

## ***Supporting Information for***

# **Nanofiber Formation via Self-Assembly of a Chiral Regioregular Poly(azomethine)**

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## **Experimental Section**

**Instrumentation.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR measurements were recorded on a JEOL JNM-EX400 instrument at 400 and 100 MHz in  $\text{CDCl}_3$  (0.05% TMS as an internal standard) at room temperature. Size exclusion chromatography (SEC) was carried out on a TOSOH UV-8020 and RI-8020 (TOSOH TSKgel  $\alpha$ -3000 column) using  $\text{CHCl}_3$  as an eluent at 40 °C, after calibration with the standard polystyrene samples. Recyclable preparative high-performance liquid chromatography (HPLC) was performed on a JAI LC-918 using  $\text{CHCl}_3$  as an eluent. FT-IR spectra were obtained using a Perkin-Elmer 1600 infrared spectrometer. UV-vis spectra were recorded on a SHIMADZU UV-3600 spectrophotometer. Circular dichroism (CD) spectra were recorded on a JASCO J-600 spectropolarimeter with  $\text{CHCl}_3$  as a solvent. Optical rotations were measured with a RUDOLPH RESEACH Autopol IV polarimeter by using  $\text{CHCl}_3$  as a solvent. Transmission electron microscopy (TEM) images were observed with a JEOL JEM-100SX operating at an accelerating voltage of 100 kV. TEM samples were prepared by depositing one drop of a desired solution on a 200 mesh copper grid covered with a carbon film and dried to remove the solvent at room temperature. Elemental analysis was performed at the Microanalytical Center of Kyoto University. Powder X-ray diffraction (XRD) patterns were taken by using  $\text{Cu K}\alpha$  radiation with a Shimadzu XRD-600.

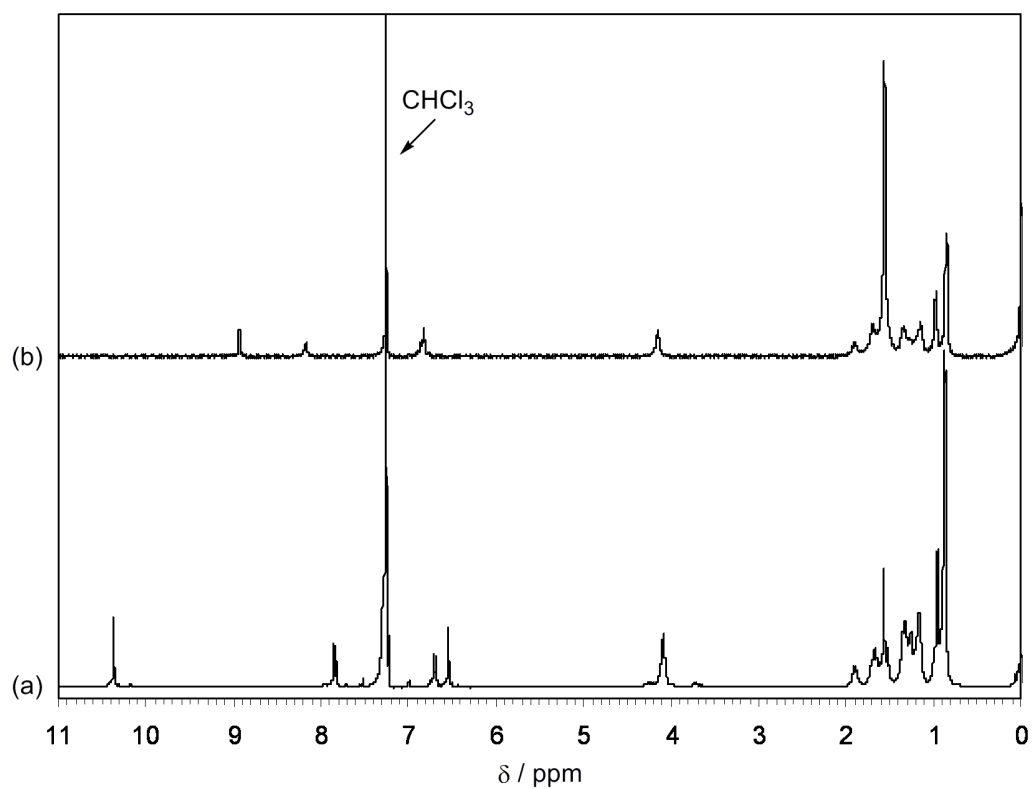
**Materials.** Unless stated otherwise, all reagents were obtained from commercial sources and used without further purification. Tetrahydrofuran (THF) was purified using a two-column solid-state purification system (Glasscontour System, Joerg Meyer, Irvine, CA). 4-Azido-2-(3',7'-dimethyloctyloxy)benzaldehyde (**1**) and the resulting racemic poly(azomethine) (**2**) were synthesized and characterized according to the literature.<sup>1</sup> (*S*)-3,7-Dimethyloctyl bromide was synthesized and characterized according to the literature.<sup>2</sup>

