SHORT COMMUNICATION

EurJOC European Journal of Organic Chemistry

DOI: 10.1002/ejoc.201201003

Cavity-Extended Pillar[5]arenes: Syntheses and Host–Guest Complexation with Paraquat and Bispyridinium Derivatives

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Keywords: Host–guest systems / Pillararenes / Pseudorotaxanes / Macrocycles / Supramolecular chemistry

Cavity-extended pillar[5]arenes containing electron-rich naphthyl groups have been demonstrated to have enhanced binding affinity to linear guests containing electron-deficient pyridinium units. The importance of size effect, charge density, cooperative effect, and C–H···π interactions were investigated, and these factors play significant roles in the complexation of these host–guest systems.

Introduction

Threaded structures, such as rotaxanes or pseudorotaxanes, with macrocyclic hosts (the "wheels") and linear guests (the "axles") have attracted considerable attention in the last decade not only because of their topological importance but also due to their application in the fabrication of artificial molecular machines, supramolecular polymers, supramolecular gels, and other functional supramolecular systems.[1] Crown ethers, cyclodextrins, cucurbiturils, and calixarenes are the four most important classes of macrocyclic hosts and have been widely studied in host–guest chemistry.[2] Pillar[*n*]arenes, mainly including pillar[5]arenes[3] and pillar[6]arenes,[4] are new macrocyclic hosts. Their repeating units are connected by methylene bridges at the *para* positions, forming a unique pillar architecture, which is different from the basket-shaped structure of *meta*-bridged calixarenes. The unique pillar structure and the easy functionalization of pillar[*n*]arenes afford them outstanding ability to selectively bind different kinds of guests and provide a useful platform for the construction of various receptors with different functions. To prepare pillar[*n*]arene-based threaded structures and large supramolecular architectures efficiently, it is necessary to increase the association strength between pillar[*n*]arenes and the guests.

A convenient strategy to enhance the binding affinity is the syntheses of improved receptors starting from a preformed molecular platform upon which additional binding sites can be introduced and oriented in space.[5] Herein, cavity-extended pillar[5]arenes **H1** and **H2** (the "wheels") containing electron-rich naphthyl groups on both sides or on one side of the pillar[5]arene backbone were designed and prepared. Compounds **G1**–**G7** (Scheme 1) with electron-deficient aromatic units were chosen as the linear guests (the "axles"). The introduction of naphthyl rings provided additional binding sites for the guests, resulting in an improvement in their association constants efficiently. We investigated the impact of size, charge density, cooperative effects, and C–H···π interactions on the complexation in these host–guest systems. These factors play significant roles in the improvement in the association constants between macrocyclic hosts **H1** and **H2** and linear guests **G1**–**G7**. ^{1}H NMR, 2D NOESY, and UV/Vis spectroscopy, in addition to ESI-MS, provided converging evidence of efficient binding.

Results and Discussion

Size effects between the hosts and guests were firstly investigated. From the single crystal structure of **H1** (Figure 1), we know that the length of **H1** is about 27 Å, which is more suitable for **G2** and **G4** than **G1** and **G3**. Figure 2e, d show the ^{1}H NMR spectra ($CDCl_3/CD_3CN$ = 2:1) of **G2** recorded in the absence and presence of 1 equiv. of **H1**, respectively. The signals related to protons H^{a2}, H^{c2}, and H^{d2} on the 4,4′-bipyridinium units shifted upfield ($\Delta\delta$ = –0.092, –0.012, and –0.146 ppm, respectively) after complexation. In addition, the broadening effects were so remarkable that the signals of H^{b2} and H^{e2} could not be observed after complexation. The peaks related to the methylene protons of guest **G2** shifted upfield dramatically and became broad (Supporting Information, Figure S7d), indicating that the long alkyl chains were located in the cavity of **H1**. On the other hand, chemical shift changes were also observed for the protons on **H1**. The peaks for protons H^2

