Supplementary Information:

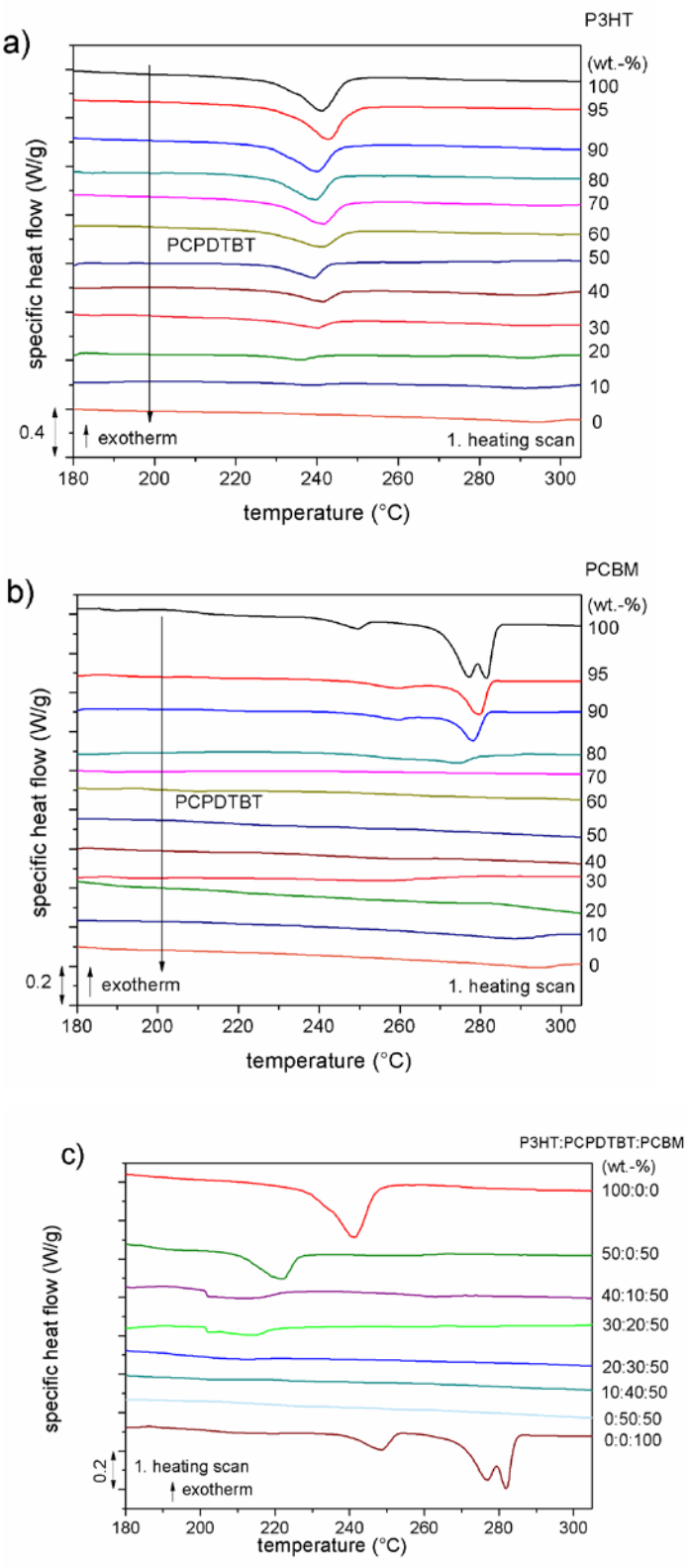

Figure S1: DSC thermograms (first heating scan, heating rate of 10 K min^{-1}) of binary mixtures: a) P3HT and PCPDTBT, b) PCBM and PCPDTBT and c) ternary mixtures with 50 wt% PCBM including the neat P3HT and PCBM. Thermograms are ploted with exotherm up.

