

# Supporting information

## Rational design of poly(fluorene)-b-poly(thiophene) block copolymers to obtain a unique aggregation behavior

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## I. Materials

All reagents were purchased and used without further purification. Reagent grade solvents were dried by a solvent purification system MBRAUN SPS 800 (columns with activated alumina). 7-bromo-2-iodo-9,9-dioctylfluorene (**5a**)<sup>1</sup>, 7-bromo-2-iodo-9,9-dihexylfluorene (**5b**)<sup>1,2</sup>, 2-bromo-5-iodo-3-((*S*)-3,7-dimethyloctyl)thiophene (**7a**)<sup>3</sup>, 2-bromo-5-iodo-3-((*S*)-2-methylbutyl)thiophene (**7b**)<sup>4</sup> were synthesized according to literature procedures.

## II. Instrumentation

<sup>1</sup>H-NMR spectra were recorded on a Bruker Avance 400 MHz spectrometer. Gel permeation chromatography (GPC) measurements were carried out on a Shimadzu LC20 GPC system. The column is a PLgel 5μm mixed-D type column and the detection system consists of a differential refractometer and a UV-vis spectrophotometer. The GPC system is calibrated towards polystyrene standards (purchased from Polymer Laboratories). Before measuring, the polymers are dissolved in THF (*c* ≈ 1 mg/mL) and filtered over a pore size of 0.2 μm. The preparative GPC measurements were performed with the same apparatus, but two PLgel 10 μm 500 Å columns were used. The concentration of the start solution in the solvatochromism experiments was approximately 0.03 mg/mL in chloroform and the methanol was added at a speed of 0.25 mL/min with an automatic infusion pump. The UV-vis spectra were measured on a Perkin Elmer Lambda 900 spectrometer. CD spectra were recorded on a JASCO J-810 spectrometer. The mass spectra were recorded using a LCQ Advantage Thermo Finnigan Electrospray Ionization (ESI) Mass Spectrometer. The elemental analysis was executed with a Thermo Scientific Flash 2000 Organic elemental analyzer.

### III. Monomer synthesis

#### *2-(7-bromo-9,9-dioctylfluorene-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (6a)*

The compound was synthesized according to an adapted literature procedure.<sup>5</sup> Under inert atmosphere and at 0°C, *t*BuLi (10.0 mmol; 6.67 mL; 1.50 M) was added to a mixture of dry THF (6.7 mL) and *t*BuMgCl (5.00 mmol; 2.94 mL; 1.70 M). This mixture was stirred for 1 hour, whereafter 1 equivalent (10.0 mmol; 11.1 mL; 0.90 M) was added to 2-bromo-7-iodo-9,9-dioctylfluorene (**5a**) (10.0 mmol; 5.95 g) in dry THF (10.0 mL) at 0°C. After 1 hour at 0°C, 2-*isopropoxy*-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (12.0 mmol; 2.45 mL) was added at 0°C and the resulting mixture was stirred for 2 hours at ambient temperature. The reaction mixture was concentrated and poured into cold pentane (0°C). The formed salts were filtered off and the solvent was removed under reduced pressure. The crude product was purified by column chromatography with heptane/dichloromethane (7/3) and the pure product was obtained as a white solid.

Yield: 3.41 g, 57%. <sup>1</sup>H NMR (CDCl<sub>3</sub> with 0.1% v/v TMS, 400 MHz) 7.80 (d, 1H), 7.72 (s, 1H), 7.66 (d, 1H), 7.57 (d, 1H), 7.45 (m, 2H), 1.95 (m, 4H), 1.37 (s, 12H), 1.10 (m, 20H), 0.82 (t, 6H), 0.56 (m, 4H). C<sub>35</sub>H<sub>52</sub>BBrO<sub>2</sub>: C<sub>calc</sub>: 70.6%, C<sub>found</sub>: 70.6%; H<sub>calc</sub>: 8.8%, H<sub>found</sub>: 8.9%

#### *2-(7-bromo-9,9-dihexylfluorene-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (6b)*

Compound (**6b**) was synthesized via the same procedure as compound (**6a**) starting from 2-bromo-7-iodo-9,9-dihexylfluorene (**5b**) (5.00 mmol; 2.70 g) and 2-*isopropoxy*-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (6.00 mmol; 1.22 mL). The crude product was purified by column chromatography with heptane/dichloromethane (7/3) and the pure product was obtained as a white solid.

Yield: 1.67 g, 62%. <sup>1</sup>H NMR (CDCl<sub>3</sub> with 0.1% v/v TMS, 400 MHz) 7.80 (d, 1H), 7.72 (s, 1H), 7.66 (d, 1H), 7.57 (d, 1H), 7.44 (m, 2H), 1.95 (m, 4H), 1.38 (s, 12H), 1.06 (m, 12H), 0.76 (t, 6H), 0.56 (m, 4H). C<sub>31</sub>H<sub>44</sub>BBrO<sub>2</sub>: C<sub>calc</sub>: 69.0%, C<sub>found</sub>: 69.0%; H<sub>calc</sub>: 8.2%, H<sub>found</sub>: 8.3%

*2-(5-bromo-4-((S)-3,7-dimethyloctylthiophene-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (8a)*

The compound was synthesized according to an adapted literature procedure.<sup>5</sup> Under inert atmosphere and at 0°C, a solution of *i*PrMgCl·LiCl in THF (6.90 mmol; 5.60 mL; 1.22 M) was added dropwise to a solution of 2-bromo-5-iodo-3-((S)-3,7-dimethyloctylthiophene (**7a**) (6.91 mmol; 2.97 g) in dry THF (15 mL). After stirring for 30 minutes, 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (8.30 mmol; 1.69 mL) was added at 0°C and the resulting mixture was stirred for 2 hours at ambient temperature. The reaction mixture was concentrated and poured into cold pentane (0°C). The formed salts were filtered off and the solvent and impurities were removed under reduced pressure. The pure product was obtained as a brown oil.

