Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information for

Supramolecular Chirality Induced by Chiral Solvation in Achiral Cyclic Azo-containing Polymers: Topological Effects on Chiral Aggregation

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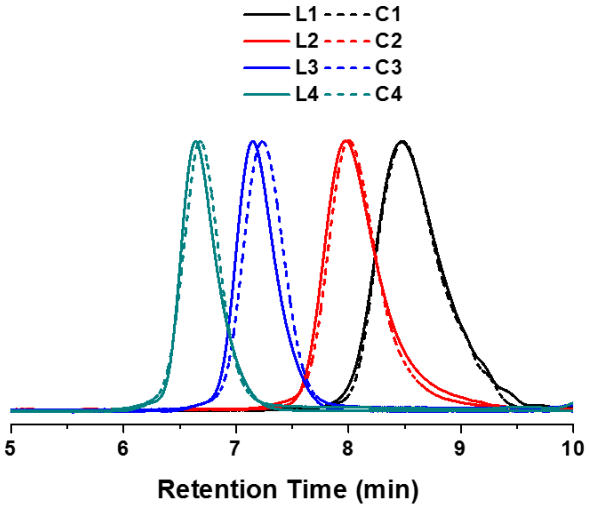
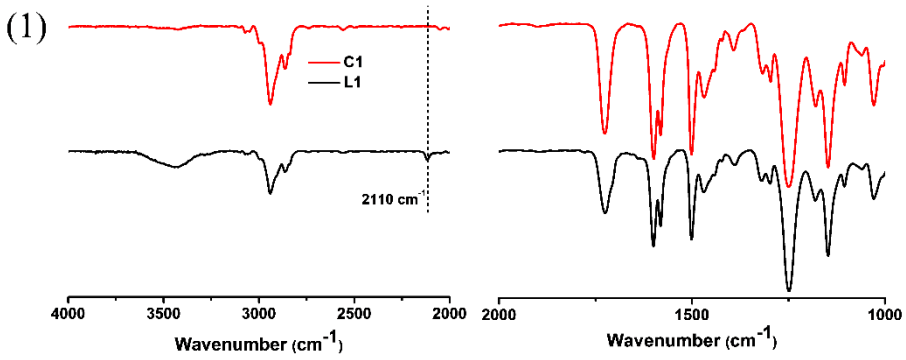


Fig. S1 GPC curves of linear and cyclic side-chain Azo polymers with different molecular weights.



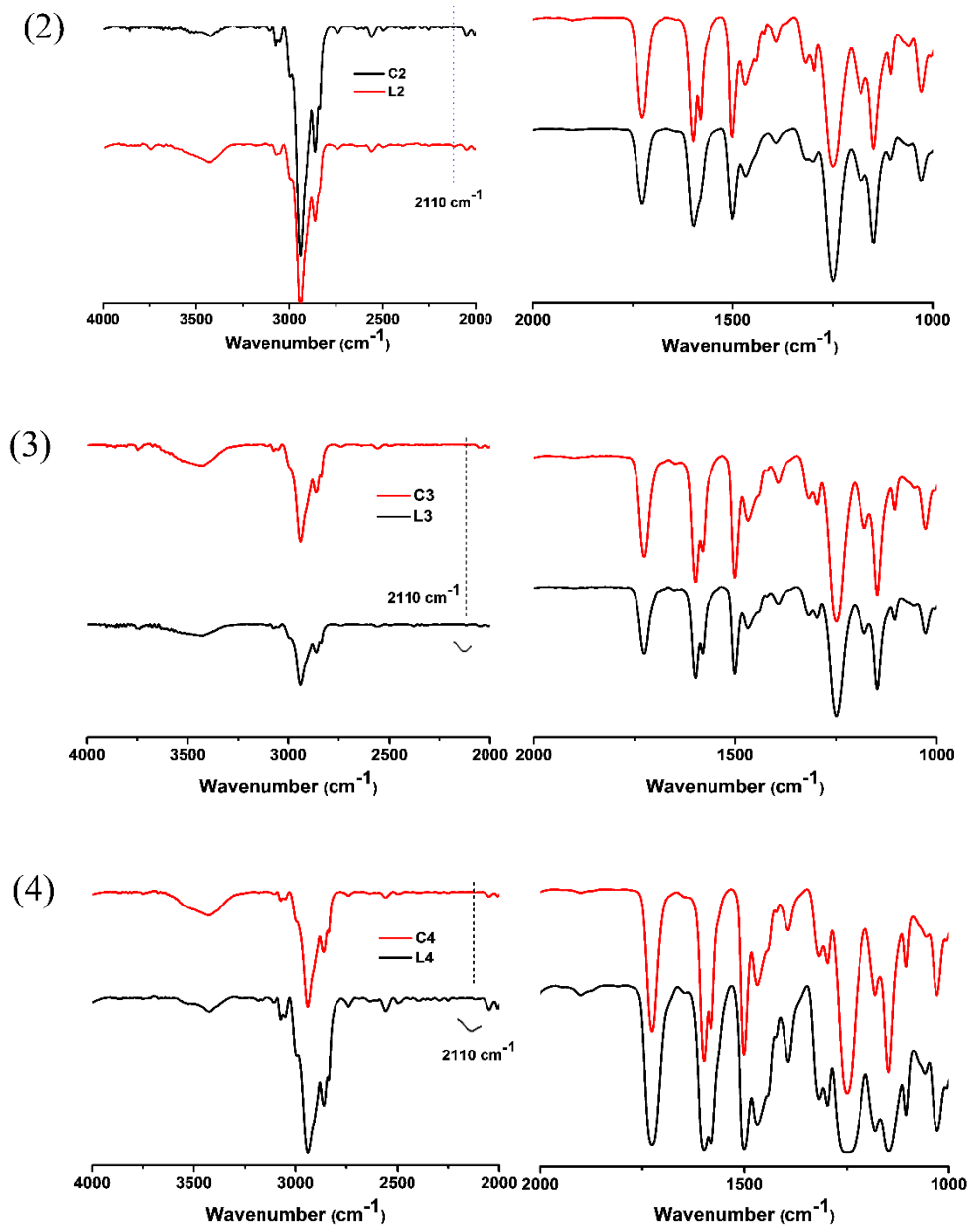
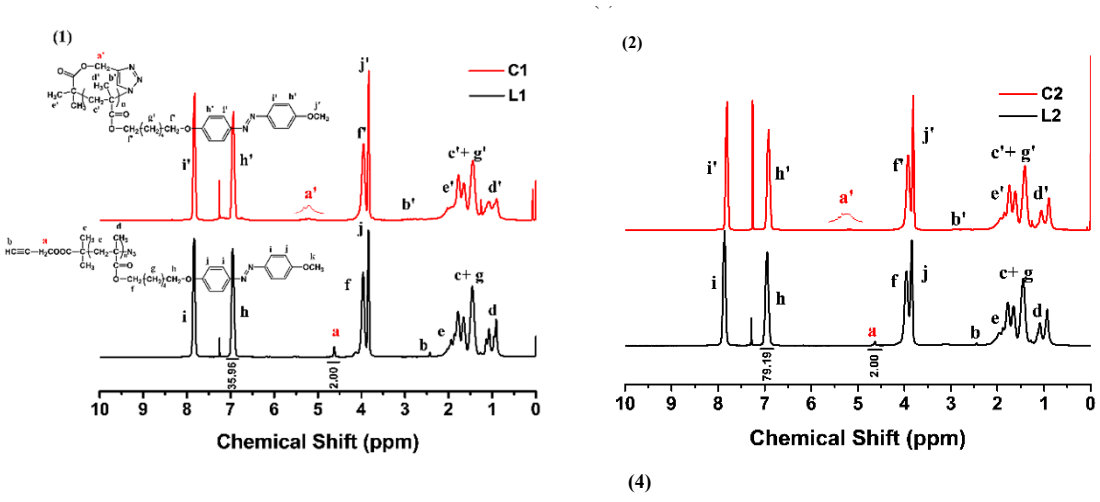


