

## Supplementary Information

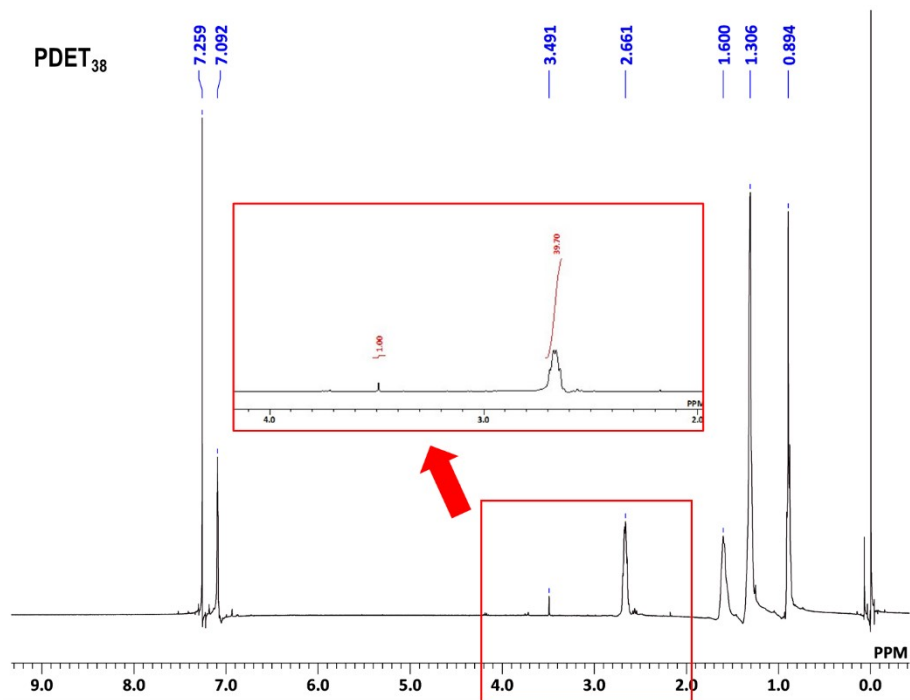
### **Coil-rod-coil triblock copolymers synthesized by macromolecular clicking and their compatibilizer effects in all-polymer solar cells**

