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Supra-dendron Gelator Based on Azobenzene-cyclodextrin Host-Guest interaction: Photoswitched Optical and Chiroptical Reversibility

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Abstract: A novel amphiphilic dendron (AZOC₈GAc) with three Lglutamic acid units and an azobenzene moiety covalently linked by an alkyl spacer was designed. The compound formed hydrogels with water in very low concentration and self-assembled into chiral twist structures. The gel showed a reversible macroscopic volume phase transition responding to pH variations and photo-irradiation. During the photo-triggered changes, although the gel showed a complete reversibility in their optical absorptions, only an incomplete chiroptical property was reached. On the other hand, the dendron could form a 1:1 inclusion complex via a host-guest interaction with α -cyclodextrin (α -CD), designated as a supra-dendron gelator AZOC₈GAc /α-CD. The supra-dendron showed a similar gelation behavior to that of AZOC₈GAc but with an enhanced photoisomerization transition efficiency and chiroptical switching capacity, which was completely reversible both in the optical and chiroptical performances. The self-assembly of the supra-dendron is a hierarchical or multi supramolecular self-assembling process. The work clear illustrates that the hierarchical and multi-supramolecular self-assembling systems endows the supramolecular nanostructures or materials with superior reversible optical and chiroptical switching.

Introduction

Stimuli-responsive supramolecular gels, which undergo reversible behaviors during the gel to sol or other macroscopic volume phase transitions upon external stimuli such as temperature, light, metal ions, electrical or magnetic field, have attracted great interests.^[1-5] A lot of soft smart materials have been fabricated based on the responsive gels, which find many applications in various fields such as biological substance release,^[6-8] mechanical shape memory,^[9-10] environmental remediation^[11-14]and so forth. Light is one of the most important stimuli since it is easily controlled and non-destructive. Thus, various photoactive gels have been developed. Those photochromic groups such as azobenzene, spiropyran or dithienylethene were well incorporated into the gels through the covalent bonds or via the supramolecular approach.[15-17] Among various photoactive gelators, the azobenzene derivative is one of the most investigated systems and many azobenzene derivatives were successfully incorporated into the functional

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gels.^[18-20]Besides the conventional optical switch upon alternative UV/Vis irradiation, the chiroptical switch, which is a reversible change of the chirality in the system, has also attracting great interest.^[21-25] In order to realize the chiroptical switch based on azobenzene, it is important to transfer the chirality to the azobenzene moiety since the azobenzene is achiral. During such chiral transfer, the self-assembly of the component molecules is necessary. However, in many cases, although the strong π - π interactions between the azobenzenes can help the self-assembly, they often cause irreversibility of trans-cis isomerization.^[26-28]Thus, it is necessary to subtly change the molecular design. An effective way is to incorporate the azobenzene moiety into the polymer system. While an alternative way could be through the host-guest inetractions between the azobenzene and cyclodextrins. Since the pioneer work of Bortolus and Monti^[29] on the azobenzene-cyclodextrin inclusion complexes, it has been well-established that transform host-guest inclusion azobenzene complex with cyclodextrins (α-CD, β-CD and γ-CD) in water and the bulky cisazobenzene would never fit in the cavity of α -CD due to the steric repulsion. In this paper, we have designed a dendron attached by the azobenzene with an alkyl spacer, as shown in Figure 1.



Figure 1 Photographs of the gels and the illustration on the reversible phase transitions of (a) conventional gelator $AZOC_8GAc$ and (b) Host-Guest inclusion supra-dendron $AZOC_8GAc/\alpha$ -CD. The $AZOC_8GAc$ gelator:0.41 wt% in all cases, $AZOC_8GAc/\alpha$ -CD mol ratio is 1/1.

With such a molecular design both the gelation ability and the optical reversibility were greatly enhanced. However, the chiroptical switching is still not satisfactory. Thus, we further fabricate the inclusion complex with cyclodextrins (CDs) and found that the dendron could from a 1:1 host-guest complex

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with α -cyclodextrin (α -CD) in Figure 1, which could be designated as supra-dendron. Such a supra-gelator shows a similar gelation behavior to that of the **AZOC**₈**GAc** but with an enhanced chiroptical switching capacity, which is completely reversible both in the optical and chiroptical performances. The self-assembly of the supra-dendron is a hierarchical or multi supramolecular self-assembling process. The results indicated that such a hierarchical self-assembly process endows the supramolecular system with more complexity and superior reversible optical as well as chiroptical switching.

