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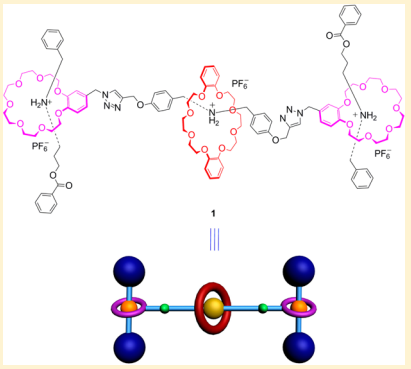
Two Stepwise Synthetic Routes toward a Hetero[4]rotaxane

Qian-Fu Luo, Lan Zhu, Si-Jia Rao, Hong Li, Qi Miao, and Da-Hui Qu*

Key Laboratory for Advanced Materials and Institute of Fine Chemicals, East China University of Science & Technology, Shanghai 200237, People's Republic of China

Supporting Information

ABSTRACT: Heterorotaxanes have been emerging as an important class of mechanically interlocked molecules and have attracted much attention in recent years. Driven by the distinguishable host−guest interactions between crown ether macrocycles and ammonium with different sizes, a novel hetero[4]rotaxane was successfully prepared by employing the combination of copper-catalyzed "click" reaction and P(n-Bu)$_3$-catalyzed esterification reaction as stoppering reactions. The hetero[4]rotaxane contains an interlocked species in which a dibenzo[24]crown-8 ring threaded by a dibenzylammonium-containing component with two benzo[21]crown-7 macrocycles at both ends to act as stoppers, and each of the two benzo[21]crown-7 rings is also threaded with a benzylalkylammonium unit to form the second interlocked species. The hetero[4]rotaxane was prepared through two different stepwise synthetic routes, and the complicated chemical structure of the hetero[4]-rotaxane was well-characterized by ^{1}H NMR spectroscopy and high-resolution electrospray ionization (HR-ESI) mass spectrometry. The investigation shows that the construction of complicated topological heterorotaxane can be achieved via distinct approaches with high efficiencies, which may provide a foundation for the construction of more sophisticated heterorotaxane systems or functional supermolecules.



INTRODUCTION

In recent years, various highly ordered and complicated mechanically interlocked molecules (MIMs)[1] have been designed, constructed, and widely used in various fields, including molecular switches and machines,[2] polymer materials,[3] drug delivery,[4] and so on. Among numerous topological architectures of MIMs, heterorotaxanes[5] have drawn much attention because of their appealing and unique structural features with the possibility for further expanded functionality. Among the macrocycles used in the construction of MIMs, crown ether derivatives have been widely used as macrocycle hosts to construct a series of supramolecular self-assembling and mechanically interlocked systems,[6] including hetero[n]-rotaxanes that contains different crown ether macrocycles. For example, Liu and co-workers[7] prepared a new twin-axial hetero[7]rotaxane derived from bis(phenylene-34-crown-10) and benzo[21]crown-7 (B21C7). Recently, a series of topologically interesting hetero[4]rotaxanes based on crown ether macrocycles have also been reported by Yin and co-workers.[8] Dibenzo[24]crown-8 (DB24C8) ring and B21C7 ring are the most extensively used crown ether macrocycles. Stoddart and co-workers[9] first demonstrated that dibenzylammonium salt can thread into a DB24C8 ring to form pseudorotaxane, while Huang and co-workers[10] for the first time found that B21C7 macrocycle can be threaded by benzylalkylammonium salts to form mechanically interlocked structures. On the basis of the two above-mentioned host−guest complexation behaviors, namely, the selective threading processes of DB24C8 ring and dibenzylammonium moiety and of B21C7 ring and benzylalkylammonium moiety, chemists have studied and constructed many hetero[n]rotaxanes using integrative self-sorting strategy.[11−13] Schalley and co-workers[13] demonstrated that the incorporation of DB24C8 and B21C7 macrocycles with two kinds of secondary ammonium in a single molecular system could lead to the formation of hetero[n]-rotaxanes by integrative self-sorting strategy. However, it still remains a necessity to develop crown ether-containing hetero[n]rotaxanes with high efficiency by various synthetic methods, which also inspired us to develop functional hetero[n]rotaxane systems. In this paper, we demonstrated two stepwise synthetic routes for the construction of a hetero[4]rotaxane that is composed of two kinds of crown ether macrocycles, B21C7 and DB24C8. The hetero[4]-rotaxane contains two kinds of interlocked species, which employ the complexation between DB24C8 and a dibenzylammonium component and between B21C7 and a benzylalkylammonium unit. The study can provide more insights and methods to construct advanced functional hetero[n]rotaxane systems with more sophisticated topological architectures.

