

# Self-Assembly and Disassembly of Vesicles as Controlled by Anion- $\pi$ Interactions

Qing He, Yu-Fei Ao, Zhi-Tang Huang, and De-Xian Wang\*

**Abstract:** Anion- $\pi$  interactions have been widely studied as new noncovalent driving forces in supramolecular chemistry. However, self-assembly induced by anion- $\pi$  interactions is still largely unexplored. Herein we report the formation of supramolecular amphiphiles through anion- $\pi$  interactions, and the subsequent formation of self-assembled vesicles in water. With the  $\pi$  receptor **1** as the host and anionic amphiphiles, such as sodium dodecylsulfate (SDS), sodium laurate (SLA), and sodium methyl dodecylphosphonate (SDP), as guests, the sequential formation of host-guest supramolecular amphiphiles and self-assembled vesicles was demonstrated by SEM, TEM, DLS, and XRD techniques. The intrinsic anion- $\pi$  interactions between **1** and the anionic amphiphiles were confirmed by crystal diffraction, HRMS analysis, and DFT calculations. Furthermore, the controlled disassembly of the vesicles was promoted by competing anions, such as  $\text{NO}_3^-$ ,  $\text{Cl}^-$ , and  $\text{Br}^-$ , or by changing the pH value of the medium.

Self-assembly by the use of amphiphiles as building blocks is an important theme in supramolecular chemistry.<sup>[1]</sup> Besides the vast amount of synthetic covalent amphiphiles, there has been great interest in supramolecular amphiphiles formed by noncovalent bonding.<sup>[1,2]</sup> The reversible nature of noncovalent bonding enables the straightforward construction of diverse supramolecular amphiphiles, and their controllable self-assembly and disassembly. The inclusion of versatile functional groups in supramolecular amphiphilic entities also enables the assembly of stimuli-responsive materials. Since early examples based on multiple hydrogen bonding<sup>[3]</sup> and electrostatic attraction,<sup>[4]</sup> noncovalent interactions such as coordination,<sup>[5]</sup> charge transfer,<sup>[6]</sup> and  $\pi$ - $\pi$  stacking<sup>[7]</sup> have also been applied as driving forces to form supramolecular amphiphiles. Macrocyclic host-guest motifs have also been used to build supramolecular amphiphilic systems, and their unique self-assemblies have attracted much attention.<sup>[8]</sup> Our interest in anion- $\pi$  interactions encouraged us to explore the possibility of applying this novel type of noncovalent bond as a driving force to induce the formation of supramolecular amphiphiles.

Anion- $\pi$  interactions between electron-rich anions and electron-deficient aromatic groups are emerging noncovalent

