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# Construction of Hetero[*n*]rotaxanes by Use of Polyfunctional Rotaxane Frameworks

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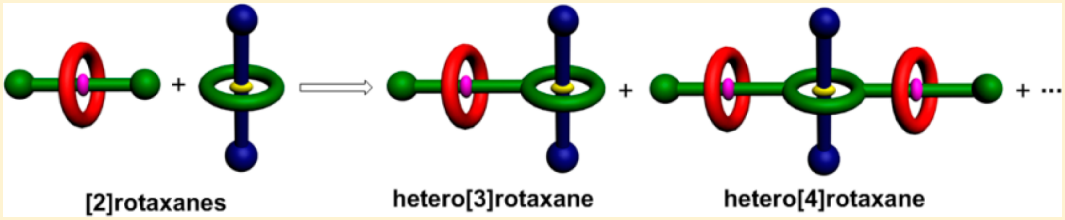
Supporting Information




**ABSTRACT:** Heterorotaxanes, one class of topological organic structures, have attracted increasing interesting during the past two decades. In general, two types of heterorotaxane structures exist, one in which two or more different macrocycles are threaded onto one dumbbell-shaped molecule and the other where one macrocycle is threaded onto two or more different dumbbell-shaped molecules. In comparison to these traditional types, another family of topologically interesting heterorotaxanes can be envisaged as arising from polyfunctional molecules that possess both host (crown ether) and guest (ammonium templates). In the present investigation, we have explored the construction of selected members of this new heterorotaxane family, which possess crown ether moieties that are wrapped around a dumbbell-shaped molecule. These structures are prepared by routes in which "stitching" processes, involving template-directed clipping reaction or olefin metathesis reactions, are used to install crown ether ring systems encircling ammonium cation centers. This is then followed by implementation of a threading-followed-by-stoppering sequence to install a second encircling crown ether ring. The results show that the polyfunctional building blocks assemble with high efficiencies. Finally, this investigation provides a foundation for future studies aimed at constructing more complicated heterorotaxane architectures, such as switchable systems, self-assembling polymers, and functional molecular machines.

## INTRODUCTION

Construction of novel topological structures has been one of the major goals of research efforts in the areas of supramolecular chemistry and self-assembly. Much attention has been given to the design and synthesis of molecular representations of mathematical topologies and to the structural analysis of these topologically interesting chemical motifs.[1] As one type of classic topological structures, mechanically interlocked molecules (MIMs), such as rotaxanes, catenanes, knots, and links, have unique structural features that enable their application in various fields, including molecular devices,[2] molecular switches and machines,[3] nanotechnology,[4] biological technology,[5] drug delivery,[4a,5b] and polymer materials.[6] As a consequence, the creation of MIMs that have novel configurations is an important aim of supramolecular self-assembly and systems chemistry.

In recent years, the focus of studies of rotaxanes has shifted from single and simple structures to those that possess functionalized and complicated structures.[7] Recently, heterorotaxanes have attracted increasing interest owing to the fact that interactions between the cyclic and linear components of these systems can lead to different chemical structures with interesting functionalities.[8] Based on a consideration of binding affinities between different host and guest components, a self-sorting strategy was developed for the efficient construction of heterorotaxanes, which have topological configurations that are similar to those of dumbbell-shaped molecules wrapped by different types of macrocyclic hosts.[9] For example, in 1996 Stoddart and co-workers[10] took advantage of the different binding affinities of dibenzo[24]crown-8 and bis(*p*-phenylene-34-crown-10) toward secondary dialkylammonium and bipyridinium ions to synthesize a novel hetero[3]pseudorotaxane.

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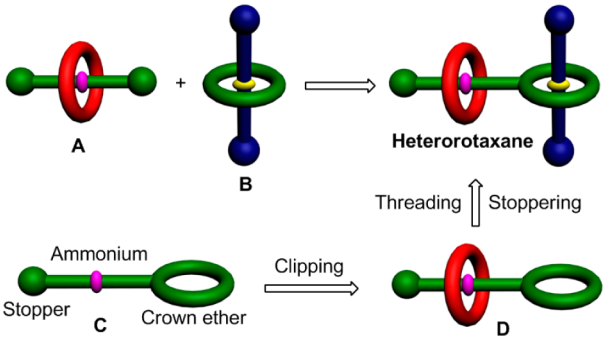
Schalley and co-workers[11,12] used the different binding behaviors of [24]crown-8 and [21]-crown-7 toward dialkylammonium ions to construct hetero[3]rotaxanes. Chiu and co-workers[13] also described the use of another self-sorting method to construct a hetero[3]rotaxane. Recently, a new twin-axial hetero[7]rotaxane derived from benzo-21-crown-7 and bis(*p*-phenylene-34-crown-10) was prepared by Liu and co-workers.[14] In addition to crown ethers, other macrocyclic hosts such as cucurbiturils,[15] cyclodextrins,[16] and others[17,18] have been utilized to construct heterorotaxanes. For example, in 2010 Wu and co-workers[19] and our group independently reported a hetero[4]-rotaxane that is generated from a crown ether and cucurbituril by employing a threading-followed-by-clipping approach.

