Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information for

Preferential Chiral Solvation Induced Supramolecular Chirality in Optically Inactive Star Azo Polymers: Photocontrollability, Chiral Amplification and Topological Effect

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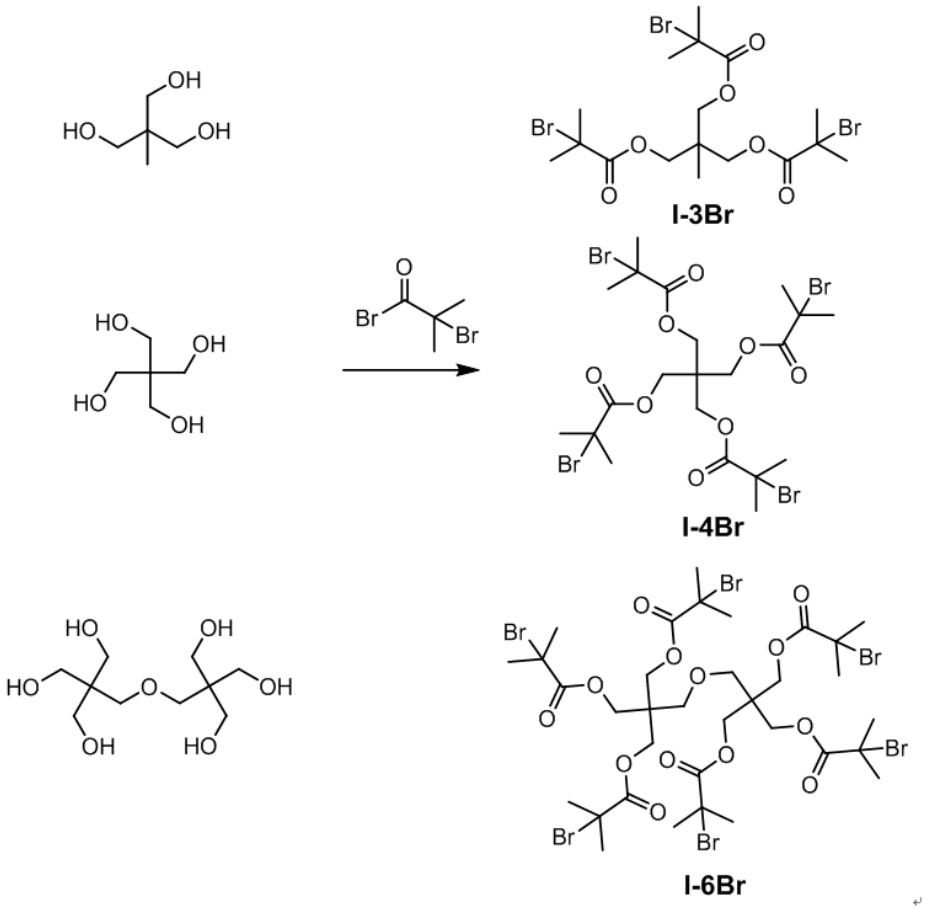


Scheme S1. The synthetic routes of multi-functional initiators.

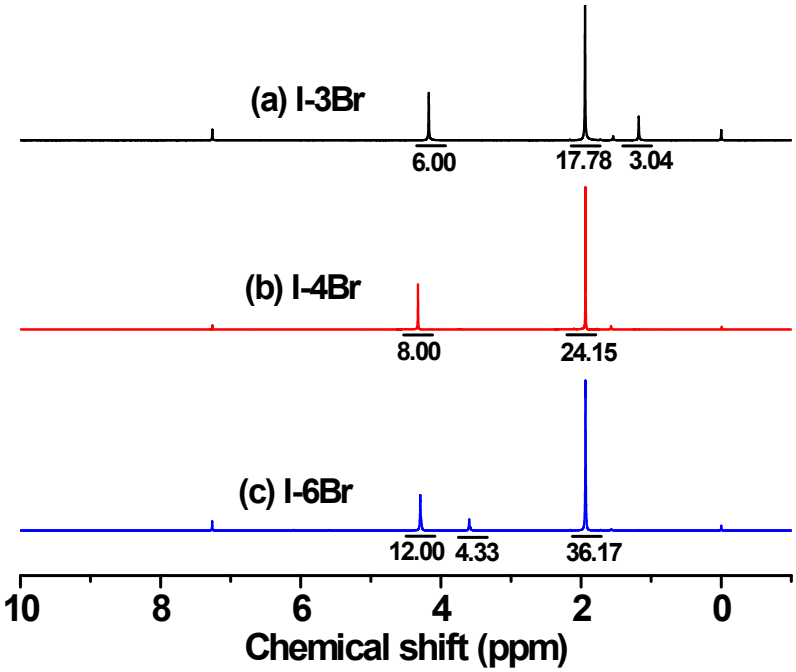


Fig. S1 ^{1}H NMR spectra of multi-functional initiators.

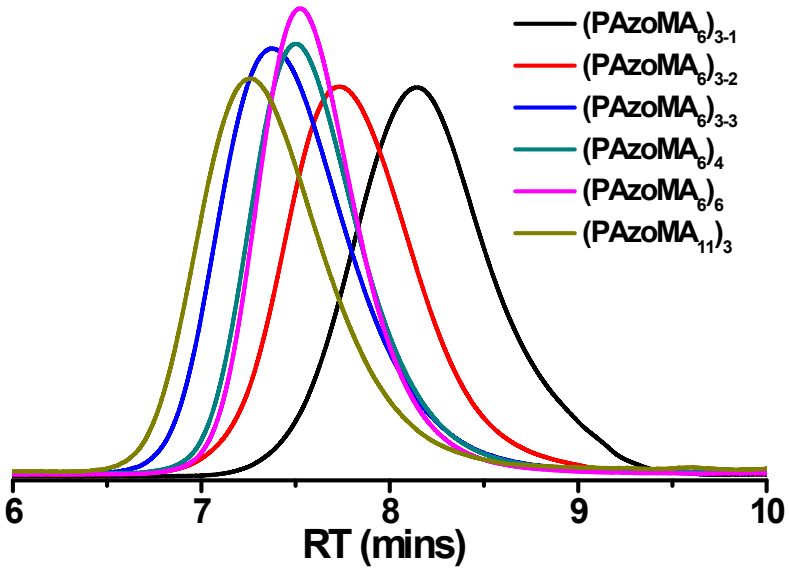


Fig. S2 GPC curves of PAzoMAs.

