

*Electronic Supplementary Information*

**Wavy supramolecular polymers formed by hydrogen-bonded rosettes**

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## 1. General

### Materials and Methods

Column chromatography was performed using 63–210  $\mu\text{m}$  silica gel. All other commercially available reagents and solvents were of reagent grade and used without further purification. The solvents for the preparation of monomers and assemblies were all spectral grade and used without further purification.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on JEOL JNM-ECA500 NMR spectrometer or Bruker AVANCE III-400M NMR spectrometer, and chemical shifts are reported in ppm ( $\delta$ ) with the signal of TMS as internal standard. APCI-MS spectra were measured on an Exactive (Thermo Fisher). UV/vis spectra were recorded on a JASCO V660 spectrophotometer equipped with a Peltier device temperature control unit using a screw-capped quartz cuvette of 1.0-cm path length. DLS measurements were conducted on Zetasizer Nano (Malvern Instruments) using noninvasive backscattering (NIBS) technology under 4.0 mW He-Ne laser (633 nm). The scattering angle was set at  $173^\circ$ . A screw-capped quartz cuvette was used for the measurements. The temperature for measurements was kept at 293 K. AFM imaging were performed under ambient conditions using Multimode 8 Nanoscope V (Bruker AXS) in Peak Force Tapping (Scanasyt) mode. Silicon cantilevers (SCANASYST-AIR) with a spring constant of  $0.4 \text{ N m}^{-1}$  and a frequency of 70 kHz (Bruker AXS) were used.

### Small-angle X-ray scattering (SAXS)

SAXS measurements were carried out at BL-10C at the Photon Factory of the High Energy Accelerator Research Organization (KEK) in Tsukuba, Japan. Solutions were loaded into cells (stainless steel surround, 20- $\mu\text{m}$ -thick quartz glass windows, 1.25-mm-path length), and the temperature was maintained at around 293 K (room temperature). An X-ray wavelength of 1.5  $\text{\AA}$  and a sample-detector distance of 1029 mm (calibrated using silver behenate) gave a detectable  $Q$  range of the order of 0.1 to  $5.9 \text{ nm}^{-1}$ . Sixty frames were collected with an exposure time of 10 s: Radiation damage was not observed, so these data were averaged to give a total integration time of 600 s. The 2D scattering data (detector: DECTRIS PILATUS3 2M) were radially averaged to yield 1D scattering intensity data [ $I(Q)$  versus  $Q$ ]. This was normalized using water as a reference, and the solvent + cell background was subtracted, to give absolute scattering intensity  $I(Q)$  in  $\text{cm}^{-1}$ . All data reduction was carried out using the software package SAngler.

### Photo-irradiation experiments

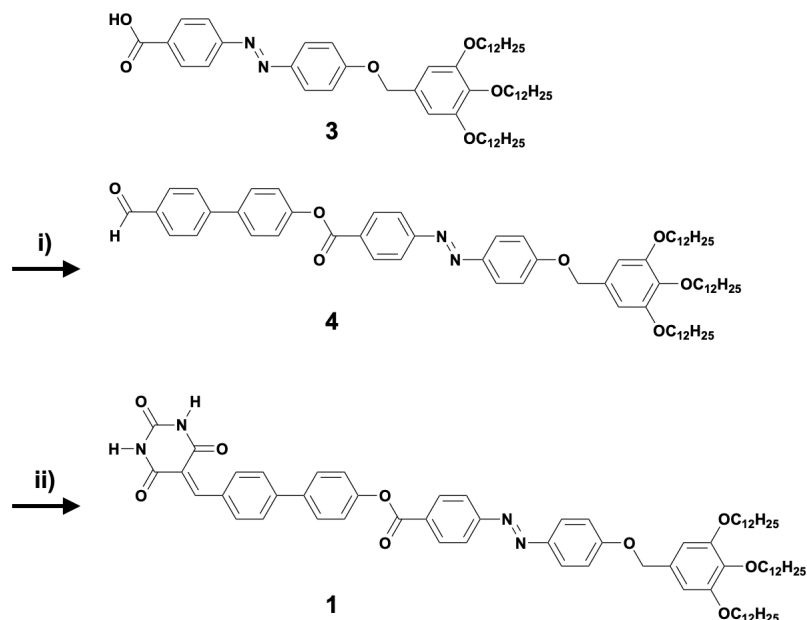
UV-light irradiation experiments of monomers and assemblies were carried out using 365-nm LED lamp ( $17 \text{ m W cm}^{-2}$ ). The sample solution was prepared in a 1-cm path length quartz cuvette. Visible-light irradiation experiments were performed using 470-nm LED lamp ( $17 \text{ m W cm}^{-2}$ ).

### Investigation of supramolecular polymerization process of $\mathbf{1}_{trans}$

The supramolecular polymerization process of  $\mathbf{1}_{trans}$  was investigated using a MCH solution ( $c = 10 \text{ }\mu\text{M}$ ). Temperature-dependent UV/vis absorption spectra upon cooling from 383 to 293 K at a rate of  $1.0 \text{ K min}^{-1}$  showed a bathochromic shift of a shoulderless absorption band at 368 nm involving fully overlapped  $\pi-\pi^*$  electronic transition of the azobenzene and the biphenyl moieties to 382 nm (Fig. S9a). The bathochromic shift suggests slipped (J-type) stacking of these chromophores upon aggregation. When this spectral change was monitored as a function of temperature, a non-sigmoidal curve characteristic of nucleation-elongation (cooperative) supramolecular polymerization was obtained (Fig. S9b).<sup>[S1]</sup> Upon decreasing concentration from 10 to  $5.0 \text{ }\mu\text{M}$ , critical nucleation temperature ( $T_e$ ) decreased while the trajectories are almost superimposable (Fig. S9b). Because heating curves of these SP solution showed complicated multi-step dissociation probably due to considerable bundling (Fig. S10), we analyzed the cooling curves by means of a modified van't Hoff plot. By plotting the natural logarithm of concentrations versus the reciprocal of  $T_e$  provided thermodynamic parameters including standard enthalpy ( $\Delta H^\circ = -50.2 \text{ kJ mol}^{-1}$ ), entropy ( $\Delta S^\circ = -42.1 \text{ J K}^{-1} \text{ mol}^{-1}$ ), and Gibbs free energy ( $\Delta G^\circ = -37.8 \text{ kJ mol}^{-1}$ ) (Fig. S9c).

