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Efficient Potassium-Ion-Templated Synthesis and Controlled Destruction of [2]Rotaxanes Based on Cascade Complexes

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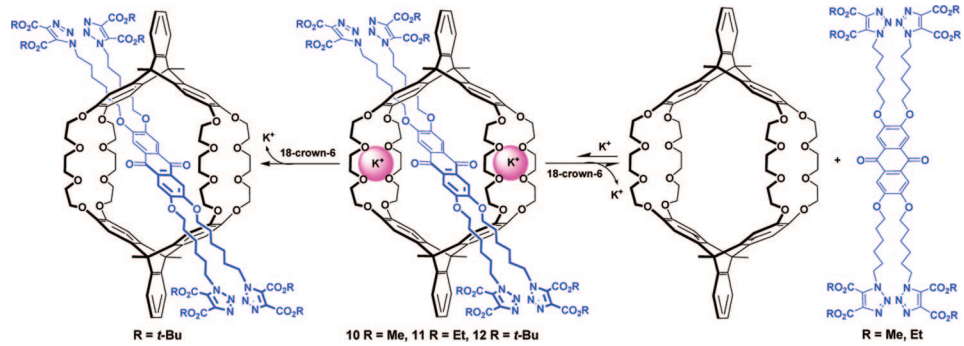

The triptycene-based macrotricyclic host can form pseudorotaxane-like cascade complexes with anthraquinone and its tetra-azide terminally functionalized derivative in the presence of potassium ions, which subsequently resulted in the synthesis of three novel potassium-ion-templated [2]rotaxanes **10**−**12** in high yields by the "threading followed by stoppering" approach. Since the potassium ions act not only as templates during the stoppering reactions but also as nonslipping chocks to shrink the inner diameter of the wheel cavity, the deslipping behaviors of the [2]rotaxanes with different triazole stoppers by peeling off the potassium ions with 18-crown-6 were further investigated. The results show that rotaxanes **10** and **11** can be destroyed, but under the same conditions the dumbbell and ring components of rotaxane **12** remain interlocked.

Introduction

Two decades ago, it was realized that metal−ligand coordination geometries could fix molecular fragments in three-demensional space such that they were predisposed to form mechanically interlocked architectures through macrocyclization or "stoppering" reactions.[1] Since then, a revolution in catenane and rotaxane synthesis has begun, and the diverse range of binding geometries exhibited by metal ions and their relatively stable interactions with ligands has been exploited for the efficient templated-directed synthesis of various supramolecular architectures[2] and interlocked molecules.[3] Although the formation of rotaxanes and catenanes has been demonstrated using transition metal ions coordinated to four (tetrahedral and square planar),[4] five (trigonal bipyramidal and square pyramidal),[5] and six (octahedral)[6] donor atoms, alkali-metal ions, which are useful templates for the synthesis of crown ethers,[7] are rarely used to direct the construction of rotaxanes and catenanes. Actually, to our knowledge, only two examples were hitherto reported. One is the use of Li^+ ion to assist the formation of a neutral bistable rotaxane,[8a] in which the reaction process utilized the slippage method with a prolonged time (14 days) to afford the rotaxane in only moderate yield. Another interesting example is a recent report on the synthesis of a slippage-derived [2]rotaxane in 7 days with Na^+ ion as template.[8b]

Cylindrical macrotricyclic polyethers[9] consist of one central cavity and two lateral circular cavities, which have new topological features with respect to the mono- and bicyclic hosts. Recently, we have designed and synthesized a novel triptycene-based macrotricyclic host **1** formed by incorporating two rigid triptycene and linking two macrocycles through four bridges,[10a] which proved to be a powerful host for complexation with

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different guests. Consequently, some new supramolecular systems with specific structures and properties have been developed.[10] As a result of the host containing two lateral crown cavities, they could bind two alkali metal ions such as potassium ions efficiently to form a new "host" with long intercationic distance, which would further bind anthraquinone with coordinated sites for the two cations to form a novel cascade complex.[11] We further deduced that if a functionalized anthraquinone was used as the guest, novel [2]rotaxanes could be achieved by a "threading followed by stoppering" approach. Moreover, the analysis of the deslipping processes could provide insight into the complementary size of the stopper boundaries and the inner diameter of the wheel cavity, which would thus allow steric demand to be measured experimentally through a supramolecular approach. Thus, destruction of the rotaxanes through deslippage of the wheel over one stopper can be informative.[12] However, most of the work about destruction of rotaxanes hitherto has been focused on deslipping kinetics and steric effects of the axles or the wheel using a synthetic approach; no one has utilized a supramolecular approach to control the destruction process of rotaxanes by changing the steric size of the wheel. In our system, because the potassium ions act not only as templates but also as nonslipping chocks thate shrink the inner diameter of the wheel cavity, destruction of the [2]rotaxanes could thus be achieved by peeling off the metal ions.

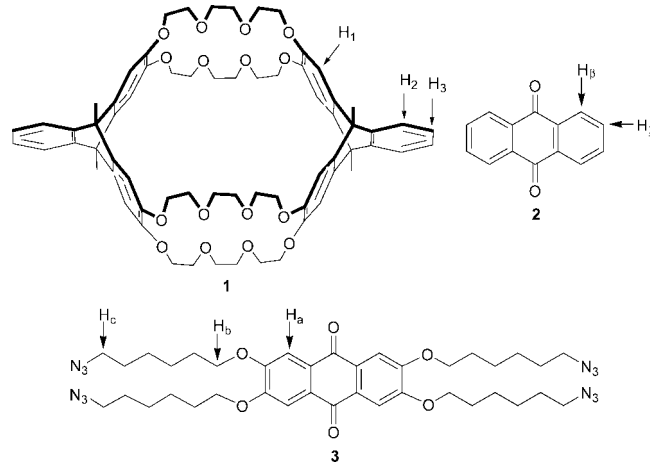

FIGURE 1. Structure and proton designations of host **1**, anthraquinone (**2**), and its derivative **3**.