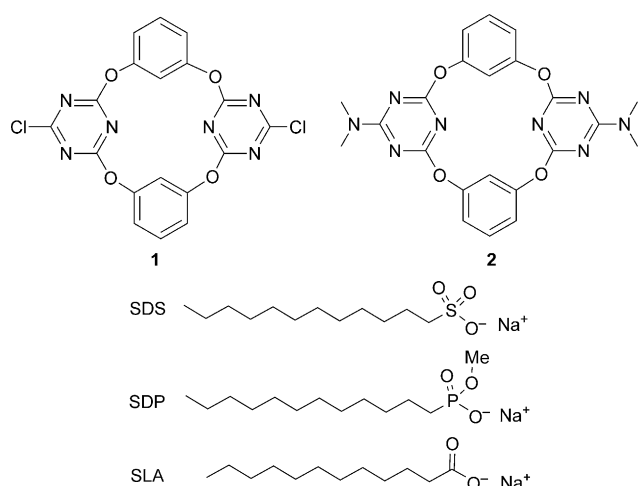
motifs.<sup>[9]</sup> Since previous theoretical studies that predict such noncovalent interactions,<sup>[10]</sup> experimental results both in the solid state and in solution have exemplified the existence of anion- $\pi$  interactions.<sup>[11]</sup> As compared to well-studied cation- $\pi$  interactions, which have been successfully applied in biological systems and chemistry,<sup>[12]</sup> the application of anion- $\pi$  interactions remains largely unexplored.<sup>[13]</sup> For example, in living systems, functions of anion- $\pi$  interactions in enzymatic catalysis and protein structure have been revealed by the groups of Frontera<sup>[13a]</sup> and Robertazzi,<sup>[13b]</sup> respectively. In the field of supramolecular chemistry, Guha and Saha<sup>[11k]</sup> reported anion sensing by the use of naphthanedimides (NDIs) as  $\pi$ -electron-deficient receptors. Matile and co-workers designed NDI-based and calixpyrrole-based transporters that can transport anions across lipid bilayer membranes.<sup>[13c,d]</sup> The Matile group also reported unprecedented catalytic reactions based on anion- $\pi$  interactions.<sup>[13e,f]</sup> Recently, we demonstrated that the size of vesicles formed with tetraoxacalix[2]arene[2]triazine-derived covalent amphiphiles can be regulated by anion- $\pi$  interactions both in THF-water and in water systems.<sup>[14]</sup> The further challenge is: could anion- $\pi$  interactions induce the formation of self-assembled aggregates in water? Specifically, could the anion- $\pi$  binding motifs be used to build supramolecular amphiphiles? To address this challenge, we report herein anion- $\pi$ -controlled self-assembly and disassembly. Our findings demonstrated that tetraoxacalix[2]arene[2]triazine and anionic surfactants can form supramolecular amphiphiles through anion- $\pi$  interactions. The resulting supramolecular amphiphiles further self-assembled into vesicles with the help of hydrophobic effects. Owing to the reversibility of anion- $\pi$  interactions, the controlled disassembly of vesicles can also be promoted by adding competitive anions or decreasing the pH value.

We initiated our studies by using **1**<sup>[15]</sup> as the host and commercially available sodium dodecylsulfate (SDS) as the guest to construct supramolecular amphiphiles (Scheme 1). In principle, SDS forms micelles above the critical micelle concentration (CMC; 8–10 mM) in water. Therefore, we chose a concentration far below its CMC for the investigation, and in such case SDSs are expected to exist as discrete molecules in solution. The procedure was carried out by quickly injecting water (1 mL) into a 1:1 mixture of **1** and SDS (60  $\mu\text{L}$ , 10 mM in THF/methanol (3:7)) to give a final concentration of  $6 \times 10^{-4}$  M. Vortexing of the aqueous mixture for 1 min produced an opalescent colloidal solution, thus indicating the formation of self-assembled aggregates. The critical aggregation concentration (CAC) was measured as  $5.0 \times 10^{-6}$  M by means of a fluorescence method with pyrene as the probe (see Figure S38 in the Supporting Information). The morphology of the aggregates was first investigated with

