Supporting Information

Molar Mass versus Polymer Solar Cell Performance: Highlighting the Role of Homocouplings

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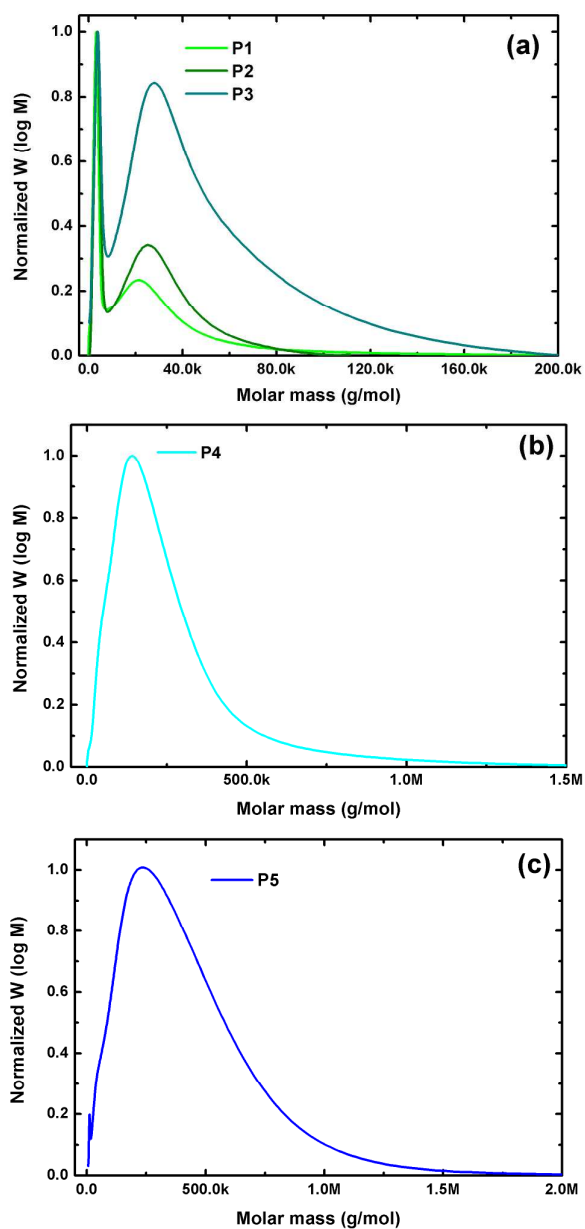# 1. GPC profiles on a linear scale

Figure S1. Molar mass distributions of the as received PTB7 batches (as measured by GPC) plotted on a linear scale: (a) P1−P3, (b) P4, (c) P5.
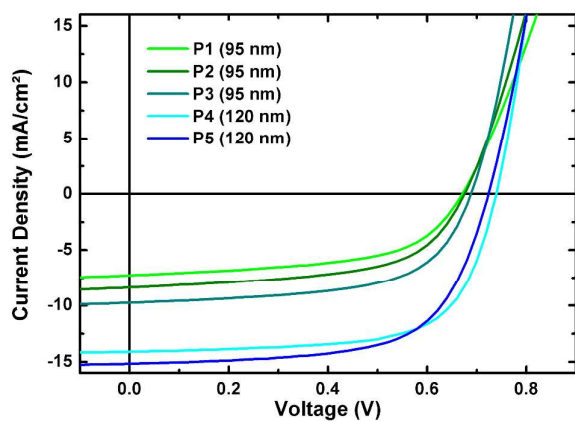
2. *J-V* curves for the optimized solar cells

Figure S2. Current density-voltage curves for the optimized solar cells prepared with the different PTB7 batches. The active area of each cell was 3 mm². The corresponding optimized active layer thicknesses are shown in the legend.

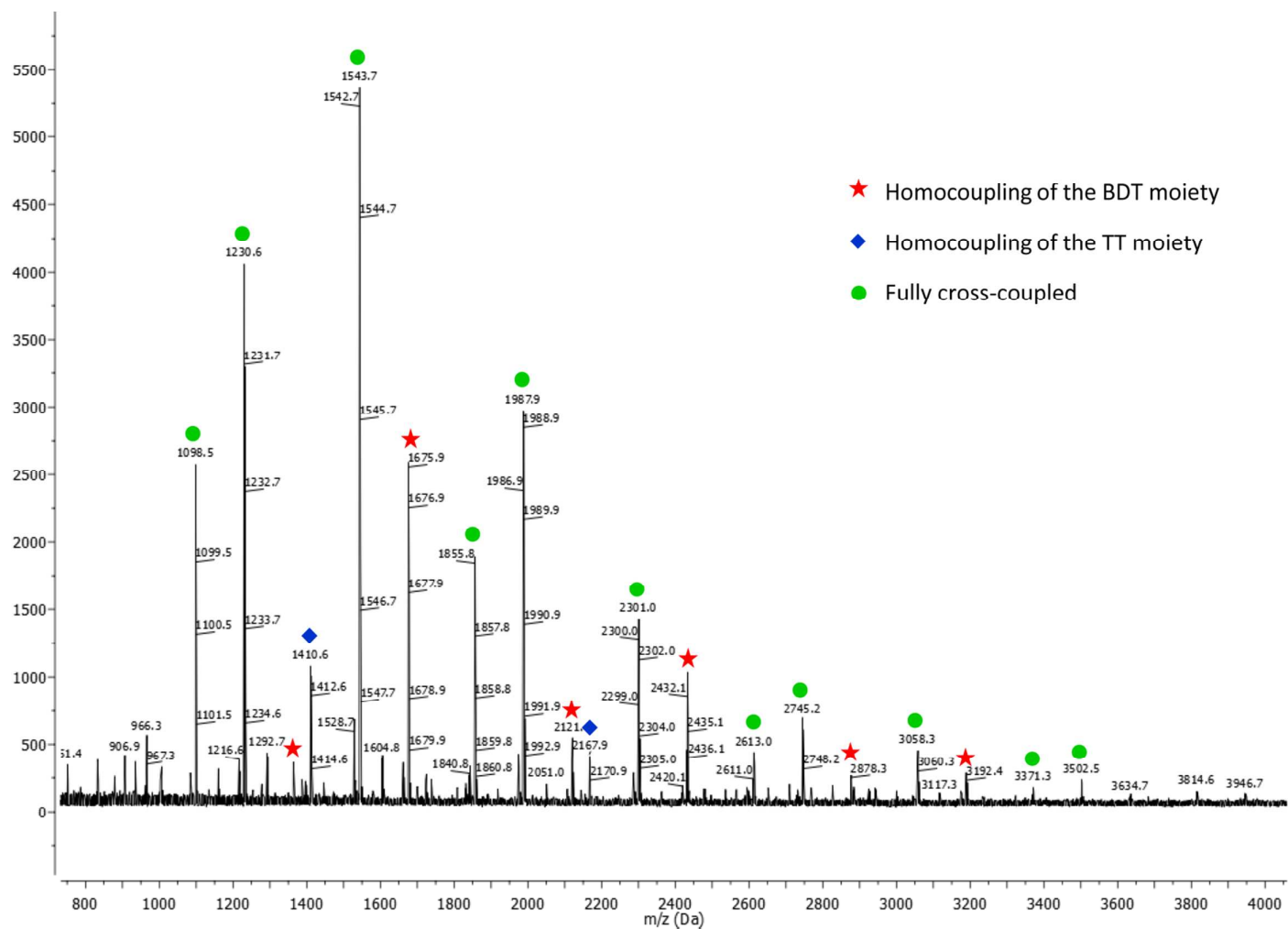## 3. MALDI-TOF mass spectra and analysis

