Supporting Information

Self-assembly of carboxylated polythiophene nanowires for improved bulk heterojunction morphology in polymer solar cells

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Surface Energy Calculation:

The method to calculate the surface energy relies on the following set of equations:[S1]

$$1 + \cos\theta = 2\sqrt{\gamma_s^d}\left(\frac{\sqrt{\gamma_l^d}}{\gamma_l^v}\right) + 2\sqrt{\gamma_s^h}\left(\frac{\sqrt{\gamma_l^h}}{\gamma_l^v}\right) \tag{1}$$

$$\gamma_s = \gamma_s^d + \gamma_s^h \tag{2}$$

In these equations, the indices h and d refer to the hydrogen bonding and dispersion force components, while s and l denote solid or liquid. γ_s refers to the surface energy of the solid, γ_l^v is the surface energy of the liquid, and θ is the contact angle of the liquid with the solid surface. The surface energy parameters were found tabulated in the literature,[S2] and the relevant values are listed below:

	γ_l^d (mJ/m^2)	γ_l^h (mJ/m^2)	γ_l^v (mJ/m^2)
H$_2$O	21.8	51.0	72.8
n-hexadecane	26.35	0	26.35

To determine γ_s, we substitute the measured contact angle and known parameters γ_l^d, γ_l^h and γ_l^v into equation (1) for both H_2O and *n*-hexadecane as solvents. This forms a system of two equations in two unknowns that may be solved to calculate γ_s^d and γ_s^h. Equation (2) is then invoked to determine γ_s.
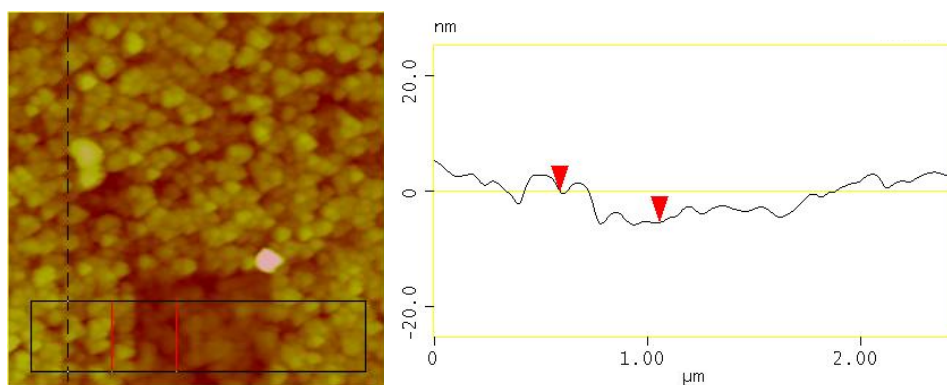

Fig. S1 Determination by AFM of the thickness of P3CPenT deposited onto an ITO surface using the solution absorption method. The average thickness measured by this technique is ~4 nm. The red triangles were generated in the AFM analysis software, but were not used in the determination of thickness.
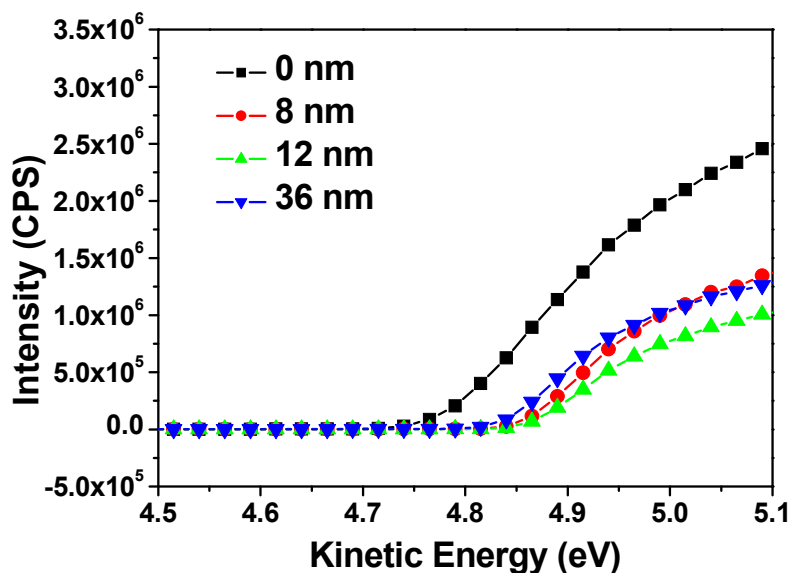

