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Polymeric Self-Assembly into Micelles and Hollow Spheres with Multiscale Cavities Driven by Inclusion Complexation

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Abstract: The inclusion complexation between β-CD (β-cyclodextrin) and adamantyl group (ADA) is used as a driving force in constructing polymeric micelles. The micelles composed of a hydrophobic core of PtBA-ADA and a hydrophilic shell of PGMA-CD show unique properties due to the presence of β-CDs on the micellar surface. The micelles can be converted to hollow spheres of PGMA-CD networks. The hollow spheres possess a central hole in the size of submicrometers and many cavities of β-CDs of 0.7 nm on the surface.

Introduction

Cyclodextrins (CDs) are a family of cyclic oligomers composed of glucopyranose units linked by α-1,4 glycosidic bonds.[1] CDs are characteristic of a hydrophilic exterior surface and hydrophobic interior cavity, which can accommodate a wide range of molecules as guests. Among the varieties of such host−guest pairs, the inclusion complex of β-CD and adamantly group (ADA) has been mostly investigated for their high association constant.[2−4] This interaction has been successfully employed from β-CD-containing and ADA-containing molecules to build supramolecular polymers[5−7] as well as supramolecular assemblies.[8−11]

In recently years, our group has developed block-copolymer-free strategies to fabricate polymeric micelles using polymer pairs as building blocks.[12,13] These novel approaches result in noncovalently connected micelles (NCCM), in which only hydrogen bonds rather than chemical bonds exist between shell and core. Rotello's group[14] has reported supramolecular vesicles formed by the self-assembly of copolymer pairs with complementary interchain hydrogen bonding. In all these self-assembly processes hydrogen bonding between the component polymers serves as the driving force, which differs from the micellization of block copolymers in selective solvents.

In the present work we, for the first time, report using the inclusion complexation as driving force to construct polymeric micelles. A hydrophilic polymer PGMA-CD containing β-CD and hydrophobic ADA-containing polymer PtBA-ADA (Scheme 1) were used as building blocks to construct micelles. Driven by the inclusion interaction between the β-CD and ADA, the micelles in aqueous media with PtBA-ADA as the core and PGMA-CD as the shell are formed. The resultant micelles stably dispersed in water possess unique characters: it contains both a hydrophobic PtBA-ADA core on a scale of hundreds of nanometers and hydrophobic cavities at a size of 0.7 nm in the shell. Taking advantages of the cavities being able to accommodate different molecules, the micellar surface can be easily modified to either hydrophobic or charged ones. Besides, by subsequently cross-linking the shell and dissolving the core, the micelles can be converted to β-CD-containing nanocages. The resultant hollow spheres contain multiscale holes: the large central ones and β-CD interior cavities.

Result and Discussion

CD-containing polymers can be obtained by either polymer modification with CD-derivatives[15−18] or polymerization of CD-containing monomers.[19,20] However, few water-soluble CD-containing homopolymers with linear structures were reported. The difficulties in preparing such polymers are associated with the synthesis of monomers with *mono*-vinyl substitution of

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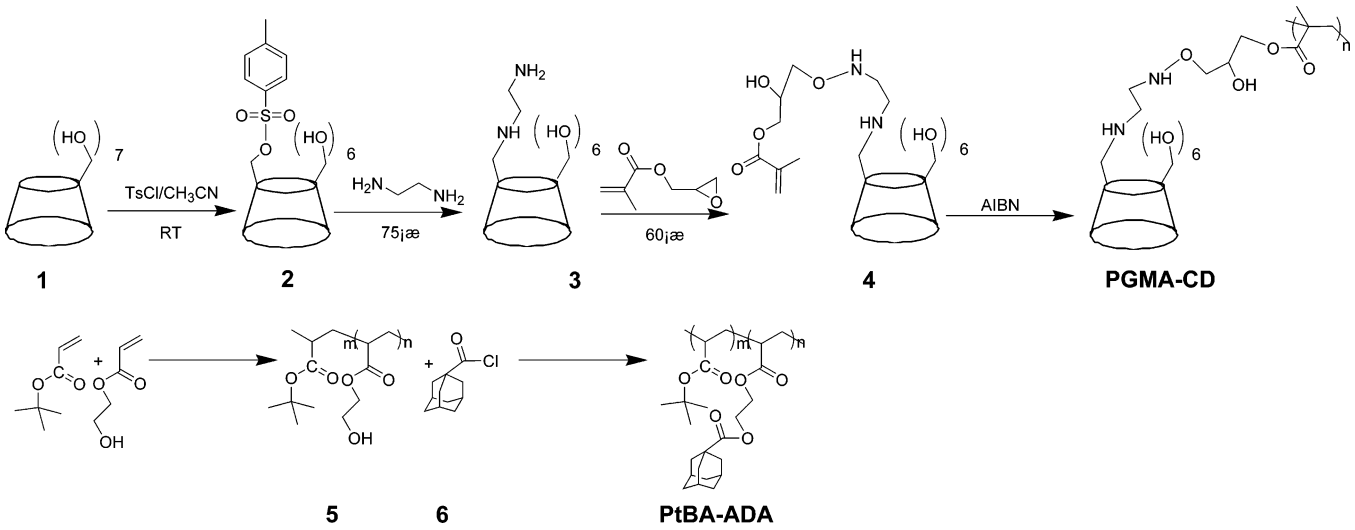
Scheme 1. Synthesis Procedures of PGMA-CD and PtBA-ADA



