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Efficient Preparation of Separable Pseudo[*n*]rotaxanes by Selective Threading of Oligoalkylammonium Salts with Cucurbit[7]uril

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Abstract: We describe the efficient preparation of well-defined, homogeneous pseudo[*n*]rotaxanes ($n=2, 3, 4, 5$) by the selective threading of oligoalkylammonium salts with cucurbit[7]uril (CB[7]) and the subsequent simple separation of the pure pseudo[*n*]rotaxanes from the complicated system. A series of well-defined oligoalkylammonium salts were prepared by stepwise synthesis and their molecular recognition and self-assembly with a solution of CB[7] in CF_3CO_2D/D_2O (1:1 v/v) were investigated. As a result of the high affinity of CB[7] to the *p*-xylene diammonium units ($\text{-}NH_2{}^+CH_2C_6H_4CH_2NH_2{}^+\text{-}$) in the oligoalkylammonium salts, the CB[7] rings threaded onto these cationic threads to form pseudorotaxane structures. Interestingly, due to the repulsive dipole–dipole electrostatic interactions between the CB[7] units and steric hindrance, the threading process exhibited a high selectivity and a unique self-assembling mode was discovered in which two CB[7] units cannot bind the same ammonium site. The as-formed well-defined pseudo[*n*]rotaxanes can be easily separated as pure compounds from the mixture by simple counterion exchange with NH_4PF_6 and the pure pseudo[*n*]rotaxanes are stable and partially soluble in normal organic solvents. Such facile preparation and separation are mainly ascribed to the high binding constant between CB[7] and the oligoalkylammonium salts and the unique solubility of CB[7] in protonic acid. As most pseudorotaxanes reported in the literature exist as a dynamic mixture and their separation is usually difficult, our research represents one good example in which pure pseudo[*n*]rotaxanes ($n=2, 3, 4, 5$) can be obtained by a simple “threading-followed-by-precipitation” method.

Keywords: counterion exchange · cucurbiturils · pseudorotaxanes · self-assembly · supramolecular chemistry

Introduction

Interlocked molecules, such as rotaxanes, catenanes, and molecular knots,[1] comprise a major research field of supramolecular chemistry and have been worthy of steadily increasing attention in recent decades[2] because they allow one to construct functional molecular devices of high sophistication.[1f,g,2h,3] For example, rotaxanes have been used as molecular switches within nanoelectronics,[4] artificial muscles,[5] macroscopic liquid transport,[6] and mesoporous-silica-mounted nanovalves.[7] Polyrotaxanes, in which cyclic rings and a linear dumbbell-like species carrying recognition sites are mechanically interlocked with each other, have been prepared by using a template-directed clipping reaction,[8] threading-followed-by-stoppering,[1e,9] slipping reaction[10] and other methods.[1h,11] Unique properties were found in polyrotaxanes compared with those of conventional covalent polymers.[12] Pseudorotaxane is a similar structure to rotaxane, in that bulk stoppers do not exist and the interlocked structures are solely stabilized by molecular recognition between macrocycles and the recognition sites on the thread. Usually pseudorotaxanes are easily formed by simply threading the thread with suitable macrocycles, and in most cases, a large excess of macrocycles has to be used to reach a maximum degree of threading. This is mainly because the binding between the macrocycles and the thread is not strong enough and a dynamic threading–dethreading process takes place; this leads to a complicated mixture of different pseudo[*n*]rotaxanes coexisting with excess macrocycles in the solution. All these make the separation of pseudorotaxanes more challenging than the purification of rotaxanes.[13] To date, although the synthesis of higher order rotaxanes has been quite successful,[8] the efficient preparation and separation of pseudorotaxanes still lags behind. A

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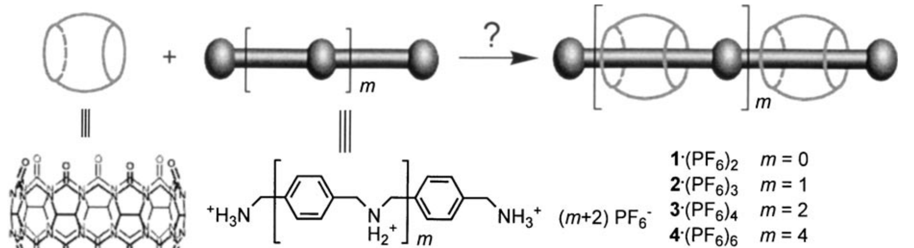
general consideration for the synthesis and separation of pure pseudorotaxanes is that the binding constant between the recognition sites and the macrocycles must be high enough so that the as-formed pseudorotaxane does not undergo a dethreading process even with the absence of excess macrocycles.

