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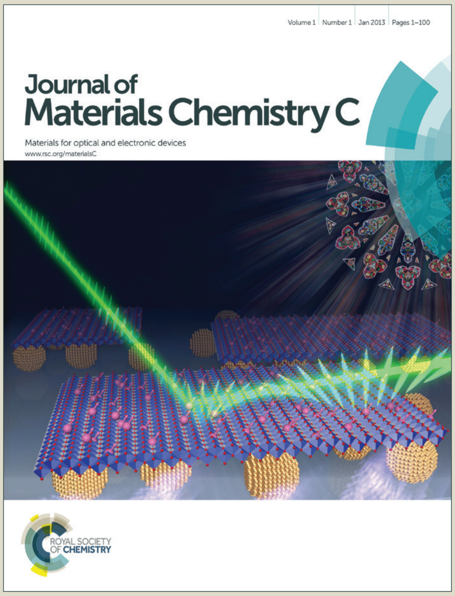

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Azobenzene Based Multistimuli Responsive Supramolecular Hydrogels

Runmiao Yang,*[a,b] Shuhua Peng,[c] Wubo Wan[b,d] and Timothy C. Hughes*[b]

Multistimuli responsive supramolecular aqueous gelators (C_4-Azo-C_5-D_{230}, C_4-Azo-C_5-D_{400}, C_4-Azo-C_5-ED_{900}), composed of alkyl chains, an azobenzene unit, and an amine terminated polyether was prepared. We studied their reversible hydrogelation into three-dimensional entangled supramolecular gels upon changes in temperature, light exposure, pH, and shear. Upon irradiation with UV light, the *trans* isomer of the C_4-Azo-C_5-D_{400} photoisomerized to the *cis* isomer, which goes to a new steady state between both isomers, resulting in disruption of the gel. Rheological measurements of the hydrogel of C_4-Azo-C_5-D_{400} suggested that the non-covalent interactions were disrupted. Likewise, high temperature also caused a reversible disruption to the gel. While the binary mixture of C_4-Azo-C_5-D_{400} and water formed gels from a solution under neutral and basic conditions, under the acidic conditions the molecules aggregated and precipitated. After intense shaking of the hydrogel, a solution separated from the gel, resulting in a rapid drop in both modulus and complex viscosity. This photoresponsive gelator can also form lyotropic liquid crystal (LLC) mesophases above 70 ^{o}C. Through rational design, multistimuli responsive hydrogelators were successful devised, potentially providing an impetus to the ‘design’ of new gelators through the incorporation of other stimuli responsive features.

Keywords: *hydrogel; azobenzene; multistimuli responsive; supramolecular; SAXS*

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† Electronic Supplementary Information (ESI) available: Synthetic procedures and characterization data for new compounds, the thermal behaviors and additional experiments for studying the hydrogel supporting the stimuli-responsive behavior.

Introduction

Gels are soft materials which are highly desirable for advanced applications in many fields such as sol-gel processes, drug delivery systems, sensors and many more.[1-5] They consist of a solvent swollen network held together by covalent bonds and/or non-covalent interactions.[6] According to the solvents contained therein, the gels can been categorized as organogels[7] or hydrogels.[8-9] While a majority of traditional hydrogels are comprised of covalently crosslinked polymer networks, supramolecular gels are formed from non-covalent interactions.[10-13] As such, these three-dimensional networks are constructed from non-covalent interactions such as hydrogen bonds, hydrophobic interactions, π–π interactions, van der Waals forces and electrostatic interactions between low molecular weight gelators (LMWGs).[14-15]

There is an increasing interest in 'active' materials which can respond or adapt to external stimuli or changing environmental conditions over traditional non-changing 'passive' materials.[16] The application of such responsive materials to supramolecular gels may lead to novel smart materials[17] which are designed to alter their physical properties upon exposure to a stimulus. A range of different stimuli for responsive systems have been reported, namely, photo, electrochemical, pH and ionic, etc.[18-20] Among these external stimuli, light has attracted much attention, since it provides a broad range of tunable parameters, e.g., wavelength, intensity, and duration, to manipulate the rheological properties of the gel. Photochromic units within these systems undergo structural transformations such as isomerisation, tautomerisation and electrocycling ring closures and openings to control gel's properties.[21] Azobenzenes have been successfully introduced into supramolecular assemblies in order to manipulate the gel's properties by reversible *trans–cis* photochemical isomerisation upon exposure to different wavelengths of light.[22-27] Due to their hydrophobicity, the azobenzene moieties are generally incorporated into polymeric hydrogelators.[28-33] Thus, LMWGs derived from azobenzene based hydrogels are still rare.[34-37] For example, Huang *et al.*[34] designed and synthesized an azo-dipeptide hydrogelator whose pH and salt effect behavior and gel formation ability were investigated in detail. Velema *et al.*[35] incorporated an azobenzene photoswitch into a dichromonyl compound. The self-assembly of dichromonyl compounds into fibers lead to the formation of a hydrogel. Ogawa *et al.*[36] prepared novel sugar-decorated nanofibers by self-assembly of low molecular weight hydrogelators composed of azobenzene and disaccharide lactones. Our group also designed and studied a novel azobenzene surfactant, which can assemble into ordered structure and viscous lyotropic liquid crystal (LLC) phases at certain water contents.[37-38]