Results and Discussion

Hydrogelation and pH-responsiveness of Azo-dendron (AZOC₅GAc)

The molecular structure of the hydrogelator AZOC₈GAc was shown in Figure 1. The solid compound was dispersed in water (1ml) and slightly heated to 50 °C, a light yellow solution could be obtained. After cooling down for some time to room temperature, transparent hydrogel could be obtained, which was confirmed by the inverted test tube method.^[30] It was found that the lowest critical gelation concentration (CGC) to form a hydrogel was near to 0.25 wt% and the sample required four hours to reach stability. Moreover, the formation of the hydrogel with the gelator concentration increasing to 0.69 wt% only needed 30 minutes. Figure 2a shows the absorption spectra of the dendron in various concentrated solution or gels. The maximum absorption peak showed a blue-shift with gelator concentration increasing, indicating the π - π stacking of the azobenzene moieties. Dynamic rheological measurements^[31-32] were performed to characterize the rheological behavior of the sample with different concentration of 0.41wt% and 0.15 wt%. From the frequency sweep measurements (Figure 2b), both G' and G" of the hydrogel sample at 0.41 wt% increased with the increasing frequency, and showing a storage modulus G' greater than the loss modulus G", which evidenced a true gel compared to sol-like sample at 0.15 wt%. As shown in Figure S 1d, the strain sweep tests were conducted for the 0.41wt% gel from 0.1% to 100% strain at 20 °C, with a constant frequency of 6.28 rad s⁻¹. When the strain increased over 50%, the G" value was greater than G', revealing the collapse of the gel networks and the dominant fluid character of the hydrogel.



Figure 2 (a) concentration-dependent UV/Vis spectra, and (b) evolution of G' and G" as a function of angular frequency $AZOC_8GAc$ assembly at different concentration, in which the sample with gelator concentration at 0.15 wt%

presents sol-like, while the samples with the gelator concentration between 0.25 wt% and 0.69 wt% form hydrogel.

Since the dendritic compound AZOC8GAc with four carboxylic acids was pH sensitive, the pH titration curve at an AZOC8GAc solution concentration of 1 mM was presented in Figure S1. The relatively flat regions of the curve correspond to the protonation constants pKa values, which were found to be 3.4±0.1 and 4.46±0.1, respectively. The corresponding compositions of AZOC₈GAc at various pH were calculated from the equation pKa = pH - lg ([base]/ [acid],^[33-34] the negative charge distribution from 0 to 4 under different pH values were obtained. Based on the above results, the assemblies formed at selected pH values showed different phase behavior and micro properties It was found that the pH value of the original hydrogel was located at 3.4, well-defined helical twists were obtained (Figure 3b), exhibited the widths ranged from 7 to 15 nm. TEM images (Figure S2) revealed the ultrafine nanofibres with an average diameter around 5 nm and further deduced the helical nanostructures may due to the helical entanglement of Nano fibers. If the system was acidified to pH 2, stable hydrogel was still obtained. In this case, thicker nanofibers with average diameter of 8 nm were obtained, but without obvious helical structures. Moreover, when increasing the sample pH to 4, the increased ionization of carboxyl group resulted in a partial hydrogel, in which helical nanostructures randomly distributed and partly relaxed. At pH 5.5 or above, the hydrogel converted to a sol and the morphologies changed completely from helixes to non-continuous packed structures. UV-Vis and CD spectra further revealed the pH responsiveness of the hydrogel (Figure 3a). For the UV-Vis spectra of the system pH fell in the range of 2-4, the maximum peak appeared at 326nm, which can be ascribed to the π - π * transition of the trans-form azobenzene moiety in an aggregated state. Upon regulating the sample to pH 5.5, the peak further shifted to 343 nm which is exactly corresponding to the disassembly with pH increasing. In the CD spectra,[35-36] the hydrogel at pH 3.4 presented a strong symmetric exciton couplet Cotton effect with a crossover at 328 nm, and positive peak and negative valley at 315 nm and 346 nm, respectively. This spectrum indicated that the chiral transfer from chiral carbon atom to achiral azobenzene head group was due to the self-assembly of the dendron. When pH changed, the CD spectrum showed also a change. An intensive negative CD splitting band was observed at pH 2 of the hydrogel, appearing a minimum negative band at 365nm and a maximum positive band at 301 nm. For the system pH at 5.5, negative CD band with decreased intensity was located at 341nm. These spectral changes reflected that the packing of the azobenzene moiety could be subtly regulated by the pH variations of the gel.

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Figure 3 (a) CD and UV-Vis spectra, (b) AFM images of the AZOC₈GAc hydrogel at different pH values. Gelator AZOC₈GAc is 0.41wt%.The inset image of Fig 3b showing the amplified defined helicity for the hydrogel at pH 3.4.