## 2. Synthesis and Analytical Data

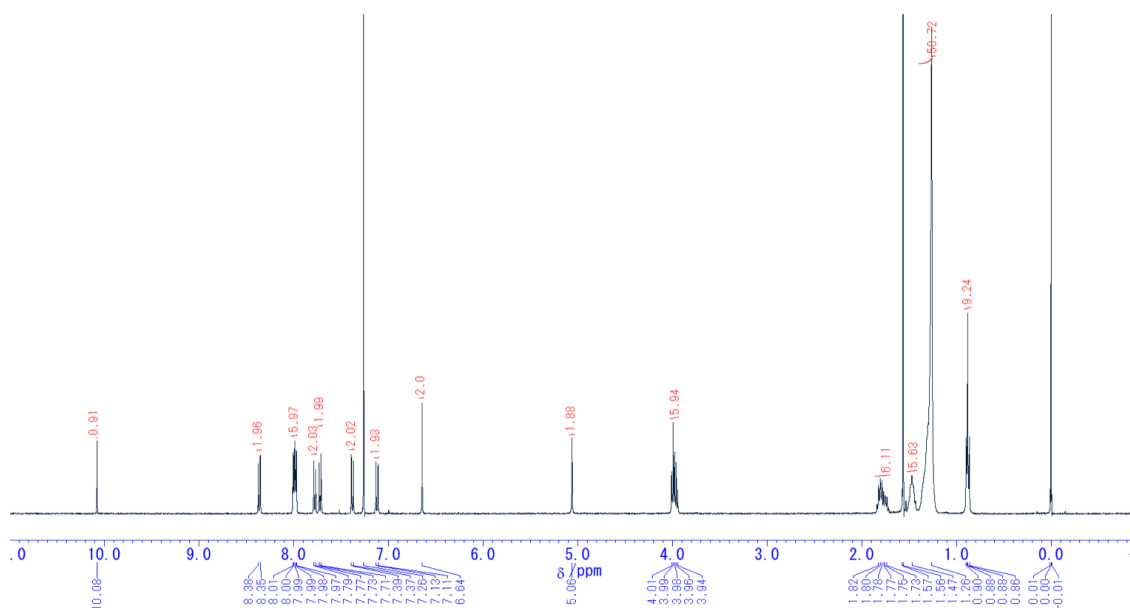
Compound **1** was synthesized according to Scheme S1.



**Scheme S1.** Synthesis of compound **1**. i) 4'-hydroxybiphenyl-4-carbaldehyde, EDCI, DMAP, CH<sub>2</sub>Cl<sub>2</sub>, r.t.; ii) barbituric acid, EtOH, reflux.

**Synthesis of compound 4:** Compound **3** (0.297 g, 0.335 mmol), 4'-hydroxybiphenyl-4-carbaldehyde (0.066 g, 0.333 mmol), 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDCI, 0.102 g, 0.532 mmol), and 4-dimethylaminopyridine (DMAP, 0.047 g, 0.385 mmol) were dissolved in dry CH<sub>2</sub>Cl<sub>2</sub> (10 mL). The mixture was stirred for overnight at room temperature under N<sub>2</sub> atmosphere. The reaction mixture was poured into water and extracted with CH<sub>2</sub>Cl<sub>2</sub>, washed with H<sub>2</sub>O and then brine. The organic layer was dried over Na<sub>2</sub>SO<sub>4</sub>, concentrated in vacuo and evaporated to dryness. The residue was purified by column chromatography over silica gel (eluent: hexane/AcOEt = 9:1) to give compound **4** as an orange solid (0.101 g, 28%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 293K):  $\delta$  (ppm) = 10.08 (s, 1H), 8.38 (d,  $J$  = 8.8 Hz, 2H), 8.01–7.97 (m, 6H), 7.79 (d,  $J$  = 8.2 Hz, 2H), 7.73 (d,  $J$  = 8.8 Hz, 2H), 7.39 (d,  $J$  = 8.7 Hz, 2H), 7.13 (d,  $J$  = 9.0 Hz, 2H), 6.64 (s, 2H), 5.06 (s, 2H), 4.01–3.94 (m, 6H), 1.82–1.73 (m, 6H), 1.47 (m, 6H), 1.26 (m, 48H), 0.90–0.86 (m, 9H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, 293K):  $\delta$  = 191.90, 164.68, 162.03, 155.85, 153.41, 151.26, 147.14, 146.28, 138.15, 137.59, 135.29, 131.31, 131.09, 130.36, 130.28, 128.59, 127.70, 125.35, 122.64, 122.36, 115.26, 106.17, 73.48, 70.78, 69.18, 31.96, 30.37, 29.80, 29.77, 29.74, 29.68, 29.45, 29.40, 26.13, 22.73, 14.16. MS (APCI):  $m/z$  calcd for C<sub>69</sub>H<sub>96</sub>N<sub>2</sub>O<sub>7</sub> = 1065.7290 [M+H]<sup>+</sup>, found 1065.7303.

**Synthesis of compound 1:** Compound **4** (0.075 g, 0.070 mmol) and barbituric acid (0.066 g, 0.515 mmol) in EtOH (10 mL) was stirred for overnight at 80 °C under reflux. The reaction mixture was cooled to room temperature and the resulting precipitates were collected by filtration and washed with hot ethanol repeatedly to give pure compound **1** as orange solids (0.067 g, 89%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 293K): δ (ppm) = 8.63 (s, 1H), 8.37–8.32 (m, 4H), 8.01–7.98 (m, 5H), 7.87 (br, 1H), 7.76 (d, *J* = 8.6 Hz, 3H), 7.40 (d, *J* = 8.6 Hz), 7.13 (d, *J* = 9.1 Hz, 2H), 6.64 (s, 2H), 5.06 (s, 2H), 4.01–3.94 (m, 6H), 1.82–1.73 (m, 6H), 1.47 (m, 6H), 1.26 (m, 48H), 0.90–0.86 (m, 9H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, 333 K): δ = 164.51, 162.18, 160.43, 159.71, 158.06, 156.08, 153.57, 151.68, 149.82, 147.42, 145.86, 138.89, 137.62, 137.34, 135.60, 133.52, 131.25, 130.51, 128.45, 127.02, 125.31, 122.63, 122.35, 115.45, 106.81, 73.56, 70.90, 69.61, 31.97, 30.47, 29.77, 29.73, 29.68, 29.60, 29.48, 29.37, 26.19, 22.69, 14.03. MS (APCI): *m/z* calcd for C<sub>73</sub>H<sub>98</sub>N<sub>4</sub>O<sub>9</sub> = 1175.7407 [M+H]<sup>+</sup>, found 1175.7423.



**Chart S1.** <sup>1</sup>H NMR spectrum of **4** in CDCl<sub>3</sub> at 293 K.

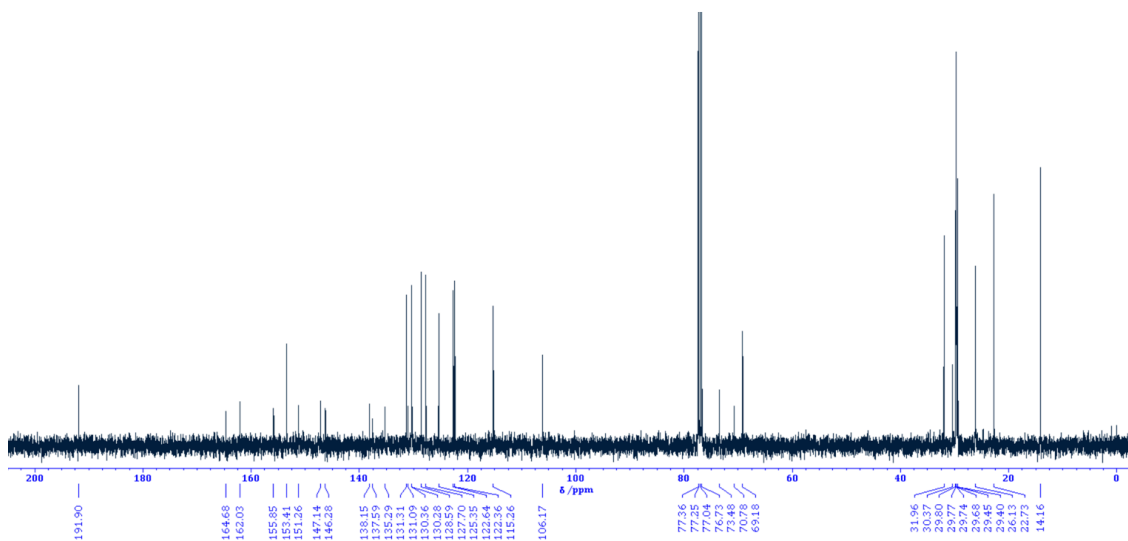


Chart S2.  $^{13}\text{C}$  NMR spectrum of 4 in  $\text{CDCl}_3$  at 293 K.

