Supporting Information

Self-catalysis in Thermal Hysteresis during Random-coil to Helix-dimer Transition of Sulfonamidohelicene Tetramer

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General method. CD spectra were measured on a JASCO J-720 spectropolarimeter. The path length 0.113 cm of quartz round cell was used. The curve fitting method was conducted by non-linear least-squares fit using Kyplot version 2.0 beta.

1. Synthesis

(*M*)-**1** was synthesized as described in our recent work.[14a)]

2. Equilibrium state

S-random-coil state in 1,3-difluorobenzene (5.0×10^{-4} M), where all the molecules are random-coil, was determined previously, $\Delta\varepsilon = -150$ $cm^{-1}M^{-1}$.[14a)] S-helix-dimer, where all the molecules are helix-dimer not containing random-coil was also determined previously, $\Delta\varepsilon =$ +980 $cm^{-1}M^{-1}$.[14a)]

All the following CD experiments were conducted quickly changing temperatures from one temperature to another.

The equilibrium states at 40, 45, 50, 55, and 60 °C were described in the reference.[14a)] The equilibrium states at 43 and 35 °C were determined as follows. A solution of (*M*)-**1** in 1,3-difluorobenzene (2.0 mL, 5.0×10^{-4} M) was prepared by dissolving (*M*)-**1** (3.2 mg) in 1,3-difluorobenzene (2.0 mL) with sonication and heating at 65 °C for 10 min. A part of the solution (0.8 mL) was transfered to a round cell, heated at 70 °C (60 min), cooled at 50 °C (20 min), cooled at 43 °C (480 min), and cooled at 35 °C (190 min). At each temperature, the solution was allowed to settle and analyzed by CD for the times described in parentheses, when $\Delta\varepsilon$ change was less than 2 $M^{-1}cm^{-1}$ within a 10 min period. Then, the equilibrium states at 43 °C with $\Delta\varepsilon =$ +840 $cm^{-1}M^{-1}$ and 35 °C with +950 $cm^{-1}M^{-1}$ were obtained (Figure S1a).

The equilibrium states in 6.0×10^{-4} M solution at 45 and 50 °C were determined as follows. A solution of (*M*)-**1** in 1,3-difluorobenzene (2.0 mL, 6.0×10^{-4} M) was prepared by dissolving (*M*)-**1** (3.8 mg) in 1,3-difluorobenzene (2.0 mL) with sonication and heating at 65 °C for 10 min. A part of the solution (0.8 mL) was transfered to a round cell, heated at 70 °C (60 min), cooled at 50 °C (20 min), cooled at 45 °C (480 min), and heated at 50 °C (130 min). At each temperature, the solution was allowed to settle and analyzed by CD for the times described in parentheses, when $\Delta\varepsilon$ change was less than 2 $M^{-1}cm^{-1}$ within a 10 min period. Then, the equilibrium states at 45 °C with $\Delta\varepsilon =$ +900 $cm^{-1}M^{-1}$ and 50 °C with +750 $cm^{-1}M^{-1}$ were obtained (Figure S1b).

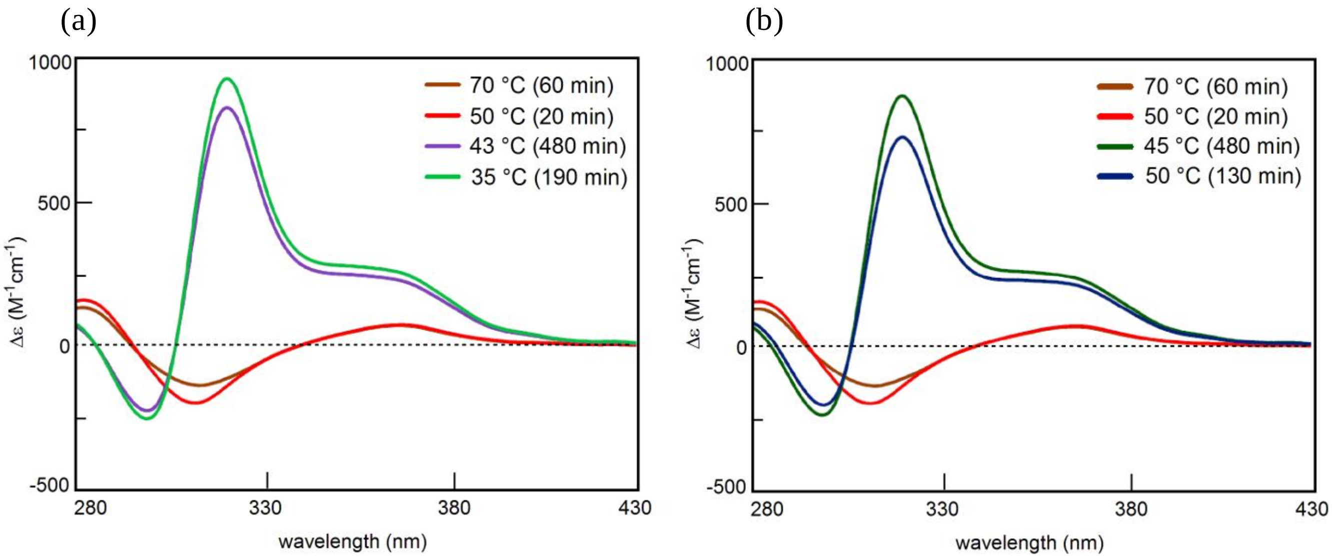


Figure S1. Equilibrium states of (*M*)-**1** followed by CD spectra in 1,3-difluorobenzene (a) at 5.0 x 10^{-4} M and (b) at 6.0 x 10^{-4} M. CD spectra were obtained at each temperature after settled for the time shown in parenthesis.

3. Stability of random-coil and helix-dimer solution

A solution of (*M*)-**1** in 1,3-difluorobenzene (2.0 mL, 5.0×10^{-4} M) was prepared by dissolving (*M*)-**1** (3.2 mg) in 1,3-difluorobenzene (2.0 mL) with sonication and heating at 65 °C for 10 min. A part of the solution (0.8 mL) was transfered to a round cell, heated at 70 °C (60 min), cooled at 50 °C (20 min), cooled at 45 °C (480 min), and heated at 50 °C (90 min), providing a helix-dimer solution. The solution was analyzed by CD at 50 °C for 180 min (Figure S1a). Another part of the solution (0.8 mL) was transfered to a round cell, heated at 70 °C (60 min), cooled at 50 °C, providing an S-random-coil solution (Figure S1b). The solution was analyzed by CD at 50 °C for 180 min. No change in CD spectra were observed during the period in both solutions (Figure 3 and S2).

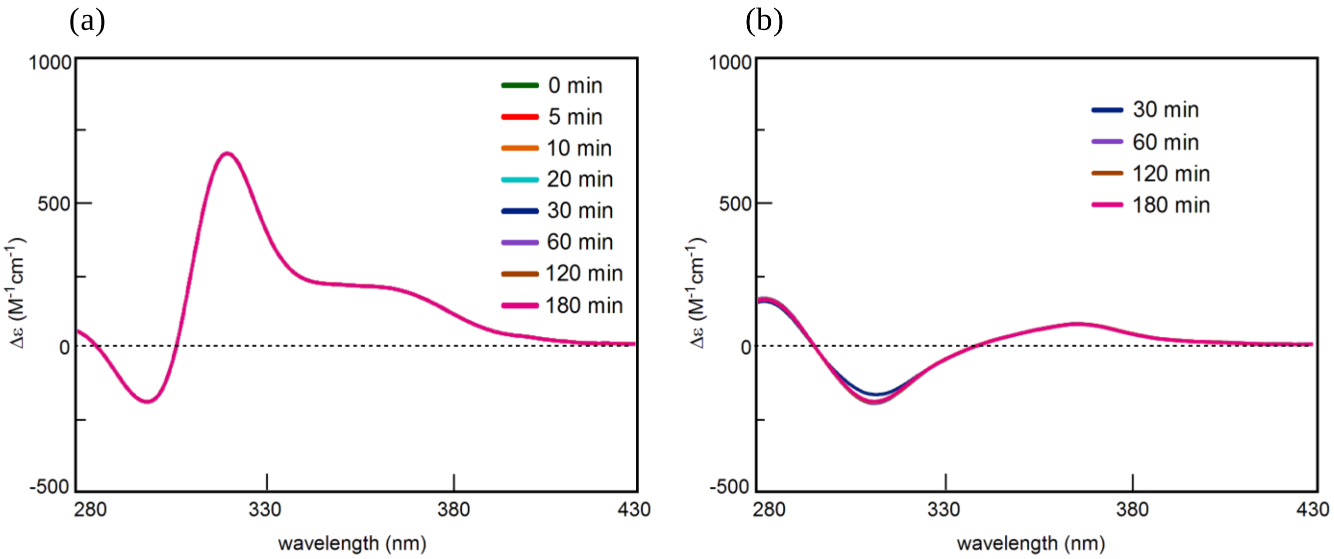
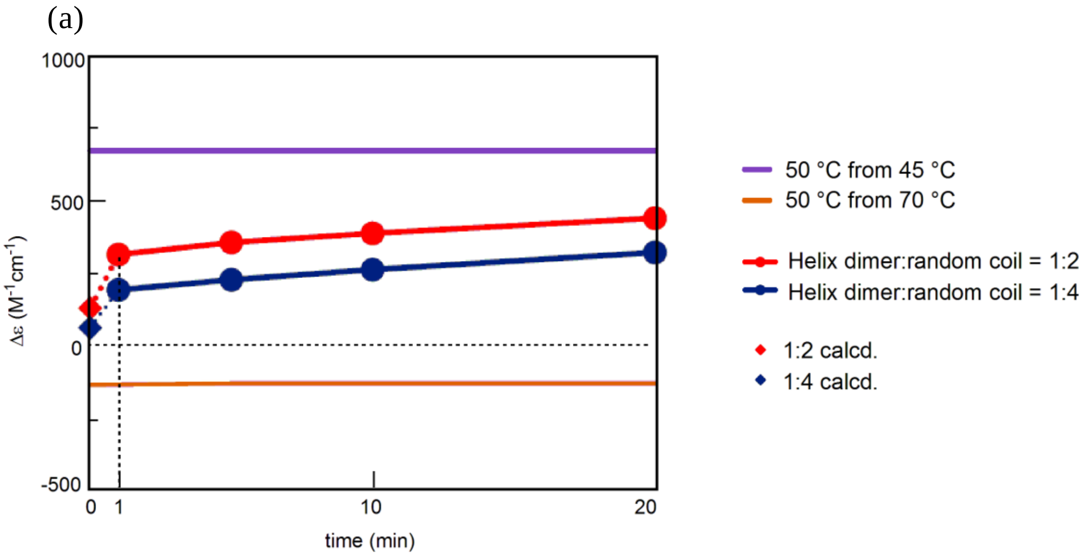


Figure S2. Stability of (*M*)-**1** followed by CD spectra (5.0 x 10^{-4} M, 50 °C) in 1,3-difluorobenzene. (a) A helix-dimer solution and (b) a random-coil solution.

