# Reversible Transition between SDS@2β-CD Microtubes and Vesicles Triggered by Temperature

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**S** *Supporting Information*

**ABSTRACT:** Switching between association and dissociation is the well-known strategy for constructing responsive materials based on the host−guest complexes of cyclodextrins (CDs). In this work, we report that temperature may also trigger self-assembly transition in the supramolecular system composed of sodium dodecyl sulfate (SDS) and β-cyclodextrin (β-CD) at a molar ratio of 1:2. We reported previously that, at this ratio, SDS and β-CD form a channel-type SDS@2β-CD supramolecular unit, which further self-assembles into non-amphiphilic vesicles and microtubes driven by hydrogen bonding. Here, we report that the vesicles and microtubes can be reversibly switched between each other upon decreasing and increasing temperature. Control experiments in heavy water suggest that water molecules play a dominating role in the hydrogen bonding between SDS@2β-CD supramolecular units at lower concentration and higher temperature. Under opposite conditions, the hydrogen bonding between CDs is dominating. Therefore, for the 5% system, we observed a vesicle to microtube transition with a decreasing temperature, whereas for the 10% system, we observed the reverse process. Both processes are reversible. This is not only an example of temperature-triggered responsiveness in non-amphiphilic self-assemblies but also a new mode of responsiveness for the host−guest inclusion systems based on CDs. This temperature-responsive process is anticipated to shed light on the design and development of novel advanced materials.
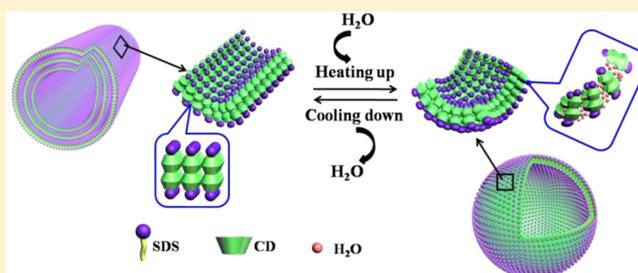
## ■ INTRODUCTION

The host−guest inclusion between cyclodextrins (CDs) and amphiphilic molecules has attracted increasing attention in the development of responsive molecular devices.[1−7] CDs are doughnut-like oligosaccharides with a hydrophilic exterior and a hydrophobic cavity.[3] The hydrophobic moiety of most amphiphiles can be included in the cavity of CDs.[8−10] As a result, the inclusion complexes become hydrophilic, which disfavors self-assembly formation via a hydrophobic effect.[11,12] Therefore, CDs are widely used to tune the properties of various supramolecular systems.[13−19] For instance, Jiang et al. reported that the surface tension and critical micelle concentrations of surfactants[13] can be increased because of the formation of inclusion complexes. Upon breaking the doughnut ring structure of CDs with α-amylase[13] or adding a competitive guest, these properties can be recovered. This rationale was also employed to tune the gel−sol transition in polymeric systems.[17,19] In azobenzene systems, the inclusion of the *trans* isomers into the cavity of CDs and the dissociation with *cis* isomers were used to create smart surface and responsive materials.[20]

The above examples have one feature in common, in that they are all based on the formation and dissociation of the inclusion complexes. However, the previous work in our group has pointed out that, when the inclusion complexes of CDs and

surfactants are formed at a molar ratio of host to guest being 2:1, the outer surface of the surfactants are completely covered by the hydroxyl groups of CDs, which are in the form of channel-type dimers.[9,15] As a result, the hydrogen bonding between these channel-type dimers occurs cooperatively to drive unamphiphilic self-assembled structures, such as vesicles, tubes, and lamellae. We found that this is a general phenomenon in surfactant systems and in long-chain polar hydrocarbons. Although these self-assemblies take the morphology just like classical amphiphilic self-assemblies, they are driven purely by hydrogen bonding, where the polarity of the head groups only influences the critical concentration for self-assembly.[9,15]

Because hydrogen bonds are sensitive to the temperature,[21] we expect that these novel self-assemblies may also be thermoresponsive. How would these hydrogen-bonding driven self-assemblies change with temperature? Herein, we report the reversible transformation between tubes and vesicles triggered by temperature in the SDS@2β-CD inclusion system. The basic self-assembling properties of the SDS@2β-CD supramolecular structures have been reported in our previous work,[22] where we

found that vesicle and tubular structures existed at the concentration range of 4−6 and 6−25% at 25 °C, respectively. In the present paper, we report that, upon a decreasing temperature, the vesicles will transform into microtubes in the concentration range of 4−6%, whereas the microtubes that are formed in the concentration range of 6−25% transform into vesicles with increasing temperature. The thermoresponsiveness of SDS@2$\beta$-CD is envisioned to open new possibilities for further applications of inclusion complexes.