Fig. S2 Ultraviolet photoelectron spectroscopy measurements of unmodified ITO and ITO modified with 8 nm, 12 nm and 36 nm of P3CPenT. Work functions are extracted from the onset.
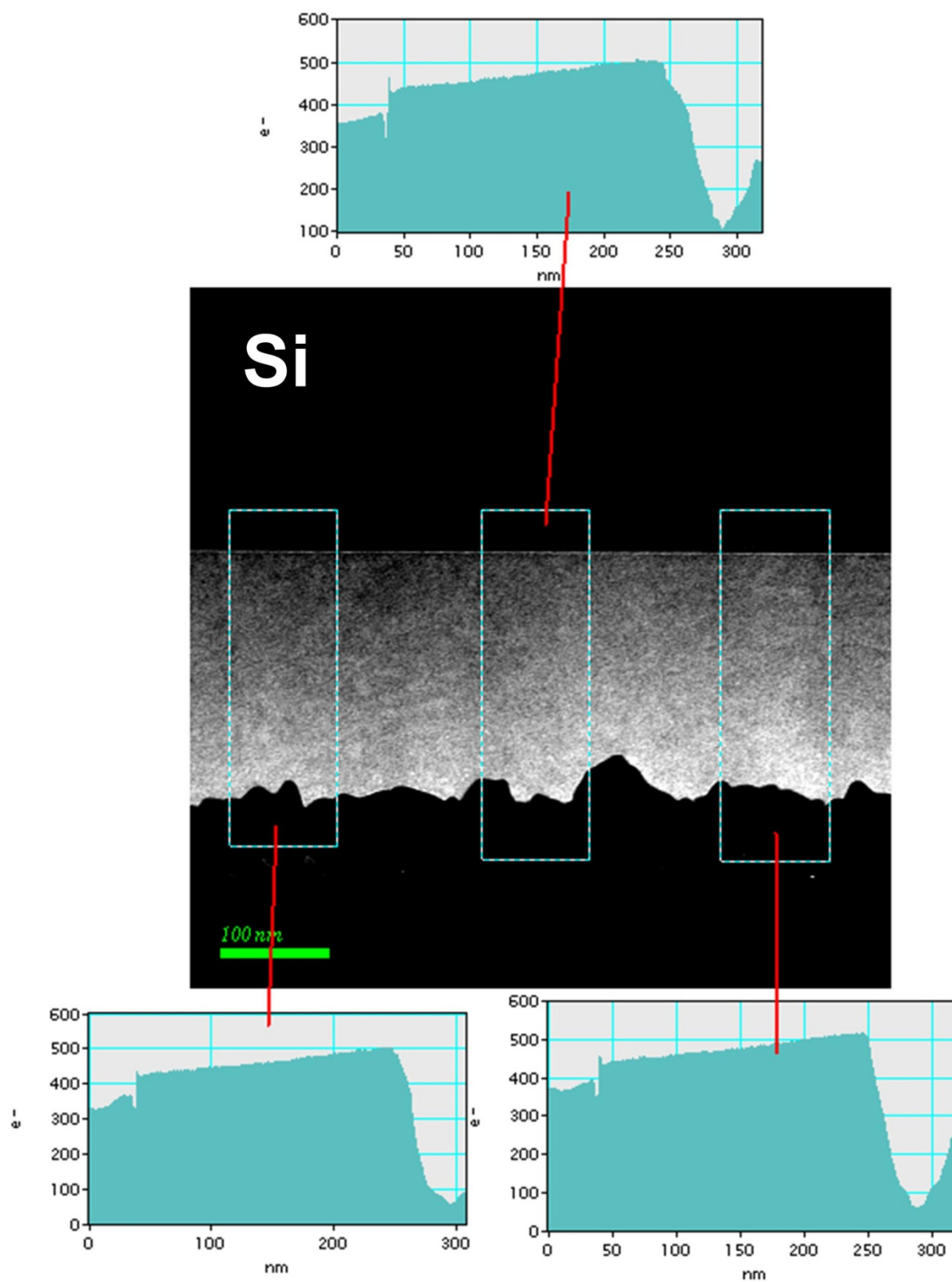
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Fig. S3 Large area cross sectional TEM images of samples with the following architecture: Si/P3HT:PCBM. Plots indicating the average pixel brightness within each rectangular area, which is related to chemical composition, are also included. The scale bars are 100 nm.

