

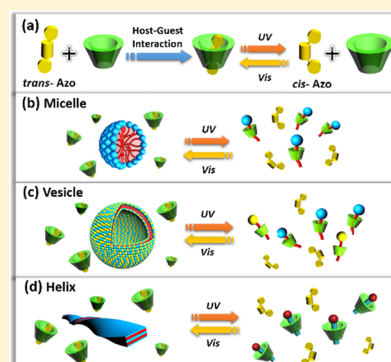
# General Approach To Construct Photoresponsive Self-Assembly in a Light-Inert Amphiphilic System

Qiang Zhao, Zhen Lian, Xuedong Gao, Yun Yan,\* and Jianbin Huang\*

Beijing National Laboratory for Molecular Sciences (BNLMS), State Key Laboratory for Structural Chemistry of Unstable and Stable Species, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, People's Republic of China

## Supporting Information

**ABSTRACT:** The ability to modulate amphiphilic aggregation reversibly with external stimuli, especially using light as a trigger, is of great importance. This has greatly contributed to the development of applications using self-assembly. However, most previously described systems are based on a specific molecular design and have shown difficulty in their application to light-inert aggregation. Here, we developed a general and effective approach to control the morphology of amphiphilic aggregates by light, which is suitable for different assemblies such as micelles, vesicles, and helices. Our strategy is to construct a photoresponsive factor into light-inert self-assemblies. On the basis of the different capabilities to form host–guest inclusions between photoresponsive azobenzene sodium and light-inert molecules with cyclodextrin, the transformation of the corresponding amphiphilic aggregation can be controlled easily and reversibly by light stimuli. Not only the nanostructure of the aggregates but also the phase behavior, such as gel formation, can be modulated upon light irradiation using this method.



## 1. INTRODUCTION

Amphiphilic molecules are able to form various well-defined self-assemblies in water, such as micelles,<sup>1–3</sup> vesicles,<sup>4–6</sup> tubes,<sup>7,8</sup> helices,<sup>9–11</sup> and so forth, which provide opportunities for their use in many applications, for example, sensors,<sup>12,13</sup> medical diagnostics,<sup>14</sup> optoelectronics,<sup>15,16</sup> and homogeneous catalysis.<sup>17</sup> Among them, smart materials, especially for photoresponsive materials, have attracted great attention recently, which provide promising potential for use in controlling morphology and functional transformation.<sup>18,19</sup> Compared with other responsive methods, light stimuli methods are advantageous because they can be easily conducted, and no extra chemical additives are needed to induce the response. Generally, the most often used method to fabricate a photoresponsive system is to introduce a light-responsive group into a molecular structure.<sup>20–22</sup> Although many successful breakthroughs in this area have been made,<sup>23–25</sup> challenges still exist to break the current limits faced by this research field. For example, synthesis, instead of utilizing a general approach, sometimes requires time-consuming processes and a specific method for each system. Moreover, the aggregation morphology and other properties of amphiphiles would be changed after chemical modifications. In fact, a study was reported by simple mixing of a light-responsive molecule such as sodium (4-phenylazo-phenoxy)-acetate with an oppositely charged light-inert surfactant cetyltrimethylammonium bromide, which constructed a photoresponsive system based on electrostatic attraction and generated multistate nanostructures including wormlike micelles, vesicles, lamellar structures, and spherical micelles by controlled ultraviolet

(UV)–visible (vis) light irradiation.<sup>26</sup> However, the shortcomings of this method are also obvious, e.g., it has seldom been applied to electrostatic repulsion or nonelectrostatic systems. Even in electrostatic attraction systems,<sup>27,28</sup> conformational variation of the light-sensitive group is not always effective at tuning the self-assembled structures. Hence, pursuing a simple and general approach to construct a phototriggered system, especially for use in light-inert self-assembly, is an urgent and challenging work. To achieve this goal, some requirements should be satisfied so that the responsive group is able to form general interactions<sup>29,30</sup> with amphiphilic molecules. Moreover, the structures of aggregates are able to be significantly modulated by a change in their light-responsive group under a light trigger.<sup>31–33</sup>

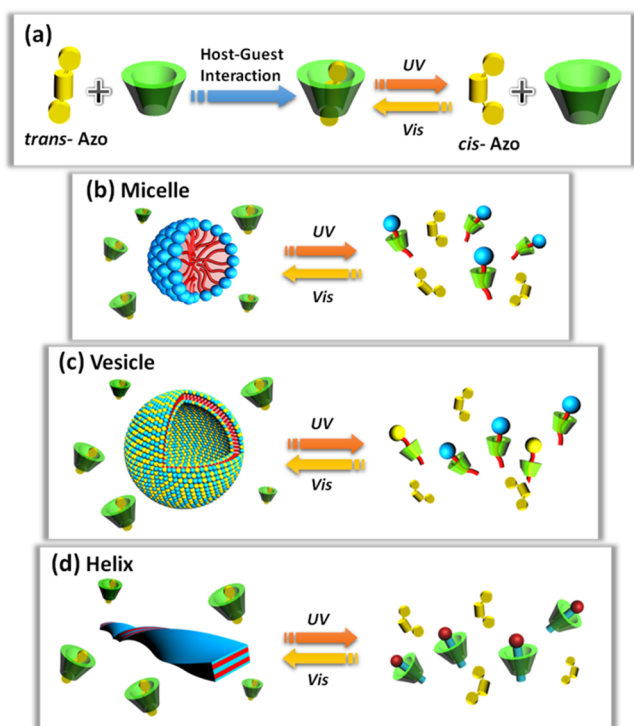
Cyclodextrin (CD) is a kind of compound that could form host–guest complexes with many molecules, particularly for surfactants, resulting in the disassembly of surfactant aggregation.<sup>34–36</sup> Considering the fact that CD cannot respond to light,<sup>37</sup> we developed 4-(phenylazo)benzoic acid sodium salt (Azo) into a system that can be inserted into the CD cavity based on stable inclusion. It forms an Azo@CD photoresponsive factor to couple with light-inert amphiphilic assemblies that successfully make a general approach for controlling the morphology of amphiphilic aggregates by UV or visible light irradiation. The key point of this strategy is the different capabilities of forming host–guest inclusions with CD,