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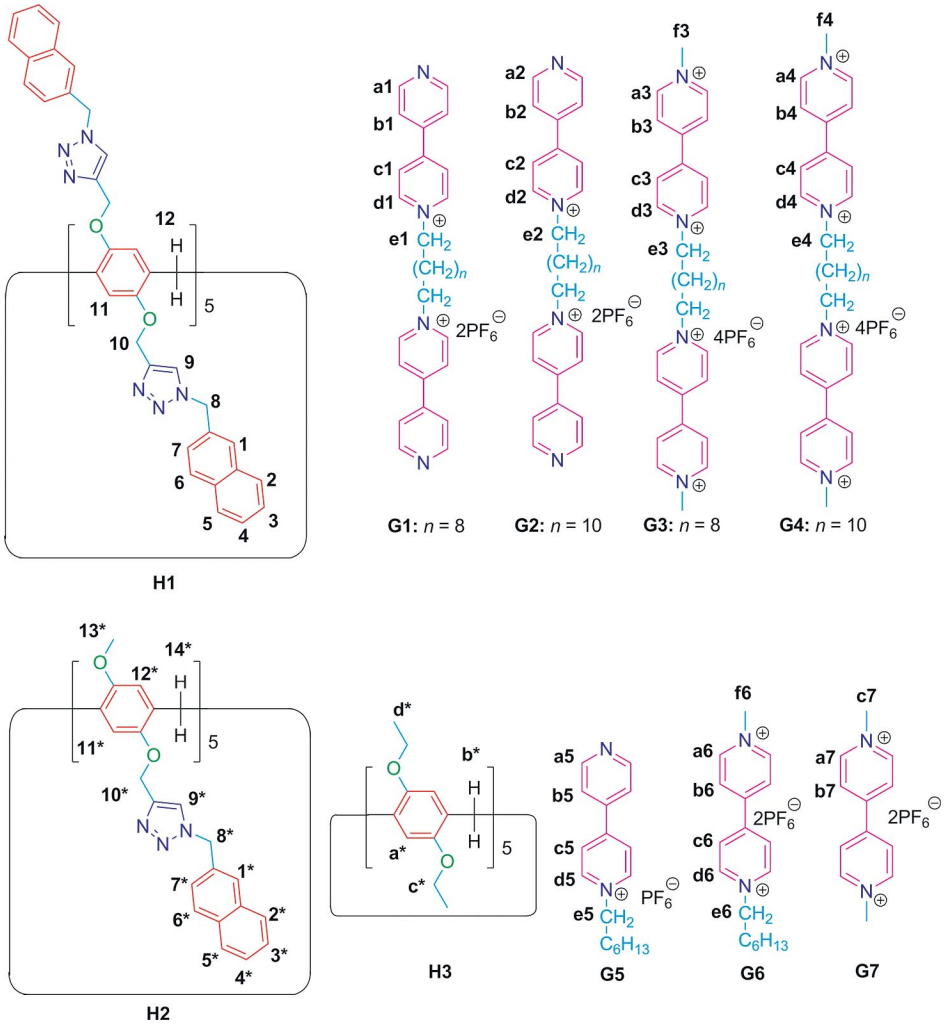
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejoc.201201003.



Scheme 1. Chemical structures of the hosts and guests.

and H^8 exhibited a downfield shift ($\Delta\delta$ = +0.051 and +0.101 ppm, respectively), whereas the signals of H^{11} and H^{12} shifted upfield. These chemical shift changes are consistent with the formation of an interpenetrated complex. We deduce that **G2** interacts with **H1** in solution and the guest molecule is included in the cavity of the host, which leads to efficient shielding of the guest protons. The corresponding association constant value (K_a) of **H1**⊃**G2** was determined to be $(1.28 \pm 0.10) \times 10^3$ M^{-1}, which is higher than that for the shorter guest **G1** with **H1** (Table 1). Similarly, the binding constant between **H1** and **G4** is $(6.25 \pm 0.56) \times 10^3$ M^{-1}, about five times that between **H1** and **G3** (Table 1). The difference in these K_a values is caused by the different sizes (lengths) of these guests. Compared with **G1** and **G3**, the lengths of **G2** and **G4** are more suitable for **H1**, so the host–guest interactions can be more easily achieved, resulting in stronger binding affinities.