Light controlled reversible morphology and chirality

As is well known, diverse light responsive supramolecular assemblies are designed as functional materials which is related to the reversible E/Z-isomerization of azobenzenes.[37-38] Our azobenzene attached dendron showed similar photoresponsiveness to the light. Figure 4 showed the supramolecular chirality changes accompanied with the morphological transformations for the conventional hydrogel upon alternative UV/Vis irradiation. As the hydrogel proceeding with reversible Gel-Sol transition stimulated by UV light (365 nm), the assembly showed the characteristic changes in the absorbance spectra (Figure 4a) with a decrease in the π - π * absorption band of the trans-form azobenzene moieties at 326 nm and the appearance of the $n-\pi^*$ transition of cis-form azobenzene groups at 431nm. Upon irradiation with visible light (420 nm), the return efficiency from cis-form to trans-form reached to 94%. Though the gel showed a complete reversible optical switching, the transition efficiency of trans to cis isomerization was only 65% based on the quantitative calculation (as seen in Figure S3),^[39-40] which may result from the azobenzene chromophores having strong π - π * interactions and being restricted heavily in the hydrogel. For the CD spectral measurements (Figure 4b), significant Cotton effect was observed in the gel state, and the CD intensity presented a slight photo driven decrease but could not recover to the original

intensity upon visible light stimuli. Therefore, the CD intensity at 346 nm was steadily decreased after several UV/Vis irradiation cycles which manifesting an irreversible supramolecular chiroptical switching, as shown in Figure 4c. Furthermore, Figure 4d revealed that the photo-triggered isomerization process from tans-azobenzene to cis-azobenzene resulted in a dramatic morphology change, during which the helical twists disassembled into lamellar fragments but the CD signal was not completely disappeared. AFM section analyses (Figure 4e and 4f) provided more precise information about the helical assembly. Most helical fibers was obtained with a height of approximately 7.8 nm and a helical pitch of around 90 nm, whereas few thinner fibrils with a diameter of around 4.3 nm and thicker helixes with height of 15nm were also observed. Depending on these analysis, it could interpret that the helical nanostructures were predominantly bundles of the nanofibers. The results discussed above indicated that the segmentally conformational change of the gelator may bring more vital effects on the stabilization of helixes than the spectral changes with respect to the supramolecular hydrogel.



Figure 4 (a) UV-Vis spectra and (b) CD spectra of AZOC₈GAc hydrogel under alternative UV/Vis irradiation (AZOC₈GAc hydrogel, Green line; the sample under UV irradiation for 15min, Red line; the sample under Vis irradiation for 30min, Blue line). (c) CD intensity of AZOC₈GAc hydrogel as a function of the irradiation cycle at 346nm. (d) AFM images revealing the morphological changes of AZOC₈GAc hydrogel under UV irradiation. (e, f) AFM sectional

analysis of AZOC₈GAc hydrogel (height along the red arrows and helical pitch labelled by blue triangles).UV light (30W at 365 nm) and visible light (40 W compact fluorescent lamp, >400nm). Gelator AZOC₈GAc is 0.41wt%, the assembly pH is 3.4.

Host-guest and light controlled reversibility of the supramolecular chirality

It is well-known that trans-azobenzene can fit into the cavity of cyclodextrin (CDs) and spontaneously form supramolecular complex.^[41-42] To this end, isothermal titration calorimetry (ITC)^[43] was carried out to determine the stoichiometry and binding constants of inclusion complexes. The titration curves of each titration were found in Figure S6 and corresponding ITC results of each titration were summarized in Table 1 of SI, revealing that complexation stoichiometry between AZOC₈GAc gelator and a-, β - or γ -cyclodextrin was approaching to be 1/1, 5/4, or 2/1. Moreover, the binding constants for the inclusion with the α -, β or γ - cyclodextrin were calculated to be 98.4 $\times 10^2$, 26.6 $\times 10^2$ and 29.1×10² M⁻¹. Thus, for host-guest inclusion complex with azobenzene, the α -CD had a higher association constant to serve as a suitable host compared with β - or γ -CD. ¹H NMR spectroscopy was further carried out to investigate the binding behavior of AZOC₈GAC with CDs. As shown in Figure 5a, in comparison with the spectrum of AZOC₈GAC assembly, peaks related to protons H_{a-d} on azobenzene part of AZOC₈GAC displayed pronounced downfield shifts after adding a- or v-CD on a stoichiometric ratio, whereas the initial signals of the azobenzene moiety still partly retain in AZOC₈GAc/β-CD inclusion. However, Figure S8 showed that the signals related to protons He, Hf on alkyl chain of AZOC8GAc displayed almost negligible downfield shifts with an increasing amount of α -CD, in which the $\Delta \delta$ values were 0.22 for $H_e,~0.08$ for $H_f,^{[44]}$ and while the peaks related to protons H₃ and H₅ located inside the cavity of α-CD exhibited gradual upfield shifts. Furthermore, 2D nuclear Overhauser enhancement spectroscopy (NOESY) of AZOC₈GAc/α-CD complex showed the clear NOE correlations between the protons H_3 and H_5 on inner $\alpha\text{-}CD$ cavity and protons on azobenzene part of AZOC₈GAc (Figure S9). All these results demonstrated that the azobenzene moiety of AZOC₈GAc was threaded into the cavity of α -CD, but the alkyl chain moiety of AZOC₈GAc just have extremely weak interaction with α-CD. The FT-IR spectra (Figure S10 a) demonstrated that in case of AZOC₈GAc/α-CD complex, the N-H stretching frequencies at 3306.5 cm⁻¹ were disappearing with the stretching frequencies of primary and secondary alcoholic groups of CDs appeared around at 3375 cm^{-1,[46]} while amide I at 1655cm⁻¹ and amide II at 1545cm⁻¹ significantly decreased associated with weakened hydrogen bonding. Therefore, NMR spectra or the FT-IR spectral study gave the supporting evidence for the formation of more stable inclusion complex between AZOC₈GAc and α-CD. As seen in Figure 5c, azobenzene moiety was exactly located inside the cavity of α-CD to form 1:1 AZOC₈GAc/α-CD inclusion while the azobenzene was not easily accessible to β-CD though it had larger cavity diameter due to lower binding constant. The X-ray diffraction patterns of four xerogels were also investigated, as shown in Figure S10 b. For the AZOC8GAc assembly, there were four diffraction peaks with the d spacing ratio of roughly 1:1/2:1/3 and 1:4, corresponding to the d spacing of 3.8 nm in a lamellar structure. Since the length of 3.8 nm was larger than the extended molecular length of 2.37nm but smaller than twice the length, indicating the interdigitated bilayer structure of the hydrogel.^[47] However, for the complex hydrogel of AZOC₈GAc/α-CD system, three diffraction peaks corresponding to the d spacings of 1.73 ,1.34,and 0.92 nm in the low angle region were observed. This means that the structure of the H-G

