Electronic Supplementary Information (ESI)

Mirror Symmetry Breaking and Restoration within μm-sized Polymer Particles in Optofluidic Media by Pumping Circularly Polarised Light

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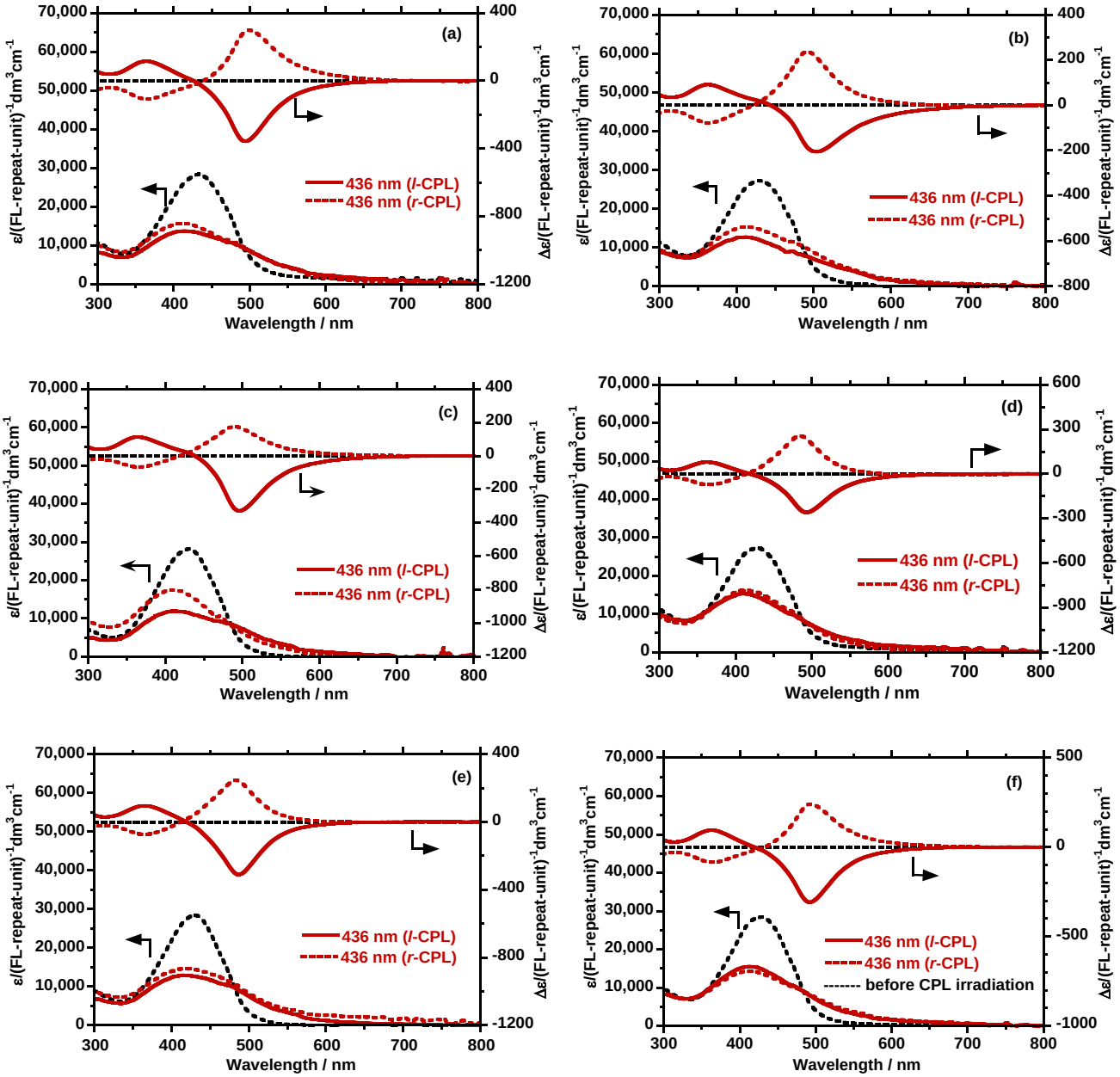

Fig. S1. CD and UV-vis spectra of **F8AZO** aggregates in (a) $CHCl_3$/ethanol (EtOH) (1.3/1.7, v/v), (b) $CHCl_3$/*n*-propanol (*n*-PrOH) cosolvent (1.1/1.9, v/v), (c) $CHCl_3$/*n*-butanol (*n*-BuOH) cosolvent (1.1/1.9, v/v), (d) $CHCl_3$/*i*-propanol (*i*-PrOH) cosolvent (1.1/1.9, v/v), (e) $CHCl_3$/*i*-butanol (*i*-BuOH) cosolvent (0.8/2.2, v/v), and (f) $CHCl_3$/*n*-pentanol (*n*-PenOH) cosolvent (0.8/2.2, v/v). These spectra were obtained by irradiating with first the 436-nm *l*-CPL (solid lines) then the 436-nm *r*-CPL (dash lines). For clarity, the CD and UV-vis spectra before CPL pumping are shown by black dotted lines.

