

Electronic Supplementary Material

Asymmetric living supramolecular polymerization of an achiral aza-BODIPY dye by solvent-mediated chirality induction and memory

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1. Materials and Methods

Chemicals and Reagents: Unless otherwise specified, all the chemicals were purchased from commercial suppliers and did not require further purification when used.

Aza-BODIPY dye **1** was synthesized as described previously.¹

UV/Vis spectroscopy: UV/Vis absorption spectra were recorded on an Agilent Technologies Cary 300 UV/Vis spectrophotometer equipped with a SPV 1×1 temperature controller. The solvents for spectroscopic studies were spectroscopic grade and used as received. The spectra were recorded in quartz cuvettes and the extinction coefficients ϵ was calculated according to Lambert-Beer's law.

Circular dichroism (CD) spectroscopy: CD spectra were recorded on a Jasco J-810 spectrophotometer equipped with Jasco CDF 426S temperature controller.

Atomic force microscopy: AFM measurements were performed under ambient conditions using a Bruker Dimension icon spectra system operating in tapping mode. Silicon cantilevers with a resonance frequency of 300 kHz were used. The sample for AFM was prepared by drop-casting (*S*)- and (*R*)-limonene solution of dye **1** ($c=1.0 \times 10^{-5}$ M) on mica surface and evaporating the solvent.

Transmission electron microscopy: Transmission electron microscopy (TEM) measurements were performed on a JEM-1400 transmission electron microscope, operating at an acceleration voltage of 120 kV. For the observation of aggregates, 400-mesh copper grids coated with carbon was dipped in a drop of sample solution of dye **1**. About 1 min after the deposition, the grid was placed on filter paper to remove solvent. Staining was performed by a drop of uranyl acetate aqueous solution (0.5 % wt) onto the copper grid. After 10 min, the liquid on the grid was removed with filter paper.

Fourier transform infrared (FT-IR) Spectroscopy: FT-IR measurements were performed on a Bruker ALPHA II infrared spectrometer. The liquid sample was prepared by holding appropriate amount of solution of dye **1** between two KBr crystal tablets. Press it into a uniform and transparent film with tablet press.

Preparation of the Aggregates II_L: Aza-BODIPY dye **1** (1.0 - 4.0 mg) was dissolved with 100 mL either (*S*)-limonene or (*R*)-limonene. By keeping the solutions at room

temperature for 8 to 20 h, **Agg. II_L** of dye **1** in (*S*)- and (*R*)-limonene was obtained. The formation of **Agg. II_L** was confirmed by UV/Vis absorption spectra.

Preparation of the Aggregates I_M: Aza-BODIPY dye **1** (1.0 - 4.0 mg) was dissolved with 100 mL MCH. By keeping the solutions at room temperature for 8 to 20 h, **Agg. II_M** of dye **1** in MCH was obtained. Then the solution was cooled rapidly at the rate of 10 K/min so that the **Agg. I_M** was obtained. The formation of **Agg. I_M** was confirmed by UV/Vis absorption spectra.

Experimental operation for multiple cyclic Living supramolecular polymerization:

Firstly, the seeds of **Agg. II_L** (**Seed_{Agg. II_L}**) was prepared by applying sonication to a **Agg. II_L** solution in (*S*)-limonene ($c_T = 5.0 \times 10^{-6}$ M) for 5 min in a water bath at 293 K. And the freshly prepared **Agg. I_M** was obtained by rapid cooling of the hot monomer solution of dye **1** in MCH ($c_T = 5.0 \times 10^{-6}$ M) from 343 K to 278 K (10 K min⁻¹) which was in a kinetically trapped inactive state. Then the equal amounts of **Agg. I_M** at 278 K (1.5 mL) was injected into **Seed_{Agg. II_L}** (1.5 mL) which has already been cooled down to 278 K. After that the mixture was warmed to 283 K to initiate the first cycle of multiple cycles of living polymerization process and kept at this temperature. After the complete transformation from **Agg. I_M** to **Agg. II_L**, half volume of the solution was removed and the remaining half was cooled down to 278 K. Then the equal amounts of **Agg. I_M** in pure MCH at 278 K (1.5 mL) was injected into the remaining solution of the first cycle and the mixture was heated to 283 K again and maintain this temperature until the transformation process was finished. The solution was cooled down to 278 K to prepare for the next cycle and the operation was repeated.

