Supporting Information for

# The role of heterogeneous nucleation in the self-assembly of oligothiophenes

Martin Wolffs, Peter A. Korevaar, Pascal Jonkheijm, Olivier Henze, W. James Feast,

Albertus P. H. J. Schenning* and E.W. Meijer*

*e-mail: a.p.h.j.schenning@tue.nl; e.w.meijer@tue.nl*

**This supporting information includes:**

- Materials and Methods
- Figure S1-S19
- References

### *Materials and Methods*

The synthesis and characterization of **T6** and **T7** has already been described.[S1] *n*-Butanol was purchased from Acros and used without purification. HPLC-grade chloroform was purchased from Biosolve. UV/Vis, CD and LD spectra were measured on a Jasco J-815 spectropolarimeter where the sensitivity, time constant and scan rate were chosen appropriately. Before starting the studies related to the cooling speeds, the **T6** solution was heated for 45 minutes at 353 K. Temperature dependent CD, LD and UV/Vis measurements were performed with a PFD-425S/15 Peltier-type temperature controller with a temperature range of 263-383 K and adjustable temperature slope on the J-815. Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectrometry has been performed on a PerSeptive Biosystems Voyager-DE PRO spectrometer. Gelpermeation chromatography was performed on a Shimadzu LC10-AT using two PL Gel 3 μm 100 Å (length per column 300 mm, diameter 7.5 mm) columns, a Shimadzu Photodiodearray SPD-M10Avp detector from 250-700 nm and chloroform as eluent with a flow rate of 1 ml/min (T = 293 K). Recycling gelpermeation chromatography was performed on a modified Shimadzu LC10-AT (*S2*) using 1 Jaigel 2.5 H (600 * 20 mm) + 1 Jaigel 2 H (600 * 20 mm) column, a Shimadzu Photodiodearray SPD-10AVp detector at 450 nm and 510 nm and chloroform as eluent with a flow rate of 3.5 ml/min (T = 293 K). Atomic Force Microscopy images were recorded under ambient conditions using a Digital Instrument Multimode Nanoscope IV operating in the tapping mode regime. Microfabricated silicon cantilever tips (NS) with a resonance frequency of approximately 300 kHz and a spring constant of about 50 Nm$^{-1}$ were used. AFM samples were prepared by dropcasting the solutions on glass. A Zeiss Axiolab microscope was used with a 50 x Zeiss objective. The camera was a Sony PowerHAD. The pictures have been captured with a Pinnacle PCTV video capturecard. The sample was deposited on a round glass cover (Menzel, 24 mm).

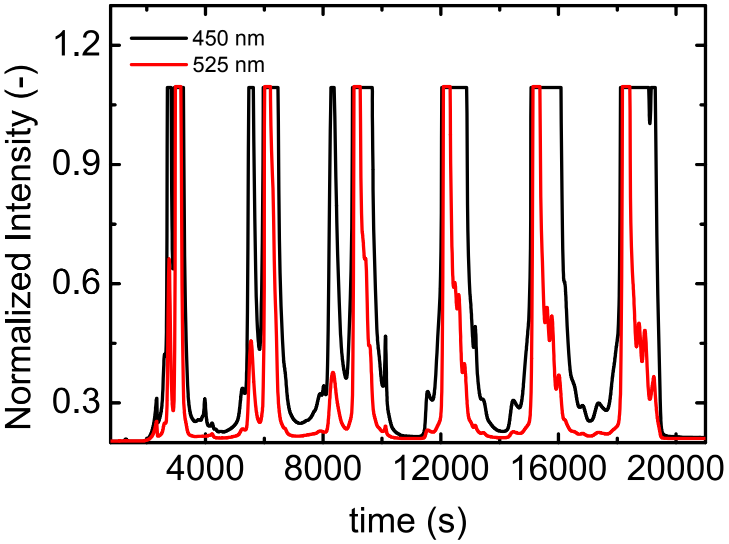

***Figure S1.*** Typical recycling GPC-chromatogram of **T6** in chloroform monitored at 450 nm (black) and 525 nm (red).

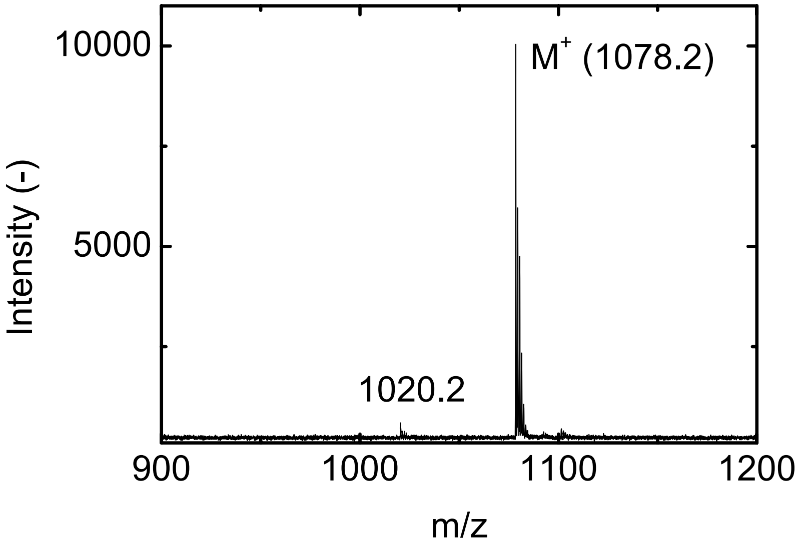

***Figure S2.*** MALDI-TOF mass spectrum of **T6** sample A. The peak at 1020.2 indicates the loss of an ethylene oxide component ($C_2H_4OCH_3$) from one tail.[S2]