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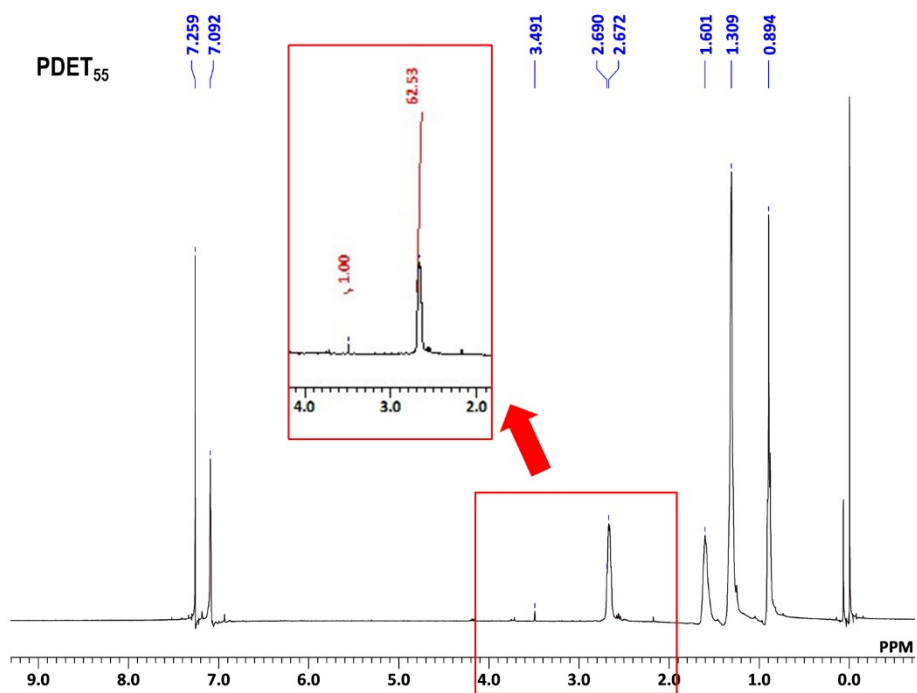
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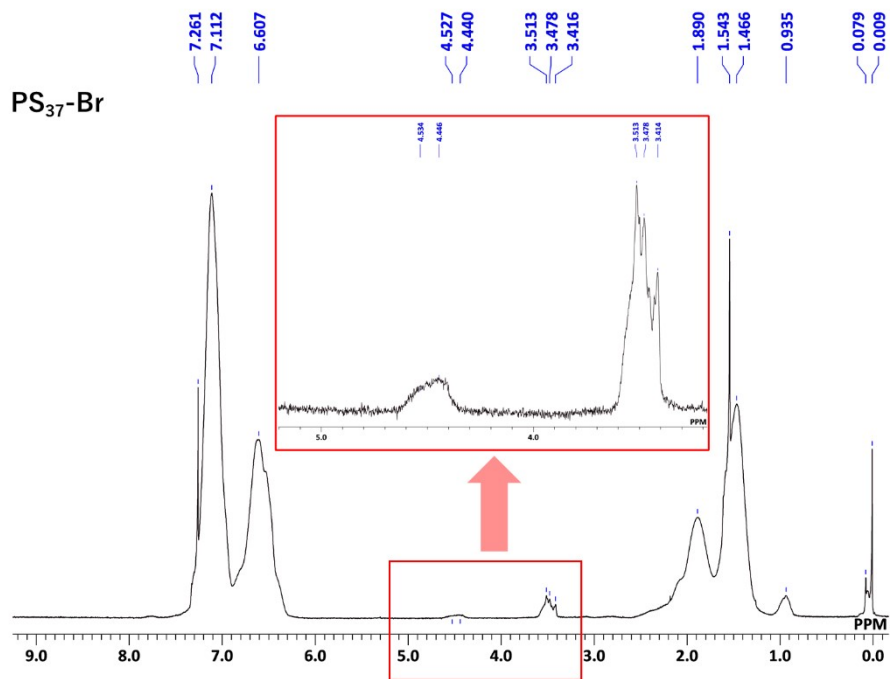
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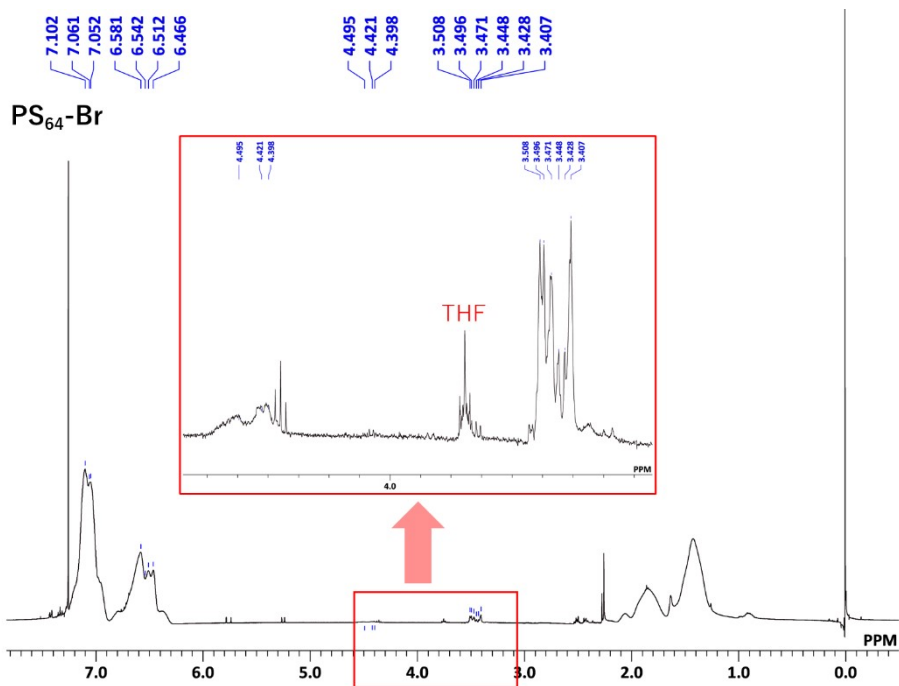
**Figure S1.** <sup>1</sup>H NMR spectrum of **PDET<sub>38</sub>** in CDCl<sub>3</sub>.



