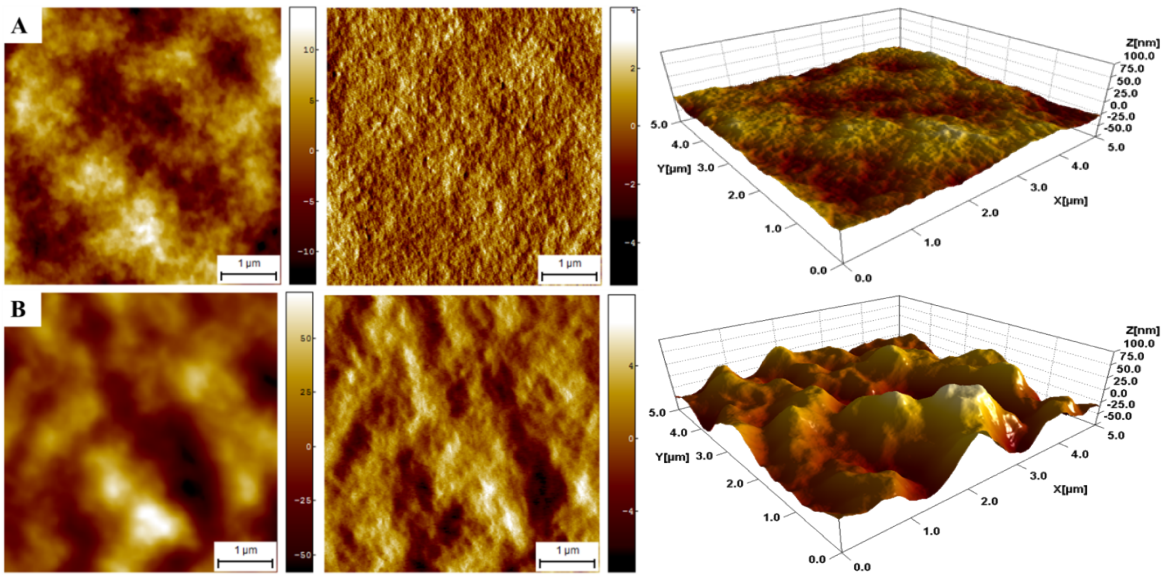
Electronic Supplementary Information (ESI)

Supplementary Information

Table ESI 1. Coating parameters used for device preparation with specification for each layer.

Layer	Material	Concentration	Speed (m/min)	Flow (ml/min)	Thickness (µm)	Temperature (°C)
Substrate	Flextrode					
Active layer	P3HT:PCBM (+Additive)	30:30 mg/mL	1.0	0.1	10	70
Compatibilizer	F010:IPA	1:4 v/v	1.0	0.1	8	70
HTL	4083:IPA	1:2 v/v	1.0	0.3	23	70
Conducting layer	F010:IPA	2:1 v/v	1.0	0.5	38	70
Conducting layer	5010:IPA	5:1 w/w	0.8	1.2	125	70
Electrode	Ag PV410		1.0			70