Received: July 29, 2016

Revised: October 19, 2016

Published: October 20, 2016

that is, *trans*-azobenzene > alkyl chain of amphiphilic molecules > *cis*-azobenzene.<sup>38–41</sup> The inclusion of *trans*-Azo@CD can stably coexist with light-inert amphiphilic aggregates under visible light. Upon UV light irradiation, with the transformation from *trans*-Azo to *cis*-Azo, CDs are released into the solution and form new inclusions with amphiphilic molecules, which lead to the disassembly of the light-inert aggregations. With alternating UV–vis light irradiation, the corresponding light control process can be repeated several times in three typical assembly systems of micelles,<sup>42,43</sup> vesicles,<sup>44–46</sup> and helices,<sup>47,48</sup> as shown in Figure 1.



**Figure 1.** Schematic illustrations of the construction (a) a photo-responsive self-assembly using Azo@CD in (b) micelle, (c) vesicle, and (d) helix systems.

## 2. EXPERIMENTAL SECTION

**2.1. Materials.** Sodium dodecyl sulfate (SDS), dodecyl trimethyl ammonium bromide (DTAB), and octadecyl trimethyl ammonium bromide (OTAB) were prepared by recrystallizing five times from

ethanol/acetone. Sodium laurate (SL) and sodium cholate (SC) were purchased from Sigma-Aldrich and were used as received.  $\beta$ -CD and  $\alpha$ -CD were purchased from Sinopharm Chemical Reagent Co., with a water content of 14%. D<sub>2</sub>O (99.9%) was purchased from Cambridge Isotope Laboratories, Inc. Aqueous solutions were prepared using Milli-Q water of 18 M $\Omega$ . Other reagents were purchased from Beijing Chemical Reagents (Beijing, China). All reagents were used as received, and the solvents were purified according to general procedures used before.

**2.2. Methods.** **2.2.1. Sample Preparation.** The SDS micelle system was a mixture of 12 mM SDS and Azo@ $\beta$ -CD (6:6 mM) in an aqueous solution. The vesicle system was a mixture of the SDS/DTAB (0.4:0.6 mM) solution with Azo@ $\beta$ -CD (6:6 mM). The helix solution was a mixture of CaCl<sub>2</sub>/SC (20:20 mM) and Azo@ $\beta$ -CD (10:10 mM). Moreover, for  $\alpha$ -CD systems, the vesicle system was a mixture of SL/OTAB (2.5:2.5 mM) with Azo@ $\alpha$ -CD (5:5 mM) in 10 mM borax buffer. The helix solution was a mixture of CaCl<sub>2</sub>/SC (20:20 mM) with Azo@ $\alpha$ -CD (10:10 mM), as described before. All solutions were then thermostatically incubated at 25 °C for 48 h to allow the formation of stable aggregates. The structural formulas of all compounds are given in Figure S1. The UV light was generated using a model FC-100/F long-wave UV (365 nm, 230 V, 50 Hz, and 0.9 A). The duration of irradiation was 4 h.

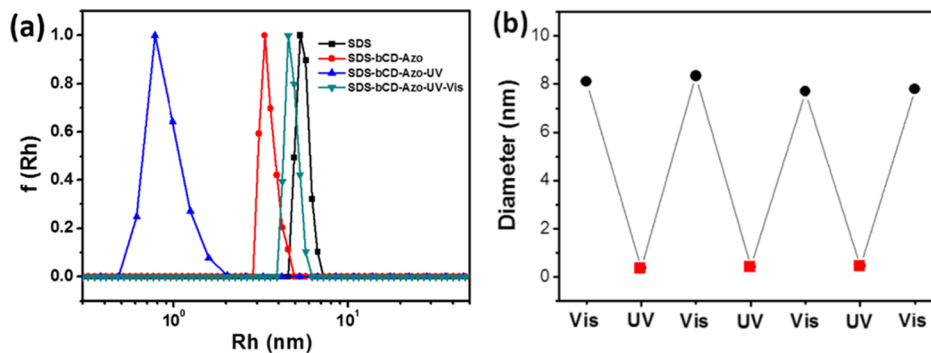
**2.2.2. Transmission Electron Microscopy.** Samples were observed using a Jeol JEM 100 CX microscope (80 kV) and JEM-2100 microscope (200 kV). Drops of samples were added onto 230-mesh copper grids coated with a formvar film. Excess water was removed using filter paper, and the samples were allowed to dry in ambient air at room temperature (RT), before transmission electron microscopy (TEM) observation. All samples were stained except for the hydrogel systems.

**2.2.3. Spectral Measurements.** UV–vis absorbance measurements were carried out on a Pgeneral TU-1810 UV–vis spectrophotometer. All spectral measurements were recorded at RT. The samples were exposed to UV light for 4 h.