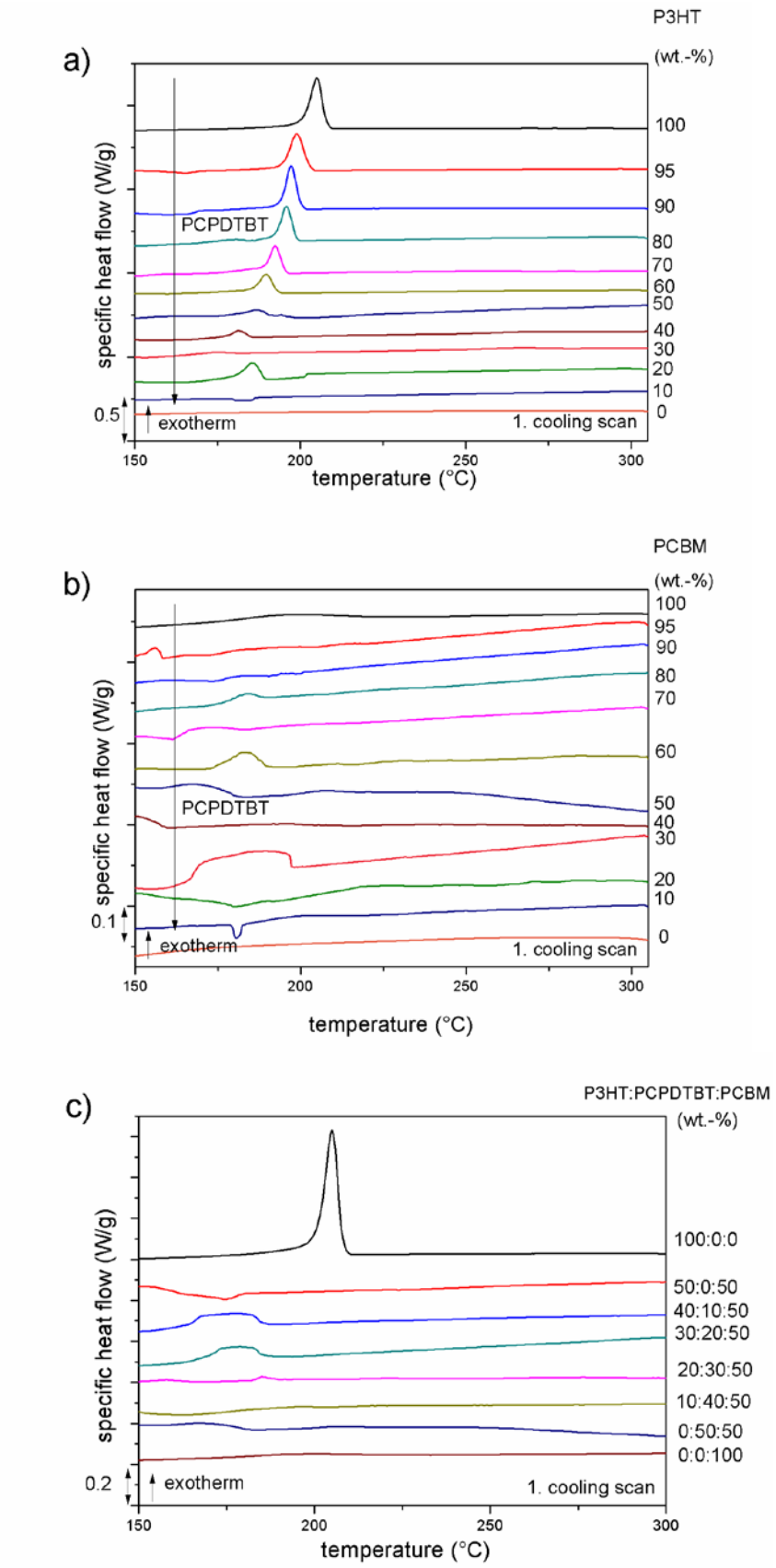

Figure S2: DSC thermograms (first cooling scan, cooling rate of 10 K min^{-1}) of binary mixtures: a) P3HT and PCPDTBT, b) PCBM and PCPDTBT and c) ternary mixtures including 50 wt% PCBM and the neat P3HT and PCBM. Thermograms are ploted with exotherm up.

