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Improved recognition of alkylammonium salts by ion pair recognition based on a novel heteroditopic pillar[5]arene receptor

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ABSTRACT

A novel pillar[5]arene-based heteroditopic receptor for ion pair recognition of alkylammonium salts with different alkyl chain lengths and different counterions was prepared, which showed the best association constant enhancement (71 times) to $n\text{-}BuNH_3^+Cl^-$ compared with monotopic receptor 1,4-dimethoxypillar[5]arene over corresponding Br^- and CF_3COO^- salts in chloroform.

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The research on cation receptors based on host–guest chemistry has attracted considerable interest in supramolecular chemistry due to their great importance in biological, analytical, catalytic, environmental applications, drug delivery, molecular machines, and so on.[1] When the cation recognition processes occur in apolar solvents, most recognition studies of cation guests were carried out with their low-coordinating counterions such as tetrafluoroborate and hexafluorophosphate where the counterion effect could be neglected, ascribed to their good solubility and weak ion-pairing binding affinity in apolar solvents. However, those low-coordinating counterions were hardly observed in our nature environment and real life system, and as a matter of fact, cation guests usually exist with Cl^-, PO_4^{3-}, HCO_3^- etc. as counterions,[2] where the coordinating power of the counterions could not be neglected due to their Coulomb interaction with the cation guests. As a consequence, it is quite important to study the recognition of cation guest with competitive coordinating counterions in apolar solvents for well understanding the role of counterions in recognition.[3]

In the cation recognition process in apolar solvents, the counterion can inhibit the cation recognition. However, on the other hand, the binding affinity can be improved by employing heteroditopic receptors, which consist of two different binding sites, thus capable of binding two ionic partners of an ion pair simultaneously.[4] In 1991, Reetz and co-workers[5] firstly reported a good example of heteroditopic receptors for potassium associated ion pairs. Due to the superior recognition ability and selectivity to ion pairs, heteroditopic receptors have been applied for helping salt dissolution, extraction, and transportation.[6] Nevertheless, to the best of our knowledge, heteroditopic receptors based on macrocycles for organic cation recognition especially with the improved binding affinity by ion pair recognition are rarely reported and most of them are based on crown ethers or calixarenes.[7] For instance, Huang and co-workers[8] reported dibenzo-24-crown-8 derivatives for the improved recognition of dibenzylammonium salts. So we are interested in developing a novel heteroditopic receptor based on new-type macrocycle host for organic cation recognition with improved binding affinity by ion pair recognition.

Recently, a new class of macrocycle host named pillar[n]arene[9] has attracted much attention of supramolecular chemists, and the emergence of monofunctionalized pillar[5]arene has expanded the application of pillar[n]arene in the areas of molecule recognition, self-assembly, supramolecular polymer construction, and so on.[9j,k,p] Unlike basket-shaped calix[n]arene, this novel host is para-bridged and displays perfectly symmetric architecture. Because of the column-shaped and π-electron rich cavity, pillar[n]arene can form inclusion complexes with organic cations like paraquats,[9a,d] alkylammoniums,[9g,n] and bis(imidazolium) derivatives.[9f] Among those organic cation guests, the recognition of alkylammoniums is rather significant and also full of challenge, because of their physiological activity[10] and applications in many fields such as herbicide detection.[11]

Therefore, in order to prove that the new designed pillar[5]arene based heteroditopic receptor could improve the recognition of the alkylammounium salts compared to monotopic one,

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the urea unit that is well known as a good anion receptor was introduced to the pillar[5]arene host to achieve a novel heteroditopic pillar[5]arene receptor **1**. With two different binding sites, a π-electron rich cavity and a urea group, it was desired that heteroditopic pillar[5]arene receptor **1** could bind both the ionic partners of alkylammonium salts (**G**) cooperatively, leading to dramatically improved recognition of the alkylammoniums (Fig. 1). On the other hand, this is also the first example of heteroditopic pillar[5]arene receptor designed for ion pair recognition of alkylammonium salts. Herein, we studied the complexation between heteroditopic receptor **1** and several alkylammonium salts with different counterions and different alkyl chain lengths, demonstrating that heteroditopic receptor **1** showed much more improved binding affinity to alkylammoniums by ion pair recognition than monotopic receptor 1,4-dimethoxypillar[5]arene (**DMP5**) which was synthesized for comparison.

