

Water-Soluble Pillar[7]arene: Synthesis, pH-Controlled Complexation with Paraquat, and Application in Constructing Supramolecular Vesicles

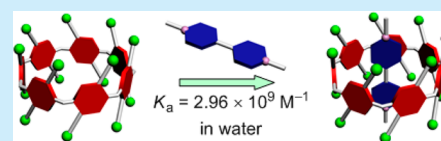
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S Supporting Information

ABSTRACT: By the introduction of 14 anionic carboxylate groups at its two rims, a water-soluble pillar[7]arene (WP7) was synthesized. Its pH-controlled complexation with paraquat **G**₁ in water was investigated. Host WP7 and guest **G**₁ formed a 1:1 [2]pseudorotaxane with a high association constant of $(2.96 \pm 0.31) \times 10^9 \text{ M}^{-1}$ in water. Furthermore, we took advantage of this novel molecular recognition motif to fabricate a supra-amphiphile based on WP7 and an amphiphilic paraquat derivative **G**₂. The morphologies and sizes of self-assemblies of **G**₂ and WP7 \supset **G**₂ were identified by transmission electron microscopy and dynamic light scattering.



The environment-responsive molecular recognition motifs have played a significant role in the progress of supramolecular chemistry and been widely used to construct different kinds of supramolecular systems, such as molecular machines,¹ molecular switches,² drug carrier materials,³ supramolecular polymers,⁴ and so on.⁵ Pillararenes,^{6–11} as a novel family of macrocyclic host molecules, have attracted growing interest since they were reported in 2008.^{6a} Because of their rigid pillar architectures, pillararenes have revealed ascendant host–guest complexation properties with different kinds of guests. On the basis of established recognition topics, rotaxanes/pseudorotaxanes,⁷ vesicles,⁸ daisy chains,⁹ and supramolecular polymers¹⁰ have been prepared to enrich the contents and applications of pillararenes in different areas.

Previously, Li et al. reported that a bis(imidazolium) dication could thread into the cavity of pillar[5]arene and its dethreading/rethreading process could be reversibly controlled by acid/base treatment.^{7a} Later, we reported the anion-responsive host–guest complexation between pillar[5]arenes and secondary ammonium salts and demonstrated that the host–guest complexation could be inhibited by addition of chloride anion.^{7e} As for pillar[6]arenes, some interesting studies have also been reported. For example, we synthesized the first water-soluble pillar[6]arene^{6m} and studied its pH-responsive host–guest binding to paraquat in water.^{8a} Similarly, Wang et al. reported its pH-controlled complexation with a ferrocene derivative.⁶ⁿ Furthermore, they studied redox-responsive complexation between per-butylated pillar[6]arene and a ferrocenium guest.^{7h} Different from the motif presented by Wang et al., we discovered another redox-responsive recognition motif based on a pillar[5]arene with mono-(ethylene oxide) substituents and paraquat.⁷ⁱ This host–guest complexation could be reversibly controlled by sequential addition and removal of Zn powder.

Pillar[7]arenes, which have seven repeating units, have larger cavities^{6g} than those of pillar[5]arenes and pillar[6]arenes. Though the syntheses of pillar[7]arenes have been reported previously,¹¹ the host–guest complexation based on pillar[7]arenes has been rarely reported. Recently, Li et al. presented the first example of pillar[7]arene-based host–guest complexation between per-ethylated pillar[7]arene and 3,5-dimethyl-1-adamantylammonium cations.^{11d} This work is of great significance and encourages researchers to exploit the potential of pillar[7]arenes in other aspects. We are interested in the host–guest chemistry of pillar[7]arenes in water. Herein, we synthesized the first water-soluble pillar[7]arene (WP7). It bears 14 anionic carboxylate groups on its two rims. We pleasantly discovered its pH-responsive binding to paraquat (**G**₁) with an extremely high association constant of $(2.96 \pm 0.31) \times 10^9 \text{ M}^{-1}$. Furthermore, we employed this new molecular recognition motif in the construction of a supra-amphiphile^{12b} based on WP7 and an amphiphilic paraquat derivative **G**₂ (Scheme 1).

