Rotaxanes

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A Twin-Axial Hetero[7]rotaxane**

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Rotaxanes are challenging and interesting because of their potential applications in nanotechnology and molecular machines.[1] Template synthesis has been widely used to realize more efficient synthesis of rotaxanes, while various protocols have been reported such as the popular "threading followed by stoppering", "slippage", and "clipping" approaches.[2] However, the synthesis of high-order rotaxanes still remains a challenge.[3,4] In this respect, it is very difficult to obtain heterorotaxanes with two or more similar rings,[5] as well as [*n*]rotaxanes with more than one axle molecule threaded through the same ring.[6]

Macrocyclic polyethers have been applied widely in the construction of various rotaxanes[7] because of the unique complexation behavior of the macrocycles toward threadlike guests such as secondary benzyl or alkyl ammonium ions.[8] Herein, we propose a strategy to integrate two different macrocyclic polyethers into one [*n*]rotaxane molecule by simultaneous twin-axial and single-axial rotaxanation (Figure 1). We firstly designed a four-component self-assembly system, which involves two macrocyclic polyethers, namely bis(*p*-phenylene-34-crown-10) (BPP34C10) and benzo-21-crown-7 (B21C7) and two secondary ammonium compounds **1** and **2**. When all materials are mixed, the [3]pseudorotaxane $\mathbf{2}_2$@BPP34C10[8b,9] and the [2]pseudorotaxane **1**@B21C7[10] are formed exclusively. The two pseudorotaxanes contain azide and alkyne groups as potential reactive sites. With the pseudorotaxanes in hand, the copper(I)-catalyzed Huisgen alkyne–azide 1,3-dipolar cycloaddition (CuAAC "click" reaction), which has often been used in rotaxane synthesis, was performed.[11] In the obtained hetero[7]rotaxane, four B21C7 rings can be stoppered by the outer phenyl groups,[10] while the central BPP34C10 is "cascade-stoppered" by the B21C7 rings.[5a] The combination of self-assembly and synthetic strategy ensures the correct position for two kinds of rings in the final product. In sharp contrast, the synthesis of higher-order rotaxanes often needs the corresponding components to contain more binding sites, which increases the synthetic difficulty; a high association constant is needed to obtain the dynamic multicomponent complex, which is required in the common "threading followed by stoppering" protocol. Our method utilizes the concept of modularization, which means that the high-order hetero[7]rotaxane is synthesized by using the highly efficient CuAAC reaction among the preorganized building blocks.

The preparation of **1** and **2** involves the condensation of the corresponding benzaldehyde with an alkyl or benzyl amine, and then reduction, protonation, and anion-exchange steps. We performed ^{1}H NMR experiments to confirm the formation of self-assembly systems in solution. It has been reported that BPP34C10 can form a 1:2 complex with secondary dibenzyl ammonium ions.[8b] From the characteristic complexation-induced chemical shifts in the ^{1}H NMR spectra, the formation of [3]pseudorotaxane $\mathbf{2}_2$@BPP34C10 and [2]pseudorotaxane **1**@B21C7 was confirmed, when the axle molecules and corresponding ring components were mixed (see Figures S28 and S38 in the Supporting Information). The signals of H_e and H_f in $\mathbf{2}_2$@BPP34C10 as well as those of H_a and H_c in **1**@B21C7 can be identified from the ^{1}H NMR spectrum of a 2:2:2:1 mixture of **1**, **2**, B21C7, and BPP34C10 (Figure 2b). These observations indicate that the two pseudorotaxanes still exist as the dominant species in the four-component system. Moreover, the ^{1}H NMR spectrum of a 1:1:1:1 mixture of **1**, **2**, B21C7, and dibenzo-24-crown-8 (DB24C8) shows that two pseudorotaxanes **1**@B21C7 and **2**@DB24C8 are predominantly formed in this four-component system (see Figure S30 in the Supporting Information).