RESULTS AND DISCUSSION

In this design, two different synthetic routes for the target heterotaxane were employed. As shown in Scheme 1, the hetero[4]rotaxane contains an interlocked species in which a DB24C8 ring is threaded by a dibenzylammonium component with two B21C7-containing rotaxanes as stoppers. Two synthetic routes can be used, shown as routes A and B; each

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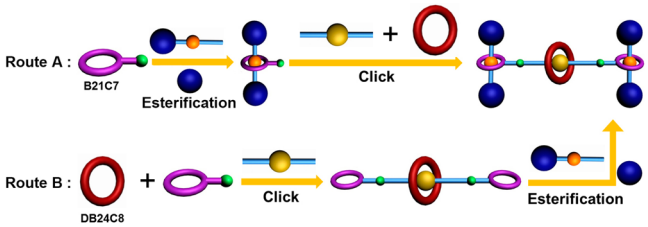
Scheme 1. Cartoon Representation of Two Stepwise Synthetic Routes for Preparation of Hetero[4]rotaxane 1

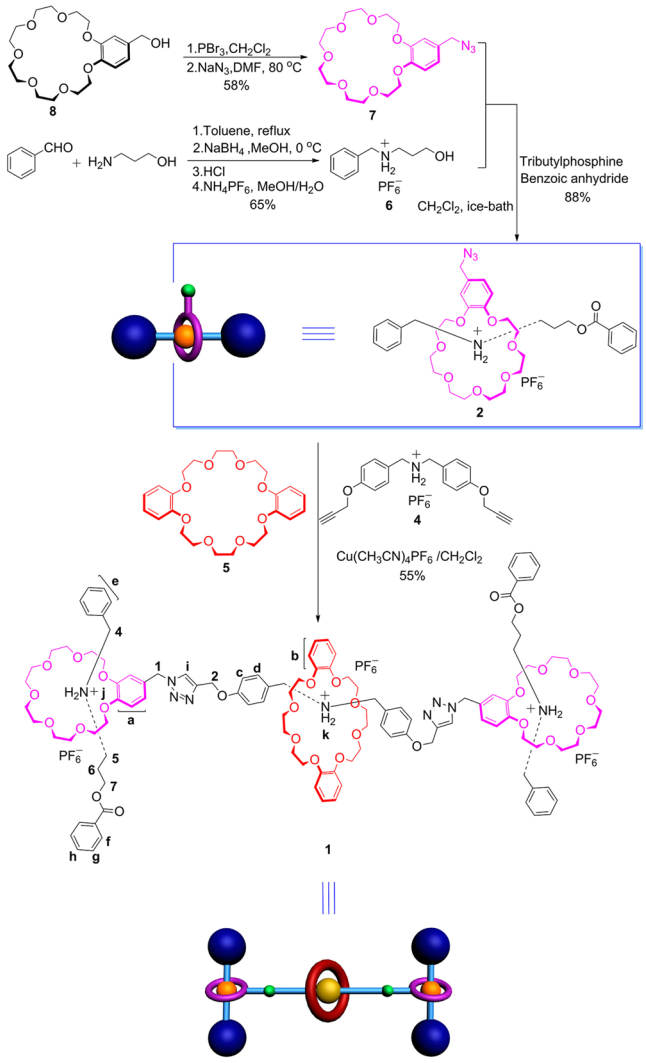


of them is composed of two stoppering reactions, in which the combination of Cu(I)-catalyzed "click" reaction between terminal azide and alkyne[14,15] and P(*n*-Bu)$_3$-catalyzed esterification[16] are used to prepare the target hetero[4]rotaxane as the stoppering reactions. Route A first involves the threading process of a benzylalkylammonium unit into an azide-functionalized B21C7 ring, which was treated by employing an esterification end-capping method to yield an azide-substituted B21C7-containing [2]rotaxane. Then the second threading process of dibenzylammonium unit into DB24C8 ring, followed by stoppering of the generated B21C7-based [2]rotaxane by the well-known copper-catalyzed click reaction, can yield the target hetero[4]rotaxane (Scheme 1, route A). On the contrary, route B involves a self-sorting process to thread DB24C8 in the first step and generate a [2]rotaxane with two B21C7 stoppers; then subsequent threading of the two B21C7 rings, followed by P(*n*-Bu)$_3$-catalyzed esterification stopping reaction, produces the target hetero[4]rotaxane (Scheme 1, route B).

