

(Supporting Information)

**Thermally Stable and Rewritable Circularly Polarized Luminescent Helical Poly(diphenylacetylene)s: Stabilization of Macromolecular Helicity Memory via Reversible Ion-pair Formation**

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## Experimental Section

### 1. Materials

Tungsten(VI) chloride ( $\text{WCl}_6$ ), amberlyst A26 (hydroxide form), and tetrakisdecylammonium hydroxide ( $\text{A}_{10}\text{OH}$ ) (10% in methanol) were purchased from Sigma-Aldrich (St. Louis, MO, USA). Tetraphenyltin ( $\text{Ph}_4\text{Sn}$ ), didodecylamine, 1-butanol, piperidine, (*S*)- and (*R*)-2-phenylglycinol ((*S*)- and (*R*)-PG), tetramethylammonium hydroxide ( $\text{A}_1\text{OH}$ ) (10% in methanol (MeOH)), tetrabutylammonium hydroxide ( $\text{A}_4\text{OH}$ ) (10% in MeOH), and tetrahexylammonium hydroxide ( $\text{A}_6\text{OH}$ ) (10% in MeOH) were obtained from Tokyo Chemical Industry (TCI, Tokyo, Japan). Copper(I) iodide ( $\text{CuI}$ ) and ethanol (EtOH) were obtained from Kanto Kagaku (Tokyo, Japan). Phosphorous pentachloride ( $\text{PCl}_5$ ) and trifluoroacetic acid were purchased from FUJIFILM Wako Pure Chemical (Osaka, Japan). 4-(4,6-Dimethoxy-1,3,5-triazin-2-yl)-4-methylmorphonium chloride (DMT-MM) was obtained from Oakwood Chemical Int. (Columbia, USA). Anhydrous tetrahydrofuran (THF), toluene, and dimethyl sulfoxide (DMSO) were purchased from Kanto Kagaku. Deionized, distilled water was used throughout for all measurements. Bis(4-heptyloxy-carbonylphenyl)acetylene (**1-Hep**) was prepared according to the reported method.<sup>1, 2</sup> Stereoregular (*cis*) poly-**1-Hep**<sup>3</sup> was synthesized by the polymerization of **1-Hep** using  $\text{WCl}_6\text{-Ph}_4\text{Sn}$  as a catalyst in a similar method reported previously.<sup>1, 2, 4, 5</sup> The number-average molar mass ( $M_n$ ) and molar-mass dispersity ( $M_w/M_n$ ) were  $1.4 \times 10^4$  and 1.6, respectively, as determined by size exclusion chromatography (SEC) with THF as the eluent. The obtained poly-**1-Hep** was converted to poly-**1-H** by alkaline hydrolysis of the ester groups according to the previously reported method.<sup>1, 2</sup> *h*-Poly-**1-H** with left-handed helicity memory ( $\Delta\varepsilon_{1st} = -22.5$ ), which was used throughout all experiments without otherwise stated, was prepared from poly-**1-H** based on the helicity induction and memory strategy using (*S*)-PG as a helix-inducer according to the previous report.<sup>2</sup>

## 2. Instruments

NMR spectra were taken on a JNM-ECA 500 or a JNM-ECA 600 (JEOL, Tokyo, Japan) (500 and 600 MHz for  $^1\text{H}$ ) spectrometer in  $\text{CDCl}_3$ ,  $\text{DMSO-}d_6$ , and  $\text{DMSO-}d_6$ - $\text{D}_2\text{O}$  using TMS (for  $\text{CDCl}_3$ ) or a solvent residual peak (for  $\text{DMSO-}d_6$  and  $\text{DMSO-}d_6$ - $\text{D}_2\text{O}$ ) as the internal standard. IR spectra were recorded with a JASCO (Hachioji, Japan) Fourier Transform IR-4700 spectrophotometer. SEC measurements were performed with a JASCO PU-2080 liquid chromatograph equipped with a UV-vis (JASCO UV-970) detector at 40 °C using a Shodex (Tokyo, Japan) KF-805L SEC column. The temperature was controlled with a JASCO CO-1560 column oven. THF was used as the eluent at a flow rate of 1.0 mL/min. The molar mass calibration curves were obtained with polystyrene standards (Tosoh, Tokyo, Japan). Absorption and circular dichroism (CD) spectra were measured in a 1.0-mm quartz cell on a JASCO V-650 spectrophotometer and a JASCO J-725 spectropolarimeter, respectively. The temperature was controlled with a JASCO PTC-348WI apparatus. The concentration of polymers was calculated based on the monomer units. Circularly polarized luminescence (CPL) spectra were obtained on a JASCO CPL-300 spectrofluoropolarimeter using a 1.0-mm quartz cell at room temperature, which was designed to gain a high S/N ratio by adjusting the angle between the incident and traveling light to 0° using a notch filter. Fluorescent (FL) spectra were measured using a 10-mm quartz cell on a JASCO FP-6300 spectrofluorometer. The fluorescent quantum yields ( $\Phi_{\text{FL}}$ ) were determined using the quinine sulfate solution in 1 N  $\text{H}_2\text{SO}_4$  as reference. High-resolution mass (HRMS) spectra were measured on a JEOL JMS-700. Elemental analyses were performed by the Research Institute for Instrumental Analysis of Advanced Science Research Center, Kanazawa University, Kanazawa, Japan.

