

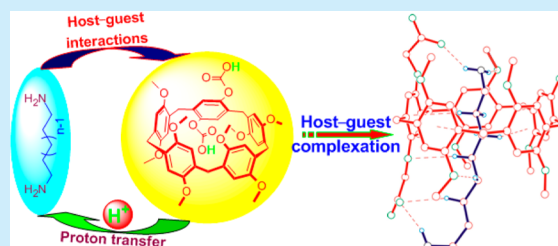
Proton Transfer in Host–Guest Complexation between a Difunctional Pillar[5]arene and Alkyldiamines

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Supporting Information

ABSTRACT: Host–guest complexation between a novel difunctional pillar[5]arene-based host **H** and alkyldiamines was fully investigated in both solution and the solid state. Proton transfer from the carboxylic acid groups to the amine units occurred in the principle by undergoing an acid–base reaction. Driven by the cooperativity of electrostatic interactions, multiple C–H $\cdots\pi$ interactions, and H-bonds, the guests penetrated into the cavity of **H** to form pseudorotaxane-type inclusion complexes with relatively high binding affinities.



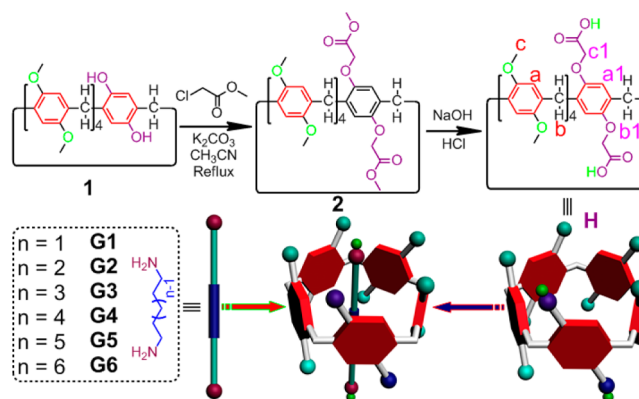
Macrocyclic molecules, such as crown ethers,¹ cyclodextrins,² calixarenes,³ and cucurbiturils,⁴ are always fascinating and attractive owing to their interesting topology structures and potential applications in the fabrication of molecular switches, molecular machines, drug delivery systems, supramolecular polymers, and other interesting host–guest systems.⁵ Pillar[*n*]arenes, mainly including pillar[5]arenes⁶ and pillar[6]arenes,⁷ a novel class of macrocycles, have recently stimulated a tremendous upsurge of interest in supramolecular chemistry and materials science since their first synthesis in 2008. Compared with the basket-shaped structure of meta-bridged calixarenes, pillar[*n*]arenes are linked by methylene (–CH₂–) bridges at para-positions of 2,5-dialkoxybenzene rings, forming a unique rigid pillar architecture, which have afforded them superior properties in host–guest recognition. Due to their unique symmetrical structure and easy functionalization, pillararenes act as useful platforms for the construction of various interesting supramolecular systems, such as liquid crystals,⁸ cyclic dimers,⁹ chemosensors,¹⁰ supramolecular polymers,¹¹ drug delivery systems,¹² transmembrane channels,¹³ and cell glue.¹⁴

Various methods, including *per*-functionalization and partial functionalization on the oxygen atom of the repeating benzene rings have been developed to functionalize pillararenes, endowing them with sophisticated structures and versatile functions. Partial oxidation of the dialkoxybenzene units on pillar[*n*]arenes (*n* = 5, 6) as reported by Huang and Ogoshi et al. can afford pillar[*n*]arene derivatives with one or more benzoquinone units.¹⁵ Reduction of the benzoquinone unit yields an even hydroxylated pillararene derivative, which can be further functionalized. Herein, we report the preparation of a difunctionalized pillar[5]arene containing two carboxylic acid moieties (**H**) and its complexation with alkyldiamines ranging from 1,5-pentanediamine to 1,10-decanediamine (**G1**–**G6**). Proton transfer from the carboxylic acids to the amino groups was achieved to provide the corresponding alkylammonium ions. Driven by the cooperativity of electrostatic interactions,

multiple C–H $\cdots\pi$ interactions, and H-bonds, the binding affinities between **H** and the guests were enhanced effectively.

