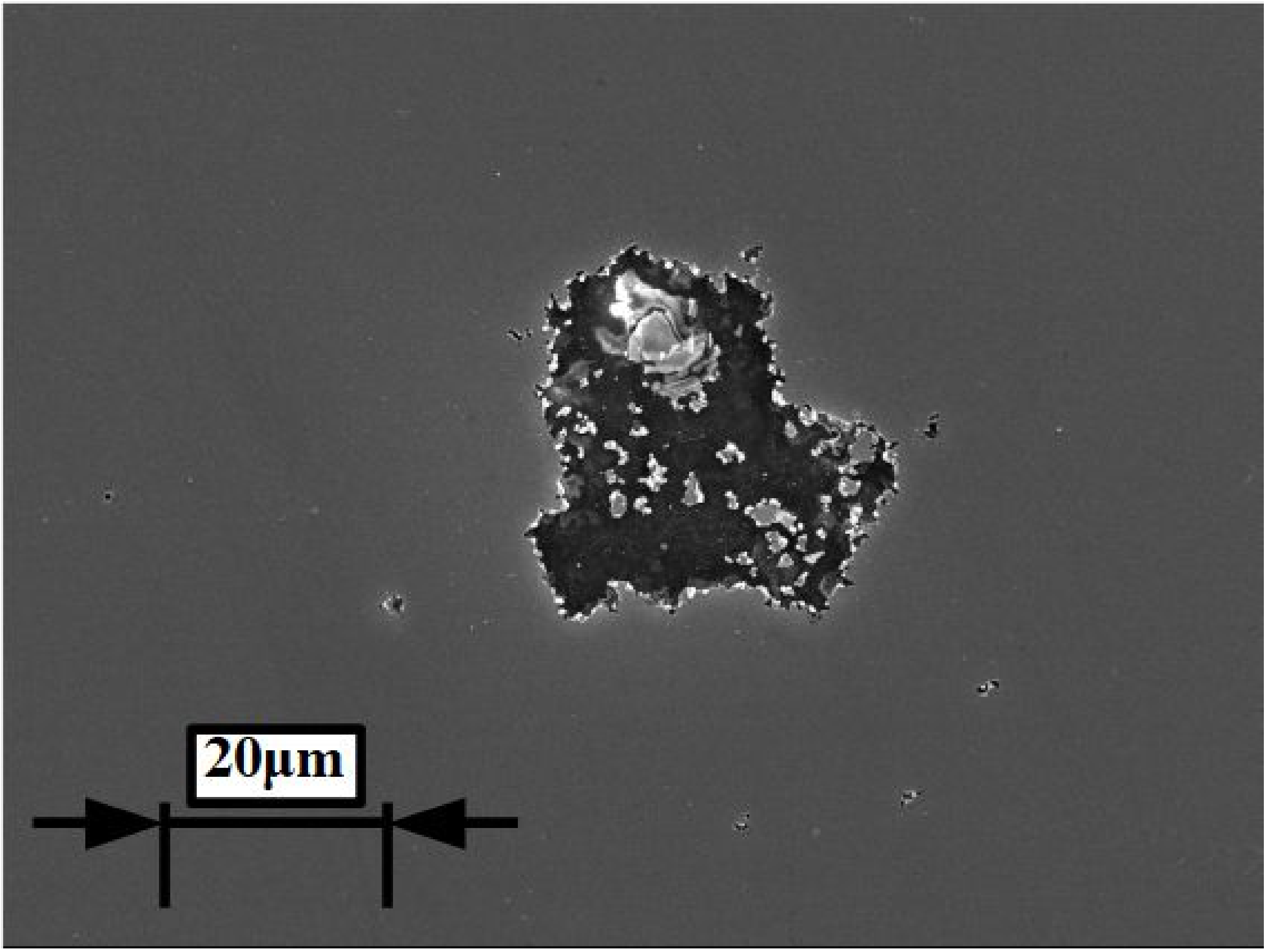

Figure S1: Top view SEM images of corona treated ITO coated PET substrate showing damage to the ITO surface. Inset scale bars represent 20 microns.

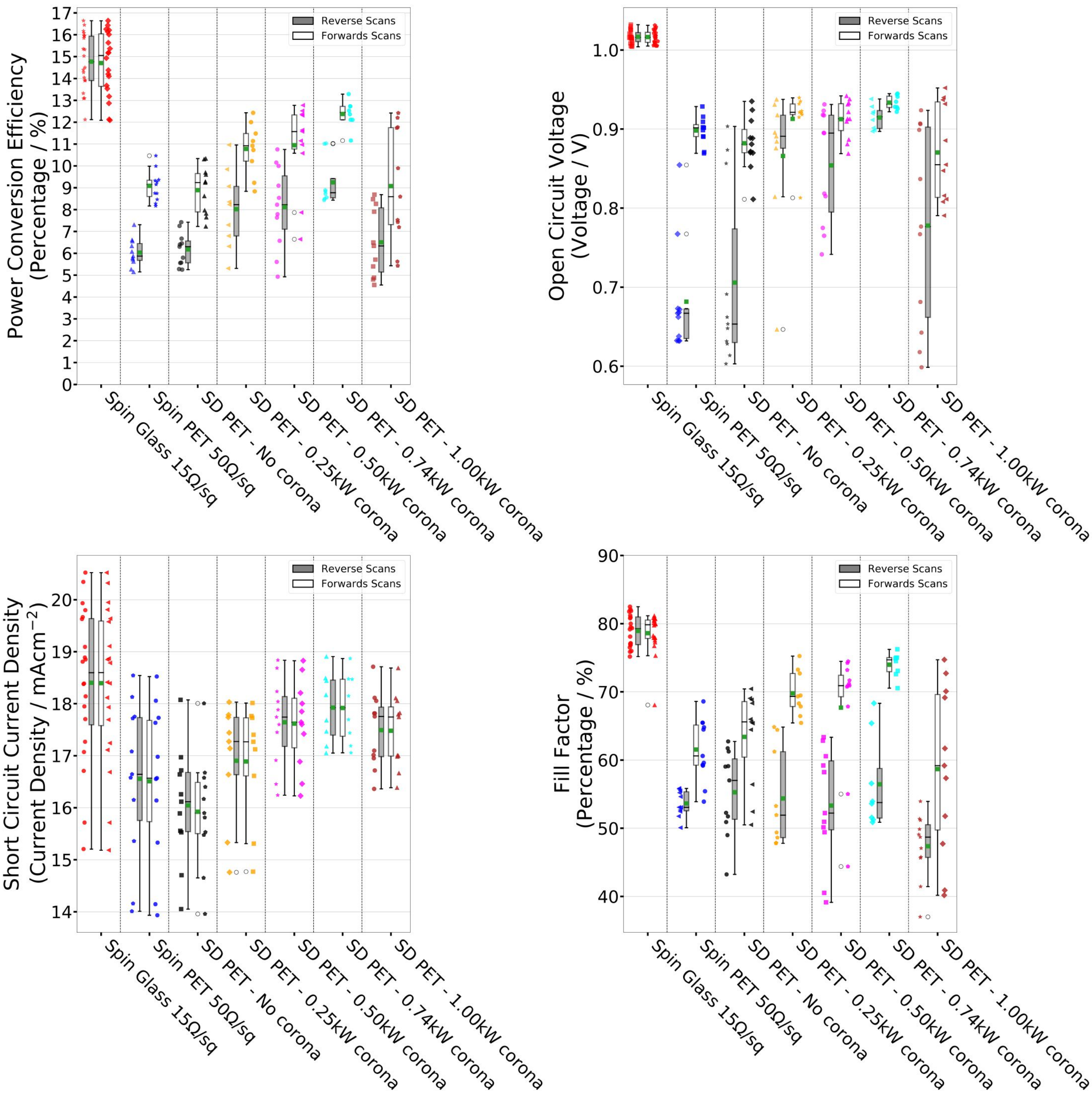

Figure S2: Box-plots of JV scan photovoltaic performance parameters for 0.09cm^2 cells with ITO coated PET substrate (50Ω/sq) corona treatment powers of 0, 0.25, 0.5, 0.74 or 1.0kW and R2R slot-die coated PEDOT:PSS HTL or spin coated HTL with no corona treatment, compared to ITO coated glass substrates (15Ω/sq) with spin coated HTL as control devices. The boxes represent the first and third quartiles, the horizontal black line the median, the upper whisker the data within 1.5 times the inter quartile range of the upper quartile and the lower whisker 1.5 times the inter quartile range of the lower quartile, green square the mean and open black dots outliers. The coloured full markers represent the individual scan results for the adjacent scan direction and corresponding split.

Table S2: MedianJV scan photovoltaic performance parameters for 0.09cm^2 cells with ITO coated PET substrate (50Ω/sq) corona treatment powers of 0, 0.25, 0.5, 0.74 or 1.0kW and R2R slot-die coated PEDOT:PSS HTL or spin coated HTL with no corona treatment, compared to ITO coated glass substrates (15Ω/sq) with spin coated HTL as control devices.

Power Setting (kW)	Scan Direction	Voc (V)	Jsc (mAcm^{-2})	FF (%)	PCE (%)
Spin Coat Glass	Forwards	1.02	18.6	80	15.0
	Reverse	1.02	18.6	80	14.8
Spin Coat PET	Forwards	0.90	16.6	61	9.2
	Reverse	0.67	16.6	53	5.9
0	Forwards	0.88	15.9	66	9.2
	Reverse	0.65	16.1	57	6.3
0.25	Forwards	0.92	17.3	69	10.9
	Reverse	0.89	17.3	52	8.2
0.5	Forwards	0.91	17.6	71	11.6
	Reverse	0.89	17.7	52	8.2
0.74	Forwards	0.93	17.9	75	12.4
	Reverse	0.92	17.9	54	8.7
1.0	Forwards	0.85	17.8	59	8.6
	Reverse	0.78	17.8	49	6.3

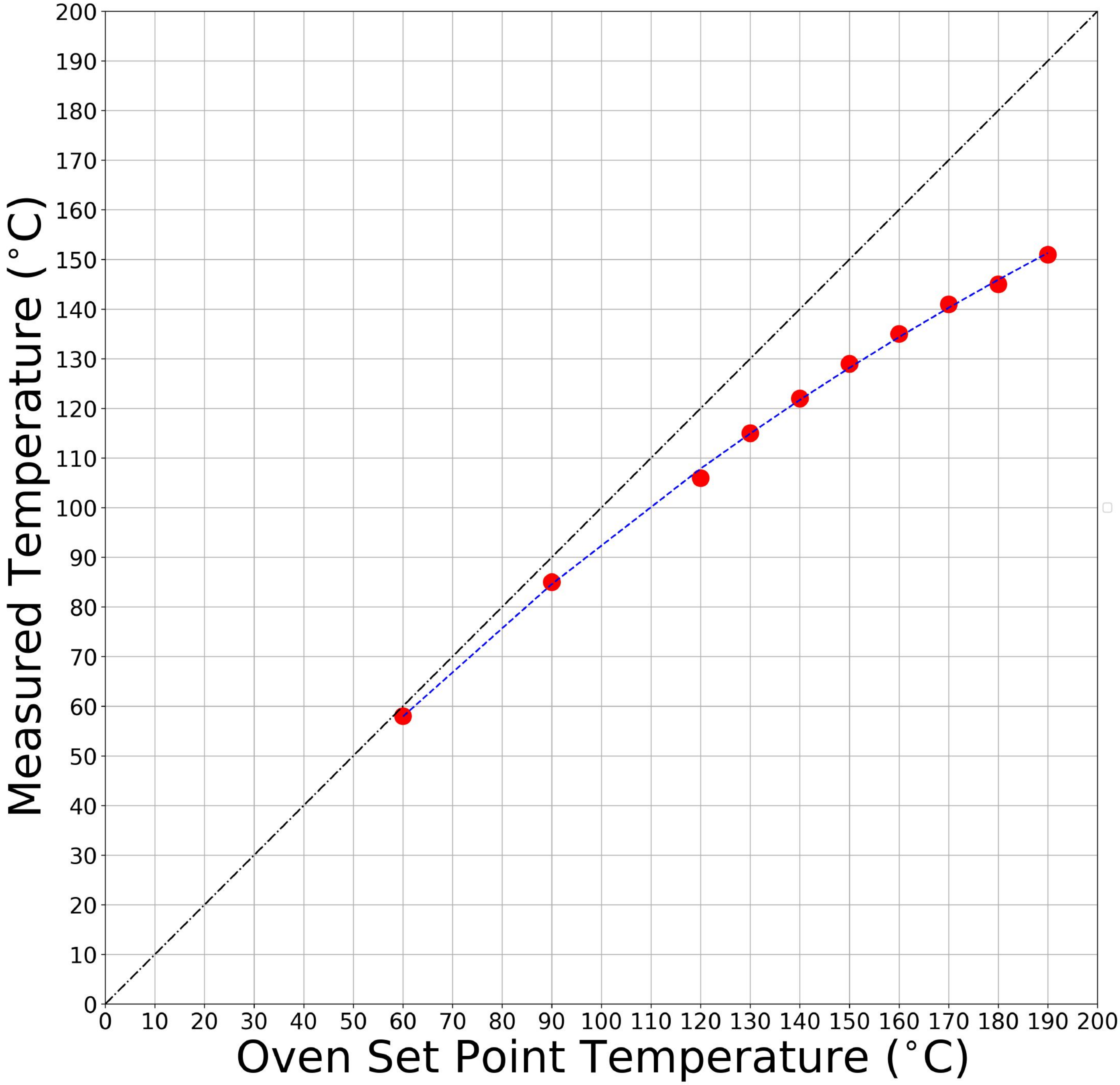

Figure S3: Oven set point temperatures and the measured temperature using a thermocouple positioned near the middle of the first oven unit, both oven units used air flow rate set points of 50% (approximately $45 \mathrm{m}^3\mathrm{hr}^{-1}$). The blue dashed line is an exponential approach fit to the measured temperatures and the black dash-dot line is a guide highlighting the deviation of the measured values from the set-points.

