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A dual thermal and photo-switchable shrinking–swelling supramolecular peptide dendron gel†

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A supramolecular dendron gel was fabricated through the co-assembly of an L-glutamic acid terminated amphiphilic dendron and a positively charged azobenzene derivative, which showed a dual thermal and photo-switched reversible volume phase transition or shrinking/swelling.

Supramolecular gels, in which small molecules self-assembled into entangled nanostructures and immobilized the solvents, have been attracting continuous interest due to their stimuli-responsiveness and many potential applications as smart materials.[1–5] Various stimuli such as the pH, metal ions, light and sound have been applied to the supramolecular gels and gel-to-sol or sol-to-gel transition was successfully realized. However, stimuli-responsive hydrogel materials with a macroscopic volume phase transition or shrinking/swelling properties, which are very necessary in consideration of application in drug release,[6–9] biosensing,[10,11] controlled microvalves,[12–14] and self-healing,[15–18] have been scarcely realized in supramolecular gels due to the inherent non-covalent bond nature. Only some examples are reported. Hamachi *et al.*[8,19] realized a thermal and pH-responsive supramolecular hydrogel by using glycosylated amino acetate as the gelator. We have developed a metal ion triggered peptide dendron gelator.[20] However, in all these systems, the triggers of shrinking and swelling are greatly involved in the gel system. A more important and remote stimulus such as light to cause the gel shrinkage or swelling has not been successful in supramolecular gel systems. Here, combining the shrinkable merits of our dendron hydro-gelator and the photoactive azobenzene, we present a strategy to construct a reversible shrinking and swelling supramolecular gel system triggered by photoirradiation.

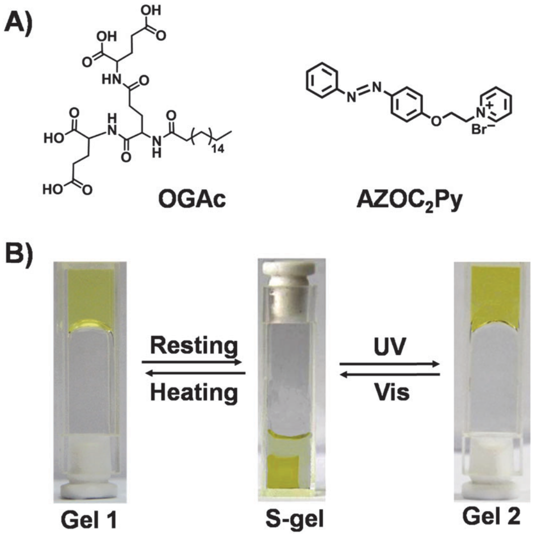

Fig. 1 (A) Molecular structure of **OGAc** and **AZOC$_2$Py**. (B) Schematic illustration of the phase transition in the co-assembled processes under multiple stimuli (photographs show the S-gel, swollen Gel 1 and Gel 2 respectively). Gelator **OGAc** is 0.13 wt%, the molar ratio of **OGAc** and **AZOC$_2$Py** is 5 : 1.

The hydrogel system is composed of an amphiphilic dendron terminated with three L-glutamic acid groups (OGAC) and a positively charged azobenzene derivative, as shown in Fig. 1. When OGAc and AZOC$_2$Py were mixed in certain ratios, they formed a transparent hydrogel initially. When such a hydrogel was kept at a room temperature of 20 °C, the gel underwent shrinkage to form a shrinking gel (S-gel), during which water was expelled. Interestingly, when the S-gel was irradiated using a UV light, the S-gel was swollen and formed a gel again (Gel 2). Gel 2 is very stable and will not change when kept at room temperature. However, if Gel 2 was subjected to visible light, then Gel 2 would change into the S-gel again. Such shrinking and swelling between the S-gel and Gel 2 can be reversibly switched by alternate Vis/UV irradiation many times. In addition, as the basic property of the gel, the S-gel can be thermally

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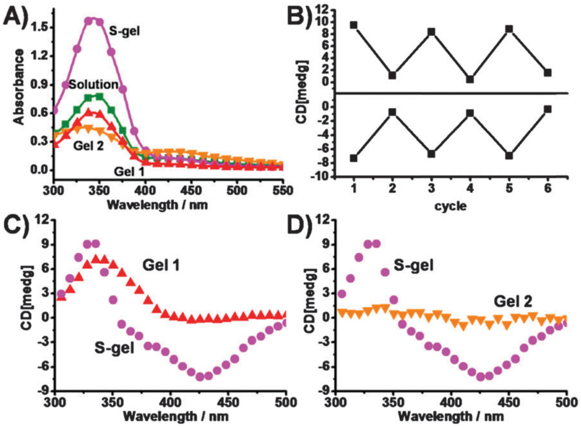