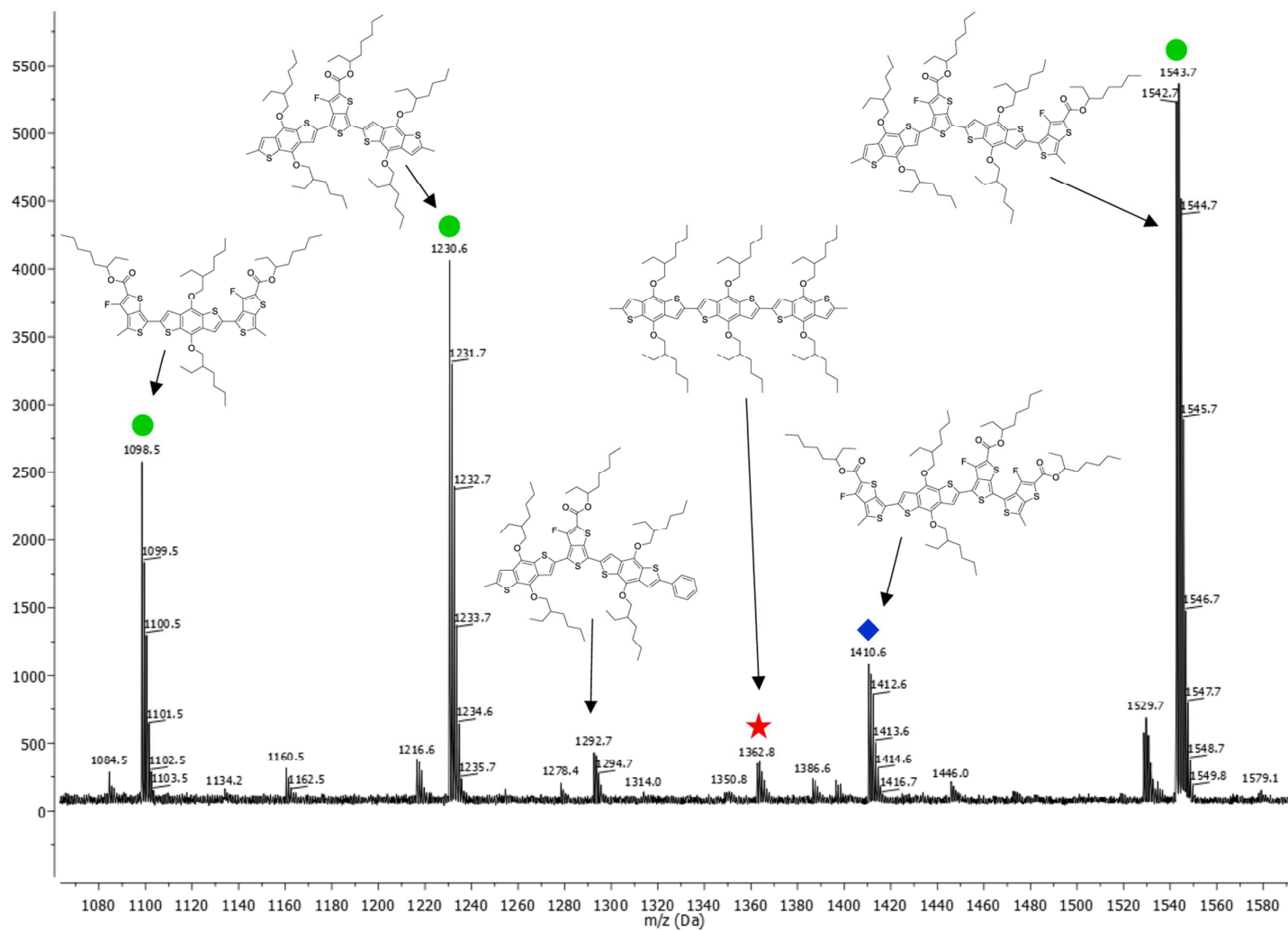**Figure S3.** MALDI-TOF mass spectrum for PTB7 batch P1.