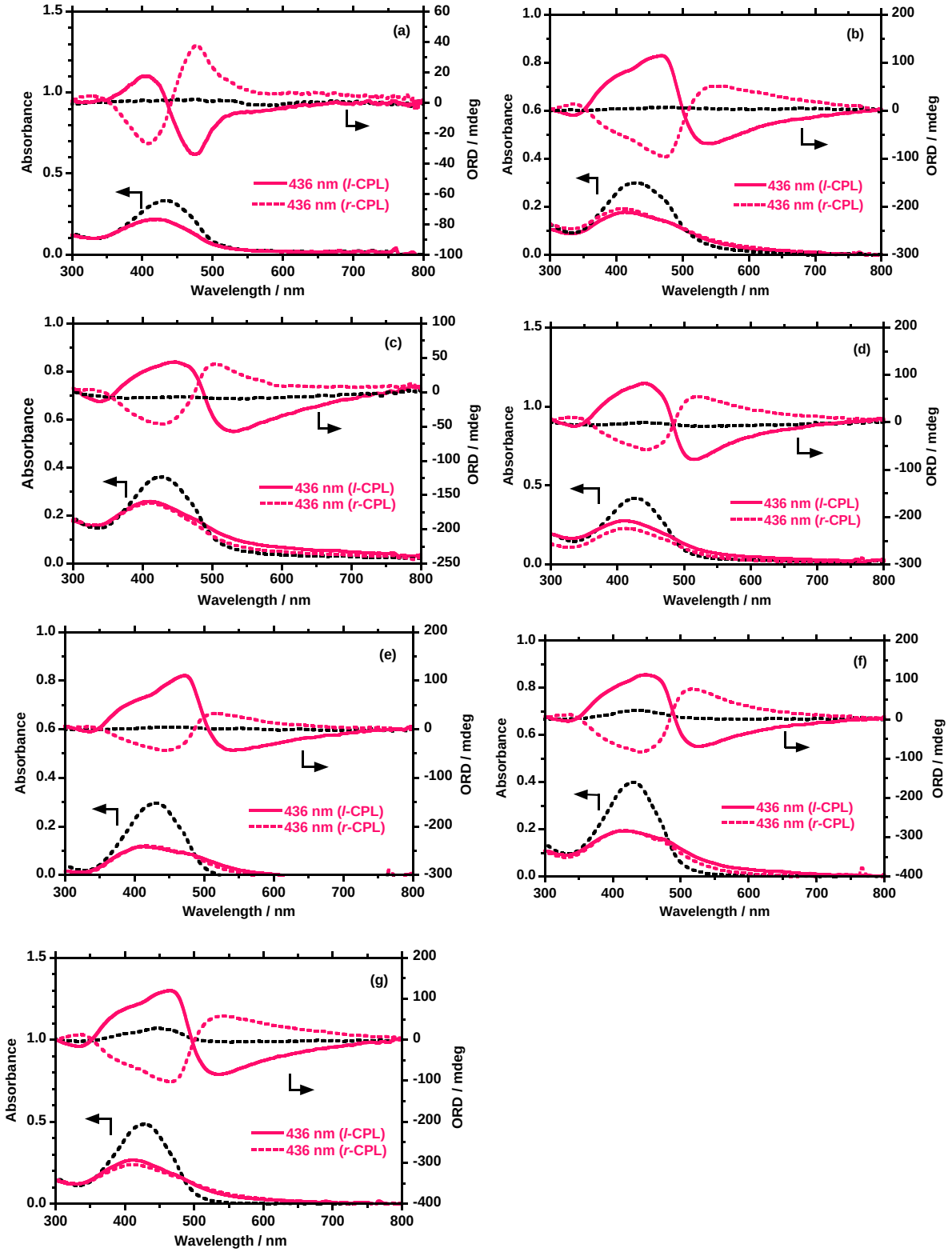

Fig. S2. ORD and UV-vis spectra of the **F8AZO** aggregates in (a) $CHCl_3$/MeOH cosolvent (1.4/1.6, v/v), (b) $CHCl_3$/EtOH cosolvent (1.3/1.7,v/v), (c) $CHCl_3$/*n*-PrOH cosolvent (1.1/1.9, v/v), (d) $CHCl_3$/*n*-BuOH cosolvent (1.1/1.9, v/v), (e) $CHCl_3$/*i*-PrOH cosolvent (1.1/1.9, v/v), (f) $CHCl_3$/*i*-BuOH cosolvent (0.8/2.2, v/v) and (g) $CHCl_3$/*n*-PenOH cosolvent (0.8/2.2, v/v). These spectra were obtained by irradiating with first the 436-nm *l*-CPL and then the 436-nm *r*-CPL. For clarity, the ORD and UV-vis spectra before CPL irradition are shown by black dotted lines.