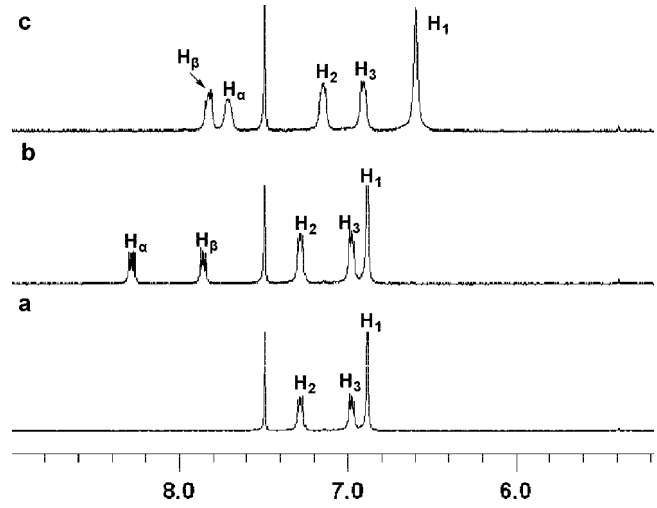

FIGURE 2. Partial ^{1}H NMR spectra (300 MHz, $CD_3CN/CDCl_3$ = 1:1, 295 K) of (a) **1**; (b) **1** and 1.0 equiv of **2**, $[\mathbf{1}]_0$ = 3.0 mM; (c) the mixture obtained after adding KPF_6 (4.0 equiv) to the solution in (b).

In this paper, we report (1) the formation of cascade complexes between host **1** with anthraquione **2** and its tetra-azide terminal derivative **3** (Figure 1) in the presence of potassium ions, (2) the synthesis of three potassium-ion-templated [2]rotaxanes through "slippage" and/or "threading followed by stoppering" approaches, and (3) the different deslipping behaviors of the [2]rotaxanes with different triazole stoppers by peeling off the potassium ions with 18-crown-6.

Results and Discussion

Cascade Complex Formation Between Host 1 and Anthraquinone. We first investigated the complexation between host **1** and anthraquinone (**2**) in solution, and found that the ^{1}H NMR spectrum of **1** and **2** (each 3.0 mM concentration) in 1:1 $CDCl_3/CD_3CN$ solution at room temperature is essentially the sum of the two components (Figure 2b). This observation indicated that no obvious complexation between **1** and **2** existed. However, it was found that the addition of solid KPF_6 into the mixture gave a yellow solution, which suggested that potassium-ion-templated complexation between **1** and **2** might occur. Further evidence for formation of the complex came from the

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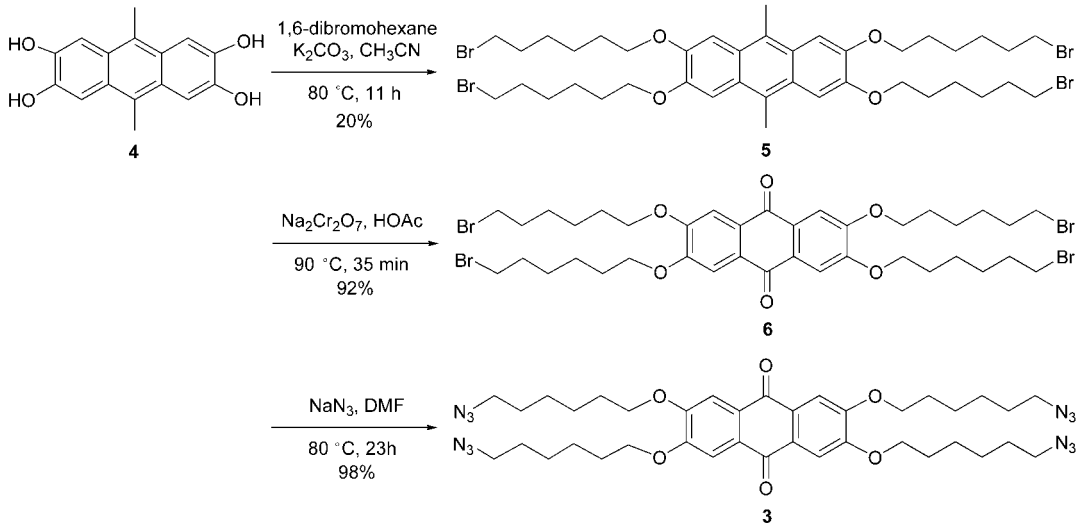
SCHEME 1. Synthesis of Anthraquinone Derivative 3



^{1}H NMR spectrum of a 1:1 mixture of **1** and **2** in the presence of potassium salts (Figure 2c), which showed a great difference compared with those for **1** (Figure 2a) and **2**. Especially, the proton signal of H_α shifted dramatically to upfield. Similarly, the upfield shifts of the signals for protons H_1-H_3 were also observed. Consequently, a novel cascade complex could be formed. According to a similar method as described before,[11c] we have chosen to titrate **2** into a solution of **1** containing a large excess of potassium salts, and under these conditions it is reasonable to assume that binding of K^+ to **1** is essentially complete. The ^{1}H NMR spectroscopic titrations afforded a quantitative estimate for the complex of **1** and **2** in the presence of 20 equiv of KPF_6 by monitoring the changes of the chemical shift of the proton H_1 of the host. The results showed that a 1:1 complex between **1** and **2** was formed by a mole ratio plot.[13] Accordingly, the apparent equilibrium constant was determined to be 9.1 ($\pm$0.8) $\times$ 10^2 M^{-1} by the Scatchard plot.[14] Moreover, the ESI-MS spectrum showed a strong peak at *m*/*z* 717.2 for **1**·**2**·$2K^+$, which provided another evidence for formation of the complex.

Furthermore, we obtained a yellow crystal of the complex **1**·**2**·$2KPF_6$ suitable for X-ray analysis by slow diffusion of ether into an equimolar mixture of **1** and **2** in 1:1 chloroform/acetonitrile solution in the presence of excess KPF_6. As shown in Figure 3, the anthraquinone ring is threaded into the host cavity to result in a cascade complex structure.[11] The intercationic distance between two potassium ions was 10.80 Å. Interestingly, it was also found that one potassium ion is nine-coordinate while the other one is ten-coordinate in which one is from the nitrogen atom of acetonitrile and the others from the oxygen atoms of the anthraquinone and the glycol chains.