By partial oxidation of 1,4-dimethoxypillar[5]arene with (NH₄)₂[Ce(NO₃)₆] as the oxidizing agent and then reduction by Na₂S₂O₄, a difunctionalized pillar[5]arene **1** with a hydroquinone repeating unit was obtained in 28% yield (Scheme 1). Methoxycarbonylmethoxy group substituted

Scheme 1. Synthetic Route to a Difunctionalized Pillar[5]arene (**H**) and Schematic Representation of **H**, **G**, and **H**⊂**G**



pillar[5]arene **2** was synthesized through etherification of dihydroxylated pillar[5]arene derivative **1**. The hydrolysis of **2** under basic conditions and further acidification in the presence of HCl afforded the dicarboxylic acid substituted pillar[5]arene **H**. ¹H NMR, ¹³C NMR, LRESIMS, HRESIMS, HMBC, HMQC, DEPT-135, COSY, and NOESY were utilized to confirm the successful synthesis of **H** (Figures S4–S10).

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The host–guest interactions between **H** and the guests (**G1**–**G6**) were first investigated by ^1H NMR spectroscopy in a mixture of chloroform-*d* and methanol-*d*₄ (1:1 in molar ratio). Compared with the spectra of free guests (**G1**–**G6**) (spectra a, e, f in Figure 1 and spectra a, e, f in Figure S11), the resonance

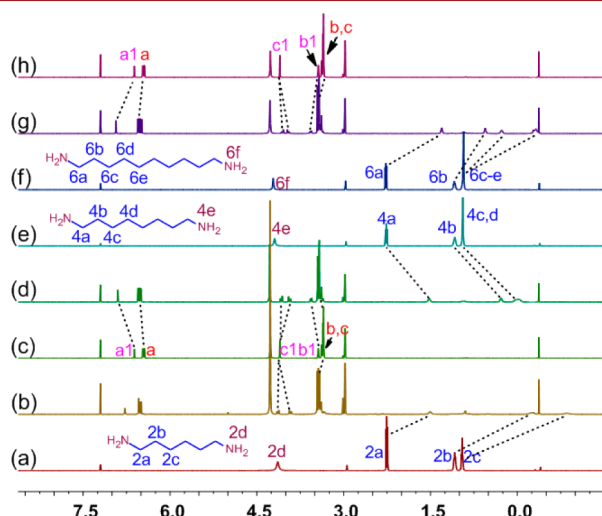


Figure 1. ^1H NMR spectra (500 MHz, chloroform-*d*/methanol-*d*₄ = 1:1, 295 K): (a) **G2** (5.00 mM); (b) **H** (5.00 mM) and **G2** (5.00 mM); (c) **H** (5.00 mM) and **G3** (5.00 mM); (d) **H** (5.00 mM) and **G4** (5.00 mM); (e) **G4** (5.00 mM); (f) **G6** (5.00 mM); (g) **H** (5.00 mM) and **G6** (5.00 mM); (h) **H** (5.00 mM).

peaks related to the methylene protons on the guests all displayed substantial upfield shifts in the presence of an equivalent amount of **H** (Figures 1 and S11). The reason was that these protons were shielded by the electron-rich cyclic structure upon forming a threaded structure between **H** and the guests.^{6c} Furthermore, extensive broadening effects were observed for the peaks corresponding to protons on the guests caused by complexation dynamics.^{7d} Yet, the protons on **H** also exhibited slight chemical shift changes due to the interactions between **H** and the guests. The resonance peaks related to protons H_a and H_{a1} on the benzene rings, H_b and H_{b1} on the methylene bridges, and H_c for the methyl group shifted downfield. Additionally, the peaks corresponding to the protons H_{c1} shifted upfield in the presence of **G3** or **G5** due to the formation of host–guest inclusion complexes. Notably, the methylene protons H_{c1} on **H** were observed to split into two overlapped doublets after the complexation with **G1**, **G2**, **G4**, or **G6**, indicating that the mobility of H_{c1} was suppressed and slow on the NMR time scale at 22 °C (Figure 1b, d, and g), indicating that H_{c1} located in the inner and outer spaces were shielded and deshielded, respectively, resulting from the formation of an inclusion complex.^{7b,16}