The impact of the charge density of the guests on the host–guest interactions in these host–guest systems was also studied. The lengths of the alkyl chains between **G1** and **G3** and between **G2** and **G4** are the same, whereas the charge densities of **G3** and **G4** (four positive charges) are higher than those of **G1** and **G2** (two positive charges). From comparison of the ^{1}H NMR spectra, similar changes in the

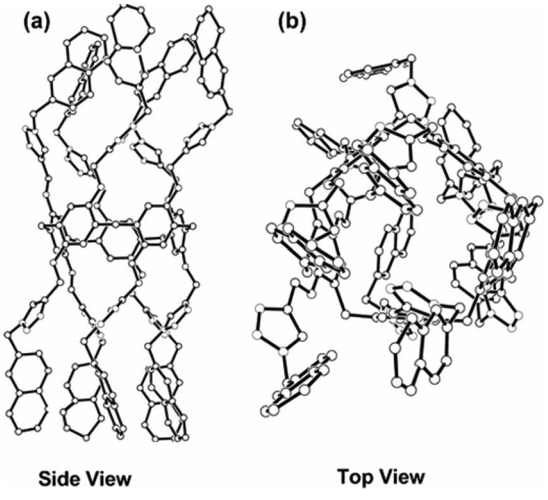


Figure 1. Ball-and-stick views of the crystal structure of **H1**. Hydrogen atoms and solvent molecules are omitted for clarity. Disorder found for some naphthalene groups is not shown.

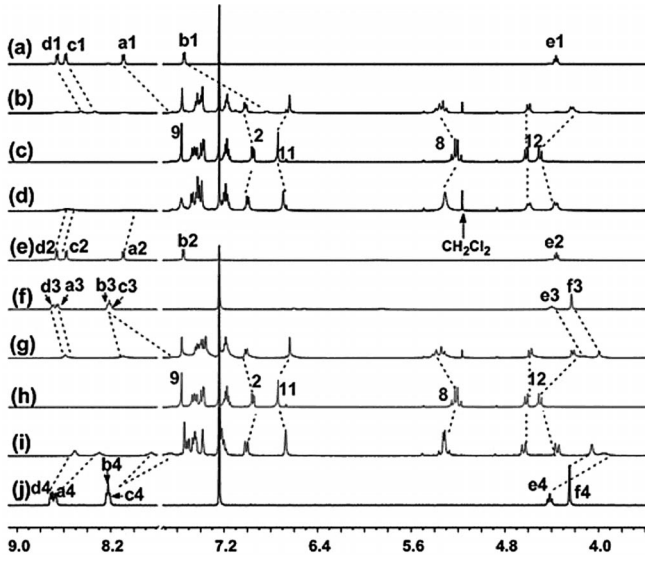


Figure 2. Partial ^{1}H NMR spectra (400 MHz, [D_1]chloroform/[D_3] acetonitrile = 2:1, room temperature): (a) **G1** (1.00 mM); (b) **G1** (1.00 mM) and **H1** (1.00 mM); (c) **H1** (1.00 mM); (d) **G2** (1.00 mM) and **H1** (1.00 mM); (e) **G2** (1.00 mM); (f) **G3** (1.00 mM); (g) **G3** (1.00 mM) and **H1** (1.00 mM); (h) **H1** (1.00 mM); (i) **G4** (1.00 mM) and **H1** (1.00 mM); (j) **G4** (1.00 mM).