Multistimuli responsive gels have properties which can respond to more than one stimuli. Apart from the azo-dipeptide hydrogels,[34] most supramolecular hydrogels containing azobenzene have been reported to respond to limited stimuli.[35-37] This is due to the challenges of incorporating additional stimuli responsive functionalities into the LMWG structure in addition to the hydrophobic azobenzene group. Due to its hydrophobicity, crystallization and precipitation of azobenzene molecules occurs, which hinders the formation of the gel. Thus, the successful design of a multiresponsive azobenzene based supramolecular hydrogel remains a significant challenge. Despite the known influence of non-covalent interactions in supramolecular gelation, it is still difficult to rationally design and functionalize small gelator molecules.[23]

With this challenge in mind, we set about rationally designing a simple yet effective azobenzene based multistimuli responsive supramolecular hydrogel. Surfactant-like molecules were synthesized by incorporating hydrophilic amino-terminated telechelic poly(propylether)s onto a hydrophobic azobenezene unit containing alkyl chains. Their ability to form hydrogels at low solids content and respond to various stimuli including heat, light, pH and stress was investigated. Small angle X-ray scattering (SAXS), optical and electron microscopy, rheology and UV-visible spectroscopy were used to characterize the self assembly of the gelator and its transition between gel and solution states. The resulting azobenzene based multistimuli responsive supramolecular hydrogels have potential to enable new applications for environmentally sensitive materials.

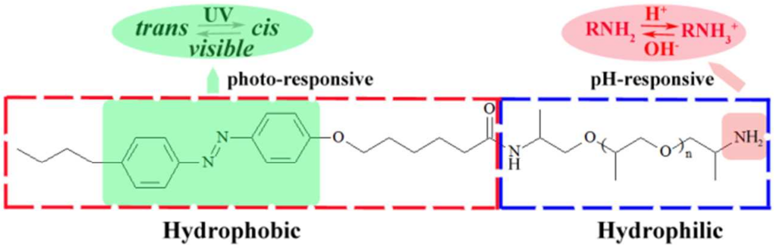
Experimental Section

Synthesis preparation, and characterization of C_4-Azo-C_5-D_{230}, C_4-Azo-C_5-D_{400}, and C_4-Azo-C_5-ED_{900} are described in detail in the Supporting Information. Poly(propylether)diamines (JEFFAMINE®, D_{230}, D_{400}, ED_{900}) were supplied by (Huntsman Corporation, USA). All other chemicals were purchased from Sigma-Aldrich and Merck and used without further purification. No purification was performed on the solvents. All the chemicals were characterized by ^{1}H and ^{13}C NMR spectroscopy on a 400 MHz Bruker Ultrashield Spectrometer (Bruker, Germany) in $CDCl_3$. Accurate mass spectra were obtained on a Thermo Scientific Q Exactive FTMS, employing ASAP probe. Photoisomerization of C_4-Azo-C_5-D_{400} was measured on a Cary 50-Bio UV-vis spectrophotometer (Varian) against a background of water in a quartz cuvette. *Trans* to *cis* isomerisation was induced by an EXFO Acticure 4000 light source via a liquid light-guide working at 365 nm wavelength. The UV light intensity was about 3.8 mW/cm^2. *Cis* to *trans* isomerisation was induced by visible light at 12.1 mW/cm^2. POM was conducted using a Nikon Eclipse 80i. SAXS experiments were performed at the Australian Synchrotron on the small/wide angle X-ray scattering beamline working at 12.0 KeV. Data reduction (calibration and integration) of data collected using a 2D detector was achieved using AXcess, a custom-written SAXS analysis program written by Dr Andrew Heron from Imperial College, London. SEM was recorded on FEI Quanta 400F ESEM. Rheology was conducted using an ARES photo-rheometer (TA Instruments, USA) connected to an EXFO Acticure 4000 UV light source (365 nm, 200 mW/cm^2) and quartz-halogen visible light source (>540 nm, 38 mW/cm^2) via liquid light-guide. A Peltier temperature controller was also connected to the rheometer to maintain the temperature. The Fourier Transform IR was conducted using the Nicolet 6700 (Thermo Fisher Scientific. USA). All measurements were made under room light conditions unless otherwise stated.

Determination of critical gelation concentration (CGC)

Typically, gelator was mixed with solvent. The mixture was heated until the gelator dissolved and a clear solution was obtained. The solutions were then cooled to room temperature and gel formation was determined by inverting the vials. The CGC was the concentration of gelator which was sufficient to form a firm gel in which the solvent did not flow out of when the tube was inverted.

Results and Discussion



Scheme 1. Chemical structure of the C_4-Azo-C_5-D_{400} and schematic representation of the design rationale for reversible multistimuli responsive hydrogel.

