



Neutral guest capture by a cationic water-soluble pillar[5]arene in water



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ABSTRACT

A cationic water-soluble pillar[5]arene offering a well-defined cavity with hydrophobic inner surface can capture neutral guests, even water-insoluble guests, into its cavity via hydrophobic forces. The binding ability depends upon guest hydrophobicity. The higher guest hydrophobicity contributes to the higher host affinity. Methanol and ethanol do not show any affinity for the host at all, because they are too hydrophilic for the host to compete with water.

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1. Introduction

Water not only provides an environment for life but also mediates, regulates, and controls many processes in nature. Therefore, supramolecular chemistry in water becomes a constantly growing research area because noncovalent interactions in aqueous media are important for obtaining a better understanding and controlling of the major processes in nature.^{1a} One of the important goals of supramolecular chemistry^{1b} is the creation of synthetic receptors that have both high affinity and high selectivity for the binding of guests in water. Although several kinds of macrocyclic receptors have been synthesized and used to encapsulate various guests in water,² the search of synthetic receptors, which can be used in water still represents a special challenge.^{1a} As a new kind of macrocyclic receptors after the early macrocycles,³ pillar[*n*]arenes, which have displayed lots of fascinating properties in the preparation of supramolecular polymers,^{5d} microtubes,⁵ⁱ vesicles,^{5j} and other interesting supramolecular systems,^{4–6} should be able to play an important role in this area. Pillar[*n*]arenes substituted by various hydrophilic groups, such as carboxylic,^{4b,5j,6c} amino^{6a} and ammonium,^{5h} show a moderate solubility in water and can bind kinds of guests in water. However, only the binding of ionic guests with these water-soluble pillar[*n*]arenes was studied. The binding of neutral guests in water by these water-soluble pillar[*n*]arenes has

never been investigated. It should be advantageous to our understanding of hydrophobic interactions if a simple system can be studied in which a guest moves from water into a well-defined host environment that excludes water to maximize the guest desolvation.^{2d} Hence, the aim of this study was to gain insight into the binding of neutral hydrophobic guests in water with a cationic water-soluble pillar[5]arene previously reported by us.

2. Results and discussion

In our previous work, we reported the synthesis of a cationic water-soluble pillar[5]arene (**H**), which is a multipoint recognition host (Fig. 1).^{5h} **H** possesses both a hydrophobic cavity and 10 charged substituents, thus providing a very efficient recognition motif for guests with multiple functional groups such as 1-octanesulfonate. The complexation mode of 1-octanesulfonate and **H** includes the incorporation of the alkyl moiety of the guest into the cavity as a result of hydrophobic interactions, which is supported by electrostatic interactions between the anionic sulfonate moieties and the cationic ammonium groups of the host. Here extended these preliminary studies to several small neutral organic molecules such as *n*-hexane and *p*-xylene (Figs. 1 and 2).

n-Hexane was briefly sonicated with D₂O, and then the ¹H NMR spectrum of the aqueous phase was recorded. By NMR spectroscopic analysis, *n*-hexane shows no water solubility (Fig. 2, spectrum c). However, when *n*-hexane was sonicated with a 4.00 mM solution of **H** in D₂O, the spectrum of the aqueous phase showed that the hydrophobic *n*-hexane was extracted into aqueous solution

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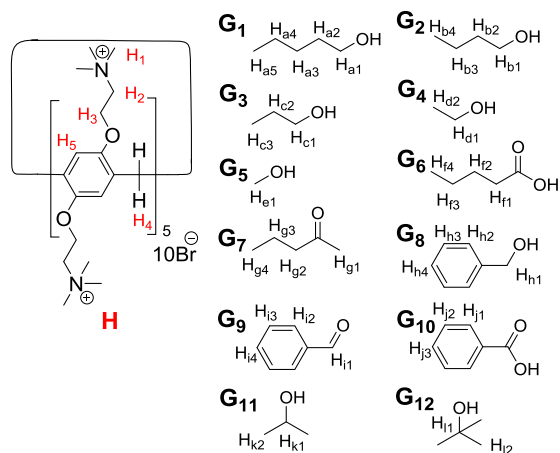


Fig. 1. Chemical structures of cationic water-soluble pillar[5]arene **H** and neutral guests studied here.