complex deviated from the lamellar. The largest d spacing of 1.73 nm is close to the single H-G molecule length with the alkyl chain inclined.



Figure 5 (a) ¹H NMR spectra (azobenzene region) (b) CD / UV-Vis spectra of AZOC₈GAc hydrogel and AZOC₈GAc/ Cyclodextrin complex. (c) Schematic illustration of the 'host-guest' inclusion mode with the stoichiometric ratio at 1:1 for α-, 5:4 for β-, and 2:1 for γ-CD, AZOC₈GAc gelator: 0.41 wt %).

With regard to the exactly complete inclusion of azobenzene with α-CD, we focused on investigations of 1:1 AZOC8GAc/α-CD complex hydrogel. Firstly, for AZOC₈GAc/α-CD complex after irradiating with 365nm UV light, ¹H NMR spectroscopy (Figure S7 c) showed the resonance peaks corresponding to the protons Ha'-d' of cis-azobenzene part arose with no obvious peak shifts which was similar to the free cis-azobenzene of AZOC₈GAc assembly upon photoirradiation (Figure S7 d). These phenomena provided evidence that AZOC₈GAc/α-CD complex exhibited excellent light responsive isomerization behavior and the cis-form azobenzene was mostly located outside the cavity of α -CD. Furthermore, it was interesting to investigate this complex assembly featuring light-controlled complete reversible optical and chiroptcial properties accompanied with morphological transformations. Figure 6a revealed the absorption peak of the complex hydrogel has redshift to 333 nm due to the host-guest inclusion between azobenzene group and cyclodextrin cavity. The exciton couplet Cotton effect from AZOC₈GAc/α-CD hydrogel observed was similar to the AZOC₈GAc hydrogel which may ascribe to the chirality transfer from the chiral center to azobenzene part through short alkyl spacer was more significant than from α-CD with inherent chirality. In addition, the host-guest interactions decreased π - π * packing of azobenzene groups and then improved the photo transition efficiency from trans to cis-form. Therefore, the spectral characterizations (Figure 6b) showed that the CD signal almost disappeared under UV irradiation, and reversely recovered by the visible light. Therefore, for AZOC₈GAc/α-CD complex, repeated photoirradiation cycles resulted in virtually the same chiroptical activity which indicated good reversibility of this chiroptical switching (Figure 6c). The AFM images described the reversible photo modulation on

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micro-level morphologies of $AZOC_8GAc/\alpha$ -CD complex. As shown in Figure 6d, the fragmental irregular nanoaggregates regulated by host-guest inclusion finally transformed into more amorphous particles upon UV irradiation. However, the same nanostructures were also obtained for the recovered sample irradiated by visible light.