β-CD. A CD carrying multiple vinyl groups, which is easily produced, leads to highly branched or cross-linked polymers. In this work, by carefully controlling the reaction conditions from both **1** to **2**[21] and **3** to **4** (Scheme 1), we succeeded in obtaining monosubstituted monomer **4**, which was confirmed by MALDI-TOF measurements (Figure S1, Supporting Information). The water soluble polymer PGMA-CD was prepared by free radical copolymerization of **4** in DMF, and its molecular weight was found to be $M_w = 1.04 \times 10^4$ by size exclusion chromatography (SEC).

The hydrophobic copolymer PtBA-ADA was prepared as follows. First the copolymer of *tert*-butyl acrylate and hydroxylethyl acrylate (**5**) was produced by ATRP polymerization. ADA groups were then introduced by the reaction of copolymer **5** with **6** (Figure S2, Supporting Information). The resultant copolymer PtBA-ADA contains ADA groups (10 mol %) and has an M_n of $1.87 \times 10^4$and $M_w/M_n = 1.28$ measured by SEC. The synthesis details of the monomers and polymers are described in the Supporting Information.

Both PtBA-ADA and PGMA-CD can be dissolved in dimethyl formamide (DMF). The viscosity of the mixed solutions of the two polymers in DMF at 25 °C shows a considerable positive deviation from the expected values by the additivity law of the component solutions (Figure S3, Supporting Information). This implies that the two polymers form a soluble complex in DMF due to the β-CD/ADA inclusion interaction.[22] The deviation decreases with increasing temperature, and at 50 °C the viscosity obeys the additivity law indicating that the inclusion interaction no longer exists. When water was added dropwise to the PtBA-ADA/DMF solution, precipitate immediately formed as expected. However, when a large volume of water was added into the *mixed* solution of PGMA-CD and PtBA-ADA in DMF over a broad range of the molar ratio of β-CD/ADA from 0.3 to 2.2, stable particles appeared. Five samples of the dispersed particles M1, M2, M3, M4, and M5 with molar ratios of β-CD to ADA being 0.33, 0.43, 1.08, 1.63, and 2.17, respectively, were used in this study. As shown in Figure 1, the size of the resultant particles of the five samples M1−M5 depends on the composition, i.e., the weight ratio of PGMA-CD to PtBA-ADA or the molar ratio of β-CD to ADA. It is interesting to see that when the molar ratio of β-CD/ADA is as small as 0.33 (M1), the polymers are still able to form stable particles. From chemical intuition, we believe that the inclusion interaction of ADA and β-CD induces the self-assembly of the two polymers forming the micelles with PtBA-ADA as the core and PGMA-CD as the shell. As shown in Figure 1, when the β-CD/ADA ratio increases, the particle size decreases first and then increases after $\langle Dh \rangle$ goes through its minimum. We may interpret the result as follows. In general, the hydrophilic PGMA-CD chains act as a stabilizer of the hydrophobic core of PtBA-ADA, so the more PGMA-CD, the smaller the core when the relative amount of the stabilizer is small (M1−M3). Meanwhile, increasing PGMA-CD may cause more chains to gather around the core leading to an increase of the shell thickness. This fact may become dominated when the β-CD/ADA ratio is large (M3−M5).