2. Data analysis for temperature-dependent spectroscopic studies

For the process of temperature-dependent research, the summation of the fractions of two species is equal to 1 if monomer and aggregate species are involved. The α_{mon} and α_{agg} represent the fraction of monomer and aggregates. When there were only monomer and one type of aggregate existing in process of temperature-dependent study, the α_{agg} could be obtained by the Eq. S1:

$$\alpha_{\text{agg}}(T) = 1 - \frac{\varepsilon(T) - \varepsilon_{\text{agg}}}{\varepsilon_{\text{mon}} - \varepsilon_{\text{agg}}} \quad (\text{S1})$$

For CD spectroscopic data, $\Delta\varepsilon_{\text{agg}}$ was used instead of ε_{agg} in equation (S1).

The data points of the molar fraction of aggregated molecules obtained in experiment as a function of temperature can be fitted by using the nucleation-elongation model (Eq. S2 and Eq. S3, for the enucleation and elongation regime respectively) proposed by Meijer et al.^{2,3} Accordingly, thermodynamic parameters including the dimensionless equilibrium constant K_a (for the activation step at the elongation temperature), elongation temperature T_e , and the elongation enthalpy change ΔH_e . The average length of the stack $N_n(T_e)$ at T_e is given by Eq. S4.

$$\alpha_{\text{agg}} = K_a^{1/3} \exp\left(2/3 K_a^{-1/3} - 1\right) \left[\frac{\Delta H_e}{RT_e^2} (T - T_e) \right] \quad (\text{S2})$$

$$\alpha_{\text{agg}} = \alpha_{\text{SAT}} \left\{ 1 - \exp \left[- \frac{\Delta H_e}{RT_e^2} (T - T_e) \right] \right\} \quad (\text{S3})$$

$$N_n(T_e) = \frac{1}{K_a^{1/3}} \quad (\text{S4})$$

The standard enthalpy change (ΔH°) and standard entropy change (ΔS°) can be determined according to the linear relationship in the van't Hoff plot applying Eq. S5, where R is the ideal gas constant.⁴

$$\ln \left[\frac{1}{c_T} \right] = - \frac{\Delta H^\circ}{RT_e} + \frac{\Delta S^\circ}{R} \quad (\text{S5})$$

3. Aggregation studies by spectroscopic methods and AFM

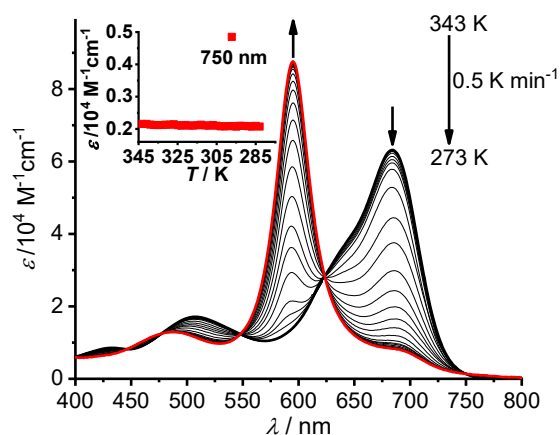


Fig. S1 Temperature-dependent UV/Vis absorption spectra of dye **1** in (*S*)-limonene ($c_T = 1.0 \times 10^{-5}$ M) upon cooling from 343 K to 273 K at 0.5 K min^{-1} . Inset: Changes of the molar extinction absorption coefficient monitored at 750 nm.