#### **(*S*)-4-Azido-2-(3',7'-dimethyloctyloxy)benzaldehyde (**1**\*)**

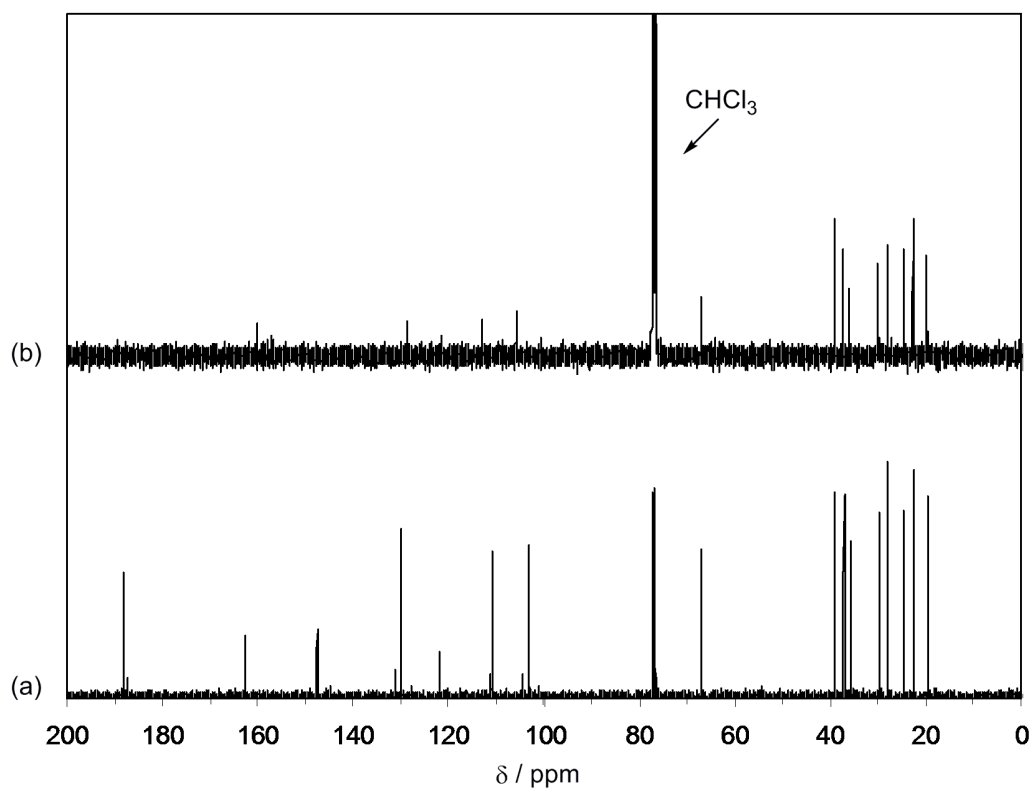
**1\*** was synthesized according to the literature procedure<sup>1</sup> by using (*S*)-3,7-dimethyloctyl bromide instead of 3,7-dimethyloctyl bromide. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ (ppm) 10.37 (s, 1 H), 7.84 (d, 1 H), 6.69 (d, 1 H), 6.54 (s, 1 H), 4.09 (t, 2 H), 1.89 (m, 2 H), 1.80–0.80 (br, 17 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ (ppm) 188.3 (CHO), 162.8 (*C*<sub>Ar</sub>–O), 147.6 (*C*<sub>Ar</sub>–N), 130.1 (*C*<sub>Ar</sub>–H), 122.0 (*C*<sub>Ar</sub>–C), 111.0 (*C*<sub>Ar</sub>–H), 103.1 (*C*<sub>Ar</sub>–H), 67.2 (CH<sub>2</sub>O), 40–19 (aliphatic carbons). MS (EI) *m/z*: 303.1947 (C<sub>17</sub>H<sub>25</sub>O<sub>2</sub>N<sub>3</sub> requires 303.1947). Anal. Calcd: C 67.30, H 8.31; Found: C 67.19, H 8.33.