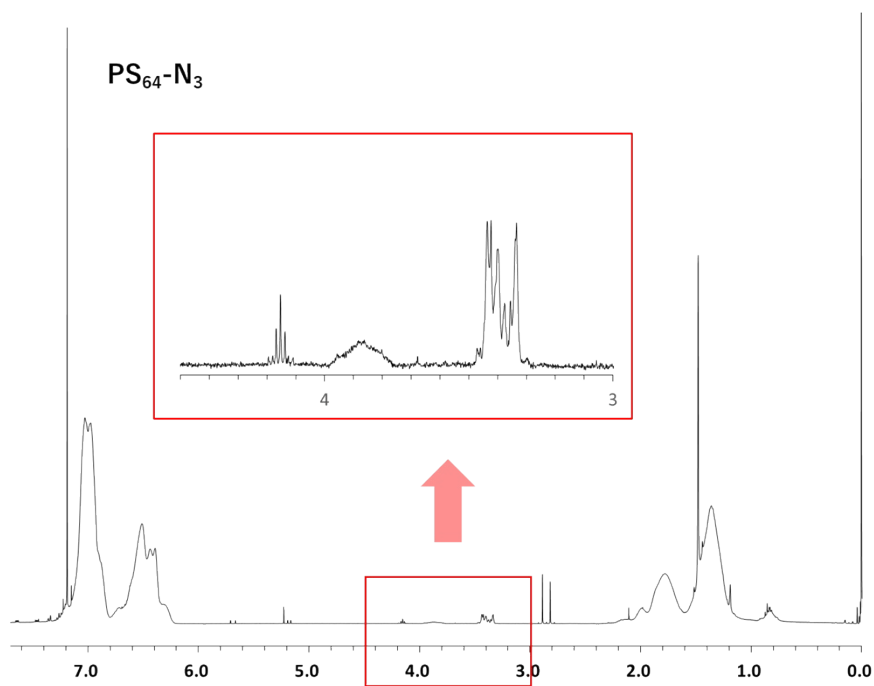
**Figure S2.** <sup>1</sup>H NMR spectrum of **PDET<sub>55</sub>** in CDCl<sub>3</sub>.



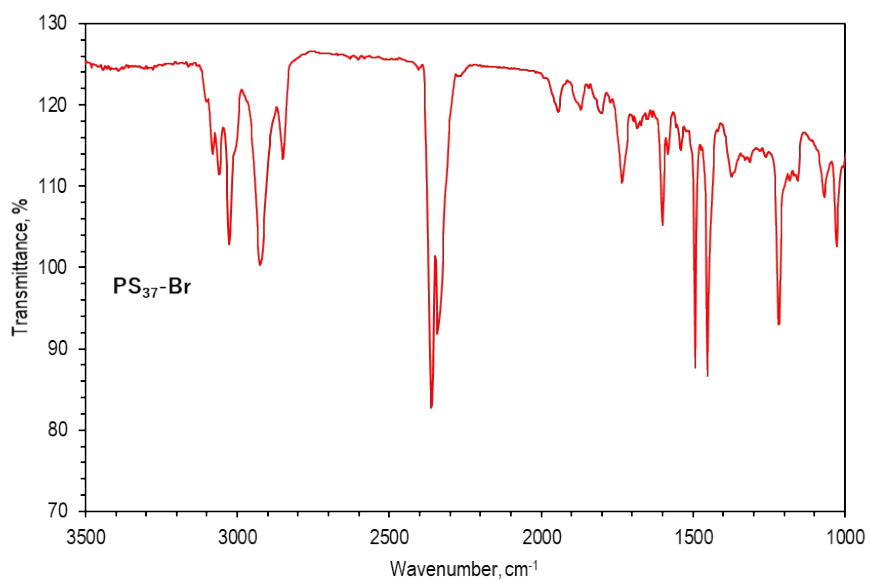
**Figure S3.** <sup>1</sup>H NMR spectrum of PS<sub>37</sub>-Br in CDCl<sub>3</sub>.