Synthesis and Complexation Study of the Tetra-Azide-Functionalized Derivative of Anthraquinone. Synthesis of the anthraquinone derivative **3** is depicted in Scheme 1. Anthracene derivative **5** was first synthesized by the reaction of 9,10-dimethyl- 2,3,6,7-tetrahydroxylanthracene and 1,6-dibromohexane in the presence of potassium carbonate. Oxidation of **5** with sodium dichromate afforded compound **6** in 92% yield, which then reacted with sodium azide in DMF to give **3** as a yellow powder in 98% yield. Compounds **3**, **5**, and **6** were characterized by their ^{1}H NMR, ^{13}C NMR, and MALDI-TOF MS spectra and elemental analyses.[14]

We then investigated the complexation between host **1** and anthraquinone derivative **3** in solution and found that the ^{1}H NMR spectrum of **1** and **3** (each 3.0 mM concentration) in 1:1 $CDCl_3/CD_3CN$ solution in the presence of potassium ions (Figure 4c) showed a great difference from those for **3** (Figure 4a) and **1**. Especially, the proton signal of H_a in **3** shifted dramatically to upfield. Interestingly, the spectrum displays three

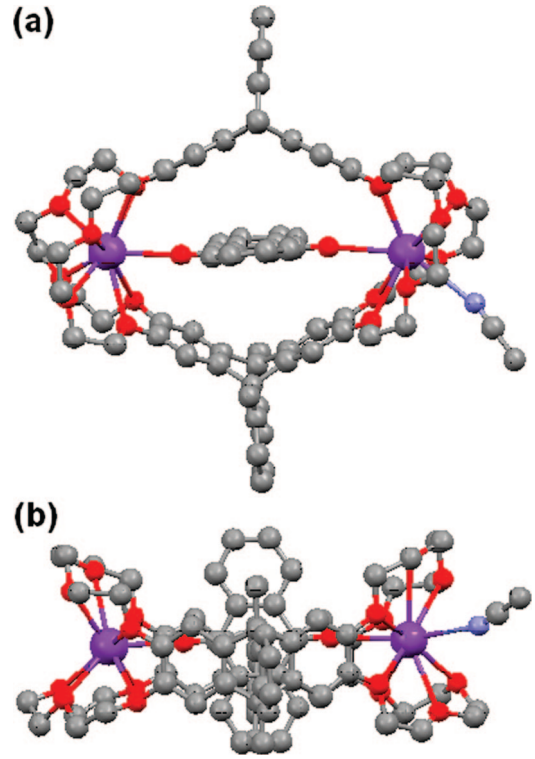
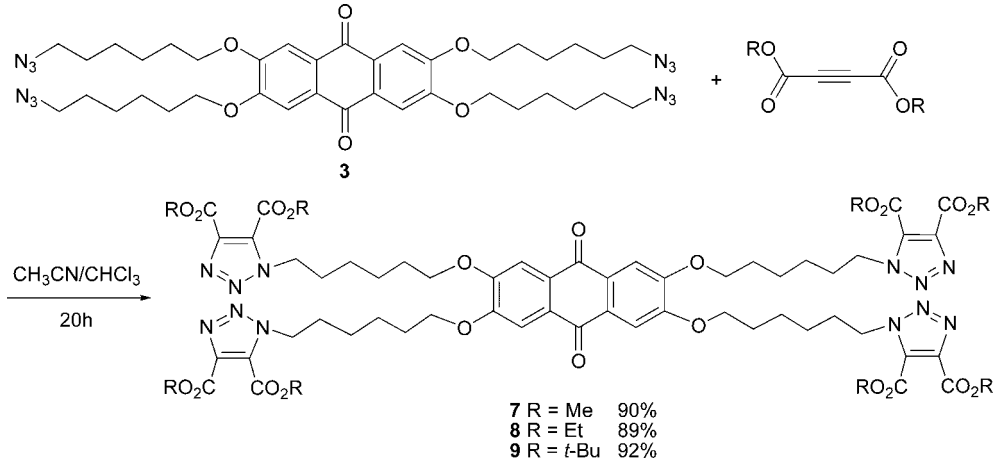


FIGURE 3. (a) Top view and (b) side view of crystal structure of **1**·**2**·$2KPF_6$. Solvent molecules, PF_6^- counterions, and hydrogen atoms are omitted for clarity.

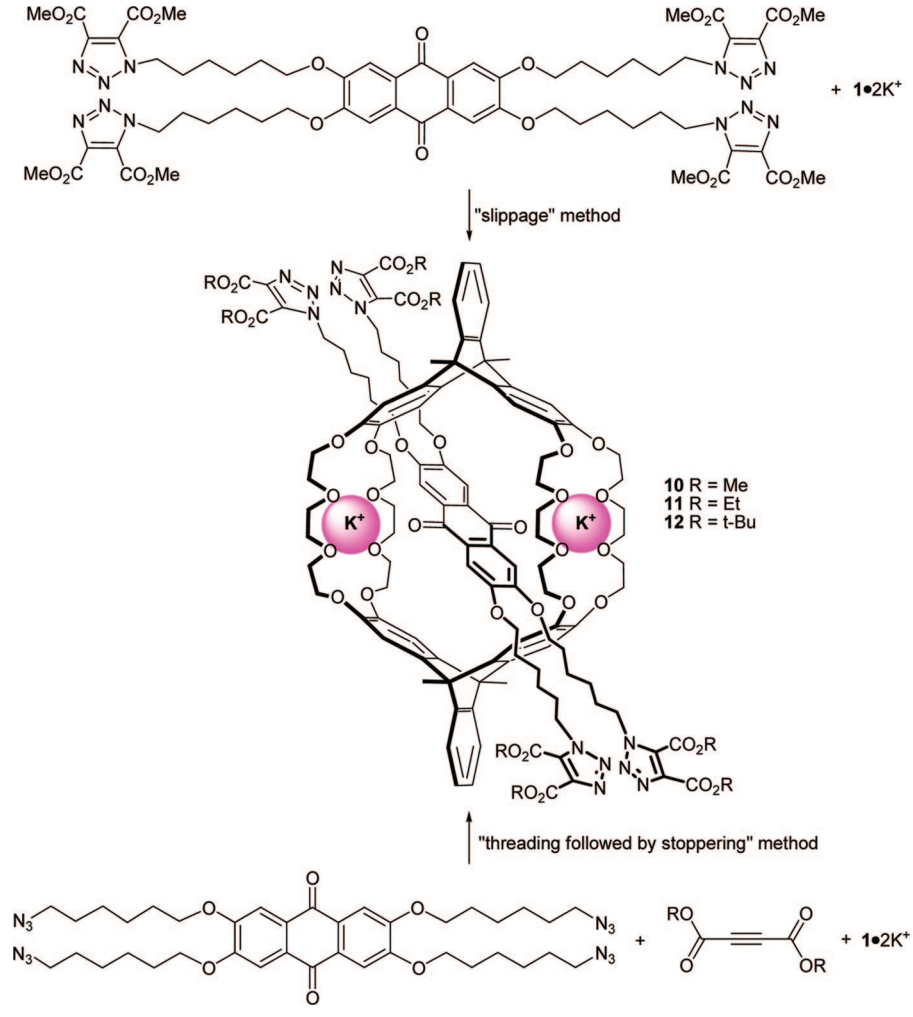
(13) Tsukube, H.; Furuta, H.; Odani, A.; Takeda, Y.; Kudo, Y.; Inoue, Y.; Liu, Y.; Sakamoto, H.; Kimura, K. In *Comprehensive Supramolecular Chemistry*; Atwood, J. L., Davies, J. E. D., MacNicol, D. D., Vögtle, F.; Lehn, J. M., Eds.; Elsevier: New York, 1996.

