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Tubular Structures Self-Assembled from a Bola-Amphiphilic Pillar[5]arene in Water and Applied as a Microreactor

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Supporting Information

ABSTRACT: Various nanomorphologies were obtained by simply changing the fabrication conditions, such as the pH of the system, different solvent, or different concentration, of bola-amphiphilic pillar[5]arene Bola-AP5. Importantly, hybrid microtubules as a microreactor were successfully prepared by directly reducing $AuCl_4^-$ on the surface of Bola-AP5-based tubular structures in water.

Self-assembly of nanomaterials to form well-ordered hierarchical structures provides great opportunities in optical, electronic, and magnetic materials and devices.[1] Among a variety of molecular building blocks for self-assembly, such as block copolymers, peptide derivatives, and lipid molecules, macrocyclic amphiphiles,[2] consisting of rigid cycles and flexible functional groups, are excellent candidates for creating well-defined supramolecular structures in selective solvents.

As a new class of macrocycles after crown ethers,[3] cyclodextrins,[4] calixarenes,[5] cucurbiturils,[6] and other macrocyclic hosts,[7] pillar[*n*]arenes[8] consist of repeating hydroquinone units linked by methylene ($-CH_2-$) bridges at their 2,5-positions with pillar-like architectures and electron-donating cavities, and their syntheses, conformational mobility, derivatization, host−guest complexation, self-assembly in water or organic solvents, and applications have been widely explored recently in various fields. Huang and co-workers synthesized the first amphiphilic pillararene and found that it could self-assemble into vesicles and then further assemble into stable microtubes in water.[9]

Although several amphiphilic pillararenes have been synthesized,[10] there are two main problems in the syntheses and application of amphiphilic pillar[5]arene. First, the yield of asymmetric pillar[5]arene is too low.[9] Second, when they self-assemble in water, the intermolecular interactions are not strong.[10] How to synthesize amphiphilic pillararenes with strong intermolecular interactions and high yields is very important in the development of macrocyclic chemistry.

Herein, we report the synthesis of a new bola-amphiphilic pillar[5]arene (Bola-AP5, Scheme 1) with 10 amino groups and 10 amide groups as hydrophilic groups. When Bola-AP5 was dissolved in water with a concentration approximately at its critical aggregation concentration (CAC), it self-assembled into vesicles then into stable microtubes after 2 weeks. However, if the system pH is too low or the concentration is too high, it could not self-assemble into tubes but formed micelles or gel-like structures. Otherwise, tubular structures could be obtained immediately when Bola-AP5 was dissolved in THF and dropped into water at a high concentration. Importantly, hybrid microtubules as a microreactor were successfully prepared by directly reducing $AuCl_4^-$ on the surface of Bola-AP5-based tubular structures in water (Scheme 1).

Bola-AP5 was successfully obtained by refluxing ester-functionalized pillar[5]arene and 1,4-butanediamine in toluene with a 45% yield. When Bola-AP5 was dissolved in pure water, its CAC value was about 4.00×10^{-4} mol/L (see the Supporting Information, Figure S4), and its amphiphilic properties change upon the addition of H^+. In a typical experiment, 1 mg of Bola-AP5 was first dissolved in 10 mL of water upon ultrasonic treatment at room temperature for 30 min. Then HCl was utilized to control the pH of the system. Figure 1 shows the dynamic light scattering (DLS) studies of Bola-AP5 in water under different pH conditions. The average diameter of the assemblies was about 100 or 120 nm when the system pH was 5 or 7, respectively (Figure 1c,d). However, the diameter of the assemblies decreased sharply to 5 nm when the system pH decreased to 4 (Figure 1b). When the system pH decreased to 2, the diameter of the assemblies was smaller than 2 nm (Figure 1a), implying that Bola-AP5 was monodispersed in this condition. The DLS studies above indicated that changing the pH of the system could induce the morphology transformations of Bola-AP5. Similar behavior was observed when the experiments were conducted under controlled pH using buffer solutions (see the Supporting Information Figure S13). The hydrochloride salt of

