Circularly Polarized Light with Sense and Wavelengths to Regulate Azobenzene Supramolecular Chirality in Optofluidic Medium

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EXPERIMENTAL SECTION

Materials. Achiral side chain azo-containing polymers (PAzoMAs) were synthesized as previously reported via atom transfer radical polymerization (ESI, Figure S14 and Figure S15),[S1] and the results are summarized in Table S2. ^{1}H nuclear magnetic resonance (NMR) peaks were ascribed to syndiotactic (*rr*)-57%, atactic (*mr*)-36%, and isotactic (*mm*)-7% methyl groups. This corresponded to 75 % racemo and 25 % meso fractions. Spectroscopic-grade DCE, MCH, methanol (MeOH) and other solvents (Dojindo, Kumamoto, Japan) were used as received.

Instrumentation. The number-average molecular weight (M_n) and polydispersity ($PDI = M_w/M_n$) of the polymers were evaluated by HLC-8320 size-exclusion chromatography (SEC, Tosoh, Tokyo, Japan) equipped with refractive index and UV detectors. Two TSKgel Super Multipore HZ-N columns (4.6 × 150 mm, 3-μm aggregate size) with molecular weights in the

range of $7 \times 10^2 - 2 \times 10^5$ g mol^{-1} were used in series. Tetrahydrofuran (THF) was used at a flow rate of 0.35 mL min^{-1} and 40 °C. These samples were calibrated with poly(methyl methacrylate) PMMA standards (Tosoh). The UV-vis and CD spectra of the solutions were measured with a JASCO J-820 spectropolarimeter (Hachioji-Tokyo, Japan) equipped with Peltier-controlled housing units. Synthetic quartz (SQ) cuvettes with a 10-mm path length (scanning rate: 100 nm min^{-1}; bandwidth: 1 nm; response time: 1 s; 0.5-nm interval sampling; single accumulation) at 25 °C were used. The changes in the g_{CD} values as a function of the photoirradiation time were evaluated at CD extremum wavelengths.[S2] Dynamic light scattering (DLS) (detector: 90°; accumulation: 30 times) measurements were performed using a DLS-6000 Otsuka Electronics instrument (Hirakata-Osaka, Japan) at 25 °C. Fluorescence optical microscopy (FOM) images were collected as jpeg data with a Nikon (Tokyo, Japan) Eclipse E400. The optofluidic reaction was set up using a CPL pumping apparatus that consisted of an Ushio (Tokyo, Japan) Optiplex BA-H501 (both with and without apertures), an USH-500SC2 ultrahigh-pressure, a 500-W Hg lamp with six narrow band-pass filters with FWHM of 10 nm (254, 313, 365, 405, 436, 546 nm) from Sigma Koki (Tokyo, Japan) and Asahi Spectra instrument (Tokyo, Japan), a Glan-Taylor prism coated with MgF$_2$ (ultrahigh-purity calcite, 230-2300 nm, Sigma Koki), a Glan-Thomson prism coated with MgF$_2$ (α-BBO, 200-900 nm, Sigma Koki), and six different λ/4 quartz waveplates suited to 254, 313, 365, 405, 436, and 546 nm (Sigma Koki). FT-IR spectra were recorded with a CaF$_2$ plate using a Horiba FT-730 IR spectrometer over a wavenumber range from 800 to 4000 cm^{-1} with a scanning speed of 5.0 mm s^{-1} for 128 scans.

We did not measure linear dichroism (LD) signals of the polymer aggregate dispersed in isotropic cosolvents based on the following reasons. In case of partially oriented samples in optically anisotropic solid films deposited on the solid substrate (for example, LB films with a dichroic ratio), external-bias oriented stretched films, and optically anisotropic sample under a high-shear flow condition, partial contribution from the LD signals may cause unfavorable artifact CD signals. To avoid these LD effects, most researchers including our group employed

all CD measurement of molecules dispersed in isotropic solutions with a very gentle stirring and/or stagnant conditions, and of molecular aggregates and polymer aggregates as their suspension states dispersed in isotropic solvents. In a series of our CD measurements in the past, sign of CD signals induced by hand of CP light source as well as induced by side chain chirality/solvent chirality showed an almost mirror-image relationship, the LD effects in this work are absent and/or negligible small if existed.

The particle sizes of the aggregates might be one of the most critical factors to efficiently employ the CPL-triggered chirality induction and restoration experiments detected by CD-signals. During the whole experiments (as shown in Figure 1) including many preliminary experiments (not given in this paper), we found by naked eyes an immediate production of very large precipitates, which were a collection of larger particle sizes, when a volume fraction of DCE/MCH ranged from 0.4/2.6 (v/v) and 0.2/2.8 (v/v). Moreover, when a volume fraction of DCE/MCH was in the range of 0.8/2.2 and 3.0/0.0 (v/v), the polymers in these cosolvents were nearly transparent due to very small aggregate sizes and/or molecularly dissolved in homogeneous solution. Finally, to experimentally obtain a long-term stability of the polymer aggregates with an appropriate aggregate size to reproducibly measure these CD spectra, the best DCE/MCH ratio was 0.5/2.5 (v/v) when DCE/MCH ranged from 0.2/2.8 (v/v) and 3.0/0.0 (v/v) as well as their refractive indices (n_{D}).