4. Mixing experiment

A solution of (*M*)-**1** in 1,3-difluorobenzene (2.0 mL, 5.0×10^{-4} M) was prepared by dissolving (*M*)-**1** (3.2 mg) in 1,3-difluorobenzene (2.0 mL) with sonication and heating at 65 °C for 10 min. A part of the solution (0.2 or 0.4 mL) was transfered to a round cell, heated at 70 °C (60 min), cooled at 50 °C (20 min), cooled at 45 °C (480 min), and heated at 50 °C (90 min), providing a helix-dimer solution. Another portion of the solution was transferred in a flask, heated at 70 °C (10 min), and cooled at 50 °C (10 min), providing an S-random-coil solution. To the helix-dimer solution in the cell adjusted to 50 °C, the S-random-coil solution was added in a ratio of 1:2 (helix-dimer:random-coil = 0.4 mL:0.8 mL) or 1:4 (helix-dimer:random-coil = 0.2 mL:0.8 mL), and the solution was allowed to settle for 180 min for CD analysis (Figures 3 and S3).



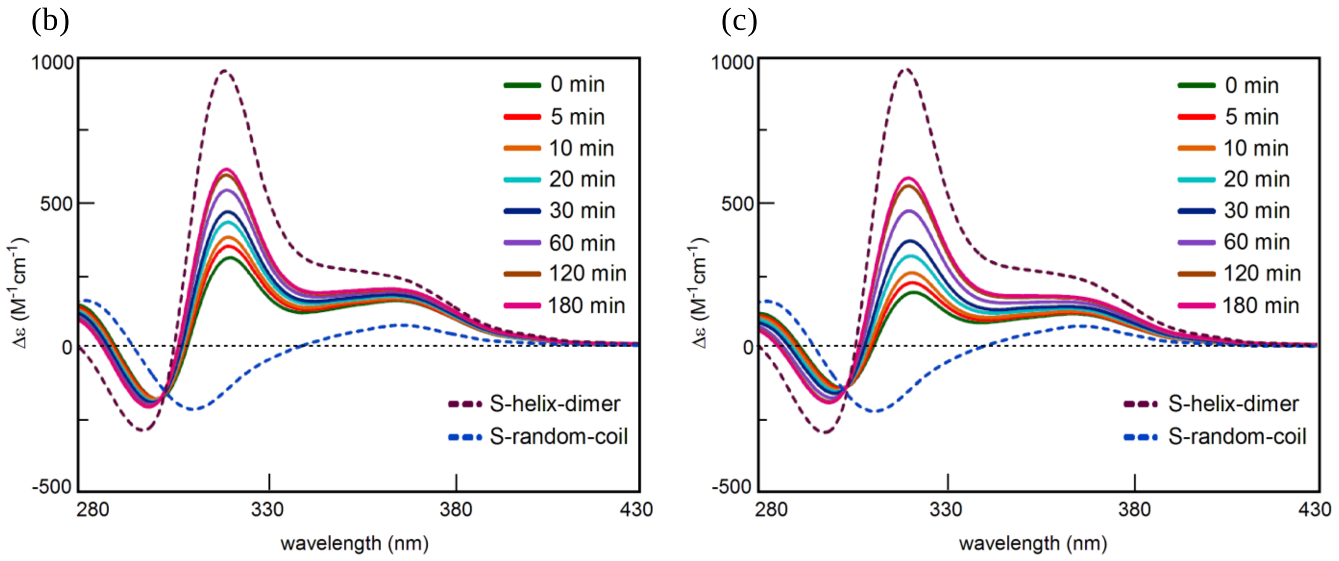
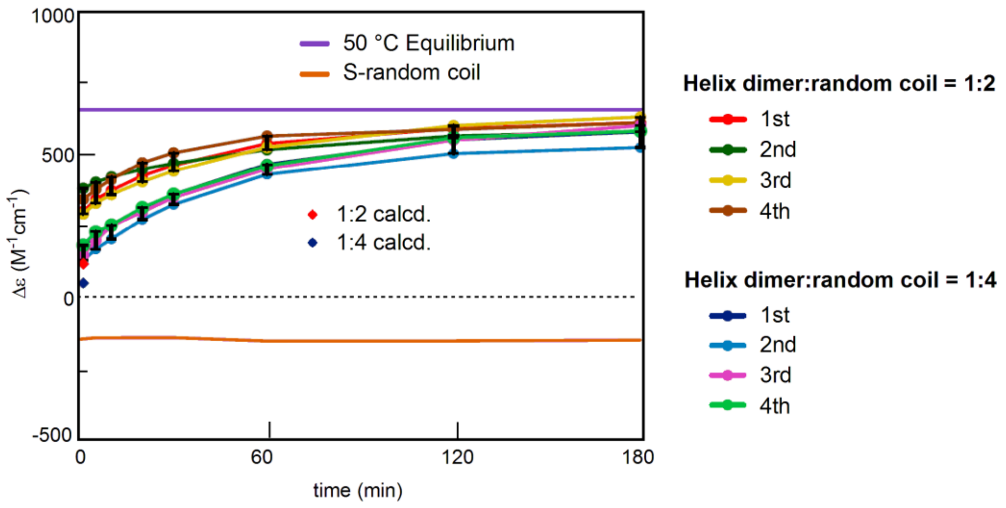


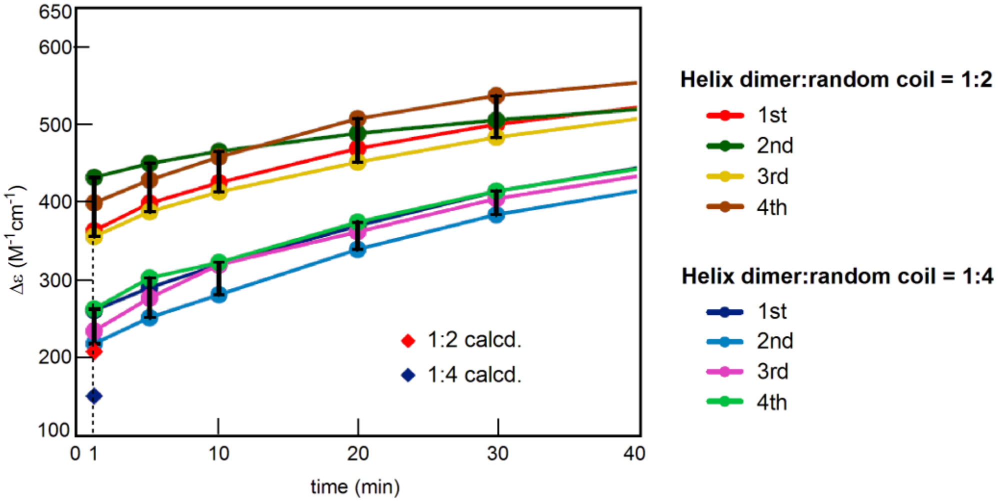
Figure S3. (a) The initial part of Δε (320 nm)/time profiles shown in Figure 3. (b and c) Reaction course followed by CD spectra (5.0×10^{-4} M, 50 °C) of (*M*)-**1** in 1,3-difluorobenzene. (b) A 1:2 mixture (helix-dimer:random-coil = 0.4 mL:0.8 mL). (c) A 1:4 mixture (helix-dimer:random-coil = 0.2 mL:0.8 mL). CD spectra of S-helix-dimer and S-random-coil were obtained in our previous work [14a].

<Reproducibility>

(a)

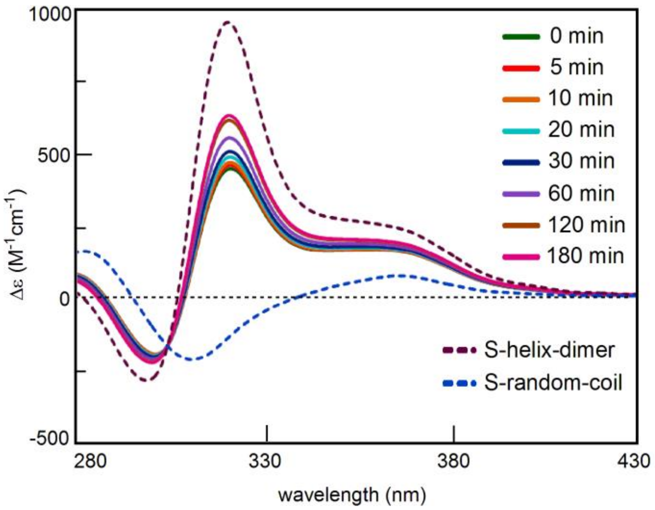


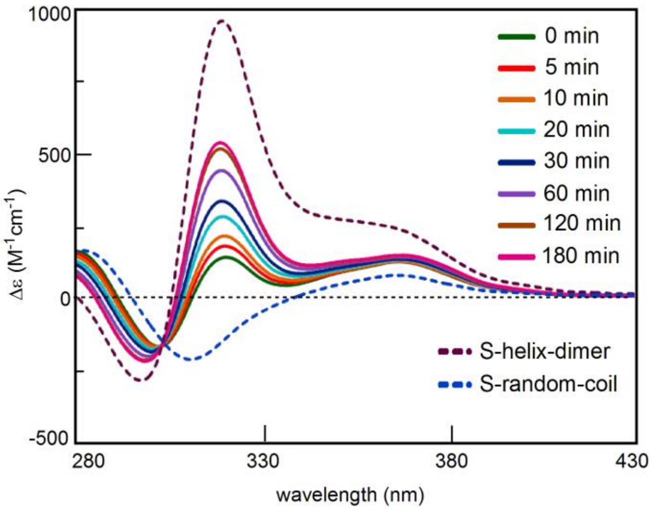
(b)