Table 1. Association constants K_a and stoichiometries for the host–guest complexes.[a]

Host	Guest	Stoichiometry	K_a [M^{-1}]
H1	**G1**	1:1	$(9.43 \pm 0.89) \times 10^2$
H1	**G2**	1:1	$(1.28 \pm 0.10) \times 10^3$
H1	**G3**	1:1	$(1.30 \pm 0.11) \times 10^3$
H1	**G4**	1:1	$(6.25 \pm 0.56) \times 10^3$
H2	**G5**	1:1	$(2.27 \pm 0.21) \times 10^2$
H2	**G6**	1:1	$(6.02 \pm 0.46) \times 10^2$
H2	**G7**	1:1	$(3.57 \pm 0.21) \times 10^2$
H3	**G6**	1:1	$(1.23 \pm 0.11) \times 10^2$

[a] Association constants and stoichiometries of these host–guest complexes were determined by ^{1}H NMR titrations ($CDCl_3/CD_3CN$ = 2:1).

chemical shifts of the protons on the hosts and guests were observed for the complexations of **H1**⊃**G** (**G** = **G3** or **G4**) and **H1**⊃**G** (**G** = **G1** or **G2**; Figure 2; Supporting Information, Figure S7), which indicated that they have similar binding modes. However, the association constant of **H1**⊃**G3** is greater than that of **H1**⊃**G1**, and the association constant of **H1**⊃**G4** is greater than that of **H1**⊃**G2** (Table 1). The main reason is that the extent of the electron deficiency of **G3** (or **G4**) is higher than that of **G1** (or **G2**), resulting in stronger interaction between **H1** and the guests with higher charge density (**G3** and **G4**). Among these four guests, the K_a value of **H1**⊃**G4** is the highest and about four times higher than those of the complexes between **H1** and **G1**–**G3**, indicating that suitable size and high charge density both play significant roles in these host–guest systems and they can efficiently enhance the binding ability between the host and the guest.

The C–H···π interactions are the weakest non-covalent interaction in supramolecular chemistry (1.5–2.5 kcal mol^{-1}).[6] However, they play significant roles in various fields, for example, in determining the conformations of molecules, crystal packing, host–guest chemistry, reaction selectivity, and the self-assembly of molecules into an organized supramolecular structure.[7] From our previous work, we know that C–H···π interactions are an important driving force in the formation of pillar[5]arene-based host–guest complexes. A supramolecular polymer,[3g] a mirror image cyclic dimer,[3i] and a molecular spring[3y] were obtained based on multiple C–H···π interactions. Compounds **H2**, **G6**, and **G7** were used as model compounds to investigate the impact of C–H···π interactions on the binding ability. ^{1}H NMR spectra showed that in the presence of **H2** (1:1 molar ratio), the peaks for the protons of **G6** exhibited upfield shifts and broadening effects compared with the free axle as a result of inclusion-induced shielding (Figure 3d; Supporting Information, Figure S8d). These changes in resonance signals suggested that the long alkyl chain of **G6** is located in the cavity of **H2**. However, guest **G7** without a long alkyl chain cannot form C–H···π interactions with **H2**. The association constant of **H2**⊃**G6** is $(6.02 \pm 0.46) \times 10^2$ M^{-1}, which is higher than that of **H2**⊃**G7** (Table 1), indicating that C–H···π interactions between the alkyl chain of **G6** and **H2** occurred and these forces stabilized the complex.