The CuAAC reaction of **1**@B21C7 and $\mathbf{2}_2$@BPP34C10 in the presence of $Cu(MeCN)_4PF_6$ and 2,6-lutidine in dichloromethane at room temperature, and subsequent alkylation of the 1,2,3-triazole[11a] resulted in the successful synthesis of hetero[7]rotaxane **5**, which was isolated in moderate yield after purification by column chromatography. The HRMS spectrum of **5** shows a signal at *m*/*z* 663.2944, which corresponds to the product after loss of six PF_6^- ions; this finding is consistent with the calculated mass isotope distribution (Figure S52 in the Supporting Information). The methylation of the 1,2,3-triazole was performed to enhance the polarity of the final product for more efficient isolation of the rotaxane from the reactants.

To further confirm the structure of hetero[7]rotaxane **5**, we synthesized hetero[4]rotaxane **4**, which contains one DB24C8 and two B21C7 rings, as well as [3]rotaxane **3** with two B21C7 rings, by following a similar procedure. We assigned all the resonances in **3** and **4** by analyzing their 1D and 2D NMR spectra. The protons H_1, H_2, H_3, and H_c on the axle component in **3** are shifted upfield when compared with free **6**, while H_a and H_b adjacent to the outer ammonium site are shifted downfield (Figure 3c) because of the complexation of the B21C7 ring. It is notable that protons H_4 in **3** can be detected because of the stabilizing effect of the hydrogen bonding interactions between the crown ether and the ammonium hydrogen atoms. On the other hand, we noted that not only the central ammonium hydrogen atoms H_8 in **3** cannot be detected, but also that H_6, H_7, and H_f remain mostly

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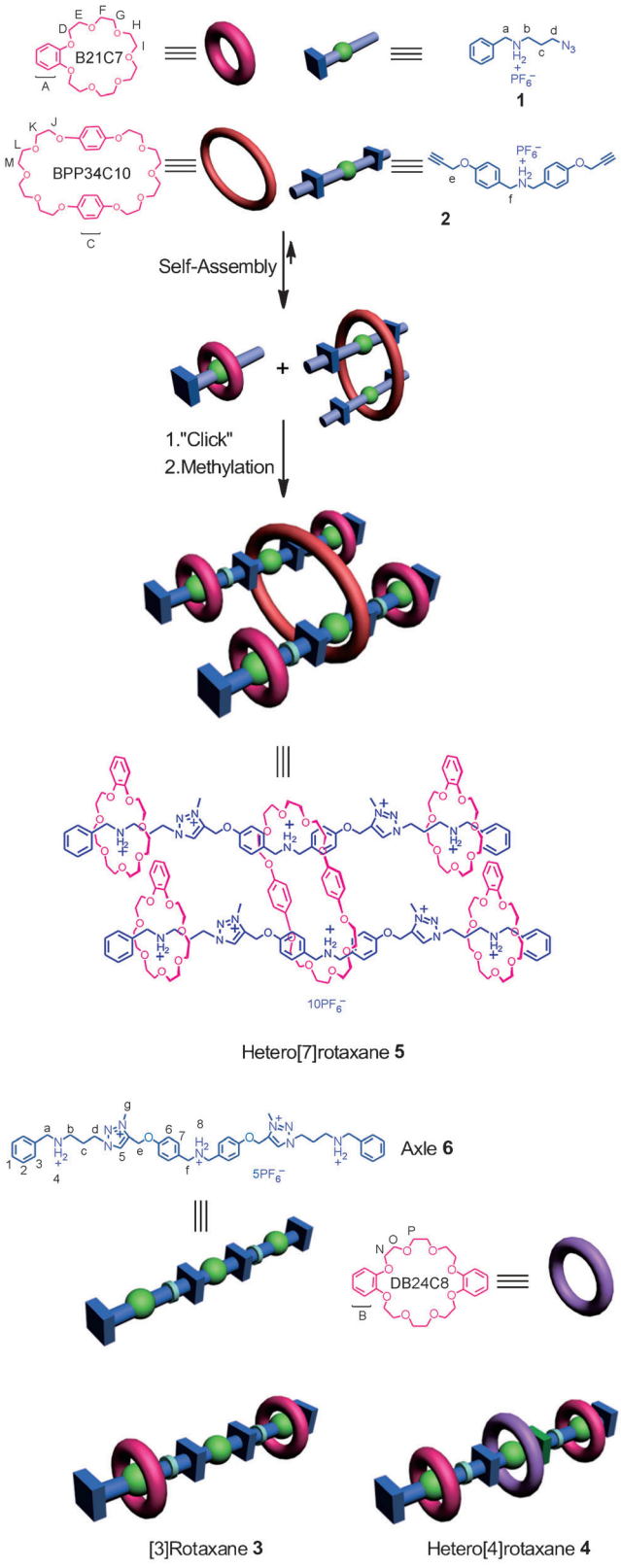