Another family of heterorotaxanes contain members that are composed of macrocycles in which different dumbbell-shaped molecules are threaded. In 2006, Anderson and co-workers[20] described a hetero[3]rotaxane containing one stilbene and one cyanine dye moiety threaded through the center of a γ-cyclodextrin molecule. Schalley and co-workers[21] also constructed a series of heterorotaxanes by employing self-assembly of hosts containing 21-crown-7 and 24-crown-8 units onto different ammonium templates.

In the effort described below, we have designed, synthesized, and investigated several new hetero[*n*]rotaxanes ($n$ = 3, 4) and hetero[5]pseudorotaxane that have unique topological structures that are different from those of the two traditional types described above. The new types of dual-functional molecules are composed of crown ether and ammonium building blocks that play the roles of respective hosts and guests. The crown ether groups in these dual-functional molecules are designed to have the ability to wrap dumbbell-shaped molecules while the ammonium components play the roles of guest templates that thread the crown ethers. The dual-functional molecules highly efficiently assemble to form novel topological hetero[*n*]rotaxanes.

**Scheme 1. Schematic Representation of the Route for Heterorotaxane Formation**



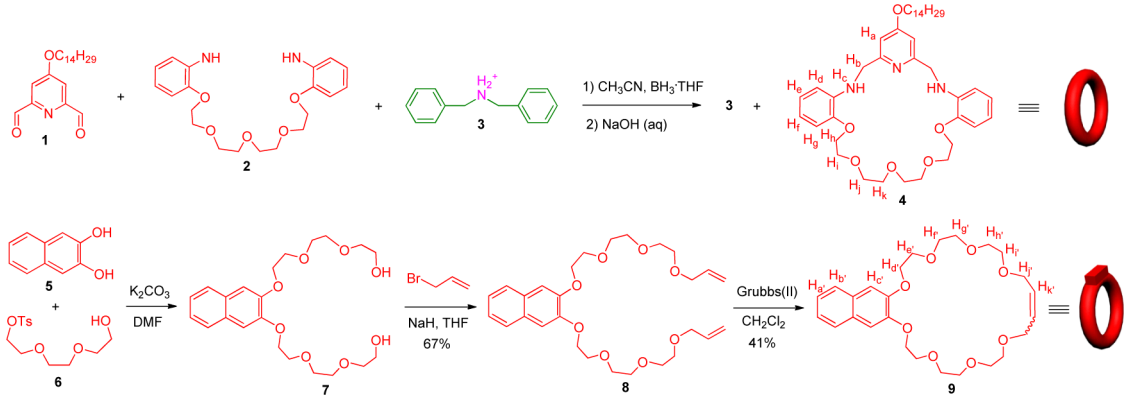

## RESULTS AND DISCUSSION

**Design of New Heterorotaxanes.** The general strategy we have developed for the preparation of novel hetero[*n*]-rotaxane is depicted pictorially in Scheme 1. In general, the heterorotaxanes are composed of two simple rotaxanes A and B, which are formed from polyfunctional host–guest building blocks. It should be noted that previous efforts have shown that dual-functional molecules of this type undergo intermolecular self-assembly to form daisy-shaped molecules and polymers.[22] Consequently, in our approach a stopper is introduced in order to avoid daisy-shaped polymer formation. The building block C contains a stopper group along with both a crown ether and an ammonium cation group. In this approach, hetero[*n*]rotaxane construction take place through a two-step self-assembly strategy in which the ammonium unit serves as a template for incorporating an encircling macrocyclic ring by using either template-directed clipping reaction or olefin metathesis reaction.[23] These processes afford intermediate D, which is then subjected to a threading-followed-by-stoppering sequence to install a second encircling crown ether ring as part of the new heterorotaxane.