#### **Chiral poly(azomethine) (**2**\*)**

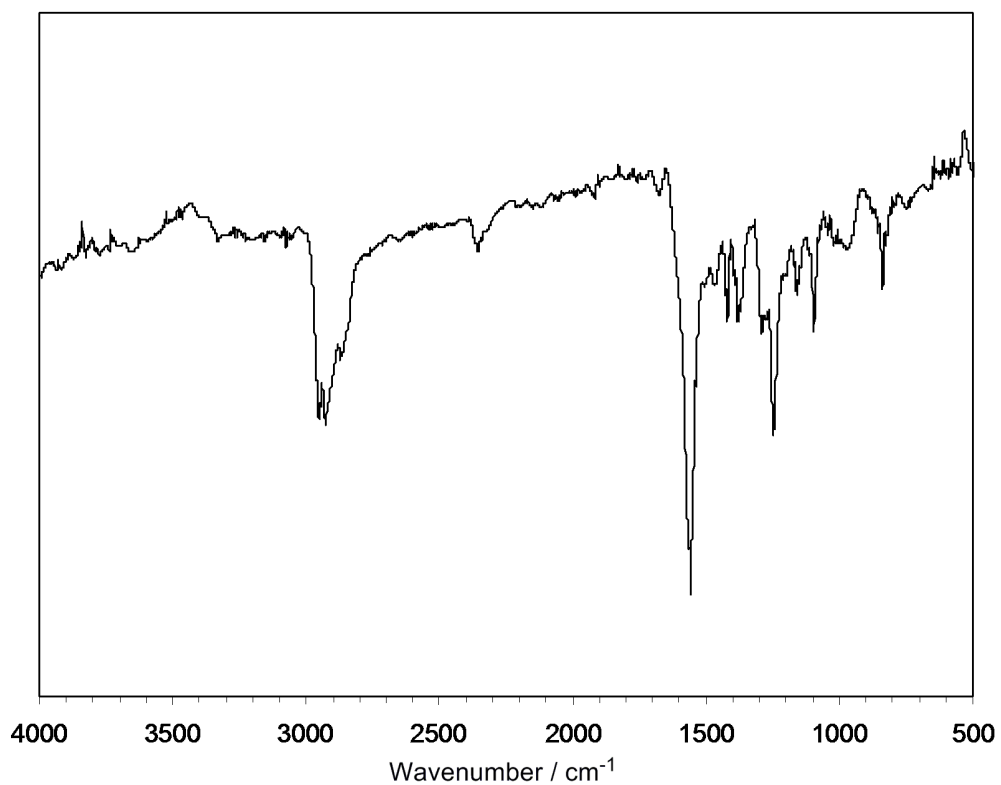
**2\*** was synthesized according to the literature procedure<sup>1</sup> by using monomer **1\*** instead of monomer **1**. In a round-bottom flask were placed a monomer, dry toluene (200 mM), and an excess amount of methyldiphenylphosphine (PMePh<sub>2</sub>) at room temperature. The reaction mixture was thoroughly deoxygenated, filled with high-purity argon, and placed in a thermostatic oil bath at 80 °C. After heating for 48 h, an excess of benzaldehyde was added to quench the polycondensation reaction. After cooling down, the reaction mixture was concentrated. Exhaustive precipitation into methanol and hexane afforded the target polymer. **2\***: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ (ppm) 8.94 (br, 1 H), 8.17 (br, 1 H), 6.85 (br, 2 H), 4.15 (br, 2 H), 1.90 (br, 2 H), 1.80–0.80 (br, 17 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ (ppm) 160.1 (N=CH), 158.0 (*C*<sub>Ar</sub>–O), 157.0 (*C*<sub>Ar</sub>–N), 128.6 (*C*<sub>Ar</sub>–H), 121.6 (*C*<sub>Ar</sub>–C), 112.9 (*C*<sub>Ar</sub>–H), 105.9 (*C*<sub>Ar</sub>–H), 70.0 (CH<sub>2</sub>O), 40–19 (aliphatic carbons). IR (ν, cm<sup>-1</sup>): 1558 (–CH=N–).



