

## A benzotri thiophene-based low band gap polymer for polymer solar cells with high open-circuit voltage

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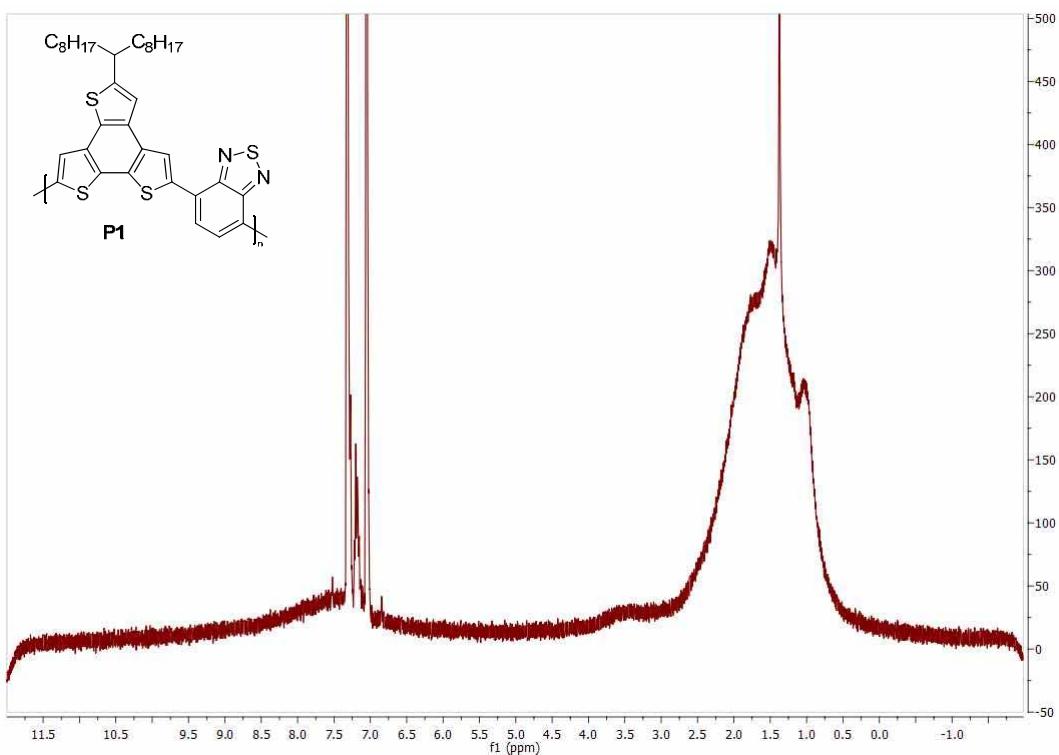
## Supporting Information

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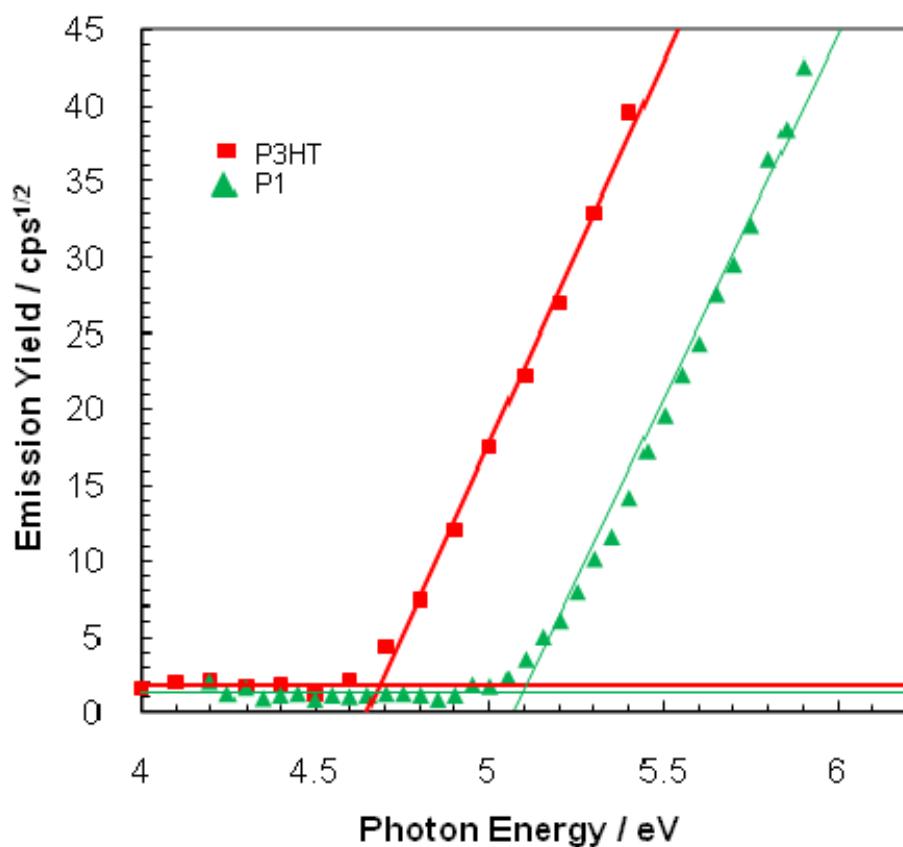
## Experimental Section

