



Fig. 1 (a) Illustration of different supramolecular self-assembly modulated by CPL handedness, right-CPL promotes the collapse of ordered structure, but left-CPL triggers the formation of new helical structure. (b) Chemical structure of 4,4'-azobenzene-linked dipeptide gelator, abbreviated to Azo-DF.

45 cm) light irradiation and too swift response to catch under 10 mW cm⁻² (D : 10 cm) irradiation, 5 mW cm⁻² (D : 32.5 cm) was regarded as the optimal light intensity in the following experiments. Meanwhile, the light intensities of left- and right-CPL were identical (Fig. S5b and c in ESI†).

First, the photo-responsiveness of Azo-DF triggered by right- or left-CPL was detected by UV-vis absorption spectra. Azo-DF gelator was dissolved in chloroform at a low concentration of 0.05 mg ml⁻¹, in which Azo-DF was in isolated state and supramolecular self-assembly would not happen. Initially, the UV-vis spectrum of Azo-DF consisted of a strong UV band with a maximum absorption peak at 326 nm, which could be ascribed to the π - π^* transition and corresponds to the vibrational structure of the typical *trans*-azobenzene (Fig. 2b). After irradiation of right- or left-CPL, two well separated bands in the UV region ($\lambda_{\text{max}} \sim 290$ nm) and visible region ($\lambda_{\text{max}} \sim 440$ nm) increased, representing the π - π^* and n - π transition of *cis*-azobenzene structure, respectively.¹³ The photo-stationary state was reached after 30 min right- or left-CPL irradiation, revealing that the typical *trans*- to *cis*-transformation of azobenzene in Azo-DF had indeed happened. It is worth noting that the amount of range caused by CPL handedness were almost equal within the error range. A consistent tendency was observed when the individual azobenzene was irradiated by the left- or right-CPL (Fig. S6 in ESI†).

Then the gelator concentration was increased to 2 mg ml⁻¹ in chloroform/methanol ($v/v = 1 : 3$), allowing the gel formation. The distinct gel-sol transition degree caused by the CPL handedness on macroscopic gel was observed. As shown in Fig. 2c, when the gel was exposed to the right-CPL irradiation, the gel showed an obvious tendency to loose and collapse after 3 h irradiation, remaining some fluffy aggregates in the 30 μ L solvents. By comparison, Azo-DF gel maintained stable in the gel state after 3 h of left-CPL irradiation, only a few solvents (12 μ L) were squeezed out. A similar solvent squeezed out situation of azobenzene gel, where a stable layered superstructure after UV light irradiation was claimed to be responsible, was reported by Jeong.¹⁴ Scanning electronic microscopy (SEM) were utilized to observe the gel morphology before and after 3 h of right- or left-CPL irradiation, respectively (Fig. 2d-f). Many long and regular ribbon-like fibres were observed. These fibres intertwined with each other and formed a dense three-dimensional (3D) network, revealing strong self-assembly capacities and linear packing pattern of Azo-DF. Large-scaled fibre distribution and enlarged view of a single fibre are shown in Fig. S7 in ESI.† After 3 h of right-CPL irradiation, the ribbon-like fibres were divided into numerous short stubs that scattered and piled up randomly, corresponding to the collapse of the gels. While after 3 h left-CPL irradiation, the intertwined ribbon-fibres were well-preserved. The arrangement of fibres became slightly loose, which explained why there some solvents were squeezed out.

Circular dichroism (CD) spectroscopy was used to monitor this self-assembly process (Fig. 2g and h). Initially, there are two weak peaks at 260 and 330 nm in the CD spectrum, which could be attributed to the molar chirality of two dipeptide arms carried by Azo-DF gelator itself. Such weak peaks were consistent with the morphology observed by SEM, where no evidential helical structure was detected. When the Azo-DF gel was irradiated with right-CPL, fluctuations around the baseline were observed in the CD spectra. But with the left-CPL irradiation, the CD spectrum (Fig. 2h) shows negative and positive cotton effect bands at 314 and 385 nm, respectively. These bands enhanced remarkably after 3 hours of the left-CPL irradiation, indicating the appearance of new helical structure during self-assembly process under the left-CPL irradiation,¹⁵ although such helical structure was not a common scenario.