Cucurbit[*n*]urils (CB[*n*]s, $n=5,6,7,8,10$) as a kind of important supramolecular host have been well known to form host–guest complexes with various guests carrying ammonium sites due to their high affinity and highly selective binding.[14–18] Furthermore, cucurbiturils have also been used in the preparation of polyrotaxanes and pseudopolyrotaxanes[19] by diversified approaches as reported by Kim and co-workers,[20] Steinke and Tuncel,[21] Liu,[22] and others.[23] One general method is to utilize the unique click chemistry of alkyne and azide in the inner cavity of cucurbituril. A (pseudo)rotaxane is then formed after the reaction. The second general procedure is to thread polymeric alkylammoniums or polyviologens with CBs. Statistic pseudopolyrotaxanes are then formed. In the latter case, excess CBs have to be used to reach a high degree of threading and thus how to purify and separate these CB-based pseudopolyrotaxanes is a challenging problem. There are a few reports on the purification and separation of crown ether and cyclodextrin-based rotaxanes by methods such as gel permeation chromatography (GPC)[24] or high-performance liquid chromatography (HPLC),[1h,25] however, these techniques are only suitable for separation of a small quantity of compounds and are only applicable to specific systems. For CB-based polyrotaxanes and pseudopolyrotaxanes, there are so far no good methods to obtain pure compounds. In addition, although the self-assembling mode of the crown ether with polyammonium salts is well known,[8d,13] the detailed binding mode of CBs with the cationic polymer thread is still unclear.[17b,26] To better understand the threading process and the self-assembling mode, we are interested in investigating the threading of well-defined oligoalkylammonium salts with CBs. The strong binding between the CBs and the oligoalkylammonium salts also makes it possible to prepare well-defined pseudo[*n*]rotaxanes in pure form.

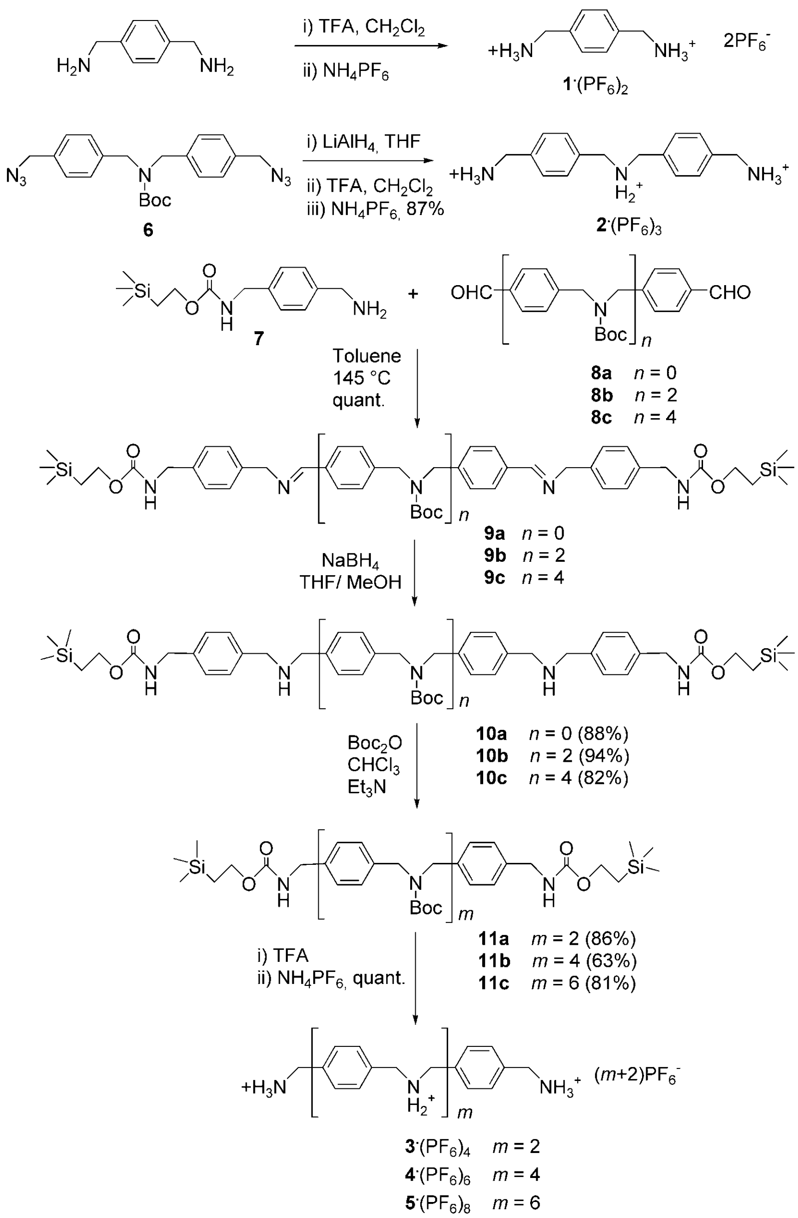
In this experiment, we synthesized a series of well-defined oligoalkylammonium salts **1**$\cdot(PF_6)_n$–**5**$\cdot(PF_6)_n$ in which the ammonium ions are linked by *p*-xylene units (Scheme 1). Such oligomers were chosen because it is known that the *p*-xylene diammonium salts can form a stable 1:1 complex with CB[6] or CB[7] under suitable conditions and they can be prepared by using reasonable synthetic methods. As represented in Scheme 1, an interesting question is whether every *p*-xylene unit can be encircled by one CB[7] ring during the threading of the oligoalkylammonium salts with excess CBs. Our detailed studies disclosed that the threading process showed high selectivity and only a limited number of CB units can be located at very specific sites on the cationic thread. At the same time, by taking advantage of the high binding constant between the CBs and the *p*-xylene diammonium units[14–18] and the unique solubility of CBs in protonic acid,[19] we found that these well-defined pseudo[*n*]rotaxanes could also be separated as pure and stable compounds from the complex systems by simple counterion exchange.