### 3. Synthesis

#### *Synthesis of tetrapiperidylphosphonium chloride*

PCl<sub>5</sub> (416 mg, 2.00 mmol) was dissolved in chlorobenzene (2.63 mL) under nitrogen and the solution was cooled to 0 °C by using an ice water bath. To this was added piperidine (2.37 mL, 24.0 mmol) dropwise slowly and the mixture was stirred at 110 °C for 27 h. After addition of 20% NaOH aq. (2.56 mL), the mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> three times and the solvent was removed by evaporation. The crude product was purified by silica-gel chromatography (eluent: CH<sub>2</sub>Cl<sub>2</sub>/MeOH =15/1, v/v) to afford tetrapiperidylphosphonium chloride as a pale yellow solid (466 mg, 1.16 mmol, 58%).

IR (KBr, cm<sup>-1</sup>): 2981, 1453, 1110. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>, r.t.): δ 3.22–3.08 (m, 16H, N<sup>+</sup>CH<sub>2</sub>), 1.75–1.55 (m, 24H, N<sup>+</sup>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>). HRMS (FAB+) Calcd for C<sub>20</sub>H<sub>40</sub>N<sub>4</sub>P<sup>+</sup> (M<sup>+</sup>): m/z = 367.2985. Found: 367.2990.

#### *Preparation of tetrapiperidylphosphonium hydroxide (POH) solution*

Tetrapiperidylphosphonium chloride (0.50 mmol) in MeOH (2.0 mL) was applied to a glass tube column (ϕ:10 (mm)) filled with Amberlyst A26 (2.5 g) and elution with MeOH (23 mL) gave POH in MeOH (0.02 M).

#### *Synthesis of h-poly-2*

To a solution of *h*-poly-1-H (23.1 mg, 86.8 μmol) and didodecylamine (123 mg, 348 μmol) in DMSO–water (5/1, v/v) (4.0 mL) was added DMT-MM (97.0 mg, 351 μmol), and the resulting mixture was stirred at room temperature overnight. After addition of CH<sub>2</sub>Cl<sub>2</sub>, the organic layer was washed with water three times and the solvent was removed by evaporation. The mixture was diluted with a small amount of CH<sub>2</sub>Cl<sub>2</sub> and poured into a large amount of MeOH, and the precipitated yellow fiber was collected by centrifugation and then dried *in vacuo* at room temperature to give *h*-poly-2 (68.0 mg, 72.5 μmol, 84%) as a red solid.

Spectroscopic data of *h*-poly-2: IR (KBr, cm<sup>-1</sup>): 1631 (ν<sub>C=O</sub> of amide). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 25 °C): δ 7.18–5.51 (br, 8H, aromatic), 4.26–2.44 (br, 8H, NCH<sub>2</sub>CH<sub>2</sub>), 1.86–1.45 (br, 8H, NCH<sub>2</sub>CH<sub>2</sub>),

1.42–1.02 (br, 72H, CH<sub>2</sub>), 1.01–0.68 (br, 12H, CH<sub>3</sub>). Elemental analysis: Calcd for C<sub>64</sub>H<sub>108</sub>N<sub>2</sub>O<sub>2</sub>·0.53H<sub>2</sub>O: C, 81.16; H, 11.61; N, 2.96. Found: C, 80.86; H, 11.47; N, 3.26.