Fig. 2 UV-Vis (A) and CD (C and D) spectra of **OGAc** co-assembled with **AZOC$_2$Py**. Gel 1 (red, regular triangle), S-gel (pink, cycle), Gel 2 (orange, inverted triangle). (B) CD intensity as a function of the irradiation cycle (331 nm, top; 427 nm, bottom). UV light (150 W at 365 nm) and visible light (40 W compact fluorescent lamp, >400 nm).

changed to Gel 1 upon heating in solution and cooling down to room temperature. Therefore with this system, a dual thermal and photo-switchable shrinking/swelling gel can be realized. So far many research studies have been devoted to the volume phase transition in polymer systems. Here, we present the first example of a photo-switchable shrinking/swelling gel in a supramolecular system.

The reversible change in the gel states and the corresponding shrinking/swelling process can be visualized or followed by spectroscopy. Fig. 2A shows UV-Vis spectral change of different gels in comparison with that of the AZOC$_2$Py aqueous solution. In solution, the absorption peak of AZOC$_2$Py appeared at 350 nm and 430 nm, respectively. In the UV-Vis spectra of Gel 1, which is as-prepared by cooling the mixed solution of OGAC and AZOC$_2$Py to room temperature, the maximum peak appears at 346 nm, which can be ascribed to the π–π* transition of the *trans*-form azobenzene moiety in an aggregated state. Upon resting to form the shrinking gel (S-gel), the peak intensity increased and shifted further to 344 nm due to the expelling of water. When the shrinkage approached equilibrium after nearly 12 hours, the shrinkage ratio was estimated to be 60% (ESI,† Table S1). Upon irradiation of the S-gel by the UV light, the peak at 344 nm decreased, while a new peak at 420 nm can be observed, which can be ascribed to the n–π* transition of *cis*-form azobenzene.[21] This indicated that upon UV irradiation, azobenzene experiences a *trans* to *cis*-form transformation and Gel 2 was composed mostly of the *cis*-form azobenzene. Upon irradiation using visible light, Gel 2 changed into the S-gel and the corresponding UV-Vis spectra back to the same one.

The OGAc gelator is chiral, we have also investigated the CD spectral changes during the shrinkage and swelling of the gel in Fig. 2C and D since CD spectra can provide much information on the molecular packing in the chiral supramolecular system.[22] In the CD spectra, a positive CD signal at 337 nm was observed for Gel 1, indicating that the molecular chirality of OGAc was transferred to the achiral AZOC$_2$Py moiety. For the shrunken gel, the strong exciton couplet Cotton effect is observed, which showed a crossover at 357 nm, and positive and negative valleys at 331 nm and 427 nm, respectively. When the S-gel was subjected to the UV light stimuli, the *trans*-azobenzene transformed into the *cis*-form, the CD signals totally disappeared. This phenomenon is the same as those of the self-assembled chiral system where azobenzene was involved.[23] This is because the *cis*-form of azobenzene is difficult to be packed well and the molecular chirality localized in the carbon atom could not be transferred to the whole system. Upon the visible light irradiation with Gel 2, the CD signals can reappear again, as shown in Fig. 2D. Such a process can be repeated many times and the CD signals changed subsequently. Fig. 2B shows a plot of the intensity change of the CD signal for the co-assembly as a function of the exposure cycles. In one direction, the shrunken hydrogel was regulated by heating/cooling to obtain the swollen Gel 1 with the transition from exciton-split to the positive CD signal. In another direction, the shrunken hydrogel could transform to swollen Gel 2 with the CD-silent signal. Thus, compared to the chiroptical switch manifesting reversible *supra*-molecular chirality between the gel and sol,[24,25] a dual thermo- and photo-driven chiroptical switch was realized displaying reversible chirality change based on *trans*–*cis* isomerization of azobenzene and the assembling to dissembling process in the gel.

In order to further clarify the assembling structure and the packing during the shrinking/swollen process, AFM and TEM of the corresponding xerogels were investigated, as shown in Fig. 3 and Fig. S1 (ESI†).

