

Supporting information

Chiral expression of co-crystallizing poly(thiophene)-*block*- poly(selenophene) copolymers

Birgitt Timmermans and Guy Koeckelberghs*

Laboratory for Polymer Synthesis, KU Leuven, Celestijnenlaan 200F - Box 2404, B-3001
Heverlee, Belgium

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II. Materials

Except for precursor monomer (*S*)-2-bromo-3-(3,7-dimethyloctyl)-5-iodothiophene (**1a**), 3-iodoselenophene (**2a**) and the precursor initiator (**3a**), 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).

III. Instrumentation

¹H NMR spectra were recorded on a Bruker Avance 300 MHz or 400 MHz spectrometer. Gel permeation chromatography (GPC) measurements were carried out with a Shimadzu LC20 apparatus (LC-20AT pump, CBM-20A controller, RID-20A and SPD-20A detectors, PLgel 5 μ m MIXED-D column). The GPC system is calibrated towards polystyrene standards (purchased from Polymer Laboratories). Before injecting, the polymers were dissolved in THF ($c \approx 1$ mg/mL) and filtered over a filter with a pore size of 0.2 μ m. The UV-vis spectra were measured on a Perkin Elmer Lambda 900 spectrometer. The CD spectra were recorded on a JASCO J-810 spectrometer. The GC-MS spectra were recorded using a Thermo Finnigan Trace GC and ITQ 9000 Mass Spectrometer. The concentration of the start solution of the solvatochromism experiments was ± 0.03 mg/mL and methanol was added at a constant speed of 0.25 mL/min via an automatic syringe pump. Differential scanning calorimetry (DSC) measurements were performed using a TA Instruments Q2000-DSC. Tzero Aluminium Hermetic pans were used and the DSC apparatus was calibrated towards indium. The samples were heated from 0°C to 200°C or 220°C and then cooled to 0°C, this was done twice. At 0°C and 200°C or 220°C, the samples were kept isothermic for 5 minutes. A heating and cooling rate of 10°C/min were used. Dynamic light scattering (DLS) measurements were executed on a Brookhaven BI-90Plus Particle Size Analyzer with a laser wavelength of 659nm, collecting of the scattered light at an angle of 90°

and an acquisition time of 60 s. The concentration of the start solution of the DLS experiments was ± 0.03 mg/mL and methanol was added at a constant speed of 0.25 mL/min via an automatic syringe pump.

IV. Synthetic procedures

Precursor monomer (*S*)-2-bromo-3-(3,7-dimethyloctyl)-5-iodothiophene (**1a**)¹, 3-iodoselenophene (**2a**)² and precursor initiator (**3a**)³ were synthesized according to literature procedures.

a) Synthesis of precursor monomer (*S*)-2-bromo-3-(3,7-dimethyloctyl)-5-iodoselenophene (**2d**)

Synthesis of (S)-3-(3,7-dimethyloctyl)selenophene (2b)

A solution of (*S*)-1-bromo-3,7-dimethyloctane (8.18 g, 37.0 mmol) in dry diethyl ether (15 mL) was added dropwise to a suspension of magnesium turnings (0.899 g, 37.0 mmol) in dry diethyl ether (10 mL) under argon atmosphere. The reaction mixture was refluxed for 3 hours, then cooled down to room temperature and cannulated to a solution of 3-iodoselenophene (**2a**) (4.75 g, 18.5 mmol) and Ni(dppe)Cl₂ (dppe = 1,3-bis(diphenylphosphino)ethane) (0.488 g, 0.925 mmol) in dry diethyl ether (10 mL) under argon atmosphere. The reaction mixture was refluxed for 2 hours, after which it was cannulated to a 2M HCl solution at 0°C. The formed precipitate was filtered off and the filtrate was extracted with diethyl ether. The organic layers were combined and consecutively washed with a saturated NaHCO₃- and saturated NaCl-solution, then dried over MgSO₄ and concentrated under reduced pressure. The crude product was purified by column chromatography (SiO₂, heptane) and a yellow oil was obtained.

Yield: 2.33 g, 23%. δ H (300 MHz, CDCl_3 , TMS): δ 7.91 (dd, $J = 5.30$ Hz, 2.5 Hz, 1H), 7.54 (m, 1H), 7.21 (dd, $J = 5.30$ Hz, 1.22 Hz, 1H), 2.60 (m, 2H), 1.58-1.72 (m, 1H), 1.35-1.53 (m, 3H), 1.02-1.35 (m, 7H); 0,91 (d, 3H), 0,86 (d, 6H). δ C (300 MHz, CDCl_3 , TMS): 145.53, 131.55, 129.79, 123.75, 39.46, 37.77, 37.27, 32.60, 29.62, 28.11, 24.85, 22.87, 19.73. GC-MS (EI) m/z: $\text{C}_{14}\text{H}_{24}\text{Se}$ [M^+], 271.

Synthesis of (S)-2-bromo-3-(3,7-dimethyloctyl)selenophene (2c)

N-bromosuccinimide (1.37 g, 7.72 mmol) was added in small quantities to a solution of **2b** (2.33 g, 8.58 mmol) in tetrahydrofuran (35 mL) at 0°C and under argon atmosphere. The reaction mixture was shielded from light and stirred overnight at room temperature. Then, a saturated NaHSO_3 -solution (35 mL) was added to the reaction mixture and the mixture was extracted with heptane. The organic layers were combined and consecutively washed with a saturated NaHSO_3 -solution, a 20% NaOH -solution and a saturated NaHCO_3 - and NaCl -solution, then dried over MgSO_4 and concentrated under reduced pressure. The crude product was purified by column chromatography (SiO_2 , petroleum ether) and a colorless oil was obtained.

Yield: 1.90 g, 63%. δ H (400 MHz, CDCl_3 , TMS): 7.48 (d, $J = 6.10$ Hz, 1H), 7.02 (d, $J = 6.10$ Hz, 1H), 2.54 (m, 2H), 1.48-1.65 (m, 1H), 1.19-1.48 (m, 6H), 1.05-1.19 (m, 3H); 0,93 (d, 3H), 0,87 (d, 6H). δ C (300 MHz, CDCl_3 , TMS): 144.57, 131.28, 130.21, 111.13, 39.45, 37.15, 36.91, 32.63, 28.48, 28.13, 24.83, 22.88, 19.75. GC-MS (EI) m/z: $\text{C}_{14}\text{H}_{23}\text{BrSe}$ [M^+], 352.

Synthesis of (S)-2-bromo-3-(3,7-dimethyloctyl)-5-iodoselenophene (2d)

Di(acetoxyiodo)benzene (0.789 g, 2.45 mmol) was added to a solution of **2c** (1.90 g, 5.44 mmol) in dichloromethane (50 mL) at 0°C under inert atmosphere. Then, iodine (0.621 g, 2.45 mmol) was added in small quantities and the reaction mixture was stirred overnight at room

temperature. Afterwards, the reaction mixture was quenched with a saturated NaHSO₃-solution (50 mL) and extracted with diethyl ether. The organic layers were combined and consecutively washed with a saturated NaHSO₃-, NaHCO₃ and NaCl-solution, then dried over MgSO₄ and concentrated under reduced pressure. The crude product was purified by column chromatography (SiO₂, petroleum ether) and a colorless oil was obtained.

Yield: 2.30 g, 89%. δ H (400 MHz, CDCl₃, TMS): 7.25 (s, 1H), 2.50 (m, 2H), 1.47-1.60 (m, 2H), 1.19-1.47 (m, 5H), 1.04-1.19 (m, 3H); 0,92 (d, 3H), 0,87 (d, 6H). δ C (300 MHz, CDCl₃, TMS): 146.64, 141.37, 114.77, 73.55, 39.41, 37.07, 36.84, 32.55, 28.17, 28.10, 24.78, 22.90, 19.73. GC-MS (EI) m/z: C₁₄H₂₂BrISe [M⁺], 478.

b) Monomer synthesis

Synthesis of monomer 1b

For the synthesis of **P1-P5**:

Precursor monomer **1a** (0.665 g, 1.55 mmol) was brought under argon atmosphere and dissolved in dry tetrahydrofuran (15.5 mL). An *i*-PrMgCl·LiCl solution (1.13 mL, 1.52 mmol, 1.34 M) was added dropwise at 0°C and the reaction mixture was stirred for 1 hour at 0°C.

For the synthesis of **P6**:

Precursor monomer **1a** (0.150 g, 0.35 mmol) was brought under argon atmosphere and dissolved in dry tetrahydrofuran (3.5 mL). An *i*-PrMgCl·LiCl solution (0.29 mL, 0.343 mmol, 1.19 M) was added dropwise at 0°C and the reaction mixture was stirred for 1 hour at 0°C.

For the synthesis of **P7**:

Precursor monomer **1a** (0.118 g, 0.275 mmol) was brought under argon atmosphere and dissolved in dry tetrahydrofuran (2.75 mL). An *i*-PrMgCl·LiCl solution (0.20 mL, 0.270 mmol, 1.34 M) was added dropwise at 0°C and the reaction mixture was stirred for 1 hour at 0°C.

Synthesis of monomer 2e

For the synthesis of **P1-P5**:

Precursor monomer **2d** (0.631 g, 1.33 mmol) was brought under argon atmosphere and dissolved in dry tetrahydrofuran (13.3 mL). An *i*-PrMgCl·LiCl solution (0.970 mL, 1.30 mmol, 1.34 M) was added dropwise at 0°C and the reaction mixture was stirred for 1 hour at 0°C.

For the synthesis of **P6**:

Precursor monomer **2d** (0.167 g, 0.35 mmol) was brought under argon atmosphere and dissolved in dry tetrahydrofuran (3.5 mL). An *i*-PrMgCl·LiCl solution (0.29 mL, 1.30 mmol, 1.19 M) was added dropwise at 0°C and the reaction mixture was stirred for 1 hour at 0°C.

For the synthesis of **P7**:

Precursor monomer **2d** (0.167 g, 0.35 mmol) was brought under argon atmosphere and dissolved in dry tetrahydrofuran (3.5 mL). An *i*-PrMgCl·LiCl solution (0.26 mL, 0.343 mmol, 1.34 M) was added dropwise at 0°C and the reaction mixture was stirred for 1 hour at 0°C.

V. Polymerization procedures

a) Synthesis of **P1**, **P2**, **P3**, **P4** and **P5**.

Four flasks charged with dppe (20.0 μmol ; 8.00 mg) and bromo-(*o*-methylbenzene)-bis(triphenylphosphine)nickel(II) **3a** (10.0 μmol ; 7.50 mg) were purged with argon and dry tetrahydrofuran (2.0 mL) was added. The reaction mixtures were stirred for 15 minutes at room temperature, after which an additional 4 mL of tetrahydrofuran was added to dilute the initiator mixture. 6 mL of the obtained solution of monomer **1b** was transferred to initiator mixture 1, 4.5 mL to initiator mixture 2, 3.0 mL to initiator mixture 3 and 1.5 mL to initiator mixture 4. Meanwhile, a fifth flask was charged with dppe (20.0 μmol ; 8.00 mg) and bromo-(*o*-methylbenzene)-bis(triphenylphosphine)nickel(II) **3a** (10.0 μmol ; 7.50 mg) and purged with argon. After a polymerization time of 45 minutes at room temperature, dry tetrahydrofuran (2.0 mL) was added to the fifth flask and the mixture was stirred for 15 minutes, after which an extra 4 mL of tetrahydrofuran was added to dilute the initiator mixture. After a polymerization time of 1 hour at room temperature, polymerization mixture 1 was quenched with HCl in tetrahydrofuran and 1/4 of the volume of mixture 2, 3 and 4 was transferred to different mass tubes charged with HCl in tetrahydrofuran in order to obtain **P1**, **P3a**, **P4a** and **P5a** respectively. Then, 1.13 mL of the obtained solution of monomer **2e** was transferred to initiator mixture 2, 2.25 mL to initiator mixture 3, 3.38 mL to initiator mixture 4 and 6 mL to initiator mixture 5. After a polymerization time of 1 hour at room temperature, the different polymerization mixtures were quenched with HCl in tetrahydrofuran in order to obtain **P2**, **P3**, **P4** and **P5**. A small aliquot of all polymerization mixtures was isolated for size exclusion chromatography before purification. The quenched polymerization mixtures were stirred for 15 minutes, after which they were precipitated in methanol and filtered. Then, the polymers were purified by a Soxhlet extraction in

methanol and chloroform. After precipitation of the concentrated chloroform solution in methanol and filtration **P1**, **P2**, **P3**, **P4** and **P5** were obtained as dark purple solids. The remaining 0.50 mL solution of the monomers was quenched with 0.50 mL D₂O for ¹H NMR analysis.

	Block 1		Block 1+2	
	\bar{M}_n (kg/mol)	Đ	\bar{M}_n (kg/mol)	Đ
P1	15.3	1.06	/	/
P2	12.5	1.06	/	/
P3	11.8	1.09	14.5	1.09
P4	6.46	1.09	15.7	1.10
P5	2.53	1.39	14.7	1.06

Yield: **P1**: 24.2 mg; **P2**: 92.0 mg; **P3**: 66.6 mg; **P4**: 72.7 mg; **P5**: 67.8 mg

b) Synthesis of P6.

