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Magnetic-Responsive Supramolecular Vesicles From Self-Organization of Amphiphilic Pillar[5]arene and Application in Controlled Release

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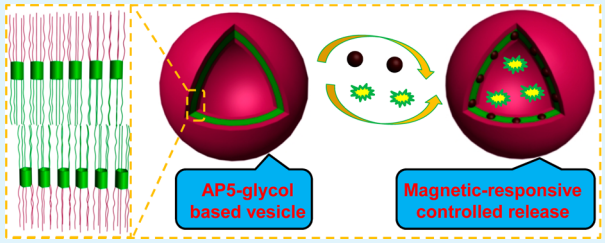
Supporting Information

ABSTRACT: A new amphiphilic pillar[5]arene (AP5-glycol) with five oligomeric glycol groups and five alkyl chains was prepared. AP5-glycol spontaneously formed bilayer vesicles in water, and these vesicles were still stable after several weeks. Additionally, when they were exposed to external physical stimuli, these vesicles also showed reversible thermal and dynamic properties. Interestingly, oleic-acid-stabilized magnetic iron oxide nanoparticles could be incorporated into the bilayer of the AP5-glycol vesicles to form hybrid magnetic-responsive supramolecular vesicles.



KEYWORDS: *supramolecular chemistry, amphiphilie, self-assembly, magnetic-responsive, host−guest interaction*

1. INTRODUCTION

In the past, amphiphilic compounds have attracted considerable attention because they can self-assembly into various structures and apply in drug delivery systems, surfactants, soft materials, and biological transfer.[1−3] Among different kinds of amphiphilic molecules, macrocyclic amphiphiles are a class of charming molecules which are synthesized based on macrocyclic compounds.[4−6] Similar to common amphiphiles, macrocyclic amphiphiles can self-assemble into various structures such as micelles, vesicles, and microtubes in water. On the other hand, macrocyclic amphiphiles can form complexes with different guests through host−guest interactions.[7−9] So, we can easily functionalize the nanostructures self-assembled from macrocyclic amphiphiles through host−guest interactions to fabricate multidimensional and smart materials.

Pillar[*n*]arenes are a new class of macrocyclic compounds after crown ethers, cyclodextrins, calixarenes, cucurbiturils, and others;[10−16] they consist of hydroquinone units linked by methylene (−CH_2−) bridges at their *para* positions, forming a pillar-like architecture; and they contain an electron-donating cavity.[17−28] Their syntheses, functionalization, host−guest complexation, self-assembly properties, and applications in different fields have been widely reported. They have been considered as "a new class of macrocycles for supramolecular chemistry".[23] In 2012, Huang and co-workers synthesized the first amphiphilic pillar[5]arene. It could self-assemble into vesicles in water and then transform into microtubes after 2 months.[20] Then, a series of amphiphilic pillar[5]arenes were synthesized and applied in various areas.[29−33] However, pillar[5]arene-based magnetic vesicles, which may have application in biomedicine due to their water-soluble, biocompatible, and biodegradable nature, have not been reported.[34]

In this study, we report a new glycol-chain functionalized amphiphilic pillar[5]arene (AP5-glycol). When AP5-glycol was dissolved in water, it spontaneously formed bilayer vesicles (Scheme 1). These vesicles showed reversible properties when the system was heated or stirred. More importantly, iron oxide nanoparticles could be incorporated into the bilayer of the AP5-glycol vesicles to form hybrid magnetic-responsive supramolecular vesicles, which could be further used in magnetic controlled release.

2. EXPERIMENTAL SECTION

2.1. Materials. Boron trifluoride etherate, hydroquinone, 1-bromododecane, $ClCH_2COOCH_3$, paraformaldehyde, NaOH, HCl, DMAP, triglycol monomethyl ether, and solvents were reagent grade.