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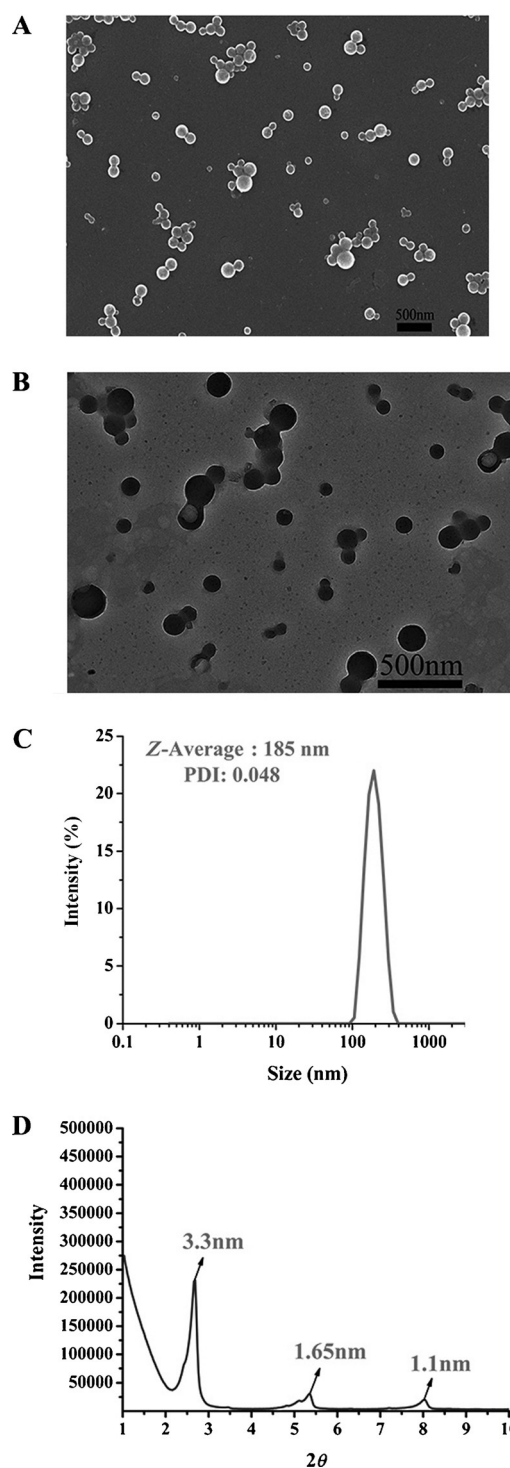


**Scheme 1.** Structures of host and guest molecules.

SEM and TEM techniques. From the SEM and TEM images (Figure 1 A,B), spherical aggregates with an average size in the range of 100–250 nm were obtained. The partially collapsed spheres observed demonstrate the hollow nature of the aggregates and thus the formation of vesicles. A cryo-TEM experiment confirmed the vesicular morphology (see Figure S22). DLS experiments revealed an average hydrodynamic diameter of the vesicles of 185 nm with a narrow size distribution ( $PDI = 0.048$ ; Figure 1 C); these results agree well with those obtained by SEM and TEM. The membrane thickness of the vesicles was determined on the basis of XRD experiments. After freeze drying of the colloidal solution, the resulting powders gave a strong diffraction peak at 3.3 nm ( $2\theta = 2.69^\circ$ ) as well as clear higher-order diffraction peaks at 1.65 (second-order) and 1.1 nm (third-order), thus demonstrating the formation of highly ordered assemblies (Figure 1 D). From the diffraction data, the thickness of the membrane was calculated to be 3.3 nm.

To gain more insight on the formation of the vesicles, we carried out SEM–EDS analysis to identify the building units of the vesicles. The experiments were carried out by scanning a small area of the surface of the vesicle and the blank background for analysis by energy-dispersive X-ray spectroscopy (EDS). Besides the carbon supporting material, the spectrum recorded from the vesicle surface showed peaks corresponding to N, O, Cl, S, and Na, which are the elements that make up **1** and SDS. In contrast, these elemental signals were not observed in the spectrum taken from the background (see Figure S15). This outcome indicated that both **1** and SDS contributed to the formation of the vesicles.

To verify that it was complexation between **1** and SDS that induced vesicle formation, we mixed **2** and SDS in a control experiment and investigated their self-assembly behavior. Compound **2** is a structural analogue of **1** in which the chloride atoms have been replaced with  $N(CH_3)_2$  groups. According to our previous results,<sup>[11d]</sup> the anion– $\pi$  binding affinity of **2** towards anions is negligible as the electron-donating  $N(CH_3)_2$  groups increase the electron density of the triazine rings and disfavor interactions with anions. The 1:1



**Figure 1.** A) SEM and B) TEM images, C) DLS (dynamic light scattering) and D) XRD results for the self-assembled vesicles formed from the mixture of **1** and SDS.  $PDI$  = polydispersity index.

mixture of **2** and SDS was prepared by the procedure used for **1** and SDS. However, SEM showed irregular morphologies rather than vesicles (see Figure S4). EDS analysis also indicated that these species with irregular morphologies were only precipitates of **2** (see Figure S17). The outcome that **2** failed to induce the formation of vesicles in turn

indicated that the anion- $\pi$  interactions between **1** and SDS are crucial during self-assembly.