A flask charged with Ni(dppe)Cl₂ (10.0 μmol; 5.30 mg) was purged with argon and dry tetrahydrofuran (6.0 mL) was added. Then, 3 mL of the obtained solution of monomer **1b** was added to 3 mL of the obtained solution of **2d** and this mixture was stirred for 2 minutes. Then, this mixture was transferred to the initiator mixture. After a polymerization time of 1 hour at room temperature, the polymerization mixture was quenched with HCl in tetrahydrofuran in

order to obtain **P6**. A small aliquot the polymerization mixtures was isolated for size exclusion chromatography before purification. The quenched polymerization mixture was stirred for 15 minutes, after which it was precipitated in methanol and filtered. Then, the polymer was purified by a Soxhlet extraction in methanol and chloroform. After precipitation of the concentrated chloroform solution in methanol and filtration, **P6** was obtained as a dark purple solid. The remaining 0.50 mL solution of the monomers was quenched with 0.50 mL D₂O for ¹H NMR analysis.

	\bar{M}_n (kg/mol)	Đ
P6	11.5	1.2

Yield: 77.9 mg

c) Synthesis of P7.

A flask charged with dppe (20.0 μmol; 8.00 mg) and bromo-(*o*-methylbenzene)-bis(triphenylphosphine)nickel(II) **3a** (10.0 μmol; 7.50 mg) was purged with argon and dry tetrahydrofuran (2.0 mL) was added. The reaction mixture was stirred for 15 minutes at room temperature, after which an additional 4 mL of tetrahydrofuran was added to dilute the initiator mixture. 3 mL of the obtained solution of monomer **2d** was transferred to the initiator mixture. After a polymerization time of 1 hour at room temperature, 1/4 of the volume of the polymerization mixture was transferred to a mass tubes charged with HCl in tetrahydrofuran in order to obtain **P7a**. Then, 2.25 mL of the obtained solution of monomer **1b** was transferred to the resulting polymerization mixture. After a polymerization time of 1 hour at room temperature,

the polymerization mixture was quenched with HCl in tetrahydrofuran in order to obtain **P7**. A small aliquot of the polymerization mixture was isolated for size exclusion chromatography before purification. The quenched polymerization mixture was stirred for 15 minutes, after which it was precipitated in methanol and filtered. Then, the polymer was purified by a Soxhlet extraction in methanol and chloroform. After precipitation of the concentrated chloroform solution in methanol and filtration **P7** was obtained as a dark purple solid. The remaining 0.50 mL solution of the monomers was quenched with 0.50 mL D₂O for ¹H NMR analysis.

	\bar{M}_n (kg/mol)	\bar{D}
P7	13.4	1.1

Yield: 56.6 mg

VI. Additional SEC elution curves

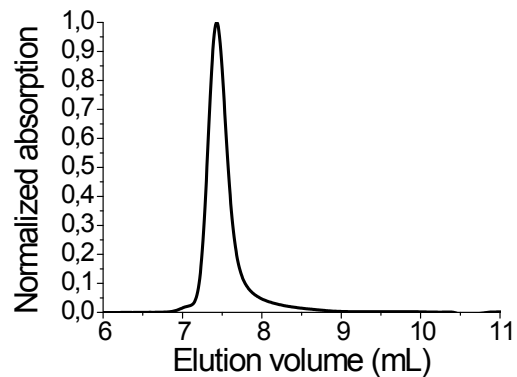


Figure S1. SEC elution curve of **P1**.

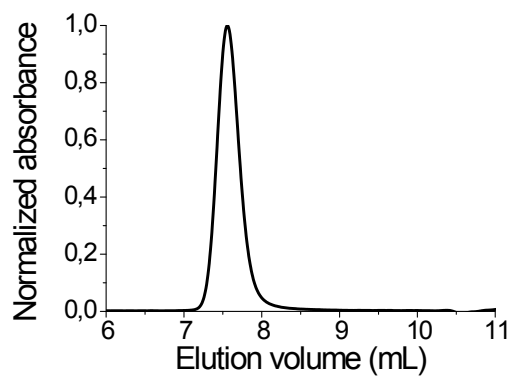


Figure S2. SEC elution curve of **P2**.

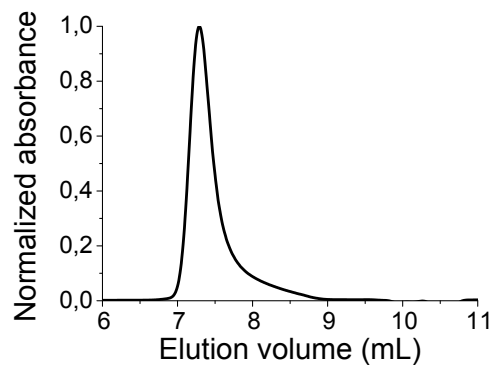


Figure S3. SEC elution curve of **P6**.

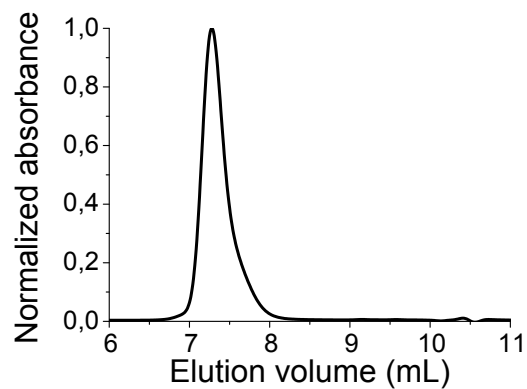


Figure S4. SEC elution curve of **P7**.

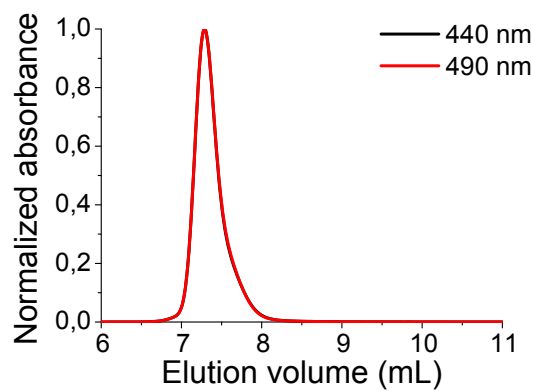


Figure S5. SEC elution curves of **P7** at 440 nm (black curve) and 490 nm (red curve).

VII. Evaluation of the detection limit of the SEC detector for poly(3-alkylselenophene) contamination in poly(3-alkylthiophene-*b*-poly(3-alkylselenophene))

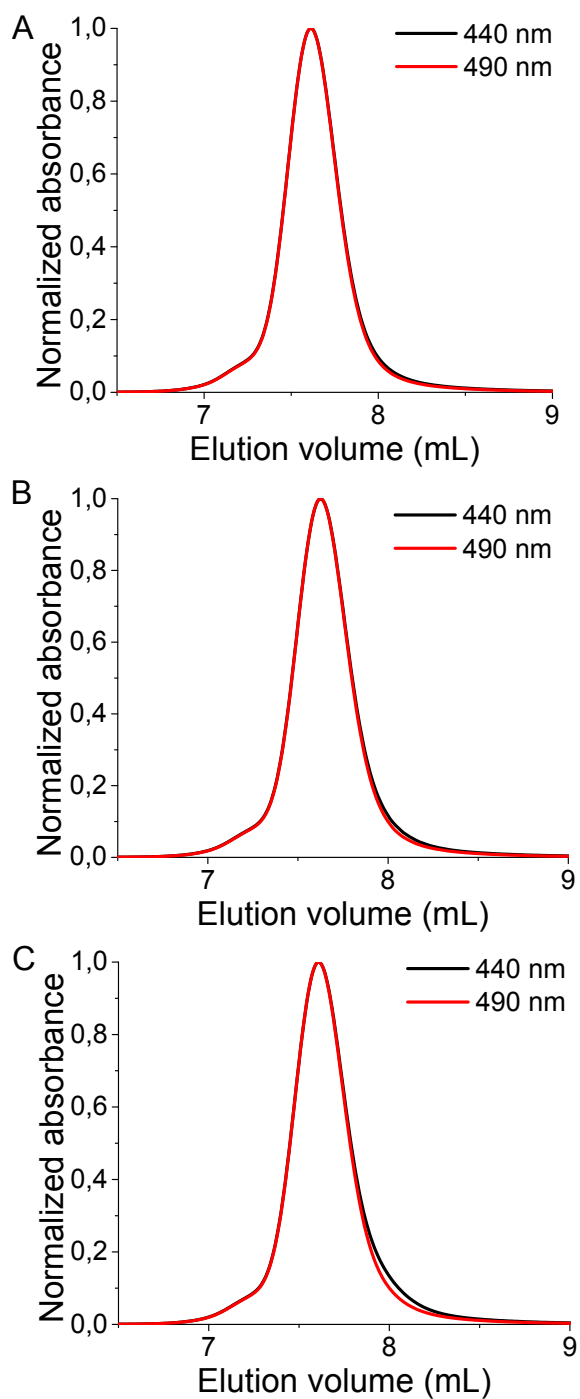


Figure S6. SEC elution curves (detection at 440 nm and 490 nm) of **P2** contaminated with different percentages of **P4a** (A: 1% of **P4a**, B: 2% of **P4a** and C: 5% of **P4a**).

VIII. Determination of the degree of polymerization

a) Via aliphatic region

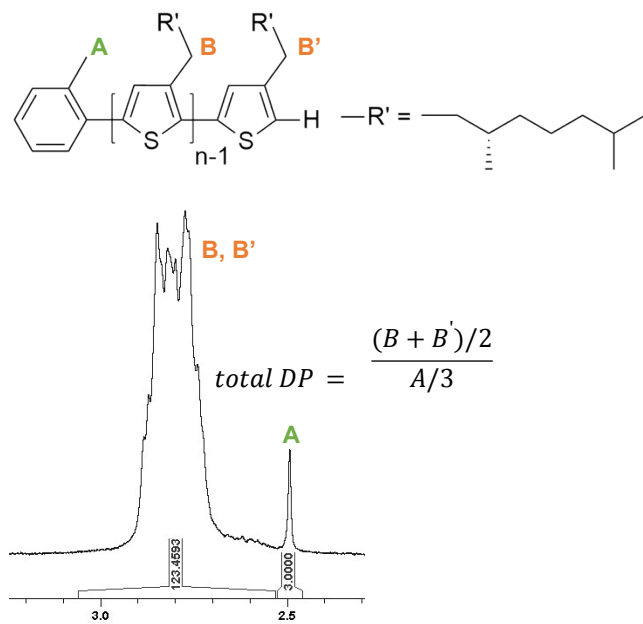


Figure S7. Determination of the degree of polymerization for **P1** via aliphatic $^1\text{H NMR}$ signals.

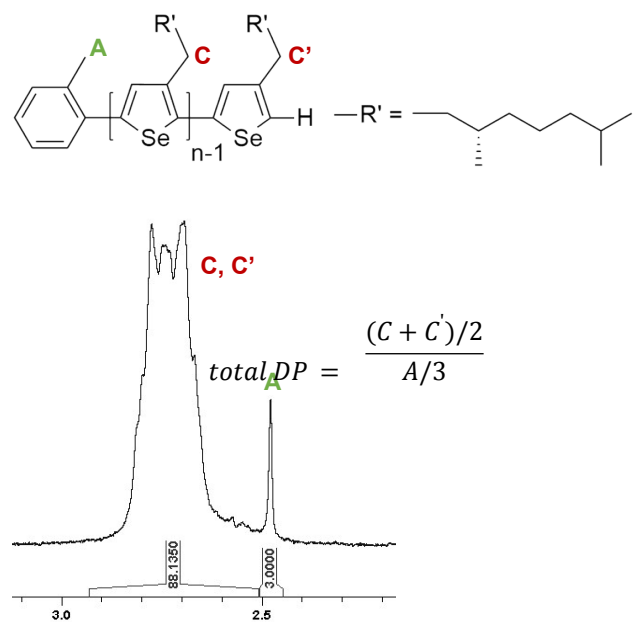


Figure S8. Determination of the degree of polymerization for **P2** via aliphatic $^1\text{H NMR}$ signals.

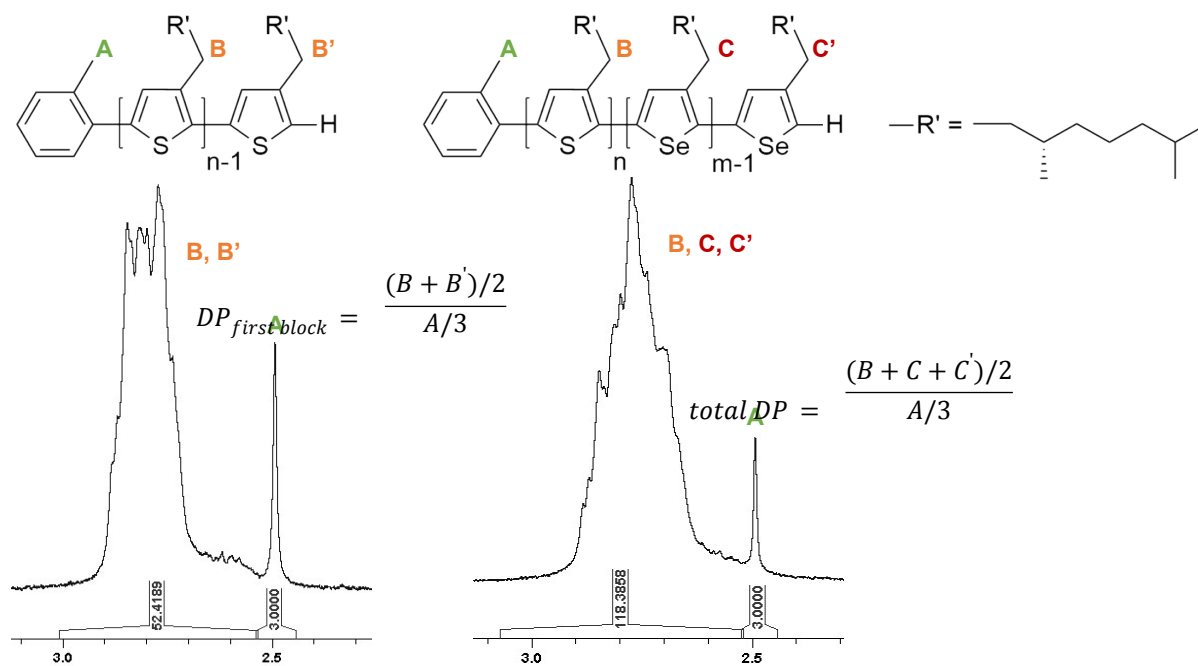


Figure S9. Determination of the degree of polymerization for **P4** via aliphatic ^1H NMR signals.