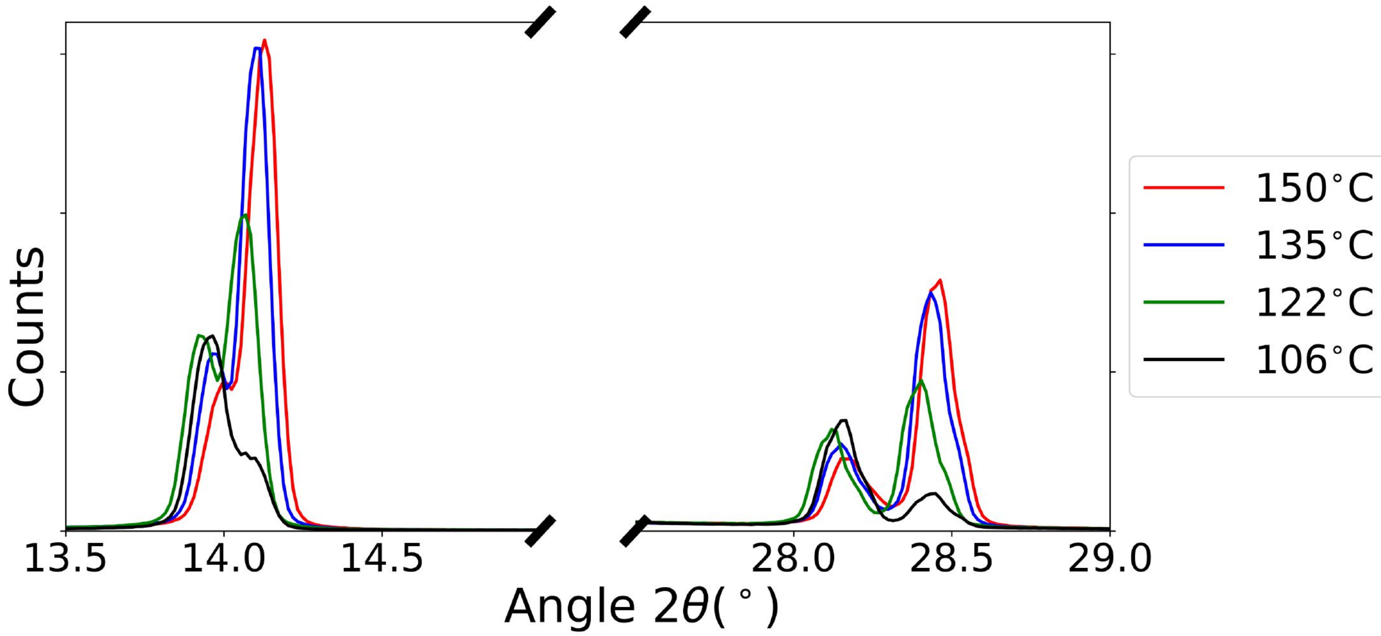

Figure S4: XRD spectra of R2R slot-die coated perovskite with various drying oven set point temperatures, 120°C set point = 106°C measured , 140°C set point = 122°C measured, 160°C set point = 135°C measured, 190°C set point = 150°C measured.

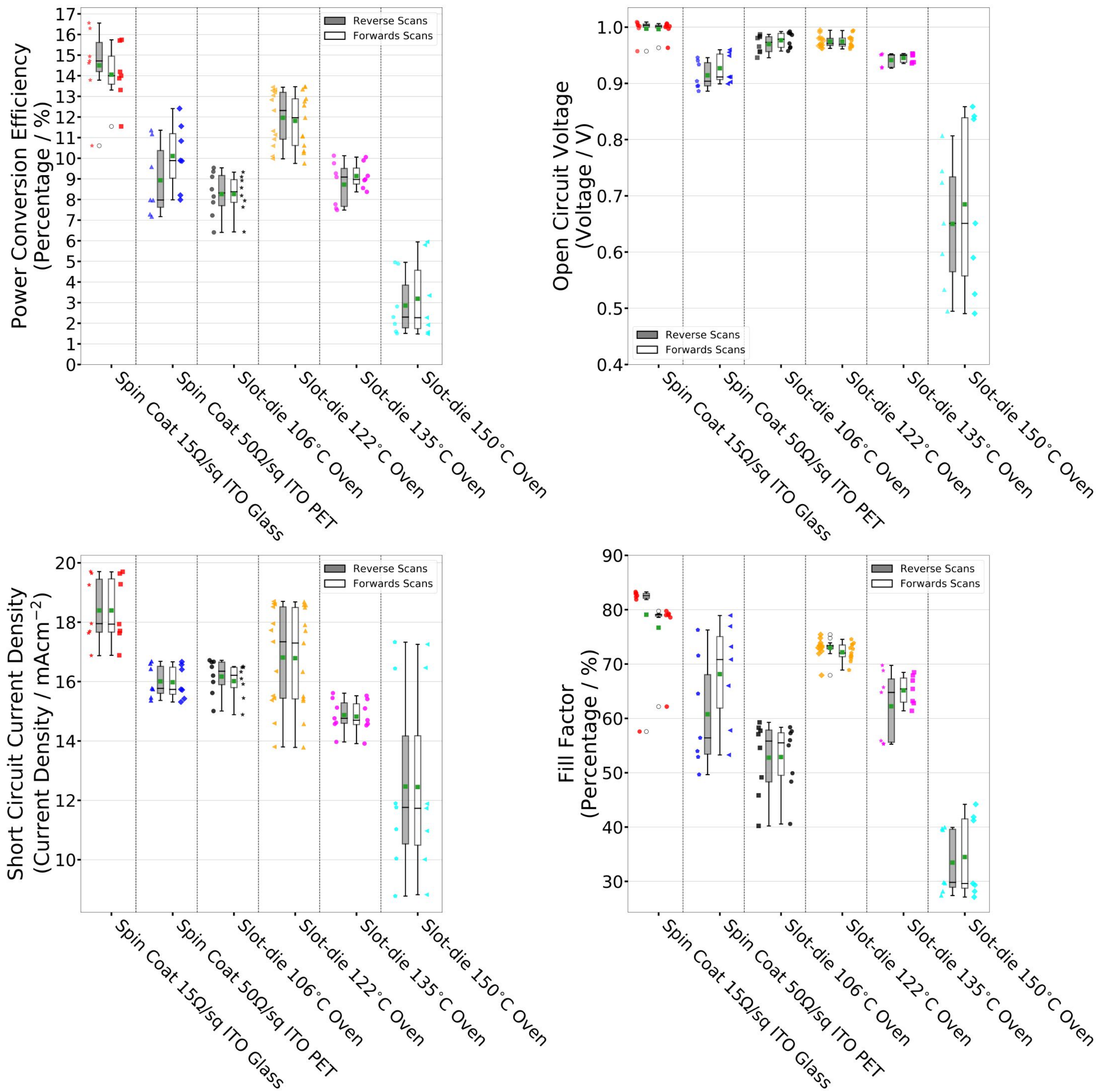

Figure S5: Box-plots of JV scan photovoltaic performance parameters for 0.09cm^2 cells with R2R slot-die coated perovskite with various drying oven set point temperatures compared to spin coated control devices with ITO coated PET substrates and ITO coated glass substrate control devices. Oven temperature 120°C set point = 106°C measured , 140°C set point = 122°C measured, 160°C set point = 135°C measured and 190°C set point = 150°C measured. The boxes represent the first and third quartiles, the horizontal black line the median, the upper whisker the data within 1.5 times the inter quartile range of the upper quartile and the lower whisker 1.5 times the inter quartile range of the lower quartile, green square the mean and open black dots outliers. The coloured full markers represent the individual scan results for the adjacent scan direction and corresponding split.

Table S3: MedianJV scan photovoltaic performance parameters for $0.09cm^2$ cells with R2R slot-die coated perovskite with various drying oven set point temperatures compared to spin coated control devices with ITO coated PET substrates ($50\Omega/sq$) and ITO coated glass substrate control devices ($15\Omega/sq$).

Oven Temperature (set point) (°C)	Scan Direction	Voc (V)	Jsc ($mAcm^{-2}$)	FF (%)	PCE (%)
Spin Glass	Forwards	1.00	17.9	79	14.0
	Reverse	1.00	18.0	83	14.7
Spin PET	Forwards	0.91	15.7	71	9.9
	Reverse	0.90	15.8	56	8.0
106 (120)	Forwards	0.98	16.2	56	8.4
	Reverse	0.97	16.4	56	8.3
122 (140)	Forwards	0.97	17.3	72	12.0
	Reverse	0.97	17.3	73	12.3
135 (160)	Forwards	0.95	14.7	65	9.0
	Reverse	0.95	14.8	65	9.1
150 (190)	Forwards	0.65	11.7	30	2.3
	Reverse	0.65	11.8	30	2.3

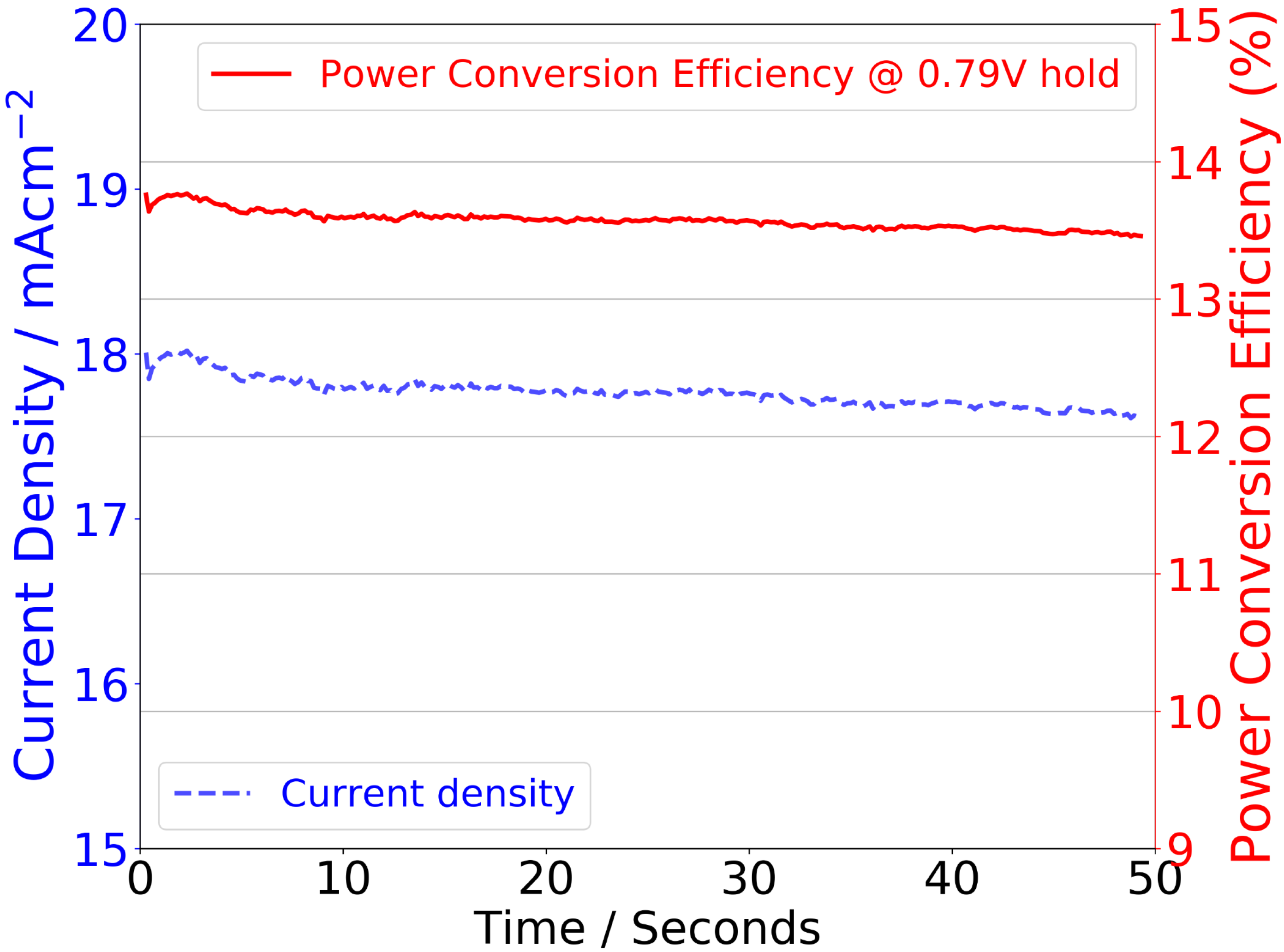

Figure S6: Stabilized power output of hero device held at maximum power point voltage over the course of 50 seconds

