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Cite this: DOI: 10.1039/c0xx00000x

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COMMUNICATION

Formation of a [2]pseudorotaxane based on a pillar[5]arene and a rigid guest in solution and in the solid state†

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Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

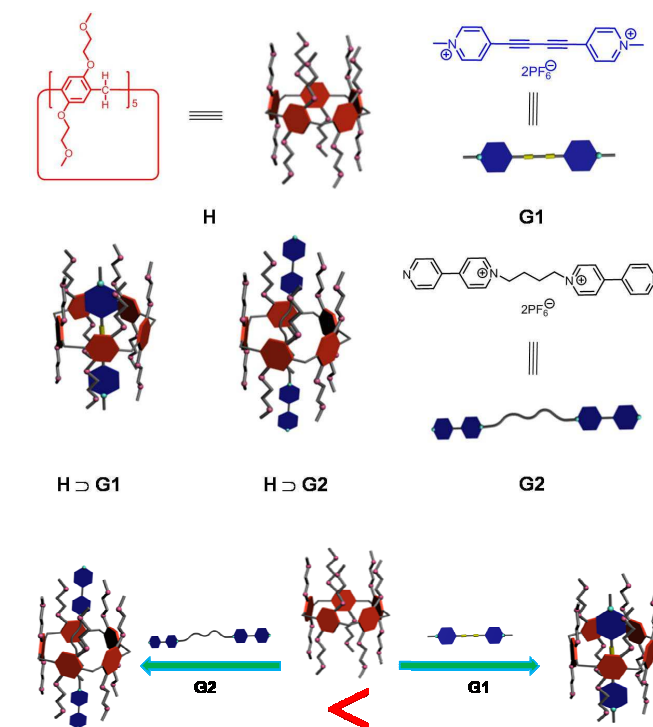
DOI: 10.1039/c0xx00000x

A pillar[5]arene with mono(ethylene oxide) substituents could form a highly stable [2]pseudorotaxane with a rigid guest both in solution and in the solid state.

In recent years, due to the contribution of threaded structures to topology and inventive applications in nanoscience, the research interest on these structures has grown rapidly.¹ As the basic threaded structures, pseudorotaxanes are the supramolecular precursors of rotaxanes and catenanes, which have drawn much attention and been widely studied. They are the fundamental building blocks for the design and fabrication of advanced supramolecular species with intriguing properties, such as functional supramolecular polymers and artificial molecular machines.² In order to increase the options available for the development of rotaxanes, catenanes, switches and machines, we have to search for new macrocyclic hosts and linear guest molecules to construct the templates of pseudorotaxanes. Up to now, the available host–guest recognition motifs which can be used in the construction of threaded and inclusion structures are still limited.³ This has hindered the development of research on inclusion structures. Therefore, the discovery of novel host–guest recognition motifs, especially the ones that have high binding constants will promote the development of supramolecular chemistry.

Pillar[*n*]arenes,⁴ a new generation of macrocyclic hosts, were first synthesized in 2008 and have gained a wide range of interests in the field of supramolecular chemistry.⁵ Compared with other macrocyclic hosts, pillar[*n*]arenes are cyclic pentamers, hexamers, or other larger polygons composed of hydroquinone units, which are connected by methylene bridges at the *para* positions, forming a unique and symmetric pillar architecture. Due to their special structures, they have exhibited unique binding abilities to various organic guests and revealed fascinating properties in the preparation of supramolecular polymers^{5d,6}, [c2]daisy chains^{5f,7} and other interesting supramolecular systems.⁸ Pillar[*n*]arenes exhibit very interesting host–guest properties with electron-deficient molecules such as paraquat derivatives and cationic molecules. As we all know, hydroxylated pillar[5]arene has active hydroxyl groups at both rims, thus we can introduce mono(ethylene oxide) groups to increase the electron donor ability of the pillar[5]arene. Complexation of pillar[5]arene **H** with paraquat and viologen derivatives has been studied recently.⁹ Here we synthesized a

novel guest **G1** possessing a π -conjugated and rigid structure with suitable size by sonogashira couplings and investigated the host–guest complexation between **H** and **G1** in both solution and the solid state. Furthermore, **H** can form a higher stable inclusion complex with rigid guest **G1** than the corresponding flexible guest **G2**, which was confirmed by various titration experiments, including fluorescence titration, UV-vis titration and ¹H NMR titration (Scheme 1).



Scheme 1 Chemical structures and cartoon representations of **H**, **G1**, **G2**, **H**⊃**G1**, and **H**⊃**G2**. Cartoon representation of complexation of pillar[5]arene **H** with **G1** and **G2**.

