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Communication

Carbon-carbon double bond in pillar[5]arene cavity: Selective binding of *cis*/*trans*-olefin isomers

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ABSTRACT

The binding behavior of pillar[5]arenes (**P5As**) towards a series of olefin guests ((*E*)-1,4-dichlorobut-2-ene (**1*E***), (*Z*)-1,4-dichlorobut-2-ene (**1*Z***), (*E*)-but-2-ene-1,4-diol (**2*E***), and (*Z*)-but-2-ene-1,4-diol (**2*Z***), as well as an alkyne derivative 1,4-dichlorobut-2-yne (**3**)) have been studied in organic solution. **P5As** exhibit considerable selectivities for the *trans*-olefin isomers (**1*E*** and **2*E***) over their *cis*-isomers (**1*Z*** and **2*Z***). The *cis/trans*-selective interactions hold the potential of utilizing **P5As** to separate olefin isomers.

As a new class of supramolecular macrocyclic hosts, pillararenes possess prism-like geometries and have π-rich cavities with multiple alkoxy or hydroxyl groups on both portals [1–11]. Pillararenes have shown excellent cavity host-guest properties towards a variety of guest molecules [12–22]. Compared with other popular macrocyclic receptors, the most peculiar binding behavior of pillararenes is the highly strong complexation of pillar[5]arenes (**P5As**) towards suitable neutral molecules in organic solution [23,24]. Our group has developed a series of α,ω-disubstituted alkane guests for **P5As** [25–30]. The guests with four-methylene bridges, which length fits the height of **P5As**'s cavity, give the strongest binding affinities.

Based on these results, we wonder if carbon-carbon double and triple bonds can be engulfed by the cavities of **P5As**. In this work, we wish to report the host-guest properties of **P5As** (**EtP5A** and **BuP5A**) towards a series of olefin guests (Scheme 1), *i.e.*, (*E*)-1,4-dichlorobut-2-ene (**1*E***), (*Z*)-1,4-dichlorobut-2-ene (**1*Z***), (*E*)-but-2-ene-1,4-diol (**2*E***), and (*Z*)-but-2-ene-1,4-diol (**2*Z***), as well as an alkyne 1,4-dichlorobut-2-yne (**3**), exhibiting interesting binding selectivities of *cis/trans* olefins. Olefins are basic feedstocks in the chemical industry. The selective recognition of an isomer of an olefin over the other is a challenging task due to their similar chemical and physical properties. Very recently, our group [31] and Huang's group [32] demonstrated the separation of *cis*- and *trans*-olefin isomers by crystalline materials of biphen[3]arene [33–35] and **P5As** at the solid-vapor phase. To the best of our knowledge, the present work is the first example of selective binding of olefin isomers by pillararenes in solution.

Fig. 1 shows the ^{1}H NMR spectra of hydrocarbons **2*Z*** and **2*E*** in $CDCl_3$ in the absence and presence of 1.0 equiv. amount of **EtP5A** host. Compared to the free **2*Z*** and **2*E*** (Figs. 1A and E), the peaks for the protons of **2*Z*** and **2*E*** (Figs. 1B and D) exhibit upfield shifts and broadening as a consequence of inclusion-induced shielding effects. Meanwhile, the host is deshielded by the presence of the guests, since proton signals of **EtP5A** derived from aromatic protons shift downfield. Therefore, we can deduce that the guest molecules are included in the cavity of the host. In addition, the chemical shifts induced by the *cis*- and *trans*-guest are different. The encapsulation-induced upfield shifts and broadening effects of methylene protons of **2*E*** are more obvious than those of **2*Z***. For example, the $\Delta\delta$ value for H_B of **2*E*** (−0.59 ppm) is much larger than that for H_b of **2*Z*** (−0.18 ppm). And the middle alkenyl protons (H_A) of **2*E*** exhibit the most remarkable complexation-induced peak broadening, because their signals cannot be observed in the ^{1}H NMR spectrum. Correspondingly, the downfield shifts of aromatic and methylene protons (H_1, H_2) of **EtP5A** caused by

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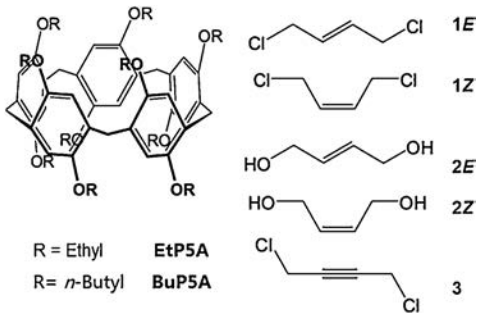

Scheme 1. Structures of the host and the guests.