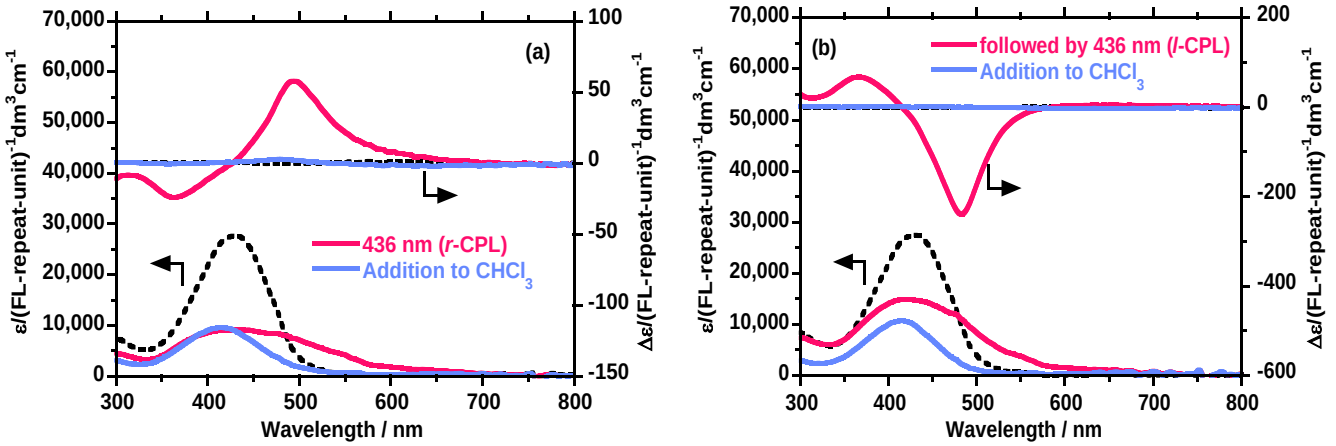

Fig. S3. (a and b) The changes in the CD and UV-vis spectra at 25 °C for **F8AZO** particles (black dotted lines, before pumping) generated in $CHCl_3$/*i*-BuOH (0.8/2.2, v/v) by pumping with the 436-nm *r*-CPL and *l*-CPL for 30 min to form the chiral **F8AZO** aggregates followed by adding 1.5 mL of the solution to 1.5 mL of $CHCl_3$. For clarity, the CD and UV-vis spectra before the CPL pumping are shown by black dotted lines.

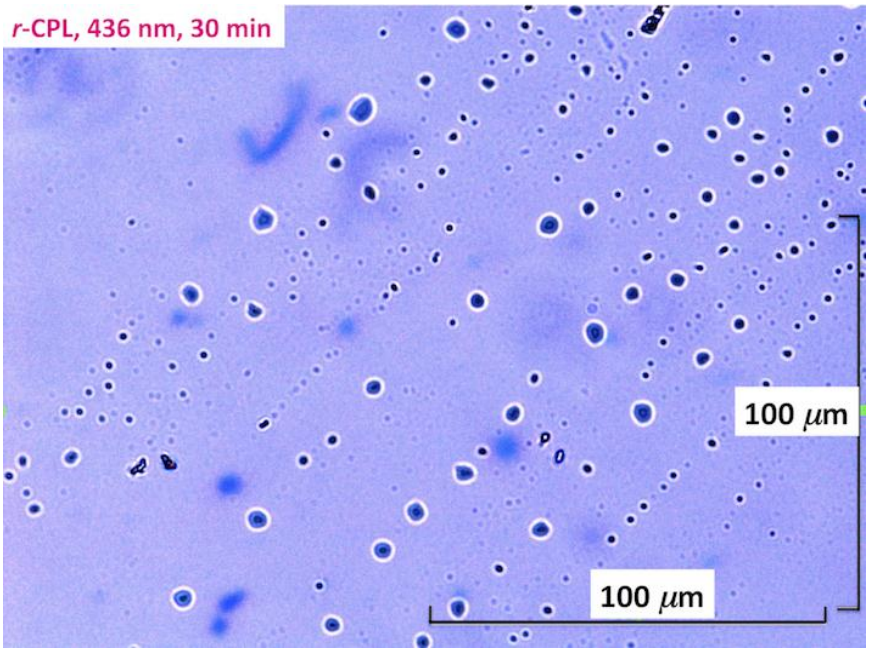

Fig. S4. Optical microscopic images of **F8AZO** aggregates dispersed in a $CHCl_3$/MeOH optofluidic solution (1.3/1.7, v/v) after the 436-nm *r*-CPL pumping for 30 min.