Fig. S2 Infrared spectra of linear- and cyclic side-chain Azo polymers



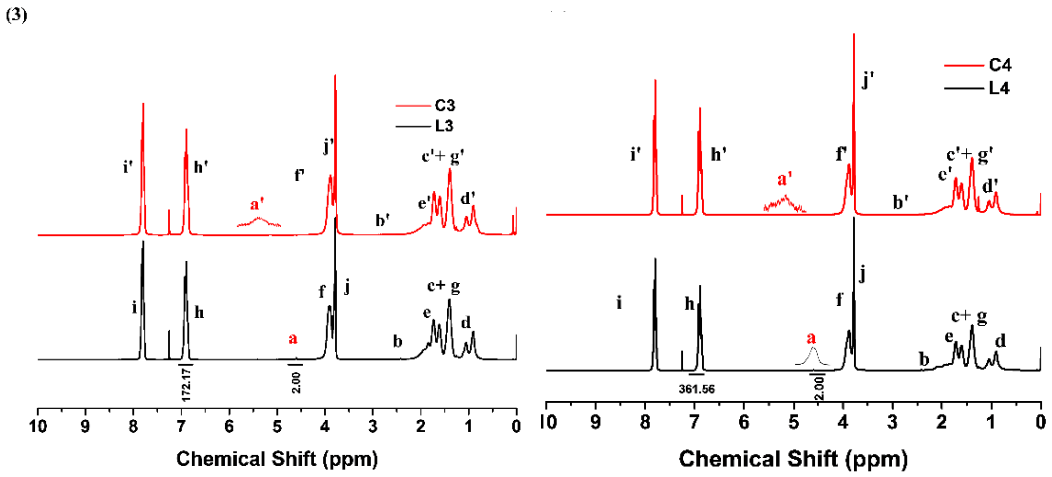


Fig. S3 ^{1}H NMR spectra of linear and cyclic Azo polymer

The molecular weight ($M_{n,NMR}$) were calculated as follows. The integral ratio of I_h and I_a is $I_h/2$, which I_h is the integrations of benzene ring (4H) of repeating units at 7.1-6.7 ppm in ^{1}H NMR spectra and I_a is set to 2 relative to the methylene next to alkynyl of the initiator. The equations of $M_{n,NMR}$ and $n_{(NMR)}$ are as follows:

$$M_{n,NMR} = [I_h/4] \times M_{monomer} + M_{initiator}$$

$$n_{(NMR)} = I_h/4$$

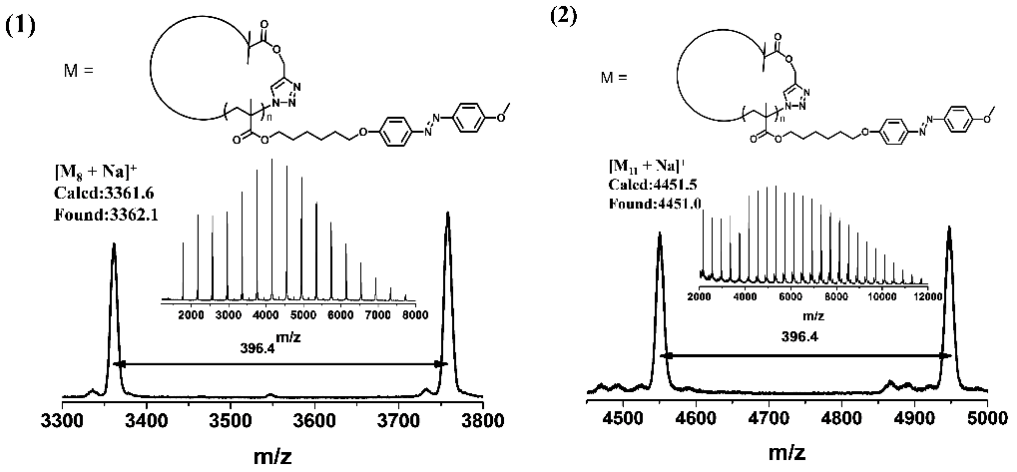


Fig. S4 Expanded MALDI-TOF mass spectra of cyclic Azo polymers (C1 and C2) with the inserted full spectra.

