Supplementary Materials

Competition and cooperation between steric hindrance and hydrogen bonding of supramolecular discs

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1. General

Materials and Methods

All commercially available reagents and solvents were of reagent grade and used without further purification. Column chromatography was performed using 63–210 mm silica gel. Solvents used for the preparation of supramolecular assemblies were spectral grade and used without further purification. Biotage Microwave Synthesizer (Model: Initiator+) was operated with a high absorption level setting. ^{1}H NMR spectra were measured in $CDCl_3$ using Bruker-AVANCE III-400M and Bruker-AVANCE III-500M spectrometers, and chemical shifts reported in parts per million (ppm, δ) are referenced to the signal of tetramethylsilane (TMS) at 0.00 ppm as internal standard. The resonance multiplicity is described as s (singlet), d (doublet), t (triplet), q (quartet), quin (quintet), dd (double doublet), br (broad multiplet), br s (broad singlet) and m (multiplet). ^{13}C NMR spectra were measured in $CDCl_3$ using Bruker-AVANCE III-500M spectrometer, and chemical shifts reported in δ (ppm) are referenced to the chemical shifts of $CDCl_3$ at 77.16 ppm. APCI-MS spectra were measured on an Exactive (Thermo Scientific) mass spectrometer.

UV–vis spectroscopy

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.

FT-IR spectroscopy

FT-IR spectra of monomeric and aggregated solutions were measured on a JASCO FT/IR-4600 spectrometer using a KBr cuvette of 1.0-mm path length and KBr substrate, respectively.

Atomic force microscopy (AFM)

AFM imaging was performed under ambient conditions using Multimode 8 Nanoscope V (Bruker AXS) in Peak Force Tapping (Scanasyst) mode. Silicon cantilevers (SCANASYST-AIR) with a spring constant of 0.4 N m^{-1} and a frequency of 70 kHz (Bruker AXS) were used. The samples were prepared by spin-coating (3000 rpm, 1 min) MCH solutions (10 μL) onto freshly cleaved highly oriented pyrolytic graphite (HOPG).

Quantum Chemical Calculations

Structure optimization and vibrational frequency estimation were performed with B3-LYP/6-31+G(d,p) level of approximation and IEF-PCM solvation model of $CHCl_3$ by using Gaussian 16 program package[S1] on an in-house computer.

Cooling curve fitting using the nucleation-elongation model

The nucleation-elongation model[S2,3] (the cooperative supramolecular polymerisation model) can be described using following two equations:

$$c_{\mathrm{m}} + \sigma \frac{K c_{\mathrm{m}}^2 (2 - K c_{\mathrm{m}})}{(1 - K c_{\mathrm{m}})^2} = c_{\mathrm{tot}} \quad (1)$$

$$a_{\mathrm{agg}} = 1 - a_{\mathrm{m}} = 1 - \frac{c_{\mathrm{m}}}{c_{\mathrm{tot}}} \quad (2)$$

Where:

- c_{tot} is the total concentration of the solute.
- c_{m} is the concentration of the monomer.
- K is the equibilium constant of elongation.
- σ is the cooperative factor, defined as K_{nuc}/K, where K_{nuc} is the equibilium constant of nucliation.

Temperature dependence of K and σ has been proposed by ten Eikelder and coworkers as follows:[S4]

$$K = \exp\left(-(\Delta H^{\mathrm{o}} - T\Delta S^{\mathrm{o}})/(RT)\right) \quad (3)$$

$$\sigma = \frac{K_{\mathrm{nuc}}}{K} = \exp\left(\Delta H^{\mathrm{o}}_{\mathrm{nuc}}/(RT)\right) \quad (4)$$

From these equations, a_{agg} can be solved while excluding temperature-dependent variables other than T, based on Cardano's formula:

$$a_{\mathrm{agg}} = F_{c_{\mathrm{tot}},\Delta H^{\mathrm{o}},\Delta S^{\mathrm{o}},\Delta H^{\mathrm{o}}_{\mathrm{nuc}}}(T) \quad (5)$$

Where ΔH^{o} is the standard enthalpy change of elongation, ΔS^{o} is the standard entropy changes of elongation and $\Delta H^{\mathrm{o}}_{\mathrm{nuc}}$ is the nucleation penalty.

Meanwhile, a_{agg} is derived from the ideal absorbance of A_{ideal} (where all molecules are agregated) at the aggregate absorption wavelength and the measured absorbance A. a_{agg} is proportional to A:

$$a_{\mathrm{agg}} = \frac{A}{A_{\mathrm{ideal}}} \propto A \quad (\because A_{\mathrm{ideal}} \text{ is a constant.}, 6)$$

Thus, the measured absorbance A is a function of T with scaling factor s.

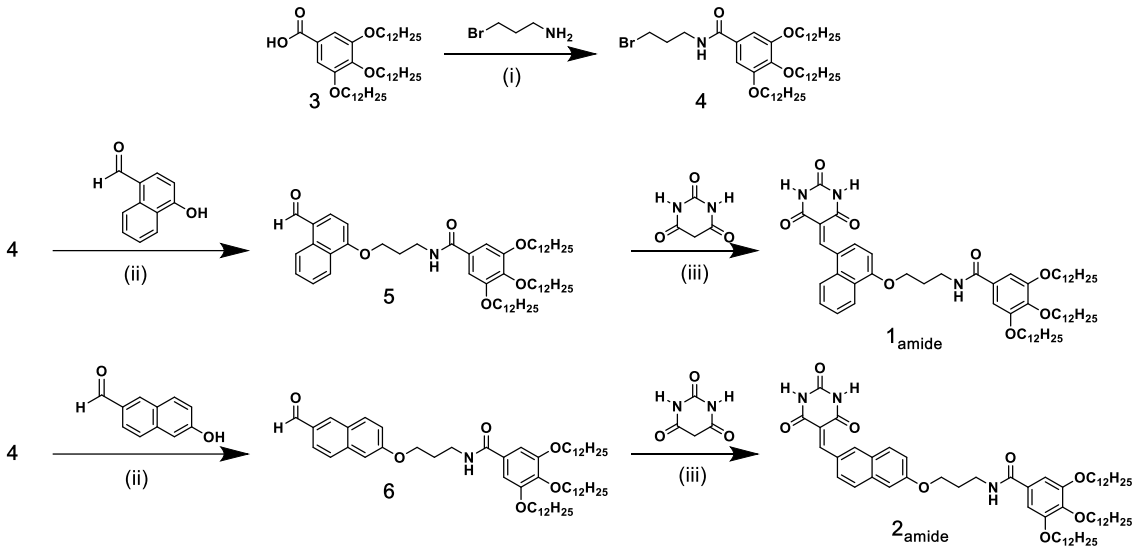
$$A = s \cdot F_{c_{\mathrm{tot}},\Delta H^{\mathrm{o}},\Delta S^{\mathrm{o}},\Delta H^{\mathrm{o}}_{\mathrm{nuc}}}(T) = F'_{c_{\mathrm{tot}},\Delta H^{\mathrm{o}},\Delta S^{\mathrm{o}},\Delta H^{\mathrm{o}}_{\mathrm{nuc}},s}(T) \quad (7)$$

$F'_{c_{\mathrm{tot}},\Delta H^{\mathrm{o}},\Delta S^{\mathrm{o}},\Delta H^{\mathrm{o}}_{\mathrm{nuc}},s}$ does not depend on T. Additionally, ΔH^{o}, ΔS^{o} and $\Delta H^{\mathrm{o}}_{\mathrm{nuc}}$ are independent of c_{tot}.