Results and Discussion

Synthesis of oligoalkylammonium salts: The stepwise synthesis of the linear oligoalkylammonium salts is shown in Scheme 2. The *p*-xylene diammonium salt **1**$\cdot(PF_6)_2$ was easily obtained by protonation of commercially available *p*-xylene diamine with trifluoroacetic acid (TFA) and followed by counterion exchange with aqueous ammonium hexafluorophosphate (NH_4PF_6). The triammonium salt **2**$\cdot(PF_6)_3$, which contains two *p*-xylene units, was synthesized from the known bisazide compound **6**.[27] The azide groups in compound **6** were reduced by lithium aluminum hydride to give amines. Subsequent deprotection of the *tert*-butoxycarbonyl (Boc) group with excess TFA and counterion exchange with NH_4PF_6 provided the desired oligoalkylammonium salts **2**$\cdot(PF_6)_3$. The syntheses of higher order oligomers **3**$\cdot(PF_6)_n$–**5**$\cdot(PF_6)_n$ were based on a similar method. We first synthesized the Boc-protected oligoalkylamines **8a–c** that contain a well-defined number of -Ph−CH$_2$−N(Boc)−CH$_2$- repeating units and two terminal aldehyde groups according to the reported procedures.[8d] Condensation reaction of compounds **8a–c** with the 2-(trimethylsilyl)ethylcarbamate (Teoc) monoprotected xylene diamine **7**[8d] in toluene gave the corresponding imines **9a–c** in nearly quantitative yields. Reduction of the imine bonds in compounds **9a–c** with $NaBH_4$ afforded the free amines **10a–c** in high yields. Compounds **10a–c** had high polarity and their purification by column chromatography was difficult. To obtain high-purity oligomers, the free amine groups in compounds **10a–c** were protected by Boc by reaction with Boc$_2$O and the obtained compounds **11a–c** could be easily purified by routine column chromatography. The pure oligomers **11a–c** were then treated with excess TFA to



Scheme 1. The schematic representation of pseudo[*n*]rotaxane formation by threading of oligoalkylammonium salts with CB[7].



Scheme 2. Synthetic route of the oligoalkylammonium salts.

remove both the Boc and Teoc groups, and at the same time, all the amine groups were protonated. For the higher order oligomers such as **11b** and **11c**, it was necessary to use neat TFA to remove all protective groups. After counterion exchange by adding saturated aqueous NH_4PF_6 to the solution, pure oligoalkylammonium salts **3**·$(PF_6)_4$, **4**·$(PF_6)_6$, and **5**·$(PF_6)_8$ containing a well-defined number of -$CH_2NH_3^+$ and -$CH_2NH_2^+CH_2$- units were obtained in nearly quantitative yields. All of the intermediate and final compounds were well characterized by standard spectroscopic techniques such as NMR spectroscopy and mass spectrometry (see the Supporting Information).