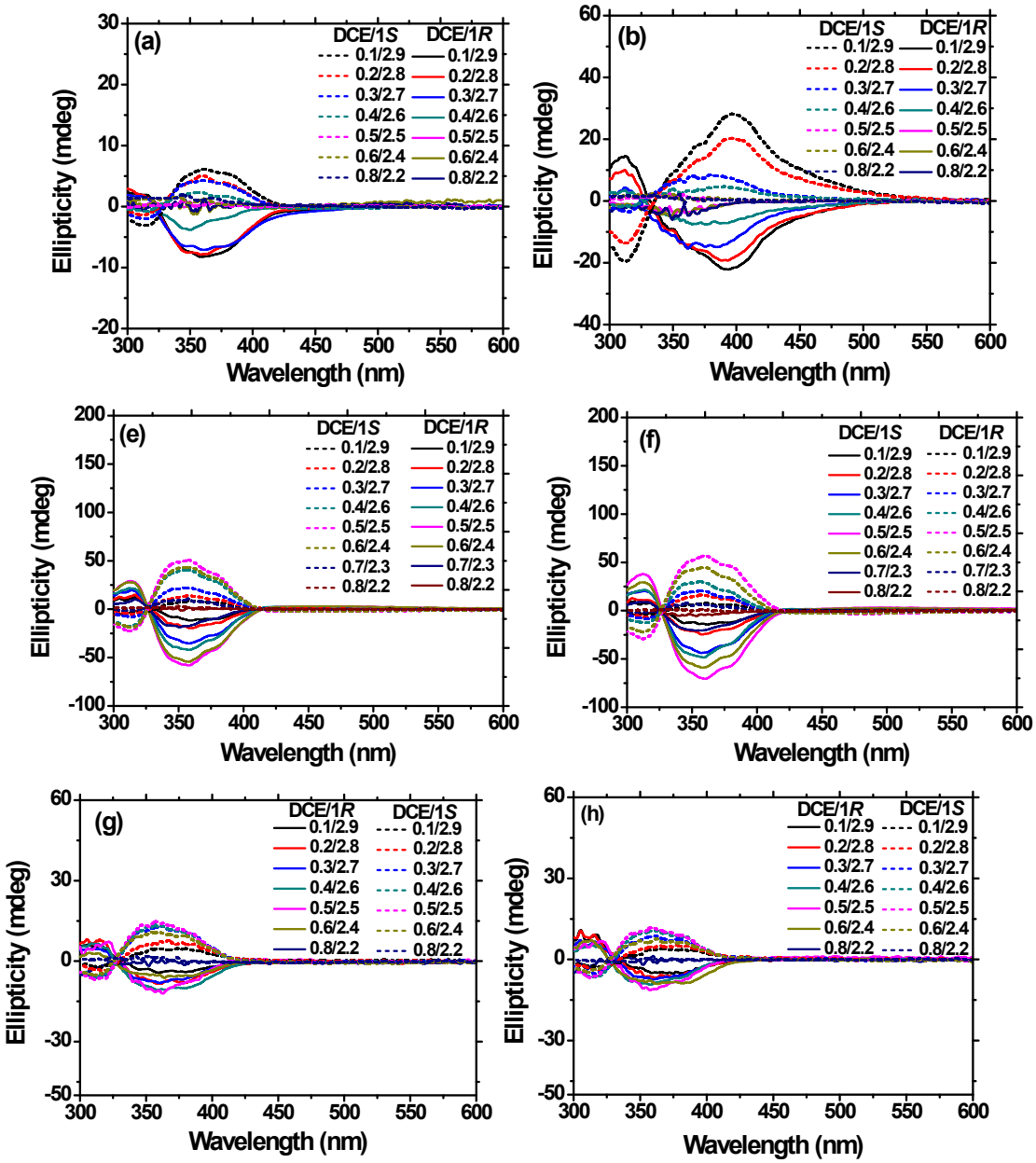
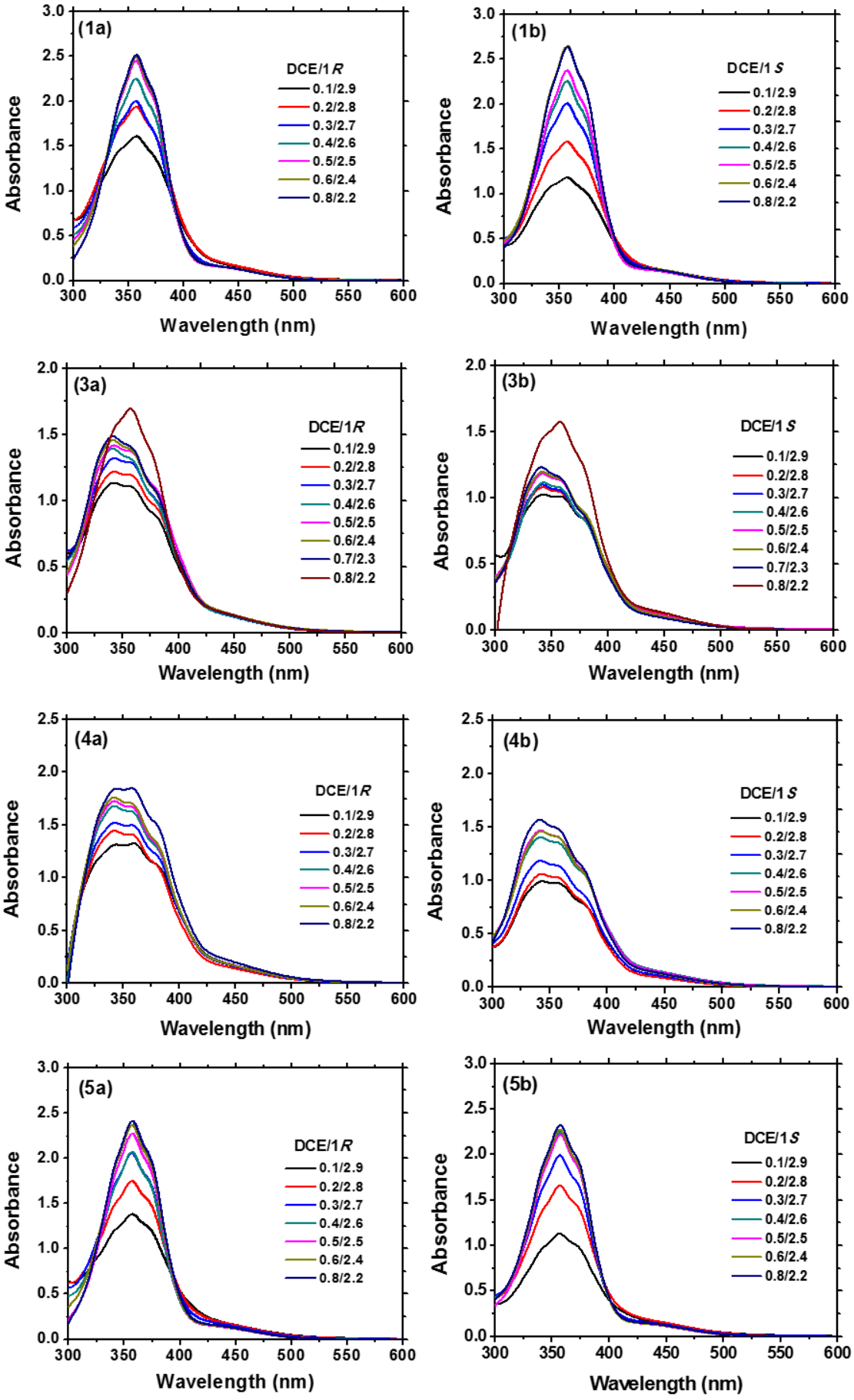


Fig. S5 Circular dichroism (CD) spectra of linear and cyclic side-chain Azo polymers aggregates with different DCE/(1*R* or 1*S*) volume fractions. (a), (e) and (g) stand for C1, C3 and C4, respectively. (b), (f) and (h) stand for L1, L3 and L4, respectively. The concentration of polymer repeating unit is 8.42×10^{-5} mol/L.


(1a)
DCE/1R
0.1/2.9
0.2/2.8
0.3/2.7
0.4/2.6
0.5/2.5
0.6/2.4
0.8/2.2
(1b)
DCE/1S
0.1/2.9
0.2/2.8
0.3/2.7
0.4/2.6
0.5/2.5
0.6/2.4
0.8/2.2
(3a)
DCE/1R
0.1/2.9
0.2/2.8
0.3/2.7
0.4/2.6
0.5/2.5
0.6/2.4
0.7/2.3
0.8/2.2
(3b)
DCE/1S
0.1/2.9
0.2/2.8
0.3/2.7
0.4/2.6
0.5/2.5
0.6/2.4
0.7/2.3
0.8/2.2
(4a)
DCE/1R
0.1/2.9
0.2/2.8
0.3/2.7
0.4/2.6
0.5/2.5
0.6/2.4
0.8/2.2
(4b)
DCE/1S
0.1/2.9
0.2/2.8
0.3/2.7
0.4/2.6
0.5/2.5
0.6/2.4
0.8/2.2
(5a)
DCE/1R
0.1/2.9
0.2/2.8
0.3/2.7
0.4/2.6
0.5/2.5
0.6/2.4
0.8/2.2
(5b)
DCE/1S
0.1/2.9
0.2/2.8
0.3/2.7
0.4/2.6
0.5/2.5
0.6/2.4
0.8/2.2
Absorbance
Wavelength (nm)