Figure S4. MALDI-TOF mass spectrum for PTB7 batch P1 (zoom from *m/z* 1070–1590 g mol^{-1}), with identification of the different species.
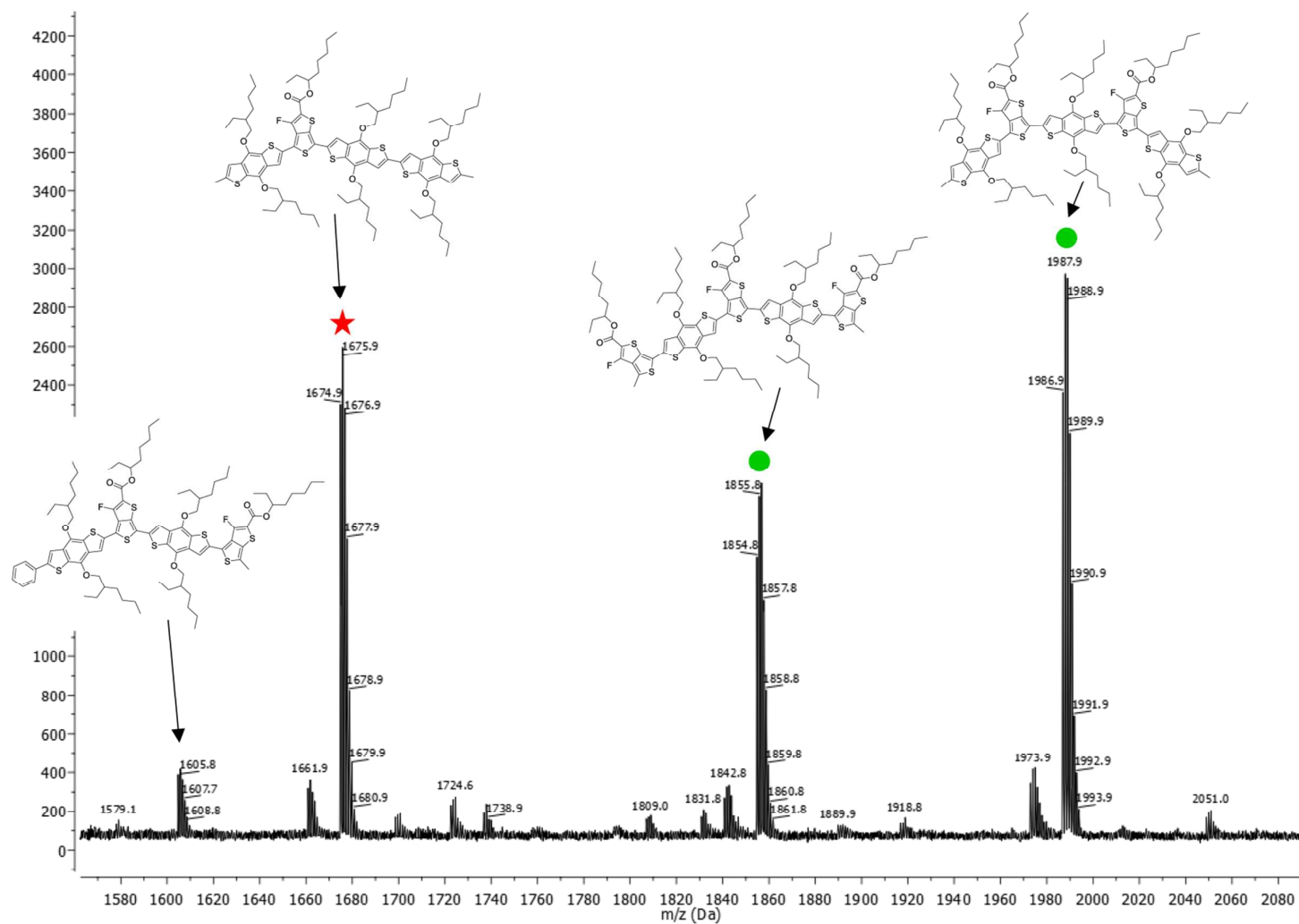
Figure S5. MALDI-TOF mass spectrum for PTB7 batch P1 (zoom from *m/z* 1570–2090 g mol^{-1}), with identification of the different species.
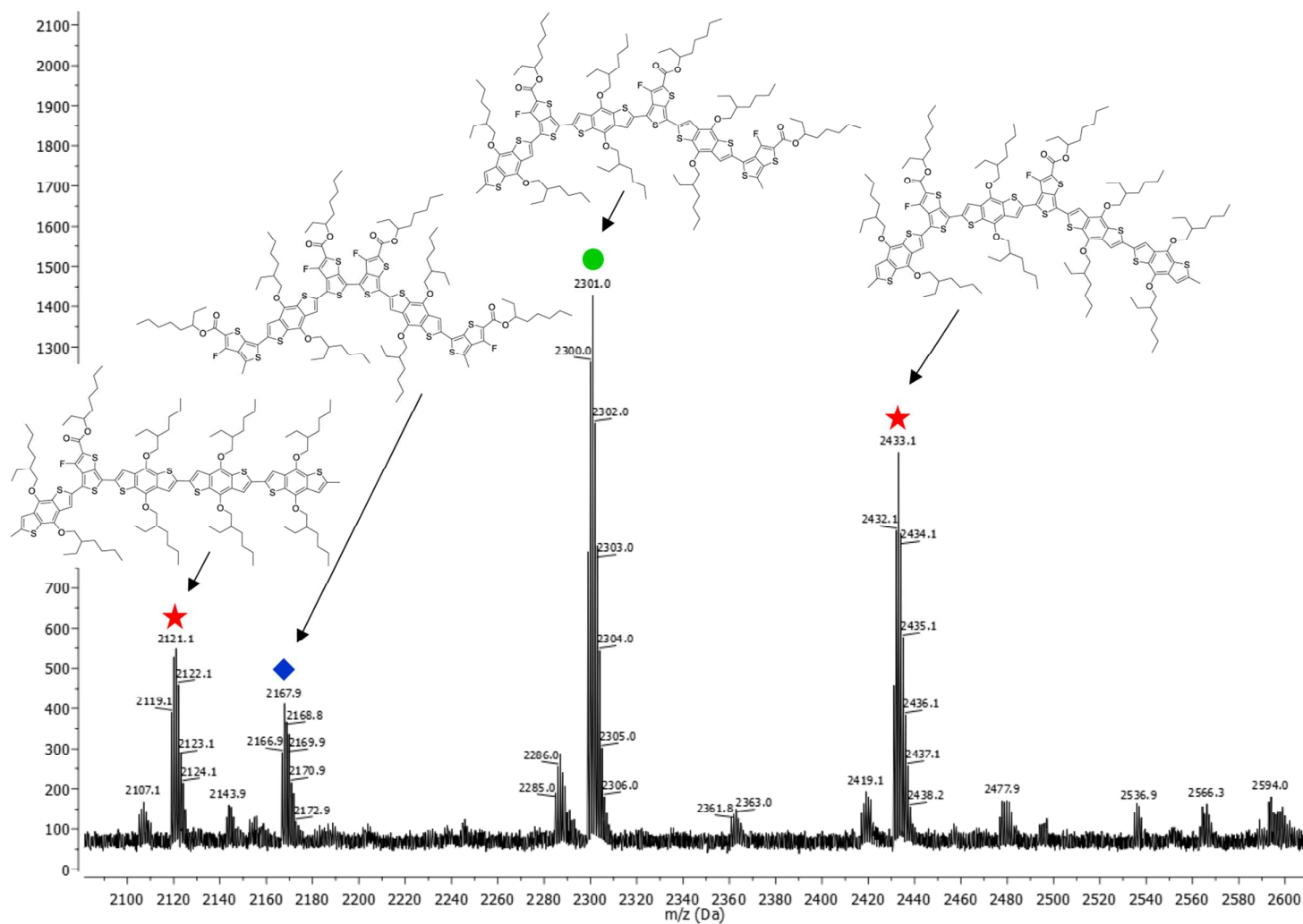
Figure S6. MALDI-TOF mass spectrum for PTB7 batch P1 (zoom from *m/z* 2090–2610 g mol^{-1}), with identification of the different species.
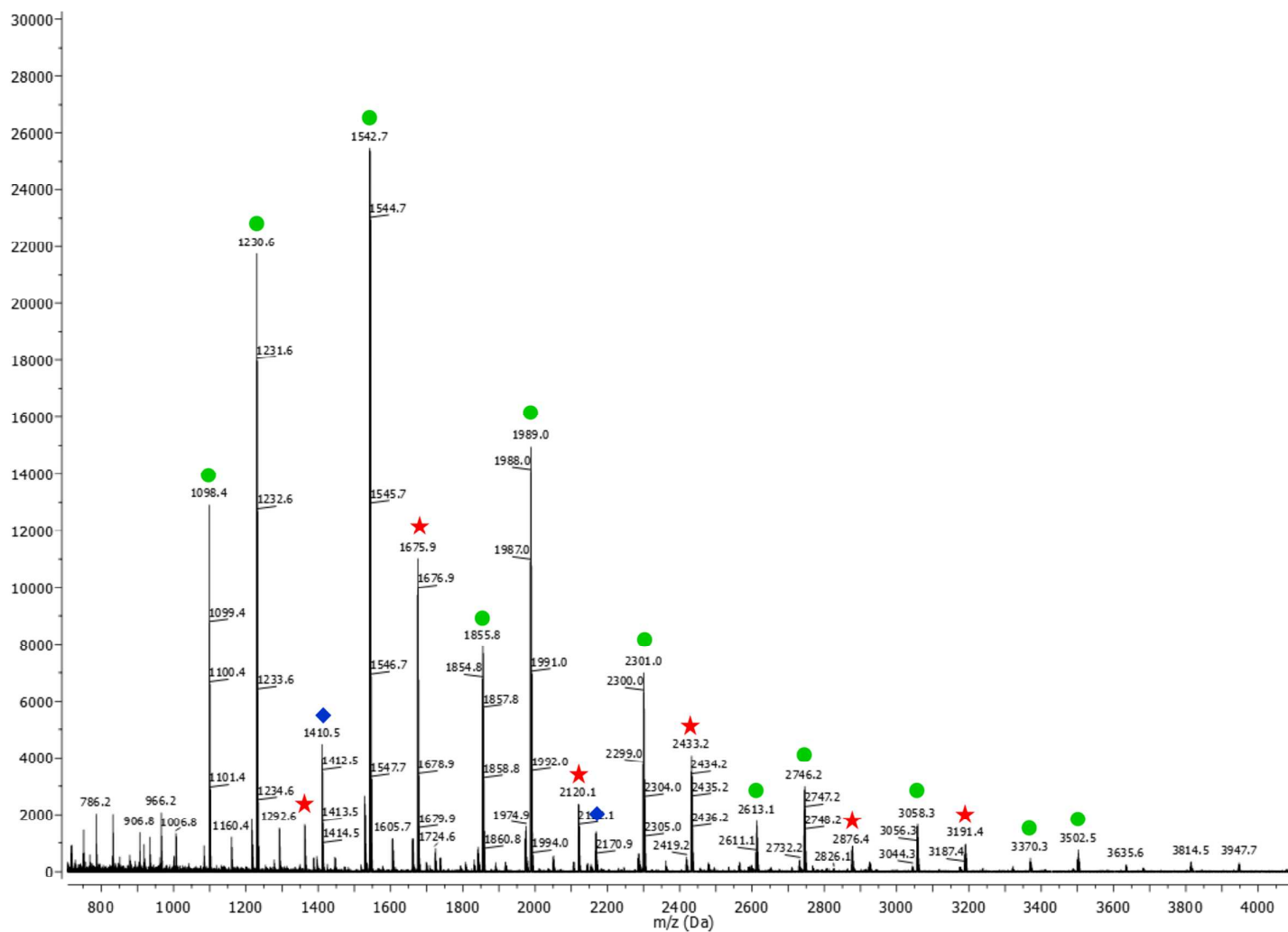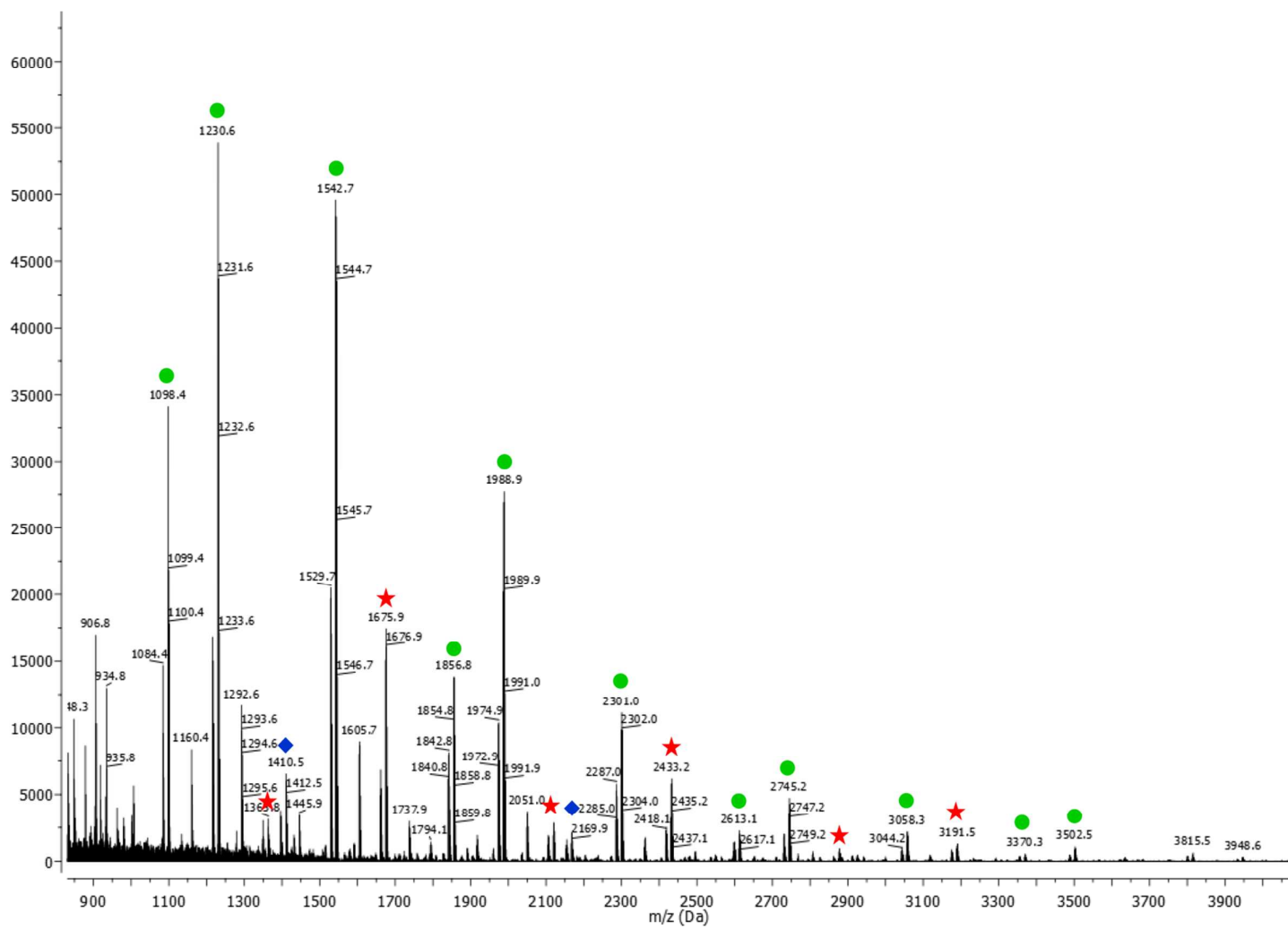
Figure S7. MALDI-TOF mass spectrum for PTB7 batch P2.