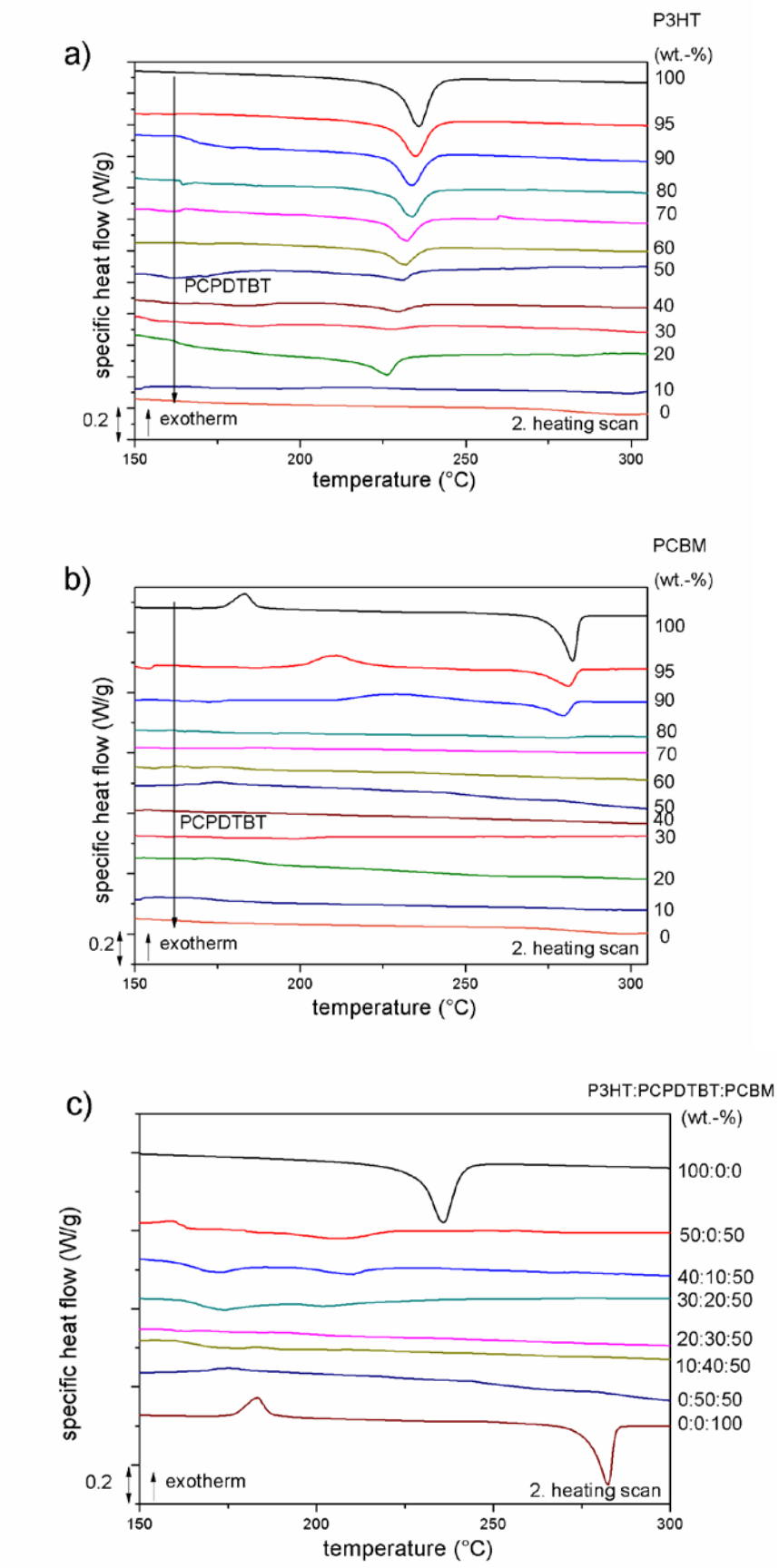

Figure S3: DSC thermograms (second heating scan, heating rate of 10 K min^{-1}) of binary mixtures: a) P3HT and PCPDTBT, b) PCBM and PCPDTBT and c) ternary mixtures with 50 wt% PCBM including the neat P3HT and PCBM. Thermograms are plotted with exotherm up.