In this paper, we designed and synthesized a series of supramolecular gelators (C_4-Azo-C_5-D_{230}, C_4-Azo-C_5-D_{400}, C_4-Azo-C_5-ED_{900}), composed of alkyl chains, an azobenzene unit, and a polyether-amine moiety, which was expected to form hydrogels exhibiting multistimuli responsive behavior (Scheme 1). The molecular design is based on the following considerations. (1) An amine and its corresponding ammonium salt can be reversibly transformed under different pH.[39-40] (2) Light irradiation can trigger the *cis* and *trans* isomerization of the azobenzene group, resulting in a conformational change, and altering the intermolecular interactions.[41] (3) Amphiphilic molecular structures conducive to forming self-assembled supramolecular gels could comprise of a polyether as the hydrophilic part and alkyl chains/azobenzene unit as the hydrophobic part.[42-43] (4) The inclusion of an alkane into the molecule will increase its gelation ability.[44-45] It was expected that incorporation of these functional groups into one molecule would lead to new multiresponsive hydrogelators.

To test this design, three new surfactants (C_4-Azo-C_5-D_{230}, C_4-Azo-C_5-D_{400}, C_4-Azo-C_5-ED_{900}) were synthesized from phenol and 4-butylaniline in a three step synthesis as shown in Scheme S1.

Synthetic details and full characterization data are provided in the supporting information. In order to test materials with a wide range of amphilicity, three different polyether diamines (D_{230}, D_{400} and ED_{900}) with varying lengths of polypropylene oxide (on average 2.5, 6.1 and 18.5 repeats units per chain, respectively) were used in the synthesis.

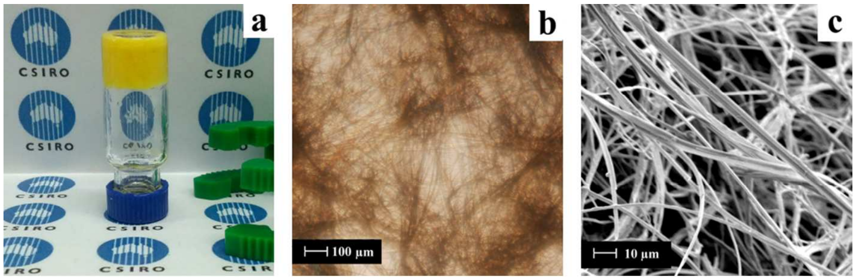


Fig. 1 C_4-Azo-C_5-D_{400} gel (20 °C) in water at 10.0 wt%: (a) photograph of the gel; (b) OM image (200× magnification); (c) SEM image.

The ability of C_4-Azo-C_5-D_{230}, C_4-Azo-C_5-D_{400}, and C_4-Azo-C_5-ED_{900} to form gels was measured in water at different concentrations, as observed by inversion of the vial (Fig. S17). C_4-Azo-C_5-D_{400} formed gels with critical gelation concentrations (CGCs) as low as 0.8 wt % while C_4-Azo-C_5-D_{230} and C_4-Azo-C_5-ED_{900} had CGCs of 1 and 2 wt %, respectively. The measured CGCs were directly comparable with those of the known azobenzene hydrogelators.[34-37]

As all three azobenzene based surfactants could form hydrogels and had similar gelation characteristics, C_4-Azo-C_5-D_{400} was selected for detailed characterization as it had the lowest CGC and was formed from a polyether diamine of intermediate chain length. Interestingly, C_4-Azo-C_5-D_{400} could also form gels when saline or PBS solution was used instead of water. For the *in situ* observation of gel, the hydrogel was rapidly cooled in liquid nitrogen before being freeze dried. Three-dimensional random entangled supramolecular fibers were observed under optical microscopy (OM) and scanning electron microscopy (SEM) imaging (Fig. 1).

We found that the concentration of the gelator had a significant impact on the gelation time and the average length of the self assembled fibers. With high gelator concentration, the gel can be formed in a short time with relatively short fibers. For example, with 10.0 wt %, the yellow colored gel could be generated rapidly within 30 minutes resulting in fibers about 2 mm in length. In contrast, at low concentrations, the gelation time was longer producing gels containing longer fibers. At 2.0 wt% the gelator took more than 12 hours to form a gel containing fibers about 5 mm in length. We may divide the process of gel formation of this system into two steps: (1) the formation of gelation point from the solution and (2) fiber growth to form three-dimensional networks. When aqueous solutions of C_4-Azo-C_5-D_{400} were cooled, decreasing the temperature causes the solubility of the hydrophobic part of the gelator to decrease. As a result, the hydrophobic part begins to aggregate into higher order structures, driven by non-covalent interactions (eg the hydrogen bonds, hydrophobic interactions and π–π interactions).[22] The formation of self assembled structures initiates aggregation into single fibers and then further into fiber aggregates to form bundles of fibers.[42] These processes were characterized by dynamic light scattering (DLS) measurements. At 50 °C the 0.2 wt% solution, contained mainly 14 and 321 nm sized particles (55.5% and 44.5%, respectively). However, upon cooling, a dramatic decrease of number of small particles and an increase in the number of large particles was observed. At 20 °C the average size of the bimodal distribution of particles was 20 and 1531 nm (6.2% and 93.8%, respectively) (Fig. S22). Thus, the structures and modes of formation of the self-assembled fibrillar networks (SAFINs) was similar to earlier reports.[27]