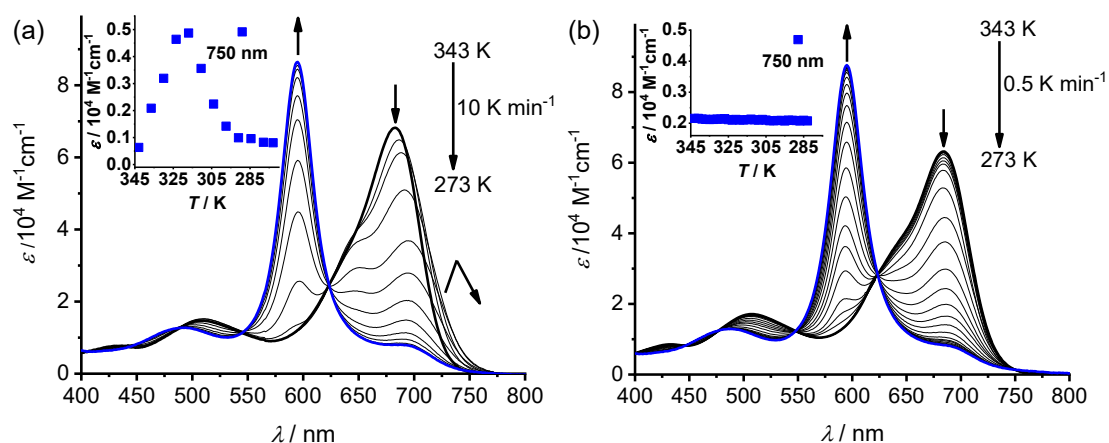


Fig. S2 Temperature-dependent UV/Vis absorption spectra of dye **1** in (*R*)-limonene ($c_T = 1.0 \times 10^{-5}$ M) upon (a) rapid cooling at 10 K min^{-1} and (b) slow cooling at 0.5 K min^{-1} from 343 K to 273 K. Insets: Changes of the molar extinction absorption coefficient monitored at 750 nm.

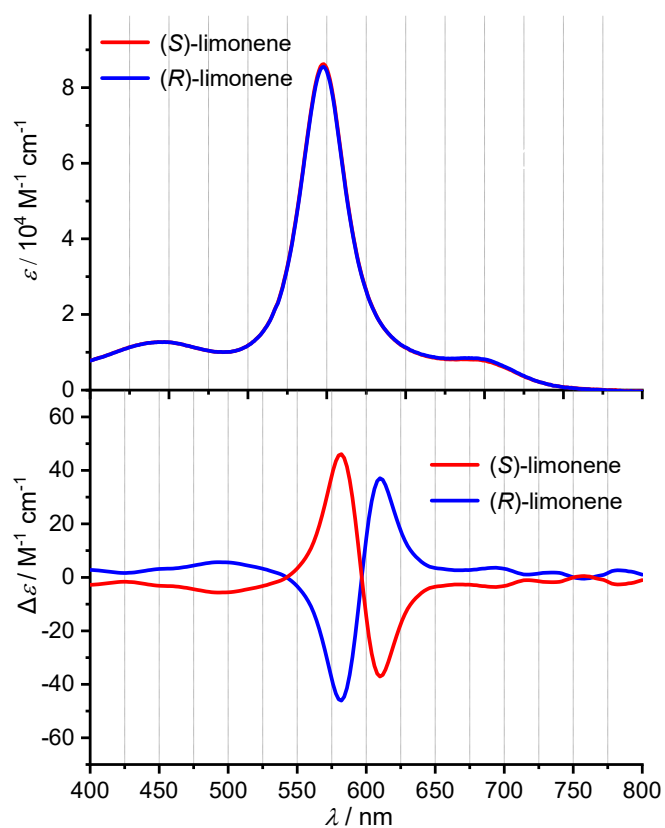


Fig. S3 UV/Vis absorption spectra (top) and CD (bottom) spectra of dye **1** in (*S*)-limonene (1.0×10^{-5} M) and (*R*)-limonene (1.0×10^{-5} M) at 273 K, respectively.