650
600
500
400
300
200
100
Δε (M⁻¹cm⁻¹)
0
1
10
20
30
40
time (min)
1:2 calcd.
1:4 calcd.
Helix dimer:random coil = 1:2
1st
2nd
3rd
4th
Helix dimer:random coil = 1:4
1st
2nd
3rd
4th

(c)

(d)


1000
500
0
-500
Δε (M⁻¹cm⁻¹)
280
330
380
430
wavelength (nm)
0 min
5 min
10 min
20 min
30 min
60 min
120 min
180 min
S-helix-dimer
S-random-coil


1000
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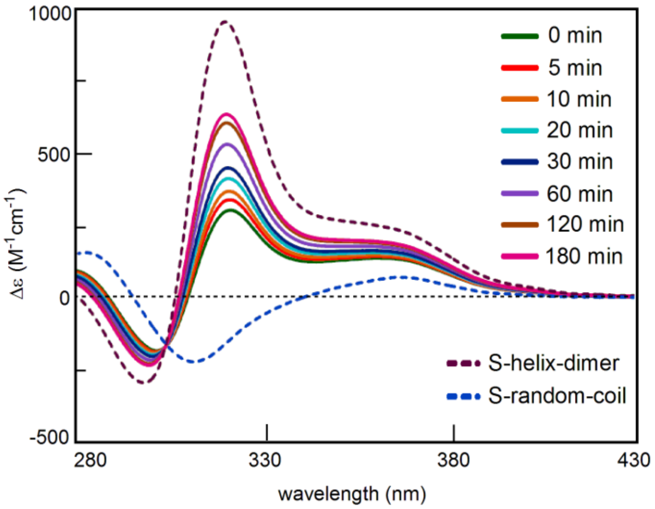
Δε (M⁻¹cm⁻¹)
280
330
380
430
wavelength (nm)
0 min
5 min
10 min
20 min
30 min
60 min
120 min
180 min
S-helix-dimer
S-random-coil

(e)

(f)


1000
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Δε (M⁻¹cm⁻¹)
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wavelength (nm)
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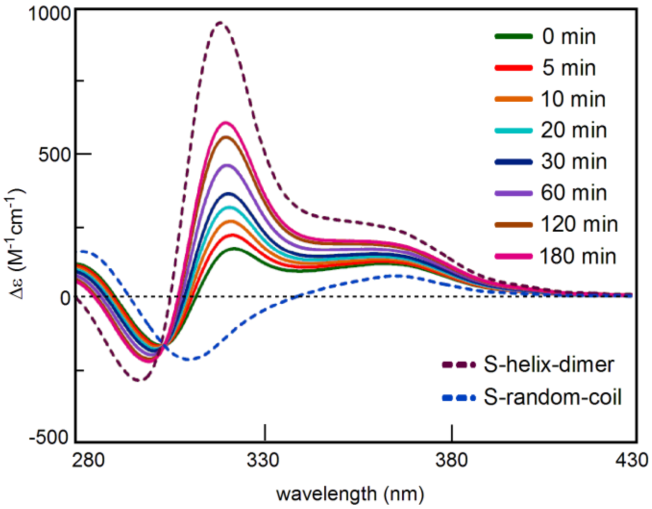
180 min
S-helix-dimer
S-random-coil


1000
500
0
-500
Δε (M⁻¹cm⁻¹)
280
330
380
430
wavelength (nm)
0 min
5 min
10 min
20 min
30 min
60 min
120 min
180 min
S-helix-dimer
S-random-coil

(g)

(h)

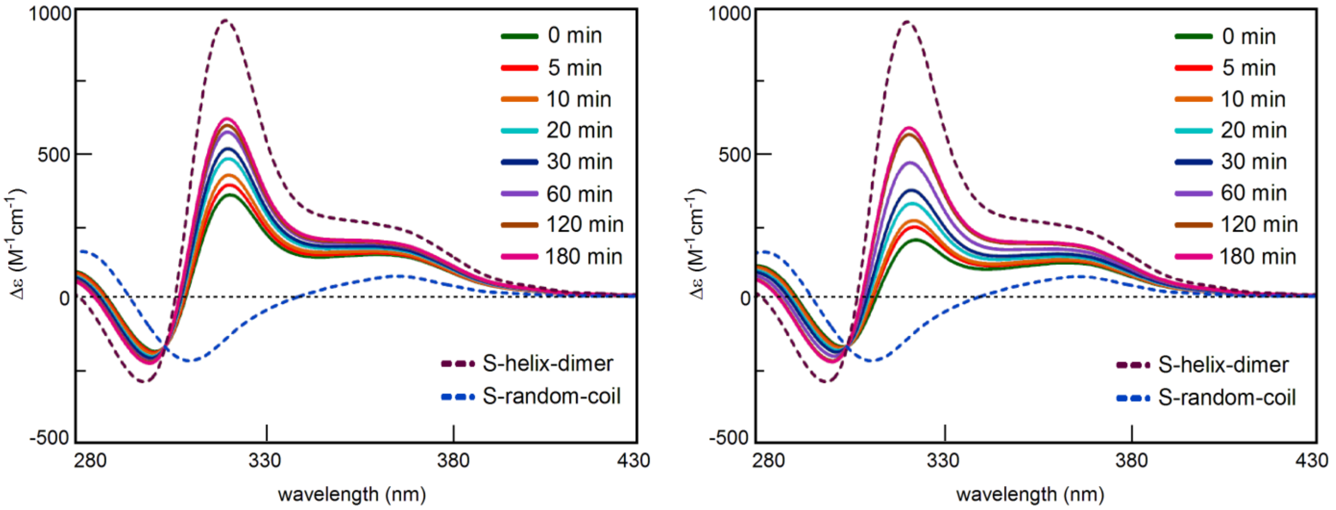


Figure S4. Reproducibility in the mixing experiments (a) Δε (320 nm)/time profiles (5.0×10^{-4} M, 50 °C) of (*M*)-**1** in 1,3-difluorobenzene. Experimets of 1:2 mixture and 1:4 mixture were conducted four times, respectively. The red, green, yellow, and brown dots show Δε change of a 1:2 mixture (helix-dimer:random-coil = 0.4 mL:0.8 mL). The blue, pale blue, pink, and pale green dots show Δε change of a 1:4 mixture (helix-dimer:random-coil = 0.2 mL:0.8 mL). The red and blue lines are drawn between the points. The red and blue squares show calculated values, based on the initial ratio of the mixture of helix-dimer:random-coil = 1:2 and 1:4, respectively. The equilibrium and S-random-coil state at 50 °C were obtained in Figure 3, and shown by purple and orange lines, respectively. The scale bars are drawn as black lines between maximum and minimum values at each time. (b) Expansion of (a). (c, d, e, f, g, and h) Reaction course followed by CD spectra (5.0×10^{-4} M, 50 °C) of (*M*)-**1** in 1,3-difluorobenzene. (c, e, and g) A 1:2 mixture (helix-dimer:random-coil = 0.4 mL:0.8 mL). (d, f, and h) A 1:4 mixture (helix-dimer:random-coil = 0.2 mL:0.8 mL). CD spectra of S-helix-dimer and S-random-coil were obtained in our previous work [14a)].

<Effect of temperature>

Mixing experiments at 35, 40, 43, and 45 °C. A solution of (*M*)-**1** in 1,3-difluorobenzene (2.0 mL, 5.0×10^{-4} M) was prepared by dissolving (*M*)-**1** (3.2 mg) in 1,3-difluorobenzene (2.0 mL) with sonication and heating at 65 °C for 10 min. A part of the solution (0.4 mL) was transfered to a round cell, heated at 70 °C (60 min), cooled at 50 °C (20 min), and cooled at 45 °C (480 min), providing a helix-dimer solution. Another portion (0.8 mL) of the solution was transferred to a flask, heated at 70 °C (10 min), and cooled at 50 °C (10 min), providing an S-random-coil solution. The S-random-coil solution was cooled at 45 °C for 5 min, and was added to the helix-dimer solution in the cell in a ratio of 1:2 (helix-dimer random-coil = 0.4 mL:0.8 mL), and the solution was settled for 180 min for CD analysis (Figure S5d and S7).

The same experiment was conducted at 35, 40, and 43 °C (Figures S5a, S5b, S5c, and S7).