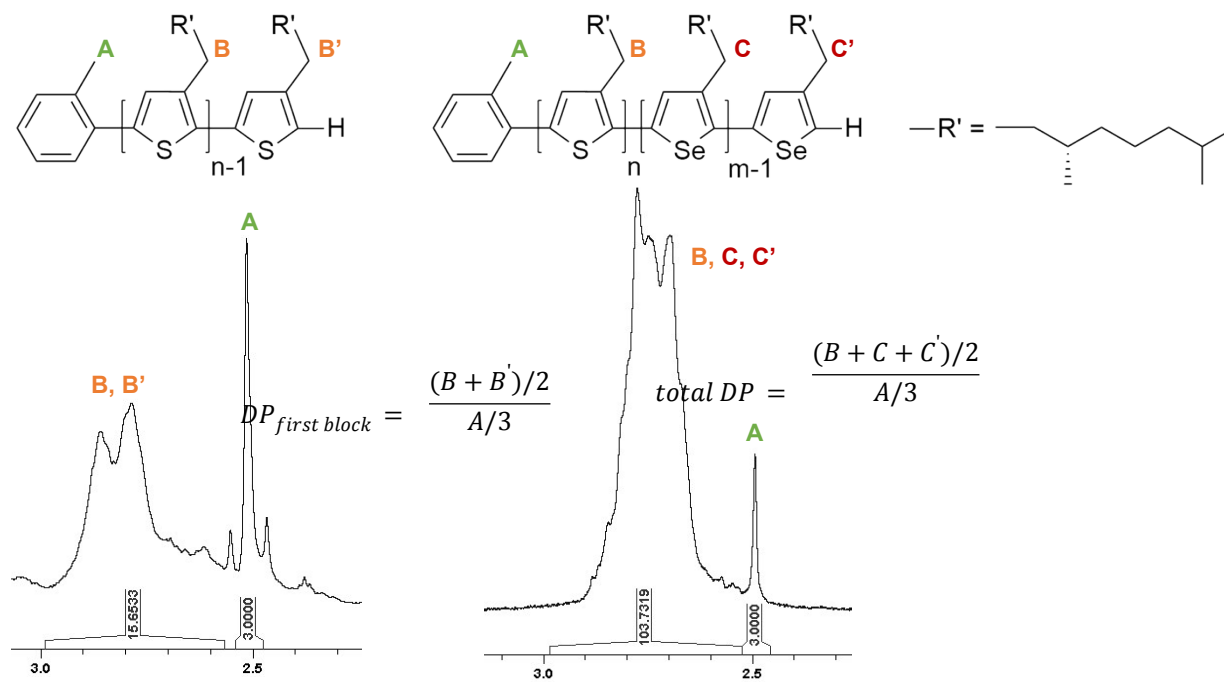


Figure S10. Determination of the degree of polymerization for **P5** via aliphatic ^1H NMR signals.

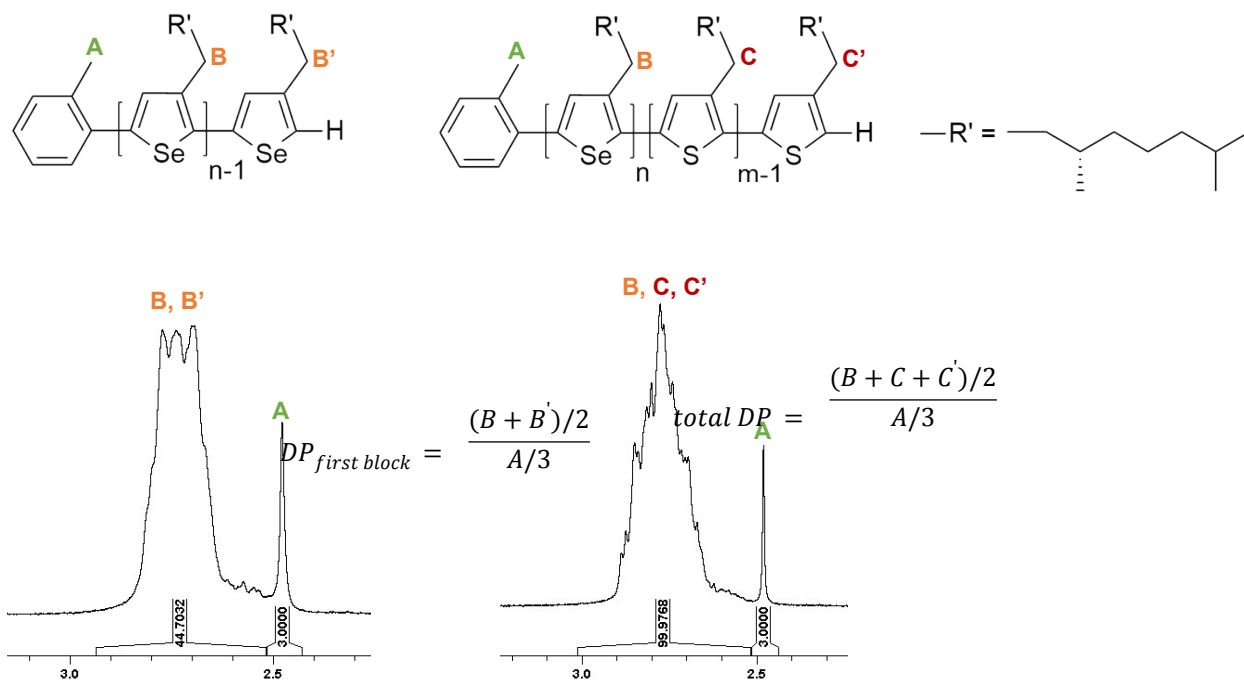


Figure S11. Determination of the degree of polymerization for **P7** via aliphatic ^1H NMR signals.

b) *Via aromatic region*

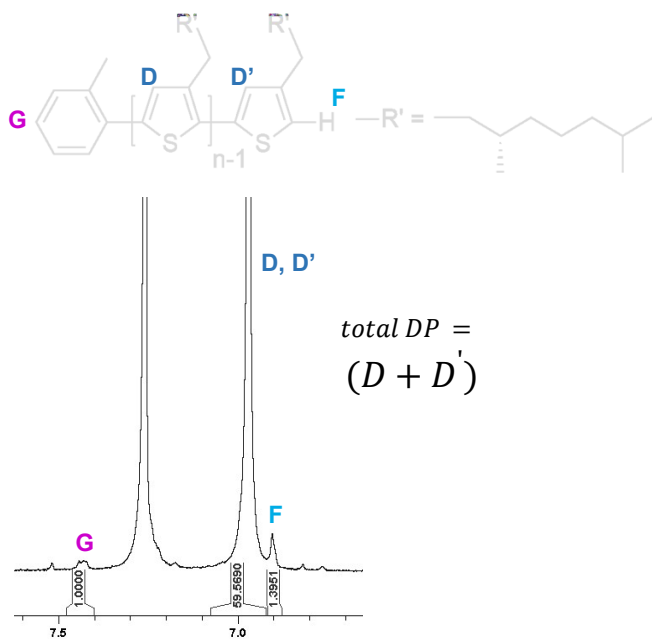


Figure S12. Determination of the degree of polymerization for **P1** via aromatic ^1H NMR signals.

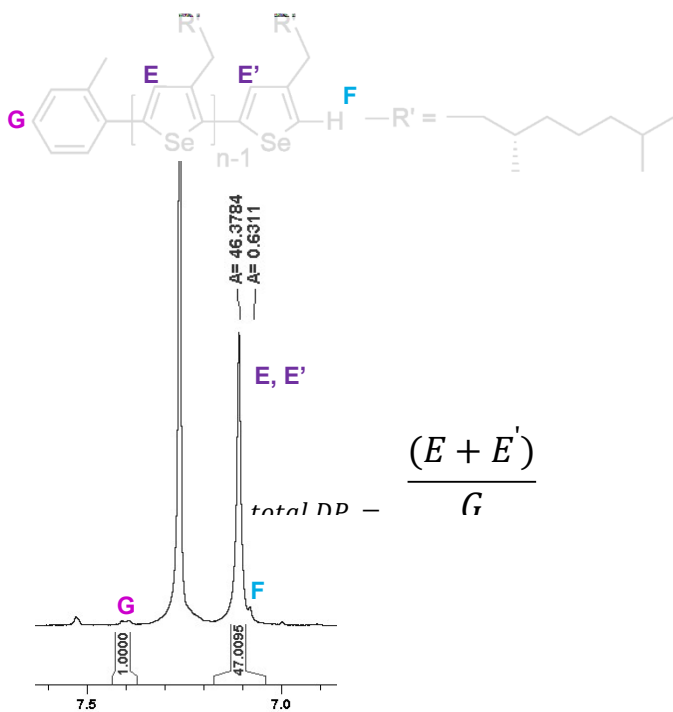


Figure S13. Determination of the degree of polymerization for **P2** via aromatic ^1H NMR signals.

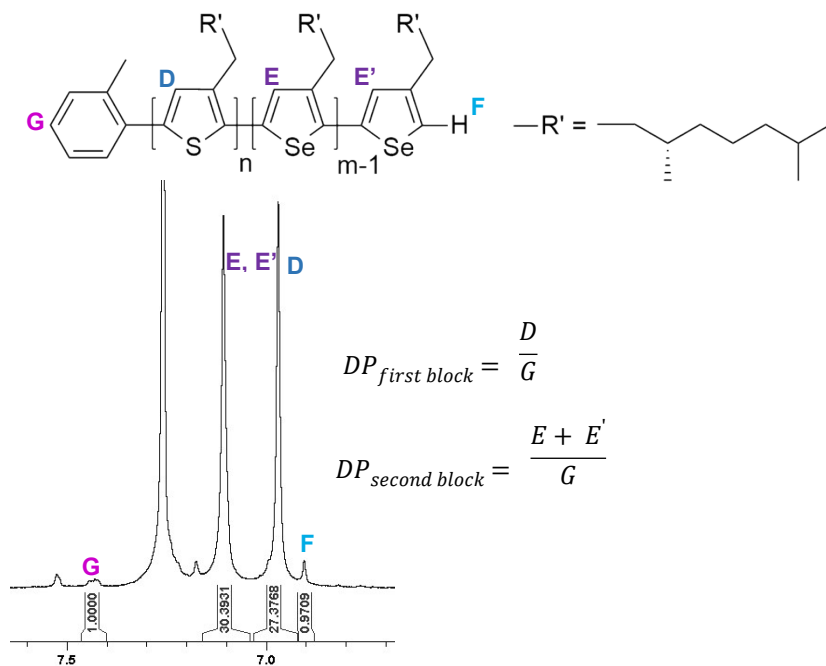


Figure S14. Determination of the degree of polymerization for **P4** via aromatic ^1H NMR signals.

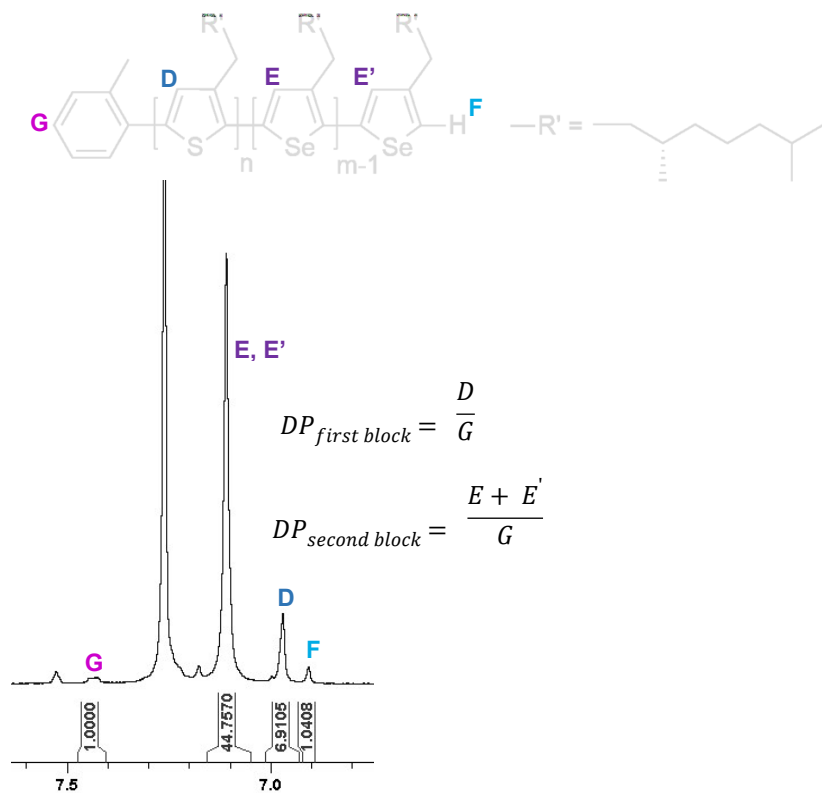


Figure S15. Determination of the degree of polymerization for **P5** via aromatic ^1H NMR signals.

