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Electronic Supplementary Information for

Circularly polarized light modulated supramolecular self-assembly for azobenzene-based chiral gel

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Part S1. Materials and Instruments

Materials. α -L-Asp-L-Phe (purity: 99%) was purchased from GL Biochem. Ltd. (Shanghai, P. R. China) and stored at $-20\text{ }^{\circ}\text{C}$. 4,4'-azodibenzoyl dichloride was purchased from Aladdin Corp. (P. R. China). Triethylamine and deuterated dimethylsulfoxide (DMSO) were purchased from Sigma-Aldrich Corp. (P. R. China). Methanol, chloroform, dichloromethane, and nitromethane with high purities (99.9%) were purchased from Sinopharm Chemical Reagent Corp. (P. R. China), and chloroform was dried by molecular sieves for 24 hours prior to use.

Instruments. Hydrogen or carbon nuclear magnetic resonance (^1H or ^{13}C NMR) experiment was carried out on an AVANCE III HD 700 MHz NMR (Bruker, Germany). Mass spectra (MS) was determined with a Q-TOF 6540 masshunter (Agilent, America). All synthesized chiral gelators were purified through Shimadzu LC-20A purity system (Japan) using a chiral chromatographic column (AS-H, 250 mm \times 4.6 mm, 5 μm , Daicel Corp., Japan). Ultraviolet and visible spectra (UV-Vis) were recorded on a Lambda 365 Ultraviolet spectrometer (PerkinElmer, America). Circular dichroism (CD) spectra were measured on a MOS-405 CD spectrometer (Bio-Logic, France). X-ray diffraction (XRD) was conducted on a PANalytical X'Pert PRO X-ray (Philips, Japan) diffractometer with Cu $K\alpha$ radiation source ($\lambda = 1.54059\text{ \AA}$). Scanning electron microscopy (SEM) was conducted with a JSM-7800F SEM (JEOL, Japan) operated at an acceleration voltage of 15 kV. Atomic force microscopy (AFM) investigation was recorded on a NanoWizard Ultra Speed AFM (JPK Instruments, Germany). Dynamic light scattering (DLS) measurement was monitored with a Zetasizer Nano ZS90 (Malvern Panalytical, UK).

Part S2. Synthesis and Characterization

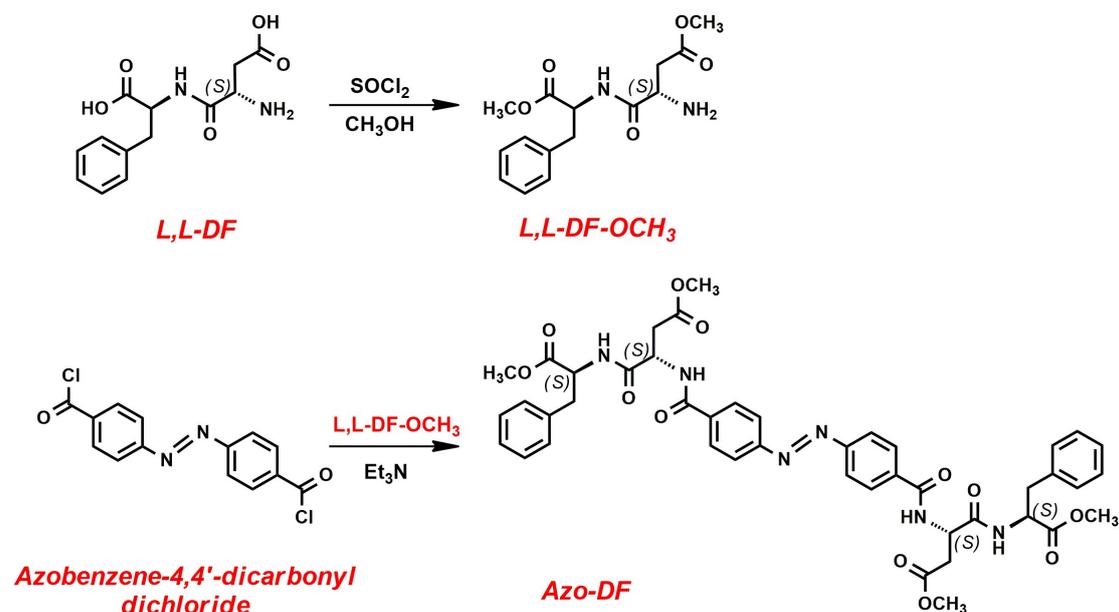


Fig. S1 Synthetic method of Azo-DF

Synthesis of α -L-Asp-L-Phe-methyl ester (L,L-DF-OCH₃): α -L-Asp-L-Phe (1.012 g, 3.6 mmol) was dissolved in 30 mL of dry methanol. Excessive thionyl chloride (1 mL, 18 mmol) was added dropwise to the reaction mixture at 0 °C, and the mixture was stirred for 3 hours at ambient temperature. After the solvent was removed by reduced pressure distillation rewash with dry methanol for three times, 1.341 g primary residue was obtained (yield: 99%).

Synthesis and characterization of Azo-L,L-DF (Azo-DF): Excessive triethylamine (Et₃N) (1.85 mL, 9 mmol) was added to a solution of L,L-DF-OCH₃ (1.341 g, 3.6 mmol) in 20 mL dry chloroform and the mixture was stirred for 10 min. Then 4,4'-azodibenzoyl dichloride (0.500 g, 1.6 mmol) in 10 mL dry chloroform was added dropwise to this mixture at ambient temperature, and continued to stir for 12 hours. After filtration and evaporation of solvent, the crude residue was purified by a silica gel column, with an elution of dichloromethane/methanol (v/v=75:1), to give target compound as orange powder (0.828 g, yield: 60%, m.p. 168 °C). This compound needed to be further purified through a Shimadzu LC-20A purity system using an AS-H chiral chromatographic column (250 mm × 4.6 mm; 5 mm; Daicel Corp., Japan).