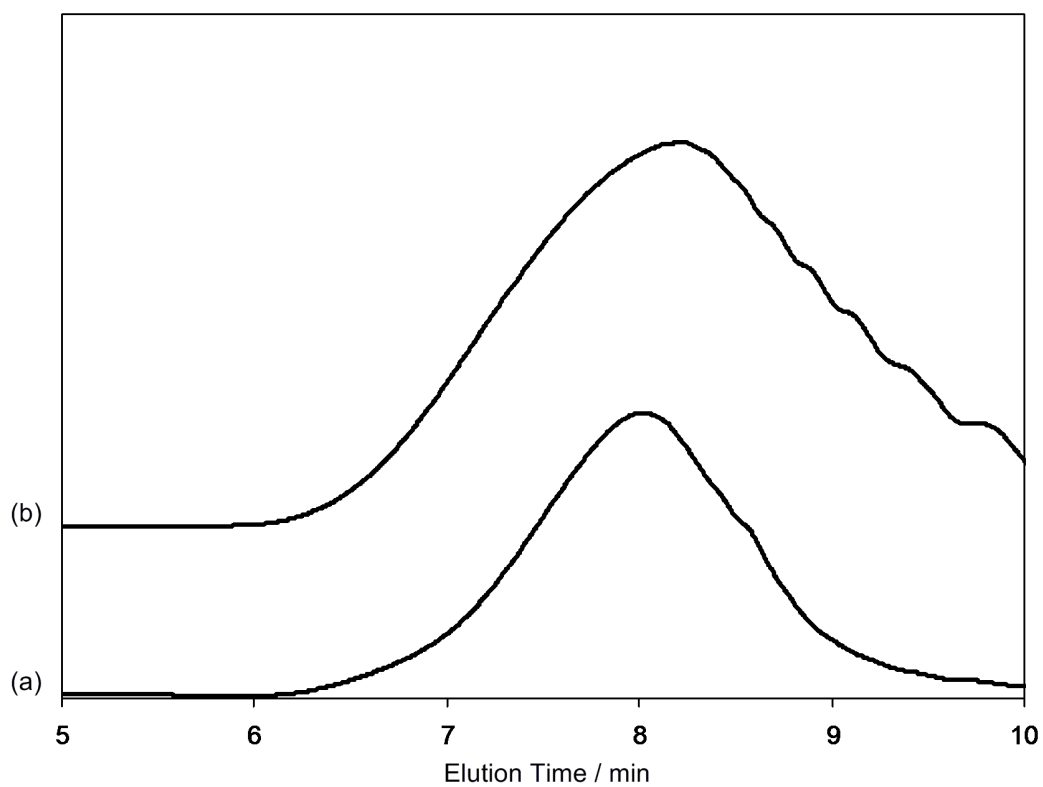
**Figure S1.**  $^1\text{H}$  NMR spectra of (a) **1\*** and (b) **2\*** in  $\text{CDCl}_3$ .