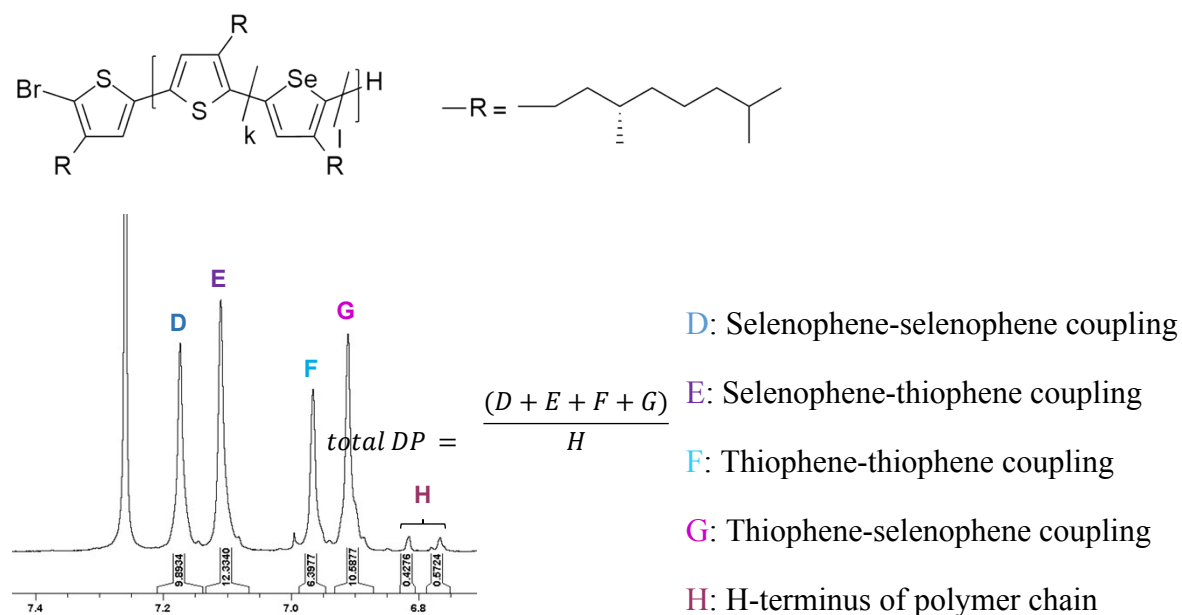


Figure S16. Determination of the degree of polymerization for **P6** via aromatic ^1H NMR signals.

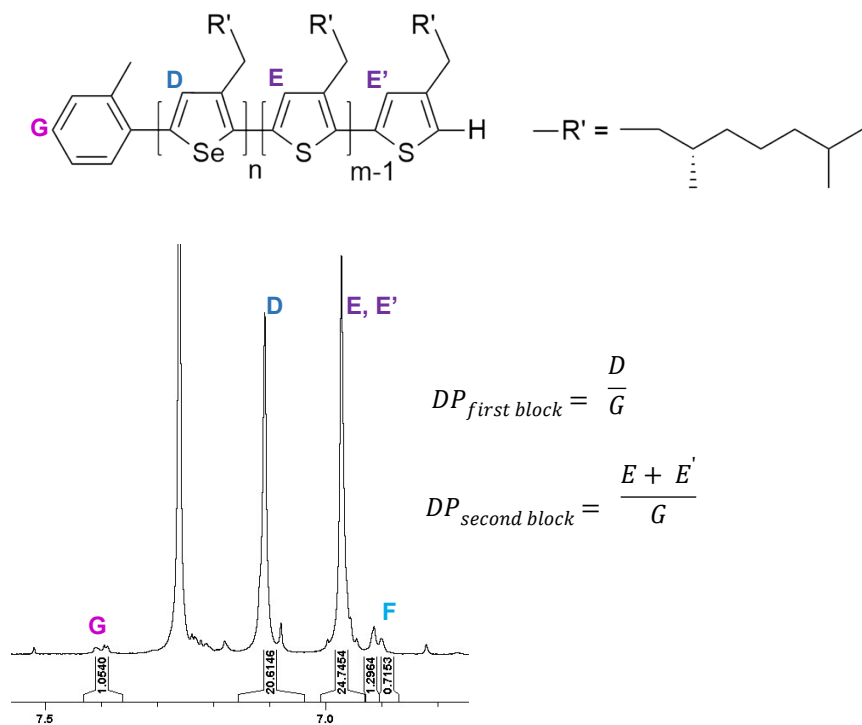


Figure S17. Determination of the degree of polymerization for **P7** via aromatic ^1H NMR signals.

IX. Additional UV-vis and CD spectra

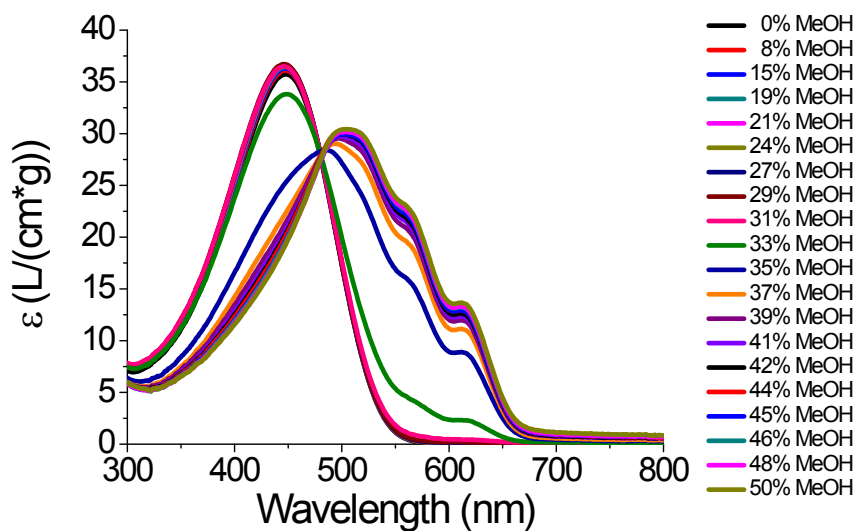


Figure S18. UV-vis spectra of the solvatochromism experiment for **P1**.

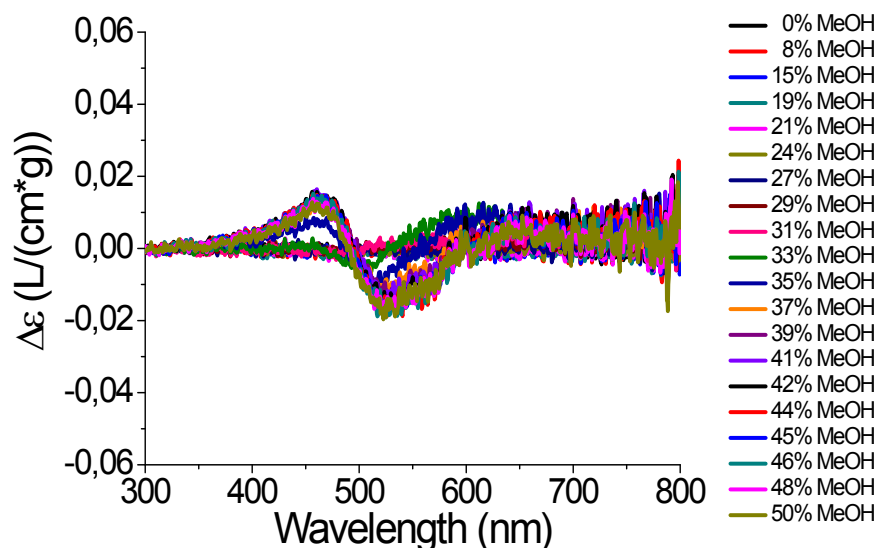


Figure S19. CD spectra of the solvatochromism experiment for **P1**.

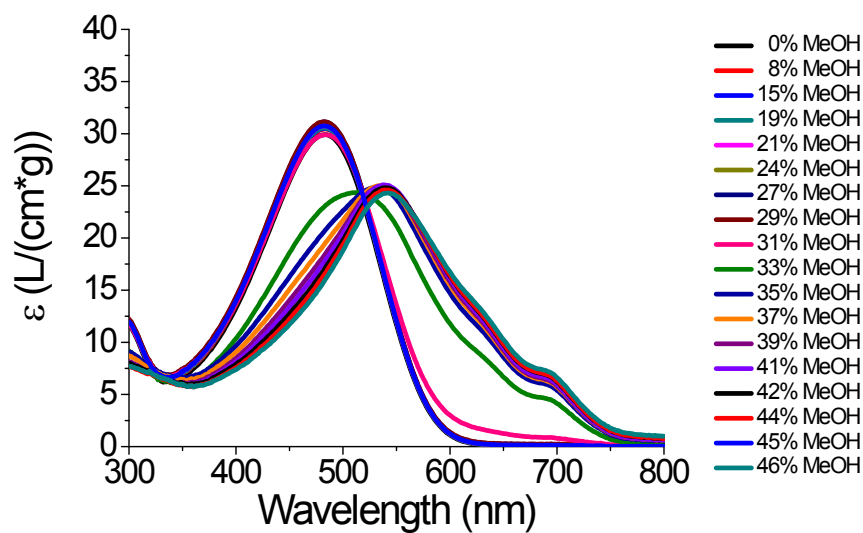


Figure S20. UV-vis spectra of the solvatochromism experiment for **P2**.

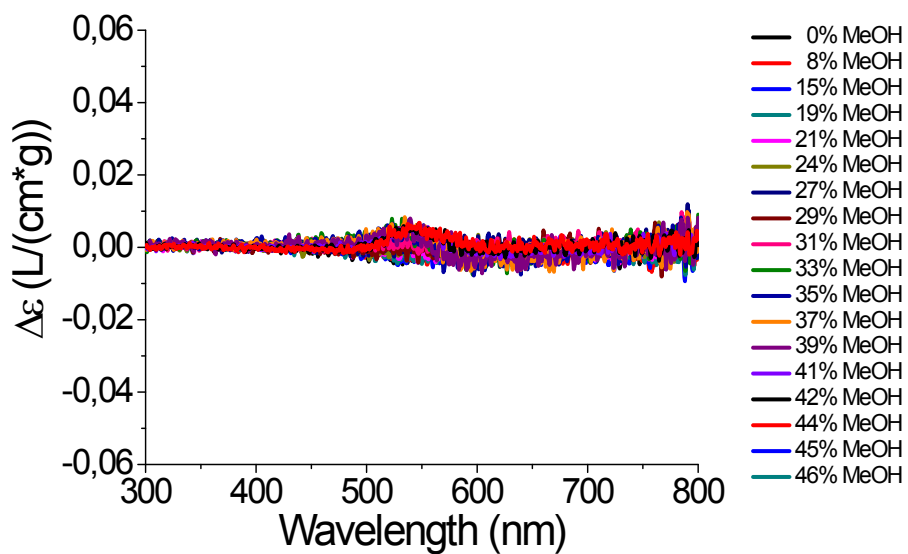


Figure S21. CD spectra of the solvatochromism experiment for **P2**.

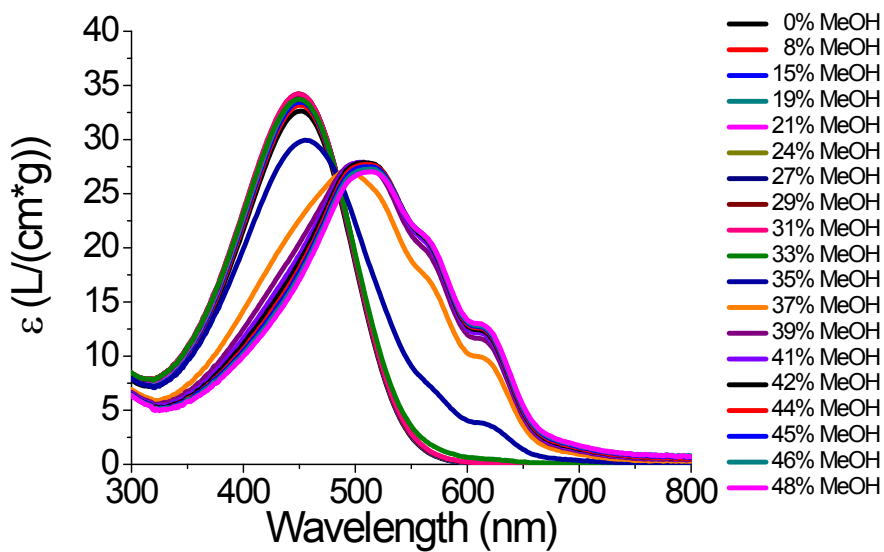


Figure S22. UV-vis spectra of the solvatochromism experiment for **P3**.

