

Supporting Information

Unexpected Chirality Transition and Inversion Mediated by Dissolution- Aggregation and Odd-Even Effect

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S1 Materials and Characterization

Materials.

Methyl (*R*)-(+)-lactate (Adamas, $\geq 98\%$), methyl (*S*)-(-)-lactate (Adamas, $\geq 98\%$), tetrabutylammonium fluoride (Aladdin, 1.0 M in THF), *tert*-butylchlorodiphenylsilane (Amethyst, $\geq 98\%$), 2-chloroethanol, 3-chloro-1-propanol, 4-chloro-1-butanol, 5-chloro-1-pentanol, 6-chloro-1-hexanol (Acros, 95%), phenol (Aladdin, AR), methacryloyl chloride (Aladdin, 95%), 4-aminoanisole (Aladdin, AR), 1,2-triphenylphosphine (Greagent, $>99\%$), diethyl azodicarboxylate (Aladdin, $\geq 97\%$), 4-dimethylaminopyridine (Macklin, 99%), *n*-(3-dimethylaminopropyl)-*n*'-ethylcarbodiimide hydrochloride (Accela, 97%), lithium aluminum hydride (Amethyst, $\geq 97\%$), dichloroethane (DCE) (Aladdin, 99%), methylcyclohexane (MCH) (Adamas, $>99\%$) were used without further purification. 2-Cyanoprop-2-yl-1-dithionaphthalate (CPDN) was synthesized according to the literature.¹ 2,2-Azobisisobutyronitrile (AIBN) was recrystallized twice from ethanol. The monomers MAzo-*L/D*-*m* (*m* = 3, 6, 7, 8, 9, and 10) were synthesized according to the previously reported procedures.^{2,3} The monomer MAzo-*L-2* was synthesized according to the previously reported procedures.^{3,4}

Characterization.

- ¹H NMR spectra were recorded on a Bruker nuclear magnetic resonance instrument (300 MHz, Bruker, Karlsruhe, Germany) using CDCl₃ as the solvent and tetramethylsilane (TMS) as the internal standard at 25 °C.
- Gel permeation chromatograph (GPC) measurements were conducted on the TOSOH HLC-8320 gel permeation chromatograph (GPC) (Tokyo, Japan), which was equipped with a refractive index and UV detectors using two TSKgel SuperMultiporeHZ-N (4.6 × 150 mm, 3.0 μm beads size) columns (Tokyo, Japan) arranged in a series. It can separate polymers in the molecular weight range of 500-190k Da. THF was used as the eluent with a flow rate of 0.35 mL/min at 40 °C. The values of the average molecular weight (*M_n*) and molecular weight distribution (*D*) of the polymer was calculated with PS standard.
- CD spectra were recorded on a JASCO J-1500 spectropolarimeter equipped with a Peltier-controlled housing unit using an SQ-grade cuvette, a single accumulation, a path length of 10 mm, a bandwidth of 2 nm, a scanning rate of 200 nm/min, and a response time of 1 s. The samples were measured at 20 °C.
- TEM images were taken with a HITACHI HT7700 operated at an accelerating voltage of 120 kV. AFM images were captured with peak force quantitative nanomechanical mapping scan mode on Multimode 8 microscope (Bruker, USA).
- The thermal behaviors were measured by TA instrument DSC 250 (New Castle, DE, USA). The heating and cooling rates were both 10 °C /min.
- The monomers were also purified by chiral high-performance liquid chromatography (HPLC). Chiral HPLC was performed on an Agilent 1200 Series chromatographs using a Daicel Chiralpak AD-H column (0.46 cm × 25 cm).

7. The IR and VCD spectra of monomers and polymers were recorded with a JASCO FVS-6000 spectrometer using a resolution of 4 cm^{-1} and a collection time of 1.7 h. The IR and VCD spectra were recorded in THF- d_8 and the concentration is about 30 mg/mL in a CaF_2 cell with 150 μm path length.

S2 Experimental Procedures

1. Synthesis of side-chain Azo-polymers.

A series of side-chain Azo-polymers were obtained by reversible addition-fragmentation chain transfer (RAFT) polymerization, where CPDN and AIBN were used as the RAFT agent and the initiator, respectively. For example, MAzo-*L*-3 (220.8 mg, 0.60 mol), CPDN (3.26 mg, 0.012 mmol), AIBN (0.656 mg, 0.004 mmol) and dried tetrahydrofuran (1.0 mL) were added into a 5 mL ampoule bottle. The reaction tube was flame-sealed under an argon atmosphere after deoxygenated with three freeze-thaw cycles. Then the polymerization was carried out at 70 °C for 4 h. Polymers of other molecular weights were obtained by changing the ratio of monomers and RAFT reagents.

2. Preparation of polymer solutions in good solvents.

First, the polymer was dissolved in a good solvent such as tetrahydrofuran (THF) or 1,2-dichloroethane (DCE), and the concentration was 1 mg/mL. Then 0.1 mL of the polymer solution was taken into an SQ-cuvette, and then the good solvent was added to 3 mL. The CD and UV-vis spectroscopy tests were then performed.

3. Preparation of the optically active polymer aggregates in mixed solvents.

A certain volume of methylcyclohexane (MCH) was added to a DCE solution containing Azo-polymers (a total of 0.1 mg of polymer, the volume of DCE varies with the proportion of mixed solvent) in an SQ-cuvette. The total volume of good solvent and poor solvent is 3 mL. After being very slightly shaken, the yellow turbid solution of Azo-polymer aggregates was measured by using the CD/UV-vis spectrometers (if the proportion of good solvent is high, the Azo-polymer will be in a dissolved state). The other polymer aggregates were produced in a similar procedure.