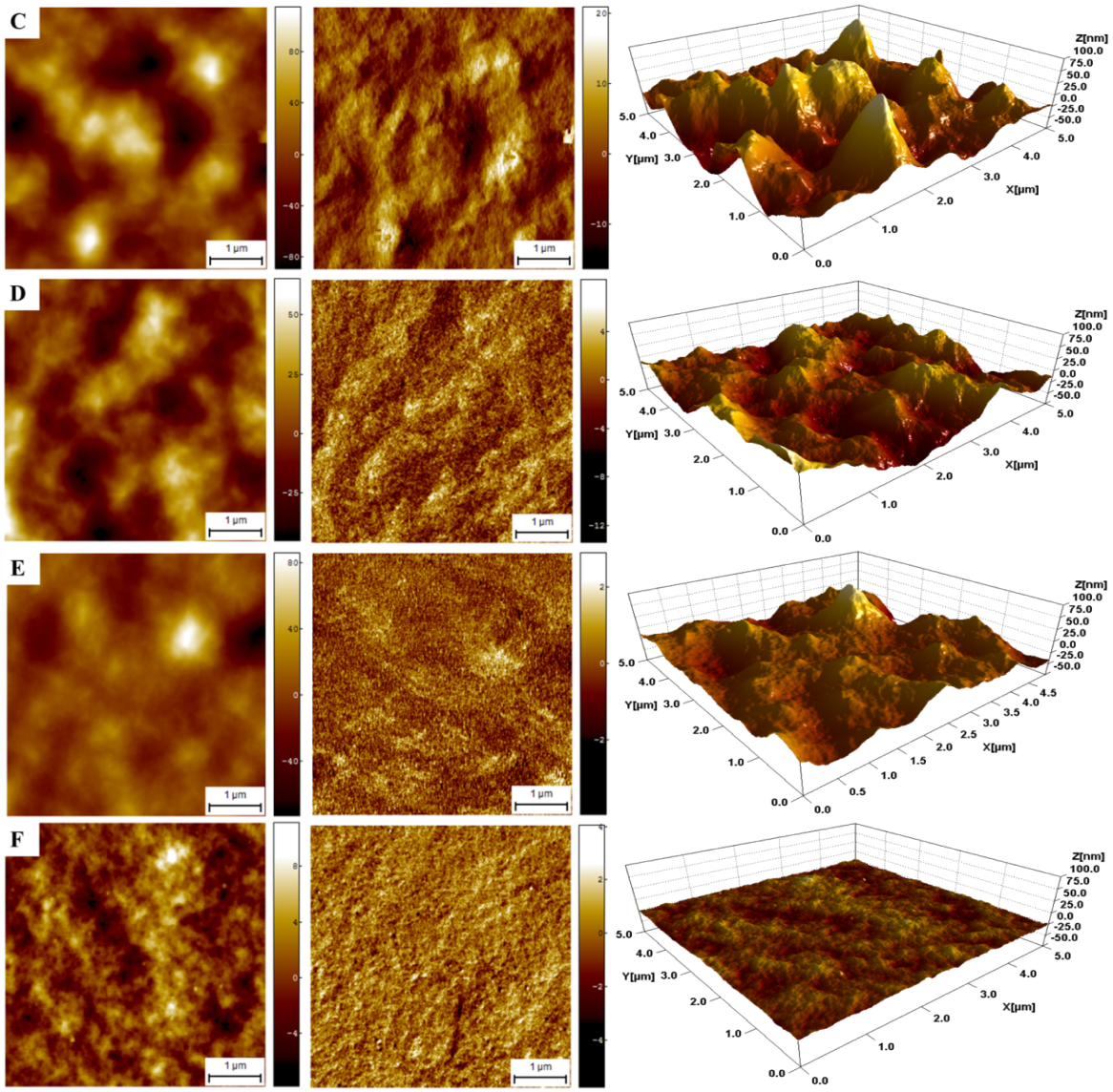


Figure ESI 1. AFM topography, corresponding phase images (5 µm x 5 µm) and 3D surface representation of the annealed samples of P3HT:PCBM blends processed without (A) and with additives: CN 3% (B), CN 5% (C), NMP 3% (D), NMP 5% (E), BARB 1% (F). The scale bars are 1 µm. 3D representation has a fix orientation and axis scale (max.100 nm; min.-50 nm) for comparison purposes.

Table ESI 2. The RMS surface roughness obtained from measurements on slot-die coated films of P3HT : PCBM blends processed without and with the additives. The data extracted from AFM topography images (5 μm x 5 μm); standard deviation is ca. 20% for all the samples.

Sample	Ref	CN 3%	CN 5%	NMP 3%	NMP 5%	BARB 1%
RMS (nm)	4.6	16.1	22.9	17.1	16.7	2.4

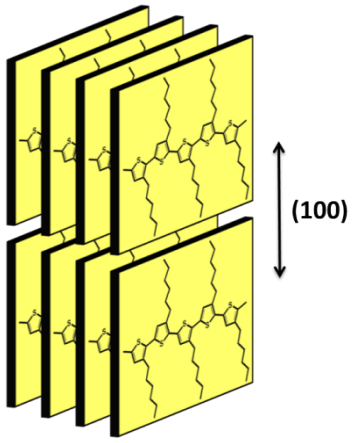


Figure ESI 2. Schematic representation of P3HT crystalline edge-on orientation and lamellar spacing at *100* reflection.