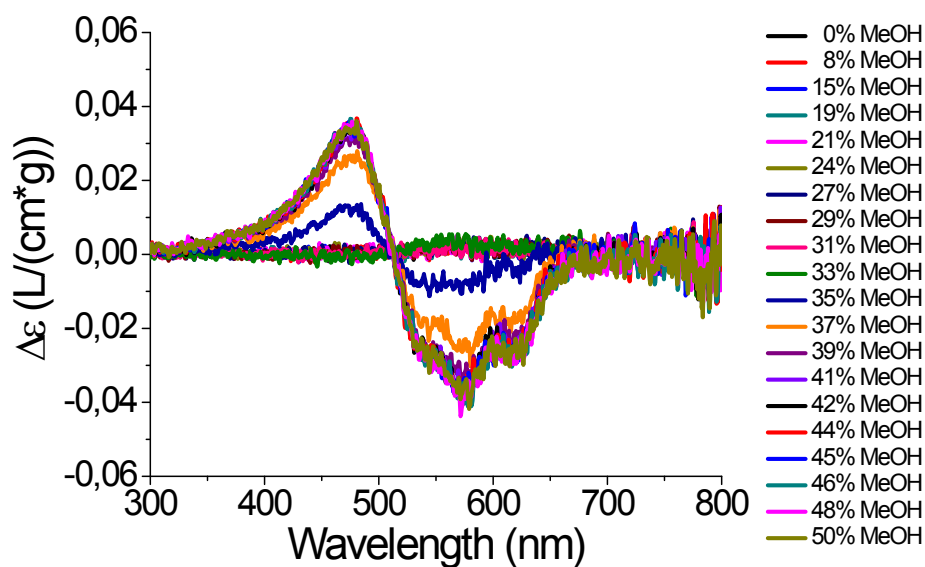


Figure S23. CD spectra of the solvatochromism experiment for **P3**.

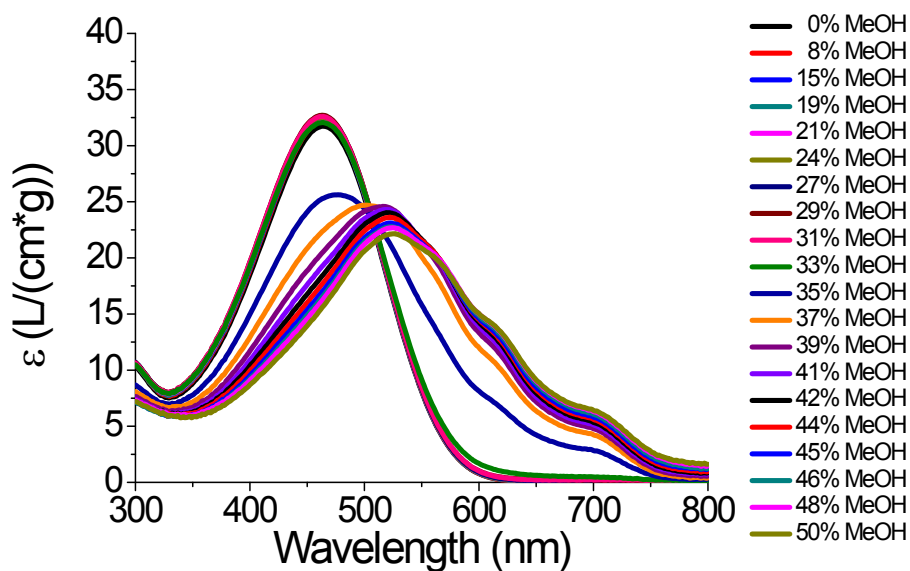


Figure S24. UV-vis spectra of the solvatochromism experiment for **P4**.

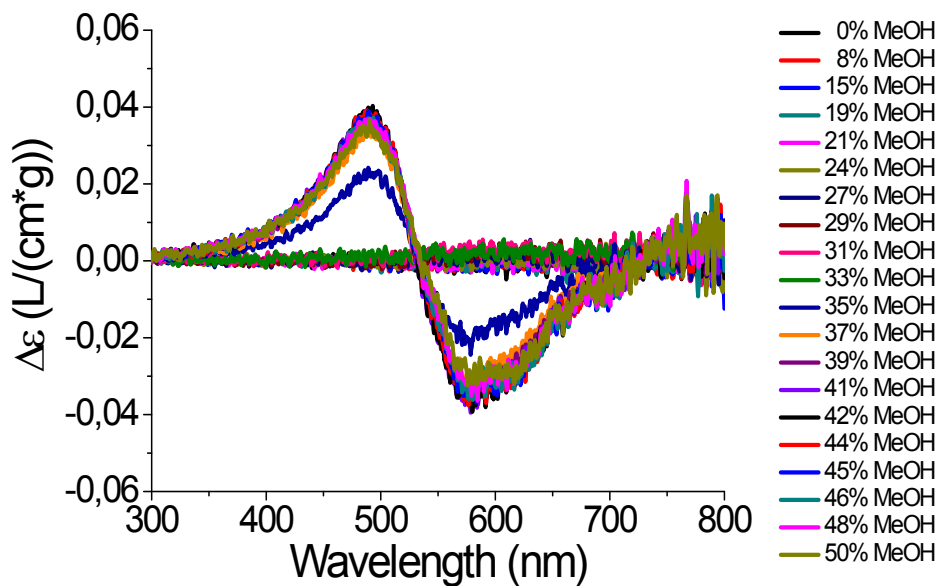


Figure S25. CD spectra of the solvatochromism experiment for **P4**.

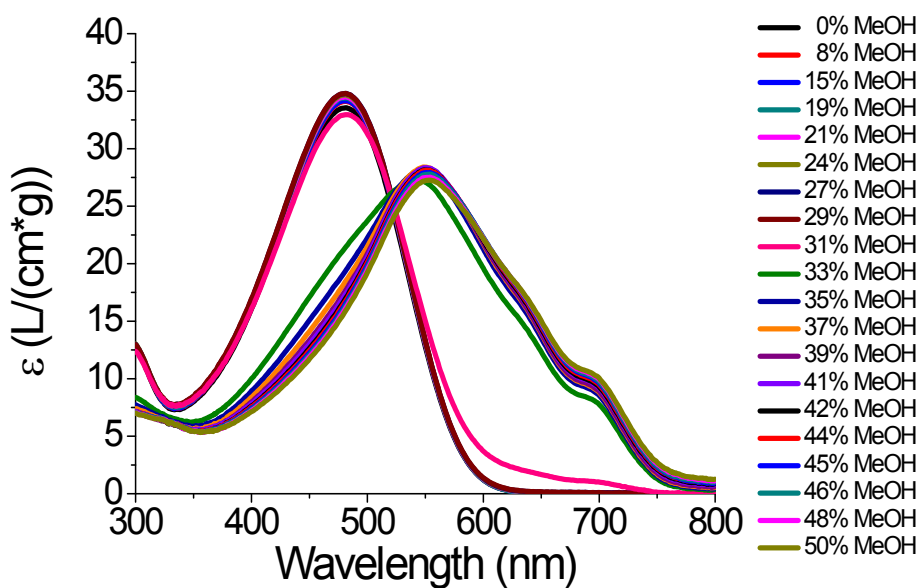


Figure S26. UV-vis spectra of the solvatochromism experiment for **P5**.

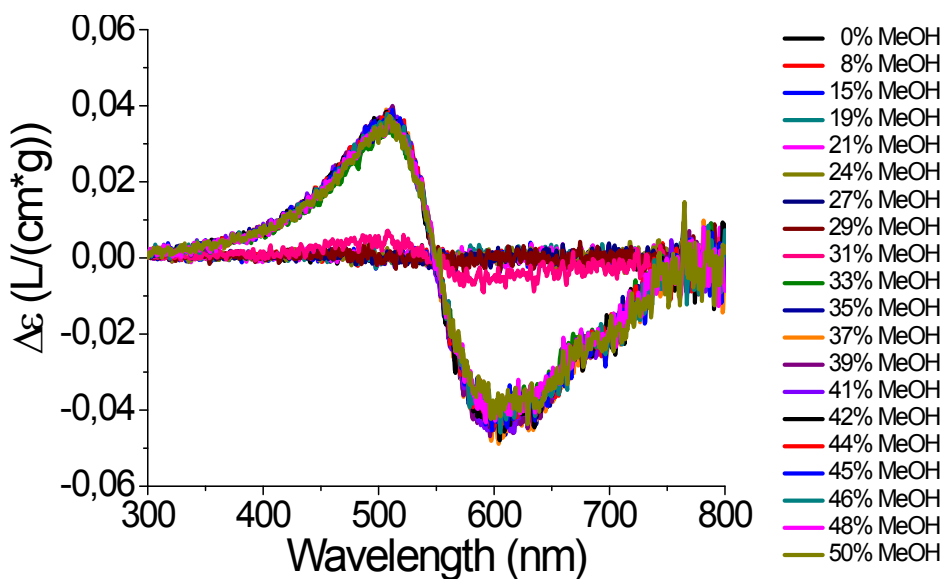


Figure S27. CD spectra of the solvatochromism experiment for **P5**.

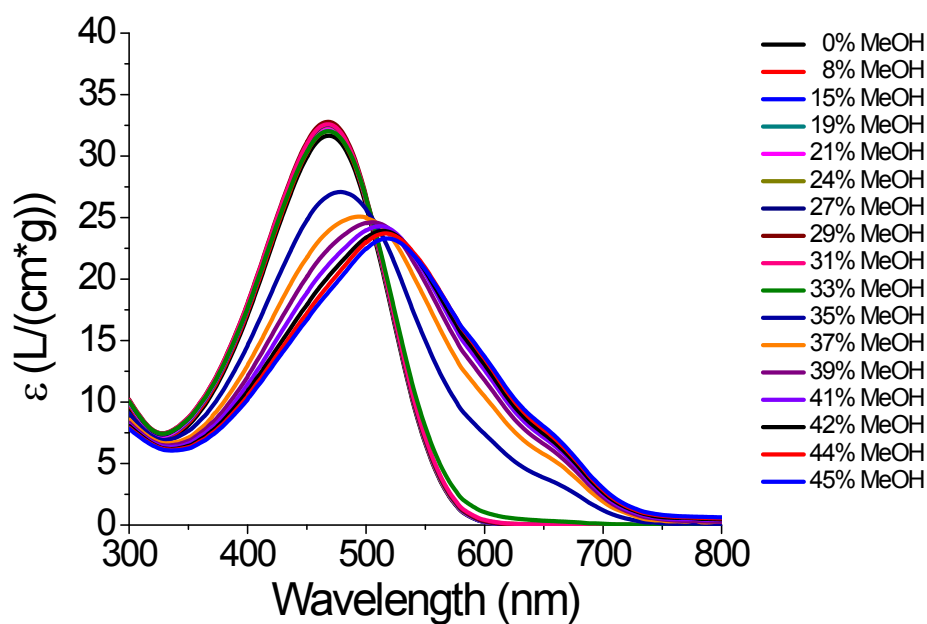


Figure S28. UV-vis spectra of the solvatochromism experiment for **P6**.

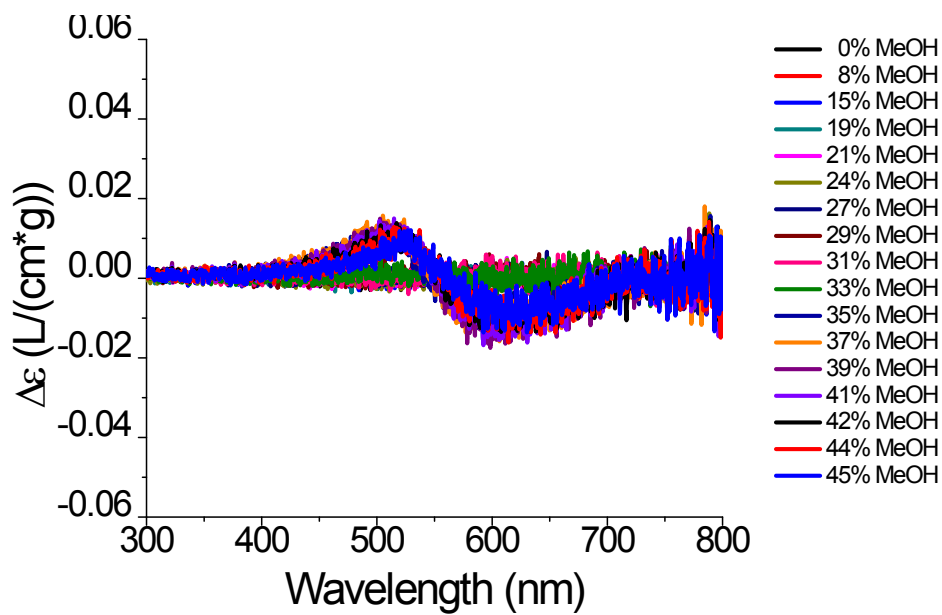


Figure S29. CD spectra of the solvatochromism experiment for **P6**.