Figure 1. Structures of compounds **1**, **2**, **6**, B21C7, BPP34C10, DB24C8, [3]rotaxane **3**, and hetero[4]rotaxane **4**, and formation of hetero[7]rotaxane **5** by the modularized four-component self-assembly strategy of **1**, **2**, B21C7, and BPP34C10.

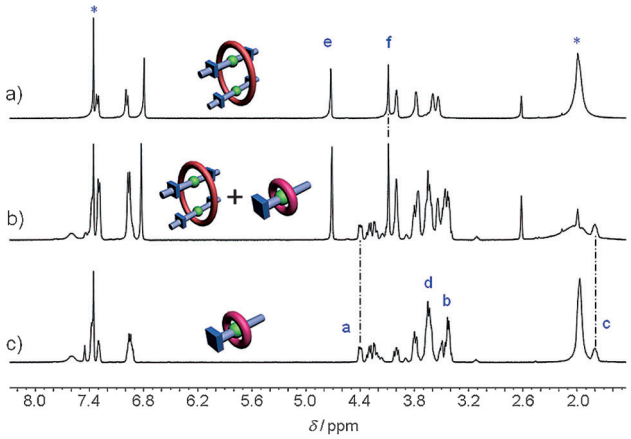

Figure 2. Partial ^{1}H NMR spectra (400 MHz, 298 K, $CDCl_3$/CD_3CN = 7:1, [**2**] = [**1**] = [B21C7] = 5.0 mM, [BPP34C10] = 2.5 mM) of a) 2:1 mixture of **2** and BPP34C10, b) 2:2:2:1 mixture of **1**, **2**, B21C7, and BPP34C10, and c) equimolar mixture of **1** and B21C7. * = solvent signal. See Figure 1 for atom labels.

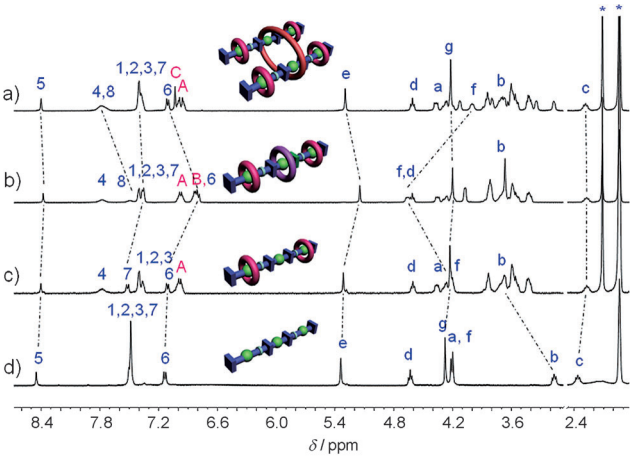

Figure 3. Partial ^{1}H NMR spectra (400 MHz, 298 K, CD_3CN) of a) hetero[7]rotaxane **5**, b) hetero[4]rotaxane **4**, c) [3]rotaxane **3**, and d) axle **6**. * = solvent signal.

in their original location, thus suggesting that the central ammonium site on the axle component in **3** is not encircled by the crown ether.