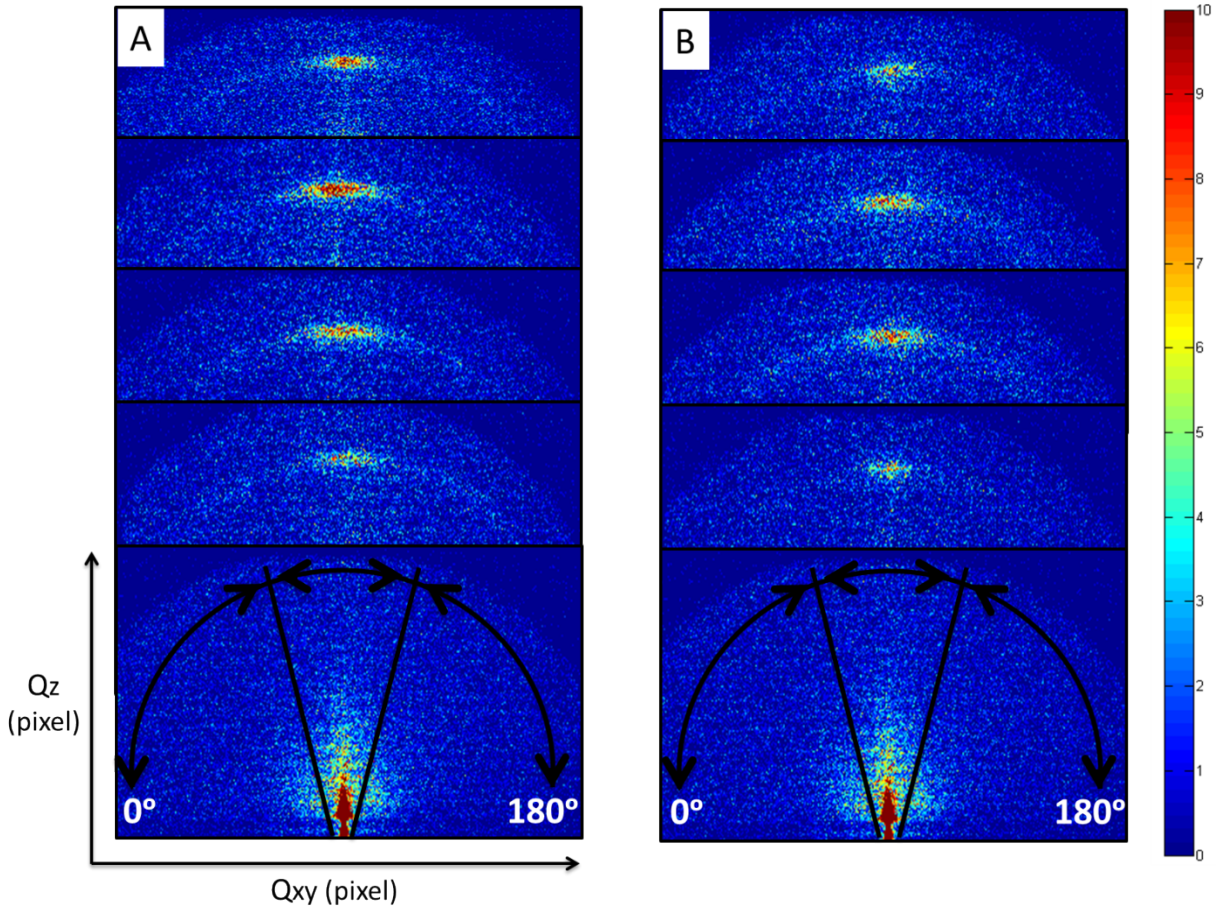
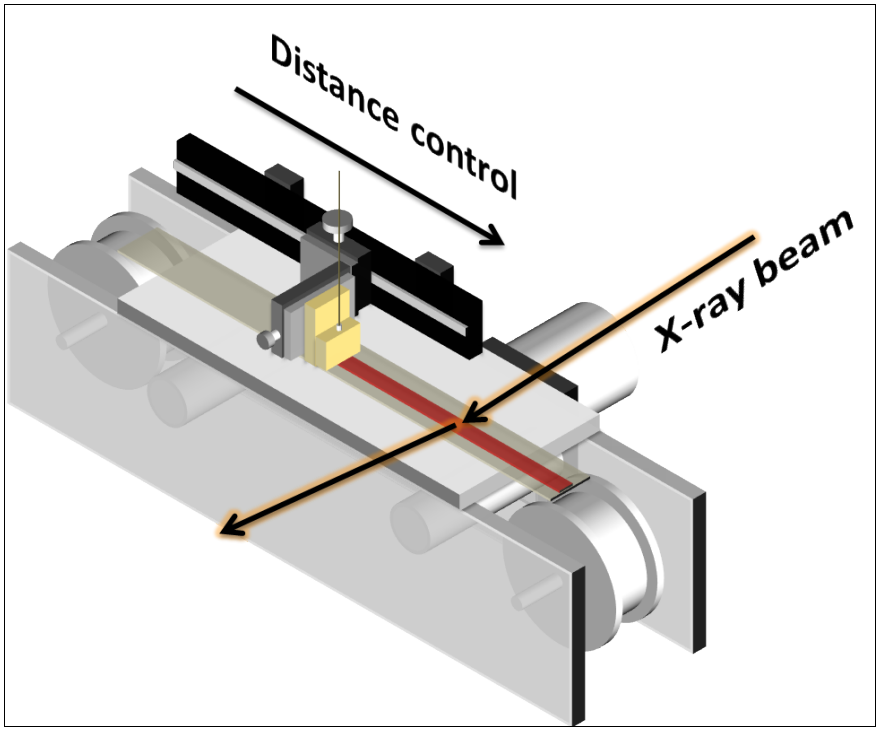