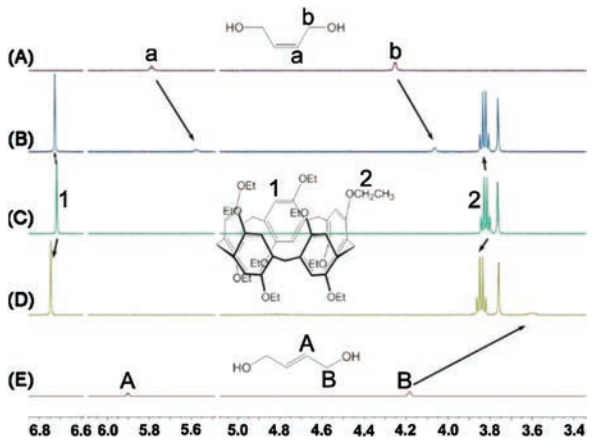

Fig. 1. ^{1}H NMR spectra (500 MHz, 298 K) of (A) **2*Z***, (B) **2*Z*+ EtP5A**, (C) **EtP5A**, (D) **2*E*+ EtP5A,** (E) **2*E*** in $CDCl_3$ at 5.0 mmol/L.

the *trans*- guest **2*E*** ($\Delta\delta_{H1}$ = 0.027 ppm, $\Delta\delta_{H2}$ = 0.020 ppm) are more obvious than those caused by the *cis*-guest **2*Z*** ($\Delta\delta_{H1}$ = 0.008 ppm, $\Delta\delta_{H2}$ = 0.006 ppm). These results suggest that the complexation between the host and the *trans*-olefin guest **2*E*** is stronger than that for the *cis*-**2*Z***. The interactions of **EtP5A** with the other olefin guests (**1*E*, 1*Z***), as well as **BuP5A** with **1*E***, **1*Z***, **2*E*** and **2*Z*** were also investigated. Similar NMR changes were observed, wherethe encapsulation-induced NMR changes of *trans*-guests were always lager that for *cis*- ones.

^{1}H NMR results suggested that both *cis*- and *trans*-olefins can be engulfed in **P5As**, however, their binding affinities were quite different. The association constants for the four olefin guests with two **P5As** in $CDCl_3$ were then tested by NMR titration methods (Table 1). The values, ranging from 10 L/mol to 210 L/mol, are lower than that for alkane compounds such as 1,4-dichlorobutane and 1,4-butanediol (Table S1 in Supporting information). This may be due to the fact that the milldle C—H bonds in olefins are less than those in the alkane guests, resulting in a smaller number of host-guest C—H$\cdots\pi$ and C–H$\cdots$O hydrogen bonds. Another possible reason is that, in comparison with olefins, alkane derivatives could effectively adjust themselves to fit the host cavity well due to their more flexible backbones.

Table 1
Association constants (K_a) for the host–guest inclusion complexation in $CDCl_3$ at 298 K.

Guest	BuP5A (L/mol)	EtP5A (L/mol)
1*E*	210 ± 20	115 ± 4
1*Z*	55 ± 3	49 ± 4
2*E*	18 ± 2	100 ± 8
2*Z*	10 ± 3	16 ± 3

For both **P5As** hosts, the association constants of *trans*-isomers are larger than those of their *cis*-isomers (Fig. 2). For example, when **BuP5A** gives a **1*E***/**1*Z*** selectivity of 3.8, the *trans*-/*cis*-isomer selectivity of **2*E***/**2*Z*** by **EtP5A** is up to 6.3. This is reasonable that *trans*-isomers having stretching structures are more suitable for **P5As**'s cavity than *cis*-isomers. The non-centrosymmetric structure of *cis*-guest leads to a lower host-guest induced-fit degree and has higher steric hindrance during the complexation, ultimately leading to a weaker host-guest interaction.