We performed fitting of A at different concentrations using shared parameters ΔH^{o},ΔS^{o},$\Delta H^{\mathrm{o}}_{\mathrm{nuc}}$ and indivisual parameters s_1, s_2, ⋯.

2. Synthesis and Analytical Data

Compounds $\mathbf{1}_{\mathbf{amide}}$ and $\mathbf{2}_{\mathbf{amide}}$ were synthesized according to Scheme 1. Synthesis of compound **3** was reported previously.[S5]



Scheme 1. Synthesis of compounds $\mathbf{1}_{\mathbf{amide}}$ and $\mathbf{2}_{\mathbf{amide}}$: i) 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC·HCl), CH_2Cl_2, r.t; ii) K_2CO_3, DMF, 150 °C, microwave; iii) MeOH, 80 °C.

Compound 4: Compound **3** (2.00 g, 2.96 mmol), 3-bromopropylamine hydrobromide (779 mg, 3.56 mmol) and 4-dimethylaminopyridine (DMAP, 360 mg, 2.95 mmol) were dissolved in 15 mL of CH_2Cl_2. To this mixture, EDC·HCl (1.13 g, 5.89 mmol) was added, and the reaction mixture was stirred for 30 min at room temperature. The mixture was diluted by $CHCl_3$ and washed with aqueous HCl (2 M) solution, water, and brine. The organic layer was dried over Na_2SO_4, filtrated and evaporated in vacuo to dryness. The residue was purified by column chromatography (*n*-hexane : EtOAc = 3 : 1) to give **4** as a white solid (1.98 g, 84% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.95 (s, 2H), 6.24 (t, J = 5.9 Hz, 1H), 4.02–3.97 (m, 6H), 3.60 (q, J = 6.4 Hz, 2H), 3.50 (t, J = 6.4 Hz, 2H), 2.21 (quin, J = 6.0 Hz, 2H), 1.84–1.70 (m, 6H), 1.50–1.43 (m, 6H), 1.30–1.26 (m, 48H), 0.88 (t, J = 6.0 Hz, 9H). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 167.63, 153.14, 141.33, 129.25, 105.71, 73.53, 69.43, 38.78, 32.17, 31.94, 31.17, 30.32, 29.76, 29.74, 29.71, 29.67, 29.65, 29.59, 29.41, 29.37, 26.09, 22.70, 14.11. HRMS (APCI): *m/z* calcd. for $C_{46}H_{85}BrNO_4$ 794.5656 $[M+H]^+$, found 794.5665.

Compound 5: Compound **4** (251 mg, 0.316 mmol) and 4-hydroxy-1-naphthaldehyde (69 mg, 0.40 mmol) were dissolved in 3 mL of DMF. To this mixture, K_2CO_3 (123 mg, 0.889 mmol) was added, and the reaction mixture was stirred for 5 min at 150 °C under microwave. The mixture was diluted by a mixture of EtOAc and *n*-hexane, and washed with water and then brine. The organic layer was dried over Na_2SO_4, filtrated, and evaporated in vacuo to dryness. The residue was purified by column chromatography (*n*-hexane : EtOAc = 3 : 1) to give **5** as a white solid (72 mg, 26% yield). ^{1}H NMR (500

MHz, $CDCl_3$): δ = 10.18 (s, 1H), 9.29 (d, *J* = 8.5 Hz, 1H), 8.28 (d, *J* = 8.0 Hz, 1H), 7.88 (d, *J* = 8.0 Hz, 1H), 7.68 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.50 (dd, *J* = 7.7, 1.2 Hz, 1H), 6.94–6.92 (m, 3H), 6.43 (t, *J* = 5.8 Hz, 1H), 4.38 (t, *J* = 5.8 Hz, 2H), 3.98 (t, *J* = 6.5 Hz, 2H), 3.90 (t, *J* = 6.5 Hz, 4H), 3.78 (q, *J* = 6.3 Hz, 2H), 2.33 (quin, *J* = 6.1 Hz, 2H), 1.78–1.70 (m, 6H) , 1.49–1.38 (m, 6H), 1.30–1.26 (m, 48H), 0.88 (t, *J* = 6.8 Hz, 9H). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 192.27, 168.54, 167.71, 159.78, 153.14, 141.18, 139.61, 131.89, 129.63, 129.36, 126.56, 125.02, 123.79, 122.13, 105.57, 103.74, 73.53, 69.30, 67.01, 37.90, 31.95, 30.33, 29.77, 29.72, 29.68, 29.66, 29.61, 29.41, 29.39, 29.34, 29.14, 26.10, 26.07, 22.72, 14.15. HRMS (APCI): *m/z* calcd. for $C_{57}H_{92}NO_6$ 886.6919 $[M+H]^+$, found 886.6926.

Compound 6: Compound **4** (245 mg, 0.308 mmol) and 6-hydroxy-2-naphthaldehyde (69 mg, 0.40 mmol) were dissolved in 3 mL of DMF. To this mixture, K_2CO_3 (0.105 mg, 0.760 mmol) was added, and the reaction mixture was stirred for 5 min at 150 °C under microwave. The mixture was diluted by a mixture of EtOAc and *n*-hexane, and washed with water and then brine. The organic layer was dried over Na_2SO_4, filtrated, and evaporated in vacuo to dryness. The residue was purified by column chromatography (eluent: n-hexane : EtOAc = 3 : 1) to give **6** as a white solid (135 mg, 49% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 10.04 (s, 1H), 8.17 (s, 1H), 7.87 (dd, *J* = 8.5, 1.5 Hz, 1H), 7.84 (d, *J* = 8.9 Hz, 1H), 7.73 (d, *J* = 8.5 Hz, 1H), 7.19 (dd, *J* = 8.9, 2.4 Hz, 1H), 7.15 (d, *J* = 2.1 Hz, 1H), 7.00 (s, 2H), 6.72 (t, *J* = 8.9 Hz, 1H), 4.23 (t, *J* = 5.8 Hz, 2H), 4.00–3.96 (m, 6H), 3.70 (q, *J* = 6.1 Hz, 2H), 2.20 (quin, *J* = 6.1 Hz, 2H), 1.79–1.71 (m, 6H), 1.50–1.39 (m, 6H), 1.30–1.25 (m, 48H), 0.88 (t, *J* = 6.8 Hz, 9H). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 191.91, 167.56, 159.24, 153.13, 141.23, 138.19, 134.13, 132.41, 131.19, 129.49, 127.98, 127.75, 123.68, 119.85, 107.06, 105.75, 73.51, 69.37, 66.63, 37.90, 31.93, 30.34, 29.75, 29.74, 29.71, 29.67, 29.65, 29.60, 29.41, 29.39, 29.37, 29.02, 26.09, 22.70, 14.11. HRMS (APCI): *m/z* calcd. for $C_{57}H_{92}NO_6$ 886.6919 $[M+H]^+$, found 886.6923.