Approach A employed for preparation of intermediate [2]rotaxanes **2** and target hetero[4]rotaxane **1** is depicted in Scheme 2. Compound **4** with a secondary dibenzylammonium center,[7] B21C7 derivative **8**,[17] and DB24C8 **5**[9] were prepared according to previous literature reports. Starting from B21C7 derivative **8** with a terminal hydroxyl group, treatment of **8** with PBr_3 can afford an unstable intermediate B21C7-containing benzyl bromide, which was directly converted into azide-functionalized B21C7 macrocycle **7** in the presence of sodium azide in 58% two-step total yield. Meanwhile, starting from benzaldehyde and propanolamine, a secondary benzylalkylammonium salt **6** with a terminal hydroxyl group was obtained through four steps in a sequence of Schiff's base reaction, reduction reaction, protonation, and anion exchange in an ideal 65% yield. Furthermore, the self-assembling [2]pseudorotaxane could be formed when **7** and **6** were mixed and dissolved simultaneously in the less polar solvent CH_2Cl_2, which was subsequently converted into [2]rotaxane **2** with an azide group in B21C7 macrocycle in a relatively high yield (88%) through the esterification reaction with benzoic anhydride using tributylphosphine [P(*n*-Bu)$_3$] as the catalyst. Finally, DB24C8 **5** and dibenzylammonium **4** with two alkyne groups were mixed and dissolved in CH_2Cl_2, and subsequently the well-known copper(I)-catalyzed Huisgen 1,3-dipolar cycloaddition reaction with azide-functionalized [2]rotaxane **2** led to formation of the target hetero[4]rotaxane **1** in 55% yield.

Chemical structures of the new intermediates and the target rotaxanes involved in this stepwise synthetic route A were confirmed by ^{1}H NMR spectroscopy. Figure 1 shows the partial ^{1}H NMR spectra of B21C7 derivative **7**, guest **6**, [2]rotaxane **2**, and hetero[4]rotaxane **1**. Compared with the ^{1}H NMR spectrum of B21C7 derivative **7** (Figure 1a), the crown ether

Scheme 2. Synthetic Route A for Formation of Hetero[4]rotaxane 1



protons in [2]rotaxane **2** (Figure 1c) exhibited significant changes, due to the binding effect of the benzylalkylammonium axle **6** and B21C7 derivative **7**. Meanwhile, in comparison with the spectrum of guest **6** (Figure 1b), the aromatic protons H$_e$ on the azide-containing [2]rotaxane **2** are shifted upfield with $\Delta\delta$ of −0.10 ppm (Figure 1c), and H$_5$, H$_6$, and H$_7$ adjacent to the outer ammonium site are shifted downfield with $\Delta\delta$ of 0.65, 0.10, and 0.55 ppm, respectively. It should be noted that protons H$_j$ in [2]rotaxane **2** can be detected because of the stabilizing effect of the hydrogen-bonding interaction between crown ether and ammonium hydrogen atoms, namely, the strong shielding effect of the crown ether ring. In addition, compared with the spectrum of [2]rotaxane **2** (Figure 1c), the protons H$_1$ in hetero[4]rotaxane **1** (Figure 1d) were shifted dramatically downfield (1.12 ppm), while the H$_j$ and H$_6$ were shifted slightly upfield. Of course, we observed the H$_i$ on the 1,2,3-triazole at 8.04 ppm, which suggested the Cu(I)-catalyzed azide−alkyne cycloaddition (CuAAC) "click" reaction between the azide [2]rotaxane and the alkyne compound **4** occurred successfully.

Meanwhile, synthetic route B toward the target hetero[4]-rotaxane **1** is shown in Scheme 3. In this approach, DB24C8 ring was first threaded by dibenzylammonium **4**, and then