Isothermal titration calorimetry (ITC) is a powerful tool for measuring the host–guest interactions, because it not only provides the association constant (K_a) but also yields the corresponding thermodynamic parameters (such as enthalpy change ΔH° and entropy change ΔS°). As shown in Figures S13–S18, the titration data were well fitted by computer simulation using the “one set of binding sites” model, indicating 1:1 complexation between **H** and the guests. It should be noted that all the data listed in Table 1 have the same feature ($\Delta H^\circ < 0$; $T\Delta S^\circ < 0$; $|\Delta H^\circ| > |T\Delta S^\circ|$), indicating that these complexations were all driven by enthalpy changes.¹⁷

Table 1. Association Constants K_a , Enthalpy Changes ΔH° , and Entropy Changes ΔS° Obtained From ITC Experiments for the 1:1 Complexes of **H** with Guests **G1**–**G6**^a

	K_a (M^{-1})	ΔH° (cal/mol)	ΔS° (cal/mol/deg)
G1	$(2.84 \pm 0.232)\text{E5}$	$-(2.11 \pm 0.120)\text{E4}$	−47.8
G3	$(3.13 \pm 0.210)\text{E5}$	$-(2.33 \pm 0.025)\text{E4}$	−51.5
G5	$(3.45 \pm 0.228)\text{E5}$	$-(2.51 \pm 0.031)\text{E4}$	−57.6
G2	$(2.39 \pm 0.237)\text{E5}$	$-(2.39 \pm 0.030)\text{E4}$	−54.1
G4	$(2.89 \pm 0.212)\text{E5}$	$-(2.42 \pm 0.116)\text{E4}$	−54.7
G6	$(3.06 \pm 0.232)\text{E5}$	$-(2.61 \pm 0.079)\text{E4}$	−60.8

^aITC experiments were conducted in the mixture of chloroform and methanol (1:1, v/v) at 303.15 K by titration of **G** (2.00 mM, 10 μL per injection) into the solution of **H** (0.100 mM).

Interestingly, the host–guest complexation in this system showed parity in K_a ($\text{HCG1} > \text{HCG2}$, $\text{HCG3} > \text{HCG4}$, $\text{HCG5} > \text{HCG6}$), ΔH° ($\text{HCG1} < \text{HCG2}$, $\text{HCG3} < \text{HCG4}$, $\text{HCG5} < \text{HCG6}$), and ΔS° ($\text{HCG1} < \text{HCG2}$, $\text{HCG3} < \text{HCG4}$, $\text{HCG5} < \text{HCG6}$) values (Table 1). Yet, the K_a values increased and the ΔH° (ΔS°) values decreased effectively accompanied by the growth of the length related to the guests owning odd (**G1**, **G3**, **G5**) and even (**G2**, **G4**, **G6**) carbon numbers, respectively.

Further evidence for the formation of stable host–guest complexes between **H** and the guests was obtained from ESI-MS. Relevant peaks were found at m/z 941.4, 955.5, 969.2, 983.6, 997.8, and 1011.7, corresponding to $[\text{HCG1} + \text{H}]^+$, $[\text{HCG2} + \text{H}]^+$, $[\text{HCG3} + \text{H}]^+$, $[\text{HCG4} + \text{H}]^+$, $[\text{HCG5} + \text{H}]^+$, and $[\text{HCG6} + \text{H}]^+$, respectively. Moreover, the peaks appearing at m/z 471.4, 478.2, 485.5, 492.3, 499.3, and 506.3 were monitored and corresponded to $[\text{HCG1} + 2\text{H}]^{2+}$, $[\text{HCG2} + 2\text{H}]^{2+}$, $[\text{HCG3} + 2\text{H}]^{2+}$, $[\text{HCG4} + 2\text{H}]^{2+}$, $[\text{HCG5} + 2\text{H}]^{2+}$, and $[\text{HCG6} + 2\text{H}]^{2+}$, respectively (Figures S19–S24). The results obtained from ESI-MS confirmed the formation of 1:1 complexes between the **H** and the corresponding guests, in agreement with the results obtained from ITC experiments.