The water-soluble pillar[7]arene WP7 was synthesized according to a method reported previously^{7b} (Scheme S1, Supporting Information). From the ¹H NMR spectrum of WP7 (Figure 1e), proton signals corresponding to phenyl protons H₁, methylene protons H₂ at both rims, and bridging methylene protons H₃ were observed as singlets, indicating that the architecture of WP7 was highly symmetrical.

The complexation between WP7 and **G**₁ was first investigated by ¹H NMR spectroscopy (Figure S10, Supporting Information). When equimolar WP7 was mixed with **G**₁ (2.00 mM), the signals related to the protons on **G**₁ became broad and shifted upfield significantly (Figure S10b, Supporting

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Scheme 1. Chemicals Used in This Study

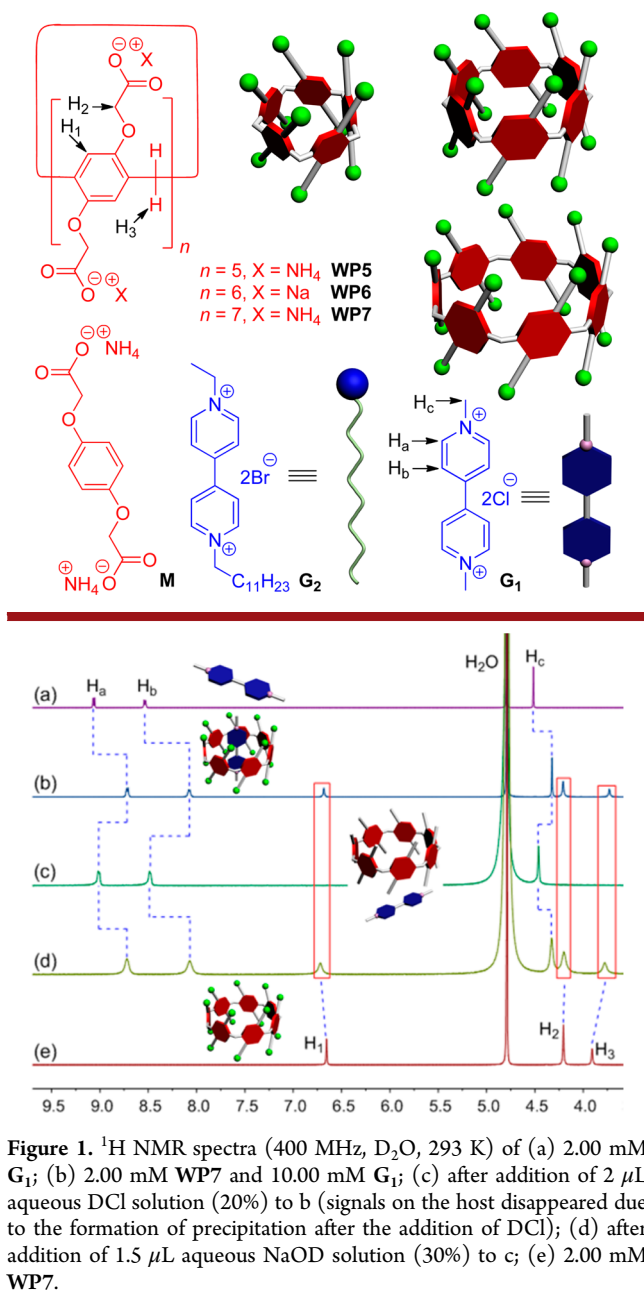


Figure 1. ^1H NMR spectra (400 MHz, D_2O , 293 K) of (a) 2.00 mM G_1 ; (b) 2.00 mM WP_7 and 10.00 mM G_1 ; (c) after addition of 2 μL aqueous DCl solution (20%) to b (signals on the host disappeared due to the formation of precipitation after the addition of DCl); (d) after addition of 1.5 μL aqueous NaOD solution (30%) to c; (e) 2.00 mM WP_7 .