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Fig. S4 Large area cross sectional TEM images of samples with the following architecture: Si/PEDOT:PSS/P3HT:PCBM. Plots indicating the average pixel brightness within each rectangular area, which is related to chemical composition, are also included. The scale bars are 100 nm.
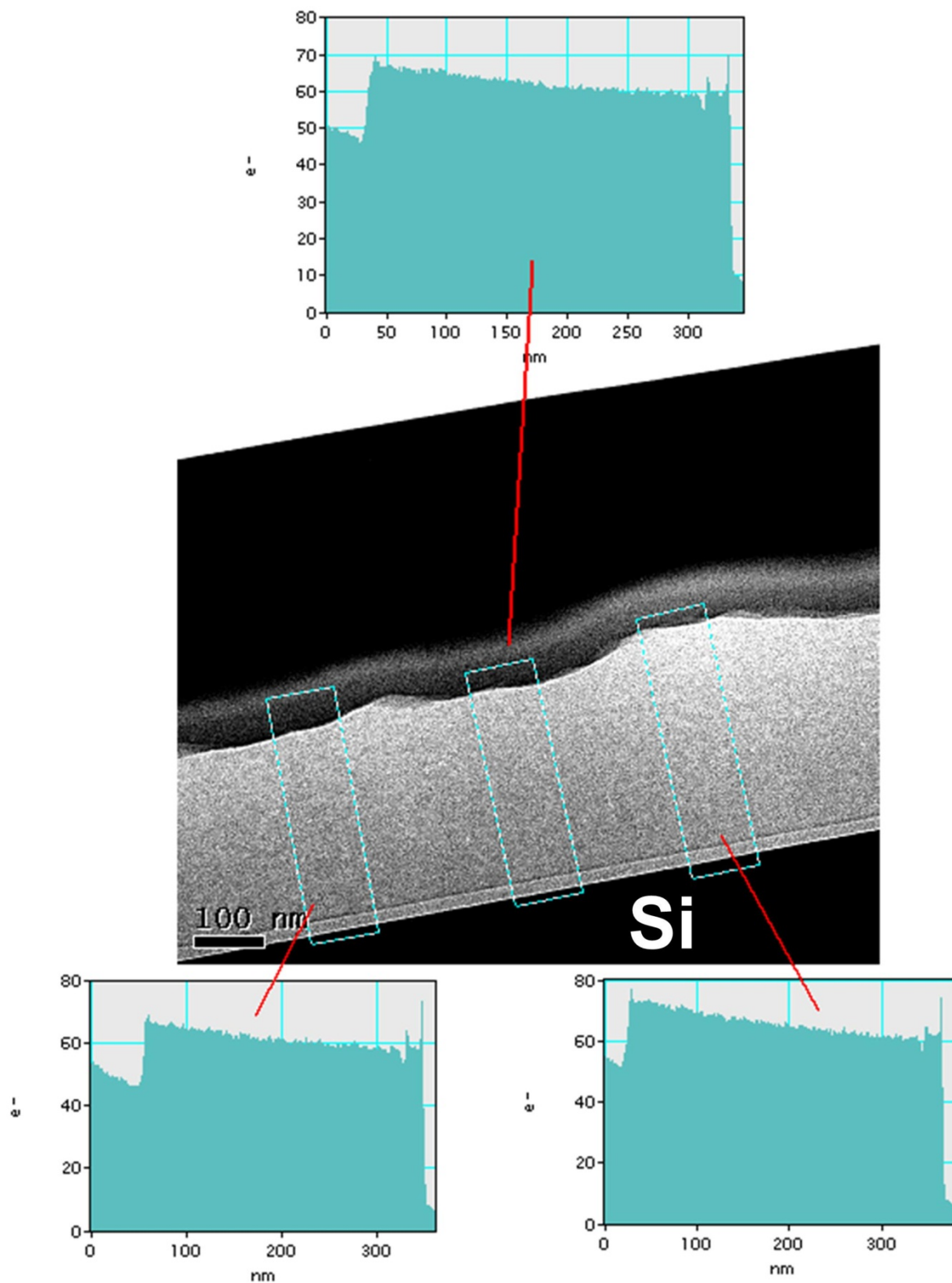
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Fig. S5 Large area cross sectional TEM images of samples with the