

# CO<sub>2</sub>-Responsive Pillar[5]arene-Based Molecular Recognition in Water: Establishment and Application in Gas-Controlled Self-Assembly and Release

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## S Supporting Information

**ABSTRACT:** Here we developed a novel CO<sub>2</sub>-responsive pillararene-based molecular recognition motif established from a water-soluble pillar[5]arene and an anionic surfactant, sodium dodecyl sulfonate (SDS). The inclusion complex acted as a supramolecular amphiphile and self-assembled into spherical bilayer vesicles as confirmed by DLS, SEM, and TEM experiments. These vesicles were disrupted upon bubbling N<sub>2</sub> or adding much more SDS to eliminate the inclusion complex. The assembly and disassembly of vesicles were successfully employed in gas and surfactant triggered releases of calcein, a water-soluble dye.

Macrocyclic compounds, which can act as supramolecular hosts to encapsulate guest molecules into their cavities, have been designed and synthesized intensively in the past decades. Next to crown ethers,<sup>1</sup> cyclodextrins,<sup>2</sup> calixarenes,<sup>3</sup> and cucurbiturils,<sup>4</sup> pillar[*n*]arenes are a new class of supramolecular hosts.<sup>5–8</sup> Different from the basket-shaped structure of meta-bridged calixarenes, pillararenes are linked by methylene bridges at para-positions of 2,5-dialkoxybenzene rings, forming a unique rigid pillar structure.<sup>6</sup> Moreover, both sides of pillararenes can be modified with functional groups in a facile way. The unique symmetrical structures and easy functionalization of pillararenes have endowed them with valuable properties in host–guest recognition.<sup>7</sup> For instance, in contrast to water-soluble cucurbiturils and cyclodextrins, pillararene-based host–guest interactions can be explored both in organic and aqueous solvents. Recently, stimuli-responsive host–guest recognition motifs based on pillararenes have been widely built whose triggers include pH, enzymes, light, temperature, etc., and further applied in supramolecular polymers and supramolecular amphiphiles.<sup>8</sup> Since host–guest recognition can be used to construct more complex supramolecular architectures,<sup>9</sup> the search of novel pillararene-based stimuli-responsive host–guest recognition motifs may significantly promote the progress of pillararenes in various areas.

CO<sub>2</sub>, a kind of benign, renewable, energy-efficient, and nonpolluting gas, has rarely been utilized as a stimulus in responsive supramolecular recognition motifs.<sup>10</sup> While CO<sub>2</sub> truly acts as a weak acid, it has advantages over normal acids, in avoiding addition of acid or base which contaminates the system with counterions and weaken the switchability due to salt accumulation.<sup>11</sup> Indeed, CO<sub>2</sub> can be completely removed from

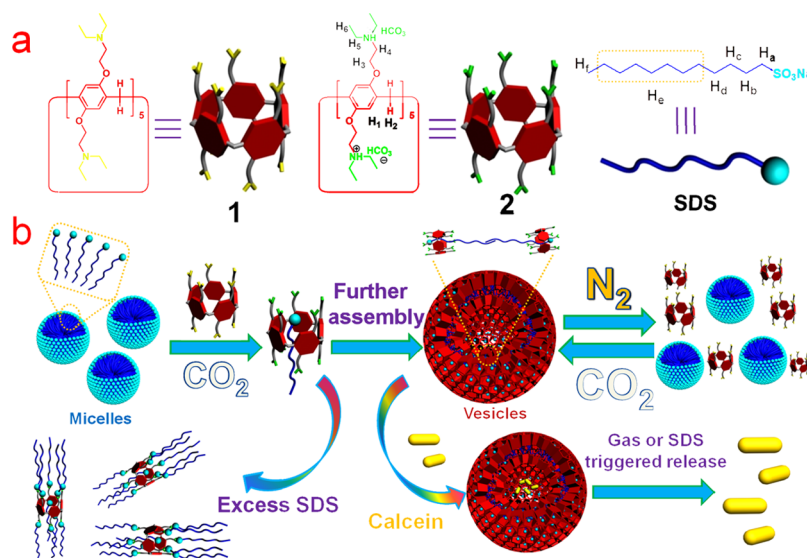
the systems simply by the passage of an inert gas (argon or nitrogen) or mild heating of the solution, which allows the CO<sub>2</sub>-reactive functional groups to recover their original forms.<sup>12</sup> Based on the advantages mentioned above, developing CO<sub>2</sub>-responsive molecular recognition motifs may be helpful to understand biological processes such as photosynthesis and fabricate novel stimuli-responsive materials such as drug delivery systems.<sup>13</sup> Recently, several wonderful works about CO<sub>2</sub>-responsive polymers were reported by Yuan et al.,<sup>11b,12d</sup> and cyclodextrin-based CO<sub>2</sub>-switchable molecular recognition was used in a polymeric self-assembly system.<sup>10</sup> However, to the best of our knowledge, pillararene-based CO<sub>2</sub>-responsive molecular recognition motifs and supramolecular amphiphiles have not been reported yet.

