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Supporting information

Influence of the dispersity and molar mass distribution of conjugated polymers on the aggregation type and subsequent chiral expression

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Contents

I. Instrumentation

^{1}H-NMR spectra were recorded on a Bruker Avance 600 MHz spectrometer in deuterated chloroform ($CDCl_3$). Size exclusion chromatography (SEC) measurements for determining the amount of unreacted monomer, and the molar mass properties of the polymers and mixtures were carried out on a Shimadzu LC20 apparatus (PLgel 5 μm MIXED-D column, LC-20AT pump, CBM-20A controller, SPD-20A and RID-20A detectors) using tetrahydrofuran (THF) as the eluent. The SEC apparatus is calibrated towards a series of polystyrene standards (Polymer Laboratories) in THF. Before the measurements, all samples were fully dissolved/diluted in THF (concentration ≈ 1 mg/mL) and filtered (pore size 0.2 μm).

Matrix-assisted laser desorption/ionization time-of-flight (MALDI-ToF) mass spectra are recorded using a Waters QToF Premier mass spectrometer. A Nd-YAG laser of 355 nm with a maximum pulse energy of 65 μJ delivered to the sample at 50 Hz repeating rate is used. Time-of-flight mass analyses is performed in the reflection mode at a resolution of about 10 000. Trans-2-(3-(4-tert-butyl-phenyl)-2-methyl-2-propenylidene)malononitrile (DCTB) is used as the matrix and is prepared as a 40 mg/ml solution in chloroform ($CHCl_3$). The matrix solution (1 μl) is applied to a stainless steel target and air-dried. Polymer samples are dissolved in $CHCl_3$ to obtain 1 mg/mL solutions. 1 μl aliquots of these solutions are applied onto the target area (already bearing the matrix crystals) and air-dried.

For the solvatochromism experiments, all polymer samples were diluted in $CHCl_3$ to obtain an initial concentration of $2.7 \pm 0.1 * 10^{-3}$ mg/mL. While constantly stirring (600 rpm), methanol (MeOH) was added to the polymer solution via an automatic syringe pump with a constant rate of 0.25 mL/min. Initially, every 5v/v% MeOH an aliquot of the solution was removed for UV-Vis and ECD measurements. After a total of 30v/v% MeOH added, steps were decreased to 2.5v/v%

MeOH to follow the transitions more clearly. Measurements were stopped after no change was noted for at least 3 subsequent measurements. The UV-vis spectra were measured on a JASCO V-730. The ECD spectra were recorded on a JASCO J-810 spectrometer. The scan rate was 200 nm/min, the step 0.2 nm, the bandwidth 1 nm and the response time 0.96 sec for both apparati.

II. Synthetic procedures

2-Bromo-3-(3,7-(*S*)-dimethyloctyl)-5-iodothiophene (**1**) was prepared according to literature procedures.[1] All other reagents were purchased and used without any further purification.

Synthesis of the polymers P1-P4

To avoid termination due to water, oven-dried glassware, dried solvents (Acros) and inert nitrogen atmosphere are used in all polymerizations. **1** (0.340 mmol; 0.146 g) was added to a polymerization tube and dissolved in dry THF (concentration = 0.1 mmol/mL). Isopropylmagnesium chloride lithium chloride complex solution in THF (0.340 mmol; 1.3 M) was slowly added while stirring at 0 °C. After 1 hour of reaction, 0.400 mL of this solution was cannulated to a dispersion of [1,3-bis(diphenylphosphino)ethane]dichloronickel(II) (Ni(dppe)Cl_2; 0.010 mmol; 0.004 g) in 1.600 mL THF while stirring to form the initiator solution. This reaction was stirred at room temperature for 5 min. Afterwards, this solution was drawn up in a Hamilton syringe, and placed in an automatic syringe pump. The initiator solution was added to the remainder of the monomer solution at a constant rate depending on the intended dispersity (see Table 1). After 10 min, the polymerization was terminated by adding a few droplets of acidified THF to the solution. The resulting polymers were precipitated in MeOH, and further purified via Soxhlet extraction in isopropylalcohol and $CHCl_3$. All polymers were dried in a vacuum oven before analysis. The polymers were characterized via SEC for their number average molar mass (