Discussion

Based on the above results, a possible mechanism concerning the novel AZOC₈GAc assembly with multi-responsiveness to chiral helixes and chiroptical properties could be proposed. The AFM or TEM images have revealed that the dendron selfassembled into helical fibrils. The FT-IR, UV/Vis spectra and Xray diffractions further confirmed that the gelator molecules formed interdigitated bilayer in which strong π - π stacking of azobenzenes groups as well as the hydrogen bond between carbonyl groups played important roles in the formation of stable hydrogel and thus produced split Cotton effect for azobenzene parts. When AZOC₈GAc hydrogel was subjected to UV irradiation, the helical structures disassembled into lamellar hydrogel collapsing. fragments with However, strong interchromophores interaction confined the complete isomerization of azobenzene groups and thus resulted in the corresponding CD signal incompletely disappearing. The visible light subsequently induced the cis-form recovering to its original packing. Meanwhile, the photo reversible CD change between trans-form and cis-form hydrogel was able to repeat several times under alternative UV / visible light irradiation. In the case of AZOC₈GAc/α-CD complex, stable hydrogel was obtained with similar exciton couplet. The strong "host-guest" interaction between azobenzene group and cyclodextrin cavity caused the

Figure 6 (a) UV-Vis spectra and (b) CD spectra of AZOC₈GAc/ α -CD hydrogel under alternative UV/Vis irradiation (AZOC₈GAc hydrogel, Light green line; the sample under UV irradiation for 15min, Red line; the sample under Vis irradiation for 30min, Blue line). (c) CD intensity of AZOC₈GAc/ α -CD hydrogel as a function of the irradiation cycle at 346nm. (d) AFM images revealing the reversible morphological changes of AZOC₈GAc/ α -CD hydrogel under alternative UV/Vis irradiation. UV light (30W at 365 nm) and visible light (40 W compact fluorescent lamp,>400 nm). (AZOC₈GAc gelator: 0.41 wt%, the molar ratio of AZOC₈GAc/ α -CD is 1/1, the co-assembly PH is 3.2).



Figure 7 Schematic illustration on the AZOC₈GAC assembly: (a) For AZOC₈GAC conventional hydrogel, the amphiphilic gelator formed interdigitated bilayer in which azobenzene groups packed face to face (π - π stacking), and then light induced the transition of azo groups from trans-form to cis-form and AZOC₈GAC hydrogel collapsed. (b) For the AZOC₈GAC/a-CD supra-hydrogel, "host-guest" interaction between azobenzene and cyclodextrin caused the lose packing and formed the nanoaggregate. Photo irradiation further caused the isomerization of Azo accompanying with the disassembly of AZOC₈GAC/a-CD complex, while partial of cis-AZOC₈GAc/a-CD complex still formed the aggregate since there are close to the cyclodextrin.

original bilayer transformed into more relaxed stacking of the supra-dendron, which formed irregular nanoaggregates. Upon irradiating the complex sample with UV light, the decreased π - π * packing of azobenzene groups due to "host-guest" interactions caused complete photo isomerization of azobenzene moieties within the **AZOC**₈**GAc**/ α -**CD** complex. Therefore, the azobenzene group came out from the cavity and led to the disassembly of the nanoaggregates. Since the cis-azobenzene is close to the cyclodextrin, some of them can still form the smaller nanoaggregate. Interestingly, the photo driven morphological and chiroptical switching was fully reversible under alternative UV/Vis irradiation with regard to the **AZOC**₈**GAc**/ α -**CD** hydrogel.

Conclusion

In summary, we demonstrated that an amphiphilic dendron $AZOC_8GAc$ with azobenzene moiety could form responsive hydrogels to pH and light. The chirality localized at the glutamic acid can be transferred to azobenzene moiety through a long alkyl spacer and generated twisted helical nanostructures and strong split Cotton effect. The hydrogel showed a reversible optical switch upon alternative UV/Vis irradiation but with

incomplete chiroptical reversibility. On the other hand, through the host-guest interaction, the dendron can be derived into a supra-dendron, in which azobenzene moiety formed a 1:1 complex with a-cyclodextrin. Such AZOC₈GAc/a-CD supradendron could form the hydrogel also. Besides the reversible optical absorption upon alternative UV/Vis irradiation, the supradendron gel showed also a complete chiroptical reversibility. This offers great potential to develop new functional supramolecular materials with the bridge between supramolecular chemistry and chiral nanostructures. Nowadays, the supramolecular self-assembly is towards more complex system to realize the new functions.^[48] The present result clear indicates that the hierarchical or multi supramolecular selfassembling endows the supramolecular system with superior responsive behaviors.

Experimental Section

Chemicals and reagents: All starting materials used in synthesis of AZOC₈GAc were obtained from commercial suppliers and used without any additional purification, in which the reactant Boc-GE was synthesized according to our previous work.^[49] All the organic solvents were purified and dried according to standard methods. Milli-Q water (18.2 MW cm) was used in all experiments.