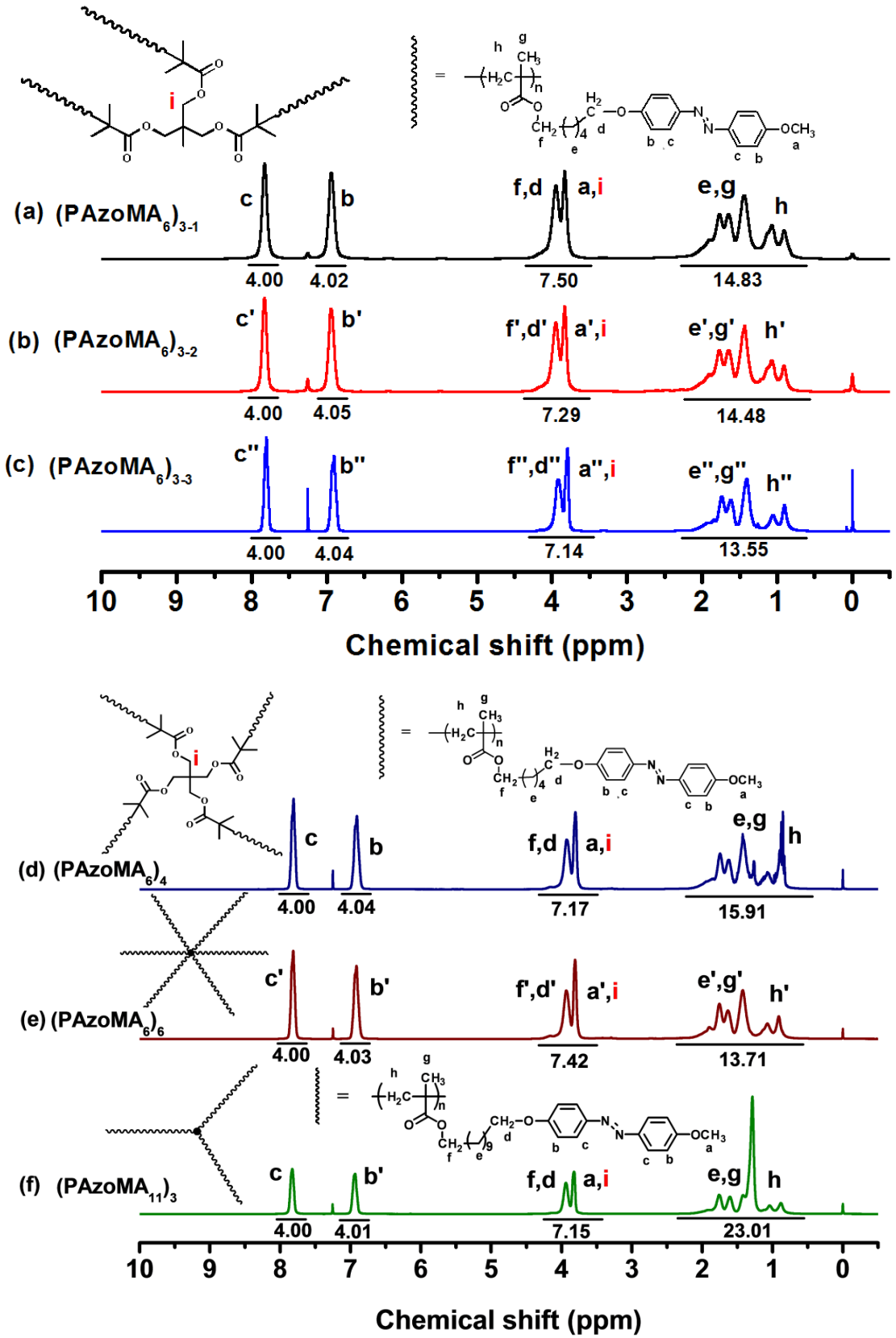


Fig. S3 ^{1}H NMR spectra of star Azo polymers $(PAzoMA_6)_3$ (a, b and c), $(PAzoMA_6)_4$ (d), $(PAzoMA_6)_6$ (e) and $(PAzoMA_{11})_3$ (f).

The $M_{n(NMR)}$ were calculated as follows. The integral ratio of I_c and $I_{(a,d,f)}$ is 4/7

theoretically. I_c is the integrations at 8.1-7.6 ppm in ^{1}H NMR spectra relative to the benzene ring (4H) of AzoMA repeating units in star PAzoMA. $I_{(a,d,f)}$ is the integrations in ^{1}H NMR spectra relative to -OCH_3, -OCH_2-, -OCH_2- (7H) of AzoMA units in star PAzoMA. $I_{(a,d,f,i)}$ is the integrations at 4.4-3.3 ppm in ^{1}H NMR spectra including $I_{(a,d,f)}$ and the multi-functional initiators (-CH_2-). Equation (S1) as follows：

$$M_{n,NMR} = (N_I)/(I_{(4.4\text{-}3.3)} - 7) \times M_{AzoMA} + M_I \qquad \text{equation (S1)}$$

For I-3Br, I-4Br and I-6Br, the N_I is 6, 8 and 16 respectively. M_{AzoMA} is the molecular weight of AzoMA monomer. M_I is the molecular weight of multi-functional initiator.