$[\alpha]_{20}^D = +56.81^\circ$ (Concentration: 5 mg/ml, in CHCl_3). $^1\text{H NMR}$ (500 MHz, d_6 -DMSO): 2.74–2.89 (m, 4H, C– CH_2), 2.96–3.08 (m, 4H, C– CH_2), 3.62 (s, 12H, OCH_3), 4.49, 4.51 (d, d, $J_1 = J_2 = 8$ Hz, 2H, C* H), 4.91, 4.94 (d, d, $J_1 = J_2 = 8.5$ Hz, 2H, C* H), 7.18–7.22 (m, 10H, Ph– H), 8.04–8.11 (m, 8H, Ph– H), 8.37 (d, $J = 7.5$ Hz, 2H, CONH), 8.86 (d, $J = 7.5$ Hz, 2H, CONH). $^{13}\text{C NMR}$ (500MHz, d_6 -DMSO): 35.9, 36.9, 50.3, 52.0, 52.4, 54.2, 123.0, 127.0, 128.7, 129.4, 129.6, 136.8, 137.5, 153.9, 165.9, 170.9, 171.1, 172.1. MS: m/z calcd. for $\text{C}_{44}\text{H}_{46}\text{N}_6\text{O}_{12}$: 850.3; found: 851.3 $[\text{M}+\text{H}]^+$. Elemental analysis calcd (%) for $\text{C}_{44}\text{H}_{46}\text{N}_6\text{O}_{12}$: C, 62.11; H, 5.45; N, 9.88. Found: C, 62.03; H, 5.40; N, 9.96.

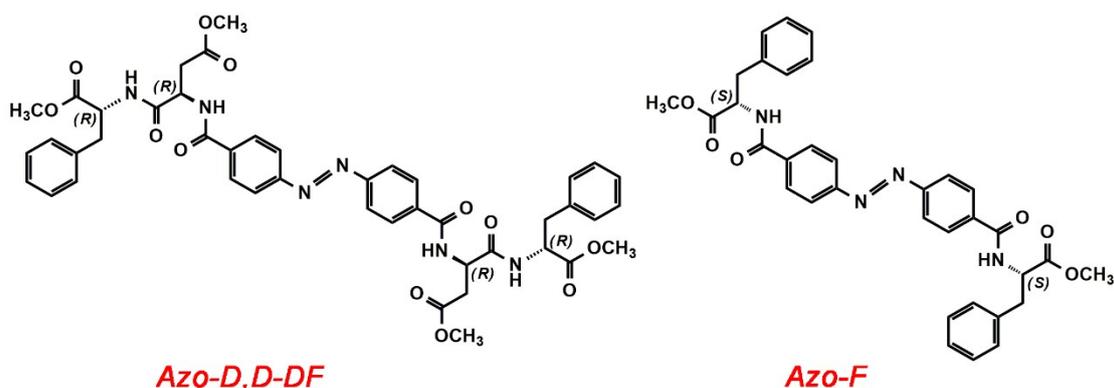


Fig. S2 Chemical structure of Azo-D,D-DF and Azo-F

Synthesis and characterization of Azo-D,D-DF: The same procedure was adopted to prepare gelator Azo-D,D-DF except the α -D-Asp-D-Phe was used as reactant (0.883g, yield: 64%, m.p. 168 °C). This compound needed to be further purified through a Shimadzu LC-20A purity system using an AS-H chiral chromatographic column (250 mm \times 4.6 mm; 5 μm ; Daicel Corp., Japan). $[\alpha]_{20}^D = -53.5^\circ$ (Concentration: 5 mg/ml, in CHCl_3). $^1\text{H NMR}$ (500 MHz, d_6 -DMSO): 2.74–2.89 (m, 4H, C– CH_2), 2.96–3.07 (m, 4H, C– CH_2), 3.62 (s, 12H, OCH_3), 4.49, 4.51 (d, d, $J_1 = J_2 = 8$ Hz, 2H, C* H), 4.91, 4.94 (d, d, $J_1 = J_2 = 8.5$ Hz, 2H, C* H), 7.19–7.23 (m, 10H, Ph– H), 8.04–8.10 (m, 8H, Ph– H), 8.37 (d, $J = 7.5$ Hz, 2H, CONH), 8.86 (d, $J = 7.5$ Hz, 2H, CONH). $^{13}\text{C NMR}$ (500 MHz, d_6 -DMSO): 35.9, 36.9, 50.3, 52.0, 52.4, 54.2, 123.0, 127.0, 128.7, 129.4, 129.6, 136.8,

137.5, 153.9, 165.9, 170.9, 171.1, 172.1. MS: m/z calcd for $C_{44}H_{46}N_6O_{12}$: 850.3; found: 851.3. $[M + H]^+$. Elemental analysis calcd (%) for $C_{44}H_{46}N_6O_{12}$: C, 62.11; H, 5.45; N, 9.88. Found: C, 62.08; H, 5.42; N, 9.93.