following architecture: Si/P3CPenT/P3HT:PCBM. Plots indicating the average pixel brightness within each rectangular area, which is related to chemical composition, are also included. The scale bars are 100 nm.
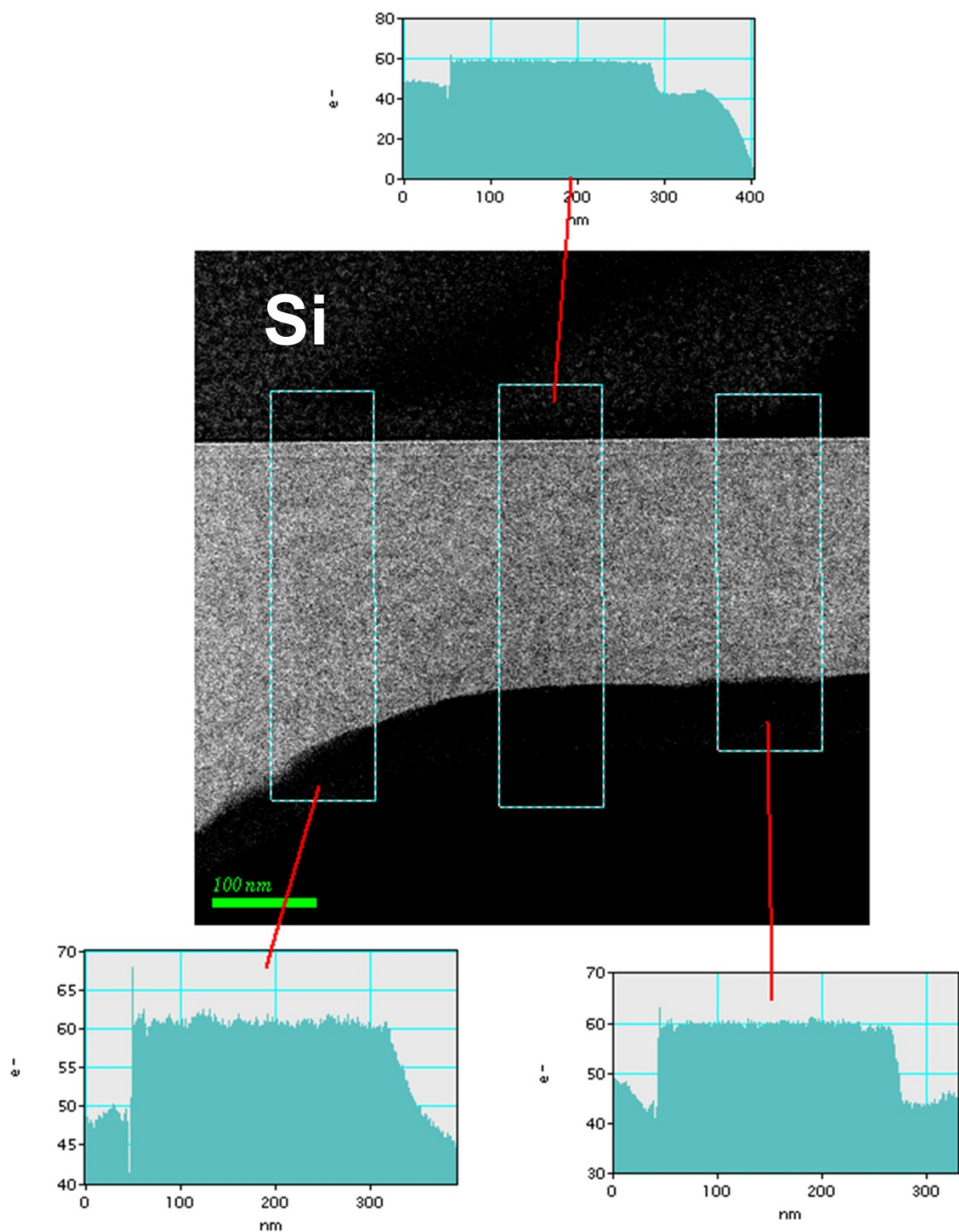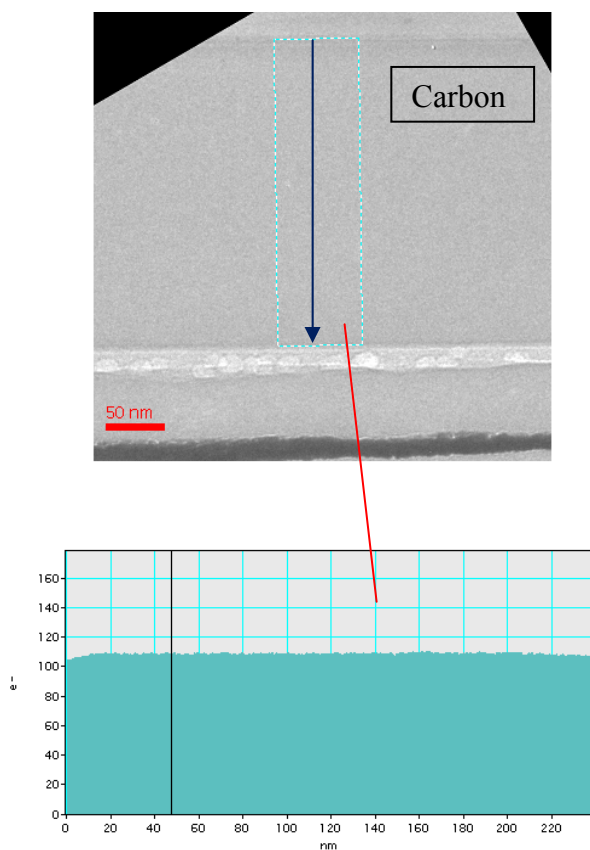
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Fig. S6 A cross sectional TEM image of a thin carbon sample which was prepared for microscopy under the same focussed ion beam conditions as the P3HT:PCBM