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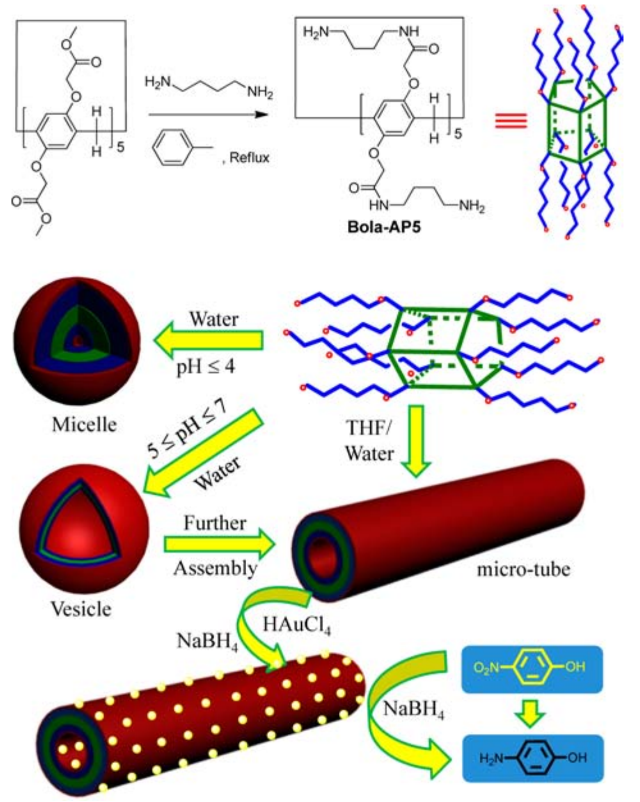
Scheme 1. Synthetic Routes and Chemical Structure of Bola-Amphiphilic Pillar[5]arene Bola-AP5 and Cartoon Representation of the Formation of Different Nanostructures as Microreactor



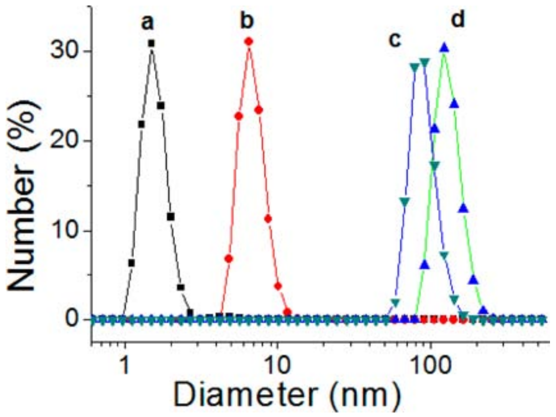


Figure 1. DLS results of Bola-AP5 dissolved in water with different pH values: (a) pH = 2, ∼1.5 nm; (b) pH = 4, ∼5 nm; (c) pH = 5, ∼100 nm; (d) pH = 7, ∼120 nm.

Bola-AP5 did not show self-assembly in water (see the Supporting Information Figure S14).

To gain better insight into the self-assembly of Bola-AP5 in water with different pH values, the resultant assemblies were analyzed on the microcosmic level by transmission electron microscopy (TEM) images and scanning electron microscopy (SEM) images. As shown in Figure 2a,b, when the system pH was 7 and 5, the peripheries and center colors of the assemblies were obviously different, indicating that the assemblies were hollow spheres. Moreover, the wall thicknesses of these vesicles were about 20 nm, which corresponds to a multiextended length of Bola-AP5 molecules, suggesting that the vesicles have multilayer walls (see the Supporting Information, Figure S5). However, the assemblies turned into small solid micelles with a diameter of about 5 nm when the system pH decreased to 4 (Figure 2c). When the system pH further decreased to 2, we could not find regular assemblies. More interestingly, the vesicles could transform into well-defined fibers with 1 mm length and 500 nm width after 4 weeks (Figure 2d). Furthermore, from the cross section of one fiber, we can see that the fibers are, in fact, microtubes (Figure 2e). The UV−vis spectrum also confirmed the further self-assembly of the vesicles in water (see Figure S6).