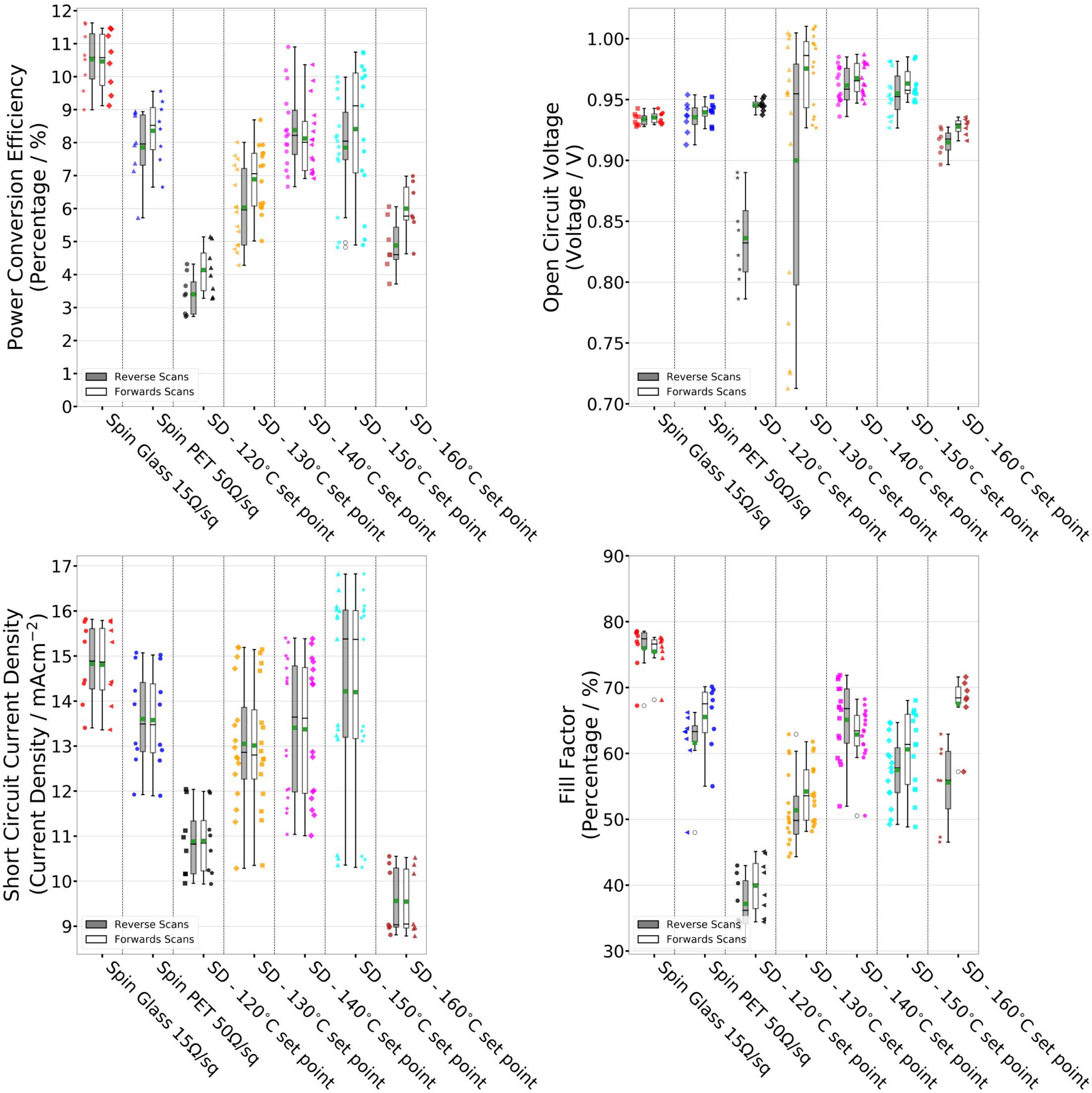

Figure S7: Box-plots of JV scan photovoltaic performance parameters for 0.09cm^2 cells with R2R slot-die coated perovskite with various drying oven set point temperatures compared to spin coated control devices with ITO coated PET substrates and ITO coated glass substrate control devices. The boxes represent the first and third quartiles, the horizontal black line the median, the upper whisker the data within 1.5 times the inter quartile range of the upper quartile and the lower whisker 1.5 times the inter quartile range of the lower quartile, green square the mean and open black dots outliers. The coloured full markers represent the individual scan results for the adjacent scan direction and corresponding split.

Table S4: MedianJV scan photovoltaic performance parameters for 0.09cm^2 cells with R2R slot-die coated perovskite with various drying oven temperatures compared to spin coated control devices with ITO coated PET substrates (50Ω/sq) and ITO coated glass substrate control devices (50Ω/sq).

Oven Temperature (°C)	Scan Direction	Voc (V)	Jsc (mAcm^{-2})	FF (%)	PCE (%)
Spin Coat Glass	Forwards	0.94	14.9	77	10.6
	Reverse	0.93	14.9	77	10.6
Spin Coat PET	Forwards	0.94	13.5	68	8.5
	Reverse	0.94	13.5	63	8.0
106	Forwards	0.95	10.8	40	4.1
	Reverse	0.83	10.8	36	3.4
115	Forwards	0.99	12.8	54	7.1
	Reverse	0.95	12.9	50	6.0
122	Forwards	0.97	13.6	63	8.0
	Reverse	0.96	13.6	67	8.2
129	Forwards	0.96	15.4	61	9.1
	Reverse	0.95	15.4	58	8.0
135	Forwards	0.93	9.0	68	5.8
	Reverse	0.92	9.0	56	4.6

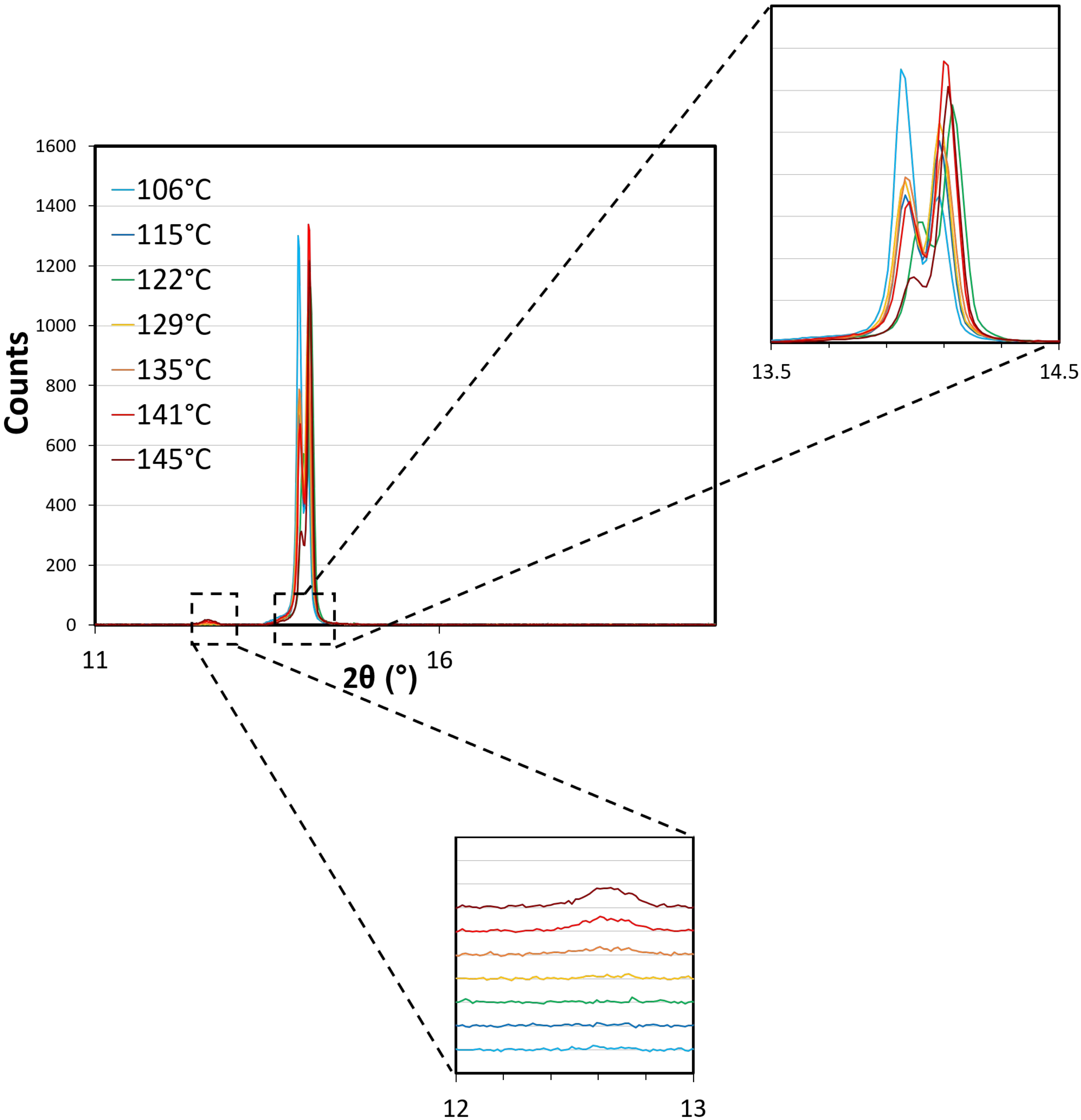

Figure S8: XRD spectra of R2R slot-die coated perovskite with various drying oven set point temperatures.

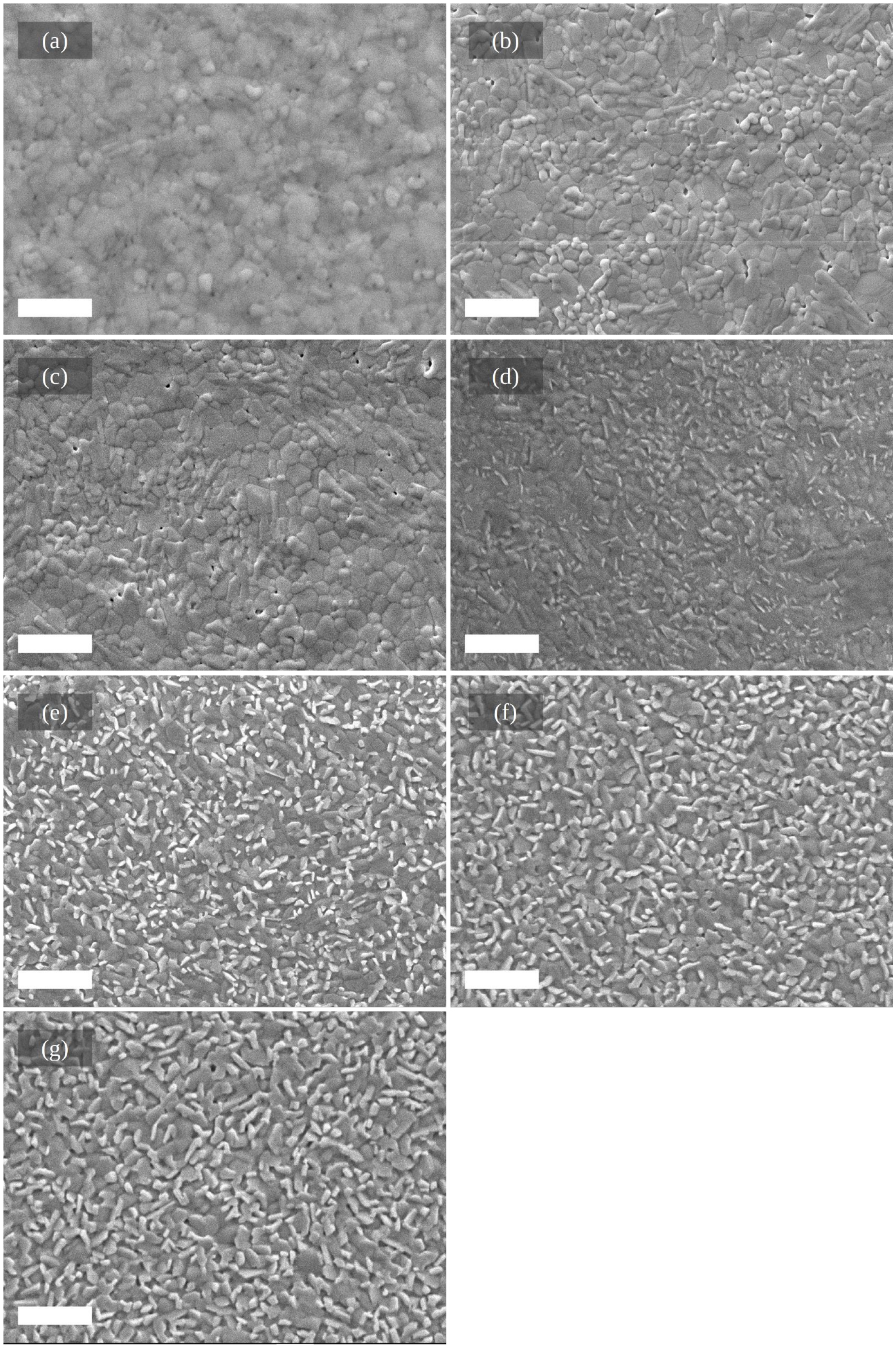

Figure S9: Top view SEM images of perovskite films R2R slot-die coated on PEDOT:PSS coated ITO coated PET substrate, at 1mmin^{-1} from a 5μm wet film thickness, with various drying oven temperatures, 106°C (120°C set point) (a), 115°C (130°C set point) (b), 122°C (140°C set point) (c), 129°C (150°C set point) (d), 135°C (160°C set point) (e), 141°C (170°C set point) (f), 145°C (180°C set point) (g). Inset scale bars represent 2 microns.