samples shown in Figure 6 of the main text and Figure S2-S4 in this supporting information section. The TEM signal intensity profile across the carbon film is also included, and the uniform profile indicates a uniform thickness of the carbon film as prepared in the FIB instrument.
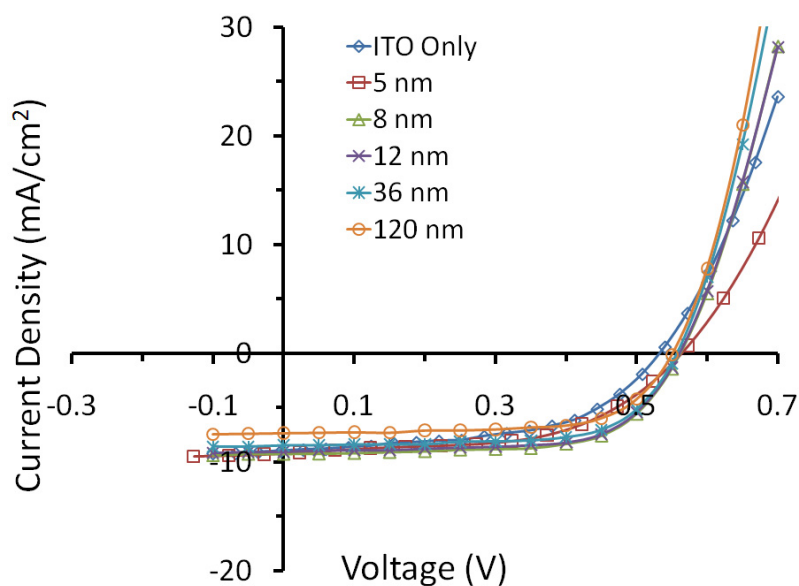
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Fig. S7 Current density-voltage curves for P3HT:PCBM PSCs fabricated with different thicknesses of P3CPenT as an HTL and illuminated with 100 mW/cm^2 simulated solar irradiation.