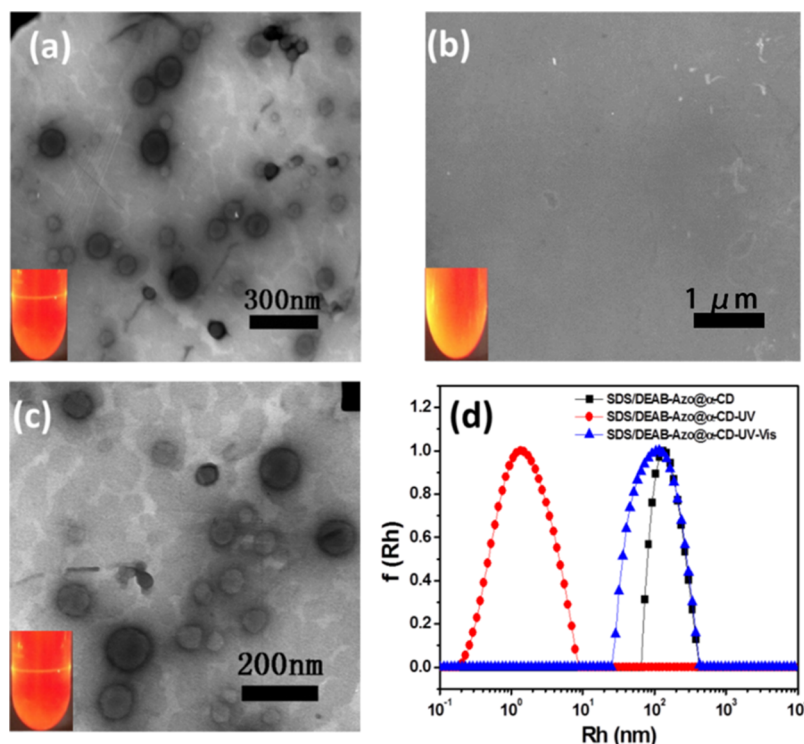
**2.2.4. Dynamic Light Scattering.** A commercialized spectrometer (Brookhaven Instruments Corporation, Holtsville, NY) equipped with a 100 mW solid-state laser (GXC-III, CNI, Changchun, China) operating at 532 nm was used to conduct dynamic light scattering (DLS) experiments. Photon correlation measurements in self-beating mode were carried out at multiple scattering angles using a BI-TurboCo digital correlator. The temperature was held at RT.

**2.2.5. <sup>1</sup>H Nuclear Magnetic Resonance.** <sup>1</sup>H NMR experiments were performed on a Bruker ARX 400 MHz spectrometer with D<sub>2</sub>O as the solvent.

**2.2.6. Rheological Measurements.** Rheological properties of Ca<sup>2+</sup>/SC, Ca<sup>2+</sup>/SC-Azo@ $\beta$ -CD, and Ca<sup>2+</sup>/SC-Azo@ $\alpha$ -CD were assessed by dynamic rheology measurements using a Thermo Haake RS300 rheometer with a cone-and-plate geometry (35 mm diameter; 0.105 mm cone gap). The temperature was kept at 25 °C, and a water trap was used to minimize water evaporation from the sample. Frequency spectra were conducted in the linear viscoelastic regime of the samples



**Figure 2.** (a) DLS test for SDS-Azo@ $\beta$ -CD and (b) diameter of SDS-Azo@ $\beta$ -CD after alternating UV and visible light irradiations. [SDS] = 12 mM, [Azo] = 6 mM, and [ $\beta$ -CD] = 6 mM.



**Figure 3.** TEM images of (a) SDS/DTAB-Azo@β-CD (b) under UV light and (c) under visible light irradiation. (d) DLS measurements. [SDS] = 0.4 mM, [DTAB] = 0.6 mM, [Azo] = 6 mM, and [β-CD] = 6 mM. The insets in panels (a)–(c) show images of the sample with the laser beam passing across it.

determined from dynamic strain-sweep measurements. In dynamic rheology measurements, a hydrogel was deformed with frequency  $f$  to give the elastic (or storage) modulus  $G'$  and viscous (or loss) modulus  $G''$ . We started with oscillation frequency sweep tests, where the stress was chosen as 1 Pa to be nondestructive to the emulsion structure, and the frequency was varied exponentially.

### 3. RESULTS AND DISCUSSION

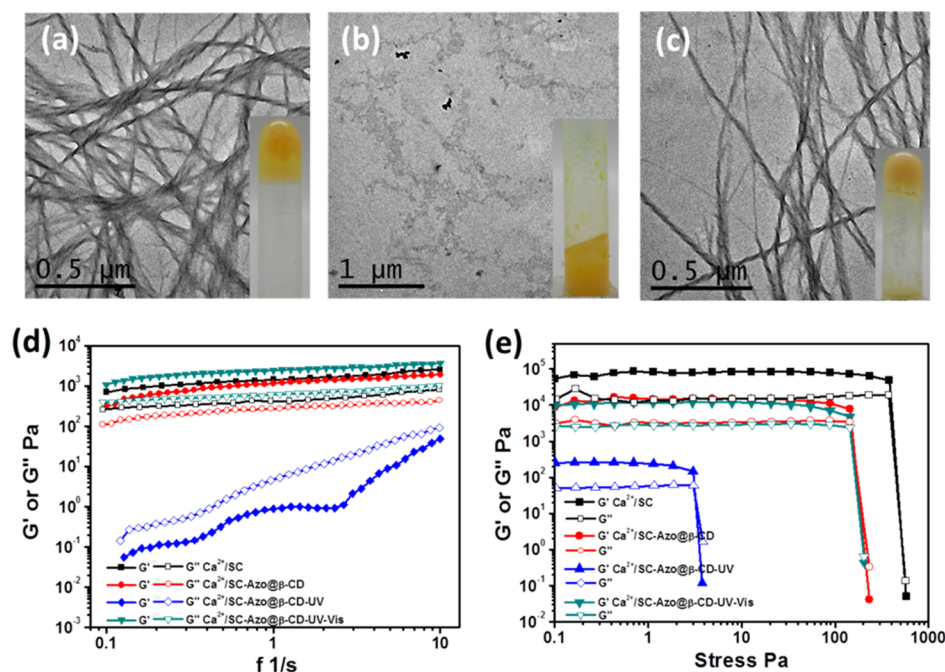
**3.1. Micelle System.** The photoresponsive factor was fabricated using Azo and β-CD and was then added into the target SDS system.<sup>49</sup> The light-triggered process of generating SDS micelles was tested using DLS (Figure 2a). The SDS micelles were stable upon the addition of the Azo@β-CD responsive factor. Both SDS and *trans*-Azo could form inclusions with β-CD by host–guest interactions, but the ability of *trans*-Azo to do so was superior to that of SDS. The binding constant of *trans*-Azo with β-CD was  $4.54 \times 10^2 \text{ mol} \cdot \text{dm}^{-3}$ , and that of *cis*-Azo with β-CD was  $1.36 \times 10^2 \text{ mol} \cdot \text{dm}^{-3}$ .<sup>50</sup> In addition, the binding constants of SDS and DTAB with β-CD were  $3.12 \times 10^2$  and  $1.49 \times 10^3 \text{ mol} \cdot \text{dm}^{-3}$ , respectively, which are between those of *trans*-Azo and *cis*-Azo.<sup>51–54</sup> Hence, the SDS-Azo@β-CD system was predominantly comprised of plenty of SDS micelles. After UV irradiation, the scattering in the solution was notably decreased, and no aggregation was found because azobenzene turns into its *cis* form upon UV irradiation, which has a lower binding ability with β-CD than SDS. This results in the formation of a SDS@β-CD inclusion that leads to the disassembly of the SDS micelles.<sup>7</sup> In addition, the scattered light recovers in response to visible light because *trans*-azobenzene reappears following exposure to visible light and recaptures β-CD to form the stable *trans*-Azo@β-CD inclusion complex in the SDS micelle solution. It is worth noting that this photostimuli process could