Threading of oligoalkylammonium salts with CBs: The pure oligoalkylammonium salts **1**·$(PF_6)_n$–**5**·$(PF_6)_n$ were then submitted for threading studies with different amount of CB[*n*]s. It was found that these oligoalkylammonium salts had poor solubility in frequently used solvent systems such as aqueous hydrochloride acid or formic acid, even when the counterions are CF_3COO^- (i.e., in the form before counterion exchange). However, they were soluble in mixed solvents of TFA and water (1:1 v/v). Therefore, all the threading processes were followed by using ^{1}H NMR spectroscopy on samples in CF_3COOD/D_2O (1:1) by varying the ratio of the CB[*n*]s to the ammonium salts. We found that upon addition of CB[6] into the solution of **1**·$(PF_6)_2$, there was no significant change in the ^{1}H NMR spectra of either **1**·$(PF_6)_2$ or CB[6], which suggests that there was no host–guest binding in such a solvent system. However, when we used the larger CB[7] instead of CB[6], obvious changes in the ^{1}H NMR spectra were observed. Upon addition of one equivalent of CB[7], the resonances of the aromatic protons and methylene protons of $\mathbf{1}^{2+}$ were shifted upfield by $\delta = 0.79$ and 0.22 ppm, respectively, which suggests that a 1:1 CB[7]–$\mathbf{1}^{2+}$ complex (i.e., a pseudo[2]rotaxane) was formed (Figure S1 in the Supporting Information). The upfield shift of the resonance for the guest molecules was attributed to the shielding effect of the CB[7] host molecule, and at the same time, a slight change to the resonance of the CB[7] was also observed, further supporting such a binding process. The absence of an exchange equilibrium of complexed and uncomplexed species in such a solvent system also indicated a high binding constant ($>10^4\,\mathrm{M}^{-1}$), which, however, cannot be directly determined by NMR spectroscopic techniques.[14b,16c,d,17b,26,28] Interestingly, such a 1:1 complex can be easily separated from the mixture solution by the addition of excess saturated NH_4PF_6 solution, and after counterion exchange, white precipitate was collected, washed with water, and dried in air to give the pure pseudo[2]rotaxane CB[7]–**1**·$(PF_6)_2$. This simple and convenient method was performed to obtain the pure pseudo[2]rotaxane as a result of the following: 1) the pseudorotaxane with PF_6^- has poor solubility in the water phase and thus precipitates from the solution; 2) the high binding constant is advantageous in preventing the pseudorotaxane from dethreading during the counterion exchange process and also to stabilize the interlocked structure in suitable organic solvents, even with the absence of excess CB[7]; and 3) any excess CB[7] will remain in the solution due to its high affinity to protonic acid. Such a simple method was also found to be very efficient in preparing pure higher order pseudo[*n*]-rotaxanes as will be discussed later. The pseudo[2]rotaxane was soluble in normal organic solvents such as acetonitrile and allowed us to characterize it by using standard spectroscopic techniques. The high-resolution electrospray ionization mass spectrum (HR-ESIMS) of CB[7]–**1**$\cdot(PF_6)_2$ in acetonitrile clearly showed three peaks that can be assigned to the $[M-2PF_6^-]^{2+}$, $[M-HPF_6-PF_6^-]^+$, and $[M+H^+-PF_6^-]^{2+}$ species, in which *M* is the 1:1 complex (Figure 1A). The lack of peaks for uncomplexed CB[7] and ammonium salts indicates that a tightly bonded pseudo[2]rotaxane complex was formed instead of the existence of a fast exchange equilibrium. In addition, the ^{1}H NMR spectrum was recorded for the complex in CD_3CN and it clearly showed a pure 1:1 complex with the proposed pseudo[2]rotaxane structure (Figure 2A). The simple NMR spectrum again suggested a tight binding between compound **1**$\cdot(PF_6)_2$ and CB[7] in acetonitrile. However, we also observed that in DMSO an obvious slow exchange equilibrium between the complexed and un-