2.2. Synthetic Routes. For synthetic routes, see Scheme S1 in the Supporting Information. Compounds **A** and **B** were prepared according to a method previously reported.[30]

2.2.1. Synthesis of Compound **C**. A mixture of compound **B** (1.81 g, 10.0 mmol) and NaOH (100 mmol) in 25 mL CH_3CH_2OH was stirred in a 100 mL round-bottom flask at 80 °C for 24 h. After the mixture cooled, HCl was added until the pH of the system was 4. Then, the solvent was removed by suction filtration, and the residue was washed with water (2 × 50 mL) to obtain compound **C** as a white solid (1.36 g, 78%). The ^{1}H NMR spectrum of compound C is shown in Figure S2 (Supporting Information). ^{1}H NMR (400 MHz, DMSO-d_6, 298 K) δ (ppm): 7.35−7.29 (m, 10H), 4.81 (s, 10H), 4.13−4.11 (m, 10H), 4.06 (s, 10H), 1.85−1.83 (m, 10H), 1.34−1.33 (m, 20H), 1.33−1.31 (m, 70H), 0.97−0.95 (m, 15H). The ^{13}C NMR spectrum of

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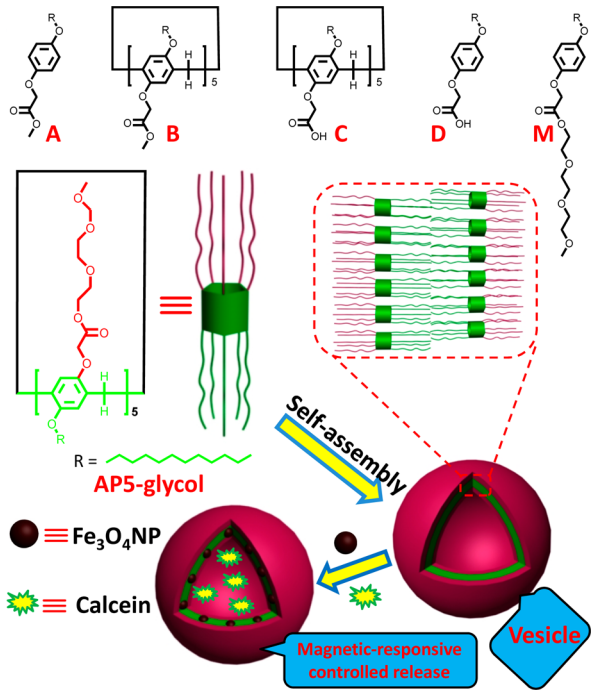
Scheme 1. Chemical Structure of AP5-Glycol and the Schematic Representation of the Formation of Bilayer Vesicles, and Further Formation of Magnetic Hybrid Vesicles in Water



C is shown in Figure S3 (Supporting Information). ^{13}C NMR (100 MHz, DMSO-d_6, 298 K) δ (ppm): 171.8, 154.7, 154.2, 117.2, 116.2, 69.6, 65.7, 38.8, 37.9, 28.9, 28.7, 26.5, 22.9, 14.0. LRESIMS is shown in Figure S4 (Supporting Information): m/z 1764.1 $[M + Na]^+$ (100%). HRESIMS: m/z calcd for $[M + Na]^+$ $C_{105}H_{160}O_{20}Na^+$, 1764.1401; found, 1764.1410; error, 0.5 ppm.