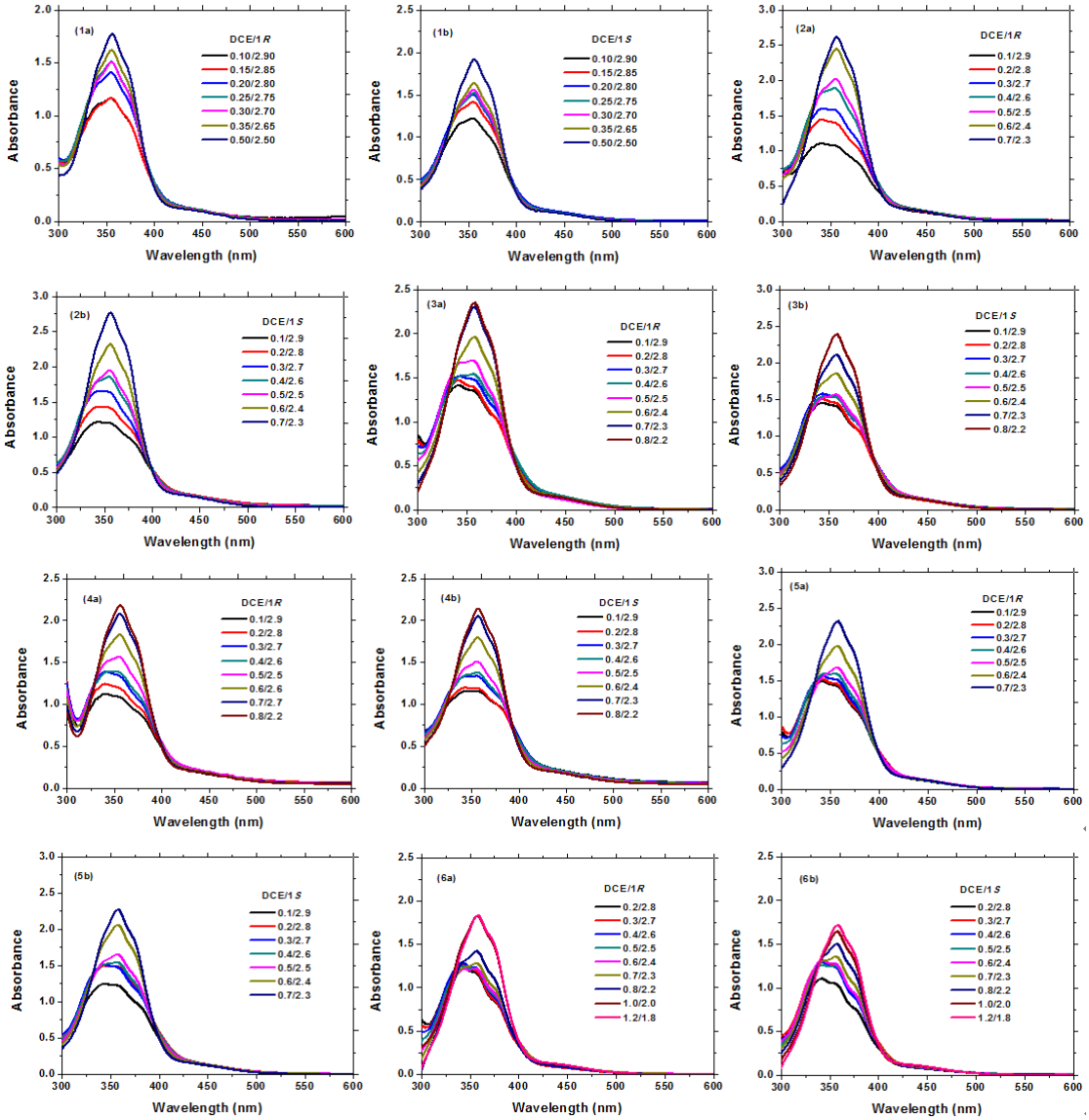
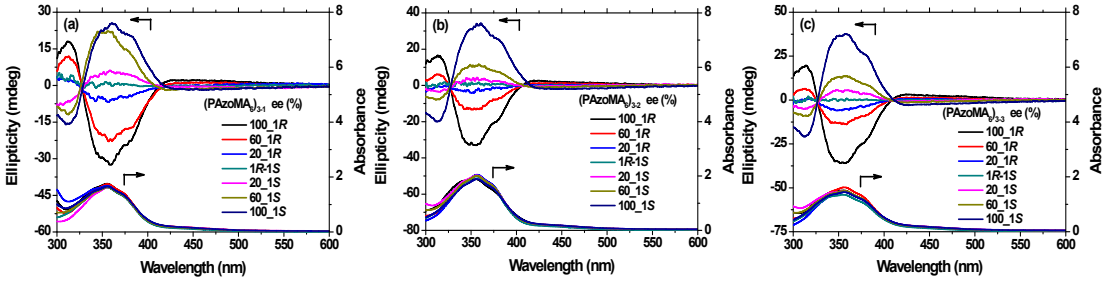


Fig. S4 UV–vis spectra of PAzoMA aggregates with different DCE/1*R* (a) and DCE/1*S* (b) volume fractions. The concentration of polymer repeating unit is 8.42 × 10^{-5} mol/L. 1-6 stands for $(PAzoMA_6)_{3\text{-}1}$, $(PAzoMA_6)_{3\text{-}2}$, $(PAzoMA_6)_{3\text{-}3}$, $(PAzoMA_6)_4$, $(PAzoMA_6)_6$ and $(PAzoMA_{11})_3$, respectively.