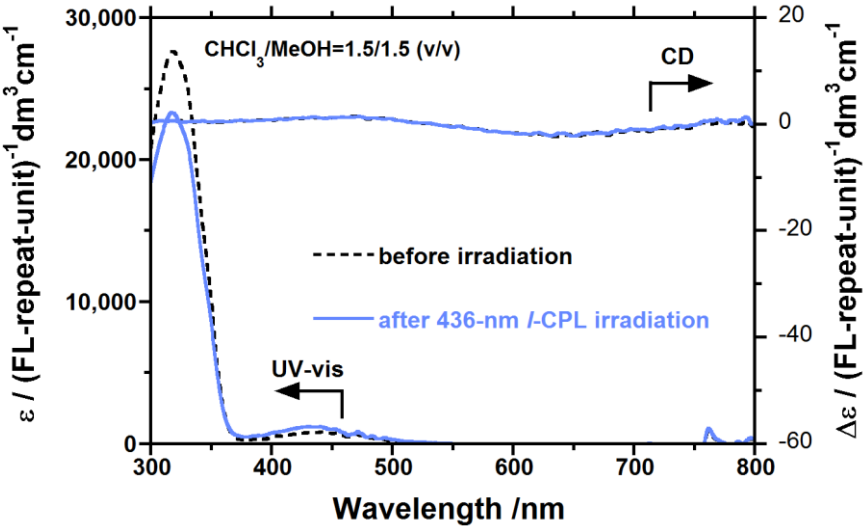

Fig. S5. CD and UV-vis spectra of molecular azobenzene particles in a $CHCl_3$/MeOH solution (1.5/1.5, v/v) pumped with *l*-CPL at 436 nm.

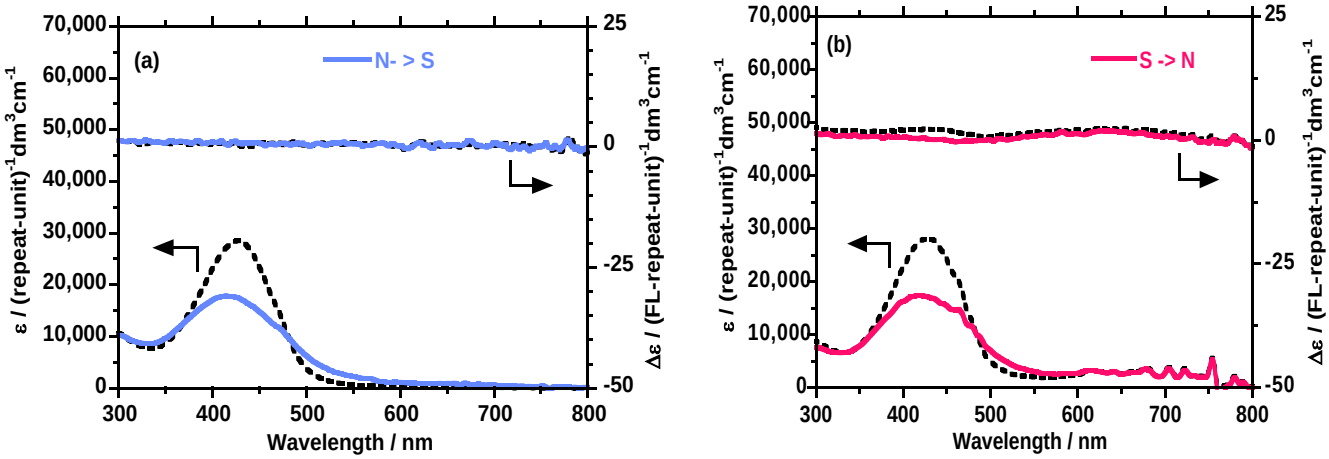

Fig. S6. CD and UV-vis spectra of **F8AZO** aggregates in a $CHCl_3$/MeOH solution (1.3/1.7, v/v) pumped with the 436-nm unpolarised light under (a) north-up and (b) south-up magnetic flux conditions with a density H_0 = 0.45 T. For clarity, the CD and UV-vis spectra before the CPL pumping are shown by black dotted lines.