3.1 Mechano response

The mechano-responsive behavior of the hydrogel reported here was investigated by rheological techniques. A hot aqueous solution of C_4-Azo-C_5-D_{400} (Fig. 2a) formed a yellow colored supramolecular gel (1.0 wt%) upon cooling (Fig. 2b). Following intense shaking, a solution separated from the three-dimensional entangled supramolecular gels (Fig. 2c). The whole three-dimensional fibrillar network could be removed using tweezers which indicated that C_4-Azo-C_5-D_{400} fibers possessed high mechanical strength (Fig. 2d). Morphological features of the fibers and solution were studied using a SEM (Fig. 3a, 3b, respectively). The process of picking up of the fibers caused orientation of the fibers (Fig. 3a) as the fibers were arranged into a well-defined direction, which was different with the random structure of freeze dried product (Fig. 1c). Residual gelator in the solution self-assembled into nano-scale assembled structures due to the amphiphilic molecular structure of C_4-Azo-C_5-D_{400} (Fig. 3b). Interestingly, after returning the fibers back to the solution, the gel slowly reformed over a few hours as determined by test tube inversion method. Depending on the temperature, a certain percentage of the gelator was generally present in solution (sol fraction). Thus, there was continuous gelator exchange occurring between the gel fiber and sol states. After reaching dynamic balance, the regeneration of the gel was consistent with previous supramolecular gels formation theory.[46]

Small angle X-ray scattering (SAXS) was used to further investigate the supramolecular structure of the gel fibers. Neat gelator fibers taken out from gel (Fig. 2) were examined by synchrotron small angle X-ray scattering (SAXS). Fig. 3c shows the one-dimensional and two-dimensional scattering pattern of the fibers. Sharp scattering peaks having the same distance between peaks were present at q = 0.134, 0.268, 0.401, 0.534, 0.668, 0.802 $Å^{-1}$, indicating the presence of a well-defined lamellar structure. The spacing of the lamellar structure was calculated to be 4.7 nm using the SAXS software.

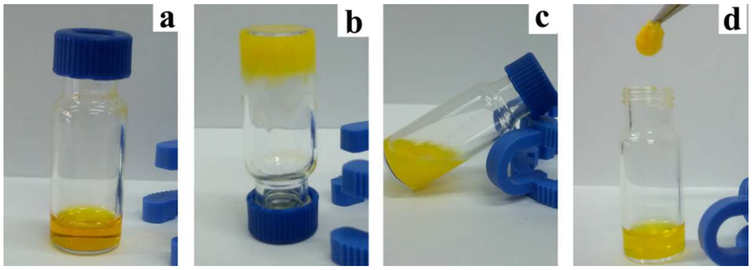


Fig. 2 Photographs of the C_4-Azo-C_5-D_{400} in water, 1.0 wt%: (a) 70 °C; (b) 20 °C; (c) shear responsive hydrogel, 20 °C; (d) separation of fiber and solution, 20 °C.

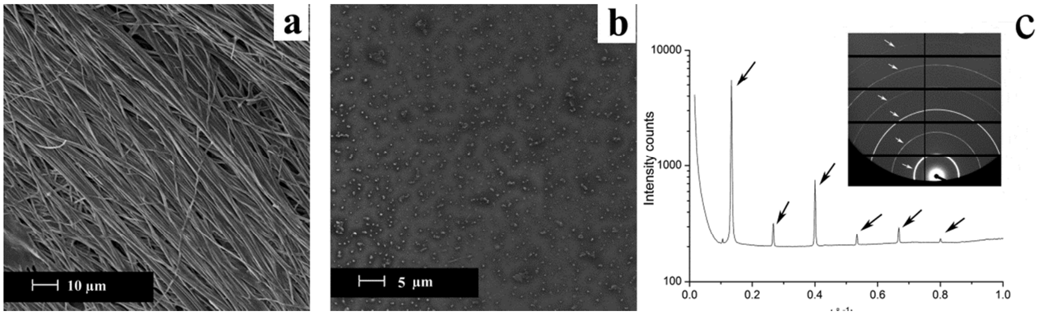


Fig. 3 (a) SEM of the C_4-Azo-C_5-D_{400} gelator fibers; (b) SEM of residual solution of the hydrogel; (c) SAXS profiles of C_4-Azo-C_5-D_{400} gelator fibers. One-dimensional and two-dimensional (insert) scattering pattern.