Heteroditopic receptor **1** was prepared by the simple modification of monofunctionalized pillar[5]arene **2**[9k] (Scheme 1). With the attachment of urea, pillar[5]arene **1** was expected to bind both alkylammonium and its counterion, forming a neutral ternary system consequently. Initially, ^1H NMR was employed to investigate the complexation between heteroditopic pillar[5]arene **1** and *n*-butylammonium salts with Cl^-, Br^-, CF_3COO^-, and PF_6^- as different counterions, respectively. Figure 2 showed the ^1H NMR spectra of **1**, *n*-butylammonium trifluoroacetate (**G4c**), and an equimolar mixture of them, respectively, in $CDCl_3$. In the presence of **1**, all peaks of **G4c** shifted upfield obviously and it only exhibited one set of peaks, indicating fast-exchanging complex on the NMR time scale. By 2D COSY spectrum of the mixture (Fig. S11, ESI), the peaks for **G4c** were accurately assigned. Therefore, the chemical shift changes of protons H_α, H_β, H_γ, H_δ, and NH_3 of **G4c** were −2.12, −2.88, −2.35, −0.83, and −2.30 ppm, respectively. Meanwhile, more importantly, urea protons H_a and H_b of **1** shifted downfield significantly from 5.04, 7.19 ppm to 6.58, 8.07 ppm, respectively, indicating the hydrogen bonding between urea and the counterion, CF_3COO^-. The cooperative binding between **1** and **G4c** also gave rise to lower resonances of the peaks for H_1, H_2, H_3, H_4, H_5, and H_6 of **1**, while no obvious chemical shift changes were observed for H_7 and H_8 of **1**. These results provided strong and direct evidence that linear *n*-$BuNH_3^+$ fully threaded into the cavity of **1**, and multiple noncovalent interactions such as urea–anion hydrogen bonding, cation–π, C–H$\cdots\pi$, and N–H$\cdots\pi$ interactions[9n,12] may contribute to the stabilization of the complex of heteroditopic receptor **1** with **G4c**. Moreover, similar complexation phenomena by ion pair recognition between heteroditopic pillar[5]arene **1** and *n*-butylammonium salts with Cl^- and Br^- (**G4a** and **G4b**) as counterions in $CDCl_3$ could also be observed from the ^1H NMR spectra of their mixtures, respectively (Figs. S7–S8, ESI). However, in these two cases, some peaks for methylene protons and urea protons could not be clearly observed because of the broadening effects[9e,9t] that occurred due to complexation dynamics where those protons were located in the cavity of pillar[5]arene and shielded by π-electron rich cyclic pillar[5]arene. What is more, due to the poor solubility of *n*-$BuNH_3^+PF_6^-$ in chloroform, the investigation of the complexation between **1** and *n*-$BuNH_3^+PF_6^-$ by ^1H NMR was limited.

Because of the relatively less remarkable broadening effect in the ^1H NMR spectra of heteroditopic receptor **1** mixed with **G4c**, the complexation between **1** and **G4c** was selected for further study by 2D NOESY NMR. From the spectrum (Fig. S12, ESI),

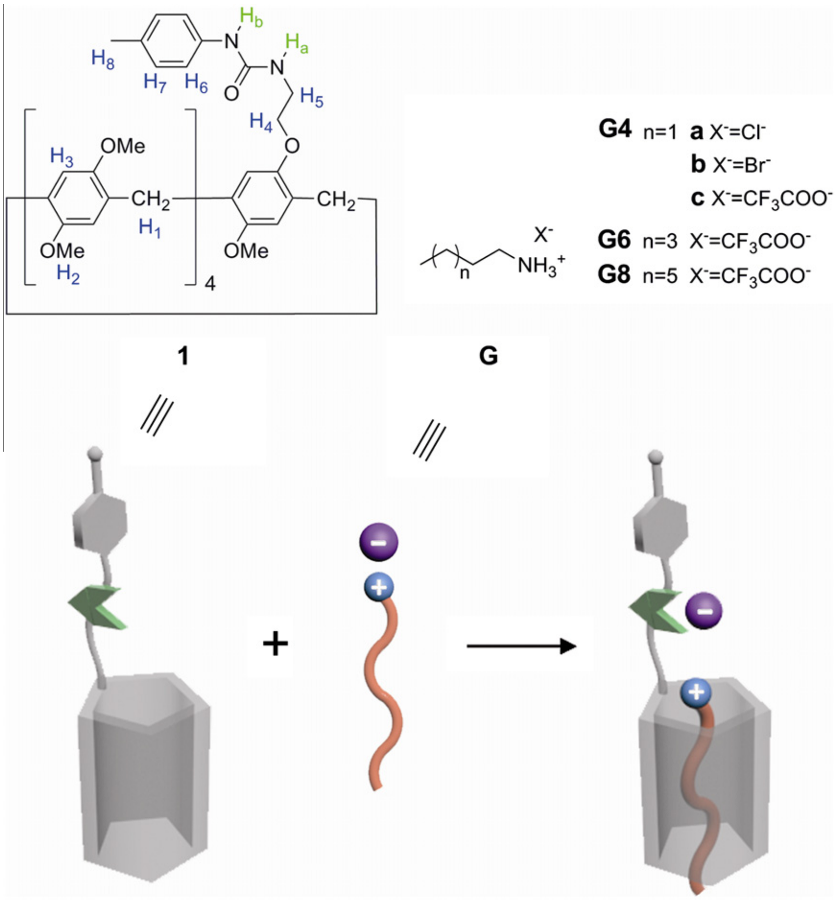

Figure 1. The cartoon representation of the complexation between heteroditopic receptor **1** and **G**.

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