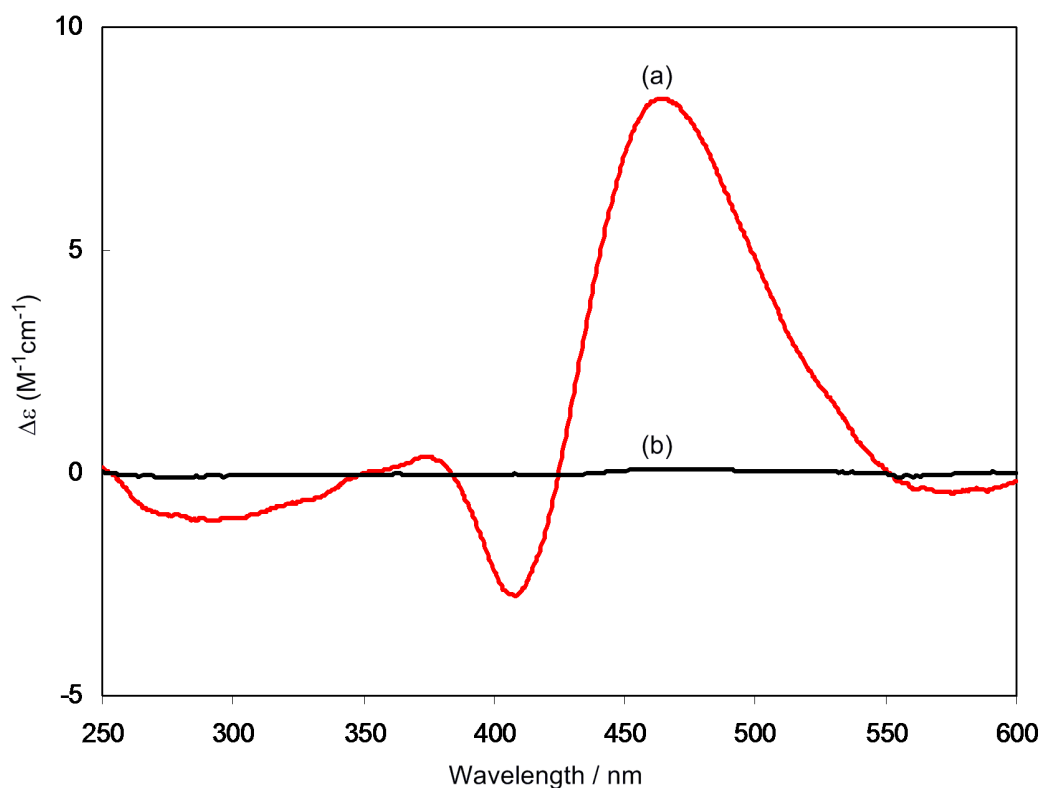
**Figure S2.**  $^{13}\text{C}$  NMR spectra of (a) **1\*** and (b) **2\*** in  $\text{CDCl}_3$ .



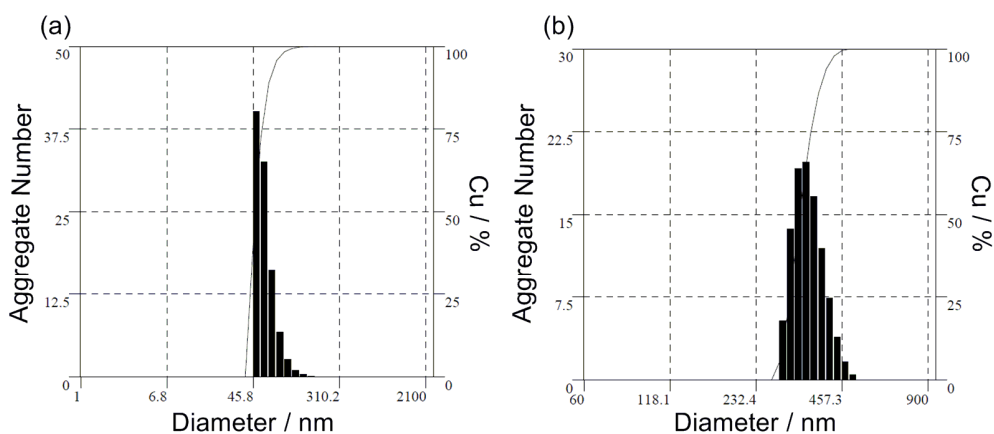
**Figure S3.** FT-IR spectrum of **2\***.