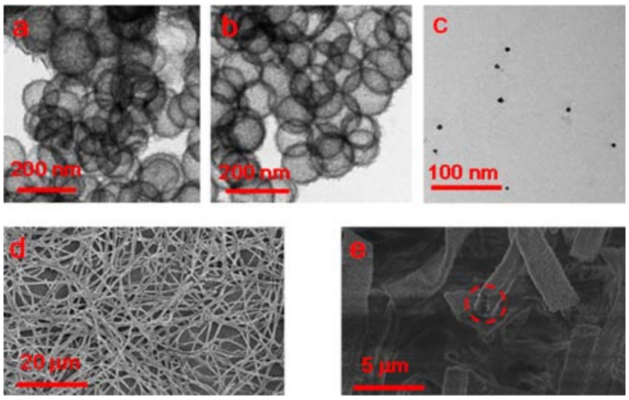


Figure 2. TEM images of Bola-AP5 self-assembled in water with different pH values: (a) pH = 7; (b) pH = 5; (c) pH = 4. SEM image (d) and cross section (e) of Bola-AP5 self-assembled in water for 4 weeks when the system pH was ∼7.

In view of the pH-induced transformation of vesicles to micelles, one can envision that hydrophilic small molecules can be encapsulated within the interior of the Bola-AP5-based vesicles when the system pH value was about 7 and can release the encapsulated molecules when the system pH decreases. As shown in Figure S7, little entrapped calcein was observed over a period of 12 h, indicating that these Bola-AP5-based vesicles were very stable. However, when the system pH of the calcein-loaded vesicles was decreased to 4, the encapsulated calcein environment was released rapidly and completely. This is because the amine groups on Bola-AP5 were quaternized when the pH of the system decreased, so the hydrophilic parts of the molecule increased, which triggered the vesicles to transform into a micellar structure (see Figure S8).[2a]

After investigating the morphologies controlled by the pH of the system, we then studied solvent influence on the self-assembly process. Bola-AP5 can be well-dissolved in THF. In a typical experiment, 1 mg of Bola-AP5 was first dissolved in 30 μL of THF, and then 120 μL of water was poured into the above solution followed by ultrasonic treatment at room temperature for 5 min. Figure S8 shows that the size distribution of the assemblies is very broad from 100 to >1000 nm. Then SEM (Figure 3a) and TEM images (Figure 3b) of the obtained assemblies confirmed that Bola-AP5 self-assembled into fibers in the THF/water solution immediately. This is quite different from the self-assembly of Bola-AP5 in pure water. Further investigation of the vertical section of a fiber showed that the fibers are actually microtubes (see Figure S9).

The solution concentration has been reported to exert a huge influence on the assembly morphology by changing the speed of aggregation.[11] In this work, different amounts of Bola-AP5 were chosen to assemble in water (pH = 7.0) with ultrasonic treatment at room temperature for 20 min and then standing for 2 weeks.

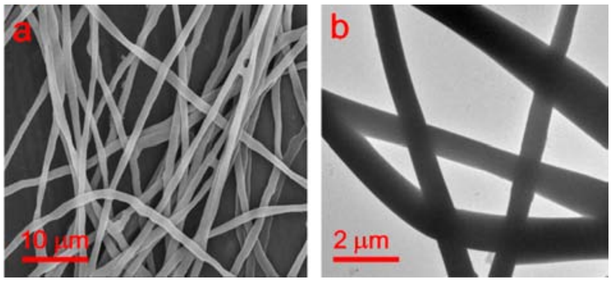


Figure 3. (a) SEM and (b) TEM images of Bola-AP5 self-assembly in a THF/water solution.

We found that Bola-AP5 could self-assemble into floccules at all concentrations. However, further SEM studies showed when the concentration of Bola-AP5 was too small (0.1 × CAC) or too high (10 × CAC), it could not self-assemble into microtubes but did form gel-like structures (Figures 4a,c). When the concentration of Bola-AP5 was approximately at its CAC, it self-assembled into well-defined microtubes (Figure 4b). This result is consistent with the pH-induced self-assembly (Figure 2d).