**Synthesis of Building Blocks.** One group of substances needed to aid spectroscopic analysis of the processes involved in heterorotaxane formation following the strategy described above, include the aza crown and normal crown ethers **4** and **9** (Scheme 2). The synthesis of **4** is accomplished by use of dibenzylammonium ion **3** as a template and aldimine-forming condensation reaction of the 4-alkoxyl-substituted 2,6-pyridinedicarboxaldehyde **1** with tetra(ethylene glycol) bis(2-aminophenyl)ether **2** followed by $BH_3$·THF-promoted reduction. The preparation of crown ether **9** is carried out via olefin metathesis reaction (41%) of the bis-olefin-containing pseudo-crown ether **8**, which is generated by substitution reaction between naphthalenediol **5** and monotosylate **6**[24] followed by O-allylation reaction of the resulting diol **7**.

The substance selected to aid spectroscopic analysis of the stopper region in the heterorotaxane forming process is the dumbbell-shaped ammonium ester **16** (Scheme 3). The route employed to prepare **16** begins with a reductive amination reaction between 3,5-dihydroxybenzaldehyde (**12**) and 5-aminopentan-1-ol (**13**), which generates amine **14** (83%). Protonation of the amine group in **14** with excess trifluoroacetic

**Scheme 2. Synthesis of Macrocycles 4 and 9**





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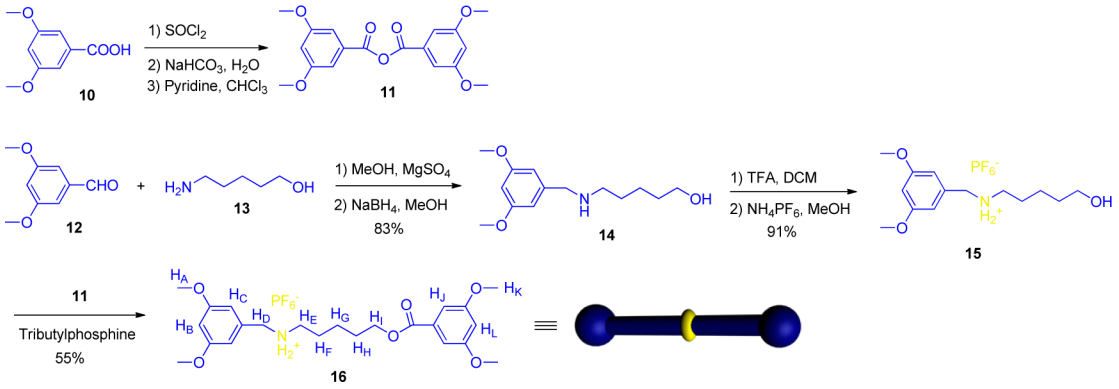
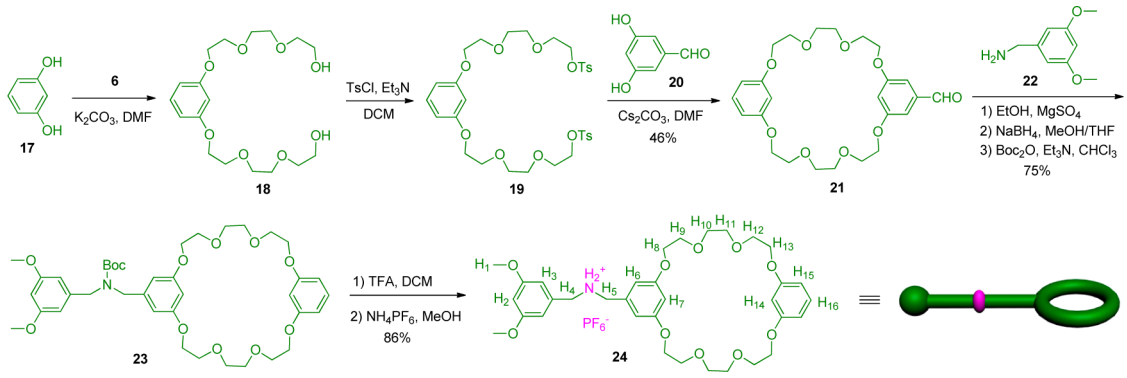
**Scheme 3. Synthesis of Dumbbell-Shaped Ammonium 16**




**Scheme 4. Synthesis of Dual-Functional Crown Ether 24**




acid followed by counterion exchange with saturated aqueous $NH_4PF_6$ affords the corresponding ammonium salt **15**. Finally, treatment of **15** with 3,5-dimethoxybenzoic anhydride (**11**), produced from the corresponding acid **10**, and catalytic tributylphosphane leads to formation of the dumbbell-shaped ammonium salt **16** in a yield of 55%. The final products and intermediates in the synthetic pathways shown in Schemes 2 and 3 as well in all of the schemes that follow were fully characterized by standard spectroscopic techniques (see Supporting Information).