Table S1. Power intensity of unpolarised and both *left*- and *right*-circularly polarised light.

Wavelength [nm]	Unpolarised light [μW cm^{-2}]	*left*-CPL [μW cm^{-2}]	*right*-CPL [μW cm^{-2}]
313	29	18	18
365	40	37	39
405	20	21	21
436	43	34	36
546	74	85	73
577	107	104	104

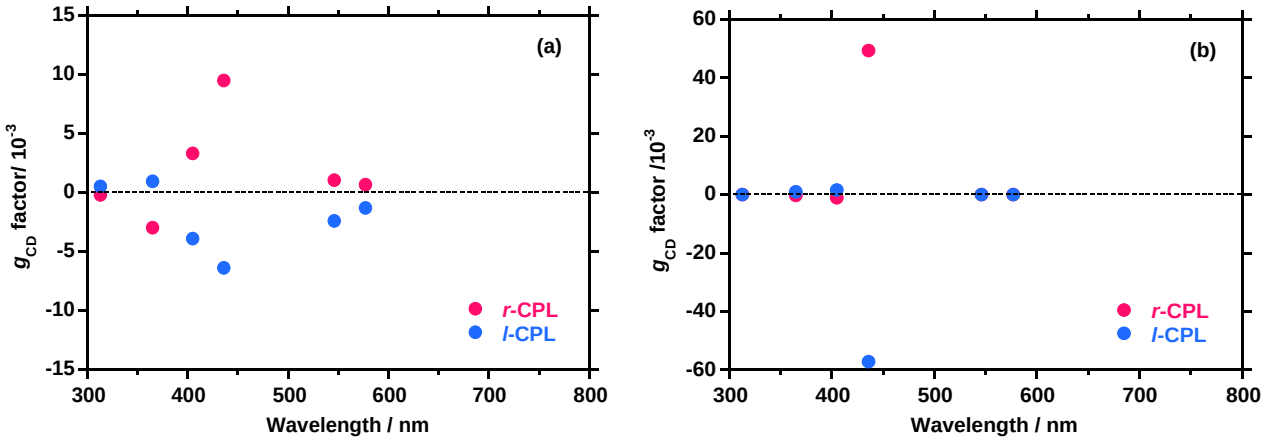

Fig. S7. The g_{CD} value of the first Cotton band as a function of the irradiating wavelength in (a) the $CHCl_3$/MeOH (1.3/1.7, v/v) and (b) $CHCl_3$/*n*-PenOH (0.7/2.1, v/v) cosolvents.

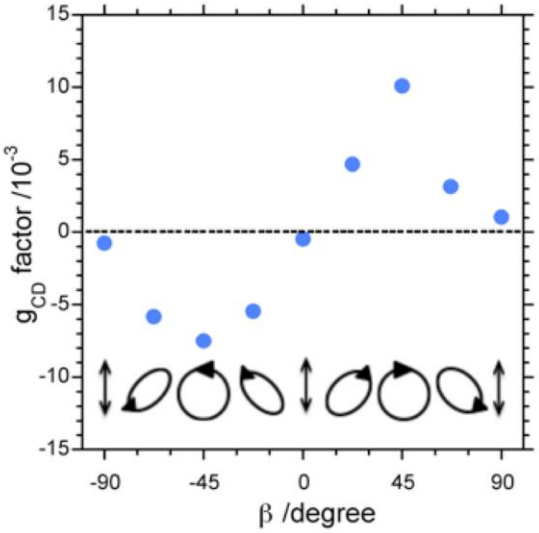

Fig. S8. The g_{CD} values of the particles in a $CHCl_3$/MeOH cosolvent (1.3/1.7, v/v) as a function of the ellipticity (β) of the 436 nm light.

