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Responsive Self-Assembly of Supramolecular Hydrogel Based on Zwitterionic Liquid Asymmetric Gemini Guest

Aoli Wu, Panpan Sun, Na Sun, and Liqiang Zheng*

Abstract: Low-molecular-weight supramolecular hydrogel was fabricated based on host-guest interaction between β -cyclodextrin (β -CD) and asymmetric Gemini zwitterionic liquid (ZIL) which contains azobenzene (Azo) and bis(trifluoromethanesulfonyl)imide (TFSI⁻). Reversible sol-gel phase transition could be triggered by light and temperature. The binding stoichiometry, main non-covalent interactions in hydrogel, photo and thermal responsive mechanisms, and inclusion complex mode were studied deeply by NMR spectroscopy, UV-vis spectroscopy, isothermal titration calorimetry (ITC) and control experiments. Interestingly, the β -CD in guest molecule can be photo-manipulated to shuttle accompanied with the change of circular dichroism (CD) signals. The reversible switches of conductivity behind the sol-gel phase transition indicating the stability of supramolecular hydrogel and their potential applications in multi-stimuli responsive electric sensor materials.

Introduction

Supramolecular gels which fabricated based on non-covalent interactions such as hydrogen bonding, host-guest, π - π stacking, and metal-coordination have attracted increasing attention due to their potential applications in smart materials, biochemistry, electrochemistry, sensors, and drug delivery.^[1] Such non-covalent interactions enable molecules cross-link dynamically which is beneficial to fabricate intelligent gels that respond to light, temperature, pH, magnetic field and other stimulus signals.^[2] Due to remotely controlled without pollution to the system, light and temperature are more competitive as external stimuli to modulate supramolecular gels reshaped and reprocessed, giving rise to non-destructive responsive materials.^[3]

It is noteworthy that, highly selective molecular recognition endows host-guest gels valuable properties that subtle structural changes on the building blocks can significantly influence the macroscopic performances of the system. Cyclodextrins, pillararenes, cucurbiturils, and crown ethers are common macrocyclic host molecules. Whereas, cyclodextrins are the most widely used in responsive supramolecular gels.^[4] It has been reported that bis(trifluoromethanesulfonyl)imide (TFSI⁻) can form inclusion complexation with β -cyclodextrin (β -CD) accompanied by temperature responsiveness due to relatively high combine energy.^[5] In addition, host-guest interaction

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between $\beta\text{-}CD$ and Azobenzene (Azo) has also been extensively studied based on the mechanism that the isomerization of Azo can be reversibly tuned by UV and visible light, which induces the changes of assembly modes and material properties. $^{[6]}$

Zwitterions with both cation and anion tethered have attracted much attention not only because ionic compounds can be easily incorporated through electrostatic interaction to obtain functional zwitterionic liquids (ZILs), but also because the ZILs combine the excellent physicochemical properties of ionic liquids (ILs) such as nonflammability, chemical and thermal stabilities, and high ionic conductivity.^[7] Based on the designability of ILs, responsive functional groups such as Azo, ferrocene (Fc), carboxyl and acrylamide are easily incorporated into the structure to fabricate multi-stimuli responsive supramolecular hydrogels. Yan et al. prepared gel based on polymer host containing β-CD and ZIL containing Fc and TFSI^{-,[8]} Temperature, anion-exchange, and redox reactions are able to induce sol-gel phase transition. Most of the researchers mainly focus on the sol-gel transition behavior, specific responsive mechanism and other performance changes behind the phase transition phenomena have been rarely studied in-depth. Instead, supramolecular host-guest hydrogels formed by small molecules are more conducive for us to study the non-covalent interactions in the system.

Herein, supramolecular hydrogel with photo and thermal responsiveness has been fabricated by using β -CD and reasonable designed asymmetric Gemini type ZIL which contains two kinds of functional guest groups Azo and TFSI⁻. The stoichiometric ratio of inclusion complex and the main non-covalent interactions present in the system were deeply investigated. It is noteworthy that the complex pattern between β -CD and Azo can be manipulated by UV light irradiation, accompanied with the changes of Cotton effect. Due to the intrinsically conductive characteristic of ZIL, the supramolecular hydrogel paves a convenient way on responsive electrical sensing materials.

Results and Discussion

Molecular structure selection and gel preparation

To fabricate low-molecular-weight supramolecular host-guest hydrogel, asymmetric ZIL denoted as AzoIPS-LiTFSI containing two different guest molecules has been masterly designed and synthesized (Scheme 2). AzoIPS-LiTFSI and β -CD were added in water at designed compositions. Then the mixture was heated to a homogeneous solution. After cooling down to room temperature, the orange hydrogel was formed instantaneously and confirmed by the inverted test tube method (Figure 1a). Interestingly, sol-gel reversible phase transition can be achieved by light irradiation and thermal treatment (Figure 1b and 1c). In order to prove the importance of this structure design

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(asymmetric ZIL), comparative tests were fabricated. As shown in Figure 1d and 1e, only suspension can be observed in the absence of AzoIPS or LiTFSI. It can be concluded that the coexistence of two kinds of guest molecules is necessary for the preparation of supramolecular hydrogel. The microstructure of the xerogel was detected by SEM (Figure S1), in which loose porous structures were constructed by stacked blocks.