Figure ESI 3. 2D pattern representation of SAXS data for the annealed (A) and non-annealed (B) samples of P3HT:PCBM blends processed without and with additives. The images are overlapped for visual comparison of the signal intensity at the *100* peak between various samples. Bottom image shows background signal and schematic representation of the integration regions used for data extraction; textured (lamellar stack aligned with the substrate) crystallinity - centered on surface around axis, integration over 70-110° azimuthal angle; un-textured (random orientation) crystallinity - integration over off-axis parts 0-70° and 110-180°. Bottom to top: background (PET substrate), Ref, CN 3%, NMP 3% and BARB 1%.

The degree of ordering of the lamellar stacking was evaluated from the *100* peak on the normal to the surface plane, corresponding to a Q_z component in reciprocal space, with $|Q| = 4\pi\sin(\theta)/\lambda$, where 2θ equals the diffraction angle, and λ is the X-ray wavelength (1.5418 Å). In the current setup, information about the inter-chain π–π packing cannot be obtained due to detector range. The out-of-plane intensities were integrated along Q_z axis in 2D patterns and converted to 1D plots. The

parameters were extracted by fitting a Gaussian function to the integrated peaks. The area obtained from the fitted curve yielded indication about the relative crystallinity. The average coherence length determined with the Scherrer equation, $2\pi D/\mathrm{FWHM}$ with D=0.9, from the full width at half maximum in Q (FWHM) of the *100* peak was considered a rough approximation of the mean size of the crystallites. The lamellar packing density of the structure was evaluated from the peak position, $2\pi/Q$. The width of the angular spread was given from FWHM of the Gaussian fitted intensity. The integrations were determined for signal collected at Q_z range of 0.30-0.47. A subtraction of the background (PET foil) signals was made prior to the data extraction.



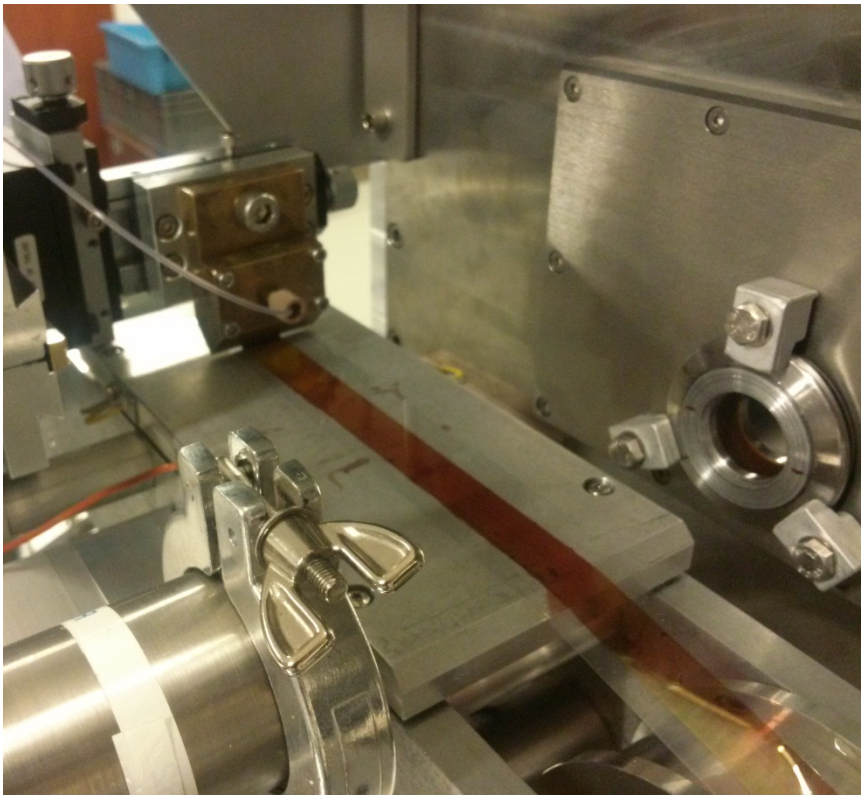


Figure ESI 4. Schematic representation and a corresponding picture of the slot-die coating device incorporated to SAXS instrument allowing control of the pump rate, speed and temperature of the film deposition. The solvent evaporation time was modified by varying the distance between the coating position versus the X-ray beam.