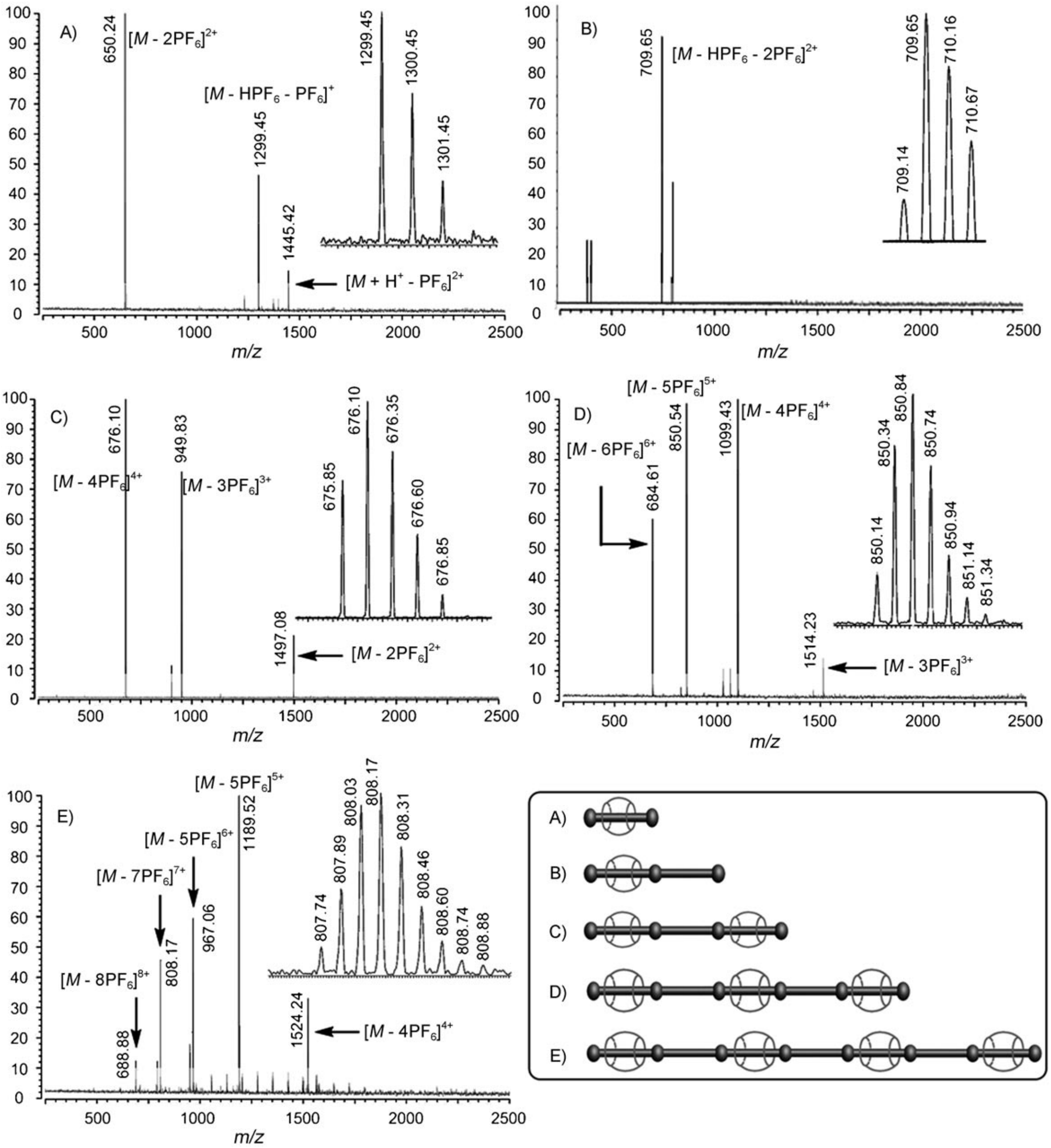


Figure 1. The high-resolution ESI mass spectra of pseudo[*n*]rotaxanes: A) CB[7]–**1**$\cdot(PF_6)_2$, B) CB[7]–**2**$\cdot(PF_6)_3$, C) CB[7]–**3**$\cdot(PF_6)_4$, D) CB[7]–**4**$\cdot(PF_6)_6$, and E) CB[7]–**5**$\cdot(PF_6)_8$.

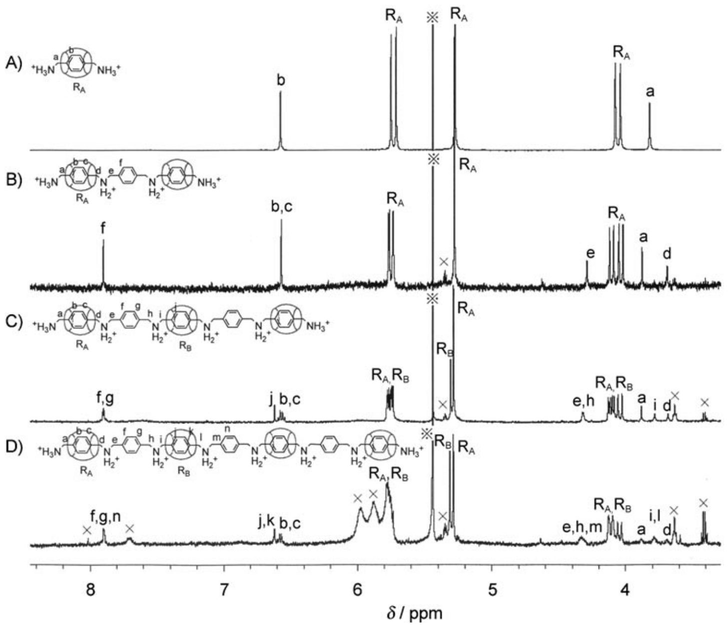


Figure 2. ^{1}H NMR spectra (500 MHz, CD_3CN, 298 K) of pseudo[*n*]rotaxanes: A) CB[7]–**1**·$(PF_6)_2$, B) CB[7]–**3**·$(PF_6)_4$, C) CB[7]–**4**·$(PF_6)_6$, and D) CB[7]–**5**·$(PF_6)_8$ (resonances labeled by "×" indicate impurities in the solvents).

complexed species existed, suggesting that the binding was also solvent-dependent.