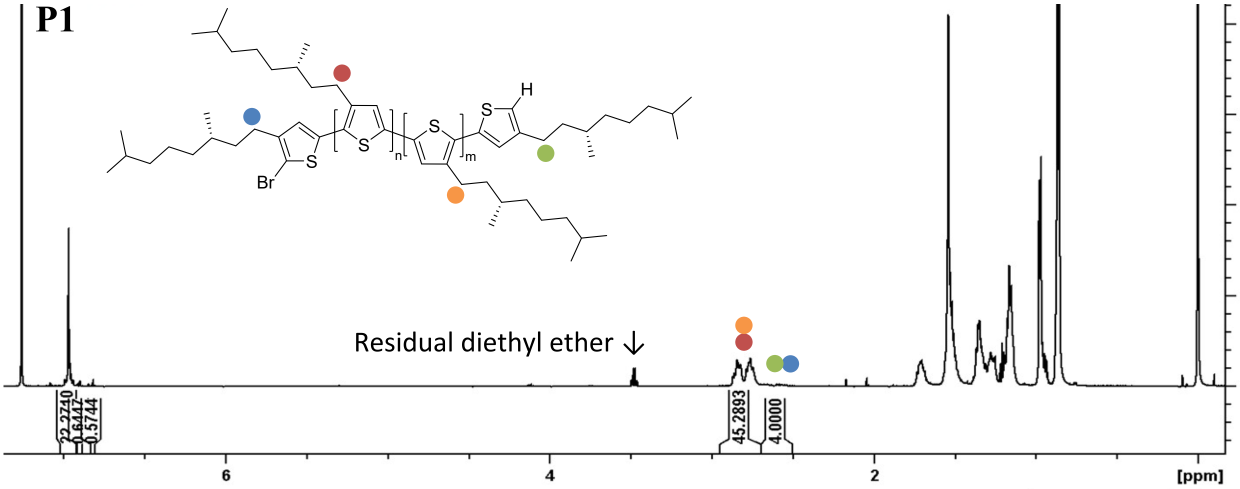
$\bar{M}_n$), weight average molar mass ($\bar{M}_w$) and dispersity (Đ) (see Table 1 and Figure 2); and with ^{1}H-NMR (see Figure S1) and MADLI-ToF (see Figure S2).

Synthesis of the polymers P5-P6

P5-6 were synthesized using a similar method as described above, except that all monomer solution was immediately added to the Ni(dppe)Cl_2 dispersion. **1** (0.340 mmol; 0.146 g) was added to a polymerization tube and dissolved in dry THF (concentration = 0.1 mmol/mL). Isopropylmagnesium chloride lithium chloride complex solution in THF (0.340 mmol; 1.3 M) was slowly added while stirring at 0 °C. After 1 hour, this solution was fully cannulated to a dispersion of Ni(dppe)Cl_2 (**P5**: 0.020 mmol; 0.009 g; **P6**: 0.006 mmol; 0.003 g) in 1.600 mL THF while stirring. After 10 min, the polymerization was terminated by adding a few droplets of acidified THF to the solution. The resulting polymers were precipitated in MeOH, and further purified via Soxhlet extraction in MeOH and $CHCl_3$. The polymers were dried in a vacuum oven before analysis. Characterization was performed via SEC for their number average molar mass ($\bar{M}_n$), weight average molar mass ($\bar{M}_w$) and dispersity (Đ) (see Table 2 and Figure 3); and with ^{1}H-NMR (see Figure S1) and MALDI-ToF (see Figure S2).

III. ^{1}H-NMR spectra

All ^{1}H-NMR spectra are taken in deuterated chloroform ($CDCl_3$) with 0.1v/v% trimethylsilane (TMS) for reference. **P6** is measured on a 400 MHz apparatus, the others on a 600 MHz apparatus. ^{1}H-NMR can be employed to calculate the number average molar mass ($\bar{M}_n$), either via the aliphatic or aromatic peaks. The external α-methylenes at 2.59 ppm (A; blue and green in Figure S1) are calibrated at 4 H-atoms, 2 for each external thiophene unit. Since one terminal thiophene unit bears a bromine atom, while the other bears a hydrogen atom, these peaks slightly shift in ppm value. However, for the sake of determining the overall number average molar mass, both of these peak are integrated together for a total of 4. Subsequently, the internal thiophene units at 2.80 ppm (B; red and orange in Figure S1) are integrated. The degree of polymerization (DP) can be calculated via DP = 4 (A+B)/2A. The DP and $\bar{M}_n$ are correlated via $\bar{M}_n$ = DP*(molar mass of the monomer unit), where the molar mass of the monomer unit is 222.4 g/mol in the case of 3-(3,7-(*S*)-dimethyloctyl)thiophene. The method to determine the $\bar{M}_n$ based on the aromatic region is similar.


P1
S
Br
H
n
m
Residual diethyl ether
22.2740
0.6442
0.5744
45.2893
4.0000
6
4
2
[ppm]
-0.0
0.5
1.0
1.5