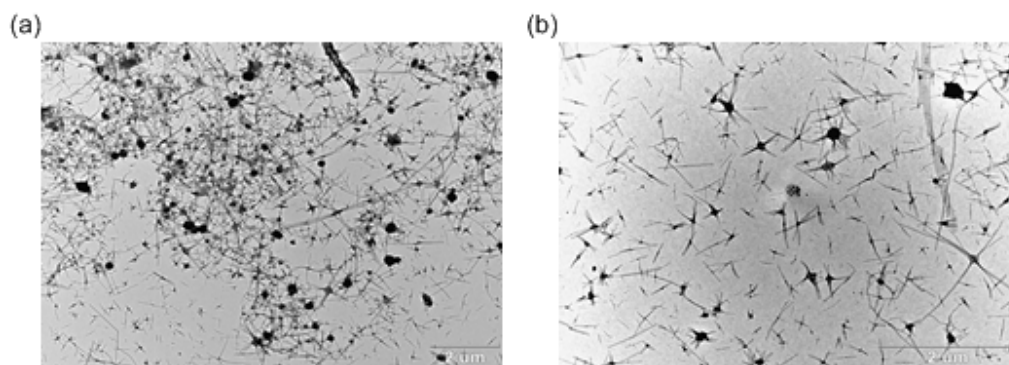
**Figure S4.** SEC traces of (a) **2\*** and (b) **2**.



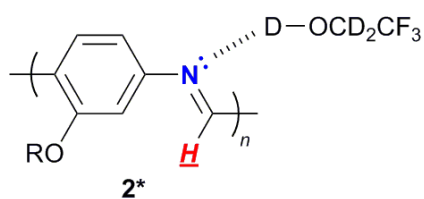
**Figure S5.** CD spectra of **2\*** in  $\text{CHCl}_3/\text{CF}_3\text{CH}_2\text{OH}$  (10/90) solutions: (a)  $1.0 \times 10^{-4}$  M and (b)  $1.0 \times 10^{-5}$  M.



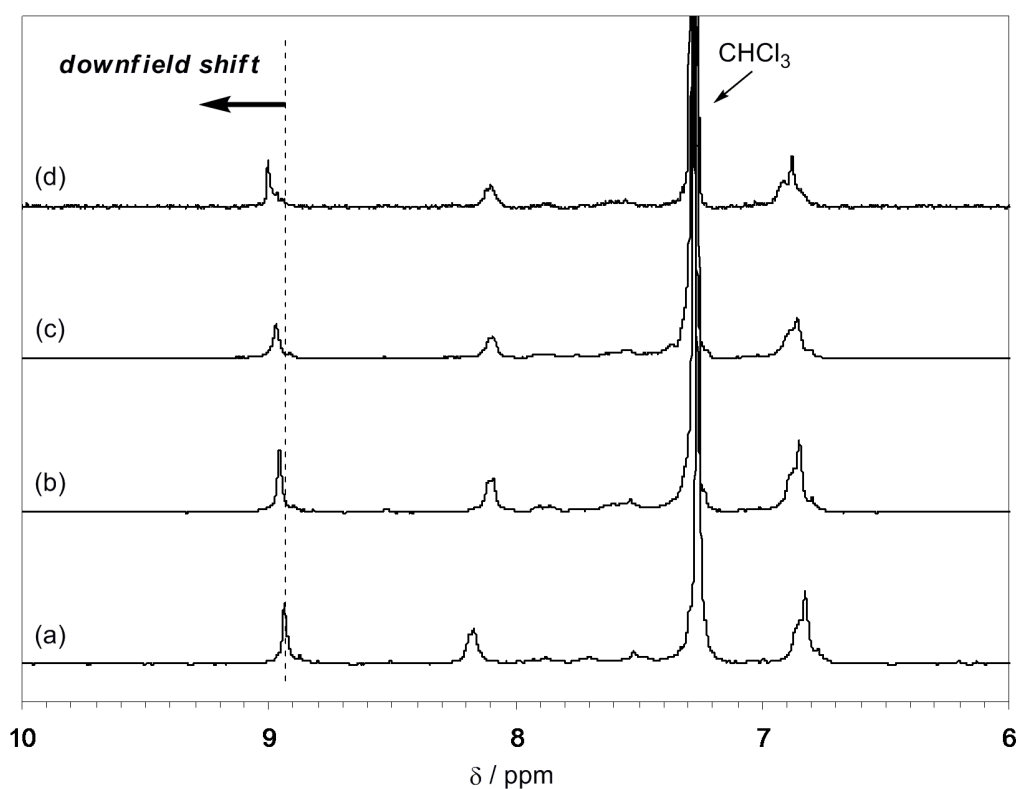
**Figure S6.** Histograms of diameters of **2\*** in  $\text{CHCl}_3/\text{CF}_3\text{CH}_2\text{OH}$  solutions ( $1.0 \times 10^{-4}$  M): (a) 20/80 and (b) 10/90.