The viscoelasticity of prepared hydrogel was detected by stress sweep mode and oscillatory sweep mode. As shown in Figure 2a, storage modulus (G') is bigger than the loss modulus (G') before the critical stress value, and both moduli are independent of the applied stress. Further increase of shear stress induces G' and G'' decrease rapidly. The oscillatory data (Figure 2b) also show that G' is thoroughly bigger than G''. In addition, G' and G'' are independent of frequency. The experimental results indicated that the system actually formed a cross-linked hydrogel.^[9]



β-CD/LiTFSI β-CD/AzoIPS β-CD/C₁₀IPS-LiTFSI β-CD/AzoIPS-LiCl

Figure 1. Preparation of supramolecular hydrogel (a) β -CD/AzoIPS-LiTFSI (3:1) and their disassembly induced by (b) UV light and (c) temperature. Comparative tests (d) β -CD/LiTFSI (1:1); (e) β -CD/AzoIPS (2:1); (f) β -CD/C₁₀IPS-LiTFSI (3:1); (g) β -CD/AzoIPS-LiCI (3:1). The concentration of β -CD was fixed at 200 mM.



Figure 2. The G' and G" of supramolecular hydrogel (β -CD/AzoIPS-LiTFSI 3:1 250 mM) (a) as a function of shear stress at a constant frequency of 1 Hz at 25.0 °C; (b) as a function of frequency at 25.0 °C.

Gel formation mechanism

In order to acquire detailed insight into the mechanism of gel formation, ¹H NMR and ¹⁹F NMR spectra were used to analyze the host-guest interaction. As shown in Figure 3a (¹H NMR spectra), significant impact of β -CD on the protons of AzoIPS-LiTFSI was observed with the increase of β -CD concentration.

The signals of H_d and H_c (7.7-7.8 ppm) show splitting and upfield shifts, while the signals of other aromatic protons (7.4-7.5 ppm) show splitting and downfield shifts, which indicating the hostguest interaction between β-CD and Azo.^[10] The overall chemical shifts for the protons of AzoIPS-LiTFSI reach the maximum at a molar ratio of 3:1, indicating 3:1 complexation of β-CD and AzoIPS-LiTFSI. In addition, the chemical shifts of the fluorine signals in the TFSI⁻ anion have also gradually moved upfield with the molar ratio of β-CD/AzoIPS-LiTFSI increased (Figure 3b, ¹⁹F NMR spectra). It can be determined that the inclusion complexation between β -CD and TFSI⁻ induces changes in the chemical environment of fluorine atoms (TFSI⁻ in D_2O and TFSI⁻ in β -CD). Compared to D_2O , a less polarized environment of β -CD cavity increases the shielding effect and causes the fluorine signal shift upfield. Similarly, it was only when the molar ratio was 3:1 that the fluorine of TFSI⁻ showed maximum upfield shift, which is consistent with the phenomenon of ¹H NMR. It is reasonably assumed that three β -CDs can be connected by one AzoIPS-LiTSFI to form inclusion complexes. According to the previous reports, β-CD tends to form inclusion complexes with TFSI⁻ or Azo with a 1:1 stoichiometric ratio.^[11] Interestingly, the chemical shifts of protons in AzoIPS almost unchanged after the molar ratio of β-CD:AzoIPS increasing to 2:1 (Figure S2), which can be inferred that one AzoIPS was combined by two β-CDs.



Figure 3. (a) Partial ¹H NMR spectra (molecular structure marked with red) for different molar ratios of β -CD to AzoIPS-LiTFSI (from 0:1 to 4:1). (b) ¹⁹F NMR spectra (using trifluoroacetic acid as an internal reference) for various molar ratios of β -CD to AzoIPS-LiTFSI (from 0:1 to 4:1). All the samples were detected in D₂O at 25.0 °C. The concentration of AzoIPS-LiTFSI was fixed at 2 mM.

Isothermal titration calorimetry (ITC) was used to further investigate the binding stoichiometry of building blocks (Azo and TFSI⁻) with β -CD and the thermodynamic mechanism behind the supramolecular self-assemble. As can be seen from Figure 4a, two binding sites were observed when β -CD was added dropwise into the aqueous AzoIPS-LiTFSI solution. The first titration jump appeared at a molar ratio of 1:1, demonstrating a strong 1:1 inclusion complexation between β -CD and AzoIPS-LiTFSI. With continued addition of β -CD, a second titration jump occurred at a molar ratio of 3:1, which demonstrated a moderate 2:1 inclusion complexation between β -CD and AzoIPS-LiTFSI. The results can be interpreted that there are two different

binding affinities of β -CD's complexation with TFSI⁻ and Azo moieties.^[12] As appeared in Figure 4b, the binding constant of complexation between β -CD and AzoIPS was 2.29 × 10³ ± 127 M⁻¹ and the stoichiometric ratio was 1.77, which was smaller than 2. It can be interpreted that there are free AzoIPS and β -CD molecules without host-guest interactions presented in the equilibrium status.