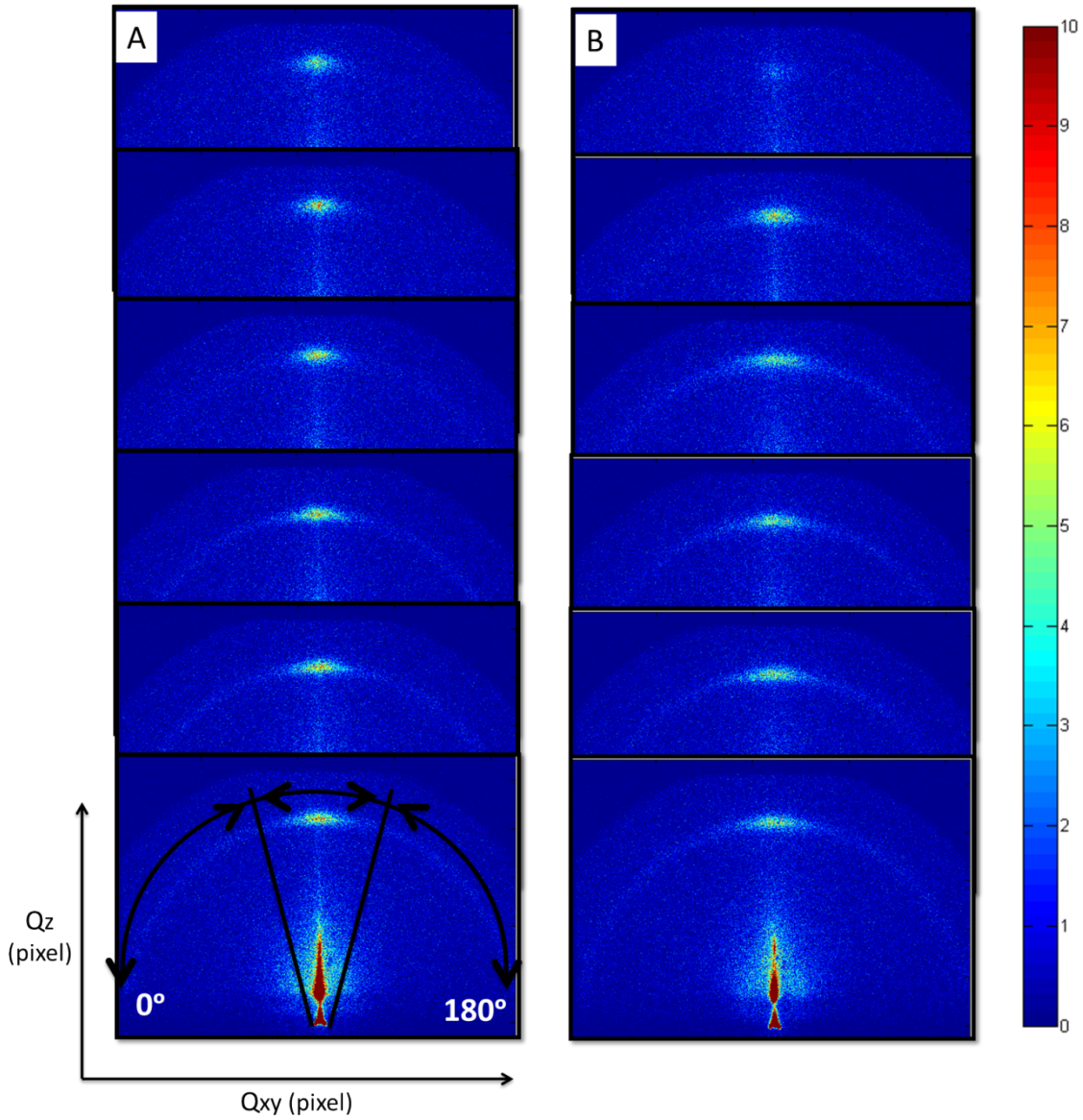


Figure ESI 5. 2D pattern representation of SAXS data for the 0% (A) CN 3% (B) samples of P3HT:PCBM blends deposited at 70°C and analyzed *in situ* with regards to two different solvent drying stages; subsequently annealed three times at 130°C with dynamic *ex situ* acquisition of each annealing process. The images are overlapped for visual comparison of the signal intensity at the *100* peak between various samples. Bottom image shows also a schematic representation of the integration regions used for data extraction; textured (lamellar stack aligned with the substrate) crystallinity - centered on surface around axis, integration over 70-110° azimuthal angle; un-textured (random orientation) crystallinity - integration over off-axis parts 0-70° and 110-180°. Top to bottom: Drying I (6.5 sec), Drying II (8.5 sec), Dry (post deposition-prior to annealing), Annealing I (21 sec), Annealing II (78 sec) and Annealing III (135 sec).

