# Chemical CD oscillation and chemical resonance phenomena in a competitive

# self-catalytic reaction system: a single temperature oscillation induces CD

# oscillations twice

Tsukasa Sawato, Yasuhiro Shinozaki, Nozomi Saito, and Masahiko Yamaguchi\*

Department of Organic Chemistry, Graduate School of Pharmaceutical Sciences,

Tohoku University, Aoba, Sendai 980-8578, Japan

\*E-mail: yama@m.tohoku.ac.jp, Fax: (+81) 22-795-6811.

# **Supporting Information**

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**General method.** CD and UV-Vis spectra were measured on a JASCO J-720 spectropolarimeter. The path length 0.0217 cm of quartz square cell was used. The cell was custom made by YAZAWA KAGAKU Co., Ltd. for 0.2 mm. The 2 mm cell and Al-made holder are brought into contact and put together into Al-housing, as shown in the following pictures. Data sampling intervals of wavelength and temperature, response time of PMT, and diameter of incident light in CD/UV-vis measurement were 0.2 nm, 0.1 K,  $\leq$  400 µs, and 8 mm, respectively. A position of the thermal sensor and cell in JASCO J-720 spectropolarimeter is shown in the following picture. Dynamic light scattering (DLS) determined at 173° scattering angle was observed by a Zetasizer Nano S90 (Malvern Panalytical Ltd.). The light source was He-Ne laser with a wavelength of 633nm. FFT analysis was performed by Excel 2013.



#### 1. Materials

The compounds (P)-1, (P)-2, (M)-2, (M)-3 were synthesized as described before.<sup>1</sup>

## 2. Determination of hetero-double-helix formation

## <Three-state experiments>

A solution of (P)-1/(M)-3 (1:1) in toluene (total 0.25 mM) was heated to 70 °C for 10 min, and cooled to 5 °C. CD and UV-vis analyses were conducted after settled for 0 min, 80 min, 5 h, 10 h, and 15 h. After 15 h, the solution was allowed to settle at room temperature for 4 days, cooled to 5 °C, and settled for 18 h. Then, CD and UV-vis analyses were conducted.



Figure S1. CD (a) and UV-vis (b) spectra of (*P*)-1/(M)-3 (1:1) in toluene (total 0.25 mM) at different periods of time.

#### <DLS analysis>

A solution of (*P*)-1/(M)-3 (1:1) in toluene (0.25 mM) was heated to 70 °C for 10 min, and DLS analysis was conducted to provide an average diameter of 0.62 nm for random-coil 2A. Then, the solution was cooled to 5 °C, and was allowed to settle for 60 h. DLS analysis was conducted to provide an average diameter of 8.7 nm for hetero-double-helix C.



Figure S2. DLS experiments of (*P*)-1/(M)-3 (1:1) in toluene (total 0.25 mM) at 70 °C (red line) and 5 °C (blue line).

#### <Determination of S-states>

A solution of (*P*)-1/(M)-3 (1:1) in fluorobenzene (total 0.5 mM) was heated at 70 °C for 10 min to provide a random coil 2A solution, and CD and UV-vis analyses were conducted. Then, the solution was cooled to 20 °C for 20 min to provide a hetero-double-helix **B** solution, and CD and UV-vis analyses were conducted. The solution was allowed to settle at room temperature for 3 days and then at 20 °C for 1 h to provide a hetero-double-helix **C** solution, and CD and UV-vis analyses were conducted.

A solution of (*P*)-1/(M)-3 (1:1) in fluorobenzene (total 1.0 mM) was heated at 80 °C for 10 min to provide a random coil 2A solution, and CD and UV-vis analyses were conducted. The solution was cooled to 20 °C for 20 min to provide a hetero-double-helix **B** solution, and CD and UV-vis analyses were conducted. The solution was allowed to settle at room temperature for 4 days and then at 20 °C for 1 h to provide a hetero-double-helix **C** solution, and CD and UV-vis analyses were conducted. Identical CD and UV-vis spectra of 0.5 and 1.0 mM solutions determined the equilibrium shifted S-states of **A**, **B**, and **C** solutions.



Figure S3. CD (a) and UV-vis (b) spectra of (P)-1/(M)-3 (1:1) in fluorobenzene (total 0.5, and 1.0 mM) at different temperatures and times.

#### 3. Thermal hysteresis experiment

#### <Effect of concentration>

A solution of (*P*)-1/(M)-3 (1:1) in toluene (total 0.25 mM) was heated at 90 °C for 10 min. Then, the solution was cooled to -5 °C, and heated to 90 °C at the rate of 2.0 K/min. The process was monitored by  $\Delta \varepsilon$  at 315 nm and  $\varepsilon$  at 315 nm employing CD and UV-vis (Figure 3). The same experiments were conducted at total 0.10, 0.20, 0.25, and 0.50 mM concentrations.