P2
Residual diethyl ether
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4.0000
6
4
2
[ppm]
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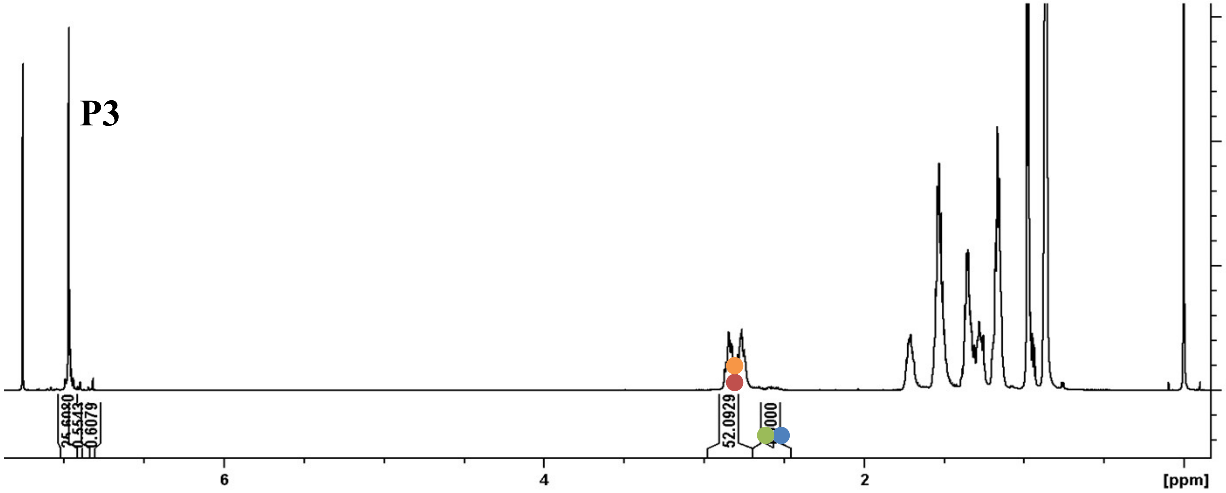
0.5
1.0
1.5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0.5543
0.6079
52.0929
4.0000
6
4
2
[ppm]
-0
1
2