be repeated several times by alternating UV and visible light irradiations (Figure 2b).

The transition of azobenzene between its *trans* and *cis* forms was confirmed using UV–vis and <sup>1</sup>H NMR. Figure S2 depicts the  $\pi$ – $\pi^*$  absorption of *trans*-azobenzene at 346 nm in the SDS-Azo@β-CD solution. The absorbance of the *cis* isomer was observed using UV light irradiation. Meanwhile, <sup>1</sup>H NMR tests revealed that the protons of *trans*-azobenzene were dominant in the SDS-Azo@β-CD solution under visible light and that the protons of *cis*-azobenzene increased after UV light irradiation (Figure S3a). The chemical shift of the alkyl group in the SDS molecule moved to high field upon UV irradiation because of the formation of the SDS@β-CD inclusion dimer by host–guest interactions when *trans*-Azo turned into its *cis* isomer under UV light (Figure S3b), which could lead to the breakup of the SDS micelle.

**3.2. Vesicle System.** Vesicles are fundamental self-assembled models for biological studies because of their bilayer membranes and inner-water environment. It has been reported that CD can bind a surfactant and affect aggregation.<sup>50</sup> Hence, cationic–anionic surfactant SDS/DTAB vesicles<sup>55</sup> were chosen to construct a light-responsive system (Figure S4). The reversible phototriggered process of SDS/DTAB-Azo@β-CD was confirmed using DLS and TEM measurements (Figure 3). In the SDS/DTAB-Azo@β-CD system, the vesicles existed (Figure 3a) with a DLS peak at 150 nm (Figure 3d), indicating that guest molecules had inserted into most of the β-CD in the solution under visible light because *trans*-Azo and β-CD could form a stable inclusion via host–guest interactions. Upon UV light irradiation, the disassembly of the vesicles (Figure 3b) is accompanied by the disappearance of the aggregation peak (Figure 3d). As *trans*-Azo turns into its *cis* isomer under UV light, it leads to the formation of SDS@β-CD and DTAB@β-





**Figure 4.** TEM images of (a)  $\text{Ca}^{2+}/\text{SC-Azo@}\beta\text{-CD}$  and  $\text{Ca}^{2+}/\text{SC-Azo@}\beta\text{-CD}$  after (b) UV and (c) visible light irradiation. Inset: images of each sample. (d) Oscillation frequency sweep test and (e) amplitude sweep test for  $\text{Ca}^{2+}/\text{SC}$ ,  $\text{Ca}^{2+}/\text{SC-Azo@}\beta\text{-CD}$ , and the samples after UV and visible light irradiation.  $[\text{CaCl}_2] = 20 \text{ mM}$ ,  $[\text{SC}] = 20 \text{ mM}$ ,  $[\text{Azo}] = 10 \text{ mM}$ , and  $[\beta\text{-CD}] = 10 \text{ mM}$ .

CD host–guest inclusions and results in the disappearance of SDS/DTAB vesicles.<sup>40,55</sup> As expected, the aggregation could reassemble under visible light (Figure 3c,d). In addition, when the light beam moved across the solution, the light path indicated the obvious existence of aggregates. After irradiation by UV light, the light path disappeared as the aggregates were broken apart (Figure 3, inset).

The photoresponsive process was also visualized by  $^1\text{H}$  NMR measurements. The  $^1\text{H}$  NMR spectra showed that, when *cis*-Azo was dominant in solution under UV irradiation, the peak of the alkyl protons in SDS and DTAB shifted to high field (Figure S5). Because the binding ability between *cis*-Azo and  $\beta\text{-CD}$  was lower than that between the surfactant (SDS, DTAB) and  $\beta\text{-CD}$ , SDS@ $\beta\text{-CD}$  and DTAB@ $\beta\text{-CD}$  channel-type dimers were formed by host–guest interactions in solution. In Figures S3 and S5,  $^1\text{H}$  NMR demonstrated that  $\beta\text{-CD}$  formed channel-type dimers because a shift of H3 and H5 was observed as H3 and H5 of  $\beta\text{-CD}$  were located at the cavity of CD. Moreover, compared with free  $\beta\text{-CD}$ , the peaks of H3 and H5 shifted to high field under visible and UV light in the mixed solutions, indicating that no free  $\beta\text{-CD}$  was released under alternating UV and visible light irradiations;  $\beta\text{-CD}$  always formed an inclusion dimer with azobenzene or the surfactants by host–guest interactions. Furthermore, the supramolecular complex could lead the SDS/DTAB vesicles to break apart, which is in agreement with the TEM and DLS results.