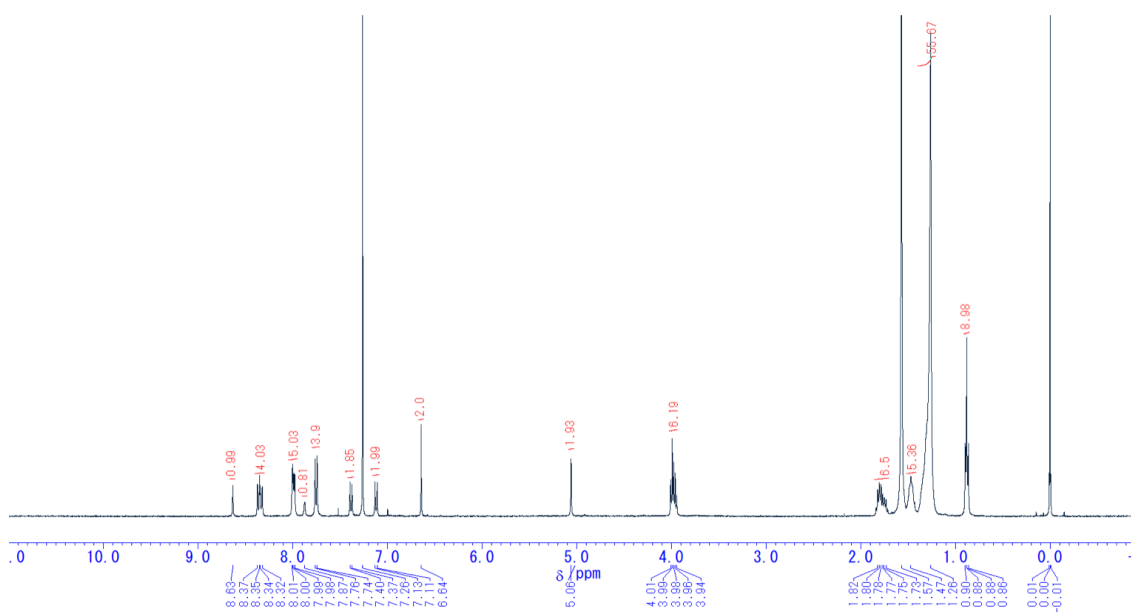
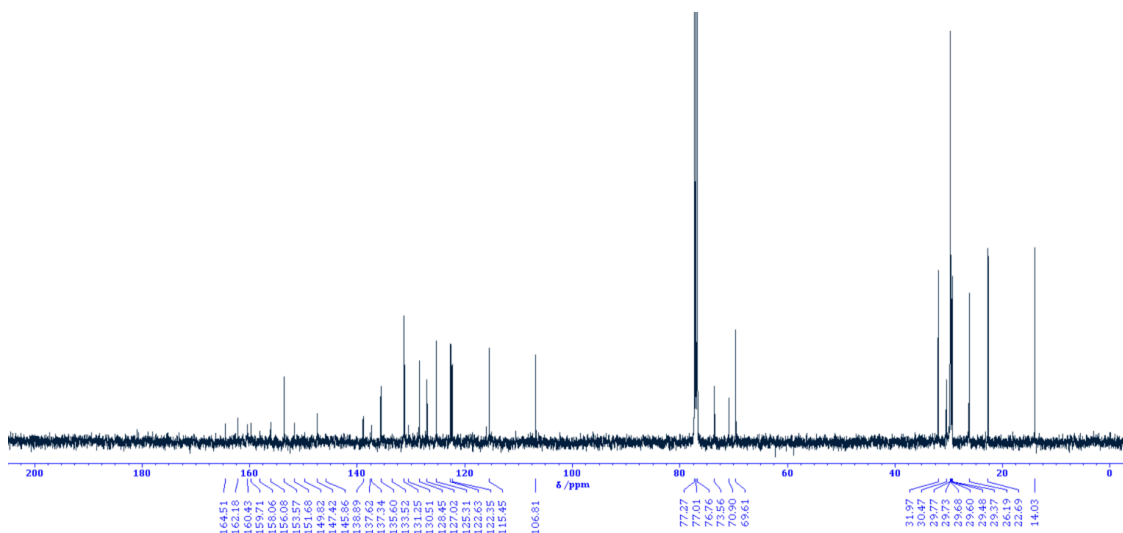
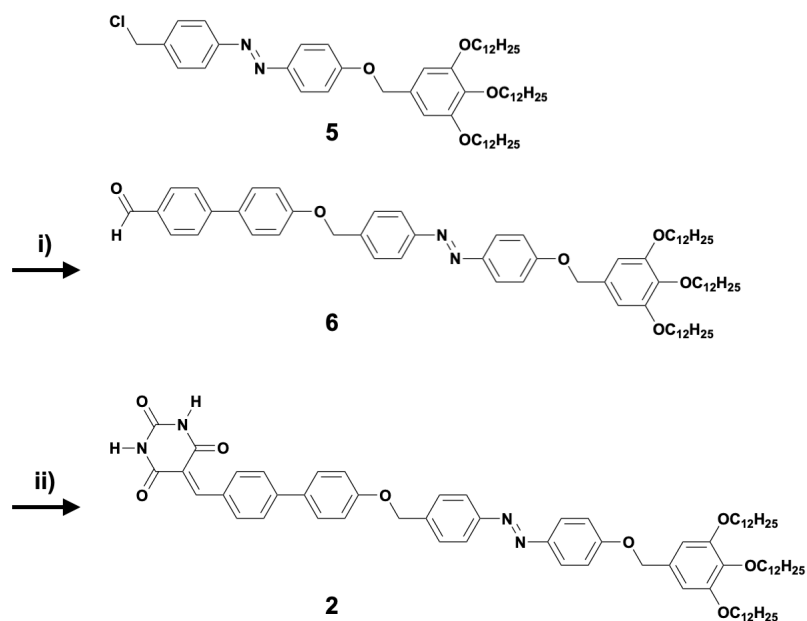


Chart S3.  $^1\text{H}$  NMR spectrum of 1 in  $\text{CDCl}_3$  at 293 K.



**Chart S4.**  $^{13}\text{C}$  NMR spectrum of **1** in  $\text{CDCl}_3$  at 333 K.

Compound **2** was synthesized according to Scheme S2.



**Scheme S2.** Synthesis of compound **2**. i) 4'-hydroxybiphenyl-4-carbaldehyde,  $\text{K}_2\text{CO}_3$ , dry DMF, 70 °C; ii) barbituric acid, EtOH, reflux.