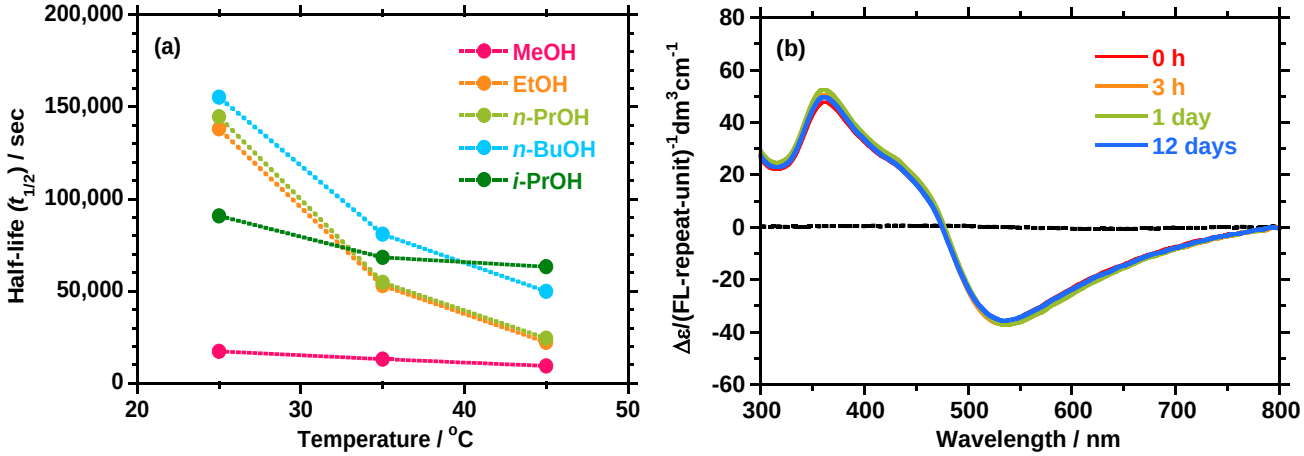

Fig. S9. (a) The half-life ($t_{1/2}$) of the CD amplitude at three temperatures (25, 35 and 45 °C). (b) The change in the CD spectra at 25 °C for **F8AZO** aggregates generated in $CHCl_3$/*i*-BuOH for four different times. For the solvent volume fractions, see Fig. 1 and ESI, Fig. S1†.

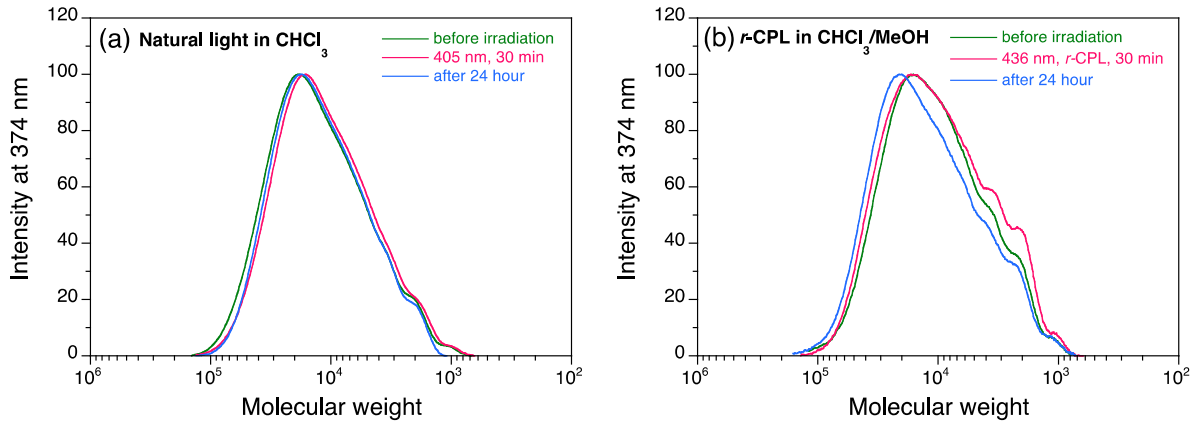

Figure S10. (*a*) Gel permeation chromatography (GPC) charts of **F8AZO** in chloroform at room temperature before the pumping with 405 nm unpolarised light (green solid curve), after the pumping for 30 min (red solid curve) and one day after pumping (blue solid curve). (*b*) GPC charts of **F8AZO** particle suspended in MeOH/chloroform = 1.7/1.3 (v/v) at room temperature before the pumping with 436 nm *r*-CPL (green solid curve) for 30 min and after pumping (red solid curve).

Table S2. Weight-averaged and number-averaged molecular weights (M_w and M_n) and polydispersity indices (*PDI*) of **F8AZO** both before and after unpolarised pumping with 405 nm light in chloroform at room temperature.

$M_w/10^3$	$M_n/10^3$	*PDI*	remarks
16.2	7.9	2.04	before the 405 nm pumping (initial *trans*)
15.3	6.8	2.24	after the 405-nm pumping (*cis*)
17.2	7.5	2.30	1 day after the 405-nm pumping (recovered *trans*)

Table S3. M_w, M_n and *PDI* of **F8AZO** particles suspended in MeOH/chloroform = 1.7/1.3 (v/v) at room temperature before the 436 nm *r*-CPL pumping, after pumping and one day after pumping.