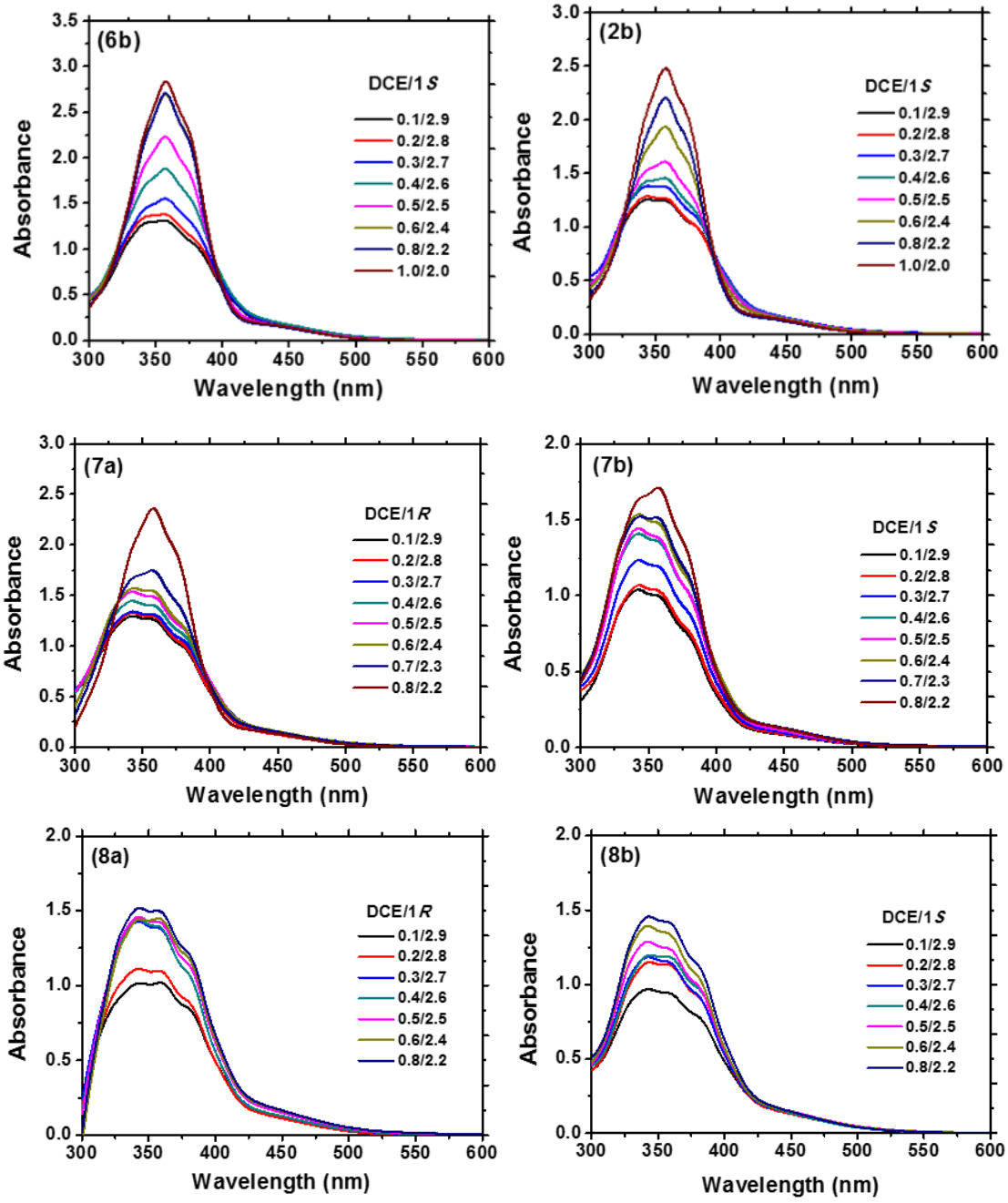


Fig. S6 UV-vis spectra of cyclic and linear Azo polymer aggregates with different DCE/1*R* (a) and DCE/1*S* (b) volume fractions. 1-4 stands for C1, C2, C3 and C4, respectively. 5-8 stands for L1, L2, L3 and L4, respectively. The concentration of polymer repeating unit is 8.42×10^{-5} mol/L.