Yield: 2.45 g, 83%. <sup>1</sup>H NMR (CDCl<sub>3</sub> with 0.1% v/v TMS, 400 MHz) 7.32 (s, 1H), 2.64-2.47 (m, 2H), 1.62-1.08 (m, 22H), 0.92 (d, 3H), 0.86 (d, 6H). <sup>13</sup>C NMR (CDCl<sub>3</sub> with 0.1% v/v TMS, 100 MHz) 143.7, 138.0, 116.4, 84.2, 37.0, 36.9, 32.5, 28.0, 27.0, 24.8, 24.7, 22.8, 22.6, 19.6. MS (ESI) *m/z*: 430 [MH<sup>+</sup>].  $[\alpha]_D^{20} = 11 \frac{^{\circ} \cdot \text{mL}}{\text{dm} \cdot \text{g}}$  (c = 0.558 in dichloromethane). C<sub>20</sub>H<sub>34</sub>BBrO<sub>2</sub>S: C<sub>calc</sub>: 56.0%, C<sub>found</sub>: 56.1%; H<sub>calc</sub>: 8.0%, H<sub>found</sub>: 8.1%

*2-(5-bromo-4-((S)-2-methylbutylthiophene-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (8b)*

Compound (**8b**) was synthesized via the same procedure as compound (**8a**) starting from 2-bromo-5-iodo-3-((S)-2-methylbutylthiophene (**7b**) (10.0 mmol; 3.69 g), *i*PrMgCl·LiCl in THF (10.0 mmol; 7.94 mL; 1.26 M) and 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-

dioxaborolane (12.0 mmol; 2.45 mL). The impurities were removed under reduced pressure and the pure product was obtained as a brown oil.

Yield: 2.52 g, 70%.  $^1\text{H}$  NMR ( $\text{CDCl}_3$  with 0.1% v/v TMS, 400 MHz) 7.28 (s, 1H), 2.57 (dd, 1H), 2.37 (dd, 1H), 1.74-1.64 (m, 1H), 1.43-1.14 (m, 14H), 0.91 (t, 3H), 0.83 (d, 3H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$  with 0.1% v/v TMS, 100 MHz) 142.5, 138.7, 117.2, 84.2, 36.4, 35.7, 32.4, 24.7, 19.0, 11.5. MS (ESI)  $m/z$ : 360  $[\text{MH}^+]$ .  $[\alpha]_D^{20} = 7.3 \frac{^\circ \cdot \text{mL}}{\text{dm} \cdot \text{g}}$  ( $c = 0.548$  in dichloromethane).

$\text{C}_{15}\text{H}_{24}\text{BBrO}_2\text{S}$ :  $\text{C}_{\text{calc}}$ : 50.2%,  $\text{C}_{\text{found}}$ : 49.4%;  $\text{H}_{\text{calc}}$ : 6.7%,  $\text{H}_{\text{found}}$ : 6.7%

#### IV. Polymerization procedures

##### *POF-b-P3OT*\*

All reagents and solvents are degassed 7 times prior to use. To the palladacycle precatalyst (**1**) (36.0  $\mu\text{mol}$ ; 18.5 mg) in THF (1.5 mL) a 4-bromotoluene solution in THF (60.0  $\mu\text{mol}$ ; 240  $\mu\text{L}$ ; 0.25 M) and a  $\text{K}_2\text{CO}_3$  solution in  $\text{H}_2\text{O}$  (3.00 mmol; 1.50 mL; 2.0 M) are added and stirred for 40 minutes at room temperature. Next, a solution of **6a** (300  $\mu\text{mol}$ ; 179 mg) in THF (15 mL) is added and the mixture is stirred during the night at room temperature. 6.00 mL (100  $\mu\text{mol}$ ) is removed from the solution and added to **3** (100  $\mu\text{mol}$ ; 20.4 mg) in THF (2.5 mL) to quench the POF block. This mixture is stirred for 1 hour at room temperature. To the remaining polymerization solution, a solution of **8a** (400  $\mu\text{mol}$ ; 172 mg) in THF (2 mL) and  $\text{K}_2\text{CO}_3$  in  $\text{H}_2\text{O}$  (0.100 mmol; 50  $\mu\text{L}$ ; 2.0 M) is cannulated. This mixture is stirred for 1 hour at  $0^\circ\text{C}$ , whereafter a solution of **4** (200  $\mu\text{mol}$ ; 42.0 mg) in THF (2.5 mL) is added and stirred for another hour to terminate the polymerization. Both terminated polymerization mixtures are concentrated, precipitated in methanol and purified by Soxhlet extraction with methanol and chloroform consecutively. The chloroform soluble fraction was concentrated and again precipitated in methanol. The block copolymer is further purified via preparative

GPC. The final homopolymer (**POF**) and the final block copolymer (**POF-*b*-P3OT\***) have a light green and dark red color, respectively. The  $\bar{M}_n$  and  $\bar{D}$  can be found in Table 1.

Yield of **POF**: 29.7 mg

Yield of **POF-*b*-P3OT\*** before preparative GPC: 151 mg

Yield of **POF-*b*-P3OT\*** after preparative GPC: 71.5 mg

C<sub>539</sub>H<sub>784</sub>S<sub>18</sub>: C<sub>calc</sub>: 82.6%, C<sub>found</sub>: 81.2%; H<sub>calc</sub>: 10.1%, H<sub>found</sub>: 10.2%

#### ***PHF-*b*-P3OT\****

The same procedure was followed as for the synthesis of **POF-*b*-P3OT\***, but monomer **6b** (300  $\mu$ mol; 162 mg) was used to synthesize the first block. Also the polymerization of the first block was done at 0°C and for 6 hours. The final homopolymer (**PHF**) and the final block copolymer (**PHF-*b*-P3OT\***) have a light green and dark red color, respectively. The  $\bar{M}_n$  and  $\bar{D}$  can be found in Table 1.

Yield of **PHF**: 25.5 mg

Yield of **PHF-*b*-P3OT\*** before preparative GPC: 125 mg

Yield of **PHF-*b*-P3OT\*** after preparative GPC: 52.6 mg

C<sub>664</sub>H<sub>956</sub>S<sub>28</sub>: C<sub>calc</sub>: 81.1%, C<sub>found</sub>: 80.8%; H<sub>calc</sub>: 9.8%, H<sub>found</sub>: 9.6%

#### ***POF-*b*-P3BT\****

The same procedure was followed as for the synthesis of **POF-*b*-P3OT\***, but monomer **8b** (400  $\mu$ mol; 144 mg) was used to synthesize the second block. Also the polymerization of the first block was done at 0°C and for 6 hours. The final homopolymer (**POF**) and the final

block copolymer (**POF-*b*-P3BT\***) have a light green and dark red color, respectively. The  $\bar{M}_n$  and  $\bar{D}$  can be found in Table 1.