$M_w/10^3$	$M_n/10^3$	*PDI*	remarks
14.6	6.3	2.32	before the 436-nm *r*-CPL pumping
14.3	5.7	2.51	after the 405-nm pumping for 30 min
17.3	6.9	2.51	1 day after the 405-nm pumping

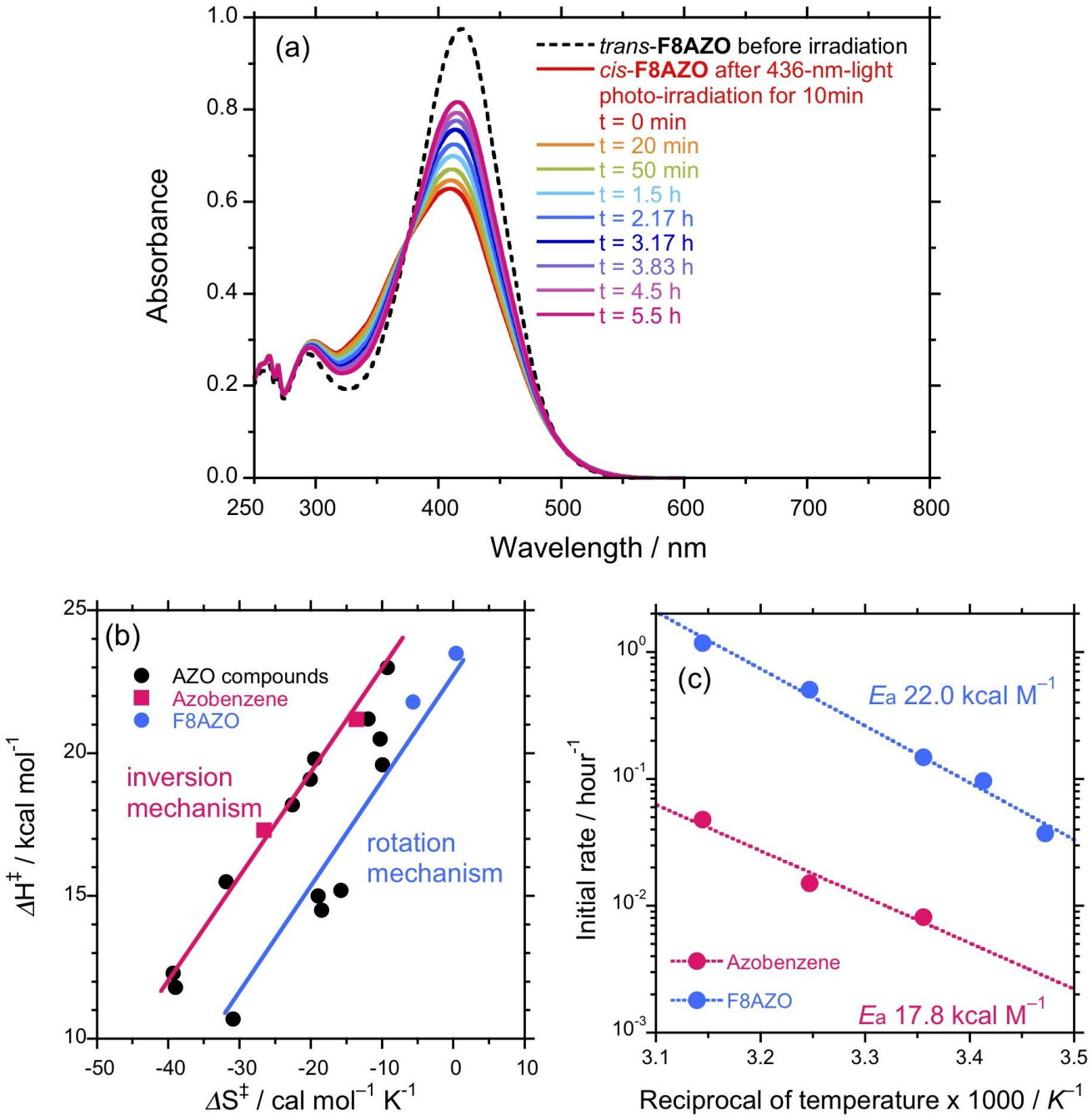

Fig. S11. (a) The change in the UV-vis spectra of the thermally-driven *cis*□*trans* isomerization of **F8AZO** in chloroform at 25 °C as a function of time after irradiating with 436-nm unpolarised light for 10 min. (b) The Eyring plots of the activation enthalpy–activation entropy ($\Delta H^{\ddagger}$–$\Delta S^{\ddagger}$) relationship[17] in the thermo-driven, *cis*□*trans* isomerization in chloroform. Data for various azobenzene derivatives (black filled circles) were obtained from Fig. 2 of ref. 17. **F8AZO** (blue filled circles) and unsubstituted azobenzene molecule (red filled squares) were used in this diagram. (c) The change in the initial rate of the thermo-driven *cis*□*trans* isomerization of **F8AZO** and **AZO** in chloroform at four different temperatures. The activation energy of the thermally-driven *cis*□*trans* isomerization was determined to be 18–22 kcal mol^{-1} by the Arrhenius plots.