X-ray powder diffraction (XRD) was implemented to further reveal the stacking structures of the xerogel. Fig. 3a shows XRD spectrum of Azo-DF xerogel before CPL irradiation, multiple sharp peaks indicated long-range molecular packing and high crystallinity of the gel structure.¹⁶ After r-CPL irradiation for 3 h, the measured XRD signals sharply diminished to bottom line (Fig. 3b), which indicated that the *trans*-to-*cis* transition of the azobenzene obviously decreased the planar symmetry of the gelators, destroying the highly ordered stacking of the gelators. This phenomenon were well consistent with the morphological changes observed by SEM. By comparison, for the gel sample after left-CPL illumination for 3 h, the crystal order was well maintained except some slight decreases in the XRD intensity. In addition, several new diffraction peaks are observed in Fig. 3c. Specifically, the peak A ($2\theta = 7.81^\circ$) splits into two bands, while two new peaks (B' and C') are found at $2\theta = 1.66^\circ$,





Fig. 2 (a) Photo of the CPL pumping system. F1: Glan–Thompson prism; F2: quarter-wave plate; s: gelator sample. (b) UV-vis spectra of Azo-DF in chloroform (0.05 mg ml^{-1}) before (dotted line) and after (solid lines) CPL illumination for 30 min. (c) Gel–sol transition of Azo-DF in chloroform/methanol ($v/v = 1 : 3$, 2 mg ml^{-1}), the gel collapsed under right-CPL irradiation, compared to only few solvent squeezing out from the gel under left-CPL irradiation. (d–f) Scanning electronic microscopy (SEM) images of Azo-DF xerogel before (d) and after 3 h irradiation of right-CPL (e) or left-CPL (f). (g and h) Circular dichroism (CD) spectra of Azo-DF gel in chloroform/methanol ($v/v = 1 : 3$, 2 mg ml^{-1}) before and after the irradiation of right-(g) or left-CPL (h). (λ : 365 nm , 5 mW cm^{-2}).

7.90° . In wide-angle region ($2\theta = 18\text{--}25^\circ$) the position of diffraction peak appears a shift,¹⁶ while the peak D splits into two peaks and the peak E decreases remarkably. These data clearly suggested that new crystalline state came into being after left-CPL illumination, moreover, the decomposition of the self-assembled structure might be largely postponed by left-CPL.

Unambiguous evidence for CPL handedness-dependent supramolecular self-assembly was provided by atomic force spectroscopy (AFM). Optimization experiments indicated that the Azo-DF could form highly ordered self-assembled pattern at a concentration of 0.5 mg ml^{-1} in chloroform. So we prepared AFM sample by dripping one drop of Azo-DF solution (0.5 mg ml^{-1} , chloroform) before and after right- or left-CPL irradiation onto freshly cleaved mica, respectively. As shown in Fig. 4a, the initially self-assembled pattern of Azo-DF presents as numerous short nanofibers evenly distributed in three directions, the



Fig. 3 XRD spectra of Azo-DF xerogels before and after 3 h irradiation of right- or left-CPL, light intensity: 5 mW cm^{-2} .

average length, width and height of these nanofibers are $2.4 \mu\text{m}$, 80 nm and 25 nm , respectively. Upon the irradiation of right-CPL for 2 h, the three-direction short nanofibers are replaced by some long and flattened ribbons with average length of more than $10 \mu\text{m}$ and height of 30 nm (Fig. 4b). After 3 h right-CPL irradiation, the self-assembled structure was hard to be detected (Fig. 4c). Such obvious change could be reasonably attributed to the weak self-assembled capacity of the gelator in a *cis*-azobenzene form, which dominated the configuration of the gelator. In comparison, when Azo-DF was irradiated by left-CPL for 2 h (Fig. 4d), rather than decomposition, those short nanofibers showed a strong tendency to aggregate, the fiber length and width were estimated to be $3.8 \mu\text{m}$ and 40 nm . A detailed enlarged view (Fig. 4e) of $1 \mu\text{m}$ shows that these nanofibers intertwined with each other to form a rope like structure. More interestingly, when the Azo-DF solution was exposed to left-CPL for 3 h (Fig. 4f), a dendritic structure was observed featured with an aggregate center over 150 nm height and numerous branches of nearly 50 nm height. The aggregation difference resulted from the CPL handedness was also monitored by dynamic light scattering (DLS) measurement (Fig. S8 in ESI[†]). The distinct self-assembly difference was well consistent with the above gel morphological changes. At the same time, the subsequent fiber growth upon left-CPL irradiation further demonstrated a special staking model of Azo-DF gelators where the supramolecular self-assembly was successfully inverted by exchanging the handedness of CPL. A nearly reversed CPL-modulated self-assembly trend was detected by using Azo-D,D-DF (Fig. S9 in ESI[†]). Considering Azo-L,L-DF and Azo-D,D-DF were not completely mirror symmetric owing to the four chiral centers, this result provided an auxiliary proof that the distinct self-assembly behaviors of the gelators were caused by CPL handedness. Compared to natural light, the introduction of CPL significantly emphasized the quantum characteristic of light orientation,^{8a} where the delicate balance between