### *Synthesis of h-poly-1-B*

*h*-Poly-1-B bearing organic cations were prepared by the treatment of *h*-poly-1-H with quaternary onium hydroxides (A<sub>n</sub>OH or POH) ([A<sub>n</sub>OH or POH]/[*h*-poly-1-H] = 2). A typical experimental procedure is described below. Tetrahexylammonium hydroxide (A<sub>6</sub>OH) (10% in MeOH) (37.2 mg, 10.0 μmol) was diluted with MeOH (1.00 mL), and *h*-poly-1-H (1.35 mg, 5.00 μmol) was added to this solution. After the mixture was stirred for 30 min at room temperature, the solvent was removed by evaporation and the residue was further dried *in vacuo* to quantitatively give *h*-poly-1-A<sub>6</sub> as a yellow film. *h*-Poly-1-Na was prepared by the treatment of *h*-poly-1-H with 0.08 M aqueous sodium hydroxide (NaOH aq.) ([NaOH]/[*h*-poly-1-H] = 4) and following re-precipitation in EtOH and washing.

### *Continuous sequence of ion-pairing, dissociation and helicity switching (Fig. 2)*

10% Tetradecylammonium (A<sub>10</sub>) hydroxide MeOH solution (596 mg, 100 μmol) as a base was diluted by MeOH (1.0 mL), and *h*-poly-1-H (13.3 mg, 50.0 μmol) was added to this mixture. The reaction mixture was stirred for 30 min at room temperature. After the reaction, the solvent was removed by evaporation and dried *in vacuo* to quantitatively afford *h*-poly-1-A<sub>10</sub> as a yellow film. The *h*-poly-1-A<sub>10</sub> (56.9 mg, 40.0 μmol) was acidified by trifluoroacetic acid (228 mg, 2.0 mmol) in DMSO (1.0 mL), and the mixture was poured into a large amount of ethyl acetate (40 mL), and the precipitated yellow solid was collected by centrifugation. After repeating this procedure three times to completely remove the residual A<sub>10</sub> cation, obtained yellow solid was dried *in vacuo* to afford *h*-poly-1-H' as a brown solid (6.38 mg, 24.0 μmol). *h*-Poly-1-H' (6.38 mg, 24.0 μmol) and (*R*)-phenylglycinol (26.3 mg, 192 μmol) were dissolved in water (2.4 mL), and the solution was stirred at 95 °C for 2 h and then at 25 °C for 24 h. The solution was acidified with 1M HCl aq. and the precipitated *h*'-poly-1-H was collected by centrifugation. After washing with water and drying *in vacuo*, *h*'-poly-1-H was obtained as a brown solid (4.30 mg, 16.2 μmol). 10% A<sub>10</sub> hydroxide MeOH solution (119 mg, 20.0 μmol) as a base was diluted by MeOH (300 μL), and *h*'-poly-1-H (2.68 mg, 10.0 μmol) was added to

this mixture. The reaction mixture was stirred for 30 min at room temperature. After the reaction, the solvent was removed by evaporation and dried *in vacuo* to quantitatively afford *h'*-poly-**1**-A<sub>10</sub> as a yellow film.

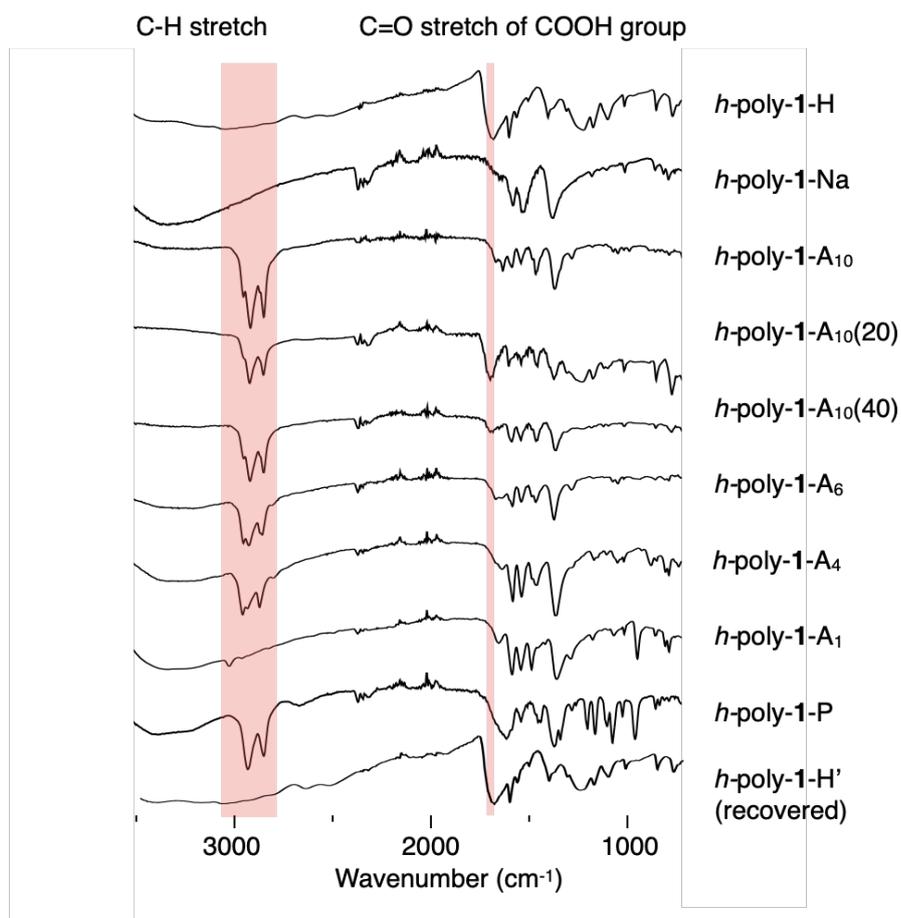
#### 4. Determination of Fluorescence Quantum Yield