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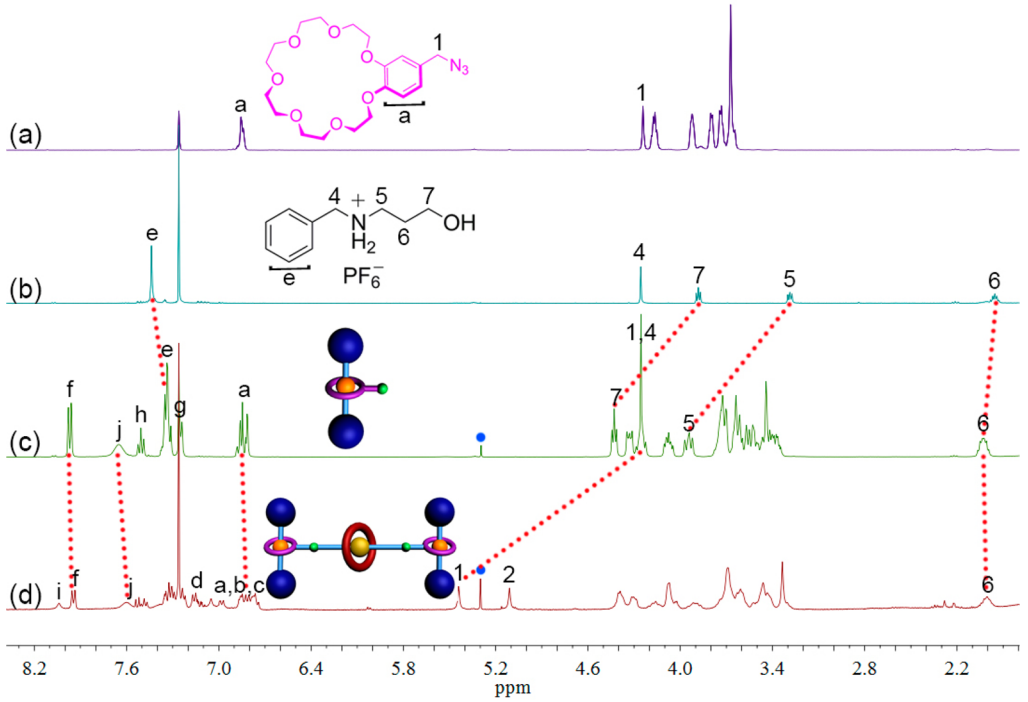
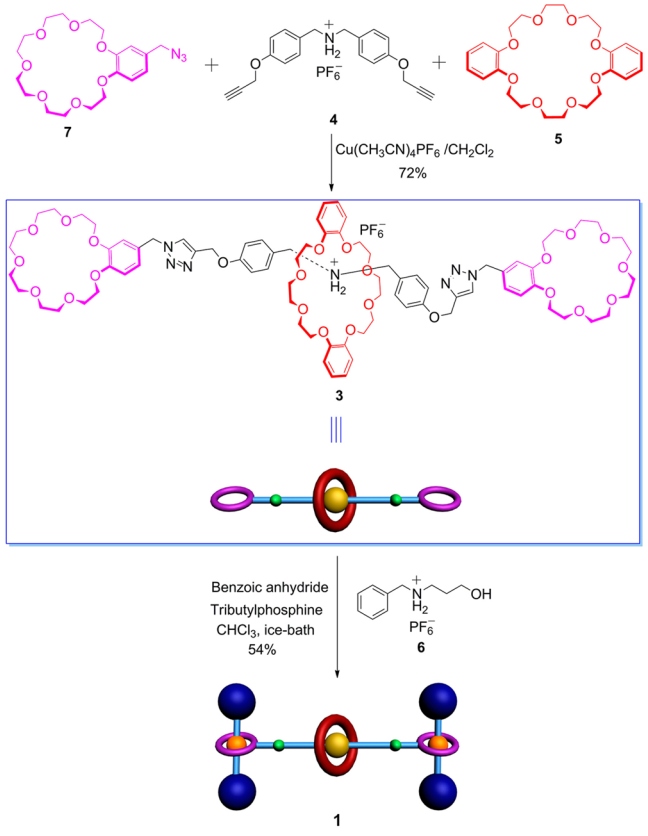


Figure 1. Partial ^{1}H NMR spectra (400 MHz, $CDCl_3$) of (a) B21C7 derivative **7**, (b) guest **6**, (c) [2]rotaxane **2**, and (d) hetero[4]rotaxane **1**. (●) Peaks from solvent CH_2Cl_2.