Yield of **POF**: 16.7 mg

Yield of **POF-*b*-P3BT\*** before preparative GPC: 82.3 mg

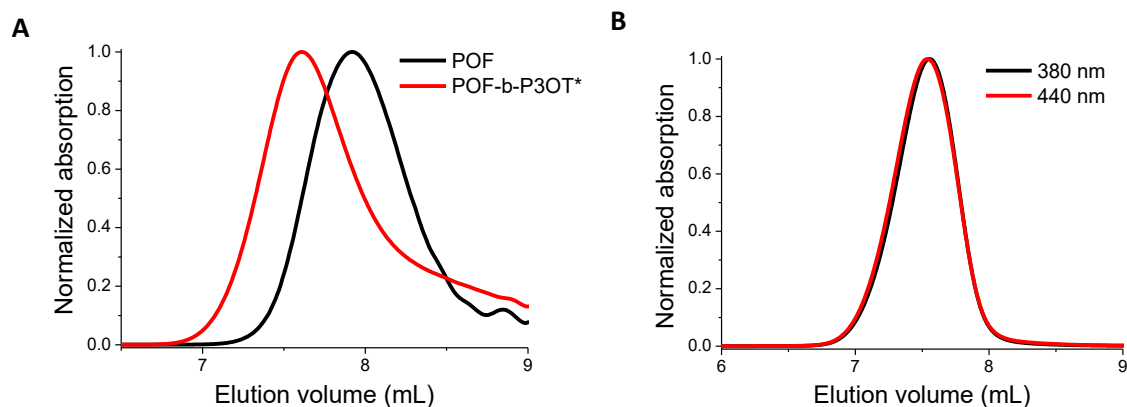
Yield of **POF-*b*-P3BT\*** after preparative GPC: 14.3 mg

C<sub>434</sub>H<sub>586</sub>S<sub>19</sub>: C<sub>calc</sub>: 81.3%, C<sub>found</sub>: 80.9%; H<sub>calc</sub>: 9.2, H<sub>found</sub>: 9.4

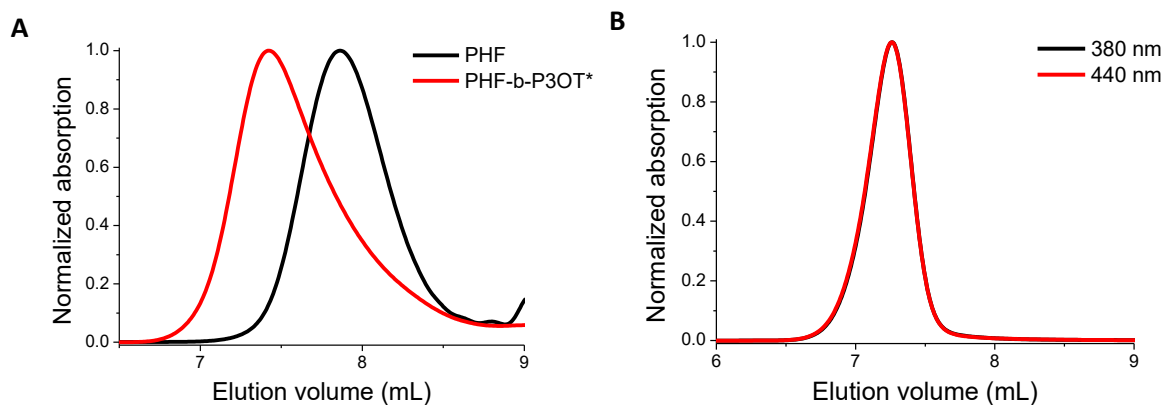
**Table 1:** Summary of  $\bar{M}_n$  and  $\bar{D}$  for the synthesized polymers.

	PF (after purification with Soxhlet extraction)		PF- <i>b</i> -PT (after purification with Soxhlet extraction and preparative GPC)	
	$\bar{M}_n$ (kg/mol)	$\bar{D}$	$\bar{M}_n$ (kg/mol)	$\bar{D}$
<b>POF-<i>b</i>-P3OT*</b>	4.9	1.3	11.7	1.2
<b>PHF-<i>b</i>-P3OT*</b>	5.7	1.2	21.3	1.1
<b>POF-<i>b</i>-P3BT*</b>	6.6	1.4	13.9	1.1

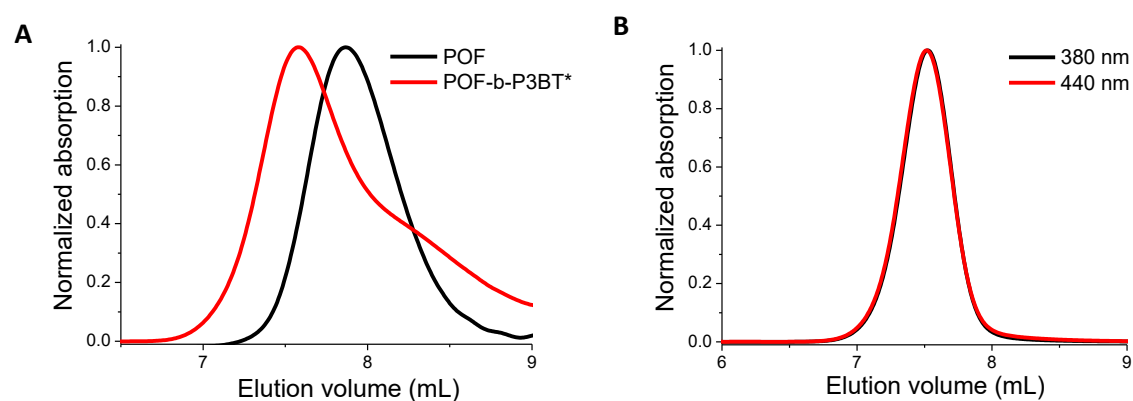
## V. Additional GPC elution chromatograms



**Figure S1:** A) GPC elution chromatograms (detection at 254 nm) for **POF-*b*-P3OT\*** before and after the addition of the second monomer. B) GPC elution chromatograms (detection at 380 nm and 440 nm) for **POF-*b*-P3OT\*** after purification.



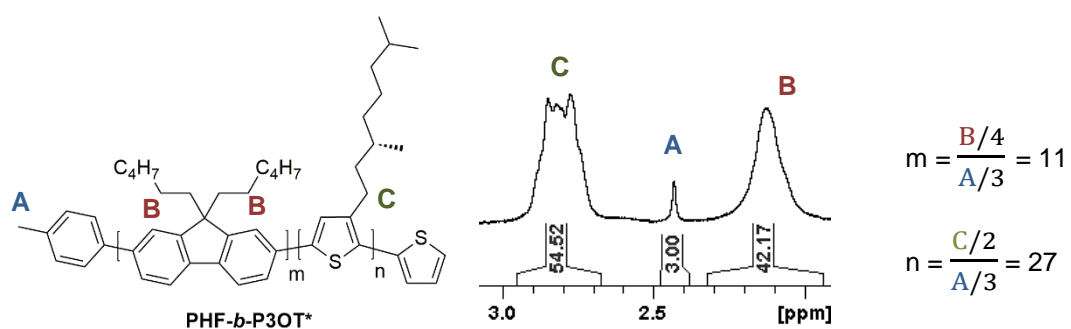
**Figure S2:** A) GPC elution chromatograms (detection at 254 nm) for **PHF-*b*-P3OT\*** before and after the addition of the second monomer. B) GPC elution chromatograms (detection at 380 nm and 440 nm) for **PHF-*b*-P3OT\*** after purification.