(14) See Supporting Information.

SCHEME 2. Synthesis of Compounds 7−9



SCHEME 3. Two Methods Used for the Synthesis of Rotaxanes 10−12



sets of resonances, namely, signals for the 1:1 complex itself, free **3**, and free host **1**, which is consistent with a recognition system that has high activation barriers for both the complexation and decomplexation steps and consequently undergoes slow rates of threading and dethreading on the NMR time scale. This is totally different from the complexation between host **1** and anthraquinone **2**, which is probably due to the alkyl chain disturbing the fast threading and dethreading of the guest molecule. The apparent association constant (K_a) for this 1:1 complex in 1:1 chloroform/acetonitrile solution was determined to be 4.8 ($\pm$0.6) $\times$ 10^3 M^{-1} by the single-point method.[15] Moreover, the ESI-MS spectrum showed a strong peak at *m*/*z*

(15) $[\mathbf{1}]_0 = 1.0$ mM, $[\mathbf{3}]_0 = 1.0$ mM, and $[KPF_6]_0 = 20.0$ mM. The binding constant was calculated on the basis of the assumption that the binding of K^+ to **1** is essentially complete in a solution of **1** containing a large excess of potassium salts. Ashton, P. R.; Chrystal, E. J. T.; Glink, P. T.; Menzer, S.; Schiavo, C.; Spencer, N.; Stoddart, J. F.; Tasker, P. A.; White, A. J. P.; Williams, D. J. *Chem. Eur. J.* **1996**, *2*, 709–728.

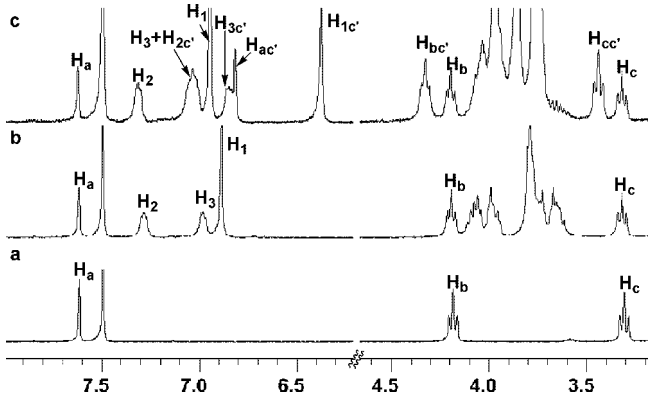


FIGURE 4. Partial ^{1}H NMR spectra (300 MHz, $CD_3CN/CDCl_3$ = 1:1, 295 K) of (a) **3**; (b) **1** and 1.0 equiv of **3**, $[\mathbf{1}]_0$ = 3.0 mM; (c) the mixture obtained after adding excess KPF_6 to the solution in (b). c′ denotes "complex" in spectrum c.

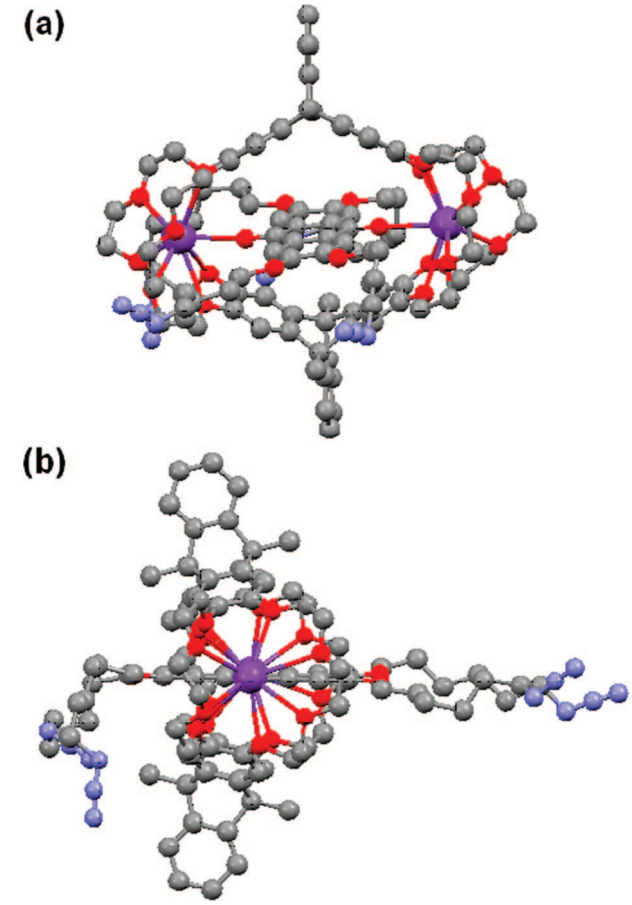


FIGURE 5. (a) Top view and (b) side view of crystal structure of **1**·**3**·2KPF_6. Solvent molecules, PF_6^- counterions, and hydrogen atoms are omitted for clarity.