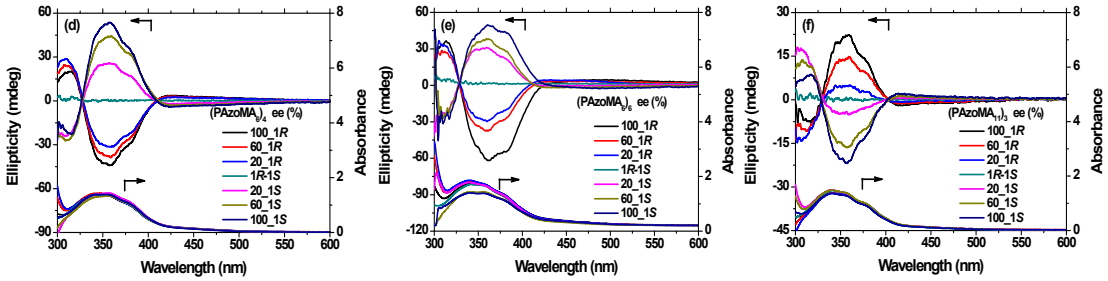
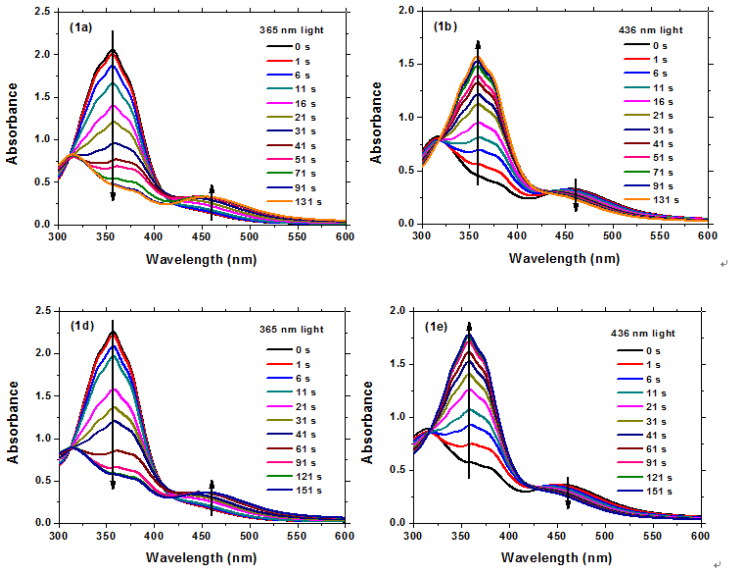
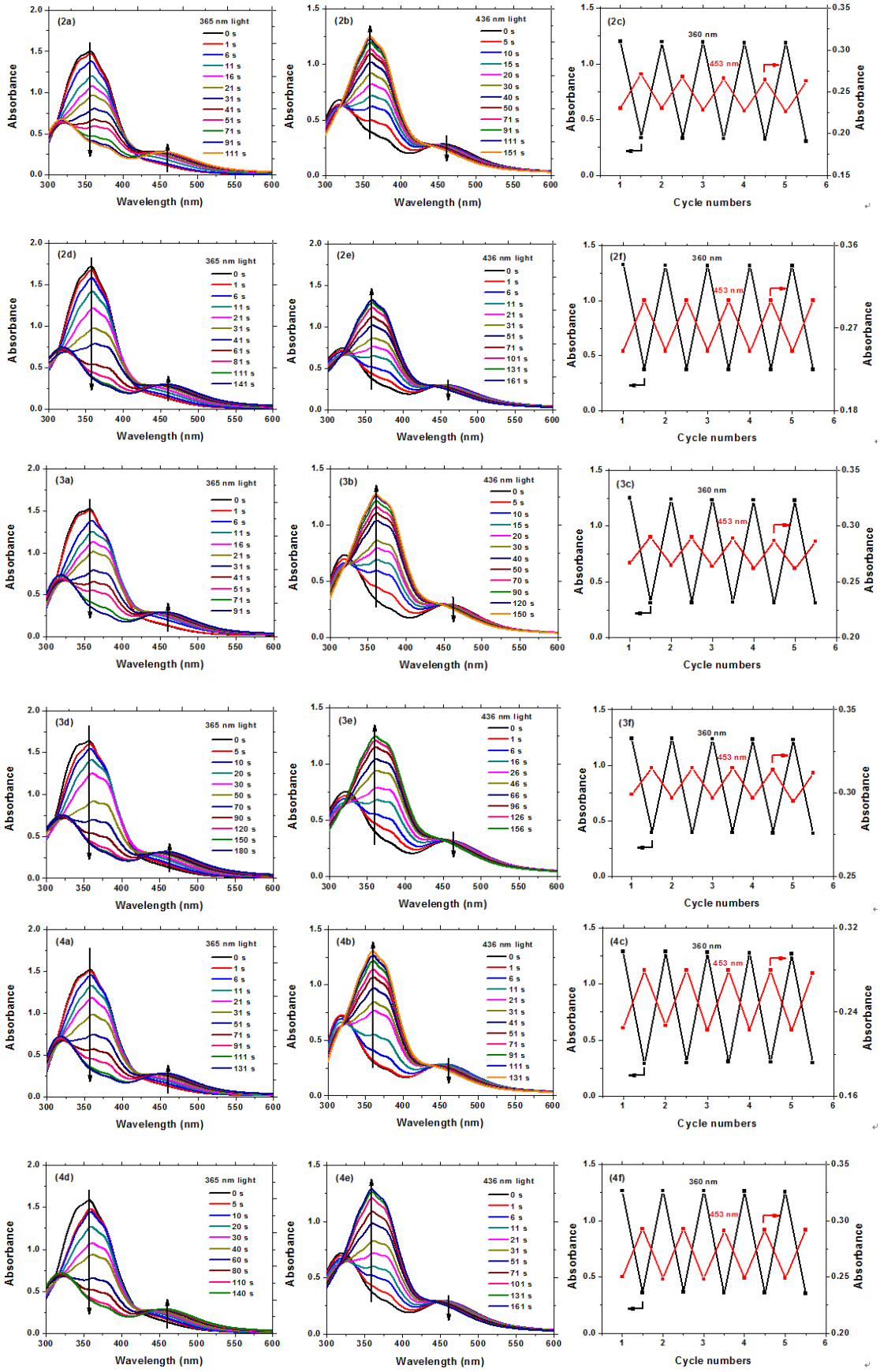


Fig. S5 Changes in CD and UV–vis spectra of PAzoMA aggregates with different enantiopurity of limonene. DCE/(1*R* + 1*S*) are 0.25/2.75, 0.4/0.6, 0.5/2.5, 0.3/2.7, 0.5/2.5 and 0.5/2.5 (v/v) for $(PAzoMA_6)_{3\text{-}1}$, $(PAzoMA_6)_{3\text{-}2}$, $(PAzoMA_6)_{3\text{-}3}$, $(PAzoMA_6)_4$, $(PAzoMA_6)_6$ and $(PAzoMA_{11})_3$ respectively. The concentration of polymer repeating unit is 8.42×10^{-5} mol/L. (a)-(f) stands for $(PAzoMA_6)_{3\text{-}1}$, $(PAzoMA_6)_{3\text{-}2}$, $(PAzoMA_6)_{3\text{-}3}$, $(PAzoMA_6)_4$, $(PAzoMA_6)_6$ and $(PAzoMA_{11})_3$, respectively.