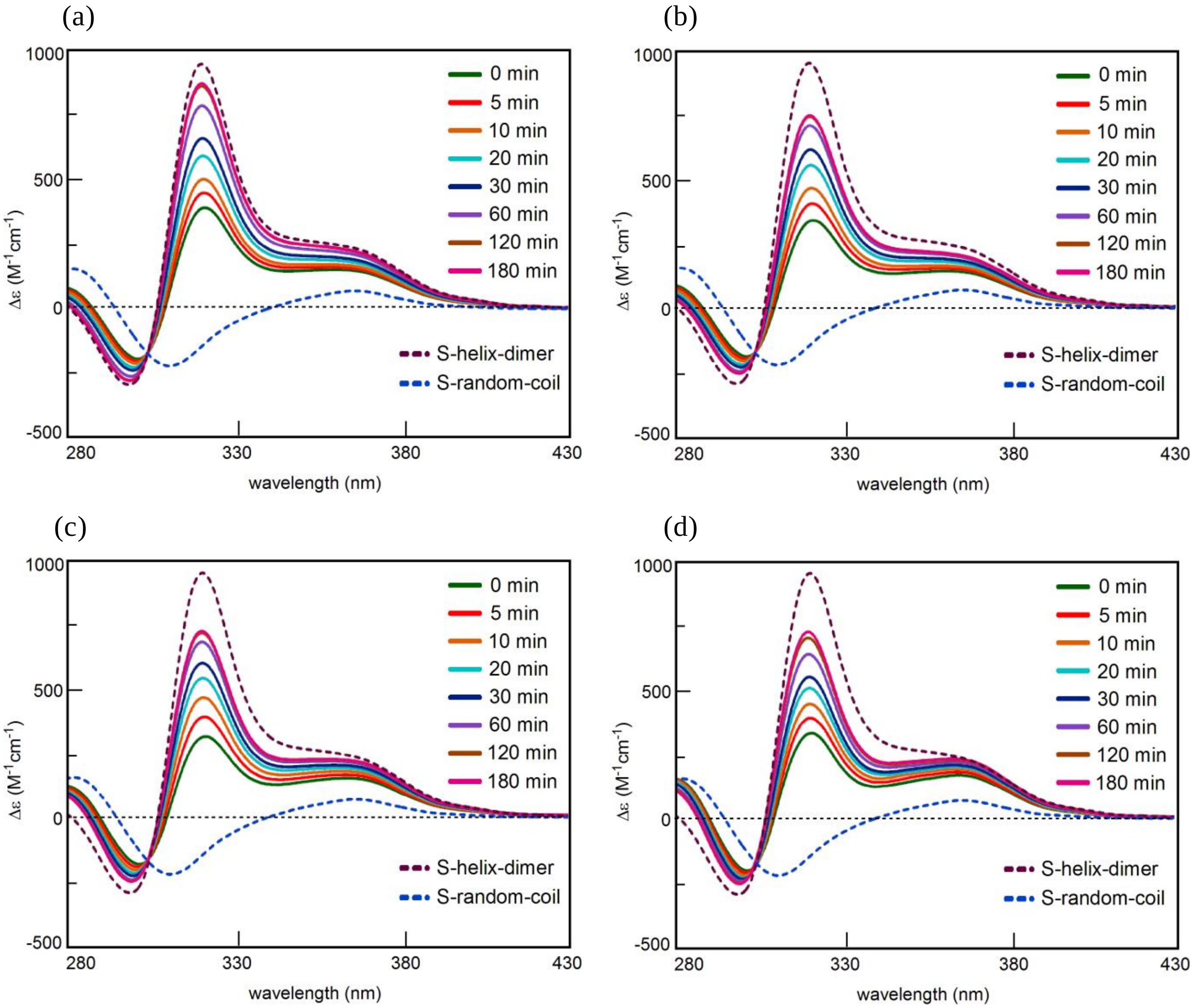


Figure S5. Reacion course followed by CD spectra (5.0 x 10^{-4} M) of (*M*)-**1** in 1,3-difluorobenzene at (a) 35 °C, (b) 40 °C, (c) 43 °C, and (d) 45 °C after mixing a helix-dimer and random-coil solution in a ratio of 1:2 (helix-dimer:random-coil = 0.4 mL:0.8 mL). CD spectra of S-helix-dimer and S-random-coil were obtained in our previous work [14a)].

Mixing experiments at 55 and 60 °C. A solution of (*M*)-**1** in 1,3-difluorobenzene (2.0 mL, 5.0×10^{-4} M) was prepared by dissolving (*M*)-**1** (3.2 mg) in 1,3-difluorobenzene (2.0 mL) with sonication and heating at 65 °C for 10 min. A part of the solution (0.4 mL) was transfered to a round cell, heated at 70 °C (60 min), cooled at 50 °C (20 min), cooled at 45 °C (480 min), and heated at 55 °C (120 min), providing a helix-dimer solution. Another portion (0.8 mL) of the solution was transferred to a flask, heated at 70 °C (10 min), and cooled at 55 °C (10 min), providing an S-random-coil solution. The S-random-coil solution was added to the helix-dimer solution in the cell in a ratio of 1:2 (helix-dimer:random-coil = 0.4 mL:0.8 mL), and the solution was settled for 180 min for CD analysis (Figures S6a and S7).

The same experiment was conducted at 60 °C, in which a helix-dimer solution was prepared by treating (*M*)-**1** solution (0.4 mL) in a round cell as follows: Heated at 70 °C (60 min), cooled at 50 °C (20 min), cooled at 45 °C (480 min), and heated at 60 °C (400 min) (Figures S6b and S7).

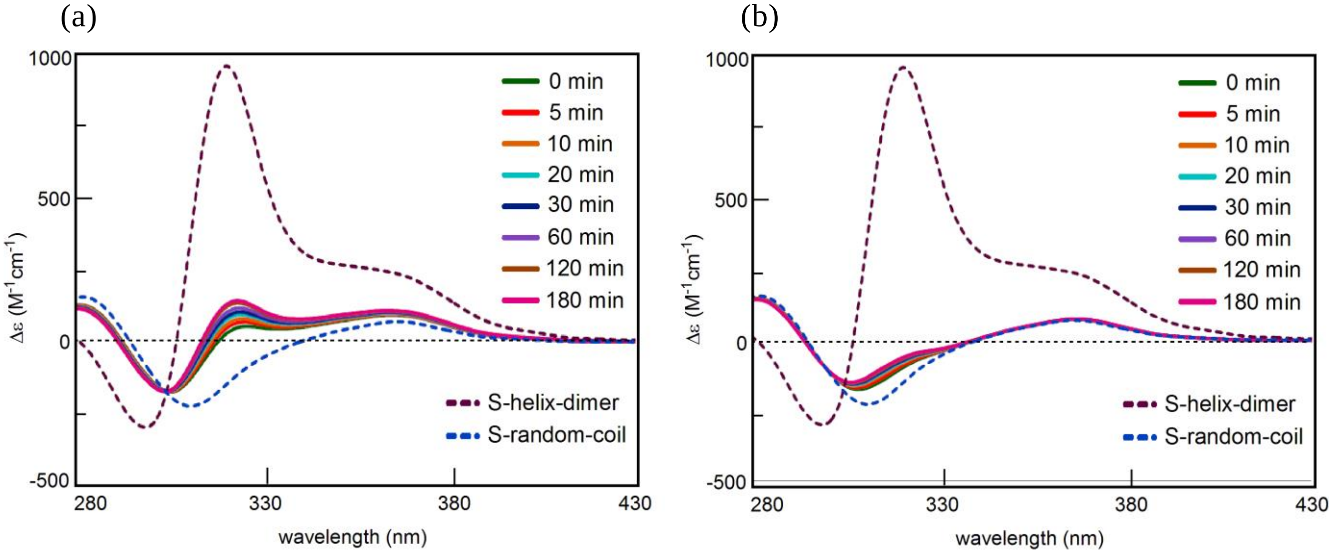


Figure S6. Reaction course followed by CD spectra (5.0 x 10^{-4} M) of (*M*)-**1** in 1,3-difluorobenzene at (a) 55 °C and (b) 60 °C after mixing the helix-dimer and random-coil solutions in a ratio of 1:2 (helix-dimer:random-coil = 0.4 mL:0.8 mL). CD spectra of S-helix-dimer and S-random-coil were obtained in our previous work [14a)].

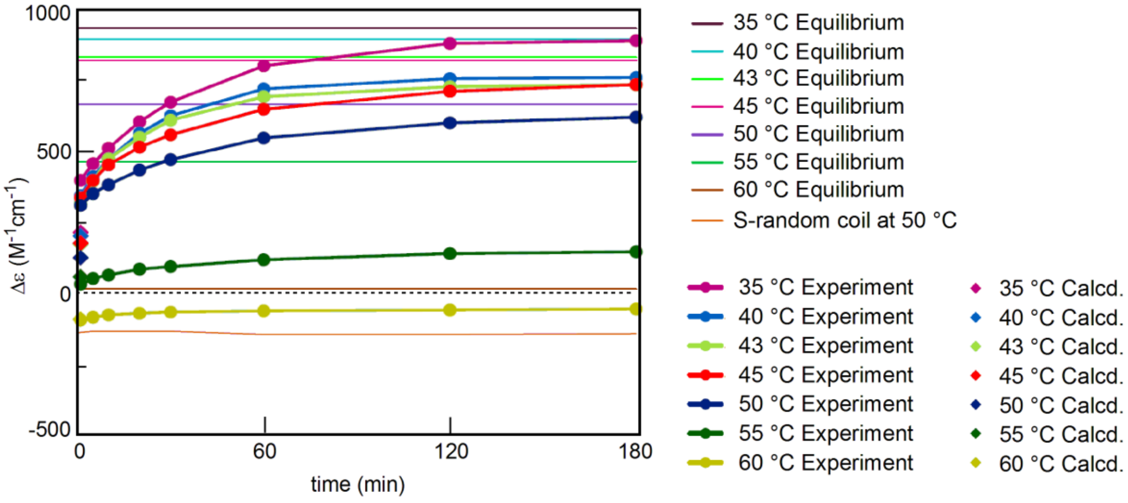


Figure S7. Summary of Δε (320 nm)/time profiles for (*M*)-**1** (1,3-difluorobenzene, 5.0 x 10^{-4} M) in the mixing experiments of helix-dimer and random-coil solutions (1:2). The dots show Δε change at 35, 40, 43, 45, 50, 55, and 60 °C. The lines are drawn between the points. The square is calculated value at each temperature, based on the initial ratio of helix-dimer:random-coil = 1:2. The straight lines show the equilibrium state at 35, 40, 43, 45, 50, 55, and 60 °C. The equilibrium and S-random-coil state at 50 °C were obtained in Figure 3, and shown by purple and orange lines, respectively.

<Effect of concentration>

A solution of (*M*)-**1** in 1,3-difluorobenzene (2.0 mL, 6.0×10^{-4} M) was prepared by dissolving (*M*)-**1** (3.8 mg) in 1,3-difluorobenzene (2.0 mL) with sonication and heating at 65 °C for 10 min. A part of the solution (0.4 mL) was transfered to a round cell, heated at 70 °C (60 min), cooled at 50 °C (20 min), cooled at 45 °C (480 min), and heated at 50 °C (130 min), providing a helix-dimer solution. Another portion (0.8 mL) of the solution was transferred to a flask, heated at 70 °C (10 min), and cooled at 50 °C (10 min), providing an S-random-coil solution. The S-random-coil solution was added to the helix-dimer solution in the cell in a ratio of 1:2 (helix-dimer:random-coil = 0.4 mL:0.8 mL), and the mixture was settled for 180 min at 50 °C for CD analysis (Figures S8 and S9).