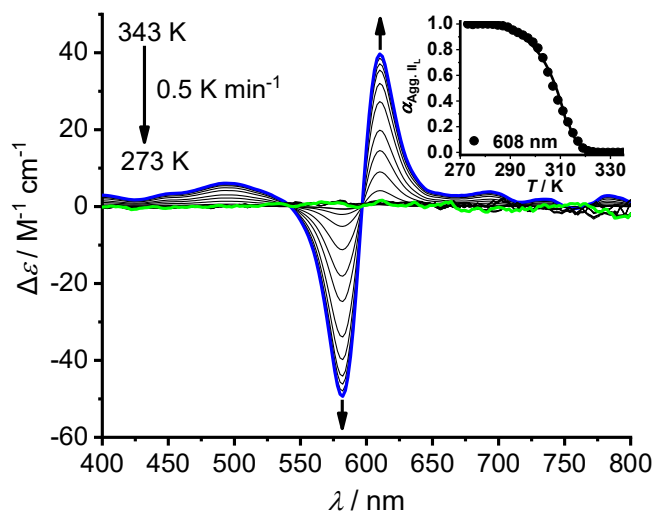


Fig. S4 Temperature-dependent CD spectra of dye **1** cooling from 343 K to 273 K in (*R*)-limonene (1.0×10^{-5} M) at 0.5 K min^{-1} . Inset: The calculated plot of molar fraction of **Agg. II_L** versus temperatures (monitored at 608 nm).

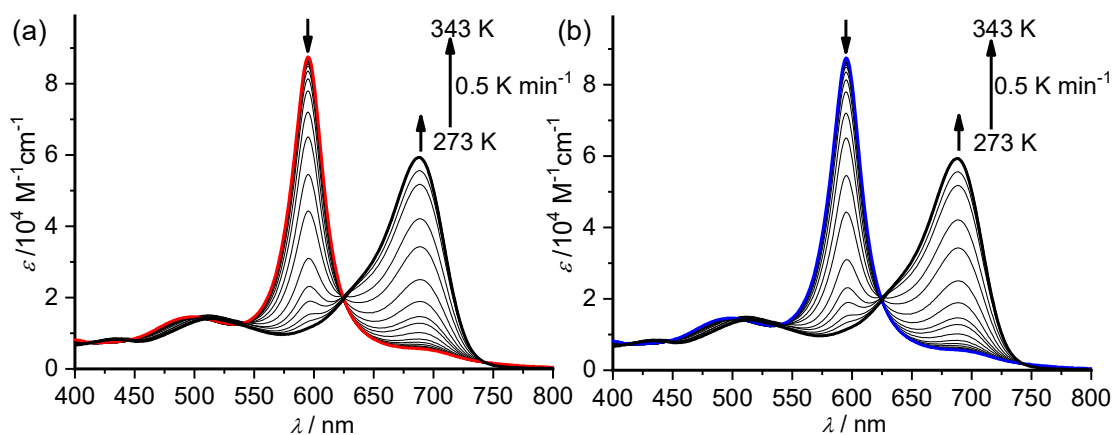


Fig. S5 Temperature-dependent UV/Vis absorption spectra of dye **1** in (a) (*S*)-limonene ($c_T = 1.0 \times 10^{-5}$ M) and (b) (*R*)-limonene ($c_T = 1.0 \times 10^{-5}$ M) upon heating from 273 K to 343 K at 0.5 K min^{-1} .