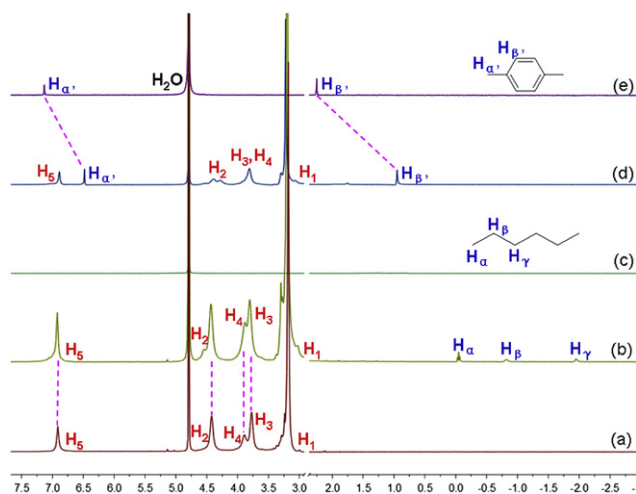


Fig. 2. ¹H NMR spectra (400 MHz, D₂O, 298 K): (a) 4.00 mM **H**; (b) *n*-hexane and 4.00 mM **H**; (c) *n*-hexane; (d) *p*-xylene and 4.00 mM **H**; (e) *p*-xylene.

and bound in the magnetically shielding region of the cavity of **H** to form a host–guest complex (Fig. 2, spectra a–c). The guest was surrounded by the surfaces made of the aromatic subunits of **H**.^{2e} Before host–guest complexation, the surfaces of the alkane chain and the inside of the cavity are ‘waterlogged.’ Therefore, the burial of hydrophobic surfaces drives the formation of the complex. Furthermore, the C–H bonds of *n*-hexane might make gentle, attractive contacts with a large fraction of the π surfaces offered by the benzene rings of **H**.^{2f,5a} C–H⋯π interactions that exist between the included *n*-hexane and **H** also contribute to the formation of the complex. Furthermore, no free alkane molecules were observed in solution; **H** extracted only those that it bound. Similarly, *p*-xylene, a larger neutral guest also with a poor water solubility (Fig. 2, spectrum e), can also be bound deeply within the shielding region of **H**, leading the signals of *p*-xylene protons H_α′ and H_β′ to shift upfield by 0.65 and 1.30 ppm, respectively (Fig. 2, spectra d and e). Unfortunately, the solubility of *n*-hexane and *p*-xylene in water is not sufficient to allow us to carry out NMR titrations with these guests. Therefore, some other neutral guests (Fig. 1) were selected because their higher solubility in water makes it possible to measure accurate association constants even for weak complexes.

The hydrophobic interactions of **H** with all guests were investigated quantitatively by ¹H NMR. When **H** and equivalent **G**₁ were mixed together in water, a host–guest complex was formed, which was in fast exchange on the proton NMR time scale. The