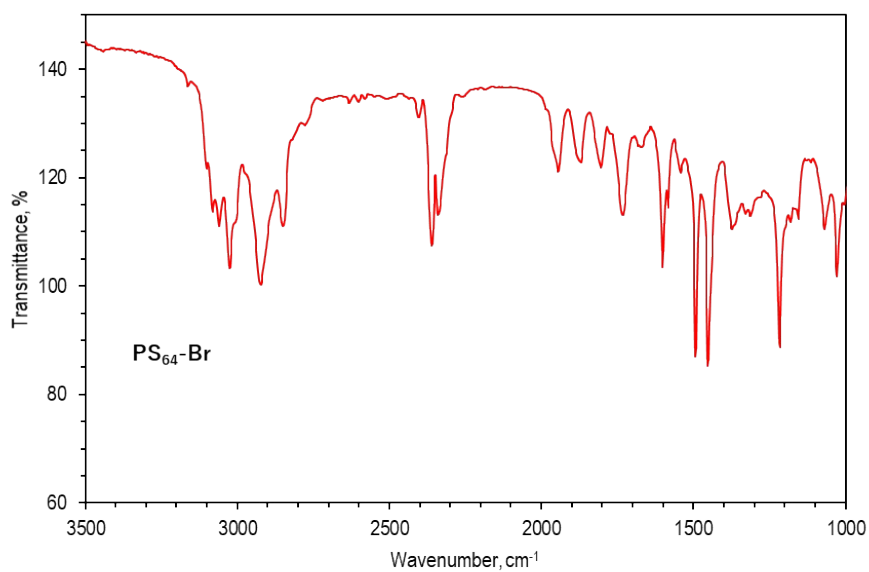
**Figure S4.** <sup>1</sup>H NMR spectrum of PS<sub>64</sub>-Br in CDCl<sub>3</sub>.



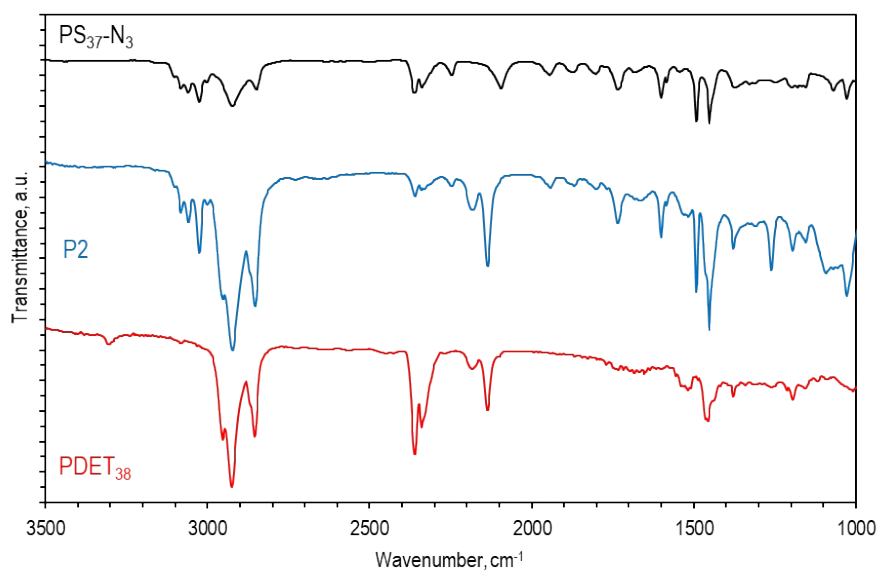
**Figure S5.**  $^1\text{H}$  NMR spectrum of  $\text{PS}_{64}\text{-N}_3$  in  $\text{CDCl}_3$ .



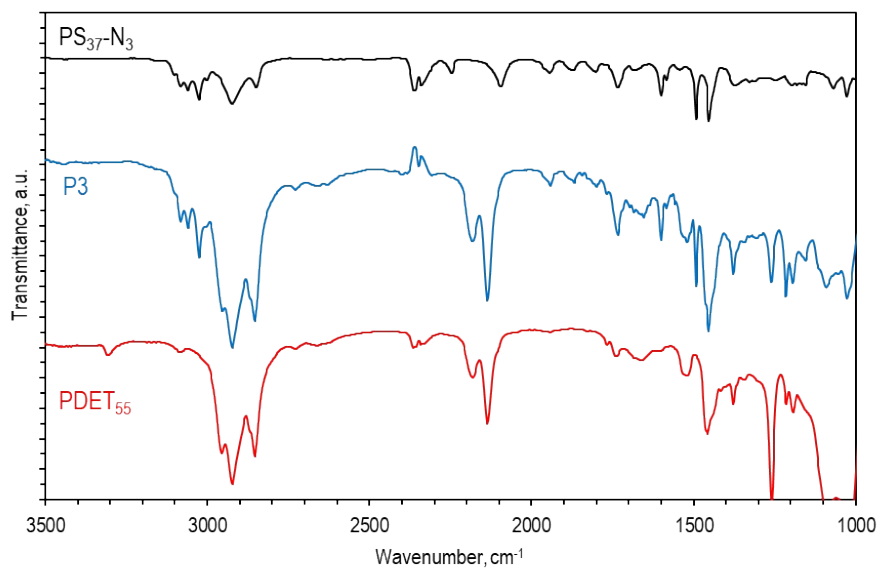
**Figure S6.** FTIR spectrum of  $\text{PS}_{37}\text{-Br}$ .