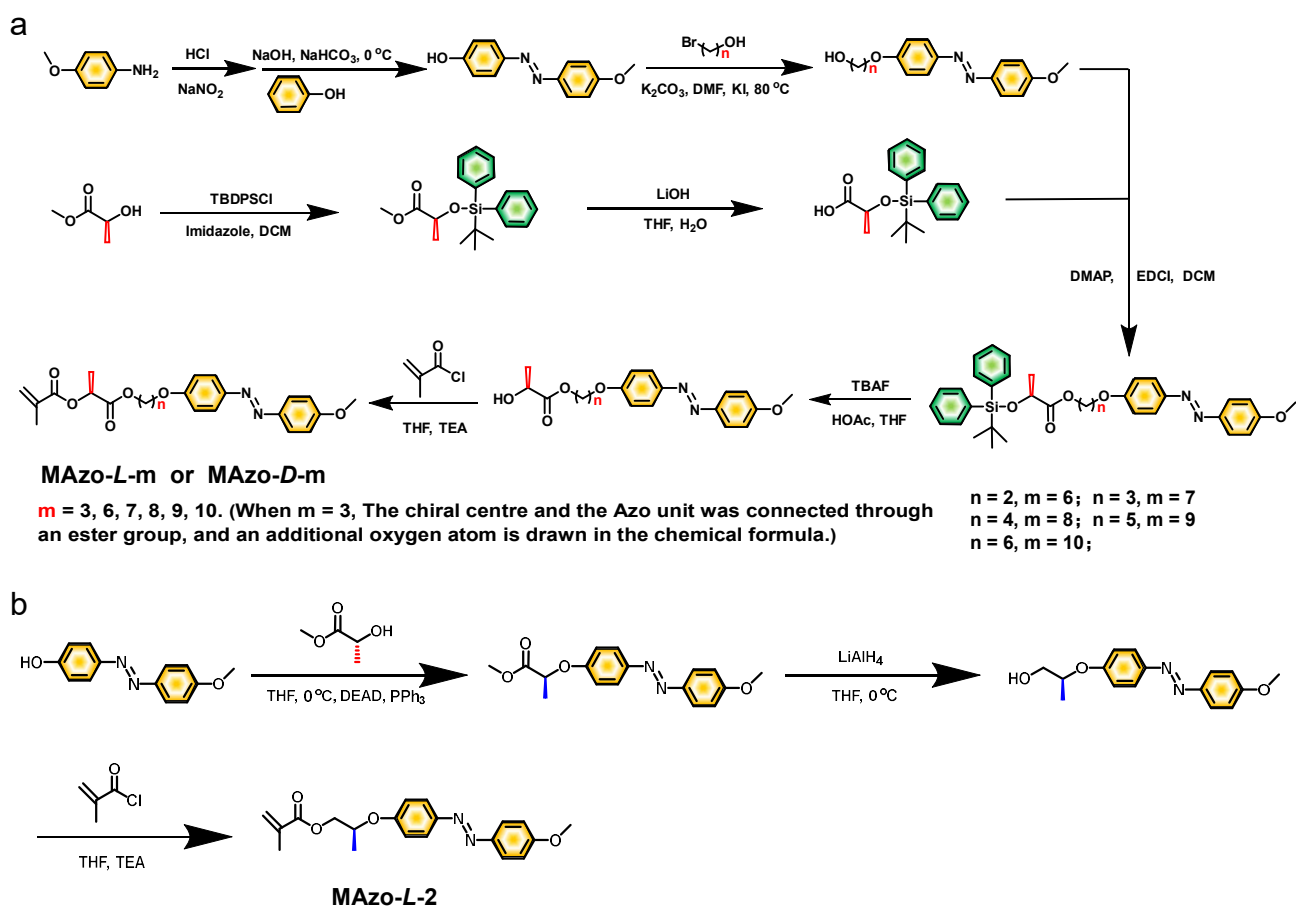
4. Heating treatment of polymer assemblies.

The heating-cooling (H-C) treatment process is to first heat up from 20 °C to 80 °C (30 °C/min), hold for a period of time (10 min), and then cool down to 20 °C (20 °C/min).

5. Filtration experiment of polymer solutions and assemblies.

In the filtration experiment, the completely dissolved solution and the assembly solution pass through the 0.45 μm syringe filter respectively, and then performed CD test.

S3 Results and Discussion



Scheme S1. Synthetic routes of chiral Azo monomers with different distances from chiral stereocenter to the Azo unit.