All chemicals were purchased from commercial suppliers unless otherwise specified.  $^1\text{H}$  NMR spectra were recorded on a BRUKER DRX400 spectrometer in d<sub>4</sub>-1,2-dichlorobenzene solution at 333 K. Number-average ( $M_n$ ) and weight-average ( $M_w$ ) molecular weights were determined with an Agilent Technologies 1200 series GPC in chlorobenzene at 80 °C, using two PL mixed B columns in series, and calibrated against narrow polydispersity polystyrene standards. UV-Vis absorption spectra were recorded on a UV-1601 Shimadzu UV-Vis spectrometer. Photo Electron Spectroscopy in Air (PESA) measurements were recorded with a Riken Keiki AC-2 PESA spectrometer with a power setting of 5 nW and a power number of 0.5. AFM images were obtained with a Picoscan PicoSPM LE scanning probe in tapping mode.

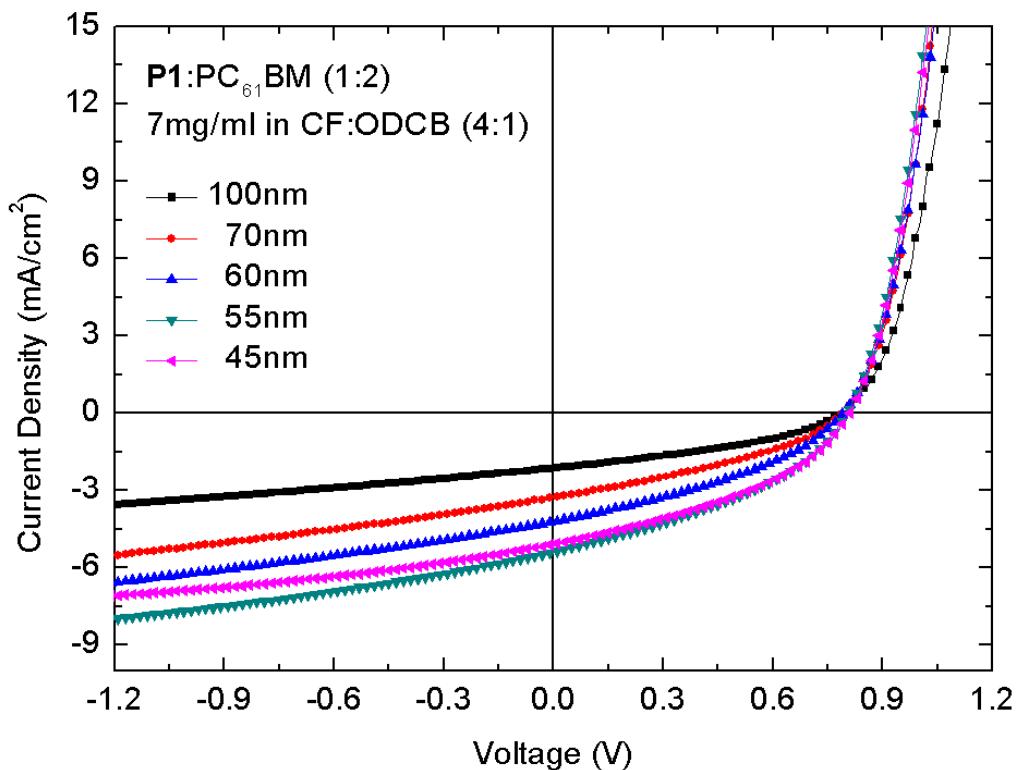
**Poly[(5-(1-octynonyl)benzo[1,2-b:3,4-b':5,6-d'']trithiophene-2,8-diyl)-alt-co-(2,1,3-benzothiadiazole-4,7-diyl)] (P1).** A 25 mL glass vial was charged with 2,8-dibromo-5-(1-octynonyl)benzo[1,2-b:3,4-b':5,6-d'']trithiophene (600 mg, 0.93 mmol), 4,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzo[c][1,2,5]thiadiazole (362 mg, 0.93 mmol), tris(dibenzylideneacetone) dipalladium (17 mg, 0.02 