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Syntheses of a pillar[4]arene[1]quinone and a difunctionalized pillar[5]arene by partial oxidation†

Chengyou Han, Zibin Zhang, Guocan Yu and Feihe Huang*

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A pillar[4]arene[1]quinone and a difunctionalized pillar[5]arene have been synthesized by partial oxidation.

Macrocyclic molecules are always fascinating and attractive due to their interesting topology and structures and excellent host–guest properties in supramolecular chemistry. Pillararenes,[1] as a new kind of host macrocycle after crown ethers,[2] cyclodextrins,[3] calixarenes[4] and cucurbiturils,[5] have become one of the most popular topics since their first synthesis in 2008.[6–9] Based on their rigid, pillar structures, a lot of host–guest systems have been developed. For example, the alkyl chain-based molecular recognition for pillar[5]arenes with C–H···π interactions as the main driving force reported by us[6a] is very important since it is the basis of the complexation between pillar[5]arenes and functionalized alkyl chain guests such as alkanediamines,[6e] bis(imidazole) derivatives,[6f] alkanediacids[6c] and alkanedinitriles.[6i] Furthermore, rotaxanes,[6e] [*c*2]daisy chains[6g] and supramolecular polymers[6h] have been prepared based on this molecular recognition.

Functionalization of pillararenes is vital in order to explore their application in different areas.[8,9] For pillar[5]arenes, there are ten oxygen atoms on the two rims of their pillar structure. So far, all the functionalization studies have been done on the oxygen atoms and two kinds of functionalization have been mentioned. One is *per*-functionalization, which means that ten positions are functionalized (see **1** in Fig. 1). The other is partial functionalization, which means that only a part of the ten positions are functionalized (see **2** in Fig. 1). There are two methods to prepare *per*-functionalized pillar[5]arenes. First, from dealkyllation of dialkylpillar[5]arene by using BBr_3, *per*-hydroxylated pillar[5]arene **1a** was obtained.[1,7f] Second, oligomerization of difunctionalized monomers, such as 1,4-bis(prop-2-ynyloxy)benzene and 1,4-bis(2-bromoethoxy)benzene, produced *per*-functionalized pillar[5]arenes **1b** and **1c**.[7a,d,f] Three ways have been developed to partially functionalize pillar[5]arenes.

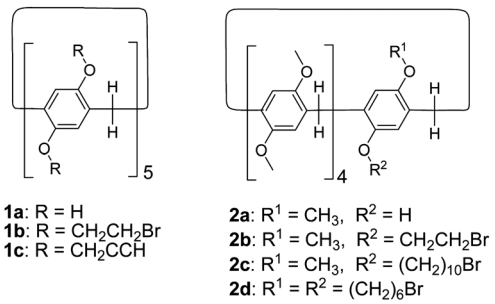
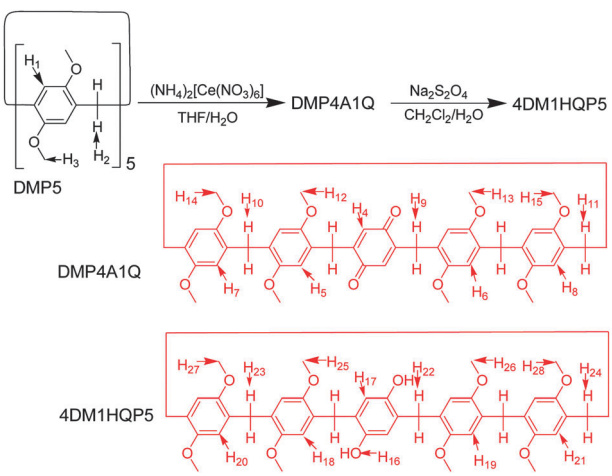


Fig. 1 Chemical structures of *per*-functionalized pillar[5]arenes **1** and partially functionalized pillar[5]arenes **2**.

First, using a small amount of BBr_3, a mono-functionalized pillar[5]arene (**2a**) was synthesized.[7b] Second, from co-oligomerization of different monomers, mono-functionalized (**2b** and **2c**) and difunctionalized (**2d**) pillar[5]arenes were prepared.[6e,7e] Third, using *in situ* cyclization and deprotection using $AlBr_3$ as the catalyst, a difunctionalized pillar[5]arene was made.[7c]

In this communication, we report a new method to functionalize pillar[5]arenes (Scheme 1). First, a pillar[4]arene[1]quinone (DMP4A1Q), a macrocycle with a benzoquinone unit replacing a dimethoxybenzene unit in the structure of DMP5, was synthesized by partial oxidation. Then reduction by $Na_2S_2O_4$



Scheme 1 Synthetic routes of a pillar[4]arene[1]quinone (DMP4A1Q) and a difunctionalized pillar[5]arene (4DM1HQP5).