General Procedure for the Preparation of the PAzoMA$_{\mathrm{S}}$ aggregates. To prepare the PAzoMA aggregates, a 0.2 mg mL^{-1} azo-containing polymer (PAzoMA) solution in a good solvent (DCE) was prepared. Then, 0.5 mL of the PAzoMA solution was added into the cuvette (1 cm × 1 cm × 3 cm), and 2.5 mL of the poor solvent was dropped in slowly (one drop per sec). The mixture was gently stirred at room temperature for 2 min to obtain stable aggregates, which were then irradiated by CPL sources for chosen irradiation times.
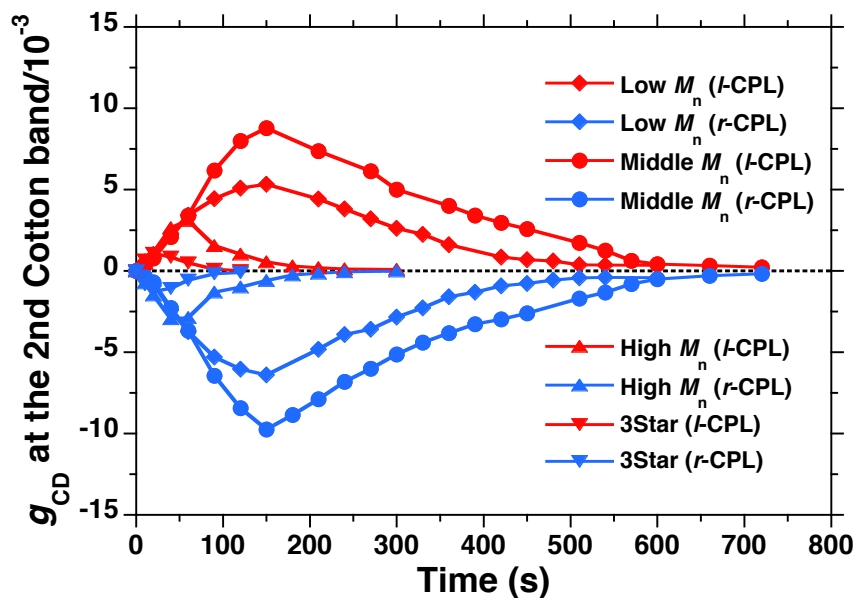
Figure S1. The g_{CD} values (at 313 nm) of linear PAzoMA and 3-star polymer aggregates of different molecular weights in DCE/MCH (0.5/2.5, v/v) under 365 nm *l*-CPL and *r*-CPL irradiation for 60 s.
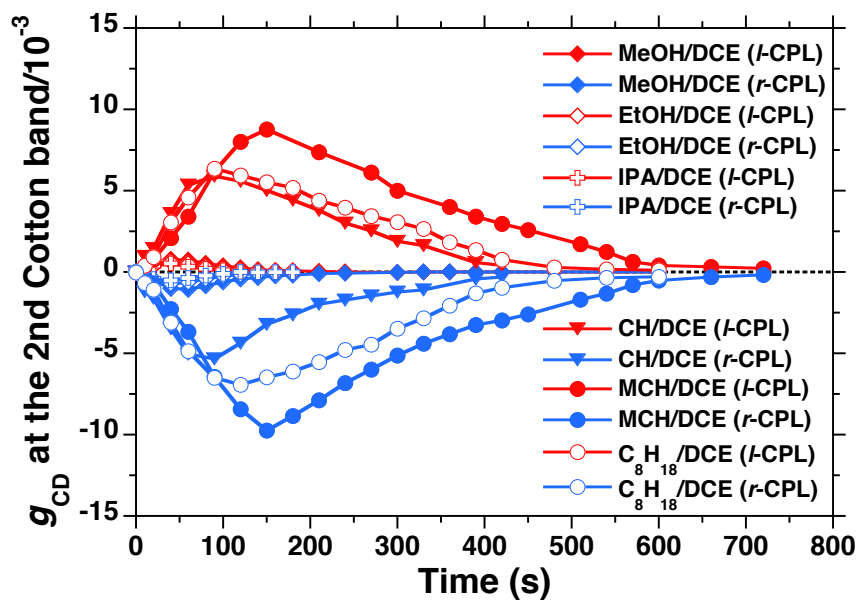