mmol), tri(o-tolyl) phosphine (23 mg, 0.08 mmol), Aliquat 336 (several drops) and toluene (20 ml). The mixture was degassed with argon for 30 minutes before 1 mL of degassed sodium carbonate solution (1.0 M) was added. The resulting biphasic mixture was degassed for 10 minutes and then heated at 120 °C in an oil bath for 72 hours. After reaction the crude polymer was precipitated in methanol and further purified by Soxhlet extractions with acetone, cyclohexane, dichloromethane and chloroform, each for 24 hours. Remaining palladium residues were removed by vigorously stirring a polymeric chlorobenzene solution with an aqueous sodium diethyldithiocarbamate solution for 1 hour at 60 °C. Afterwards the organic phase was separated from the aqueous phase and washed several times with water. The polymeric solution was concentrated under reduced pressure and precipitated into methanol. **P1** (434 mg, 0.67 mmol, 72 %) was recovered as a dark blue solid. GPC (chlorobenzene, 80 °C):  $M_n = 41.1$  kDa,  $M_w = 253.7$  kDa, PDI = 6.2.  $^1\text{H}$  NMR (400 MHz, 1,2-dichlorobenzene-d<sub>4</sub>, 60 °C):  $\delta$  (ppm) 8.4-6.8 (br, 5H), 3.8-3.1 (br, 1H), 2.8-0.5 (br, 34H).



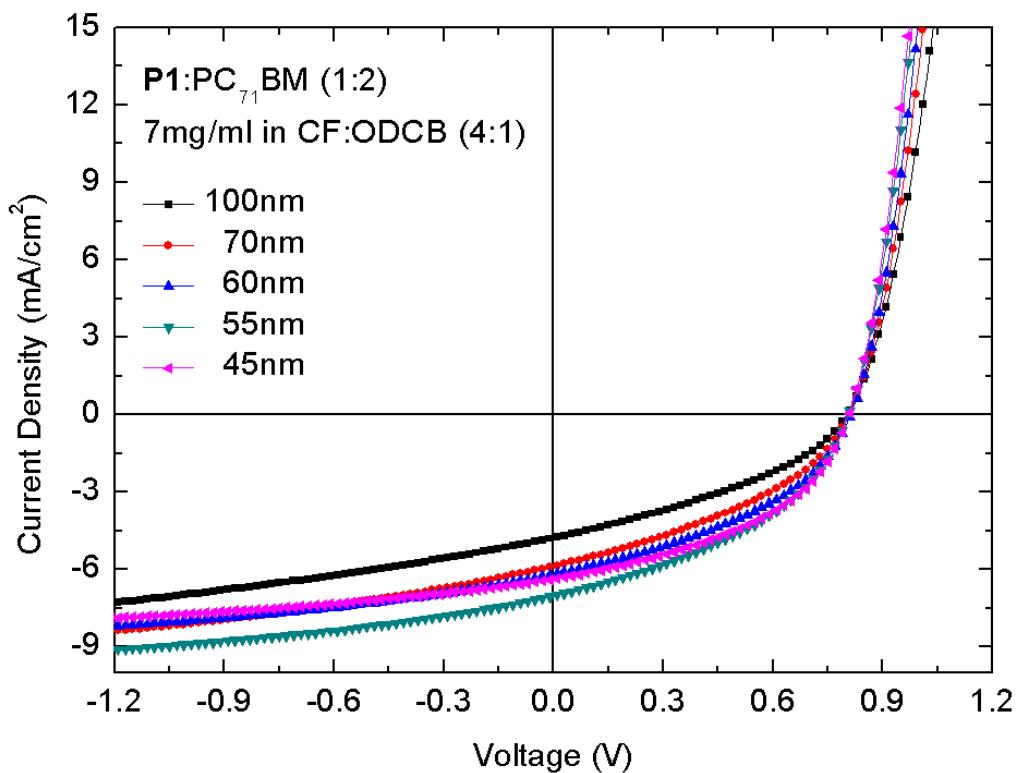
**Figure S1** <sup>1</sup>H NMR spectrum of P1.