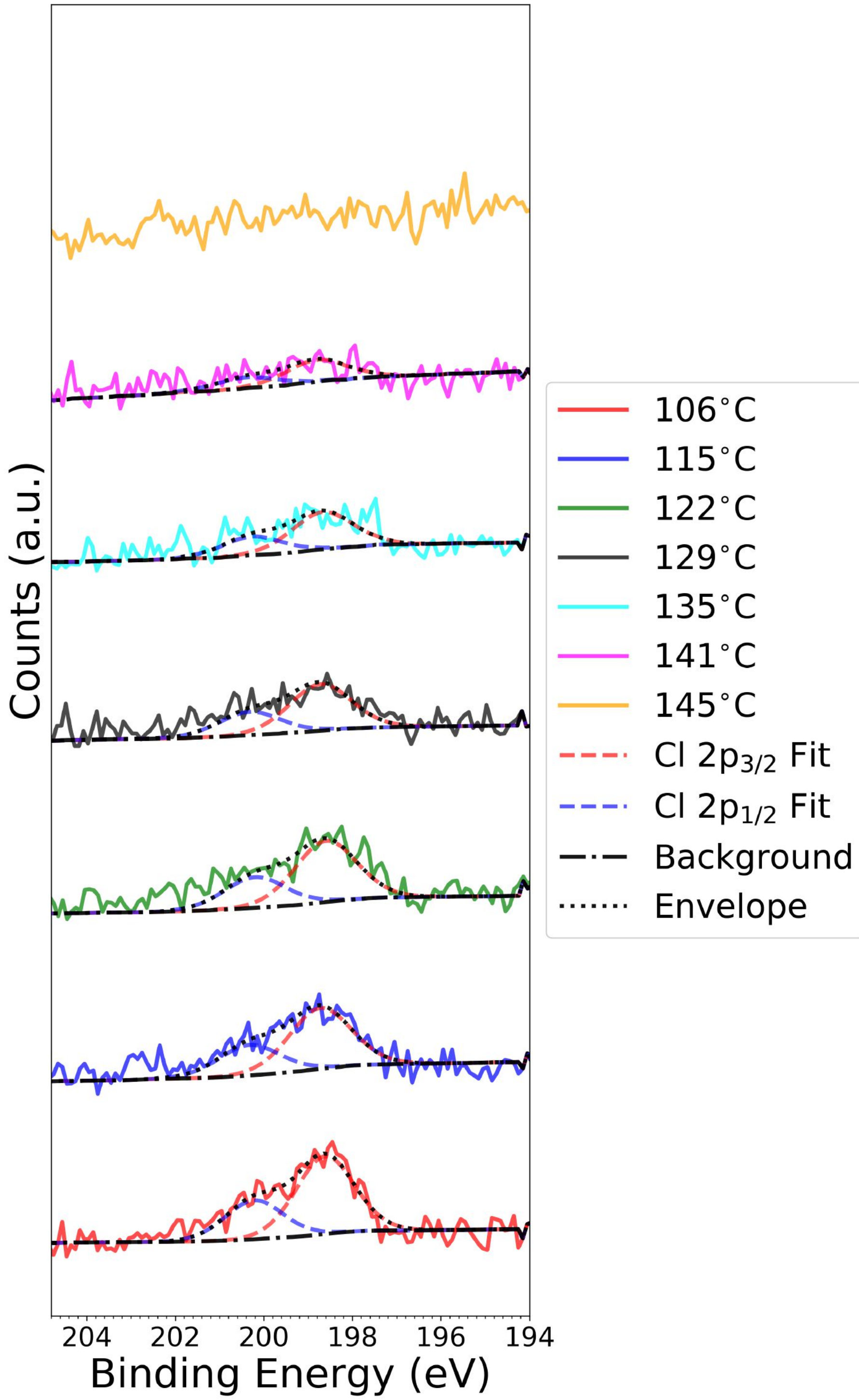

Figure S10: X-ray photoelectron spectroscopy spectra showing the change in the chloride $2p_{3/2}$ and $2p_{1/2}$ peaks for perovskite films R2R slot-die coated on PEDOT:PSS coated ITO coated PET substrate, at $1\mathrm{mmin}^{-1}$ from a 5μm wet film thickness, with various drying oven temperatures, 106°C (120°C set point), 115°C (130°C set point), 122°C (140°C set point), 129°C (150°C set point), 135°C (160°C set point), 141°C (170°C set point), 145°C (180°C set point).

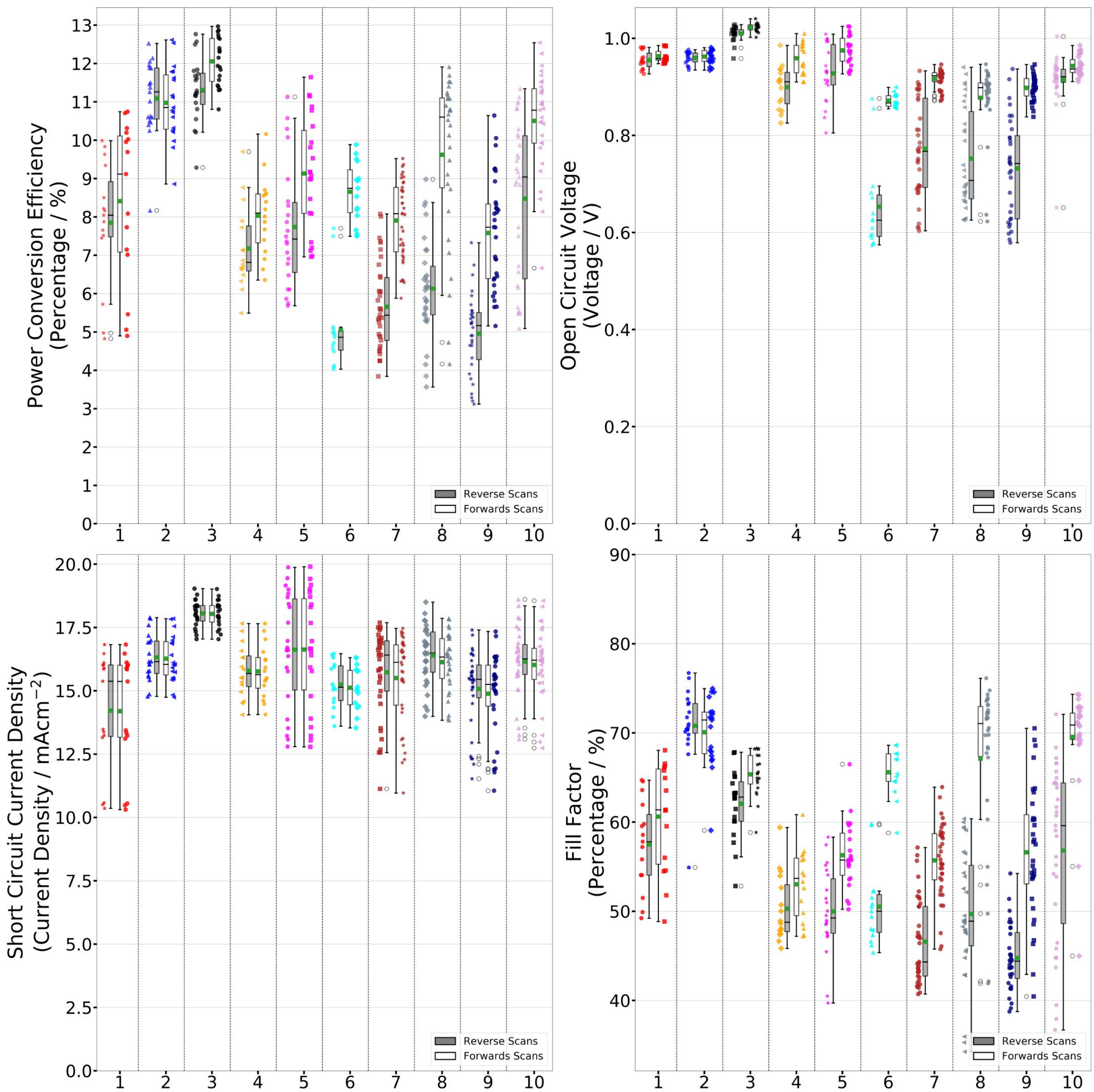

Figure S11: Box-plots of JV scan photovoltaic performance parameters for 0.09cm^2 cells with R2R slot-die coated perovskite from a 5μm wet film thickness and an oven temperature of 129°C (set-point of 150°C) for 10 separate batches of devices made over the course of six months. The boxes represent the first and third quartiles, the horizontal black line the median, the upper whisker the data within 1.5 times the inter quartile range of the upper quartile and the lower whisker 1.5 times the inter quartile range of the lower quartile, green square the mean and open black dots outliers. The coloured full markers represent the individual scan results for the adjacent scan direction and corresponding split.

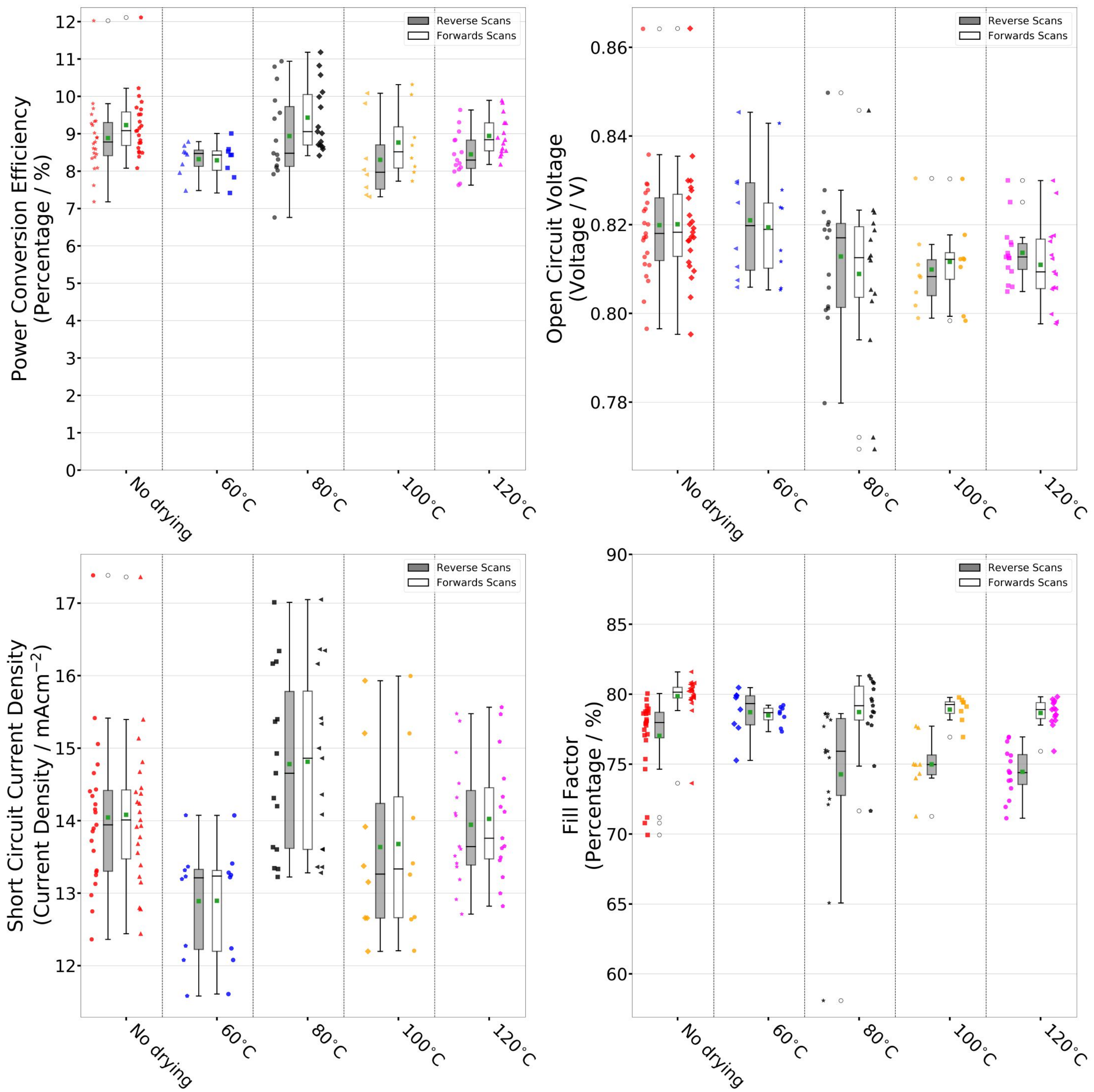

Figure S12: Box-plots of JV scan photovoltaic performance parameters for 0.09cm^2 spin coated cells with PCBM films with no drying or drying on a hot-plate for 5 minutes at 60, 80, 100 or 120°C. The boxes represent the first and third quartiles, the horizontal black line the median, the upper whisker the data within 1.5 times the inter quartile range of the upper quartile and the lower whisker 1.5 times the inter quartile range of the lower quartile, green square the mean and open black dots outliers. The coloured full markers represent the individual scan results for the adjacent scan direction and corresponding split.