## ■ EXPERIMENTAL SECTION

**Materials.** Sodium dodecyl sulfate (SDS, 99%) was purchased from Acros Organics Co. and used as received. $\beta$-Cyclodextrin ($\beta$-CD) was purchased from Sinopharm Chemical Reagent Co. with a water content of 14%. Ultrapure water was used throughout the work.

**Sample Preparation.** The samples were prepared according to procedures in ref 9.

**Dynamic Light Scattering (DLS) Measurements.** DLS measurements were conducted on an ALV/DLS/SLS5022F light scattering apparatus, equipped with a 22 mW He−Ne laser (632.8 nm wavelength). The samples were filtered with 450 nm filters. The scattering angle was fixed at 90°.

**Transmission Electron Microscopy (TEM) Observation.** The morphology of the self-assemblies was observed in a JEOL-100 CX II transmission electron microscope. The samples were prepared with negative-staining and freeze-fracture methods. For a negatively stained specimen, a drop of sample was placed on 230-mesh copper grids coated with Formvar film. Excess water was removed with filter paper, followed by negatively staining the film with uranyl acetate. After removal of the excess staining liquid by filter paper, the samples were placed at room temperature to dry for TEM observation. For freeze-fractured methods, a small amount of sample was placed on a 0.1 mm thick copper disk and then covered with a second copper disk. The sample was frozen by plunging into liquid propane, cooled by liquid nitrogen. Fracturing and replication were performed on a freeze-fracture apparatus (BalzersBAF400, Germany) at −140 °C. Pt/C was deposited at an angle of 45° to shadow the replicas, and C was deposited at an angle of 90° to consolidate the replicas. The resulting replicas were observed in a JEM-100CX electron microscope.

**Differential Scanning Calorimetry (DSC).** DSC measurements were carried out on a Q2000 DSC (TA Instruments, New Castle, DE) instrument. The sample was placed in an alumina crucible with air as the reference. The heating rate was 2 K/min from 15 to 60 °C for a 10% SDS@2$\beta$-CD sample. For a 5% sample, the heating rate was 2 K/min from 60 to 4 °C.

**Confocal Laser Scanning Microscopy (CLSM).** The samples were stained by Nile red according to the following method. A total of 15 $\mu$L of stock solution of Nile red in acetone (1 mg/mL) was added to a test tube. A desired amount of SDS@2$\beta$-CD aqueous solution was then added to the tube after volatilization of the acetone. The stained samples were allowed to equilibrate for 24 h. A drop of the samples was sealed between two slides, whose temperature was controlled by the circulator bath and then ready for CLSM observation. The CLSM experiments were conducted in florescence modes on A1R-si CLSM (Nikon, Japan).

**Fourier Transform Infrared Spectroscopy (FTIR) Measurements.** FTIR measurements were performed on Nicolet Magna IR 750 equipped with infrared microspectrography. The samples were frozen in liquid nitrogen and subsequently lyophilized for 48 h before FTIR measurements.

## ■ RESULTS AND DISCUSSION

**Reversible Transformation between Microtubes and Vesicles in the 10% SDS@2$\beta$-CD System.** We first studied the effect of the temperature on the SDS@2$\beta$-CD system at $C_{total}$ = 10%. At 25 °C, this system contains mainly microtubes, which has been reported in the previous work of our group.[22]

These microtubes scatter strongly, so that the system is highly turbid. However, upon elevating the temperature, the turbidity drops significantly. Figure 1 shows that a sharp drop of the
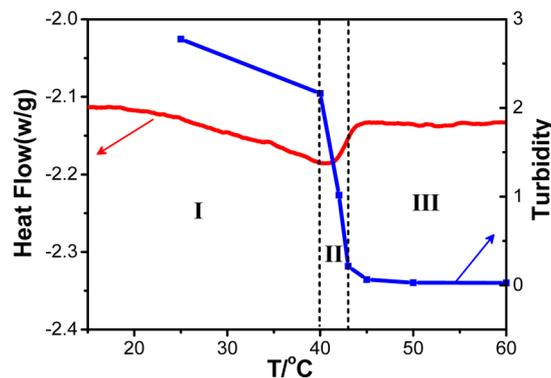