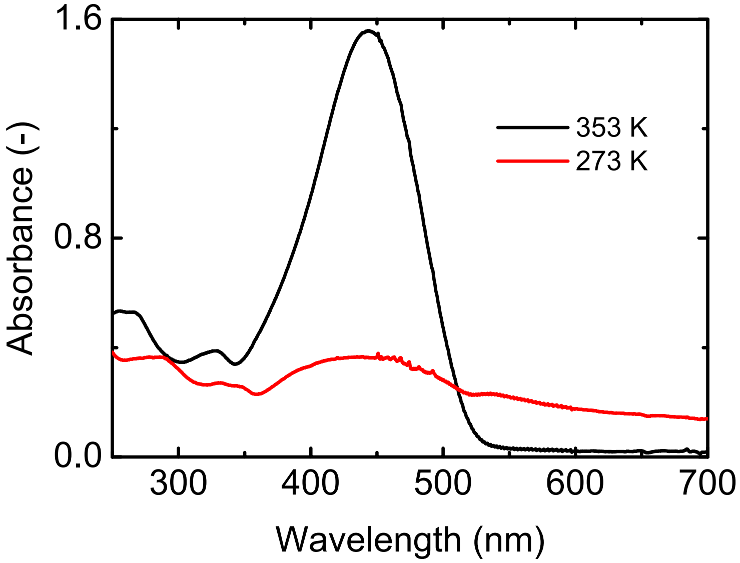

***Figure S3.*** UV/Vis spectra of **T6** sample C in *n*-butanol at 353 K (black) molecularly dissolved state and 273 K (red) assembled state (c = 2.6 x $10^{-5}$ M).

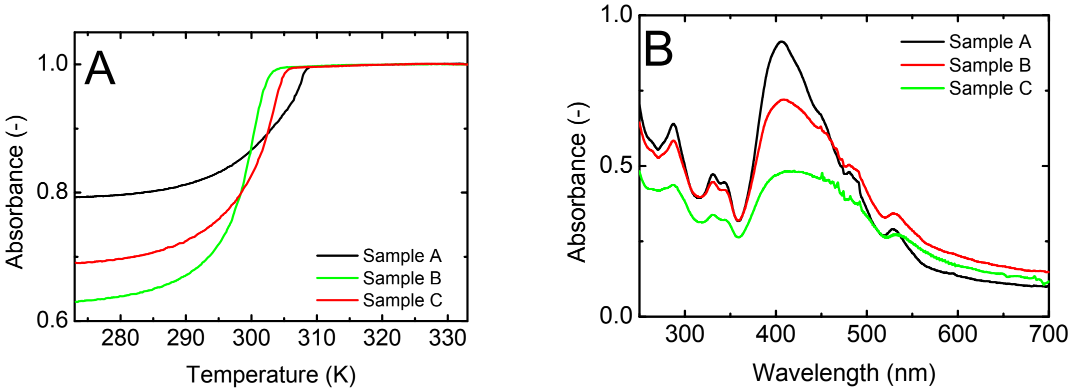

***Figure S4.*** **A.** Temperature dependent UV/Vis spectroscopy of **T6** in *n*-butanol, sample A (99.6 %, black), B (99.9 %, red) and C (99.9+ %, green) ($\lambda = 415$ nm, $c = 2.6 \times 10^{-5}$ M, $\Delta T = -60$ K/hr) **B.** UV/Vis spectra after cooling with 60 K/hr ($c = 2.6 \times 10^{-5}$ M, $T = 273$ K).