The mechano-responsive behavior of the hydrogels was further investigated by rheological measurements. Plots of storage (G') and loss (G'') modulus as a function of shear strain are shown in Fig. 4a. It can be clearly observed that at initial strain values, the value of G' (about 25 kPa) was greater than G'' (about 5 kPa), indicating a dominant elastic characteristic of the sample. When the strain was initiated, the G' and G'' of the gels decreased with increasing strain. At low strain, a sharp decrease of G' was observed, representing a partial breakup of the gel. Specifically, the complex viscosity rapidly decreased from about 5.5 kPa·s down to around 0.6 Pa·s. Likewise a reduction for the loss modulus (G'') was observed, which dropped from around 5 kPa to 1 kPa. Frequency sweep experiments were also conducted to thoroughly study the mechanical properties of the gel (Fig. 4b). In all cases, the value of G'' was below the value of G' for all frequencies. The G'' and G' showed no obvious frequency dependence in the frequency range of 0.1−100 rad/s, which indicated a slightly more elastic response of the network. This behavior is typical of colloidal gels, which at higher deformation frequencies elicits an elastic response from the local structure but can relax at lower frequencies. The complex viscosity plummeted from about 16 kPa·s down to around 0.1 kPa·s upon the frequency range of 0.1−100 rad/s. Specifically, at low frequency values (0.1–5 rad/s), a sharp decrease of the complex viscosity was observed, representing a partial breakup of the gel. Thereby confirming that the shear driven processes were a result of changes in the self assembled structure. By applying a shear force to the gel, the fibers were broken indicating that C_4-Azo-C_5-D_{400} formed a true gel-like material. It was fabricated from aggregates resulting in a network-forming nano/microscale assemblies that yielded a gel held together by relatively weak non-covalent interaction, which dissociated rapidly upon applied shear.[47] Upon removal of the mechanical stimuli, the non-covalent interactions become the dominant force resulting in reformation of the gel through self assembly of the C_4-Azo-C_5-D_{400} into fibers and bundles.

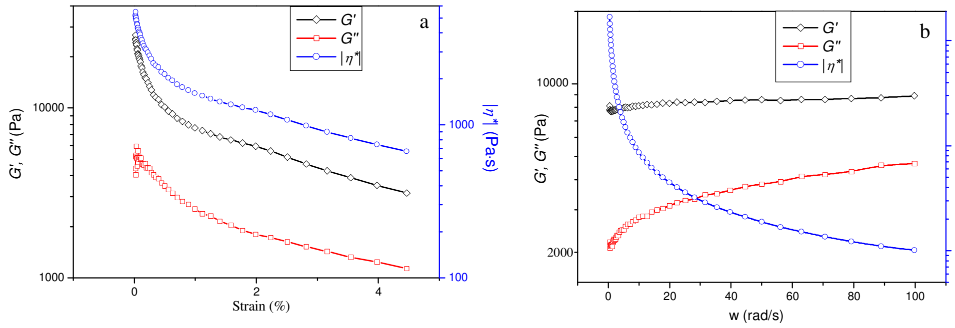


Fig. 4 (a) Effect of strain sweep on the storage modulus G' and loss modulus G'' for the C_4-Azo-C_5-D_{400} hydrogel (10.0 wt %). The data were obtained at a constant frequency of 5 rad/s and 25 °C; (b) Effect of frequency sweep on the atorage modulus G' and loss modulus G'' for the C_4-Azo-C_5-D_{400} hydrogel (10.0 wt %). The data were obtained at a strain of 1.0 % and 25 °C.

3.2 pH response

It is known that an amine and its corresponding ammonium salt can be reversibly protonated/de-protonated under different pHs. The samples were rapidly cooled in liquid nitrogen and freeze dried to get rid of water. The results of the gelator FT-IR pH study are presented in Fig. S18. Characteristic amide peaks at 1600 cm^{-1} were observed at pH=7 and 14, while this peak intensity weaken at pH=1. Moreover, peaks at 3400 cm^{-1} for the amine band were also observed. This peak signal was biggest at pH=14 and almost disappeared at pH=1. At pH=1, a new broad peak appeared at 2400-3200 cm^{-1} and 1620-1700 cm^{-1} corresponding to the formation of an ammonium salt was observed. It was expected that this transformation would also alter the intermolecular interactions. As shown in Fig. 5f, adding C_4-Azo-C_5-D_{400} gelator into water can promote aggregation of the gelator into high order assemblies resulting in gelation of the solution. Under alkaline or neutral conditions, POM images of the gel showed that the fibers as bright regions under polarized light (Fig. 5b, 5e, respectively), which together with its high viscosity and ordered SAXS peaks, suggest the formation of a liquid crystalline-like structure.[37] However, the gel was destroyed resulting in a yellow precipitate under acid conditions (Fig. 5i). The precipitation product showed no bright regions under polarized light by POM (Fig. 5h), confirming the loss of the organized self assembled structure. Interestingly, when base was added, adjusting the pH to the neutral, the gel phase was regenerated after further heating and cooling. Such a pH triggered gel-sol transitions could be repeated many times. This pH responsive behavior may be useful in controlling the release of drugs as pH responsive hydrogels have shown to be promising candidates drug delivery systems.[48-50]