Scheme 3. Synthetic Route B for Construction of Hetero[4]rotaxane 1



B21C7 derivative **7** with a terminal azide group was chosen as a terminal stoppering group to yield rotaxane **3**.[18] The secondary dibenylammonium salts **4** with two alkyne groups at two ends and DB24C8 in CH_2Cl_2 solution can form the self-assembling [2]pseudorotaxane, which can further react with B21C7 derivative **7** in the presence of $[Cu(CH_3CN)_4PF_6]$ as the catalyst to get a new [2]rotaxane **3**, with one DB24C8 ring encircled on the dibenzylammonium station and the other two B21C7 rings situated at each side of the structure, in 72% yield. Subsequently, secondary benzylalkylammonium ion **6** was added to the CH_2Cl_2 solution of [2]rotaxane **3** with two B21C7 macrocycle at both ends, and the benzylalkylammonium ion **6** was threaded into the cavities of B21C7 rings to form [4]pseudorotaxane. This self-complexing [*n*]pseudorotaxane should be converted into the target hetero[4]rotaxane **1** in moderate yield (54%) through the esterification reaction with benzoic anhydride under the condition of $[P(n\text{-}Bu)_3]$ as the catalyst. It should be noted that the two different stepwise synthetic routes yield the same target compound hetero[4]-rotaxane **1**, which was confirmed by ^{1}H NMR spectroscopy and high-resolution electrospray (HR-ESI) mass spectrometry.

Partial ^{1}H NMR spectra of compound DB24C8, [2]rotaxane **3**, hetero[4]rotaxane **1**, and B21C7 derivative **7** involved in route B are shown in Figure 2. Compared with the spectrum of DB24C8 (Figure 2a), aromatic protons H_b and methylene protons on the DB24C8 ring of [2]rotaxane **3** (Figure 2b) exhibited obvious changes due to the stabilizing effect of the hydrogen-bonding interaction between crown DB24C8 and benzylammonium axle **4**. After the B21C7 moieties were end-capped by phenyl groups through esterification, H_2 and the two terminal azido protons H_i shifted downfield, while protons H_1 in B21C7 shifted upfield. The proton signals of crown ring of B21C7 and DB24C8 in the ^{1}H NMR spectrum of hetero[4]-rotaxane **1** also exhibited significant changes, due to the effect of the diammonium axle at similar positions compared with the spectrum of **3** (Figure 2c). Furthermore, the structures of hetero[4]rotaxane **1** and [2]rotaxanes **2** and **3** were also confirmed by HR-ESI mass spectroscopy. HR-ESI mass spectra

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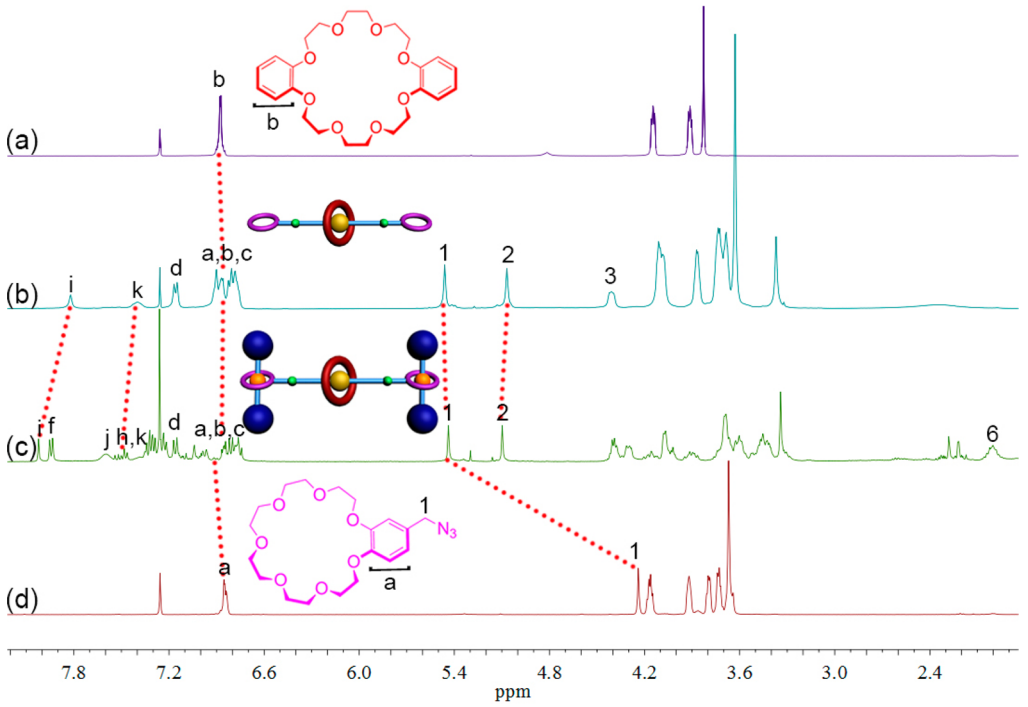