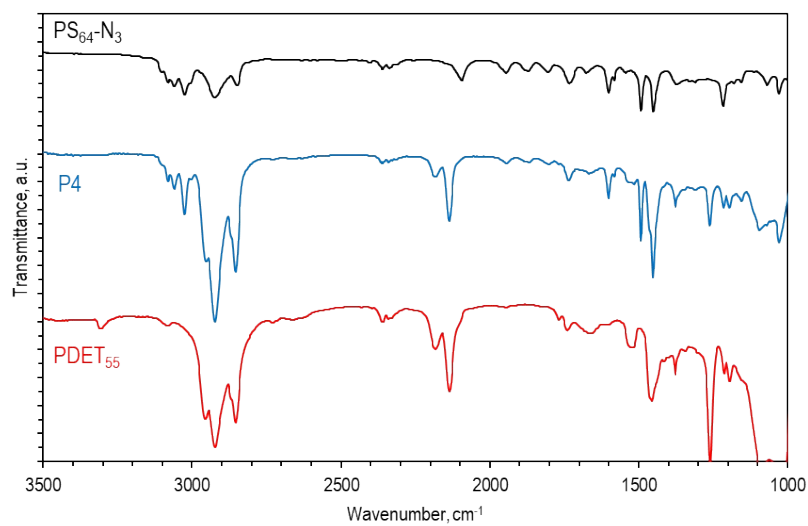
**Figure S7.** FTIR spectrum of PS<sub>64</sub>-Br.



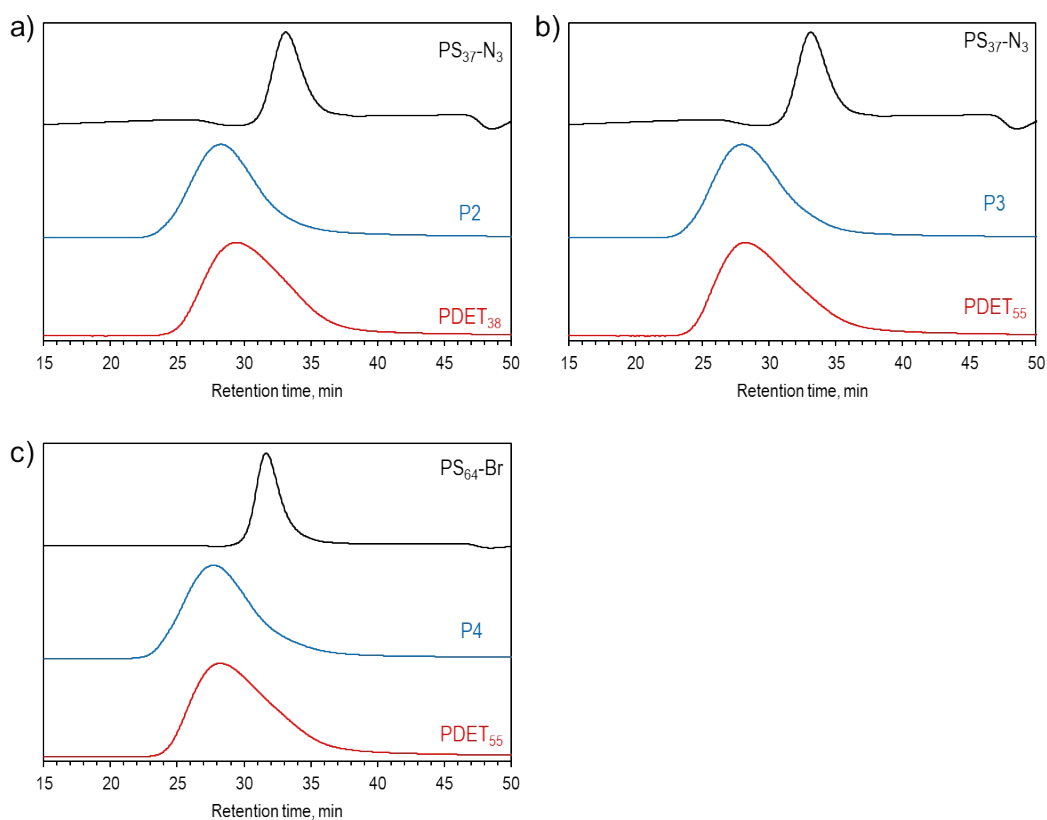
**Figure S8.** Comparison of FTIR spectra of PS<sub>37</sub>-N<sub>3</sub>, PDET<sub>38</sub> and P2.