Compound $\mathbf{1}_{\mathbf{amide}}$: Compound **5** (52 mg, 0.059 mmol) and barbituric acid (36 mg, 0.28 mmol) were dissolved in 8 mL of MeOH. The reaction mixture was stirred 19 h at 80 °C and then cooled to room temperature to obtain precipitates. The precipitates were collected by filtration and washed thoroughly with $CHCl_3$ to give pure compound $\mathbf{1}_{\mathbf{amide}}$ (55 mg, 94%) as a yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$, 323 K): δ = 9.32 (s, 1H), 8.64 (d, *J* = 8.4 Hz, 1H), 8.30 (d, *J* = 8.4 Hz, 1H), 8.05–8.02 (m, 2H), 7.86 (s, 1H), 7.63 (t, *J* = 7.1 Hz, 1H), 7.49 (t, *J* = 7.0 Hz, 1H), 6.95 (s, 2H), 6.92 (d, *J* = 8.6 Hz, 1H), 6.32 (t, *J* = 5.8 Hz, 1H), 4.39 (t, *J* = 6.5 Hz, 2H), 3.99 (t, *J* = 6.5 Hz, 2H), 3.93 (t, *J* = 6.5 Hz, 4H), 3.75 (q, *J* = 6.3 Hz, 2H), 2.31 (quin, *J* = 6.1 Hz, 2H), 1.78–1.71 (m, 6H), 1.47–1.40 (m, 6H), 1.33–1.26 (m, 48H), 0.88 (t, *J* = 6.8 Hz, 9H). ^{13}C NMR (126 MHz, $CDCl_3$, 323 K): δ = 167.63, 162.90, 160.48, 160.29, 156.82, 153.20, 148.40, 141.71, 135.48, 134.46, 129.36, 128.82, 126.09, 123.52, 123.01, 121.64, 106.14, 104.26, 73.53, 69.57, 67.14, 37.81, 31.87, 30.32, 29.68, 29.67, 29.63, 29.60, 29.58, 29.54, 29.42, 29.36, 29.31, 29.28, 26.06, 22.61, 13.96. HRMS (APCI): *m/z* calcd. for $C_{61}H_{94}N_3O_8$ 996.7035 $[M+H]^+$, found 996.7035.

Compound $\mathbf{2}_{\mathbf{amide}}$: Compound **6** (52 mg, 0.059 mmol) and barbituric acid (36 mg, 0.28 mmol) were dissolved in 3 mL of MeOH. The reaction mixture was stirred 3 h at 80 °C and then cooled to room temperature to obtain precipitates. The precipitates were

collected by filtration and washed thoroughly with $CHCl_3$ to give pure compound **2**$_{\mathbf{amide}}$ (54 mg, 92%) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$, 323 K): δ = 10.04 (s, 1H), 8.17 (s, 1H), 7.88–7.83 (m, 2H), 7.73 (d, J = 8.5 Hz, 1H), 7.19 (dd, J = 8.9, 2.4 Hz, 1H), 7.15–7.14 (m, 1H) 7.01 (s, 2H), 6.77 (br s, 1H), 4.23 (t, J = 5.7 Hz, 2H), 4.00–3.94 (m, 6H), 3.71 (q, J = 6.1 Hz, 2H), 2.21 (quin, J = 6.0 Hz, 2H), 1.80–1.70 (m, 6H), 1.50–1.38 (m, 6H), 1.30–1.25 (m, 48H), 0.88 (t, J = 6.9 Hz, 9H). ^{13}C NMR (125 MHz, $CDCl_3$, 323 K): δ = 167.52, 160.40, 160.13, 153.21, 147.33, 141.74, 138.53, 137.96, 132.01, 130.64, 129.49, 128.16, 127.90, 126.80, 119.76, 114.61, 107.07, 106.20, 73.53, 69.64, 66.81, 37.90, 37.21, 31.88, 31.87, 30.33, 29.66, 29.63, 29.60, 29.58, 29.53, 29.44, 29.36, 29.30, 29.28, 29.18, 26.07, 22.61, 13.96. HRMS (APCI): *m/z* calcd. for $C_{61}H_{94}N_3O_8$ 996.7035 $[M+H]^+$, found 996.7027.

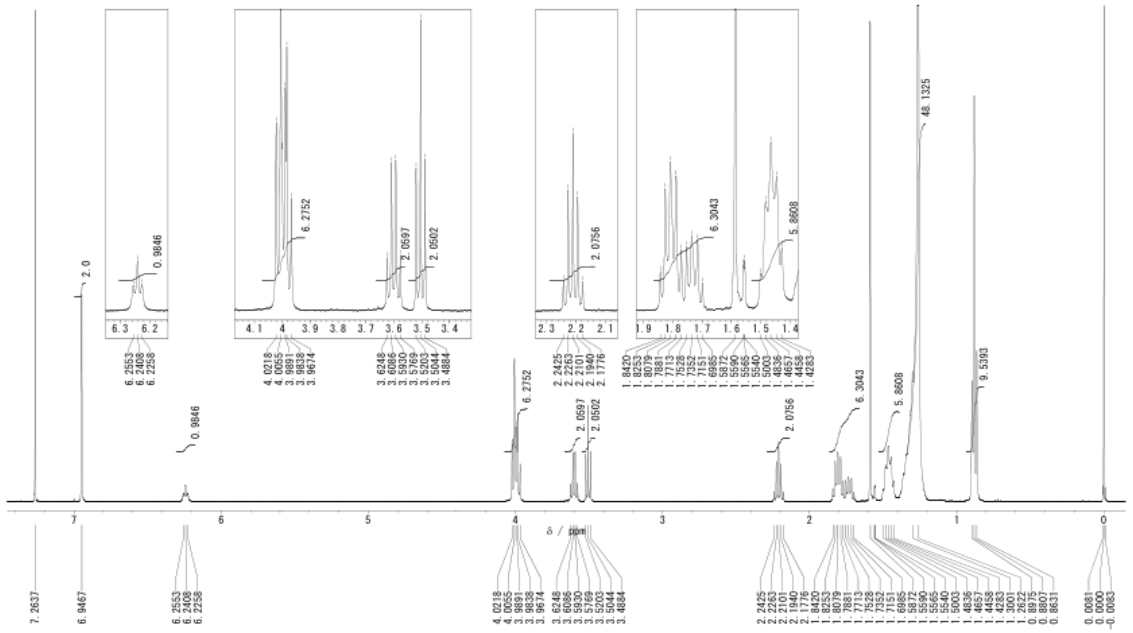


Chart S1. ^{1}H NMR spectrum of **4** in $CDCl_3$.