It is noteworthy that, the thermodynamics of the interaction between β-CD and LiTFSI in water is relatively complicated (Figure 4c). The overall binding process is a coexistence of endothermic (positive signals) and exothermic (negative signals) steps, leading to significantly different titration curves. Therefore, it is unsuitable to obtain the thermodynamic information by fitting the titration curve. However, according to our previous report,^[13] the binding stoichiometry of β -CD and TFSI⁻ was 0.859. In general, the real stoichiometric ratio between AzoIPS-LiTFSI and β-CD was smaller than 3:1 due to the coexistence of free quest molecules and inclusion complex in the supramolecular system. It is well known that, the driving force for inclusion complexation is usually the exothermic host-quest interaction. The presence of competitive interaction can shed light on the complicated binding process.^[14] It should be noted that, there exists strong hydrogen bonds between TFSI⁻ anions and water molecules, due to the heavily fluorinated of selected TFSI⁻ anion. During the titration of β -CD, TFSI⁻ released from water and entered into the cavity of β-CD to form hydrogen bonding with the hydroxyl group in β -CD. Therefore, positive signals in the titration curve may be caused by the destruction of hydrogen bonds between TFSI⁻ anions and water molecules.



Figure 4. Titration data of β -CD (15 mM) titrated into (a) AzoIPS-LITFSI (0.5 mM) (b) AzoIPS (0.75 mM) (c) LITFSI (1.5 mM) recorded at 25.0 °C.

Temperature-dependent ¹⁹F NMR spectra were carried out to prove the presence of hydrogen bonding. As shown in Figure S3, the fluorine signal of AzoIPS-LiTFSI solution is at about -77.519 ppm at 25.0 °C. Significant upfield shift can be observed with the increasing of temperature (-77.782 ppm at 50.0 °C). Upon cooling, the original fluorine signal of TFSI⁻ anion was observed again. Therefore, it can be concluded that there are hydrogen bonding between TFSI⁻ anion and water molecules. As a control experiment (Figure 5), the same experimental phenomenon was obtained (from -77.908 ppm at 25.0 °C to -78.127 ppm at 50.0 °C) for β -CD/AzoIPS-LiTFSI complex (molar ratio 3:1) due to the presence of hydrogen bonds between β -CD and TFSI⁻. However, the chemical shifts from 25.0 °C to 50.0 °C are different for pure AzoIPS-LiTFSI (0.263 ppm) and in the presence of β -CD (0.219 ppm). The possible explanation is that partial TFSI⁻ anions escape from the cavity of β -CDs, inducing the change of polarizable environment. The above results further confirmed the host-guest interaction between β -CD and TFSI⁻ and revealed the mechanism of the thermo-responsive sol-gel transition.



Figure 5. Temperature-dependent $^{19}\mathsf{F}$ NMR spectra of $\beta\text{-CD/AzoIPS-LiTFSI}$ (3:1 6 mM) in D₂O. The sample was heated from 25.0 to 50.0 °C and then cooled down to 25.0 °C (from bottom to top).

It is well known that hydrophobic interaction and reasonable size-compatible fit between the cavity of β -CD and guest molecule are the main driving forces for the β-CD inclusion complexes. The selected hydrophobic TFSI⁻ anion and Azo group are suitable size-matched host-guest pairs with β -CD, which promotes the binding. Obviously, oversized guest molecule cannot be entrapped in the β -CD cavity, and oversized β-CD cavity cannot ensure van der Waals force (which is strictly dependent on the distance between two molecules) to stabilize the host-guest interaction.^[15] As can be seen from Figure 1f, unstable hydrogel was obtained after the Azo was replaced by decyl due to relatively long distance between alkyl chain and the cavity of β-CD. When the TFSI⁻ was replaced by hydrophilic and small sized Cl⁻, supramolecular hydrogel could not form (Figure 1g). It can also be concluded that host-guest interaction is the necessary prerequisite for the formation of supramolecular hydrogel.

As ion dissociator, zwitterion AzoIPS can dissolve inorganic salt LiTFSI. As can be seen from Figure 6, the absorption band of AzoIPS located at 1159 cm⁻¹ belonging to C-H in-plane vibration of imidazole. The bands at 1186 and 1043 cm⁻¹ ascribed to the S=O stretching vibrations.^[16] For LiTFSI, the peaks at 1140, 1198 and 1061 cm⁻¹ attributed to the C-SO₂-N bond and CF₃ symmetric stretching vibration respectively.^[13] For AzoIPS-LiTFSI, these absorption peaks significantly shift to 1193, 1137, and 1051 cm⁻¹, indicating the electrostatic interaction between AzoIPS and LiTFSI.