**Figure 1.** Variation in absorbance (blue line) and DSC (red line) curves for the SDS@2$\beta$-CD ($C_{total}$ = 10%) system against the temperature.

absorbance occurs at 42 °C. The absorbance−temperature curve can be divided into three regions, where the corresponding self-assembled structures were given in Figure 2. At a temperature below 40 °C (region I, Figure 1), the turbidity decreases slowly and microtubes are the major structures (panels a, d, and e of Figure 2). However, as the temperature amounts to 43 °C (region III), vesicles become dominant (panels c and g of Figure 2). These vesicles are still
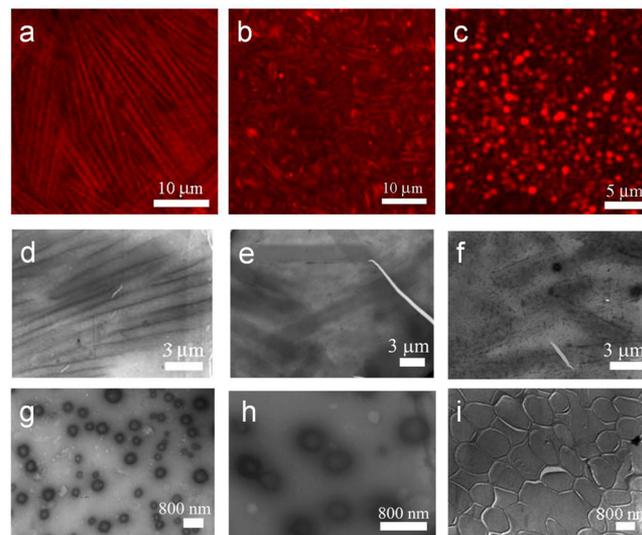


**Figure 2.** (a, b, and c) Images acquired by CLSM in fluorescence at 25, 42, and 50 °C, respectively. (d−h) TEM micrographs (from d to h, 25, 40, 42, 43, and 60 °C, respectively). (i) Freeze-fracture transmission electron microscopy (FF-TEM) micrographs at 43 °C of the SDS@2$\beta$-CD ($C_{total}$ = 10%) system. It is noted that the size and morphology for panels g and i are a little bit different, although they were acquired for the same sample at the same temperature of 43 °C. This is probably because, at this temperature, the structures are very sensitive to temperatures. For FF-TEM measurements, directly freezing the sample from 43 °C may lead to a temperature drop before the sample is completely frozen. Therefore, the structures obtained in FF-TEM may represent a state at a lower temperature, so that there are discrepancies for images obtained from direct TEM and FF-TEM observations.

stable at 60 °C (Figure 2h), suggesting that the concentration of 10% is much higher than the critical concentration for vesicle formation. In contrast, the vesicles formed in the 4−6% systems would disappear as the temperature was elevated to 60 °C. In the second region, where the turbidity drops steeply, both the microtubes and vesicles were observed. This signifies that prominent phase transition occurs in the narrow temperature range between 40 and 43 °C. In combination with the DSC measurements, where a broad endothermic peak was observed, the transition temperature between the microtubes and vesicles was estimated about 42 °C. According to the DSC results, the enthalpy change is about 9.18 kJ/mol, which is consistent with the heat of melting of very long and stiff tubes formed in aqueous mixtures of 2-phenylbenzimidazole-5-sulfonic acid and cetyltrimethylammonium bromide.[23]

It is worth noting that the transition between microtubes and vesicles was completely reversible (see Figure S1 of the Supporting Information). Upon decreasing the temperature from 60 to 25 °C, both the turbidity and the microtubes recovered. This inspires that the vesicles formed in the 4−6% region at 25 °C, which we reported previously,[9] may be transformed into tubes with a decreasing temperature. To verify this, in the following, we studied the phase and self-assembly transition in the 5% system.