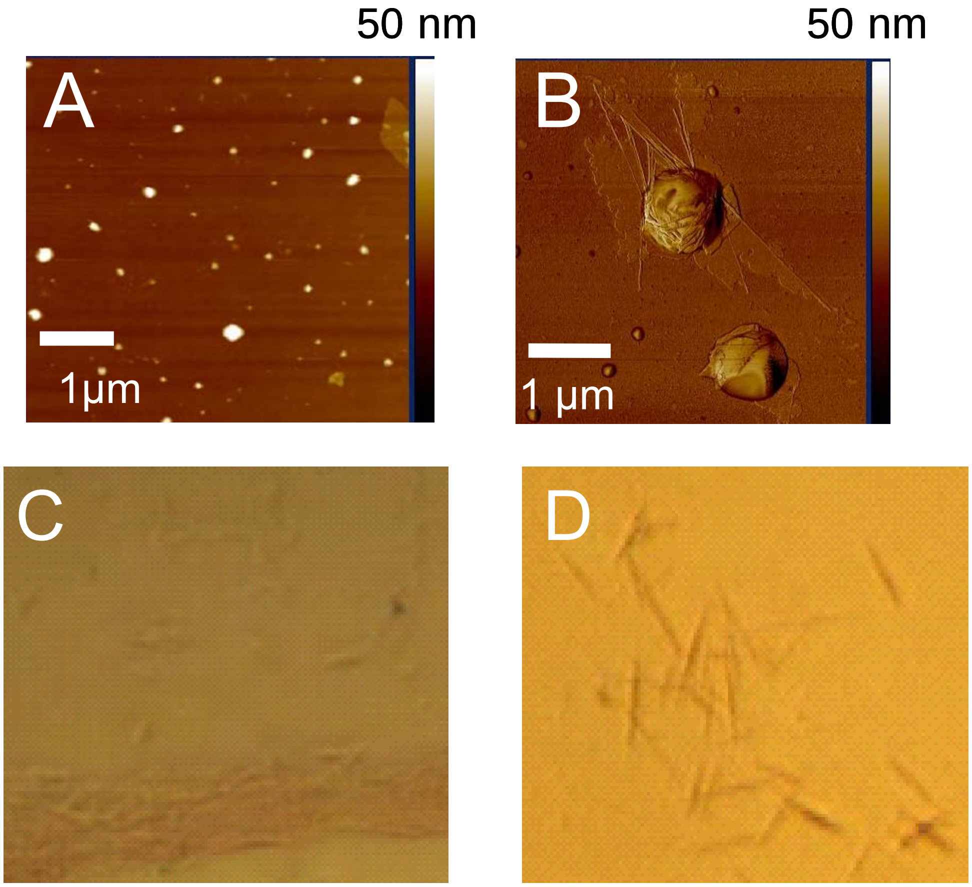

***Figure S5.*** Tapping mode AFM images in the middle of an evaporated drop on a glass substrate (top) and optical microscopy images at the edge of the drop (50 x enlarged) (bottom) that contained a **T6** solution in *n*-butanol after cooling the solution at 60 K/hr (**A**, **C**) or 4 K/hr (**B**) and 6 K/hr (**D**) (c = 2.6 x $10^{-5}$ M, sample B).

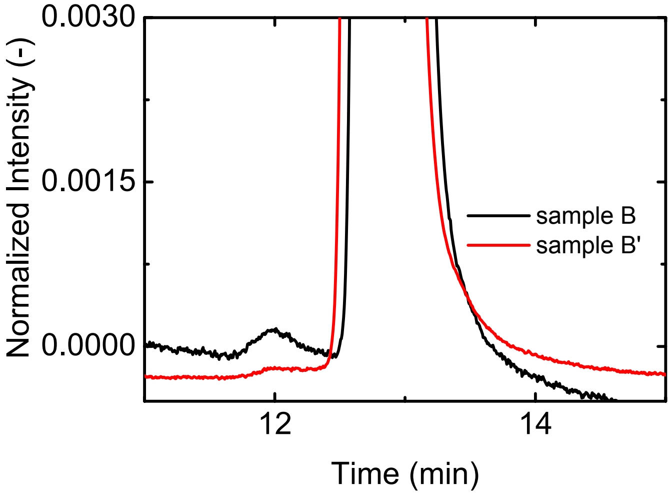

***Figure S6.*** GPC-chromatograph for sample B and B' of **T6** at λ = 450 nm.

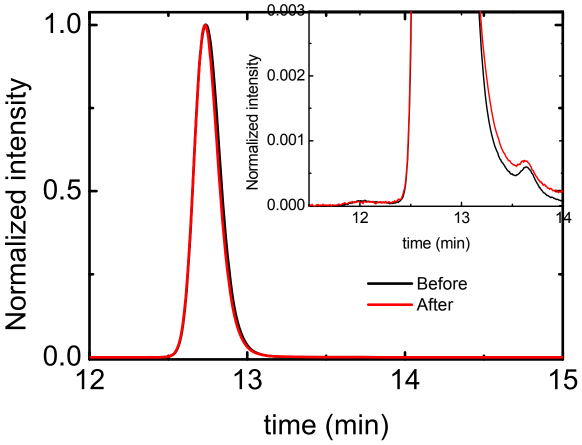

***Figure S7.*** GPC-chromatograph of a sample of **T6** before (black) and after (red) measurements in *n*-butanol at λ = 450 nm.

