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Selective and Effective Binding of Pillar[5,6]arenes toward Secondary Ammonium Salts with a Weakly Coordinating Counteranion

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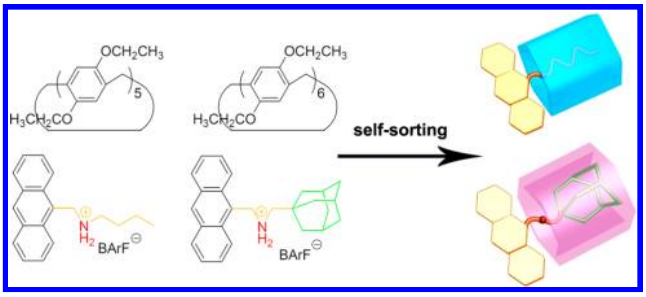
ABSTRACT



The selective and effective binding of secondary ammoniums with a weakly coordinating tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (BArF) counteranion by per-ethylated pillar[5,6]arenes is reported. The construction of a first pillararene-based self-sorting system consisting of two wheels and two axles is also described.

Rotaxanes, and their pseudorotaxane precursors, have been attracting considerable attention not only for their topological importance but also due to their inventive applications.[1] They have usually been constructed by using supramolecular macrocyclic hosts as the ‘wheels’ and linear guest molecules as the ‘axles’. Pillararenes are a new class of cyclophanes that exhibit intriguing and peculiar host–guest properties. They are made up of hydroquinone units linked by methylene bridges and possess the symmetrical pillar architecture.[2–5] Pillararenes’ structural characteristics make the hosts suitable to develop pseudorotaxanes with linear guest molecules. Our previous papers have reported the formation of a series of threaded complexes between pillar[5]arenes (P5As) with dicationic 1,4-bis(imidazolium)butanes, bis(pyridinium) derivatives and

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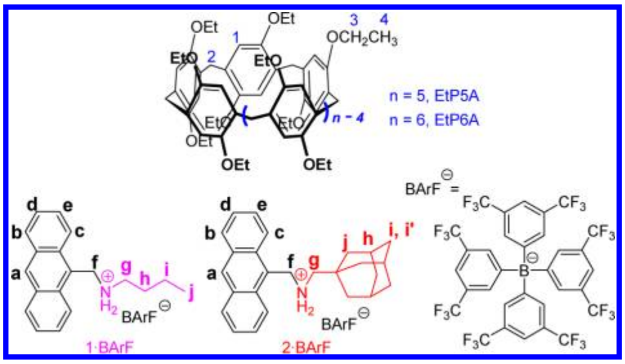
paraquat derivatives as well as neutral bis(imidazole) derivatives, alkanedinitriles, and 1,4-dihalobutanes.[4]

It is well-known that secondary ammonium salts have been widely used in fabricating interpenetrated geometries as linear axle components. Crown ethers,[1h,6] cucurbiturils,[1g,7] calixarenes,[8] and other cyclic macrocycles[9] have been successfully threaded onto suitable secondary ammonium salts to fabricate pseudorotaxane topologies. Especially, the threading of secondary ammonium derivatives through the annulus of large crown ethers was the genesis of the interpenetrated structures such as rotaxanes and catenanes. Very recently, when we prepared this paper, Huang et. al[3f] reported the complexation between per-methylated P5A and *n*-octylethyl ammonium hexafluorophosphate ($\mathrm{PF_6}^-$), giving a moderate association constant (K_a) value of 1.09 (±0.31) × 10^3 M^{-1}. To date, the binding abilities of secondary ammonium salts by pillar[6]arenes (P6As) have not been investigated as yet.

Herein, we report the highly effective self-assembly of [2]pseudorotaxanes between P5A/P6A with two secondary ammonium cations with the tetrakis[3,5-bis(trifluoromethyl)-phenyl]borate (BArF^-) counteranion (**1**•BArF and **2**•BArF) induced by very loose ammonium ion pairs, and the construction of a pillararene-based self-sorting system consisting of four components.

