

# An Amphiphilic Pillar[5]arene: Synthesis, Controllable Self-Assembly in Water, and Application in Calcein Release and TNT Adsorption

Yong Yao, Min Xue, Jianzhuang Chen, Mingming Zhang, and Feihe Huang\*

MOE Key Laboratory of Macromolecular Synthesis and Functionalization, Department of Chemistry, Zhejiang University, Hangzhou 310027, P. R. China

**S** Supporting Information

**ABSTRACT:** An amphiphilic pillar[5]arene was made. It could self-assemble to form vesicles and multiwalled microtubes in water. Dynamic light scattering, transmission electron microscopy, scanning electron microscopy, atomic force microscopy, and UV-vis and FTIR spectroscopy were employed to characterize its self-assembly process and the resultant assemblies. The vesicles could encapsulate calcein within their interiors under neutral conditions and release it in response to a decrease in pH. The microtubes, which have primary amine groups on their surfaces, could adsorb TNT through donor-acceptor interactions.

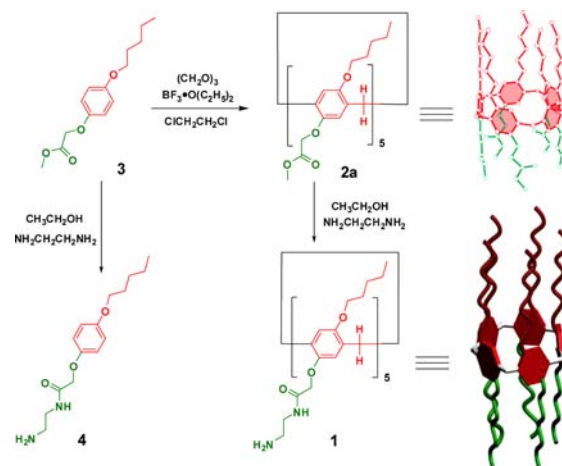
Amphiphiles are a class of fascinating molecules bearing both hydrophilic and hydrophobic groups.<sup>1</sup> When they are dispersed in water, their hydrophilic components preferentially interact with the aqueous phase while their hydrophobic portions tend to reside in the air or in the nonpolar solvent or to gather together in order to decrease the free energy of the hydrophilic-hydrophobic interface.<sup>2</sup> Therefore, the amphiphiles can spontaneously aggregate to form different assemblies depending on the repelling and coordinating forces between the hydrophilic and hydrophobic parts of the component molecules and the surrounding medium.<sup>2e</sup> Inspired by this, scientists have devoted considerable efforts to the design and fabrication of artificial supramolecular structures from the self-assembly of amphiphiles for their wide application in chemistry, biology, and materials science.<sup>3</sup> Although various linear amphiphiles such as surfactants and amphiphilic block copolymers that can self-assemble into zero-dimensional (0D) or one-dimensional (1D) structures have been prepared,<sup>4</sup> macrocyclic amphiphiles have rarely been made and employed in the fabrication of supramolecular structures. The macrocycles can locate hydrophilic and hydrophobic chains to the respective sides. This can promote their self-assembly into various well-defined architectures. Moreover, in view of the rich research results on the host-guest chemistry of macrocycles,<sup>5</sup> the use of macrocyclic amphiphiles in the fabrication of multidimensional and hierarchical self-assemblies is important since it may provide interesting new topological structures based on the self-selectivity of host-guest interactions and novel functions due to the environmental responsiveness of host-guest interactions.<sup>6</sup>

As a new class of supramolecular hosts, pillar[*n*]arenes, especially pillar[5]arenes, are useful and interesting macrocyclic compounds that present a hydrophobic core sandwiched

between two functionalizable rims.<sup>7</sup> Their repeating units are connected by methylene bridges at the para positions, forming a unique rigid pillar architecture that differs from the basket-shaped structure of meta-bridged calixarenes. They can easily be chemically modified, making them promising candidates for applications in nanomaterials, molecular recognition, ion transport, supramolecular polymers, and so on.<sup>7</sup> However, to the best of our knowledge, amphiphilic pillar[*n*]arenes have not been explored to date. Herein we report the synthesis of the first amphiphilic pillar[5]arene, its controllable self-assembly in water, and its application in calcein release and TNT adsorption.