Table S5: MedianJV scan photovoltaic performance parameters for 0.09cm^2 spin coated cells with PCBM layer dried on a hot-plate at various temperatures for 5 minutes.

Drying Temperature (°C)	Scan Direction	Voc (V)	Jsc (mAcm^{-2})	FF (%)	PCE (%)
None	Forwards	0.82	14.0	80	9.1
	Reverse	0.82	13.9	78	8.8
60	Forwards	0.82	13.2	79	8.4
	Reverse	0.82	13.2	79	8.5
80	Forwards	0.81	14.9	79	9.1
	Reverse	0.82	14.7	76	8.5
100	Forwards	0.81	13.3	79	8.5
	Reverse	0.81	13.3	75	8.0
120	Forwards	0.81	13.8	79	8.8
	Reverse	0.81	13.6	74	8.3

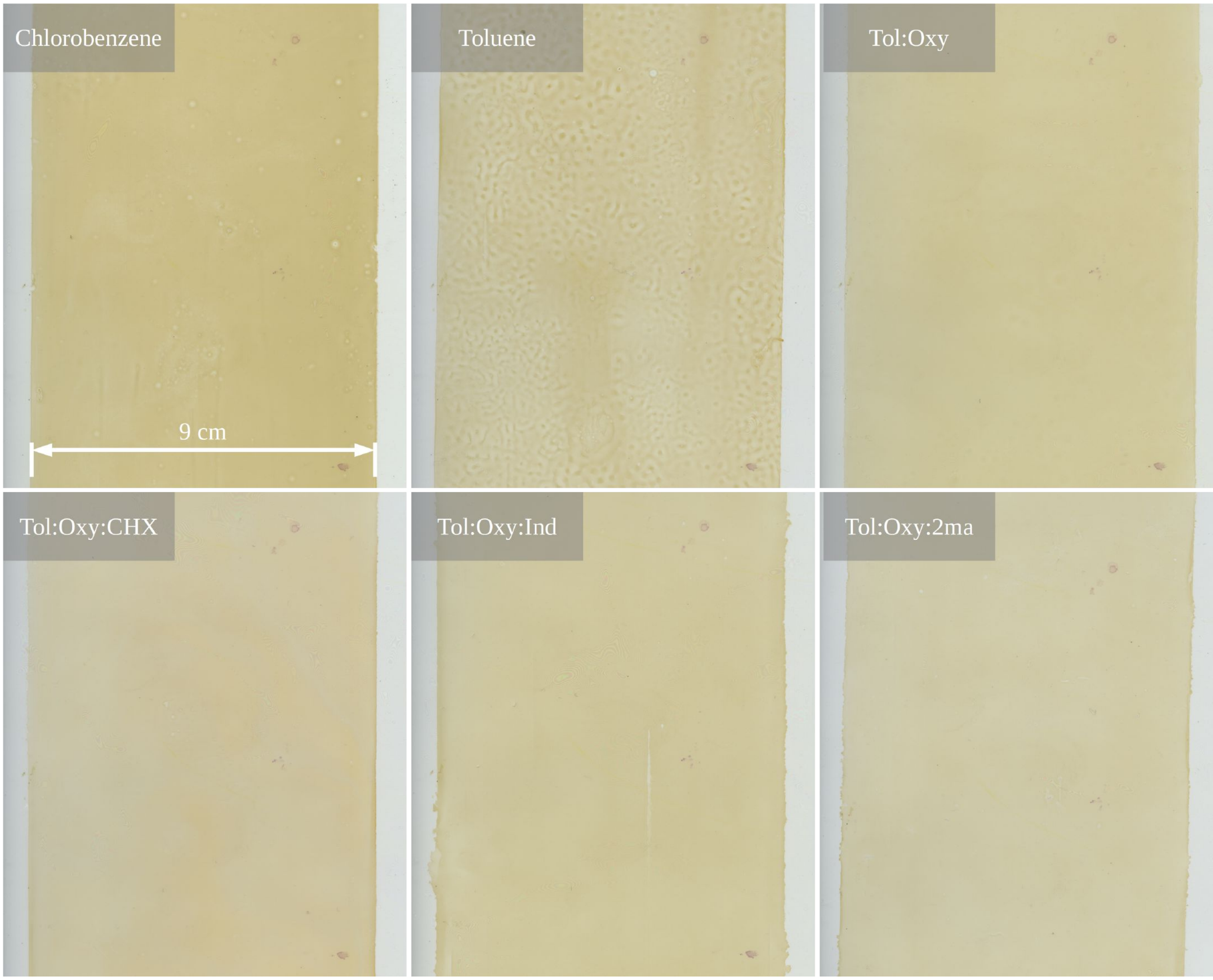

Figure S13: Images of PCBM dry films deposited by slot-die coating a 5μm wet film on bare PET substrate, using 10mgml^{-1} inks with solvent systems of either chlorobenzene, toluene, toluene:O-xylene (7:3v/v) (Tol:Oxy), toluene:O-xylene:cyclohexanone (6:3:1v/v) (Tol:Oxy:CHX), toluene:O-xylene:indan (6:3:1v/v) (Tol:Oxy:Ind), toluene:O-xylene:2-methylanisole (6:3:1v/v) (Tol:Oxy:2ma).

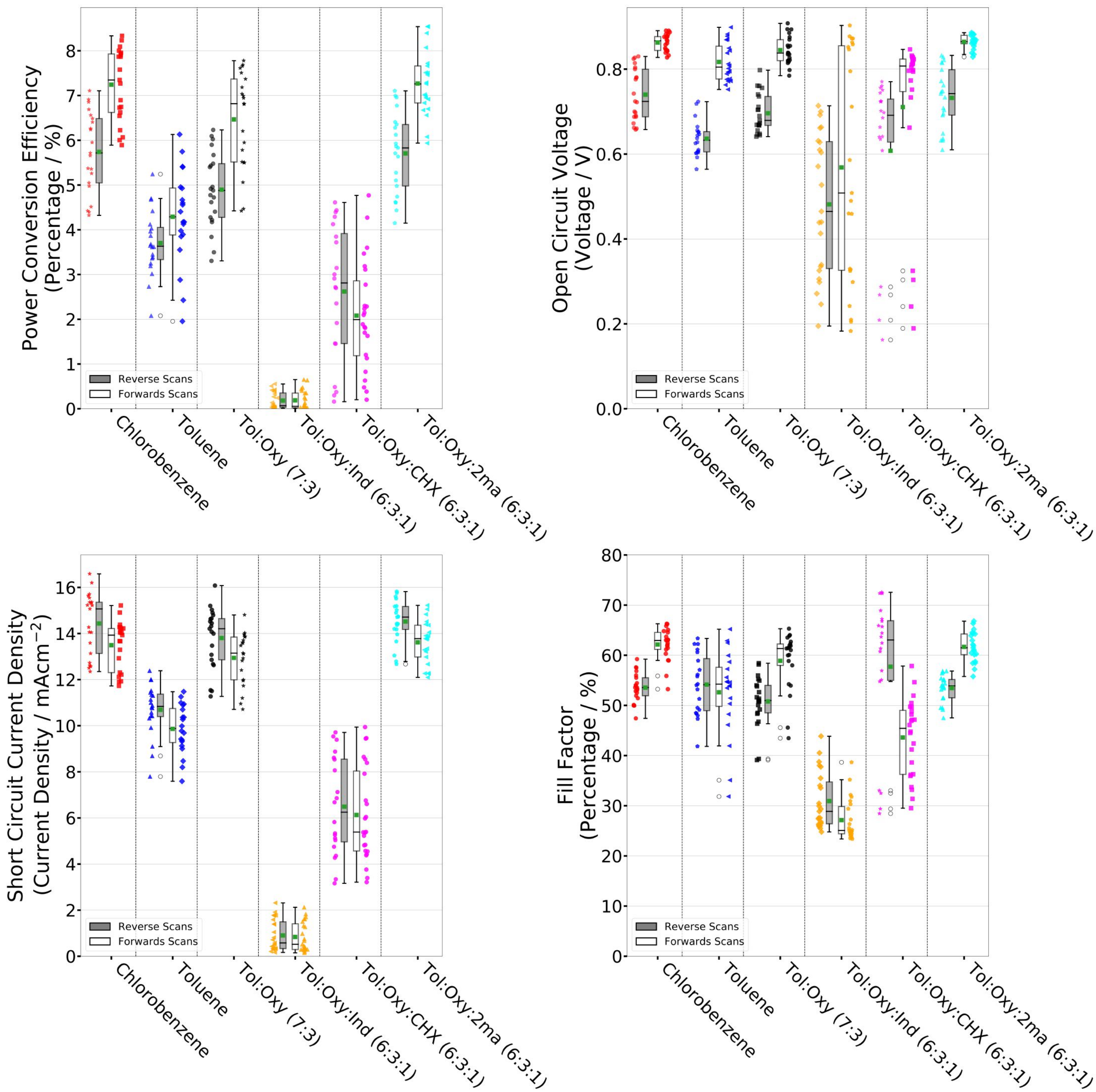

Figure S14: Box-plots of JV scan photovoltaic performance parameters for 0.09cm^2 cells made on R2R coated perovskite with S2S coated PCBM films from various solvent system inks, in the x-axis split labels Tol = toluene, Oxy = O-xylene, CHX = cyclohexanone, Ind = indan, 2ma = 2-methylanisole. The boxes represent the first and third quartiles, the horizontal black line the median, the upper whisker the data within 1.5 times the inter quartile range of the upper quartile and the lower whisker 1.5 times the inter quartile range of the lower quartile, green square the mean and open black dots outliers. The coloured full markers represent the individual scan results for the adjacent scan direction and corresponding split.

Table S6: MedianJV scan photovoltaic performance parameters for 0.09cm^2 cells made on R2R coated perovskite with S2S coated PCBM films from various solvent system inks, solvent system abbreviations are Tol = toluene, Oxy = O-xylene, CHX = cyclohexanone, Ind = indan, 2ma = 2-methylanisole.

Solvent System	Scan Direction	Voc (V)	Jsc (mAcm^{-2})	FF (%)	PCE (%)
Chlorobenzene	Forwards	0.87	13.9	63	7.3
	Reverse	0.72	15.1	54	5.7
Toluene	Forwards	0.80	9.9	54	4.3
	Reverse	0.63	10.8	54	3.6
Tol:Oxy (7:3)	Forwards	0.84	13.2	61	6.8
	Reverse	0.68	14.2	51	4.9
Tol:Oxy:Ind (6:3:1)	Forwards	0.51	0.5	25	0.1
	Reverse	0.46	0.6	29	0.1
Tol:Oxy:CHX (6:3:1)	Forwards	0.81	5.4	45	2.0
	Reverse	0.69	6.2	63	2.8
Tol:Oxy:2ma (6:3:1)	Forwards	0.86	13.8	61	7.3
	Reverse	0.74	14.7	54	5.8

Table S7: Rheology of $10 \mathrm{mgml}^{-1}$ PCBM inks for slot-die coating

Solvent System	Surface Tension (mNm^{-1})	Viscosity (mPa·s)
Chlorobenzene	33.7	1.04
Toluene	28.3	0.81
Toluene:O-xylene (7:3)	29.5	0.92
Toluene:O-xylene:cyclohexanone (6:3:1)	29.7	0.93
Toluene:O-xylene:2-methylanisole (6:3:1)	29.9	0.87
Toluene:O-xylene:indan (6:3:1)	29.3	0.88

Table S8: Median JV scan photovoltaic performance parameters for 0.09cm^2 cells with R2R slot-die coated PCBM layers from various different wet film thicknesses.