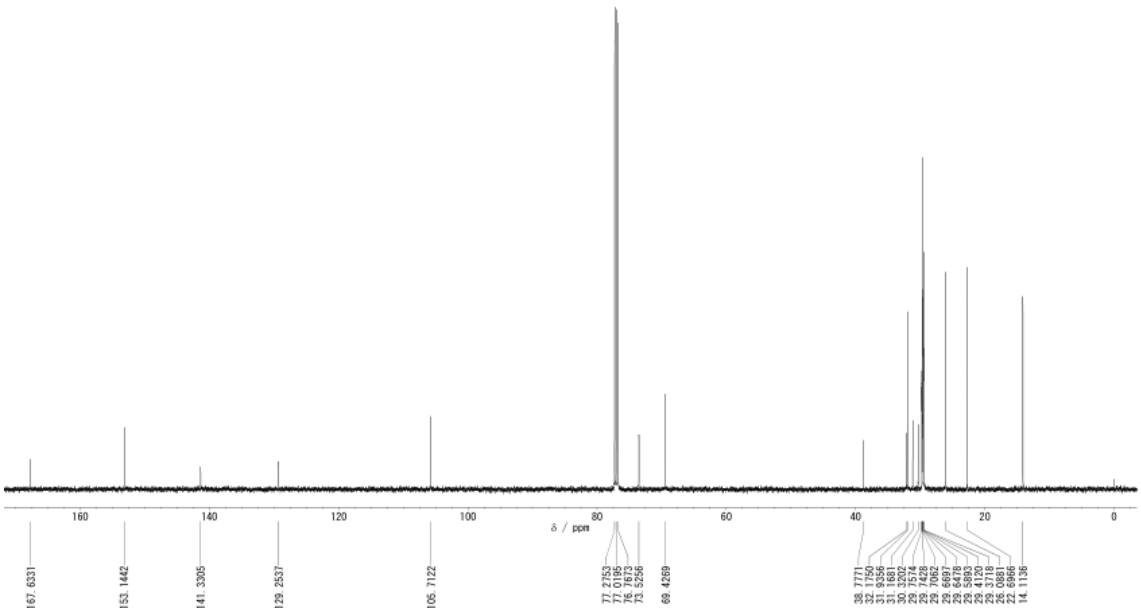


Chart S2. ^{13}C NMR spectrum of **4** in $CDCl_3$.

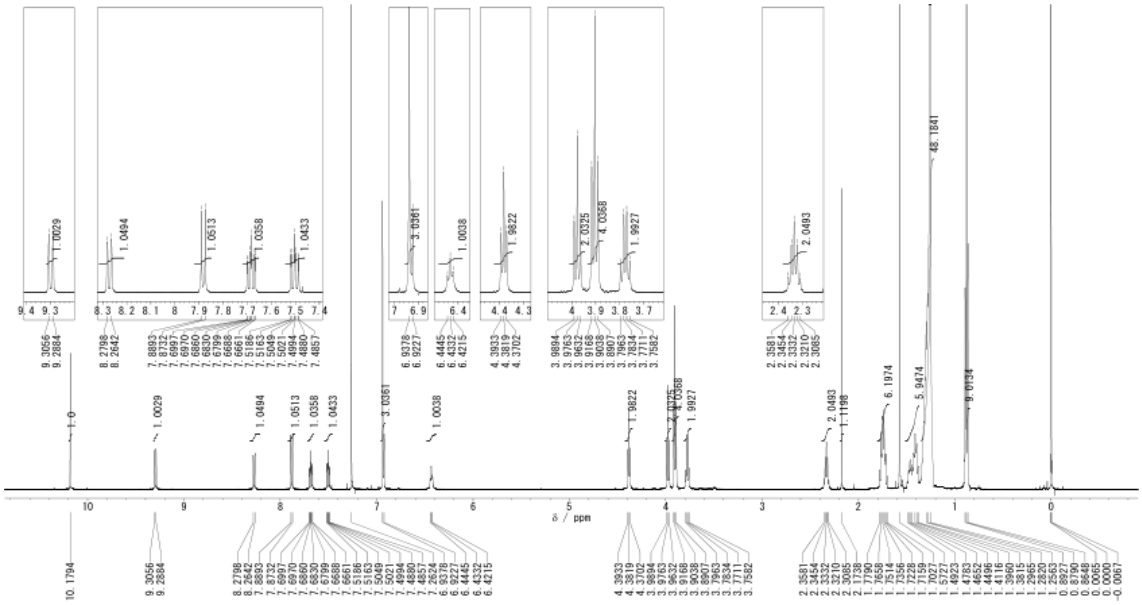


Chart S3. ^{1}H NMR spectrum of **5** in $CDCl_3$.

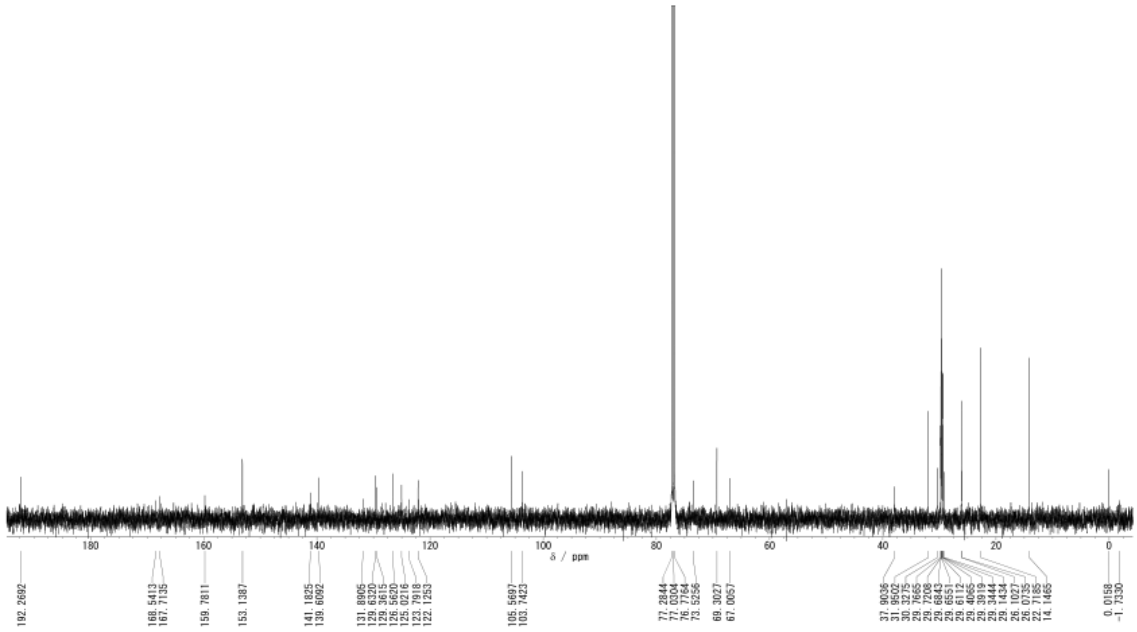


Chart S4. ^{13}C NMR spectrum of **5** in $CDCl_3$.