999.6 for **1**·**3**·2K^+, which provided further evidence for formation of the complex.[14]

We also obtained a yellow crystal of the complex **1**·**3**·2KPF_6 suitable for X-ray analysis by slow diffusion of diisopropyl ether into an equimolar mixture of **1** and **3** in 1:1 chloroform/acetonitrile solution in the presence of excess KPF_6. As shown in Figure 5, the anthraquinone ring is threaded into the host cavity to result in a cascade complex with pseudorotaxane-type structure. Both of the potassium ions are nine-coordinate, in which one is from the oxygen atom of the anthraquinone and

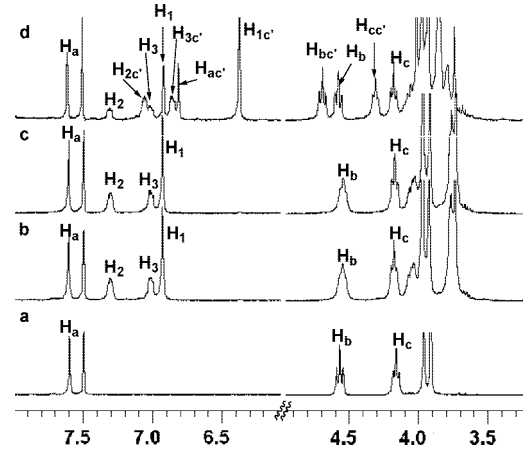


FIGURE 6. Partial ^{1}H NMR spectra (300 MHz, $CD_3CN/CDCl_3$ = 1:1) of (a) **7**; (b) the mixture obtained after adding KPF_6 (excessive) to solution of **1** and 1.0 equiv of **7**, $[\mathbf{1}]_0$ = 3.0 mM; (c) the solution in (b) heated at 333 K for 2 h; (d) the solution in (b) heated at 333 K for 20 h. c′ denotes "complex" in spectrum d.

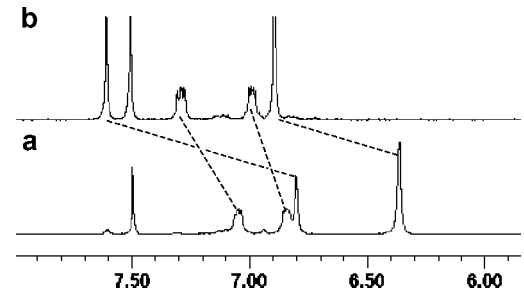


FIGURE 7. Partial ^{1}H NMR spectra (300 MHz, $CD_3CN/CDCl_3$ = 1:1, 295 K) of (a) rotaxane **10**, $[\mathbf{10}]_0$ = 2.0 mM; (b) the mixture obtained after adding 18-crown-6 (4.0 equiv) to (a).

the others from the oxygen atoms of the glycol chains. Moreover, the four functionalized alkyl chains penetrate through the central cavity of the macrotricyclic host, which provided us the opportunity to further proceed to the stoppering reactions.

Synthesis of [2]Rotaxanes Through "Slippage" and/or "Threading Followed by Stoppering" Approaches. Initially, the stoppering reactions in the absence of host **1** and KPF_6 were investigated. Consequently, the thread molecules **7**, **8**, and **9** could be easily synthesized in high yields by the 1,3-dipolar cycloaddition reactions between the tetra-azide-functionalized anthraquinone **3** and three different dialkyl acetylenedicarboxylates in acetonitrile and chloroform (Scheme 2).

We then tested the complexation between host **1** and thread **7** by NMR. As shown in Figure 6, the ^{1}H NMR spectrum of a 1:1 mixture of **1** and **7** in 1:1 $CDCl_3/CD_3CN$ solution is essentially the sum of the two components, which suggests that there is insufficient complexation to be detected by NMR. The addition of solid KPF_6 also did not cause any significant change of the spectrum, which implied that the triazole stopper is so big that compound **7** could not thread the host cavity freely. After heating at 333 K for 2 h, the spectrum remained unchanged. However, we detected a new set of signals after the solution was heated at 333K for 20 h (Figure 6d). The appearance of this new set of signals is similar to those of complex **1**·**3**·2K^+, which means the free energy of activation for the slippage of thread over macrocyclic host could be overcome, and a new slippage rotaxane was formed.

We thus used this slippage method to prepare a [2]rotaxane. Consequently, after the mixture was heated at 353 K for 4 d,