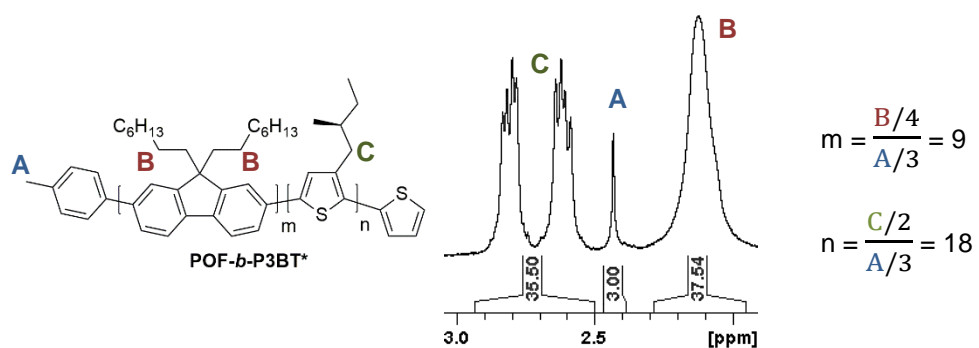
**Figure S3:** A) GPC elution chromatograms (detection at 254 nm) for **POF-*b*-P3BT\*** before and after the addition of the second monomer. B) GPC elution chromatograms (detection at 380 nm and 440 nm) for **POF-*b*-P3BT\*** after purification.



## VI. Determination of the degree of polymerization

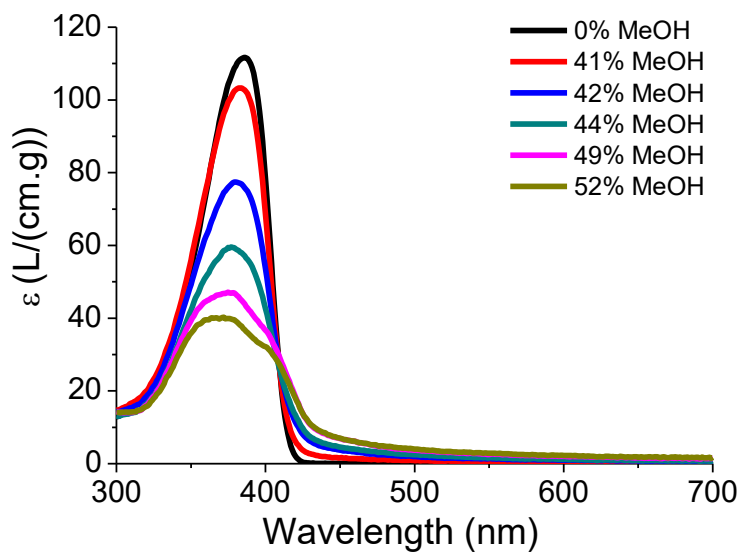


**Figure S4:** Determination of degree of polymerization for **PHF-*b*-P3OT\***.

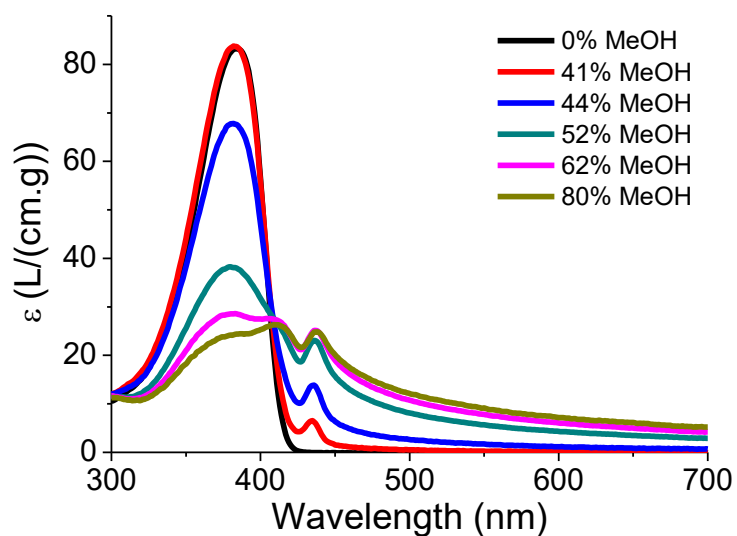


**Figure S5:** Determination of degree of polymerization for **POF-*b*-P3BT\***.

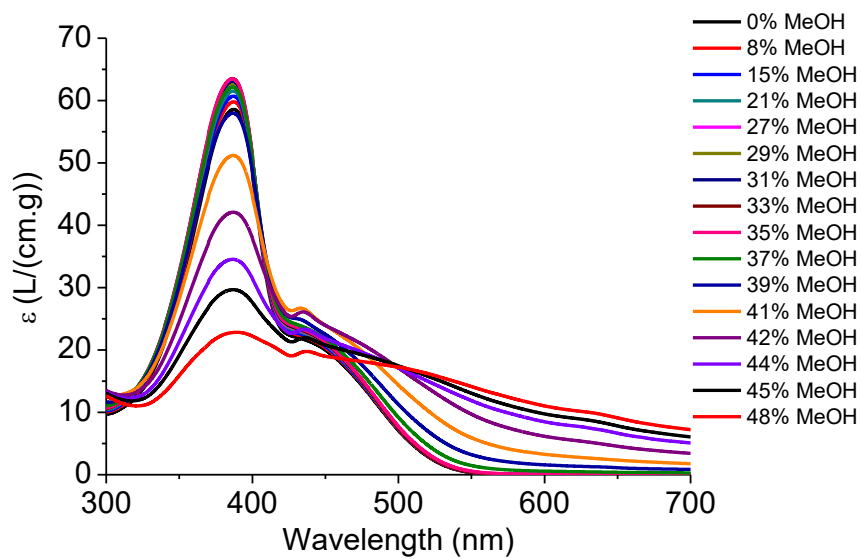
## VII. Additional UV vis and CD spectra