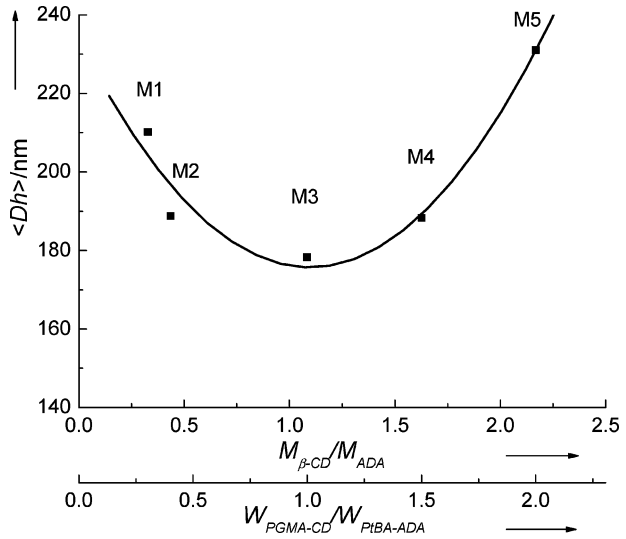


Figure 1. $\langle Dh \rangle$ of PGMA-CD/PtBA-ADA micellar solutions as a function of composition (molar ratio of β-CD moieties to ADA groups and weight ratio of PGMA-CD to PtBA-ADA). All the solutions have the same PtBA-ADA concentration of 8.13×10^{-5} g mL^{-1}; in the final solution the volume ratio of water to DMF is 40/1.

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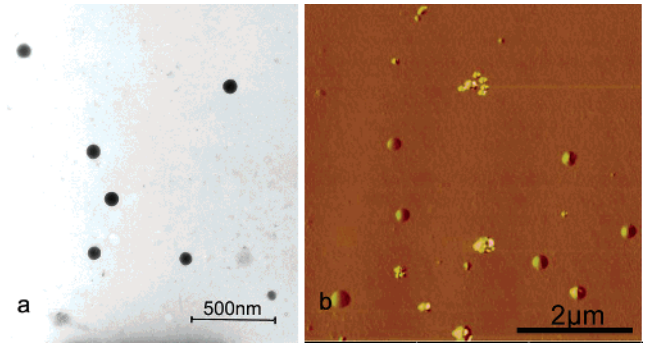

Figure 2. Electromicroscopy observations of micelles: (a) TEM image and (b) height-contrast AFM image of PGMA-CD/PtBA-ADA micellar solutions (M3)

The morphology of the particles explored by TEM and AFM is shown in Figure 2a and 2b. The TEM image displays spherical particles with an average size around 100 nm and a low polydispersivity, smaller than that from DLS measurements. It could be attributed to the low density of the outer shell composed of hydrophilic PGMA-CD chains causing a weak contrast to the background. This opinion is supported by AFM observation giving the particle diameter around 150−200 nm shown in Figure 2b. Over the whole range of the CD/ADA ratio we studied, only global particles were observed by TEM and AFM observations, and the sizes of the particles are generally in accordance with those found in DLS measurements.

^{1}H−^{1}H Nuclear Overhauser Effect (NOE) measurements of the PGMA-CD/PtBA-ADA micelles in water provided direct evidence of the inclusion interaction. NOE technique is widely used in supramolecular chemistry[23−25] as it is very sensitive to the interproton distance. No NOE could be observed if the interproton distance is larger than about 0.4 nm.[26] As shown in Figure 3, in PGMA-CD/PtBA-ADA micellar solutions (M3) irradiation of Ha of ADA induced both NOE signals of H3 and H5 existing in the interior of a β-CD. Similarly, signals of Ha, Hb, and Hc of ADA were observed when H3 or H5 of the β-CD was selectively presaturated. These results clearly indicate the immediate proximity between the protons of ADA and those in the cavities of β-CD, which confirms that the ADA groups are trapped by the cavities of the β-CD forming inclusion complexes.

It was interesting to find that, in the mixed solution of PGMA-CD and PtBA-ADA in DMF, respective presaturation of Ha, Hb, and Hc of ADA gave only the significant signal of H3 but not that of H5 which is closer to the smaller rim of the β-CD (Figure S4, Supporting Information). This means that Ha, Hb, and Hc are too far from H5 to present its detectable signals. In other words, in DMF, PGMA-CD and PtBA-ADA form relatively loose interactions.

