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Preprint Title Construction of pillar[4]arene[1]quinone/1,10-dibromodecane pseudorotaxanes in solution and the solid state

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Publication Date 22 Sep. 2020

Article Type Full Research Paper

Supporting Information File 1 CIF for H·G.cif; 1.3 MB

Supporting Information File 2 bjoc-pseudorotaxanes-SI.pdf; 559.5 KB

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The definitive version of this work can be found at <https://doi.org/10.3762/bxiv.2020.109.v1>

Construction of pillar[4]arene[1]quinone/1,10-dibromodecane pseudorotaxanes in solution and the solid state

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Abstract

We report novel pseudorotaxanes based on the complexation between a pillar[4]arene[1]quinone and 1,10-dibromodecane. The complexation is found to have a 1:1 host–guest complexation stoichiometry in chloroform but a 2:1 host–guest complexation stoichiometry in the solid state. From single crystal X-ray diffraction, the linear guest molecules thread into cyclic pillar[4]arene[1]quinone host molecules in the solid state, stabilized by CH \cdots π interactions and hydrogen bonds.

Keywords

pseudorotaxanes; host-guest chemistry; pillararenes; pillar[4]arene[1]quinones; supramolecular chemistry

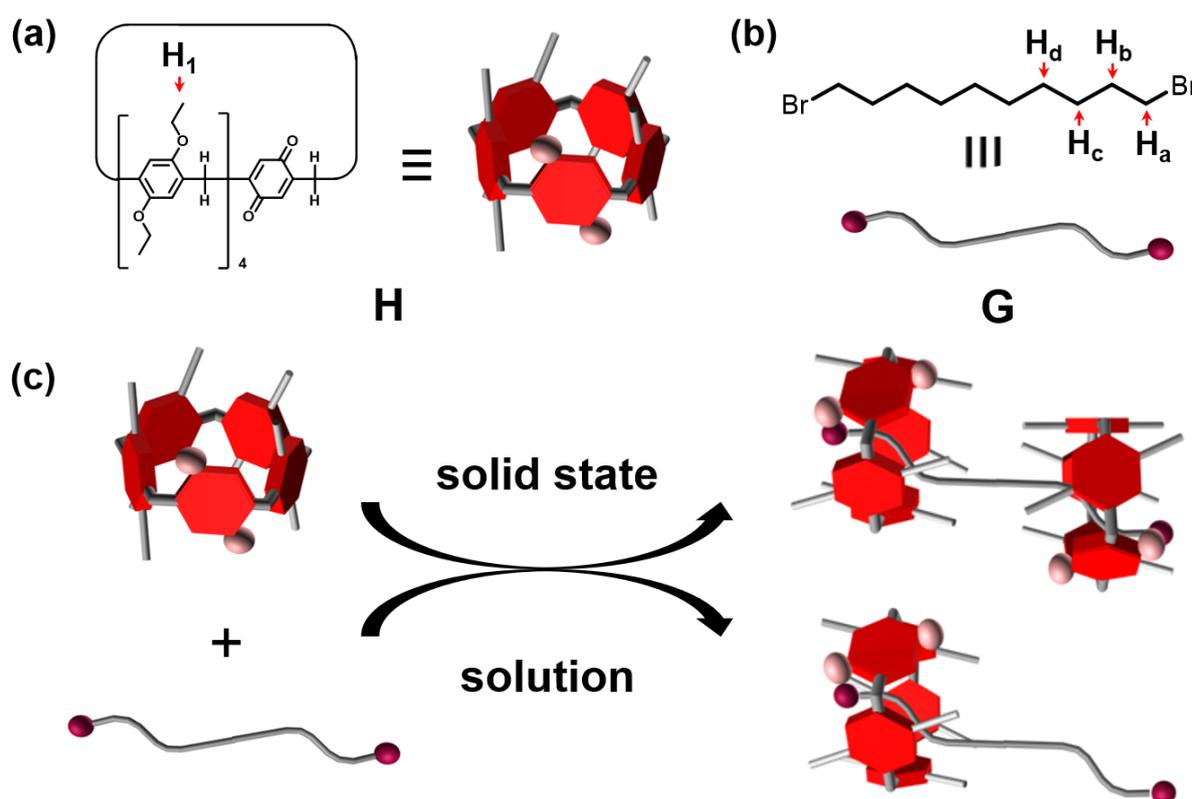
Introduction

Relying on the research of basic science, supramolecular chemistry has become an important means of constructing functional materials from the bottom up, as well as an important way to create new substances with functions [1-5]. Through ingenious designs and the applications of molecular recognition and self-assembly strategies, many exquisite supramolecular architectures have been fabricated, including molecular switches, molecular logic gates, molecular machines, supramolecular polymers, etc [6-11]. Pseudorotaxanes not only are used as the supramolecular precursors for the synthesis of rotaxanes and catenanes, but also play an important role in the construction of supramolecular architectures and chemical topology [12-23]. Seeking new systems to produce pseudorotaxanes is always a hot topic in supramolecular chemistry.