Information). A possible reason was that these protons were located in the cavity of WP_7 and shielded by the electron-rich cylinder. To further study the chemical shift changes of the protons on G_1 , excess G_1 (3 equiv and 5 equiv) was added. From the spectrum of 2.00 mM WP_7 and 10.0 mM G_1 (Figure S10d, Supporting Information), the peaks corresponding to the protons on both WP_7 and G_1 were observed clearly. On the other hand, the protons on WP_7 also showed slight chemical shift changes. Furthermore, 2D NOESY experiments were conducted with a solution of 5.00 mM WP_7 and 25.0 mM G_1 . As shown in Figure 2, correlation signals were observed between protons H_a or H_b on G_1 and protons H_{1-3} on WP_7 , respectively. Additionally, H_c on G_1 also correlated with H_1 on WP_7 , indicating that guest G_1 was threaded into the cavity of macrocyclic host WP_7 .

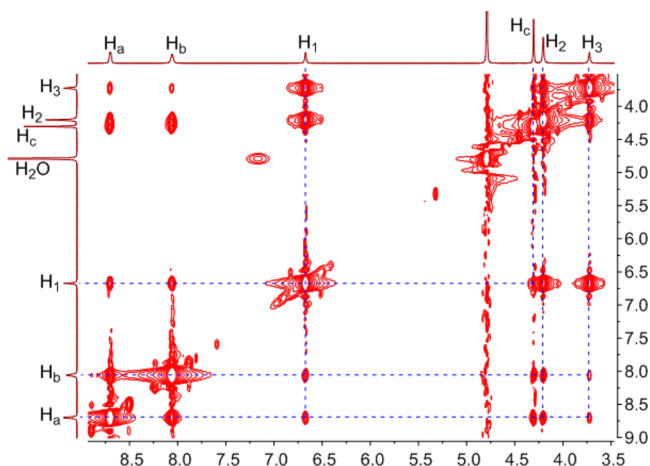


Figure 2. 2D NOESY NMR (500 MHz, D_2O , 293 K) spectrum of a solution of WP_7 (5.00 mM) and G_1 (25.00 mM).

The association constant for the complexation between WP_7 and G_1 was estimated by means of fluorescence titrations at room temperature in water. Upon gradual addition of G_1 into a WP_7 solution, the fluorescence intensity was quenched efficiently, confirming that the achievement of host–guest complexation between WP_7 and G_1 (Figure S12, Supporting Information). A mole ratio plot was fitted to show the 1:1 complexation stoichiometry between WP_7 and G_1 (Figure S13, Supporting Information), in good agreement with the result obtained from ESI-MS (Figure S17, Supporting Information). A peak at m/z 926.8 for $[\text{WP}_7\text{G}_1 - 2\text{Cl} - 14\text{NH}_3]^{2+}$ was monitored, which further proved the 1:1 complexation stoichiometry. According to ^1H NMR, 2D NOESY, the mole ratio plot, and ESI-MS, we can draw a conclusion that WP_7 and G_1 formed a 1:1 [2]pseudorotaxane in water mainly driven by multiple electrostatic interactions. The association constant (K_a) for WP_7G_1 was calculated to be $(2.96 \pm 0.31) \times 10^9 \text{ M}^{-1}$ (Figure S14, Supporting Information), which is much higher than the corresponding K_a value $((8.20 \pm 1.70) \times 10^4 \text{ M}^{-1})$ for WP_5G_1 ^{7b} and even higher than that for WP_6G_1 $((1.02 \pm 0.10) \times 10^8 \text{ M}^{-1})$.^{8a} Further evidence for the formation of the [2]pseudorotaxane based on WP_7 and G_1 was received from UV–vis absorption spectroscopy. When WP_7 was added into G_1 , a bright brick-red color appeared immediately (Figure S11, Supporting Information). The UV–vis spectrum of an equimolar solution (10^{-4} M) of WP_7 and G_1 revealed a notable typical charge-transfer band (Figure S15, Supporting Information), indicating the complexation between electron-rich WP_7 and electron-deficient G_1 .