Figure 6. FTIR spectra of AzoIPS, LiTFSI and AzoIPS-LiTFSI.

Photo-responsive mechanism

As can be seen from Figure 1b, UV irradiation of the hydrogel produced a fluid sol state. It has already been known that trans-Azo can be entrapped into the cavity of β -CD due to its size matching and hydrophobic nature. Trans-cis isomerization caused by UV light illumination will induce size changes and hydrophilicity enhancement of the Azo. Therefore, Azo moiety may exclude from the cavity of β -CD. To study the mechanism of the photo-responsive sol-gel transition, UV-vis and ¹H NMR spectroscopy were used to confirm *trans-cis* photoisomerization. Figure 7a shows the UV-vis absorbance spectra of β-CD/AzoIPS-LiTFSI (3:1 0.12 mM) aqueous solution with different UV irradiation times. Without UV light treatment, a strong absorption peak located at about 320 nm is belong to the π - π * transition of Azo. After UV irradiation for 2 min, significantly intensity decrease and blue shift (300 nm) of this peak was observed. Meanwhile, the intensity of absorption band located at 425 nm which ascribed to the $n-\pi^*$ transition increased slightly.^[17] Obviously, longer irradiation time cannot bring significant change in the UV-vis spectra due to maximum transcis photoisomerization has been finished. After visible light irradiation for 20 min, trans-AzoIPS-LiTFSI was obtained again. In addition, the reversible trans-cis transition of β-CD/AzolPS-LiTFSI complex can be repeated more than five times without decomposition of the components (Figure 7b).

¹H NMR spectra were detected to further prove the *trans-cis* isomerization and calculate the content of *trans*-isomers before and after UV illumination. By calculating the proton signals shown in Figure 7c, about 80% *trans*-content present in the complex before UV light treatment. After UV irradiation over 30 min, shielding effect and magnetically anisotropic effect caused by the change of polarity induce corresponding proton signals of *cis*-Azo appear in upfield position. Meantime, the content of *trans*-isomer was reduced to 15%. The results can be determined that UV and visible light treatment cannot achieve complete conversion. It is noteworthy that, UV illumination translocates the original protons of *trans*-isomer moves to an opposite direction compared with Figure 3a (the molar ratio of β -

CD/AzoIPS-LiTFSI from 0:1 to 3:1). As a control experiment, ¹H NMR spectra without addition of β -CD was detected and shown in Figure S4. There is no significant chemical shift was observed after UV irradiation. The results of ¹H NMR spectra demonstrate that the photoisomerization of Azo changes the inclusion mode of β -CD and guest molecules.

It is well known that there is chiral center in β-CD. Inclusion complexation between achiral guest chromophore and β-CD could induce circular dichroism (CD) signal in which information about complexation mode could be obtained. As shown in Figure 7d, no CD signal for AzoIPS-LiTFSI or β-CD aqueous solutions could be detected. While, for β-CD/AzoIPS-LiTFSI complex, CD signal was observed (blue curve) at the wavelengths similar to the UV-vis absorption spectra of trans-Azo. It can be clearly observed that, two strong positive Cotton signals ascribing to π - π * transition of Azo emerge at 264 nm and 320 nm and a weak negative Cotton signal corresponding to n- π^* transition appears at about 465 nm with a splitting band at about 360 nm, indicating strong host-quest interaction between chiral β -CD and achiral Azo. It is the chiral β -CD that leading to the chirality of the complexation. The results suggest that the π - π^* transition dipole of Azo is parallel to the principal axis of β -CD. while n- π^* transition dipole of Azo is perpendicular to the axis of β-CD.^[18] After UV irradiation, significant CD signal transition was observed, which is corresponding to the UV-vis absorption spectra of cis-Azo. That is, the decreased positive Cotton effect at about 300 nm and increased intensity of Cotton effect at about 400 nm. This spectrum (magenta curve) shows the positive and negative CD signals corresponding to π - π * and n- π^* transitions of the *cis*-Azo respectively, demonstrating that *cis*-Azo moiety entrapped in the β -CD cavity and the both transition moments are tilted to the principal axis of β-CD, while the trans-Azo moiety excluded from the β -CD.^[10,19]



Figure 7. UV-vis absorption spectra of β -CD/AzoIPS-LiTFSI aqueous solution (3:1 0.12 mM) (a) with different UV irradiation times; (b) the maximum absorption intensity after exposed to alternate UV and visible light. (c) ¹H NMR spectra of β -CD/AzoIPS-LiTFSI (3:1 6 mM) in D₂O before and after UV illumination. (d) CD spectra of AzoIPS-LiTFSI, and β -CD aqueous solution as well as β -CD/AzoIPS-LiTFSI complex before and after UV irradiation.