**Synthesis of compound 6:** Compound **5** (0.118 g, 0.133 mmol), 4'-hydroxybiphenyl-4-carbaldehyde (0.030 g, 0.151 mmol),  $\text{K}_2\text{CO}_3$  (0.104 g, 0.752 mmol) were dissolved in dry DMF (10 mL). The mixture was stirred for overnight at 70 °C under  $\text{N}_2$  atmosphere. The reaction mixture was poured into water and extracted with hexane/AcOEt = 3:1 mixture,

washed with H<sub>2</sub>O and then brine. The organic layer was dried over Na<sub>2</sub>SO<sub>4</sub>, concentrated in vacuo and evaporated to dryness. The residue was purified by column chromatography over silica gel (eluent: hexane/CHCl<sub>3</sub> = 1:9) to give compound **6** as an orange solid (0.086 g, 62%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 293K): δ(ppm) = 10.04 (s, 1H), 7.94–7.90 (m, 6H), 7.73 (d, *J* = 8.2 Hz, 2H), 7.61–7.58 (m, 4H), 7.11 (d, *J* = 2.5 Hz, 2H), 7.09 (d, *J* = 2.7 Hz, 2H), 6.64 (s, 2H), 5.21 (s, 2H), 5.04 (s, 2H), 4.00–3.94 (m, 6H), 1.82–1.73 (m, 6H), 1.47 (m, 6H), 1.26 (m, 48H), 0.89–0.86 (m, 9H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, 293K): δ = 191.92, 161.36, 159.12, 153.39, 152.49, 147.12, 146.70, 139.02, 138.11, 134.74, 132.51, 131.24, 130.35, 128.59, 127.96, 127.11, 124.82, 122.88, 115.45, 115.13, 106.16, 73.47, 70.72, 69.69, 69.17, 31.95, 30.36, 29.79, 29.77, 29.73, 29.67, 29.45, 29.39, 26.12, 22.72, 14.15. MS (APCI): *m/z* calcd for C<sub>69</sub>H<sub>98</sub>N<sub>2</sub>O<sub>6</sub> = 1051.7498 [M+H]<sup>+</sup>, found 1051.7505.

**Synthesis of compound 2:** Compound **6** (0.072 g, 0.068 mmol) and barbituric acid (0.070 g, 0.546 mmol) in EtOH (10 mL) was stirred for overnight at 80 °C under reflux. The reaction mixture was cooled to room temperature and the resulting precipitates were collected by filtration and washed with hot ethanol repeatedly to give pure compound **2** as orange solids (0.062 g, 78%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 293K): δ(ppm) = 8.61 (s, 1H), 8.34 (d, *J* = 8.5 Hz, 2H), 7.97 (br, 1H), 7.94–7.91 (m, 4H), 7.84 (br, 1H), 7.72 (d, *J* = 8.5 Hz, 2H), 7.66 (d, *J* = 8.7 Hz, 2H), 7.60 (d, *J* = 8.5 Hz, 2H), 7.11–7.08 (m, 4H), 6.64 (s, 2H), 5.21 (s, 2H), 5.04 (s, 2H), 4.00–3.94 (m, 6H), 1.82–1.73 (m, 6H), 1.47 (m, 6H), 1.26 (m, 6H), 0.89–0.86 (m, 9H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, 333 K): δ = 162.73, 161.53, 160.46, 159.93, 159.61, 153.55, 152.75, 148.26, 147.42, 146.56, 139.08, 138.83, 135.86, 132.41, 131.41, 130.60, 128.59, 127.90, 126.48, 124.80, 122.90, 115.75, 115.35, 106.79, 73.55, 70.86, 69.98, 69.59, 31.96, 30.46, 29.77, 29.72, 29.67, 29.60, 29.48, 29.36, 26.19, 22.69, 14.02. MS (APCI): *m/z* calcd for C<sub>73</sub>H<sub>100</sub>N<sub>4</sub>O<sub>8</sub> = 1161.7614 [M+H]<sup>+</sup>, found 1161.7629.





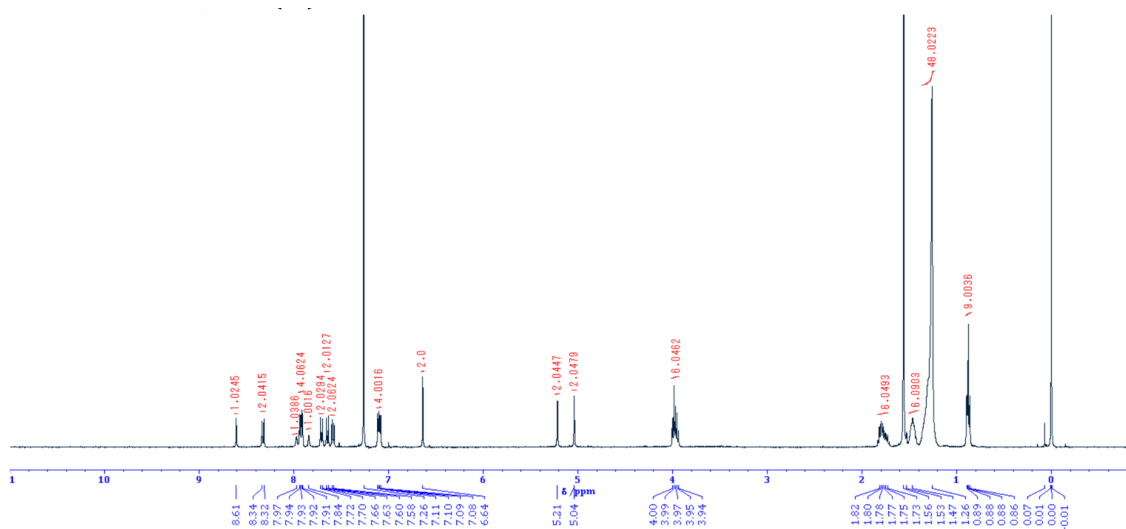


Chart S7.  $^1\text{H}$  NMR spectrum of **2** in  $\text{CDCl}_3$  at 293 K.