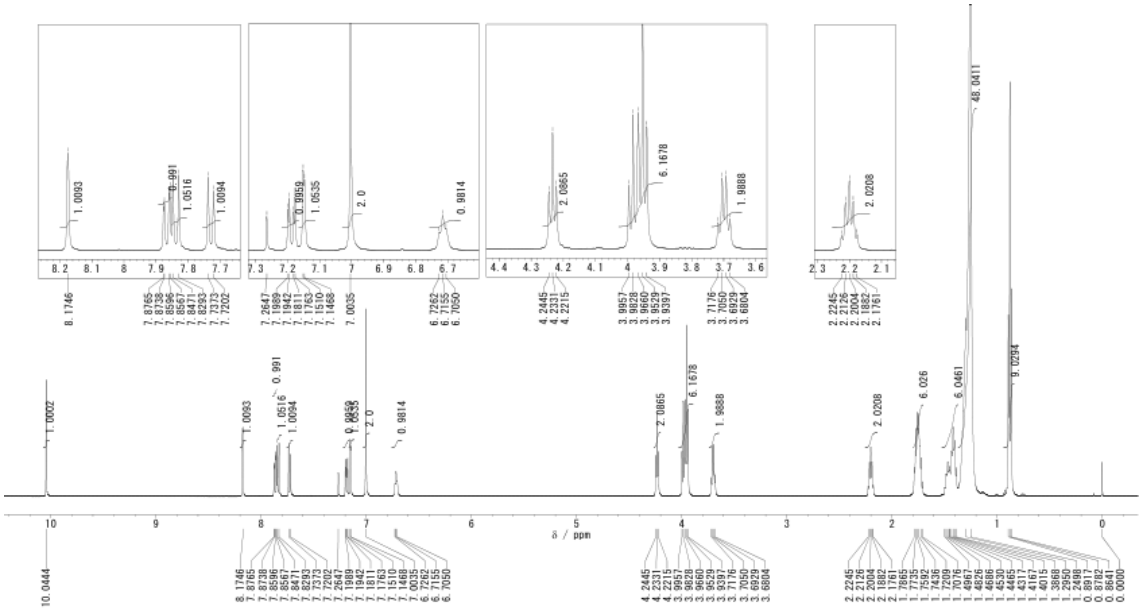


Chart S5. ^{1}H NMR spectrum of **6** in $CDCl_3$.

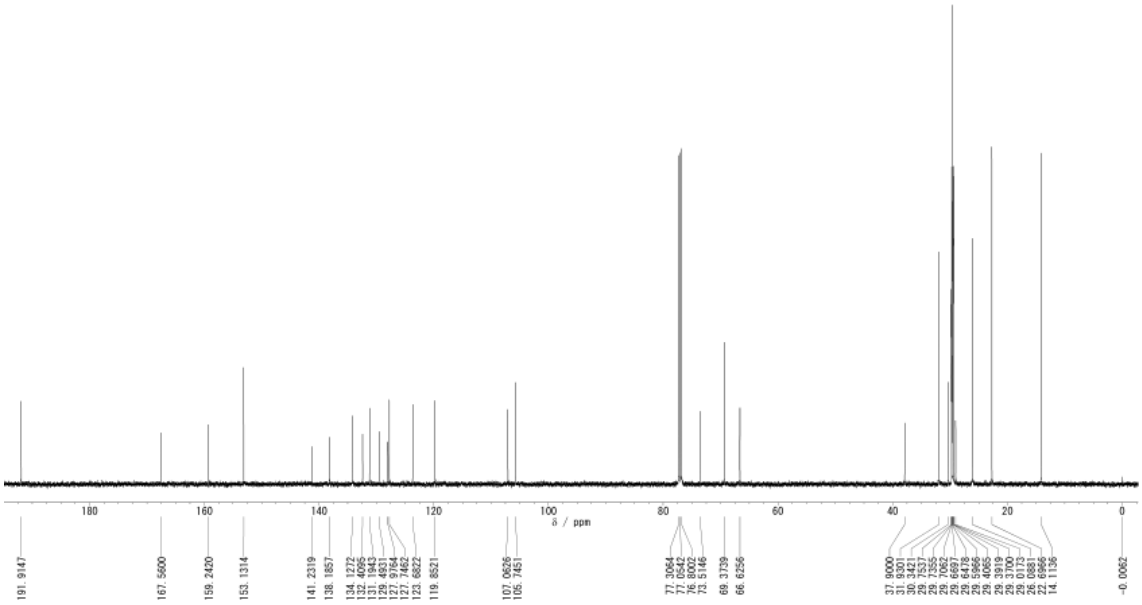


Chart S6. ^{13}C NMR spectrum of **6** in $CDCl_3$.

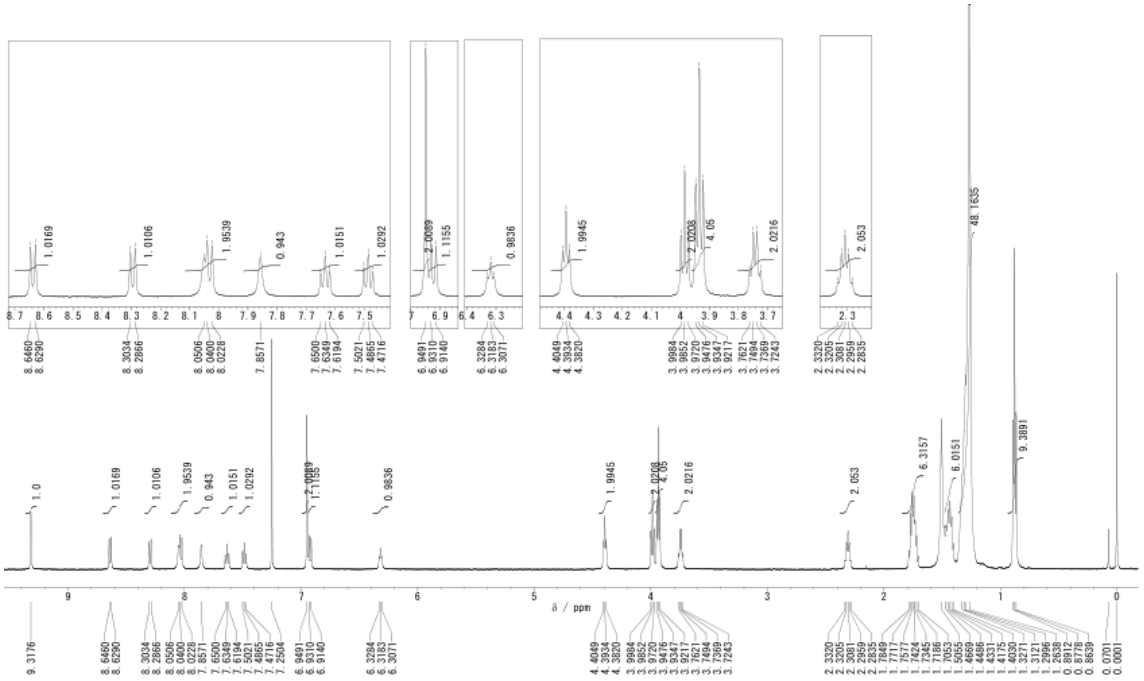


Chart S7. ^{1}H NMR spectrum of $\mathbf{1}_{\mathbf{amide}}$ in $CDCl_3$.