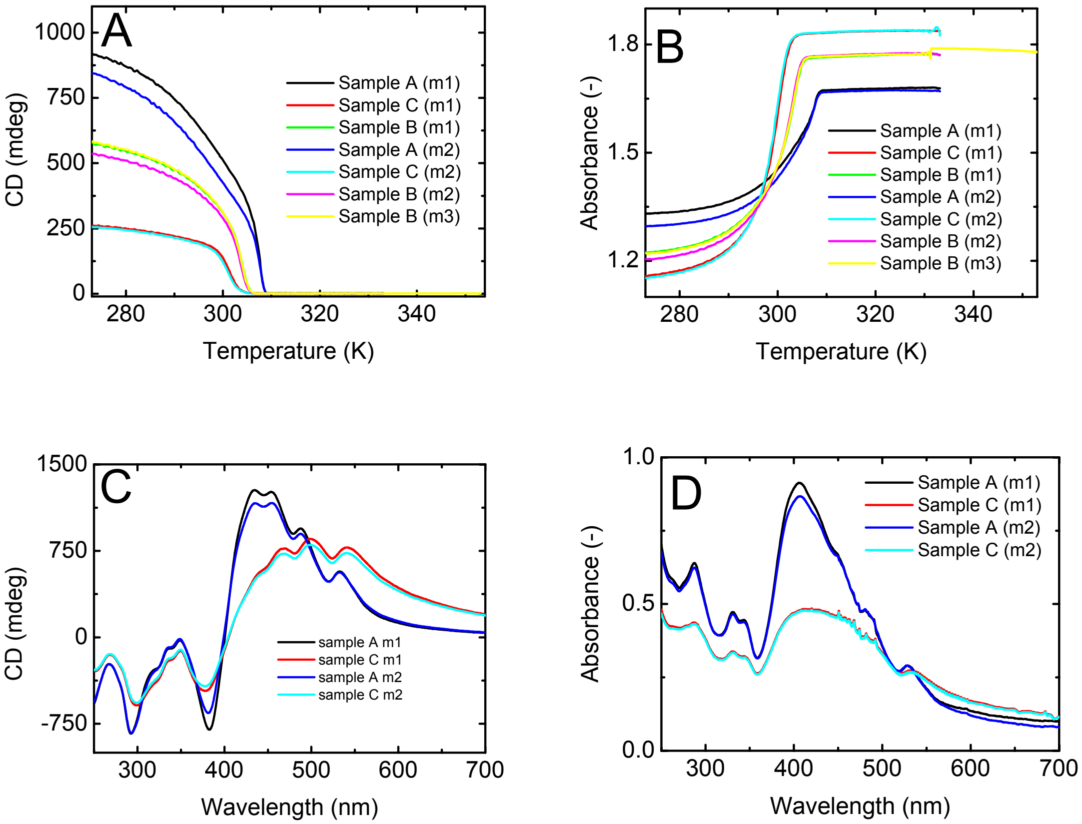

***Figure S8.*** **A**. Cooling curves in CD of **T6** samples A, B and C in *n*-butanol; m*x* stands for the first (x = 1), second (x = 2) and the third (x = 3) measurement (λ = 415 nm, ΔT = -60 K/hr, c = 2.6 x $10^{-5}$ M) **B.** Cooling curves in UV/Vis of **T6** samples A, B and C in *n*-butanol (λ = 415 nm, ΔT = -60 K/hr, c = 2.6 x $10^{-5}$ M). CD (**C**) and UV/Vis (**D**) spectra of **T6** after cooling (T = 273 K, c = 2.6 x $10^{-5}$ M)

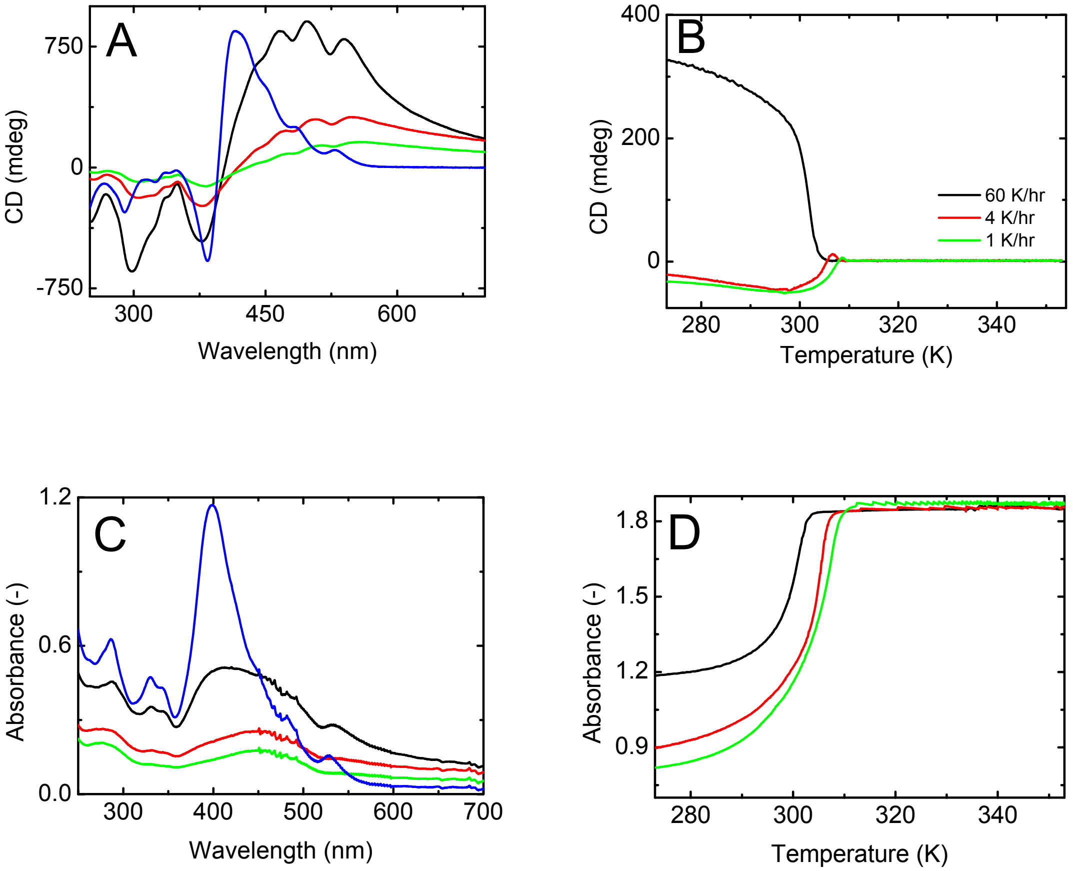

***Figure S9.*** **A.** CD-spectra of sample C after quenching in an ice bath (blue), 60 K/hr cooling (black), 4 K/hr cooling (red) and 1 K/hr cooling (green), the same codes and concentration were used for B, C and D ($c = 2.6 \times 10^{-5}$ M, T = 273 K) **B.** CD Cooling curves for **T6** ($\lambda = 415$ nm). **C.** UV/Vis spectra of sample C (T = 273 K) **D.** Cooling curves in UV/Vis for **T6** ($\lambda = 415$ nm).