The size/shape fit between *trans*-isomer and **P5A** cavity was then confirmed by a single crystal structure of **1*E*⊂BuP5A**. Guests **1*E*** and **BuP5A** (1:1, molar ratio) were completely dissolved in methylene chloride, and then covered with a layer of ethyl acetate solution at room temperature. We successfully obtained single crystals of **1*E*⊂BuP5A** complex suitable for X-ray analysis. It was found that there are nine (week) C–H$\cdots$Cl hydrogen bonding interactions between the two chlorine atoms of **1*E*** and **BuP5A**'s two portals (Fig. 3). Besides, there exist quadruple C–H$\cdots$O and quadruple C–H$\cdots\pi$ interactions between the guest protons with the host's oxygen atoms and benzenes. The main driving forces of host-guest encapsulation are multiple C—H$\cdots$Cl (O) and C—H$\cdots\pi$ interactions.

Crystallographic data for **1*E*** ⊂**BuP5A** CCDC: 1962361: colorless, $C_{79}H_{116}Cl_2O_{10}$, *FW* 1296.61, triclinic, space group *P-1*, a = 12.214(2), b = 14.805(3), c = 21.747(4), α = 89.735(3), β = 89.579(3), γ = 75.559 (3), v = 3808.3(11) Å^3, Z = 2, Dc =1.131 g/cm^3, T = 173(2) K, μ = 0.140 mm^{-1}, 22,779 measured reflections, 13,315 independent reflections, 846 parameters, 9 restraint, F000 = 1408, R_1 = 0.1453, wR_2 = 0. 0.3355 (all data), R_1 = 0.1023, wR_2 = 0.2829 [$I > 2\sigma(I)$], max. residual density 1.084 e/Å^3, and goodness-of-fit (F^2) = 1.031.

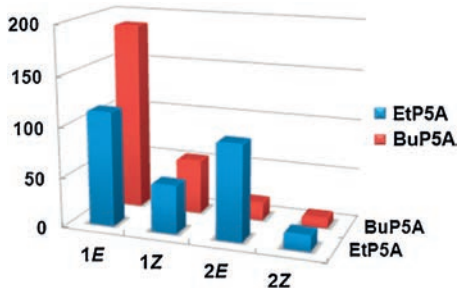

Fig. 2. Bar graph of the K_a values of the hosts **EtP5A** (blue bar) and **BuP5A** (red bar) and four olefinic guests **1*E***, **1*Z***, **2*E*** and **2*Z***.

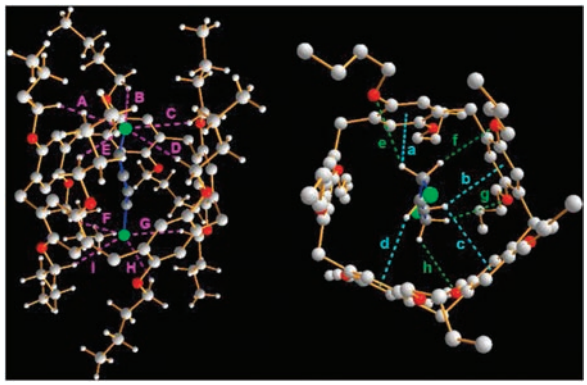

Fig. 3. Single-crystal structure of **1*E*⊂BuP5A**. Pink dashes (A-I) represent C–H$\cdots$Cl, bright blue dashes (a-d) represent C–H$\cdots\pi$ and green dashes (e-h) represent C–H$\cdots$O interactions between **1*E*** and **BuP5A**.

After studying these olefin guests, we also examined if carbon-carbon triple bond can be included in **P5As** cavity. An alkyne compound, 1, 4-dichloro-2-butyne (**3**) was chosen as the guest. The complexation-induced chemical shifts of **EtP5A** and **BuP5A** with **3** in the NMR spectrum were so small that the K_a values for **3** are very small and cannot be determined accurately. No C–H$\cdots\pi$ interactions can be formed between the middle sp bonding carbon atoms of **3** and benzene rings of **P5As**.

In summary, we report here that besides well reported α,ω-disubstituted alkane guests, olefin guests bearing double-double bonds can also be efficiently bound by the cavities of **P5As** to form inclusion complexes in organic solution. Host-guest C—H$\cdots\pi$ and C—H$\cdots$O hydrogen bonding interactions provide the main driving forces for the binding events. Particularly, the association constants of *trans*-isomers are higher than those of *cis*-ones for all the host-guest pairs, and the largest isomer selectivity of **2*E***/**2*Z*** by **EtP5A** is up to 6.3. This work expands the guest moieties for pillar[5]arenes from alkane derivatives to olefins. The interesting binding selectivity of *cis*-/*trans*-isomers could find potential applications in olefin separation.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.cclet.2020.02.037.

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