Electronic Supplementary Information (ESI)

Amphiphilic chiral block-poly(thiophene)s: Tuning the blocks.

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A. ¹H and ¹³C NMR spectra

Figure S1: 1H NMR spectrum of 2.



3

Figure S2: ¹³C NMR spectrum of 2.



4

Figure S3: ¹H NMR spectrum of 3.



Figure S4: ¹³C NMR spectrum of 3.



Figure S5: ¹H NMR spectrum of 4.



Figure S6: ¹³C NMR spectrum of 4.



Figure S7: ¹H NMR spectrum of P2.



Figure S8: ¹H NMR spectrum of P4.



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Figure S9: ¹H NMR spectrum of P5.



Figure S10: ¹H NMR spectrum of P6.



B. UV-vis & CD spectroscopy

1. In solution

i. Neutral media

Figure S11: UV-vis, CD and gabs spectra for the solvatochroism experiments of **P2** in a neutral THF/MeOH mixture. The ratio THF/MeOH is given in the legend.



Figure S12: UV-vis, CD and g_{abs} spectra for the addition of acid to P2 in a neutral THF/MeOH mixture of THF/MeOH 40/60.

The ratio THF/MeOH is given in the legend.



Figure S13: g_{abs} spectra of *P3* in a neutral *THF/MeOH* mixture. The ratio THF/MeOH is 40/60.





The ratio THF/MeOH is given in the legend.





Figure S15: UV-vis, CD and g_{abs} spectra for the addition of acid to P4 in neutral THF/MeOH 40/60 mixture. The ratio THF/MeOH is given in the legend.



Figure S16: UV-vis, CD and g_{abs} spectra for the solvatochroism experiments of P5 in a neutral THF/MeOH mixture. The ratio THF/MeOH is given in the legend.







Figure S18: UV-vis, CD and g_{abs} spectra for the solvatochroism experiments of **P6** in a neutral THF/MeOH mixture. The ratio THF/MeOH is given in the legend.



Figure S19: UV-vis, CD and g_{abs} spectra for the addition of acid to **P6** in a neutral THF/MeOH 20/80 mixture. The ratio THF/MeOH is given in the legend.

ii. Acidic media



Figure S20: UV-vis, CD and g_{abs} spectra for the solvatochroism experiments of **P2** in an acidic THF/MeOH mixture. The ratio THF/MeOH is given in the legend.



Figure S21: UV-vis, CD and g_{abs} spectra for the addition of base to **P2** in an acidic THF/MeOH 40/60 mixture. The ratio THF/MeOH is given in the legend.



Figure S22: UV-vis, CD and g_{abs} spectra for the solvatochroism experiments of P4 in an acidic THF/MeOH mixture. The ratio THF/MeOH is given in the legend.



Figure S23: UV-vis, CD and g_{abs} spectra for the addition of base to **P4** in an acidic THF/MeOH 40/60 mixture. The ratio THF/MeOH is given in the legend.



Figure S24: UV-vis, CD and g_{abs} spectra for the solvatochroism experiments of P5 in an acidic THF/MeOH mixture. The ratio THF/MeOH is given in the legend.



Figure S25: UV-vis, CD and g_{abs} spectra for the addition of base to P5 in an acidic THF/MeOH 20/80 mixture. The ratio THF/MeOH is given in the legend.



Figure S26: UV-vis, CD and g_{abs} spectra for the solvatochroism experiments of **P6** in an acidic THF/MeOH mixture. The ratio THF/MeOH is given in the legend.



Figure S27: UV-vis, CD and g_{abs} spectra for the addition of base to **P6** in an acidic THF/MeOH 20/80 mxiture. The ratio THF/MeOH is given in the legend.

2. In film

Films were prepared by spin coating from neutral or acidified THF solutions (1200 rpm, 20 s) and the solutions were filtered with a $0.20 \mu m$ filter prior to spin coating.

i. Spincoated from neutral media

Figure S28: UV-vis, CD and g_{abs} *spectra for the annealing experiments with* **P2** *with fast cooling.* Each run, the film is annealed for 1 min at the temperature given in the legend and <u>cooled fast at room T.</u>













-0.02 300

400

500

Wavelength (nm)

600

700

Figure S31: UV-vis, CD and g_{abs} spectra for the annealing experiments with **P4** with fast cooling. Each run, the film is annealed for 1 min at the temperature given in the legend and cooled fast at room T.















Figure S35: UV-vis, CD and g_{abs} spectra for the annealing experiments with **P6** with slow cooling. Each run, the film is annealed for 1 min at the temperature given in the legend and cooled slow at 2 °C min⁻¹.

I, II an III holds different measurements of the same film but under different angles. .



ii. Spincoated from acidic media

Figure S36: UV-vis, CD and g_{abs} spectra for the annealing experiments with P2 with fast cooling. Each run, the film is annealed for 1 min at the temperature given in the legend and <u>cooled fast at room T</u>.









Figure S38: UV-vis, CD and g_{abs} spectra for the annealing experiments with **P4** with fast cooling. Each run, the film is annealed for 1 min at the temperature given in the legend and <u>cooled fast at room T</u>.













Figure S42: UV-vis, CD and g_{abs} spectra for the annealing experiments with **P6** with different film thicknesses and fast cooling.

Each run, the film is annealed for 1 min at the temperature given in the legend and <u>cooled fast at room T</u>. The concentration of the solution in mg/ml used for spincoating is given at the end of the label in the legend.



Figure S43: UV-vis, CD and g_{abs} spectra for the annealing experiments with P6 with different film thicknesses and slow cooling.

Each run, the film is annealed for 1 min at the temperature given in the legend and <u>cooled slow at 2 °C min⁻¹</u>. The concentration of the solution in mg/ml used for spincoating is given at the end of the label in the legend.



C. Polarizing optical microscopy (POM)

Figure S44: POM picture of the P6 polymer sample during slow cooling from 90 °*C*. The picture of the defect texture was taken at 68 °C ($100 \times$ magnification).



D. Differential scanning calorimetry (DSC) of polymers P1-P6

The polymers were first heated well above their melting temperature, kept at this temperature for 15 minutes and then slowly cooled down at 2° C min⁻¹. Finally, the melting temperatures were also determined by reheating the samples at 10° C min⁻¹.