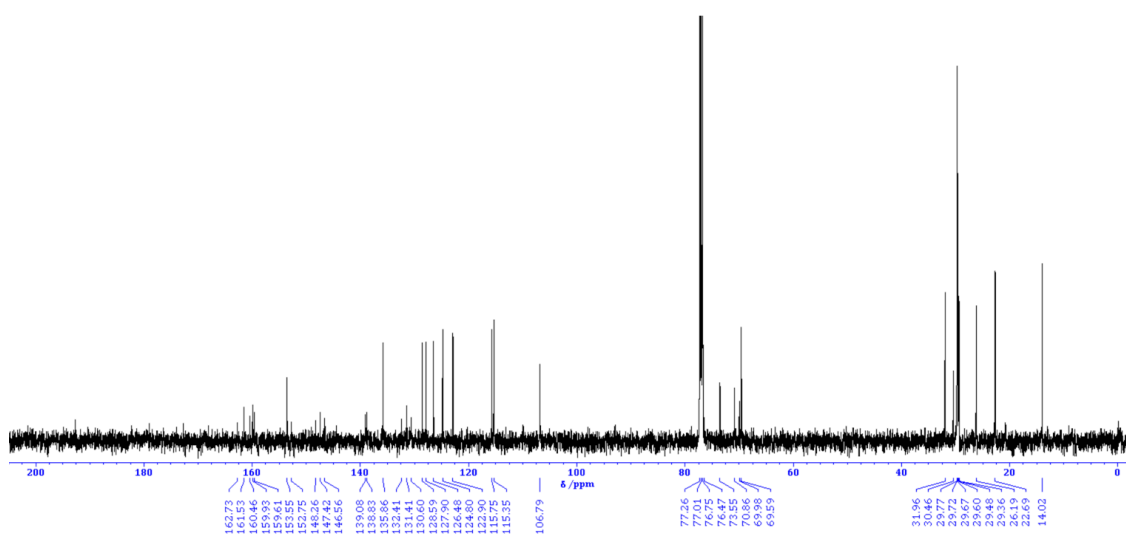
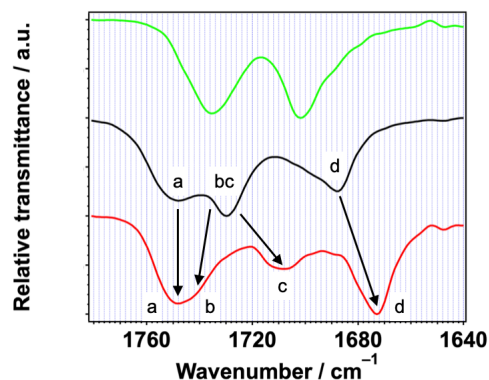
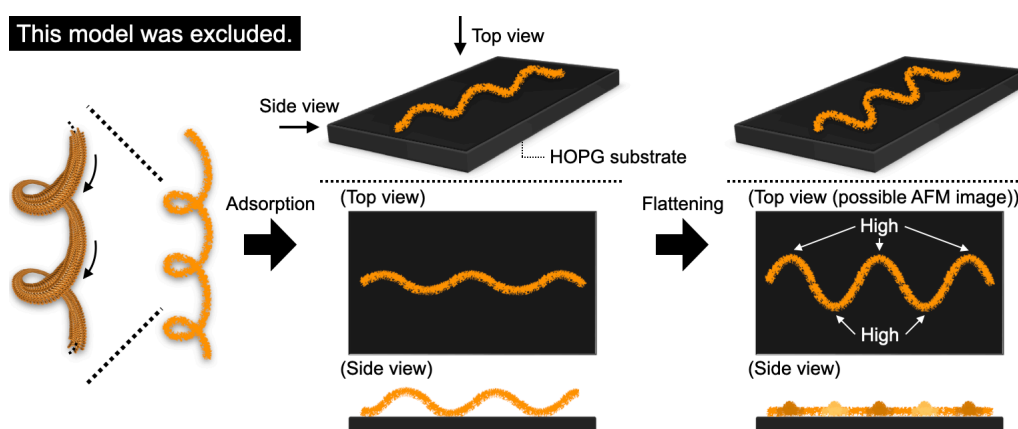


Chart S8.  $^{13}\text{C}$  NMR spectrum of **2** in  $\text{CDCl}_3$  at 333 K.

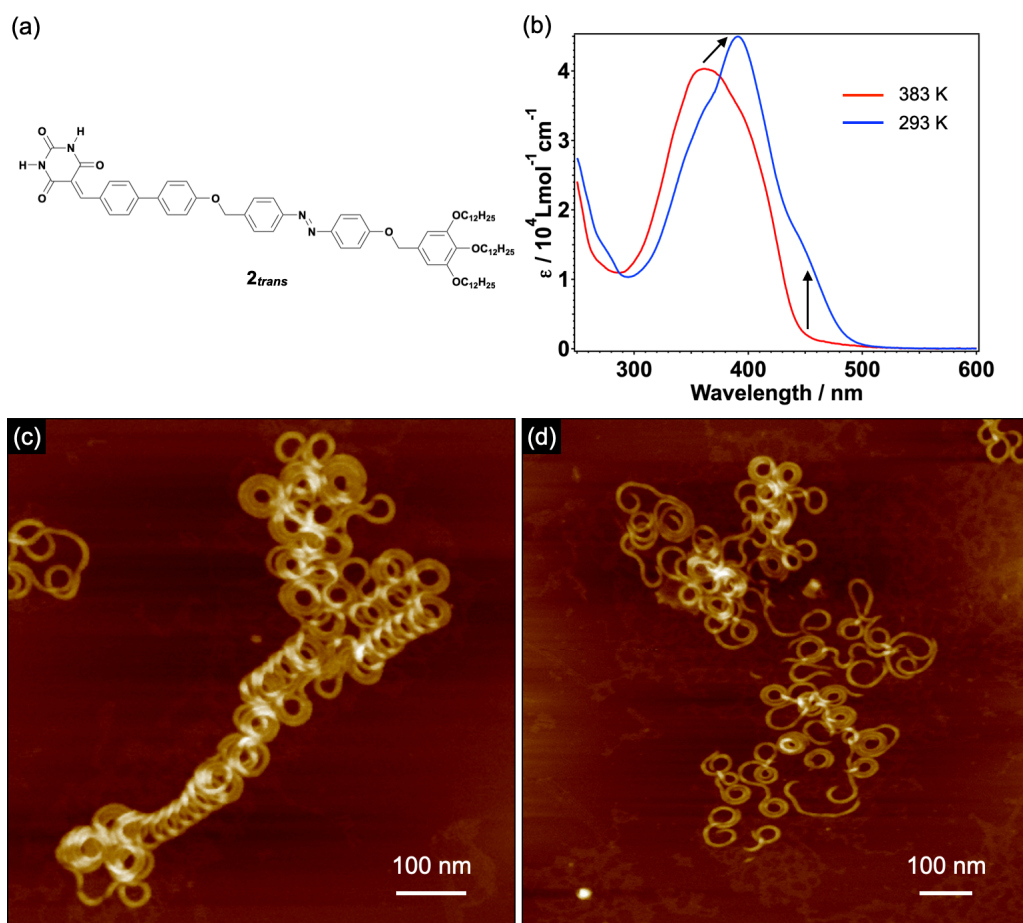
### 3. Supporting Figures



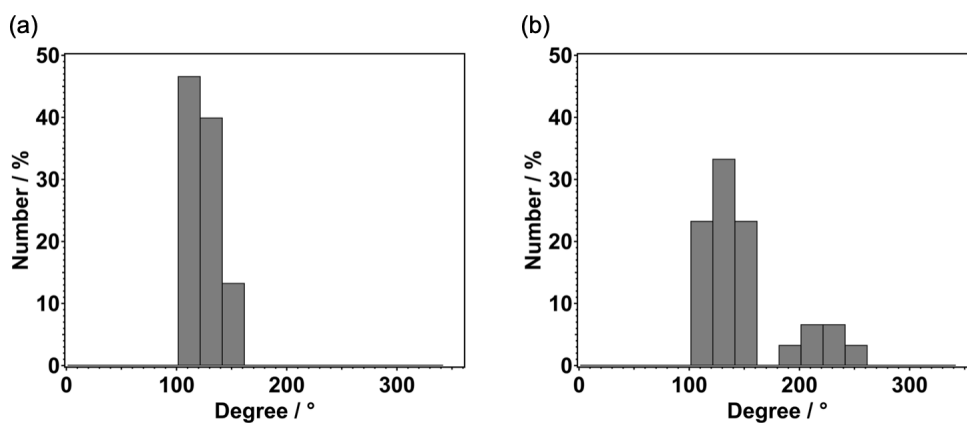
**Fig. S1** FT-IR spectra of the solutions of precursor compound **4** in chloroform (green line), monomeric **1<sub>trans</sub>** in chloroform (black line), and self-assembled **1<sub>trans</sub>** in MCH (red line).  $c = 100 \mu\text{M}$ . Peaks a, c and d are ascribable to C=O stretching vibrational bands of the barbituric acid group, and peak b is ascribable to that of the ester linkage.