**Reversible Transformation between Vesicles and Microtubes in the 5% SDS@2$\beta$-CD System.** The turbidity for the vesicular system at 5% is very low. However, upon decreasing the temperature, the turbidity increases significantly (Figure 3). Microtubes were observed coexisting with vesicles
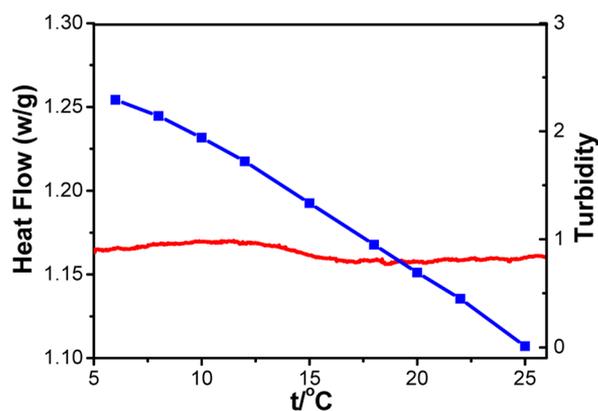


**Figure 3.** Variation in turbidity (blue line, measured at 630 nm) and DSC (red line) curves for the SDS@2$\beta$-CD ($C_{total}$ = 5%) system against the temperature.

as the temperature drops to 18 °C (Figure 4). However, no obvious transformation enthalpy was observed in this process. To understand this phenomenon better, the critical aggregation concentrations (CACs) for the microtubes and vesicles at different temperatures were estimated using DLS and TEM techniques. We found that the CACs for both the vesicles and microtubes drop with decreasing the temperature (Table 1). As the temperature decreased to 18 °C, the CAC for the microtubes becomes 5%, while that for the vesicles decreases to 1%. As the temperature dropped to 4 °C, the CACs for the microtubes and vesicles were further reduced to 2.5 and 0.5%, respectively. This suggests that the transition from vesicles to microtubes with a decreasing temperature is probably related to the change of their respective CACs. Because the CAC of the vesicles is always lower than that of the microtubes, vesicles and
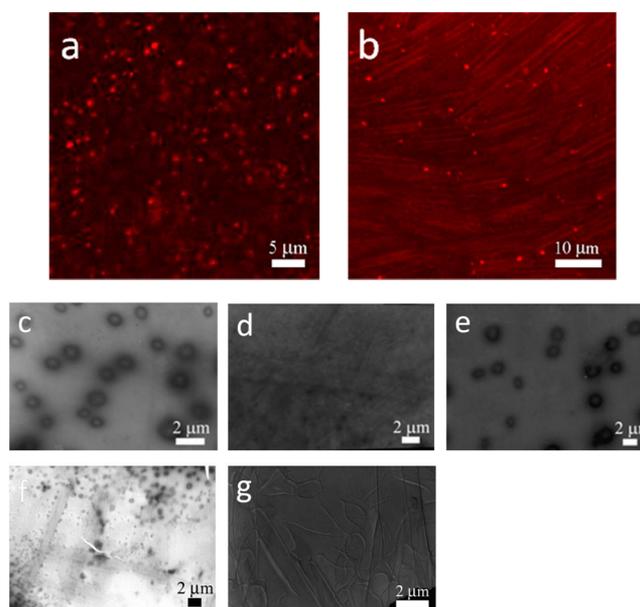


**Figure 4.** (a and b) Images acquired by CLSM in fluorescence at 25 and 15 °C, respectively. (c) TEM micrographs at 25 °C. (d and e) TEM micrographs at 18 °C. (f and g) TEM and FF-TEM micrographs at 4 °C of the SDS@2$\beta$-CD ($C_{total}$ = 5%) system.

**Table 1. CACs of Microtubes and Vesicles at Different Temperatures[a]**

| $t$ (°C) | $C_{tubes}$ (%) | $C_{vesicles}$ (%) |
| --- | --- | --- |
| 25 | 6 | 4 |
| 18 | 5 | 1 |
| 15 | 4 | 1 |
| 4 | 2.5 | 0.5 |

[a]$C$ is the total mass concentration of $\beta$-CD and SDS.

microtubes coexist from 18 to 4 °C in this concentration range. Meanwhile, owing to the respective CACs of vesicles and microtubes dropping with the decreasing temperature, coexistence of the microtubes and vesicles was also found in the concentration range of 6−25% when the temperature was below 25 °C.