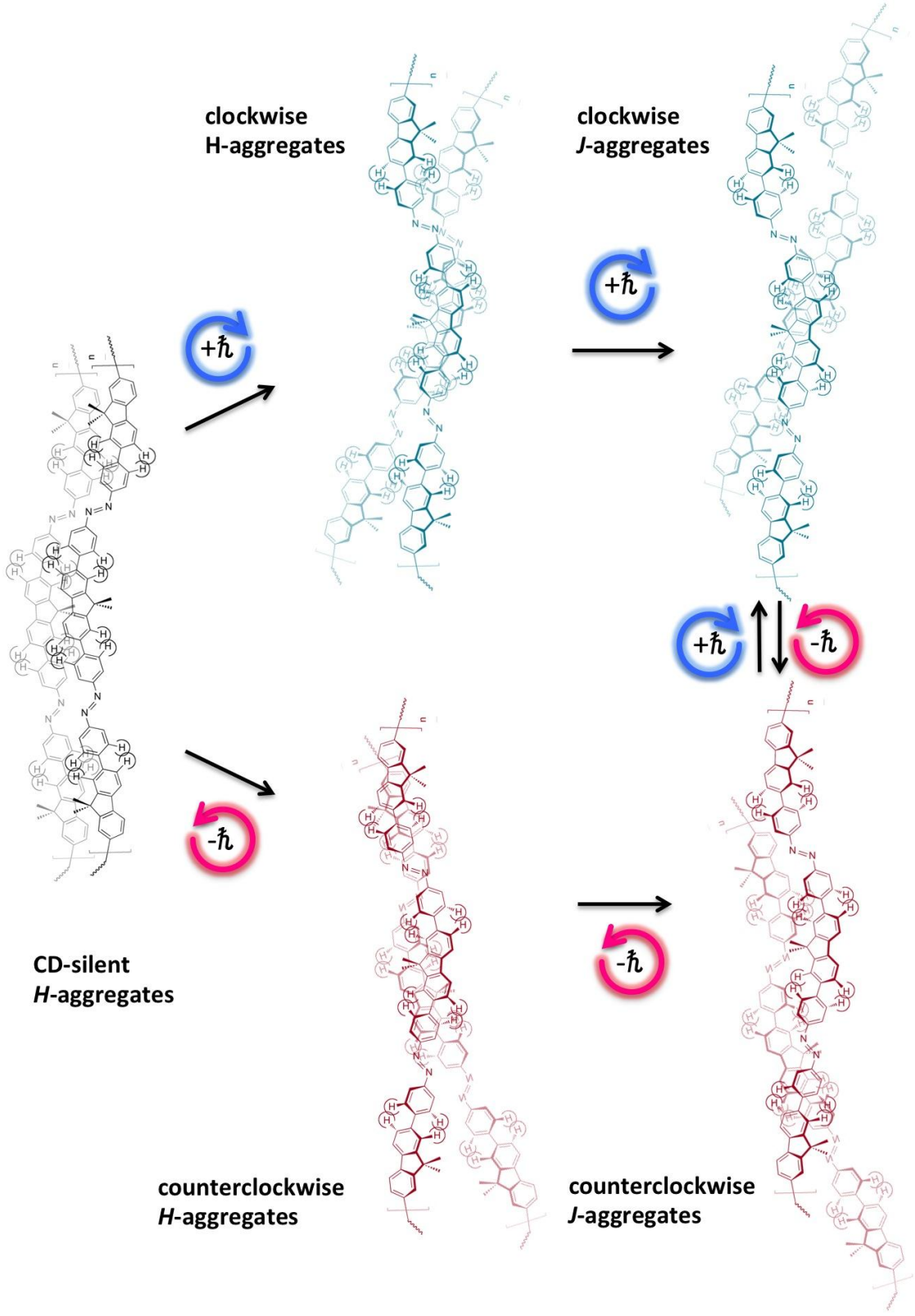

Fig. S12. A proposed model of the chiroptical generation, racemization, inversion, and retention of **F8AZO** aggregates suspended in a surrounding optofluidic medium controlled by *l*-CPL and *r*-CPL pumping.