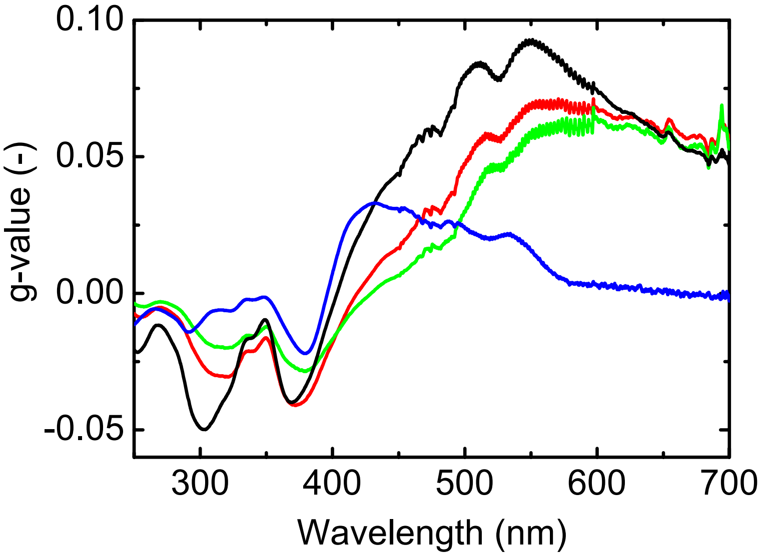

***Figure S10.*** CD-spectra, plotted in g-value, of a **T6** sample C after quenching in an ice bath (blue), 60 K/hr cooling (black), 4 K/hr cooling (red) and 1 K/hr cooling (green) (c = 2.6 x $10^{-5}$ M, T = 273 K)

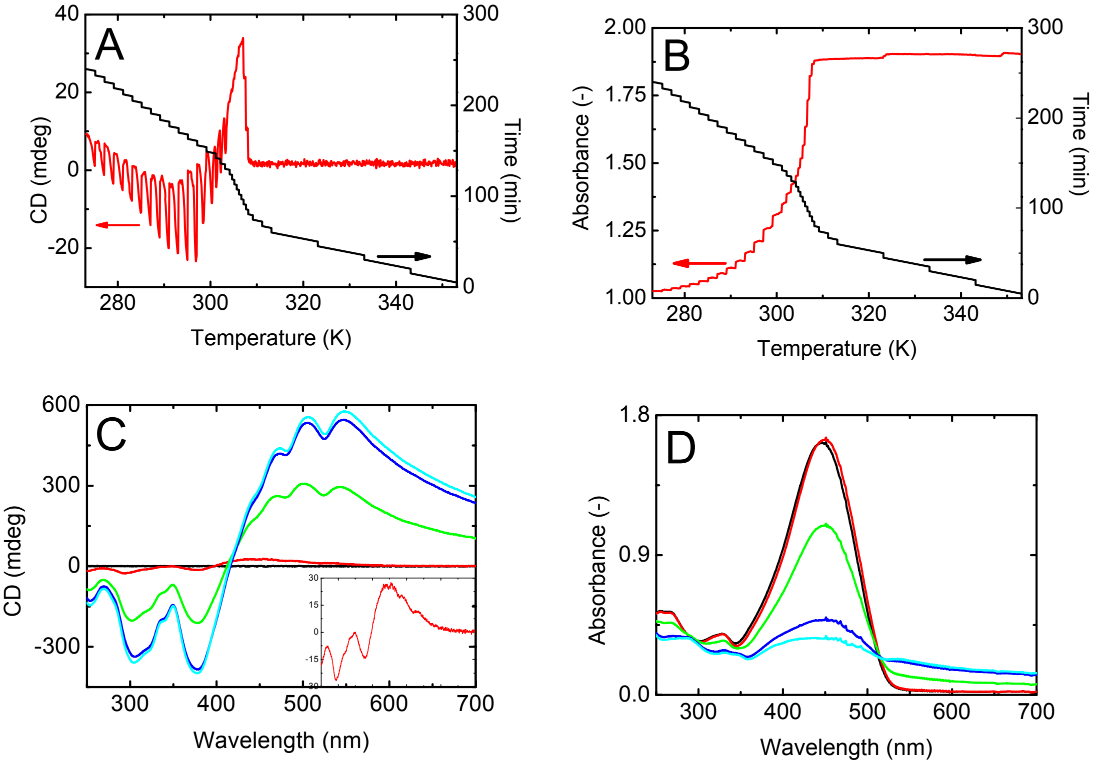

***Figure S11.*** Cooling curve in CD (**A**) and UV/Vis (**B**) of **T6** in *n*-butanol where several annealing steps were conducted (red, left axis) (c = 2.6 x $10^{-5}$ M, ΔT = 60 K/hr, λ = 415 nm, sample C) and the temperature profile (black, right axis) belonging to this cooling protocol. The waves in the CD are caused by a decrease in flow induced LD during the annealing steps (see Figure S14) CD spectra (**C**) and UV/Vis spectra (**D**) of the solution at different points in the self-assembly process during the annealing steps (T = 333 K (black), 308 K (red), 305 K (green), 289 K (dark-blue) and 273 K (light-blue)). The inset in **C** shows the enlarged CD spectrum at T = 308 K.