Figure S2. The g_{CD} value (at 313 nm) of PAzoMA$_2$ aggregates in different mixed solvents under *l*-CPL and *r*-CPL irradiation at 365 nm: $M_{n,GPC}$ = 7700 g mol^{-1}, *PDI* = 1.20. [Conc]$_0$ = 0.1 mg 3 mL^{-1}. $V_{good\ solvent}$ = 0.5 mL, and $V_{poor\ solvent}$ = 2.5 mL in SQ rectangular cuvettes.
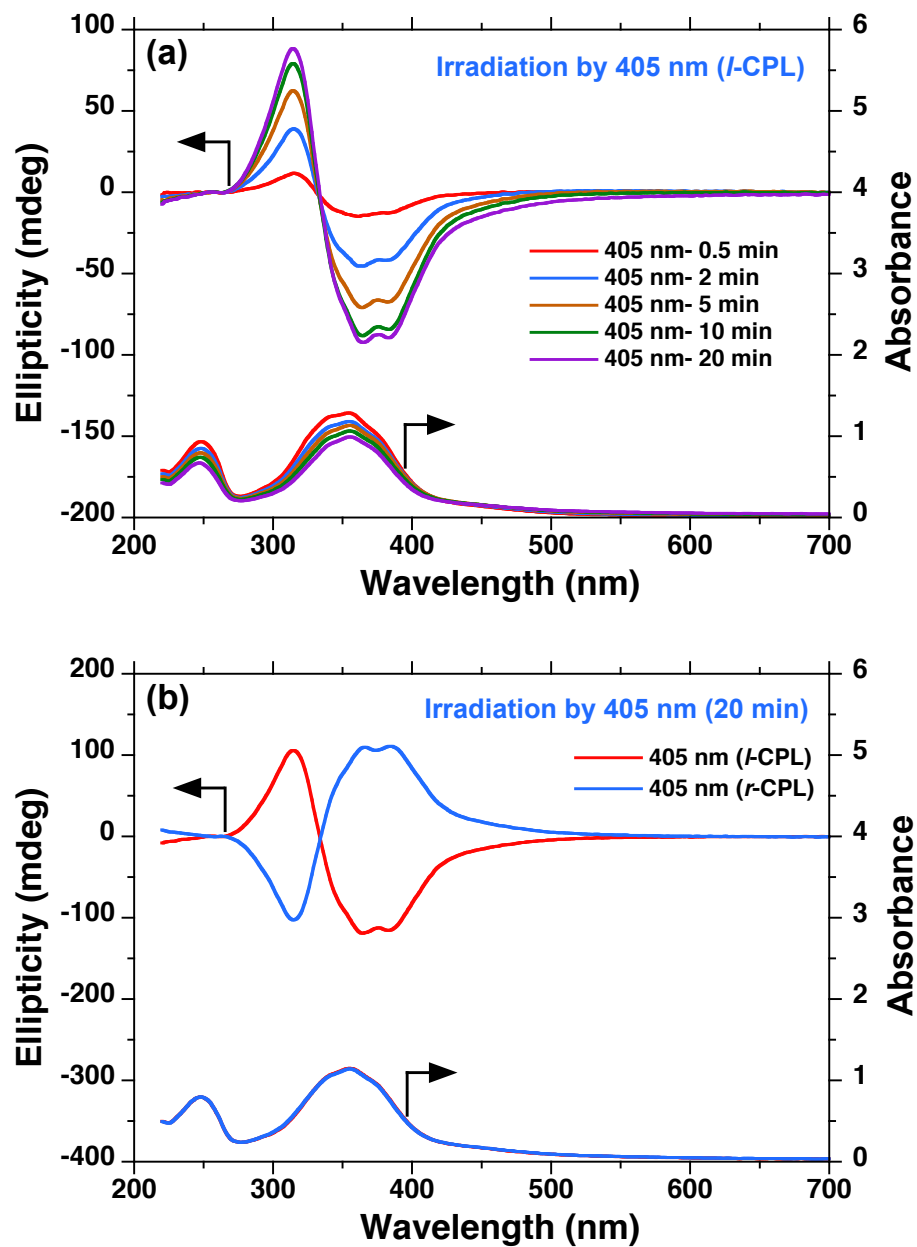
Figure S3. (a) CD and UV-vis spectra of PAzoMA$_2$ aggregates in DCE/MCH (0.5/2.5, v/v) exposed to 405 nm *l*-CPL irradiation for different durations. (b) CD and UV-vis spectra of PAzoMA$_2$ aggregates exposed to 405 nm *l*-CPL and *r*-CPL irradiation for 20 min.
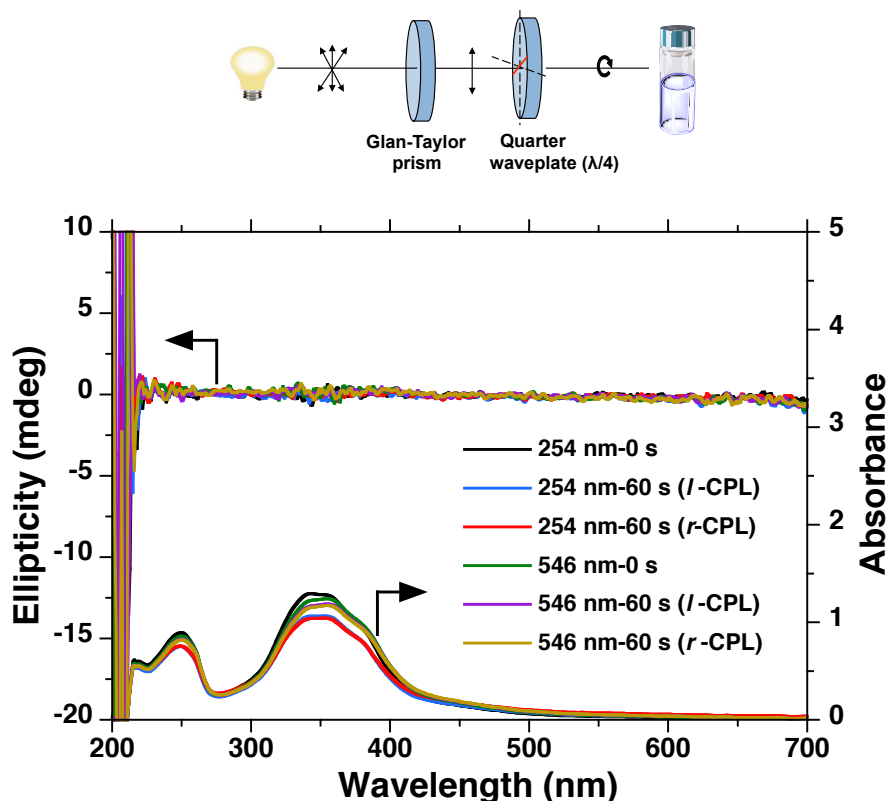
Figure S4. CD and UV-vis spectra of PAzoMA$_2$ aggregates in DCE/MCH (0.5/2.5, v/v) under 254-/546-nm *l*-CPL and *r*-CPL irradiation for different durations.