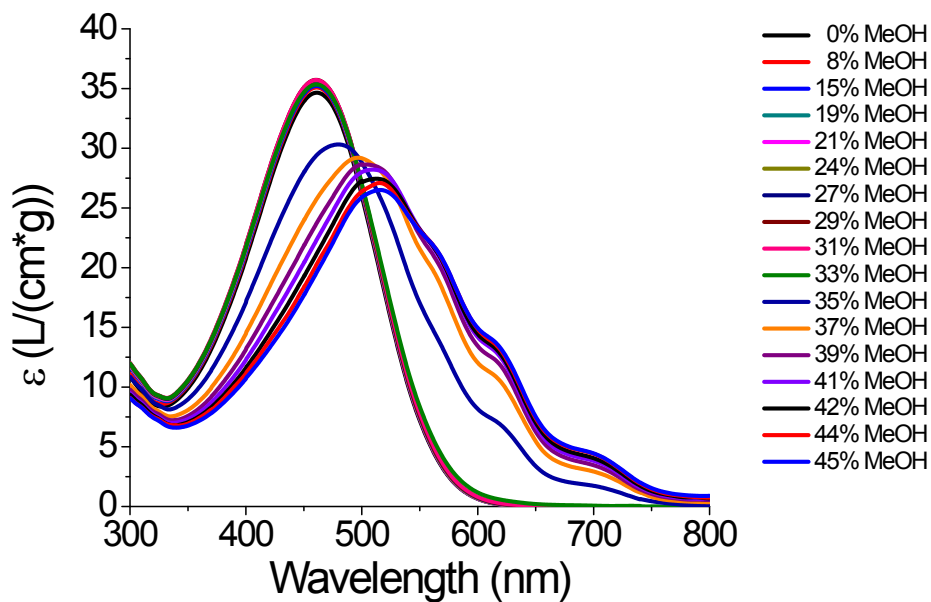


Figure S30. UV-vis spectra of the solvatochromism experiment for **P7**.

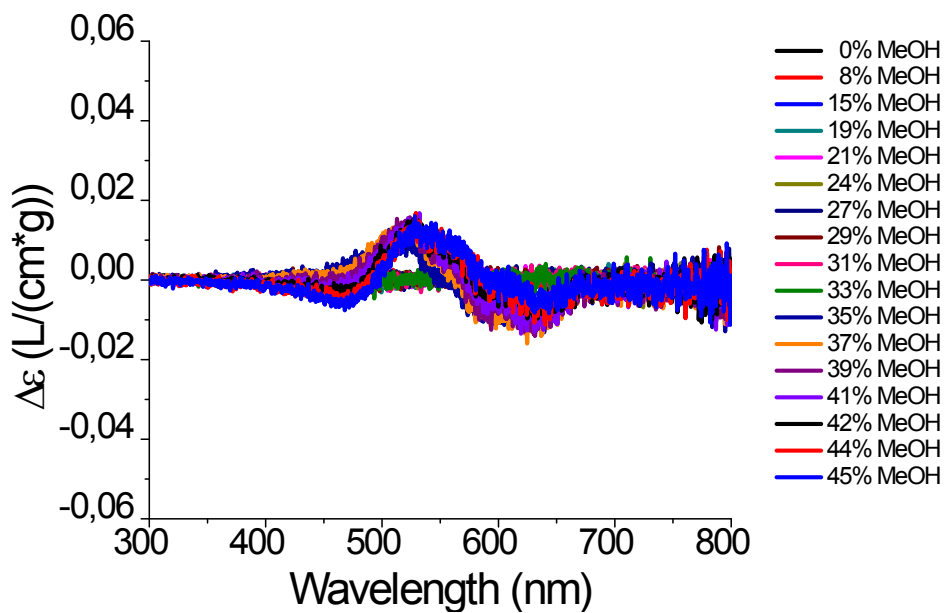


Figure S31. CD spectra of the solvatochromism experiment for **P7**.

X. Determination of the extent of the intermolecular order in P1 and P2.

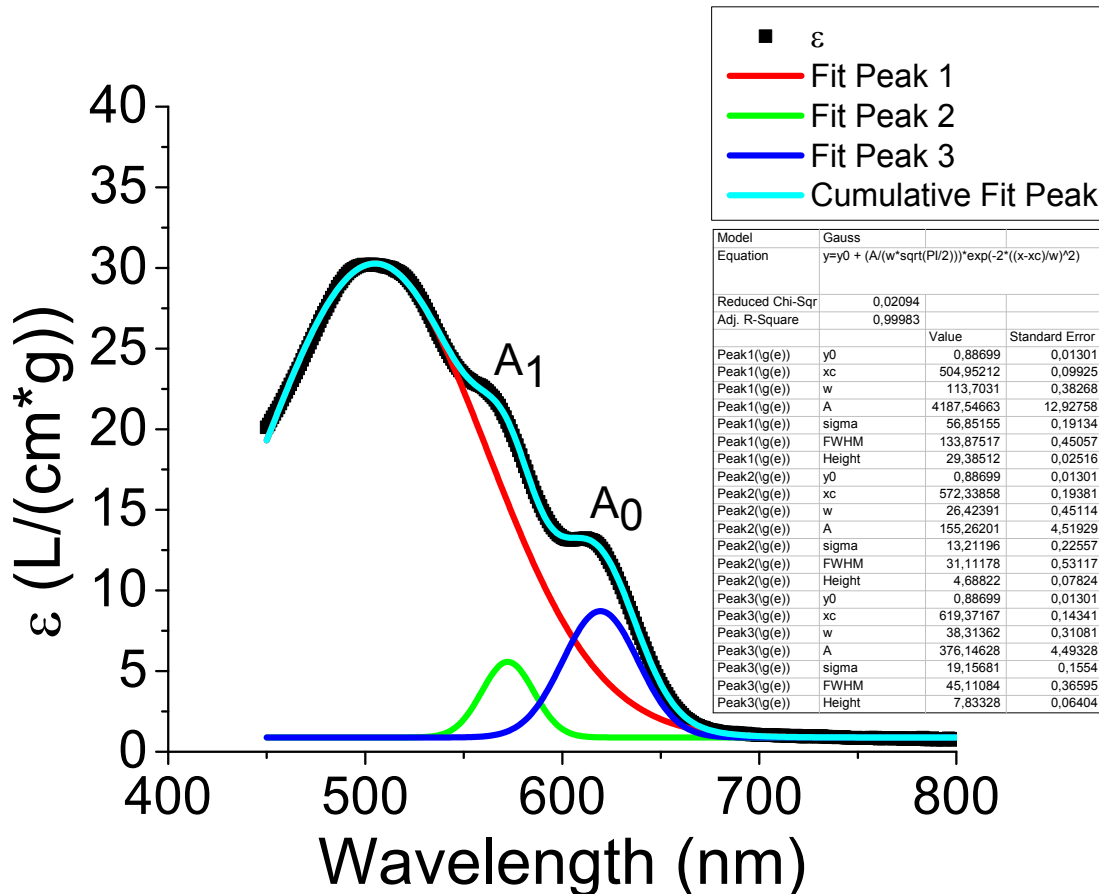


Figure S32. Deconvoluted UV-vis spectrum (of 46% MeOH) of P1.

Using the ratio $\frac{A_0}{A_1}$ (with A_0 = the integration of the absorption band of the 0-0 transition and with A_1 = the integration of the absorption band of the 0-1 transition) as a measure for the amount of the intermolecular order in the aggregated polymer chains^{4,5}:

$$\frac{A_0}{A_1} = \frac{376.15}{155.26} = 2.42$$

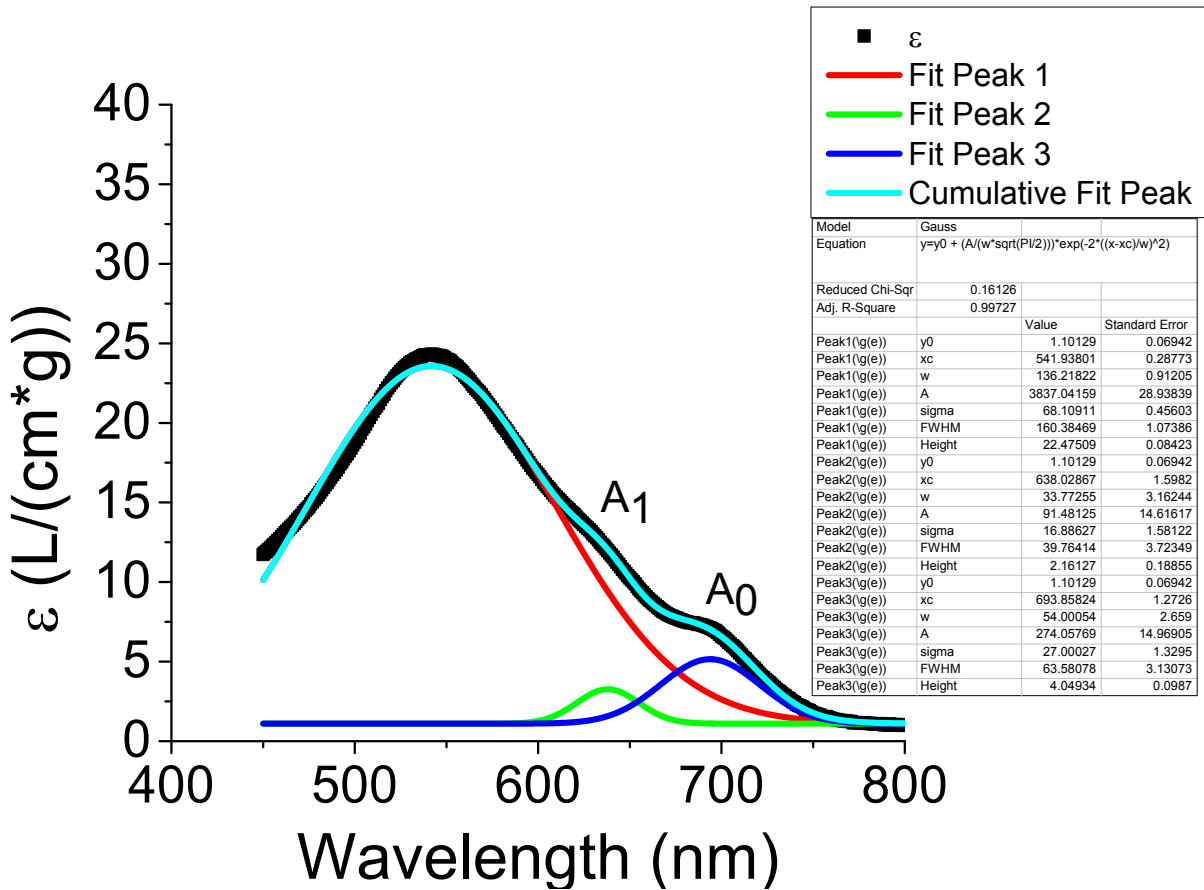


Figure S33. Deconvoluted UV-vis spectrum (of 46% MeOH) of **P2**.

Using the ratio $\frac{A_0}{A_1}$ (with A_0 = the integration of the absorption band of the 0-0 transition and with A_1 = the integration of the absorption band of the 0-1 transition) as a measure for the amount of the intermolecular order in the aggregated polymer chains^{4,5}:

$$\frac{A_0}{A_1} = \frac{274.06}{91.48} = 3$$

XI. Dynamic light scattering measurements

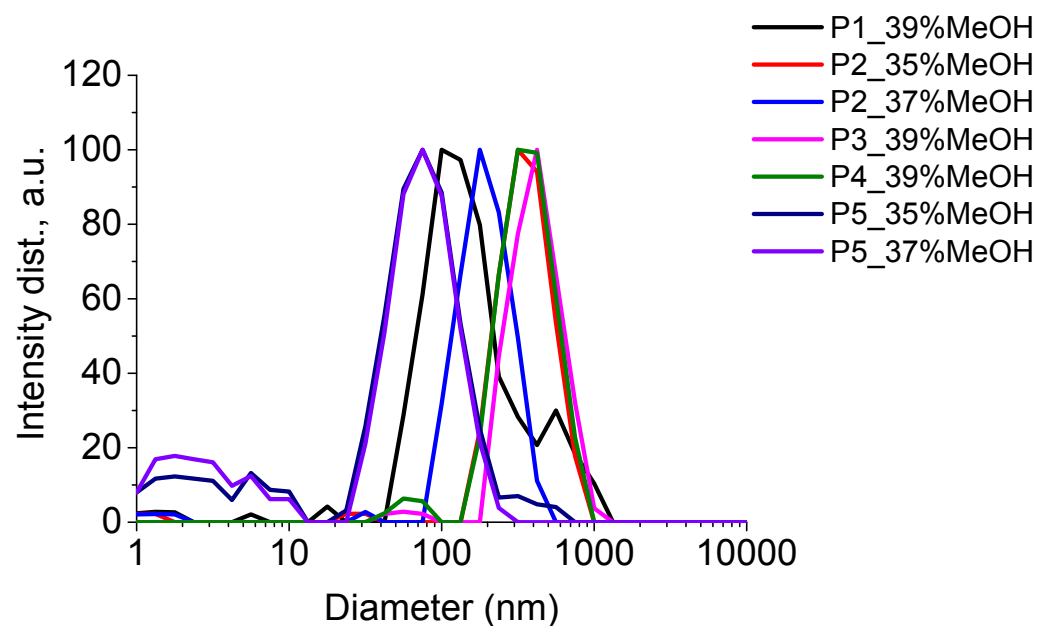
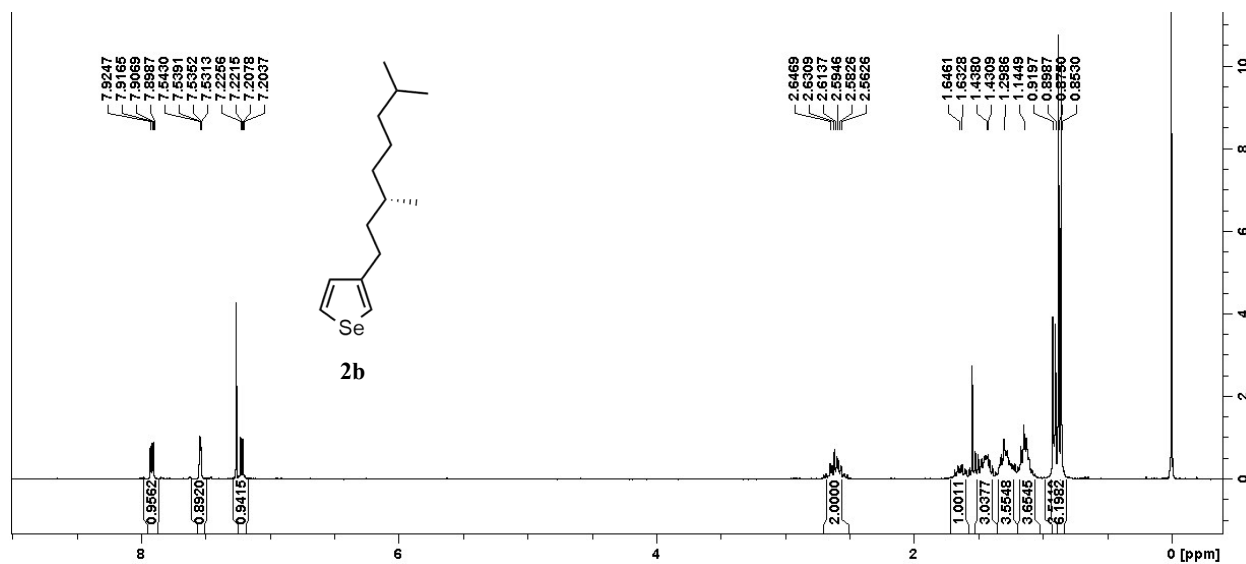