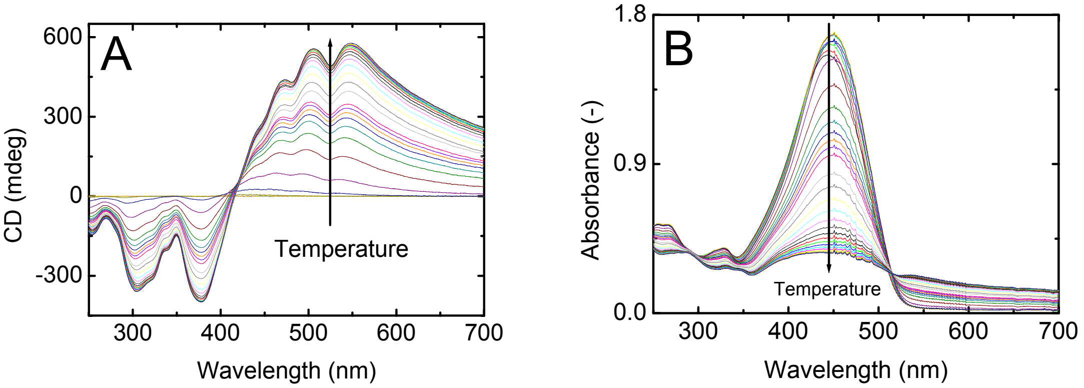

***Figure S12.*** CD (**A**) and UV/Vis (**B**) spectra of **T6** at the different annealing temperatures applied during the stepwise cooling run. The arrow indicates a decrease in temperature.(c =2.6 x $10^{-5}$ M, sample C)

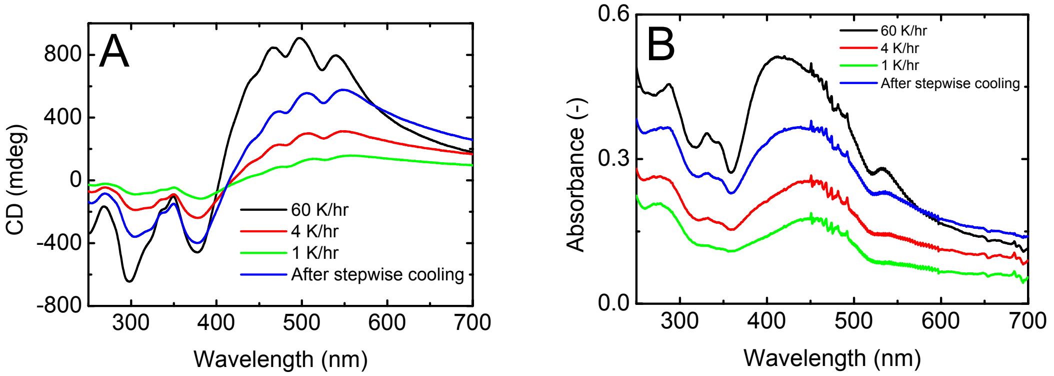

***Figure S13.*** CD (**A**) and UV/Vis (**B**) spectra after cooling a solution of **T6** with continuous cooling rates of 60 K/hr (black), 4 K/hr and 1 K/hr (green) and stepwise cooling with 60 K/hr (blue) (c = 2.6 x $10^{-5}$ M, T = 273 K, sample C)

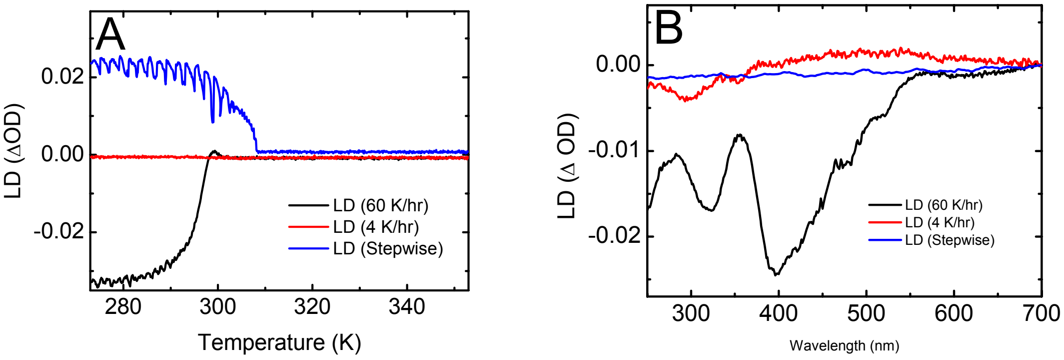

***Figure S14.*** Temperature dependent (**A**) and wavelength dependent (**B**, T = 273 K) linear dichroism measurement on a **T6** solution in *n*-butanol while continuous cooling at 60 K/hr (black) or 4 K/hr (red) and stepwise cooling (blue) (c = 2.6 x $10^{-5}$ M, sample B).

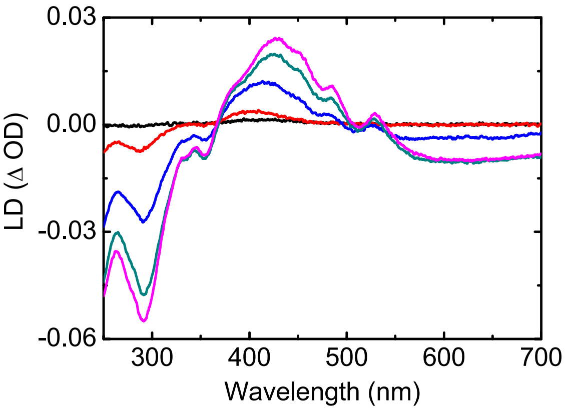

***Figure S15.*** LD measurements of a solution of **T6** at different points in the self-assembly process during stepwise cooling (c = 2.6 x $10^{-5}$ M, T = 333 K (black), 308 K (red), 305 K (blue), 289 K (dark-green) and 273 K (purple), sample B)