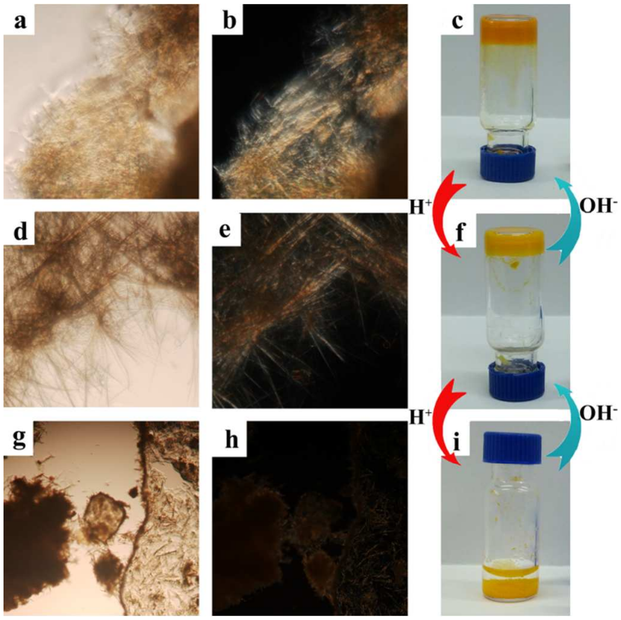


Fig. 5 POM images (200× magnification) for C_4-Azo-C_5-D_{400} (10 wt%) in water (a) natural light, pH=14; (b) polarized light, pH=14; (d) natural light, pH=7; (e) polarized light, pH=7; (g) natural light, pH=1; (h) polarized light, pH=1; and (c, f, i) photographs of the C_4-Azo-C_5-D_{400} in water under corresponding pH. 20 ^{o}C.

3.3 Light response

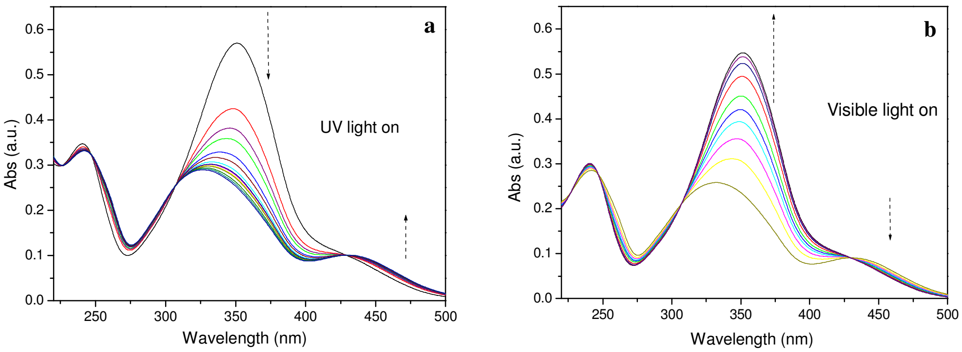


Fig. 6 C$_4$-Azo-C$_5$-D$_{400}$ in water at 20 ^{o}C (0.002 wt %), (a) Change in absorption of UV-Vis spectra over time under UV light (365 nm, 3.8 mW/cm^2); (b) Change in absorption of UV-Vis spectra over time under visible light (12.1 mW/cm^2).

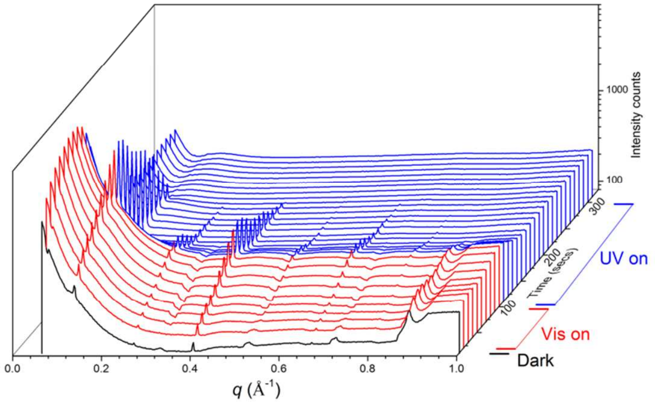


Fig. 7 Time resolved synchrotron SAXS patterns for the C$_4$-Azo-C$_5$-D400 in water (2.0 wt %), upon UV light (365 nm, 790 mW/cm^2) exposure and visible light (200 mW/cm^2) at 25 ºC.

Azobenzene compounds are well-known for their reversible photoisomerization between the *trans* and *cis* forms under alternating UV and visible light irradiation.[51] In order to investigate the light-responsive behavior of the C$_4$-Azo-C$_5$-D$_{400}$ in water, the UV/Vis spectroscopic studies of dilution solutions were performed. C$_4$-Azo-C$_5$-D$_{400}$ shows a broad absorption around 320-350 nm mainly due to the *trans* form of the azobenzene group. As shown in Fig. 6(a), UV irradiation results in the *trans-cis* isomerization, indicated by the decay of the maximum absorption band and the generation of a new absorption. Importantly for practical applications, this photo-induced isomerization is reversible (Fig. 6(b)), as the azo-surfactant in *cis* form relaxes to *trans* form after exposure to visible light or slower in the dark.