Scheme 1. Structure and Proton Designations of EtP5A/EtP6A Hosts and Secondary Ammonium Guests



Previous works have well demonstrated the size–fit relationship between the alkyl chain and P5A's cavity.[4] Thus the secondary ammonium $\mathbf{1}^+$ guest containing an *n*-butyl unit was expected to strongly bind with P5A. Considering that the diameter of the internal cavity of P6A (ca. 6.7 Å)[2b] is similar to those for *β*-cyclodextrin (*β*-CD, ca. 6.0 Å)[10] and cucurbit[7]uril (CB7, with a portal diameter of ca. 5.4 Å and an internal diameter of ca. 7.3 Å),[1g,10,11] we want to explore whether adamantane derivatives, which fit the cavity size of *β*-CD and CB7, would be suitable guests for P6As. Therefore, we designed ammonium $\mathbf{2}^+$ which had an adamantane group. Both guests contain a 9-anthracene unit in the other end. The 9-anthracene unit is too bulky to be bound by P5A and P6A, which will simplify our discussion. Potentially, $\mathbf{1}^+$ and $\mathbf{2}^+$ would be excellent matches, in size and shape, with P5A and P6A, respectively.

We first studied the complexation of the two secondary ammoniums with the $\mathrm{PF_6}^-$ counteranion by per-ethylated P5A/P6A (EtP5A/EtP6A). However, no obvious interaction was observed between **2**•$\mathrm{PF_6}$ and EtP6A (Figure 1b), and the binding between **1**•$\mathrm{PF_6}$ and EtP5A was very weak ($K_a = 61 \pm 8\ \mathrm{M}^{-1}$).[12] It is well documented that ion-pairing effects hamper the complexation of charged species by neutral receptors,[13] and the type of counteranions often affects the association strength during the course of host–guest complexation dramatically.[4b,8,14] We therefore explored whether and to what extent the use of a very weakly coordinating counteranion, BArF^- (Scheme 1), would improve the host–guest complexation.

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(12) The association constant of **1**•$\mathrm{PF_6}\subset$EtP5A was much less than that for *n*-octylethyl ammonium hexafluorophosphate and per-methylated P5A [$K_a = (1.09 \pm 0.31) \times 10^3\ \mathrm{M}^{-1}$, ref 3f], which may be caused by the increase of the guest size.

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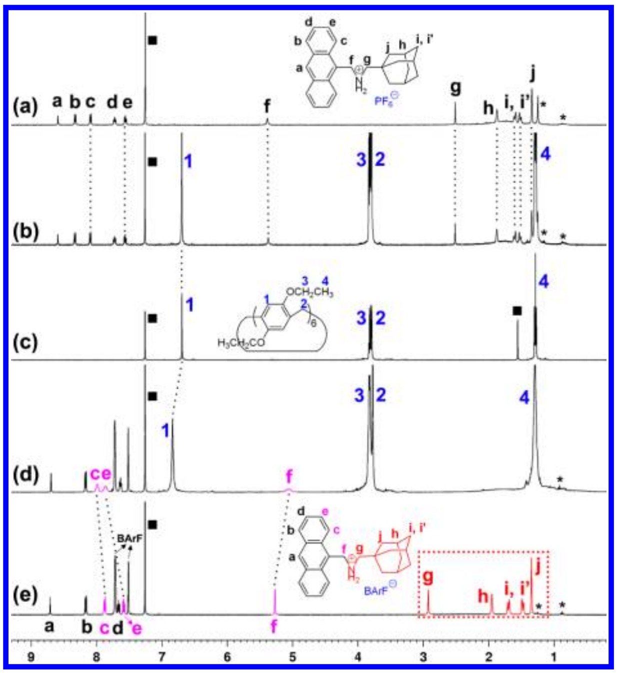

Figure 1. ^{1}H NMR spectra (500 MHz, 298 K) of (a) **2**•PF$_6$; (b) **2**•PF$_6$ + EtP6A; (c) EtP6A; (d) **2**•BArF + EtP6A, and (e) **2**•BArF in CDCl$_3$ at 4.0−4.5 mM. "■" indicates CHCl$_3$/H$_2$O. "*" indicates solvent impurities.

Figure 1e and 1d show the ^{1}H NMR spectra of **2**•BArF in CDCl$_3$ recorded in the absence and presence of ~1 equiv of EtP6A. Upon addition of the host, the NMR response of **2**•BArF was fast. The peaks for the methylene protons and adamantane protons of **2**•BArF exhibited substantial upfield shifts and broadening effects compared to the free axle. The $\Delta\delta$ value for methylene H$_f$ was −0.21 ppm. And the broadening effects were so remarkable that the proton signals of methylene H$_g$ and adamantane group (H$_{h,\ i,\ i',\ \text{and}\ j}$) could not be observed in the ^{1}H NMR spectrum. Variable-temperature and -concentration ^{1}H NMR experiments showed that the complexation induced broadening effects of guest's adamantane signals in higher temperatures/concentrations were less remarkable than those in lower temperatures/concentrations (Figures S26 and S27). For example, at 308 K, the adamantane signals of **2**•BArF could be observed in the NMR spectrum of a 1:1 host−guest mixture at 13.0 mM, with obvious upfield shifts compared to the free axle as a consequence of inclusion-induced shielding effects (Figure S27d).[15] At the same time, the signals corresponding to the "outer" protons (H$_a$, H$_b$ and H$_d$) of the anthracene group remain almost unaffected with respect to the free axle. Yet, the "inner" H$_c$ and H$_e$ experience broadening and small downfield shifts, which is characteristic of the protons being located at just outside the host's cavity portal.[16]