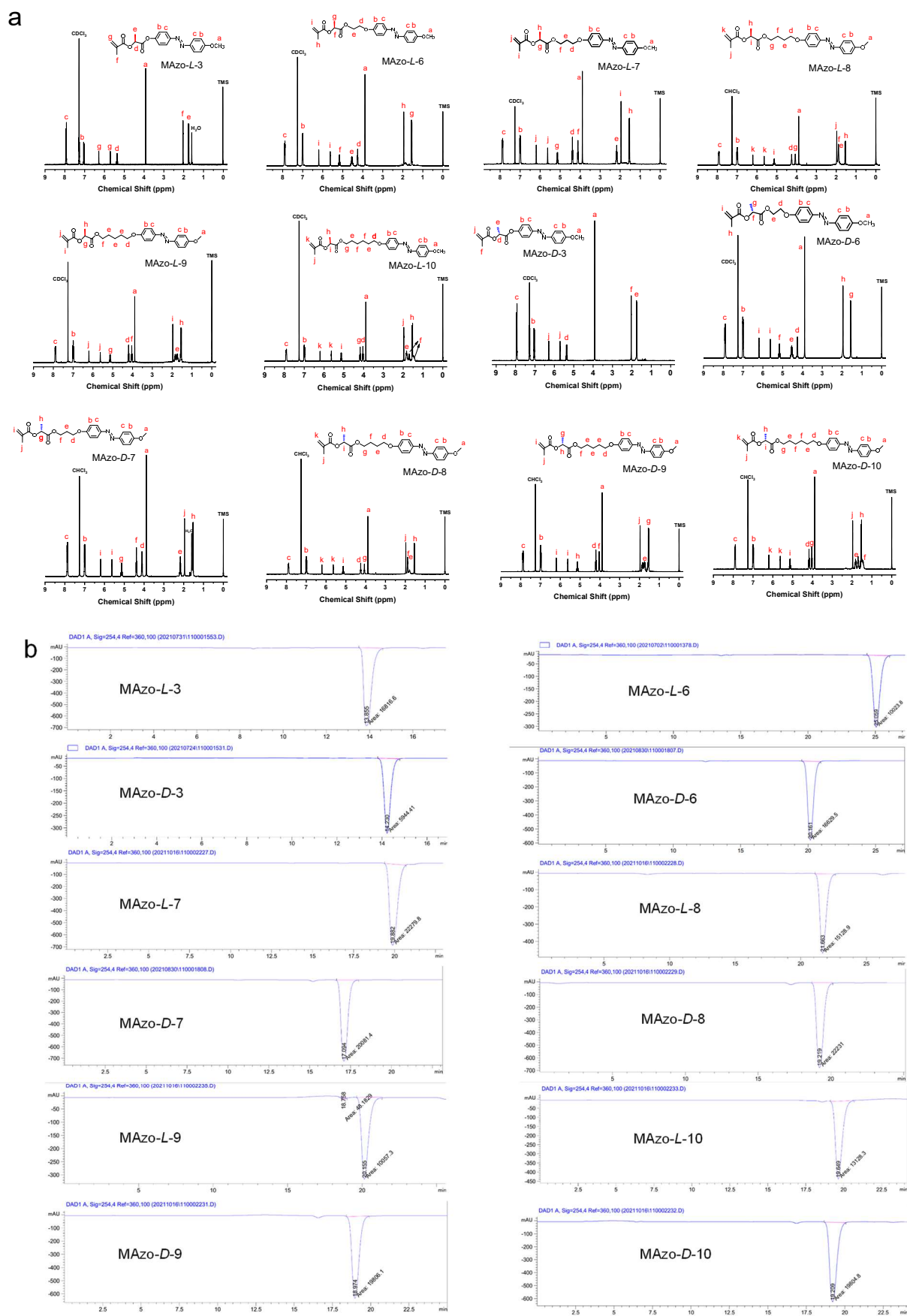


Figure S1. (a) ^1H NMR spectra of the chiral Azo monomers. (b) HPLC spectra of the chiral Azo monomers.

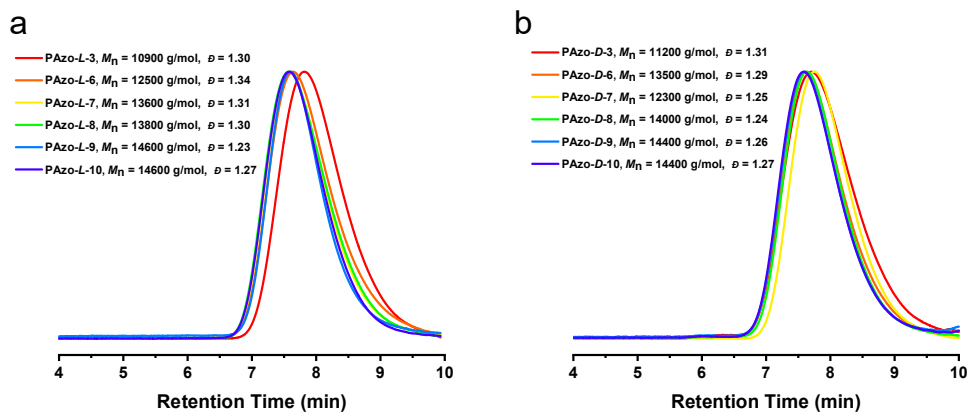


Figure S2. SEC curves of side-chain Azo-polymers.

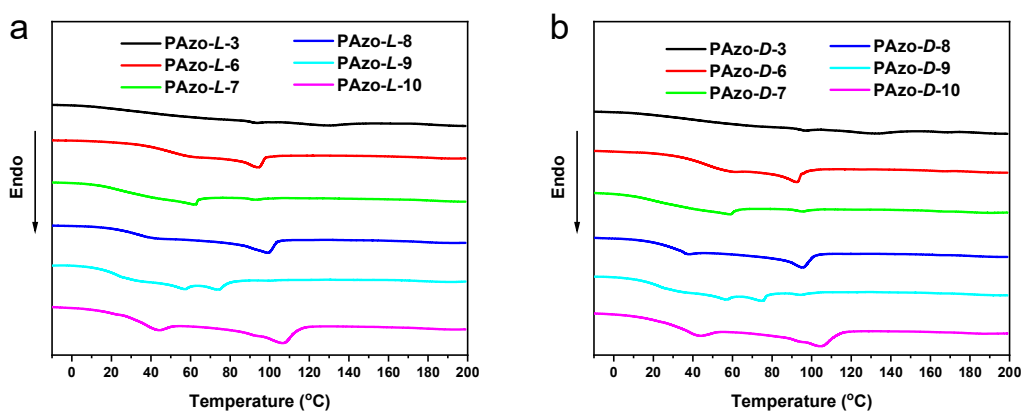


Figure S3. The second heating DSC curves of Azo-polymers.

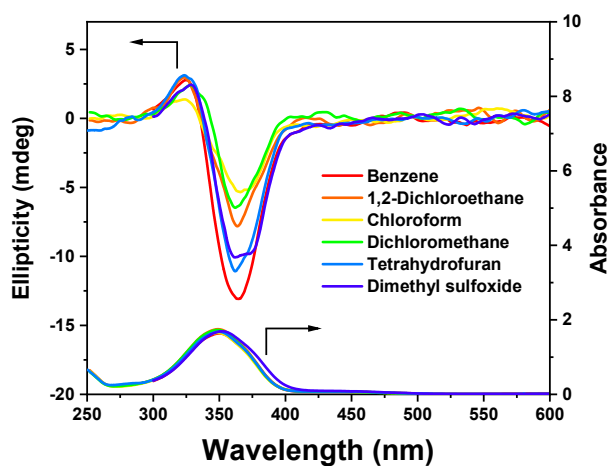


Figure S4. CD and UV-vis spectra of polymer PAzo-L-3 in different good solvents.

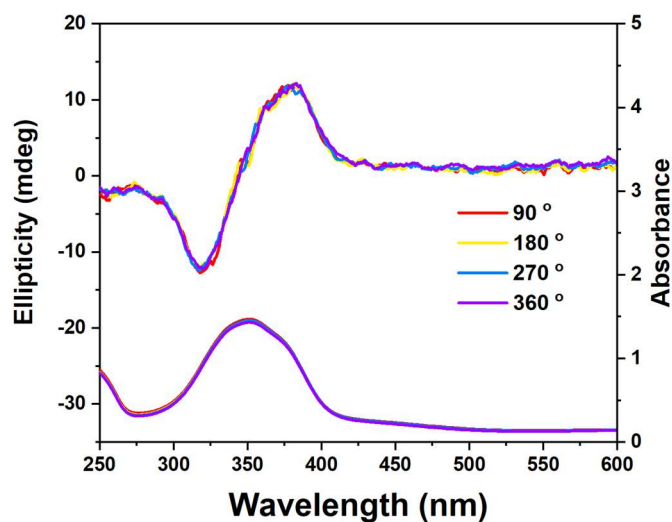


Figure S5. CD spectra of the PAzo-*L*-3 assemblies with different rotation angles.