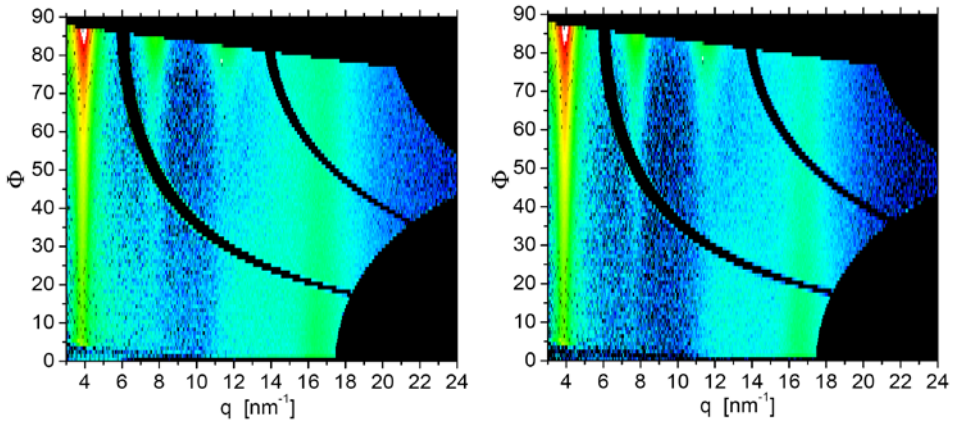

Figure S4: Two-dimensional GiWAXS detector pattern obtained for the as-coated and annealed P3HT films (intensity scale 10000).

For the conversion of mass fractions into volume fractions we assumed a density of about 1 g/cm^3 for PCPDTBT and 1.1 g/cm^3 for P3HT. Since PCPDTBT is less crystalline than P3HT its density should be lower than that of P3HT. For PCBM density values ranging from 1.3 g/cm^3 up to 1.5 g/cm^3 are reported [Ref. (S1-S3)]. This leads to an average PCBM volume fraction of 0.43 ±0.02.

Table S1: Normalization to PCBM volume fraction

Density PCBM [g/cm3]	P3HT:PCPDTBT wt%					
	50:0	40:10	30:20	25:25	20:30	0:50
	PCBM vol%					
1.3 Ref.(2)	45	45	45	45	44	44
1.5 Ref.(2)	42	42	41	41	41	41

Table S2: Device performance of ternary cells with higher PCBM content

ratio P3HT:PCPDTBT:PCBM wt%	Voc (V)	Jsc (mA/cm²)	FF (%)	PCE (%)
polymer:fullerene 1:2 wt%				
45:15:120	0.56±0.01	3.6±0.6	42±4.5	0.8±0.2
50:10:120	0.57±0.01	3.5±0.4	39±0.7	0.8±0.1
polymer:fullerene 1:3 wt%				
20:05:75	0.48±0.02	4.2±0.6	31±1.8	0.6±0.1
15:10:75	0.57±0.01	2.9±0.3	36±2.4	0.6±0.1

References

S1. A.C. Arias, J. Macromol. Sci. Polym. Rev. 2006, **46**, 103.
S2. J. W Kiel, B. J. Kirby, C. F. Majkrzak, B. B. Maranville, M. E. Mackay, Soft Matter 2010, **6**, 641.
S3. C. W. T. Bulle-Lieuwma, W. J. H. van Gennip, J. K. J. van Duren, et al. Appl. Surf. Sci. 2003, **203**, 547.