The anion- $\pi$  interactions between **1** and SDS were further confirmed by high-resolution MS, crystallographic analysis, spectroscopic titrations, and DFT optimization. A peak for the **1**-SDS complex was clearly observed in the HRMS spectrum, and the isotopic peaks were in line with those in the simulated spectrum (Figure 2A,B). To gain deep insight into the structure of the complex on a molecular level, methyl sulfate (as the tetraethylammonium salt) was chosen as the anionic head group of SDS, and the complexation was studied both in the solid state and in solution. Fortunately, slow evaporation of a mixture solution of **1** and tetraethylammonium methyl sulfate in dichloromethane and *n*-hexane gave single crystals of  $\text{Et}_4\text{N}^+(\text{1} \cdot \text{CH}_3\text{SO}_3^-)$  in good quality. Crystallographic analysis revealed that methyl sulfate locates within the V-shaped cavity, with one of two oxygen atoms (O3) sitting over each triazine ring. The distances from O3 to the triazine planes and centroids are 2.959 and 2.980 Å, respectively, thus indicating the formation of typical anion- $\pi$  interactions (Figure 2C). Spectroscopic titration of **1** with tetraethylammonium methyl sulfate in acetonitrile confirmed the host-anion interaction and gave an association constant of  $1036 \text{ M}^{-1}$  (see Figure S42). On the basis of these results, we carried out DFT optimization at the B3LYP/6-31 + G\* level to probe the structure of the complex **1**-SDS. The calcu-

lated result gave an energetically favorable structure of the supramolecular amphiphile with the anionic head group of SDS located inside the V-shaped electron-deficient cavity of **1** (Figure 2D). The length of the supramolecular amphiphile, on the base of DFT modeling, is around 2.1 nm.

The combined results described above enabled us to sketch out the formation of vesicles; that is, **1** and SDS formed supramolecular amphiphilic complexes through anion- $\pi$  interactions, and the supramolecular amphiphiles self-assembled into vesicles with the cooperation of hydrophobic effects of the long alkyl chains (Figure 3). A comparison of the extended molecular length of the supramolecular amphiphilic complex (2.1 nm) and the measured membrane thickness of the vesicles (3.3 nm) indicated that a double-layer membrane is formed.

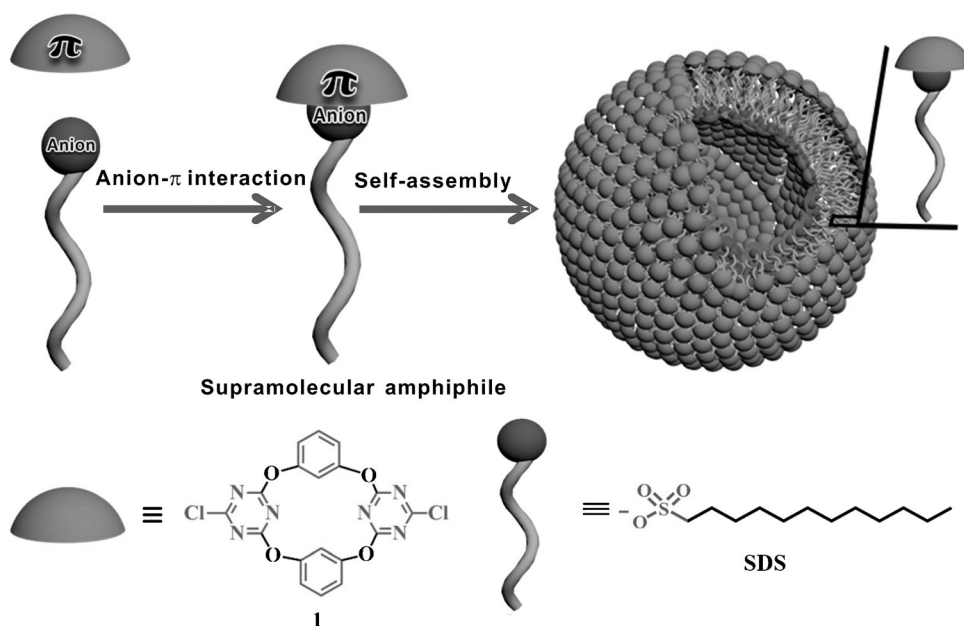


Figure 3. Illustration of the formation of vesicles as induced by anion- $\pi$  interactions.