In addition, the ratio of the components of every nano-object was calculated by integrating the peak areas from  $^1\text{H}$  NMR (Figure S6). In the SDS-Azo@ $\beta\text{-CD}$  system, 93%  $\beta\text{-CD}$  formed inclusion dimers with *trans*-Azo under visible light. After UV light irradiation, 70% of  $\beta\text{-CD}$  was released and formed the SDS@ $\beta\text{-CD}$  complex in solution. On the other hand, in the SDS/DTAB-Azo@ $\beta\text{-CD}$  system, 88% of  $\beta\text{-CD}$  formed inclusion dimers with *trans*-Azo under visible light. After UV light irradiation, 59% of  $\beta\text{-CD}$  was released and formed the SDS@ $\beta\text{-CD}$  complex in solution.

**3.3. Helix System.** Helices are ubiquitous in nature and have an exclusive structure that has attracted the interest of researchers because of their potential uses in biological and material applications. Our research group previously reported that metal ions/SC assemble into hierarchical nanostructures, forming a super hydrogel in aqueous solution.<sup>48,56–58</sup> The  $\text{Ca}^{2+}/\text{SC}$  helix system was chosen as a hydrogel model (Figure S7 and inset) and evaluated for its phototriggered transformation upon the addition of Azo@ $\beta\text{-CD}$ . TEM and rheology measurements were used to measure the structure and hydrogel properties of  $\text{Ca}^{2+}/\text{SC-Azo@}\beta\text{-CD}$ . Before UV irradiation, hierarchical nanostructures were the dominant form in this system (Figure 4a). After UV irradiation,  $\beta\text{-CD}$  bound with SC, and the helical structure disassembled (Figure 4b). This process is also reversible upon visible light irradiation (Figure 4c). Moreover, the morphological change in aggregation was accompanied by a solution phase transformation of the hydrogel (Figure 4a–c, inset).

Dynamic rheology experiments were carried out to investigate the mechanical properties of the hydrogels. A nondestructive frequency sweep showed that the  $\text{Ca}^{2+}/\text{SC-Azo@}\beta\text{-CD}$  hydrogel exhibited typical solid-like rheological behavior with the storage modulus  $G'$  ( $\sim 1200 \text{ Pa}$ ) dominating the loss modulus  $G''$  ( $\sim 250 \text{ Pa}$ ) over the investigated oscillating frequency as well as the  $\text{Ca}^{2+}/\text{SC}$  hydrogel, as shown in Figure 4d. When UV light was turned on, the  $\text{Ca}^{2+}/\text{SC-Azo@}\beta\text{-CD}$  hydrogel showed liquid-like properties, and this is also a reversible process under visible light. In addition, an amplitude sweep ( $f = 1 \text{ Hz}$ ) indicated a weak dependence of  $G'$  and  $G''$  in the  $\text{Ca}^{2+}/\text{SC-Azo@}\beta\text{-CD}$  hydrogel upon applied stress until the yield stress ( $\sim 150 \text{ Pa}$ ) was achieved, as shown in Figure 4e. Upon UV light irradiation, the yield stress ( $\sim 3 \text{ Pa}$ ) was significantly decreased because SC and  $\beta\text{-CD}$  formed inclusion dimers, resulting in the deformation of the hydrogels. This mechanism was reversible upon alternating UV–vis light irradiation. Overall, both the nanostructure and the phase

behavior of the  $\text{Ca}^{2+}$ /SC hydrogel can be controlled by the addition of Azo@ $\beta$ -CD upon UV–vis light irradiation.

**3.4.  $\alpha$ -CD System.** This method was applicable to  $\alpha$ -CD as well, exhibiting a general approach for amphiphilic self-assembly. We utilized Azo@ $\alpha$ -CD inclusions in SL/OTAB vesicles<sup>59</sup> and  $\text{Ca}^{2+}$ /SC helices. In the SL/OTAB-Azo@ $\alpha$ -CD system, the formation of vesicles could be tuned by UV–vis light, which is similar to our observations with other vesicle systems (Figure S8). The photoresponsive process was confirmed by 2D NMR measurements (Figure S9). A NOESY spectrum showed a correlation of  $\text{H}_\text{a}$  and  $\text{H}_\text{b}$  in *trans*-Azo and  $\text{H}_2$ ,  $\text{H}_3$ , and  $\text{H}_4$  in  $\alpha$ -CD, which indicated that *trans*-Azo formed an inclusion with  $\alpha$ -CD under visible light (Figure S9a,b). After UV light irradiation, *trans*-Azo turned into its *cis* form, and the correlating peaks of azobenzene and  $\alpha$ -CD disappeared. Instead,  $\alpha$ -CD formed another inclusion dimer with SL and OTAB, which was accompanied by the correlation between  $\text{H}_\text{A}$  in SL/OTAB and  $\text{H}_2$ ,  $\text{H}_3$ , and  $\text{H}_4$  in  $\alpha$ -CD (Figure S9a,c). These results demonstrated that  $\alpha$ -CD could form different complexes in azobenzene and surfactant-mixed solutions under visible and UV light irradiations, similar to that for the  $\beta$ -CD system. In the  $\text{Ca}^{2+}$ /SC-Azo@ $\alpha$ -CD hydrogel, both the nanostructure and the gel phase were successfully controlled by UV–vis light, as shown by TEM and rheology measurements (Figure S10). Thus, macrocycles such as  $\beta$ -CD and  $\alpha$ -CD can form Azo@CD inclusions by host–guest interactions and can modulate the formation of a light-inert assembly into a photoresponsive system, suggesting that more phototriggered systems using nonphotoresponsive aggregations can be designed.