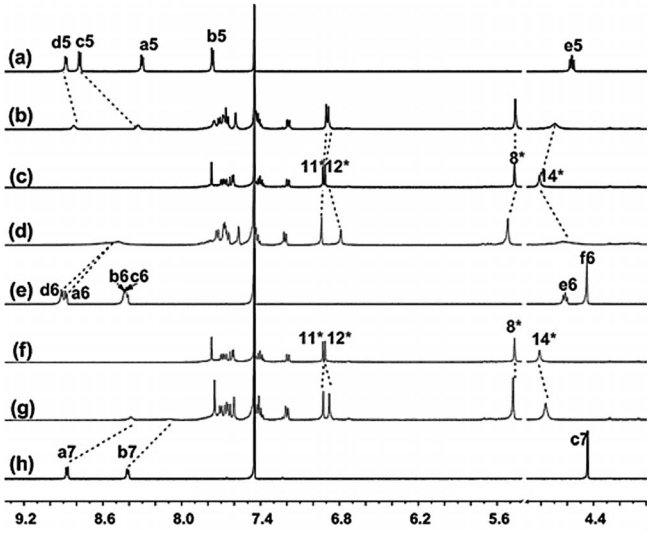


Figure 3. Partial ^{1}H NMR spectra (400 MHz, [D_1]chloroform/[D_3]-acetonitrile = 2:1, room temperature): (a) **G5** (1.00 mM); (b) **G5** (1.00 mM) and **H2** (1.00 mM); (c) **H2** (1.00 mM); (d) **G6** (1.00 mM) and **H2** (1.00 mM); (e) **G6** (1.00 mM); (f) **H2** (1.00 mM); (g) **G7** (1.00 mM) and **H2** (1.00 mM); (h) **G7** (1.00 mM).

Cooperative effects[8] can efficiently enhance the binding ability in host–guest systems. For **H1**, there are 5 electron-rich naphthyl groups on both sides of the pillar[5]arene cavity, so it provides 10 additional binding sites for the guests containing two 4,4′-bipyridinium units (**G1**–**G4**). For **H2**, it can only provide five additional binding sites. Compared with **G6** with only one electron-deficient 4,4′-bipyridinium

unit, **G4** with two electron-deficient 4,4′-bipyridinium units can interact with **H1** cooperatively. The K_a value of **H1⊃G4** is about nine times larger than that of **H2⊃G6** (Table 1). When **G4** threads into the cavity of **H1**, its two tetravalent cationic 4,4′-bipyridinium units interact with electron-rich naphthyl groups on both sides of **H1** cooperatively, which enhance the association constant significantly.

Further evidence for the formation of stable host–guest complexes between the cavity-extended pillar[5]arene-based hosts and the guests were obtained from UV/Vis absorption spectra and electrospray ionization (ESI) mass spectrometry. A series of solutions with different host–guest ratios were prepared. Figures S42–S48 (Supporting Information) show that upon addition of the corresponding guests, the absorbance increased gradually and blueshift phenomena were observed, indicating that interactions occurred between the electron-rich naphthyl units and the electron-deficient 4,4′-bipyridinium units. ESI-MS was also used to characterize the complexes between hosts **H1**–**H3** and guests **G1**–**G7**[9] (Supporting Information, Figures S10–S17). The relevant peaks were found at *m*/*z* = 1638.0, 1653.2, 1194.5, 1811.9, 2042.6, 1029.3, 986.8, and 684.7, corresponding to $[\mathbf{H1}\supset\mathbf{G1} - 2PF_6]^{2+}$, $[\mathbf{H1}\supset\mathbf{G2} - 2PF_6]^{2+}$, $[\mathbf{H1}\supset\mathbf{G3} - 2PF_6 + H]^{3+}$, $[\mathbf{H1}\supset\mathbf{G4} - 2PF_6]^{2+}$, $[\mathbf{H2}\supset\mathbf{G5} - PF_6]^{+}$, $[\mathbf{H2}\supset\mathbf{G6} - 2PF_6]^{2+}$, $[\mathbf{H2}\supset\mathbf{G7} - 2PF_6]^{2+}$, and $[\mathbf{H3}\supset\mathbf{G2} - 2PF_6]^{2+}$, respectively, which confirmed the formation of 1:1 complexes between the hosts and the corresponding guests.

2D NOESY is a useful tool to study the relative positions of building components in host–guest inclusion complexes. From the 2D NOESY spectrum of an equimolar mixture of **G4** and **H1**, NOE correlation signals were observed between the middle methylene protons H^g, H^h, H^i, H^j, and H^k of axle **G4** and protons H^8, H^{10}, and H^{11} on **H1** (Figure 4), suggesting that the middle alkyl chain of **G4** was deeply threaded into the pillar[5]arene cavity. This inclusion complex can be considered to have a 1:1 [2]pseudorotaxane structure.