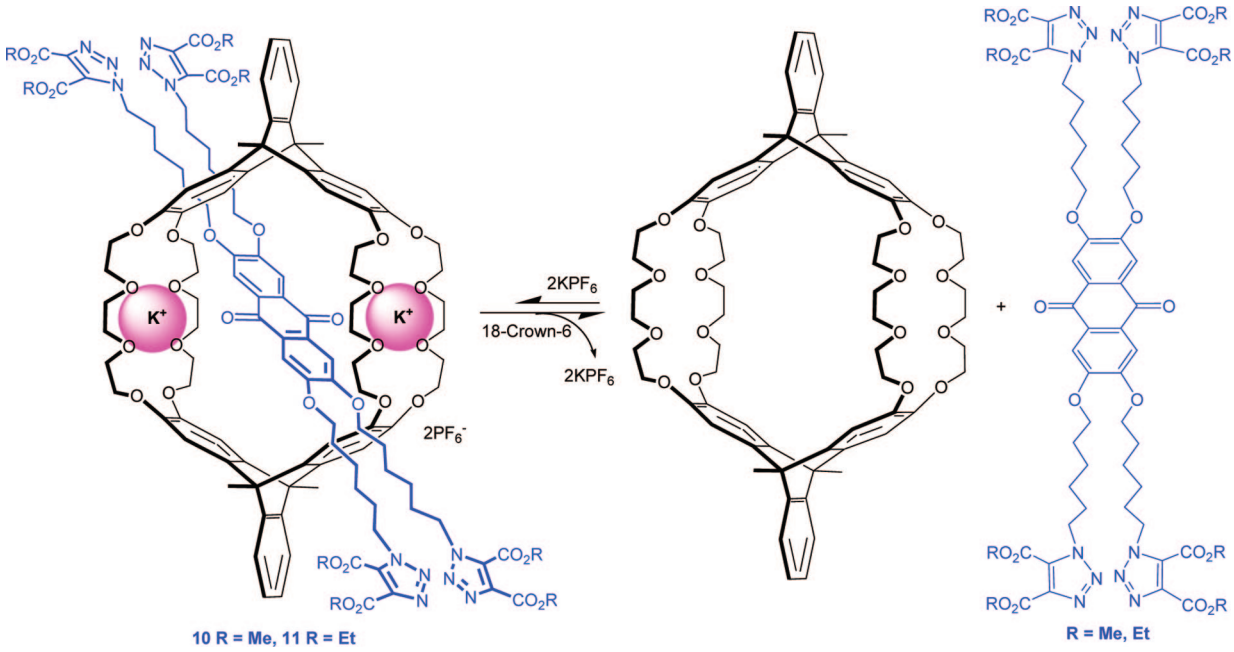


FIGURE 8. Illustration of the controlled dethreading and threading of the rotaxanes **10** and **11**.

31% of the corresponding [2]rotaxane **10** was isolated by column chromatography. However, when we mixed **1**, **3**, and dimethyl but-2-ynedioate together in the presence of KPF_6, it was found that after the mixture was heated in 1:1 chloroform/acetonitrile solution at 353 K for 20 h, rotaxane **10** could be isolated in 80% yield from the reaction mixture by column chromatography. This result means that the "threading followed by stoppering" method is more efficient than the slippage method in our system (Scheme 3).

In the case of **8**, it was found that the ^{1}H NMR spectrum of a 1:1 mixture of **1** and **8** in the presence of potassium ions showed no changes after it was heated at 333 K for 2 d.[14] Even after 10 d, only few new signals for the threaded **8** were detected. This to some extent means that it is very hard for **8** to thread the host, and the size of the trazole stoppers of **8** is the complementary size of the inner diameter of the wheel cavity. For the thread **9** with the four bulky *tert*-butyl-substituted trazole groups, it was supposed to be not able to form [2]rotaxane with host **1** via the slippage method. However, we found that the "threading followed by stoppering" approach could be employed successfully for the synthesis of rotaxanes **11** and **12** (Scheme 3). Under similar conditions as used before, rotaxanes **11** and **12** could be obtained in 81% and 78% yield, respectively. The fact that the [2]rotaxanes **10**, **11**, and **12** survive column chromatography might indicate that the two arms of the threads on each side of the wheel worked together to prevent the deslippage of the [2]rotaxanes. The ^{1}H NMR spectra showed that the dumbbell and ring components are present in not only equal stoichiometry but also interlocked with one another. Moreover, their MALDI-TOF mass spectra provided further evidence for formation of the [2]rotaxanes.[14]

Deslipping Behaviors of Potassium-Ion-Templated [2]Rotaxanes with Different Triazole Stoppers. Because the potassium ions act not only as templates during the stoppering reaction but also as nonslipping chock which shrink the inner diameter of the wheel cavity, we speculated that peeling off the potassium ions of the [2]rotaxanes might disturb their stabilities to some extent. As was expected, the addition of 18-crown-6 to the 1:1 $CDCl_3/CD_3CN$ solution of [2]rotaxane **10** immediately resulted in a very different ^{1}H NMR spectrum compared to the original (Figure 7). The aromatic proton signals of the [2]rotaxane shifted dramatically downfield almost to the original positions of uncomplexed thread and wheel, which suggested that the two components of the [2]rotaxane were separated, and the rotaxane **10** was destroyed through deslippage of the wheel over one stopper. Similar to **10**, [2]rotaxane **11** also showed the dethreading process to give the host and compound **8** when the potassium ions were peeled off by the addition of 18-crown-6 (Figure 8). Since **8** could hardly thread the wheel in the presence of potassium ions, the result that the triazole stoppers of **8** could dethread of the host indicated that the inner diameter of the wheel cavity could be changed by the supramolecular approach, and an extending process might occur with the wheel when the potassium ions were peeled off. However, the addition of 18-crown-6 to the solution of rotaxane **12** did not result in the destruction of the rotaxane,[14] which implied that the triazole stoppers of **12** are sufficiently sterically bulky to prevent dethreading of the anthraquinone derivative through the cavity of the macrotricyclic host. Thus, besides the rotaxane **12**, both **10** and **11** could be destructed easily through deslippage of the wheel over one stopper by peeling off the alkali-metal ions; on the other hand, the threading process for compounds **7** and **8** hardly could proceed at an elevated temperature (Figure 8).

Conclusion

In summary, we have demonstrated that the triptycene-based macrotricyclic host **1** could form pseudorotaxane-like cascade complexes with anthraquinone and its tetra-azide terminally functionalized derivative in the presence of potassium ions. Accordingly, we have synthesized three novel potassium-ion-templated [2]rotaxanes efficiently in high yields by the "threading followed by stoppering" approach and also have proven that the two arms of the thread on each side of the rotaxanes worked cooperatively to prevent the deslippage of the wheel over one stopper. Since the potassium ions act not only as templates during the stoppering reactions but also as nonslipping chocks

to shrink the inner diameter of the cavity, we further investigated the deslipping behaviors of the [2]rotaxanes with different triazole stoppers by peeling off the potassium ions with 18-crown-6, and the results showed that rotaxanes **10** and **11** could be destroyed, but under the same conditions the dumbbell and ring components of rotaxane **12** remained interlocked. We believe that the results presented here would provide us insight into the complementary size of the stopper boundaries and the inner diameter of the wheel cavity and thus allow us to further design and optimize the function of the triptycene-based macrotricyclic supramolecular systems.