2D NOESY NMR spectroscopy was further employed to investigate the complexation between **H** and the guests (**G1**–**G6**), because it is a useful tool to study the relative positions of the components in host–guest inclusion complexes (Figures 2 and S25–S30). Nuclear Overhauser effect (NOE) correlations were observed between the signals related to methylene protons on the guests and protons on **H**, suggesting that alkyldiamines penetrated into the cavity of **H** to form inclusion complexes. From our previous studies,^{6e} we knew that the

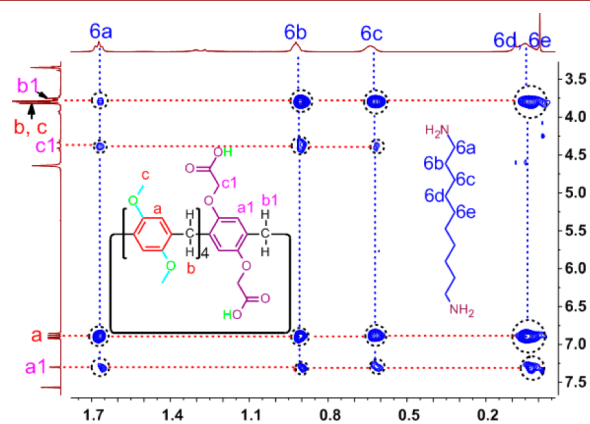


Figure 2. Partial NOESY NMR spectrum (500 MHz, chloroform-*d*/methanol-*d*₄ = 1:1, 295 K) of **H** (5.00 mM) and **G6** (5.00 mM).

cavity of pillar[5]arene could only encapsulate four methylenes. However, the pillar-shaped cavity can vibrate along the alkyl chain, thus causing upfield shifts of protons on more methylenes.^{6e} In all reported pillar[5]arene based host–guest systems with long alkyl guests, this conclusion is in accordance with their crystal structures.

Single-crystal X-ray analyses (Figure 3) further confirmed the formation of host–guest inclusion complexes. Crystals of

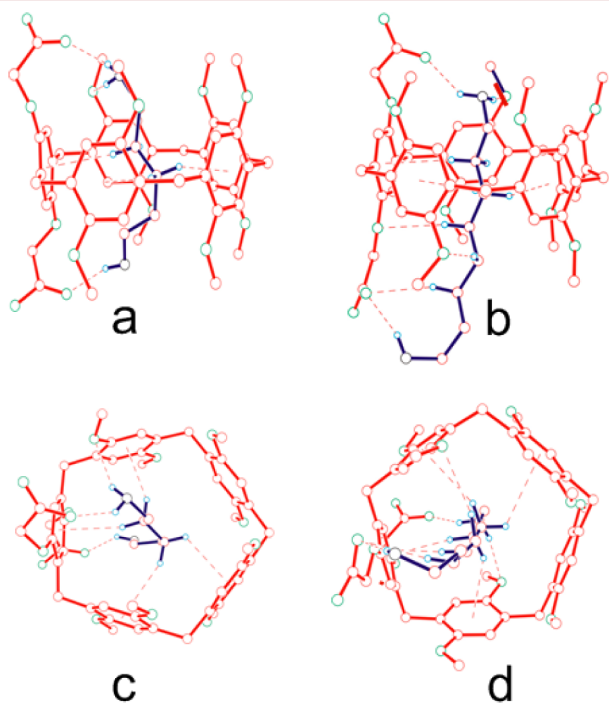


Figure 3. Views of the crystal structures of **H₂G1** (a and c) and **H₂G4** (b and d). Hydrogens except the ones participating in the formation of C–H... π interactions and hydrogen bonds were omitted for clarity. The purple dotted lines indicate C–H... π interactions and hydrogen bonds.