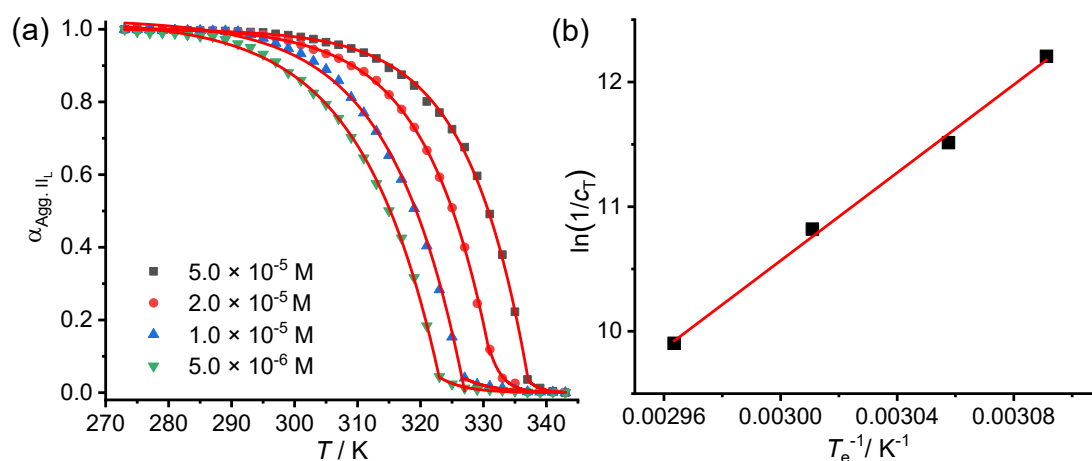


Fig. S6 (a) Molar fraction of **Agg. II_L** in (*S*)-limonene monitored by temperature-dependent UV/Vis absorption spectra at 595 nm in the heating process from 273 K to 343 K at the rate of 0.5 K min^{-1} . (b) The van't Hoff plot for heating process of **Agg. II_L** in (*S*)-limonene (5.0×10^{-6} M to 5.0×10^{-5} M).

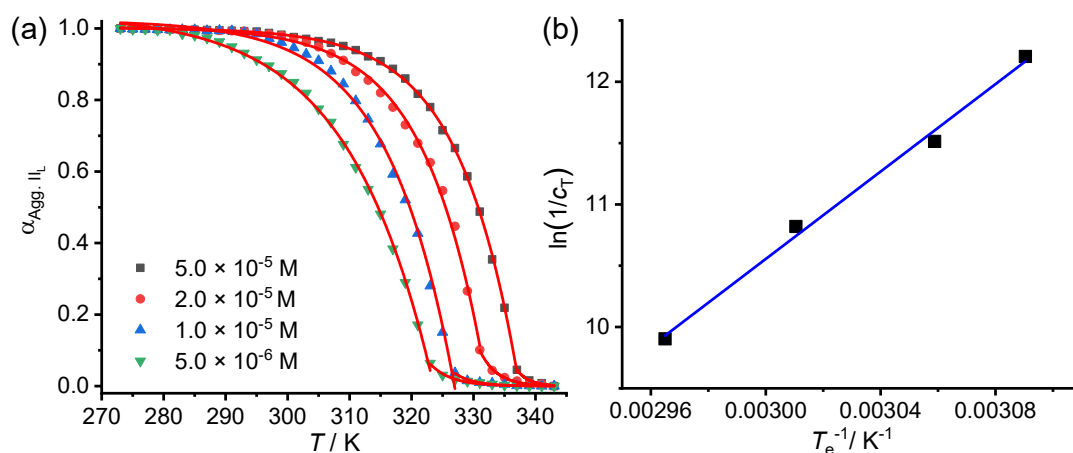


Fig. S7 (a) Molar fraction of **Agg. II_L** in (*R*)-limonene monitored by temperature-dependent UV/Vis absorption spectra at 595 nm in the heating process from 273 K to 343 K at the rate of 0.5 K min⁻¹. (b) The van't Hoff plot for heating process of **Agg. II_L** in (*R*)-limonene (5.0 × 10⁻⁶ M to 5.0 × 10⁻⁵ M).

Table S1 Thermodynamic parameters of aza-BODIPY **1** in chiral limonene solution.

		<i>(S)</i> -Limonene		<i>(R)</i> -Limonene	
<i>c</i> _T /	<i>T</i> _e /	ΔH_e /	<i>T</i> _e /	ΔH_e /	
10 ⁻⁵ M	K	kJ mol ⁻¹	K	kJ mol ⁻¹	
0.5	324 ± 0.5	-173 ± 2.5	324 ± 0.6	-175 ± 1.6	
1.0	327 ± 0.3	-173 ± 2.1	327 ± 0.8	-175 ± 2.8	
2.0	332 ± 0.4	-170 ± 1.8	332 ± 0.5	-172 ± 1.9	
5.0	337 ± 0.4	-174 ± 3.4	337 ± 0.6	-174 ± 2.5	