Long nanofibers were observed for the as-prepared gel. After shrinking, the fibers become thicker and straight (Fig. 3B).

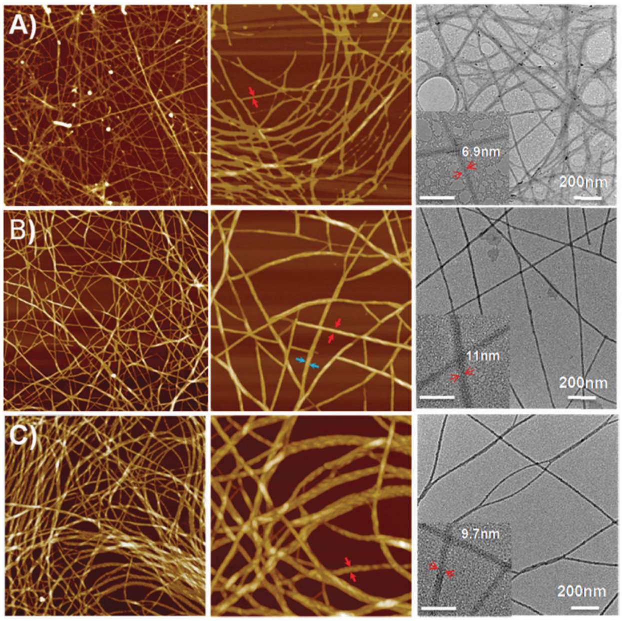

Fig. 3 AFM (left) and TEM (right) images of **OGAc** co-assembled with **AZOC$_2$Py**. (A) Gel 1, (B) S-gel, (C) Gel 2. The AFM images were 5 μm × 5 μm and middle column was 2 μm × 2 μm (arrows with different colours represented different diameters). All the TEM images are 200 nm × 200 nm and the inset images show amplified structures in which the arrows indicated the diameters of nanofibers.

For the swelling Gel 2, many helical structures are observed (Fig. 3C), which seemed to be due to the helical entanglement of the nanofibers. Such changes in the chiral structures reflected a slightly different packing of the molecules in the gels.[26] AFM analysis indicated that these nanofibers fell in the range of several nanometers. TEM measurements further confirmed the thickness of the nanofibers or nanohelices, which fell in the range of 6.9–11 nm, in correspondence with the AFM measurements.

The X-ray diffraction patterns of three xerogels were further investigated, as shown in Fig. S4 (ESI†). One diffraction peak was observed for all these xerogels, indicating the less ordered packing of the gelator molecules. The two theta (2θ) values were observed to be 2.08, 2.28 and 2.08, respectively. According to the Braggs equation, the d-spacings were estimated to be 4.2, 3.9, and 4.2 nm for the as-prepared, S-gel, and Gel 2, respectively. Previously, we have reported that OGAc itself could self-assemble into a bilayer structure with a layer distance of 3.9 nm. From the similarity of the two systems, it can be suggested that a bilayer structure was essentially kept in the present gel. However, upon adding $AZOC_2Py$, both alkyl chain and the packing of the azobenzene seemed to be more tilted.

We have further investigated the FT-IR spectra of the xerogels, as shown in Fig. S5 (ESI†). It was found that upon shrinking, both the vibration bands assigned to COO^- at 1600 cm^{-1} became more obvious, indicating the electrostatic interaction between $AZOC_2Py$ and OGAC.