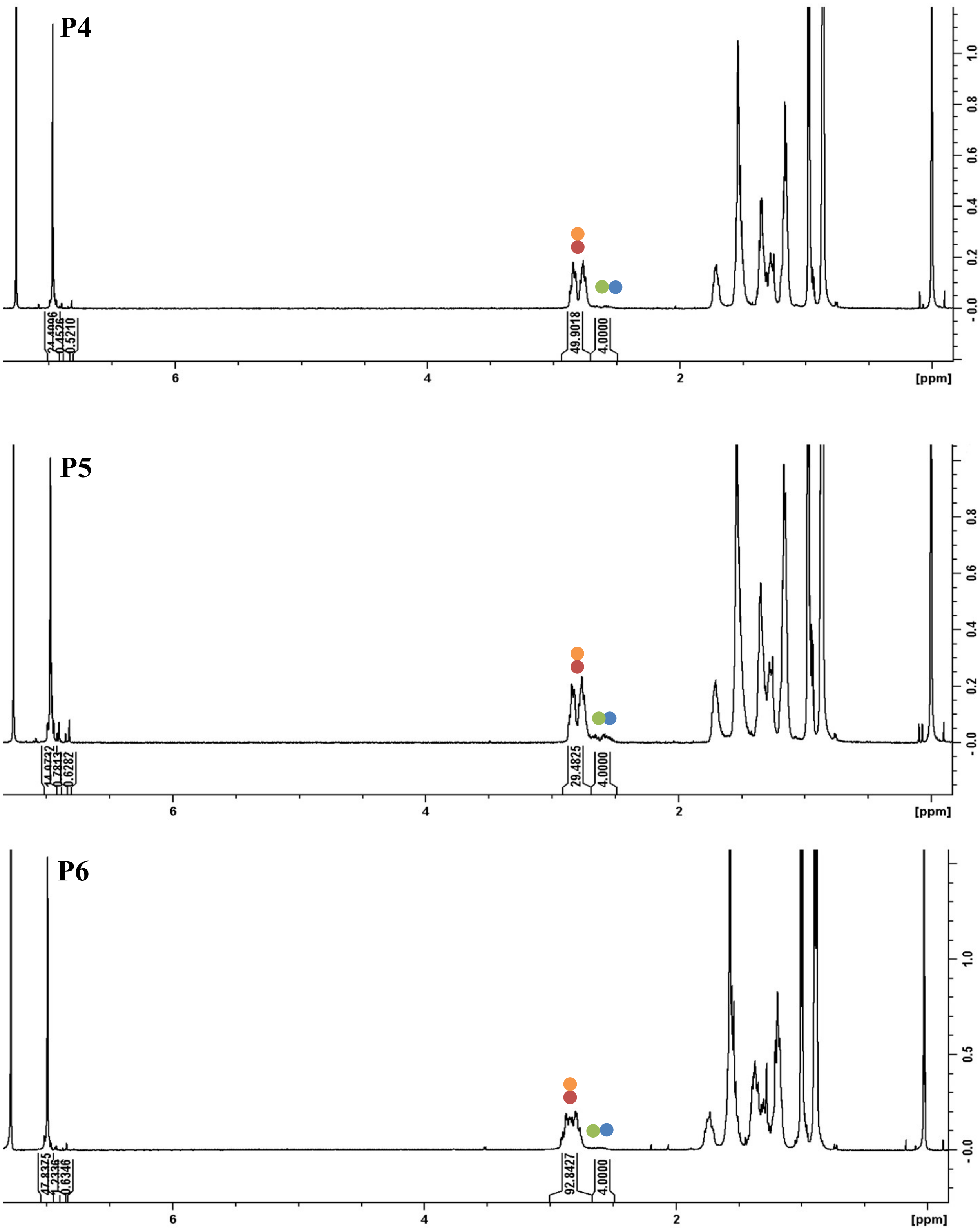
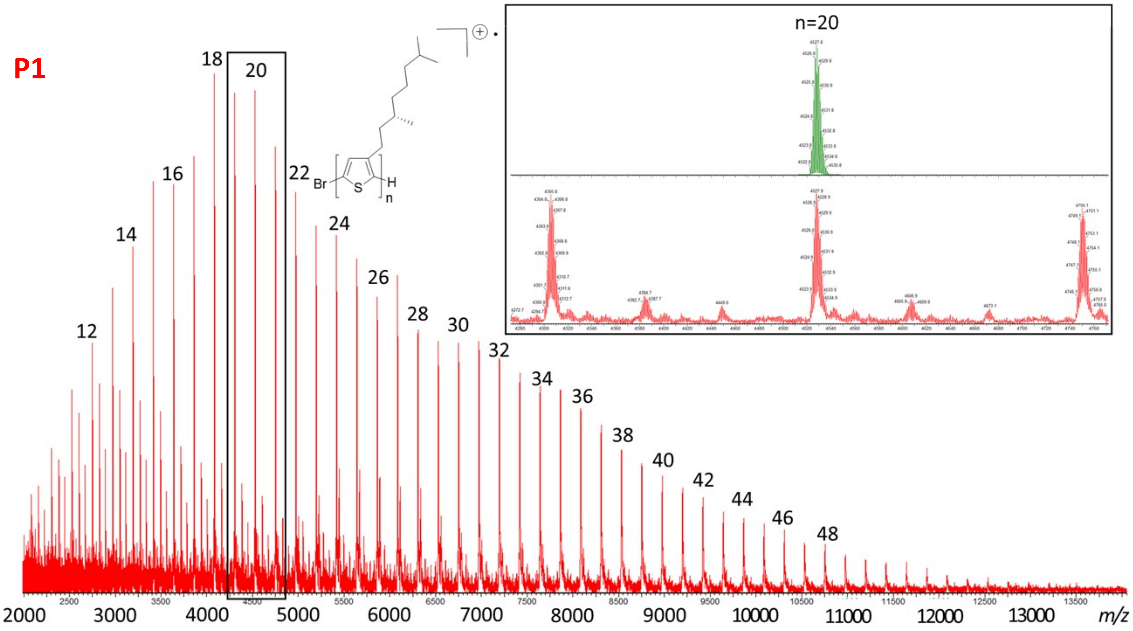
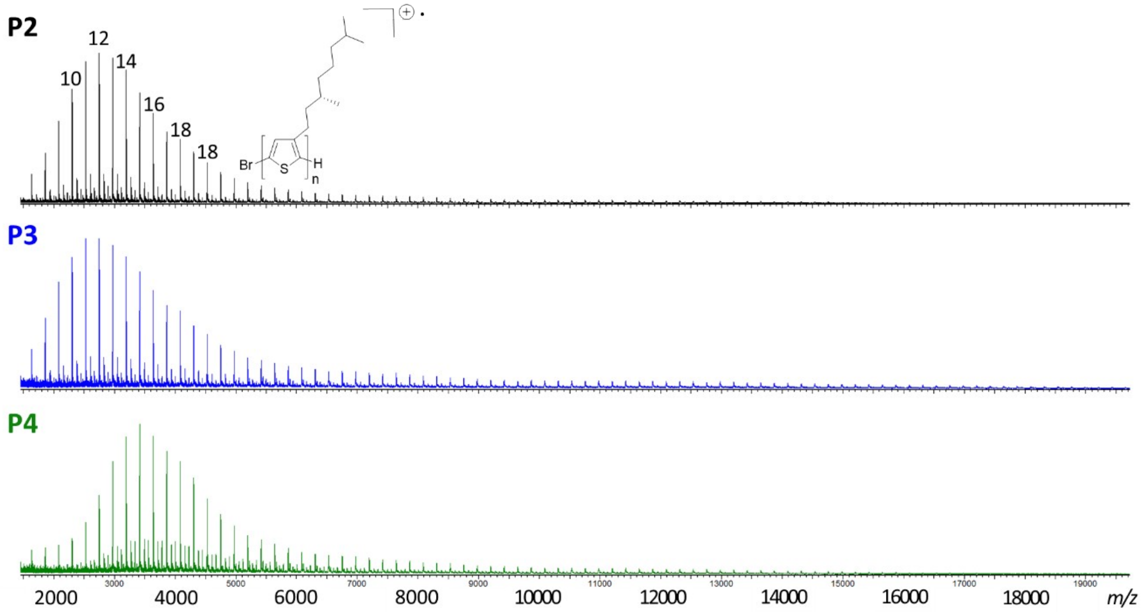


Figure S1. The ^{1}H-NMR data of **P1-P6**, calibrated at 4 H atoms for the external α-methylenes (green and blue) at 2.59 ppm. Internal α-methylenes are indicated with orange and red (see inset).

