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Self-assembly of Supramolecular Amphiphile Constructed by Hydrophilic Calix[4]arene Derivative and Phenol Palmitate

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Self-assembly of supramolecular amphiphile consisting of 25,27-bispolyethyleneglycol-calix[4]arene (2mPEG-C[4]A) and phenol palmitate has been studied in a water/dioxane cosolvent. Based on the host-guest interaction of 2mPEG-C[4]A and phenol palmitate, a supramolecular calixarene amphiphile can be readily constructed. Interestingly, by only adjusting the molar ratio of calix[4]arene hosts to benzene derivatives, various morphologies with different size appear. Because of the weak interaction between 2mPEG-C[4]A and phenol palmitate, the formation of these assemblies is dynamic. Such a dynamic behavior can be applied in the controlled release of dyes and drugs.

Keywords: Calixarene, host-guest interaction, self-assembly, dynamics

1 Introduction

As the third generation of supramolecular hosts, calixarenes are versatile macrocyclic compounds which present a hydrophobic core and two functionalizable rims. Controlled self-assembly of amphiphilic calixarenes is a challenging topic in the field of chemical biology and materials science, since it provides the spontaneous generation of a well-defined aggregation under thermodynamic equilibrium (1). In a pioneering paper published in the late 1980s, Regen and co-workers (2) reported that p-tert-butylcalix[6]arene produced stable monolayer at the air/water interface having a limiting area of 260 Å^2/molecule and a film thickness of 10 Å. Through a small-angle X-ray scattering study of sulfonated calix[6]arene amphiphiles, Shinkai et al. (3) observed the existence of micelles. Most of the early studies of amphiphilic calixarenes focused on the formation of micelles or membranes (4–6). Recently, considering the potential applications in sensors and drug delivery systems, the morphology control of calixarene amphiphiles and their stimuli-responsive property have attracted much attention (7–11). For example, Lee reported that amphiphilic calixarene tetramers consisting of four alkyl chains at the small rim and four dibranched hydrophilic chains at the large rim could endow the aggregates with high stability and pH-responsive property (12). Houmadi realized the self-assembly of a calix[6]arene functionalized at the small rim by three imidazolyl moieties and at the large rim by three hydrophilic sulfonate groups. The presence of imidazole group in the hydrophobic core of the amphiphilic calix[6]arene makes the aggregates responsive to both pH and metal ions (13). Very recently, Jiang reported the self-assembly of amphiphilic calix[6]crowns (14). Upon an increase of the medium polarity, the morphology of the aggregates of calix[6]crowns evolved from vesicles to the coexistence of vesicles and nanotubles, and finally to nanotubes only. Among all of the abovementioned building blocks, the hydrophobic and hydrophilic parts are linked by covalent bonds. Without destroying the bonds, the two opposite parts cannot be separated. Contrarily, self-assembly of supramolecular calixarene amphiphile in which the hydrophilic and hydrophobic building blocks are connected by non-covalent interaction has been hardly reported.

The molecular recognition between calix[4]arenes and benzene derivatives can drive the self-assembly of calixarenes (15). In the present study, this kind of host-guest interaction has been used to construct a new type of supramolecular calixarene amphiphile in which the hydrophobic and hydrophilic parts are connected by supramolecular interaction. Interestingly, different

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2 Experimental

2.1 Materials

4-Tert-butylphenol, formaldehyde, phenol, potassium carbonate, acetonitrile, 1,4-dioxane, tetrahydrofuran, petroleum ether, CH_3OH and CH_2Cl_2 were purchased from Sinopharm Chemical Reagent Company. Polyethylene glycol monomethyether (mPEG, Mn = 550) was purchased from Alfa Aesar. p-Methyl benzene sulfonic chloride and palmitoyl chloride were from Aldrich. Deionized water with 18.2 MΩ cm^{-1} was used in all experiments.