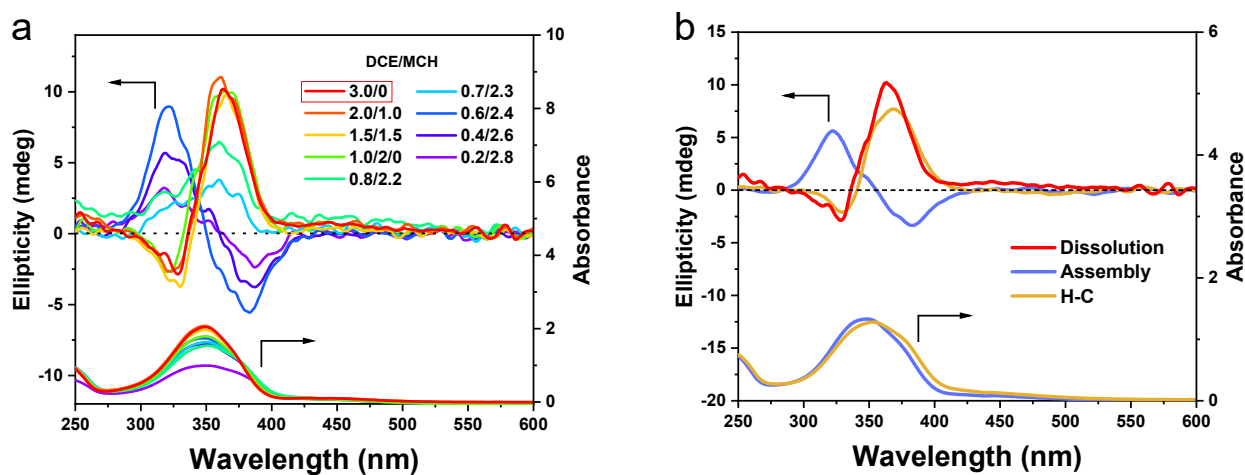


Figure S6. (a) CD and UV-vis spectra of PAzo-*D*-3 in mixed DCE/MCH solvents with different volume ratios. (b) CD and UV-vis spectra of PAzo-*D*-3 in pure DCE solvent, DCE/MCH (0.6/2.4, v/v) mixed solvent and after H-C treatment.

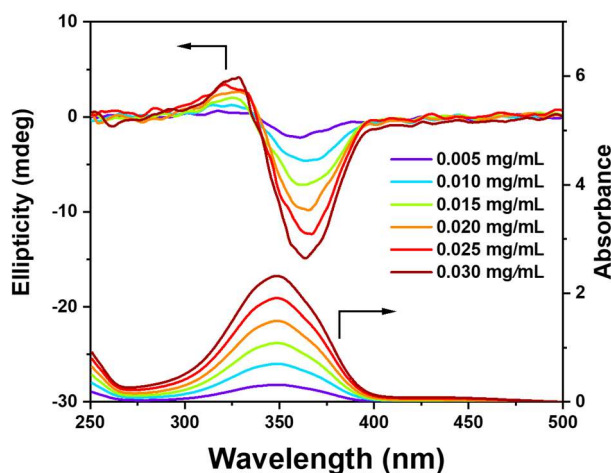


Figure S7. CD and UV-vis spectra of PAzo-*L*-3 measured in THF at 20 °C with different concentrations.

Table S1. Specific optical rotations of some Azo monomers and polymers.

sample ^a	MAzo-L-3	PAzo-L-3	MAzo-L-10	PAzo-L-10
$[\alpha]_{589}^{25}$	-16.0	-178.8	-4.2	-21.8

^a Specific optical rotation of monomer and polymer was measured at a concentration of 5.0 mg/mL in THF at 25 °C.

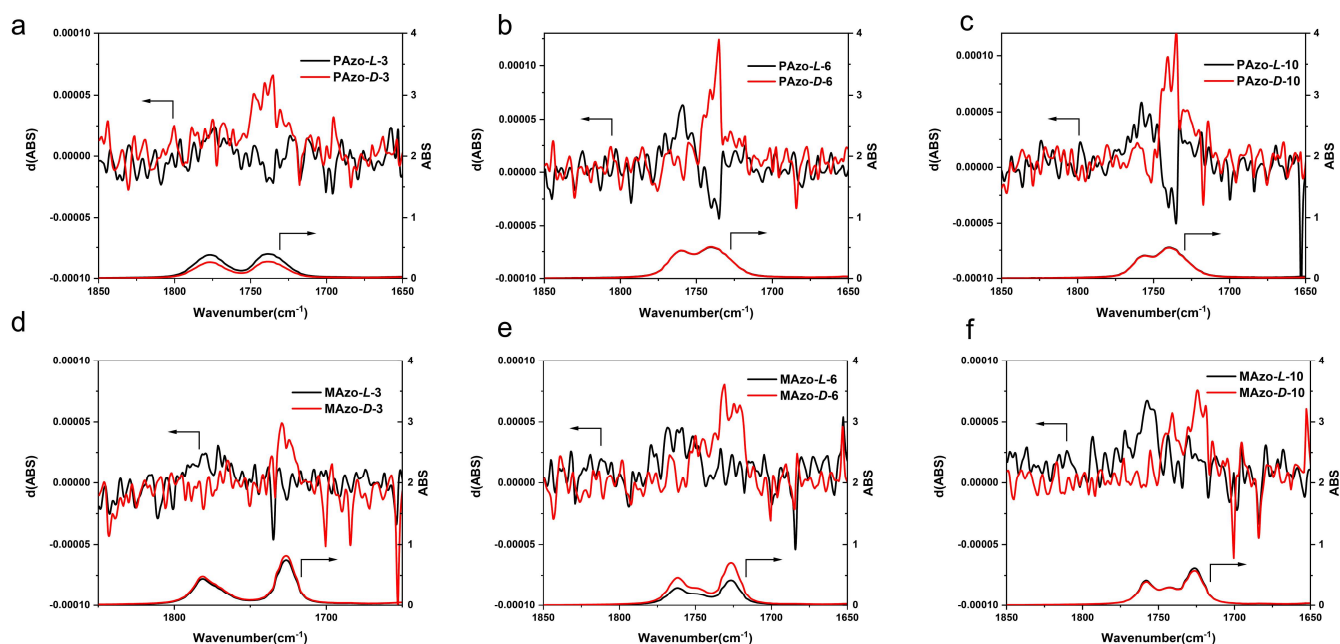


Figure S8. IR and VCD spectra of Azo monomers and polymers in THF-*d*₈.