Wet Film Thickness (μm)	Scan Direction	Voc (V)	Jsc (mAcm^{-2})	FF (%)	PCE (%)
Spin coated	Forwards	0.90	16.3	71	10.6
	Reverse	0.71	16.5	49	6.1
5	Forwards	0.80	11.8	56	5.2
	Reverse	0.58	11.7	56	3.6
7.5	Forwards	0.87	13.5	65	7.6
	Reverse	0.56	13.7	52	4.0
10	Forwards	0.92	12.5	67	7.7
	Reverse	0.62	12.8	56	4.7
12.5	Forwards	0.93	13.8	59	8.0
	Reverse	0.71	13.8	50	5.2

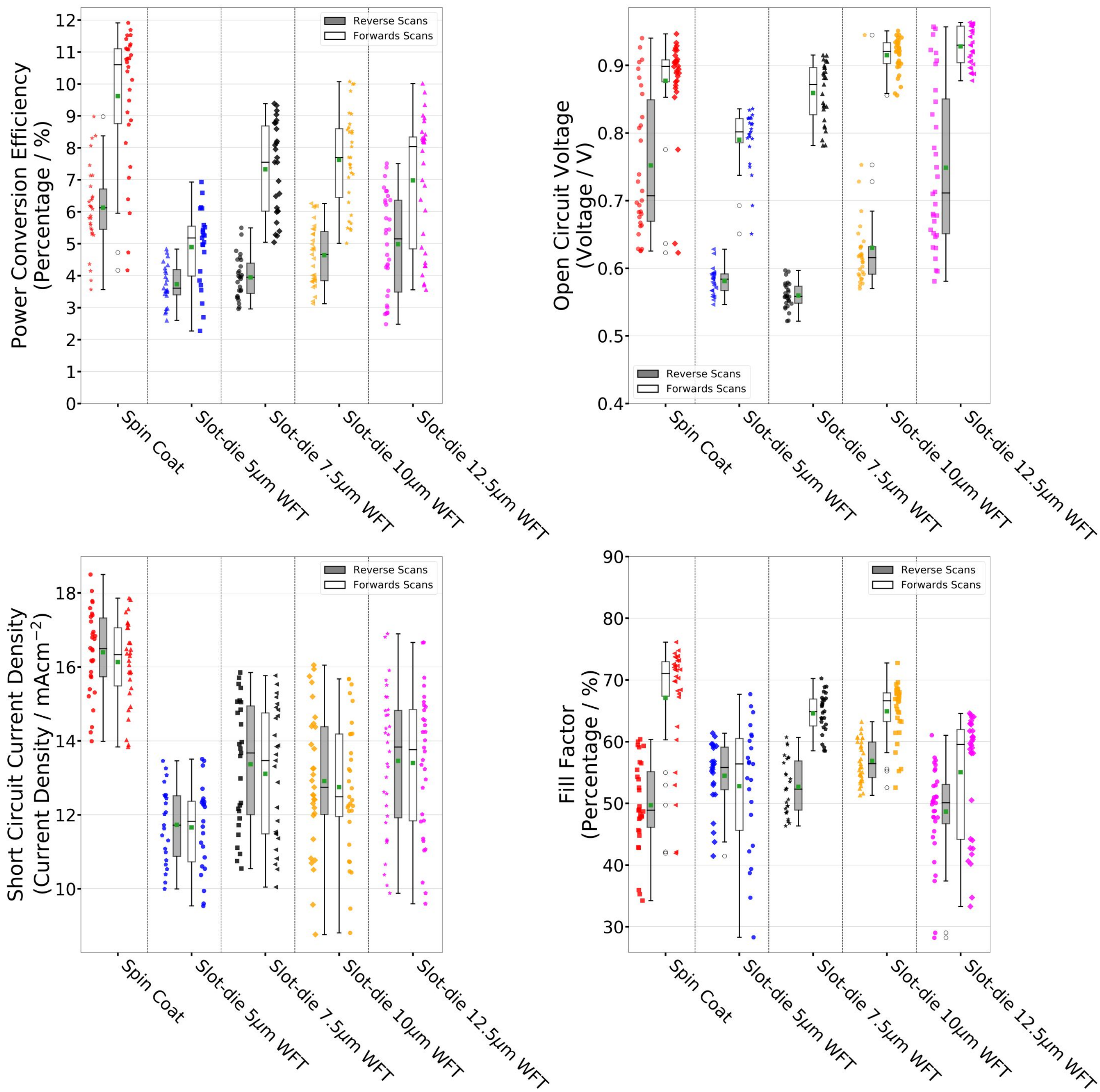

Figure S15: Box-plots of JV scan photovoltaic performance parameters for 0.09cm^2 cells made with R2R coated PCBM films deposited from various wet film thicknesses of 5, 7.5, 10 and 12.5μm. The boxes represent the first and third quartiles, the horizontal black line the median, the upper whisker the data within 1.5 times the inter quartile range of the upper quartile and the lower whisker 1.5 times the inter quartile range of the lower quartile, green square the mean and open black dots outliers. The coloured full markers represent the individual scan results for the adjacent scan direction and corresponding split.

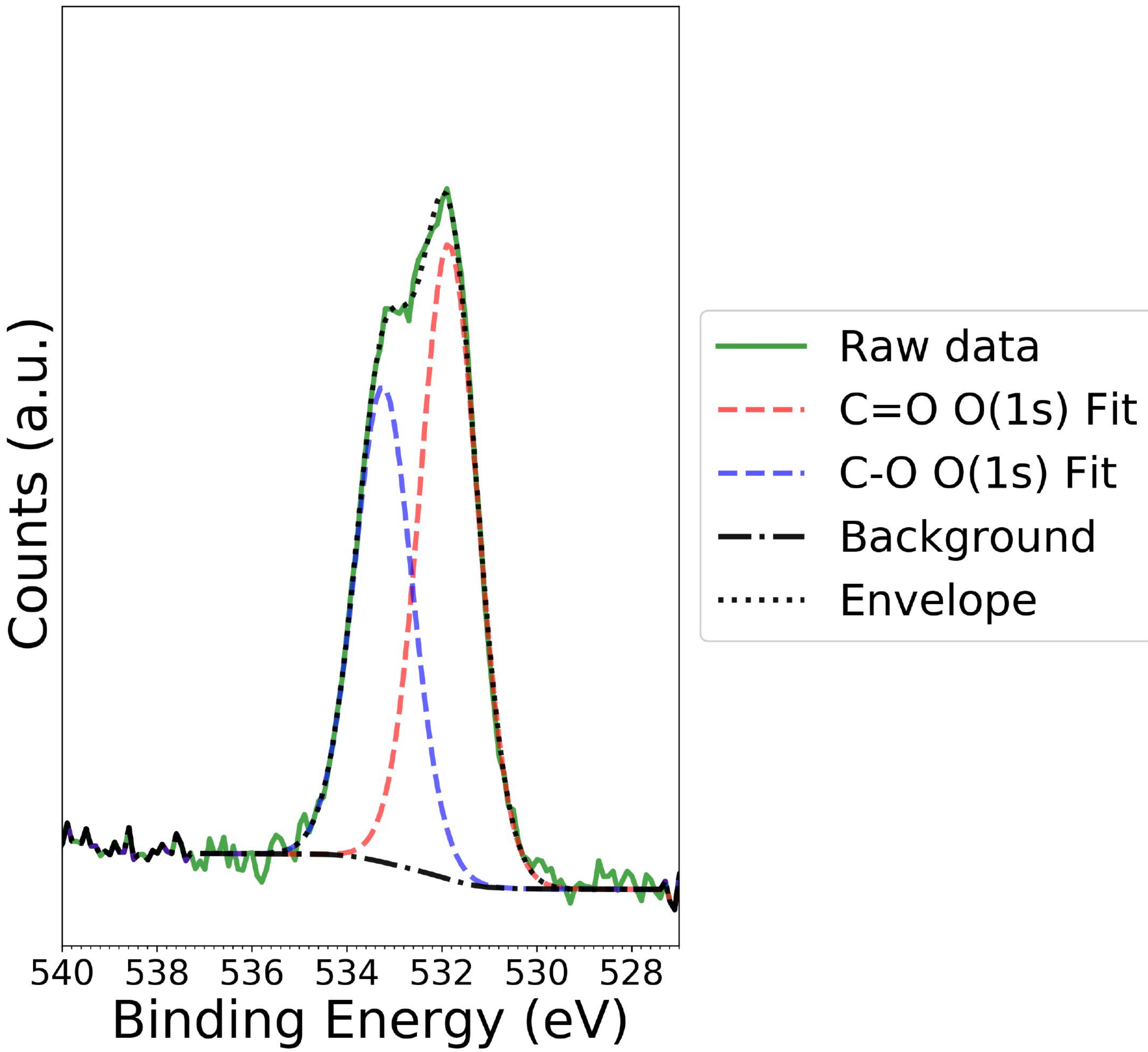

Figure S16: X-ray photoelectron spectroscopy spectra showing the O(1s) peaks for R2R slot-die coated PCBM.

Table S9: X-ray photoelectron spectroscopy elemental distribution data for R2R slot-die coated PCBM film and R2R coated BCP films with various wet film thicknesses, given in atomic %. Some silicon was detected that is attributed to contamination of the samples from handling with gloves and in plastic containers.

Sample	Carbon	Iodine	Nitrogen	Oxygen	Lead	Silicon
PCBM Only	94.9	0.05	0.08	4.6	0.02	0.31
BCP 5μm WFT	94.8	0.20	0.89	3.8	0.02	0.23
BCP 7.5μm WFT	94.4	0.16	0.37	4.9	0.04	0.19
BCP 10μm WFT	93.8	0.52	0.68	4.7	0.09	0.26
BCP 12.5μm WFT	95.1	0.25	0.47	3.8	0.07	0.30
BCP 15μm WFT	94.1	0.32	0.75	4.2	0.08	0.58

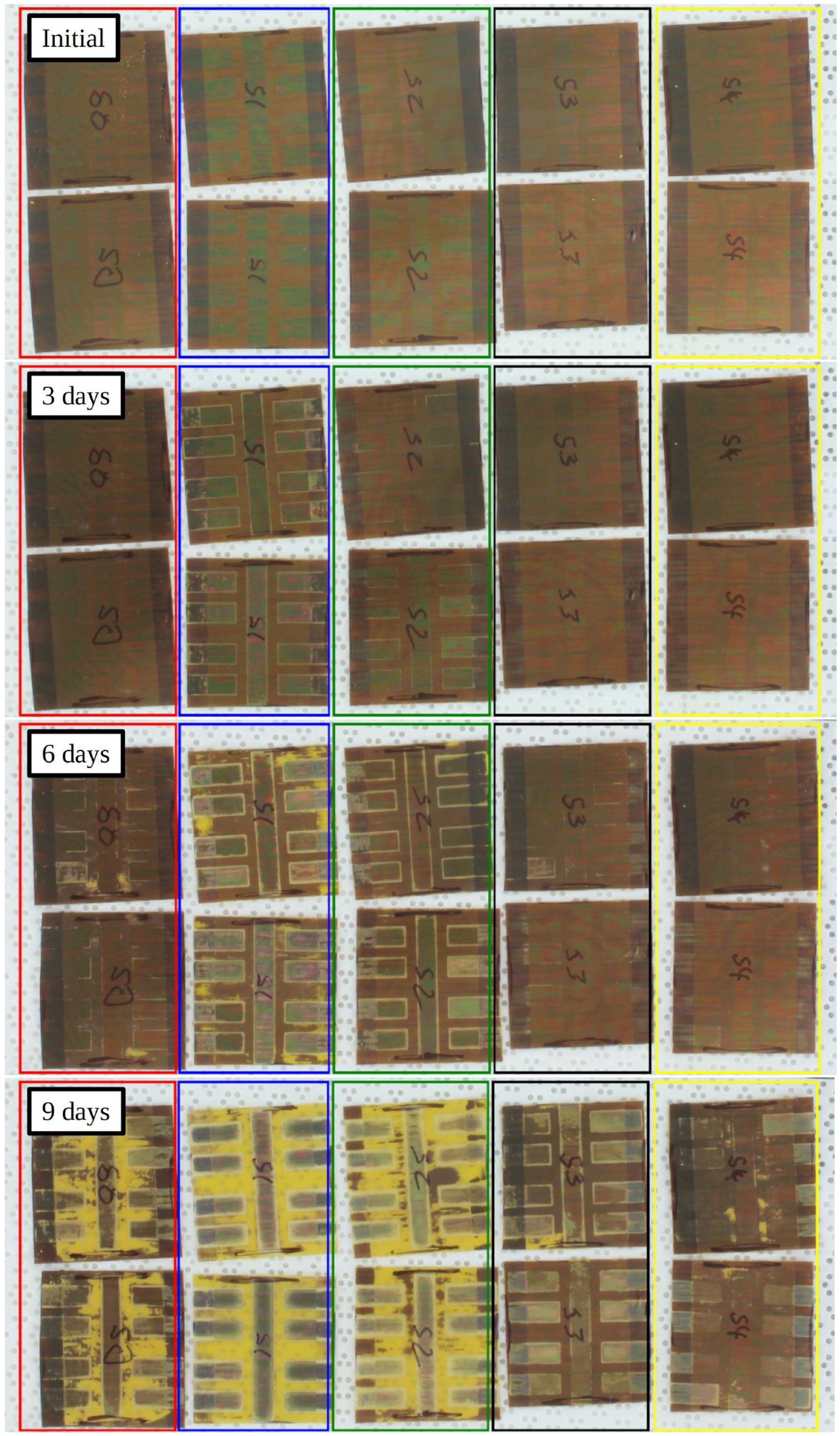

Figure S17: Images of devices with spin coated or slot-die coated PCBM with various film thicknesses, stored in a light box and photographed at regular intervals over the course of 9 days. The devices enclosed by the red boxes are have spin coated PCBM films of approximately 70nm, the devices enclosed by the blue boxes have slot-die coated PCBM films from a 5μm wet film thickness (approximately 40nm dry film), the devices enclosed by the green boxes have slot-die coated PCBM films from a 7.5μm wet film thickness (approximately 60nm dry film), the devices enclosed by the black boxes have slot-die coated PCBM films from a 10μm wet film thickness (approximately 80nm dry film) and the devices enclosed by the yellow boxes have slot-die coated PCBM films from a 12.5μm wet film thickness (approximately 100nm dry film).