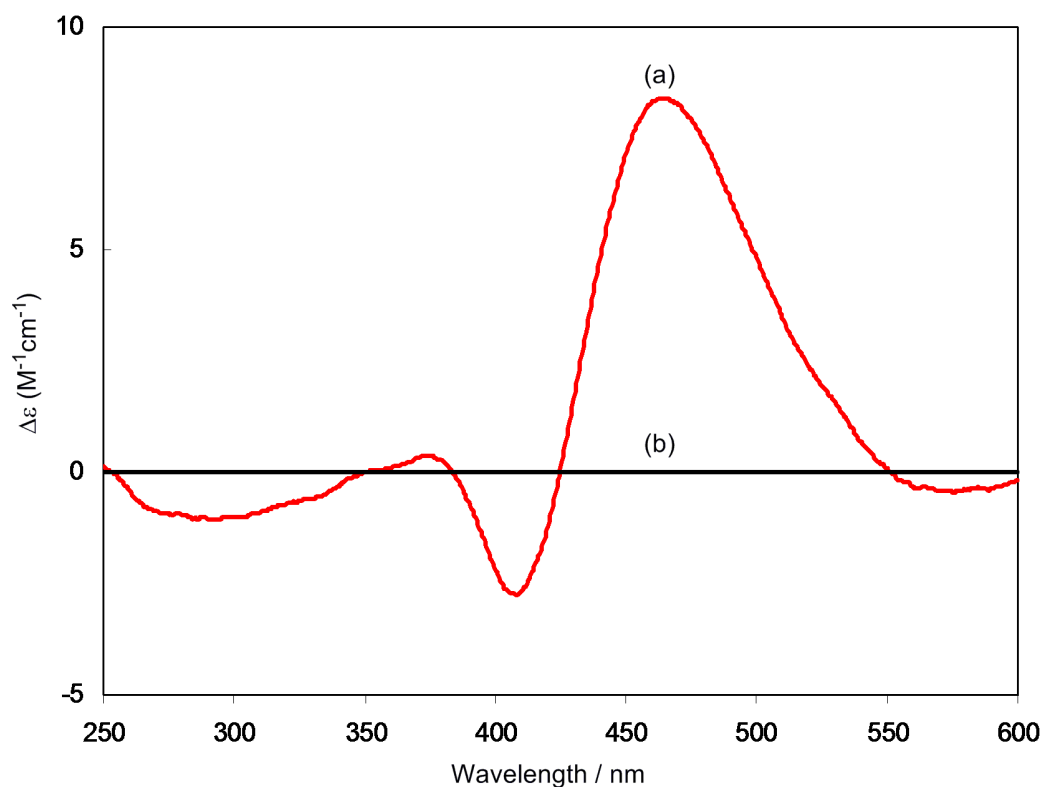
**Figure S7.** TEM images of **2\*** from  $\text{CHCl}_3/\text{CF}_3\text{CH}_2\text{OH}$  solutions ( $1.0 \times 10^{-4}$  M): (a) 100/0 and (b) 10/90.



**Chart 1**



**Figure S8.**  $^1\text{H}$  NMR spectra of **2\*** in  $\text{CDCl}_3/\text{CF}_3\text{CD}_2\text{OD}$  solutions: (a) 100/0, (b) 90/10, (c) 80/20, and (d) 50/50.



**Figure S9.** CD spectra of (a) **2\*** and (b) **2** in  $\text{CHCl}_3/\text{CF}_3\text{CH}_2\text{OH}$  (10/90) solutions. The concentration of both samples is  $1.0 \times 10^{-4}$  M.

## References

1. J. Miyake and Y. Chujo, *Macromolecules*, 2008, **41**, 9677–9682.
2. F. Vera, R. M. Tejedor, P. Romero, J. Barbera, M. B. Ros, J. L. Serrano and T. Sierra, *Angew. Chem., Int. Ed.*, 2007, **46**, 1873–1877.