As far as we know, no studies were reported yet regarding CP light source driven chirality induction experiments of azobenzene derivatives using shorter wavelengths (200−320 nm) as light source. This is because the intense *π*-*π** and/or *n*-*π** transitions exist at ≈ 350 nm associated with weak electronic transitions at ≈ 400–500 nm. We think that most researchers had no interests of these shorter wavelength light sources (313 nm and 254 nm) that are readily available by commercial Hg-source. We employed CP light source driven chirality induction experiment using one of such shorter wavelengths (254 nm) and a longer 546 nm for comparison. As shown in Figure S4, any clear CD signals were not detected. It is difficult to employ these experiments in DCE-MCH solutions shorter than 220 nm due to the existence of their inherent cut-off wavelengths. Furthermore, both band-path filter and the corresponding quarter waveplate shorter than 250 nm were not available at my laboratory. CP high-energy sources at UV-Synchrotron Orbital Radiation Facility (UV-SOR) located at Okazaki, Japan, is one candidate to further prove this experiment.
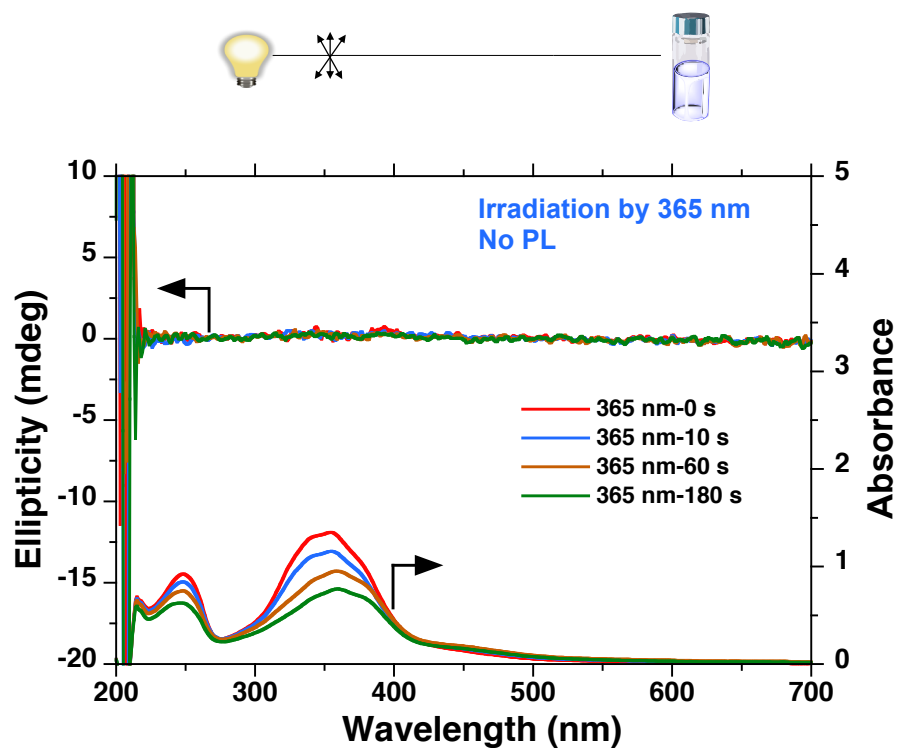
Figure S5. CD and UV-vis spectra of PAzoMA$_2$ aggregates in DCE/MCH (0.5/2.5, v/v) irradiated with 365 nm non-polarized light.
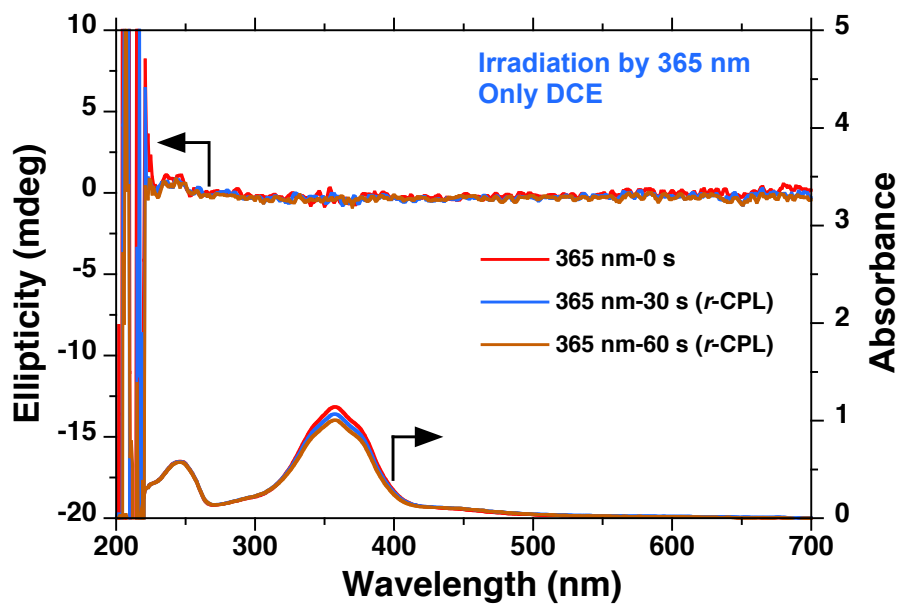