Pillar[5]arene **H** was synthesized according to a previously reported procedure (Scheme S1).¹⁰ The individual solutions of **H** and **G1** in acetonitrile are colourless. However, due to the charge-transfer interactions between the electron-rich aromatic rings of host **H** and the electron-poor pyridinium rings of guest **G1**, equimolar solutions of **H** and **G1** are orange-red (Fig. S4, ESI†), directly proving the complexation. The recognition possibilities

of **H** to guest **G1** were also investigated by ^1H NMR. Partial proton NMR spectra of **H**, **G1** and a mixture of **H** and **G1** are shown in Fig. 1. The addition of 1.0 equiv. of **G1** to a solution of **H** in acetonitrile- d_3 led to the signals of *N*-methyl protons H_{1a} , pyridinium protons H_{1b} and pyridinium protons H_{1c} on **G1** shifting upfield by 0.10, 0.25 and 0.19 ppm, respectively (Fig. 1). All these chemical shift changes indicated that the complexation of **H** with **G1** took place in solution.

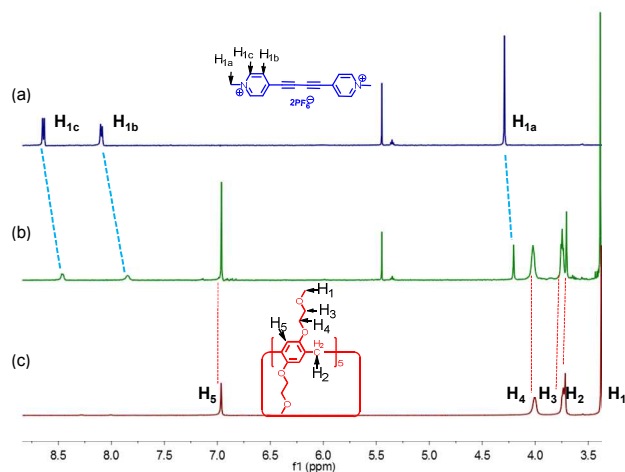


Fig. 1 Partial ^1H NMR spectra (400 MHz, CD_3CN , 25 $^\circ\text{C}$): (a) 1.00 mM **G1**; (b) 0.500 mM **H** and guest **G1**; (c) 1.00 mM guest **H**.

To further explore the binding mode between **H** and **G1**, a 2D NOESY experiment was carried out. The NOESY spectrum (Fig. S3, ESI †) of an equimolar solution of **H** and **G1** shows correlation between the signal of protons H_4 of **H** and that of protons H_{1c} on the pyridinium rings of **G1**, implying that guest **G1** was threaded into the cavity of pillar[5]arene **H**.

Additionally, electrospray ionization mass spectrometry of an equimolar solution of **H** and **G1** exhibited peaks at $m/z = 1570.0$ (100%) and 712.5 (18%) (Fig. S2, ESI †), corresponding to $[\text{H}\supset\text{G1}-\text{PF}_6]^+$ and $[\text{H}\supset\text{G1}-2\text{PF}_6]^{2+}$, respectively, which revealed a 1:1 stoichiometry for the complexation between **H** and **G1**. No peaks related to the complexes with other stoichiometries were found.

The most direct evidence for the formation of a 1:1 inclusion complex between **H** and **G1** was obtained from single crystal X-ray analysis. The crystal structure of **H}\supset\text{G1}** was grown by slow diffusion of isopropyl ether into an equimolar acetonitrile solution of **H** and **G1**. The crystal structure of **H}\supset\text{G1}** shows that **G1** is threaded through the cavity of host **H** to form an inclusion complex in the solid state, which is stabilized by hydrogen bonding interactions and $\text{C}-\text{H}\cdots\pi$ interactions (Fig. 2). The inclusion of guest **G1** into the cavity of host **H** in the solid state is in accordance with the above-mentioned significant upfield chemical shift of protons H_{1b} and H_{1c} in solution. Six hydrogen bonds (A, B, C, D, E, F) form between four hydrogen atoms of guest **G1** and six oxygen atoms on the mono(ethylene oxide) substituents of pillar[5]arene **H**. Not only three *N*-methylene hydrogen atoms but also a pyridinium hydrogen atom are involved in these

hydrogen bonding interactions. The $\text{H}\cdots\pi$ -plane distances of the two hydrogen atoms of guest **G1** (G, H, I) are 2.836, 2.813 and 2.411 \AA , shorter than 3.05 \AA , implying the existence of $\text{C}-\text{H}\cdots\pi$ interactions.^{5a} The six hydrogen bonds and three $\text{C}-\text{H}\cdots\pi$ interactions are the main driving forces to form the [2]pseudorotaxane between **H** and **G1**. The crystals of **H}\supset\text{G1}** have a red color due to charge-transfer interactions between the electron-rich aromatic rings of **H** and the electron-poor pyridinium rings of **G1**.