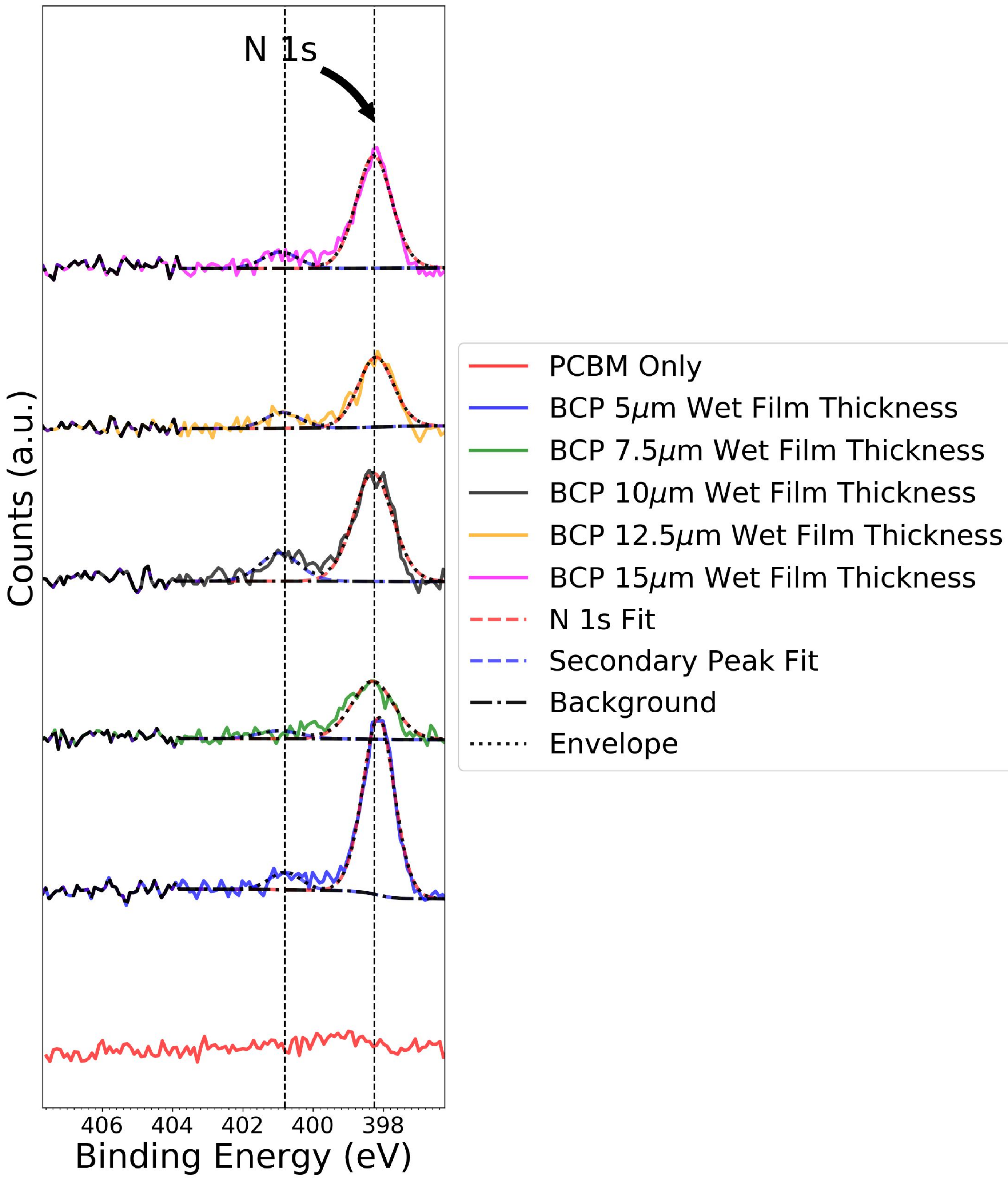

Figure S18: X-ray photoelectron spectroscopy spectra showing the change in the N 1s peak for R2R slot-die coated BCP layers from various wet film thickness on PCBM, also showing the ambiguous secondary N 1s peak.

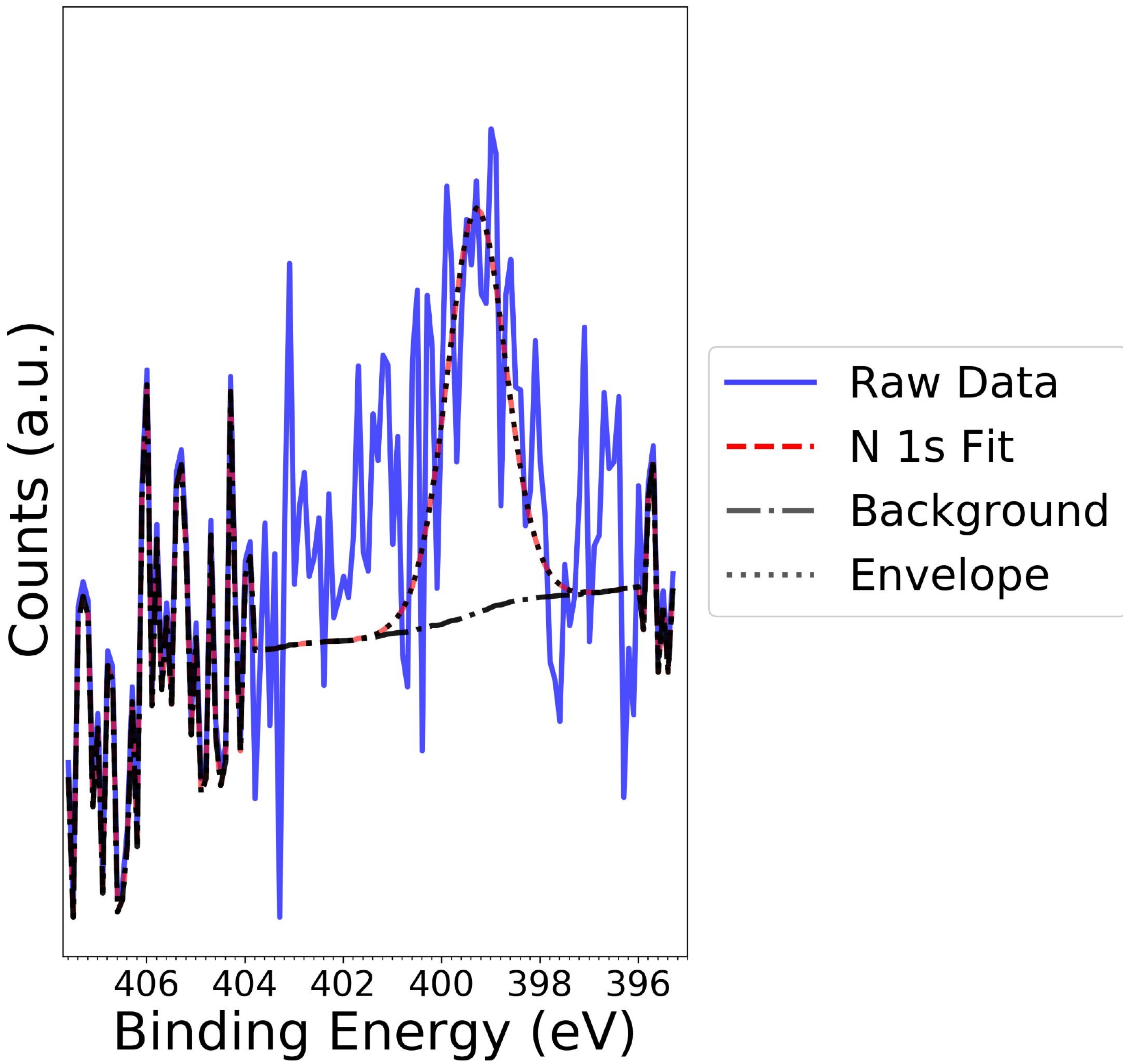

Figure S19: X-ray photoelectron spectroscopy spectra showing the small N 1s peak for R2R slot-die coated PCBM, possibly associated with methylammonium group of the underlying perovskite layer.

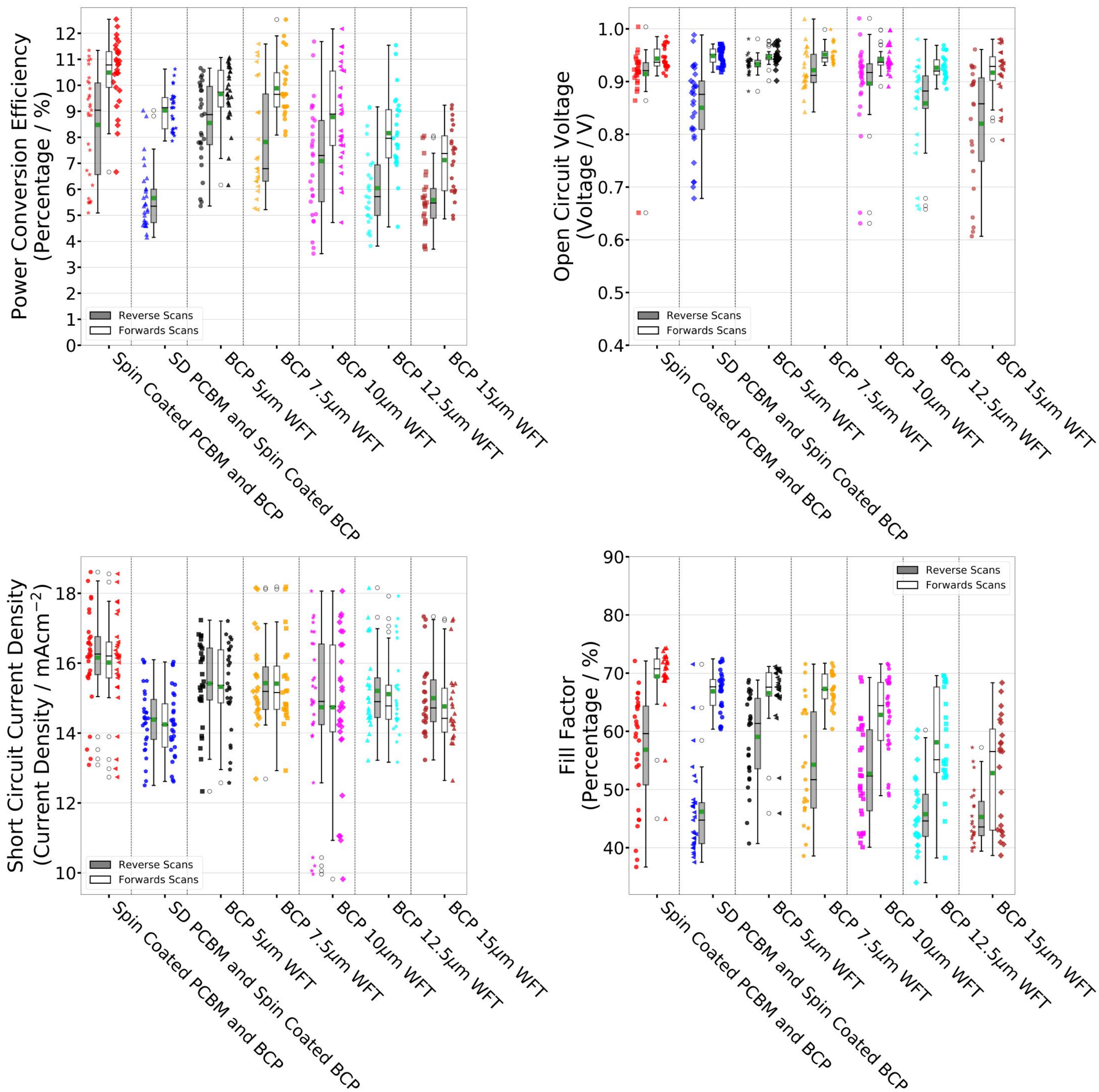

Figure S20: Box-plots of JV scan photovoltaic performance parameters for 0.09cm^2 cells made with R2R coated BCP films deposited from various wet film thicknesses of 5, 7.5, 10 and 12.5 and 15μm. The boxes represent the first and third quartiles, the horizontal black line the median, the upper whisker the data within 1.5 times the inter quartile range of the upper quartile and the lower whisker 1.5 times the inter quartile range of the lower quartile, green square the mean and open black dots outliers. The coloured full markers represent the individual scan results for the adjacent scan direction and corresponding split.

Table S10: Median JV scan photovoltaic performance parameters for 0.09cm^2 cells made with R2R coated BCP films deposited from various wet film thicknesses of 5, 7.5, 10 and 12.5 and 15μm.