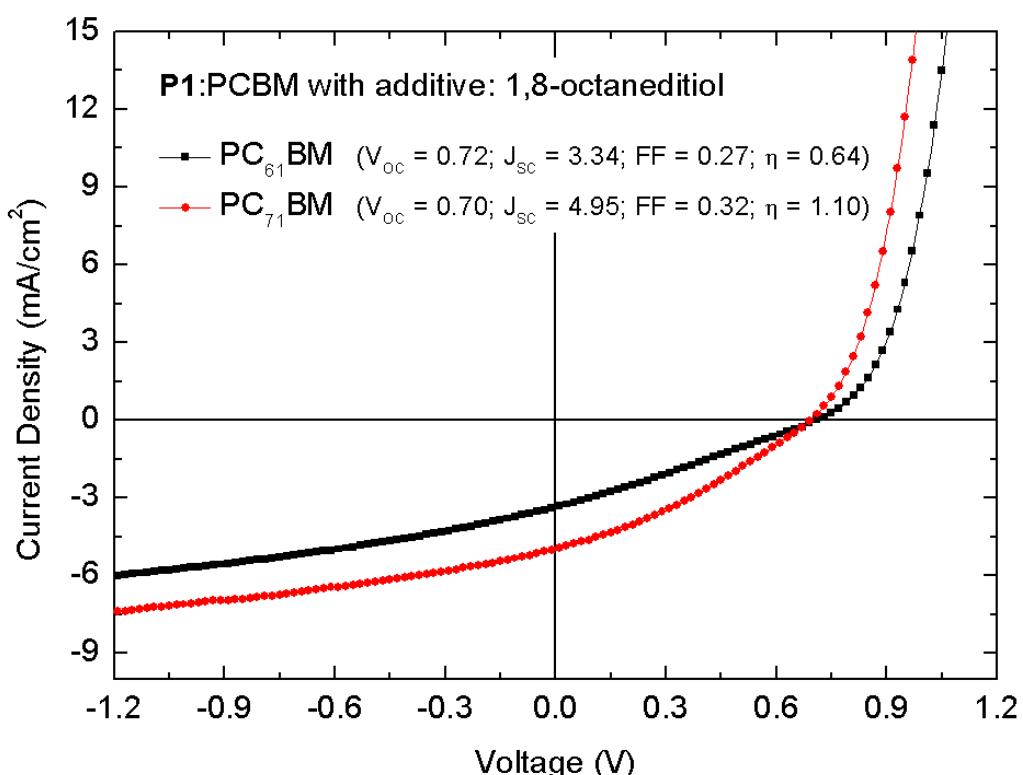
**Figure S2** Photo Electron Spectroscopy in Air (PESA) spectra of thin films of P3HT and P1.