The fluorescence quantum yields ( $\Phi$ ) were calculated by using the following equation;

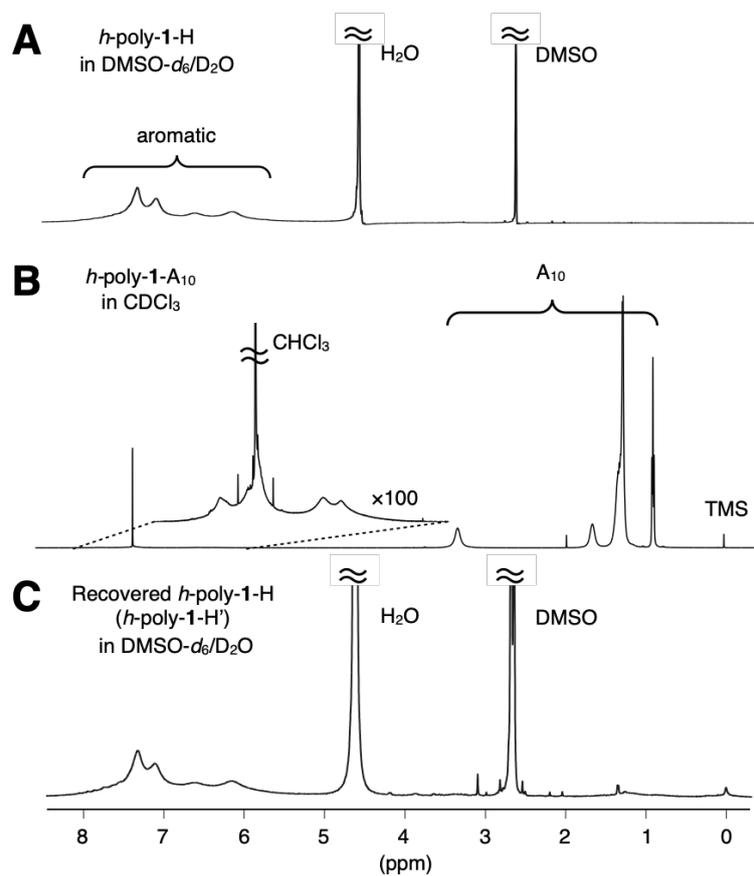
$$\Phi_S = \Phi_R \times (A_R \times F_S \times \eta_S^2 \times D_S) / (A_S \times F_R \times \eta_R^2 \times D_R) \quad (1)$$

where  $A$  is the absorbance at excitation wavelength,  $F$  is the area under FL curve,  $\eta$  is the refractive index of the solvent.<sup>6</sup> The subscripts  $S$  and  $R$  denote the respective values of the sample and the reference substance, respectively. Quinine sulfate in sulfuric acid (0.1 M) was used as a reference substance ( $\Phi_R = 0.55$ ).<sup>7</sup>