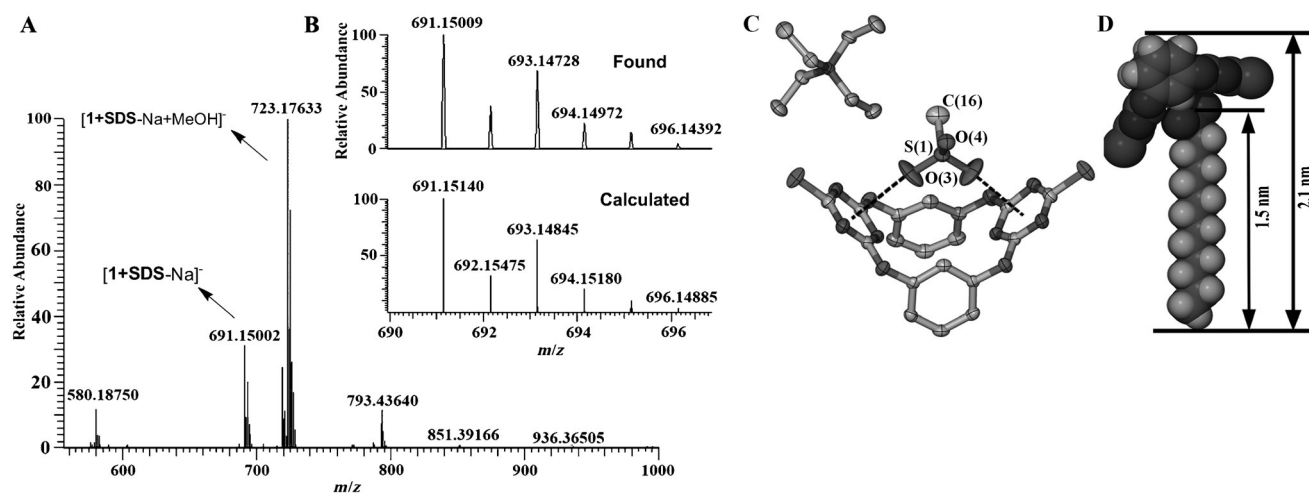
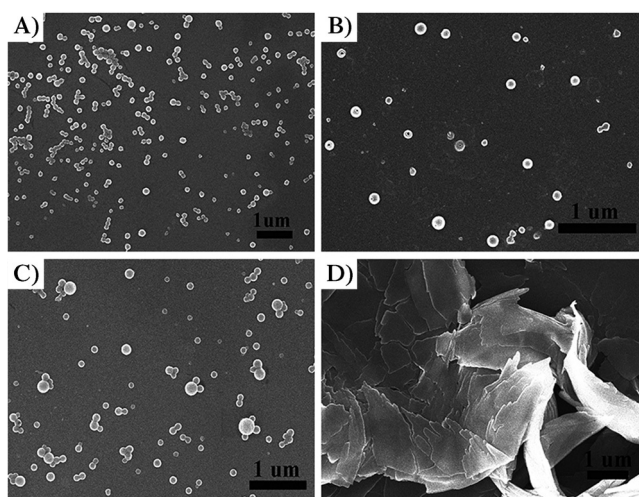


Figure 2. A,B) HRMS spectra of the complex of **1** and SDS. C) Crystal structure of the  $\text{Et}_4\text{N}^+(\text{1} \cdot \text{CH}_3\text{SO}_3^-)$  complex. D) DFT-optimized supramolecular amphiphilic model of **1** and SDS.