The threading of **2**·$(PF_6)_3$ with CB[7] was then conducted under similar conditions. The ^{1}H NMR spectrum of compound **2**·$(PF_6)_3$ in CF_3COOD/D_2O (1:1) showed simple resonances at $\delta = 7.50$ and 4.24 ppm (Figure 3B), which can be assigned to the aromatic and methylene protons, respectively. Upon addition of one equivalent of CB[7], the resonances of $\mathbf{2}^{3+}$ were split into two sets of resonance peaks, with one set showing an upfield shift and the second set displaying a downfield shift (Figure 3C). The upfield shift of the resonance peaks for aromatic protons (H_b, H_c) and methylene protons (H_a, H_d) suggested that one of the xylene units was encircled with CB[7], and the resonance assigned to the uncomplexed xylene unit showed a downfield shift because of the effect of adjacent carbonyl oxygen atoms on CB[7] (see detailed assignment in Figure 3C).[16,28,29] Interestingly, addition of more CB[7] (2 equiv) did not change the spectrum, and the approximate 1:1 integration ratio of the resonances for the complexed and uncomplexed phenyl rings indicated that only one CB[7] ring threaded onto the **2**·$(PF_6)_3$ to form a pseudo[2]rotaxane. Addition of an excess of aqueous NH_4PF_6 to the solution resulted in precipitation of the as-formed pseudo[2]rotaxane with PF_6^- as counterions, whereas the excess CB[7] still remained in the acidic solution. Again, we found that the obtained pseudo[2]rotaxane was a stable complex in acetonitrile, even with the absence of the excess CB[7]. The HR-ESIMS recorded in acetonitrile disclosed a peak at *m*/*z* 709.65 for $[M-HPF_6-2PF_6^-]^{2+}$ with well-resolved isotope distribution. This further confirmed the formation of a pseudo[2]rotaxane (Figure 1B). Unfortunately, the very poor solubility of the pseudo[2]rotaxane in acetonitrile limited detailed NMR spectroscopic analysis. These results suggested that the placement of two CB[7] molecules at two neighboring *p*-xylene units was not favorable. Such a unique self-assembling mode also agreed well with Steinke's mode[21b,23f] and can be attributed to significant repulsive dipole–dipole electrostatic interactions of the polar carbonyl-rimmed portals between two CB[7] molecules when they bind with the same ammonium site. In addition,

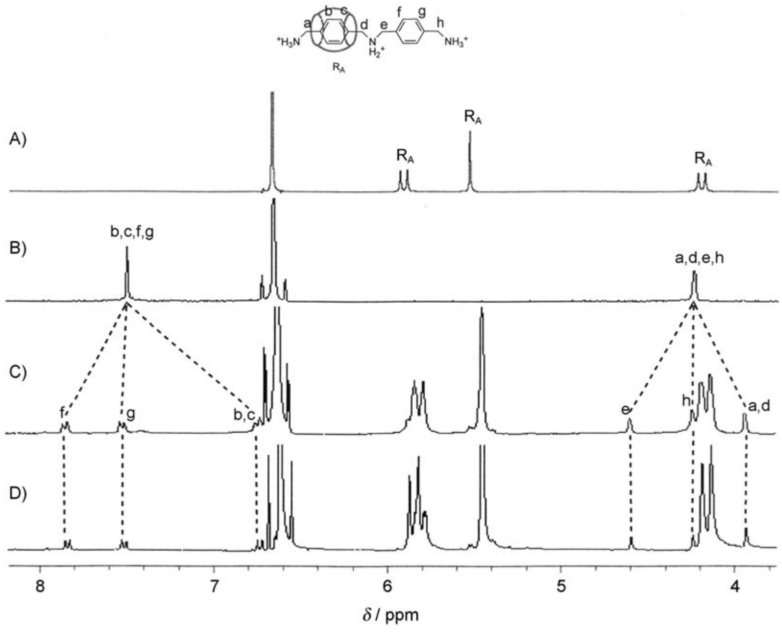


Figure 3. ^{1}H NMR spectra (300 MHz, $CF_3COOD/D_2O = 1:1$, 298 K) of A) CB[7], B) **2**·$(PF_6)_3$, C) CB[7]/**2**·$(PF_6)_3 = 1:1$, and D) CB[7]/**2**·$(PF_6)_3 = 2:1$.

the steric interactions will also prevent two CB[7] rings from threading onto two adjacent *p*-xylene units. If this self-assembling mode is also applicable to the higher order oligoalkylammonium salts, one can expect that at the maximum degree of threading, pseudo[3]rotaxane, pseudo[4]rotaxane, and pseudo[5]rotaxane will be formed for **3**$\cdot$(PF$_6$)$_4$, **4**$\cdot$(PF$_6$)$_6$, and **5**$\cdot$(PF$_6$)$_8$, respectively.