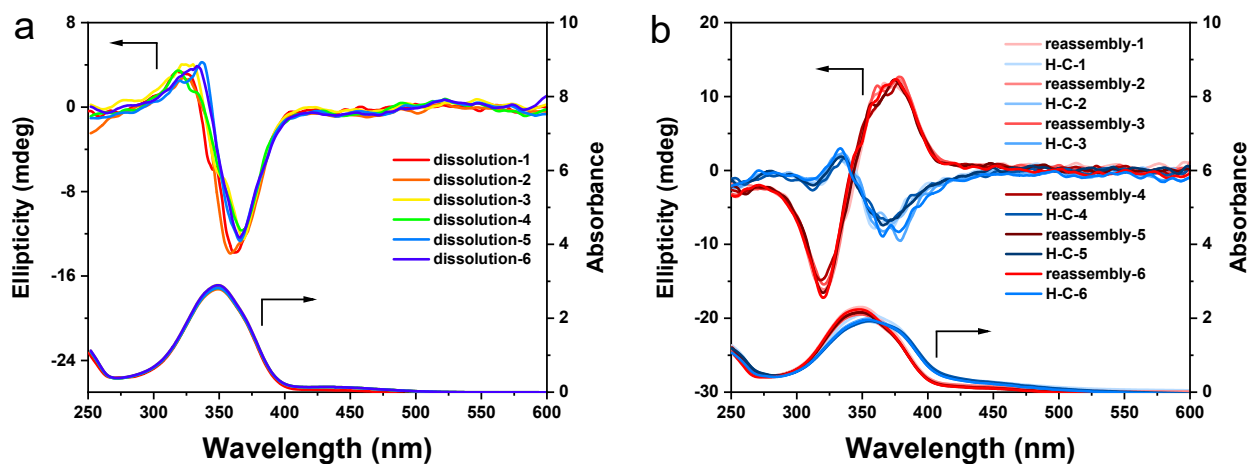


Figure S9. CD and UV-vis spectra of polymer PAzo-L-3 subjected to cyclic operations of dissolution, reassembly and H-C treatment. PAzo-L-3 in (a) dissolved state and (b) aggregated state and after H-C treatment.

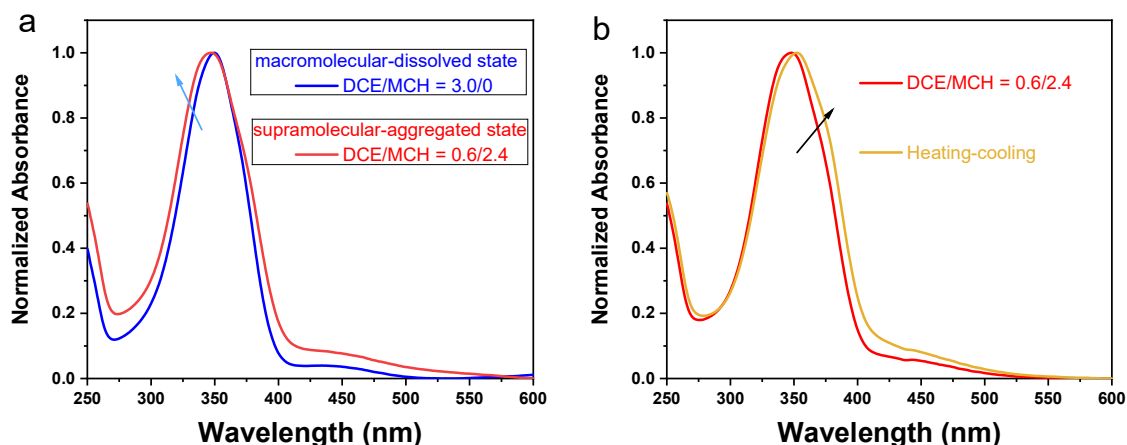


Figure S10. (a) The normalized UV-vis absorption spectra of PAzo-*L*-3 in dissolved state (DCE/MCH = 3.0/0, v/v) and aggregated state (DCE/MCH = 0.6/2.4, v/v). (b) The normalized UV-vis absorption spectra of PAzo-*L*-3 directly assembled in mixed solvent (DCE/MCH = 0.6/2.4, v/v) and thermally treated after assembly.

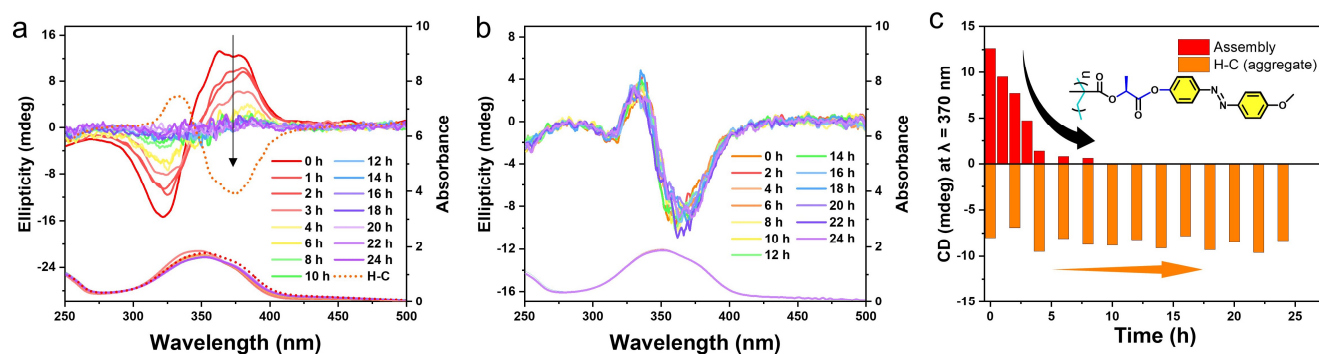


Figure S11. (a) Time-dependent CD spectra of PAzo-*L*-3 in the kinetic *H*-aggregated state (DCE/MCH = 0.6/2.4, v/v). (b) Time-dependent CD spectra of PAzo-*L*-3 after H-C treatment in the thermally stable *J*-aggregated state (DCE/MCH = 0.6/2.4, v/v). (c) Changes of the maximum CD values in a) and b).