2.2 Synthesis

2.2.1. *Synthesis of 25,27-bispolyethyleneglycolcalix [4]arene*

4-Tert-butyl calix[4]arene is a typical kind of calixarene and can be synthesized from 4-tert-butylphenol and formaldehyde (16). The mPEG reacted with the p-methyl benzene sulfonic chloride, producing the mPEG-OTs (17). 1.29 g 4-tert-butyl calix[4]arene, 3.67 g mPEG-OTs and 0.559 g potassium carbonate were dissolved in 70 ml anhydrous acetonitrile in a 250 ml three-neck flask. The mixture was heated to reflux, and stirred for 3 days under the N_2 atmosphere. The solvent was removed by rotary evaporator when the reaction stopped. The remainder was dissolved in 50 ml CH_2Cl_2 and washed with 30 ml deionized water for three times, and then organic phase was dried with anhydrous $MgSO_4$. After filtration, the solvent was removed. 3.2 g of a slightly yellow dope was obtained. Column chromatography was employed to purify the product. The eluent compositions were CH_2Cl_2:CH_3OH=20:1. After purification, 2.6 g 25,27-bispolyethyleneglycolcalix[4]arenes (2mPEG-C[4]A) were obtained and the total yield was 70%. ^1H-NMR ($CDCl_3$, 400 MHz): δ =7.24 (s, 2H, Ar-OH), 7.04 (s, 4H, ArH), 6.78 (s, 4H, ArH), 4.37 (d, 4H, J=13.30, $ArCH_2Ar$), 4.17, 3.95, 3.82, 3.56-3.64 (br, 106H, OCH_2CH_2O), 3.38 (s, 6H, OCH_3), 3.29 (d, 4H, J=13.30, $ArCH_2Ar$), 1.28 (s, 18H, $C(CH_3)_3$), 0.96 (s, 18H, $C(CH_3)_3$); ^{13}C-NMR ($CDCl_3$, 400 MHz): δ = (159.10, 156.07, 155.47, 137.19, 133.47, 128.87, 127.51, 122.73, 73.92, 72.89, 72.12, 70.85, 70.75, 69.58, 59.21, 30.91); IR (3149.7, 3033.5, 2947.8, 2908.1, 2868.3, 1666.3, 1635.7, 1479.7, 1351.2, 1299.2, 1241.1, 1106.5).

2.2.2. *Synthesis of phenol palmitate*

In a 100 ml round bottom flask, 1.87 g palmitoyl chloride, 0.7 g phenol and 0.845 g potassium carbonate were dissolved in 50 ml acetonitrile. Refluxing for 12 h, the solvent was removed by rotary evaporator. The crude product was recrystallized with CH_2Cl_2:petroleum ether=10:1. After purification, 2.2 g white crystal was obtained and the total yield was 93%. ^1H-NMR (DMSO-d_6, 400 MHz): δ =7.37 (t, 2H, J=7.825, ArH), 7.22 (t, 1H, J=7.825, ArH), 7.08 (d, 2H, J=7.825, ArH), 2.55 (t, 2H, J=7.825, $COOCH_2$), 1.75 (t, 2H, CH_2), 1.26 (br, 24H, CH_2CH_2), 0.884 (t, 3H, J=7.043, CH_3); ^{13}C-NMR (DMSO-d_6, 400 MHz): δ =(182.32, 161.32, 139.01, 135.47, 131.12, 37.47, 31.9, 29.62, 29.3, 22.72, 14.10); IR (2954.20, 2849.76, 1747.96, 1590.33, 1472.42, 1457.60, 1382.12, 1202.87, 1149.25, 934.27, 764.04, 716.77).

2.3 Self-assembly of Supramolecular Calixarene Amphiphile

5 mg 2mPEG-C[4]A was dissolved in 10 ml dioxane. Then, phenol palmitate with a different amount was added into a dioxane solution (Table 1). Under vigorous stirring, deionized water was slowly injected into 10 ml prepared solution over 30 min at 15°C. The appearance of bluish opalescence suggested the formation of nanoscale aggregates.

2.4 *^1H*-NMR Titration

^1H-NMR titration was employed to determine the complexation ratio of the host and guest (18–20). The experiments were carried out on a Varian MERCURY plus-400 spectrometer. 10^{-3} mmol of 2mPEG-C[4]A and phenol palmitate were dissolved in 10 ml dioxane-d_8, and the molar ratio of these two compounds varied from 10:1 to 1:10. Then, 50 μl D_2O was slowly added into the solution with a microsyringe. The solution was mixed and stored overnight at room temperature before NMR measurement. To minimize intermolecular interaction, the concentrations of 2mPEG-C[4]A and phenol palmitate were kept in the range of 0.5–1.5 mg/ml well below the critical micelle concentration (CMC).