Figure S8. MALDI-TOF mass spectrum for PTB7 batch P3.
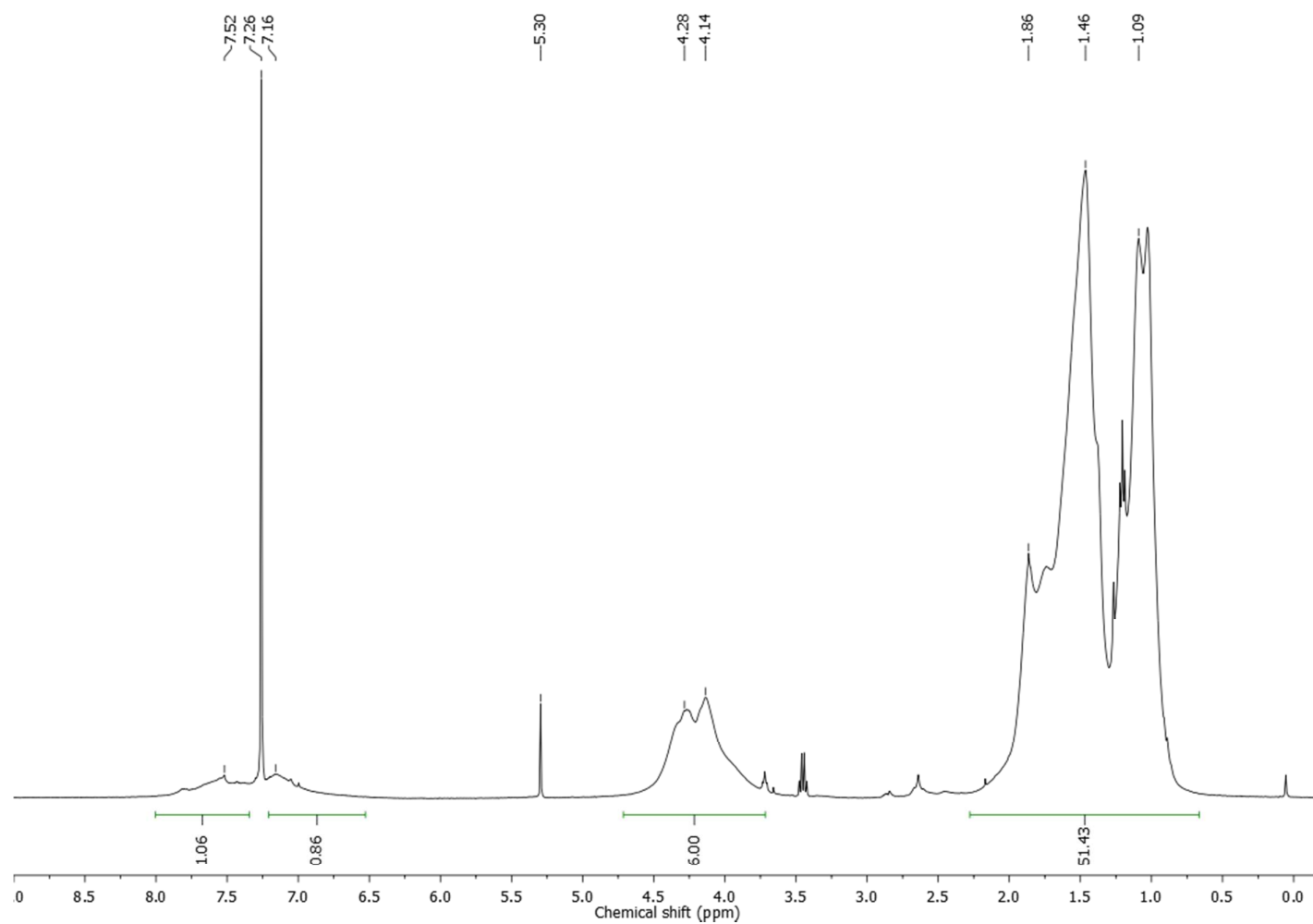
4. ^{1}H NMR spectra of P1 and P4