To further confirm this assumption and to understand the exact self-assembling mode, threading of **3**$\cdot$(PF$_6$)$_4$, **4**$\cdot$(PF$_6$)$_6$, and **5**$\cdot$(PF$_6$)$_8$ with CB[7] was conducted using a similar approach. In all cases, a gentle heating of the solution was needed to obtain clear solutions. Upon addition of various amounts of CB[7], the resonances of $\mathbf{3}^{4+}$ experienced a similar upfield and downfield shift (Figure 4). When four equivalents of CB[7] were added, a simple ^{1}H NMR spectrum was obtained that clearly showed that a symmetric pseudo[3]rotaxane had formed, in which the two CB[7] rings encircled the two terminal xylene units with the central xylene unit uncomplexed (Figure 4F). As a result, the resonances for the complexed phenyl rings (H$_b$, H$_c$) showed an upfield shift to $\delta = 6.89$ (doublet) and 6.77 ppm (doublet), and the resonance for the central uncomplexed phenyl rings (H$_f$) displayed a downfield shift to $\delta = 8.02$ ppm as a singlet. Similar changes were observed for the methylene protons of $\mathbf{3}^{4+}$ and the integration ratio between the two sets of resonances showed the expected value of 2:1. We also found that to reach a maximum degree of threading, an excess of CB[7] had to be added, as one can see that the addition of two equivalents of CB[7] resulted in an equilibrium of both pseudo[3]rotaxane and pseudo[2]rotaxane in solution (Figure 4D). The pure pseudo[3]rotaxane again was obtained by simple counterion exchange with NH$_4$PF$_6$, and it was also interesting that the sample had a higher solubility in acetonitrile than the pseudo[2]rotaxane obtained from **2**$\cdot$(PF$_6$)$_3$, probably because there were two CB[7] units encircling the cationic thread. ^{1}H NMR spectra of the pure pseudo[3]rotaxane in acetonitrile clearly supported such a self-assembling mode (Figure 2B). In addition, the HR-ESIMS exhibited three peaks at *m/z* 676.10 for $[M{-}4\,\mathrm{PF_6}^-]^{4+}$, 949.83 for $[M{-}3\,\mathrm{PF_6}^-]^{3+}$ and 1497.08 for $[M{-}2\,\mathrm{PF_6}^-]^{2+}$ (Figure 1C), further confirming the proposed structure. Based on these results, it will be natural to expect that the threading of **4**$\cdot$(PF$_6$)$_6$ and **5**$\cdot$(PF$_6$)$_8$ with excess CB[7] will lead to the formation of pseudo[4]rotaxane and pseudo[5]rotaxane with the CB[7] rings located at specific sites. In fact, our experimental data did support this assumption. The threading of **4**$\cdot$(PF$_6$)$_6$ and **5**$\cdot$(PF$_6$)$_8$ with CB[7] was followed by ^{1}H NMR spectroscopic measurements (Figures S2 and S3 in the Supporting Information). In both cases, a large excess of CB[7] was required to reach a maximum degree of threading, and finally, simple NMR spectra were obtained that can be assigned to the highly symmetric pseudo[4]rotaxane and pseudo[5]rotaxane, respectively. It was clear that for **4**$\cdot$(PF$_6$)$_6$, three CB[7] molecules were located at the two terminal and one central xylene units. Similarly for **5**$\cdot$(PF$_6$)$_8$, four CB[7] molecules are located along the cationic thread with one uncomplexed xylene unit bridged between neighboring CB[7] rings (see the models in Figures 1 and 2). Such a self-assembling mode was further proved by the ^{1}H NMR spectroscopic and HR-ESIMS measurements of the pure pseudo[*n*]rotaxanes, which were obtained by similar counterion exchange. As shown in Figure 2, simple ^{1}H NMR spectra were obtained for the pseudo[4]rotaxane in CD$_3$CN and it was in agreement with the proposed structure (Figure 2C). The collection of the ^{1}H NMR spectra of the pseudo[5]rotaxane was a little more challenging because of its poor solubility. After a long time, a relatively clear ^{1}H NMR spectrum was obtained, which again supported our expectation (Figure 2D).[30] The HR-ESIMS measurements further proved the formation of these pseudo[*n*]rotaxanes (Figure 1D, E). The mass spectrum of the pseudo[4]rotaxane formed from **4**$\cdot$(PF$_6$)$_6$ showed peaks at *m/z* 684.61 for $[M{-}6\,\mathrm{PF_6}^-]^{6+}$, 850.54 for $[M{-}5\,\mathrm{PF_6}^-]^{5+}$, 1099.43 for $[M{-}4\,\mathrm{PF_6}^-]^{4+}$ and 1514.23 for $[M{-}3\,\mathrm{PF_6}^-]^{3+}$; the pseudo[5]rotaxane from **5**$\cdot$(PF$_6$)$_8$ displayed peaks at *m/z* 688.88 for $[M{-}8\,\mathrm{PF_6}^-]^{8+}$, 808.17 for $[M{-}7\,\mathrm{PF_6}^-]^{7+}$, 967.06 for $[M{-}6\,\mathrm{PF_6}^-]^{6+}$, 1189.52 for $[M{-}5\,\mathrm{PF_6}^-]^{5+}$ and 1524.24 for $[M{-}4\,\mathrm{PF_6}^-]^{4+}$. All the peaks gave well-resolved isotope distributions in agreement with the calculated values.