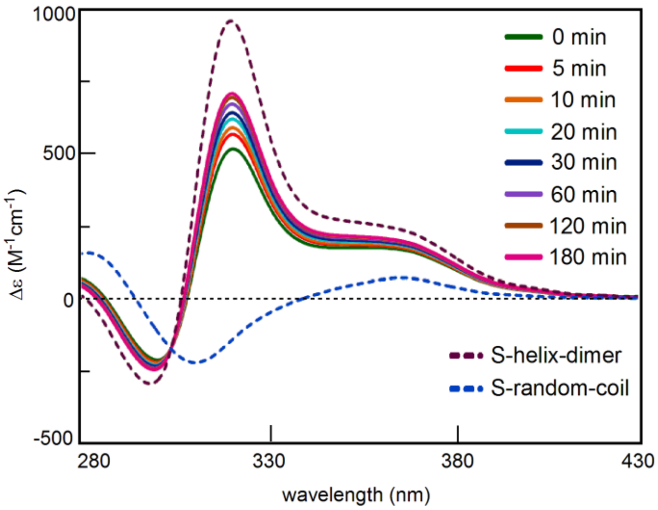


Figure S8. Reaction course followed by CD spectra (6.0 x 10^{-4} M, 50 °C) of (*M*)-**1** in 1,3-difluorobenzene after mixing helix-dimer and random-coil solutions in a ratio of 1:2 (helix-dimer:random-coil = 0.4 mL:0.8 mL). CD spectra of S-helix-dimer and S-random-coil were obtained in our previous work [14a)].

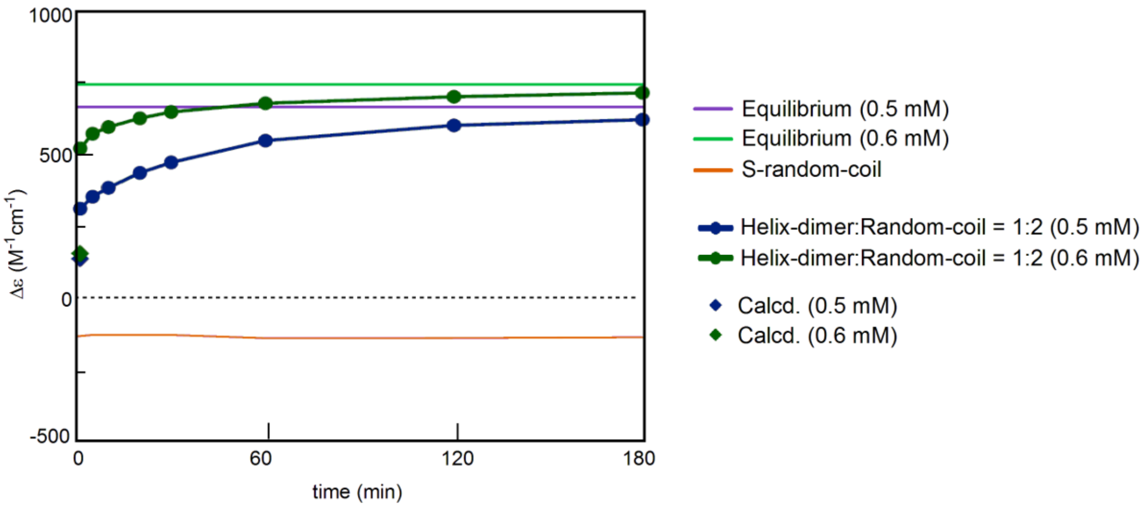


Figure S9. Concentration effect shown by Δε (320 nm)/time profiles for (*M*)-**1** (1,3-difluorobenzene, 5.0 x 10^{-4} and 6.0 x 10^{-4}M) after mixing helix-dimer and random-coil solutions in a 1:2 ratio. Blue and green dots show Δε change at 0.5 mM and 0.6 mM, respectively. Blue and green lines are drawn between the points. Blue and green squares are calculated values based on the initial ratio of helix-dimer : random-coil = 1:2. The purple and pale green lines show equilibrium state at 5.0 x 10^{-4} M and 6.0 x 10^{-4}M, respectively. The equilibrium and S-random-coil state at 50 °C were obtained in Figure 3, and shown by purple and orange lines, respectively.

5. Resetting random-coil after mixing experiment

A solution of (*M*)-**1** in 1,3-difluorobenzene (2.0 mL, 5.0×10^{-4} M) was prepared by dissolving (*M*)-**1** (3.2 mg) in 1,3-difluorobenzene (2.0 mL) with sonication and heating at 65 °C for 10 min. A part of the solution (0.4 mL) was transfered to a round cell, heated at 70 °C (60 min), cooled at 50 °C (20 min), cooled at 45 °C (480 min), and heated at 50 °C (90 min), providing a helix-dimer solution. Another portion of the solution was transferred in a flask, heated at 70 °C (10 min), and cooled at 50 °C (10 min), providing an S-random-coil solution. At 50 °C, to the helix-dimer solution in the cell, S-random-coil solution was added in a ratio of 1:2 (helix-dimer : random-coil = 0.4 mL:0.8 mL), and the solution was settled at 50 °C for 180 min for CD analysis (Figure S10a). Then, the solution was heated at 70 °C (70 °C-2) (60 min), cooled at 50 °C (50 °C-2) (20 min), and cooled at 45 °C (45 °C-2) (480 min). Heating at 70 °C-2 regenerated S-random-coil, and cooling at 50 °C-2 provided helix-dimer as indicated by CD analysis (Figure S10b).

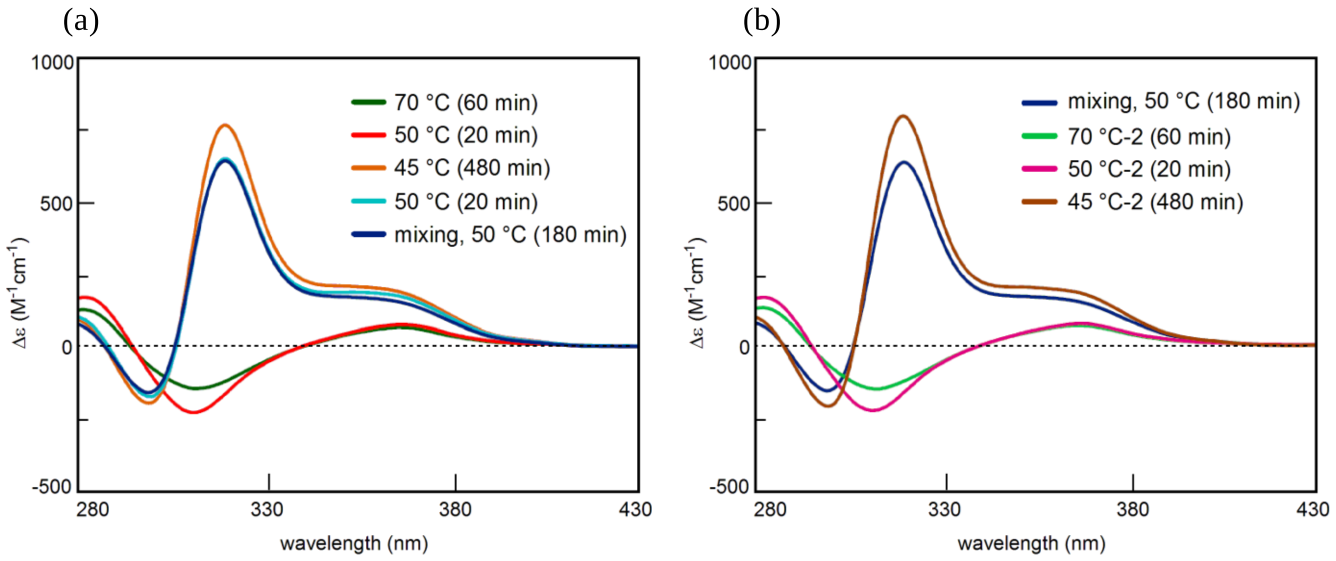


Figure S10. Resetting experiment shown by CD (5.0 x 10^{-4} M) spectra of (*M*)-**1** in 1,3-difluorobenzene. (a) The mixing experiment was conducted as described above. (b) After mixing experiment (helix-dimer:random-coil = 1:2) at 50 °C, the solution was settled for 180 min. Then, the solution was heated at 70 °C for 60 min (70 °C-2), cooled at 50 °C for 20 min (50 °C-2), cooled at 45 °C (45 °C-2), and allowed to settle for 480 min. CD spectrum was obtained at each temperature after settled for the time shown in parentheses.

6. Background experiment

A solution of (*M*)-**1** in 1,3-difluorobenzene (2.0 mL, 5.0×10^{-4} M) was prepared by dissolving (*M*)-**1** (3.2 mg) in 1,3-difluorobenzene (2.0 mL) with sonication and heating at 65 °C for 10 min. The solution was heated at 70 °C (60 min), cooled at 50 °C (20 min), cooled at 45 °C (480 min), and heated at 50 °C (90 min), providing a helix-dimer solution. A portion of the helix-dimer solution (0.4 mL) was transferred to a round cell at 50 °C, to which another portion of the helix-dimer solution (0.8 mL) was added at 50 °C, and CD spectra was obtained at 50 °C for 180 min (Figure S11a). No change of spectra was observed.

A solution of (*M*)-**1** in 1,3-difluorobenzene (2.0 mL, 5.0×10^{-4} M) was prepared by dissolving (*M*)-**1** (3.2 mg) in 1,3-difluorobenzene (2.0 mL) with sonication and heating at 65 °C for 10 min. The solution was heated at 70 °C (60 min), and cooled at 50 °C (20 min), providing an S-random-coil solution. A portion of the S-random-coil solution (0.4 mL) was transferred to a round cell at 50 °C, to which another portion of the S-random-coil solution (0.8 mL) was added, and CD analysis was conducted for 180 min (Figure S11b). No change of spectra was observed.