The Synthetic procedures of gelator AZOC $_8$ GAc:The syntheses of AZOC $_8$ OH, AZOC $_8$ GAc illustrated in Scheme S1. More details of syntheses and characterization of these compounds were provided in the ESI.

Preparation and characterize of hydrogel: The typical hydrogel was spontaneously formed by adding AZOC8GAc gelator (1.5, 2.5,4.1, 5.5, 6.9 mg) to pure water (1 mL) respectively, which was slightly heated to a light yellow solution at 50 °C and then rest at room temperature for 30 minutes. The stability of hydrogel increased with concentration. Dynamic rheological measurements were performed to demonstrate viscoelastic property of AZOC₈GAc hydrogel (0.41 wt%, the total volume was 1ml). The hydrogels at various pH values was prepared by mixing AZOC₈GAc with different pH aqueous solutions, which were adjusted by NaOH and HCl solutions. For AZOC₈GAc/cyclodextrins (CDs) complex, The gelator (4.1mg) was dissolved in water to form transparent aqueous solution. Then, an aqueous solution of α -CD, β -CD or γ -CD was mixed into the above solution, respectively. Subsequently, the mixed solution was heated and cooled down, resulting in the rapid formation of coassembled hydrogel. The mol ratio of α -CD, β -CD or γ -CD to AZOC₈GAc was kept at 1, 0.8, 0.5, respectively and the total volume was kept at 1ml. Photo-regulated experiment was carried out by UV light (30 UVA lamp, λ =365 nm. 20cm away from the sample) at cool condition and further converted the sample from Gel to Sol. The hydrogel obtained (0.41 wt%, the total volume was 1ml) by the above methods were firstly diluted with water, cast on a freshly cleaved mica surface and then dried in a vacuum for AFM measurements. For the TEM measurements, a small amount of diluted hydrogel was placed onto carbon coated copper grid and dried in a vacuum or exposed to UV light. As for FT-IR spectra and XRD measurements, the samples were cast onto silicon slices and dried as mentioned above. In the process of measuring the UV and CD spectra of hydrogels, a quartz cuvette with 0.1 mm width was used. All the samples for the characterizations were irradiated by UV (30 W UV lamp with main light at 365 nm) and visible light (40 W compact fluorescent lamp, >400 nm visible light) alternatively to see their changes.

Potentiometric pH Titration: AZOC₈GAc was first dissolved in water at a concentration of 1.0 mM, and then the sample pH was adjusted to 11 with 0.1 M NaOH aqueous solution. Then 0.1 M HCl was gradually added into this solution in small portions. The titration process was monitored

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with a METTLER TOLEDO/FE20 PH meter at a room temperature around 20 °C. The electrode was calibrated with a standard buffer solution before being used. Three titrations were performed, and the mean pKa values were calculated.

The calculation of stoichiometry and binding constant 'Ka' of the AZOC₈GAc-cyclodextrin inclusion complexes: Isothermal titration calorimetric measurements (ITC) were performed on a MicroCal AutoiTC200 instrument, which was composed of a reference cell and a sample cell of 400ul. Stock solutions of host (1 mM, 1 mL) and guest (10 mM, 0.5 mL) in water were prepared using volumetric glassware. Before each titration, all the solutions were degassed and kept constant temperature. In a typical run, a 200µL syringe was full of guest (10 mM) and the cell was loaded with host (1 mM, 400ul). The titration of the host with the guest was carried out at 298 K, 20 injections of 2 µL with a equilibration time interval of 120s each injection. Each injection of ligand resulted in a heat pulse that is integrated with respect to time and normalized for concentration to generate a titration curve of kcal/mol vs molar ratio (guest/host). The resulting isotherm was fitted to a binding model to generate the affinity (K_D), stoichiometry (n) and enthalpy of interaction (Δ H). All the data were analyzed with Microcal Origin 7.0 software provided by the manufacturer.