Synthesis and characterization of Azo- F: The same procedure was adopted to prepare gelator Azo-F except the L-Phenylalanine was used as reactant (yield: 48%, m.p. 143 °C). This compound needed to be further purified through Shimadzu LC-20A purity system using an AS-H chiral chromatographic column (250 mm × 4.6 mm, 5 μm, Daicel Corp., Japan). $[\alpha]_{20}^D = +120.4^\circ$ (c: 5 mg/mL, $CHCl_3$). 1H NMR (500 MHz, $CDCl_3$): 3.26-3.37 (m, 4H, C- CH_2), 3.82 (s, 6H, OCH_3), 5.12-5.16 (m, 2H, C* H), 6.70 (d, $J=7.5$ Hz, 2H, CONH), 7.17 (d, $J=7$ Hz, 4H, Ph- H), 7.27-7.35 (m, 6H, Ph- H), 7.89-7.99 (m, 8H, Ph- H). ^{13}C NMR (500 MHz, $CDCl_3$): 37.9, 52.5, 53.7, 122.8, 123.2, 127.3, 127.9, 128.1, 128.7, 129.4, 135.8, 136.1, 154.3, 166.0, 172.0. MS: m/z calcd for $C_{34}H_{32}N_4O_6$: 592.2; found: 593.3. $[M+H]^+$. Elemental analysis calcd. (%) for $C_{34}H_{32}N_4O_6$: C, 68.91; H, 5.44; N, 9.45. Found: C, 68.88; H, 5.42; N, 9.49.

UV-Vis absorption spectral measurement: Azo-DF gelator was dissolved in chloroform at a low concentration of 0.05 mg/mL. UV-Vis spectra were obtained from the samples in a quartz cuvette (light path: 10 mm, volume: 4 mL).

SEM observation: The Azo-DF xerogel samples were prepared by removing the mixed solvent (chloroform/methanol (v/v=1:3), 2 mg/mL) from Azo-DF gels (before and after 3h of left- or right-CPL irradiation) under vacuum. After being stuck on the conducting resin, the xerogels were sprayed with gold on their surface.

XRD measurements: The xerogel samples for XRD were prepared by the same method used in the SEM measurement. Differently, at least 50 mg dry powder was needed to be filled in the measurement cell. XRD patterns were recorded in the range of $2\theta=5\sim 30^\circ$ at a scan rate of 0.05 °/s.

CD spectra measurements: The Azo-DF gel in chloroform/methanol (v/v=1:3) mixed solvent (2 mg/mL) was prepared through a typical heating-cooling process. Then the

gel was transferred into a quartz cuvette. The quartz cuvette is composed by two quartz waveplates with 0.1 mm optical path length interspace. CD spectra were recorded in a range from 220 nm to 450 nm at a scan rate of 1 nm/min at 25°C. Considering the volatility of the mixed organic solvent, the raw data were processed by the subtraction of the cuvette itself.¹

AFM observation: AFM samples were prepared by dropping one drop of Azo-DF solution (12 μ L, 0.5 mg/mL, chloroform) before and after left/right-CPL irradiation onto a freshly cleaved mica, and allowing them to dry in dark.

DLS measurement: DLS measurements were obtained in a glass cuvette (light path: 10 mm, volume: 1.5mL). Because of the measure range of DLS was 2 nm~3 μ m, a suitable concentration of Azo-DF solution in chloroform of 0.1 mg/mL was selected.

Part S3 Possible self-assembly modes of Azo-DF and the corresponding experimental evidence

Numerous literatures have clearly pointed out that π - π stacking between two adjacent phenyl groups could be served as the driven force for the supramolecular self-assembly of the gel.² In order to validate this point, we proved the crucial roles of phenyl through the following control experiment, in which the gelation abilities of three gelators, Azo-DF, Azo-F, Ben-F³, were tested.