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365 nm light
0 s
1 s
6 s
11 s
16 s
21 s
31 s
41 s
51 s
71 s
91 s
111 s
Absorbance
Wavelength (nm)
(2b)
436 nm light
0 s
5 s
10 s
15 s
20 s
30 s
40 s
50 s
71 s
91 s
111 s
151 s
Absorbnace
Wavelength (nm)
(2c)
360 nm
453 nm
Absorbance
Cycle numbers
(2d)
365 nm light
0 s
1 s
6 s
11 s
21 s
31 s
41 s
61 s
81 s
111 s
141 s
Absorbance
Wavelength (nm)
(2e)
436 nm light
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1 s
6 s
11 s
21 s
31 s
51 s
71 s
101 s
131 s
161 s
Absorbance
Wavelength (nm)
(2f)
360 nm
453 nm
Absorbance
Cycle numbers
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6 s
11 s
16 s
21 s
31 s
41 s
51 s
71 s
91 s
Absorbance
Wavelength (nm)
(3b)
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Wavelength (nm)
(3c)
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Absorbance
Cycle numbers
(3d)
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Wavelength (nm)
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(4a)
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Absorbance
Cycle numbers

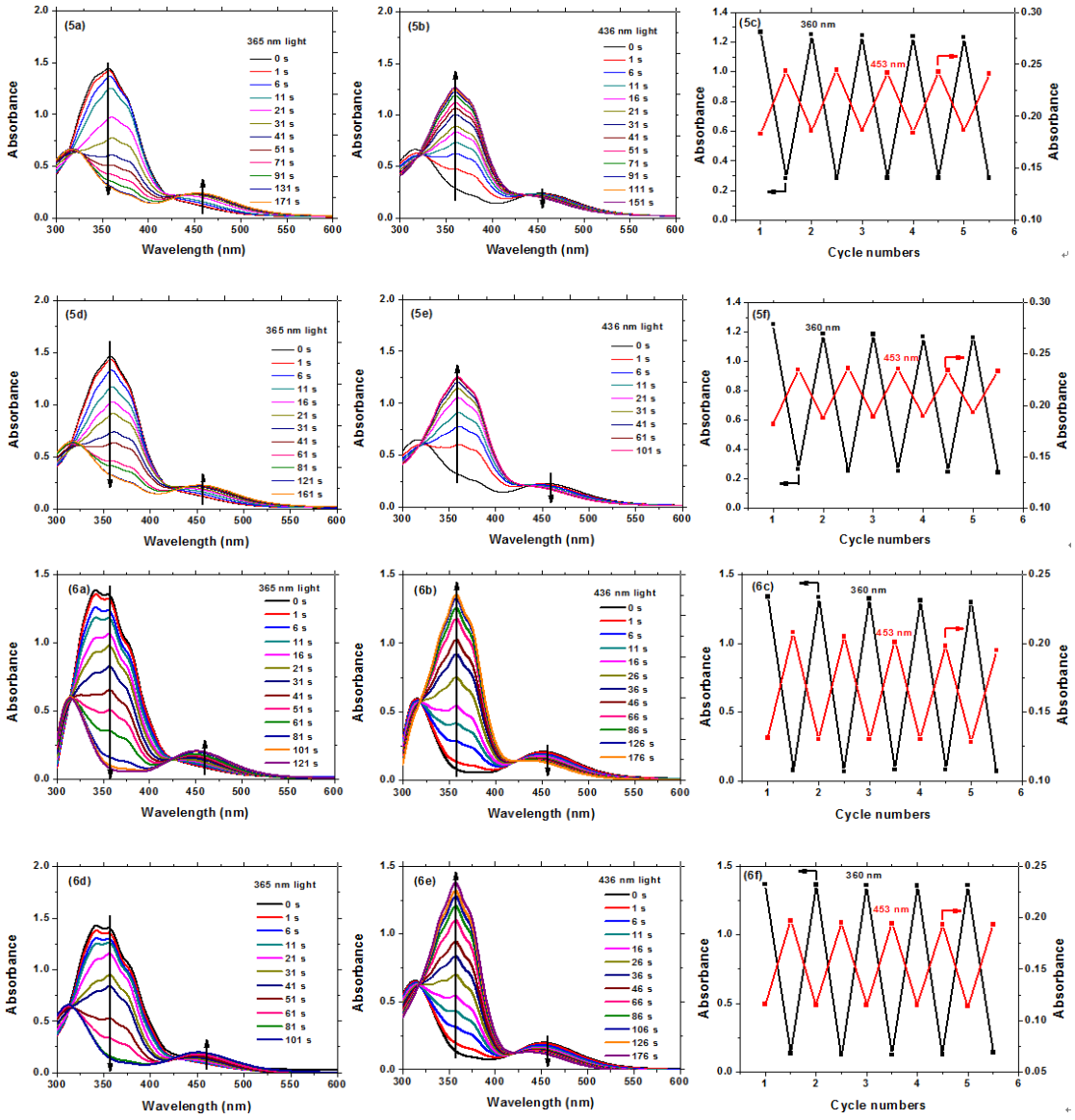


Fig. S6 Photoisomerization switching of the UV-vis spectra ((a,b) DCE/1*R* and (d,e) DCE/1*S*) of PAzoMA aggregates by irradiation with 365 nm and 436 nm light. UV-vis spectra ((c) DCE/1*R* and (f) DCE/1*S*) of PAzoMA aggregates by alternating irradiation with 365 nm and 436 nm light. The irradiation times for 365 nm light and 436 nm light are both 3 min. 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. 1-6 stands for $(PAzoMA_6)_{3\text{-}1}$, $(PAzoMA_6)_{3\text{-}2}$, $(PAzoMA_6)_{3\text{-}3}$, $(PAzoMA_6)_4$, $(PAzoMA_6)_6$ and $(PAzoMA_{11})_3$, respectively.