The phase diagram for the SDS@2$\beta$-CD inclusion system was composed on the basis of the TEM and DLS results. The results are shown in Figure 5. This diagram tells that, in the broad temperature range of 4−60 °C, the effective region of
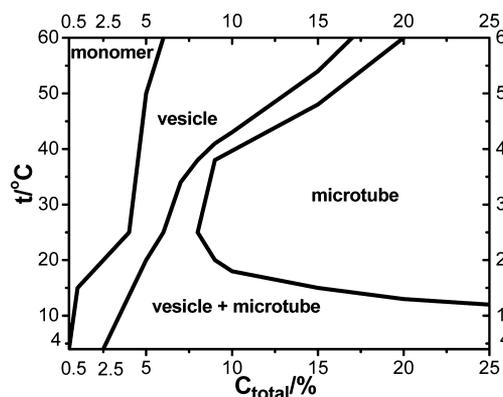


**Figure 5.** Phase diagram for the SDS@2$\beta$-CD complex system.
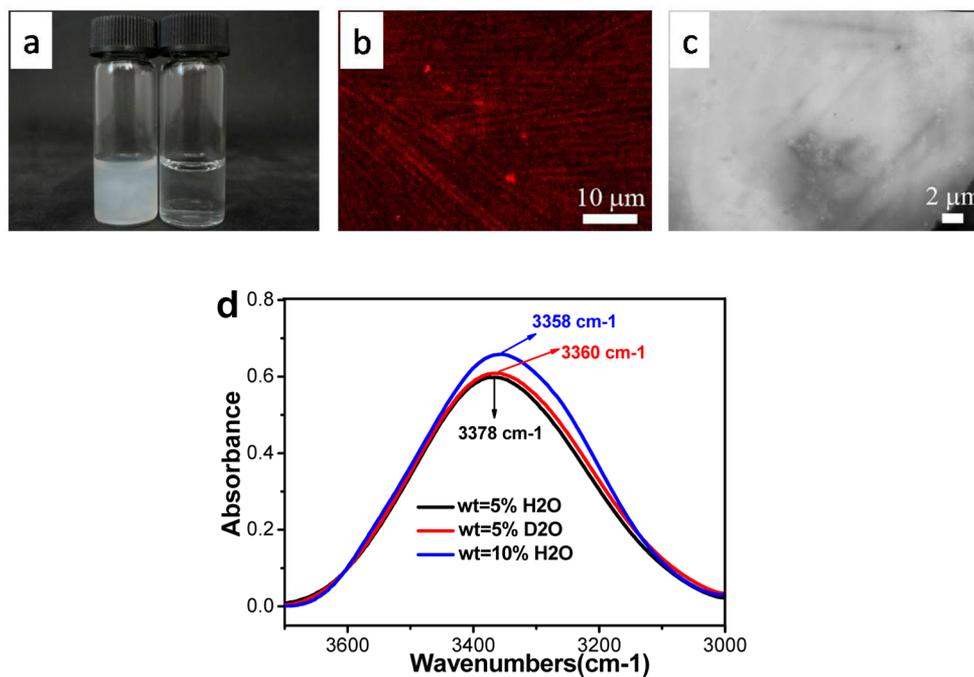
**Figure 6.** (a) Macroscopic images of the 5% SDS@2$\beta$-CD sample in D$_2$O (left) and H$_2$O (right) at 25 °C. (b and c) CLSM and TEM micrographs for the 5% SDS@2$\beta$-CD sample in D$_2$O at 25 °C, respectively. (d) IR results of the lyophilized 5% sample in H$_2$O and D$_2$O, separately, and the 10% sample in H$_2$O.

vesicles would be enlarged from 0.5 to 20%, while the microtubes could be formed at a concentration from 2.5 to 25%. This means that the temperature is a powerful means for switching the reversible transformation between microtubes and vesicles.