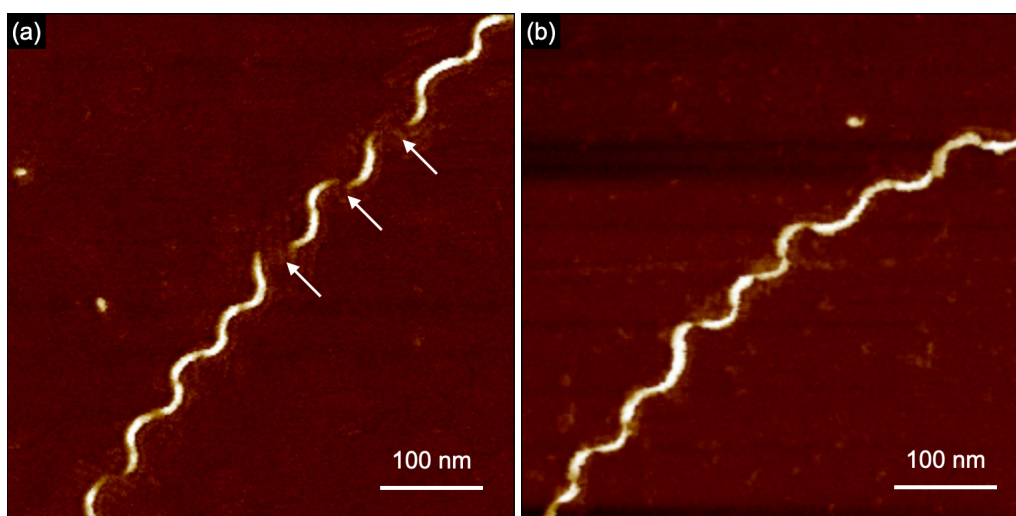
**Fig. S2** Schematic illustration of the adsorption and the following flattening of a loosely folded helicoidal structure to HOPG substrate. If the SPs of **1<sub>trans</sub>** have such a loose helicoidal structure, thicker area of fiber should be observed periodically at twisted parts of the fibers upon flattening on the substrate as shown by the side view. Since such structural features were not observed by AFM, we excluded this structure model.



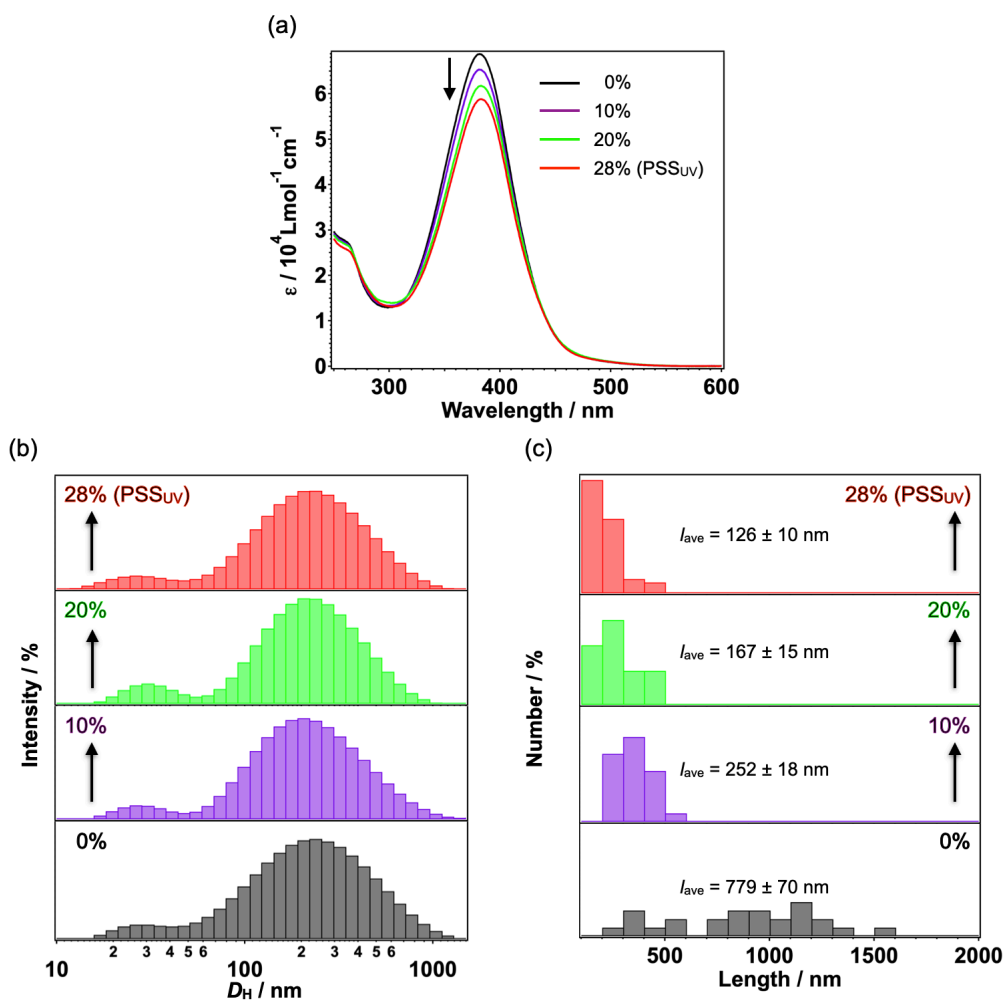
**Fig. S3** (a) Chemical structure of **2<sub>trans</sub>**. (b) UV/vis absorption spectra of **2<sub>trans</sub>** ( $c = 10 \mu\text{M}$ ) in MCH at 383 and 293 K upon naturally cooling. (c,d) AFM images of (c) helicoidal and (d) randomly coiled SPs of **2<sub>trans</sub>** prepared by naturally cooling a MCH solution ( $c = 19 \mu\text{M}$ ) from 383 to 293 K. Samples were prepared by spin-coating the solution onto HOPG substrate.