Based on the above results, a possible mechanism for the gel shrinking and swelling can be proposed, as shown in Fig. 4. The amphiphilic gelator OGAC formed basically interdigitated bilayer units and $AZOC_2Py$ was attached at the headgroup of OGAC. Due to the additional $AZOC_2Py$ in the headgroup the bilayer did not roll into a nanotube. Instead, they formed the nanofiber structure, which is from a multi-bilayer structure composed of OGAC/$AZOC_2Py$, as confirmed from AFM and TEM. For the as-prepared Gel 1, $AZOC_2Py$ distributed separately on the surface of each bilayer through the electrostatic interactions, as confirmed by the CD spectrum of Gel 1, in which only a positive CD signal was observed. Since the azobenzene moiety is hydrophobic and has a strong π–π stacking tendency, it aggregated when Gel 1 was kept at room temperature. As a result, water molecules were expelled from the fiber and the gel shrunk. This can be verified from two points. Evidence is obtained from the CD spectrum of the S-gel, in which a strong exciton couplet was observed due to the π–π stacking of the azobenzene moiety. The other evidence is the change in the layer distance, which was diminished upon shrinking. In addition, the slight shift of the absorption maximum confirmed the aggregation of the azobenzene. All these suggested that the azobenzene moiety was aggregated during the gel shrinkage. Upon photo irradiation of the S-gel, the *trans–cis* isomerization for azobenzene was experienced. This process causes the volume change of the azobenzene moiety and the surrounding water was taken into the bilayer again and the S-gel swell into Gel 2. If visible light was applied to Gel 2, the gel shrunk again due to the isomerization of azobenzene. Since $AZOC_2Py$ was attached to the headgroup of OGAC, during such a change, the basic bilayer structures were not destroyed and the neighboring fibers were connected. Different from most of the gels containing the azobenzene moiety,[23] the present gel showed swelling than collapsing due to the strong interaction between the OGAc molecules. Thus, we obtained unambiguously a reversible shrinking/swelling supramolecular gel using alternative UV/Vis photo-irradiation.

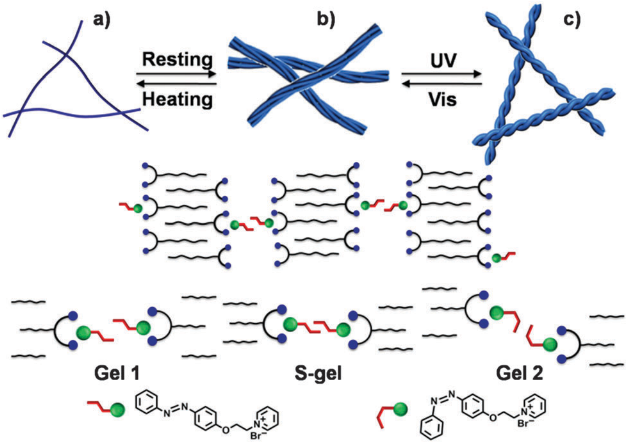

Fig. 4 Illustration of the hierarchical co-assembly of an amphiphilic dendron (**OGAc**) with the azobenzene derivative (**$AZOC_2Py$**). Top: (a) thin fibrils formed in a fresh hydrogel. (b) Thick fibrous bundles *via* strong π–π stacking upon shrinking of Gel 1. (c) Helices obtained in the swollen hydrogel after UV-photoirradiation. Bottom: the packing of the azobenzene and OGAc. **OGAc** formed a bilayer structure, in which the azobenzene moiety was embedded. In the as-prepared gel, the azobenzene moiety separately existed due to a lower ratio (**$AZOC_2Py$/OGAc**, 1 : 5). During the shrinkage of the gel, the π–π stacking of the *trans*-azobenzene increased and the neighboring fiber assembled together. Upon *trans–cis* isomerization by UV light, the layer distance was slightly expanded. However, the whole gel structure was retained due to strong interaction between the OGAc gelators, thus causing the swelling of the gel rather than collapsing.

It should be noted that Gel 2 is different from Gel 1. Gel 2 did not show any CD spectrum and the azobenzene moiety is in the *cis* form, while Gel 1 showed CD spectra and the azobenzene moiety is in the *trans* form. Only in the *trans* form the chirality of the molecules can be transferred to the whole nanostructure. Moreover, there is a reversible change between Gel 1 and the S-gel upon thermal treatment since Gel 1 was formed by cooling the solution to room temperature.

We demonstrated a reversible shrinking/swelling behavior in the supramolecular gel upon photoirradiation and thermal switch. The gel was composed of an amphiphilic dendron and a positively charged azobenzene derivative. It was confirmed that the amphiphilic gelator and the azobenzene moiety formed a multi-bilayer structure through the electrostatic interaction. Upon resting the as-prepared gel at room temperature, the azobenzene moiety experienced aggregation, which caused the shrinkage of the gel. Upon photoirradiation of the shrinking gel, the *trans–cis* isomerization occurred, which led to the swelling of the shrunken gel. Such a process can be repeated. As a result, using the combination of OGAC and the azobenzene derivative, we obtained a dual thermal and photo-switchable shrinking–swelling supramolecular peptide dendron gel. The work provided a new strategy to develop photo switchable smart soft materials with volume phase transition.

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