Table ESI 3. Structural data extracted from dynamic *in situ* and *ex situ* SAXS measurement of the films processed from pure P3HT:PCBM chlorobenzene solution and with 3% CN v/v additive. Drying I and II correspond to 6.5 and 8.5 sec drying time at 70°C respectively, Annealing I, II and III refer to 21, 78 and 135 sec of annealing time at 130°C respectively; inter-layer spacing (*d*), mean coherence length (L) of the *100* out-of-plane peak. The calculated parameters represent the integration over 70-110°, corresponding to crystalline texture (TEXT), and integrated sum of signals collected over 0-70° and 110-180°, corresponding to the un-textured crystallinity (RANDOM) acquired for 45 min each.

REFERENCE				
Index	d_{TEXT} (Å)	L_{TEXT} (Å)	d_{RANDOM} (Å)	L_{RANDOM} (Å)
Drying I	16.5	219	17.5	90
Drying I	16.5	232	17.5	100
Dry	16.5	236	17.4	217
Annealing I	17.0	278	17.6	255
Annealing II	17.1	290	17.6	222
Annealing III	17.1	305	17.5	215
CN 3% ADDITTIVE				
Index	d_{TEXT} (Å)	L_{TEXT} (Å)	d_{RANDOM} (Å)	L_{RANDOM} (Å)
Drying I	17.0	158	-	-
Drying I	16.8	211	17.3	132
Dry	16.8	205	17.4	170
Annealing I	17.2	248	17.5	182
Annealing II	17.2	265	17.5	184
Annealing III	17.2	274	17.5	163

Table ESI 4. Solar cell parameters of the annealed and non-annealed P3HT:PCBM based devices prepared without and with CN additive at 3% v/v concentration.

Sample	PCE (%)	FF (%)	V_{OC} (V)	J_{SC} (mA cm^{-2})
Annealed				

Ref	1.71	49.20	0.50	6.97
CN 3%	2.01	54.70	0.54	6.85
Non-Annealed				
Ref	1.38	51.80	0.47	5.61
CN 3%	1.92	52.62	0.53	6.86

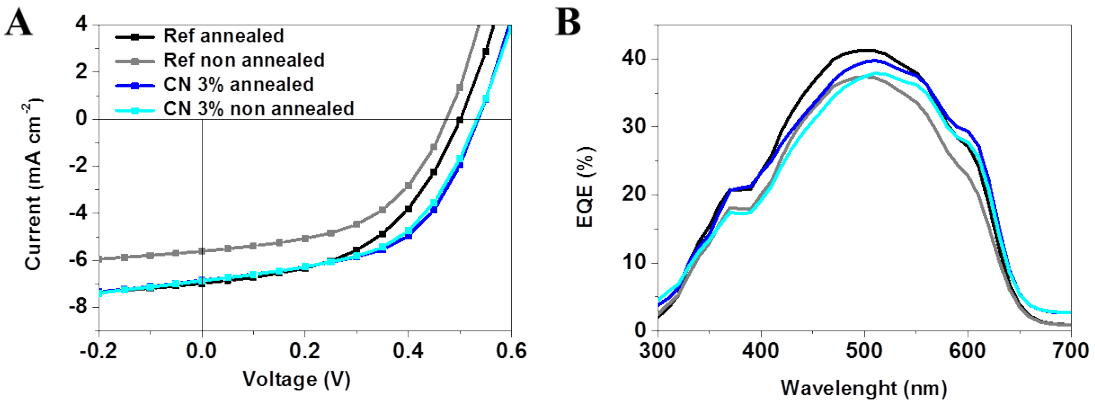
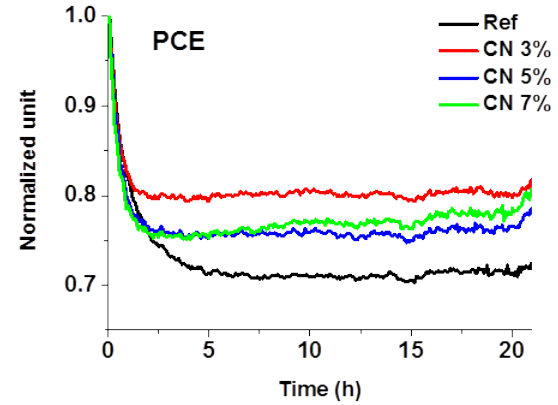
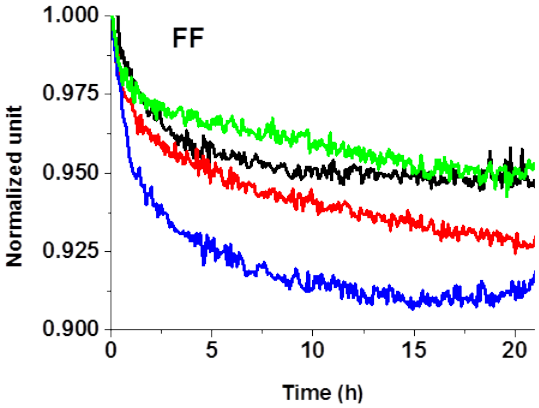
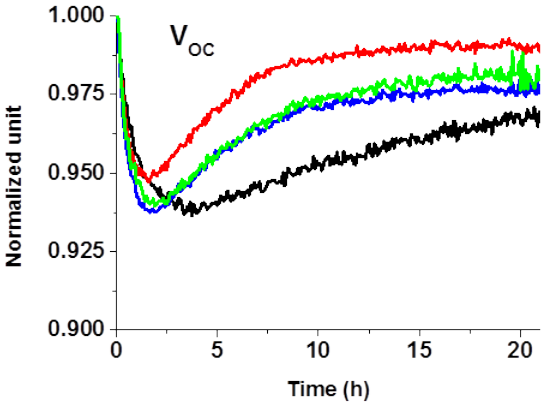
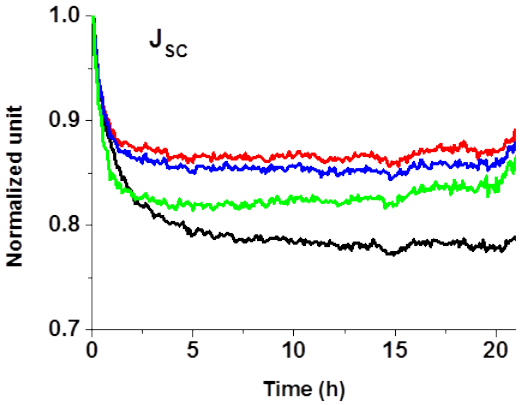