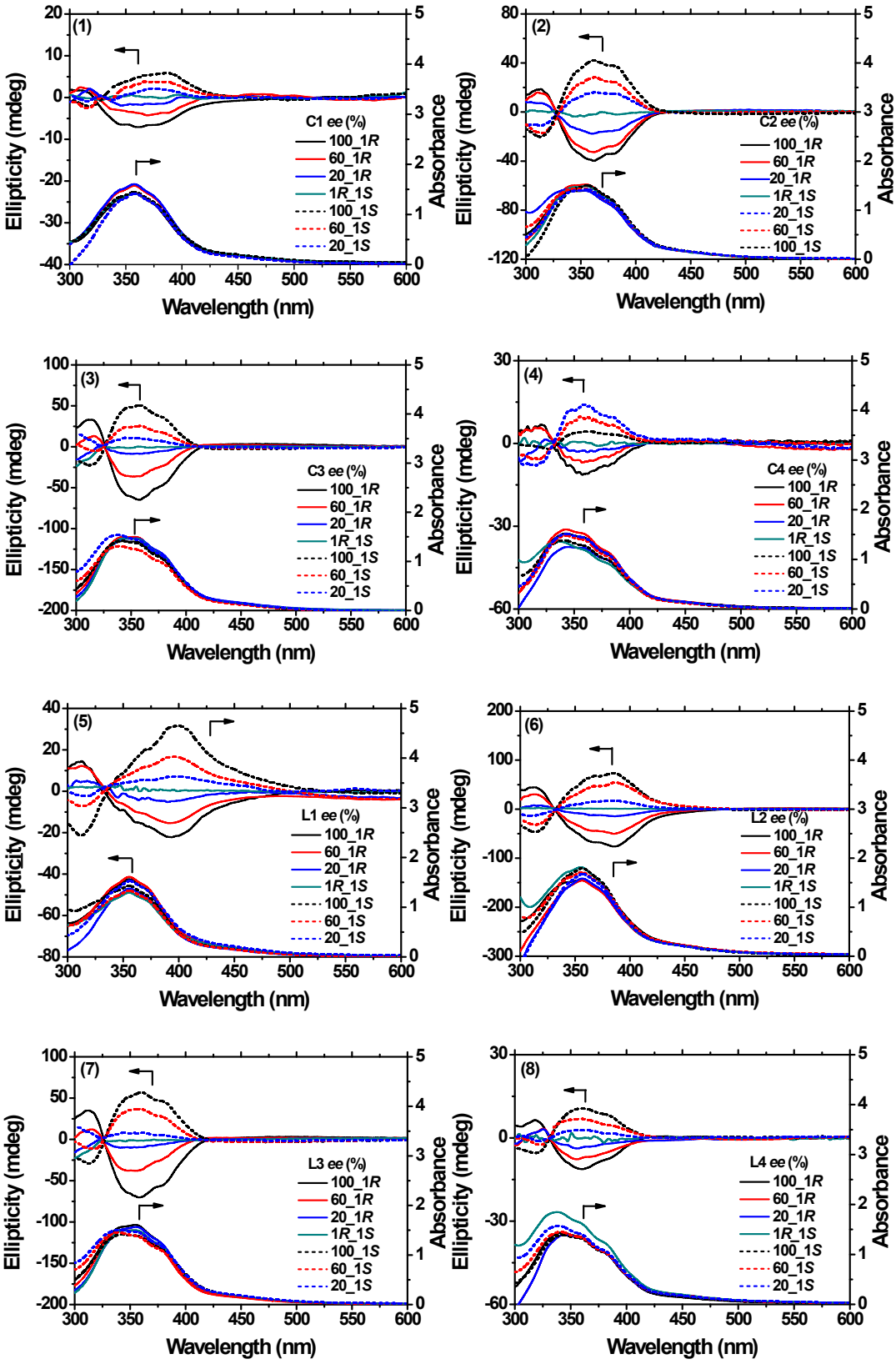
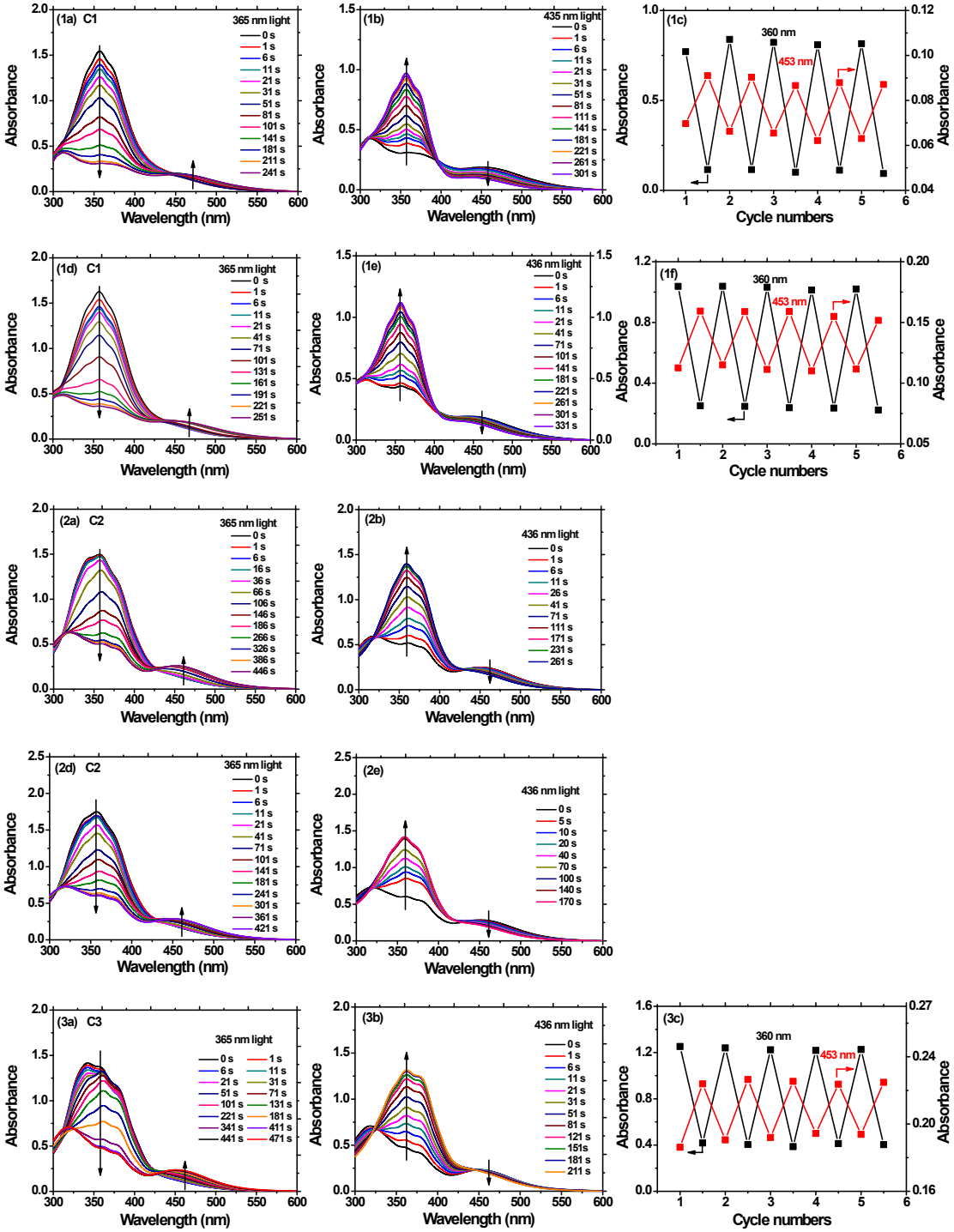
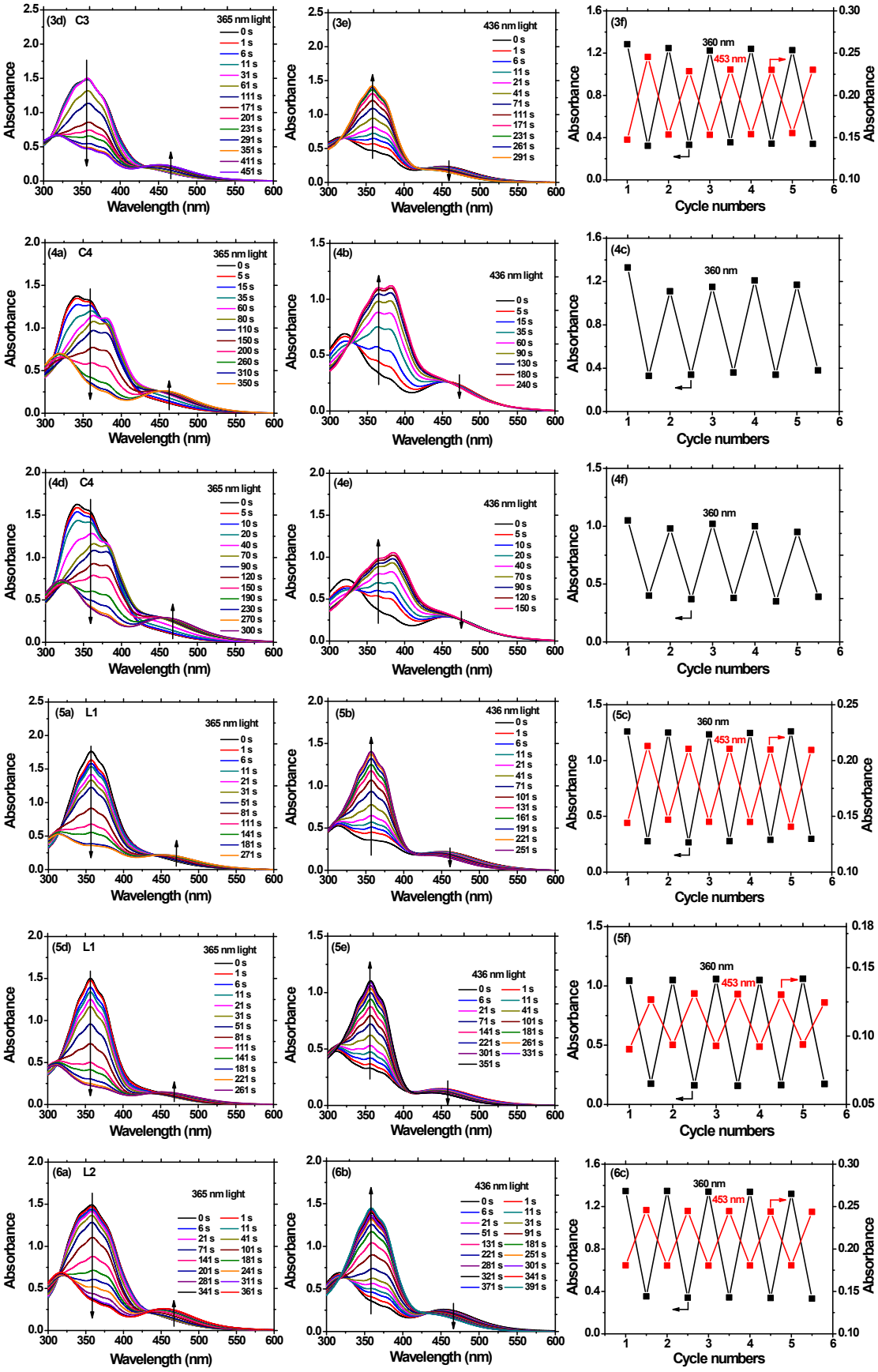


Fig. S7 The changes in CD and UV-vis spectra of Azo polymer aggregates with different enantiopurity of limonene. DCE/(1*R*+1*S*) are 0.1/2.9, 0.5/2.5, 0.5/2.5 and 0.5/2.5 (v/v) for L1, L2, L3 and L4 respectively, and 0.1/2.9, 0.4/2.6, 0.5/2.5 and 0.5/2.5

(v/v) for C1, C2, C3 and C4 respectively. The concentration of polymer repeating unit is 8.42×10^{-5} mol/L. 1-4 stands for C1, C2, C3 and C4, respectively. 5-8 stands for L1, L2, L3 and L4, respectively.