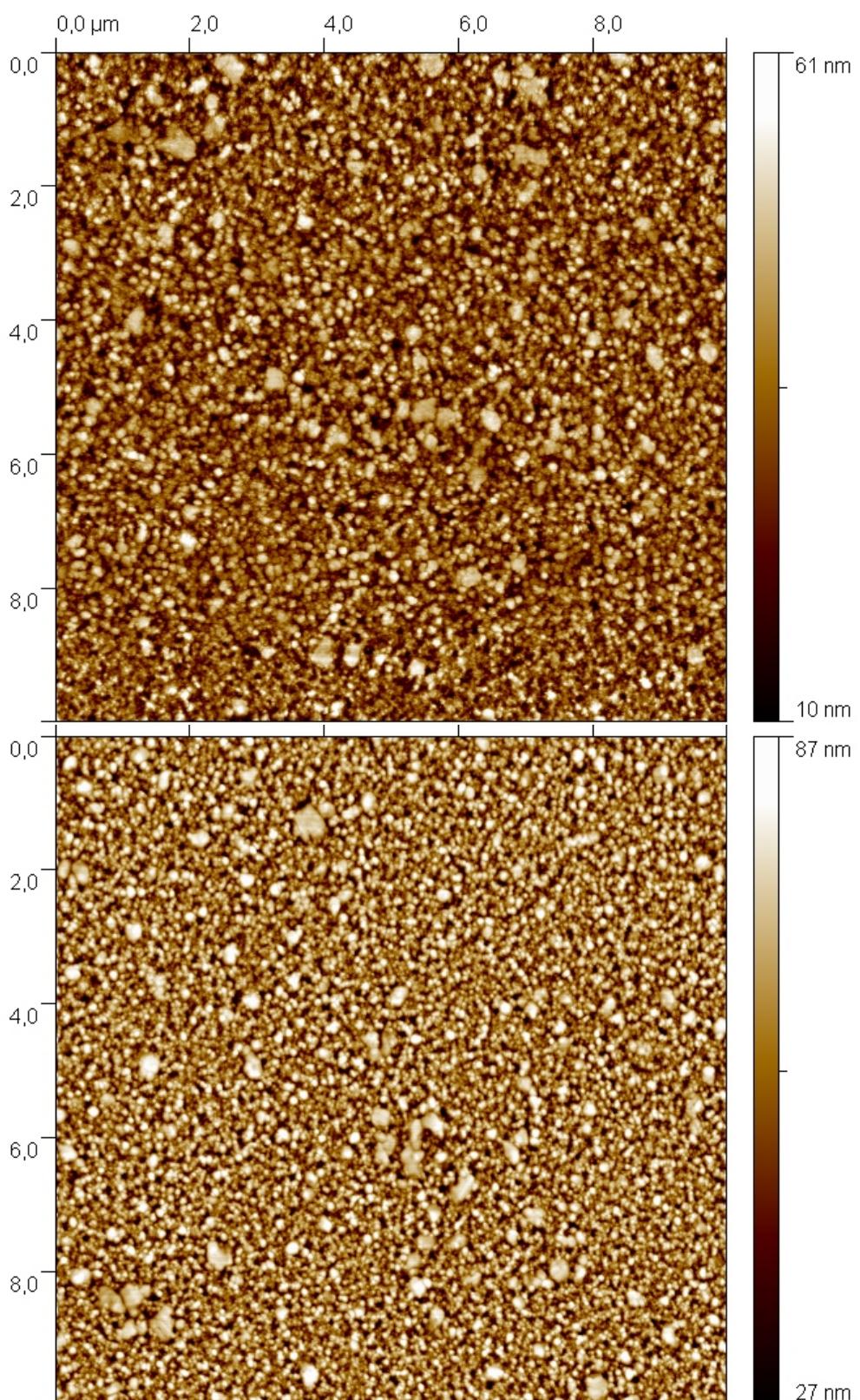
**Figure S3** *J-V* characteristics of the **P1:PC<sub>61</sub>BM** devices with different thicknesses of the photoactive layer under 100 mW/cm<sup>2</sup> AM1.5G simulated solar illumination.