2.2.2. Synthesis of AP5-Glycol. A mixture of compound **C** (0.17 g, 0.100 mmol), triglycol monomethyl ether (10.3 g, 2.00 mmol), 1-(3′-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC, 1.77 g, 0.800 mmol), and 4-dimethylaminopyridine (DMAP, catalytic amount) was stirred in 50 mL of $ClCH_2CH_2Cl$ overnight. The solution was evaporated in vacuo, and the residue was purified by flash column chromatography on silica gel (CH_2Cl_2/methanol = 1/1, v/v) to afford AP5-glycol as a white oil (0.19 g, 76%). The ^{1}H NMR spectrum of compound AP5-glycol is shown in Figure S5 (Supporting Information). ^{1}H NMR (400 MHz, DMSO-d_6, 298 K) δ (ppm): 7.38 (s, 10H), 4.80 (s, 10H), 4.52 (s, 10H), 4.11 (s, 10H), 4.00 (s, 10H), 3.60−3.51 (m, 65H), 1.81 (s, 10H), 1.34−1.31 (m, 90H), 0.96 (s, 15H). The ^{13}C NMR spectrum of AP5-glycol is shown in Figure S6 (Supporting Information). ^{13}C NMR (100 MHz, DMSO-d_6, 298 K) δ (ppm): 169.4, 154.7, 154.2, 117.2, 116.1, 73.7, 70.4, 69.9, 69.6, 69.5, 69.0, 62.2, 57.8, 38.8, 28.9, 28.7, 26.5, 22.9, 14.0. LRESIMS is shown in Figure S7 (Supporting Information): m/z 1274.7 $[M + 2K]^{2+}/2$ (100%). HRESIMS: m/z calcd for $[M]^+$ $C_{140}H_{230}O_{35}$, 2471.6218; found, 2471.6218; error, 0 ppm.

2.2.3. Synthesis of Compound M. A mixture of compound **A** (1.75 g, 5.00 mmol) and NaOH (100 mmol) in 25 mL CH_3CH_2OH was stirred in a 100 mL round-bottom flask at 80 °C for 24 h. After the mixture cooled, HCl was added until the pH of the mixture was 4. Then, the solvent was removed, and the residue was washed with water (2 × 50 mL) to obtain compound **D** as a white solid. Then, a mixture of compound **D** (0.67 g, 2.00 mmol), 1-(3′-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC, 1.77 g, 0.800 mmol) triglycol monomethyl ether (10.3 g, 2.00 mmol), and 4-dimethylaminopyridine (DMAP, catalytic amount) were stirred in 50 mL of CH_2Cl_2 overnight. The solution was evaporated in vacuo, and the residue was purified by flash column chromatography on silica gel (dichloromethane/methanol =1/1, v/v) to afford **M** as a white oil (0.74 g, 76%). The ^{1}H NMR spectrum of compound **M** is shown in Figure S8 (Supporting Information). ^{1}H NMR (400 MHz, DMSO-d_6, 298 K) δ (ppm): 6.97 (s, 2H), 6.81 (s, 2H), 4.90 (s, 2H), 4.28 (s, 2H), 4.08 (s, 2H), 3.76 (s, 2H), 3.57−3.46 (m, 11H), 1.74−1.23 (m, 20H), 0.97 (s, 3H). The ^{13}C NMR spectrum of **M** is shown in Figure S9 (Supporting Information). ^{13}C NMR (100 MHz, DMSO-d_6, 298 K) δ (ppm): 169.4, 154.7, 154.2, 117.2, 116.2, 73.7, 70.4, 69.9, 69.6, 69.5, 69.0, 62.2, 57.8, 38.9, 28.9, 28.7, 26.4, 22.9, 14.0. LRESIMS is shown in Figure S10 (Supporting Information): m/z 505.3 $[M + Na]^+$ (100%). HRESIMS: m/z calcd for $[M + Na]^+$ $C_{27}H_{46}O_7Na$, 505.3141; found, 505.3142; error, 0.2 ppm.

2.3. Characterization. NMR spectra were recorded with a Bruker Avance DMX 500 spectrophotometer or a Bruker Avance DMX 400 spectrophotometer using the deuterated solvent as the lock and the residual solvent or TMS as the internal reference. Low-resolution electrospray ionization mass spectra were recorded with a Bruker Esquire 3000 Plus spectrometer. High-resolution mass spectrometry experiments were performed with IonSpec 4.7 T FTMS. Elemental analysis was performed with a Vario MICRO cube. Transmission electron microscopy (TEM) images were carried out on a JEM-1200EX instrument, and the accelerating voltage was 100 kV. Scanning electron microscopy (SEM) images were carried out on a JEOL 6390LV instrument. Dynamic light scattering (DLS) studies were carried out on a Nano-ZS ZEN3600 instrument at room temperature.