As the inclusion interaction takes place mainly at the interface between the core and shell in PGMA-CD/PtBA-ADA, we believe that a great deal of β-CD cavities would remain intact in the shell, which endows the micelles with a series of unique

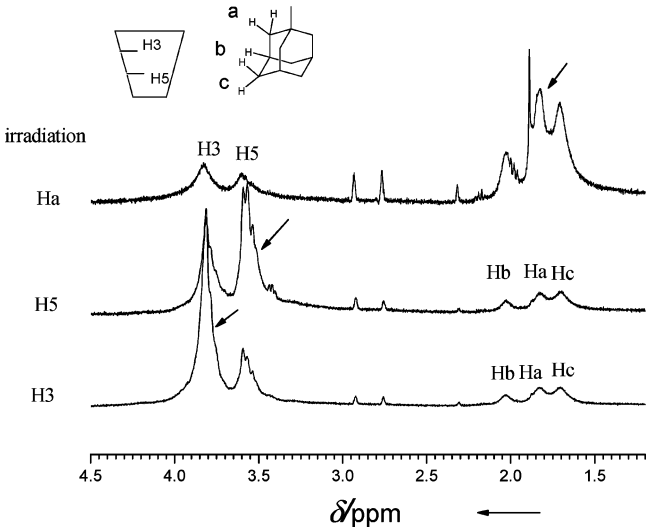

Figure 3. NMR NOE difference spectra of PGMA-CD/PtBA-ADA micelles (M3). Ha of adamantyl groups (upper), H5 (middle), and H3 (lower) of β-CD moieties were irradiated, respectively. Difference spectra were obtained by subtracting the FID data from those of the control experiment obtained by irradiation at a no-resonance area.

properties. These CD cavities provide a broad range of opportunities for further surface modifications of the micelles by incorporating different kinds of functional molecules. In fact, surface modification of nanoentities is an important step to make them meet different requirements in various areas. Surface modification of nanoparticle is often characterized by measuring the zeta potential of the solutions.[27] For illustrating such possible further developments, adamantyl derivatives containing respective anionic or cationic groups, i.e., 1-adamantanecarboxyl acid (ADA-ca) and 2-adamantanamine hydrochloride (ADA-amine), were used as the model guest compounds. The zeta-potential measurements of PGMA-CD/PtBA-ADA micellar solutions (M3) in the presence and absence of ADA-ca and ADA-amine against pH were performed. At the neutral pH range, the PGMA-CD/PtBA-ADA micelles have a neutral surface. However, it could be converted to negatively (−40 mv) or positively (20 mv) charged ones simply by adding ADA-ca and ADA-amine in the solutions, respectively. Clearly, the transition from a neutral surface to an anionic or a cationic surface was realized via the inclusion interaction between the β-CD on the micellar surface and the ADA derivatives. Furthermore, the isoelectronic point (IEP) of the micellar solutions shifted to opposite directions: from 7 to 5 by adding ADA-ca and from 7 to 8 by adding ADA-amine.

The loading behavior of the micelles was also studied using fluorescent chromophore 8-anilino-1-naphthalene sulfonate (ANS) as a model guest leading to a better understanding of the structure of the micelles. It is well-known that the fluorescent characters of ANS largely depend on its microenvironment and an apparent intensity increase and peak blue shift can be observed when ANS molecules move from water to the β-CD cavities forming the inclusion complex.[28,29] We first measured the fluorescence emission of ANS in water containing PGMA-

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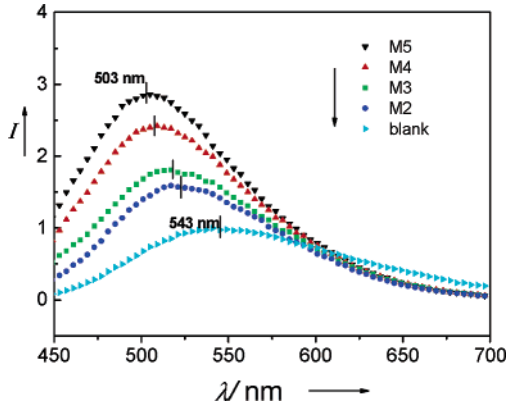

Figure 4. Fluorescence spectra of ANS in M2 (blue), M3 (green), M4 (red), and M5 (black) solutions. The β-CD molar concentrations (in 10^{-5} M) are 2.44 (M2), 6.11 (M3), 9.17 (M4), and 12.2 (M5). The bottom curve is for ANS in water; ANS concentration is 5×10^{-5} M. The excitation wavelength is 370 nm, and the emission was recorded from 450 to 700 nm.