**Mechanism for the Reversible Transformation between Microtubes and Vesicles Induced by the Temperature.** We have verified in our previous work that hydrogen bonding is the major driving force for the self-assembly formation in the surfactant@2$\beta$-CD inclusion systems. However, by then, we did not go into details about the hydrogen bonding in these systems. Do these hydrogen bonds simply occur between $\beta$-CDs? Are water molecules involved in the hydrogen bonding? To answer these questions, a control experiment was performed by replacing water with D$_2$O.[21] It is well-known that D$_2$O has a stronger ability in self-forming D−O−D bonds.[24] If water molecules were involved in the hydrogen bond formation, replacing water with D$_2$O will probably lead to a self-assembly transition. Figure 6 shows that the turbidity of the 5% SDS@2$\beta$-CD system in D$_2$O is significantly higher than that in water at 25 °C. CLSM and TEM results demonstrated that microtubes rather than vesicles were observed. Meanwhile, for the 10% SDS@2$\beta$-CD system, replacing water with D$_2$O did not lead to self-assembly changes. Therefore, it is supposed that water molecules have played an important role in the vesicle formation but not in that for microtubes. To further verify this conclusion, the infrared (IR) measurements for the lyophilized 10% sample in H$_2$O and 5% SDS@2$\beta$-CD samples in H$_2$O and D$_2$O, respectively, were conducted. It can be clearly seen in Figure 6d that the 5% sample in D$_2$O exhibits only the OH vibration (3360 cm$^{-1}$), instead of the OD vibration (2200−2740 cm$^{-1}$).[25] This is because the −OD of the frozen sample in liquid nitrogen was replaced again by −OH because of the quick exchange with H$_2$O during the subsequently lyophilized process.[25,26] For this

reason, the hydrogen bonds for the 5% system lyophilized from both H$_2$O and D$_2$O are all formed between OH groups. However, it is obvious that the OH vibration for the vesicles formed in H$_2$O occurs at 3378 cm$^{-1}$, whereas that for the microtubes formed in D$_2$O has shifted to a lower wavenumber of 3360 cm$^{-1}$. This suggests that there are more hydrogen bonds formed with H$_2$O in the vesicles than in the microtubes.[27] Because both systems are formed out of the same amount of SDS@2$\beta$-CD, the only possible reason for the extra hydrogen bonds in the vesicles should be contributed by "structural water"; namely, some H$_2$O molecules have been involved in the hydrogen bonding. If this is true, we expect that the wavenumber for the microtubes should be always lower than that for the vesicles, regardless of the concentration of the original suspensions, because the OH vibration depends only upon the nature of the hydrogen bonds rather than the concentrations for the lyophilized systems.[27] This is indeed the case. Figure 6d demonstrates that the OH vibration in the 10% system, where microtubes are present, occurs at a lower wavenumber (3358 cm$^{-1}$) when compared to that for the 5% system (3378 cm$^{-1}$), which forms vesicles. On the basis of these facts, we conclude that the microtubes are driven predominantly by the hydrogen bonds between the hydroxyl groups of CDs, whereas those for the vesicles are driven coorperatively by the hydrogen bonding between water and CDs.

According to the above information, the temperature-dependent reversible transition between microtubes and vesicles is probably because the different effects of the temperature on the hydrogen bonds between H$_2$O and that between $\beta$-CD. To verify it, the vibration of hydrogen bonds in the 5 and 10% systems with varying temperatures was conducted (Figure 7). With increasing the temperature, the wavenumbers in both systems shift toward higher values, suggesting the weakening of the hydrogen bonds.[28] According
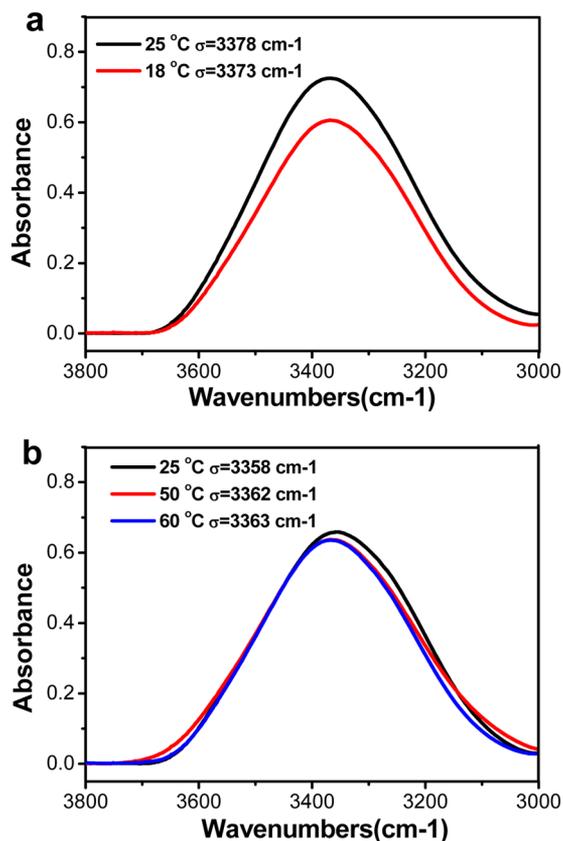
**Figure 7.** IR results of the hydrogen bonds for the (a) 5% and (b) 10% SDS@2β-CD systems at different temperatures.