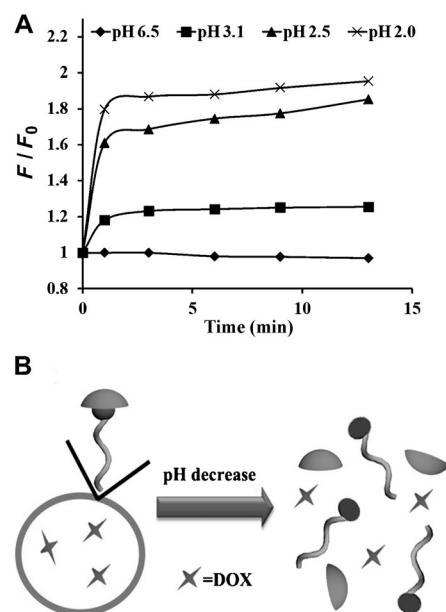


The controllable self-assembly and disassembly, or the responsiveness of self-assemblies, is an important theme in supramolecular chemistry.<sup>[1,8a]</sup> The reversible nature of anion- $\pi$  interactions led us to envision the controlled disassembly of the vesicles described above under different conditions. For example, the presence of competing anions that interact more strongly with **1** would disrupt the binding between SDS and **1** and lead to disassembly. Alternatively, protonation of the anionic head of SDS (through a decrease in the pH value) would have the same effect. To verify this hypothesis, we first investigated the effect of various anions, including  $\text{NO}_3^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{SCN}^-$ , and  $\text{ClO}_4^-$ , on the vesicles. As shown by SEM, the effects of anions can be separated into two groups. Upon the addition of 3 equivalents of  $\text{NO}_3^-$  or  $\text{Br}^-$  or 5 equivalents of  $\text{Cl}^-$  to the vesicle solution, for example, complete disassembly of the vesicles occurred, as indicated by the irregular morphologies observed in the SEM images instead of vesicles (Figure 4D; see also Figures S8–S10). However, the addition of up to 20 equivalents of  $\text{SCN}^-$  or  $\text{ClO}_4^-$  had almost no effect on the vesicles (Figure 4B; see also Figure S11). The disassembly of the vesicles, therefore, could be ascribed to the competitive interaction of  $\text{NO}_3^-$ ,  $\text{Cl}^-$ , and  $\text{Br}^-$ , versus SDS, with **1**.<sup>[11f]</sup>



**Figure 4.** Effects of anions on the disassembly of the vesicles formed by **1** and SDS: A) in the absence of anions; B) in the presence of NaSCN (20 equiv); C) in the presence of  $\text{NaNO}_3$  (1 equiv); D) in the presence of  $\text{NaNO}_3$  (3 equiv).