Figure S6. CD and UV-vis spectra of PAzoMA$_2$ in pure DCE solution after 365 nm *r*-CPL irradiation.
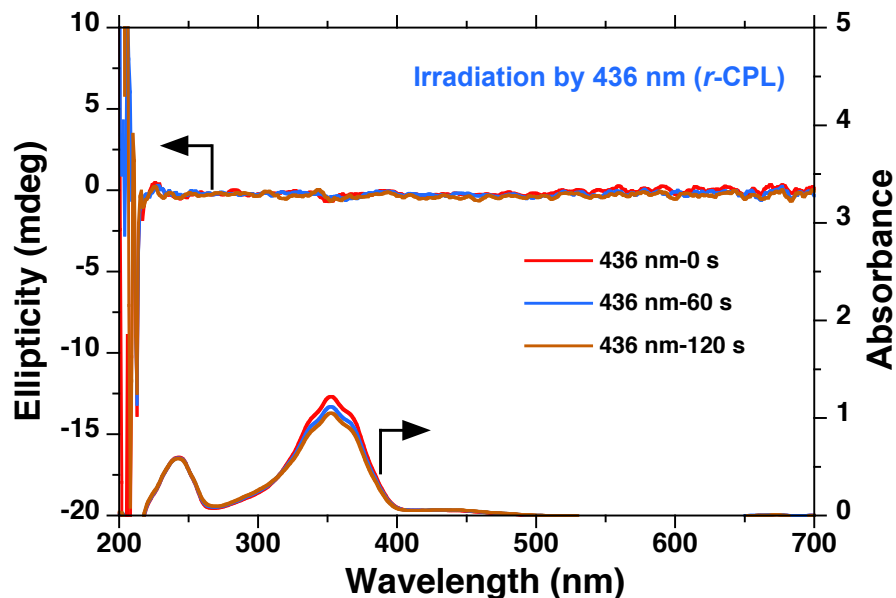
Figure S7. CD and UV-vis spectra of monomer aggregates in DCE/MCH (0.1/2.9, v/v) subjected to 436 nm *r*-CPL irradiation for different times.
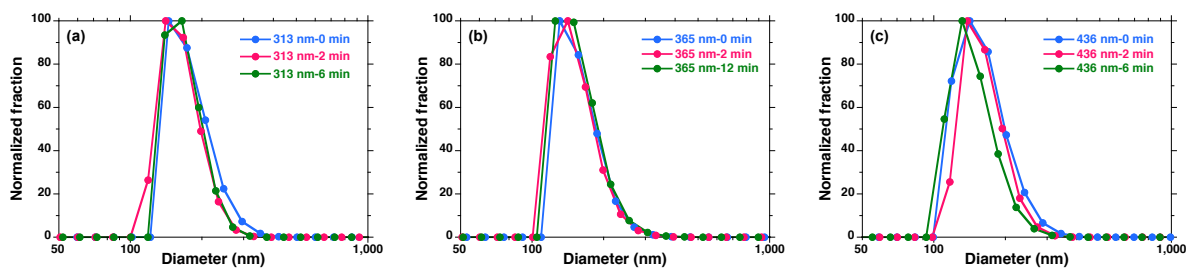

Figure S8. DLS plots of PAzoMA$_2$ aggregates in DCE/MCH (0.5/2.5, *v/v*) before and after *r*-CPL irradiation: (a) 313 nm, (b) 365 nm, and (c) 436 nm.
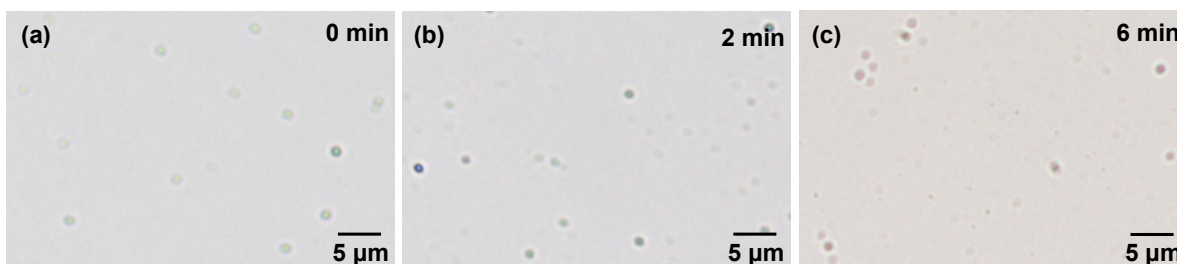