As a new class of supramolecular macrocyclic hosts, pillararenes have received extensive attention in recent years due to their unique pillar structures and rich environmental responsiveness [24-29]. There are more and more reports about pillararenes complexing with different guest molecules to construct pseudorotaxanes [30-35]. Previously, our group for the first time demonstrated that alkyl chains can be encapsulated in the pillar[5]arene cavity, forming [2]pseudorotaxanes driven by the $\text{CH}\cdots\pi$ interactions [36-37]. This discovery facilitated the preparation of threaded structures based on the pillar[5]arene/alkyl chain recognition motif. Benefiting from these results, various compounds with different substituents on the alkyl chains have

been used to prepare pseudorotaxanes with pillar[5]arenes, and have shown potential applications in different fields [38-43].

So far, fabricating pseudorotaxanes containing more than two components is still a difficult task. Here, we reported new pseudorotaxanes based on pillar[4]arene[1]quinone **H** and 1,10-dibromodecane **G** (Scheme 1). The pillar[4]arene[1]quinone was prepared by partial oxidation of perethylated pillar[5]arene according to previous reports [44-45], which is composed of four 1,4-diethoxybenzene subunits and one benzoquinone subunit. We found that **H** and **G** can be used to build a [3]pseudorotaxane in the solid state, but a [2]pseudorotaxane in solution.



Scheme 1: Chemical structures and cartoon representation: (a) pillar[4]arene[1]quinone **H**; (b) 1,10-dibromodecane **G**; (c) schematic representation of the pseudorotaxanes based on **H** and **G**.

Results and Discussion

Host–guest complexation in the solid state

Cocrystals of **H** and **G** were obtained by slow evaporation of their solution in methanol. The X-ray crystallography revealed that two host molecules complex one guest molecule, forming a [3]pseudorotaxane in the solid state (Figure 1). In the crystal structure, the alkyl chain of the guest is threaded through the cavities of the two host molecules, which is stabilized by multiple CH $\cdots\pi$ interactions and hydrogen bonds. Specifically, there are four hydrogen atoms on the guest molecule to form multiple CH $\cdots\pi$ interactions with the benzene rings of the host. In addition, the two bromine atoms at the end of the guest molecule are outside the host cavities and form moderate hydrogen bonds with the hydrogens on the ethoxy groups.