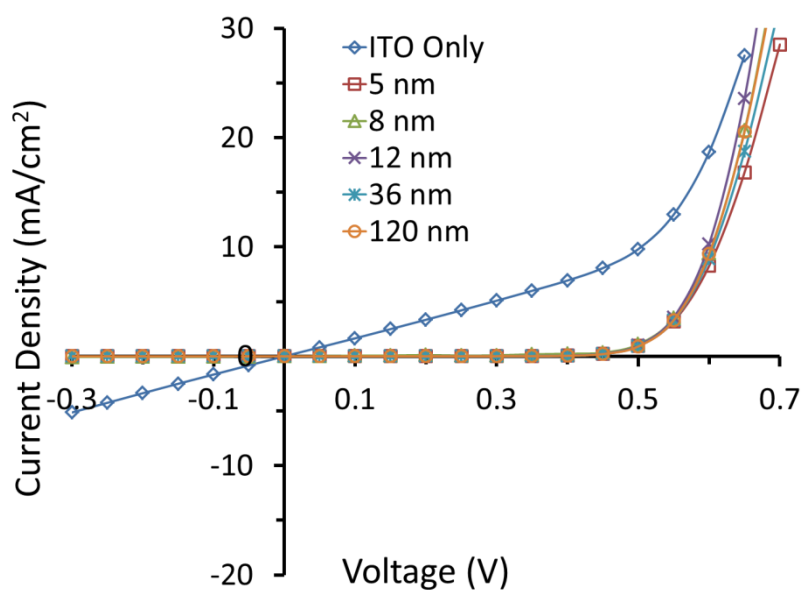
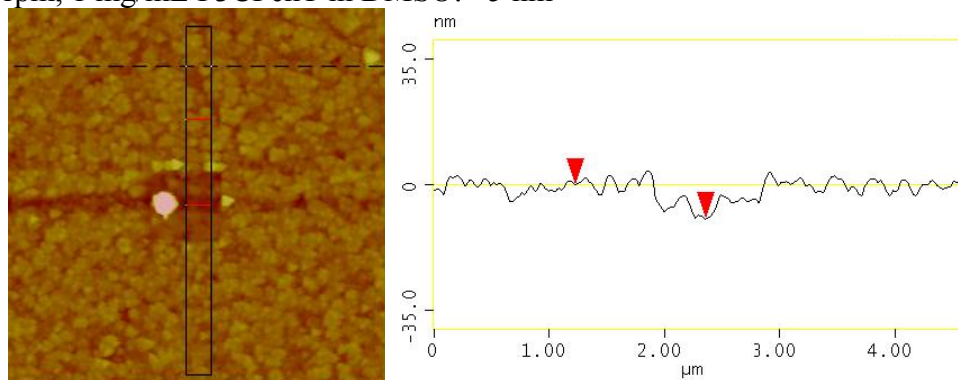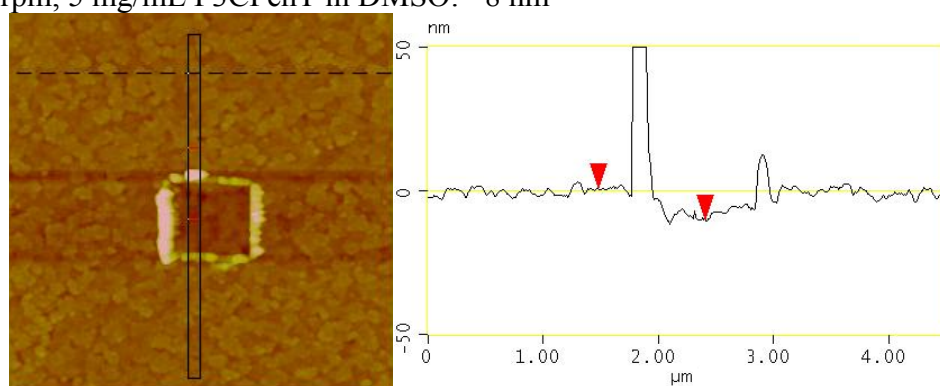**Fig. S8** Current density-voltage curves for unilluminated P3HT:PCBM PSCs fabricated with different thicknesses of P3CPenT as HTL.
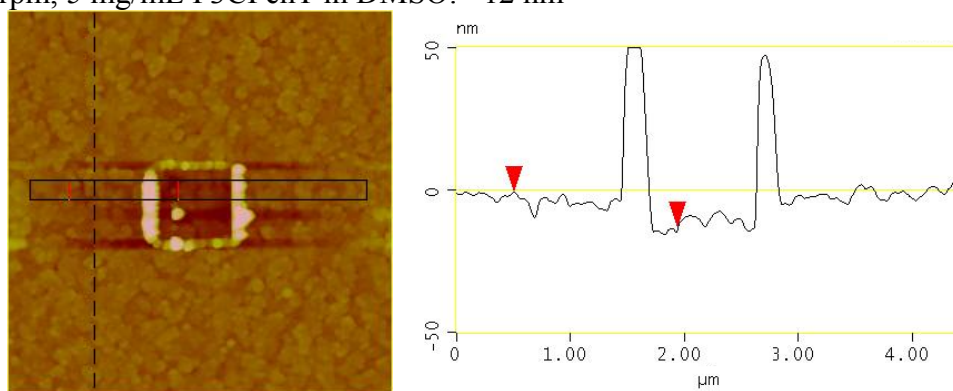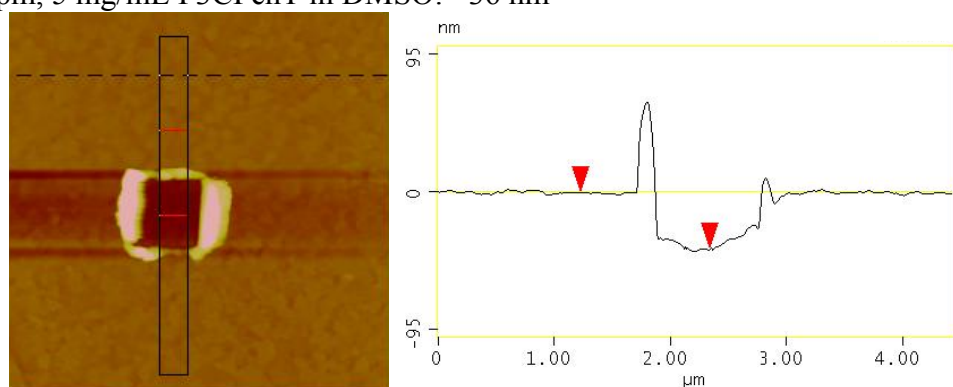
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(a) 3000 rpm, 1 mg/mL P3CPenT in DMSO: ~5 nm