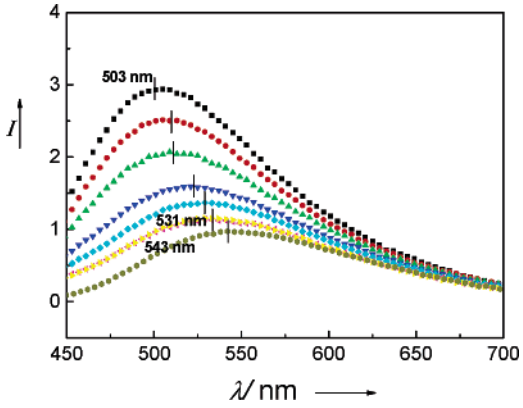

Figure 5. Fluorescence spectra of ANS in M5 solutions after addition of different amounts of ADA-ca: The final concentrations (in 10^{-5} M) of ADA-ca are 0 (black), 2.29 (red), 9.16 (green), 153 (blue), 458 (cyan), 1220 (magenta), and 5800 (yellow). The bottom curve is for ANS in water; ANS concentration is 5×10^{-5} M.

CD with different concentrations (Figure S5, Supporting Information). The intensity and the blue shift of the ANS emission increase with the concentration of the β-CD. When the β-CD molar content in the solutions is equal to that of ANS (5×10^{-5} M), the emission intensity is increased 8 times and the peak shifts from 543 to 489 nm. Similar observations were made for the solutions of ANS with the PGMA-CD/PtBA-ADA micelles. As shown in Figure 4, compared to the blank solution of ANS in water, all the micellar solutions of M2, M3, M4, and M5 cause an apparent increase in the emission intensity and a blue shift of the emission peak of ANS, which indicates that the CD cavities in the micelles have the ability to accommodate the ANS molecules. Furthermore, the effects of the micelles on the emission behavior of ANS are clearly intensified when the molar ratio of β-CD to ADA increases in the sequence from M2 to M5. This result is understandable as the increase in the molar ratio of β-CD to ADA in the micelles from M2 to M5 means more β-CD cavities are available. We now discuss the two extreme cases of M2 and M5 being used. In the case of M2 where the ratio of molar content of β-CD to ADA is only 0.43, we still observed an apparent emission intensity increase and blue shift. It means that even when the molar amount of β-CD is much less than that of ADA, there are still empty β-CD cavities in the micelles. This conclusion is in accordance with our model for the micelles, i.e., the ADA/β-CD complex mainly exists in the core−shell interface area of the micelles and a great part of the ADA groups are buried in the micellar core. Therefore, free β-CD cavities are always available in the surface area. In the case of M5 in which the β-CD exceeds largely (the molar ratio of β-CD to ADA is 2.17), the emission peak shifts to 503 nm and the intensity is increased about 3 times. Obviously, these effects of M5 on the emission of ANS are much less pronounced than that observed for PGMA-CD on solutions of ANS (Figure S5, Supporting Information). It implies that, for the micelles with a high PGMA-CD content, the PGMA-CD shell is rather thick so that the ANS molecules may not be able to reach the β-CD cavities existing in the interior part of the shell.

It was reported that the stability constant of the inclusion complexes of β-CD and ADA group is ca. 100 times as high as that of the complexes of β-CD with ANS.[2] Taking advantage