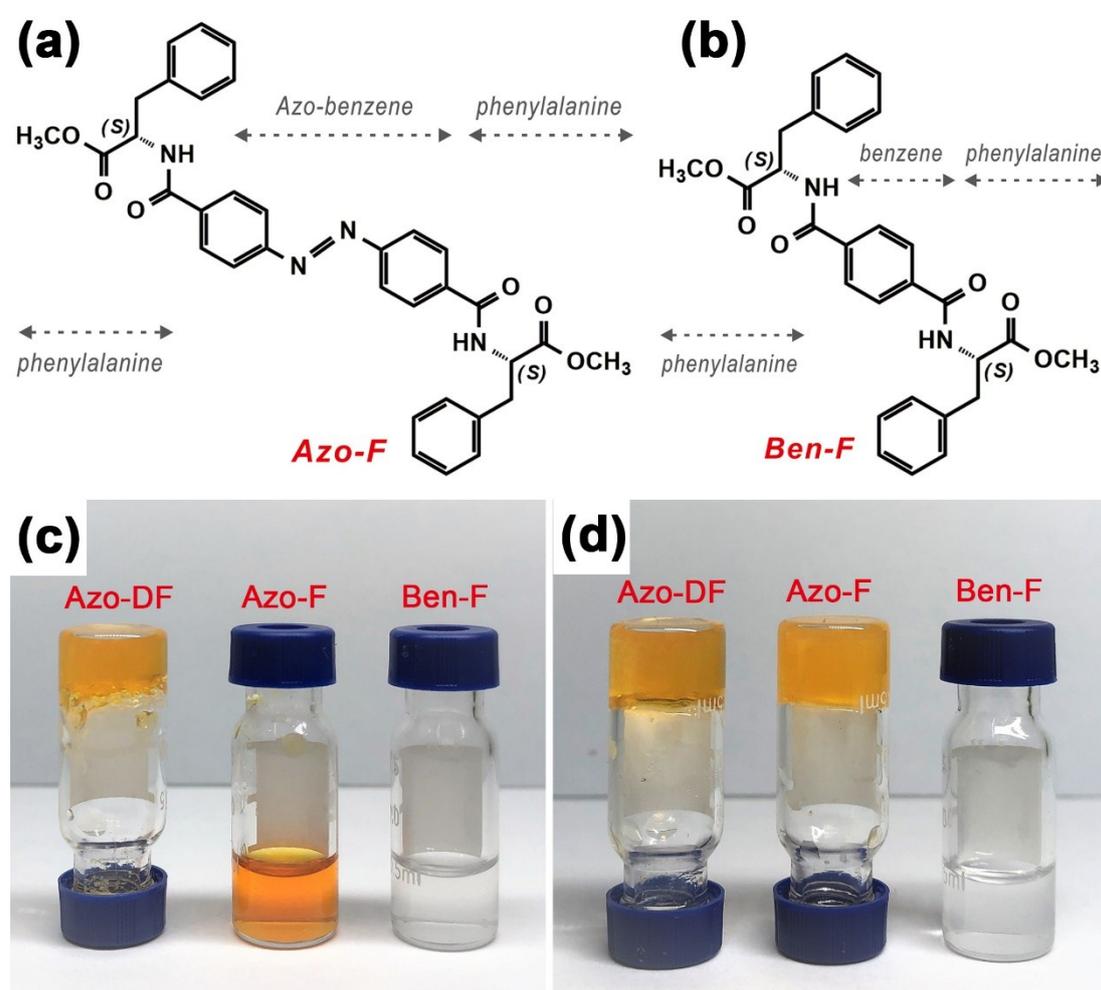


Fig. S3 Control experiment demonstrated the necessary of phenyl and azobenzene groups in self-assembly process. (a-b) Chemical structures of gelators in the control group: Azo-F (a) and Ben-F (b). (c-d) Photographs for comparing the gelation capabilities between Azo-DF in nitromethane (5 mg/mL), Azo-F in nitromethane (5 mg/mL), and Ben-F in ethanol without ultrasonic treatment (c) and with ultrasonic treatment (d). Azo-DF could form unstable gel only through a heating-cooling process; Azo-DF and Azo-F formed stable gels after ultrasonic treatment for 30 s and 10 min, respectively; Ben-F failed to form gel in both situations.

The structures of Azo-F and Ben-F are shown as Fig. S3a and S3b, respectively. It was investigated Azo-DF and Azo-F could form stable gels in nitromethane (5 mg/mL),⁴ while Azo-DF had stronger gelation capacity than Azo-F in this case. As shown in Fig. S3c and S3d, through a typical heating–cooling process, Azo-DF could form a macroscopic gel, although with a little bit of loose on the top of the gel. It was after ultrasonic treatment for 30 s that a stable Azo-DF gel formed, while an additional 10 minutes of ultrasonic treatment on Azo-F was needed to form a macroscopic organogel. Ben-F with only one phenyl in the center could not form gel neither in nitromethane, ethanol or other mixed solvent.³ This control experiment indicated that the central *trans*-azobenzene unit and the terminal phenyl groups contributed to the gel formation collectively, while Asp helped to form a pre-organized structure of the gelator.

Presuming the existence of phenyl is the vital driving force for the supramolecular self-assembly, as well as the linear and planar conformation of Azo-DF in the initial *trans*-form, we proposed three possible self-assembly modes of Azo-DF through quantum chemistry calculation, as illustrated in Fig. S4.