to the literature, the extent of changing in the hydrogen bond with the variation of the temperature follows the following order:[21,29] water−water < water−CD < CD−CD. This means that with increasing the temperature, the strength of the hydrogen bond between water decreases slower than that between CDs. Therefore, in the 10% system, it is possible that the hydrogen bonding between CDs becomes weaker than that between CD and water or water and water with increasing the temperature. This allows water molecules to participate in the hydrogen bonding between two neighboring SDS@2βCD tiles as the temperature elevates. Namely, water molecules act as

mediators between the SDS@2βCD units. Such a molecular model allows for larger curvature formation, which leads to microtube-to-vesicle transition in the process of promoting the temperature. Similarly, in the opposite process, the hydrogen bonds between CDs become the strongest, which facilitates the formation of the microtube transition. The proposed transition mechanism is illustrated in Scheme 1.

## ■ CONCLUSION

In conclusion, we achieved the reversible transition between microtubes and vesicles by variation of the temperature in the SDS@2β-CD supramolecular systems. The transition from vesicles to microtubes occurred as the temperature dropped, while the microtubes would convert into vesicles with the increase of the temperature. The achievement of the transformation between the microtubes and vesicles depends upon the variation of the strength of hydrogen bonds. At low temperatures and high concentrations, the hydrogen bonding between CDs is very strong, so that microtubes are the favorite structures. Under opposite conditions, the hydrogen bonding between water and CDs becomes dominant. The mediation of water molecules between the channel-type SDS@2β-CD units allows for larger curvature for the self-assembled structures. Therefore, vesicles are generated. This intelligent behavior provides us with the new prospective of stimulus−responsive chemistry in inclusion complexes based on CDs. We expect that this will be a cornerstone for constructing advance materials of this class.

## ■ ASSOCIATED CONTENT

### Ⓢ Supporting Information
Reversible ultraviolet−visible (UV−vis) results. This material is available free of charge via the Internet at http://pubs.acs.org.

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### Notes
The authors declare no competing financial interest.

**Scheme 1. Schematic Aggregate Morphology Transition of SDS@2β-CD Complexes with the Variation of the Temperature**
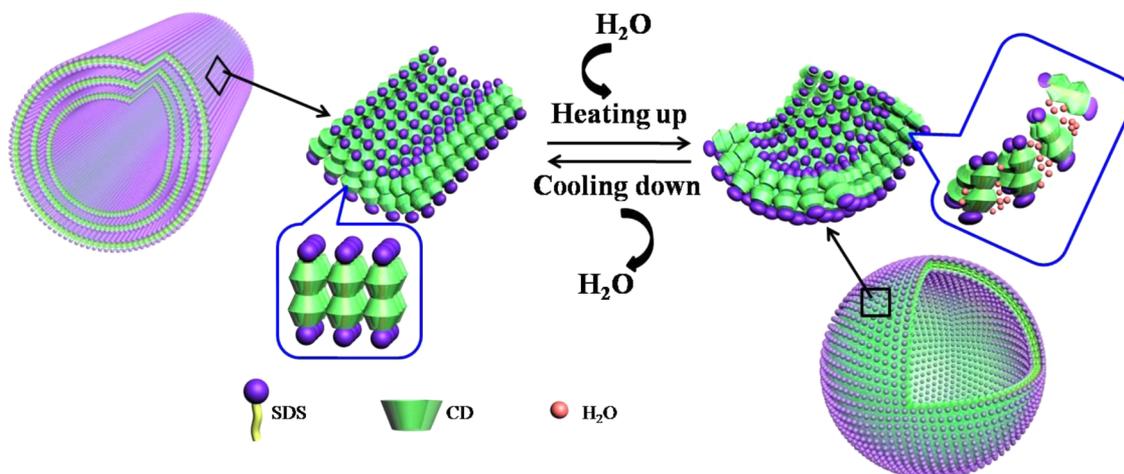
## ACKNOWLEDGMENTS

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