Figure 2. Partial ^{1}H NMR spectra (400 MHz, $CDCl_3$) of (a) DB24C8, (b) [2]rotaxane **3**, (c) hetero[4]rotaxane **1**, and (d) B21C7 derivative **7**.

of hetero[4]rotaxane **1**, [2]rotaxane **2**, and [2]rotaxane **3** exhibited strong peaks at *m*/*z* 705.6850, 681.3495, and 1576.7595, respectively, which correspond to the species that lose PF_6^- ion: $[\mathbf{1} - 3PF_6^-]^{3+}$ (Figure S15, Supporting Information), $[\mathbf{2} - PF_6^-]^+$ (Figure S9, Supporting Information), and $[\mathbf{3} - PF_6^-]^+$ (Figure S12, Supporting Information).

As described above, both stepwise synthetic routes could give the desired product effectively, with combinational stoppering yields of 48% and 39% for routes A and B, respectively. In fact, we had tried one-pot assembly through the self-sorting concept in threading-followed-by-stoppering to form the target hetero[4]rotaxane from five different kinds of components, such as guests **4** and **6**, hosts **5** and **7**, and stoppering benzoic anhydride, in the presence of two kinds of catalysts; however, no desired product was formed. Both addition sequences of the two kinds of catalysts did not give the desired product. Once $[Cu(CH_3CN)_4PF_6]$ met PBu_3, it produced amounts of precipitate rapidly, which may be due to coordination between PBu_3 and Cu(I) to form metal complex; then the reaction did not work.

It should be mentioned that the chemical structure of hetero[4]rotaxane **1** is stereochemically more complicated than it has been drawn in Scheme 2, which is due to the direction of threading of the benzylalkylammonium component and the asymmetric features of the B21C7 ring. Although there is free rotation about the link between B21C7 and the rest of the thread, this does not remove the isomerism, as the B21C7 macrocycle is inherently unsymmetrical. The direction of threading of the ester component can be either syn or anti when the triazole thread is drawn in a symmetrical conformation. Theoretically, the molecule exists as two diastereoisomers: the anti product has a pair of enantiomers, while the syn product is meso. However, this isomerism has no discernible effect on the ^{1}H NMR spectrum and is hard to detect, and thus no selectivity is observed between diastereoisomers. It should be noted that the stereoisomerism in rotaxane systems has been described variously as "cyclochirality" by Schill[19] and Vögtle and co-workers[20] or planar chirality by Takata and co-workers,[21] Lee and co-workers,[22] and Bordoli and Goldup,[23] due to the features of the mechanical bond, that is, the relative orientation of macrocycle and thread.

CONCLUSION

We have designed and constructed a novel, highly ordered hetero[4]rotaxane **1** through two distinct synthetic routes that employ the combination of CuAAC and esterification as stoppering reactions. Combinational utilization of the two kinds of reactions allows precise positional control step-by-step for the final hetero[4]rotaxane product and will thus be beneficial for the construction of more complicated interlocked molecules with well-defined structures and functions.

EXPERIMENTAL SECTION

General Methods and Materials. All solvents were reagent-grade, which were further dried and distilled prior to use following standard procedures. The molecular structures of the unknown compounds were confirmed via ^{1}H NMR, ^{13}C NMR, and HR-ESI mass spectroscopy.

Synthesis of 7. A mixture of **8** (1.93 g, 5.0 mmol) and phosphorus tribromide (2.70 g, 10 mmol) was stirred in dry CH_2Cl_2 (30 mL) at room temperature under argon atmosphere for 24 h. After removal of the solvent, the crude product was dissolved in *N*,*N*-dimethylformamide (DMF); then sodium azide (0.65 g, 10 mmol) was added in portions and the mixture was stirred at 80 °C for 12 h. After cooling, the solvent was evaporated off under reduced pressure, and then water (30 mL) was added. The mixture was extracted by CH_2Cl_2 (3 × 50 mL). The organic layer was dried over anhydrous sodium sulfate and then concentrated. The crude product was purified via column chromatography (SiO_2, CH_2Cl_2/MeOH = 300/1) to give **7** (0.92 g, 58%) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 6.86−6.85 (m, 3H), 4.25 (s, 2H), 4.19−4.16 (m, 4H), 3.93 (m, 4H), 3.81−3.80 (m, 4H), 3.74 (m, 4H), 3.68 (m, 8H). ^{13}C NMR (400 MHz, $CDCl_3$, 298 K) 148.9, 128.3, 121.3, 114.2, 113.9, 71.0, 70.9, 70.8, 70.4, 69.6,

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69.2, 54.4. HRMS (ESI) (m/z) $[M + K^+]^+$ calcd for $C_{19}H_{29}N_3O_7K$, 450.1643; found, 450.1637.