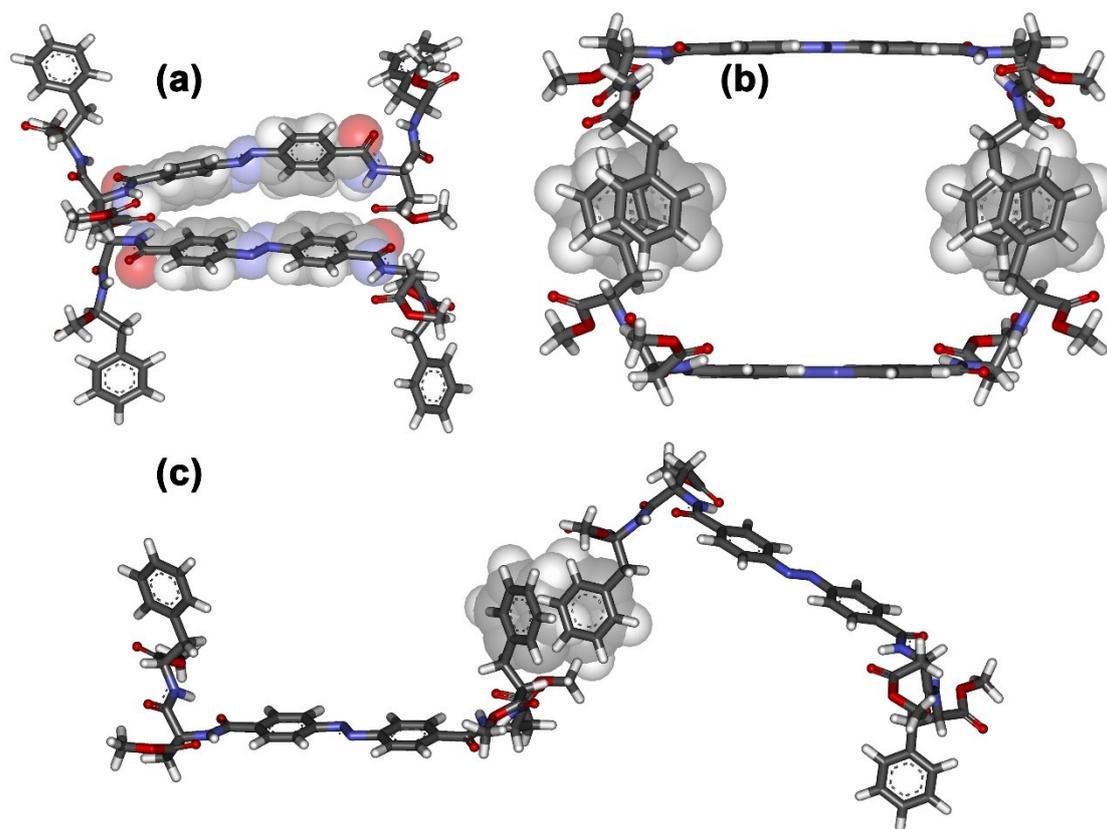


Fig. S4 Three possible binding models between two gelators: (a) a layer mode driven by π - π stacking between two azobenzene units; (b) a ring mode or (c) a chain mode driven by π - π stacking between two terminal benzene units of Azo-DF before CPL irradiation, obtained from quantum chemical calculation (Gaussian, density functional theory (DFT)), at 6-31 g level of theory, solvent: chloroform).

Part S4 CPL pumping system

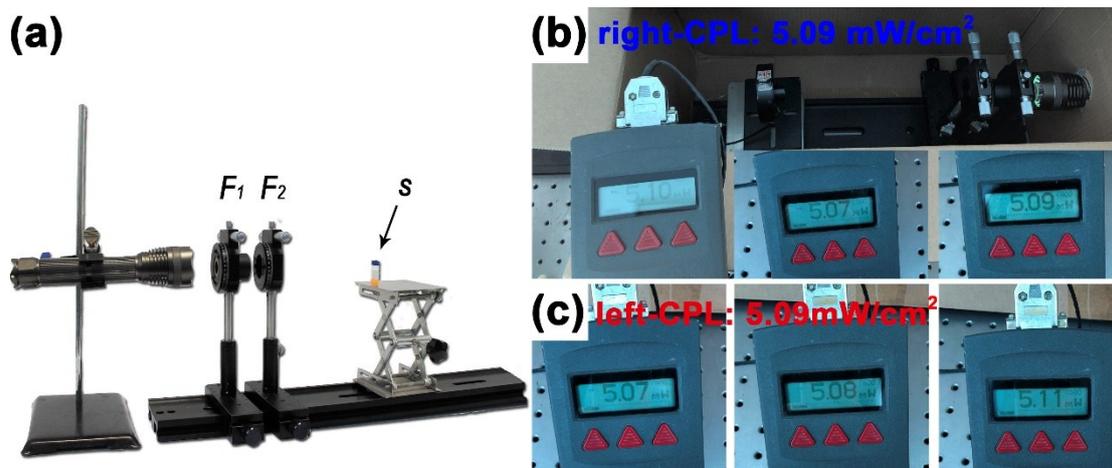


Fig. S5 (a) Photo of the CPL pumping system. F_1 : Glan–Thompson prism; F_2 : quarter-wave plate; s : gelator sample. (b-c) Photographs showing the light intensities of right-CPL (b) and left-CPL (c), measured by a Nova-oriel power meter (Ophir, Israel).

The CPL pumping platform (Fig. S5a and Fig. 2a in manuscript) was consisted of an LED-UV (365 nm) light torch (SCOUT UVFLUXS-3W, 20 mW/cm²), a Glan–Thompson prism (200–900 nm) and a quarter-wave plate. The LED-UV light torch could eliminate the influence of temperature efficiently. When the UV light passes through the Glan–Thompson prism, a linearly polarized light comes into being. Left-CPL will be generated after the linearly polarized light through the quarter-wave plate with clockwise 45° transmission angle. By rotating the quarter-wave plate 90° relative to the previous angle, the handedness of CPL can be altered to right-CPL. The emitted beam diameter was about 20 mm, which was large enough to cover the whole gelator sample. Considering the influence of light intensity, the intensity-dependent photo-responsiveness was studied by changing the distance between the LED-UV torch and the sample. Owing to subtle changes under 3 mW/cm² (distance: 45 cm) light irradiation and too swift response to catch under 10 mW/cm² (distance: 10 cm) irradiation, 5 mW/cm² (distance: 32.5 cm) was regarded as the optimal light intensity in the following experiments. The optimal location of the sample table is determined through the power meter (Fig. S5b, Ophir, Israel).

Part S5 Supplementary Table and Figures

Gelation abilities of **Azo-DF** was tested in various solvents at room temperature by a typical heating-cooling procedure. The results are shown in Table S1 (G=gel; P=precipitate; S=soluble; I=insoluble), and the minimum gelation concentrations are also presented (mg/mL).

Table S1 Gelation abilities of Azo-DF in various organic solvents or mixed solvents.