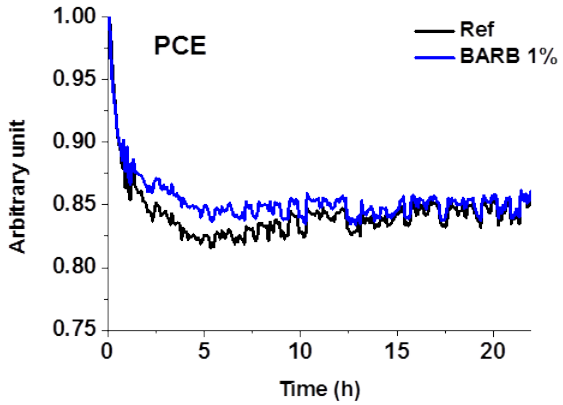
Figure ESI 6. J-V curves (A) and EQE spectra (B) of the annealed and non-annealed devices (area of 1 cm^2) coated without and with the 3% CN additive.

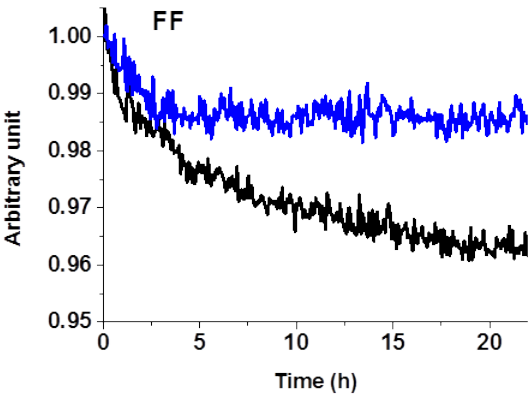

PCE
Ref
CN 3%
CN 5%
CN 7%
Normalized unit
Time (h)

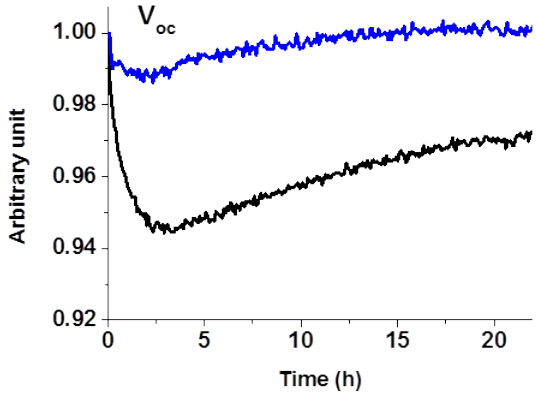

FF
Normalized unit
Time (h)