(3d) C3
365 nm light
0 s
1 s
6 s
11 s
31 s
61 s
111 s
171 s
201 s
231 s
291 s
351 s
411 s
451 s
Absorbance
Wavelength (nm)
(3e)
436 nm light
0 s
1 s
6 s
11 s
21 s
41 s
71 s
111 s
171 s
231 s
261 s
291 s
Absorbance
Wavelength (nm)
(3f)
360 nm
453 nm
Absorbance
Absorbance
Cycle numbers
(4a) C4
365 nm light
0 s
5 s
15 s
35 s
60 s
80 s
110 s
150 s
200 s
260 s
310 s
350 s
Absorbance
Wavelength (nm)
(4b)
436 nm light
0 s
5 s
15 s
35 s
60 s
90 s
130 s
180 s
240 s
Absorbance
Wavelength (nm)
(4c)
360 nm
Absorbance
Cycle numbers
(4d) C4
365 nm light
0 s
5 s
10 s
20 s
40 s
70 s
90 s
120 s
150 s
190 s
230 s
270 s
300 s
Absorbance
Wavelength (nm)
(4e)
436 nm light
0 s
5 s
10 s
20 s
40 s
70 s
90 s
120 s
150 s
Absorbance
Wavelength (nm)
(4f)
360 nm
Absorbance
Cycle numbers
(5a) L1
365 nm light
0 s
1 s
6 s
11 s
21 s
31 s
51 s
81 s
111 s
141 s
181 s
271 s
Absorbance
Wavelength (nm)
(5b)
436 nm light
0 s
1 s
6 s
11 s
21 s
41 s
71 s
101 s
131 s
161 s
191 s
221 s
251 s
Absorbance
Wavelength (nm)
(5c)
360 nm
453 nm
Absorbance
Absorbance
Cycle numbers
(5d) L1
365 nm light
0 s
1 s
6 s
11 s
21 s
31 s
51 s
81 s
111 s
141 s
181 s
221 s
261 s
Absorbance
Wavelength (nm)
(5e)
436 nm light
0 s
1 s
6 s
11 s
21 s
41 s
71 s
101 s
141 s
181 s
221 s
261 s
301 s
331 s
351 s
Absorbance
Wavelength (nm)
(5f)
360 nm
453 nm
Absorbance
Cycle numbers
(6a) L2
365 nm light
0 s
1 s
6 s
11 s
21 s
41 s
71 s
101 s
141 s
181 s
201 s
241 s
281 s
311 s
341 s
361 s
Absorbance
Wavelength (nm)
(6b)
436 nm light
0 s
1 s
6 s
11 s
21 s
31 s
51 s
91 s
131 s
181 s
221 s
251 s
281 s
301 s
321 s
341 s
371 s
391 s
Absorbance
Wavelength (nm)
(6c)
360 nm
453 nm
Absorbance
Absorbance
Cycle numbers

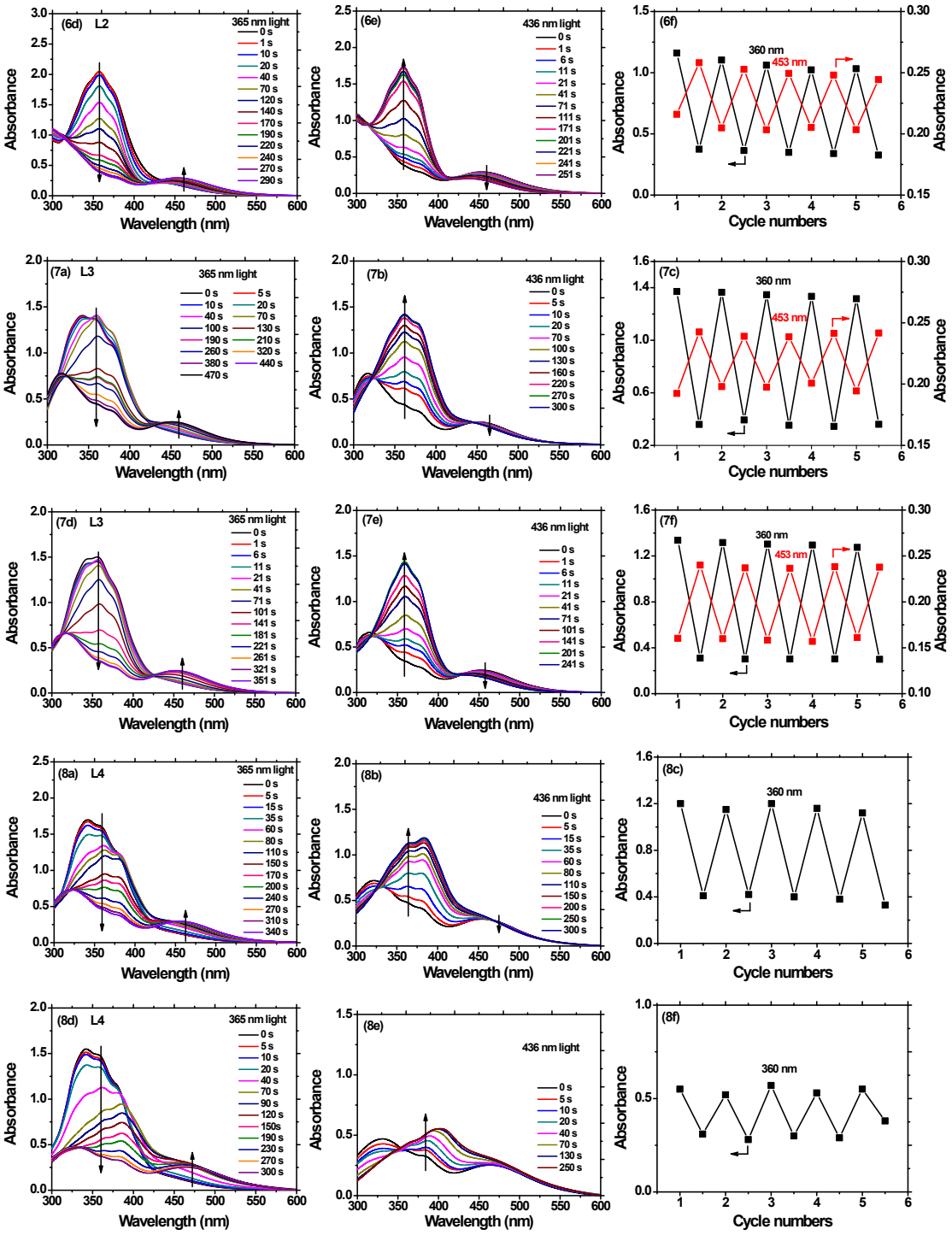
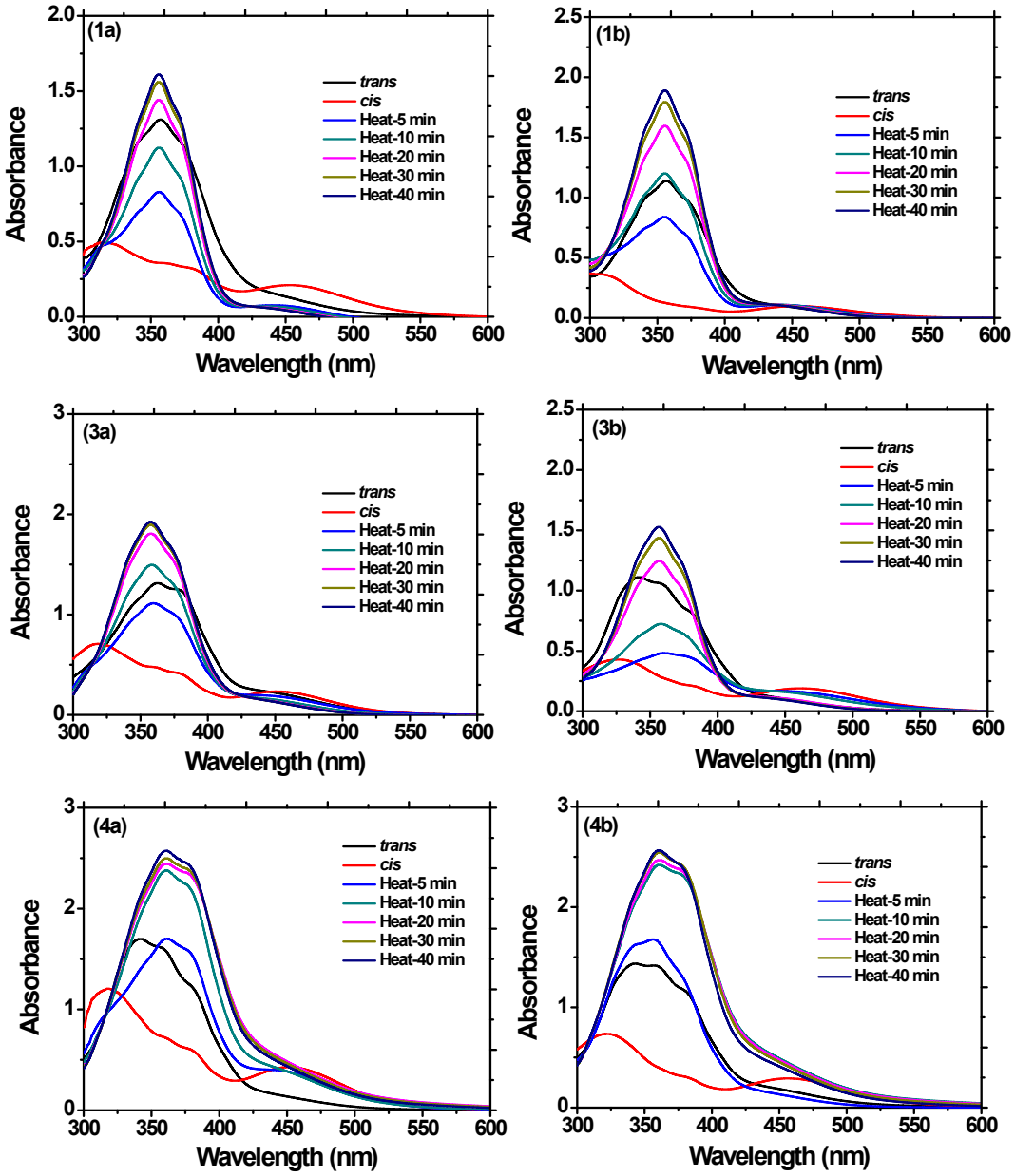