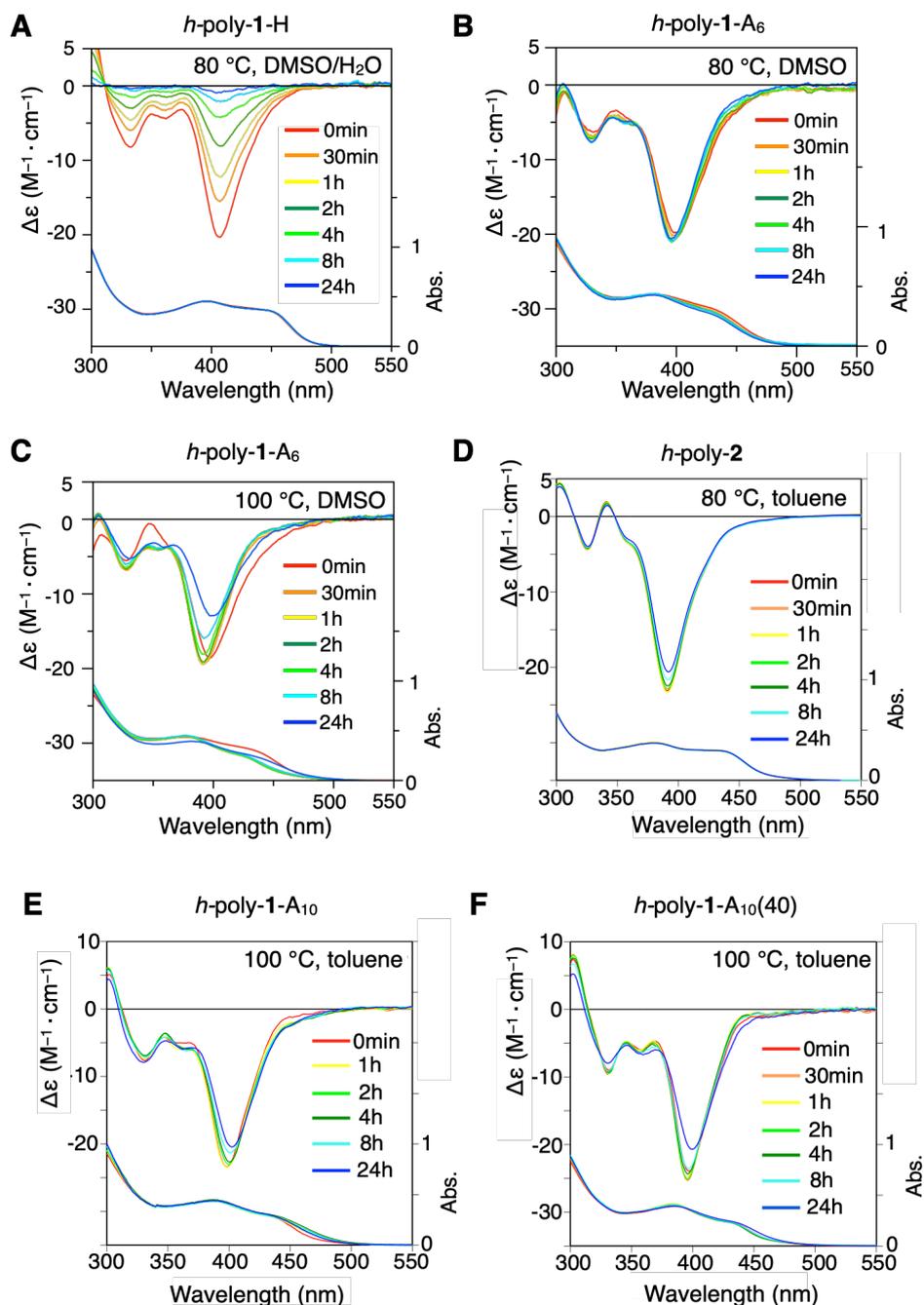
## 5. Supporting Data



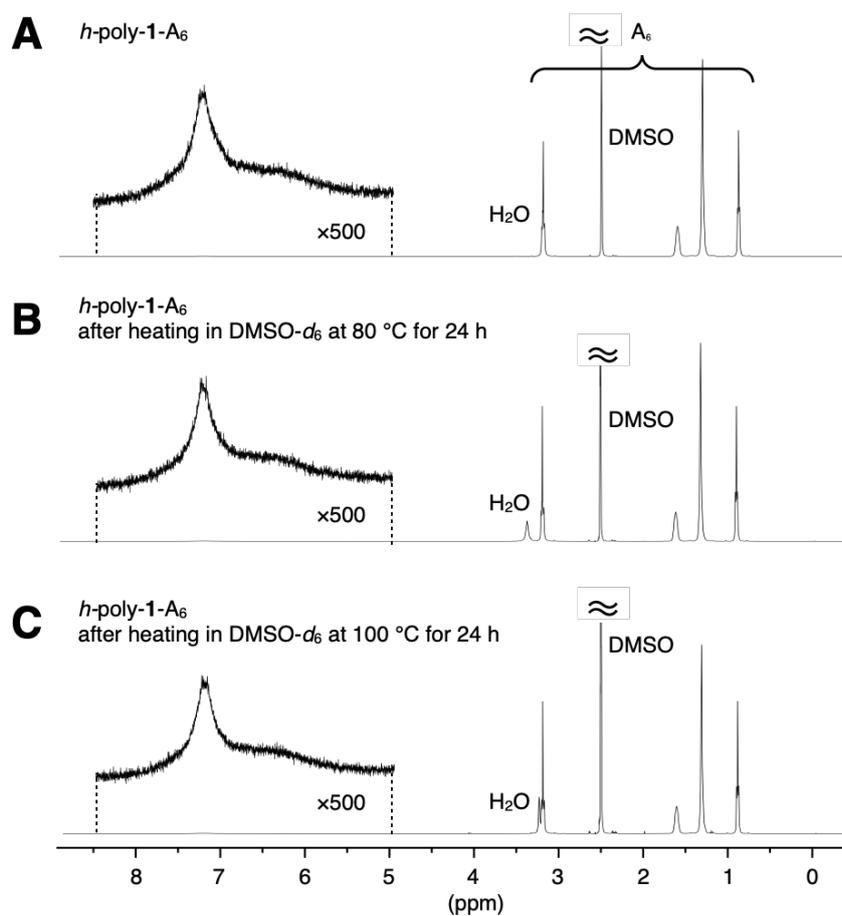
**Fig. S1.** IR (ATR) spectra of *h*-poly-1-H, *h*-poly-1-B, and *h*-poly-1-H'.



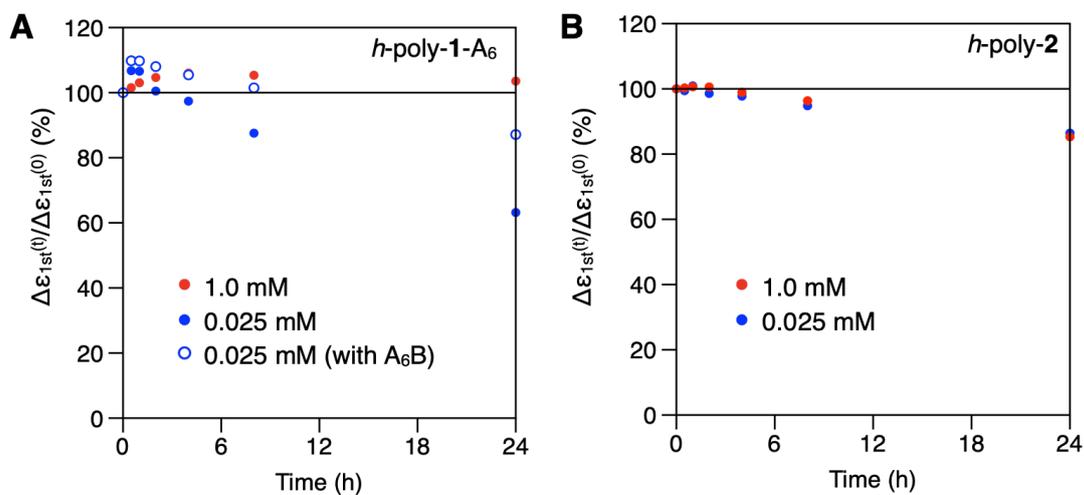
**Fig. S2.** <sup>1</sup>H NMR spectra of (A) *h*-poly-1-H in D<sub>2</sub>O–DMSO-*d*<sub>6</sub> (1/1, v/v), (B) *h*-poly-1-A<sub>10</sub> in CDCl<sub>3</sub>, and (C) *h*-poly-1-H' in D<sub>2</sub>O–DMSO-*d*<sub>6</sub> (1/1, v/v) at 25 °C.