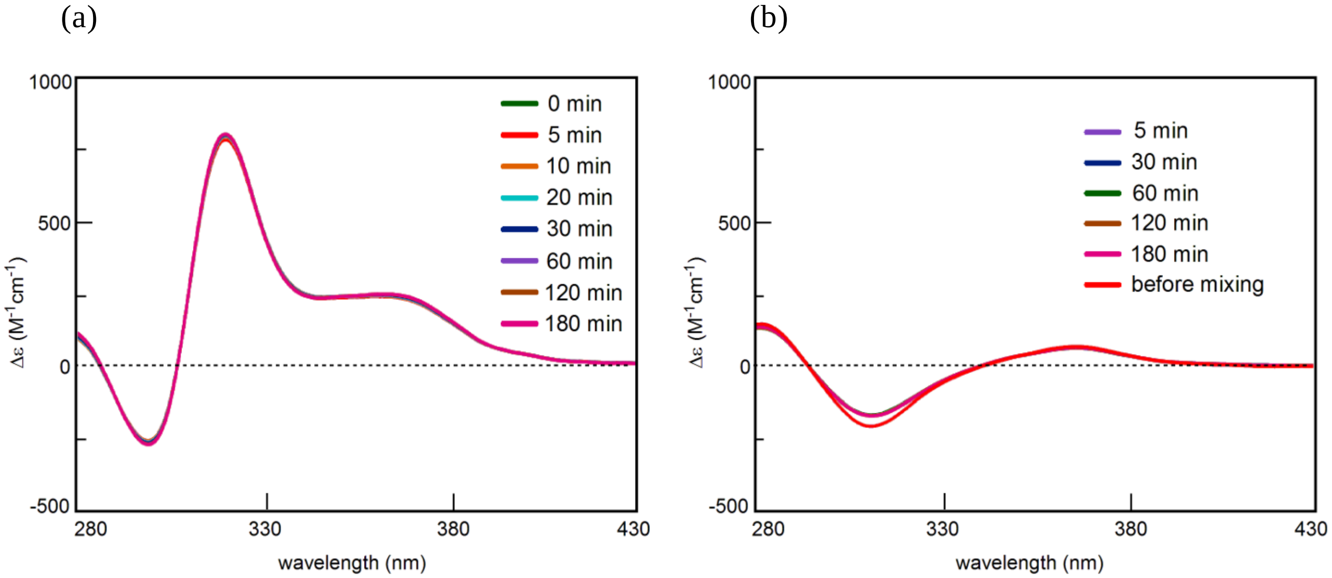


Figure S11. Background experiments followed by CD spectra (5.0 x 10^{-4} M, 50 °C) of (*M*)-**1** in 1,3-difluorobenzene. (a) A 1:2 mixture (0.4 mL:0.8 mL) of a helix-dimer solution and a helix-dimer solution. (b) A 1:2 mixture (0.4 mL:0.8 mL) of a random-coil solution and a random-coil solution.

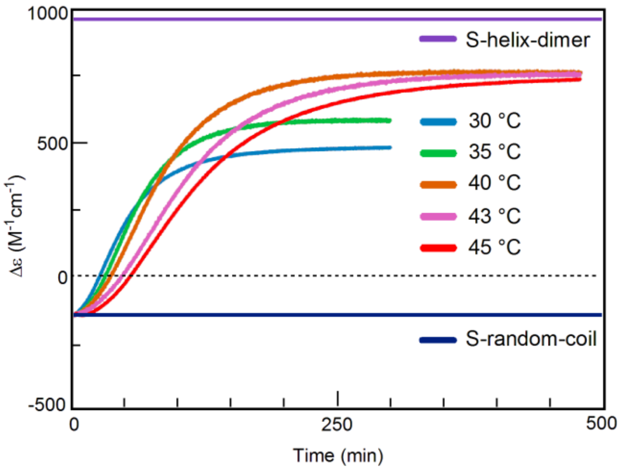
7. Kinetic analysis

A solution of (*M*)-**1** in 1,3-difluorobenzene (2.0 mL, 5.0×10^{-4} M) was prepared by dissolving (*M*)-**1** (3.2 mg) in 1,3-difluorobenzene (2.0 mL) with sonication and heating at 65 °C for 10 min. A part (0.8 mL) of the solution was transfered to a round cell, heated at 70 °C (60 min), and cooled at 50 °C (20 min), providing an S-random-coil solution. Then, the solution was cooled to either 45 °C (480 min), 43 °C (480 min), 40 °C (480 min), 35 °C (300 min), or 30 °C (300 min) and settled at each temperature during the time in parentheses. The structural change was monitored by Δε at 320 nm (Figure S12a). The reproducibility at 40 °C was confirmed 3 times (Figure S13).

Experiments to obtain time-dependent CD spectra were conducted. A solution of (*M*)-**1** in 1,3-difluorobenzene (2.0 mL, 5.0×10^{-4} M) was prepared by dissolving (*M*)-**1** (3.2 mg) in 1,3-difluorobenzene (2.0 mL) with sonication and heating at 65 °C for 10 min. A part (0.8 mL) of the solution was transfered to a round cell, heated at 70 °C (60 min), and cooled at 50 °C (20 min), providing an S-random-coil solution. Then, the solution was cooled to either 45 °C (450 min), 43 °C (420 min), 40 °C (420 min), 35 °C (300 min), or 30 °C (300 min) and settled at each temperature during the time in parentheses. The structural change was monitored by CD analyses (Figure S14).

The rearranged [**A**]/time profiles were obtained from Δε/time profiles, and were compared with calculated profiles obtained by curve fitting according to the equation 6.

(a)



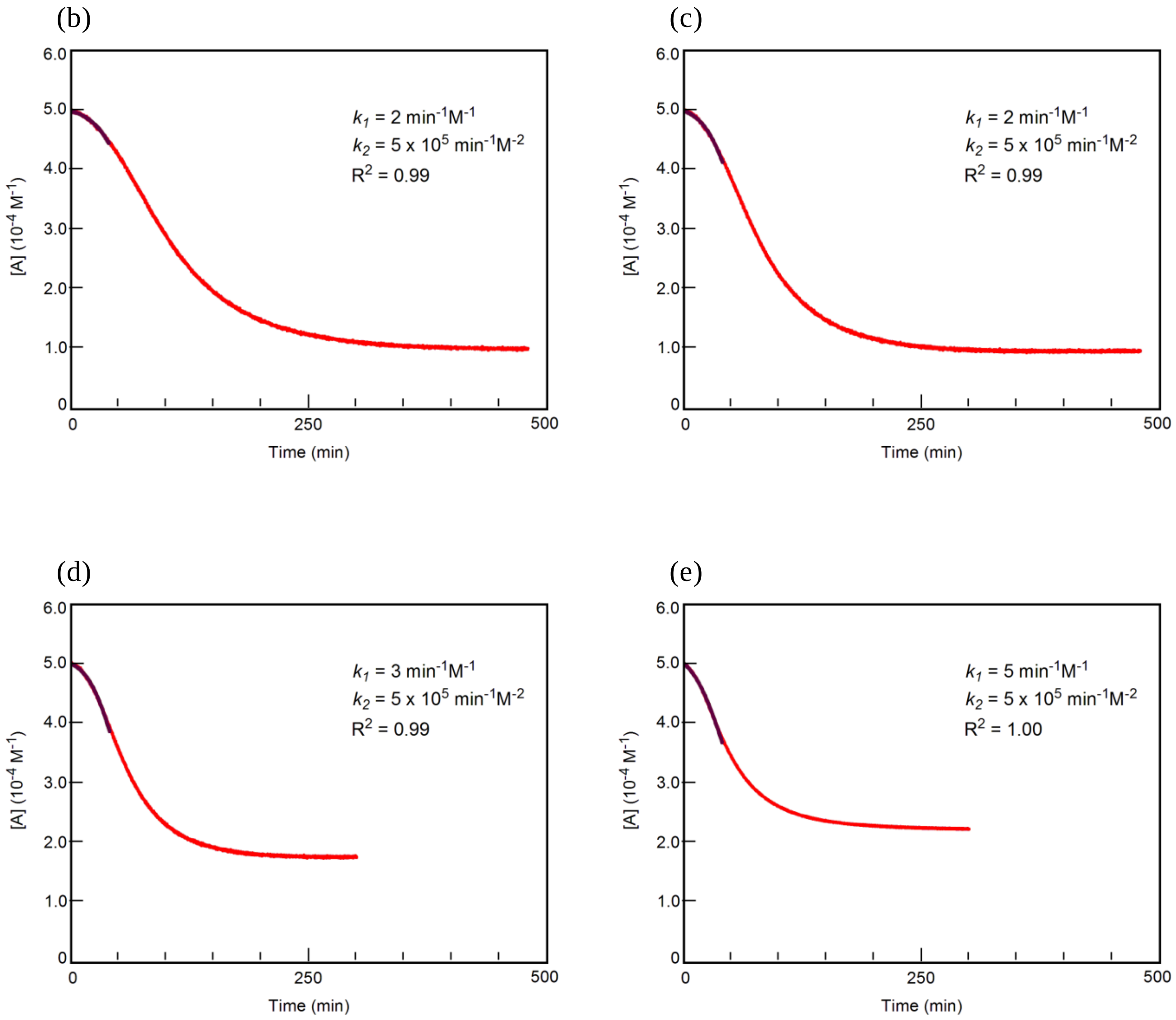


Figure S12. (a) Δε (320 nm)/time profiles (1,3-difluorobenzene, 5.0 x 10^{-4} M) of (*M*)-**1**. The solution was first heated at 70 °C (60 min), and cooled at 50 °C (20 min). Then the solution was cooled either at 43 °C (480 min), 40 °C (480 min), 35 °C (300 min) or 30 °C (300 min), and allowed to settle at each temperature. The Δε values of S-helix-dimer and S-random-coil was obtained in our previous work [14a)]. (b-e) Constant-temperature experiments at 43 °C (b), 40 °C (c), 35 °C (d), and 30 °C (e) are shown by [**A**]/time profiles (1,3-difluorobenzene, 5.0 x 10^{-4}). Calculated [**A**]/time profiles are shown in purple lines, which are obtained by curve-fitting of experimental [**A**]/time profiles between 0-40 min.