Experimental Section

Synthesis of 2,3,6,7-Tetrakis(6-bromohexyloxy)-9,10-dimethylanthracene (5). A suspension of K_2CO_3 (1.10 g, 8 mmol) in anhydrous CH_3CN (30 mL) under argon atmosphere was stirred vigorously for 5 min and then heated to 80 °C. To the mixture were added 2,3,6,7-tetrahydroxy-9,10-dimethylanthracene (0.27 g, 1 mmol) and 1,6-dibromohexane (2.46 mL, 16 mmol). The reaction mixture was stirred at 80 °C for 11 h under an argon atmosphere. After cooling to ambient temperature, the mixture was filtered and washed with CH_2Cl_2 (20 mL). The filtrate was concentrated under reduced pressure to give a reddish brown oil, which was redissolved in CH_2Cl_2 (50 mL) and washed with water. The organic layer was dried over anhydrous magnesium sulfate. After removal of the solvent, the resulting oil was subjected to column chromatography over silica gel (eluent CH_2Cl_2/petroleum ether, 1:1) to provide 0.18 g (20%) of **5** as a light yellow solid. Mp: 132−133 °C. ^{1}H NMR (300 MHz, $CDCl_3$): 1.58−1.61 (m, 16H), 1.91−1.98 (m, 16H), 2.91 (s, 6H), 3.45 (t, J = 7 Hz, 8H), 4.18 (t, J = 7 Hz, 8H), 7.40 (s, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): 14.7, 25.4, 28.0, 29.1, 32.8, 33.7, 68.5, 104.5, 123.6, 125.9, 148.6. MS (MALDI-TOF): m/z 922.4 $[M]^+$. Anal. Calcd for $C_{40}H_{58}Br_4O_4$: C, 52.08; H, 6.34; Br, 34.65. Found: C, 52.31; H, 6.39; Br, 34.94.

Synthesis of 2,3,6,7-Tetrakis(6-bromohexyloxy)anthracene-9,10-dione (6). A mixture of $Na_2Cr_2O_7$ (0.75 g, 2.5 mmol) and **5** (0.46 g, 0.5 mmol) suspended in acetic acid (20 mL) was heated to 90 °C for 35 min and then cooled to room temperature. The resulting yellow solid was filtered, washed with water to remove the unreacted $Na_2Cr_2O_7$, and finally washed with Et_2O. The solid was dried in the air to yield **6** (0.43 g, 92%) as a yellow crystalline power. Mp: 146−147 °C. ^{1}H NMR (300 MHz, $CDCl_3$): 1.54−1.58 (m, 16H), 1.88−1.94 (m, 16H), 3.44 (t, J = 7 Hz, 8H), 4.19 (t, J = 7 Hz, 8H), 7.64 (s, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): 25.2, 27.9, 28.8, 32.7, 33.6, 69.1, 109.6, 128.3, 153.3, 182.2. MS (MALDI-TOF): m/z 924.4 $[M]^+$, 947.3 $[M + Na]^+$. Anal. Calcd for $C_{38}H_{52}Br_4O_6 \cdot 0.1CH_2Cl_2$: C, 49.05; H, 5.64; Br, 34.26. Found: C, 49.34; H, 5.74; Br, 34.14.

Synthesis of 2,3,6,7-Tetrakis(6-azidohexyloxy)anthracene-9,10-dione (3). A mixture of **6** (0.46 g, 0.5 mmol) and sodium azide (0.16 g, 2.4 mmol) was heated at 80 °C in DMF for 23 h. The solvent was evaporated, and the residues were redissolved in CH_2Cl_2 (20 mL) and washed with water. The organic layer was dried over anhydrous magnesium sulfate. Evaporation of the solvent yielded the title compound as a yellow solid (0.45 g, 98%). Mp: 103−104 °C. ^{1}H NMR (300 MHz, $CDCl_3$): 1.43−1.59 (m, 16H), 1.61−1.71 (m, 8H), 1.87−1.96 (m, 8H), 3.30 (t, J = 7 Hz, 8H), 4.19 (t, J = 7 Hz, 8H), 7.64 (s, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): 25.6, 26.4, 28.78, 28.81, 51.3, 69.0, 109.5, 128.2, 153.3, 182.0. MS (MALDI-TOF): m/z 772.7 $[M]^+$, 795.7 $[M + Na]^+$, 811.6 $[M + K]^+$. Anal. Calcd for $C_{38}H_{52}N_{12}O_6$: C, 59.05; H, 6.78; N, 21.75. Found: C, 58.89; H, 6.99; N, 21.81.

General Procedure for the Synthesis of Compounds 7−9. A solution of tetra-azide **3** (77 mg, 0.1 mmol) and dialkyl acetylenedicaboxylate (1.2 mmol) was heated at 80 °C in 1:1 chloroform/acetonitrile solution (8 mL) for 20 h. The reaction mixture was cooled to room temperature, and the solvent was evaporated. The residue was separated by chromatography over silica gel to yield the target compound as yellow solid.

Compound 7. Yield: 90%. Mp: 97−98 °C.^{1}H NMR (300 MHz, $CDCl_3$): 1.39−1.61 (m, 16H), 1.84−2.01 (m, 16H), 3.97 (s, 12H), 4.00 (s, 12H), 4.17 (t, J = 7 Hz, 8H), 4.62 (t, J = 7 Hz, 8H), 7.62 (s, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): 24.1, 24.8, 27.4, 28.8, 49.2, 51.4, 52.1, 67.7, 108.2, 127.0, 128.5, 138.7, 151.8, 157.7, 159.3, 180.7. MS (MALDI-TOF): m/z 1363.9 $[M + Na]^+$, 1379.9 $[M + K]^+$. Anal. Calcd for $C_{62}H_{76}N_{12}O_{22}$: C, 55.52; H, 5.71; N, 12.53. Found: C, 55.52; H, 5.92; N, 12.49.

Compound 8. Yield: 89%. Mp: 82−83 °C.^{1}H NMR (300 MHz, $CDCl_3$): 1.38−1.43 (m, 24H), 1.38−1.60 (m, 16H), 1.84−2.00 (m, 16H), 4.17 (t, J = 7 Hz, 8H), 4.40−4.49 (m, 16H), 4.60 (t, J = 7 Hz, 8H), 7.62 (s, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): 13.9, 14.2, 25.4, 26.1, 28.7, 30.1, 50.3, 61.8, 62.8, 69.0, 109.5, 128.3, 129.8, 140.3, 153.1, 158.6, 160.3, 182.0. MS (MALDI-TOF): m/z 1476.1 $[M + Na]^+$, 1492.1 $[M + K]^+$. Anal. Calcd for $C_{70}H_{92}N_{12}O_{22}$: C, 57.84; H, 6.38; N, 11.56. Found: C, 57.83; H, 6.63; N, 11.66.