Figure S9. Optical microscope images of PAzoMA$_2$ aggregates in DCE/MCH (0.5/2.5, *v/v*) before and after *r*-CPL (436 nm) irradiation.
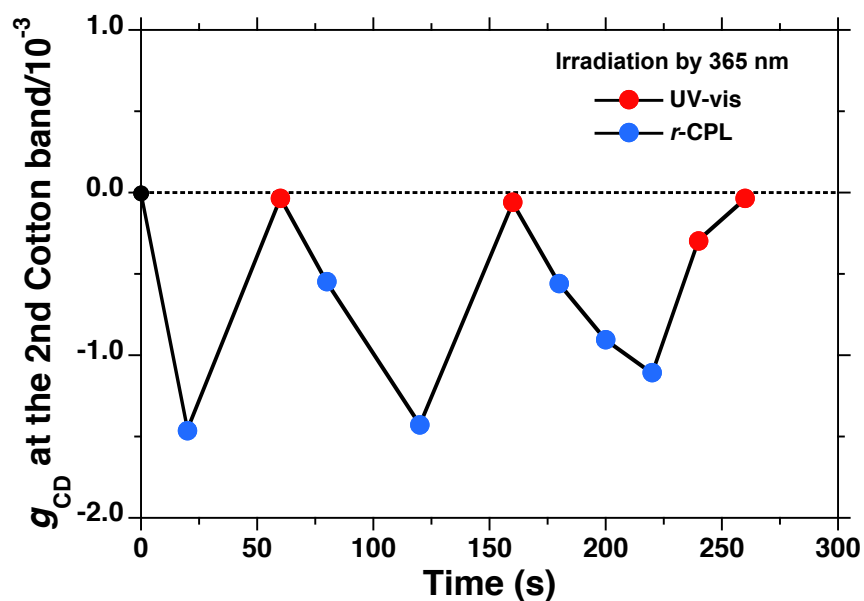
Figure S10. Chiroptical switching in the g_{CD} values (at 313 nm) of PAzoMA$_2$ aggregates in DCE/MCH (0.5/2.5, v/v) irradiated with 365 nm r-CPL and alternating non-polarized CP light.
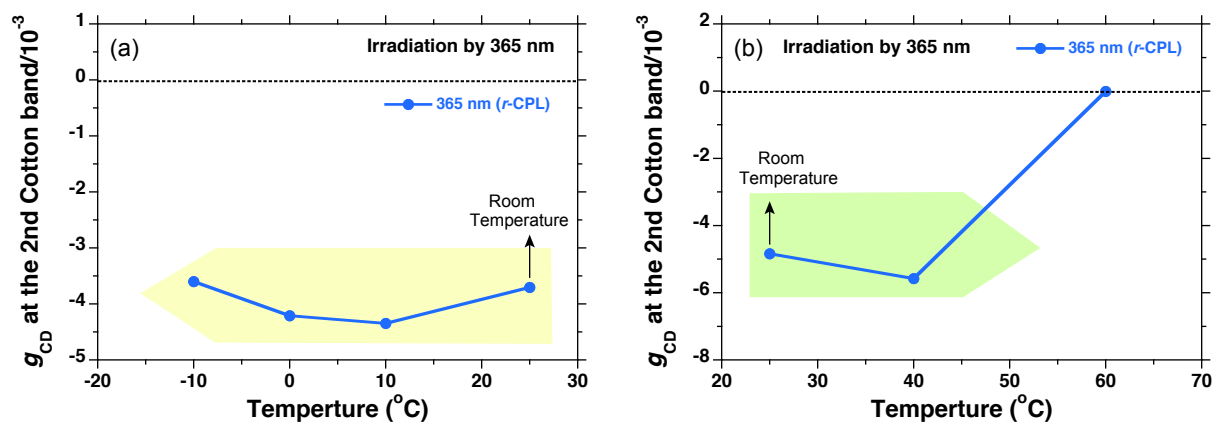

Figure S11.The g_{CD} value at the second Cotton band (313 nm) of PAzoMA$_2$ aggregates as a function of temperature in (a) cooling process from 25 °C to −10 °C and (b) heating process from 25 °C to 60°C. The optically active aggregates were generated in DCE-MCH (0.5/2.5 (v/v) by exposing r-CPL at 365 nm for 60 sec.

The degree of the optically activity (evaluated as the magnitude of the g_{CD} value at the second Cotton band, 313 nm) of PAzoMA$_2$ aggregates depended on temperature of DCE-MCH