(b) 3000 rpm, 5 mg/mL P3CPenT in DMSO: ~8 nm

(c) 2000 rpm, 5 mg/mL P3CPenT in DMSO: ~12 nm

(d) 600 rpm, 5 mg/mL P3CPenT in DMSO: ~36 nm

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(e) 1000 rpm, 15 mg/mL P3CPenT in DMSO: ~120 nm

Fig. S9 Determination of the average thickness of P3CPenT deposited on ITO surfaces by AFM. In (a), spin casting at 3000 rpm with 1 mg/mL P3CPenT in DMSO is found to lead to film thicknesses of ~5 nm, in (b), spin casting at 3000 rpm with 5 mg/mL P3CPenT in DMSO is found to lead to film thicknesses of ~8 nm, in (c), spin casting at 2000 rpm with 5 mg/mL P3CPenT in DMSO is found to lead to film thicknesses of ~12 nm, in (d), spin casting at 600 rpm with 5 mg/mL P3CPenT in DMSO is found to lead to film thicknesses of ~36 nm, and in (e), spin casting at 1000 rpm with 15 mg/mL P3CPenT in DMSO is found to lead to film thicknesses of ~120 nm. The red triangles were generated in the AFM analysis software, but were not used in the determination of thickness. In each panel, the AFM image dimensions are 5 μm x 5 μm.

Fig. S10 Influence of PEDOT:PSS HTL thickness over P3HT:PCBM device performance. Each point represents the average of 4 PV devices.

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Fig. S11 Normalized absorption spectra of P3HT and P3CPenT films.

Fig. S12 Degradation of photovoltaic parameters for P3HT:PCBM BHJ devices fabricated with PEDOT:PSS (30 nm) or P3CPenT (12 nm) as an HTL. A) J_{sc}; B) V_{oc}; C) FF and D) PCE.
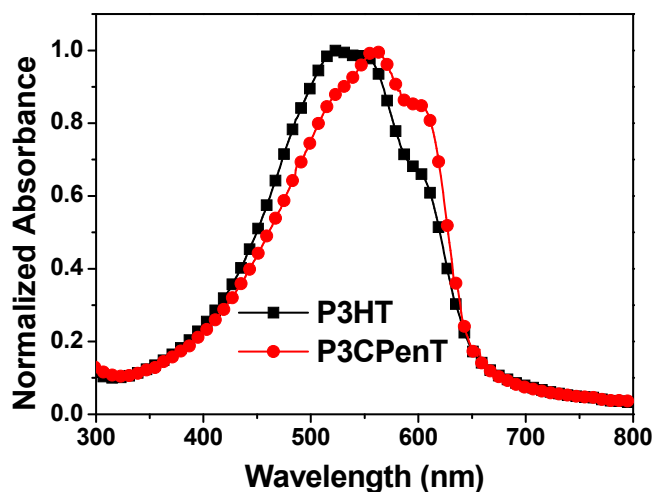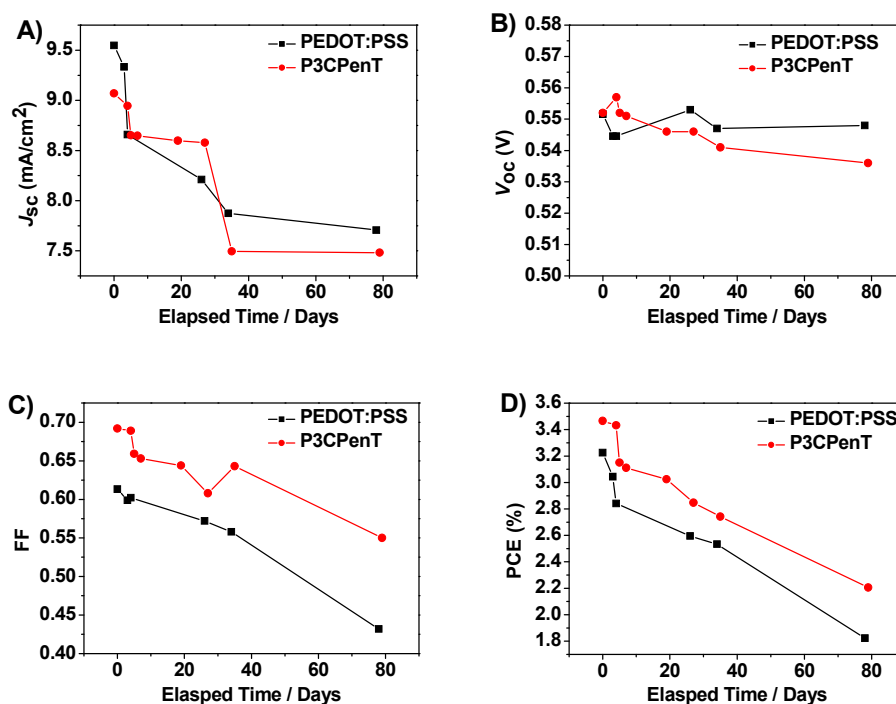
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Fig. S13 Current density-voltage curves for unilluminated P3HT:PCBM PSCs fabricated with different hole transport layers including ITO only, PEDOT:PSS and P3CPenT NWs.