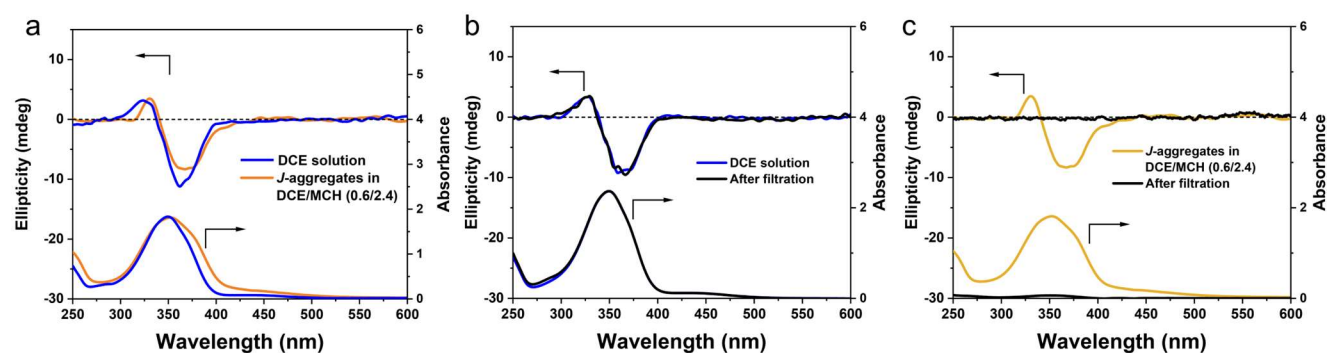


Figure S12. (a) CD and UV-vis absorption spectra of PAzo-*L*-3 in DCE solution and after H-C treatment. (b) CD and UV-vis absorption spectra of PAzo-*L*-3 before and after filtration in DCE solution. (c) CD and UV-vis absorption spectra of H-C-treated PAzo-*L*-3 aggregates (DCE/MCH = 0.6/2.4, v/v) before and after filtration (0.45 micron syringe filter selected).

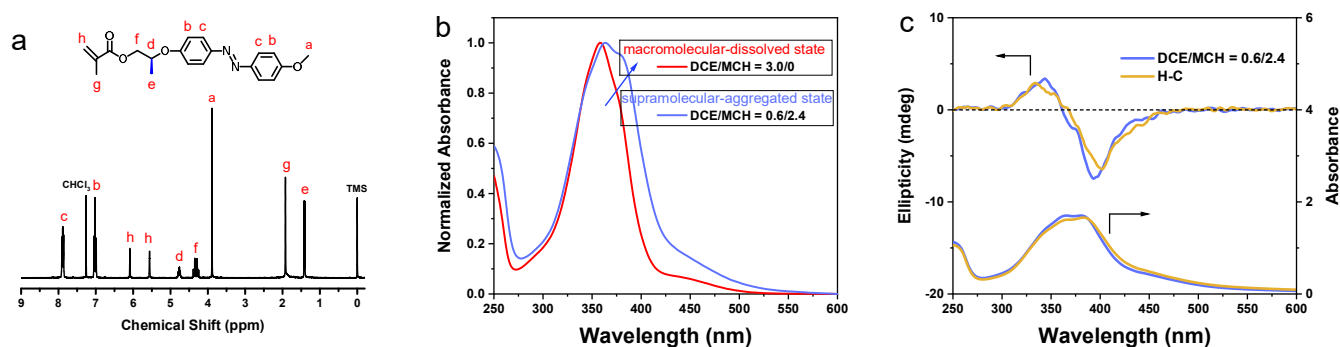


Figure S13. (a) ¹H NMR spectra of MAzo-L-2. (b) UV-vis absorption spectra of PAzo-L-2 in macromolecular-dissolved state (DCE/MCH = 3.0/0, v/v) and supramolecular-aggregated state (DCE/MCH = 0.6/2.4, v/v). (c) CD and UV-vis absorption spectra of PAzo-L-2 assembled in mixed solvent (DCE/MCH = 0.6/2.4, v/v) and after H-C treatment.

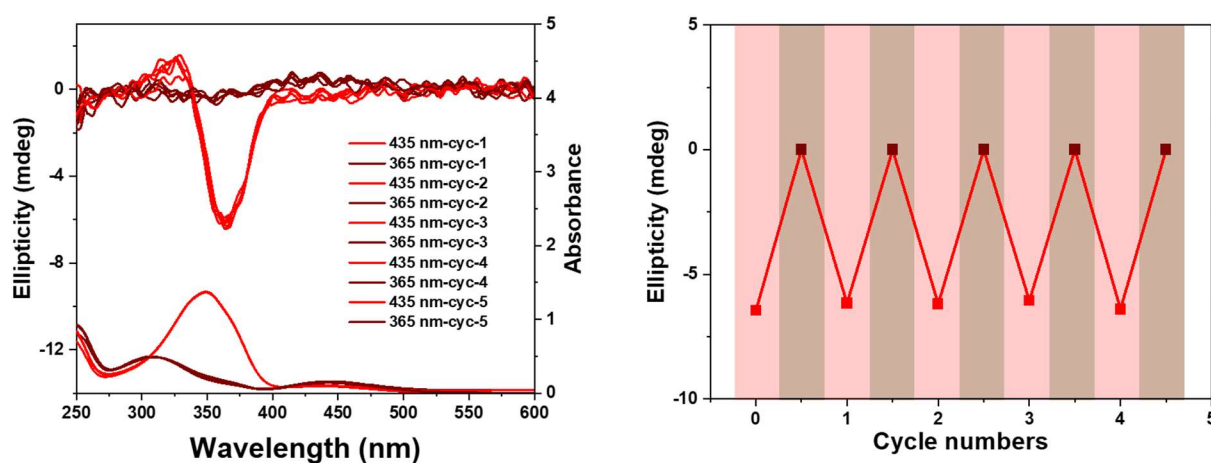


Figure S14. The chiroptical switch of PAzo-L-3 in dissolved state regulated by the alternating irradiation of 365 nm UV light and 435 nm visible light.