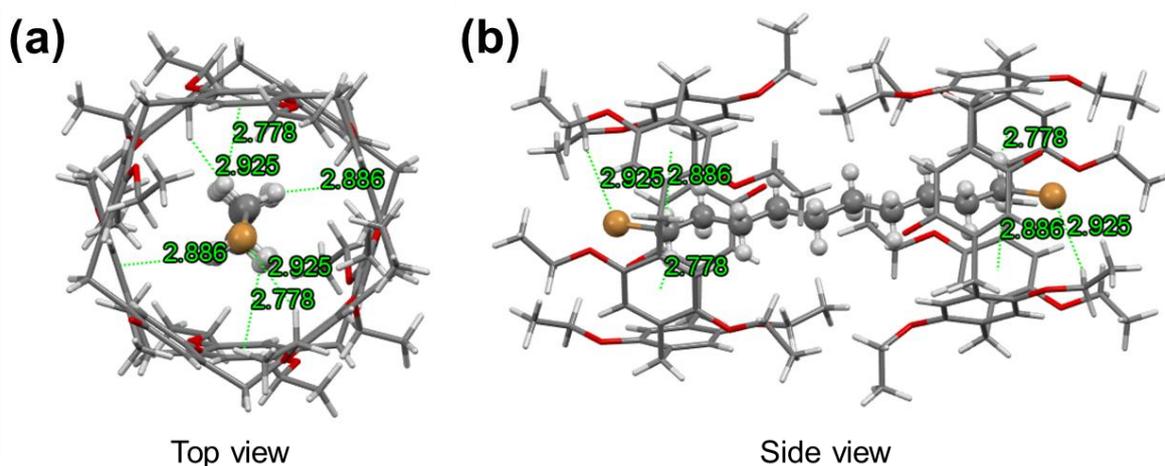


Figure 1: Crystal structures of the [3]pseudorotaxane between **H** and **G** in the solid state. Color code: C, gray; Br, orange; O, red; H, white. CH $\cdots\pi$ distance (Å): 2.778, 2.886, 2.778, 2.886; CH \cdots Br distance (Å): 2.925, 2.925.

Host–guest complexation in solution

In order to further study the host–guest binding properties of **H** and **G**, we explored the complexation in solution by ^1H NMR spectroscopy. As depicted in Figure 2, after the addition of 1.0 equiv. of **G** to a solution of **H**, all protons on **G** shifted upfield, which meant the threading of the alkyl part of the guest into the electron-rich cavity of the host, confirming the complexation between **H** and **G**.

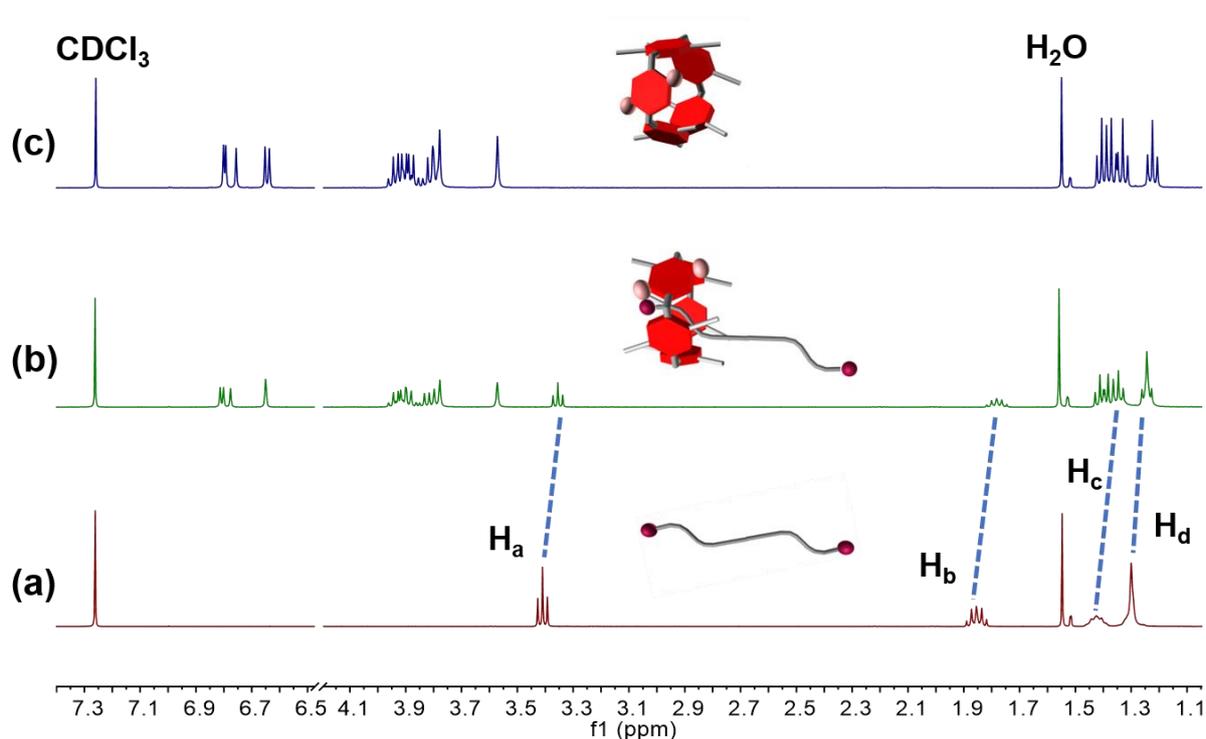


Figure 2: ^1H NMR spectra (500 MHz, CDCl_3 , 298K): (a) 6.00 mM **G**; (b) 3.00 mM **G** + 3.00 mM **H**; (c) 6.00 mM **H**.