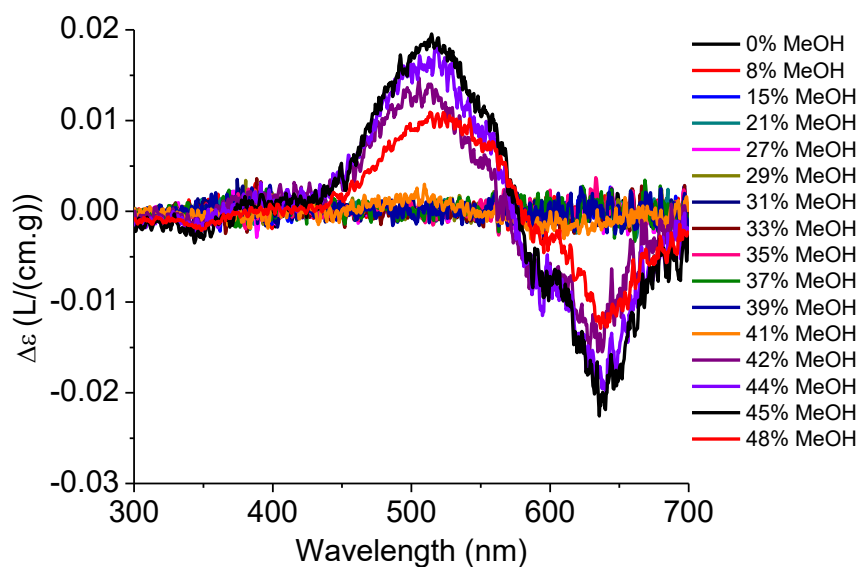
**Figure S6:** Absorption spectra of the solvatochromism experiments for poly(9,9-dihexylfluorene). The polymer was dissolved in chloroform and gradually more methanol was added.



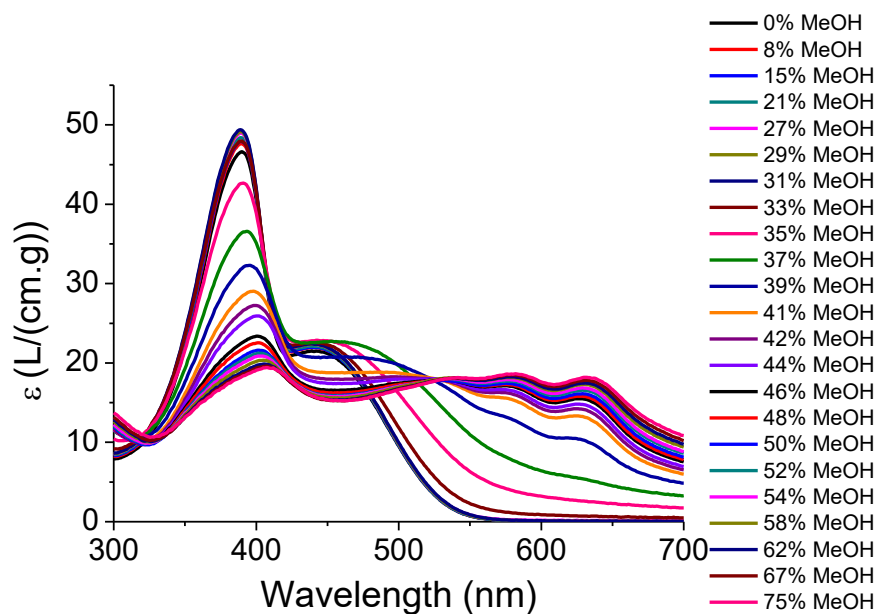
**Figure S7:** Absorption spectra of the solvatochromism experiments for poly(9,9-dioctylfluorene). The polymer was dissolved in chloroform and gradually more methanol was added.



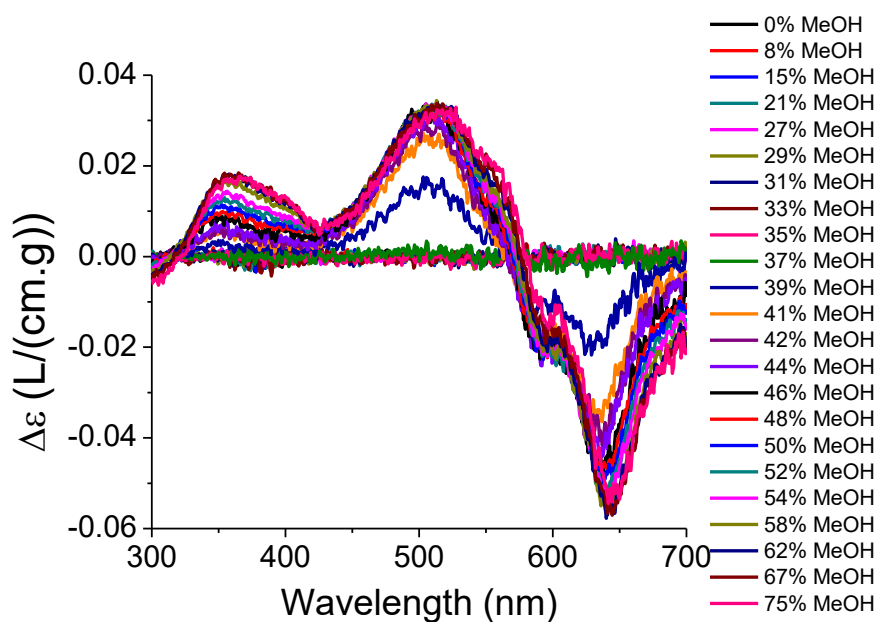
**Figure S8:** Absorption spectra of the solvatochromism experiments for **POF-*b*-P3OT\***. The polymer was dissolved in chloroform and gradually more methanol was added.



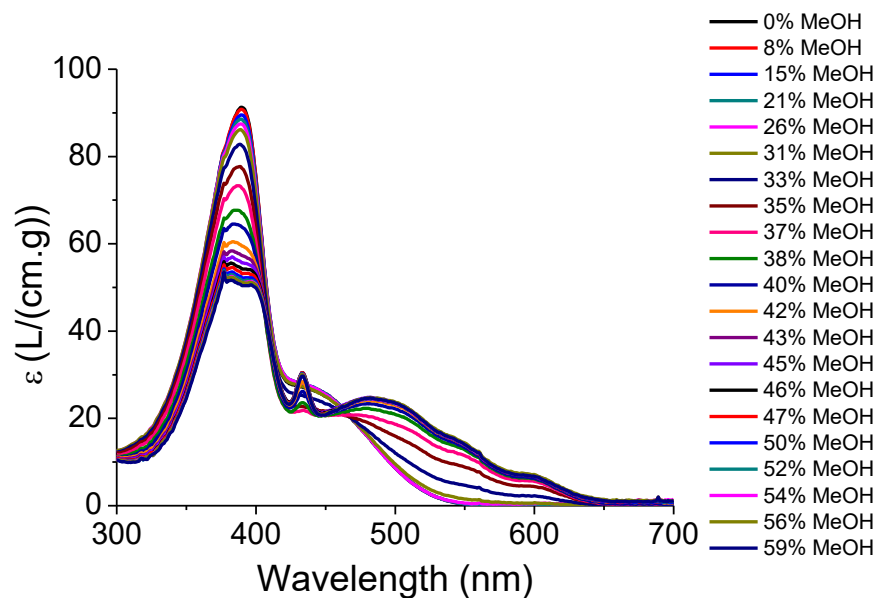
**Figure S9:** CD spectra of the solvatochromism experiments for **POF-*b*-P3OT\***. The polymer was dissolved in chloroform and gradually more methanol was added.