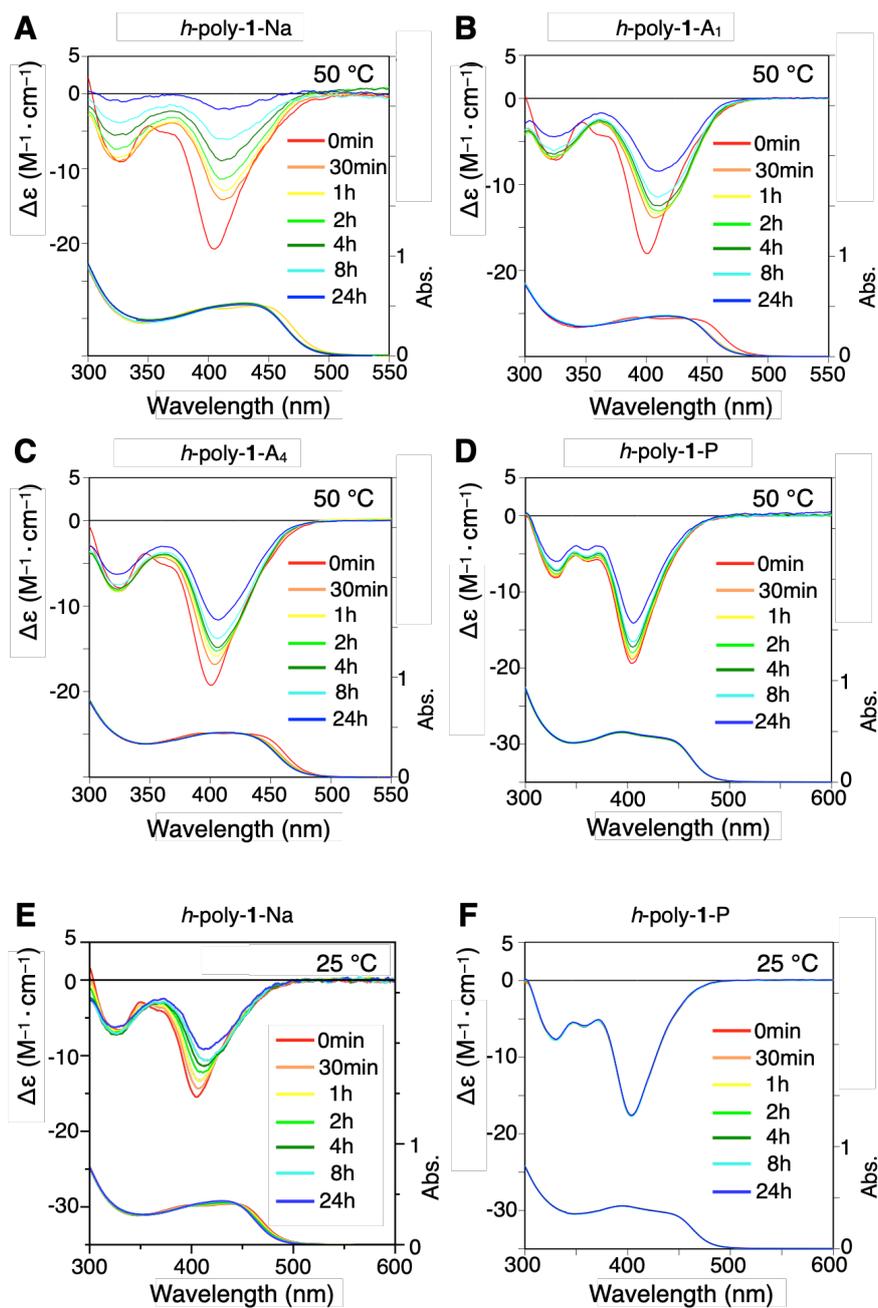
**Fig. S3.** CD and absorption spectral changes of (A) *h*-poly-1-H in H<sub>2</sub>O–DMSO (1/1, v/v), (B, C) *h*-poly-1-A<sub>6</sub> in DMSO, (D) *h*-poly-2 in toluene, (E) *h*-poly-1-A<sub>10</sub> in toluene, and (F) *h*-poly-1-A<sub>10</sub>(40) in toluene at (A, B, D) 80 °C and (C, E, F) 100 °C with time, measured at 25 °C. [Polymer] = 1.0 mM.