With the consideration of using CO<sub>2</sub> as a stimulus to construct a novel supramolecular amphiphile via pillararene-based host–guest interactions, we first established a new CO<sub>2</sub>-responsive pillar[5]arene-based host–guest recognition motif in water (Scheme 1). Pillar[5]arene **1** containing 10 tertiary amine groups at the two rims was designed and synthesized. Upon protonation by CO<sub>2</sub>, the tertiary amine parts were changed into cationic tertiary ammonium salt groups. Thus, water-insoluble pillar[5]arene **1** was turned into water-soluble pillar[5]arene **2**, making **2** a fantastic receptor for anionic guests. Sodium dodecyl sulfonate (SDS), an anionic surfactant which has been widely used in life, industry, and scientific research, threaded into the cavity of **2** mainly through CH–π, electrostatic, and hydrophobic interactions, forms a 1:1 [2]pseudorotaxane in water. Interestingly, this [2]pseudorotaxane also acted as a supramolecular amphiphile and self-assembled into spherical bilayer vesicles in water. The bilayer vesicles were destroyed simply by heating or bubbling N<sub>2</sub> to eliminate CO<sub>2</sub> as **2** turned back into **1**, thus eliminating the host–guest complexation between **2** and SDS. More intriguingly, upon addition of excess SDS, the vesicles were also disrupted because the anionic part of SDS acted as an anionic counterion to replace the bicarbonate anion in water, making the pillar[5]arene part hydrophobic. Vesicles disassembled by N<sub>2</sub> or heat could form again upon bubbling with CO<sub>2</sub>, while vesicle removal with excess SDS was irreversible. The gas-induced assembly and disassembly process was totally reversible without the accumulation of other species. Furthermore, those vesicles

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Scheme 1. (a) Chemical Structures and Cartoon Representations of 1, 2, and SDS and (b) Cartoon Representation of Gas-Controlled Self-Assembly and Dual-Trigged Release of Calcein<sup>a</sup>



<sup>a</sup>Blue solid particles represent micelles. Red hollow spheres represent vesicles.

were used in dual-triggered release of an encapsulated water-soluble dye calcein (Scheme 1).

Pillar[5]arene **1** was synthesized and characterized by <sup>1</sup>H NMR, <sup>13</sup>C NMR, LRESIMS, and MALDI-TOF MS (Figures S1–S3). Then **1** was well dispersed in water (1.00 mM, 3.00 mL) by treatment with ultrasound and turned to **2** upon bubbling CO<sub>2</sub> (0.4 MPa, 1 min). The complexation between **2** and SDS in water was first investigated by <sup>1</sup>H NMR spectroscopy (Figure 1). The <sup>1</sup>H NMR spectrum of an equimolar (1.00 mM) D<sub>2</sub>O solution of **2** and SDS (Figure 1b) indicated that the complexation between **2** and SDS was rapidly exchanging on the <sup>1</sup>H NMR time scale. When equimolar **2** was mixed with SDS,

H<sub>a</sub>, H<sub>b</sub>, H<sub>c</sub>, H<sub>d</sub>, and H<sub>e</sub> on SDS shifted upfield, while no obvious chemical shift changes were observed for H<sub>f</sub> after complexation. Furthermore, the overlapped signal corresponding to H<sub>e</sub> was split into seven peaks after complexation. On the other hand, slight chemical shift changes were also observed for the protons of **2**.

A 2D NOESY NMR study of an aqueous solution of **2** (5.00 mM) and SDS (5.00 mM) was performed to investigate the relative spatial positions of this host–guest complex. As shown in Figure S4, clear correlation signals were observed between protons H<sub>a–e</sub> on SDS and protons H<sub>1–3</sub> on **2**, respectively, indicating that part of SDS penetrated into the cavity of **2** with the sulfonate group close to the ammonium salt groups on **2**.