2.5 Dynamic Light Scattering (DLS)

The self-assembly behavior of this new type of supramolecular calixarene amphiphile was studied by dynamic light

Table 1. Experimental parameters for self-assembly of 2mPEG-C[4]A and phenol palmitate

Entry	*2mPEG-C[4]A (mmol)*	*Phenol Palmitate (mmol)*	*Dioxane/ Water (ml)*	*Molar Ratio*
1	2.96	0.29	10/2	10:1
2	2.96	0.58	10/2	5:1
3	2.96	2.96	10/2	1:1
4	2.96	14.8	10/2	1:5
5	2.96	29.6	10/2	1:10

scattering (DLS). DLS measurements were carried out at 25°C by using Zetasizer Nano-S (Malvern Instruments, Ltd., Malvern, Worcestershire, U.K.). A 40 mW He-Ne laser ($\lambda = 632$ nm) was used, and the scattered light was collected at different angles from 20 to 150° by the PM detector (diaphragm 100 μm).

2.6 Transmission Electron Microscopy (TEM)

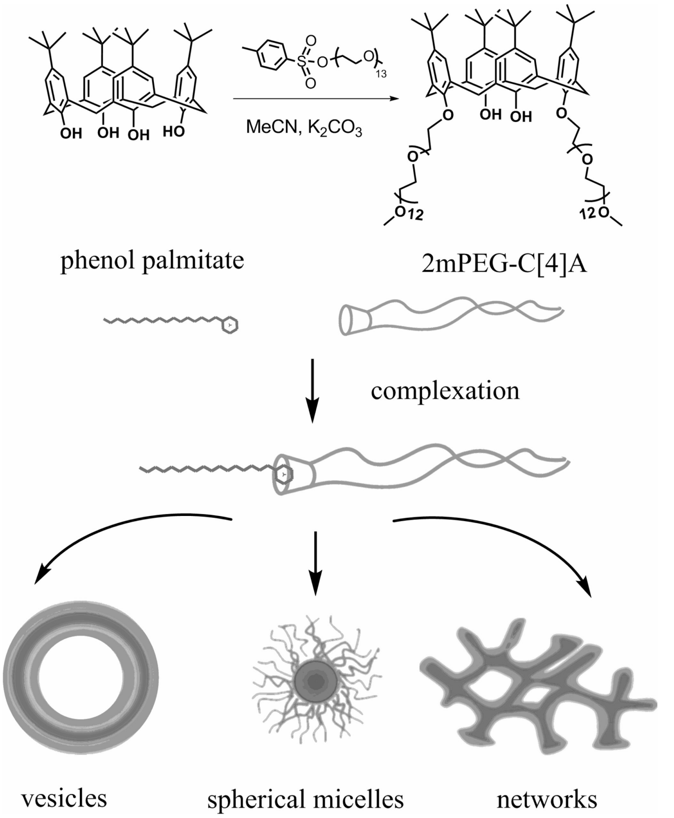
10 μl calixarene solution was deposited onto a holey carbon copper grid and dried with the freeze-drying procedure at -60°C for 24 h. TEM experiments were performed on a Jeol JEM-2010 microscope operating at an accelerating voltage of 200 kV.

2.7 Fluorescence Measurement

Pyrene was dissolved in dioxane with the concentration of 6×10^{-4} M. Deionized water was added to 2mPEG-C[4]A and phenol palmitate solution prepared as sample 3 in Table 1. A small amount of pyrene solution was mixed with sample 3 under continuous magnetic stirring. The final concentration of pyrene probe was 6×10^{-6} M which was suitable for fluorescence measurement. The solution was dropped into a quartz cuvette and fluorescence spectra were recorded at excitation wavelength of 333.0 nm using a Varian Cary spectrometer. Then, the fluorescent intensity was measured as a function of time. After 3 h, appropriate 100 μl amount of water was added to the solution to destroy the complex. Then, the fluorescence intensity was measured again at different time.