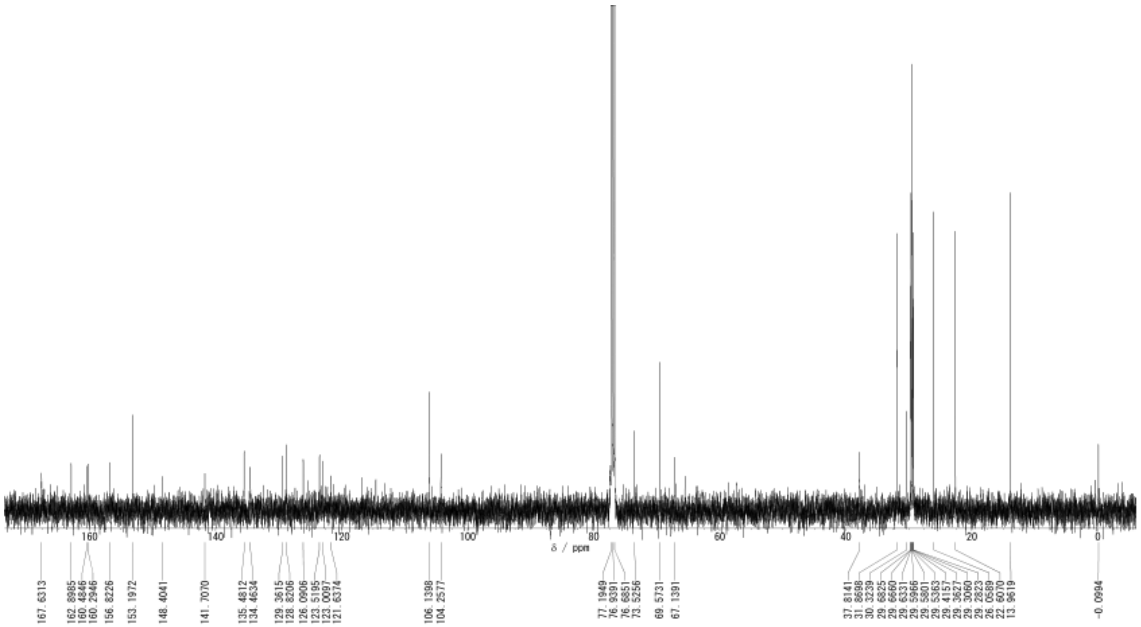


Chart S8. ^{13}C NMR spectrum of $\mathbf{1}_{\mathbf{amide}}$ in $CDCl_3$.

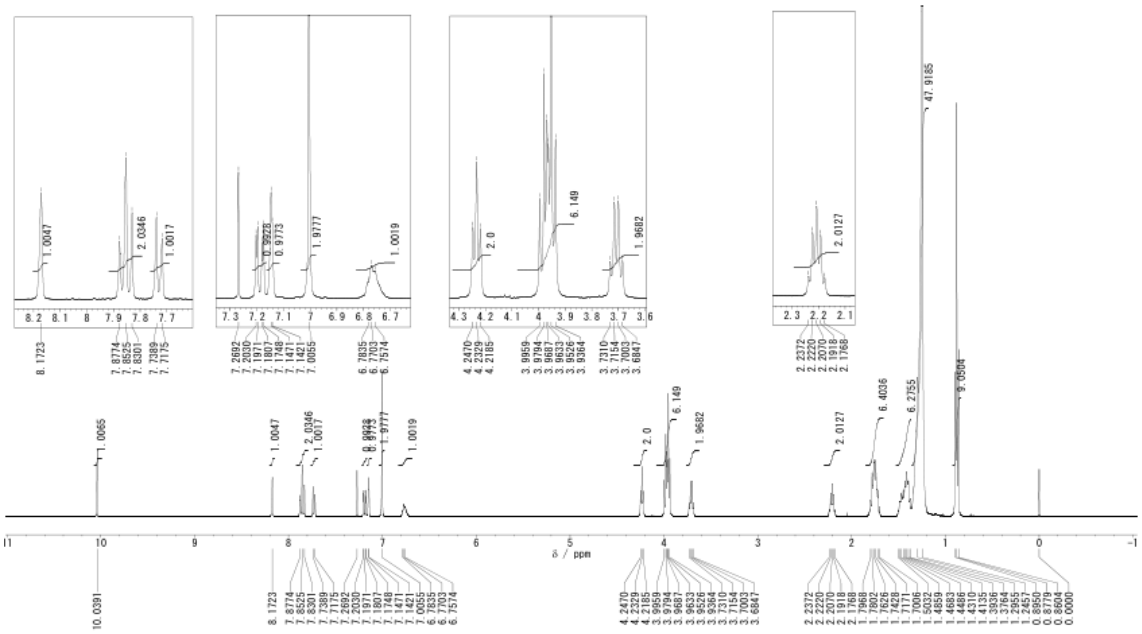


Chart S9. ^{1}H NMR spectrum of **2$_{amide}$** in $CDCl_3$.

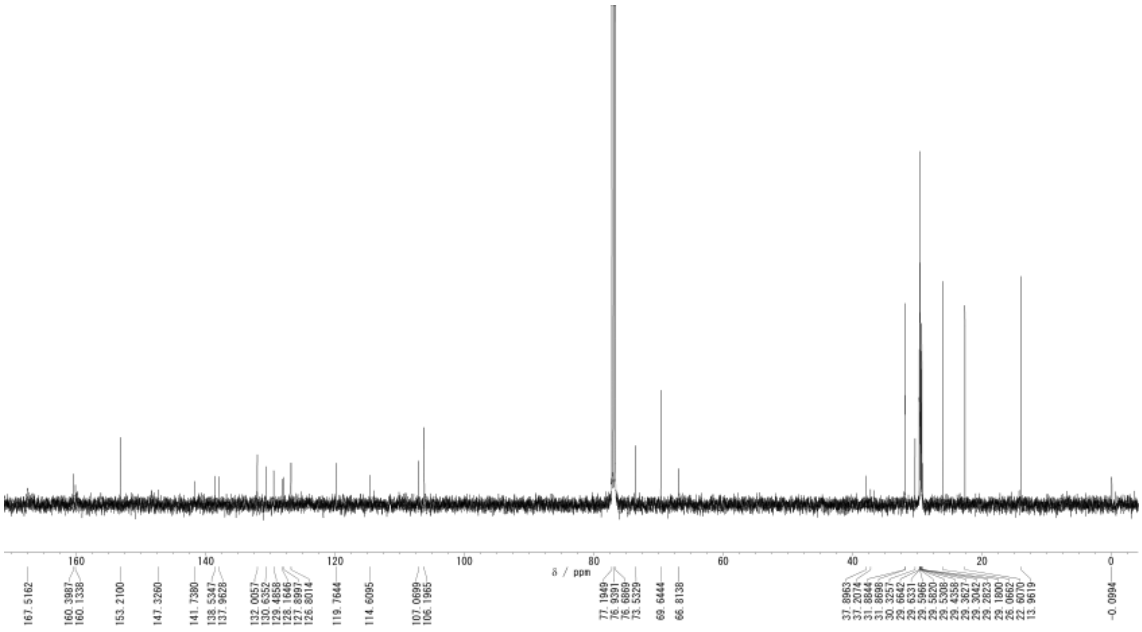


Chart S10. ^{13}C NMR spectrum of **2$_{amide}$** in $CDCl_3$.

2. Supporting Figures

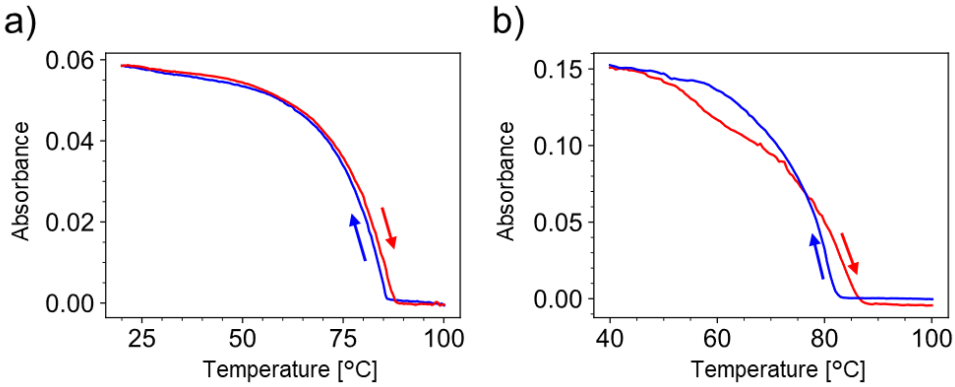


Figure S1. Cooling (blue) and heating (red) curves of (a) $\mathbf{1}_{\mathbf{amide}}$ (c = 30 μM) and (b) $\mathbf{2}_{\mathbf{amide}}$ (c = 10 μM) were obtained by plotting absorbance at λ = 500 nm and 470 nm, respectively, as a function of temperature in MCH (cooling and heating rate: 1.0 °C min^{-1}).