Amphiphilic pillar[5]arene **1** was designed to contain five amino groups as the hydrophilic head and five alkyl chains as the hydrophobic tail (Scheme 1) to endow the aggregates with

## Scheme 1. Syntheses of Amphiphilic Pillar[5]arene **1** and Its Monomeric Analogue **4**

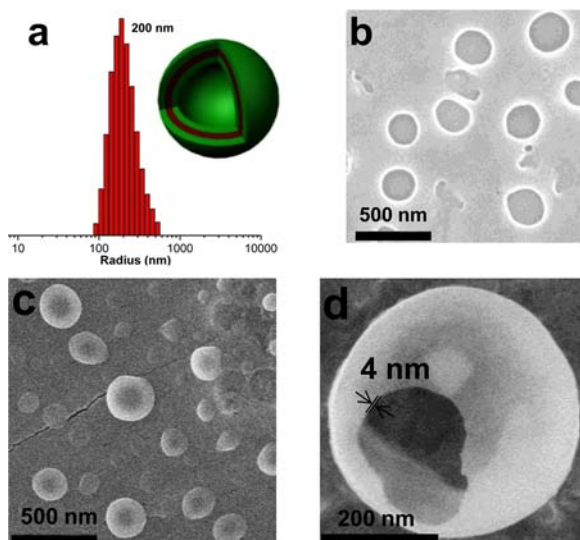


enhanced stability and a pH-responsive character. To prepare **1** (Scheme 1), the nonsymmetric monomer **3** was first synthesized [Scheme S2 in the Supporting Information (SI)]. Next, condensation of **3** with boron trifluoride etherate as the catalyst in  $\text{CH}_2\text{ClCH}_2\text{Cl}$  afforded the four constitutional isomers **2a–2d** (Scheme S3),<sup>7h</sup> among which **2a** is the one having all five ester functional groups on the same side, as confirmed by its crystal structure (Scheme 1). At last, compound **1** was obtained by refluxing a solution of **2a** and 1,2-ethanediamine in ethanol.

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When amphiphilic pillar[5]arene **1** was dissolved in water, the water surface tension ( $\gamma$ ) as a function of the concentration of **1** ( $C$ ) was measured to determine its critical micelle concentration (CMC) in water (Figure S14 in the SI).<sup>2e,6b</sup> There were two linear segments in the  $\gamma$  versus  $C$  curve and a sudden reduction in the slope, implying that the CMC is  $\sim 1.5 \times 10^{-4}$  M. The aggregation behavior of **1** in water was then investigated using dynamic light scattering (DLS), scanning electron microscopy (SEM), and transmission electron microscopy (TEM). The DLS experiment was performed with a  $2.0 \times 10^{-4}$  M aqueous solution of **1** over a scattering angle range of  $90^\circ$ . **1** showed aggregation behavior with a narrow size distribution, indicating well-equilibrated structures. The average hydrodynamic radius ( $R_H$ ) of **1** was observed to be  $\sim 200$  nm (Figure 1a), which greatly

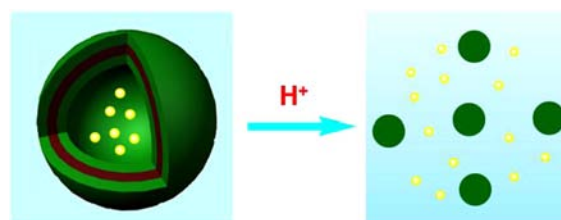


**Figure 1.** (a) DLS results at a scattering angle of  $90^\circ$  for the vesicles formed by **1** ( $2.0 \times 10^{-4}$  M) in water. (b) SEM and (c) TEM images of aggregates of **1** ( $2.0 \times 10^{-4}$  M) in water. (d) SEM image of a ruptured vesicle.