MOE Key Laboratory of Macromolecular Synthesis and Functionalization, Department of Chemistry, Zhejiang University, Hangzhou 310027, P. R. China. E-mail: fhuang@zju.edu.cn; Fax: +86-571-8795-3189; Tel: +86-571-8795-3189

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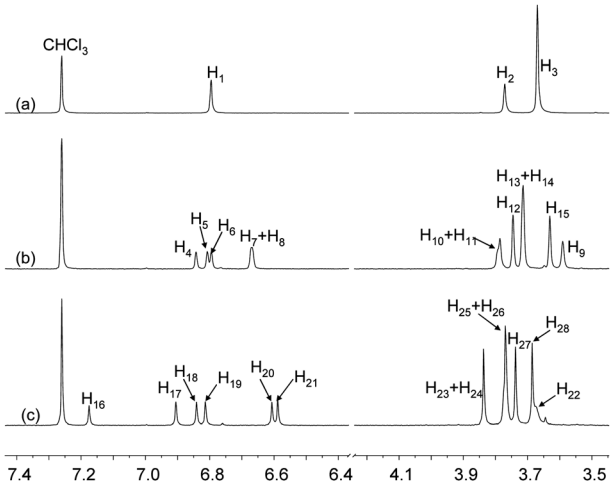

Fig. 2 Partial ^{1}H NMR spectra (400 MHz, $CDCl_3$, 22 °C): (a) DMP5; (b) DMP4A1Q; (c) 4DM1HQP5.

afforded a difunctionalized pillar[5]arene (4DM1HQP5) with a hydroquinone repeating unit quantitatively.

The ^{1}H NMR spectra of DMP5, DMP4A1Q and 4DM1HQP5 are shown in Fig. 2. When DMP5 was partially oxidated to DMP4A1Q, a new peak corresponding to protons H_4 on the benzoquinone unit appeared. The protons on the benzene rings next to the benzoquinone unit split into two peaks (H_5 and H_6), indicating the loss of symmetry. Protons H_7 and H_8 on the remaining benzene rings did not split because of their minor chemical environmental difference resulting from being far from the benzoquinone unit. Bridging methylene protons H_{10} and H_{11} and methyl protons H_{13} and H_{14} showed the same phenomena. 4DM1HQP5 has the same symmetry as DMP4A1Q, so its spectrum is similar to that of DMP4A1Q except one new peak corresponding to protons H_{16} on the hydroxyl groups of the hydroquinone moiety.

We obtained the crystal structures of DMP4A1Q and 4DM1HQP5 using single crystals grown by slow diffusion of *iso*-propylether to their individual dichloromethane solutions at rt (Fig. 3). From these crystal structures, it is clear that the pillar structure of DMP5 is still kept in DMP4A1Q and 4DM1HQP5 after oxidation and then reduction. Interestingly, there are two dichloromethane molecules in each of the crystal structures of DMP4A1Q and 4DM1HQP5: one in the cavity of the pillar structure, and the other on a rim of the pillar structure. The dichloromethane molecule inside the cavity has two C–H···π interactions with the neighbouring benzene rings. The C–H···π distances, 2.62–3.01 Å, were shorter than 3.05 Å, and the C–H···π angles, 136°–175°, were larger than 90°, indicating the existence of the C–H···π interactions (**A**, **B**, **D** and **E** in Fig. 3) between the dichloromethane molecules and the benzene rings on DMP4A1Q or 4DM1HQP5.[6a] The two dichloromethane molecules on the rims of the pillar structures of in the two crystal stuctures have hydrogen bonds with the oxygen atoms of the benzoquinone unit (**C** in Fig. 3) or the hydroquinone moiety (**F** in Fig. 3). Moreover, the hydrogens on the hydroxyl groups of the hydroquinone have two intramolecular hydrogen bonds with the oxygen atoms on the neighbouring benzene rings (**G** and **H** in Fig. 3).

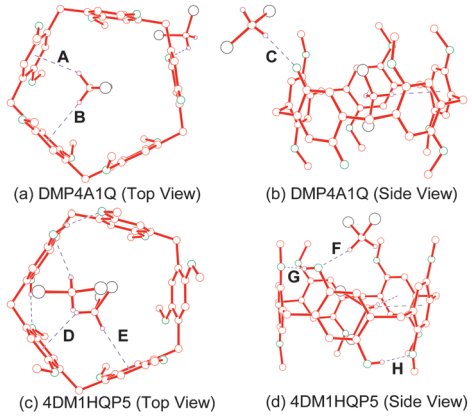

Fig. 3 Ball-stick views of the crystal structures of DMP4A1Q⊃$(CH_2Cl_2)_2$ (a and b) and 4DM1HQP5⊃$(CH_2Cl_2)_2$ (c and d). Hydrogens, except the ones on the solvent molecules and hydroxyl groups, were omitted for clarity. Carbon atoms are red, oxygen atoms are green and chlorine atoms are black. The blue dashed lines indicate C–H···π interactions (**A**, **B**, **D** and **E**) and hydrogen bond interactions (**C**, **F**, **G** and **H**). C–H···π interaction parameters: C–H···π distance (Å), C–H···π angle (deg) **A**, 2.63, 149; **B**, 3.01, 175; **D**, 2.62, 136; **E**, 2.65, 171. Hydrogen bond parameters: H···O distance (Å), C(O)–H···O angle (deg), C(O)···O distance (Å) **C**, 2.27, 129, 2.99; **F**, 2.51, 153, 3.42; **G**, 1.88, 165, 2.70; **H**, 1.92, 173, 2.76.