IV. MALDI-ToF results





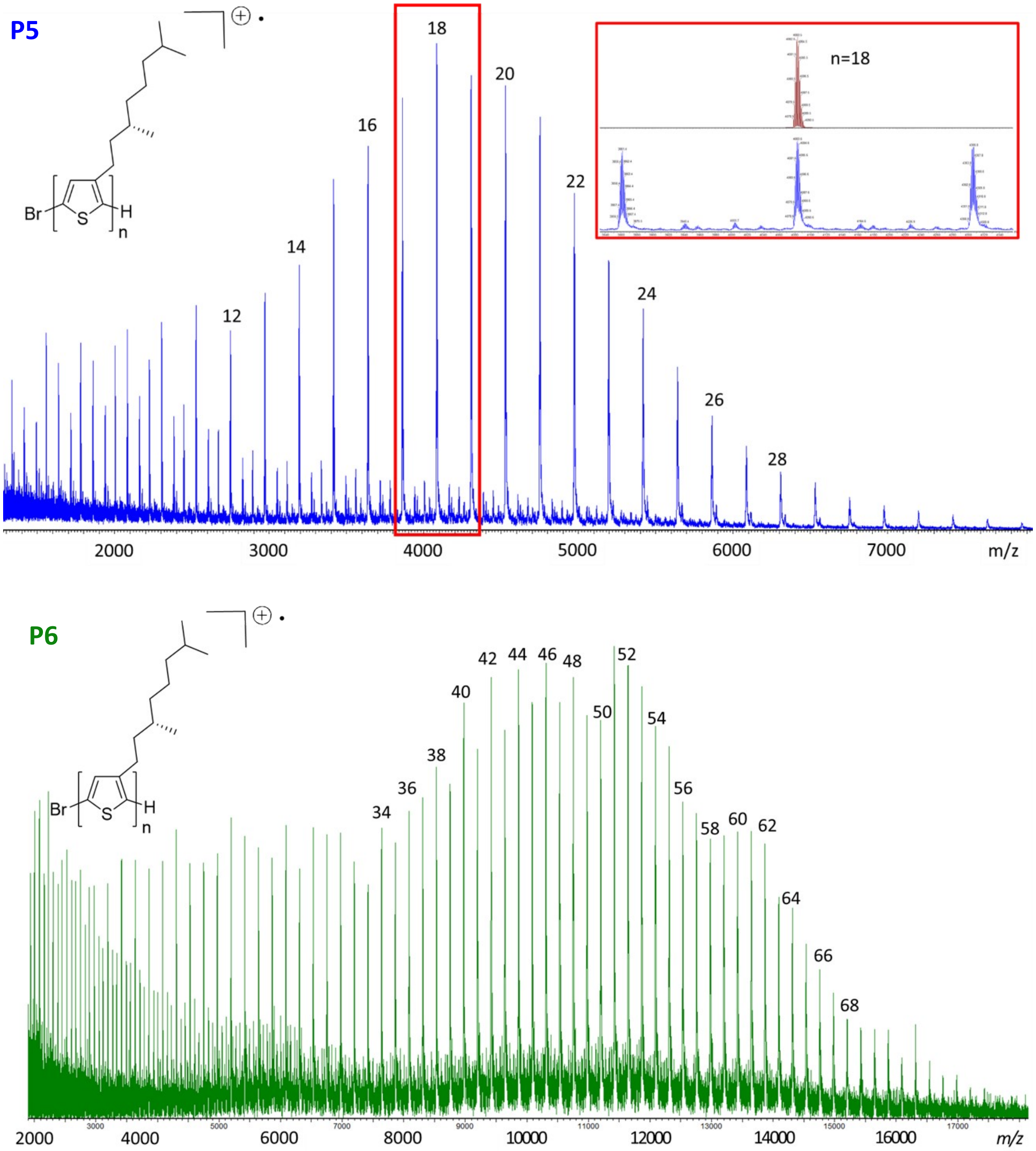
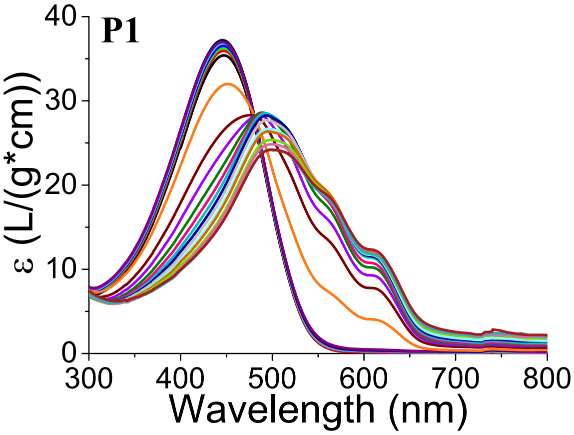
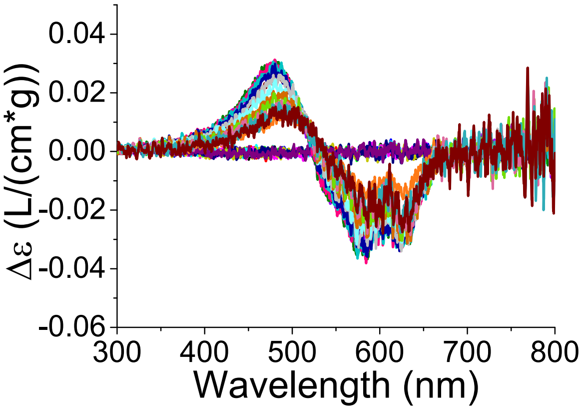
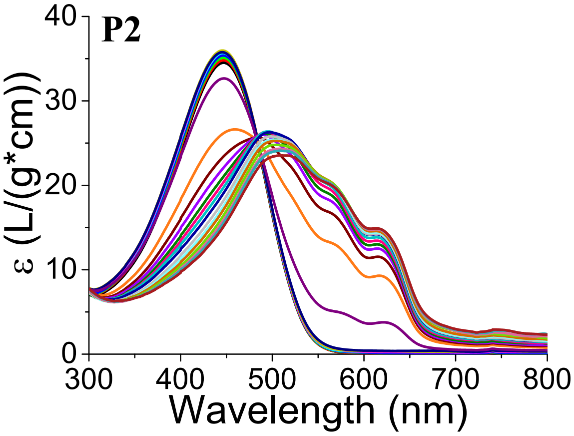