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2D ROESY ¹H NMR technique was used to detect the position of AzoIPS moiety correlated with β -CD. As shown in Figure S5 (β -CD/AzoIPS-LiTFSI 3:1 15 mM), only protons of Azo group display correlation peaks with the inner protons of host molecule. However, no significant correlation signals between the alkyl protons of AzoIPS-LiTFSI and β -CD protons were observed, demonstrating that other parts of AzoIPS-LiTFSI apart from Azo group and TFSI⁻ anion do not have host-guest interaction with β -CD. Combine with above results, β -CD only includes *trans*-Azo moiety and TFSI⁻ anion.

In order to get detailed insight into the effect of UV light irradiation on the inclusion mode of β -CD and AzoIPS moiety, partial 2D ROESY ¹H NMR spectra for the mixture of β -CD and AzoIPS-LiTFSI before and after UV illumination was exhibited (Figure 8). The hydrogen atoms on various carbons are labeled. Before UV irradiation (Figure 8a), these spectra display the correlation peaks between the protons of C₃, C₆ and C₅ in β -CD and the protons (H_a, H_b, H_c, H_d, and H_e) in the *trans*-Azo moiety indicating that only Azo group included in the β -CD. Figure 8b shows the 2D ROESY ¹H NMR spectrum of complex after UV irradiation. The correlation signals between β -CD protons and *trans*-Azo protons were obviously weakened instead of the partial protons for *cis*-Azo. Interestingly, new correlation peaks between C₃ protons and H_f were observed, which demonstrate the sliding of β -CD on the position of guest molecule.



Figure 8. Partial 2D ROESY ¹H NMR spectra for the mixture of β -CD and AzoIPS-LiTFSI with the concentration of β -CD 15 mM (molar ratio 3:1 D₂O/DMSO 9/1, v/v).

To understand the correlation mode of Azo and β-CD better, density functional theory (DFT) calculations were used to optimize the structures of trans- and cis-AzoIPS-LiTFSI (Scheme 1a and 1b). The needed lengths of groups were marked in the picture. According to above experimental results and the structure parameters of β -CD in the literature,^[20] the possible inclusion mode between β-CD and trans- or cis-AzoIPS-LiTFSI can be described in Scheme 1c. Before UV light treatment, one Azo group included in two β-CDs, which is benefit for the hydroxyl in β -CD to form hydrogen bonding with other adjacent β-CD. Thus, tightly linked host molecules induce the formation of stable supramolecular hydrogel. After UV irradiation, one β-CD escaped from Azo. Therefore, β-CDs are not able to connect with each other. The loss of cross-linking points disrupts the stability of hydrogel. For thermal responsiveness, the destruction of hydrogen bonds at elevated temperature also induces sol-gel phase transition. Therefore, it can be concluded that host-quest interaction between β-CD and two kinds of quests, electrostatic interaction between imidazole cation and TFSI⁻ anion, and hydrogen bonds between β-CDs as well as β -CD and TFSI⁻ promote the formation of supramolecular hydrogel. (Scheme 1d)



Scheme 1. Optimized structures of (a) *trans*-AzoIPS-LiTFSI, (b) *cis*-AzoIPS-LiTFSI by DFT calculations. Color code for atoms: dark gray, carbon; light gray, hydrogen; dark blue, nitrogen; light blue, fluorine; red, oxygen; yellow, sulfur; purple, lithium. (c) Inclusion mode between β -CD and AzoIPS-LiTFSI before and after UV irradiation. (d) Diagram of gel formation mechanism.

Conductivity of hydrogel

Based on the charged character of AzoIPS-LiTFSI and thermalresponsive sol-gel transition of the supramolecular hydrogel, alternating current impedance was used to study the conductive performance of the prepared supramolecular hydrogel (Figure 9). The ionic conductivity of sample at 25.0 °C is 1.84×10^{-4} S·cm⁻¹, which increases to 2.93×10^{-4} S·cm⁻¹ at 40.0 °C (sol solution at this temperature). Interestingly, significant reversible switching of conductivity was achieved accompanying with thermalresponsive sol-gel phase transition. Moreover, the cyclic conductivity conversion could be repeated many times without addition of any supporting electrolytes. Such performance is beneficial greatly for the potential application on temperature sensitive soft materials.



Figure 9. Conductivities of the supramolecular hydrogel (β -CD/AzoIPS-LiTFSI 3:1 200 mM) at gel phase (25.0 °C) and sol solution (40.0 °C) induced by alternating temperature changes at 25.0 and 40.0 °C, respectively.