Apparatus and measurements: The UV/Vis and CD spectra were detected using JASCO UV-550 and JASCO J-810 spectrophotometers, respectively. Fourier transform infrared (FT-IR) spectra were recorded on a JASCO FT/IR-660 plus spectrophotometer with a wavenumber resolution of 4 cm⁻¹at room temperature. X-ray diffraction (XRD) was achieved on a Rigaku D/Max-2500 X-ray diffractometer (Japan) with CuK_a radiation (λ =1.5406Å), which was operated at 45 kV, 100 mA. AFM was performed by using Fastscan mode (Nanoscope IIIa, Digital Instruments) with a pyramidal Si3N4 tip. The HR-TEM images were obtained on a Tecnai G2 F20 U-TWIN operating at accelerating voltages of 200 kV. PH value was obtained on the METTLER TOLEDO/FE20 PH at a room temperature around 20 °C. Rheological measurements were conducted on Discovery DHR-1 Rheometer (TA Instruments) using a 20mm parallel plate geometry in a Peltier plate. The frequency-sweep spectra were measured in a constant strain (0.1%) mode over the frequency range of 0.1-100 rad s⁻¹ at 20°C. The strain-sweep spectra were measured in a constant frequency of 6.28 rad s^{-1} over the strain range of 0.1-100% at 20 °C.TLC was performed on silica gel HF254 flake and column chromatography was carried out with 230-400 mesh silica gel. Isothermal titration calorimetric measurement (ITC) were performed on a MicroCal Auto-iTC200 instrument. ¹H NMR spectra and¹³C NMR spectra were recorded with a Bruker Fourier 300 (300 MHz) spectrometer in CDCI3 or DMSO-d⁶ by using Me4Si as an internal standard.¹H NMR spectra or 2D-NOESY spectra of assembly were recorded with a Bruker Avance DMX 400 spectrophotometer or a Bruker Avance DMX 600 spectrophotometer in D₂O. MS spectra were determined with BEFLEX III for the ESI mass spectrometer. Elemental analyses were performed on a Carlo-Erba-1106 instrument. All the photographs of the gel were taken by using a Canon EOS60D.

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Keywords: supra-dendron • chiroptical switching • chiral twist • supramolecular hydrogel • photoresponsiveness

References

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- [1] L. Zhang, X.F. Wang, T. Y. Wang, M.H. Liu, Small 2015, 11, 1025-1038.
- [2] Z. Y. Yu, J. Zhang, R. J. Coulston, R. M. Parker, F. Biedermann, X. Liu, O.A. Scherman, C. Abell, *Chem. Sci.* 2015, *6*, 4929-4933.
- [3] E. A. Appel, X.J. Loh, S. T. Jones, F. Biedermann, C. A. Dreiss, O. A. Scherman, J. Am. Chem. Soc. 2012, 134, 11767-11773.
- [4] Z. Tao, K. Peng, Y.J. Fan, Y.F. Liu, H.Y. Yang, *Polym. Chem.* 2016, 7, 1405-1412.
- [5] Q. W. Zhang, D. H. Qu, X. Ma, H. Tian, Chem. Commun. 2013, 49, 9800-9802.
- [6] B. Yan, J. C. Boyer, D. Habault, Y. Zhao, N. R. Branda, J. Am. Chem. Soc. 2012, 134, 16558-16561.
- [7] K. Schneider, J. Karchera, Z. L. Pianowski, Chem. Commun. 2016, 52, 3143-3146.
- [8] J. Yu, W. Ha, J.N. Sun, Y.P. Shi, ACS Appl. Mater. Interfaces 2014, 6, 19544-19551.
- [9] W. Feng, W.F. Zhou, Z. H. Dai, A. Yasin, H. Y. Yang, J. Mater. Chem. B 2016, 4, 1924-1931.
- [10] K. Miyamae, M. Nakahata, Y. Takashima, A. Harada, Angew. Chem. Int. Ed. 2015, 54, 8984-8987.
- [11] B. Adhikari, G. Palui, A. Banerjee, Soft Matter 2009, 5, 3452-3460.
- [12] B. O. Okesola, S. K. Suravaram, A. Parkin, D. K. Smith, *Angew.Chem. Int. Ed.* 2016, 55, 183 -187.
- [13] S. Song, L. Feng, A. X. Song, J.C. Hao, J. Phys. Chem. B 2012, 116, 12850-12856.
- [14] B. Xue, M. Qin, J.H. Wu, D.J. Luo, Q. Jiang, W. Wang, Y. Li, Y. Cao, ACS Appl. Mater. Interfaces 2016, 8, 15120-15127.
- [15] M.X. Dong, A. Babalhavaeji, S. Samanta, A. A. Beharry, G.A. Woolley, Acc. Chem. Res. 2015, 48, 2662-2670.
- [16] X. Y. Yao, T. Li, J. Wang, X. Ma, H. Tian, Adv. Optical Mater. 2016, DOI: 10.1002/ adom.201600281.
- [17] E. R. Draper, D. J. Adams, Chem. Commun. 2016, 52, 8196-8206.
- [18] F. Xie, L. Qin, M. H. Liu, Chem. Commun. 2016, 52, 930-933.
- [19] H. Yamaguchi, Y. Kobayashi, R. Kobayashi, Y. Takashima, A. Hashidzume, A. Harada, *Nat. Commun.* 2012, 3, 603-607.
- [20] W. R. Zhao, L. Feng, L. Xu, W. L. Xu, X. Sun, J. C. Hao, *Langmuir* 2015, 31, 5748-5757.
- [21] R. Afrasiabi, H. B. Kraatz, Chem. Eur. J. 2015, 21, 7695-7700.
- [22] R. Afrasiabi, H. B. Kraatz, Chem. Eur. J. 2013, 19, 15862 -15871.
- [23] E. K. Todd, X. S. Meng, J. P. Gao, Z. Y. Wang, J. Am. Chem. Soc. 2005. 127, 11552-11553.
- [24] Y. Zhao, N. A. A. Rahim, Y. J. Xia, M. Fujiki, B. Song, Z. B. Zhang, X. L. Zhu, W. Zhang, *Macromolecules* **2016**, *49*, 3214-3221.
- [25] W. Zhang, K. Yoshida, X. L. Zhu, M. Fujiki, *Macromolecules* 2011, 44, 5105-5111.
- [26] L. Zhang, L. Qin, X. F. Wang, H. Cao, M. H. Liu, Adv. Mater. 2014, 26, 6959-6964.
- [27] H. Cao, J. Jiang, X. F. Zhu, P. F. Duan, M.H. Liu, Soft Matter 2011, 7, 4654-4660.
- [28] P. F. Duan, Y. G. Li, M. H. Liu, J. Phys. Chem. B 2011, 115, 3322-3329.
- [29] P. Bortolus, S. Monti, J. Phys. Chem. 1987, 91, 5046-5050.
- [30] P. F. Duan, L. Qin, X. F. Zhu, M. H. Liu, Chem. Eur. J. 2011, 17, 6389-6395.
- [31]S. Samai, C. Sapsanis, S. P. Patil, A. Ezzeddine, B. A. Moosa, H. Omran, A. H. Emwas, K. N. Salama, N. M. Khashab, *Soft Matter* **2016**, *12*, 2842-2845.
- [32] J. Zhang, H. Q. Wang, X. Y. Li, S. S. Song, A. X. Song, J. C. Hao, J. Phys. Chem. B 2016, 120, 6812–6818.
- [33]X. Huang, M. W. Cao, J. B. Wang, Y. L. Wang, J. Phys. Chem. B 2006, 110, 19479-19486.
- [34] L. Qin, F. Xie, P. F. Duan, M. H. Liu, Chem. Eur. J. 2014, 20, 15419-15425.
- [35] G. A. Hembury, V. Borovkov, Y. Inoue, Chem. Rev. 2008, 108,1-73.
- [36] M. H. Liu, L. Zhang, T. Y. Wang, Chem. Rev. 2015, 115, 7304-7397.
- [37] H. M. Dhammik, S. C. Burdette, Chem. Soc. Rev. 2012, 41, 1809-1825.
- [38] Y. Kageyama, N. Tanigake, Y. Kurokome, S. Iwaki, S. Takeda, K. Suzuki, T. Sugawara, *Chem. Commun.* **2013**, *49*, 9386-9388.
- [39] L. Stricker, E. C. Fritz, M. Peterlechner, N. L. Doltsinis, B. J. Ravoo, J. Am. Chem. Soc. 2016, 138, 4547-4554.