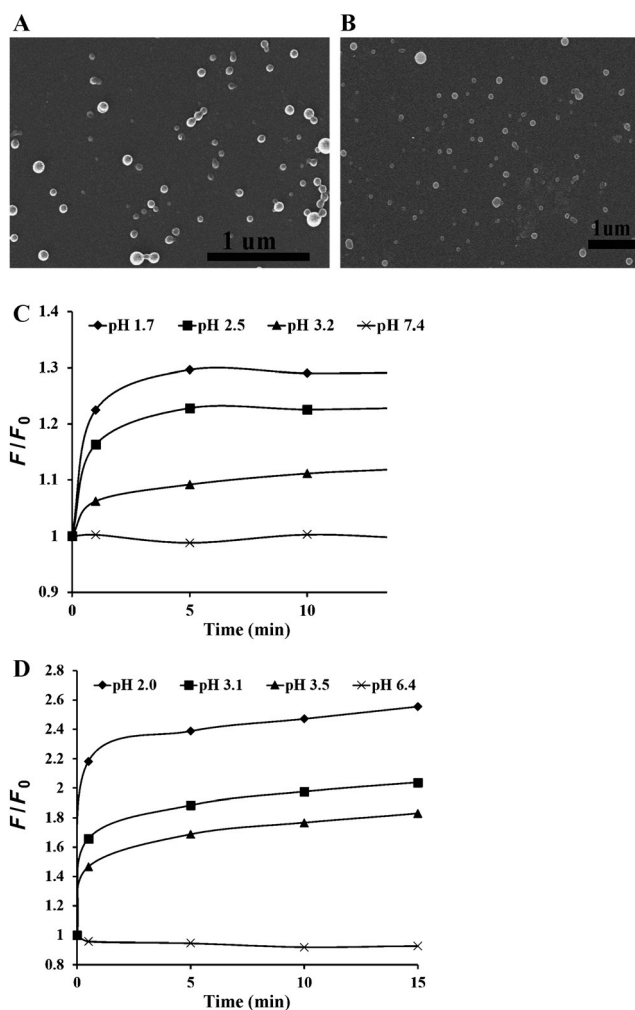
Alternatively, the controllable disassembly of the vesicles at lower pH values was observed in a drug-release experiment. The water-soluble drug doxorubicin (DOX,  $5 \times 10^{-5} \text{ M}$ ) was incubated with the mixture of **1** and SDS, and after self-assembly, it was encapsulated in the vesicles. Then repeat dialysis was performed to remove the free DOX outside the vesicles. The release of DOX was monitored on the basis of changes in fluorescence intensity.<sup>[8f]</sup> The fluorescence intensity of the encapsulated DOX remained constant at pH 6.5, thus indicating that no release occurred at all (Figure 5). In contrast, significantly enhanced intensity was recorded as the pH value decreased. For example, the relative fluorescence



**Figure 5.** A) pH-mediated release of DOX from inside the vesicles formed by **1** and SDS. B) Illustration of the pH-mediated release of DOX.

intensity increased from 1 at pH 6.5 to 1.89 at pH 2.0 (Figure 5A). Since the fluorescence intensity of DOX alone is not affected by changes in the pH value (see Figure S38), the results indicated the pH-mediated release of DOX. As the pH value decreased, protonation of the sulfate anionic head group of SDS occurred, and its anion- $\pi$  interactions with **1** were weakened, thus leading to the concomitant disassembly of the vesicles and release of DOX (Figure 5B).

Encouraged by the results with SDS and **1**, we further extended the protocol to the use of sodium laurate (SLA; CMC = 20–30 mM) and sodium methyl dodecylphosphonate (SDP; CMC = 8 mM).<sup>[16]</sup> As demonstrated by a combination of STM, TEM, cryo-TEM, DLS, and XRD measurements, 1:1 mixtures (total concentration:  $1 \times 10^{-4} \text{ M}$ ) of **1** and SLA or SDP yielded assembled vesicles with an average diameter of 128 and 143 nm, respectively (Figure 6A,B; for other Figures, see the Supporting Information). The CAC values of the two supramolecular amphiphiles were  $7.5 \times 10^{-6} \text{ M}$  (**1**/SLA) and  $7.1 \times 10^{-6} \text{ M}$  (**1**/SDP; see Figures S39 and S40). We investigated the mechanism of formation of the vesicles by the same protocols used for **1** and SDS. For example, HRMS measurements indicated the formation of a 1:1 complex between **1** and SLA or SDP (see Figures S32 and S33). Spectroscopic titrations of **1** with methyl methylphosphonate and acetate (as their quaternary ammonium salts) in acetonitrile gave association constants of 3372 and  $7846 \text{ M}^{-1}$ , respectively (see Figures S43 and S44). We also determined the crystal structure of  $\text{Me}_4\text{N}^+(1\text{-CH}_3\text{COO}^-)$ . In spite of some disorder, it clearly showed that the carboxylate group is located in the cavity and participates in an anion- $\pi$  interaction and possible  $\pi$ - $\pi$  stacking with one of the triazine rings (see Figure S35). Furthermore, DFT calculations at the B3LYP/6-31 + G\* level gave energetically favorable 1:1 supramolecular amphiphiles composed of **1** and SLA or SDP (see Figure S36). Therefore,