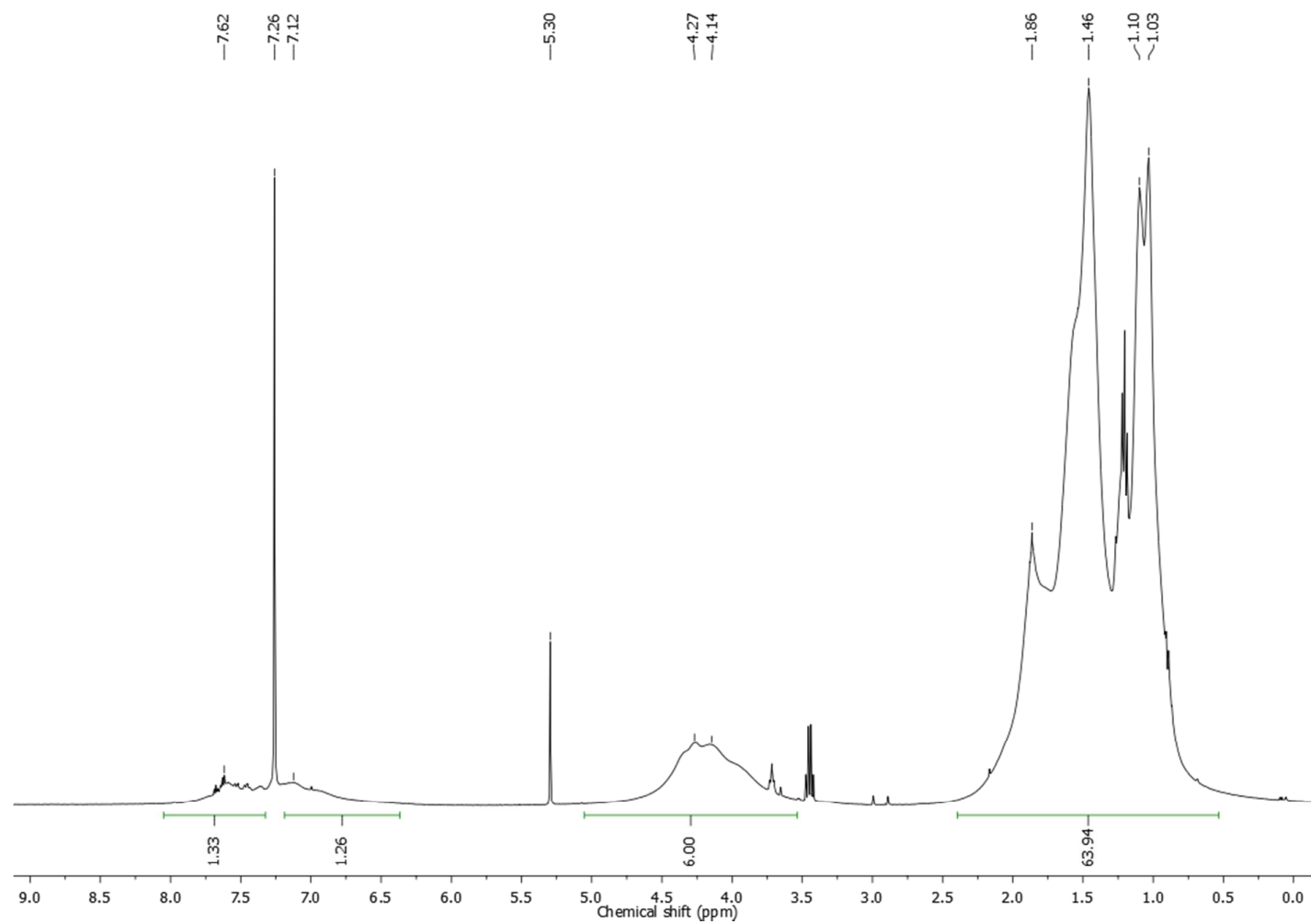**Figure S9.** ^{1}H NMR spectrum of PTB7 batch P1 (400 MHz, CDCl$_3$:CS$_2$ 1:3).