Fig. S8 Photoisomerization switching of the UV-vis spectra ((a, b) DCE/1*R* and (d, e) DCE/1*S*) of linear and cyclic Azo polymer aggregates by irradiation with 365 nm and 436 nm light. The UV-vis spectra ((c) DCE/1*R* and (f) DCE/1*S*) of linear and cyclic Azo polymer aggregates are switched by alternating irradiation with 365 nm and 436 nm light. The absorbance change for *trans*- and *cis*-form is taken from 360 nm (black)

and 453 nm (red), respectively. The concentration of polymer repeating unit is 8.42 × 10^{-5} mol/L. 1-4 stands for C1, C2, C3 and C4, respectively. 5-8 stands for L1, L2, L3 and L4, respectively.



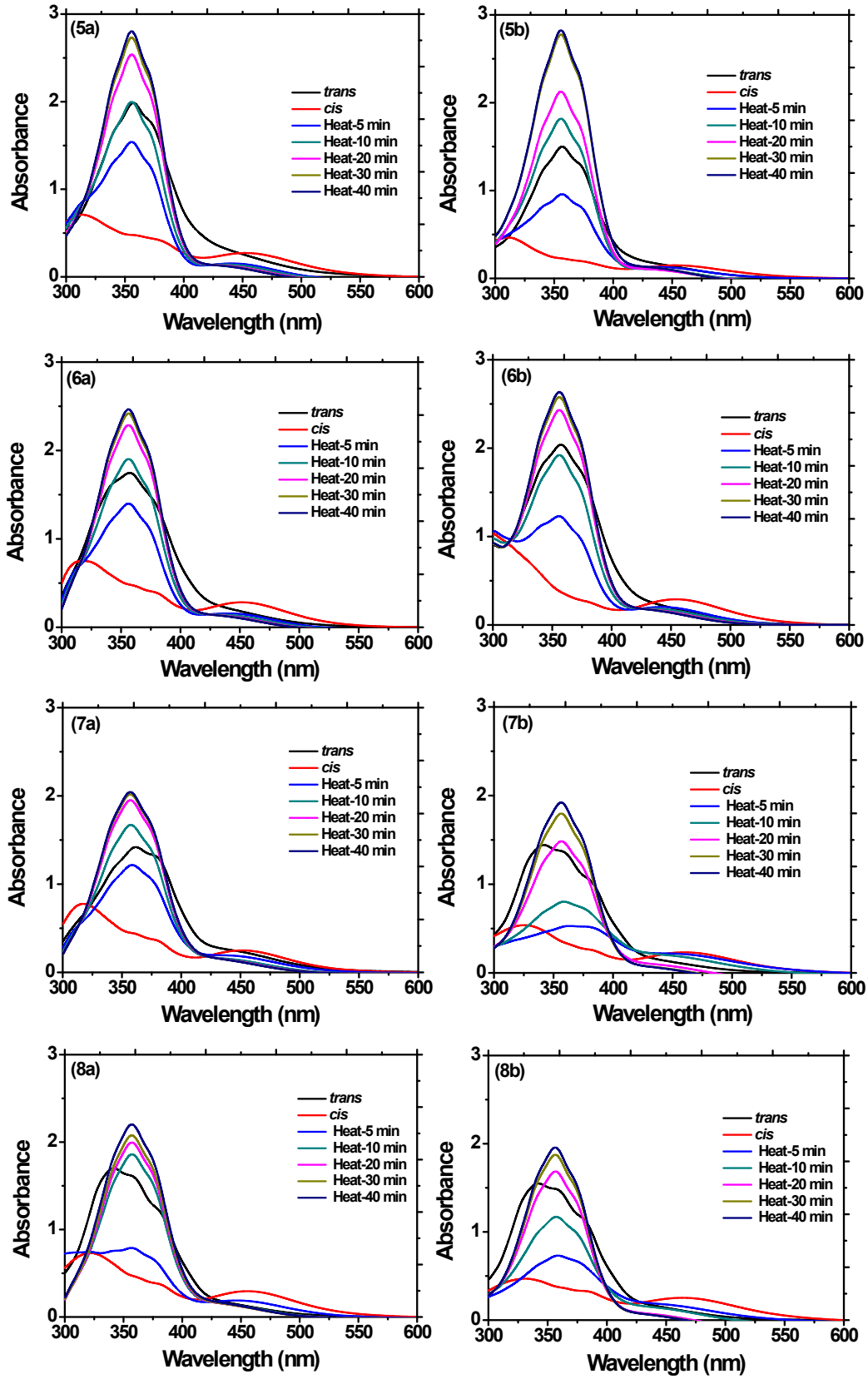
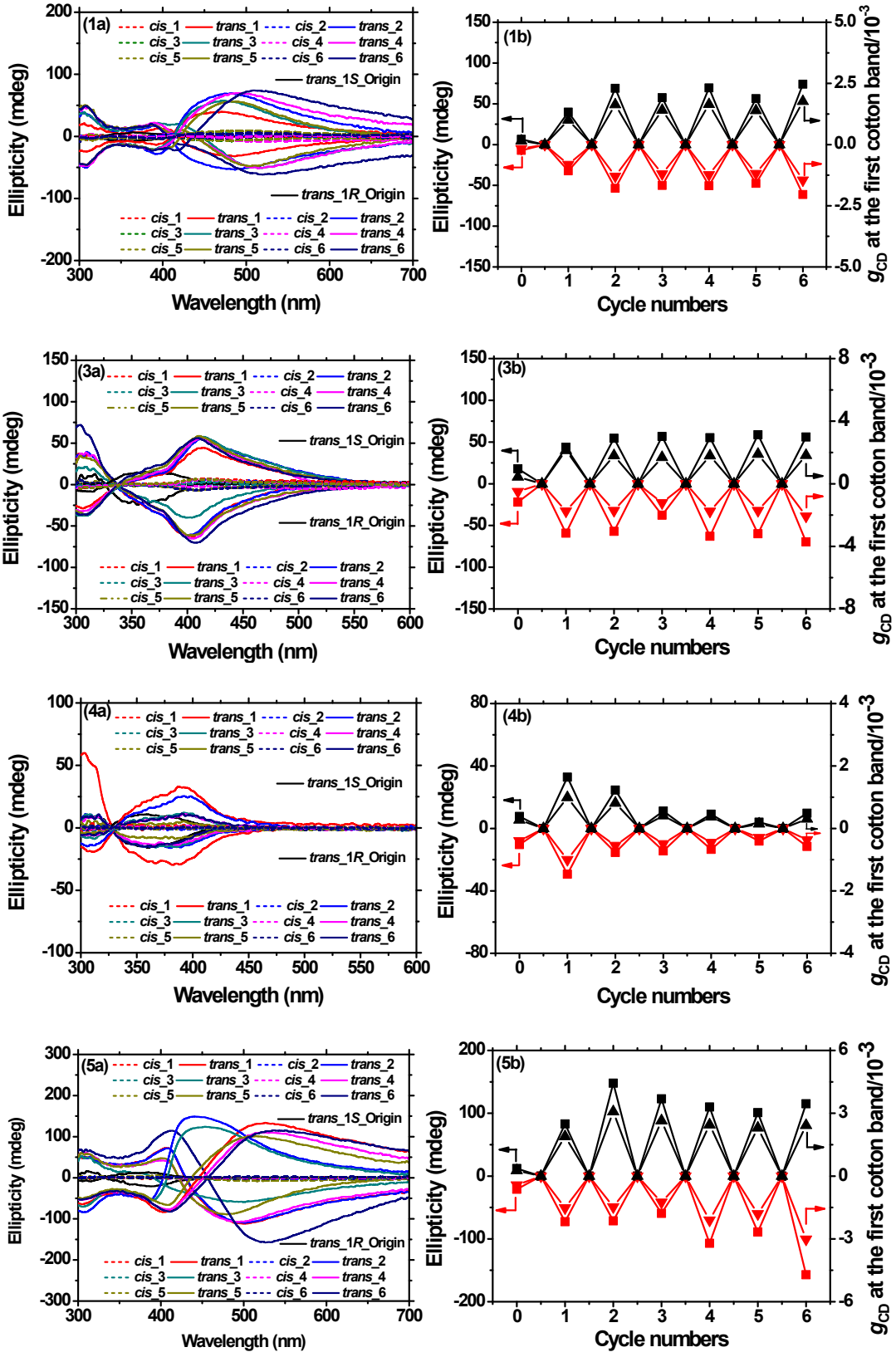