Solvent	CHCl₃	CH₂Cl₂	CH₃OH	CHCl₃/CH₃OH (v/v=1:3)
Azo-DF	S	P	P	G (2.0)
Solvent	1,4-dioxane	Nitromethane	Acetone	Benzene
Azo-DF	S	G (5.0)	P	I

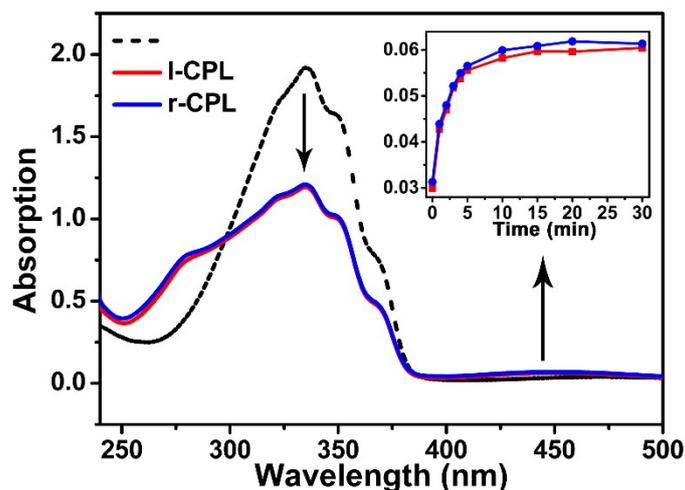


Fig. S6 UV-vis spectra of Azo-DF in chloroform (0.05 mg/ml) before (dotted line) and after (solid lines) CPL illumination for 30 min

UV-vis spectra of azobenzene molecule upon CPL irradiation was detected by dissolving 4,4'-azobenzoyl dichloride in chloroform with high purities (0.02 mg/ml) before and after CPL irradiation. Three characteristics of the spectra could be observed.

- (1) The initially strong UV band with a maximum absorption peak at 326 nm could be ascribed to the $\pi-\pi^*$ transition and corresponds to the vibrational structure of the typical *trans*-azobenzene;
- (2) After irradiation of left- or right-CPL, two well separated bands in the UV region ($\lambda_{\max}\sim 290$ nm) and visible region ($\lambda_{\max}\sim 440$ nm) increased, representing the $\pi-\pi^*$ and $n-\pi$ transition of *cis*-azobenzene structure, respectively;
- (3) The amount of variations caused by CPL handedness were almost equal within the error range.

Such result corresponded with the typical UV-vis spectrum of *trans*- to *cis*-isomerization of azobenzene,⁵ which indicated that the *trans*- to *cis*- transformation of azobenzene in Azo-DF had indeed happened. Before the irradiation of CPL, linear and planar conformation of *trans*-azobenzene contributed to the self-assembly as well as the gel formation of Azo-DF. While with the irradiation of CPL within the UV region, the UV-light irradiation-induced *trans*-to-*cis* transition broke such molecular symmetry and led to the collapse of self-assembled structures. And during this phase, it was the interaction between chiral dipeptide sequences and CPL handedness that we convinced might determine the collapse or continuingly self-assembly of Azo-DF.

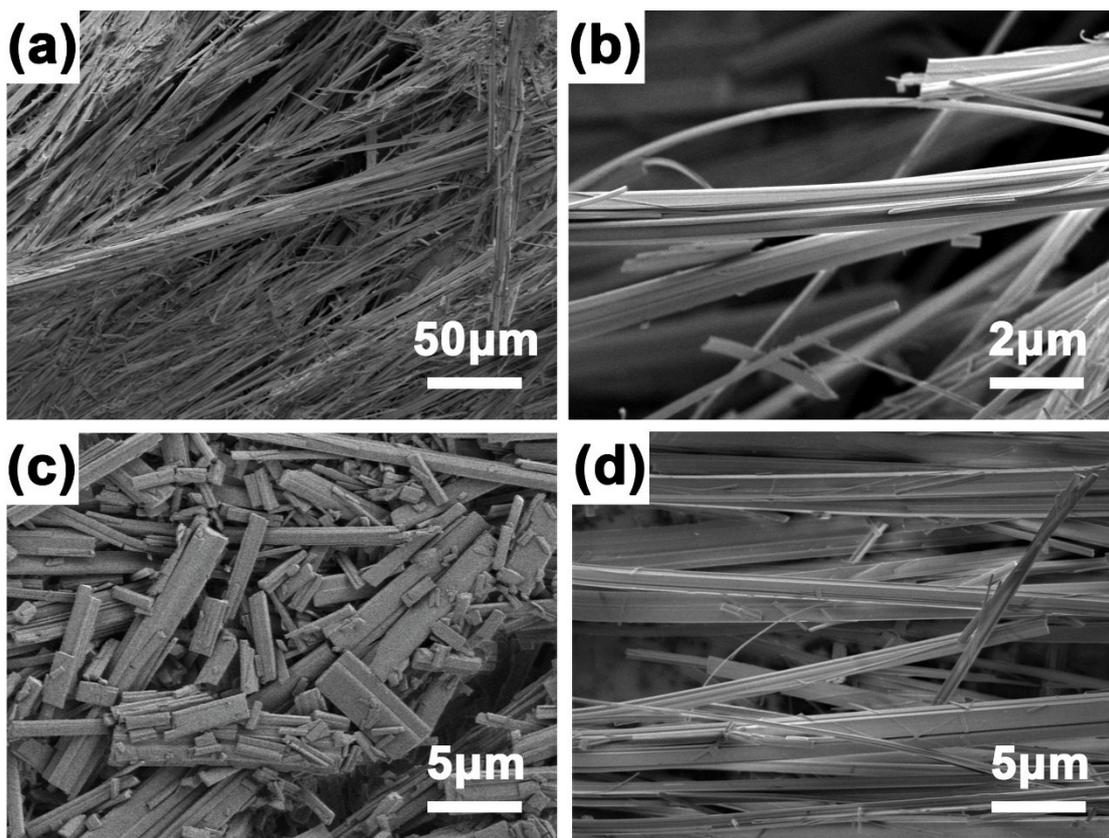


Fig. S7 Scanning electronic microscopy (SEM) images of Azo-DF xerogel before (a-b) and after right-CPL (c) or left-CPL irradiation (d) for 3 hours.