In summary, we proposed a simple and effective approach to construct a general photoresponsive system with Azo@CD and amphiphilic aggregations, which can be applied in different single surfactant or mixed surfactant systems to produce many kinds of assemblies such as micelles, vesicles, and helices. In addition, the nanostructure and the phase behavior, such as gel formation, can both be controlled using this method. Furthermore, this general strategy can be applied to many other kinds of systems, for example, nanoparticles,<sup>60</sup> polymers, or polymer surfactant assemblies, and it can regulate phase behaviors that are closely related to self-assembly, for instance, the aqueous biphasic system (ABS) and emulsion. We successfully constructed an Azo@CD photoresponsive factor with both  $\alpha$ -CD and  $\beta$ -CD. On the basis of this, more responsive factors could be designed using other macrocyclic molecules such as cucurbituril. It is also expected that other stimuli-responsive factors (temperature, pH) will be developed based on this strategy. This new method is not only helpful for obtaining a better scientific understanding in the field of light-controlled assemblies but also for opening new vistas in the construction and application of smart materials.

## ■ ASSOCIATED CONTENT

### ■ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.langmuir.6b02836.

<sup>1</sup>H NMR, DLS, TEM, and rheology measurements (PDF)

## ■ AUTHOR INFORMATION

### Corresponding Authors

\*E-mail: yunyan@pku.edu.cn (Y.Y.).

\*E-mail: JBHuang@pku.edu.cn (J.H.).

### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (21422302, 21573011, and 21273013), the National Basic Research Program of China (973 Program, 2013CB933800), and the Doctoral Program of Higher Education of China.

## ■ REFERENCES

- (1) Kresge, C. T.; Leonowicz, M. E.; Roth, W. J.; Vartuli, J. C.; Beck, J. S. Ordered mesoporous molecular sieves synthesized by a liquid-crystal template mechanism. *Nature* **1992**, *359*, 710–712.
- (2) Israelachvili, J. N.; Mitchell, D. J.; Ninham, B. W. Theory of self-assembly of hydrocarbon amphiphiles into micelles and bilayers. *J. Chem. Soc., Faraday Trans. 2* **1976**, *72*, 1525–1568.
- (3) Dubertret, B.; Skourides, P.; Norris, D. J.; Noireaux, V.; Brivanlou, A. H.; Libchaber, A. In vivo imaging of quantum dots encapsulated in phospholipid micelles. *Science* **2002**, *298*, 1759–1762.
- (4) Yin, H.; Zhou, Z.; Huang, J.; Zheng, R.; Zhang, Y. Temperature-induced micelle to vesicle transition in the sodium dodecylsulfate/dodecyltriethylammonium bromide system. *Angew. Chem., Int. Ed.* **2003**, *42*, 2188–2191.
- (5) Waterston, R. H.; et al. Initial sequencing and comparative analysis of the mouse genome. *Nature* **2002**, *420*, 520–562.
- (6) Lavallée, Y.; Dingwell, D. B.; Johnson, J. B.; Cimarelli, C.; Hornby, A. J.; Kendrick, J. E.; von Aulock, F. W.; Kennedy, B. M.; Andrews, B. J.; Wadsworth, F. B.; Rhodes, E.; Chigna, G. Thermal vesiculation during volcanic eruptions. *Nature* **2015**, *528*, 544.
- (7) Jiang, L.; Yan, Y.; Drechsler, M.; Huang, J. Enzyme-triggered model self-assembly in surfactant–cyclodextrin systems. *Chem. Commun.* **2012**, *48*, 7347–7349.
- (8) Jiang, L.; de Folter, J. W. J.; Huang, J.; Philipse, A. P.; Kegel, W. K.; Petukhov, A. V. Helical colloidal sphere structures through thermoreversible co-assembly with molecular microtubes. *Angew. Chem., Int. Ed.* **2013**, *52*, 3364–3368.
- (9) Datta, S.; Bhattacharya, S. Ag<sup>+</sup>-induced reverse vesicle to helical fiber transformation in a self-assembly by adjusting the keto–enol equilibrium of a chiral salicylideneaniline. *Chem. Commun.* **2015**, *51*, 13929–13932.
- (10) Gillissen, M. A. J.; Koenigs, M. M. E.; Spiering, J. J. H.; Vekemans, J. A. J. M.; Palmans, A. R. A.; Voets, I. K.; Meijer, E. W. Triple helix formation in amphiphilic discotics: Demystifying solvent effects in supramolecular self-assembly. *J. Am. Chem. Soc.* **2014**, *136*, 336–343.
- (11) Peterca, M.; Percec, V.; Imam, M. R.; Leowanawat, P.; Morimitsu, K.; Heiney, P. A. Molecular structure of helical supramolecular dendrimers. *J. Am. Chem. Soc.* **2008**, *130*, 14840–14852.
- (12) Scherf, U.; Gutacker, A.; Koenen, N. All-conjugated block copolymers. *Acc. Chem. Res.* **2008**, *41*, 1086–1097.
- (13) Broz, P.; Driamov, S.; Ziegler, J.; Ben-Haim, N.; Marsch, S.; Meier, W.; Hunziker, P. Toward intelligent nanosize bioreactors: A pH-switchable, channel-equipped, functional polymer nanocontainer. *Nano Lett.* **2006**, *6*, 2349–2353.
- (14) Guo, D.-S.; Wang, K.; Wang, Y.-X.; Liu, Y. Cholinesterase-responsive supramolecular vesicle. *J. Am. Chem. Soc.* **2012**, *134*, 10244–10250.
- (15) Zhao, Q.; Wang, Y.; Qiao, Y.; Wang, X.; Guo, X.; Yan, Y.; Huang, J. Conductive porphyrin helix from ternary self-assembly systems. *Chem. Commun.* **2014**, *50*, 13537–13539.