cosolvent (0.5/2.5 (v/v)), as shown in Figure S11. The optically active aggregates were generated in the cosolvent by exposing r-CPL at 365 nm for 60 sec. The g_{CD} value in the range of -10 °C and 40 °C kept an almost constant value ranging from ca. -3.6 and -5.5 x 10^{-3}. These magnitudes somehow depended on cooling down (from 25 °C to -10 °C, Figure S11(a)) and heating up (from 25 °C to 60 °C, Figure S11(b)) processes. The temperature of -10 °C was the lowest measurable temperature in J-820 CD spectrometer. However, the g_{CD} value abruptly diminished when the cosolvent reached at 60 °C. Possibly, DCE molecules penetrated to an interior of the aggregates, thus, turning into swollen (loose) aggregates. Chirally assorted, CD-active stacks of *trans*-azobenzene moieties was racemized in the swollen state. The upper temperature of the chiroptical memory function may be 60 °C in the cosolvent. However, when one can produce the cosolvent-free PAzoMA$_2$ aggregates (xero-aggregates), the upper temperature should increase upto Tg values of similar azobenzene containing polymers.[S3] We demonstrated recently solvent-free chiral polymer xero-aggregates using a silicone grease.[S4]
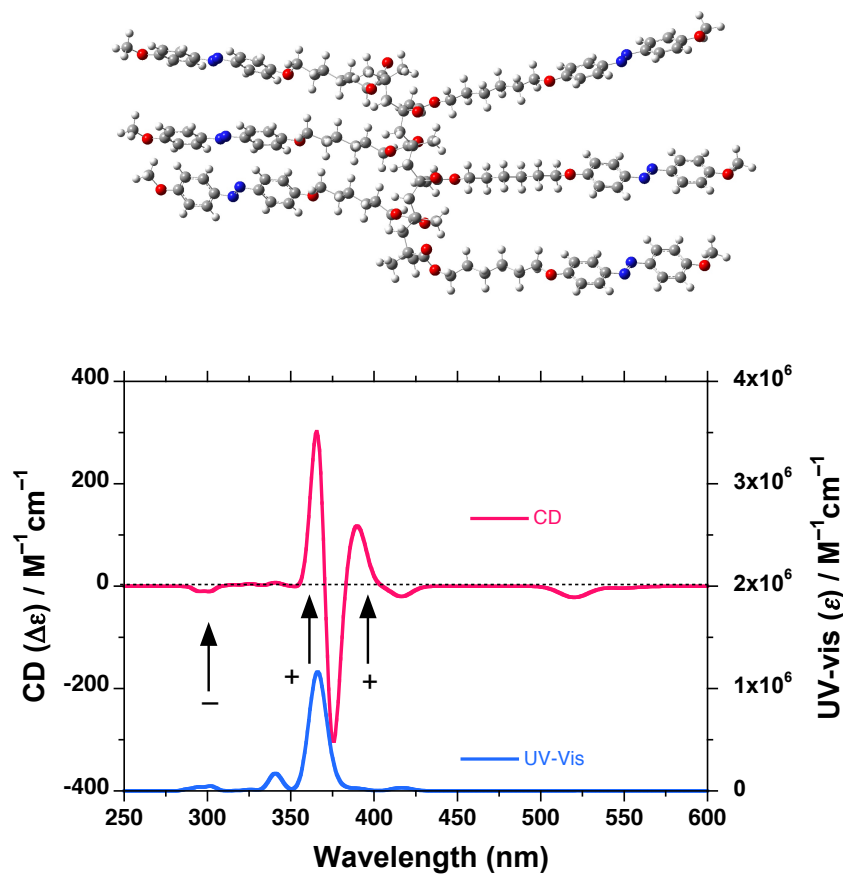
Figure S12. (top) Slight disorder of six *trans*-azobenzene side chains. (bottom) Simulated CD and UV-vis spectra of the model (half-width at half-height = 0.3 eV width).
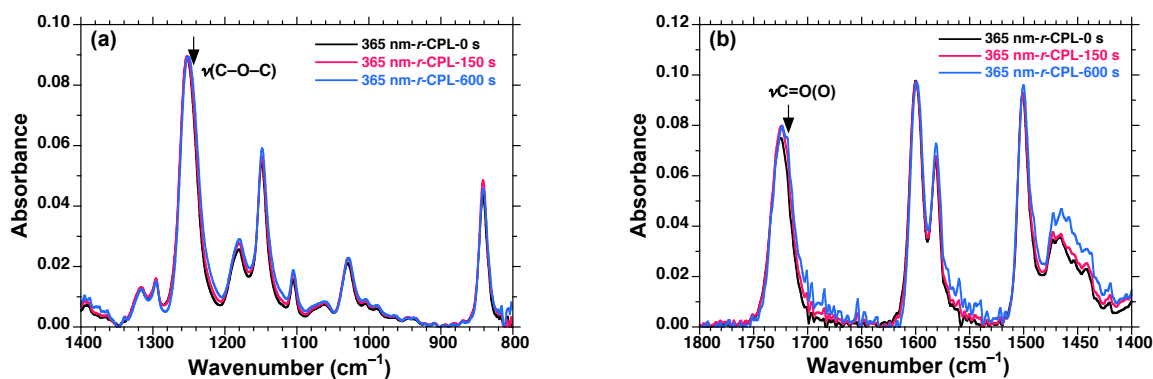

Figure S13. FT-IR spectra of PAzoMA$_2$ aggregates in DCE/MCH (0.5/2.5, *v/v*) exposed to 365 nm *r*-CPL irradiation vs. the irradiation time: (a) local area from 1400 cm^{-1} to 800 cm^{-1} and (b) local area from 1800 cm^{-1} to 1400 cm^{-1}.