3. RESULTS AND DISCUSSION

3.1. Self-Assembly of AP5-Glycol in Water. For investigating the self-assembly behavior of AP5-glycol in aqueous solutions, we first determine its critical aggregate concentration (CAC) through water surface tension (γ, Figure 1a).[5,20] The junction of the $\gamma-C$ plot indicates its CAC value is

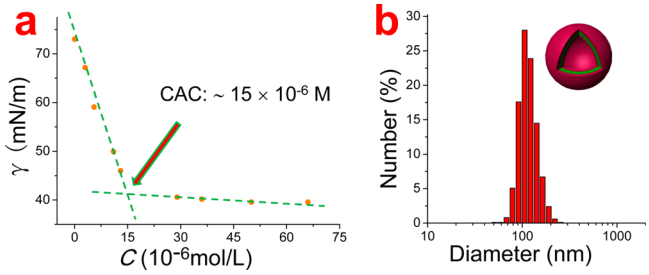


Figure 1. (a) Water surface tension (γ) as a function of the concentration of AP5-glycol (C). (b) DLS studies of AP5-glycol self-assembly in water.

about 1.50 × 10^{-5} M. Then, we used DLS to investigate its aggregation behavior. DLS studies were performed with a solution of AP5-glycol (2.00 × 10^{-5} M) over a scattering angular range of 30−145° at room temperature (25 °C). From Figure 1b, we can draw a conclusion that AP5-glycol self-assembly into well-defined structures and the diameters of the aggregates are distributed with a narrow size. The average diameter of AP5-glycol assemblies was about 100 nm, which exceeded the length of AP5-glycol (~3 nm), suggesting that the AP5-glycol assemblies were vesicles rather than simple solid micelles.

Then, TEM was used to investigate the aggregation behavior of AP5-glycol in water. As shown in Figure 2a, obvious difference between the periphery and the center of the spheres could be seen, indicating that these hollow assemblies were vesicles rather than simple micelles. The average diameter of these vesicles was about 120 nm (Figure 2a). From Figure 2b we could also estimate that the thickness of the vesicles was

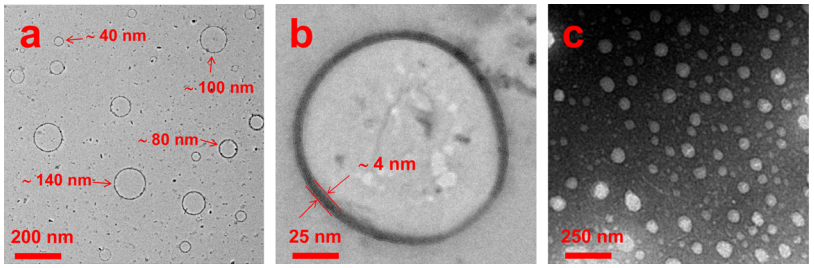


Figure 2. (a) TEM image of AP5-glycol self-assembly into vesicles in water. (b) Enlargement of vesicle shown in panel a. (c) SEM image of AP5-glycol self-assembly into vesicles in water.

about 4 nm. However, the model compound **M** could only self-assemble into small solid micelles with a diameter about 5 nm under the same conditions (Figure S11, Supporting Information). The above comparison indicated that the framework of pillar[5]arene played a significant role in controlling the self-assembly of AP5-glycol. The vesicles self-assembled from AP5-glycol were also confirmed by SEM image. As shown in Figure 2c, the diameter of the aggregates was about 120 nm, consistent with the DLS and TEM results.