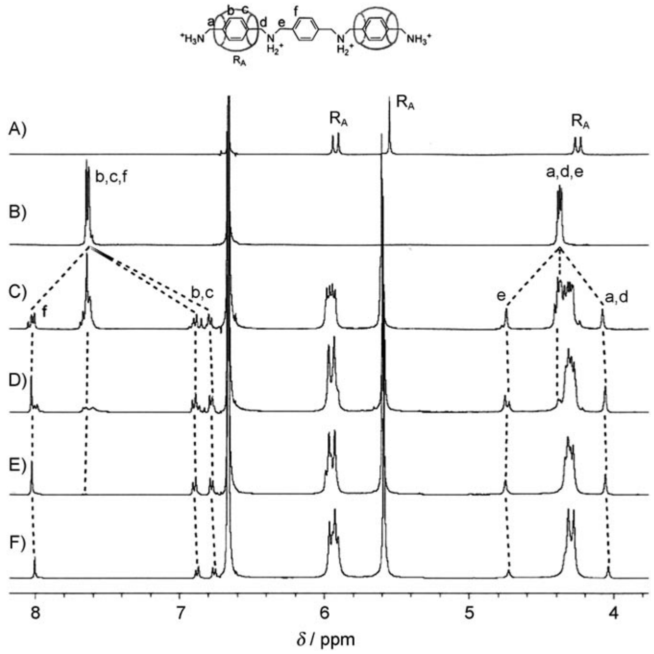


Figure 4. ^{1}H NMR spectra (500 MHz, CF$_3$COOD/D$_2$O = 1:1, 298 K) of A) CB[7], B) **3**$\cdot$(PF$_6$)$_4$, C) CB[7]/**3**$\cdot$(PF$_6$)$_4$ = 1:1, D) CB[7]/**3**$\cdot$(PF$_6$)$_4$ = 2:1, E) CB[7]/**3**$\cdot$(PF$_6$)$_4$ = 3:1, and F) CB[7]/**3**$\cdot$(PF$_6$)$_4$ = 4:1.

Conclusions

In conclusion, a series of well-defined, higher order pseudo[*n*]rotaxanes ($n = 2$, 3, 4, 5) have been prepared in pure form by using a simple "threading-followed-by-precipitation" approach. To the best of our knowledge, the obtained pseudo[5]rotaxane represents the longest pure pseudorotaxane to date. By taking advantage of the tight binding properties between the CB[7] and xylene diammonium units, well-defined pseudodorotaxanes are formed in solution by a simple threading process, and the as-formed pseudo[*n*]rotaxanes can be easily separated from the complicated mixture by simple counterion exchange. Our studies also disclosed an interesting self-assembling mode during the threading of a series of oligoalkylammonium salts with CB[7], and this suggested the importance of the interactions between the macrocycles during the threading process. In this specific case, the repulsion and steric hindrance between the CB[7] molecules on the thread led to a unique self-assembling mode. Furthermore, our research forms the basis for constructing more complicated supramolecular architectures as well as switchable systems in the future.

Experimental Section

Details on the starting materials, experimental procedures, characterization data for all new compounds, selected ^{1}H NMR spectra for some key intermediate oligomers, and ^{1}H NMR spectra recorded during the threading of **1**$\cdot$(PF$_6$)$_2$, **4**$\cdot$(PF$_6$)$_6$, and **5**$\cdot$(PF$_6$)$_8$ with CB[7] are given in the Supporting Information.

Acknowledgements

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[30] It should be noted that after a long scanning time, resonances of around $\delta = 6$ ppm for a trace amount of NH_4PF_6 in the solvent appeared in the ^1H NMR spectrum, which dominate the major impurities.

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