Figure S4.  $\Delta \varepsilon$  (315 nm)/temperature profiles (a) and  $\varepsilon$  (315 nm)/temperature profiles (b) of (*P*)-1/(*M*)-**3** (1:1) in toluene (total 0.10 mM, green line; total 0.20 mM, yellow line; total 0.25 mM, red line; total 0.50 mM, blue line) under heating/cooling rate of 2.0 K/min. The solution was cooled from 90 °C to -5 °C, and then heated to 90 °C.

#### <Effect of oligomer structure>

A solution of (P)-1/(M)-2 (1:1) in toluene (total 0.25 mM) was heated to 90 °C for 10 min. then the solution was cooled to 5 °C, and heated to 90 °C at the rate of 2.0 K/min.

A solution of (*P*)-2/(M)-3 (1:1) in toluene (total 0.25 mM) was heated to 90 °C for 10 min. then the solution was cooled to 5 °C, and heated to 90 °C at the rate of 2.0 K/min.



Figure S5.  $\Delta \varepsilon$  (315 nm)/temperature profiles (a) and  $\varepsilon$  (315 nm)/temperature profiles (b) of (*P*)-1/(*M*)-2 (1:1, green line), (*P*)-1/(*M*)-3 (1:1, red line) and (*P*)-2/(*M*)-3 (1:1, blue line) in toluene (total 0.25 mM) under heating/cooling rate of 2.0 K/min between 90 °C and -5 °C.

#### <Effect of temperature rate>

A solution of (*P*)-1/(M)-3 (1:1) in toluene (total 0.25 mM) was heated to 90 °C for 10 min. Then, the solution was cooled to -5 °C, and heated to 90 °C at the rate of 1.0, 2.0, and 5.0 K/min (Figure 3).

A solution of (*P*)-1/(M)-3 (1:1) in toluene (total 0.25 mM) was heated at 90 °C for 10 min. then the solution was cooled to -5 °C, and heated to 60 °C at the rate of 0.1 K/min.



Figure S6.  $\Delta \varepsilon$  (315 nm)/temperature profiles (a) and  $\varepsilon$  (315 nm)/temperature profiles (b) of (*P*)-1/(*M*)-**3** (1:1) in toluene (total 0.25 mM) under heating/cooling rate of 0.1 K/min. The solution was cooled from 60 °C to -5 °C, and then heated to 60 °C.



# Figure S7. $\Delta \varepsilon$ (315 nm)/temperature profiles (a) and $\varepsilon$ (315 nm)/temperature profiles (b) of (*P*)-1/(*M*)-3 (1:1) in toluene (total 0.25 mM) under heating/cooling rate of 2.0 K/min. The solution was cooled from 90 °C to -5 °C, and then heated to 90 °C (red line); cooled from 70 °C to -10 °C, and then heated to 70 °C (blue line).

#### 4. Temperature oscillation experiment

A solution of (*P*)-1/(M)-3 (1:1) in toluene (total 0.25 mM) was heated to 70 °C for 10 min, cooled to -5 °C at the rate of 2.0 K/min. Then, temperature was oscillated between -5 and 38 °C at the rate of 2.0 K/min (Figure 4a).

The experiment was repeated 3 times to confirm reproducibility as shown in Figure S8.



Figure S8. Temperature oscillation of (*P*)-1/(M)-3 (1:1) in toluene (total 0.25 mM) between 38 and - 5 °C at the rate of 2.0 K/min.



Figure S9. Raw data of temperature oscillation of (P)-1/(M)-3 (1:1) in toluene (total 0.25 mM) between 38 and -5 °C at the rates of 1.0 K/min (yellow line), 2.0 K/min (red line), 3.0 K/min (green line), and 4.0 K/min (purple line).

#### 5. Effect of temperature change rate in temperature oscillation

A solution of (*P*)-1/(*M*)-3 (1:1) in toluene (total 0.25 mM) was heated to 70 °C for 10 min. Then, the solution was cooled to -5 °C, and oscillated between -5 °C and 38 °C at the rate of 1.0 K/min; 2.0 K/min; 3.0 K/min; 4.0 K/min, as shown by  $\Delta \varepsilon$  (315 nm)/time and  $\varepsilon$  (315 nm)/time profiles.



<Oscillation between 38 and -5 °C at 1.0 K/min>

Figure S10. Temperature oscillation of (*P*)-1/(M)-3 (1:1) in toluene (total 0.25 mM) between 38 and -5 °C at the rate of 1.0 K/min.



Figure S11. Temperature oscillation of (P)-1/(M)-3 (1:1) in toluene (total 0.25 mM) between 38 and -5 °C at the rate of 2.0 K/min. Profiles (a) and (c) are identical with Figures 4a and 4c, respectively.



Figure S12. Temperature oscillation of (*P*)-1/(M)-3 (1:1) in toluene (total 0.25 mM) between 38 and -5 °C at the rate of 3.0 K/min.



Figure S13. Temperature oscillation of (*P*)-1/(M)-3 (1:1) in toluene (total 0.25 mM) between 38 and -5 °C at the rate of 4.0 K/min.