3 Result and Discussion

The host-guest interaction between calix[4]arenes and benzene derivatives is used to construct the supramolecular calixarene amphiphile. The preparation route is given in Scheme 1. Firstly, both 2mPEG-C[4]A and phenol palmitate were synthesized. In order to improve its aqueous solubility, the calix[4]arene was modified with two mPEG chains. The mPEG reacted with the p-methyl benzene sulfonic chloride to produce the mPEG-OTs with a high purity, as shown in Figure 1a. Under catalyzing with weak base, mPEG-OTs chains were reacted with the hydroxyl groups at contraposition of lower rim of calix[4]arene. After purification by silica gel column separation, bis-substituted product was obtained. The structure of 2mPEG-C[4]A is verified by ^{1}H NMR spectrum in Figure 1b. From the integral area of 7.1 (s, 4H, ArH) and 3.6 ppm (br, 106H, OCH_2CH_2O), it can be calculated that two hydroxy groups at the lower rim of calix[4]arene have been reacted. Moreover, the tert-butyl proton signals divide into two groups with equal integral area, demonstrating the bis-substituted calix[4]arene derivatives. The double peaks at 4.4 and 3.3 ppm are the signals of bridging methylene groups. Their coupling split is readily observed, indicating the cone conformation of calix[4]arene. The calixarene host with stable cone conformation can offer the best function of molecular recognition and keep unique morphology in the solution. This mPEG-modification provides the calix[4]arene with high aqueous solubility, so 2mPEG-C[4]A is an excellent hydrophilic building block for supramolecular self-assembly. On the other hand, the hydrophobic building block was prepared by the reaction of palmitoyl chloride and phenol. The structure of phenol palmitate guest can be confirmed by the ^{1}H NMR spectrum in Figure 1c.



Sch. 1. Self-assembly of supramolecular amphiphile consisting of hydrophilic 25,27-bispolyethyleneglycolcalix[4]arene and hydrophobic phenol palmitate.

Figure 2a shows the FTIR spectrum of 2mPEG-C[4]A. In the C–H stretching region, the 3030 cm^{-1} band comes from the stretching vibrations of benzene ring; the 2954 and 2870 cm^{-1} bands are related to the asymmetric and symmetric $-CH_3$ stretching vibration, respectively, while the 2910 cm^{-1} corresponds to the asymmetric stretching vibrations of methylene group. The 1100 cm^{-1} band results from the C—O—C asymmetric stretching vibration. For the phenol palmitate guests, Figure 2b displays the appearance of the stretching vibrations of benzene ring at 3030 cm^{-1}, the asymmetric and symmetric $-CH_3$ stretching vibrations at 2954 and 2865 cm^{-1}, the asymmetric and symmetric $-CH_2-$ stretching vibrations at 2911 and 2847 cm^{-1}, the carbonyl stretching vibrations at 1740 cm^{-1}. Both ^{1}H-NMR and FTIR results confirm the successful preparation of 2mPEG-C[4]A host and phenol palmitate guest.

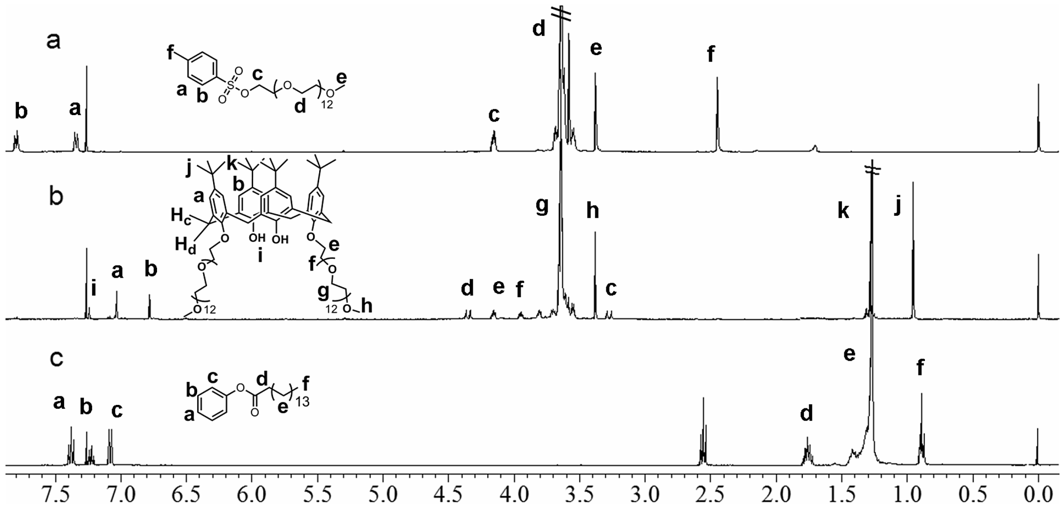


Fig. 1. ^{1}H-NMR spectra of mPEG-OTs (a), 2mPEG-C[4]A (b), phenol palmitate (c).