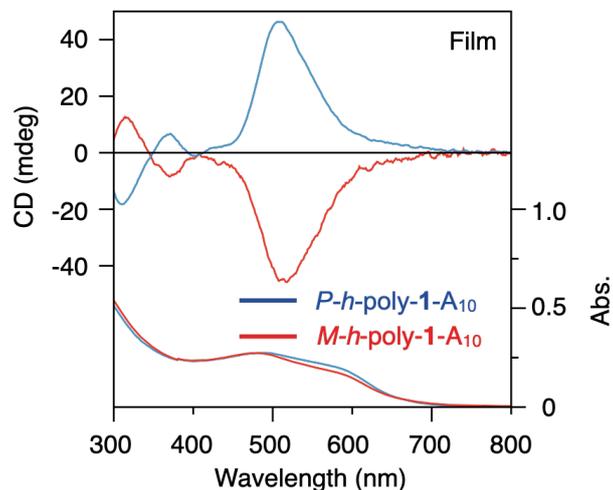
**Fig. S4.** <sup>1</sup>H NMR spectra of (A) *h*-poly-1-A<sub>6</sub>, (B) *h*-poly-1-A<sub>6</sub> after heating in DMSO-*d*<sub>6</sub> at 80 °C for 24 h, and (C) *h*-poly-1-A<sub>6</sub> after heating in DMSO-*d*<sub>6</sub> at 100 °C for 24 h, measured in DMSO-*d*<sub>6</sub> at 25 °C.



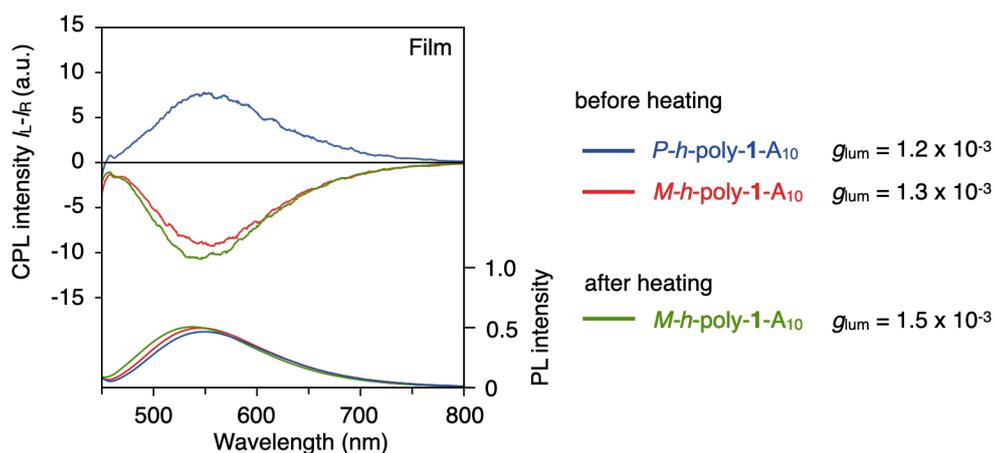
**Fig. S5.** Time-dependent ICD intensity changes ( $\Delta\varepsilon_{1st}^{(t)}/\Delta\varepsilon_{1st}^{(0)}$ ) of (A) *h*-poly-1-A<sub>6</sub> (1.0 mM (red) and 0.025 mM (blue)) in DMSO at 80 °C in the absence (closed circle) and presence (open circle) of tetrahexylammonium bromide (A<sub>6</sub>B) (2.0 mM) and (B) *h*-poly-2 (1.0 mM (red) and 0.025 mM (blue)) in toluene at 80 °C. All CD measurements were performed at 25 °C after standing at designated temperatures.



**Fig. S6.** CD and absorption spectral changes of (A, E) *h-poly-1-Na*, (B) *h-poly-1-A<sub>1</sub>*, (C) *h-poly-1-A<sub>4</sub>*, and (D, F) *h-poly-1-P* in H<sub>2</sub>O at (A–D) 50 °C and (E, F) 25 °C with time, measured at 25 °C. [Polymer] = 1.0 mM.



**Fig. S7.** CD (top) and absorption (bottom) spectra of *M*- (red) and *P-h*-poly-**1**-A<sub>10</sub> (blue) cast films on quartz disks from acetone solution, measured at room temperature.



**Fig. S8.** CPL (top) and PL (bottom) spectra of *M*- (red, green) and *P-h*-poly-**1**-A<sub>10</sub> (blue) cast films on quartz disks from acetone solution before (red, blue) and after (green) heating at 100 °C for 24 h, measured at 25 °C. Excited at 350 nm.

## 6. Supporting References

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