To investigate whether the binding affinity between the cavity-extended pillar[5]arene-based hosts and these guests can be efficiently enhanced by introduction of electron-rich naphthyl groups, 1,4-bis(ethoxy)pillar[5]arene **H3** was used as the control compound. The association constant of **H3⊃G6** was determined to be $(1.23 \pm 0.11) \times 10^2$ M^{-1}, which was lower than that of **H2⊃G6** (Table 1). As a result of the introduction of five naphthyl rings on one side of the pillar[5]arene, **H2** has five additional naphthyl binding sites for the 4,4′-bipyridinium unit when it complexes with **G6**, which improved the association constant.

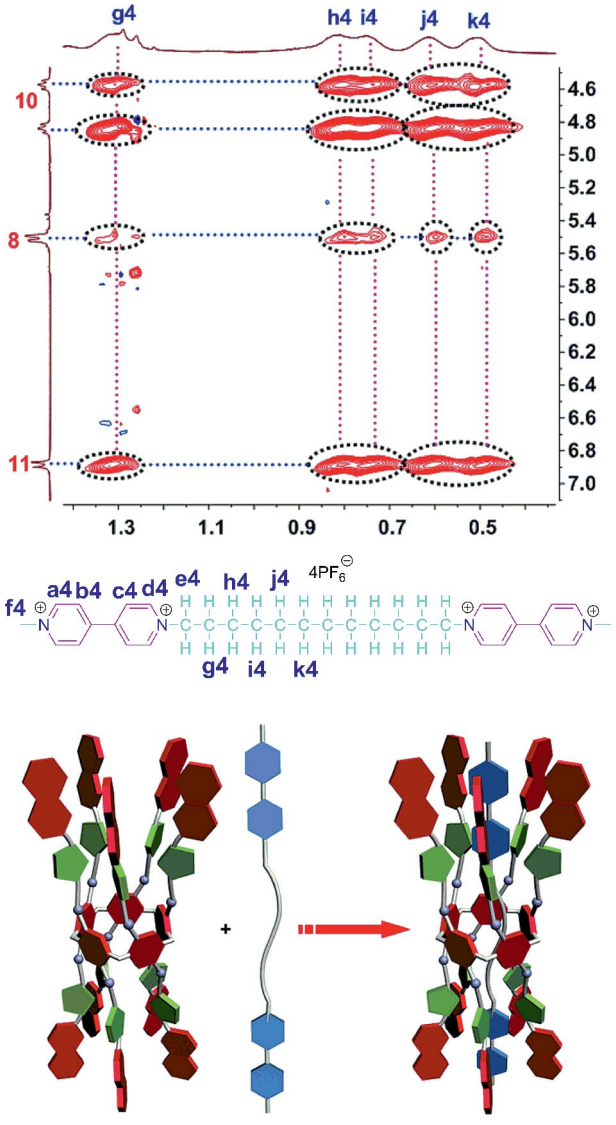


Figure 4. 2D ^{1}H–^{1}H NOESY spectrum of **H1⊃G4** ([D_1]chloroform/[D_3]acetonitrile = 2:1) and cartoon representation of the formation of this [2]pseudorotaxane.

Conclusions

In conclusion, novel cavity-extended pillar[5]arene-based hosts containing electron-rich naphthyl groups were designed and synthesized. By introduction of additional binding sites for the guests with electron-deficient 4,4′-bipyridinium units, the binding affinity could be enhanced efficiently. The impacts of size effects, charge density, cooperative effects, and C–H···π interactions on the complexation in these host–guest systems were investigated. These multiple non-covalent interactions jointly contribute to the formation of the complex and considerably reinforce the stability of the complex. The present efficient recognition motifs based on the cavity-extended pillar[5]arenes can be used in the fabrication of functional mechanically interlocked structures and large supramolecular systems.

Supporting Information (see footnote on the first page of this article): Synthetic procedures, characterization data, crystal data for **H1**, ^{1}H NMR titrations, and UV/Vis data.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (20834004, 91027006, and 21125417), the Fundamen-

tal Research Funds for the Central Universities (2012QNA3013), Program for New Century Excellent Talents in University, and Zhejiang Provincial Natural Science Foundation of China (R4100009).

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Received: July 26, 2012
Published Online: September 13, 2012