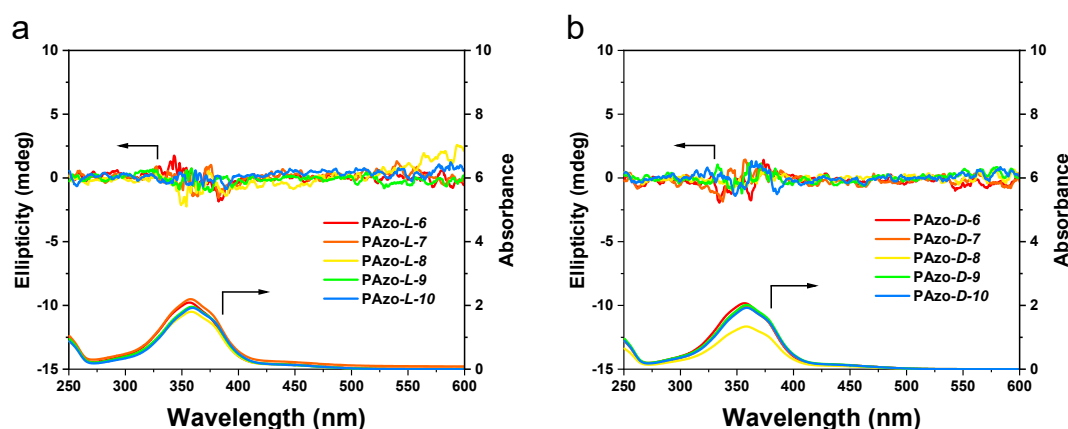


Figure S15. CD and UV-vis spectra of (a) L-type Azo-polymers and (b) D-type Azo-polymers in DCE.

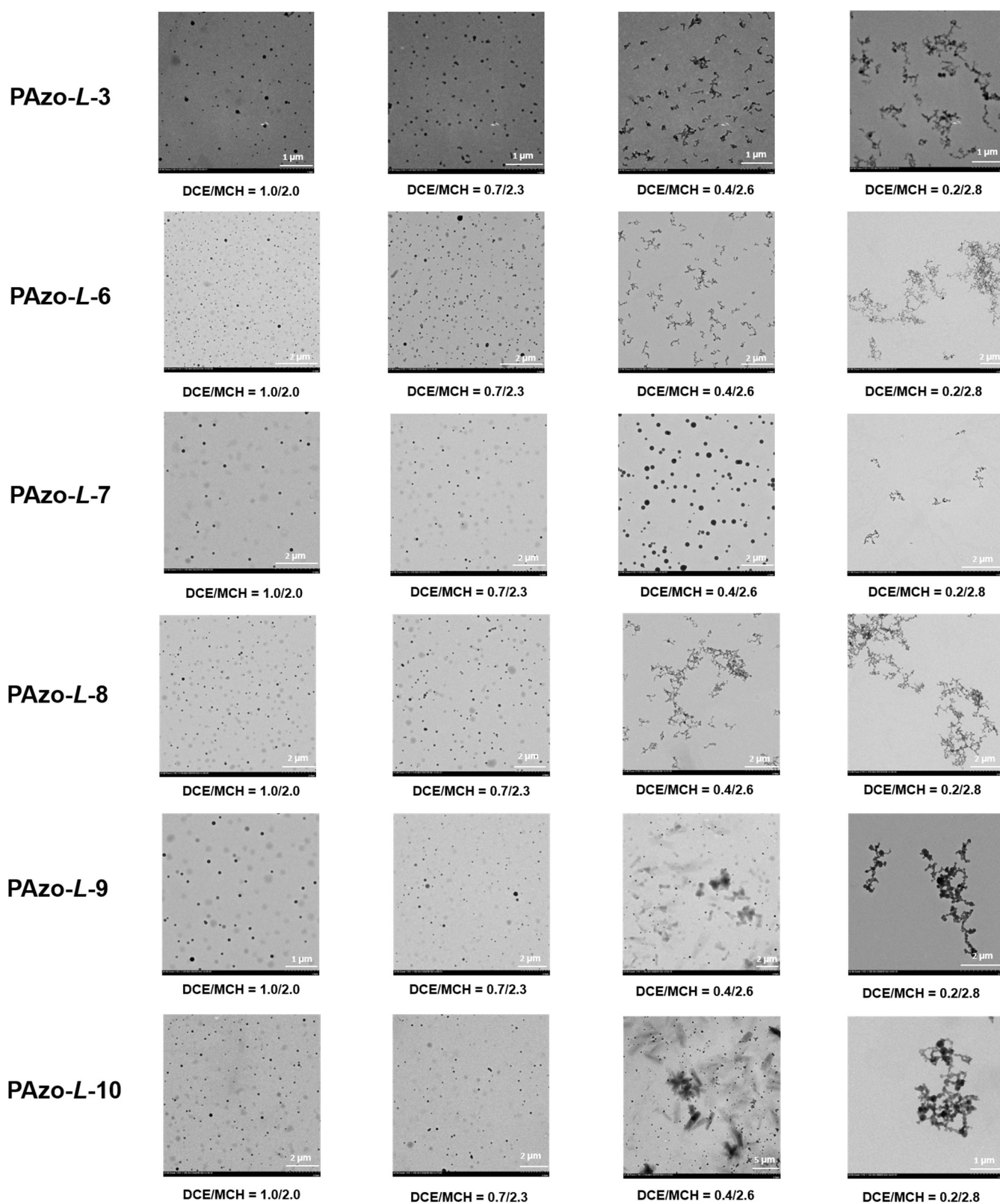


Figure S16. TEM images of Azo-polymer assemblies in DCE/MCH mixed solvents.