2mPEG-C[4]A can be dissolved in water and a polar organic solvent such as dioxane, whereas, the phenol palmitate is only dissolved in weakly polar organic solvents such as THF and dioxane. Dioxane is the common one that dissolves both of 2mPEG-C[4]A and phenol palmitate. Mixing 2mPEG-C[4]A and phenol palmitate in a dioxane/water cosolvent, bluish opalescence appeared immediately, suggesting the formation of nanoscale aggregates. To clarify the driving force of self-assembly, ^{1}H-NMR titration experiments were performed. As shown in Figure 1, the resonance signals at 7.05 and 7.40 ppm come from H_a of 2mPEG-C[4]A and H_a of phenol palmitate respectively. Figure 3 gives the change of peak area ratio of the host and guest molecules as a function of the molar ratio. According to the slope transition in the titration curves, it can be found that 1:1 stoichiometric complex between 2mPEG-C[4]A and phenol palmitate is formed. The ^{1}H NMR titration result suggests that the benzene group of phenol palmitate enters into the cavity of the calix[4]arene via the host-guest interaction, which induces the inclusion complexation between the 2mPEG-C[4]A host and phenol palmitate guest.

The morphology of nanoscale aggregates was examined by transmission electron microscopy (TEM). Figure 4 shows that when the molar ratio of 2mPEG-C[4]A to phenol palmitate is 10:1 (sample 1 in Table 1), the aggregates are spherical with a diameter ranging from 80 to 310 nm. All of the assemblies show a strong contrast between the center and the periphery, which is typical of vesicular structure. Unlike other work, the vesicles form spontaneously just by addition of water without any further treatment like sonication. Obviously, it is caused by the self-assembly of the supramolecular amphiphile consisting of 2mPEG-C[4]A and phenol palmitate. Although the polydispersity of vesicles is large, all of vesicles have a uniform membrane thickness of about 10 nm. Molecular simulation gives a simple estimate of 7 nm for the molecular size of phenol

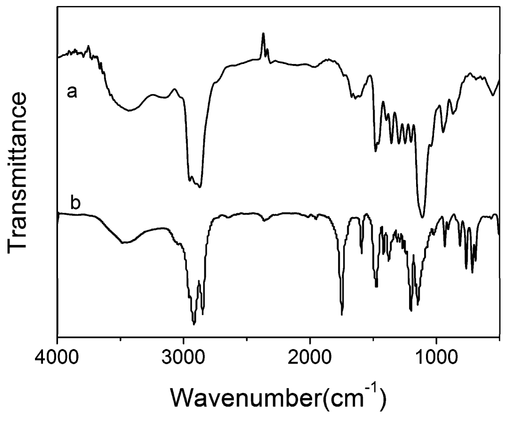


Fig. 2. FTIR spectra of 2mPEG-C[4]A (a) and phenol palmitate (b).

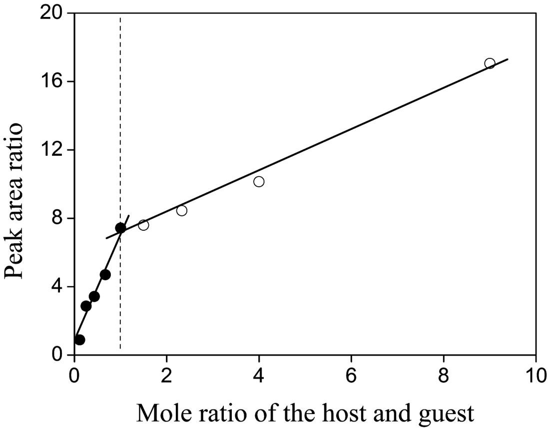


Fig. 3. ^{1}H-NMR peak area ratio changes as a function of the 2mPEG-C[4]A and phenol palmitate mole ratio.