3.2. Stability Study of AP5-Glycol Vesicles in Water. The response of these vesicles toward external stimuli, such as heating, sonicating, stirring is very important. We first determined the thermal-responsiveness of the vesicles. As shown in Figure 3, DLS studies were used to track the change

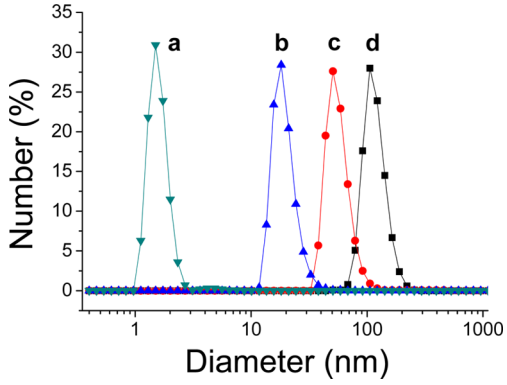


Figure 3. DLS results of the transformation process of the vesicles formed by AP5-glycol during the heating process: (a) 80; (b) 60; (c) 40; and (d) 20 °C.

of the vesicle when a solution of AP5-glycol (2.00×10^{-5} M) was heated to 80 °C. The DLS results showed that the diameter of the vesicles decreased as the temperature increased. At last, there were no vesicles when the temperature was 80 °C (Figure 3a). This transformation process was also confirmed by TEM images (Figure S12, Supporting Information). When the system was cooling to room temperature, AP5-glycol self-assembled into vesicles again. These results suggested that the supramolecular vesicles of AP5-glycol in water showed excellent thermal reversible properties. After that, we also used DLS studies to track the transformation of the vesicles when the system was under ultrasonic conditions. When the system was exposed to ultrasound, the vesicles disappeared in 5 min. However, when we removed the ultrasound, the vesicles formed again after 10 min (Figure S14, Supporting Information). Vigorous stirring can also induce vesicle transformation into small solid aggregates (Figure S15, Supporting Information). The above studies indicated that the supramolecular AP5-glycol vesicles could be re-formed after they were destroyed by external stimuli. All of the above investigations confirmed that the AP5-glycol vesicles had dynamic reversible properties, which is a very important characteristic of soft materials.

3.3. Preparation of Magnetic Hybrid Vesicles in Water. Magnetic nanoparticles stabilized by oleic acid were synthesized as described.[35] The average size of the iron oxide nanoparticles was around 4 nm, according to TEM (Figure 4a). These magnetic nanoparticles can be easily precipitated with a permanent magnet, indicating they are highly superparamagnetic (Figure 4b).

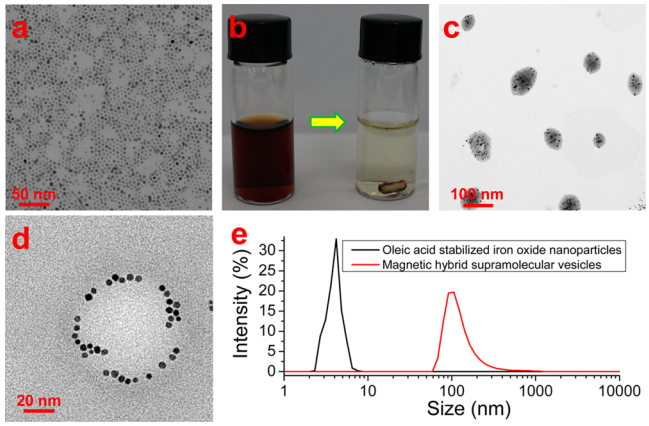


Figure 4. (a) TEM image of oleic-acid-coated iron oxide nanoparticles. (b) Optical images of iron oxide nanoparticles dissolved in *n*-hexane and then precipitated with a permanent magnet. (c) TEM image of superparamagnetic hybrid vesicles. (d) TEM image of a collapsed superparamagnetic hybrid vesicle. (e) DLS studies of oleic-acid-coated iron oxide nanoparticles and superparamagnetic hybrid vesicles.