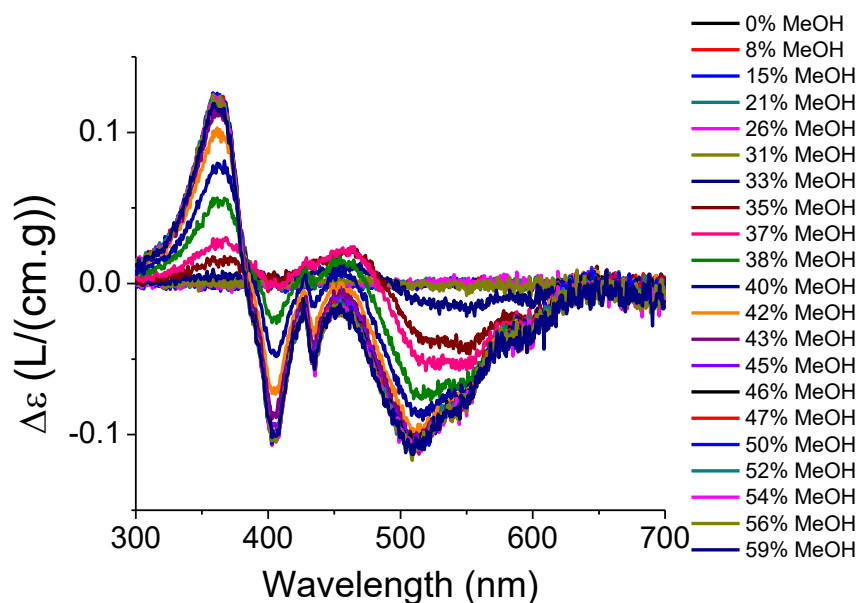
**Figure S10:** Absorption spectra of the solvatochromism experiments for **PHF-*b*-P3OT\***. The polymer was dissolved in chloroform and gradually more methanol was added.



**Figure S11:** CD spectra of the solvatochromism experiments for **PHF-*b*-P3OT\***. The polymer was dissolved in chloroform and gradually more methanol was added.

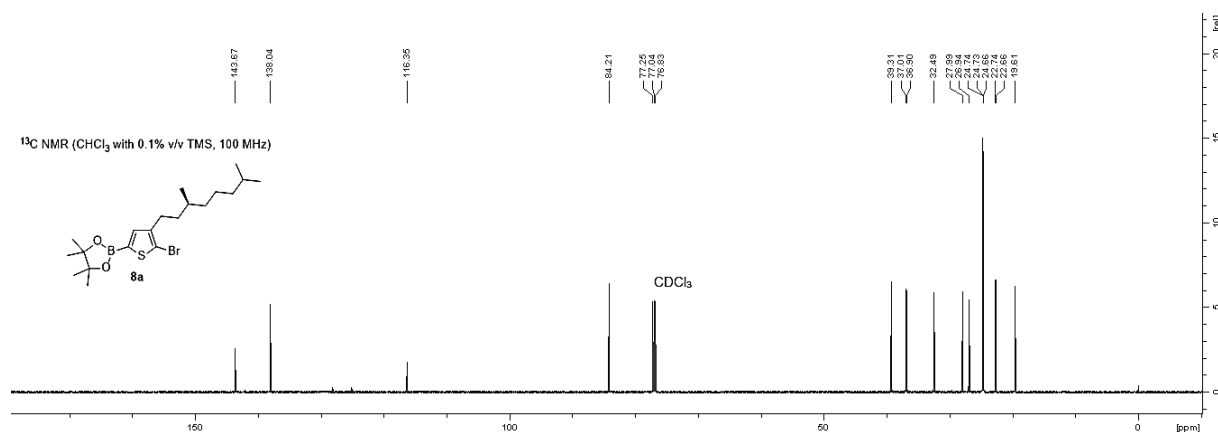
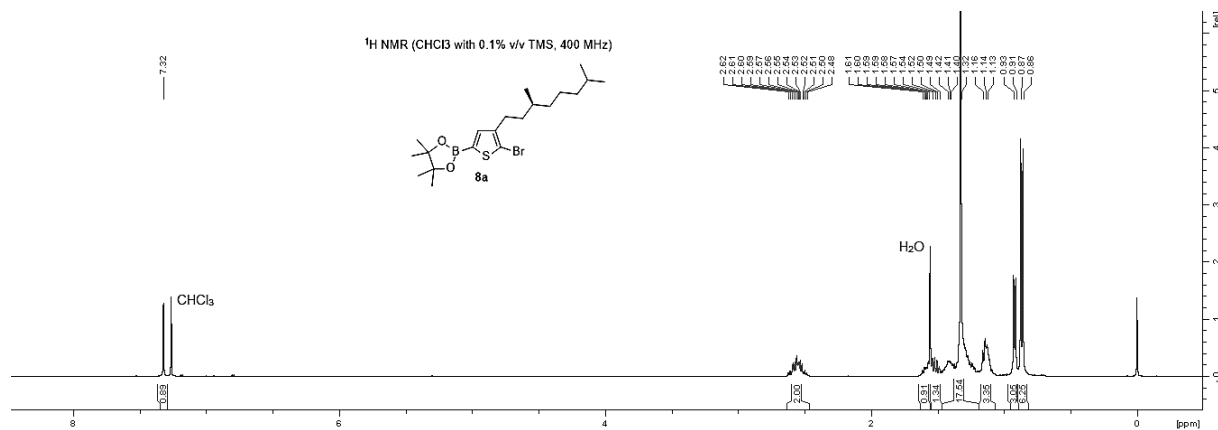
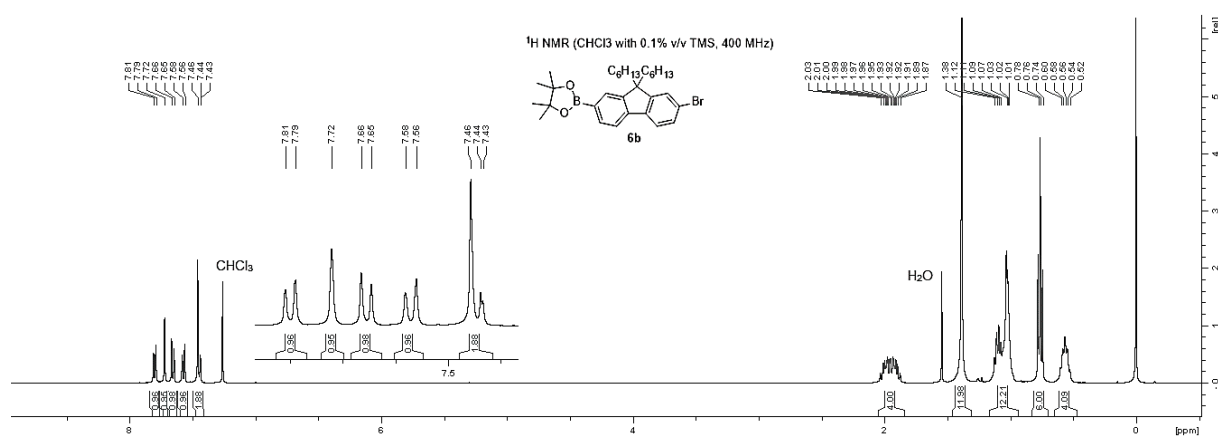
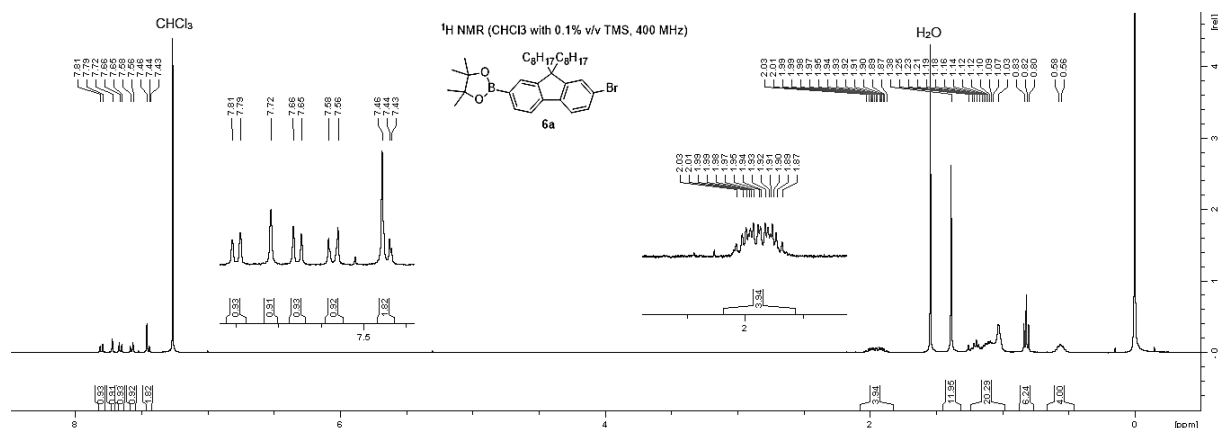