exceeds the corresponding extended molecular length of **1** ( $\sim 2$  nm), suggesting that these aggregates were vesicular entities rather than simple micelles. Further evidence for the formation of vesicles from **1** was provided by TEM experiments. As shown in Figure 1b, the TEM image revealed an obvious color contrast between the peripheries and centers of the spheres, characteristic of the projection images of hollow spheres. The formation of spherical aggregates from **1** was also confirmed by SEM experiments (Figure 1c). The resultant micrograph showed spherical aggregates with diameters of  $\sim 200$  nm, consistent with the results obtained from the above-mentioned DLS and TEM experiments. Moreover, the wall thickness of the vesicles was  $\sim 4$  nm, as observed from a ruptured vesicle (Figure 1d and Figure S16), indicating that the vesicles had a bilayer wall.

More importantly, the vesicular structure appeared to transform into a micellar structure with a decrease in pH. The effect of pH on the aggregation behavior of **1** was investigated by DLS measurements. As shown in Figure S15, a decrease in pH induced a dramatic decrease in the aggregate diameter from 200 nm at pH 7 to 10 nm at pH 3, while the aggregates maintained a narrow size distribution. This unique aggregation behavior seems to be due to a transition from a vesicular structure to a micellar structure (Figure S17a inset). Therefore, one can envision that the vesicles formed by **1** encapsulate hydrophilic guest molecules

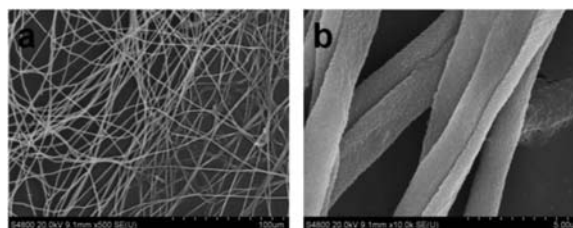
within their interiors under neutral conditions and release the guest molecules in response to a decrease in pH. This stimuli-responsive nanocapsule might have potential applications in selective drug delivery in tissues having a lower pH, such as infected tissues and tumor tissues.<sup>4</sup> With this in mind, calcein as a model hydrophilic guest was encapsulated in the vesicles. Release of calcein from the interiors of the vesicles was accompanied by an increase in fluorescence emission as the free calcein in solution was dequenched. As shown in Figure S17b, no leakage of entrapped calcein was observed over a period of 1 day, indicating that these vesicles were stable toward leakage. However, exposure of the calcein-loaded vesicles to a pH 4 environment resulted in rapid and complete release of the encapsulated calcein. This result can be explained by considering a pH-triggered vesicle-to-micelle transition. The decrease in pH results in the quaternization of the amine groups. This increases the surface area of the hydrophilic headgroup, triggering the collapse of the vesicular structure into a micellar structure with concomitant release of the encapsulated calcein (Figure 2).<sup>4</sup>



**Figure 2.** Schematic representation of a pH-triggered vesicle-to-micelle transition of the aggregates of **1** and the subsequent release of encapsulated calcein.

Additionally, floccules were observed in solution after 2 weeks (Figure S18b), and the floccules were found to become consistently larger and darker as the incubation time increased. The aggregation behavior of **1** in water as a function of aging time was investigated by UV-vis spectroscopy (Figure S18a). The characteristic peak at  $\sim 290$  nm, which is due to the absorbance of free **1** in solution caused by the formation of floccules. For comparison, the noncyclic monomeric analogue **4** was synthesized (Scheme 1) and allowed to self-assemble in water under the same experimental conditions. However, no floccules formed even after 4 months, indicating that the pillar[5]arene frame plays a significant role in the self-assembly process of **1**.