Figure S10. ^{1}H NMR spectrum of PTB7 batch P4 (400 MHz, CDCl$_3$:CS$_2$ 1:3).

5. XRD data

Table S1. Alkyl stacking distance and coherence length of the studied PTB7:PC$_{71}$BM blend films.

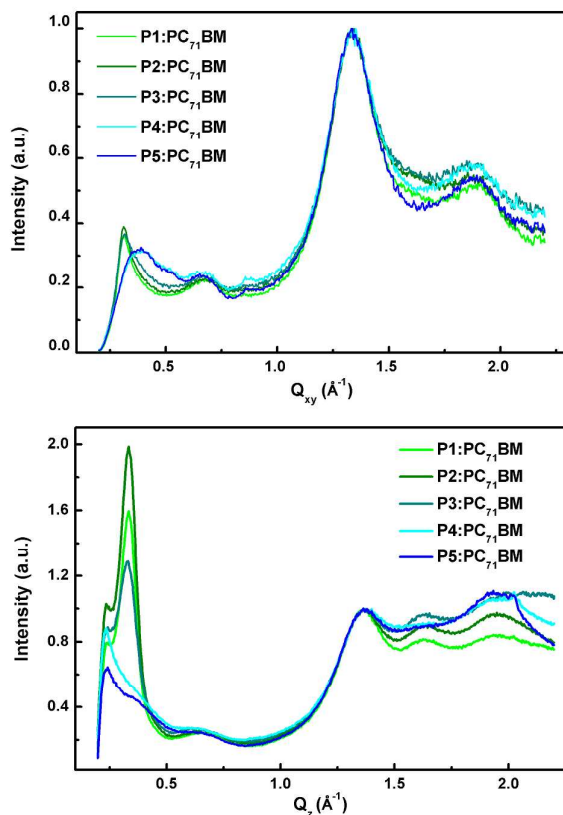| Batch	Alkyl coherence length (Å)	Alkyl stacking distance (Å)	π-π coherence length (Å)	π-π stacking distance (Å)
P1	71 ±8	20.1 ±0.3	28 ±9	3.9 ±0.1
P2	72 ±8	20 ±0.3	26 ±9	3.9 ±0.1
P3	57 ±6	19.9 ±0.3	22 ±9	3.9 ±0.1
P4	29 ±9	17.4 ±0.3	22 ±9	3.9 ±0.1
P5	29 ±9	17.4 ±0.3	15 ±9	3.9 ±0.1