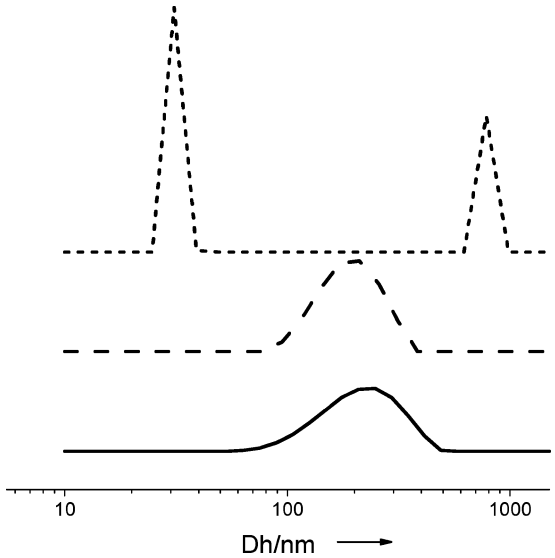

Figure 6. DLS measurements of M3 solutions, before (solid) and after shell cross-linking (dash) and then treated in DMF at 50 °C (short dash).

of this fact we may be able to replace the ANS molecules included in the cavities of β-CD by adding ADA-ca. The solutions of M5 with ANS loaded were used to test this opinion by fluorescence measurements. As shown in Figure 5, the emission intensity of ANS (5×10^{-5} M) decreases gradually and the emission peak shifts back when more ADA-ca is added. When a greater excess amount of ADA-ca (0.012 M) is added, both the emission intensity and the peak position of ANS no longer change with a further increase of the concentration ADA-ca. In this case, the peak position reaches 531 nm, and the emission intensity is quite close to that of the blank solution of ANS in water. The results indicate that the included ANS can be mostly but not completely replaced by ADA-ca.

Polymeric hollow spheres have great potential for the encapsulation of large quantities of guest molecules.[30−32] To develop a hollow nanostructure from the PGMA-CD/PtBA-ADA micelles, shell cross-linking and core removal were

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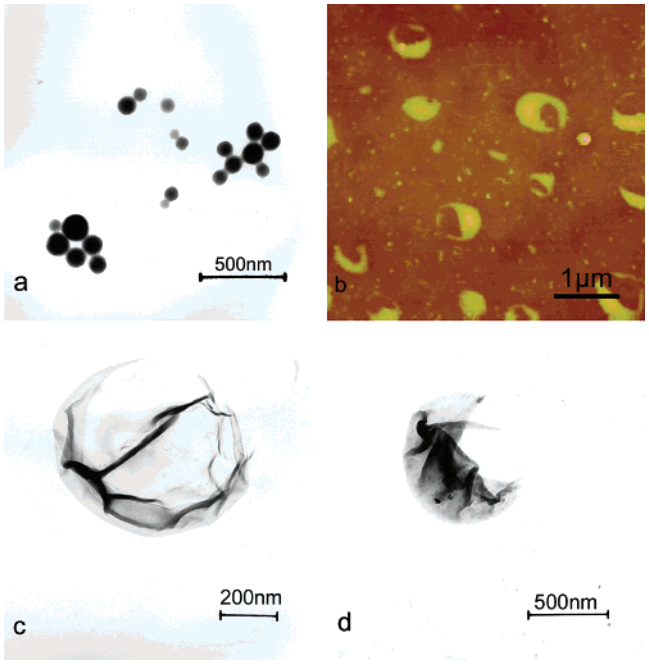

Figure 7. TEM (a) image of cross-linked micelles M3 and AFM (b) and TEM (c and d) images of the corresponding hollow spheres.

performed.[12,13,33,34] The resultant hollow aggregates are expected to have multiscale cavities, i.e., a large central hydrophilic cavity and the inherent inner hydrophobic cavities of β-CD molecules (7.5−8.3 Å).[1] Epichlorohydrin has been widely used to react with hydroxyl groups for cross-linking CD-containing polymers.[35−37] However, it is not practical in the present case, as the required strong basic condition could induce hydrolysis of t-BA group and destroy the structure of PGMA-CD/PtBA-ADA particles. Therefore, we used biochemical reagent glutaraldehyde (GA) for cross-linking the amino groups[38] in PGMA-CD. As shown in Figure 6 the Dh distribution curve of the micelles varied little after the cross-linking reaction. In other words, the reaction did not alter the integrity of the micelles as we desired. For removing the core of PtBA-ADA, we need a solvent which could not only dissolve PtBA-ADA but also destroy the inclusion interaction between β-CD and ADA. As we mentioned above, in DMF at a higher temperature (50 °C) the inclusion interaction between β-CD and ADA disappeared as indicated by the viscosity measurement (Figure S3, Supporting Information). Therefore, the micellar solution was treated with DMF around 50 °C overnight. The resultant solutions show a bimodal size distribution (Figure 6) with a peak located at about 20−30 nm and another one ranging from 500 to 900 nm. The former could be attributed to the free PtBA-ADA chains from exclusion of the PGMA-CD/PtBA-ADA complex,[39] and the latter, to the hollow spheres. Compared to the size of the micelles in water, the diameter of the hollow spheres is much expended as a result of strong swelling of the cross-linked PGMA-CD in DMF[40] (Figure S6, Supporting Information).