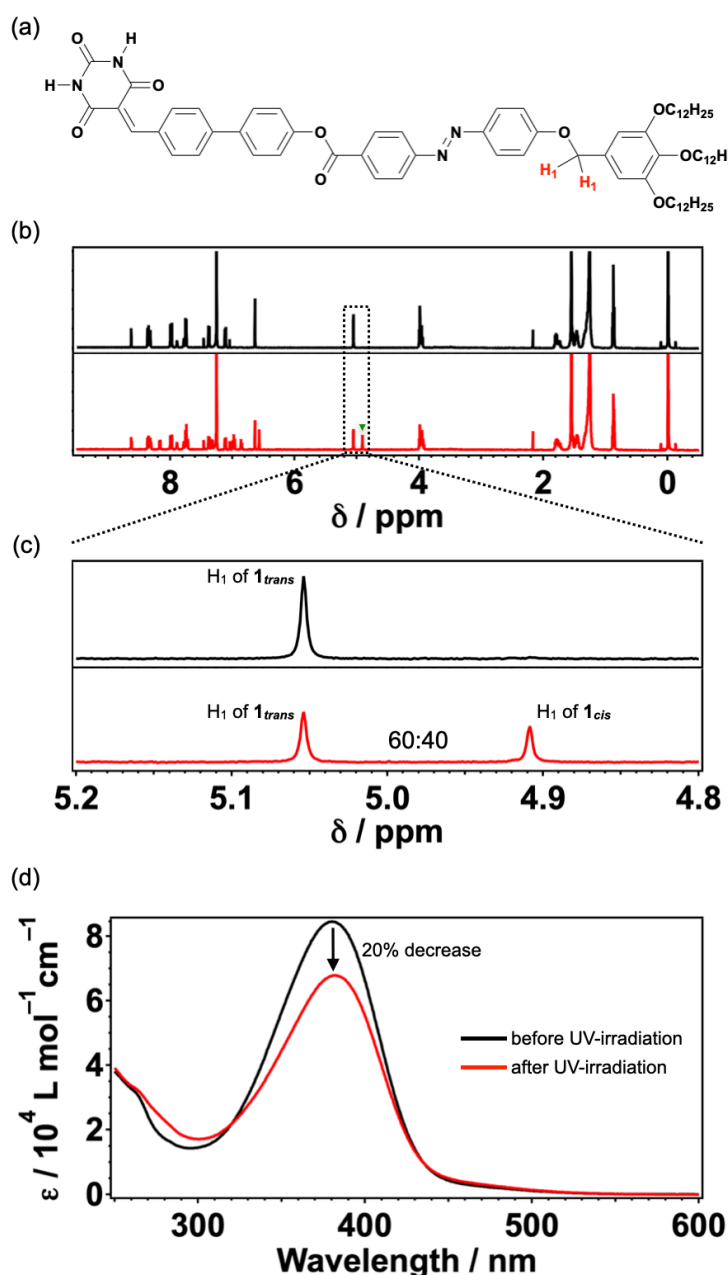
**Fig. S4** (a,b) Histograms of central angle  $\theta$  of curves in wavy SPs of  $\mathbf{1}_{trans}$  prepared by cooling a MCH solution at a rate of (a)  $1.0 \text{ K min}^{-1}$  and (b)  $0.1 \text{ K min}^{-1}$ . The  $\theta$  values were evaluated by manually fitting circles for randomly selected 30 curves of an AFM image of each SP fiber.



**Fig. S5** (a,b) AFM images of wavy SPs of  $\mathbf{1}_{trans}$  prepared by cooling a MCH solution ( $c = 5.0 \mu\text{M}$ ) at a rate of  $1.0 \text{ K min}^{-1}$ . Samples were prepared by (a) spin-coating and (b) drop-casting the solution onto HOPG substrate. White arrows in (a) indicate defects where the material was dissociated.

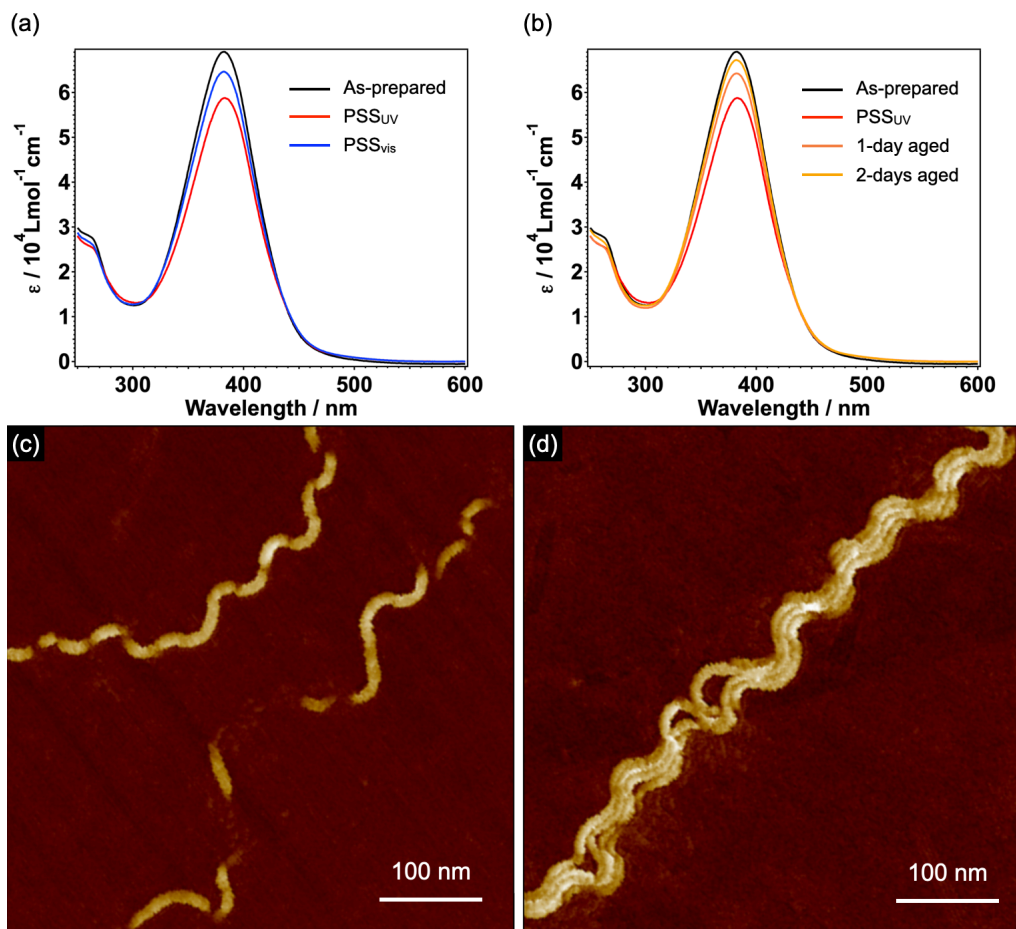


**Fig. S6** (a) UV/vis absorption spectral change of a SP solution of **1** ( $c = 10 \mu\text{M}$ ) in MCH upon UV-light irradiation. (b) DLS size distribution of the SP solution of **1** at different content of **1**<sub>cis</sub> (0, 10, 20, 28%) upon UV-light irradiation. (c) AFM length distribution of the intact nanofiber domains of SPs upon spin-coating the MCH solution onto HOPG substrate at different **1**<sub>cis</sub> content.