Conclusions

In summary, we have prepared photo and thermal responsive supramolecular hydrogel based on β -CD and rational designed asymmetric Gemini ZIL guest. The complex ratio between β -CD and two kinds of guest molecules Azo and TFSI⁻, as well as photo and thermal responsive mechanism has been meticulous studied. The coexistence of two kinds of host-guest interactions and hydrogen bonding are the requirements for the formation of hydrogel. Interestingly, one *trans*-Azo group can be included in two β -CDs. In addition, the β -CD in AzoIPS-LiTFSI can be photo-manipulated to shuttle accompanied with the change of CD signals. The conductive properties may highlight the potential applications of stimuli-responsive hydrogel on electrical sensing materials.

Experimental Section

Materials

Nitrosobenzene (98%), *p*-toluidine (99%), *N*-bromosuccinimide (99%) and benzoyl peroxide (98%), imidazole (99%), *1*,3-propanesultone (99%), lithium bis(trifluoromethanesulfonyl)imide (LiTFSI, 99%), lithium chloride (LiCI) (99%), *1*-bromodecane (98%) were purchased from J&K Scientific Co., Ltd. Trifluoroacetic acid (99%), β-CD (96%) was purchased from Aladdin Chemical Reagent Co., Ltd. Organic solvents were purchased from Shanghai Chemical Co., Ltd. All the above materials were used without further purification. Ultra-pure water was used throughout the experiment. The purity of the products was confirmed by ¹H NMR on a Bruker Avance 400 MHz NMR.

Synthesis

AzoBr (1) AzoBr was synthesized according to the previous report.^[21]

Azomim (2) Imidazole (0.68 g), NaOH (0.44 g) and ultra-pure water (0.44 mL) were added to a neck round bottom flask. AzoBr (2.5 g) was dissolved in THF and added dropwise into the above mixture at 60 °C under N₂ atmosphere. After refluxed for 3 days, THF was removed by rotary evaporation. The crude product was extracted three times with CH₂Cl₂/H₂O. The organic layer was concentrated and dried under vacuum. ¹H NMR (CDCl₃, δ): 5.21 (s, 2H), 6.94 (s, 1H), 7.13 (s, 1H), 7.26-7.30 (m, 2H), 7.48-7.61 (m, 4H), 7.89-7.93 (m, 4H).

AzoIPS (3) Azomin (1.8 g, 6.9 mmol) was dissolved in acetone. An equimolar amount of 1,3-propanesultone (0.84 g, 6.9 mmol) dissolved in acetone was added dropwise to the solution in ice bath under N₂ atmosphere. The mixture was then stirred for 5 days at room temperature. After that, the solution was filtered and the solid was purified with acetone for three times. The orange powder AzoIPS was dried under a vacuum at room temperature. ¹H NMR (DMSO, δ): 2.07-2.17 (m, 2H), 2.39-2.45 (t, 2H), 4.31-4.37 (t, 2H), 5.54 (s, 2H), 7.57-7.64 (m, 5H), 7.82-7.95 (m, 6H), 9.34 (s, 1H).

AzoIPS-LiTFSI (4) AzoIPS-LiTFSI was obtained by dissolving equimolar AzoIPS and LiTFSI in MeOH/H₂O mixture solvent. After stirring overnight, the solvent was removed by rotary evaporation. The product was dried under vacuum at room temperature.

AzoIPS-LiCI The synthesis of AzoIPS-LiCI (Figure S6a) is similar to the synthesis AzoIPS-LiTFSI.

C₁₀**IPS** The synthesis of C₁₀IPS (Figure S6b) is similar to the previous report.^[22] ¹H NMR (D₂O, δ): 0.66-0.71 (t, 3H), 1.08-1.12 (m, 14H), 1.68-1.73 (m, 2H), 2.13-2.21 (m, 2H), 2.72-2.77 (t, 2H), 4.00-4.06 (t, 2H), 4.18-4.23 (t, 2H), 7.34-7.39 (m, 2H).





Scheme 2. Synthetic routes of AzoIPS-LiTFSI.

Sample preparation

The hydrogels were prepared by weighing all components at designed compositions in a screw-capped sample tube. The β -CD and AzoIPS-LiTFSI were mixed at different molar ratios. The concentration indicated in the article was the molar concentration of β -CD unless otherwise specified. The mixtures were homogenized at 60 °C and equilibrated at room temperature.

Photoisomeric experiments

To achieve *trans-cis* isomerization, the samples in quartz tube were illuminated with a LUYOR-3109 UV light at room temperature. After photoisomerization, all the samples were wrapped with aluminum foil to prevent the transformation from *cis*- to *tans*-isomer.

NMR

 ^1H NMR and ^{19}F NMR spectra were recorded on a Bruker Avance 400 MHz NMR with D_2O as solvent at 25.0 °C. For ^{19}F NMR measurements, trifluoroacetic acid in D_2O was used as an external reference (-79.45 ppm). 2D ROESY ^1H NMR spectra were recorded by using D_2O/DMSO (9:1 v/v) mixed solvent at 25.0 °C.