In order to estimate the association constant ( $K_a$ ) of the complex between **2** and SDS, we carried out isothermal titration calorimetry (ITC) experiments to provide thermodynamic insight. The  $K_a$  value of **2**∩SDS was determined to be  $(4.6 \pm 0.5) \times 10^5 \text{ M}^{-1}$  in 1:1 stoichiometry (Figure S5), which was further confirmed by electrospray ionization mass spectrometry (ESI-MS, Figure S6). ESI-MS revealed a clear peak at  $m/z$  1177.4 for  $[\mathbf{2} \cap \text{SDS} - 3\text{HCO}_3^- - \text{Na}^+ + 3\text{H}_2\text{O}]^{2+}$ , and no peaks related to other complex stoichiometries were observed. The binding affinity of this host–guest system can be attributed to the cooperativity of multiple electrostatic interactions between the cationic tertiary ammonium salt groups on the rigid pillar[5]-arene receptor platform and the anionic sulfonate part on SDS, CH- $\pi$ , and hydrophobic interactions between the alkyl chain and the host. Therefore, according to <sup>1</sup>H NMR, 2D NOESY, ITC and mass spectrometry investigations, we conclude that in solution, the guest molecule SDS, as an axle, was threaded through the cavity of the cyclic host **2** to construct a 1:1 inclusion complex.

It is well-established that the neutral tertiary amines and cationic tertiary ammonium salt groups can be reversibly interconverted by bubbling with CO<sub>2</sub> or N<sub>2</sub>, respectively.<sup>11c,12d</sup> Hence, the dethreading/rethreading process of **2**∩SDS can be controlled by alternatively bubbling with CO<sub>2</sub> or N<sub>2</sub>, making the complexation totally gas responsive. When a solution of equimolar **2** and SDS was bubbled with N<sub>2</sub>, the transparent solution gradually became turbid as the cationic tertiary

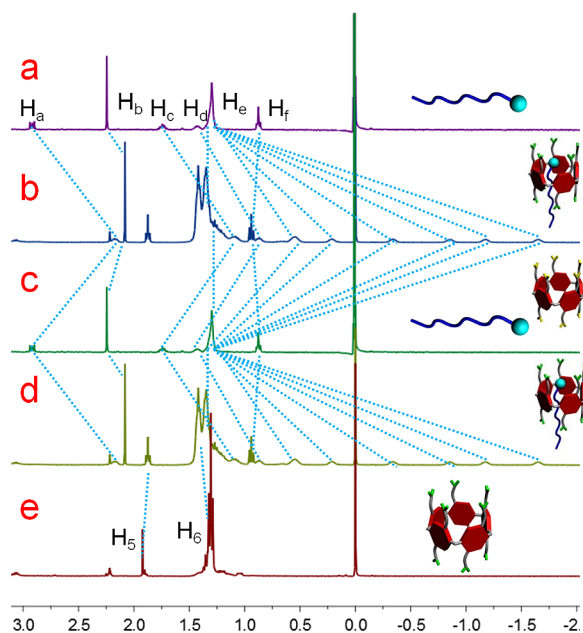
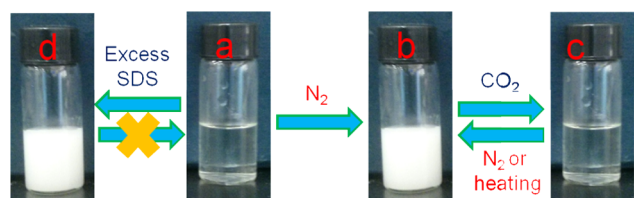


Figure 1. Partial <sup>1</sup>H NMR spectra (400 MHz, D<sub>2</sub>O, 293 K): (a) SDS (1.00 mM); (b) **2** (1.00 mM) and SDS (1.00 mM); (c) after bubbling b with N<sub>2</sub>; (d) after bubbling c with CO<sub>2</sub>; (e) **2** (1.00 mM).

ammonium salt groups on **2** were slowly deprotonated into hydrophobic tertiary amine groups by  $N_2$ , making water-soluble **2** transform to water-insoluble **1**. However, as expected, the turbid dispersion slowly turned transparent upon bubbling with  $CO_2$  (Figure 2), resulting from the protonation of the tertiary