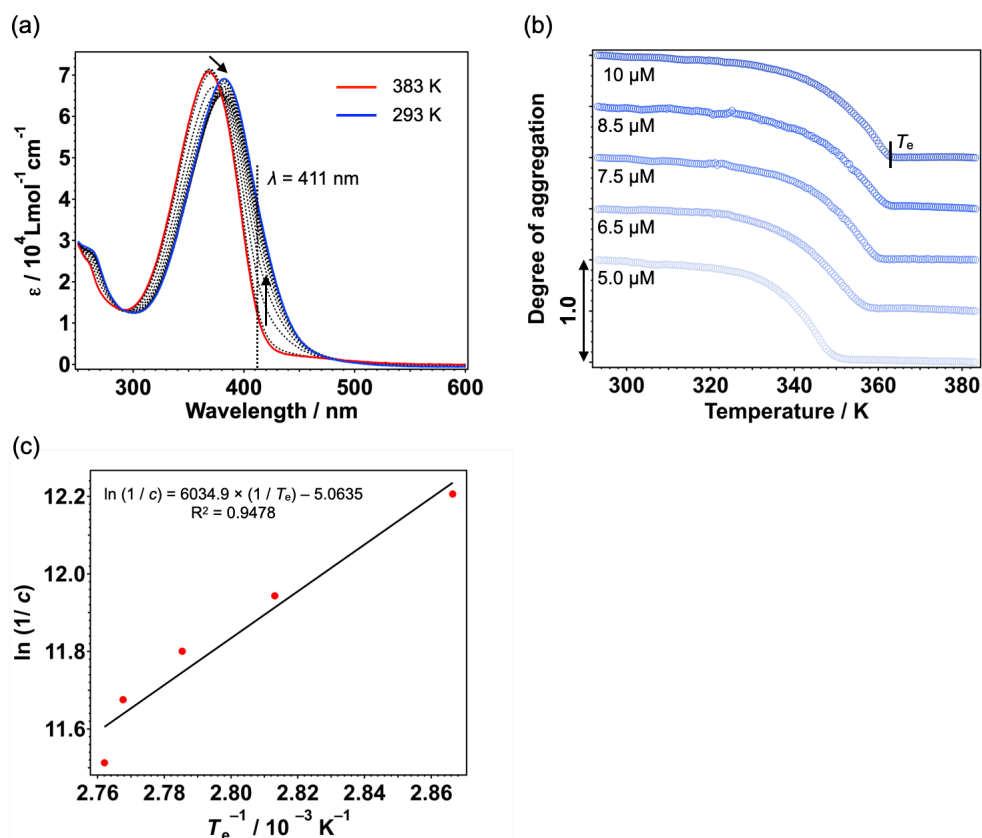
**Fig. S7** (a) Chemical structure of **1<sub>trans</sub>** highlighting benzylic hydrogens ( $H_1$ ). (b) Full  $^1H$  NMR spectra of **1** ( $c = 500 \mu M$ ) in  $CDCl_3$  before (black) and after (red) irradiation with UV-light for 1.5 min to reach a photostationary state (PSS). (c) Partial  $^1H$  NMR spectra of **1<sub>trans</sub>** and **1<sub>cis</sub>** showing the change of the benzylic proton signals. From the integration of these signals, **1<sub>trans</sub>**:**1<sub>cis</sub>** ratio at the PSS was estimated to be 60:40. (d) UV/vis spectra of a  $CHCl_3$  solution of **1** ( $c = 10 \mu M$ ) before (black) and after (red) irradiation with UV-light for 1 min to reach a PSS. The maximum absorption intensity at 380 nm showed 20% decrease upon UV-irradiation, which corresponds to the 40% *trans*-to-*cis* isomerization

according to the NMR analysis. This relationship has been used as a reference to calculate photoisomerization yield of azobenzene unit in MCH.

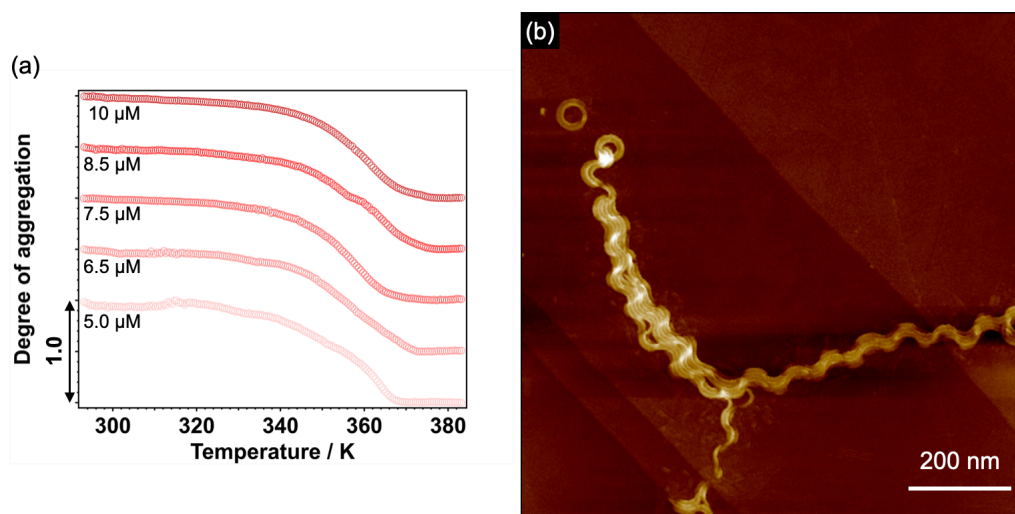


**Fig. S8** (a) UV/vis absorption spectra of a SP solution of **1** ( $c = 10 \mu\text{M}$ ) in MCH in the as-prepared state, PSS<sub>UV</sub>, and PSS<sub>vis</sub>. (b) UV/vis absorption spectra of the SP solution in the as-prepared state, PSS<sub>UV</sub>, and after 1 and 2-days aging from the PSS<sub>UV</sub>. (c,d) AFM images of SPs of **1** (c) at the PSS<sub>vis</sub> and (d) after 2-days aging from the PSS<sub>UV</sub>. These samples were prepared by spin-coating the solutions onto HOPG.





**Fig. S9** (a) Temperature-dependent UV/vis absorption spectra of  $\mathbf{1}_{trans}$  ( $c = 10 \mu\text{M}$ ) in MCH upon cooling from 383 to 293 K at a rate of  $1.0 \text{ K min}^{-1}$ . (b) Cooling curves of  $\mathbf{1}_{trans}$  obtained by plotting the degree of aggregation (calculated from the absorption change at  $\lambda = 411 \text{ nm}$ ) as a function of temperature at  $c = 5.0, 6.5, 7.5, 8.5,$  and  $10 \mu\text{M}$ . (c) van't Hoff analysis of  $\mathbf{1}_{trans}$  by plotting natural logarithm of the monomer concentration as a function of  $T_e^{-1}$ . The black line shows the corresponding linear fit. The analysis provided thermodynamic parameters including standard enthalpy ( $\Delta H^\circ = -50.2 \text{ kJ mol}^{-1}$ ), entropy ( $\Delta S^\circ = -42.1 \text{ J K}^{-1} \text{ mol}^{-1}$ ), and Gibbs free energy ( $\Delta G^\circ = -37.8 \text{ kJ mol}^{-1}$ ).



**Fig. S10** (a) Heating curves of  $\mathbf{1}_{trans}$  obtained by plotting the degree of aggregation (calculated from the absorption change at  $\lambda = 411$  nm) as a function of temperature at  $c = 5.0, 6.5, 7.5, 8.5,$  and  $10 \mu\text{M}$  in MCH. (b) AFM image of bundled wavy SPs of  $\mathbf{1}_{trans}$  prepared by cooling the MCH solution ( $c = 10 \mu\text{M}$ ) from 383 to 293 K at a rate of  $1.0 \text{ K min}^{-1}$ . The sample was prepared by spin-coating the solution onto HOPG substrate.

#### 4. Supporting References

[S1] (a) D. Zhao and J. S. Moore, *Org. Biomol. Chem.*, 2003, **1**, 3471–3491; (b) T. F. A. De Greef, M. M. J. Smulders, M. Wolfs, A. P. H. J. Schenning, R. P. Sijbesma and E. W. Meijer, *Chem. Rev.*, 2009, **109**, 5687–5754; (c) C. Rest, R. Kandanelli and G. Fernández, *Chem. Soc. Rev.*, 2015, **44**, 2543–2572.