From the above results, we can unambiguously deduce that the guest's adamantane unit is included in the cavity of the host, which thus leads to efficient shielding of the guest protons (H$_{g-j}$).[15] An ESI mass experiment also confirms the host−guest binding. In the ESI spectrum of an equimolar mixture of **2**•BArF and EtP6A (Figure S20), only two intense peaks were observed, one for the 1:1 complex [**2**⊂EtP6A]$^+$ (m/z 1424.7) and one for uncomplexed guest **2**$^+$ (m/z 356.2). The 1:1 binding stoichiometry was also demonstrated by a Job plot based on proton NMR data (Figure S21).

Table 1. Association Constant (K_a/M^{-1}) for Complexation of Neutral Guests with P5A Dimers in CDCl$_3$ at 298 K

	1•PF$_6$	**1**•BArF	**2**•PF$_6$	**2**•BArF
EtP5A	61 ± 8	3.4 (±0.4) × 10$^{4\,b}$	^{a}	^{a}
EtP6A	^{a}	38 ± 4	^{a}	3.4 (±0.2) × 10^3

^{a} NMR changes are too small to allow the calculation of K_a. ^{b} 0.05% (v%) DMSO-d_6 in CDCl$_3$.

The association constant of **2**•BArF⊂EtP6A was measured by ^{1}H NMR titration methods to be 3.4 (±0.2) × 10^3 M^{-1} in CDCl$_3$ (Table 1 and Figure S23). To the best of our knowledge, the resulting host−guest complex represents the most efficient recognition motif based on P6As.[17] Thermodynamic parameters (Figures S28 and S29) indicate that the complexation between EtP6A and **2**•BArF is synergistically contributed to by both enthalpy and entropy changes ($\Delta H° = -11.1$ kJ mol^{-1}, $T\Delta S° = 9.0$ kJ mol^{-1}). The complexation of **2**•BArF by the smaller EtP5A host was then examined. As expected, no signal changes were observed for the guest upon addition of EtP5A. Since the adamantane unit was too large in comparison with P5A's cavity, the **2**•BArF⊂EtP5A inclusion complex did not form.

Figure S15 shows the sequential addition of 0.3, 0.7, and 1.2 equiv of EtP5A to a solution of **1**•BArF in CDCl$_3$. Slow exchange on the NMR time scale was observed for this complex. From integrations of all peaks, the stoichiometry of the complex was determined to be 1:1, which was also been proved by ESI mass experiment (Figure S19). The resonances of the new species are consistent with the formation of an interpenetrated geometry. The peaks for n-butyl protons of **1**•BArF exhibit substantial upfield shifts and broadening effects compared to the free axle ($\Delta\delta = -1.34$ to -3.10 ppm for H$_{g-j}$) as a consequence of inclusion-induced shielding effects,[16] indicating that the wheel is fully threaded by the axle's butyl unit. The forces stabilizing the complex are very significant, since the free guest is never observed in the presence of 1 equiv of the EtP5A wheel or more, suggesting very strong binding affinities in CDCl$_3$. The association constant for this complex in CDCl$_3$ can not be determined using the

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(17) Although the binding behavior of P5As has been well investigated, the host−guest properties of P6As have been rarely explored. Only two types of guests, tetraalkyl ammonium hexafluorophosphate and paraquat bis(hexafluorophosphate), were reported to be suitable guests for P6A. See ref 5b−5d.

^{1}H NMR single point method.[4f,18] The addition of a very small amount of polar DMSO-d_6 (0.05%, v%) to a $CDCl_3$ solution of **1**•BArF and EtP5A resulted in a rapid NMR response. The K_a value for **1**•BArF⊂EtP5A is determined to be 3.4 (±0.4) × 10^4 M^{-1} (Figures S24 and S25) in the $CDCl_3$/DMSO-d_6 mixed solvent by ^{1}H NMR titration methods, which is 560 times larger than that for **1**•PF_6⊂EtP5A (61 ± 8 M^{-1}) in pure $CDCl_3$. The drastic counteranion effects unambiguously indicate the significant superiority of $BArF^-$ to PF_6^-, due to the inducing effect of the weakly coordinating $BArF^-$ that gives free "naked" secondary ammoniums.