It is well-established that neutral carboxylic groups and anionic carboxylate groups can be converted reversibly by adjusting the solution pH. On the basis of this characteristic of anionic carboxylate groups, the dethreading/rethreading process of the complex WP_7G_1 can be controlled by the acid/base treatment. ^1H NMR provided powerful evidence for the pH-controlled complexation between WP_7 and G_1 . When a solution of WP_7 and G_1 was added with an aqueous DCl solution, the brick-red color disappeared immediately and yellow precipitates appeared (Figure S16, Supporting Information). From ^1H NMR spectroscopy, the signals for all protons on the host disappeared and the resonance peaks related to protons on the guest returned to their original positions just as free G_1 (Figure 1c). Because the anionic carboxylate groups on WP_7 were protonated to neutral carboxylic acid groups, the

water-soluble host precipitated from the solution associated with the disassembly of the inclusion complex, whereas the water-soluble guest **G**₁ kept dissolved in D₂O. On the other hand, it was comprehensible that the insoluble carboxylic acid groups would be deprotonated when the solution was made basic, so the macrocyclic host would become soluble in water again after addition of NaOD. As expected, the colorless solution returned to be brick-red at once upon addition of a NaOD solution (Figure S16, Supporting Information). Also, The peaks corresponding to protons H_{a-c} on **G**₁ shifted upfield and became broad as well showed in the ¹H NMR spectrum (Figure 1d), indicating the reformation of the [2]-pseudorotaxane based on **WP7** and **G**₁. To summarize, the dethreading and rethreading processes of the complex **WP7**⊃**G**₁ could be easily controlled by changing the solution pH.

With this novel pillar[7]arene/paraquat molecular recognition motif in hand, we further applied it to construct a supra-amphiphile based on **WP7** and an amphiphilic paraquat derivative **G**₂ (Scheme 1). In order to study the aggregation behavior of this supra-amphiphile, fluorescence spectroscopy experiments using pyrene as the probe were conducted. As revealed in Figure S19 (Supporting Information), in the presence of **G**₂ (0.100 mM), the quenching of the excited pyrene molecules was not evident, which suggested that **G**₂ can not aggregate at this concentration, coinciding with the critical aggregation concentration (CAC) of **G**₂ (3.44×10^{-4} M) reported previously.^{8a} However, the relative fluorescence intensity of pyrene was quenched remarkably as revealed in the fluorescence spectra (Figure S20, Supporting Information) performed with the solution of **WP7** (5.00×10^{-5} M) upon gradual addition of **G**₂ (0 to 1.84×10^{-4} M) in the presence of pyrene. This notable fluorescence quenching can be explained by the fact that nonpolar pyrene is dissolved near the Stern layer in aggregates, which proves the formation of amphiphilic aggregation.^{8a,12a} Undoubtedly, **WP7** itself has no chance to aggregate in aqueous solution. Contrast experiments revealed that the addition of **WP7** to a **G**₂ solution in the presence of pyrene could induce the formation of aggregation, but the model compound **M** could not (Figure S19, Supporting Information), which suggested that the host–guest complexation between **WP7** and **G**₂ is the essential factor leading to the amphiphilic aggregation.

Based on the above results, we knew that **WP7**⊃**G**₂ could assemble into microaggregates arising from the host–guest complexation between **WP7** and **G**₂. Therefore, we determined the best molar ratio between **WP7** and **G**₂ leading to supramolecular self-assembly. By pyrene-based fluorescence spectra, a plot of fluorescence intensity at 375 nm as a function of **WP7** concentration with a fixed **G**₂ concentration at 1.00×10^{-4} M was made (Figure S21, Supporting Information), where an inflection point at **WP7**/**G**₂ molar ratio of 0.5 appeared, representing the best molar ratio for the amphiphilic assembly. When the **WP7**/**G**₂ molar ratio was 0.5, the CAC value of **WP7**⊃**G**₂ was estimated to be about 4.10×10^{-5} M (Figure S18, Supporting Information) by concentration-dependent conductivity, which was much lower than that of **G**₂ due to the complexation of **WP7**.