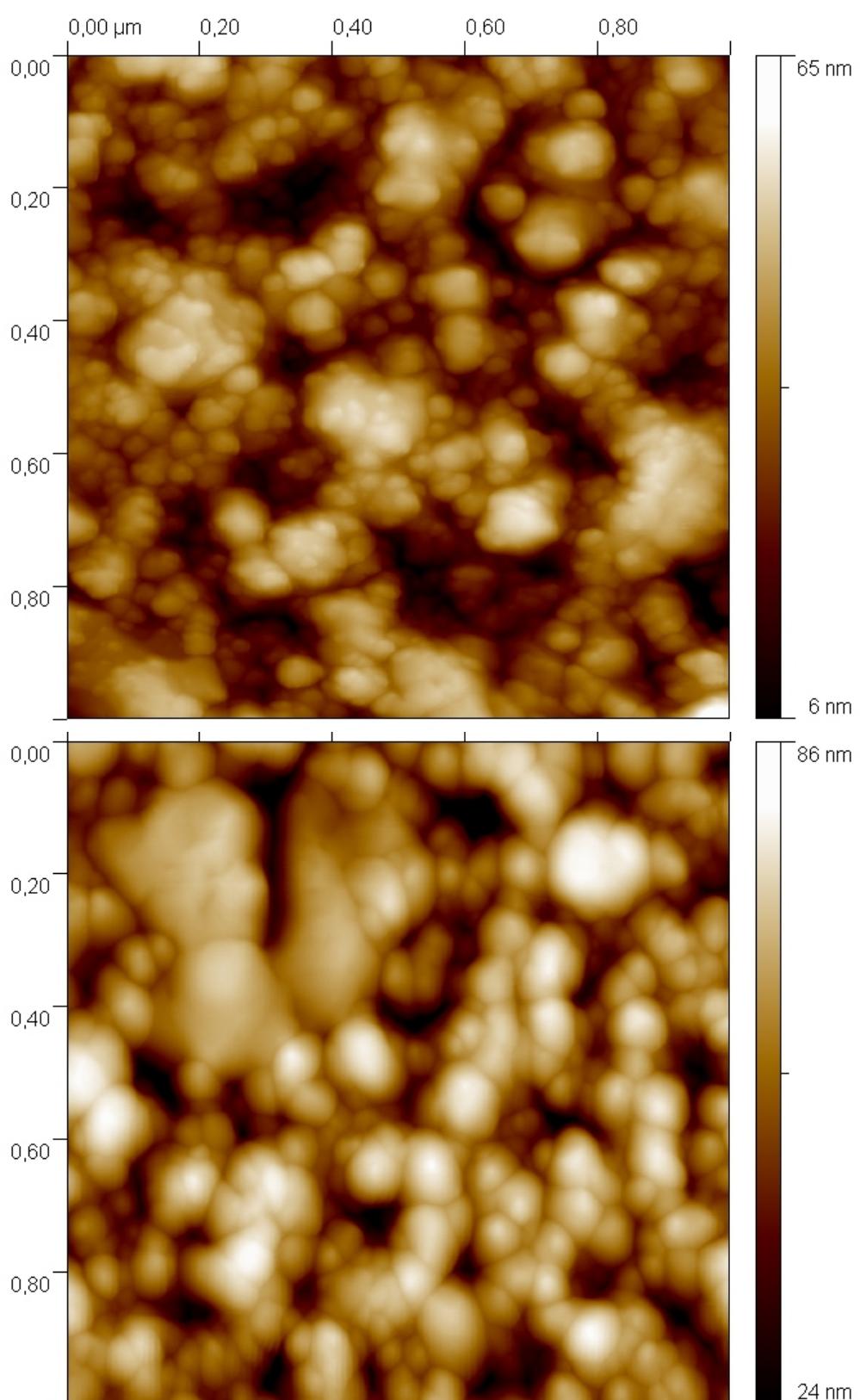
**Figure S4** *J-V* characteristics of the **P1:PC<sub>71</sub>BM** devices with different thicknesses of the photoactive layer under 100 mW/cm<sup>2</sup> AM1.5G simulated solar illumination.



**Figure S5**  $J$ - $V$  characteristics of the best P1:PCBM devices with 1,8-octanedithiol additive under 100 mW/cm<sup>2</sup> AM1.5G simulated solar illumination.



**Figure S6** AFM images (tapping-mode,  $10 \times 10 \mu\text{m}$ ) of **P1:PC<sub>61</sub>BM** (top) and **P1:PC<sub>71</sub>BM** (bottom) blends; both samples are 55 nm thick 1:2 **P1**:fullerene blends.



**Figure S7** AFM images (tapping-mode,  $1 \times 1 \mu\text{m}$ ) of **P1:PC<sub>61</sub>BM** (top) and **P1:PC<sub>71</sub>BM** (bottom) blends; both samples are 55 nm thick 1:2 **P1**:fullerene blends.