**Figure 6.** A,B) SEM images of self-assembled vesicles formed by **1** and SDS (A), and **1** and SLA (B). C,D) pH-mediated release of DOX from inside the vesicles formed by **1** and SLA (C), and **1** and SDP (D). Scale bars: 1 μm.

in analogy with **1** and SDS, the formation of supramolecular amphiphiles between **1** and SDP or SLA was revealed, as well as the subsequent formation of self-assembled vesicles. Finally, the release of DOX from inside the vesicles formed by **1** and SLA or SDP was also observed when the pH value was decreased, thus indicating that the formation and disassembly of these vesicles could be mediated by changes in the pH value as well (Figure 6C,D; see also Figures S13 and S14).

In summary, we have demonstrated that a 1:1 mixture of host molecule **1** and an anionic guest, such as SDS, SLA, or SDP, led to the formation of self-assembled vesicles. The vesicular morphology of the self-assemblies was confirmed by a combination of SEM, TEM, and DLS studies. Through HRMS, spectroscopic titration, crystal-structure analysis, DFT calculations, and control experiments, **1** was shown to form supramolecular amphiphilic complexes with SDS, SLA, and SDP. The supramolecular amphiphilic complexes further self-assembled into vesicles with the cooperation of hydrophobic effects. The disassembly of the vesicles

was promoted by competing anions, such as  $\text{NO}_3^-$ ,  $\text{Cl}^-$ , and  $\text{Br}^-$ , or by a decrease in the pH value. Thus, this study demonstrated that anion- $\pi$  interactions can induce the formation of self-assembled vesicles in water. It suggests future applications of anion- $\pi$  interactions in the fabrication of stimuli-responsive materials and the development of drug-delivery systems.

## Experimental Section

**Preparation of vesicles:** Stock solutions of 1:1 mixtures ( $5 \times 10^{-3}$  M) were prepared by dissolving equimolar amounts of **1** and SDS, SDP, or SLA in a mixture of THF and methanol (v/v, 3:7). A small volume of the stock solution (60 μL for **1** and SDS, 10 μL for **1** and SDP or SLA) was transferred to a sample bottle. Doubly distilled water (1 mL) was injected quickly to a final concentration of  $6 \times 10^{-4}$  M for **1** and SDS, and  $1 \times 10^{-4}$  M for **1** and SDP or **1** and SLA. Vortexing of the aqueous mixture for 1 min produced an opalescent colloidal solution.

**Dynamic light scattering:** DLS measurements were carried out at 25 °C with an LLS spectrometer (ALV/SP-125) equipped with a multi- $\tau$  digital time correlator (ALV-5000). Light of  $\lambda = 632.8$  nm from a solid-state He-Ne laser (22 mW) was used as the incident beam. The measurement was performed at a scattering angle of 90°. The correlation function was analyzed from the scattering data by the CONTIN method to obtain the distribution of diffusion coefficients ( $D$ ) of the solutes. The apparent hydrodynamic radius  $R_h$  was deduced from  $D$  by the Stokes-Einstein equation  $R_h = k_B T / (6\pi\eta D)$ , in which  $k_B$  is the Boltzmann constant,  $T$  is the temperature in kelvin, and  $\eta$  is the viscosity of the solvent.

**X-ray diffraction:** Samples for XRD measurement were prepared by direct lyophilization of 30 mL of freshly prepared vesicular solution in a vacuum freeze drier. XRD analysis was performed on an X-ray diffractometer (SW, X'PERT) with nickel-filtered  $\text{Cu}_{K\alpha}$  radiation ( $\lambda = 1.54060$  Å) at 40 kV and 10 mA.

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**Keywords:** anion- $\pi$  interactions · host-guest systems · self-assembly · supramolecular amphiphiles · vesicles

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- [16] The new surfactant compound SDP was synthesized, and its CMC was measured as 8 mM by means of a fluorescence method with pyrene as the probe (see Figure S34).

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