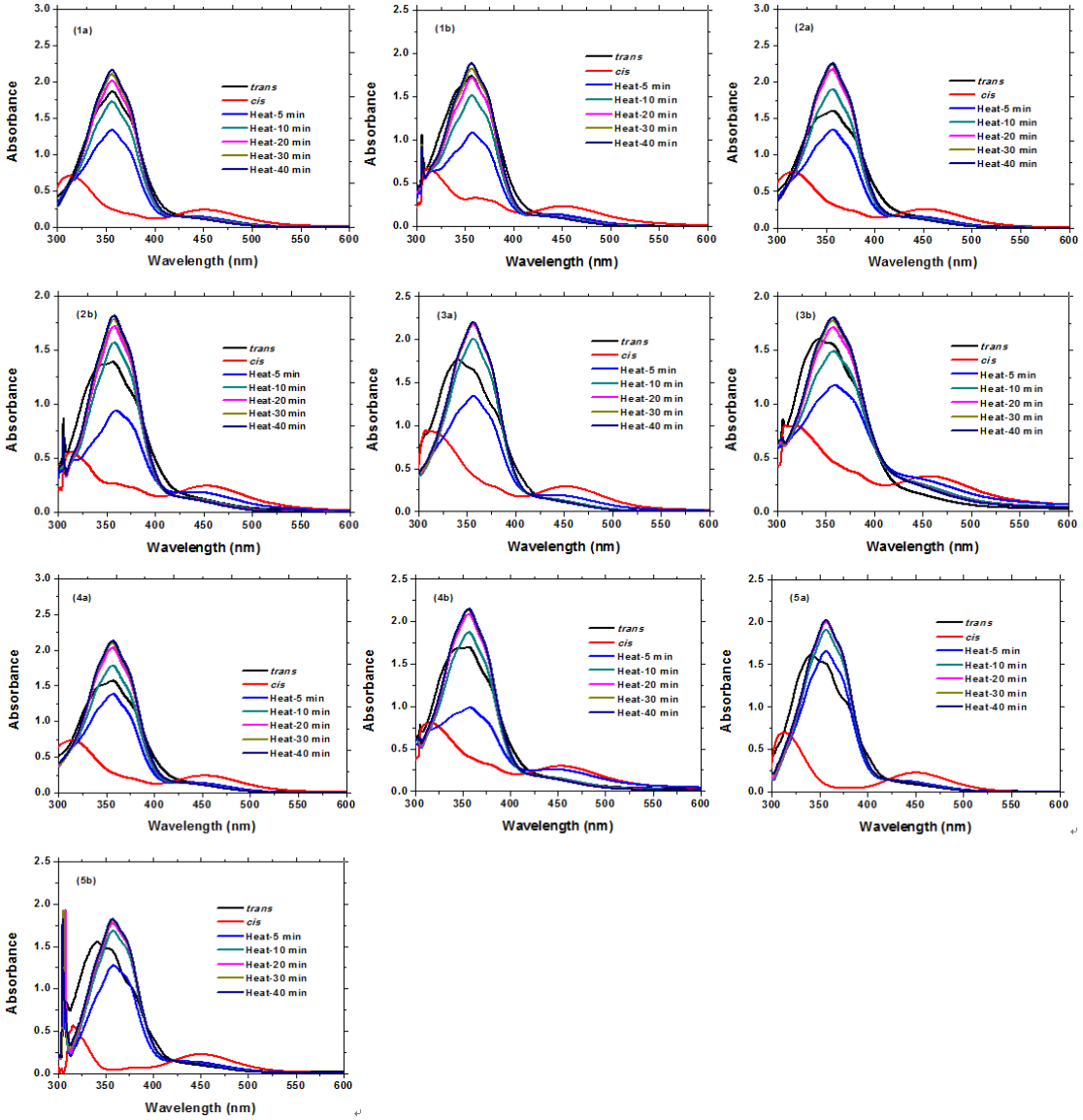
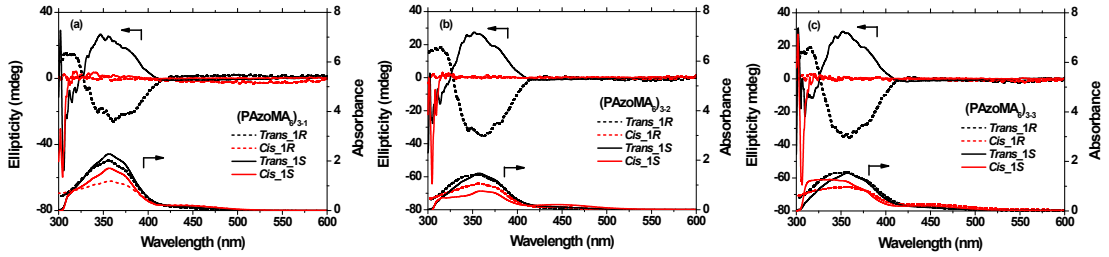


Fig. S7 The changes of UV-vis spectra with heating time in the process of thermal isomerization at 60 °C ((a) DCE/1*R* and (b) DCE/1*S*). The concentration of polymer repeating unit is 8.42 × 10^{-5} mol/L. 1-5 stands for $(PAzoMA_6)_{3\text{-}2}$, $(PAzoMA_6)_{3\text{-}3}$, $(PAzoMA_6)_4$, $(PAzoMA_6)_6$ and $(PAzoMA_{11})_3$, respectively.



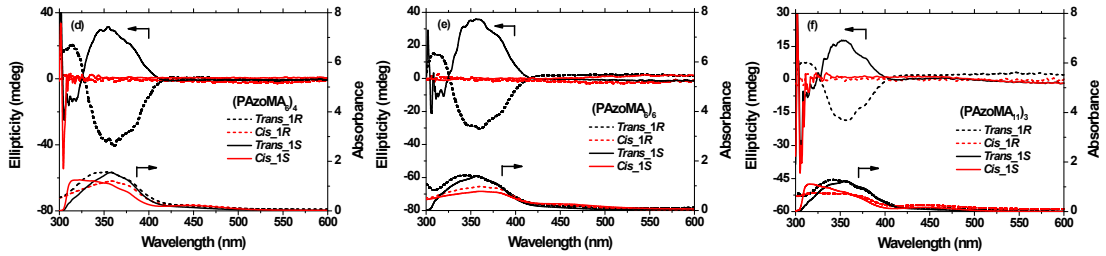


Fig. S8 Changes in CD and UV-vis spectra of *trans*- (original) and *cis*-form (irradiated by 365 nm light for 3 min) of PAzoMA aggregates in mixed solvents. The concentration of polymer repeating unit is 8.42 × 10^{-5} mol/L. (a)-(f) stands for $(PAzoMA_6)_{3\text{-}1}$, $(PAzoMA_6)_{3\text{-}2}$, $(PAzoMA_6)_{3\text{-}3}$, $(PAzoMA_6)_4$, $(PAzoMA_6)_6$ and $(PAzoMA_{11})_3$, respectively.