Synthesis of 6. A solution of benzaldehyde (2.12 g, 20 mmol) and propanolamine (1.50 g, 20 mmol) in dry toluene (80 mL) was refluxed for 24 h under argon atmosphere. After cooling, the solvent was removed under vacuum, and the residue was dissolved in MeOH (50 mL). To the solution was added $NaBH_4$ (1.52 g, 40 mmol) in portions at 0 °C. After the mixture was stirred for 12 h, the solution was poured into water, and the mixture was extracted by CH_2Cl_2 (3 × 50 mL). The organic layer was evaporated off to give the free amine compound. Concentrated HCl was added into a solution of the amine in MeOH (20 mL) to adjust the pH < 2 at room temperature. After the mixture was stirred for 2 h, the solvent was then evaporated off under reduced pressure. The residue was dissolved in MeOH (10 mL), and then saturated NH_4PF_6 (30 mL) solution was added. After the mixture was stirred for 3 h, the solvent was removed under vacuum and deionized water (30 mL) was added. The mixture was extracted by CH_2Cl_2 (3 × 50 mL). The organic layer was dried over anhydrous sodium sulfate and then concentrated. The crude product was purified via column chromatography (SiO_2, CH_2Cl_2) to give **6** (5.29 g, 65%) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 7.44 (m, 5H), 4.26 (s, 2H), 3.90−3.87 (t, J = 5.2 Hz, 2H), 3.30−3.28 (t, J = 5.2 Hz, 2H), 1.98−1.93 (m, 2H). ^{13}C NMR (400 MHz, CD_3COCD_3, 298 K) δ = 131.3, 130.0, 129.6, 129.1, 60.2, 51.3, 47.0, 27.6. HRMS (ESI) (m/z) $[M - PF_6^-]^+$ calcd for $C_{10}H_{16}NO$, 166.1232; found, 166.1225.

Synthesis of 2. To a solution of **7** (0.314 g, 0.76 mmol) and **6** (0.216 g, 0.69 mmol) in dry dichloromethane (5.00 mL) was added benzoic anhydride (0.235 g, 1.04 mmol), followed by tributylphosphine (1 μL, 0.014 mmol). The reaction mixture was stirred for 3 h at 0 °C and for another 2 h at room temperature under argon atmosphere. After evaporation, the residue was subjected to silica gel column chromatography (SiO_2/CH_2Cl_2) to give **2** (0.860 g, 88%) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 7.98−7.96 (m, 2H), 7.65 (s, 2H), 7.53−7.49 (m, 1H), 7.35−7.31 (m, 5H), 7.24 (m, 2H), 6.88−6.81 (m, 3H), 4.44−4.41 (t, 2H), 4.35−4.31 (m, 2H), 4.26 (m, 4H), 4.10−4.05 (m, 2H), 3.97−3.92 (t, 2H), 3.73−3.35 (m, 20H), 2.07−1.99 (m, 2H). ^{13}C NMR (400 MHz, $CDCl_3$, 298 K) δ 166.4, 147.0, 146.8, 133.3, 132.2, 130.0, 129.5, 129.0, 128.7, 128.4, 121.5, 111.9, 111.8, 71.4, 71.0, 70.9, 70.5, 69.6, 68.4, 61.9, 54.4, 51.3, 44.4, 26.5, 14.1, 11.4. HRMS (ESI) (m/z) $[M - PF_6^-]^+$ calcd for $C_{36}H_{49}N_4O_9$, 681.3500; found, 681.3495.