The proton signals of the two outer ammonium sites and the resonances of B21C7 in the ^{1}H NMR spectrum of hetero[4]rotaxane **4** are at similar positions to those in the spectrum of **3** (Figure 3b), thus indicating that the two B21C7 rings are still located on the outer ammonium sites of the axle component. Moreover, the resonance of the central ammonium hydrogen atoms H_8 can be found in the spectrum. The signals of hydrogen atoms H_6 and H_7 on the phenyl rings and of H_e near the central ammonium site are shifted upfield, and the signal of H_f is shifted downfield. In addition, the protons H_B of the catechol rings in DB24C8 and the ethylidene protons also show their characteristic pattern. These combined observations not only validate the formation of

hetero[4]rotaxane **4**, but are also useful for analyzing the structure of hetero[7]rotaxane **5**.

As can be seen in the ^{1}H NMR spectrum of **5** (Figure 3a), the chemical shifts of protons on the outer ammonium sites and B21C7 rings of **5** are consistent with those of **3** and **4**, thus suggesting that the location of B21C7 remains unchanged. The central ammonium hydrogen atom H_8 can still be found in the spectrum of **5**, but is more downfield-shifted than in the spectrum of **4**. H_6 and H_e are also downfield-shifted. These observations indicate that this site is bound to a ring component through a different binding mode. One explanation is that the shielding effect from the catechol rings of DB24C8 influences hydrogen atoms H_6 and H_e in **4**, while the location of the hydroquinone rings of BPP34C10 does not result in a similar shielding effect in **5**. Moreover, the signal of H_f is shifted upfield compared with both the other rotaxanes and the uncomplexed axle molecule; this observation is consistent with the twin-axial rotaxanation of BPP34C10.[8b,12] Significant changes in the chemical shifts of the protons in B21C7 and BPP34C10 of **5** are also observed (Figure S56 in the Supporting Information).

The NOESY spectrum of **5** in CD_3CN (Figure 4) shows a cross-peak (peak Q) between the protons H_f adjacent to the

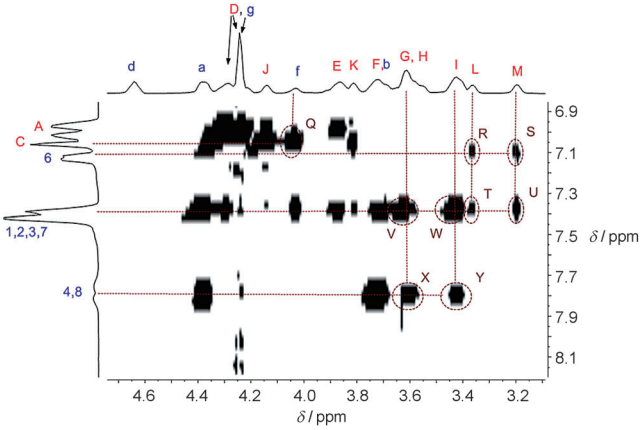

Figure 4. Partial NOESY spectrum (400 MHz, 298 K, CD_3CN) of **5**.

central ammonium center and H_C on the BPP34C10 ring, and the cross-peaks (peaks R, S, T, and U) between the polyether protons (H_L and H_M) and the phenyl protons (H_6 and H_7) on the axle component, thus clearly indicating that BPP34C10 is located near the central site on the axle. Furthermore, cross-peaks (peaks V, W, X, and Y) between the polyether protons (H_G, H_H, and H_I) of B21C7 and the outer ammonium protons H_4 and phenyl protons (H_1, H_2, and H_3) are also observed, thus confirming the location of the B21C7 rings. The energy-minimized structure of **5** obtained by molecular modeling is also consistent with the proposed structure (Figure 5).