Superparamagnetic hybrid vesicles (SMHV) were obtained by absorbing oleic-acid-stabilized iron oxide nanoparticles into the bilayer of the AP5-glycol vesicles during preparation of the vesicles. To this purpose, a drop of the oleic-acid-stabilized iron oxide nanoparticles dissolved in *n*-hexane was added into the aqueous solution of AP5-glycol. After the solution was stirred for 1 h, *n*-hexane was evaporated and iron oxide nanoparticles were encapsulated into the bilayer of the vesicles. The resulting SMHV were investigated by TEM and DLS studies. In the TEM image, it could be seen that the iron oxide nanoparticles were confined to the SMHV (Figure 4c) and that the SMHV had a diameter of around 100 nm. From a collapsed superparamagnetic hybrid vesicle, we can see that magnetic nanoparticles were around the vesicles, which confirmed that nanoparticles were absorbed in the bilayer of the vesicles

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(Figure 4d). The DLS studies also confirmed these results (Figure 4e). When dissolved in water, AP5-glycol can self-organize into bilayer vesicles because the hydrophobic alkyl chains can aggregate together and the oligo(ethylene glycol) moieties can cover the surfaces of the hydrophobic parts. These bilayers could accommodate iron oxide nanoparticles in the hydrophobic membrane interior, even though the average diameter of the particles is almost the same as the thickness of the bilayer.[36]

3.4. Magnetic-Responsive Controlled Release. The hybrid vesicles appeared to transform into irregular structures when an external magnetic field was added. We used DLS studies to investigate the external magnetic field effect on the self-assembly behavior of AP5-glycol. As shown in Figure 5a,

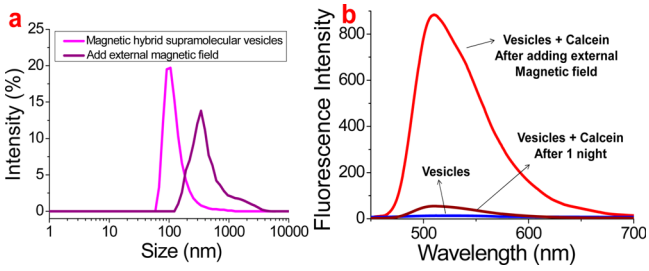

Figure 5. (a) DLS results of superparamagnetic hybrid vesicles before and after adding external magnetic field. (b) Fluorescence emission spectra of hybrid vesicles and of vesicles and calcein after one night and after adding an external magnetic field for 1 h.

adding an external magnetic field induced a dramatic change in the aggregate diameter, which was mainly due to the transition of the aggregates from vesicular structures to irregular structures. Therefore, one could envision that the vesicles formed by AP5-glycol might be able to encapsulate hydrophilic guest molecules within their interiors under neutral conditions and release the guest molecules in response to an external magnetic field. We encapsulated calcein in the hybrid vesicles. When the calcein is released from the interiors of the hybrid vesicles, the fluorescence emission as the free calcein will increase. From the fluorescence spectra (Figure 5b), we found that even after one night without the external magnetic field, almost no leakage of entrapped calcein was observed. However, exposure of the system to an external magnetic field resulted in the release of the encapsulated calcein. This phenomenon can be explained by considering a magnetic triggered vesicle-to-irregular structure transition.

4. CONCLUSIONS

In summary, we synthesized a new amphiphilic pillar[5]arene (AP5-glycol) with five alkyl chains and five oligomeric glycol groups. The AP5-glycol could self-assemble into reversible responsive supramolecular vesicles in water, while the model molecule **M** could not under the same condition, indicating that the framework of pillar[5]arene is very important when AP5-glycol form self-assembly in water. DLS studies, TEM, and SEM images have been used to characterize the self-assembly process and the resulting assemblies. The supramolecular vesicles were confirmed to be bilayer with a diameter about 100 nm. These vesicles were still stable after several weeks. Additionally, under external physical stimuli, these vesicles also showed reversible thermal and dynamic properties. More interestingly, iron oxide nanoparticles could be incorporated into the bilayer of the AP5-glycol vesicles to form hybrid magnetic-responsive supramolecular vesicles, and these hybrid vesicles could be used in magnetic controlled release.

■ ASSOCIATED CONTENT

Supporting Information

Experimental details, ^{1}H NMR, ^{13}C NMR, SEM images, TEM images, DLS studies, and other materials. 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.

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