- [40] C. E. Weston, R. D. Richardson, P. R Haycock, A. J. P. White, M. J. Fuchter, J. Am. Chem. Soc. 2014, 136, 11878-11881.
- [41] Y. Takashima, M. Nakahata, A. Harada, Acc. Chem. Res. 2014, 47, 2128-2140.
- [42] X.Y. Zheng, Z. G. Shuai, X. Zhang, D. Wang, J. Phys. Chem. B 2012, 116, 823–832.
- [43] X.D. Chi, X.F. Ji, D.Y. Xia, F.H. Huang, J. Am. Chem. Soc. 2015, 137, 1440-1443.
- [44] H. Qian, D.S. Guo, Y. Liu, Chem. Eur. J. 2012, 18, 5087 5095.
- [45] M. Mic, S. Neamt, M. Palage, M. Bogdan, J Incl Phenom Macrocycl Chem 2015, 83, 257–265.
- [46]R. Rajamohan, S. K. Nayaki, M. Swaminathan, Journal of Molecular Liquids 2016, 22, 918-925.
- [47] L. Qin, P. F. Duan, F. Xie, M. H. Liu, Chem Commun. 2013, 49, 10823-10825.
- [48] J. M. Lehn, Angew. Chem. Int. Ed. 2013, 52, 2836 2850
- [49] P. F. Duan, M. H. Liu, Phys. Chem. Chem. Phys. 2010, 12, 4383-4389

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Fan Xie, Long Qin and Minghua Liu *

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Supra-dendron gelator based on Azobenzene-cyclodextrin Host-Guest interaction: Photoswitched Optical and Chiroptical reversibility

The constructed dendron hydrogel showed a reversible optical switching but an incomplete chiroptical switching. While the supra-dendron composed of 1:1 inclusion complex with α -CD displayed both complete reversible optical and chiroptical switching.