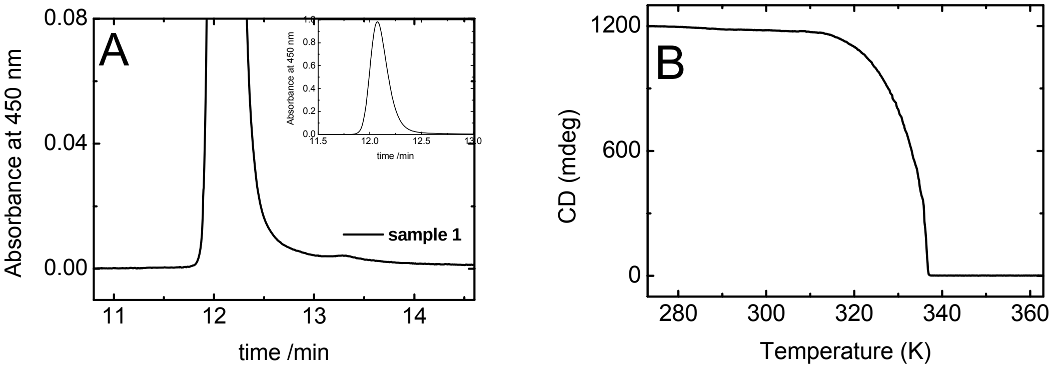

***Figure S16.*** The 100 x zoom normalized GPC-trace of **T7** (**A**) where the inset shows the full trace at λ = 450 nm and the temperature dependent cooling curve in *n*-butanol (**B**), (c = 2.6 x $10^{-5}$ M, λ = 425 nm, ΔT = - 60 K/hr).

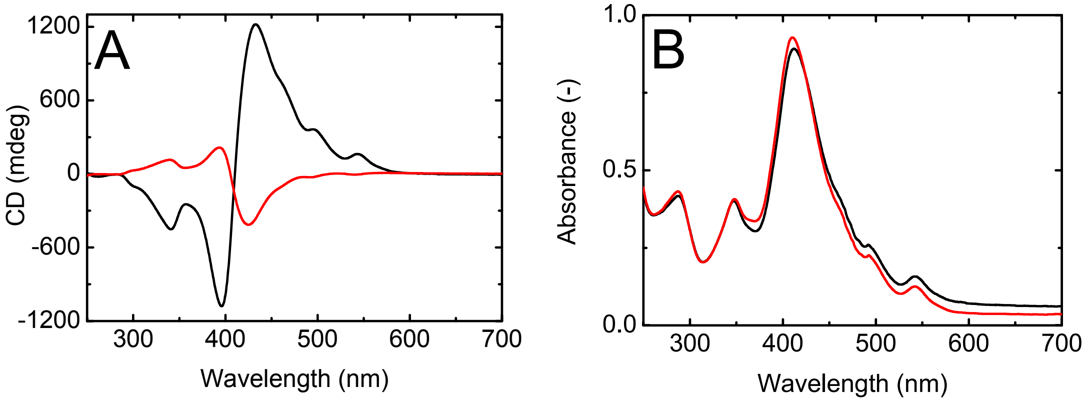

***Figure S17.*** **A.** CD-spectra of **T7** after quenching in an ice batch (red), 60 K/hr cooling (black), the same codes and concentration were used for B (c = 2.6 x $10^{-5}$ M, T = 273 K). **B.** UV/Vis spectra of **T7** (T = 273 K).