Isothermal titration calorimetry (ITC)

ITC experiment was carried out with Microcal VP-ITC apparatus at 25.0 °C. The β -CD solution was titrated into the 1.4 mL AzoIPS-LiTFSI solution via a 300 μ L syringe with the total injection of 29 drops.

UV-vis and FTIR spectroscopy

The UV-vis spectroscopy measurements of 0.12 mM β -CD/AzoIPS-LiTFSI (3:1) aqueous solutions before and after different UV irradiation times were carried out on a UV-4100 spectrophotometer. The ultra-pure water was utilized as a blank in the experiments. FTIR (PerkinElmer Spectrum Two) was carried out at room temperature.

Rheological measurements

The rheological measurement was examined by Haake Rheostress 6000 rheometer with a cone-plate system (C35/1 Ti) at 25.0 °C. For each sample, dynamic frequency sweep measurement was recorded in the linear viscoelastic region, which was determined from dynamic stress sweep measurement.

Scanning electron microscope (SEM)

The morphology of xerogel was characterized by SEM (JEOL JSM-6700F) after platinum sputter coating. The xerogel was obtained by freeze-dry of hydrogel.

Circular dichroism (CD)

CD spectra were studied on a JASCO J-810 spectropolarimeter. Two quartz plates with 0.1 mm path length were used to obtain the spectra.

Density functional theory (DFT)

DFT calculations were used to simulate the optimum configuration of *trans*- and *cis*-AzoIPS-LiTFSI. Gaussian 09 package with the hybrid B3LYP functional and the 6-31G (d, p) basis set were performed.

Conductivity measurements

Conductivities of the hydrogels at different conditions were determined by an electrochemical impedance spectroscopy technique with 0.2 V oscillating voltage in the frequency range from 1 Hz to 10 MHz using ITO glasses as cell electrodes and teflon as a spacer. The conductivities (σ) were calculated using the following equation:^[23]

 $\sigma = \frac{l}{RA}$

where R is the resistance; and I and A are the thickness and area of the sample, respectively.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: supramolecular hydrogel • stimuli-responsive • azobenzene • zwitterionic liquid • host-guest interaction

- a) Z. Wei, J. H. Yang, J. Zhou, F. Xu, M. Zrínyi, P. H. Dussault, Y. Osada, Y. M. Chen, *Chem. Soc. Rev.* **2014**, *43*, 8114-8131; b) T. Shimizu, N. Kameta, W. Ding, M. Masuda, *Langmuir* **2016**, *32*, 12242-12264; c) M. Zhang, D. Xu, X. Yan, J. Chen, S. Dong, B. Zheng, F. Huang, *Angew. Chem. Int. Ed. Engl.* **2012**, *51*, 7011-7015; *Angew. Chem.* **2012**, *124*, 7117-7121; d) Y. Hu, D. Xie, Y. Wu, N. Lin, A. Song, J. Hao, *Chem. Eur. J.* **2017**, *23*, 15721-15728.
- a) S. Dong, Y. Luo, X. Yan, B. Zheng, X. Ding, Y. Yu, Z. Ma, Q. Zhao, F. Huang, *Angew. Chem. Int. Ed. Engl.* 2011, *50*, 1905-1909; *Angew. Chem.* 2011, *123*, 1945-1949; b) S. Matsumoto, S. Yamaguchi, S. Ueno, H. Komatsu, M. Ikeda, K. Ishizuka, Y. Iko, K. V. Tabata, H. Aoki, S. Ito, H. Noji, I. Hamachi, *Chem. Eur. J.* 2008, *14*, 3977-3986.
- [3] a) H. Zhou, C. Xue, P. Weis, Y. Suzuki, S. Huang, K. Koynov, G. K. Auernhammer, R. Berger, H.-J. Butt, S. Wu, *Nat. Chem.* 2017, *9*, 145-151; b) Y. Guo, Y. Gong, Y. Gao, J. Xiao, T. Wang, L. Yu, *Langmuir* 2016, *32*, 9293-9300; c) C. Wang, K. Hashimoto, R. Tamate, H. Kokubo, M. Watanabe, *Angew. Chem. Int. Ed. Engl.* 2018, *57*, 227-230; *Angew. Chem.* 2018, *130*, 233-236.
- [4] a) M. Nakahata, Y. Takashima, H. Yamaguchi, A. Harada, Nat. Commun. 2011, 2, 511; b) Y. Chen, X.-H. Pang, C.-M. Dong, Adv. Funct. Mater. 2010, 20, 579-586; c) S.-S. Hou, Y.-Y. Hsu, J.-H. Lin, J.-S. Jan, ACS Macro Lett. 2016, 5, 1201-1205.
- [5] a) Y. He, Q. Chen, C. Xu, J. Zhang, X. Shen, J. Phys. Chem. B 2009, 113, 231-238; b) S. Amajjahe, S. Choi, M. Munteanu, H. Ritter, Angew. Chem. Int. Ed. Engl. 2008, 47, 3435-3437; Angew. Chem. 2008, 120, 3484-3486; c) S. Amajjahe, H. Ritter, Macromolecules 2008, 41, 3250-3253.
- a) H. Chen, X. Ma, S. Wu, H. Tian, Angew. Chem. Int. Ed. Engl. 2014, 53, 14149-14152; Angew. Chem. 2014, 126, 14373-14376; b) H.