The larger EtP6A host can also bind with **1**•BArF, showing a very small association constant (38 ± 4 M^{-1}), which is reasonable since the *n*-butyl group of $\mathbf{1}^+$ is very small in comparison with P6A's cavity.

Based on the results above, the construction of a four-component self-sorting system was then considered. Self-sorting phenomena are familiar in biological systems, such as DNA replication, translation, and transcription. The present self-sorting system consisting of two pillararenes (EtP5A and EtP6A) and two ammonium ions (**1**•BArF and **2**•BArF) should have high fidelity since **2**•BArF is not able to be bound by EtP5A and the K_a value of **1**•BArF with EtP5A is much larger (890 times) than that for EtP6A. Thermodynamic properties thus control the preference of EtP5A for **1**•BArF and EtP6A for **2**•BArF. As can be seen from Figure S18, the pseudorotaxanes **1**•BArF⊂EtP5A and **2**•BArF⊂EtP6A are significantly dominant in the equimolar mixture of **1**•BArF, **2**•BArF, EtP5A, and EtP6A, since the response signals of the four-component mixture (Figure S18b) are almost the superposition of those for **1**•BArF/EtP5A (Figure S18a) and **2**•BArF/EtP6A (Figure S18c).

An ESI mass spectrum of the equimolar mixture of **1**•BArF, **2**•BArF, EtP5A, and EtP6A in CH_3OH also confirmed perfect self-sorting. As can be seen from Figure 2, only two intense peaks for the host–guest complexes are observed, one for $[\mathbf{1}\subset\mathrm{EtP5A}]^+$ (*m*/*z* 1154.7) and one for $[\mathbf{2}\subset\mathrm{EtP6A}]^+$ (*m*/*z* 1424.7). Meanwhile, the signal for $[\mathbf{1}\subset\mathrm{EtP6A}]^+$ is very weak at *m*/*z* 1332.6, while no complex ion of $[\mathbf{2}\subset\mathrm{EtP5A}]^+$ is detected at all (*m*/*z* 1246.5). To the best of our knowledge, this is the first pillararene-based self-sorting system.

In conclusion, the highly effective self-assembly of pillar[5,6]arene/secondary ammonium salt [2]pseudorotaxanes can be fabricated through the inducing effect of the weakly coordinating $BArF^-$ that gives free "naked" secondary ammonium cations. Guest **2**•BArF having an adamantane unit fits the cavity of EtP6A very well but cannot be bound by EtP5A. The binding affinity of **1**•BArF, possessing an *n*-butyl group, by EtP5A is much stronger than that for EtP6A. Based on the strong binding and high selectivity, a high-fidelity self-sorting system consisting of two pillararenes and two secondary ammonium salts is constructed. We believe that these excellent motifs will be applicable in the fabrication of large and complex supramolecular systems, and the self-sorting behavior observed for the two pillar[*n*]arenes could be used as the basis for separating pillar[5]arene and pillar[6]arene.

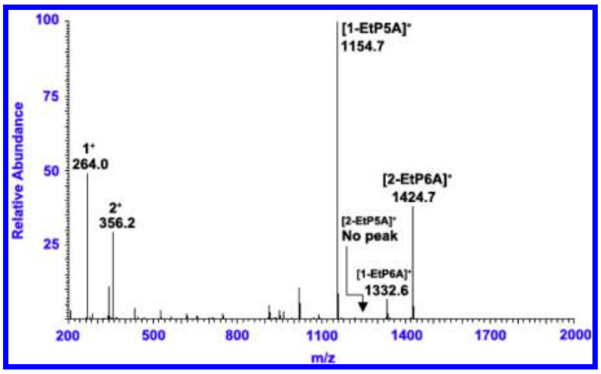

Figure 2. ESI mass spectrum of an equimolar mixture of **1**•BArF, **2**•BArF, EtP5A, and EtP6A in methanol solution. The concentration of host/guest is about 0.5 μmol/L.

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Supporting Information Available. Additional ^{1}H NMR spectra, Job plots, ESI mass spectra, and determination of the association constants. This material is available free of charge via the Internet at http://pubs.acs.org.

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The authors declare no competing financial interest.