Synchrotron SAXS is a powerful method for exploring dynamic changes in supramolecular structures.[37-38, 52-53] We also carried out synchrotron *in situ* SAXS measurements to obtain structural information of the gelator under Vis/UV light exposure (Fig. 7). After measuring the initial gel in dark, the visible light was switched on. The SAXS profiles of peaks, which is clear evidence of lamellar fibers structure, increase in intensity. When the visible light was switched off and UV light turned on immediately, all the scattering peaks which appeared under visible light disappeared, indicating that the gelator molecules completely dissolved forming a solution with loss of their original structure. As shown in Fig. 7, the SAXS profiles at the solution state were smoothed which means UV irradiation results in the *trans-cis* isomerization to form typical of homogeneous solutions.[54] If the solution was irradiated under visible light and set aside for a few hours, the supramolecular gels can reform, demonstrating the reversibility of the photoisomerization and subsequent self assembly of the gelator into a fibrous network.

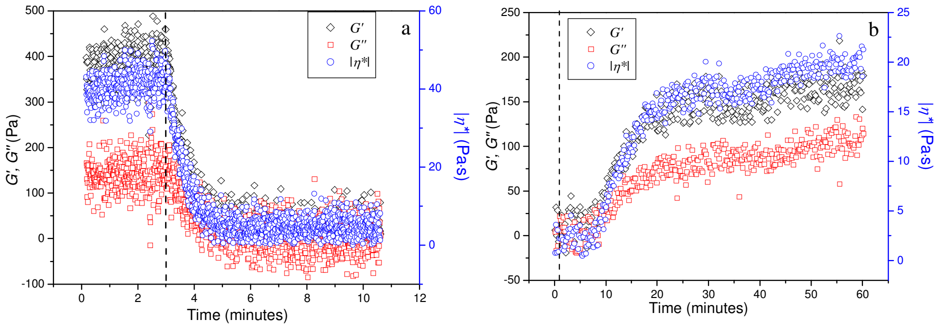


Fig. 8 Real-time photo-rheology measurements. C_4-Azo-C_5-D_{400} in water at 20 ^{o}C (2.0 wt %). (a)The data were obtained at a constant frequency of 5 rad/s and a strain of 1.0 %. UV turned on at 3 min; (b) The data were obtained at a constant frequency of 5 rad/s and a strain of 1.0 %. Visible light turned on at 1.0 min.

Dynamic changes in rheological properties of materials upon exposure to light can be readily measured using photorheology.[55-56] The dynamic changes to the storage modulus (G') and the loss modulus (G'') with time were clearly observed under UV light exposure (Fig. 8a). In the beginning without UV exposure, the G' was greater than G'' indicating an elastic response. However, during exposure of the hydrogel (2.0 wt %) to UV light (from 3 mins), a dramatic decrease of modulus was observed and a new plateau value was reached within 2 min. To assess reversibility of this process, the material was then exposed to visible light (Fig. 8b) which demonstrated the partial recovery of the rheological properties upon exposure of visible light. However, the rate of recovery was relatively slow comparing to exposure with UV light. As shown in Fig. 6b, modulus and complex viscosity were restored to only half of the initial values before UV light irradiation even after exposure to visible light for 1 hour. For the solution to completely return to the initial state took more than 12 hours. In contrast, when the same experiments were performed at a high concentration (10.0 wt %) of the gelator, the gel to sol transition took a longer time while regeneration of the gel take a shorter time (Fig. S15, S16).

3.4 Thermo response

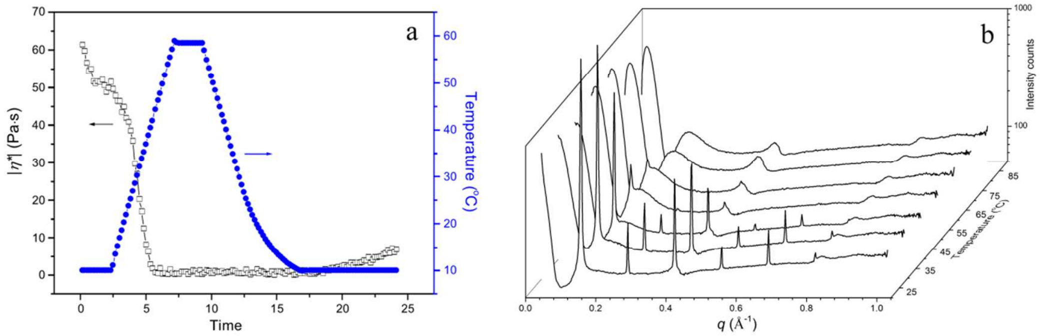


Fig. 9 (a) Plot of complex viscosity against the temperature of C_4-Azo-C_5-D_{400} in water (2.0 wt%). The data were obtained at a constant frequency of 5 rad/s and a strain of 1.0 %; (b) Temperature dependence of the synchrotron SAXS profiles for the C_4-Azo-C_5-D_{400} in water (2.0 wt%)

The reversible nature of the non-covalent interactions that hold the network structure results in the inherent ability of LMWGs to respond to thermal stimuli. Representative photographs of the surfactant during sol to gel studies are shown in Fig. S21. An orange colored solution in water (10.0 wt %) was formed by heating. Upon cooling, the yellow colored gel could be generated. The gel formed rapidly within 30 minutes at 10.0 wt %, but took more than 12 hours at 2.0 wt %. This thermally driven reversible gel-sol phase transition could also be repeated many times simply by repeated heating and cooling cycles. A rheological study showed a reversible change in complex viscosity with change in temperature (Fig. 9a). Initially, at 10 ^{o}C the sample was viscous liquid with a $|\eta*|$ ~ 50 Pa·s. when the temperature was increased, a dramatic decrease of complex viscosity was observed. Specifically, the complex viscosity reached a new steady state of $|\eta*|$ ~ 2 Pa·s at 50 ^{o}C which was maintained until the temperature was decreased. Upon a reduction in temperature, the complex viscosity slowly increased. However, the trend in increasing complex viscosity indicates that the sample should take more than 12 hours at 2.0 wt% to regain a gel-like state.