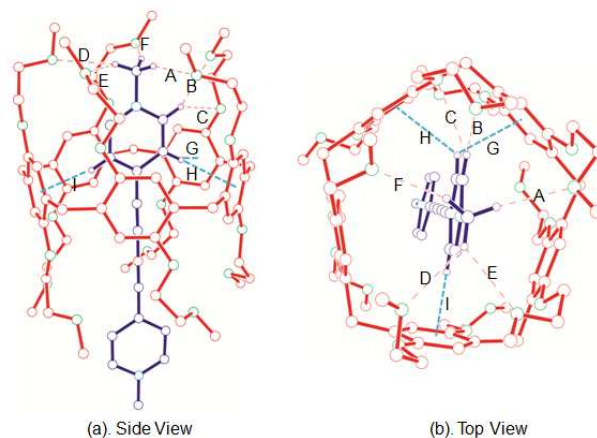


Fig. 2 Ball-stick views of the crystal structure of **H}\supset\text{G1}** (a and b). Host **H** is red, guest **G1** is blue, nitrogens are sky blue, oxygens are green, and hydrogens are purple. PF_6^- counterions, solvent molecules and hydrogens except the ones involved in hydrogen bonding between **H** and **G1** were omitted for clarity. The red dashed lines indicate hydrogen bonds (A, B, C, D, E and F) and $\text{C}-\text{H}\cdots\pi$ interactions (G, H and I). Hydrogen bond parameters: $\text{H}\cdots\text{O}$ distance (\AA), $\text{C}\cdots\text{O}$ distance (\AA), $\text{C}-\text{H}\cdots\text{O}$ angle (deg): A, 2.511, 3.431, 160.23; B, 2.447, 3.312, 154.74; C, 2.696, 4.959, 130.97; D, 2.720, 3.510, 132.62; E, 2.638, 3.342, 130.44; F, 2.480, 3.383, 156.79. $\text{C}-\text{H}\cdots\pi$ interactions parameters: $\text{C}-\text{H}\cdots\pi$ distance (\AA), $\text{C}-\text{H}\cdots\pi$ angle (deg): G, 2.836, 123.79, H, 2.813, 124.91, I, 2.411, 164.93.

The association constant for the complexation between **H** and **G1** was estimated by means of fluorescence titrations at room temperature in acetonitrile. Upon gradual addition of **G1** into an **H** solution, the fluorescence intensity was quenched efficiently, confirming the achievement of host-guest complexation between **H** and **G1**. A mole ratio plot was fitted to show the 1:1 complexation stoichiometry between **H** and **G1**. The association constant (K_a) for **H}\supset\text{G1}** was calculated to be $(3.33 \pm 0.41) \times 10^4 \text{ M}^{-1}$ (Fig. S5–S7, ESI †), which is higher than the corresponding K_a value $((1.92 \pm 0.15) \times 10^3 \text{ M}^{-1})$ for **H}\supset\text{G2}** (Fig. S8–S10, ESI †). The association constants (K_a) of **H}\supset\text{G1}** was also determined in acetonitrile by using a UV-vis titration method to be $(5.0 \pm 0.8) \times 10^4 \text{ M}^{-1}$ (Fig. S13, ESI †). The association constants (K_a) of **H}\supset\text{G2}** was measured by a ^1H NMR titration experiment to be $(1.45 \pm 0.38) \times 10^3 \text{ M}^{-1}$ in acetonitrile (Fig. S14–S15, ESI †). The above results suggesting that **H** and **G1** are strongly bonded, which is in agreement with the results obtained from the fluorescence titrations experiment. The reason why **G1** binds more tightly with **H** may be due to the rigid, conjugated structure of **G1**, and is better fitted in the cavity of pillar[5]arene **H** compared with **G2**.

In summary, we investigated the complexation between pillar[5]arene **H** and two different guests. Pillar[5]arene **H** can

form a 1:1 complex with guest **G1** both in solution and in the solid state. The formation of this complex was confirmed by ¹H NMR, electrospray ionization mass spectrometry, 2D NOESY and single crystal X-ray analysis. Compared with guest **G2**, **G1** showed a much higher binding constant, indicating that its rigid and conjugated structure enhance the complexation ability of the guest, as well as the matched cavity of **H** with **G1**. The good binding ability of pillar[5]arene **H** with guest **G1** makes this novel host-guest recognition motif have a broad potential application in the fabrication of new functional supramolecular systems and interlocked structures.

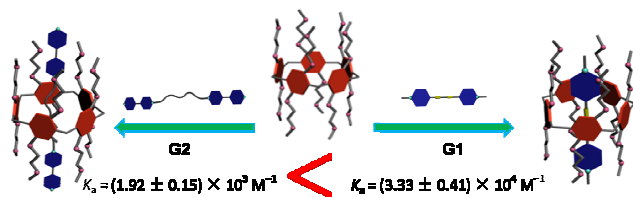
This work was supported by the Fundamental Research Funds for the Central Universities.

Notes and references

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† Electronic Supplementary Information (ESI) available: [Synthetic procedures, characterizations.]. See DOI: 10.1039/c0xx00000x.

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Colour Graphic:**Text:**

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