complexation of **G**₁ and **H** took place through inclusion of the alkyl unit into the pillar[5]arene cavity, which was proved by upfield shifts of all the protons (H_{a1}, H_{a2}, H_{a3}, H_{a4} and H_{a5}) of **G**₁ in the ¹H NMR spectra (Fig. 3). Binding of **G**₁ made the shielding effect of H₁ and H₃ on **H** a little diminished, causing the signals of H₁ and H₃ to move downfield to 3.28 and 3.91 ppm, respectively, while leaving the other peaks (H₂, H₄ and H₅) of **H** unchanged. The two most upfield-shifted singlets of encapsulated **G**₁ at δ_H=0.00 and 0.19 were assigned to H_{a3} and H_{a4}, respectively, supported by the analysis of the COSY spectrum of the complex (Fig. S2). After complexation, the peak for H₂ was further split into two separate peaks, corresponding to the methylene protons close to the alcohol head group of **G**₁ and the methylene protons close to the alkyl tail group of **G**₁, respectively. This phenomenon might result from the asymmetric structure of **G**₁. The 2D ¹H NMR NOESY spectrum of an equimolar mixture of **H** and **G**₁ (Fig. S3) showed correlations between phenyl protons H₅ of **H** and all the protons (H_{a1}, H_{a2}, H_{a3}, H_{a4} and H_{a5}) of **G**₁. There were correlations between protons H₂ of **H** and protons H_{a1}/H_{a2}/H_{a5} of **G**₁, while no correlations between protons H₂ of **H** and protons H_{a3}/H_{a4} of **G**₁ were observed. There were correlations between protons H₃ of **H** and protons H_{a5} of **G**₁, while no correlations between protons H₃ of **H** and protons H_{a1}/H_{a2}/H_{a3}/H_{a4} of **G**₁ were observed. Furthermore, there were correlations between protons H₄ of **H** and protons H_{a2}/H_{a5} of **G**₁, while no correlations between protons H₄ of **H** and protons H_{a1}/H_{a3}/H_{a4} of **G**₁ were observed. These phenomena suggested that **G**₁ was fully encapsulated by **H** to form a [2]pseudorotaxane with the middle two methylene groups (H_{a3}/H_{a4}) of **G**₁ bound deeply within the cavity. The alcohol head group and the tail methyl group (H_{a5}) pointed to the trimethylammonium rims of **H**. Further support for the suggested binding pattern came from theoretical calculations. The minimized-energy structure of complex **H**⊃**G**₁ shows that **G**₁ is threaded through the cavity of **H** with its alcohol head close to the trimethylammonium groups of **H** and the middle part included in the cavity (Fig. S45).

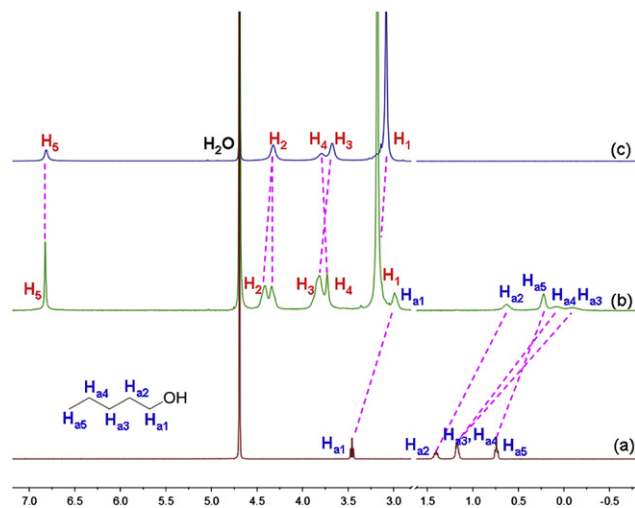


Fig. 3. ¹H NMR spectra (400 MHz, D₂O, 298 K): (a) 4.00 mM **G**₁; (b) 4.00 mM **G**₁ and **H**; (c) 4.00 mM **H**.

The affinity of **H** and **G**₁ in water was measured by NMR titration at 298 K. The titration was conducted at a constant **G**₁ concentration (4.00 mM) by monitoring changes in the chemical shift of protons H_{a2} of **G**₁ with increasing **H** concentration. A mole ratio plot for the complexation of **H** and **G**₁ showed that the stoichiometry of the complex was 1:1 (Fig. S6). The association constant (*K*_a) of **H**⊃**G**₁ was calculated to be (1.03±0.37)×10² M⁻¹ in D₂O, using a nonlinear curve fitting analysis (Fig. S5). Based on this association

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