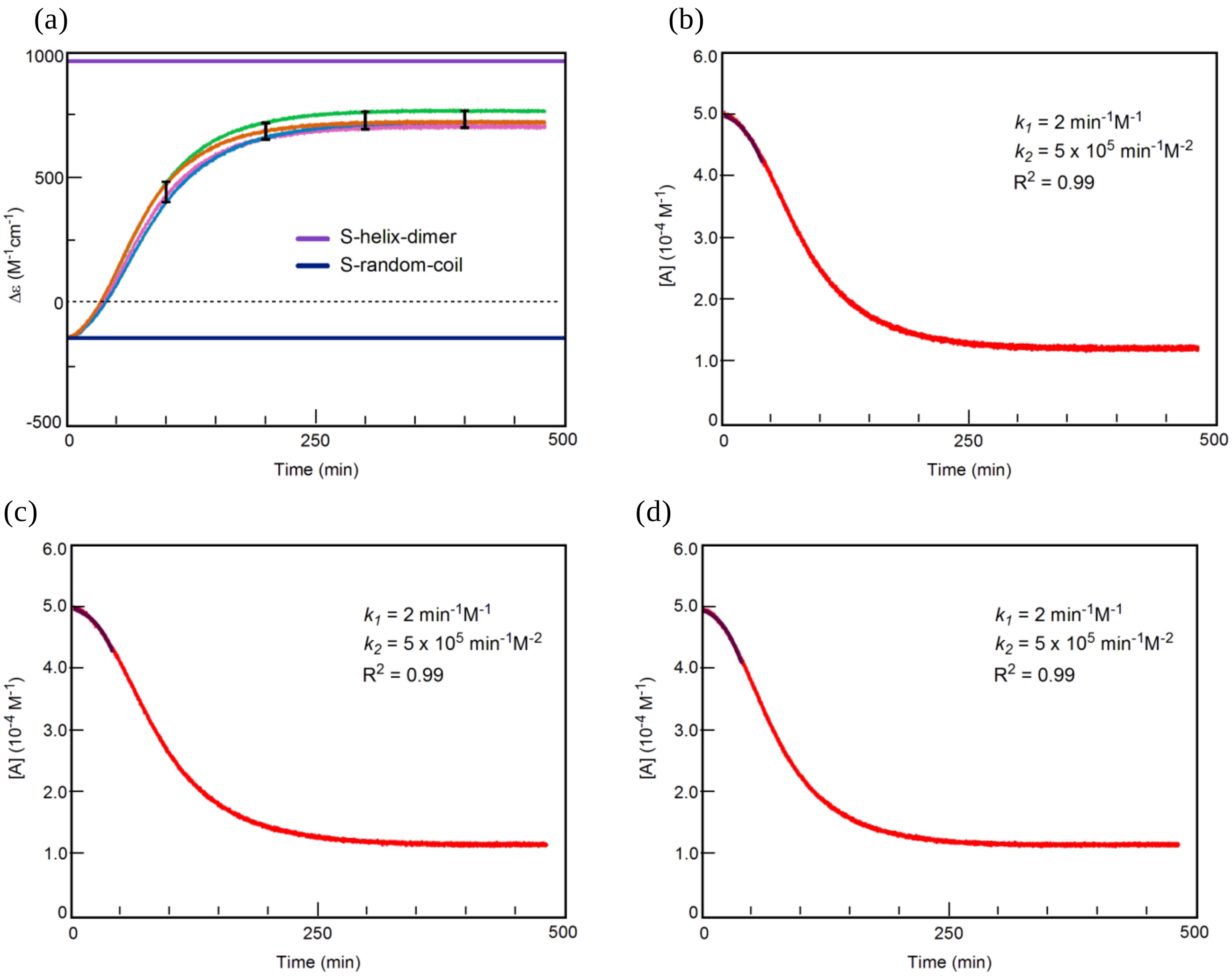
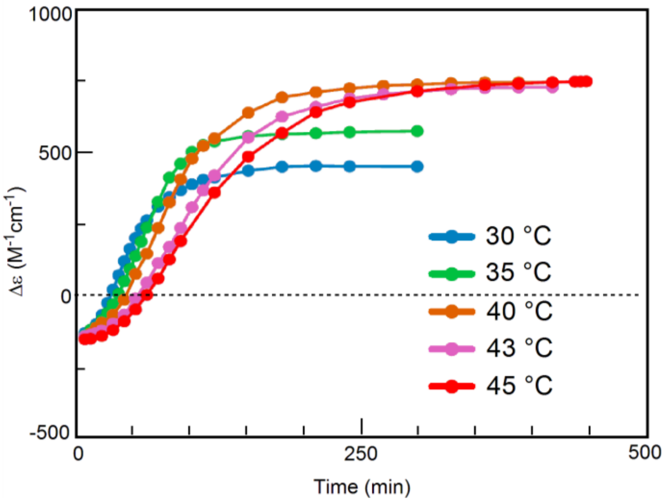
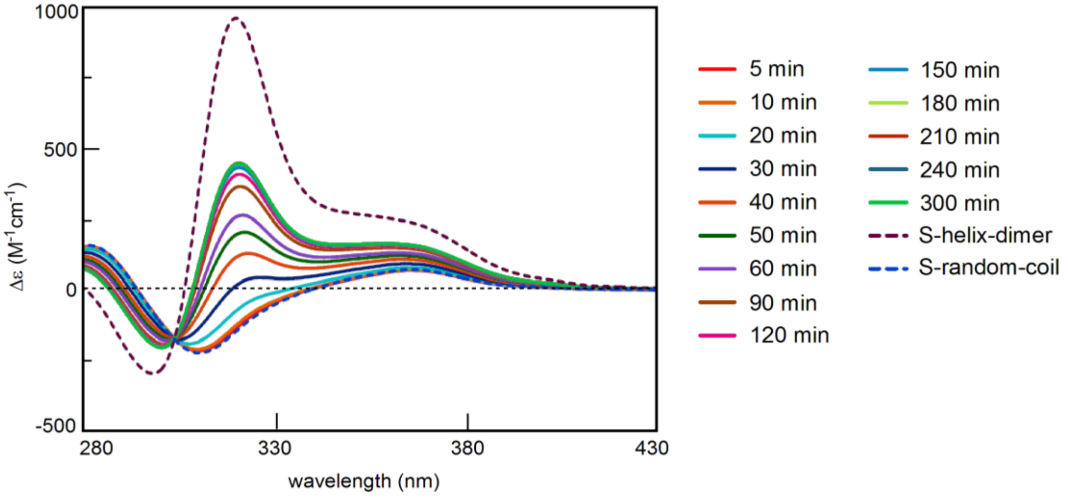


Figure S13. (a) Δε (320 nm)/time profiles (1,3-difluorobenzene, 5.0 x 10^{-4} M, 40 °C) of (*M*)-**1**. The solution was first heated at 70 °C (60 min), and cooled at 50 °C (20 min). Then the solution was cooled at 40 °C, and allowed to settle for 480 min. The same experiments were conducted 4 times (Figure S13b, S13c, and S13d). The scale bars are drawn as black lines between maximum and minimum values at 100, 200, 300, and 400 min. The Δε values of S-helix-dimer and S-random-coil was obtained in our previous work [14a)]. (b-d) Constant-temperature experiments at 40 °C on (b) second, (c) third, and (d) forth trial are shown by [**A**]/time profiles (1,3-difluorobenzene, 5.0 x 10^{-4}). Calculated [**A**]/time profiles are shown in purple lines, which are obtained by curve-fitting of experimental [**A**]/time profiles between 0-40 min.

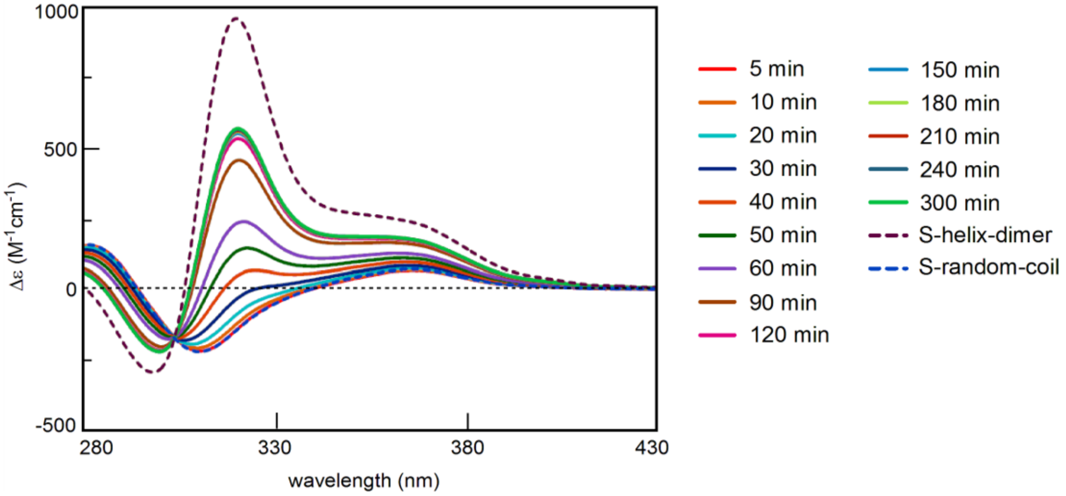
(a)


1000
500
0
-500
Δε (M-1cm-1)
0
250
500
Time (min)
30 °C
35 °C
40 °C
43 °C
45 °C

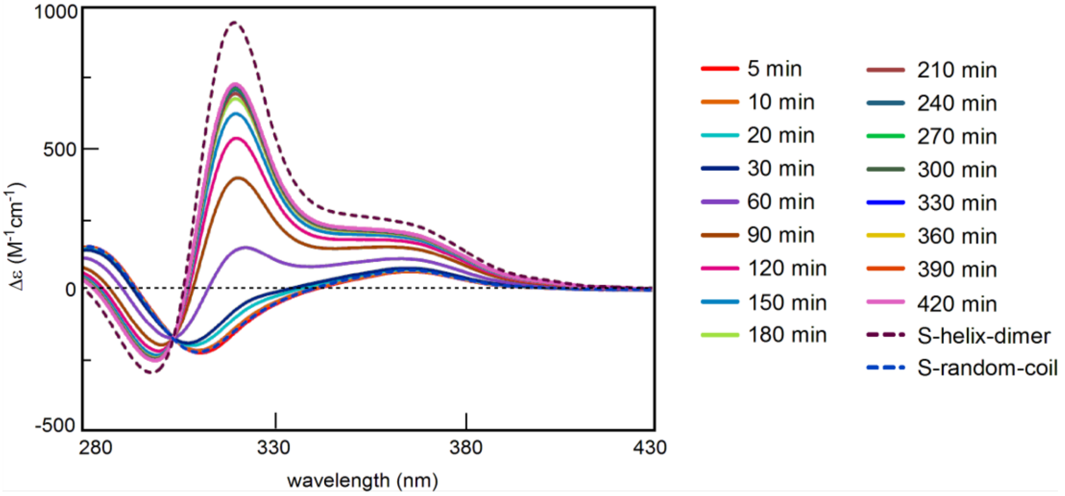
(b)


1000
500
0
-500
Δε (M-1cm-1)
280
330
380
430
wavelength (nm)
5 min
10 min
20 min
30 min
40 min
50 min
60 min
90 min
120 min
150 min
180 min
210 min
240 min
300 min
S-helix-dimer
S-random-coil