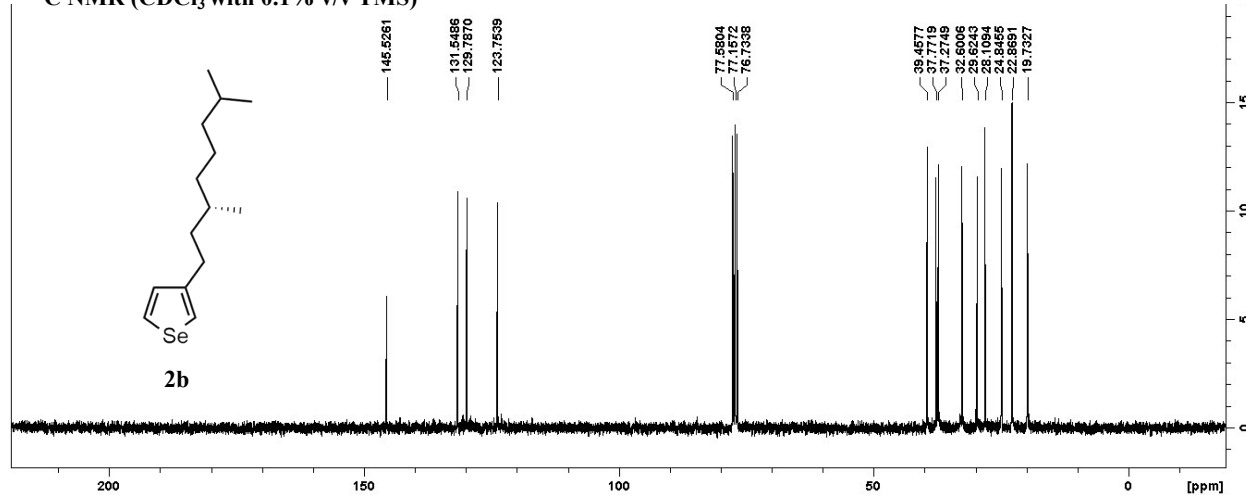
Figure S34. NNLS_FixedScale spectra of the DLS measurements of **P1-P5**.

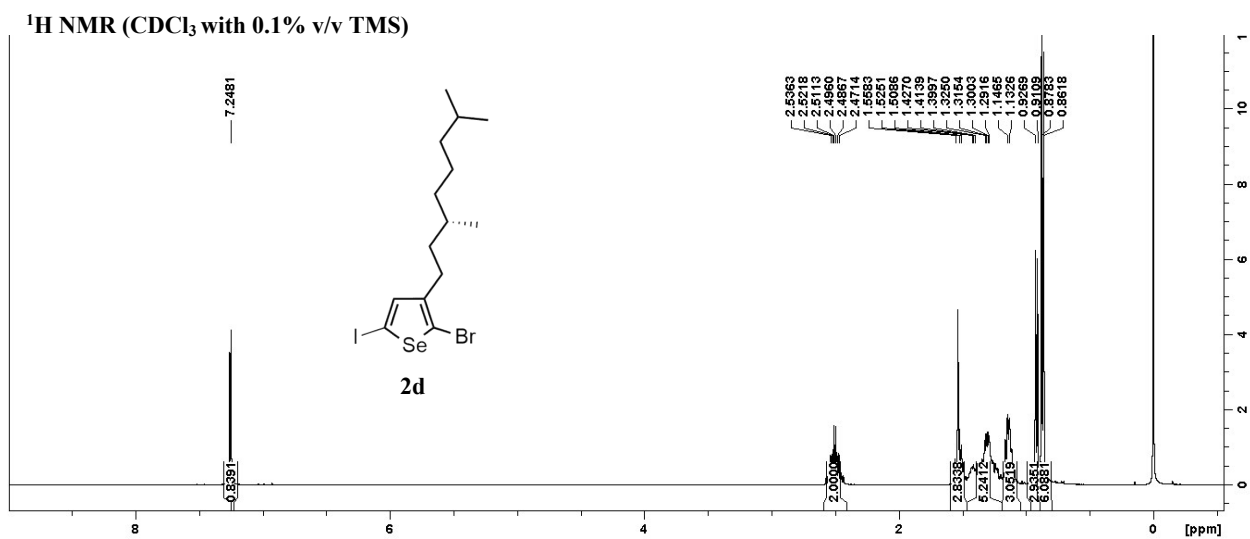
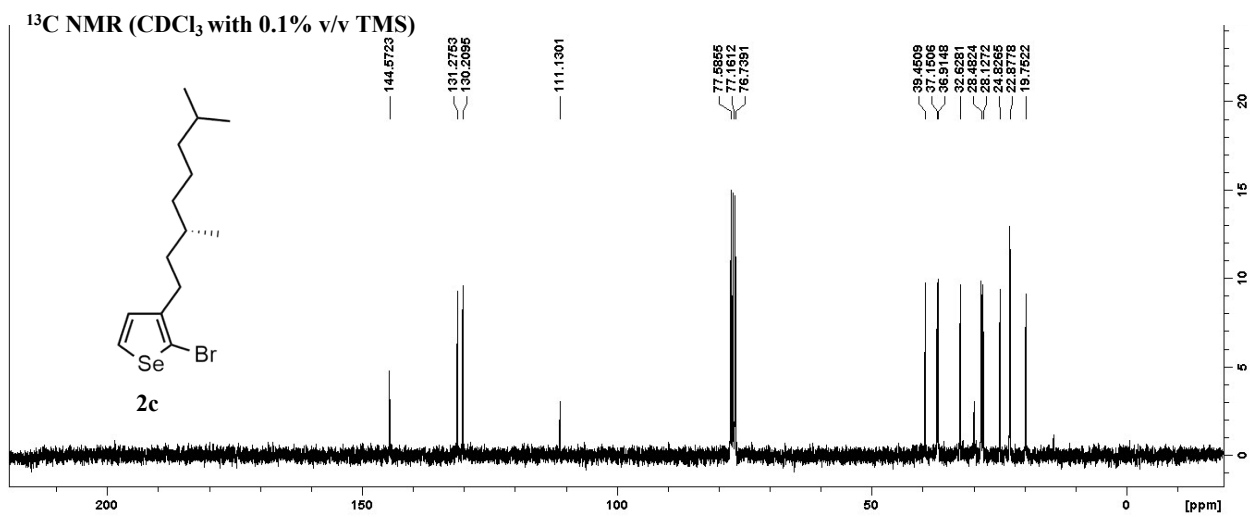
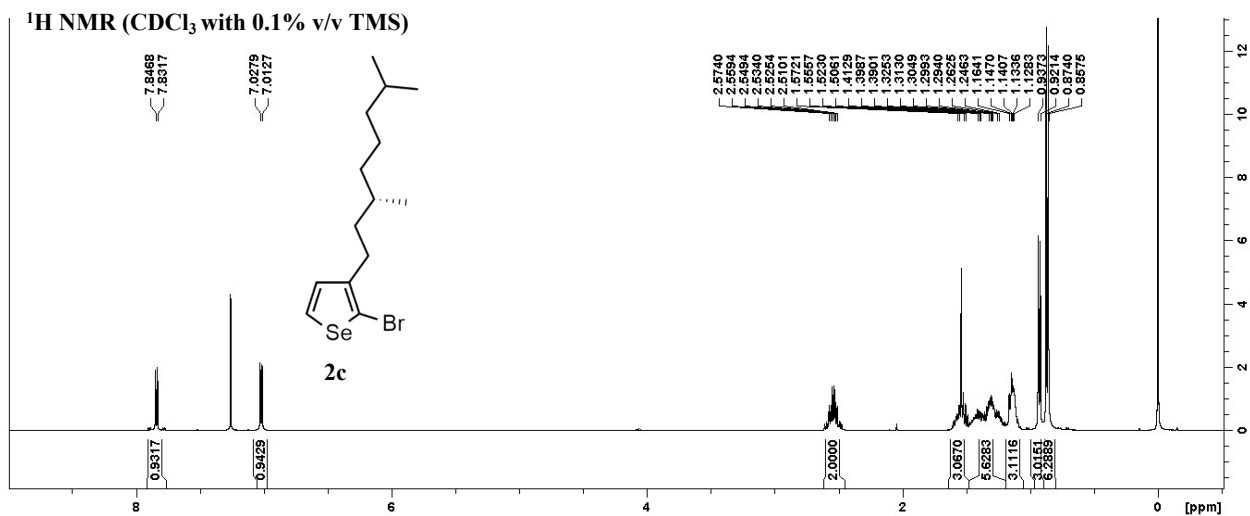
XII. ¹H NMR spectra

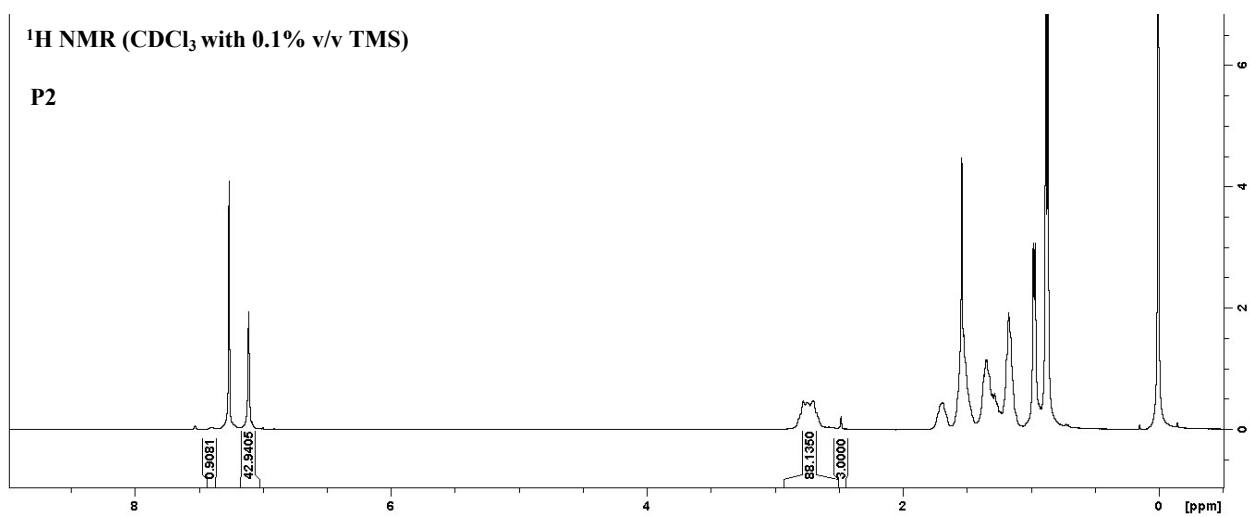
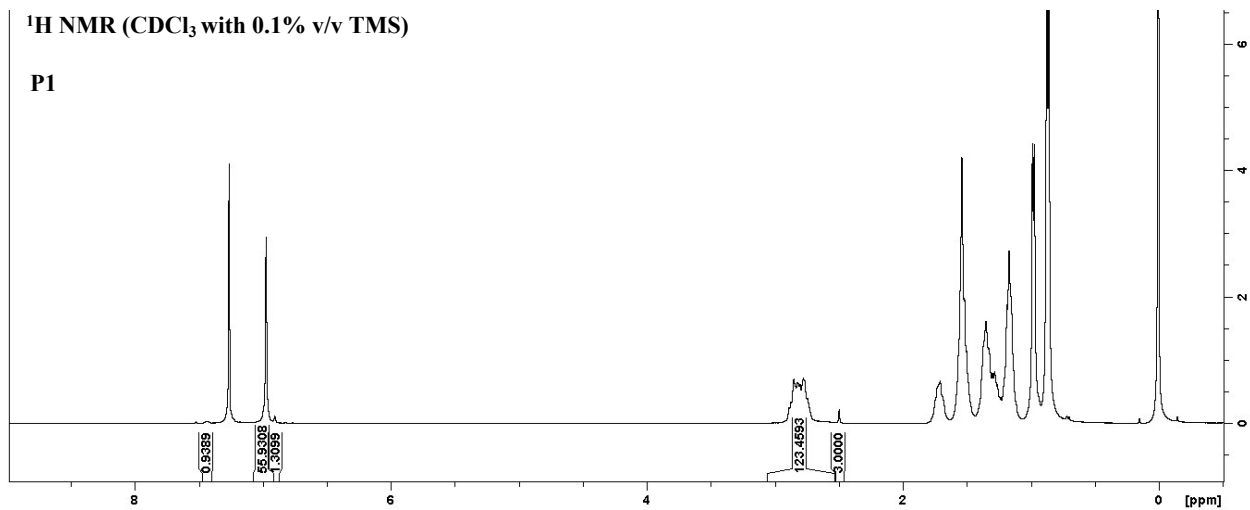
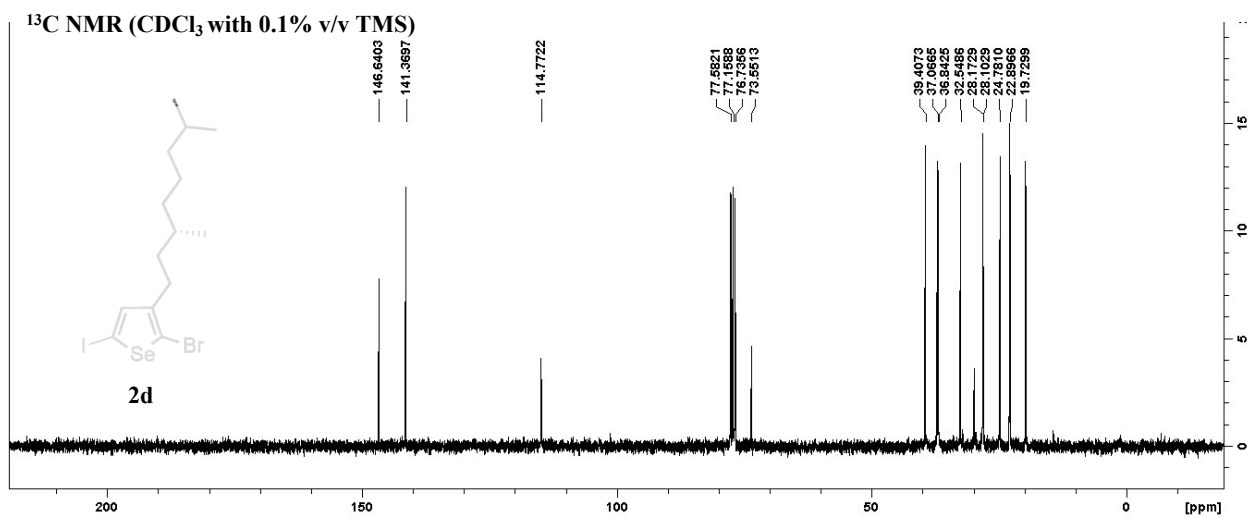
¹H NMR (CDCl₃ with 0.1% v/v TMS)