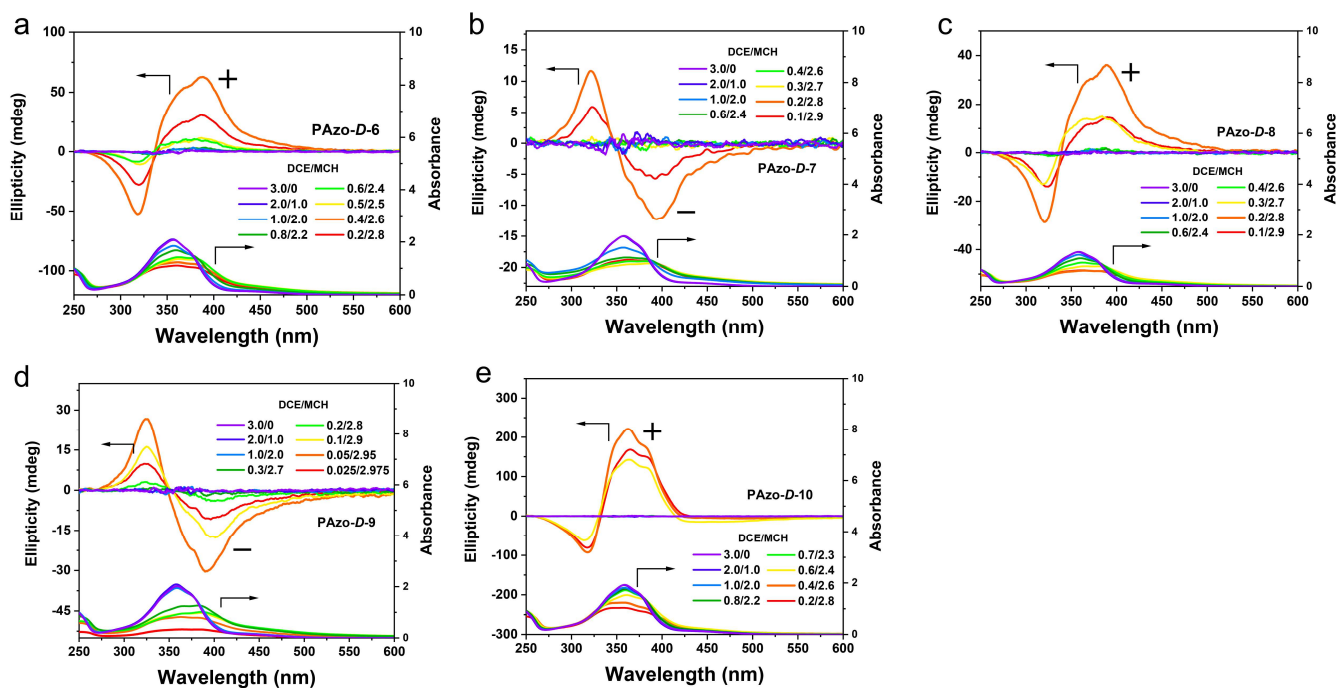


Figure S17. CD and UV-vis spectra of PAzo-D-m (m = 6, 7, 8, 9, and 10) in mixed solvents with different DCE/MCH volume ratios.

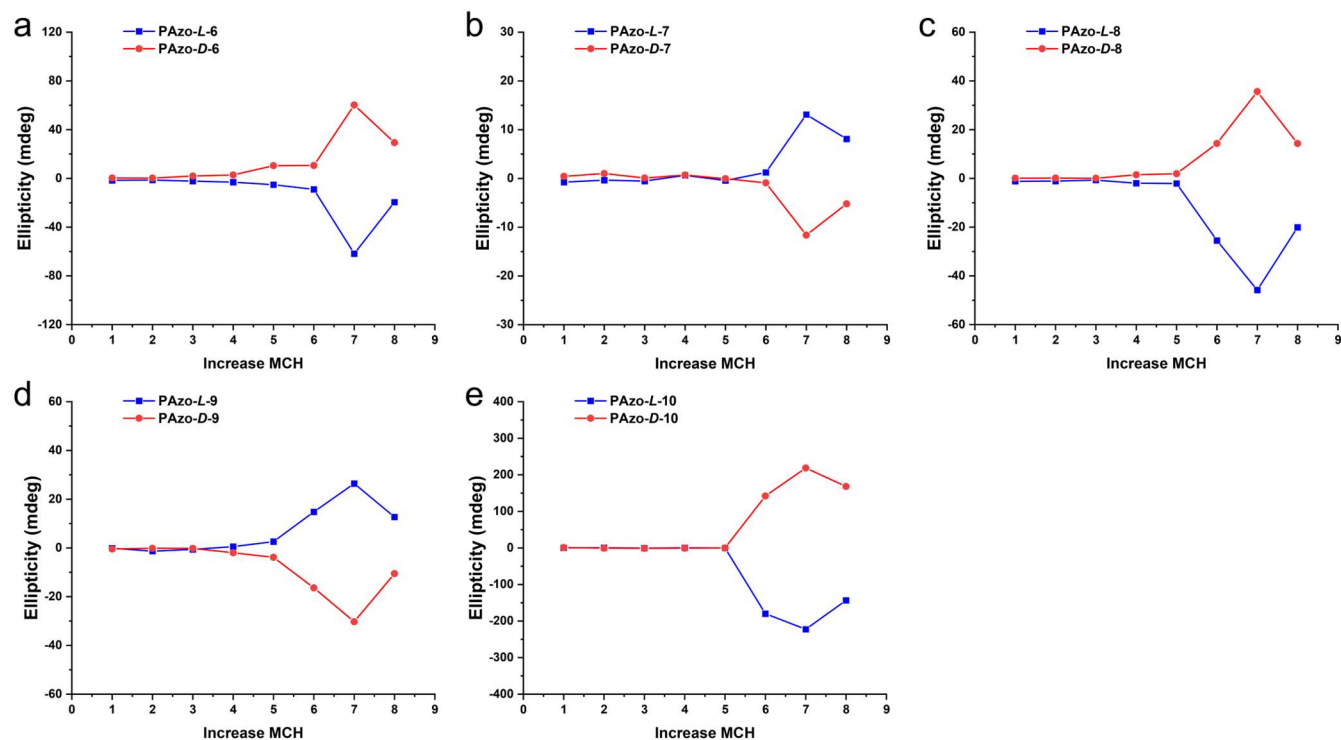


Figure S18. The change of CD maximum values of PAzo-L/D-m (m = 6, 7, 8, 9, and 10) in mixed DCE/MCH solvents with the increase of MCH volume contents.

S4 References

- 1 Z. Zhang, W. Wang, H. Xia, J. Zhu, W. Zhang and X. Zhu, *Macromolecules*, 2009, **42**, 7360.
- 2 W. Xie, B. Zou, D. Pei and D. Ma, *Org. Lett.*, 2005, **7**, 2775.
- 3 J. del Barrio, R. M. Tejedor, L. S. Chinelatto, C. Sánchez, M. Piñol and L. Oriol, *J. Mater. Chem.*, 2009, **19**, 4922.
- 4 A. Khan, C. Kaiser and S. Hecht, *Angew. Chem. Int. Ed.*, 2006, **45**, 1878.