H₂G1 and **H₂G4** were grown by slow evaporation of a solution containing equimolar concentrations of **H** and the corresponding guest in a dichloromethane/methanol mixture. The crystal structures of **H₂G1** and **H₂G4** gave direct proof that the alkyl chain of the guests was located in the cavity of **H** to form stable 1:1 [2]pseudorotaxane-type host–guest complexes. The C–H... π distances, 2.62–3.01 Å, were shorter than 3.05 Å, and the C–H... π angles were larger than 90°, implying the formation of multiple C–H... π interactions between the host and guest. Furthermore, the guests in the cavity of **H** formed H-bonds with the O-atoms of the hydroquinone moiety. More interestingly, proton transfer from the carboxyl groups to the amines on the guest occurred in principle by undergoing an acid–base reaction, resulting in the formation of corresponding carboxylate anions and alkylammonium cations inside its cavity.¹⁸ Electrostatic interactions can be further achieved, which play a critical role in the formation of host–guest inclusion complexes. The guest locates inside the cavity of **H** with ammonium groups pointed at the carboxylate anion to achieve electrostatic interactions. Compared with **G1** (Figure 3a and c), the length of **G4** was longer than the height of the host; a section of the alkyl chains bends to make the length suitable for the host (Figure 3b and d).

As listed in Table 1, the K_a values of complexes could reach a magnitude of 10^5 M^{-1} in the mixture of chloroform and methanol (1:1 in molar ratio) at 30 °C determined by ITC. Compared with the association constant between 1,4-dimethoxypillar[5]arene (**DMP5**) and **G1** ($670 \pm 73.8 \text{ M}^{-1}$), the corresponding K_a values in these systems were enhanced significantly (Figure S31). The high binding affinities of these host–guest systems were attributed to the cooperativity of electrostatic interactions between the carboxylate anionic groups on the rigid pillar[5]arene receptor platform and the cationic ammonium groups, multiple C–H... π interactions, and H-bonds between the alkyl chain and the host. The alkyl chains in these host–guest complexes exhibited excellent flexibility which could bend to form electrostatic interactions effectively with the host. Yet, a greater number of C–H... π interactions and H-bonds could be established associated with the increase of the lengths of the guests, resulting in the enhancement of binding affinities of the host–guest complexes. For the guests containing an odd or even carbon number, we speculated that the numbers of C–H... π interactions and H-bonds might be different, resulting in the appearance of parity in the host–guest complexation. Moreover, the polarization effect that C-atoms in a hydrocarbon compound exhibit, owing alternately to positive and negative charges, could play an important role in the odd/even effect.¹⁹

In conclusion, a novel difunctional pillar[5]arene-based host **H** containing two carboxyl units was designed and synthesized. Host–guest complexation between **H** and alkyldiamine ranging from 1,5-pentanediamine to 1,10-decanediamine (**G1**–**G6**) was investigated by using ¹H NMR, ITC, 2D NOESY, and X-ray crystallographic analysis. Proton transfer from the carboxylic acid groups to the amines on the guest could be achieved in principle by undergoing an acid–base reaction. Driven by the cooperativity of electrostatic interactions, multiple C–H... π interactions, and H-bonds, the guests penetrated into the cavity of **H** to form stable 1:1 [2]pseudorotaxane-type host–guest inclusion complexes, showing relatively high binding affinities. The new recognition motif exemplified the enormous potential applications in various fields, including supramolecular polymers, nanoelectronics, sensors, and drug and gene delivery systems.

■ ASSOCIATED CONTENT

§ Supporting Information

Synthetic procedures, characterizations, X-ray crystallographic files (CIF) for **H₂G1** and **H₂G4** (CCDC 916495 and 916493), 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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