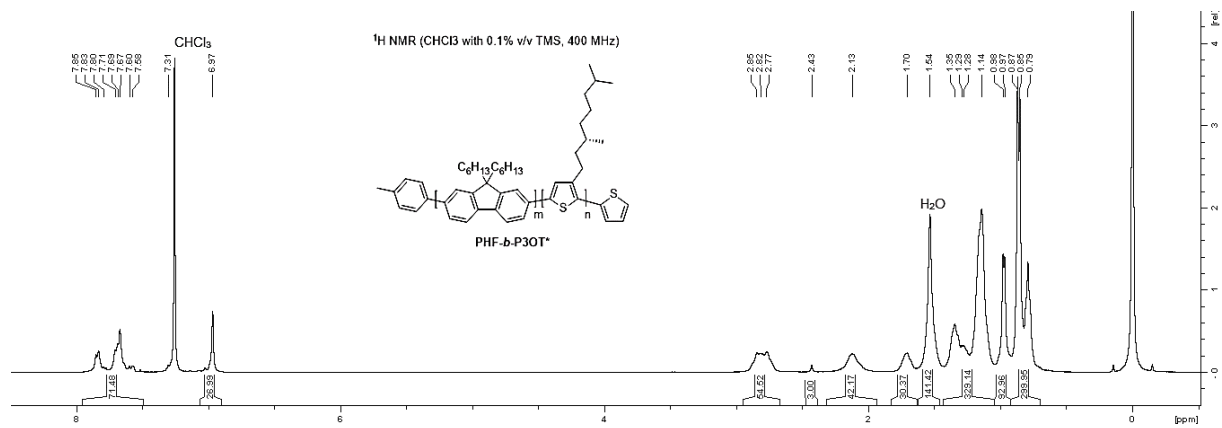
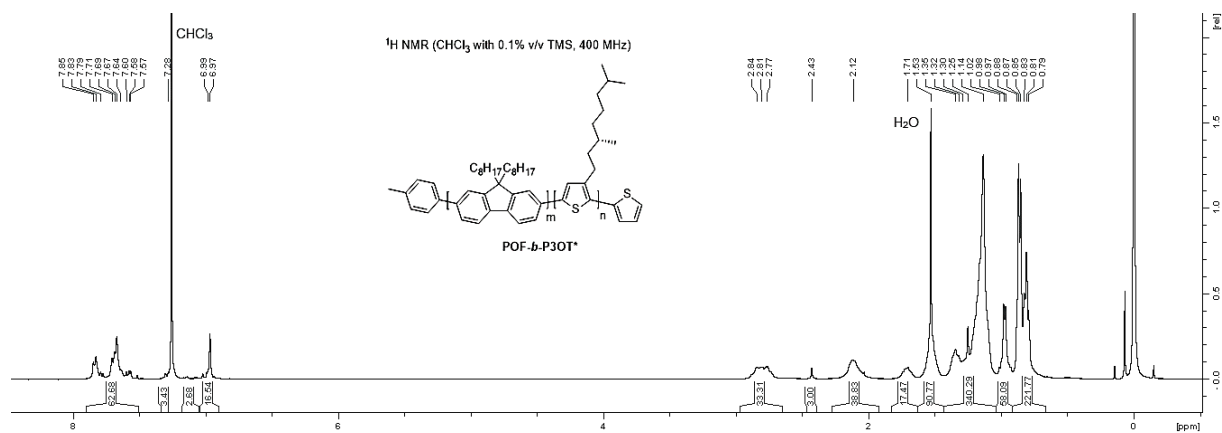
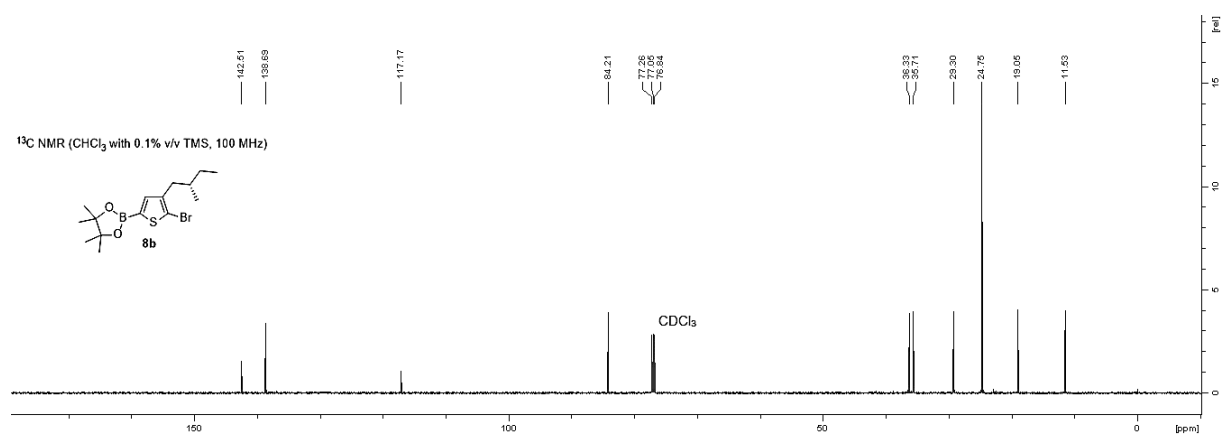
**Figure S12:** Absorption spectra of the solvatochromism experiments for **POF-*b*-P3BT\***. The polymer was dissolved in chloroform and gradually more methanol was added.