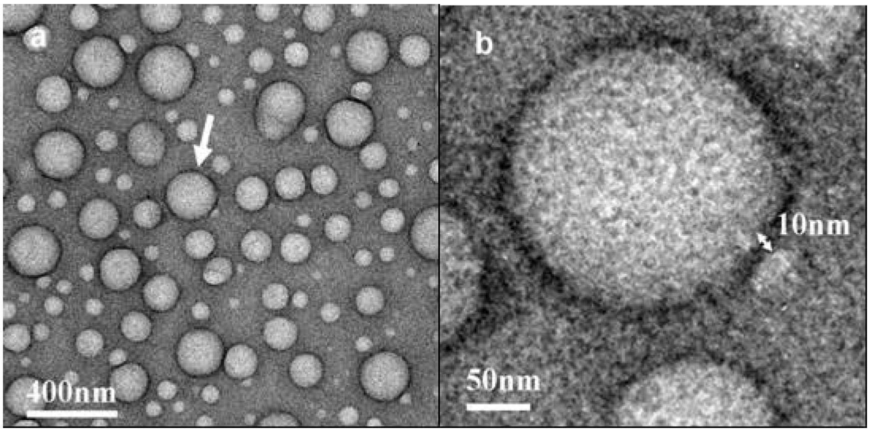


Fig. 4. TEM micrograph of self-assembled structures obtained from sample 1 (a) and one of vesicles amplified at the different scale (b).

palmitate with 2mPEG-C[4]A. The thickness of wall is a little smaller than the double molecular size of the complex. The stacking of alkyl chain might not be perfect and the PEG chain could also shrink during the drying procedure, so a bilayer model of membranes is acceptable (21–24). In such a model, the alkyl chains aggregate together and are direct inward. In the meantime, 2mPEG-C[4]A hosts are aligned with their hydrophilic mPEG chains facing the solution phase.

To investigate the effect of the host/guest molar ratio on the aggregates' morphology, the hydrophilic 2mPEG-C[4]A block was fixed at 0.5 mg/ml while the concentration of hydrophobic phenol palmitate was increased from 0.1 to 13.6 mg/ml. Figure 5 shows that the size and morphology of the self-assembled objects change with phenol palmitate concentration. When the weight fraction of hydrophilic 2mPEG-C[4]A block is high such as host:guest=10:1, the vesicles with an average size of 270 nm are given in Figure 5a. These vesicles shrink with increasing weight fraction of hydrophobic phenol palmitate. For example, Figure 5b shows that the average vesicle diameter is only 170 nm at host:guest=5:1. At the stoichiometric complexation of 2mPEG-C[4]A and phenol palmitate, the normally spherical micelles about 130 nm form (Figure 5c), owing to the strong hydrophobic aggregation between phenol palmitate chains. Further increasing the guest content, the spherical micelles become larger and larger (host:guest=1:5, Figure 5d). Finally, the net-work aggregates with a few spherical micelles are mainly presented at a high guest concentration (host:guest=1:10, Figure 5e), which can be attributed to