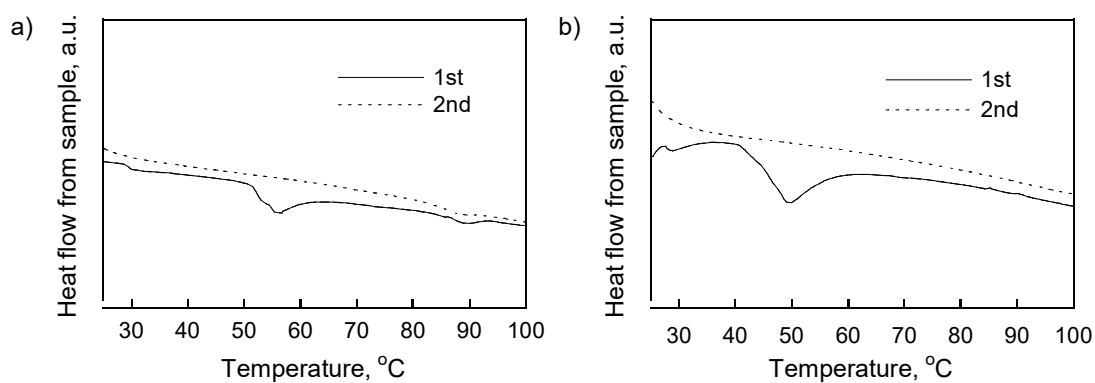
**Figure S9.** Comparison of FTIR spectra of PS<sub>37</sub>-N<sub>3</sub>, PDET<sub>55</sub> and P3.



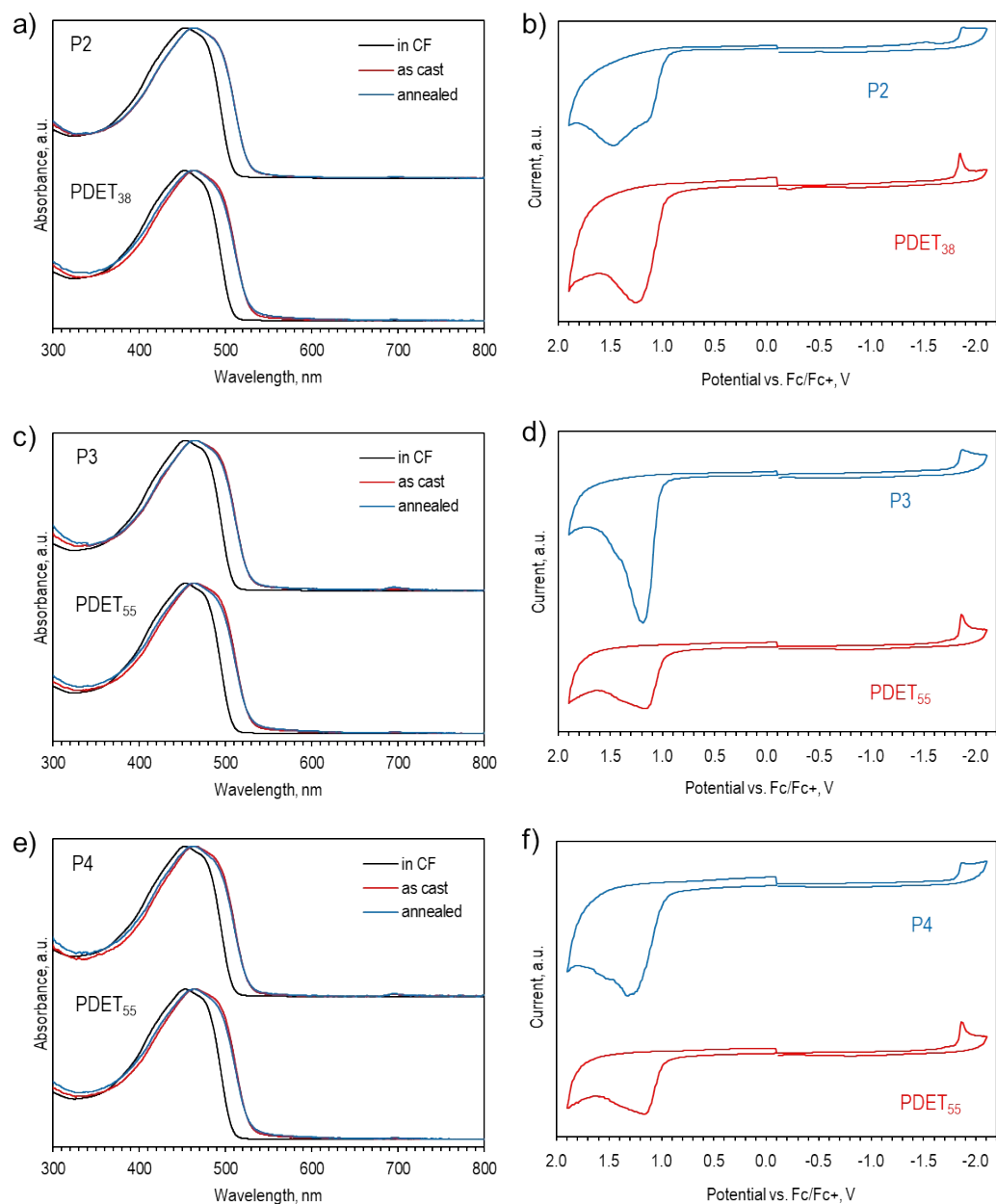
**Figure S10.** Comparison of FTIR spectra of PS<sub>64</sub>-N<sub>3</sub>, PDET<sub>55</sub> and P4.