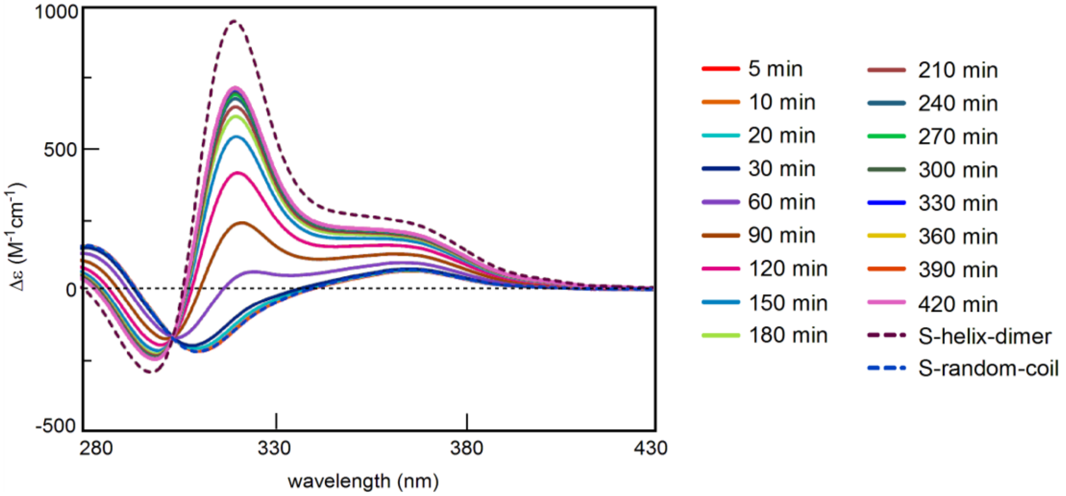
(c)


1000
500
0
-500
Δε (M-1cm-1)
280
330
380
430
wavelength (nm)
5 min
10 min
20 min
30 min
40 min
50 min
60 min
90 min
120 min
150 min
180 min
210 min
240 min
300 min
S-helix-dimer
S-random-coil

(d)


1000
500
0
-500
Δε (M^{-1}cm^{-1})
280
330
380
430
wavelength (nm)
5 min
10 min
20 min
30 min
60 min
90 min
120 min
150 min
180 min
210 min
240 min
270 min
300 min
330 min
360 min
390 min
420 min
S-helix-dimer
S-random-coil

(e)


1000
500
0
-500
Δε (M^{-1}cm^{-1})
280
330
380
430
wavelength (nm)
5 min
10 min
20 min
30 min
60 min
90 min
120 min
150 min
180 min
210 min
240 min
270 min
300 min
330 min
360 min
390 min
420 min
S-helix-dimer
S-random-coil

(f)

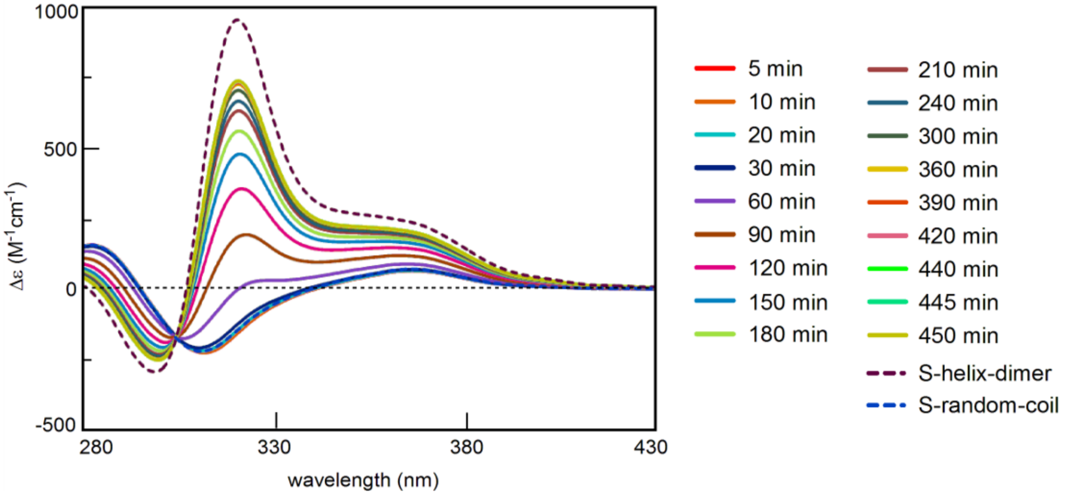

1000
500
0
-500
Δε (M^{-1}cm^{-1})
280
330
380
430
wavelength (nm)
5 min
10 min
20 min
30 min
60 min
90 min
120 min
150 min
180 min
210 min
240 min
300 min
360 min
390 min
420 min
440 min
445 min
450 min
S-helix-dimer
S-random-coil

Figure S14. (a) Δε (320 nm)/time profiles (1,3-difluorobenzene, 5.0 x 10^{-4} M) of (*M*)-**1**. The solution was first heated at 70 °C (60 min), and cooled at 50 °C (20 min). Then the solution was cooled at 30 °C, 35 °C, 40 °C, 43 °C, and 45 °C, respectively, each of which was allowed to settle for 300-480 min. (b-f) Reaction course followed by CD spectra (1,3-difluorobenzene, 5.0 x 10^{-4} M) of (*M*)-**1** in 1,3-difluorobenzene at 30 °C (b), 35 °C (c), 40 °C (d), 43 °C (e), and 45 °C (f), which was obtained in the same experiment shown in Figure S14a. CD spectra of S-helix-dimer and S-random-coil were obtained in our previous work [14a)].

<Determination of the initial rate constants k_1 and k_2 in the formation of helix-dimer B from random-coil A>

Bimolecular reaction (reaction 1) and self-catalytic reaction (reaction 2) are considered.

$$2\text{ Random-coil }(\mathbf{A}) \overset{k_1}{\rightarrow} \text{Helix-dimer }(\mathbf{B}) \qquad \text{(reaction 1)}$$

$$2\text{ Random-coil }(\mathbf{A}) + \text{Helix-dimer }(\mathbf{B}) \overset{k_2}{\rightarrow} 2\text{ Helix-dimer }(\mathbf{B}) \qquad \text{(reaction 2)}$$

The observed Δε ($\Delta\varepsilon_{obs}$) is described as shown in equation 1, in which [**A**] and [**B**] are concentrations of **A** and **B**, respectively.

$$\Delta\varepsilon_{obs} = \Delta\varepsilon_A([\mathbf{A}]/[\mathbf{A}_0])+\Delta\varepsilon_B(2[\mathbf{B}]/[\mathbf{A}_0]) \qquad \text{(eq. 1)}$$

The total concentration [$\mathbf{A}_0$] of **A** and **B** is defined as shown in equation 2.

$$[\mathbf{A}_0] = [\mathbf{A}] + 2[\mathbf{B}] \qquad \text{(eq. 2)}$$

Substitution for [**B**] in equation 1 and solving for [**A**] gives equation 3.

$$[\mathbf{A}] = [\mathbf{A}_0](\Delta\varepsilon_{obs} - \Delta\varepsilon_B)/(\Delta\varepsilon_A - \Delta\varepsilon_B) \qquad \text{(eq. 3)}$$

The observed $\Delta\varepsilon_{obs}$ is transformed to [**A**] using equation 3 with [$\mathbf{A}_0$] = 5.0 x 10^{-4} M, $\Delta\varepsilon_A$ = –150 $cm^{-1}M^{-1}$, and $\Delta\varepsilon_B$ = +980 $cm^{-1}M^{-1}$.

The reaction rate of the formation of helix-dimer **B** from random-coil **A** can be expressed in equations 4, where [**A**], [**B**], k_1, and k_2 are concentration of **A**, concentration of **B**, rate constant of reaction 1, and rate constant of reaction 2, respectively. Equation 4 shows the rate containing both reaction 1 and reaction 2.

$$-\mathrm{d}[\mathbf{A}]/\mathrm{dt} = k_1 [\mathbf{A}]^2 + k_2 [\mathbf{A}]^2[\mathbf{B}] \quad \text{(eq. 4)}$$

Solving the differential equation 4 gives equation 5 as a function of time *t*.

$t = [2/(2k_1 + k_2[\mathbf{A}_0])]\{[(1/[\mathbf{A}]) - (1/[\mathbf{A}_0])] + [k_2/(2k_1 + k_2[\mathbf{A}_0])] \times \ln[[\mathbf{A}_0](2k_1 + k_2([\mathbf{A}_0] - [\mathbf{A}]))/2k_1[\mathbf{A}]]\}$ (eq. 5)

The rate constants k_1 and k_2 at each temperature are obtained by non-linear least-squares fit using Kyplot version 2.0 beta (Figures S12 and S13).
The reaction rate constants k_1 and k_2 for the formation of helix-dimer of (*M*)-**1** (1,3-difluorobenzene, 5.0×10^{-4} M) are obtained using the change of [**A**] at the initial 40 min.

At 43 °C, $k_1 = 2\ \mathrm{M^{-1}min^{-1}}$ and $k_2 = 5 \times 10^5\ \mathrm{min^{-1}M^{-2}}$ (Figure S12)
At 40 °C, $k_1 = 2\ \mathrm{M^{-1}min^{-1}}$ and $k_2 = 5 \times 10^5\ \mathrm{min^{-1}M^{-2}}$ (Figure S12)
At 35 °C, $k_1 = 3\ \mathrm{M^{-1}min^{-1}}$ and $k_2 = 5 \times 10^5\ \mathrm{min^{-1}M^{-2}}$ (Figure S12)
At 30 °C, $k_1 = 5\ \mathrm{M^{-1}min^{-1}}$ and $k_2 = 5 \times 10^5\ \mathrm{min^{-1}M^{-2}}$ (Figure S12).

In order to compare the rate of bimolecular reaction 1, equation 6 was obtained as a function of time *t*.

$$[\mathbf{A}] = [\mathbf{A}_0]/(1+k_1[\mathbf{A}_0]t) \quad \text{(eq. 6)}$$

The calculated reaction curve was drawn by using equation 6 and the rate constant k_1 at 40 °C obtained by equation 5 in a green line (Figure 4).

8. Reference

14a. Shigeno, M.; Kushida, Y.; Yamaguchi, M. *Chem. Eur. J.* **2013**, *19*, 10226.