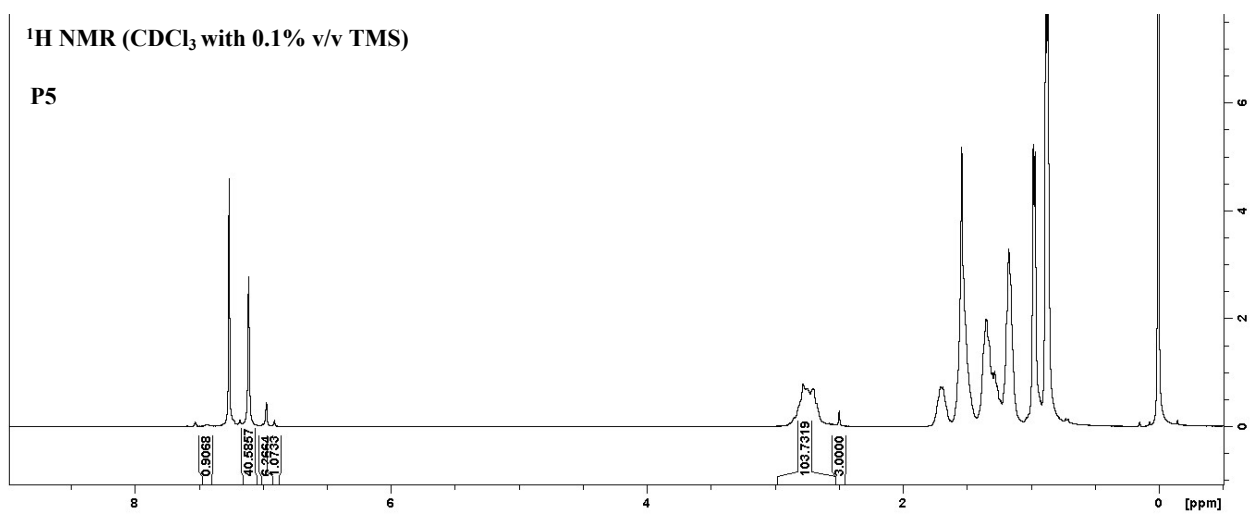
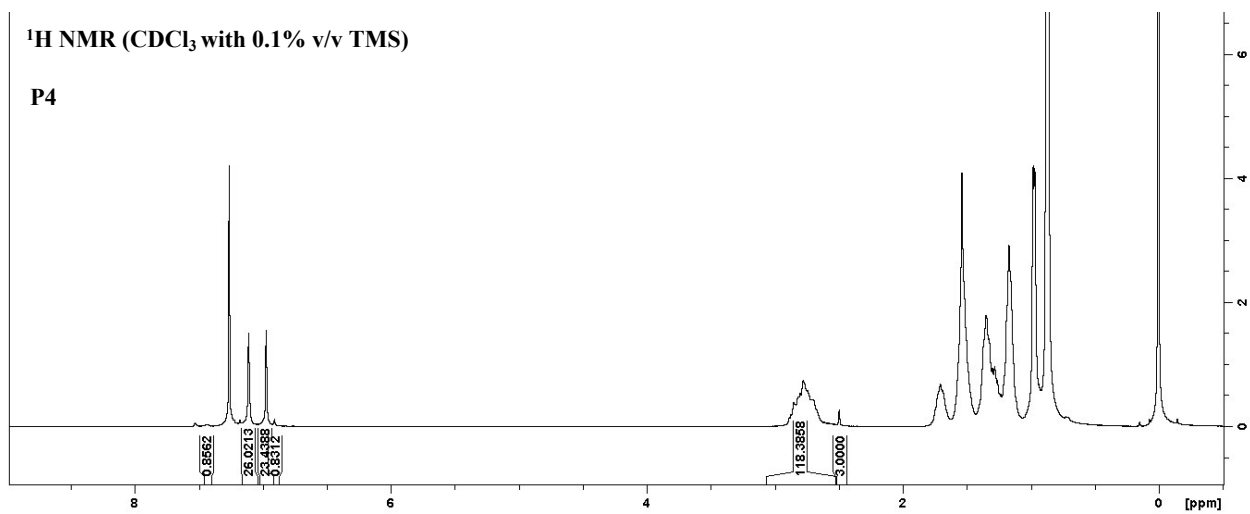
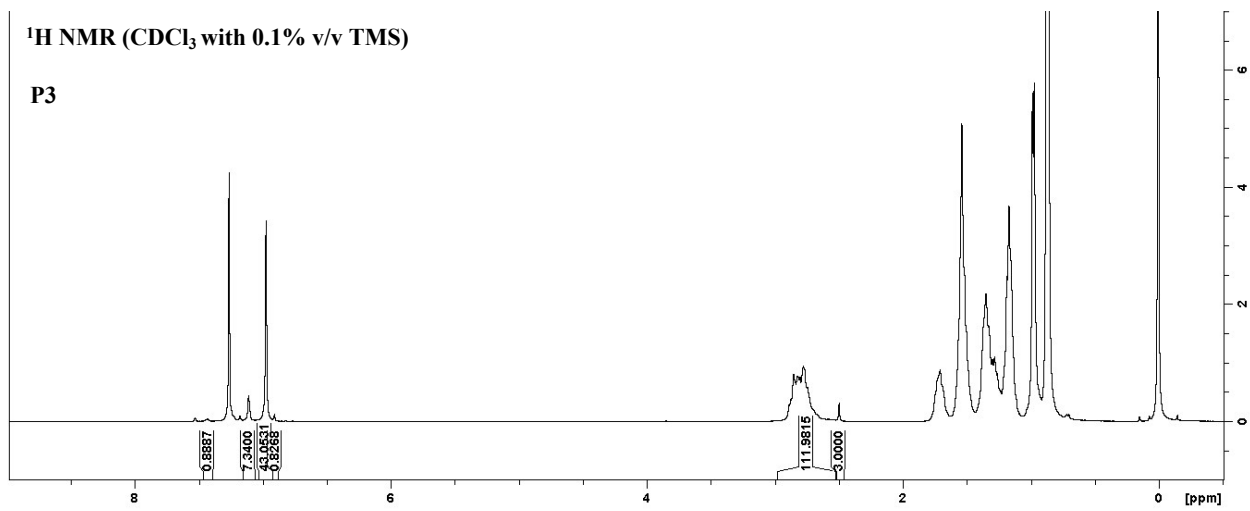


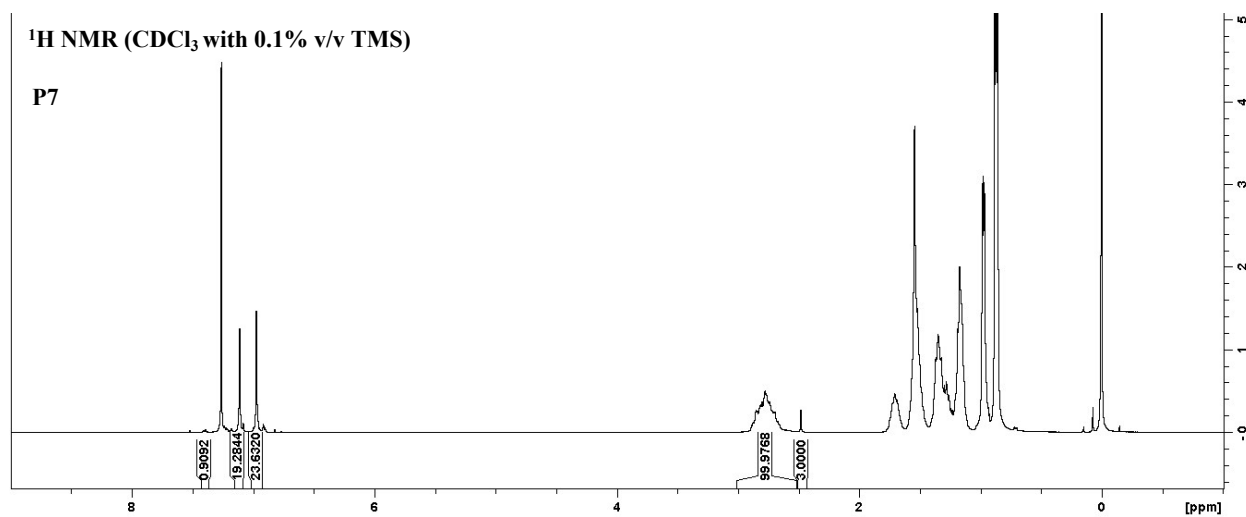
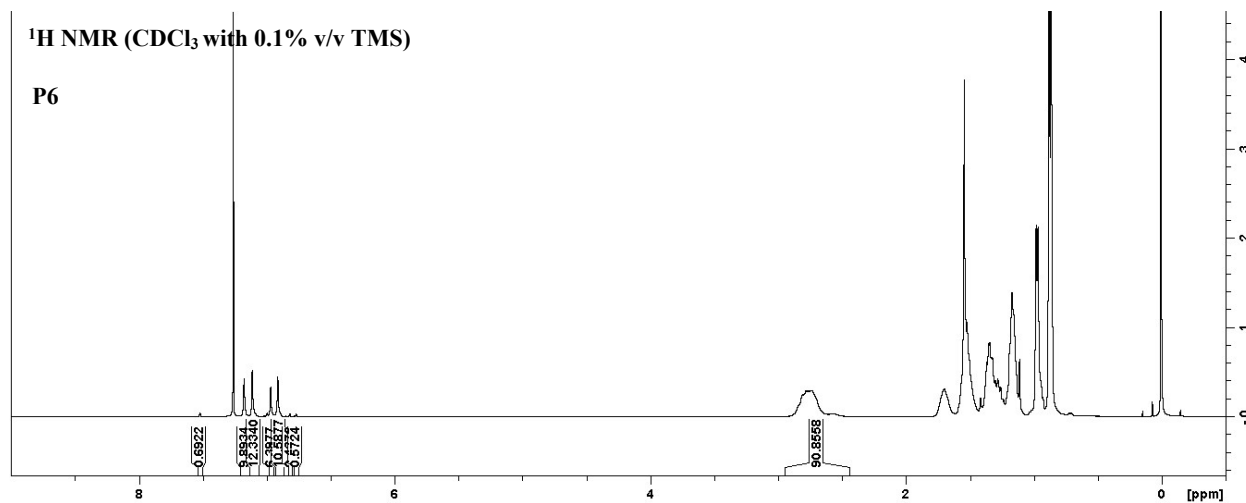
¹³C NMR (CDCl₃ with 0.1% v/v TMS)











XIII. References

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