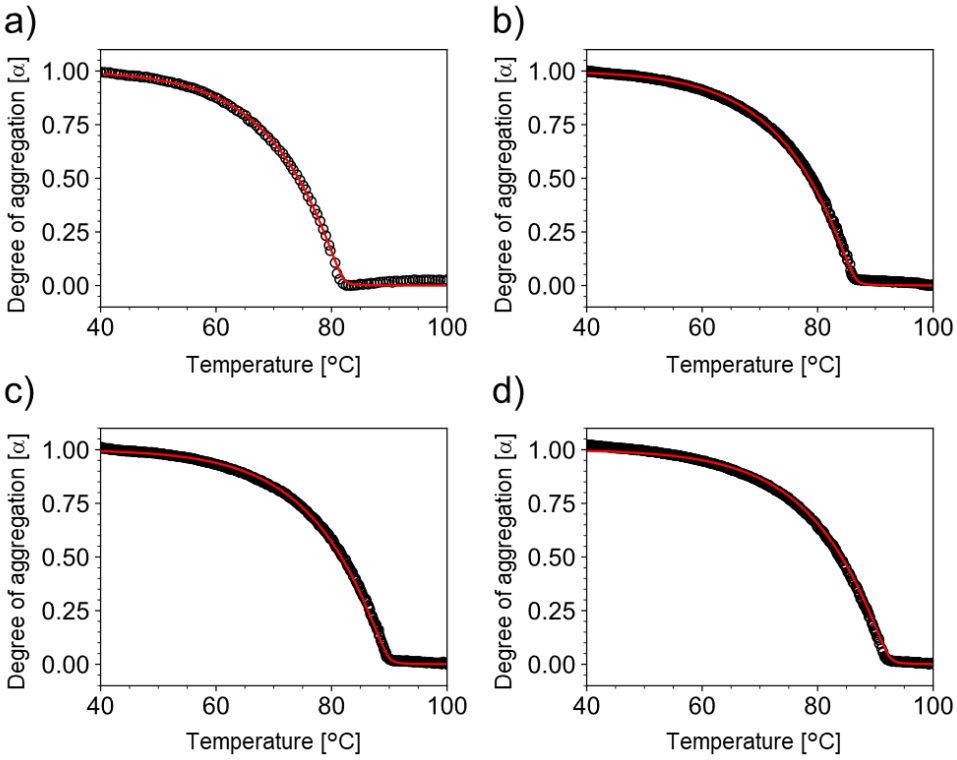


Figure S2. a–d) Plots of degree of aggregation (a) of $\mathbf{1}_{\mathbf{amide}}$ in MCH at c = 20 μM (a), 30 μM (b), 40 μM (c), 50 μM (d) as a function of temperature during the cooling processes (cooling rate = 1.0 °C min^{-1}). The red solid lines were obtained by fitting the cooling curves to the nucleation-elongation model proposed by Zhao and Moore.[S3]

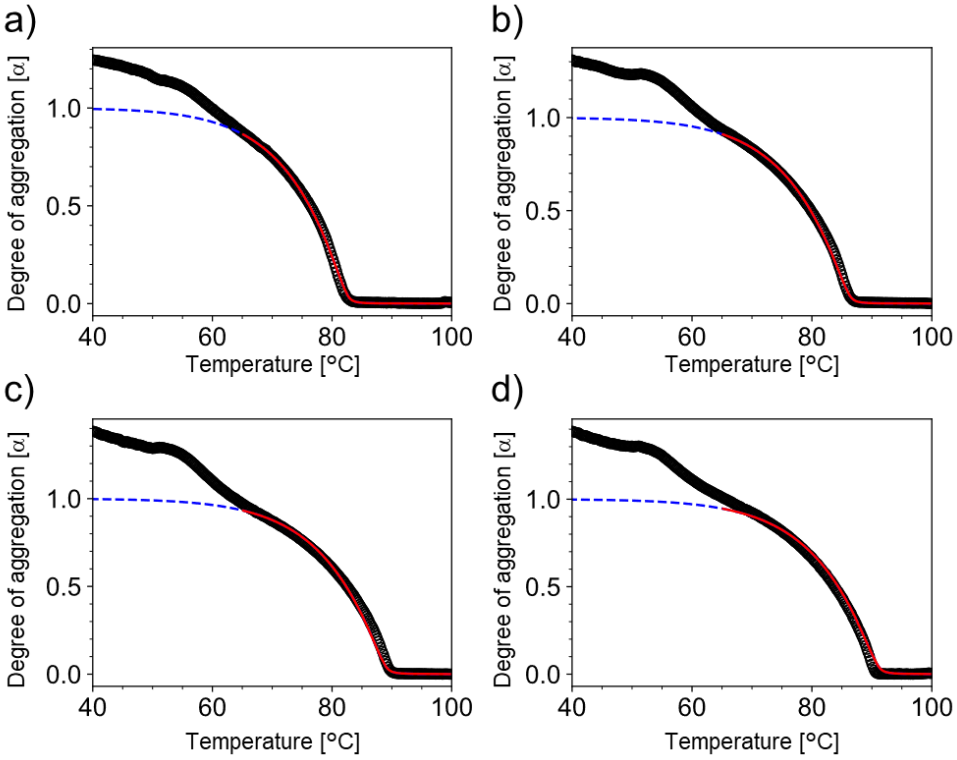


Figure S3. a–d) Plots of degree of aggregation (*a*) of $\mathbf{2}_{\mathbf{amide}}$ in MCH at c = 20 μM (a), 30 μM (b), 40 μM (c), and 50 μM (d) as a function of temperature during cooling processes (cooling rate =1.0 °C min^{-1}). The blue dash and red solid lines were obtained by fitting the cooling curves, excluding the secondary transition occurring below 65 °C, to the nucleation-elongation model proposed by Zhao and Moore.[S3] The red lines represent fitted regions.