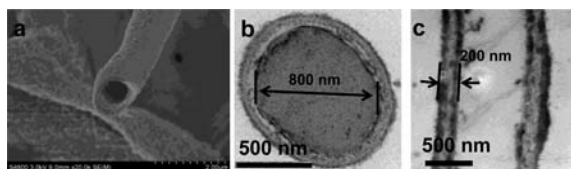
The morphology of the aggregates was examined by SEM (Figure 3), TEM (Figure S20), and atomic force microscopy (AFM) (Figure S19). The overview of the aggregates provided by SEM demonstrated that the floccules were actually microfibrils (Figure 3a). AFM and TEM images (Figures S19 and S20)



**Figure 3.** SEM images of the amphiphilic pillar[5]arene **1**-based microfibrils: (a) overview of the microfibrils; (b) enlarged image of (a).

and an enlarged SEM image (Figure 3b) of individual microfibers showed that the average diameter of the microfibers was  $\sim 1.2 \mu\text{m}$ .

Furthermore, the SEM images of the floccules showed that some of the microfibers were oblate (Figure S21), suggesting that the fibers should not be solid. It can be seen from the cross-section of a microfiber that the microfibers are actually hollow (Figure 4a and Figure S22). To explore the fine structures of



**Figure 4.** (a) SEM image of the cross-section of a microfiber; (b) TEM image of the cross-section of a microfiber; (c) TEM image of the vertical section of a microfiber.

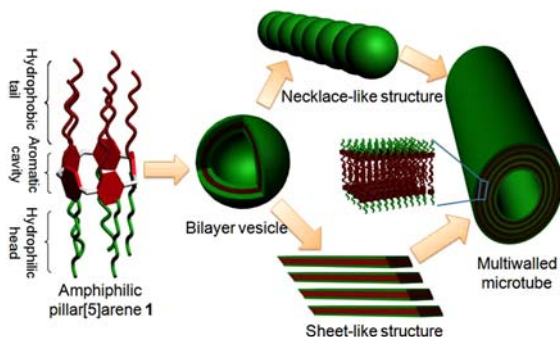
these microfibers, an ultrathin slice of a microfiber was observed by TEM. The results (Figure 4b,c) clearly showed that the microfibers were in fact microtubes with an exterior diameter of  $\sim 1.2 \mu\text{m}$ , a thickness of  $\sim 200 \text{ nm}$ , and an inner diameter of  $\sim 800 \text{ nm}$ .

To study the mechanism of the self-assembly process, the Fourier transform IR spectra of a powder sample of **1** and of the microtubes self-assembled from **1** were compared (Figure S23). It was observed that the N–H stretching and carbonyl bands of the powder were at  $3396$  and  $1676 \text{ cm}^{-1}$ , respectively, and shifted to  $3393$  and  $1671 \text{ cm}^{-1}$ , respectively, in the microtubes. The decrease in the wavenumber suggests an enhancement of the hydrogen-bonding strength and also shows that stronger and more ordered hydrogen bonds are formed in the microtubes.<sup>6b</sup> In addition, the antisymmetric and symmetric stretching vibrations of the  $\text{CH}_2$  alkyl chains in the microtubes were at  $2924$  and  $2854 \text{ cm}^{-1}$ , respectively, while the corresponding peaks for the powder sample were at  $2926$  and  $2856 \text{ cm}^{-1}$ . It is well-known that the symmetric and antisymmetric stretching vibrations of  $\text{CH}_2$  can be used as sensitive indicators of the order of alkyl chains, with increases in the frequencies and band widths being associated with the increasing numbers of gauche defects and disorder.<sup>8</sup> Therefore, the decrease in wavenumber in going from the powder to the microtubes suggested an increase in the number of van der Waals interactions between neighboring alkyl chains in the microtubes.

Further investigation provided us with deeper insight into the nature of the self-assembly. It was interesting that vesicular structures appeared to transform into microtubes with increasing incubation time (Figure S24), suggesting a possible mechanism for the formation of the microtubes. This observation was very important since it highlighted the significance of vesicles in the self-assembly process to form microtubes. Figure S24a shows an SEM image of the floccules after an incubation time of 2 weeks, in which a large number of vesicles and several microtubes can be seen. The number of vesicles decreased when the floccules self-assembled for 1 month (Figure S24b). Furthermore, when the incubation time was increased to 2 months, a large number of microtubes and only a few vesicles were observed (Figure S24c). Remarkably, almost all of the vesicles were converted to microtubes after 4 months (Figure S24d). Simultaneously, some necklacelike and sheetlike structures were also found in the intermediates (Figure S25). With an increase in the incubation time, these structures were also gradually converted to

microtubes. After 4 months, there were no sheetlike or necklacelike structures, indicating that all of these structures had been converted to microtubes.