Yamaguchi, Y. Kobayashi, R. Kobayashi, Y. Takashima, A. Hashidzume, A. Harada, *Nat. Commun.* **2012**, *3*, 603.

- [7] a) S. Ueda, J. Kagimoto, T. Ichikawa, T. Kato, H. Ohno, *Adv. Mater.* **2011**, *23*, 3071-3074; b) B. Soberats, M. Yoshio, T. Ichikawa, S. Taguchi, H. Ohno, T. Kato, *J. Am. Chem. Soc.* **2013**, *135*, 15286-15289; c) X. Peng, H. Liu, Q. Yin, J. Wu, P. Chen, G. Zhang, G. Liu, C. Wu, Y. Xie, *Nat. Commun.* **2016**, *7*, 11782; d) A. Wu, X. Gao, P. Sun, F. Lu, L. Zheng, *Angew. Chem. Int. Ed. Engl.* **2018**, *57*, 4025-4029; *Angew. Chem.* **2018**, *130*, 4089-4093.
- [8] C. Yuan, J. Guo, M. Tan, M. Guo, L. Qiu, F. Yan, ACS Macro Lett. 2014, 3, 271-275.
- [9] W. Miao, D. Yang, M. Liu, Chem. Eur. J. 2015, 21, 7562-7570.
- [10] D. Taura, S. Li, A. Hashidzume, A. Harada, *Macromolecules* **2010**, *43*, 1706-1713.
- a) S. Amajjahe, H. Ritter, *Macromolecules* 2008, *41*, 716-718; b) Q.
 Zhao, Y. Wang, Y. Yan, J. Huang, *ACS Nano* 2014, *8*, 11341-11349.
- [12] L. Chen, Z. Huang, J.-F. Xu, Z. Wang, X. Zhang, Polym. Chem. 2016, 7, 1397-1404.
- [13] A. Wu, F. Lu, P. Sun, X. Qiao, X. Gao, L. Zheng, *Langmuir* 2017, 33, 13982-13989.
- [14] G. Zhang, B. Keita, C. T. Craescu, S. Miron, P. de Oliveira, L. Nadjo, *Biomacromolecules* 2008, 9, 812-817.

- [15] D. Ondo, M. Tkadlecová, V. Dohnal, J. Rak, J. Kvíčala, J. K. Lehmann, A. Heintz, N. Ignatiev, J. Phys. Chem. B 2011, 115, 10285-10297.
- [16] Z. H. Li, Q. L. Xia, L. L. Liu, G. T. Lei, Q. Z. Xiao, D. S. Gao, X. D. Zhou, *Electrochim. Acta* 2010, 56, 804-809.
- [17] a) Y. Lin, X. Cheng, Y. Qiao, C. Yu, Z. Li, Y. Yan, J. Huang, *Soft Matter* 2010, *6*, 902-908; b) Y. Guo, Y. Gong, Z. Yu, Y. Gao, L. Yu, *RSC Adv.* 2016, *6*, 14468-14473.
- a) N. Yoshida, H. Yamaguchi, M. Higashi, J. Chem. Soc. Perkin Trans
 1994, 2, 2507-2513; b) P. Duan, L. Qin, M. Liu, Langmuir 2011, 27,
 1326-1331; c) Y. Li, M. Liu, J. Colloid Interf. Sci. 2007, 306, 386-390.
- [19] X.-P. Qiu, E. V. Korchagina, J. Rolland, F. M. Winnik, *Polym. Chem.* 2014, 5, 3656-3665.
- [20] G. Yu, K. Jie, F. Huang, Chem. Rev. 2015, 115, 7240-7303.
- [21] A. Wu, F. Lu, P. Sun, X. Gao, L. Shi and L. Zheng, *Langmuir* 2016, *32*, 8163-8170.
- [22] P. Sun, F. Lu, A. Wu, L. Shi, L. Zheng, Soft Matter 2017, 13, 2543-2548.
- [23] J. Luo, A. H. Jensen, N. R. Brooks, J. Sniekers, M. Knipper, D. Aili, Q. Li, B. Vanroy, M. Wübbenhorst, F. Yan, L. V. Meervelt, Z. Shao, J. Fang, Z.-H. Luo, D. E. De Vos, K. Binnemans, J. Fransaer, *Energy Environ. Sci.* 2015, *8*, 1276-1291.

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Reversible sol-gel phase transition of prepared supramolecular hydrogel could be triggered by light and temperature. UV irradiation changes the inclusion complex mode between β -CD and Azo, while thermal treat influences the hydrogen bonding between β -CD and TFSI⁻.

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