Figure S11. 2-Dimensional X-ray diffraction patterns for the studied PTB7:PC$_{71}$BM blend films.
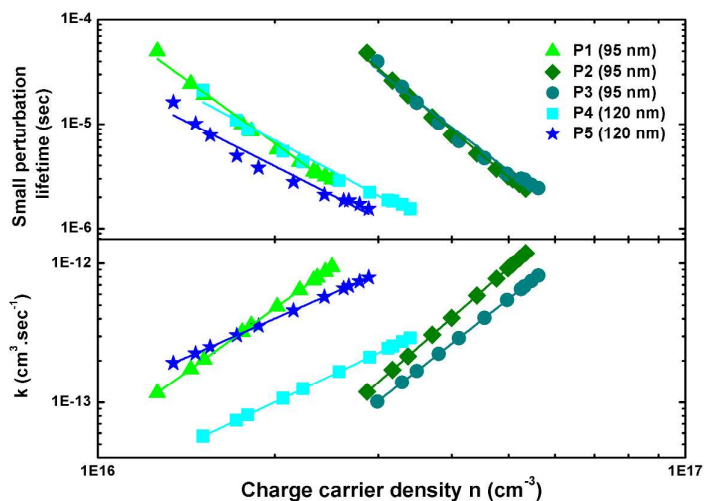
6. TPV/TPC analysis

Figure S12. Small perturbation lifetime and recombination coefficient *k* in function of the charge carrier density as determined by TPV/TPC for the cells with optimal layer thickness.
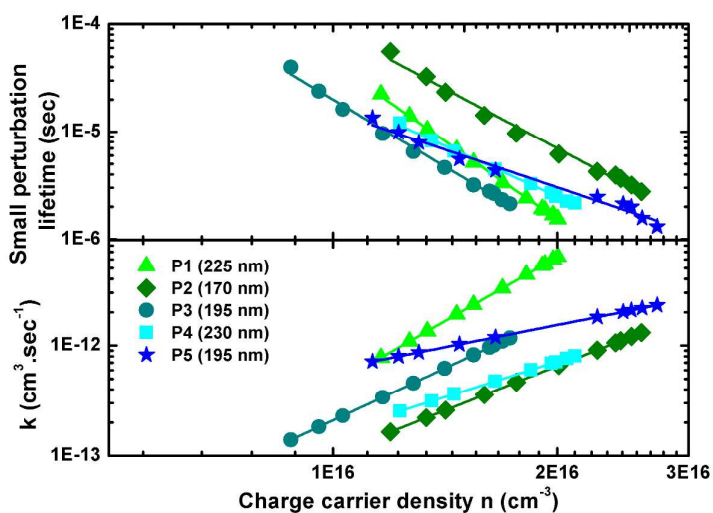

Figure S13. Small perturbation lifetime and recombination coefficient *k* in function of the charge carrier density as determined by TPV/TPC for cells with thicker active layers (>170 nm).
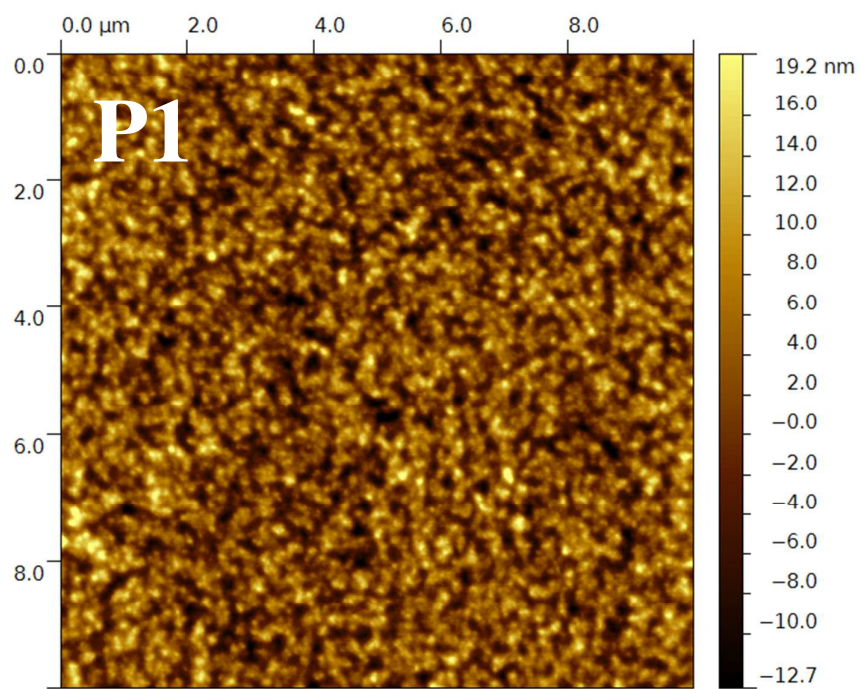
7. AFM images

Figure S14. PF-QNM AFM image (10x10 μm) for the PTB7:PC$_{71}$BM blend film based on P1.
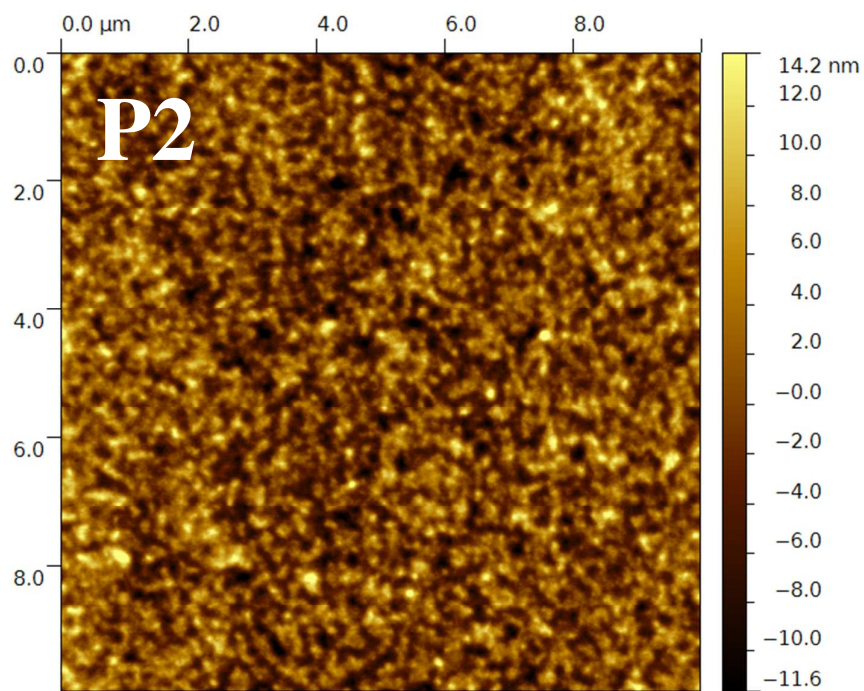