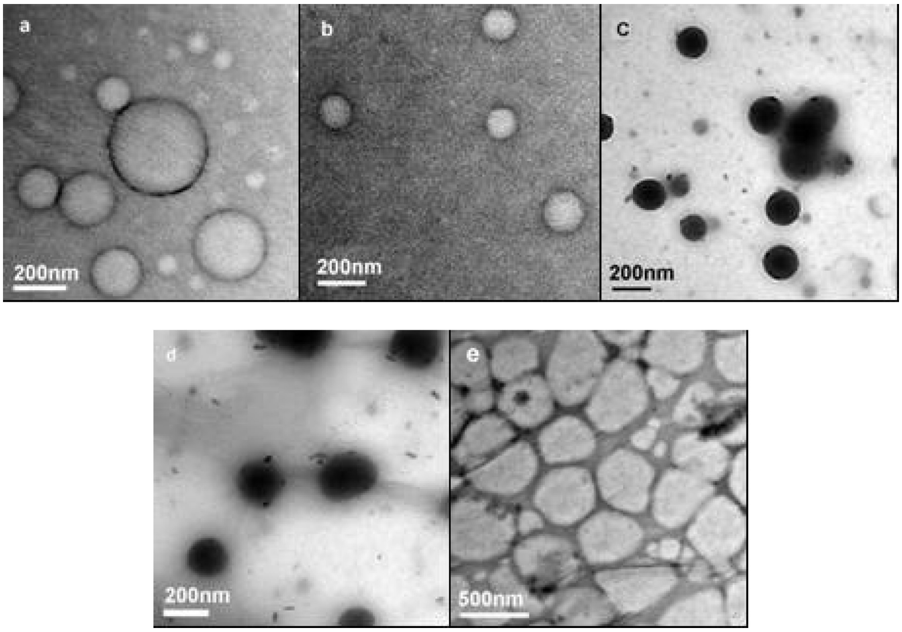


Fig. 5. TEM measurement for the morphology changes of sample 1-5 (a–e).

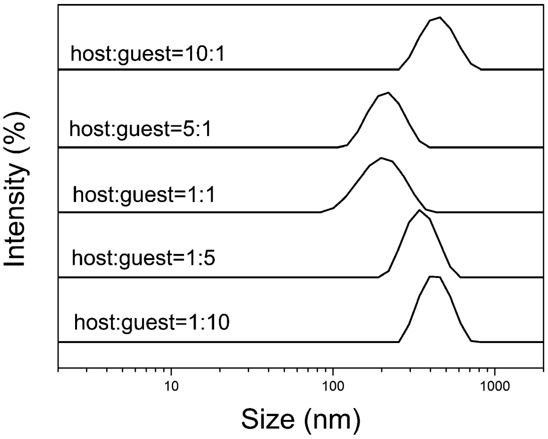


Fig. 6. DLS measurements of size and size distributions of sample 1–5.

both the decreased repulsion among the hydrophilic chains and the increased surface tension resulting from the increased hydrophobic-hydrophilic balance (25, 26).

The change of aggregates' size with guest concentration is also measured by dynamic light scattering (DLS) technique, as shown in Figure 6. When the molar ratio of 2mPEG-C[4]A to phenol palmitate is 10:1, the average diameter of aggregates is about 420 nm. The aggregates shrink to 195 nm at the stoichiometric complexation between host and guest. However, the size of aggregates increases again when the phenol palmitate is excess. Generally speaking, the size determined by DLS is much larger than that from TEM. It is reasonable because TEM and DLS show the different morphology in a solid or swollen state, respectively (27, 28). The polydispersity index (PDI) for all of samples is close to 0.4, indicating the relatively broad size distribution. Both TEM and DLS observations show that the size and morphology of the self-assembled objects depend on the molar ratio of the host to guest. Changing the weight fraction of host or gust affects the hydrophilic-hydrophobic balance, thus, the morphology and size of self-assembled object can be readily adjusted.

Considering that 2mPEG-C[4]A and phenol palmitate are connected by weak interaction, the assemblies are dynamically stable. Such a dynamic behavior should be very useful in the controlled release of dyes and drugs. Pyrene is a widely used fluorescent probe for its photophysical characteristics. Because it is strongly hydrophobic, pyrene is preferentially solubilized into the interior of the hydrophobic region in aqueous media. This change in the microenvironment of the probes is reflected by variations in its emission spectra. The intensity ratio of the first to the third band of the pyrene emission spectrum, I_1/I_3, can be characterized as an indicator of the polarity of the pyrene environment