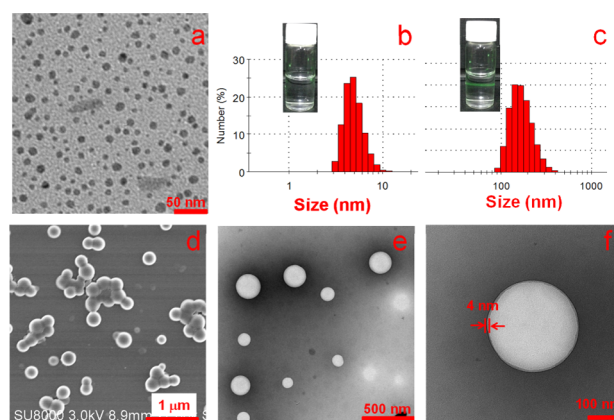


**Figure 2.** Photographs of aqueous solutions: (a) 1.00 mM **2** and SDS dissolved in water; (b) after bubbling a with  $N_2$  (0.5 MPa, 3 min) or heating; (c) after bubbling b with  $CO_2$  (0.4 MPa, 2 min); (d) after adding excess SDS to a.

amine groups and the recovery of water-soluble **2**.  $^1H$  NMR provided strong evidence for the gas-controlled complexation between **2** and SDS. Compared with the spectrum of **2** and SDS in  $D_2O$ , the signals for the protons on **2** disappeared after bubbling with  $N_2$  or heating the solution. Meanwhile, the chemical shifts of  $H_{a-e}$  on SDS returned to their original states as did those of other protons of SDS (Figure 1c), indicating that SDS dethreaded from the cavity of **2**. On the other hand, the signals corresponding to protons on SDS shifted upfield remarkably, and the peaks of  $H_{a-e}$  became broad again by protonation of the tertiary amine groups of **1** upon bubbling with  $CO_2$ , indicating the recovery of the complex between **2** and SDS (Figure 1d). Moreover, the dethreading/rethreading process could be reproduced over several cycles. Alternatively bubbling with  $CO_2$  and removing it by bubbling with  $N_2$  to or heating a solution of **2** and SDS induced a huge change in the transmittance of the dispersion using a visual wavelength of 339 nm (Figures 2a–c and S7).

Interestingly, upon addition of excess SDS, the solution became turbid and a precipitate formed (Figure 2d). The  $^1H$  NMR spectrum of the precipitate in chloroform-*d* showed that anionic dodecyl sulfonate groups acted as counteranions to replace bicarbonate anions, leading to a decrease of the water solubility of **2**. Moreover, there was still a guest molecule threaded through the cavity of **2** (Figure S8). Besides, in a 2D diffusion-ordered  $^1H$  NMR spectroscopy (DOSY) experiment, the observation of a single band confirmed that a single product formed, implying that the dodecyl sulfonate groups became the counteranions of **2** when the SDS concentration was sufficiently high (Figure S9).

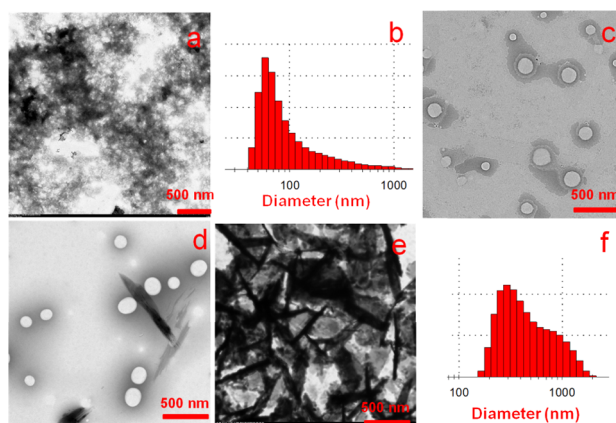
As reported by previous literature,<sup>14</sup> SDS (the critical aggregation concentration value  $\sim 8.00 \times 10^{-3}$  M) as a surfactant self-assembled into micelles, which was confirmed by DLS and TEM experiments (Figure 3a,b). Intriguingly,  $2\text{CSDS}$  served as a supramolecular amphiphile with the pillar[5]arene head as the hydrophilic portion and the alkyl chain on SDS as the hydrophobic part. The self-assembly behavior of  $2\text{CSDS}$  in water was investigated by DLS, SEM, and TEM. The critical aggregation concentration value of  $2\text{CSDS}$  in water was measured to be  $\sim 2.00 \times 10^{-4}$  M by plotting the conductivity of equimolar solutions of **2** and SDS as a function of concentration (Figure S10). The Tyndall effect was observed for a solution of  $2\text{CSDS}$  (Figure 3c), indicating the self-assemblies were more than 100 nm in diameter. DLS results (Figure 3c) showed that the aggregates of  $2\text{CSDS}$  have an



**Figure 3.** (a) TEM image and (b) DLS result of SDS ( $1.00 \times 10^{-2}$  M) in water; (c) DLS and Tyndall effect, (d) SEM image, (e) TEM image, and (f) enlarged TEM image of  $2\text{CSDS}$  ( $4.00 \times 10^{-4}$  M) in water.