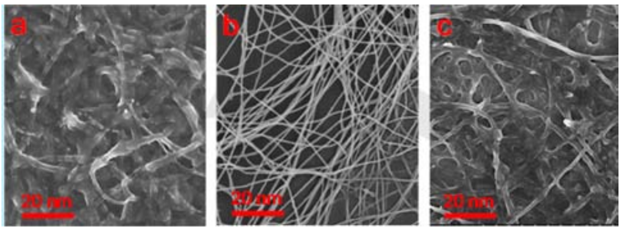


Figure 4. SEM images of Bola-AP5 self-assembly in water with different concentrations: [C] = (a) 0.1 CAC, (b) 1 CAC, and (c) 10 CAC.

As is well-known, amino groups, carboxylic groups, or sulfydryl groups can act as stabilizers for preparing gold nanoparticles. The obtained nanotubes in this work have numerous amino groups on their exterior surfaces. Therefore, we can prepare hybrid microtubes by reducing $HAuCl_4$ on the surface of the tubular structures directly. As shown in Figure 5, gold nanoparticles were distributed on the surfaces of the microtubes, and the hybrid microtubes remained in their original tubular structures. Furthermore, from the vertical section of one hybrid microtube, we can see that there were no nanoparticles in the interior of the tubes (Figure 5e).

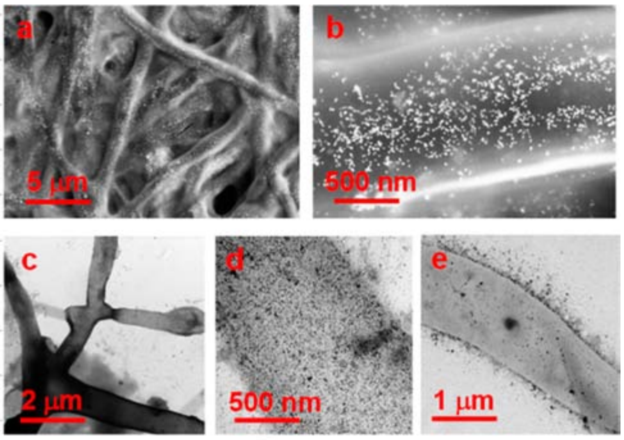
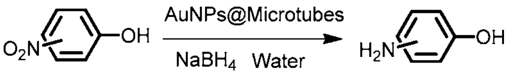


Figure 5. (a) SEM and (b) enlarged SEM images of AuNP microtubes (for this sample, we were unable to spray gold nanoparticles before SEM studies). TEM images of AuNP microtubes (c−e).

After we prepared the hybrid microtubes successfully, we further used them as recycled catalysts for reduction of nitroaniline by $NaBH_4$. The catalytic activity of AuNP microtubes is shown in Table 1. All of the substrates were reduced with yields of about 95−99% in only 30 min (see Figures S10-S12). Moreover, the AuNP microtube catalyst can be easily recovered and reused for many catalytic cycles without any loss of reactivity and conversion ratio. We were unable to conduct control experiments with gold nanoparticles that were not supported on a microtube.

Table 1. Reducing Nitro Aromatic Compounds Catalyzed by AuNP Microtubes



entry		cycle 1	cycle 2	cycle 3	cycle 4
1	*o*	96%	95%	95%	96%
2	*p*	97%	97%	96%	97%
3	*q*	99%	99%	99%	99%

In conclusion, various characterization methods, including ^1H NMR, DLS, UV−vis spectroscopy, TEM, and SEM, were performed to investigate the self-assembly behaviors of a new amphiphilic pillar[5]arene in water. When dissolved in water, the morphology of its assemblies transformed from vesicles to micelles with the decrease of pH. When the pH value was 5−7, the vesicles further self-assembled into well-defined microtubes after 2 weeks. However, when Bola-AP5 was dissolved in THF first and then dropped into water, it self-assembled into microtubes immediately. More interestingly, the concentration of Bola-AP5 has a huge influence on the assembly morphology. Only when the concentration was close to its CAC could it further self-assemble into microtubes. While under other concentrations, it only self-assembled into gel-like structures. Importantly, hybrid microtubules as a microreactor were successfully prepared by directly reducing $AuCl_4^-$ on the surface of Bola-AP5-based tubular structures in water. This work provides a new method to directly create microreactors and will have potential applications in industry.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.5b01910.

Synthetic details, self-assembly of Bola-AP5 in water, and controlled release of small molecules (PDF)

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Notes

The authors declare no competing financial interest.

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