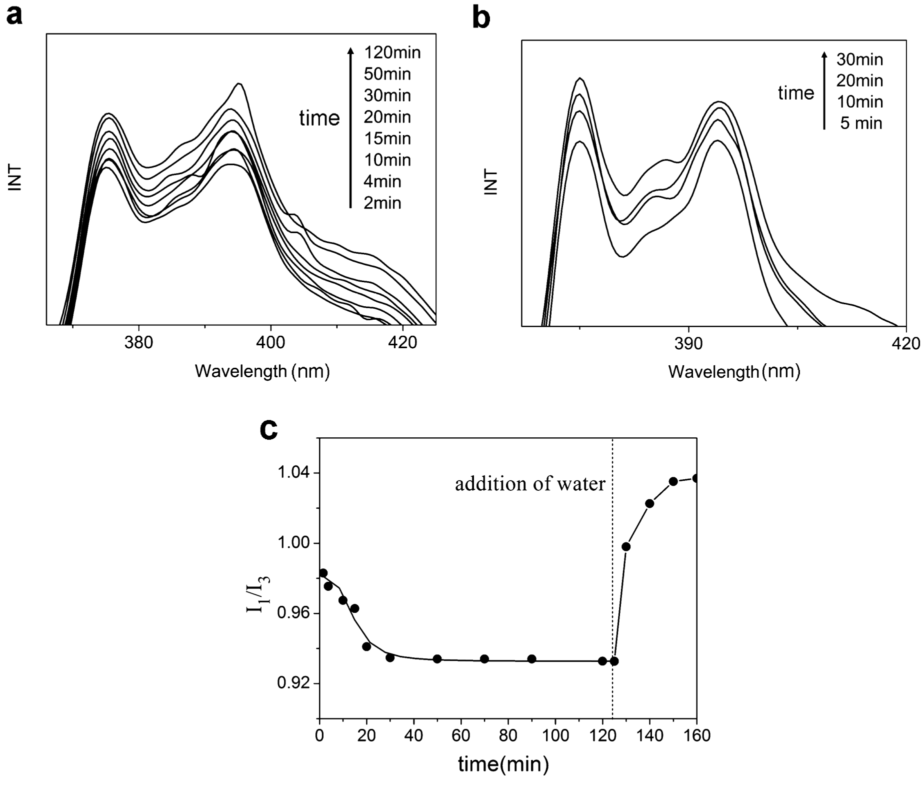


Fig. 7. Emission spectra of pyrene probe in assembly solution (a), and deconstruction of assemblies by dropping small mount of water (b), I_1/I_3 value variation before and after addition of water (c).

(29, 30). In this study, emission spectra of pyrene in aggregation solution were measured as a function of time until two hours later when the system was stable and no change in the emission spectra was observed. Subsequently, 100 μl deionized water was added into solution to break the connection between 2mPEG-C[4]A and phenol palmitate. This can be validated by the precipitation of guest molecules because of the strong hydrophobic property of alkyl chain. Figure 7 shows that after addition of pyrene, I_1/I_3 decreases from 0.99 to 0.93 gradually during 2 hours. In this process, free pyrenes enter into a less polar solubilization site of the aggregates, presumably in the interior layer of the micelle. In short, pyrene was found to have a limited solubility in the mixed solvent of dioxane and water. The addition of deionized water destroys the assembly, so I_1/I_3 rises up to 1.02 in 6 min and then levels off. This demonstrates a burst release of the probe pyrene from the hydrophobic core into the solvent, because of the deconstruction of self-assembled object. This apparent discrepancy results from the dynamic behavior of the noncovalent amphiphilic assembly. In comparison with the traditional diblock copolymer or other amphiphiles of which the hydrophobic and hydrophilic parts are connected by chemical bond, the noncovalent amphiphiles can be disconnected by changing the environment condition instead of breaking the covalent bond.

4 Conclusions

In conclusion, we have constructed a new type of supramolecular calixarene amphiphile using 2mPEG-C[4]A and phenol palmitate through the host-guest interaction. The hydrophilic building block can be implemented by the reaction of tert-butyl calix[4]arene and mPEG-OTs, while the phenol palmitate is used as the hydrophobic building block. ^{1}H NMR and FTIR results confirm the successful preparation of 2mPEG-C[4]A host and phenol palmitate guest. The hydrophilic-hydrophobic balance can be easily adjusted by the weight fraction of hydrophilic or hydrophobic building block. Therefore, various assemblies with different morphology or size can be obtained in a water/dioxane cosolvent. When the weight fraction of hydrophilic 2mPEG-C[4]A block is high, the large vesicles appear. Vesicles shrink with increasing weight fraction of hydrophobic phenol palmitate. At the stoichiometric complexation of 2mPEG-C[4]A and phenol palmitate, the normally spherical micelles form. Further increasing the guest content, the spherical micelles become larger and larger, finally to the net-work aggregates. The encapsulation and controlled release of pyrene molecules by supramolecular calix[4]arene assemblies have been performed. The experimental results demonstrate that the encapsulated molecules can be released by only changing the environment condition.

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