average diameter of  $\sim 200$  nm with a narrow size distribution, indicating that some spherical assemblies formed. Spherical assemblies around 200 nm in diameter were observed in SEM images (Figure 3d), strongly supporting the DLS result. A TEM experiment was further conducted, and hollow spherical assemblies with a thin shell were observed, suggesting that  $2\text{CSDS}$  self-assembled into vesicles in water (Figure 3e). The wall thickness of the hollow vesicles was measured to be about 4.2 nm by small-angle X-ray scattering (Figure S11) and 4.0 nm based on an enlarged TEM image (Figure 3f). Moreover, this thickness corresponds to about twice of the length of a  $2\text{CSDS}$  complex (Figure S12), indicating that the vesicles have bilayer walls.

Not surprisingly, the vesicles collapsed into irregular assemblies upon bubbling with  $N_2$  (0.5 MPa, 3 min), because the complex  $2\text{CSDS}$  was destroyed, forming a precipitate (Figure 4a). DLS showed that this precipitate possessed a wide size distribution, suggesting the formation of irregular assemblies (Figure 4b). We wondered whether vesicles could be reformed upon bubbling with  $CO_2$  through the solution. As expected, vesicular aggregates emerged again, while there still existed some irregular assemblies upon bubbling with  $CO_2$  (0.4 MPa) for 1 min (Figure 4c). Moreover, bubbling with  $CO_2$  for more than 3



**Figure 4.** (a) TEM image and (b) DLS results for  $2\text{CSDS}$  ( $4.00 \times 10^{-4}$  M) in water after bubbling with  $N_2$  (0.5 MPa, 3 min); (c) TEM image of a after bubbling with  $CO_2$  (0.4 MPa, 1 min); (d) TEM image of a after bubbling with  $CO_2$  (0.4 MPa, 3 min); (e) TEM image and (f) DLS result of a after adding 10 equiv of SDS.



min caused the complete reformation of vesicles and the disappearance of irregular assemblies (Figure 4d), indicating the time-dependent self-assembly process. Additionally, according to the repeated cycles performed before, we demonstrated that the formation and disruption of vesicles could be realized several times without the accumulation of other species. Furthermore, as shown in Figure 4e, the addition of excess SDS led to the disruption of vesicles. The corresponding DLS results exhibited a wide size distribution from 30 to 800 nm, strongly supporting the disruption of vesicles (Figure 4f).

Depending on the gas-controlled assembly and disassembly and guest-induced disassembly of vesicles, controlled release experiments were then performed. Calcein, as a hydrophilic fluorescent guest which could be encapsulated into the interior of the vesicles, was chosen as the model compound. A solution of calcein-loaded vesicles was dialyzed until free calcein molecules were almost all removed. Upon bubbling with N<sub>2</sub> or adding SDS, the release percentage of calcein molecules from the vesicles was obtained by checking the fluorescence change in the solution (Figures S13 and S14). Interestingly, the release rate with the N<sub>2</sub> treatment was much slower than by adding SDS due to the relatively slow vesicle disruption caused by N<sub>2</sub> treatment. At last, the release amount with both treatments was almost the same, indicating the total collapse of the vesicles.

In conclusion, a CO<sub>2</sub>-responsive molecular recognition motif was built from a tertiary amine-modified pillar[5]arene and SDS in water and it was used in the construction of supramolecular vesicles and gas controlled release. Compared with cyclodextrin-based CO<sub>2</sub>-switchable molecular recognition,<sup>10</sup> this CO<sub>2</sub>-responsive pillar[5]arene-based host-guest complex formed with the addition of CO<sub>2</sub>, while cyclodextrin-based CO<sub>2</sub>-switchable molecular recognition was disrupted after bubbling CO<sub>2</sub>. Moreover, the formation and destruction of this CO<sub>2</sub>-responsive pillar[5]arene-based host-guest complex can be visually judged due to the change of the solution transmittance. In addition, the hydrophobic alkyl chains of SDS could be threaded into the cyclodextrin cavity with the sulfonate groups outside the cavity, which is different from our system. This new CO<sub>2</sub>-responsive molecular recognition motif and self-assembly systems based on it have potential use in drug delivery and sensors and should be beneficial for us to better understand biological processes.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b05960.

Experimental details, synthesis of pillararene 1, NMR spectra, and other materials (PDF)

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### Notes

The authors declare no competing financial interest.

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