Compared to the images shown in Figure 2, the morphology of the cross-linked micelles M3 shown in Figure 7a does not display a substantial change of the micelles in shape and size caused by cross-linking. However, dramatic changes took place when the micellar core was removed: after being treated with DMF at 50 °C overnight, discrete and collapsed hollow spheres in a size range of about 500−1000 nm were observed in the AFM image (Figure 7b). It implies that the hollow spheres with thin walls cannot keep their overall integrity under the drying process for AFM measurements. In addition, many small particles about 20 nm scattered were observed as well, which can be obviously attributed to the free PtBA-ADA polymer chains.[39] The TEM results (Figure 7c, 7d) are in agreement with that of AFM showing typical images of collapsed thin-wall hollow spheres, which is reminiscent of the hollow structures obtained by a layer-by-layer technique reported in the literature.[41,42]

Conclusion

As summarized schematically in Figure 8, we developed a new route to fabricate noncovalently connected micelles (NCCM) of PGMA-CD/PtBA-ADA in aqueous media based on host−guest interaction of β-CD and ADA. The presence of the β-CD cavities in the micellar shell provides broad opportunities to modify the micellar surface to meet different requirements in applications. Via shell cross-linking and core removal of the micelles, hollow spheres composed of β-CD-containing polymers were also obtained. These hollow spheres possess multiscale holes, i.e., the large central one at a size of submicrometers and many small β-CD cavities at 0.7 nm.

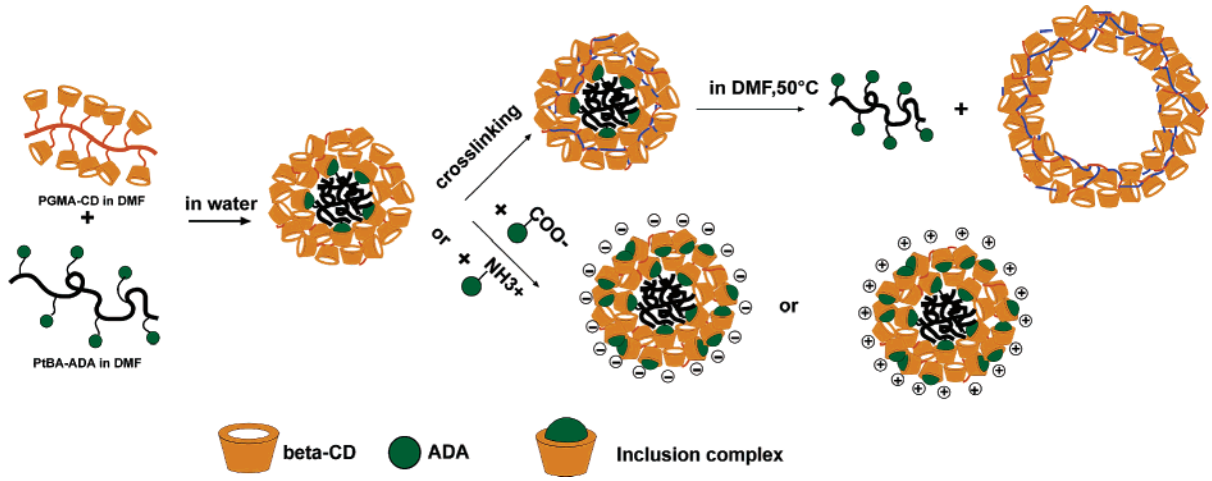

Figure 8. An illustration of PGMA-CD/PtBA-ADA micelles and their characters.

Acknowledgment. The National Natural Science Foundation of China (NNSFC, Project No. 50333010) is acknowledged for supporting this research.

Supporting Information Available: Details of synthesis, micellization, hollow spheres preparation, and the characterizations are shown in the Supporting Information. This material is available free of charge via the Internet at http://pubs.acs.org.

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