Synthesis of 1 (Route A). To a solution of **2** (0.187 g, 0.226 mmol) in dry CH_2Cl_2 (2.0 mL) were added **4** (0.034 g, 0.075 mmol), DB24C8 (0.051 g, 0.113 mmol), and $[Cu(MeCN)_4]PF_6$ (0.056 g, 0.15 mmol). The reaction mixture was stirred at room temperature under argon atmosphere for 24 h. Then the solution was poured into a saturated aqueous solution of ethylenediaminetetraacetic acid (EDTA). The mixture was extracted by CH_2Cl_2 (3 × 30 mL). The organic layer was dried over anhydrous sodium sulfate and then concentrated. The crude product was purified by column chromatography (SiO_2, CH_2Cl_2/MeOH = 200/1) to afford **1** (0.207 g, 55%) as a pale powder. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 8.04 (s, 2H), 7.96−7.94 (m, 4H), 7.60 (s, 4H), 7.54−7.47 (m, 4H), 7.34−7.29 (m, 10H), 7.24−7.22 (m, 4H), 7.17−7.15 (m, 6H), 7.05 (m, 2H), 6.99−6.97 (m, 2H), 6.85−6.74 (m, 12H), 5.44 (s, 4H), 5.11 (s, 4H), 4.40−4.29 (m, 15H), 4.20−4.16 (m, 5H), 4.07−4.03 (m, 10H), 3.95−3.86 (m, 5H), 3.74−3.52 (m, 29H), 3.53−3.42 (m, 15H), 3.34−3.30 (m, 9H), 2.01 (m, 4H). ^{13}C NMR (400 MHz, $CDCl_3$, 298 K) δ 166.4, 158.9, 147.7, 147.6, 147.5, 147.1, 138.5, 133.4, 132.2, 130.8, 130.1, 129.7, 129.5, 129.0, 128.4, 124.5, 124.0, 121.8, 119.1, 115.0, 112.9, 112.7, 71.3, 70.9, 70.1, 69.6, 68.6, 68.4, 44.4, 41.4, 37.4, 34.9, 34.5, 31.9, 31.6, 31.5, 30.2, 29.7, 29.4, 22.7, 14.1, 11.4. HRMS (ESI) (m/z) $[M - 3PF_6^-]^{3+}$ calcd for $C_{116}H_{150}N_9O_{28}/3$, 705.6858; found, 705.6850.

Synthesis of 3. A mixture of **7** (0.17 g, 0.28 mmol), **4** (0.10 g, 0.28 mmol), crown ether **5** (0.10 g, 0.28 mmol), and $[Cu(CH_3CN)_4]PF_6$ (0.11 g, 0.28 mmol) was stirred in dry CH_2Cl_2 (5 mL) at room temperature for 24 h under argon atmosphere. Then the solution was poured into a saturated aqueous solution of EDTA. The mixture was extracted by CH_2Cl_2 (3 × 50 mL). The organic layer was dried over anhydrous sodium sulfate and then concentrated. The crude product was purified via column chromatography (SiO_2, CH_2Cl_2/MeOH = 100/1) to give **3** (1.39 g, 72%) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 7.82 (s, 2H), 7.40 (s, 2H), 7.17−7.15 (m, 4H), 6.90−6.79 (m, 18H), 5.46 (s, 4H), 5.07 (s, 4H), 4.41 (s, 4H), 4.11−4.09 (m, 16H), 3.88−3.87 (m, 8H), 3.74−3.73 (m, 24H), 3.69−3.63 (m, 16H), 3.37 (m, 8H). ^{13}C NMR (400 MHz, $CDCl_3$, 298 K) δ 158.8, 149.2, 147.4, 143.5, 130.7, 127.7, 124.1, 123.5, 121.8, 121.7, 114.8, 114.4, 114.2, 112.9, 71.0, 70.9, 70.6, 70.5, 70.1, 69.6, 69.3, 69.2, 68.3, 61.7, 53.9, 51.9, 29.6. HRMS (ESI) (m/z) $[M - PF_6^-]^+$ calcd for $C_{82}H_{110}N_7O_{24}$, 1576.7602; found, 1576.7595.

Synthesis of 1 (Route B). To a solution of **3** (0.50 g, 1.47 mmol) and **6** (0.53 g, 1.47 mmol) in dry $CHCl_3$ (5.00 mL) was added benzoic anhydride (0.50 g, 2.20 mmol), followed by tributylphosphine (10.4 μL, 0.150 mmol). The reaction mixture was stirred for 3 h at 0 °C and for 2 h at room temperature under argon atmosphere. After evaporation, the residue was subjected to silica gel column chromatography (SiO_2/CH_2Cl_2/MeOH = 200/1) to give **1** (0.86 g, 54%) as a pale white powder.

■ ASSOCIATED CONTENT

Supporting Information

Characterization data for all new compounds, including ^{1}H NMR, ^{13}C NMR, and HR-ESI spectra of target hetero[4]-rotaxane **1** and [2]rotaxanes **2** and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail dahui_qu@ecust.edu.cn; fax +86-21 64252288.

Notes

The authors declare no competing financial interest.

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