- (16) Li, B.; Han, W.; Jiang, B.; Lin, Z. Crafting threads of diblock copolymer micelles via flow-enabled self-assembly. *ACS Nano* **2014**, *8*, 2936–2942.
- (17) Jordan, P. C.; Patterson, D. P.; Saboda, K. N.; Edwards, E. J.; Miettinen, H. M.; Basu, G.; Thielges, M. C.; Douglas, T. Self-assembling biomolecular catalysts for hydrogen production. *Nat. Chem.* **2016**, *8*, 179–185.
- (18) Song, J.; Huang, P.; Duan, H.; Chen, X. Plasmonic vesicles of amphiphilic nanocrystals: Optically active multifunctional platform for cancer diagnosis and therapy. *Acc. Chem. Res.* **2015**, *48*, 2506–2515.
- (19) Bansal, A.; Zhang, Y. Photocontrolled nanoparticle delivery systems for biomedical applications. *Acc. Chem. Res.* **2014**, *47*, 3052–3060.
- (20) Aznar, E.; Marcos, M. D.; Martínez-Mañez, R.; Sancenón, F.; Soto, J.; Amorós, P.; Guillem, C. pH- and photo-switched release of guest molecules from mesoporous silica supports. *J. Am. Chem. Soc.* **2009**, *131*, 6833–6843.
- (21) Nihei, M.; Kurihara, M.; Mizutani, J.; Nishihara, H. Synthesis of azo-conjugated metalladithiolenes and their photo- and proton-responsive isomerization reactions. *J. Am. Chem. Soc.* **2003**, *125*, 2964–2973.
- (22) Kim, J.; Lee, J.; Kim, W. Y.; Kim, H.; Lee, S.; Lee, H. C.; Lee, Y. S.; Seo, M.; Kim, S. Y. Induction and control of supramolecular chirality by light in self-assembled helical nanostructures. *Nat. Commun.* **2015**, *6*, 6959.
- (23) Gunnlaugsson, T. Supramolecular pathways: Accessible self-assembly. *Nat. Chem.* **2016**, *8*, 6–7.
- (24) Dance, A. Micromanagement with light. *Nature* **2015**, *528*, 291–294.
- (25) Brongersma, M. L.; Cui, Y.; Fan, S. Light management for photovoltaics using high-index nanostructures. *Nat. Mater.* **2014**, *13*, 451–460.
- (26) Lin, Y.; Cheng, X.; Qiao, Y.; Yu, C.; Li, Z.; Yan, Y.; Huang, J. Creation of photo-modulated multi-state and multi-scale molecular assemblies via binary-state molecular switch. *Soft Matter* **2010**, *6*, 902–908.
- (27) Wang, X.; Hu, J.; Liu, G.; Tian, J.; Wang, H.; Gong, M.; Liu, S. Reversibly switching bilayer permeability and release modules of photochromic polymersomes stabilized by cooperative noncovalent interactions. *J. Am. Chem. Soc.* **2015**, *137*, 15262–15275.
- (28) Chen, S.; Bao, L.; Ou, E.; Peng, C.; Wang, W.; Xu, W. A cationic azobenzene-surfactant-modified graphene hybrid: Unique photo-response and electrochemical behavior. *Nanoscale* **2015**, *7*, 19673–19686.
- (29) Vallavoju, N.; Sivaguru, J. Supramolecular photocatalysis: Combining confinement and non-covalent interactions to control light initiated reactions. *Chem. Soc. Rev.* **2014**, *43*, 4084–4101.
- (30) Wang, A.; Shi, W.; Huang, J.; Yan, Y. Adaptive soft molecular self-assemblies. *Soft Matter* **2016**, *12*, 337–357.
- (31) Diguët, A.; Yanagisawa, M.; Liu, Y.-J.; Brun, E.; Abadie, S.; Rudiuk, S.; Baigl, D. UV-induced bursting of cell-sized multi-component lipid vesicles in a photosensitive surfactant solution. *J. Am. Chem. Soc.* **2012**, *134*, 4898–4904.
- (32) Kloxin, A. M.; Kasko, A. M.; Salinas, C. N.; Anseth, K. S. Photodegradable hydrogels for dynamic tuning of physical and chemical properties. *Science* **2009**, *324*, 59–63.
- (33) Du, J.-Z.; Long, H.-Y.; Yuan, Y.-Y.; Song, M.-M.; Chen, L.; Bi, H.; Wang, J. Micelle-to-vesicle morphological transition via light-induced rapid hydrophilic arm detachment from a star polymer. *Chem. Commun.* **2012**, *48*, 1257–1259.
- (34) Wang, Y.; Ma, N.; Wang, Z.; Zhang, X. Photocontrolled reversible supramolecular assemblies of an azobenzene-containing surfactant with  $\alpha$ -cyclodextrin. *Angew. Chem., Int. Ed.* **2007**, *46*, 2823–2826.
- (35) Yamaguchi, H.; Kobayashi, Y.; Kobayashi, R.; Takashima, Y.; Hashidzume, A.; Harada, A. Photoswitchable gel assembly based on molecular recognition. *Nat. Commun.* **2012**, *3*, 603.
- (36) Houk, K. N.; Leach, A. G.; Kim, S. P.; Zhang, X. Binding affinities of host–guest, protein–ligand, and protein–transition-state complexes. *Angew. Chem., Int. Ed.* **2003**, *42*, 4872–4897.
- (37) Lin, Y.; Cheng, X.; Qiao, Y.; Yu, C.; Li, Z.; Yan, Y.; Huang, J. Creation of photo-modulated multi-state and multi-scale molecular assemblies via binary-state molecular switch. *Soft Matter* **2010**, *6*, 902–908.