The supramolecular chirality of the azobenzene-containing polymers was discussed in details in three papers (*Polym. Chem.* **2015**, *6*, 4230–4239; *Polym. Chem.* **2015**, *6*, 7045–7052; *Polym. Chem.* **2017**, *8*, 1906–1913). For example, the *trans*-to-*cis* photoisomerization process should cause the breaking in supramolecular chirality due to weakening in π-π stacking interactions that result in ill-ordered packing structures. This discussion is consistent with the present results under a prolonged UV irradiation more than 600 s, as proven from Figure 2b (CD/UV-vis data). On the other hand, the *cis*-to-*trans* photoisomerization process should allow to restore the supramolecular chirality. From the comparative FT-IR spectra (Figure 6 and Figure S13) associated with Figure 2a (CD/UV-vis spectra), we concluded that only small fractions of *trans*-isomers have changeable to *cis*-isomers upon CP light irradiation. Although we expected the marked changes in the stretching and bending modes of N=N bonds and azobenzene rings, we could not see any clear evidence of vibration modes due to *cis*-azobenzene in mid-IR region upon irradiating weak, incoherent light power of 30.0 μW cm^{-2} at 365 nm disregard of *l*- and *r*-CP light sources.
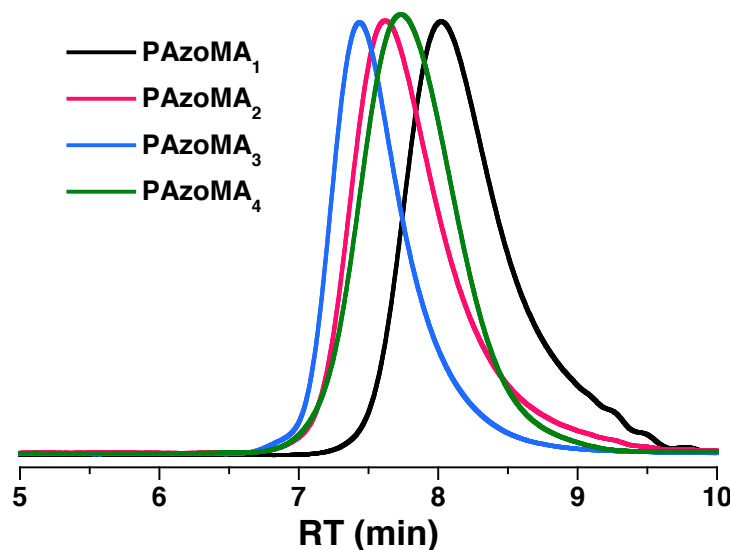

Figure S14. The GPC curves of PAzoMAs.

Table S1. Particle sizes of the PAzoMA$_2$ aggregates before and after *r*-CPL irradiation.

Wavelength (nm)		*d* (nm)	
313	236 (0 min)	194 (2 min)	193 (6 min)
365	248 (0 min)	226 (2 min)	235 (12 min)
436	239 (0 min)	207 (2 min)	205 (6 min)

Table S2. Molecular weight characteristics of PAzoMAs.

Polymer	Ratio^a	Time (h)	Conv (%)^b	$M_{n,th}$ (g mol^{-1})^c	$M_{n,GPC}$ (g mol^{-1})	M_w/M_n	DP_n
PAzoMA$_1$	15:1:2:2	16	80.2	4800	4900	1.22	12
PAzoMA$_2$	30:1:2:2	16	78.7	9300	7700	1.20	19
PAzoMA$_3$	50:1:2:2	16	76.8	15200	13500	1.20	34
PAzoMA$_4$^{d}	25:1:2:2	12	77.3	8200	8100	1.16	19

^{a} Polymerization ratio: [AzoMA]$_0$/[Initiator]$_0$/[CuBr]$_0$/[HMTETA]$_0$ for the homopolymerization. ^{b} Precipitated in methanol and determined gravimetrically. ^{c} Calculated by $M_{n,th}$ = ([Monomer]$_0$/[EBIB]$_0$) × $M_{Monomer}$ × conversion%. ^{d} 3-armed Azo polymer.
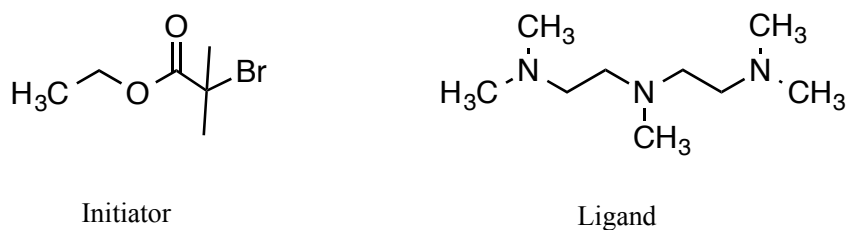
Initiator   Ligand

Figure S15. The chemical structures of the initiator and ligand in ATRP.

Light power sources

313 nm and 32.0 μW cm^{-2} for *l*- and *r*-CP light sources

365 nm and 30.0 μW cm^{-2} for *l*- and *r*-CP light sources

405 nm and 38.0 μW cm^{-2} for *l*- and *r*-CP light sources

436 nm and 32.0 μW cm^{-2} for *l*- and *r*-CP light sources

For Figure S5, red points:

365 nm and 38 μW/cm^2 for non-CP light (i.e., equal amounts of *l*- and *r*-CP light)

No detectable Cotton CD effects of CP-AAS experiments

254 nm and 15.5 μW cm^{-2} for *l*- and *r*-CP light sources

546 nm and 30.0 μW cm^{-2} for *l*- and *r*-CP light sources

References

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(S2) Eliel, E. L.; Wilen, S. H.; Mander, L. N. In *Stereochemistry of Organic Compounds*, Wiley, 1994, Chapter 13, pp 991−1118.

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(S4) Duong, S. T.; Fujiki, M. *Polym. Chem.* **2017**, *8*, 4673–4679.