Pillar[5]arene **1** has five hydrophilic amino headgroups, a hydrophobic pillar[5]arene cavity, and five hydrophobic alkyl tails, so it can be considered as an amphiphilic molecule. A possible mechanism for the generation of microtubes is shown in Figure 5. It is proposed that molecules of **1** initially undergo tail-



**Figure 5.** Schematic illustration of the self-assembly process of amphiphilic pillar[5]arene **1** into microtubes.

to-tail packing to form bilayer vesicles. Subsequently, some bilayer vesicles are transformed into necklacelike structures when they are close to each other, while other bilayer vesicles fuse into large vesicles, with sheetlike structures being formed by rupture of these large vesicles. These necklacelike structures then further fuse into microtubes.<sup>6c,e</sup> At the same time, the sheetlike structures could subsequently roll-up via hydrogen-bonding interactions, which could also lead to the generation of microtubes (Figure 5).<sup>6a,b</sup> Taken together, the studies described above suggested that hydrophobic interactions<sup>9</sup> of alkyl chains provide the driving force for the formation of vesicles. Furthermore, aromatic stacking<sup>10</sup> between the pillar[5]arene frames and hydrogen-bonding interactions between the amino groups and acylamino groups contribute to the generation of microtubes and account for the stability of the resulting architectures.<sup>6d</sup> All of these factors lead to the formation of the microtubular structures, in which the hydrophobic surfaces are shielded from the polar solvent whereas the hydrophilic chains (primary amine groups) are in contact with the aqueous environment.

2,4,6-Trinitrotoluene (TNT) is a leading example of nitroaromatic explosives with significant detrimental effects on the environment and human health. How to curb TNT is a challenging mission today.<sup>11</sup> The supramolecular microtubes in the present work can be considered as electron donors because they contain primary amines on their inner and outer walls. Therefore, we envisioned that TNT could be adsorbed on the surfaces of the microtubes through donor–acceptor (D–A) interactions. A decrease in the characteristic absorbance of TNT from 0.342 to 0.065 after the microtubes were immersed in an aqueous solution of TNT confirmed that TNT was indeed adsorbed by the microtubes (Figure S26). Furthermore, this characteristic absorbance did not decrease after free **1** or **4** was added to an aqueous solution of TNT.

In conclusion, the results described here demonstrate that amphiphilic pillar[5]arene **1** can self-assemble to form well-defined vesicles under neutral conditions. These vesicles were observed to transform into small globular micelles at low pH. This transformation can be used to trigger the controlled release

of encapsulated calcein. Moreover, these vesicles underwent further self-assembly to produce microtubes after 4 months, and the resultant microtubes could adsorb TNT driven by D–A interactions. However, monomeric molecule 4 could neither assemble into microtubes nor adsorb TNT under the same conditions, indicating that the pillar[5]arene frame plays a significant role in controlling self-assembly of 1 in aqueous media. In contrast to previous studies that mainly dealt only with the formation of 0D or 1D morphologies in water,<sup>2,3,6</sup> this work indicates that both 0D and 1D aggregates can be obtained from a simple building block. It will stimulate further studies on macrocyclic amphiphiles that can self-assemble to produce aggregates with potential applications in biological systems and materials science.

## ■ ASSOCIATED CONTENT

### Supporting Information

Experimental details; NMR spectra; SEM, TEM, and AFM images; and other supporting materials. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## ■ AUTHOR INFORMATION

### Corresponding Author

fhuang@zju.edu.cn.

### Notes

The authors declare no competing financial interest.

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