#### 6. Effect of temperature range in temperature oscillation

A solution of (*P*)-1/(*M*)-3 (1:1) in toluene (total 0.25 mM) was heated to 70 °C for 10 min. Then, the solution was cooled to -5 °C, and oscillated between -5 °C and 30 °C; -5 °C and 36 °C; -5 °C and 40 °C; -5 °C and 45 °C at the rate of 2.0 K/min, as shown by  $\Delta \varepsilon$  (315 nm)/time profiles.



<Oscillation between 45 and -5 °C>

Figure S14. Temperature oscillation between 45 and -5 °C of (P)-1/(M)-3 (1:1) in toluene (total 0.25 mM) at the rate of 2.0 K/min.

<Oscillation between 40 and -5 °C>



Figure S15. Temperature oscillation between 40 and -5 °C of (P)-1/(M)-3 (1:1) in toluene (total 0.25 mM) at the rate of 2.0 K/min.



Figure S16. Temperature oscillation between 36 and -5 °C of (P)-1/(M)-3 (1:1) in toluene (total 0.25 mM) at the rate of 2.0 K/min.



Figure S17. Temperature oscillation between 30 and  $-5 \degree C$  of (*P*)-1/(*M*)-3 (1:1) in toluene (total 0.25 mM) at the rate of 2.0 K/min.

#### 7. Determination of equilibrium state

#### <Cooling experiments>

Solutions of (*P*)-1/(*M*)-3 (1:1) in toluene (total 0.25 mM) were heated at 70 °C for 10 min. Then, the solutions were cooled to 60, 50, 40, and 30 °C, and were allowed to settle for 30 min. Then,  $\Delta \epsilon$  (315 nm) were obtained (Figure S17). At 40 °C, the solution was allowed to settle for 4 days, and confirmed not to change by  $\Delta \epsilon$  (315 nm). The experiment was conducted by cooling the solution to 25 °C and allowing to settle for 10 days. Then,  $\Delta \epsilon$  (315 nm) and CD spectrum were obtained (Figures S17 and S18c).

#### <Heating experiments>

Solution of (*P*)-1/(M)-3 (1:1) in toluene (total 0.25 mM) were heated to 70 °C for 10 min. Then, the solutions were cooled to 5 °C, and was allowed to settle for 4 to 8 days, which provided CD spectra for C (Figure S18a). Then, the solutions were heated to 20, 25, and 30 °C, and were allowed to settle for 3 to 5 days. CD spectra were obtained during the process (Figures S18b, 18c, and S18d). Another solution was heated at 90 °C for 10 min, snap-cooled to -35 °C for 15 min, and heated to 25 °C. The solution was allowed to settle for 10 days, and CD spectrum was obtained (Figure S18c).

An equilibrium curve was obtained by the above experiments (Figure S17).



Figure S18. Equilibrium states for of (*P*)-1/(*M*)-3 (1:1) in toluene (total 0.25 mM) shown by  $\Delta \varepsilon$  (315 nm)/temperature profiles. Cooling experiment (red diamonds): Solutions were heated to 70 °C, cooled to 60, 50, 40, and 30, and were allowed to settle for 30 min. Then,  $\Delta \varepsilon$  (315 nm) were obtained. A solution was cooled to 25 °C, and was allowed to settle for 10 days. Then,  $\Delta \varepsilon$  (315 nm) and CD spectrum were obtained. Heating experiment (blue circles): Solutions were heated to 70 or 90 °C, cooled to 5 or -35 °C, heated to 30, 25, and 20 °C, and were allowed to settle for several days. Then, CD spectra were obtained (Figure S18). Arrows indicate changes of  $\Delta \varepsilon$  (315 nm) under isothermal condition.



Figure S19. CD spectra of (*P*)-1/(M)-3 (1:1) in toluene (total 0.25 mM) by heating experiment at 5 °C (a), 20 °C (b), 25 °C (c), and 30 °C (d). CD spectrum obtained by snap-cooling experiment at 25 °C was added in Figure S18c.

#### 8. Domain analysis

 $\Delta \epsilon$  (315 nm)/time profiles of (*P*)-**1**/(*M*)-**3** (1:1) in toluene (total 0.25 mM) under different heating/cooling rates (Figures 6b and S19) were taken from Figures S9a, S10a, S11a, and S12a. Figure 6b is a part of Figure S19.



Figure S20. Detail results of Figure 6b.  $\Delta \epsilon$  (315 nm)/time profiles of (*P*)-1/(*M*)-3 (1:1) in toluene (total 0.25 mM) between -5 and 38 °C under heating/cooling rate of 1.0 K/min; 2.0 K/min; 3.0 K/min; 4.0 K/min. Temperature was decreased from 70 °C to -5 °C. Domains, where self-catalytic 2A+B-to-2B (red shade) and 2A+C-to-2C (blue shade) reactions predominate, are shown. Equilibrium curve is also shown (black dashed line).

### 9. References

1. M. Shigeno, Y. Kushida, M. Yamaguchi, J. Am. Chem. Soc. 2014, 136, 7972-7980.