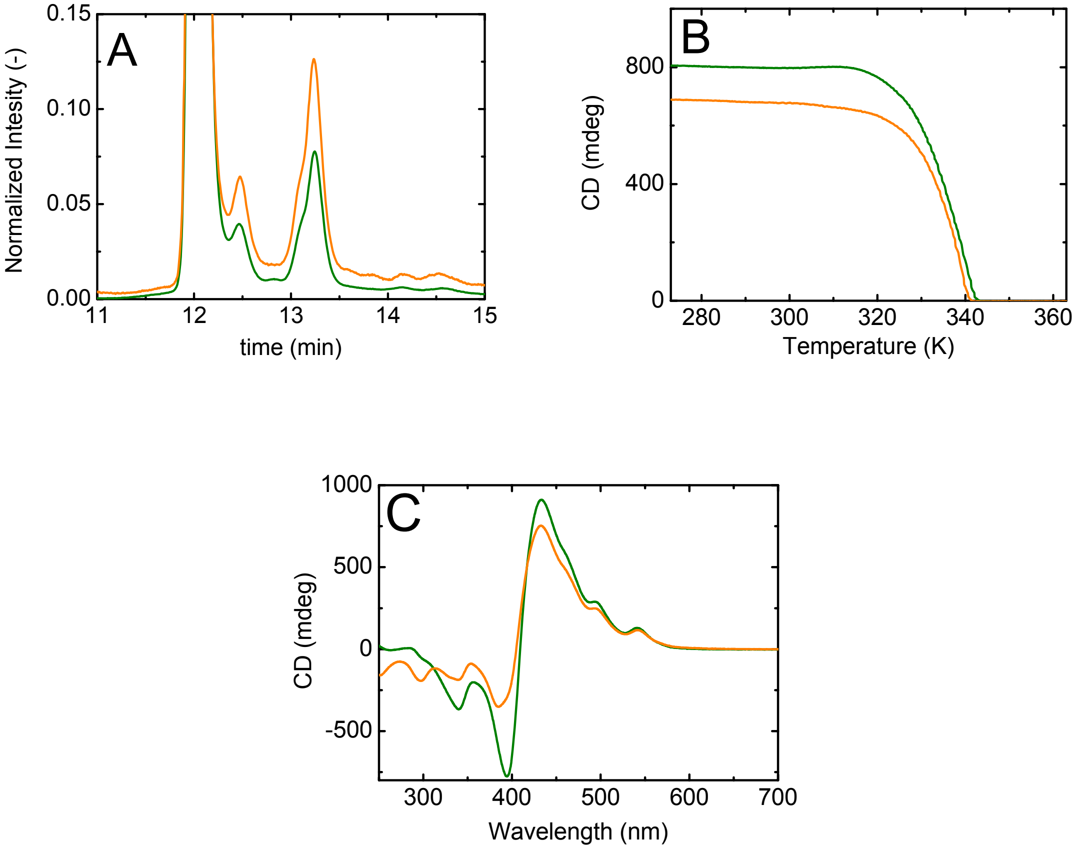

***Figure S18.*** **A.** Zoom in of the GPC trace at λ = 254 nm of **T7** (sample 2) before first cooling and annealing experiment (green, purity = 79 %) and before second cooling and annealing experiment (orange, purity = 72 %). **B.** First (green) and second (orange) cooling curves with 60 K/hr of **T7** in *n*-butanol (sample 2, 1-butanol, 2.6 x $10^{-5}$ M, λ = 425 nm) **C.** CD spectra after first (green) and second (orange) cooling run of **T7** (sample 2, c = 2.6 x $10^{-5}$ M, T= 273 K)

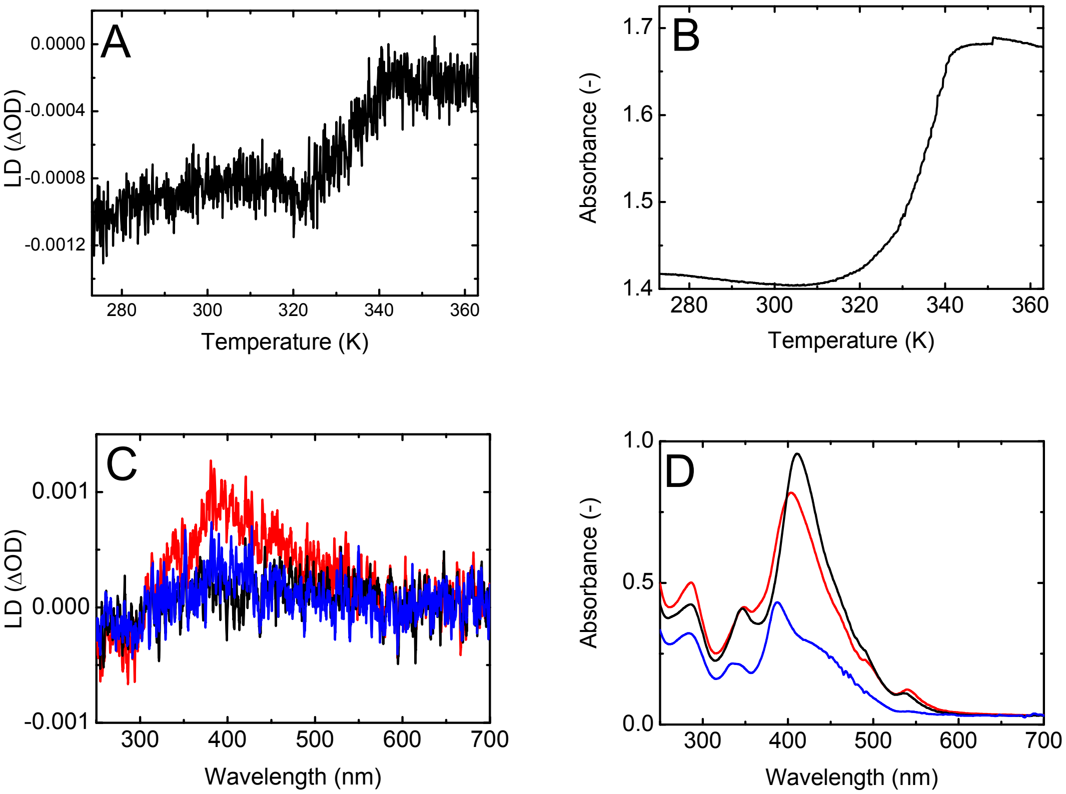

***Figure S19.*** Cooling curves of **T7** (sample with purity of 76 % (λ = 254 nm) / 82 % (λ = 450 nm) at 60 K/hr in LD (**A**) and UV/Vis (**B**), (2.6 x $10^{-5}$ M, λ = 425 nm). LD (**C**) and UV/vis (**D**) spectra of **T7** in *n*-butanol (2.6 x$10^{-5}$ M) after quenching (red), cooling at 60 K/hr (black) and annealing (blue) (c = 2.6 x $10^{-5}$ M)

## References

S1. O. Henze, W. J. Feast, F. Gardebien, P. Jonkheijm, R. Lazzaroni, P. Leclère, E. W. Meijer, A. P. H. J. Schenning, *J. Am. Chem. Soc.*, 2006, **128**, 5923.

S2. R. J. Abbel, M. Wolffs, R. A. A. Bovee, J. L. J. van Dongen, O. Henze, W. J. Feast, E. W. Meijer, A. P. H. J. Schenning, manuscript in preparation.