In conclusion, we have described a methodology for preparing high-order hetero[*n*]rotaxanes through the combination of self-assembly and covalent synthetic "click" chemistry. This strategy allows precise positional control in the final [*n*]rotaxane product and will thus be beneficial for

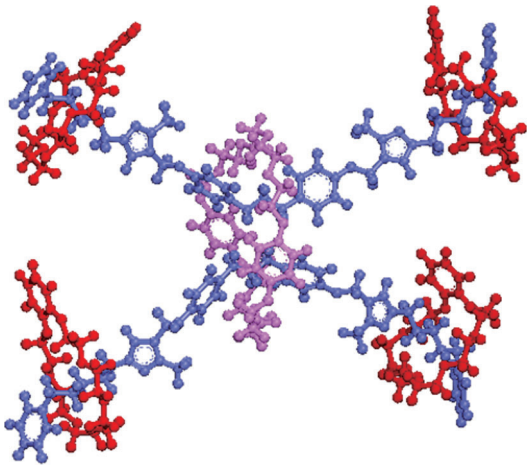

Figure 5. Energy-minimized structure of **5** obtained by a molecular modeling study. The geometry was optimized by the molecular mechanics method with dreiding forcefield. B21C7 is shown in red, axle **6** in blue, and BPP34C10 in violet.

the construction of more complicated interlocked molecules with well-defined structures and functions.

Experimental Section

General synthetic procedure as exemplified by the synthesis of hetero[7]rotaxane **5**: $Cu(MeCN)_4PF_6$ (373 mg, 1.00 mmol) and 2,6-lutidine (12 μL, 0.10 mmol) were added to a solution of **1** (246 mg, 0.73 mmol), **2** (150 mg, 0.332 mmol), B21C7[13] (475 mg, 1.33 mmol), and BPP34C10[14] (107 mg, 0.20 mmol) in dichloromethane (1.00 mL). The reaction mixture was stirred for 24 h at room temperature, and CH_3CN (5 mL) and CH_3I (5 mL) were subsequently added. The mixture was heated at 40 °C for 4 days after which the solvent was removed under reduced pressure. The crude product was suspended in acetone (40 mL), a saturated aqueous solution of NH_4PF_6 was added, and the mixture stirred until the suspension became clear. The solvent was removed and water (100 mL) was added to the residue. The resulting mixture was then filtered, washed with water, and dried. The residue was purified by column chromatography on silica gel (eluent: 20:1 acetone/MeOH) to afford **5** as a white solid (338 mg, 42%). ^{1}H NMR (400 MHz, CD_3CN): $\delta = 8.40$ (s, 4H; H_5), 7.79 (s, 12H; H_4, H_8), 7.39 (m, 28H; H_1, H_2, H_3, H_7), 7.11 (d, $J = 8.5$ Hz, 8H; H_6), 7.03 (s, 8H; H_C), 6.97 (m, 16H; H_A), 5.30 (s, 8H; H_c), 4.61 (t, $J = 7.1$ Hz, 8H; H_d), 4.37 (m, 8H; H_a), 4.30–4.20 (m, 28H; H_D, H_g), 4.13 (s, 8H; H_J), 4.00 (s, 8H; H_f), 3.85 (m, 16H; H_E), 3.80 (s, 8H; H_K), 3.75–3.64 (m, 24H; H_F, H_b), 3.62–3.53 (m, 32H; H_G, H_H), 3.42 (m, 16H; H_I), 3.34 (s, 8H; H_L), 3.17 (s, 8H; H_M), 2.29 ppm (m, 8H; H_c); ^{13}C NMR (100 MHz, CD_3CN) $\delta = 157.9$, 152.2, 146.5, 139.3, 132.0, 131.5, 129.7, 129.5, 129.1, 128.6, 124.2, 121.1 115.5, 114.7, 111.8, 70.8, 70.7, 70.3, 70.1, 70.0, 69.9, 69.4, 68.0, 67.5, 57.6, 51.3, 51.2, 50.8, 43.5, 38.3, 25.6 ppm; HRMS (ESI): *m/z*: calcd for $C_{184}H_{264}F_{24}N_{18}O_{42}P_4^{6+}$: 663.2945 [$(M\text{-}6PF_6)^{6+}$]; found: 663.2944.