Matrix-assisted Laser Desorption/Ionization Time of Flight Mass Spectrometry (MALDI-TOF MS) was conducted to investigate the complexation properties. However, no peak related to the complex but only peaks of **H** were found, implying weak host–guest interactions between **H** and **G** (Figure S3-S4).

A Job plot based on the proton NMR data was made to determine the complexation stoichiometry between **H** and **G**. The formation signified a 1:1 binding stoichiometry

in chloroform-*d* at room temperature (Figures S5-S6). Combined with the mass spectrometry results, we believed that the different stoichiometry ratios of the complexation in the solid state and solution could be owing to the competitive role of solvent molecules in the combination of **H** and **G**. The association constant (K_a) value calculated by the non-linear curve-fitting method was $20.0 \pm 2.4 \text{ M}^{-1}$ (Figures S7-S8), which agreed well with the inference above.

To further explore the geometry of the complexation in solution, we performed a NOESY study (Figure 3). Only one correlative peak between proton H_1 of **H** and H_a of **G**, which agreed with the formation of the complexation: the alkyl chains of **G** were encapsulated into the cavity of **H**. This further indicated that the interactions between **H** and **G** were weak.

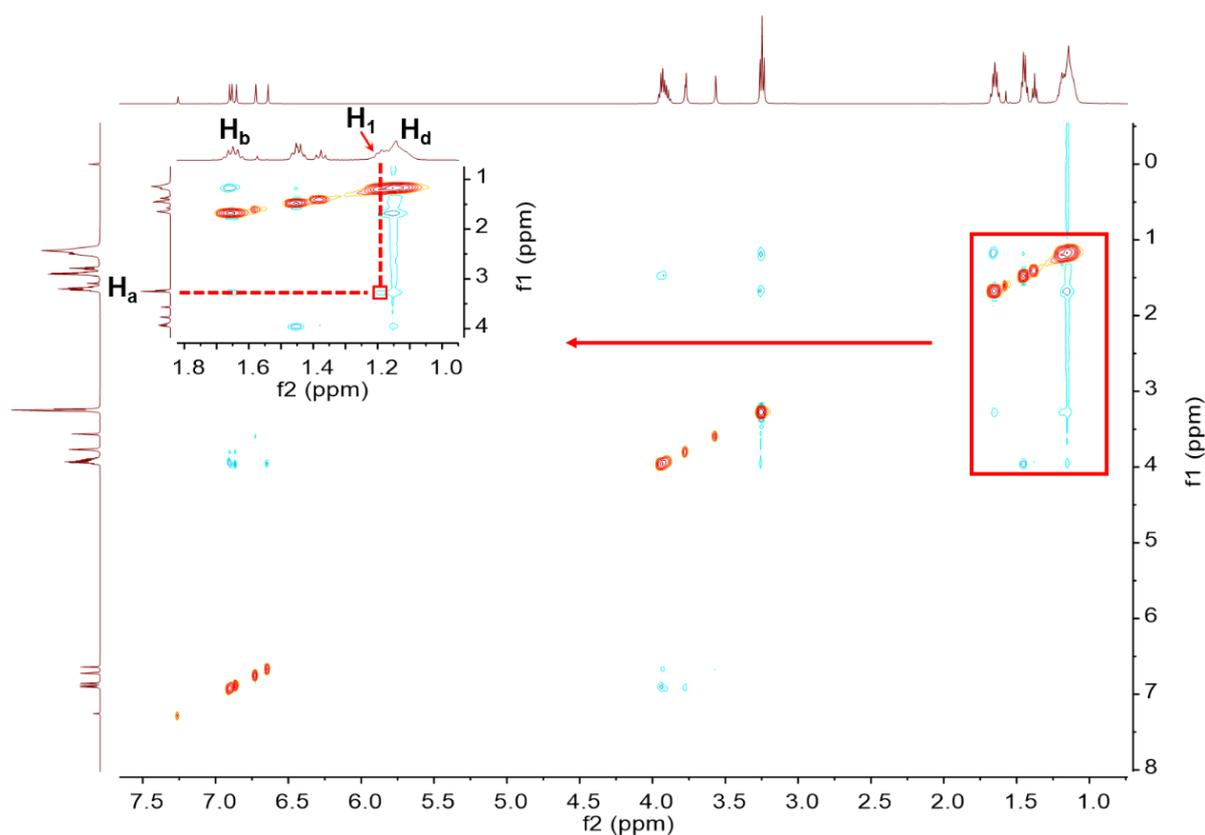


Figure 3: NOESY spectrum of a solution of **H** and **G** (500 MHz, chloroform-*d*, 298K).

Ultraviolet-visible property of the complexation in solution

Due to the red characteristic of **H**, we wondered the influence of **G** on the optical properties of **H**, so a UV-vis spectroscopy experiment was carried out. We investigated the changes in the UV-vis absorption of the complex at different guest concentrations of 0.5 equivalent and 1 equivalent. As shown in Figure 4, the concentration of **G** did not affect the maximum UV-vis absorption wavelength. This also indicated that the interactions between **H** and **G** were weak.