- (38) Rau, H. Spectroscopic properties of organic azo compounds. *Angew. Chem., Int. Ed.* **1973**, *12*, 224–235.
- (39) Beharry, A. A.; Woolley, G. A. Azobenzene photoswitches for biomolecules. *Chem. Soc. Rev.* **2011**, *40*, 4422–4437.
- (40) Jiang, L.; Yan, Y.; Huang, J.; Yu, C.; Jin, C.; Deng, M.; Wang, Y. Selectivity and stoichiometry boosting of  $\beta$ -cyclodextrin in cationic/anionic surfactant systems: When host–guest equilibrium meets biased aggregation equilibrium. *J. Phys. Chem. B* **2010**, *114*, 2165–2174.
- (41) Harada, A. Cyclodextrin-based molecular machines. *Acc. Chem. Res.* **2001**, *34*, 456–464.
- (42) Wennerström, H.; Lindman, B. Micelles. Physical chemistry of surfactant association. *Phys. Rep.* **1979**, *52*, 1–86.
- (43) Dubertret, B.; Skourides, P.; Norris, D. J.; Noireaux, V.; Brivanlou, A. H.; Libchaber, A. In vivo imaging of quantum dots encapsulated in phospholipid micelles. *Science* **2002**, *298*, 1759–1762.
- (44) Discher, D. E.; Eisenberg, A. Polymer vesicles. *Science* **2002**, *297*, 967–973.
- (45) Jain, S.; Bates, F. S. On the origins of morphological complexity in block copolymer surfactants. *Science* **2003**, *300*, 460–464.
- (46) Fendler, J. H. Surfactant vesicles as membrane mimetic agents: Characterization and utilization. *Acc. Chem. Res.* **1980**, *13*, 7–13.
- (47) Hartgerink, J. D.; Beniash, E.; Stupp, S. I. Self-assembly and mineralization of peptide-amphiphile nanofibers. *Science* **2001**, *294*, 1684–1688.
- (48) Qiao, Y.; Lin, Y.; Wang, Y.; Yang, Z.; Liu, J.; Zhou, J.; Yan, Y.; Huang, J. Metal-driven hierarchical self-assembled one-dimensional nanohelices. *Nano Lett.* **2009**, *9*, 4500–4504.
- (49) Iwadare, Y.; Suzawa, T.  $\zeta$ -Potentials of natural and synthetic fibers in SDS solutions and the viscosity of SDS solutions above critical micelle concentration. *Bull. Chem. Soc. Jpn.* **1970**, *43*, 2326.
- (50) Harada, A. Cyclodextrin-based molecular machines. *Acc. Chem. Res.* **2001**, *34*, 456–464.
- (51) Palepu, R.; Richardson, J. E.; Reinsborough, V. C. Binding constants of  $\beta$ -cyclodextrin/surfactant inclusion by conductivity measurements. *Langmuir* **1989**, *5*, 218–221.
- (52) Kahle, C.; Holzgrabe, U. Determination of binding constants of cyclodextrin inclusion complexes with amino acids and dipeptides by potentiometric titration. *Chirality* **2004**, *16*, 509–515.
- (53) Dotsikas, Y.; Loukas, Y. L. Efficient determination and evaluation of model cyclodextrin complex binding constants by electrospray mass spectrometry. *J. Am. Soc. Mass Spectrom.* **2003**, *14*, 1123–1129.
- (54) Mwakibete, H.; Cristantino, R.; Bloor, D. M.; Wyn-Jones, E.; Holzwarth, J. F. Reliability of the experimental methods to determine equilibrium constants for surfactant/cyclodextrin inclusion complexes. *Langmuir* **1995**, *11*, 57–60.
- (55) Kaler, E. W.; Murthy, A. K.; Rodriguez, B. E.; Zasadzinski, J. A. Spontaneous vesicle formation in aqueous mixtures of single-tailed surfactants. *Science* **1989**, *245*, 1371–1374.
- (56) Qiao, Y.; Lin, Y.; Wang, Y.; Li, Z.; Huang, J. Metal-driven viscoelastic wormlike micelle in anionic/zwitterionic surfactant systems and template-directed synthesis of dendritic silver nanostructures. *Langmuir* **2011**, *27*, 1718–1723.
- (57) Qiao, Y.; Lin, Y.; Zhang, S.; Huang, J. Lanthanide-containing photoluminescent materials: From hybrid hydrogel to inorganic nanotubes. *Chem.—Eur. J.* **2011**, *17*, 5180–5187.
- (58) Qiao, Y.; Wang, Y.; Yang, Z.; Lin, Y.; Huang, J. Self-templating of metal-driven supramolecular self-assembly: A general approach toward 1D inorganic nanotubes. *Chem. Mater.* **2011**, *23*, 1182–1187.

(59) Mao, M.; Huang, J.; Zhu, B.; Ye, J. The transition from vesicles to micelles induced by octane in aqueous surfactant two-phase systems. *J. Phys. Chem. B* **2002**, *106*, 219–225.

(60) Kundu, P. K.; Samanta, D.; Leizrowice, R.; Margulis, B.; Zhao, H.; Börner, M.; Udayabhaskararao, T.; Manna, D.; Klajn, R. Light-controlled self-assembly of non-photoresponsive nanoparticles. *Nat. Chem.* **2015**, *7*, 646–652.