Fig. S9 The changes of UV-vis spectra with heating time in the process of thermal isomerization at 60 °C ((a) DCE/1*R* and (b) DCE/1*S*). The concentration of polymer

repeating unit is 8.42×10^{-5} mol/L. 1-4 stands for C1, C2, C3 and C4, respectively. 5-8 stands for L1, L2, L3 and L4, respectively.



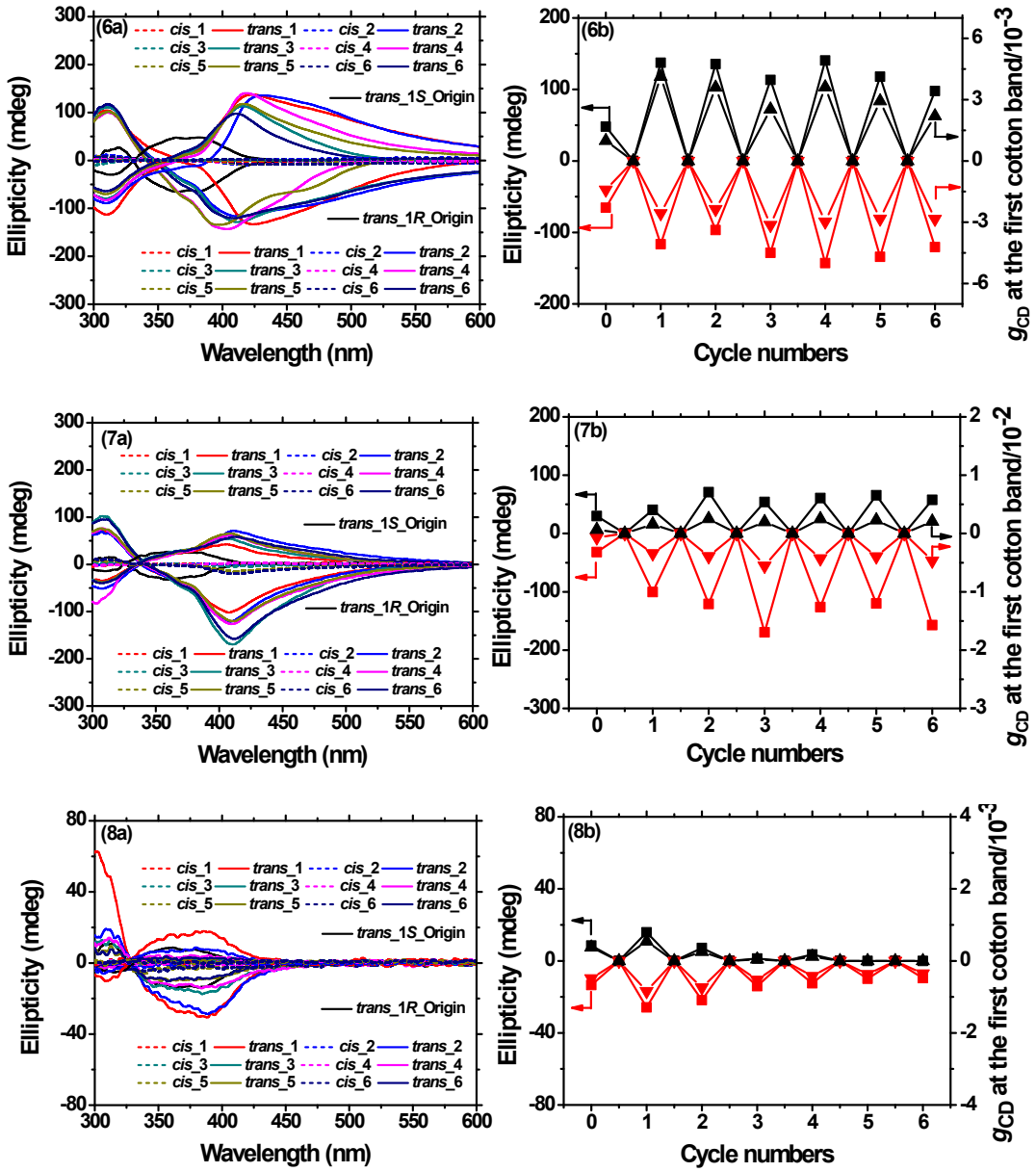


Fig. S10 Changes in CD spectra (a) and the maximum CD and g_{CD} values (b) of Azo polymer aggregates in DCE/(1*R* or 1*S*) during 365 nm light irradiation (3min) and heating treatment (60 °C for 40 min then cooling to room temperature). The concentration of polymer repeating unit is 8.42×10^{-5} mol/L. 1-4 stands for C1, C2, C3 and C4 respectively. 5-8 stands for L1, L2, L3 and L4, respectively.