**Figure S13:** CD spectra of the solvatochromism experiments for **POF-*b*-P3BT\***. The polymer was dissolved in chloroform and gradually more methanol was added.

# VIII. NMR spectra

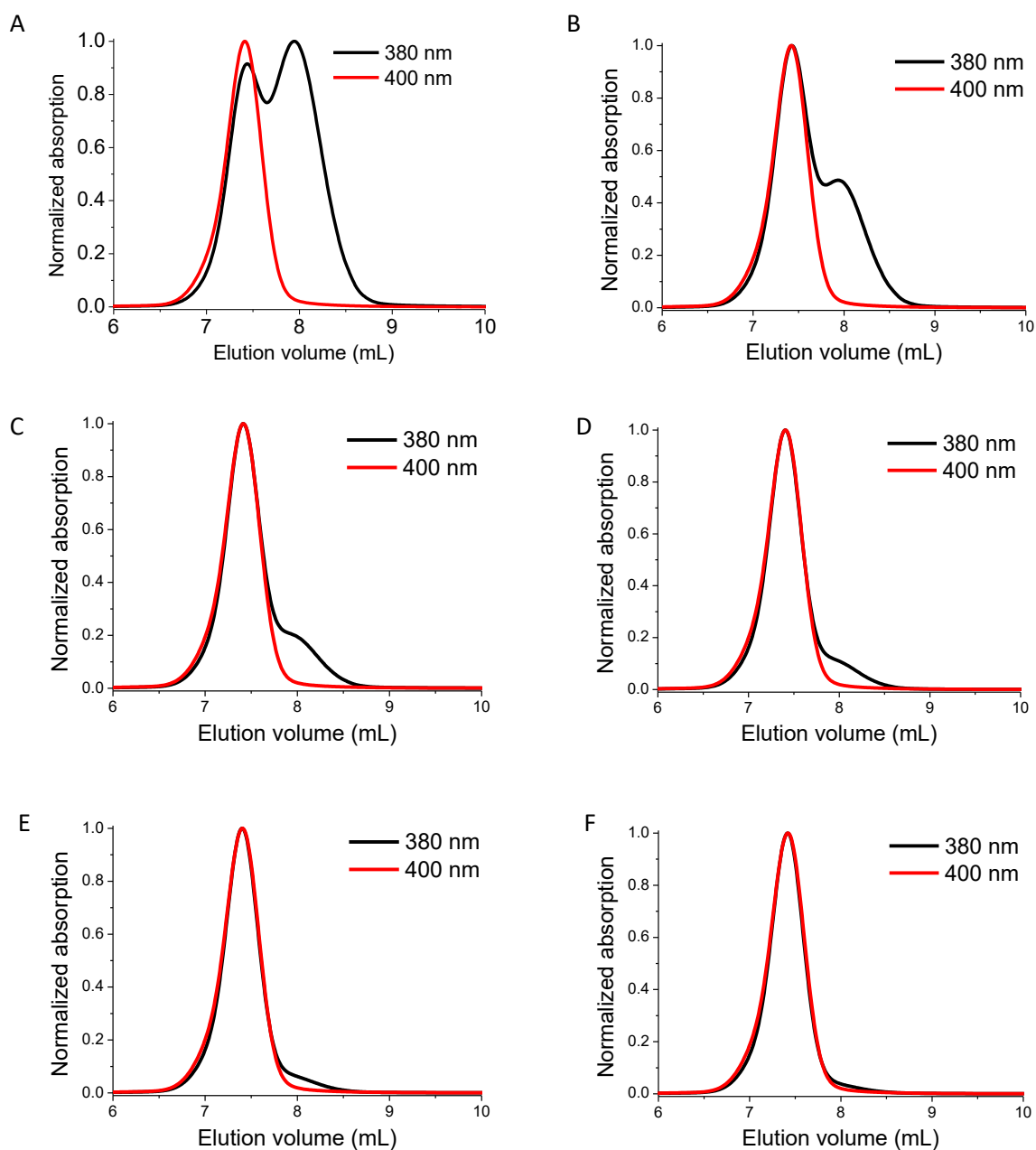








## IX. Determination of detection limit of PF homopolymer contamination in PF-*b*-PT copolymers



**Figure S14:** GPC elution chromatograms (detection at 380 nm and 440 nm) for mixtures of POF-*b*-P3BT\* and POF. A until F are mixture with 50%, 25%, 10%, 5%, 2.5% and 1.25% of POF, respectively.

## X. References

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