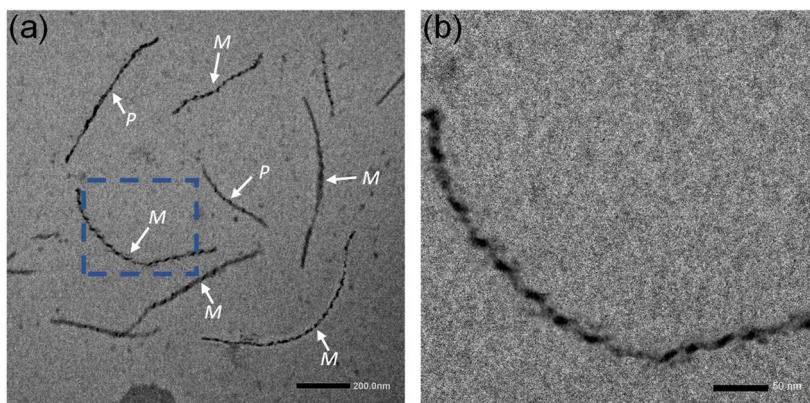


Fig. S8 (a) TEM image for **Agg. II_L** in (*S*)-limonene solution (1.0×10^{-5} M). (b) Zoomed image of one left-handed (*M*) nanofiber along the blue dashed box of (a)

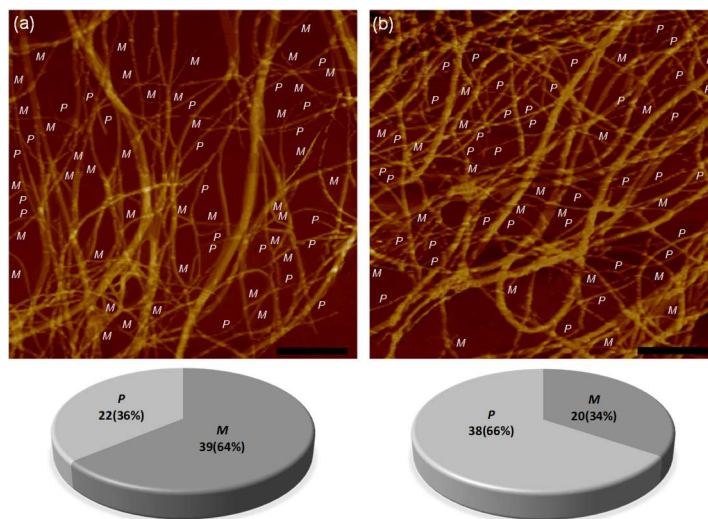


Fig. S9 AFM height image by drop-casting (a) (*S*)-limonene and (b) (*R*)-limonene solution (5.0×10^{-5} M) of dye **1** and the statistical graph of *M* and *P* helices.

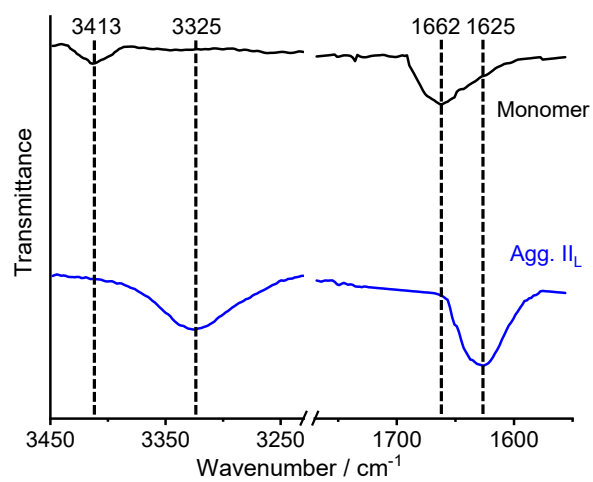


Fig. S10 FT-IR spectra of the N-H and C=O stretching vibration region for monomeric dye **1** ($c_T = 1.0 \times 10^{-5}$ M) in CHCl₃, and **Agg. II_L** in (*S*)-limonene ($c_T = 1.0 \times 10^{-5}$ M).