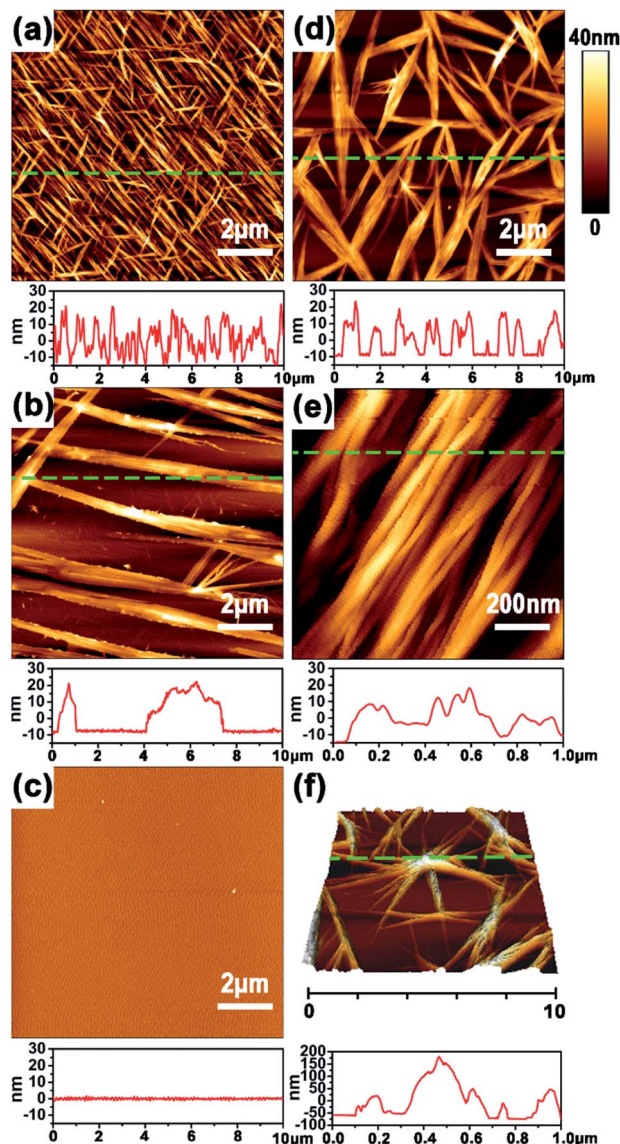


Fig. 4 AFM images of the self-assembled morphologies and the corresponding section profiles of Azo-DF in chloroform (0.5 mg ml^{-1}) before (a) and after 2 h (b) or 3 h (c) of right-CPL irradiation; (d–f) Azo-DF after 2 h (d and e) or 3 h (f) of left-CPL irradiation.

the isomerization of azobenzene and the chiral preference of the dipeptide played an important role in the dissociation or supramolecular self-assembly of Azo-DF gelators.^{13b,17} The possible mechanism is described in Part S6 in ESI.†

In conclusion, we observed an unconventional chiral effect: azobenzene-based chiral gelator showed a collapse tendency under the right-CPL irradiation, by contrast, intensive self-assembly emerged when the gelator was irradiated with left-CPL. Such CPL handedness-triggered self-assembly difference might arise great interest in the potential of CPL sources in controlling the supramolecular self-assembly of chiral molecules or polymers as well as for exploring their roles in the fabrication of function materials, moreover, inspiring rethought of some vital chemical and biological processes from the unique perspective of “dynamic molecular chirality”.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (51473131, 51533007 and 21775116), DICP Innovation Funding (DICP-RC201801). G. Qing acknowledges Wuhan Morning Light Plan of Youth Science and Technology.

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