Transmission electron microscopy (TEM) and dynamic light scattering (DLS) were employed to visualize the morphology and assembly size of the **WP7**⊃**G**₂ supra-amphiphile. As reported previously,^{8a} **G**₂ itself self-assembled in water to form solid spherical micelles with the average diameter about 7.0 nm

(Figure 3a, b). However, upon addition of **WP7** to obtain the best molar ratio solution, vesicles rather than micelles were

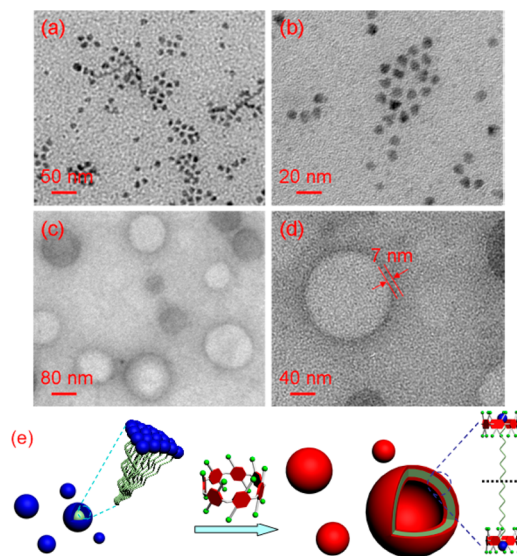


Figure 3. TEM images: (a) **G**₂; (b) enlarged image of **G**₂; (c) **WP7**⊃**G**₂; (d) enlarged image of **WP7**⊃**G**₂. (e) Illustration of the formation of the aggregates.

observed (Figure 3c). The DLS result exhibited that the average diameter of aggregates formed by **WP7**⊃**G**₂ was around 164.2 nm as revealed in Figure S22 (Supporting Information), which was in good accordance with the corresponding value (~ 160 nm) measured from the TEM image in Figure 3c. Incidentally, the average size of micelles formed by **G**₂ was also detected by DLS with the identical solution, giving a value of ~ 10 nm. It was noted that the thickness of the vesicles was measured to be ~ 7 nm (Figure 3d), which was just equal to the extended length of two [2]pseudorotaxane based on **WP7** and **G**₂, indicating the vesicles had a bilayer membrane.

It is well-known that the microassembled structure of the aggregates formed by an amphiphile is determined by the curvature of the membrane.^{8a,12a} After complexation with **WP7**, the water-soluble 4,4'-bipyridinium unit of **G**₂ threaded into the cavity of **WP7**, forming a [2]pseudorotaxane-type supra-amphiphile. When this supra-amphiphile is dissolved in water, the packing structure of the pseudorotaxanes is in an antiparallel pattern. Therefore, with the steric hindrance and the electrostatic repulsion generated from the insertion of **WP7** molecules, a vesicular structure with lower curvature was formed, resulting in the transformation from micelles to vesicles (Figure 3e).

In conclusion, we synthesized the first water-soluble pillar[7]arene (**WP7**) and investigated its pH-controlled complexation with paraquat **G**₁ in water. We demonstrated that **WP7** and **G**₁ formed a 1:1 [2]pseudorotaxane with a high association constant of $(2.96 \pm 0.31) \times 10^9$ M⁻¹ mainly driven by multiple electrostatic interactions. Furthermore, we used this novel recognition motif to construct a supra-amphiphile based on **WP7** and an amphiphilic paraquat derivative **G**₂. The host–guest complex **WP7**⊃**G**₂ self-assembled in water into supra-molecular vesicles. TEM and DLS were applied to identify the morphologies and sizes of self-assemblies of **G**₂ and **WP7**⊃**G**₂. Future work will aim at controlled release and drug-delivery on the basis of this novel molecular recognition motif.

■ ASSOCIATED CONTENT

■ Supporting Information

Synthesis, characterization, stoichiometry and association constant determination, UV-vis data, fluorescence spectra, DLS results, 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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