4. Studies on the seeded supramolecular polymerization in MCH/limonene mixture and the racemization process

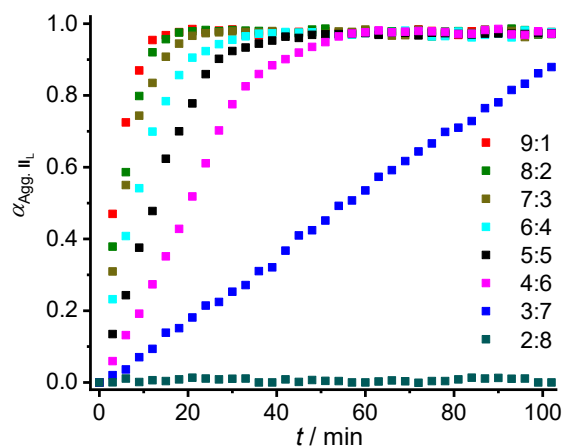


Fig. S11 The kinetic curves for the transformation of **Agg. I_M** to **Agg. I_L** monitored by CD spectroscopy at 283 K in the mixed solvent of (*S*)-limonene/MCH ($c_T = 5.0 \times 10^{-6}$ M) from 9:1 to 2:8.

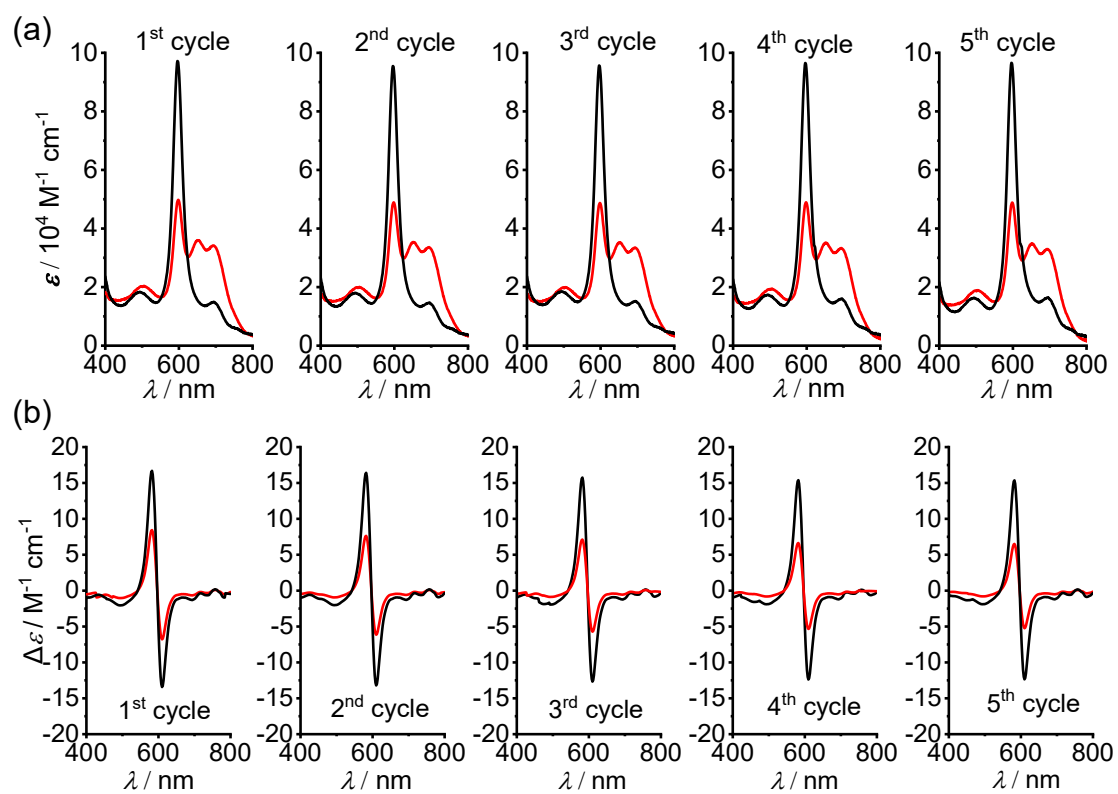


Fig. S12 The initial (red) and final (black) UV/Vis absorption spectra (a) and CD spectra (b) for each cycle of the LSP process in MCH/limonene ($[\text{Seed}_{\text{Agg. III}} \text{ in } (S)\text{-limonene}] = [\text{Agg. I}_{\text{M}} \text{ in MCH}] = 5.0 \times 10^{-6} \text{ M}$).

5. References

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