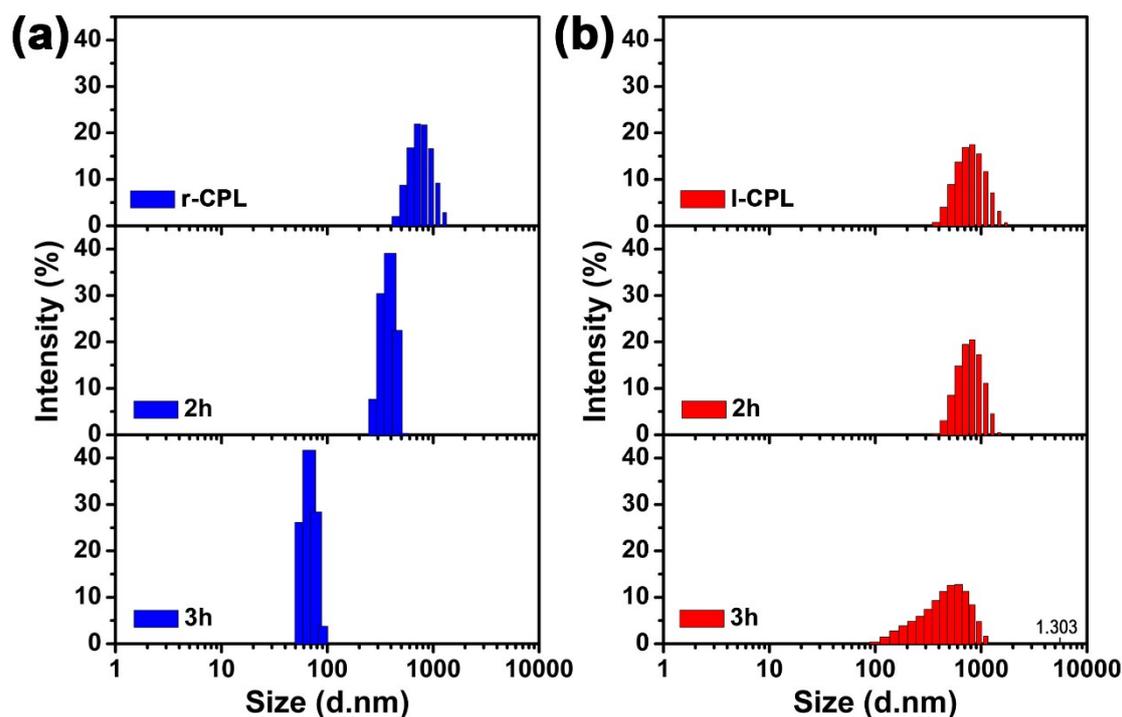


Fig. S8 Dynamic light scattering measurements of Azo-DF in chloroform before and after right-CPL (a) or left-CPL (b) irradiation.

The particle size of the self-assembled fibers decreased gradually with the increase of right-CPL irradiation time, and finally decreased to average 69 nm after 3h, which was consistent with the phenomena observed by AFM. By contrast, the particle size increased gradually irradiated by left-CPL. (The average particle size was outranged after 3h irradiation by left-CPL. As shown by Fig.S7b 3 h situation, the peak was broadened with wider size range. Moreover, there were more than one peak showing up in the result with some fluctuation.)

It is worth noting that we presume DLS as a good complement to SEM and AFM test. And in some degree, the collected DLS data might not reliable enough because of the following three reasons.

(1) Our gelator self-assembled into long and thin fibers in both chloroform/methanol mixture and chloroform solutions, which had been clearly displayed by SEM and AFM observations. These long fibers are difficult to be described by the typical DLS theory, which usually fits to spherical or semi-spherical particles but not fit the long fibers.

(2) After left-CPL irradiation, many larger self-assembles with average diameter of 10 μm were found by AFM, the size of these self-assembles has been out of range of

DLS with an optimal measurement range from 2 nm to 3 μm (Malvern Zetasizer Nano ZS90 DLS).

(3) DLS is difficult to be served as a real-time detection method for monitoring the dynamic changes of self-assembles because the CPL pumping system could not integrated into the DLS system easily. The principal of DLS technique is detecting the fluctuating behavior of particles by scattering light that particles reflect. The introduction of CPL (performing irradiation and detection at the same time) would disturb the scattering light received by detector. On the other hand, in each experiment, the gelator sample was irradiated by CPL, 100 μL gelator solution was collected and diluted to 1.5 mL, then the sample was detected by DLS, which usually took more than 20 min.