Hetero[4]rotaxane **4**: Yield 72%. ^{1}H NMR (400 MHz, CD_3CN) $\delta = 8.38$ (s, 2H; H_5), 7.78 (s, 4H; H_4), 7.49 (s, 2H; H_8), 7.40 (s, 6H; H_1, H_2), 7.36 (m, 8H; H_3, H_7), 6.98 (m, 8H; H_A), 6.81 (m, 12H; H_B, H_6), 5.15 (s, 4H; H_c), 4.62 (m, 8H; H_f, H_d), 4.35 (m, 4H; H_a), 4.28 (m, 4H; H_D), 4.20 (m, 10H; H_D, H_g), 4.07 (s, 8H; H_N), 3.82 (m, 16H; H_E, H_O), 3.67 (m, 20H; H_F, H_B, H_b), 3.61–3.51 (m, 16H; H_G, H_H), 3.46–3.39 (m, 8H; H_I), 2.26 ppm (m, 4H; H_c); ^{13}C NMR (100 MHz, CD_3CN) $\delta =$ 157.1, 147.1, 146.5, 139.4, 132.0, 130.9, 129.7, 129.4, 129.1, 128.6, 125.6, 121.1, 120.8, 114.2, 112.1, 111.9, 70.8, 70.7, 70.4, 70.3, 70.1, 69.9, 69.4,

68.0, 67.5, 57.4, 51.3, 50.8, 43.5, 38.4, 25.6 ppm; HRMS (ESI): *m*/*z*: calcd for $C_{102}H_{144}F_6N_9O_{24}P^{4+}$: 506.2494 [(M-4PF$_6$)$^{4+}$]; found: 506.2491.

[3]Rotaxane **3**: Yield 76 %. ^{1}H NMR (400 MHz, CD_3CN) $\delta = 8.41$ (s, 2H; H_5), 7.77 (s, 4H; H_4), 7.52 (d, $J = 8.4$ Hz, 4H; H_7), 7.38 (m, 10H; H_1, H_2, H_3), 7.30–7.26 (m, 2H; H_8), 7.11 (d, $J = 8.4$ Hz, 4H; H_6), 6.98 (d, $J = 9.3$ Hz, 8H; H_A), 5.32 (s, 4H; H_e), 4.61 (t, $J = 6.8$ Hz, 4H; H_d), 4.38–4.32 (m, 4H; H_a), 4.31–4.16 (m, 18H; H_g, H_f, H_D), 3.84 (m, 8H; H_E), 3.67 (m, 12H; H_F, H_b), 3.55 (m, 16H; H_G, H_H), 3.45–3.36 (m, 8H; H_I), 2.32–2.22 ppm (m, 4H; H_c); ^{13}C NMR (100 MHz, CD_3CN) $\delta = 157.8$, 146.5, 139.3, 132.0, 131.9, 129.7, 129.6, 129.1, 128.6, 124.0, 121.1, 114.7, 111.9, 70.8, 70.7, 70.3, 70.1, 69.4, 68.0, 57.5, 51.3, 50.8, 50.4, 43.5, 38.4, 25.6 ppm; HRMS (ESI): *m*/*z*: calcd for $C_{78}H_{110}N_9O_{16}^{3+}$: 476.2685 [(M-5PF$_6$-2H)$^{3+}$]; found: 476.2692.

Axle **6**: See the Supporting Information for detailed synthetic procedure. Yield 91 %. ^{1}H NMR (400 MHz, CD_3CN) $\delta = 8.45$ (s, 2H; H_5), 7.49 (m, 14H; H_1, H_2, H_3, H_7), 7.14 (d, $J = 8.4$ Hz, 4H; H_6), 5.34 (s, 4H; H_e), 4.63 (t, $J = 6.9$ Hz, 4H; H_d), 4.28 (s, 6H; H_g), 4.21 (m, 8H; H_a, H_f), 3.16 (m, 4H; H_b), 2.36 ppm (m, 4H; H_c); ^{13}C NMR (100 MHz, CD_3CN) $\delta = 157.9$, 139.4, 131.9, 129.9, 129.8, 129.6, 128.9, 123.8, 114.8, 57.8, 51.5, 50.5, 50.4, 44.1, 38.3, 24.8 ppm; HRMS (ESI): *m*/*z*: calcd for $C_{42}H_{53}N_9O_2^{2+}$ [(M-5PF$_6$-3H)$^{2+}$]: 357.7156; found: 357.7173.

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