Table S1 Summarized contact angles of Si substrates modified by PEDOT:PSS or P3CPenT.

	Water contact angle (°)	n-Hexadecane contact angle (°)	Surface energy (mJ/m^2)
Unmodified Si	9	9	72
Si modified by PEDOT:PSS	4	10	73
Si modified by P3CPenT	47	4	54

Table S2 The average (over nine devices) photvoltaic performance of PSCs made with P3CPenT HTLs cast from DMSO and pyridine. For DMSO-casting, a 5 mg/mL solution was spin-cast at 1000 rpm, and for pyridine-casting, a 2.5 mg/mL solution was spin-cast at 3000 rpm, both for 5 minutes. The resulting P3CPenT films were both measured via ellipsometry to be 11 nm thick. All HTL spin-casting was done at 90 °C, and the samples were annealed subsequently in air at 90 °C.

Casting Solution	J_{sc} (mA/cm^2)	V_{oc} (V)	FF	PCE (%)	R_s (Ω cm^2)	R_{sh} (kΩ cm^2)
DMSO	7.62 (0.40)	0.58 (0.004)	0.60 (0.01)	2.67 (0.12)	6.65 (0.67)	0.71 (0.13)
Pyridine	6.57 (0.34)	0.57 (0.003)	0.58 (0.02)	2.17 (0.09)	7.76 (0.63)	0.58 (0.23)

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Table S3 Average photovoltaic parameters of devices fabricated with various HTLs: only ITO, PEDOT:PSS (30 nm), P3CPenT (8 nm) and dip-cast P3CPenT. Standard deviations are included in parentheses. The fourth entry confirms that PSCs based on P3CPenT HTLs formed by dip-casting/absorption methods are also functional.

HTL	J_{sc} (mA/cm^2)	V_{oc} (V)	FF	PCE (%)	R_s (Ω cm^2)	R_{sh} (kΩ cm^2)	Best PCE (%)
Only ITO	9.24 (0.16)	0.52 (0.01)	0.51 (0.01)	2.44 (0.1)	6.03 (0.12)	0.34 (0.09)	2.5
PEDOT:PSS	9.24 (0.09)	0.55 (0.003)	0.61 (0.006)	3.1 (0.13)	8.17 (0.14)	1.78 (0.03)	3.4
P3CPenT	9.26 (0.18)	0.56 (0.002)	0.67 (0.006)	3.42 (0.12)	6.45 (0.20)	1.81 (0.04)	3.7
P3CPenT*	9.17 (0.06)	0.56 (0.005)	0.60 (0.005)	3.06 (0.06)	6.73 (0.17)	1.79 (0.13)	3.1

* This P3CPenT layer was formed by immersing an ITO-coated substrate into P3CPenT solution (DMSO) as described in the experimental section.

References

S1   D. K. Owens and R. C. Wendt, *J. Appl. Polym. Sci.,* 1969, **13**, 1741.
S2   B. Jańczuk and E. Chibowski, *J. Coll. Inter. Sci.*, 1983, **95**, 268.