**Figure S11.** GPC curves of a) **P2**, PS<sub>37</sub>-N<sub>3</sub> and **PDET<sub>38</sub>**, b) **P3**, PS<sub>37</sub>-N<sub>3</sub> and **PDET<sub>55</sub>**, and c) **P4**, PS<sub>64</sub>-Br and **PDET<sub>55</sub>**.



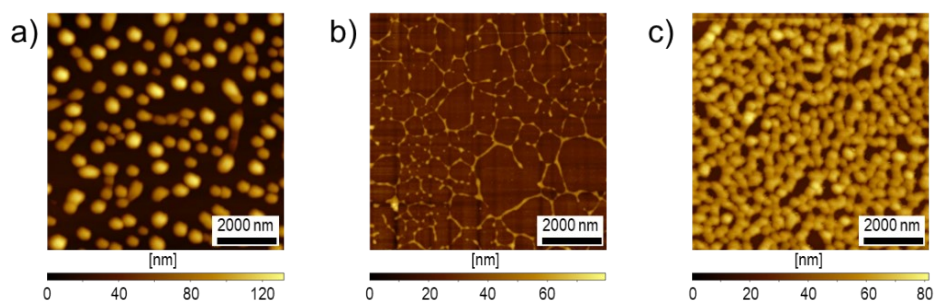
**Figure S12.** The 1st and 2nd heating scans of DSC curves of a) PS<sub>37</sub>-N<sub>3</sub> and b) **P1**.