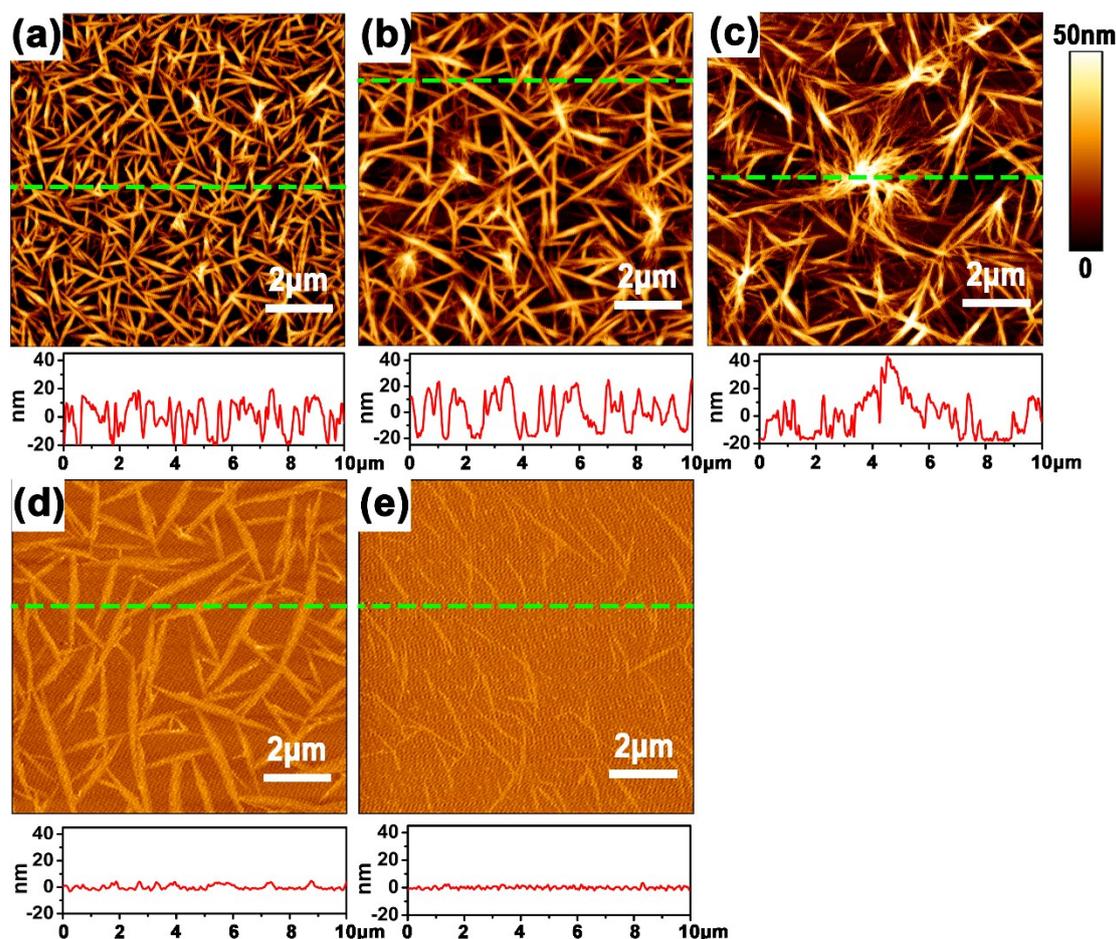


Fig. S9 AFM images of the self-assembled morphologies and the corresponding section profiles of Azo-D,D-DF in chloroform (0.5 mg/mL) before (a) and after 2 h (b) or 3 h (c) of right-CPL irradiation; (d-e) Azo-D,D-DF after 2 h (d, e) or 3 h (f) of left-CPL irradiation.

In the case of Azo-L,L-DF, an assembly and a disassembly of Azo-L,L-DF under left- and right-CPL irradiation were observed, respectively. While in the case of Azo-D,D-DF under right- or left-CPL irradiation, we observed a reversed tendency. Considering the original of Azo-L,L-DF and Azo-D,D-DF, the initial self-assembly morphology of Azo-D,D-DF was slightly different with that of Azo-L,L-DF (Fig. 4a in manuscript and Fig. S9a). Upon the irradiation of right-CPL, the nanofibers of Azo-D,D-DF showed an obvious tendency to aggregate (Fig. S9b), and after r-CPL irradiating for 3 h, several small dendritic structures with an aggregate center of 30~40 nm height were observed (Fig. S9c). When Azo-D,D-DF was irradiated by left-CPL for 2 h, the nanofibers decomposed rapidly with an average height of 6 nm (Fig. 9d). And after the irradiation of right-CPL for 3 h, only some thin fibers could be detected (Fig. 9e).

Such reversed results are in correspond with our hypothesis of the possible mechanism in some way, while it is worth noting that, there are four chiral centers in Azo-DF, and the CD spectra of L, L-azo-DF and D, D-azo-DF at 0.05 mg/mL in chloroform were not mirrior symmetry. We supposed this result as an auxiliary proof that the distinct self-assembly behaviors of gelators were caused by the CPL handedness.

Part S6 Possible mechanisms of CPL modulated self-assembly for Azo-DF

There are several possible mechanisms that we have thought about.

From the perspective of the isomerization of azobenzene, the undetectable energy transition (four additional low-lying triplet states, $3(n\pi^*)$ and $3(\pi\pi^*)$ have never been directly observed⁶), the reorientation of azobenzene in molecule might not be successive (when transition dipole moments are perpendicular to the polarization axis of the pump light, absorption could be no longer possible⁷), and the degrees of freedom when an azobenzene is in the center of the molecule (because of less mobility compares to those in an azobenzene group in the side⁸). From the perspective of CPL pumping system, the introduction of CPL might emphasize the quantum characteristic of light orientation, for example, the chiral dipeptide sequences in the side chain might preferentially interact with CPL with a kind of handedness, leading to stronger self-assembly tendency of the molecule⁹. This might restrict the orientation caused by *trans*-to-*cis* realignment of azobenzene. Such delicate balance postponed the dissociation of Azo-DF gel and contributed to a more compact self-assembled structure. While in-depth mechanism explanation relies on the close cooperation with experts in photocatalysis and photophysics, which is one of our follow-up actions.

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