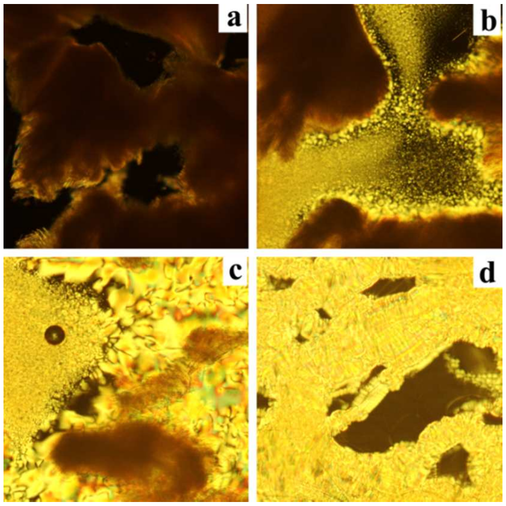


Fig. 10 Representative POM textures of the C_4-Azo-C_5-D_{400} in water, 10 wt%, polarized light, under different temperature (a)20 ^{o}C; (b) 72 ^{o}C; (c) 74 ^{o}C; (d)78 ^{o}C, (100× magnification).

As discussed above, C_4-Azo-C_5-D_{400} in water can self-assemble into lamellar structures which then aggregate and rearrange into fibers, resulting in the formation of hydrogel through non-covalent interactions. In contrast, upon heating the mixture above 70 ^{o}C a new self organized structure was observable upon POM observation, suggesting that that the C_4-Azo-C_5-D_{400} water mixture at high temperature forms a lyotropic liquid crystals. As shown in Fig. 10 and Fig. S24, the distinct POM textures and DSC curve for C_4-Azo-C_5-D_{400} in different temperatures confirmed the existence of different LLC phases between 70-80 ^{o}C.

One peculiar phenomena for the gel was that a clear thermal transition from the gel to sol state was observed upon heating. Fig. 9b shows that lamellar packed fibrils were formed in the gel state and the solvent molecules could be present between the fibrils ($T<55^{o}C$). It was clear that gelator molecules and water can self assemble to form supramolecular structures. But these sharp single peaks were completely lost if the sample was heated higher than 55 ^{o}C. Although the fiber structure disappeared, multiple peaks in the SAXS spectrum strongly suggesting that at high temperatures the gelator self assembles into other nano-scale self assembled structures. Thus, synchrotron SAXS experiments also confirmed the loss of an organized network structure at high temperatures.

Conclusions

Based upon a simple molecular design, the synthesis of novel amphiphilic surfactants (C_4-Azo-C_5-D_{230}, C_4-Azo-C_5-D_{400}, C_4-Azo-C_5-ED_{900}) and their self-assembly and gelation characteristics in water was described. Detailed analysis of hydrogels from C_4-Azo-C_5-D_{400} including investigation by dynamic light scattering (DLS), polarized microscopy, scanning electron microscopy (SEM), and small angle x-ray scattering (SAXS) revealed that this novel gelator formed well-ordered nanofibers in binary mixtures with water. The hydrogels formed from the gelators exhibited multistimuli responsive behavior upon exposure to external stimuli including changes in pH, light exposure, mechanical stress and temperature. Detailed characterization of the transition between the gel and sol states indicated that disruption of relatively weak non-covalent interactions upon exposure to the stimulus was the driving force behind the reversible changes in bulk properties. C_4-Azo-C_5-D_{400}/water mixtures also formed ordered lyotropic liquid crystalline (LLC) phases at certain water contents. Together, these prominent features of the C_4-Azo-C_5-D_{400} hydrogel make it an excellent intelligent soft material with promising potential applications in the area of stimuli triggered drug delivery systems or smart rheological fluids.

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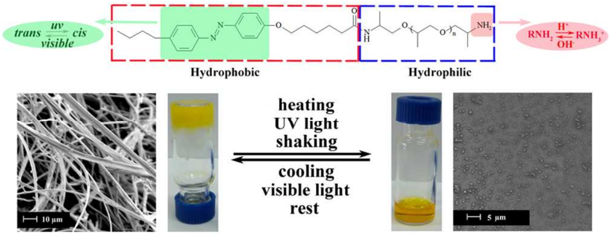
Abstract graphic



Multiresponsive hydrogels capable of reversible transitions to solutions upon changes in light, heat, shear and pH were prepared from low molecular weight azobenzene hydrogelators.