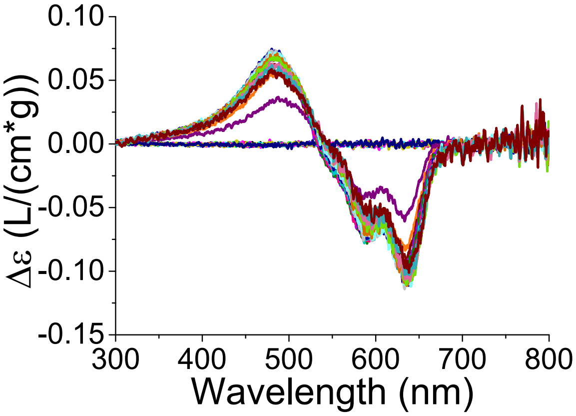
Figure S2. MALDI-ToF data of **P1-P6**. In **P1** and **P5**, an inset is visible with a zoomed in and analysed set of peaks. These peaks are similarly visible in the other MALDI-ToF spectra and are therefore not shown again.

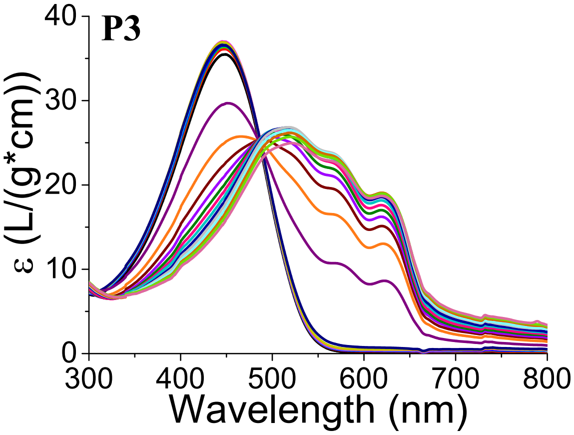
V. UV-Vis and ECD measurement repeats

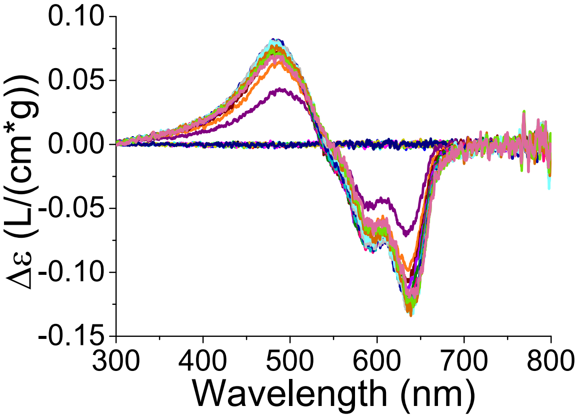


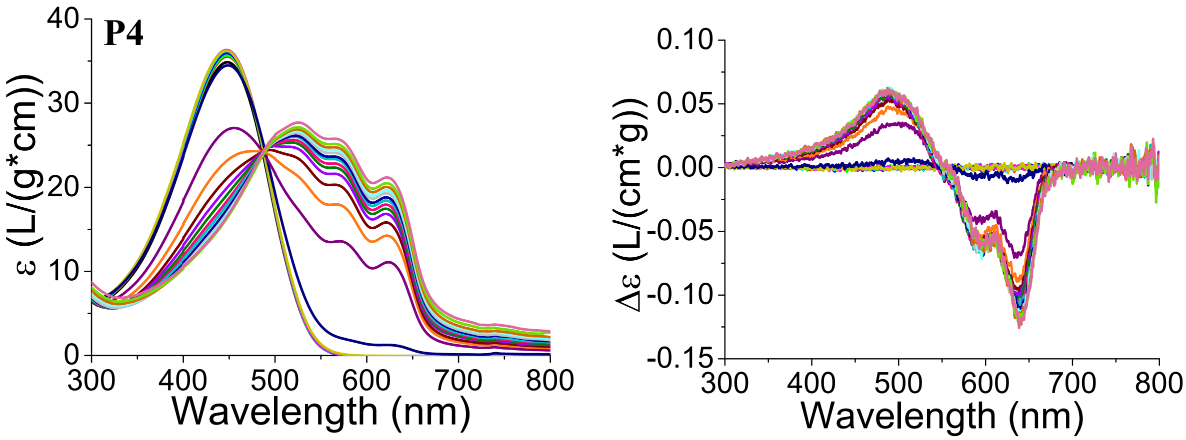


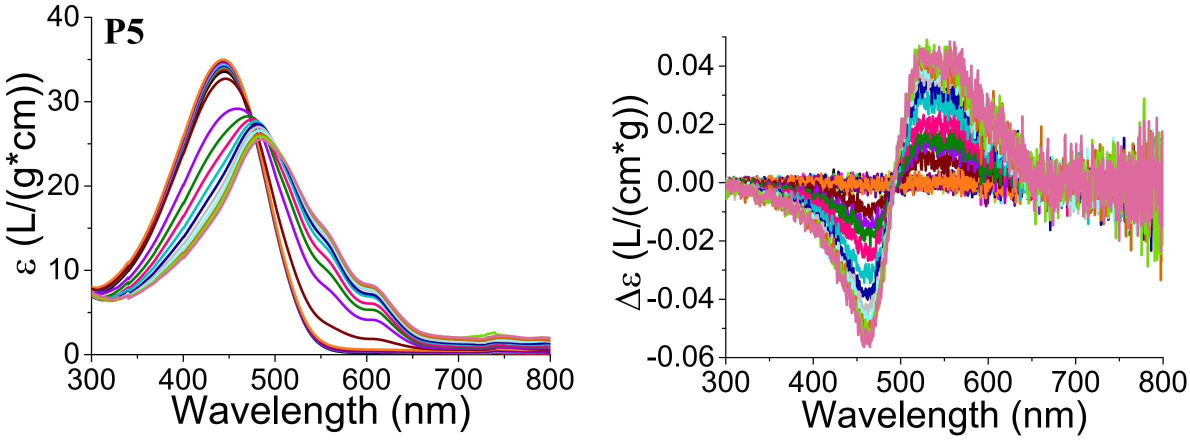


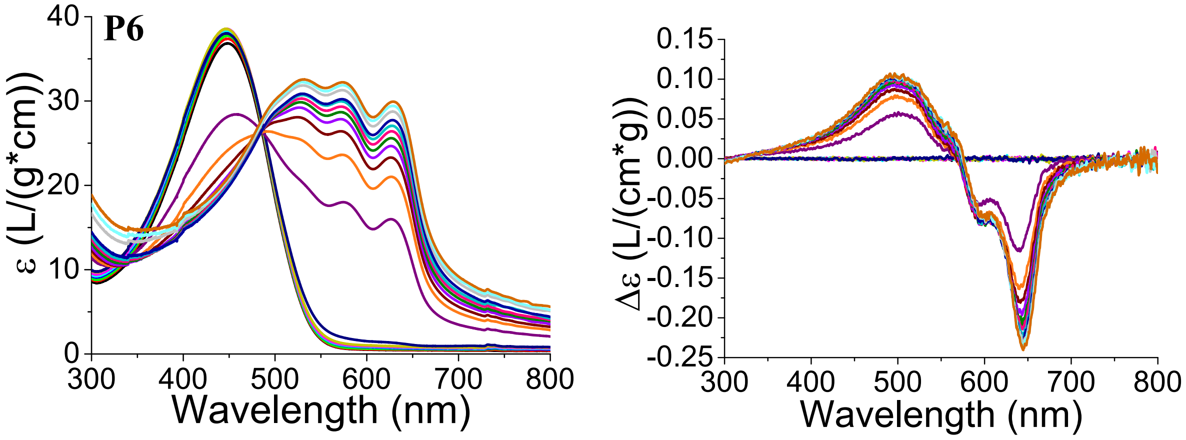







P4
ε (L/(g*cm))
0
10
20
30
40
300
400
500
600
700
800
Wavelength (nm)
Δε (L/(cm*g))
0.10
0.05
0.00
-0.05
-0.10
-0.15
300
400
500
600
700
800
Wavelength (nm)


P5
ε (L/(g*cm))
0
10
20
30
40
300
400
500
600
700
800
Wavelength (nm)
Δε (L/(cm*g))
0.04
0.02
0.00
-0.02
-0.04
-0.06
300
400
500
600
700
800
Wavelength (nm)


P6
ε (L/(g*cm))
0
10
20
30
40
300
400
500
600
700
800
Wavelength (nm)
Δε (L/(cm*g))
0.15
0.10
0.05
0.00
-0.05
-0.10
-0.15
-0.20
-0.25
300
400
500
600
700
800
Wavelength (nm)