**Figure S13.** Comparison of UV-vis absorption spectra and CV curves of the polymers.

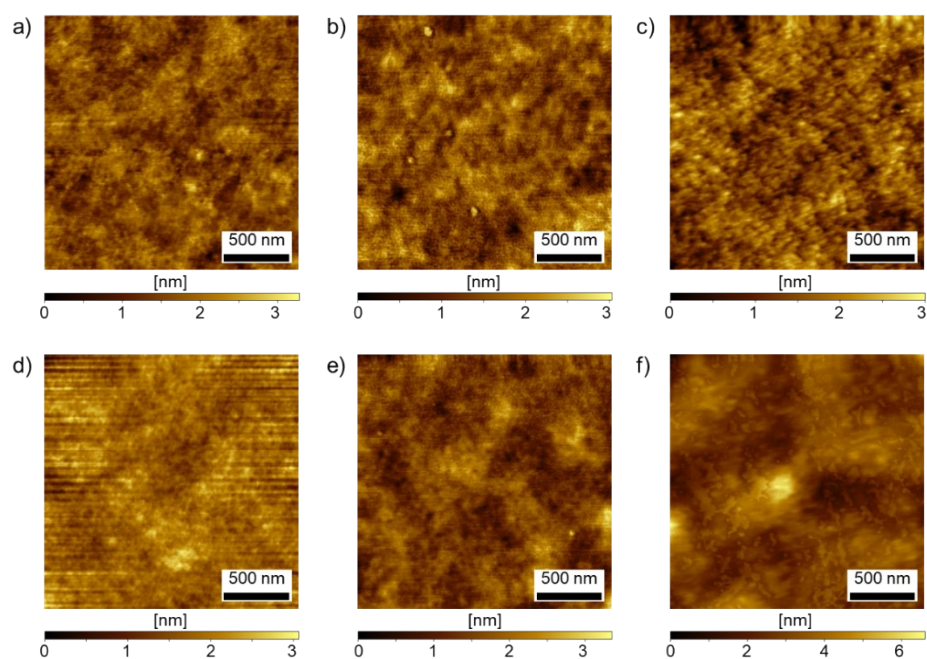
UV-vis absorption spectra in chloroform (CF), as-cast film and annealed film of a) **P2** and **PDET<sub>38</sub>**, c) **P3** and **PDET<sub>55</sub>**, and e) **P4** and **PDET<sub>55</sub>**. CV curves of b) **P2** and **PDET<sub>38</sub>**, d) **P3** and **PDET<sub>55</sub>**, and f) **P4** and **PDET<sub>55</sub>**, measured in CH<sub>3</sub>CN with 0.1 M (nC<sub>4</sub>H<sub>9</sub>)<sub>4</sub>NPF<sub>6</sub>.





**Figure S14.** Larger scan area images of the annealed films of a) **P2**, b) **P3** and c) **P4**.

Films were annealed on a hot plate at 120 °C for 30 min.



**Figure S15.** AFM topography images of the films of **PDET<sub>29</sub>** a) as-cast, b) annealed at 100 °C and c) annealed at 200 °C. AFM topography images of the films of **P1** d) as-cast, e) annealed at 100 °C and f) annealed at 200 °C.

**Table S1.** Properties of the synthesized homopolymers.

Polymer <sup>a)</sup>	GPC <sup>b)</sup>			<sup>1</sup> H NMR <sup>c)</sup>		Functionality, %
	$M_n$ (kg mol <sup>-1</sup> )	$\bar{D}$	DP	$M_n$ (kg mol <sup>-1</sup> )	DP	
<b>PDET<sub>29</sub></b>	6.26	3.06	29	6.12	29	
<b>PDET<sub>38</sub></b>	8.14	2.82	38	8.50	40	
<b>PDET<sub>55</sub></b>	11.77	2.83	55	13.38	62	
<b>PS<sub>37</sub>-Br</b>	3.97	1.05	37	3.79	35	90 <sup>d)</sup>
<b>PS<sub>64</sub>-Br</b>	6.85	1.05	64	6.61	62	91 <sup>d)</sup>

<sup>a)</sup> Labeled according to the degree of polymerization (DP) determined by GPC: **PDET<sub>DP</sub>** and **PS<sub>DP</sub>-Br**. <sup>b)</sup> Measured with *o*-dichlorobenzene at 40 °C and molecular weights estimated by comparing to polystyrene standards. <sup>c)</sup> For **PDET**, estimated from the ratio of the <sup>1</sup>H NMR peak areas of the terminal alkyne and the repeat DET units. For **PS-Br**, estimated from the ratio of the <sup>1</sup>H NMR peak areas of the terminal methoxy group and repeat benzene rings. <sup>d)</sup> Azido-functionality calculated from the <sup>1</sup>H NMR peak areas of the methoxy group and the  $\alpha$ -hydrogen on the other end of the polymer chain. See Figure 1 for the details of the evaluation of the <sup>1</sup>H NMR results.

**Table S2.** Detailed energy loss of the fabricated all-PSCs.

	$E_{gap}$ (eV)	$V_{oc}$ (eV)		$E_{loss}$ (eV)	$f$ (eV <sup>2</sup> )	$\lambda$ (eV)	$E_{CT}$ (eV)	$\Delta E_1$ (eV)	$\Delta E_2$ (eV)	$\Delta E_3$ (eV)
<b>Control</b>	1.481	0.878		0.603	0.0204	0.279	1.42	0.267	0.061	0.276
<b>1 wt% P1</b>	1.487	0.885		0.602	0.0154	0.212	1.44	0.262	0.047	0.293
<b>1 wt% PDET</b>	1.516	0.862		0.654	0.0204	0.141	1.46	0.275	0.056	0.323