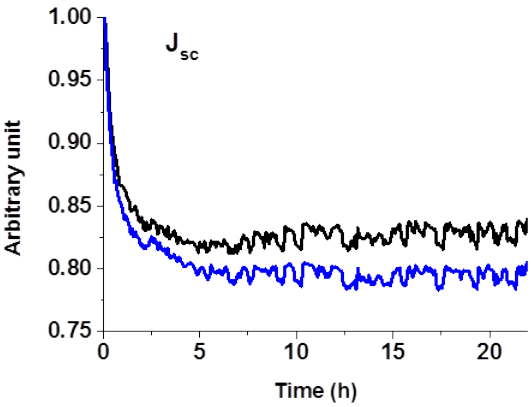

V_OC
Normalized unit
Time (h)


J_SC
Normalized unit
Time (h)


PCE
Ref
BARB 1%
Arbitrary unit
Time (h)


FF
Arbitrary unit
Time (h)


V_oc
Arbitrary unit
Time (h)


J_sc
Arbitrary unit
Time (h)

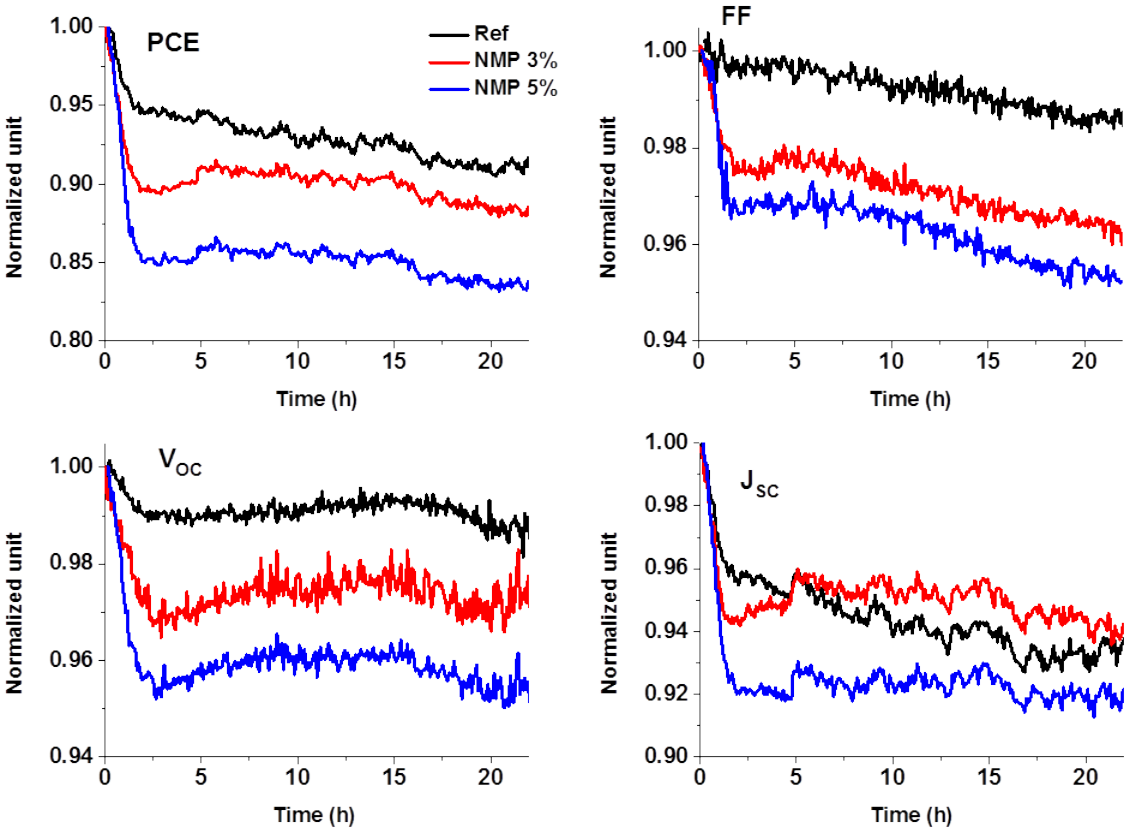


Figure ESI 7. Representative examples of degradation curves for devices fabricated with CN, BARB and NMP with the best performing device architectures;"3 layer" for CN and BARB, "5010" for NMP. The normalized PCE, FF, Voc and Jsc are plotted over time; curves of the reference tested concomitantly with the samples are presented for comparison.