Compound 9. Yield: 92%. Mp: 45−46 °C.^{1}H NMR (300 MHz, $CDCl_3$): 1.38−1.48 (m, 8H), 1.50−1.66 (m, 80H), 4.17 (t, J = 7 Hz, 8H), 4.57 (t, J = 7 Hz, 8H), 7.62 (s, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): 25.4, 26.2, 27.9, 28.1, 28.7, 30.2, 50.1, 68.9, 82.8, 84.8, 109.4, 128.2, 130.5, 141.4, 153.1, 157.7, 159.6, 182.1. MS (MALDI-TOF): m/z 1669.9 $[M + Na]^+$, 1716.1 $[M + K]^+$. Anal. Calcd for $C_{86}H_{124}N_{12}O_{22} \cdot 3C_6H_{14} \cdot CH_2Cl_2$: C, 62.39; H, 8.38; N, 8.31. Found: C, 62.32; H, 8.19; N, 8.40.

Synthesis of Rotaxane 10 by Slippage Approach. A mixture of host **1** (34 mg, 0.03 mmol), **7** (81 mg, 0.06 mmol), and KPF_6 (55 mg, 0.3 mmol) in 1:1 (v/v) chloroform/acetonitrile (8 mL) was heated at 80 °C for 4 d. The reaction mixture was cooled to room temperature, and the solvent evaporated. The residue was chromatographed over silica gel to yield compound **10** as a yellow solid.

General Procedure Using the "Threading Followed by Stoppering" Approach to Synthesize Rotaxanes 10−12. A mixture of tetra-azide **3** (46 mg, 0.06 mmol), dialkyl acetylenedicaboxylate (1.2 mmol), host **1** (34 mg, 0.03 mmol), and KPF_6 (55 mg, 0.3 mmol) in chloroform/acetonitrile (1:1, 8 mL) was heated at 80 °C for 20 h. The reaction mixture was cooled to room temperature, and the solvent was evaporated. The residue was separated by chromatography over silica gel to yield the target compound as a yellow solid.

Rotaxane 10. Yield: 80%. Mp: 117−118 °C.^{1}H NMR (300 MHz, $CD_3CN/CDCl_3$ = 1:1): 1.50−1.72 (m, 28H), 1.96−2.12 (m, 16H), 3.75−4.03 (m, 72H), 4.21−4.35 (m, 8H), 4.66 (t, J = 7 Hz, 8H), 6.35 (s, 8H), 6.79 (s, 4H), 6.81−6.85 (m, 4H), 7.02−7.05 (m, 4H). ^{13}C NMR (75 MHz, $CD_3CN/CDCl_3$ = 1:1): 12.9, 24.7, 25.2, 28.2, 29.0, 46.4, 49.6, 59.2, 61.1, 67.8, 68.2, 69.5, 107.9, 109.8, 119.0, 123.6, 124.8, 129.3, 138.9, 141.8, 144.5, 147.7, 151.0, 158.2, 159.9, 177.9. MS (MALDI-TOF): m/z 2528.9 $[M - K - 2PF_6]^+$. HRMS (MALDI-TOF) calcd for $C_{130}H_{152}N_{12}O_{38}K$ $[M - K - 2PF_6]^+$ 2527.9962, found 2527.9953.

Rotaxane 11. Yield: 81%. Mp: 106−107 °C.^{1}H NMR (300 MHz, $CD_3CN/CDCl_3$ = 1:1): 1.32−1.44 (m, 24H), 1.53−1.64 (m, 8H), 1.66−1.78 (m, 20H), 2.00−2.13 (m, 16H), 3.78−4.00 (m, 48H), 4.25−4.33 (m, 8H), 4.35−4.50 (m, 16H), 4.68 (t, J = 7 Hz, 8H), 6.36 (s, 8H), 6.80 (s, 4H), 6.83−6.86 (m, 4H), 7.03−7.06 (m, 4H). ^{13}C NMR (75 MHz, $CD_3CN/CDCl_3$ = 1:1): 12.8, 13.0, 24.7, 25.3, 28.2, 29.0, 46.4, 49.5, 60.9, 62.1, 67.8, 68.2, 69.5, 107.9, 109.8, 119.0, 123.6, 124.8, 129.3, 139.1, 141.8, 144.5, 147.7, 150.9, 157.7, 159.5, 177.9. MS (MALDI-TOF): m/z 2640.2 $[M - K - 2PF_6]^+$. HRMS (MALDI-TOF) calcd for $C_{138}H_{168}N_{12}O_{38}K$ $[M - K - 2PF_6]^+$ 2640.1214, found 2640.1253.

Rotaxane 12. Yield: 78%. Mp: 92−93 °C.^{1}H NMR (300 MHz, $CD_3CN/CDCl_3$ = 1:1): 1.51−1.66 (m, 80H), 1.68−1.75 (m, 20H), 2.01−2.08 (m, 16H), 3.78−4.00 (m, 48H), 4.28 (t, J = 7 Hz, 8H), 4.63 (t, J = 7 Hz, 8H), 6.36 (s, 8H), 6.80 (s, 4H), 6.83−6.86 (m, 4H), 7.03−7.06 (m, 4H). ^{13}C NMR (75 MHz, $CD_3CN/CDCl_3$ = 1:1): 24.7, 25.3, 26.8, 26.9, 28.2, 28.6, 29.1, 46.4, 49.3, 67.7, 68.2,

69.5, 81.9, 84.2, 107.9, 109.8, 119.0, 123.6, 124.8, 130.1, 140.0, 141.8, 144.5, 147.6, 150.9, 156.8, 158.8, 177.9. MS (MALDI-TOF): *m/z* 2864.4 $[M - K - 2PF_6]^+$. HRMS (MALDI-TOF) calcd for $C_{154}H_{200}N_{12}O_{38}K$ $[M - 2K^+Na - 2PF_6]^+$ 2848.3979, found 2848.4057.

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Supporting Information Available: Copies of ^1H NMR, ^{13}C NMR, and MS spectra of new compounds and the rotaxanes **10**, **11**, and **12**; characterization and determination of the association constants for the complexes; X-ray crystallographic files in CIF format for the complexes. This material is available free of charge via the Internet at http://pubs.acs.org.

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