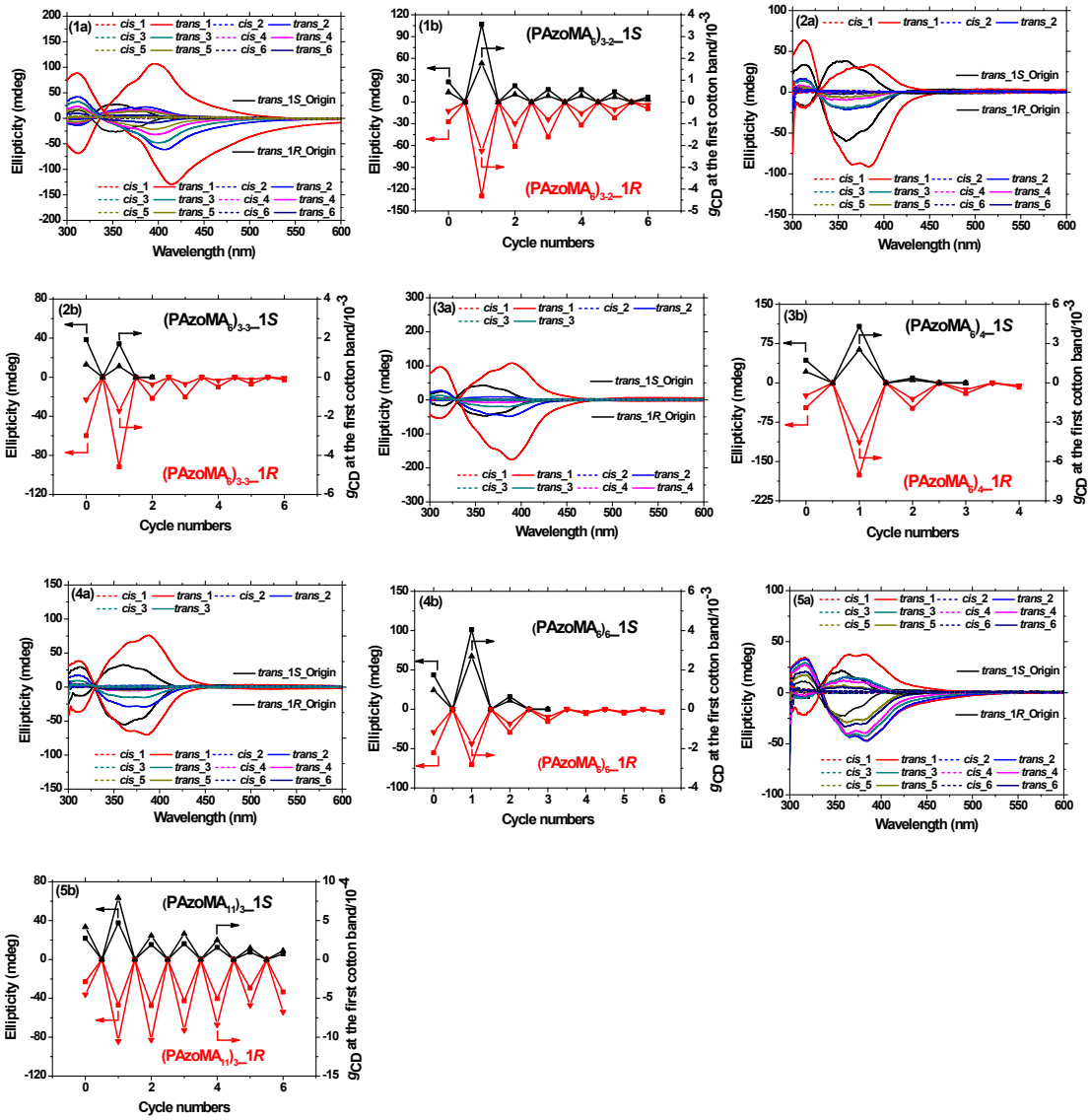
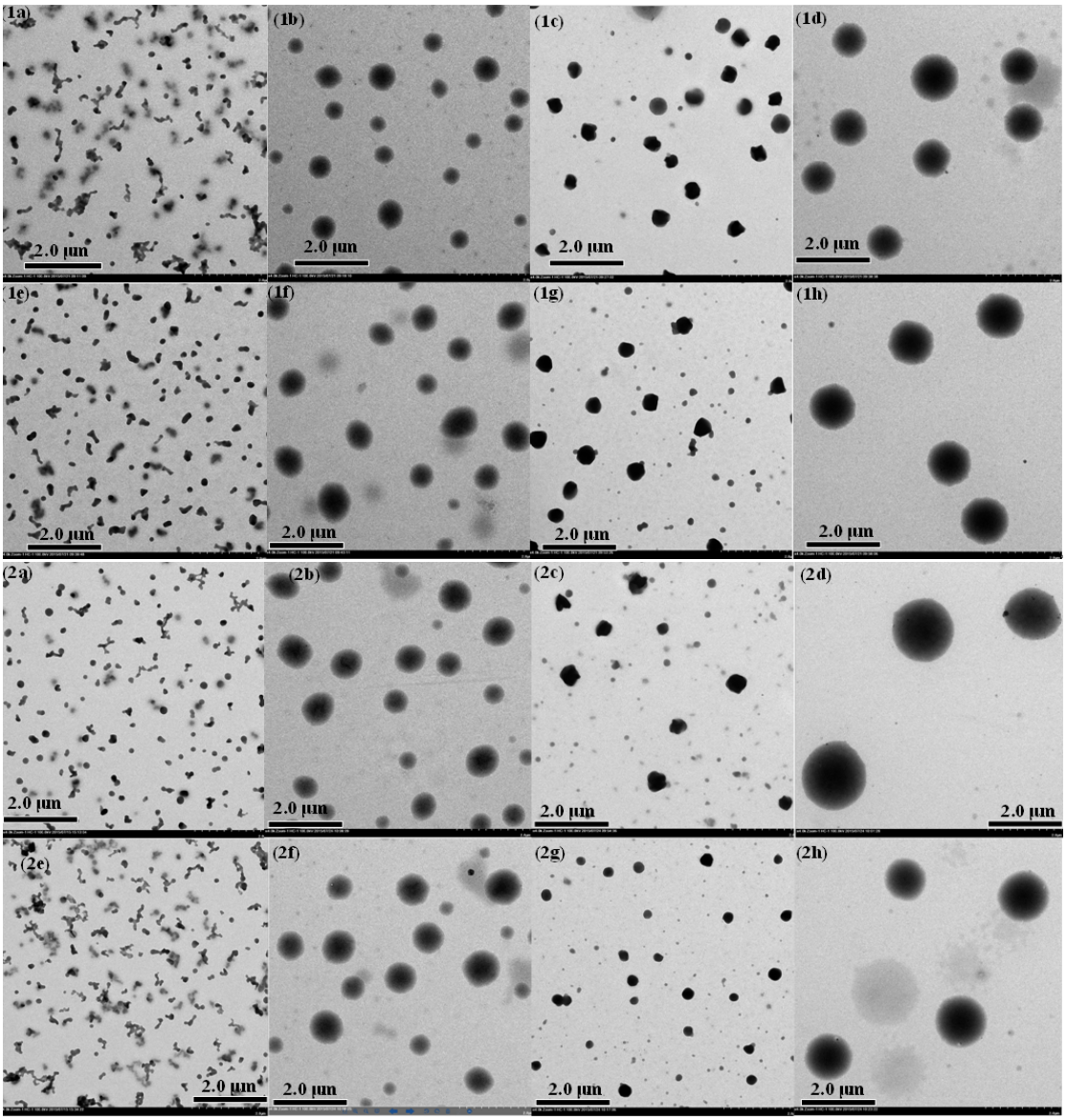