We further studied the host–guest binding properties of DMP4A1Q and 4DM1HQP5 using *n*-octylethyl ammonium hexafluorophosphate (**3**) as a model guest. Compared with the ^{1}H NMR spectra of DMP4A1Q and **3** (spectra a and c in Fig. 4), the ^{1}H NMR spectrum of an equimolar solution of DMP4A1Q and **3** shows no chemical shift changes and no signal doubling, indicating no complexation or weak complexation between DMP4A1Q and **3** in chloroform-*d*. A possible reason is that the benzoquinone unit is electron-deficient so it may repel

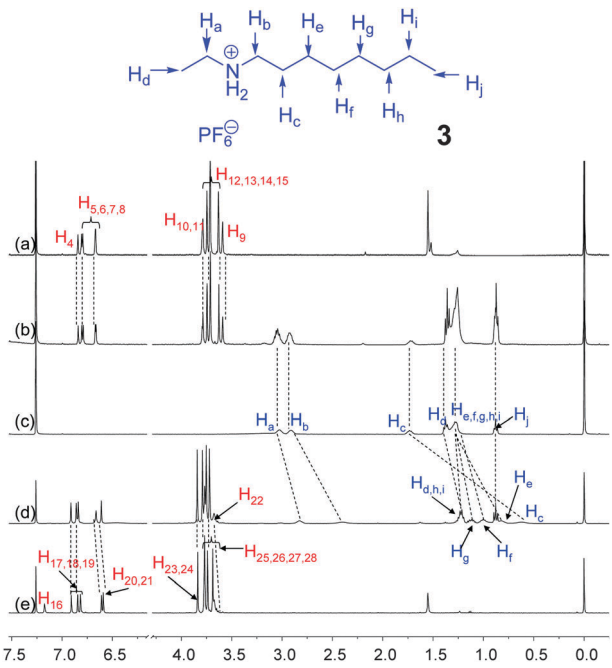

Fig. 4 Partial ^{1}H NMR spectra (400 MHz, $CDCl_3$, 22 °C): (a) 8.00 mM DMP4A1Q; (b) 8.00 mM DMP4A1Q and **3**; (c) 8.00 mM **3**; (d) 8.00 mM 4DM1HQP5 and 7.00 mM **3**; (e) 8.00 mM 4DM1HQP5.

the positive dialkylammonium part out of the pillar[5]arene cavity. The ^{1}H NMR spectrum (spectrum d in Fig. 4) of a solution of 4DM1HQP5 and **3** in chloroform-*d* shows only one set of peaks, indicating fast-exchange complexation between 4DM1HQP5 and **3** on the ^{1}H NMR time scale at 22 °C. After complexation, protons H_{17-28} on 4DM1HQP5 showed small chemical shift changes (spectra d and e in Fig. 4). The significant upfield chemical shift changes for H_a, H_b, H_c and H_e indicate that these methylene protons were located in the shielding region of the cyclic pillar structure. However, the small chemical shift changes of methyl protons H_d and H_j show that these protons were out of the cyclic pillar structure. These phenomena indicated that the linear guest **3** was threaded through the cavity of cyclic host 4DM1HQP5 to form a [2]pseudorotaxane in solution with the methylene protons H_a, H_b, H_c and H_e in the cavity of 4DM1HQP5 and the methyl protons H_d and H_j out of the cavity of 4DM1HQP5. This complexation geometry is similar to that of DMP5⊃**3**.[8g] A molar ratio plot indicated that the complexation stoichiometry between 4DM1HQP5 and **3** was 1 : 1 (Fig. S8, ESI†), which was confirmed by a low-resolution electrospary ionization mass spectrometry peak at *m*/*z* 880.5 corresponding to $[4DM1HQP5⊃\mathbf{3}–PF_6]^+$ (Fig. S10, ESI†). The association constant of 4DM1HQP5⊃**3** in chloroform-*d* was determined to be 1.70 (±0.70) × 10^3 M^{-1} (Fig. S9, ESI†). It is higher than the corresponding association constant value, 1.09 (±0.31) × 10^3 M^{-1}, of DMP5⊃**3**.[8g] One possible reason is that the steric hindrance becomes smaller after the loss of two methyl groups from DMP5 to 4DM1HQP5. Another possible reason is that the intramolecular hydrogen bonds (**G** and **H** in Fig. 3) make 4DM1HQP5 more rigid than DMP5, preorganizing it for the binding of **3**.

In conclusion, a pillar[4]arene[1]quinone and a difunctionalized pillar[5]arene were synthesized by partial oxidation. With this new functionalized method, partially functionalized pillararenes can be made for applications in various research areas.

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