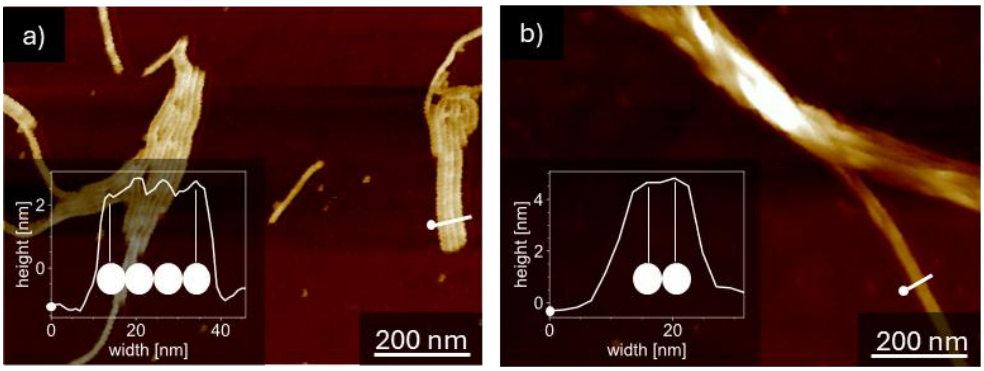


Figure S4. a,b) AFM images and section analysis (insets) of supramolecular polymers formed in a solution of $\mathbf{1}_{\mathbf{amide}}$ (a) and $\mathbf{2}_{\mathbf{amide}}$ (b) in MCH (c = 50 μM).

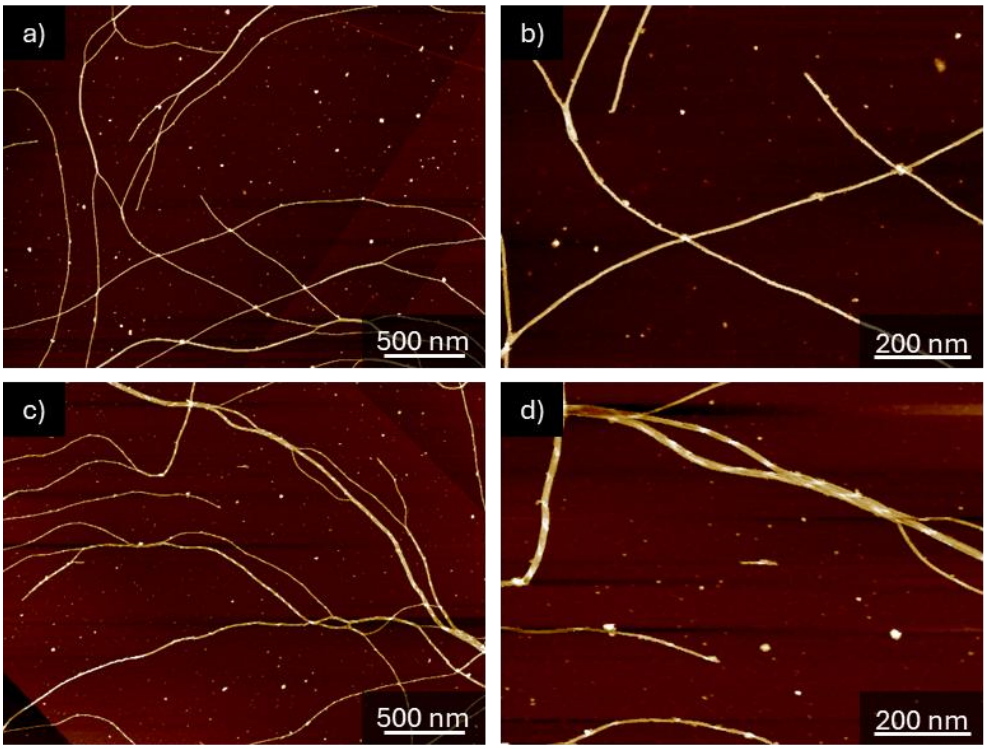


Figure S5. a–d) AFM images of supramolecular polymers formed in a solution of $\mathbf{2}_{\mathbf{amide}}$ (c = 50 μM) in MCH at 70 °C (a,b) and 50 °C (c,d).

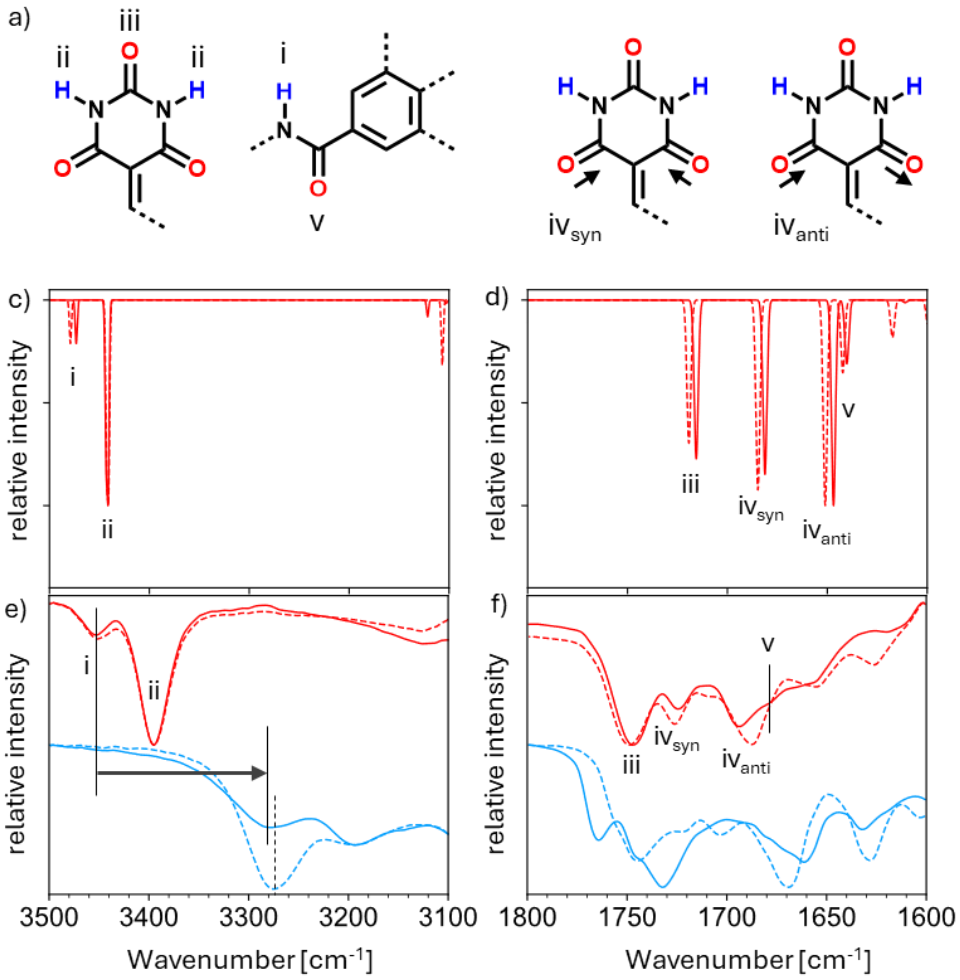


Figure S6. a) Assignments of C=O and N–H stretching vibration modes for **1**$_{amide}$ and **2**$_{amide}$. c,d) Calculated IR spectra of **1**$_{amide}$ (solid line) and **2**$_{amide}$ (dash line) in $CHCl_3$ by DFT calculation (B3-LYP/6-31+G(d,p)) and a linear correlation[S6]. e,f) IR spectra of $CHCl_3$ solutions (c = 2 mM, red lines) and nanofiber films (on KBr substrate, blue lines) of **1**$_{amide}$ (solid lines) and **2**$_{amide}$ (dash lines). For the spectra of $CHCl_3$ solutions, peaks were assigned with the corresponding vibration modes.

4. Supporting References

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