Fig. S9 Changes in CD spectra (a) and the maximum CD and g_{CD} values (b) of PAzoMA aggregates in DCE/(1*R* or 1*S*) during 365 nm light irradiation (3 min) and heating-cooling treatment (60 °C for 40 min then cooling to room temperature). The concentration of polymer repeating units is 8.42×10^{-5} mol/L. 1-5 stands for the $(PAzoMA_6)_{3\text{-}2}$, $(PAzoMA_6)_{3\text{-}3}$, $(PAzoMA_6)_4$, $(PAzoMA_6)_6$ and $(PAzoMA_{11})_3$, respectively.



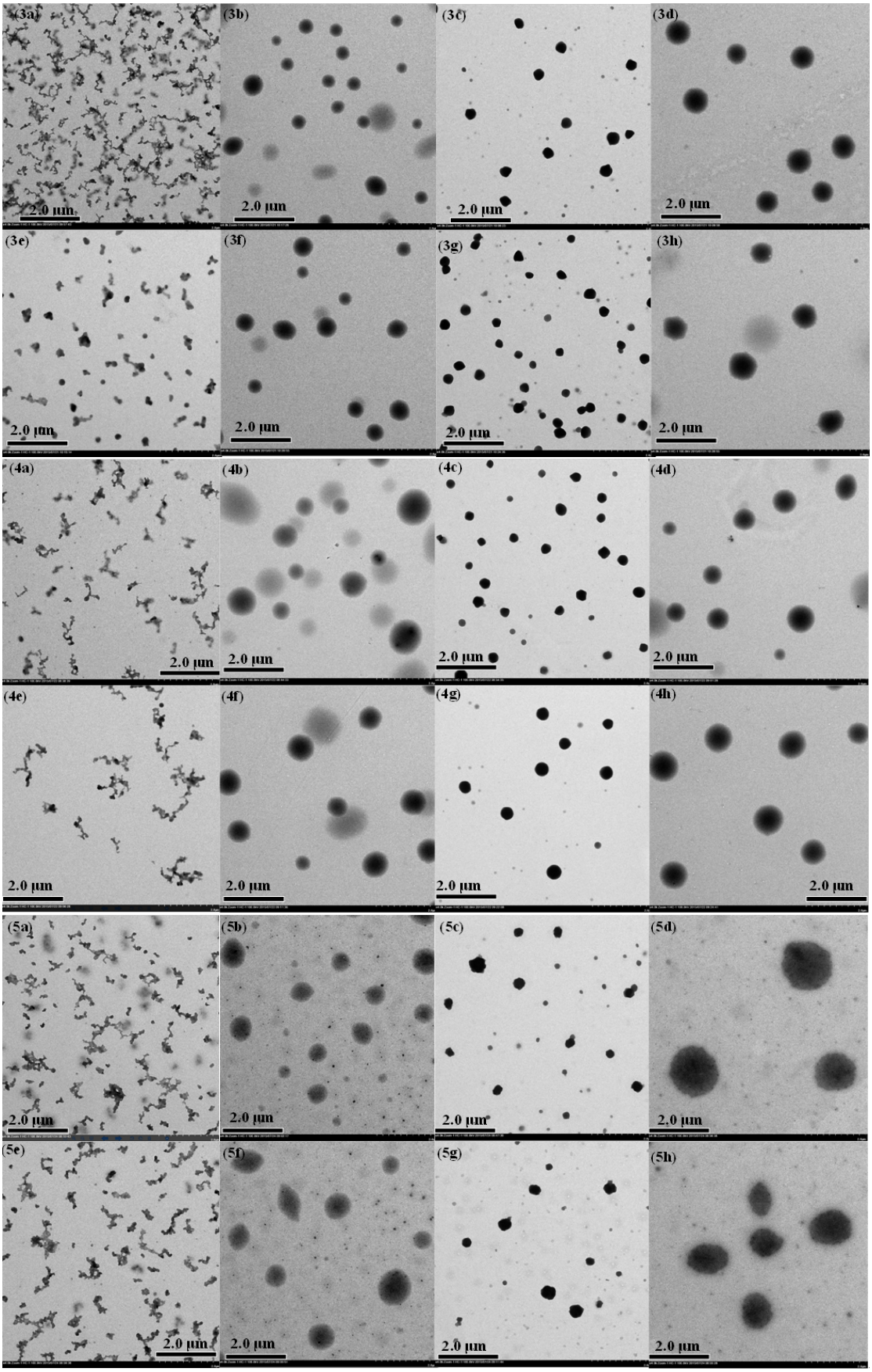


Fig. S10 TEM images of PAzoMA aggregates during chiroptical switching process. (a-d for 1*R*/DCE and e-h for 1*S*/DCE). The original *trans*-form (a and e), after the

first 3 min 365 nm light irradiation (b and f), after the heating-cooling treatment (c and g), after the second 3 min 365 nm light irradiation (d and h). 1-5 stands for the $(PAzoMA_6)_{3\text{-}2}$, $(PAzoMA_6)_{3\text{-}3}$, $(PAzoMA_6)_4$, $(PAzoMA_6)_6$ and $(PAzoMA_{11})_3$, respectively.