Figure S15. PF-QNM AFM image (10x10 μm) for the PTB7:PC$_{71}$BM blend film based on P2.
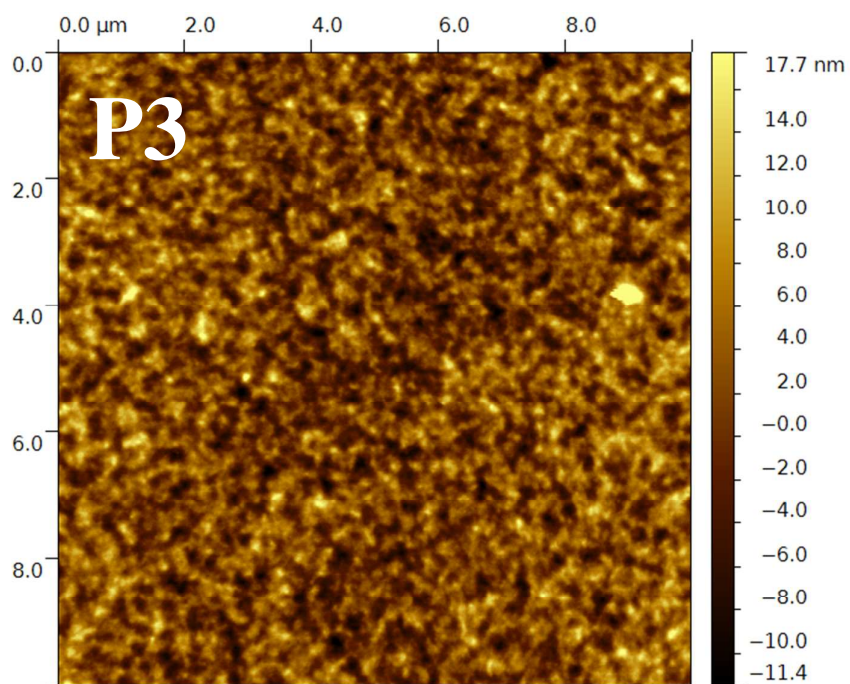
Figure S16. PF-QNM AFM image (10x10 μm) for the PTB7:PC$_{71}$BM blend film based on P3.
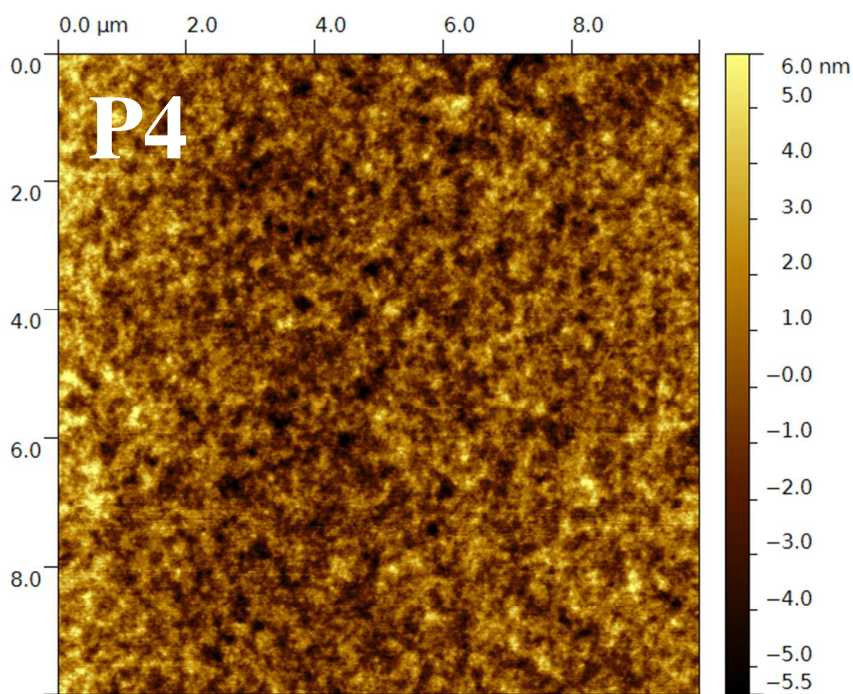

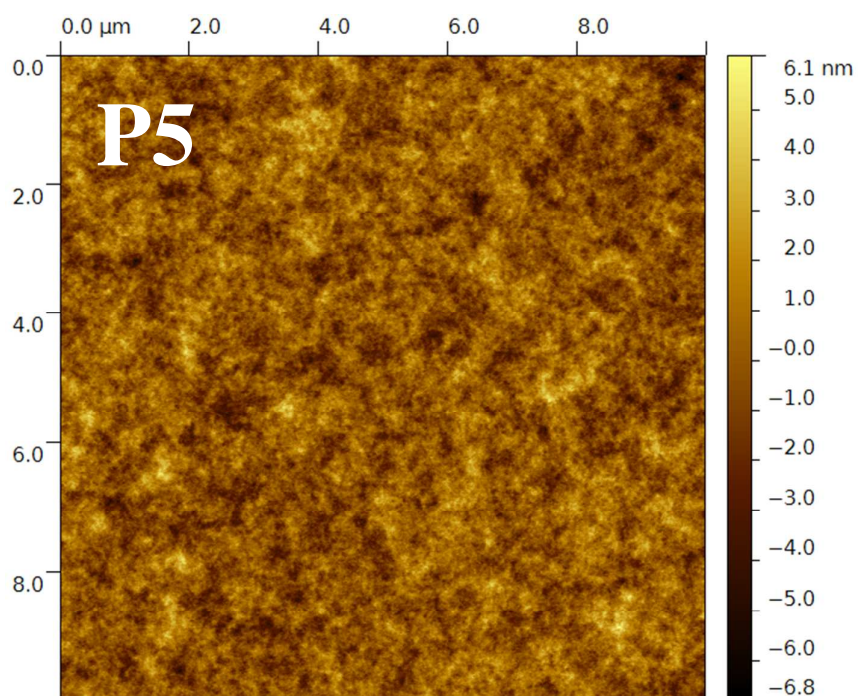**Figure S17.** PF-QNM AFM image (10x10 μm) for the PTB7:PC$_{71}$BM blend film based on P4.

Figure S18. PF-QNM AFM image (10x10 μm) for the PTB7:PC$_{71}$BM blend film based on P5.