Wet Film Thickness (μm)	Scan Direction	Voc (V)	Jsc (mAcm^{-2})	FF (%)	PCE (%)
Spin Coated PCBM and BCP	Forwards	0.94	16.2	71	10.8
	Reverse	0.92	16.3	60	9.0
SD PCBM and Spin Coated BCP	Forwards	0.95	14.2	68	9.1
	Reverse	0.88	14.4	45	5.3
BCP 5μm WFT	Forwards	0.94	15.4	68	9.7
	Reverse	0.93	15.4	61	8.9
BCP 7.5μm WFT	Forwards	0.94	15.2	67	9.7
	Reverse	0.91	15.2	52	6.8
BCP 10μm WFT	Forwards	0.94	14.8	64	8.9
	Reverse	0.92	14.9	52	7.3
BCP 12.5μm WFT	Forwards	0.92	14.8	55	8.0
	Reverse	0.88	14.9	45	5.7
BCP 15μm WFT	Forwards	0.93	14.4	57	7.4
	Reverse	0.86	14.7	44	5.5

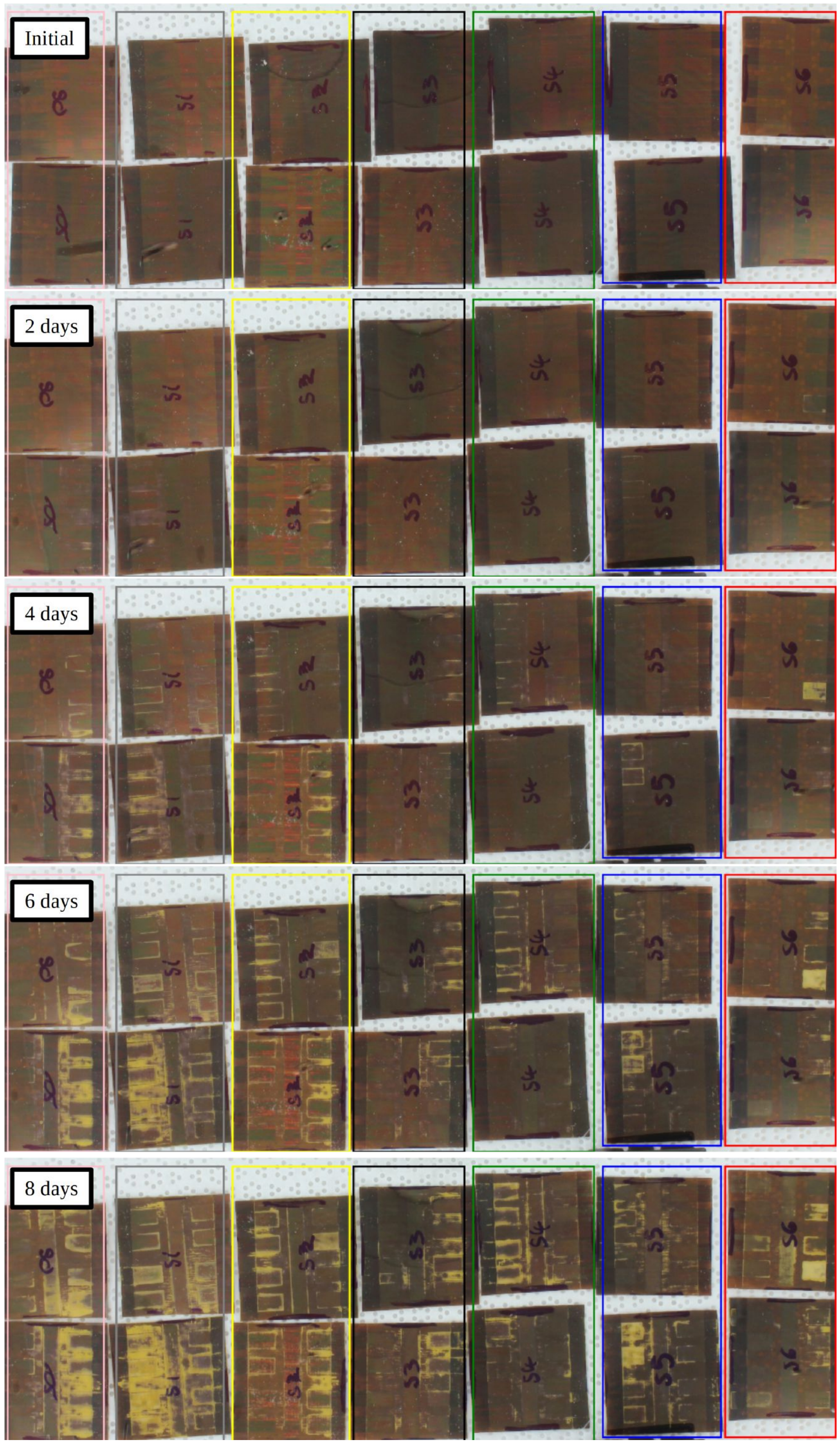

Figure S21: Images of devices with spin coated or slot-die coated BCP with various film thicknesses, stored in a light box and photographed at regular intervals over the course of 8 days. The devices enclosed by the red boxes are have spin coated PCBM films and spin coated BCP films, the devices enclosed by the gray boxes are have slot-die coated PCBM films and spin coated BCP films, the devices enclosed by the yellow boxes have slot-die coated BCP films from a 5μm wet film thickness, the devices enclosed by the black boxes have slot-die coated BCP films from a 7.5μm wet film thickness, the devices enclosed by the green boxes have slot-die coated BCP films from a 10μm wet film thickness, the devices enclosed by the blue boxes have slot-die coated BCP films from a 12.5μm wet film thickness and the devices enclosed by the red boxes have slot-die coated BCP films from a 15μm wet film thickness.

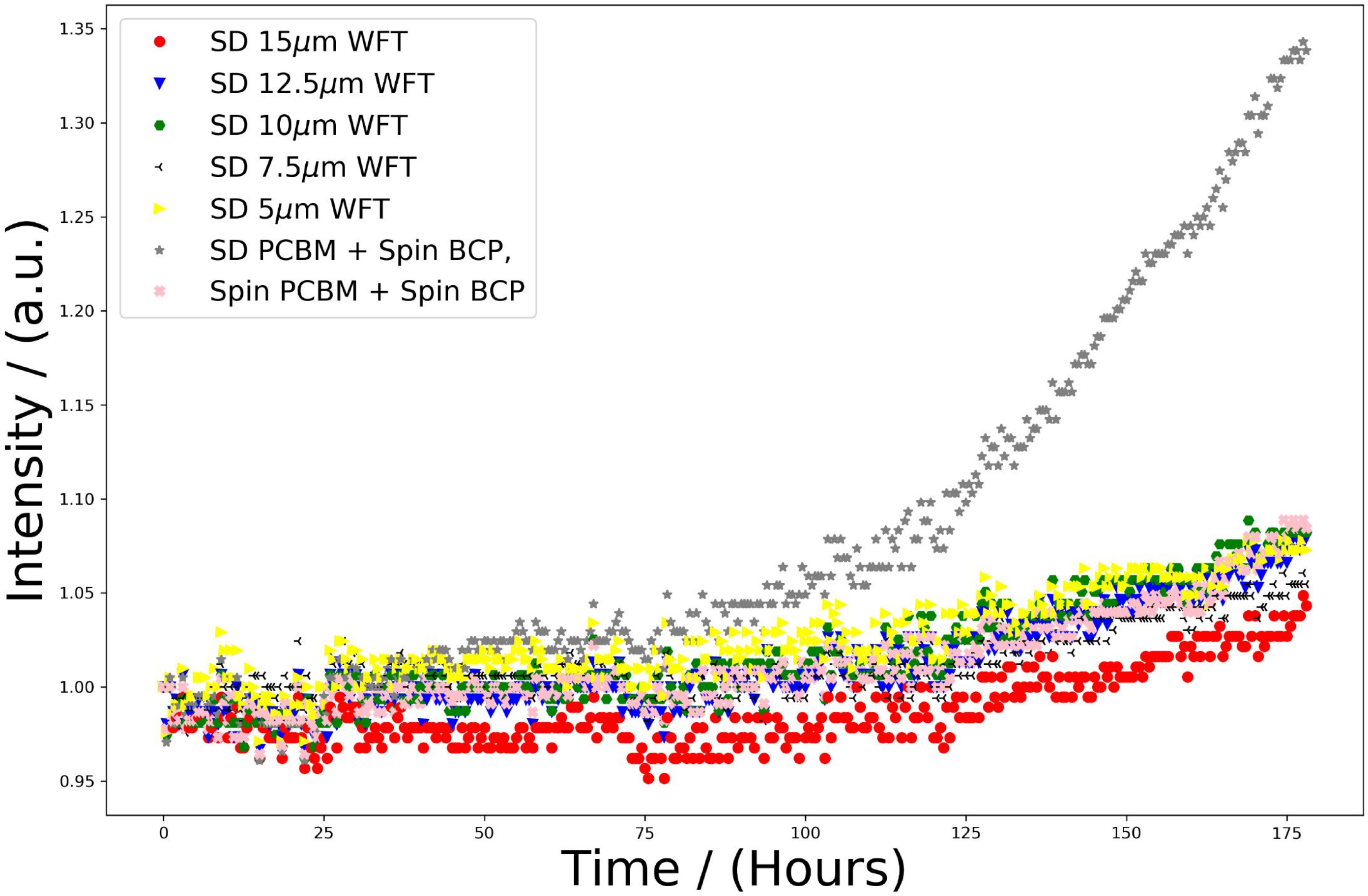

Figure S22: Average red RGB color channel intensity of device areas over time, normalized to the initial value, for images of devices with spin coated or slot-die coated BCP with various film thicknesses, stored in a light box and photographed at regular intervals over the course of 8 days. For devices with spin coated PCBM and spin coated BCP (pink x), slot-die coated PCBM and spin coated BCP (grey star), slot-die coated PCBM and slot-die coated BCP from a 5μm wet film thickness (yellow right pointing triangle), slot-die coated PCBM and slot-die coated BCP from a 7.5μm wet film thickness (black tri-point), slot-die coated PCBM and slot-die coated BCP from a 10μm wet film thickness (green hexagon), slot-die coated PCBM and slot-die coated BCP from a 12.5μm wet film thickness (blue down pointing triangle) and slot-die coated PCBM and slot-die coated BCP from a 15μm wet film thickness (red circle).

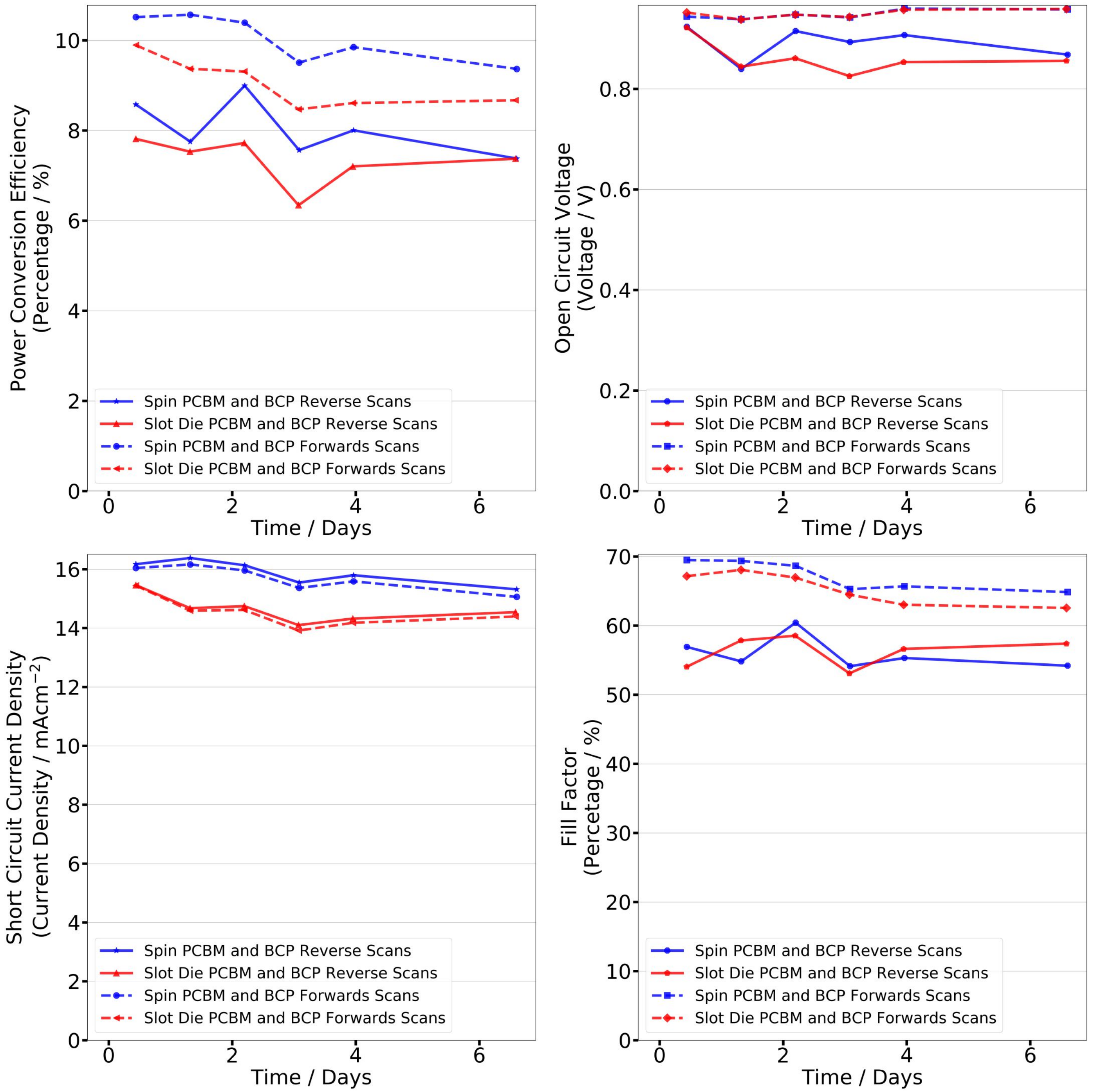

Figure S23: Dark shelf-life storage JV scan lifetime measurements of R2R devices with spin coated PCBM and BCP or slot-die coated PCBM and BCP layers, stored in a glove-box and measured periodically over the course of approximately 6 days.

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