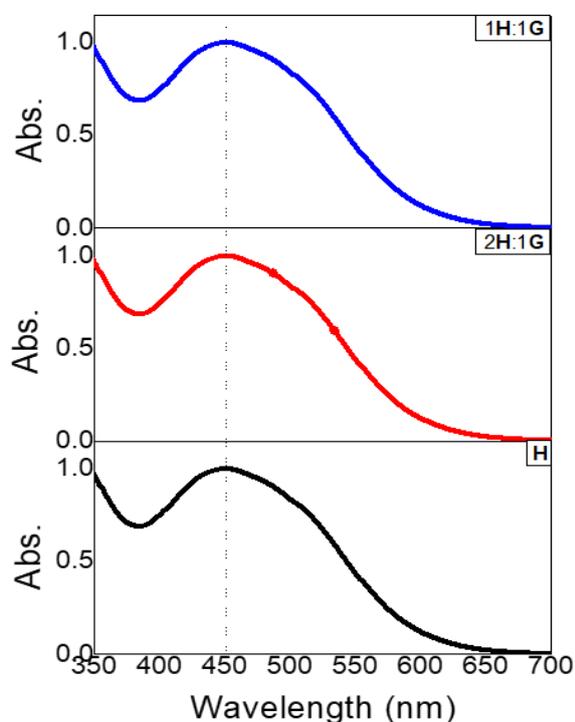


Figure 4: Normalized Ultraviolet-visible spectra: **H** (bottom); **H** with addition of 0.5 equiv. **G** (middle); **H** with addition of 1 equiv. **G** (top). [**H**] = 3.00 mM.

Conclusion

In summary, we constructed novel pseudorotaxanes based on a pillar[4]arene[1]quinone and 1,10-dibromodecane. X-ray single crystal diffraction

analysis showed that an alkane molecule threaded into cavities of two pillar[4]arene[1]quinone molecules, forming a [3]pseudorotaxane in the solid state. However, ^1H NMR experiments revealed that the pillar[4]arene[1]quinone encapsulated the guest molecule with 1:1 stoichiometry to form [2]pseudorotaxane in solution. One possible reason may be that the interactions between **H** and **G** were weak and there was a complexation competition with solvent molecules. Furthermore, the addition of **G** did not change the maximum UV-vis absorption wavelength of **H**. The bromine atoms at the ends of the guest molecule provide convenience for the further capping of pseudorotaxanes to construct rotaxanes, which will broaden the potential applications of pillararene derivatives in the manufacture of sophisticated supramolecular architectures and functional supramolecular systems.

Supporting Information

Supporting Information File 1:

File Name: bjoc-pseudorotaxanes-SI

File Format: pdf

Title: Supporting Information

Supporting Information File 2:

File Name: CIF file for **H•G**

File Format: cif

Title: CIF file for **H•G**

Acknowledgements

We thank sincerely the financial support of the National Natural Science Foundation of China NSFC (22035006) and the fundamental research funds for the central universities.

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