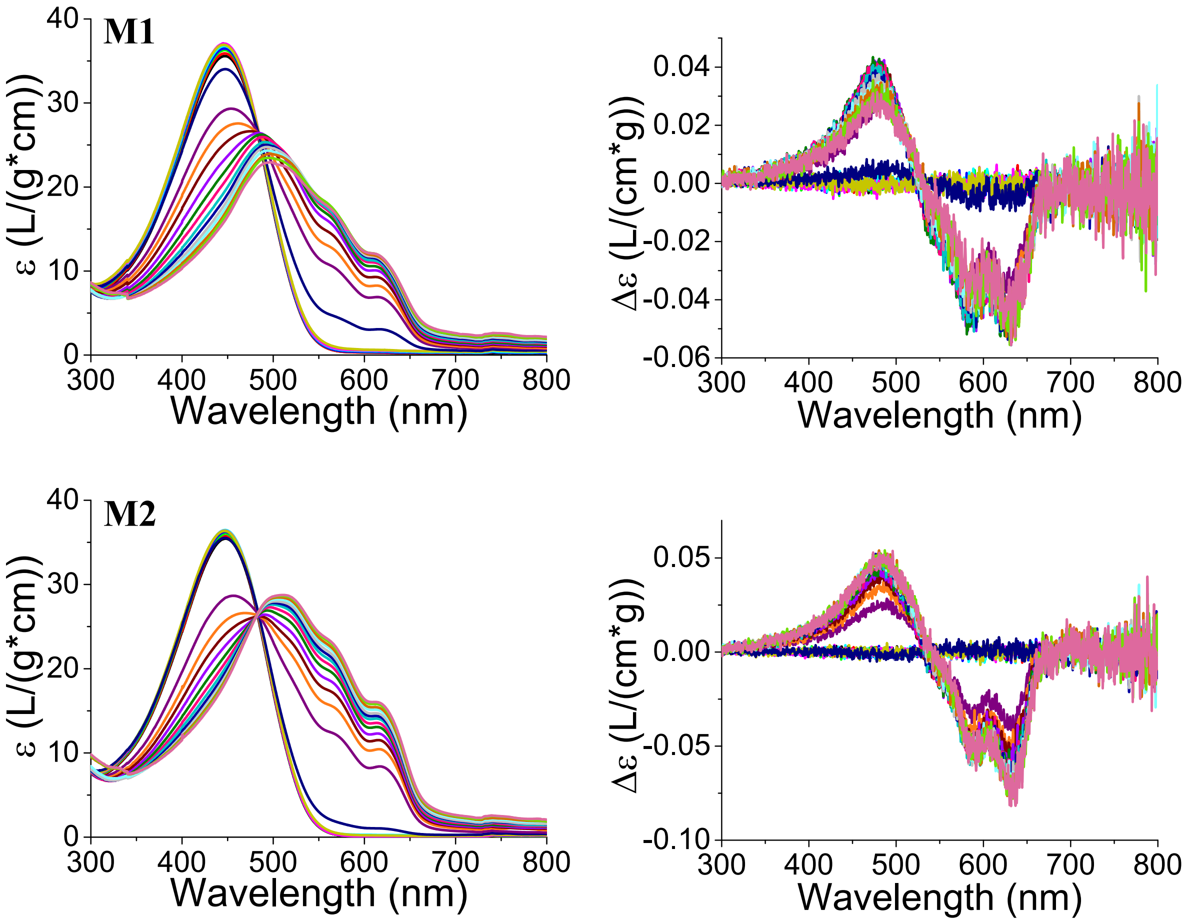


Figure S3. Repetitions of the UV-Vis (left) and ECD (right) measurements for **P1-P6** and **M1-M2** (see also Figure 3 and Figure 5). Note that the y-axis in the ECD measurements differs to show each individual spectrum clearly.

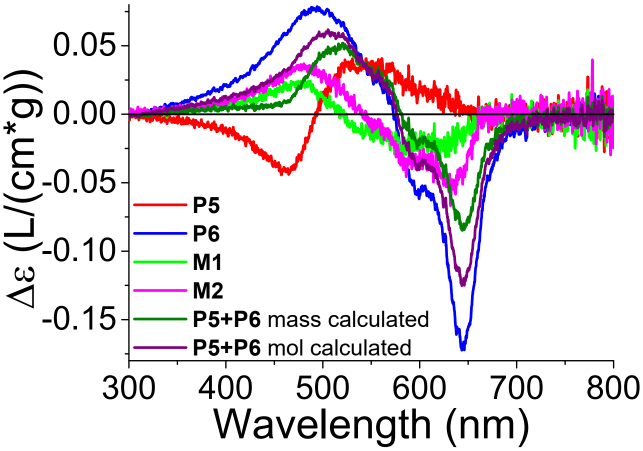


Figure S4. Comparison of **M1-M2** and their comprising polymers **P5-P6**. Weighted averages for **M1** (mass calculated) and **M2** (mol calculated) are also included to show the deviation between a perfect mixture, and the incorporation of disorder as a result of the presence of both type I and II since the long range interaction (monosignate Cotton effect at ~645 nm) is less pronounced.

VI. References

(1) Van Den Bergh, K.; Cosemans, I.; Verbiest, T.; Koeckelberghs, G. Expression of Supramolecular Chirality in Block Copoly(Thiophene)S. *Macromolecules* **2010**, *43* (8), 3794–3800. https://doi.org/10.1021/ma100266b.