With model compounds **4**, **9**, and **16** in hand, we set out to synthesize the dual-functional structural components of the heterorotaxanes. One key substance **24**, containing a crown ether and an ammonium structural unit, was synthesized utilizing the route shown in Scheme 4. Treatment of 3,5-dihydroxybenzaldehyde **20** with the pseudo-crown ether **19**,[25] formed by a route starting with bisphenol **17** and monotosylate **6**, in the presence of $Cs_2CO_3$ produces the aldehyde-substituted crown ether **21** in 46% yield. Reductive amination of **21** with 3,5-dimethoxybenzylamine (**22**) gives the precursor of the Boc-protected amino crown ether **23**, produced for the purpose of convenient purification. Boc deprotection with trifluoroacetic acid (TFA) in dry dichloromethane followed by counterion exchange with saturated aqueous $NH_4PF_6$ gives the target ammonium tethered bis(*m*-phenylene)-26-crown-8 **24**.

A similar synthetic strategy was employed to prepare the dual-functional crown ether **30**, which contains two ammonium groups and one crown ether host unit (Scheme 5). The sequence was initiated by treatment of 3,5-dihydroxybenzaldehyde (**25**) with the bistosylate **27**, generated from **25**. This process produces crown ether **28** (54%), which then undergoes reductive amination with 3,5-dimethoxybenzylamine **22** followed by N-protection by use of $Boc_2O$ to form the bis-substituted crown ether **29** (69% over three steps). Subsequent deprotection and counterion exchange affords the bisammonium tethered crown ether **30**. A single crystal of **30** suitable for crystallographic analysis was obtained by diffusion of isopropyl ether into an acetonitrile solution at room temperature (Figure S1, Supporting Information). X-ray crystallographic analysis of **30** shows that it exists in a highly ordered packed structure in the solid state (Table S1, Supporting Information).

The triangular-shaped trisammonium tethered crown ether **34** was prepared employing the pathway outlined in Scheme 6. The route begins with $Cs^+$ template-controlled reaction of 3,5-dihydroxybenzaldehyde **25** with bistosylate **31**, which forms the key trisaldehyde intermediate **32** (43%). Reductive amination of **32** with amine **22** followed by Boc protection (for the purpose of purification), deprotection, and ion exchange then gives **34**.

**Hetero[*n*]rotaxane Assembly.** A reductive amination-based stitching process was employed to affix a macrocyclic ring on the side-chain ammonium residue in the dual-functional substrate **24**. This process was accomplished by mixing **24** with dialdehyde **1** and bisaniline derivative **2** in $CD_3CN$ (pictorially represented in Scheme 7). The observation of a broad singlet at 9.76 ppm for ammonium $NH_2^+$ protons as well as a singlet at 8.24 ppm for imine (CH=N) protons in $^1H$ NMR spectra of the crude reaction mixture shows that macrocyclic bisimine formation has taken place in a reversible manner (Figure S2, Supporting Information). Reduction of the imine moieties in this substance with $BH_3$·THF followed by chromatographic purification then generates the kinetically stable [2]rotaxane-1 (78%).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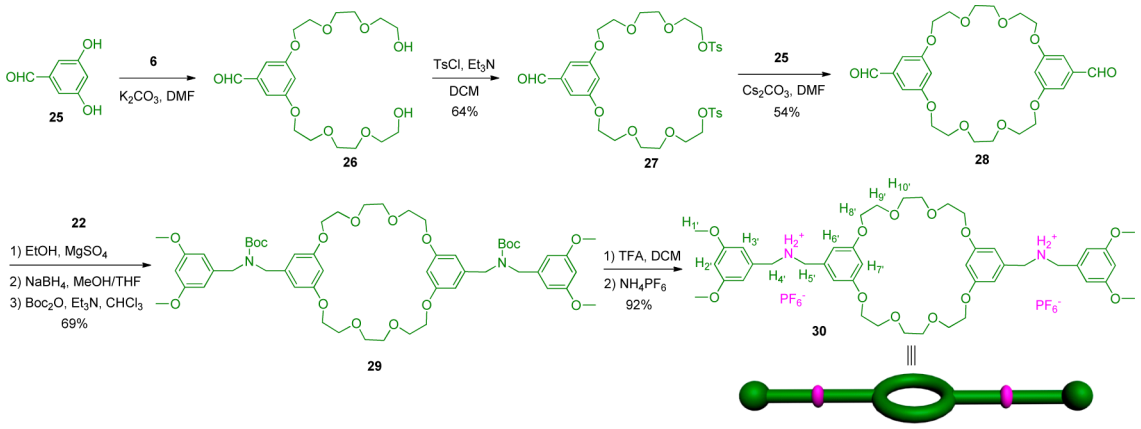
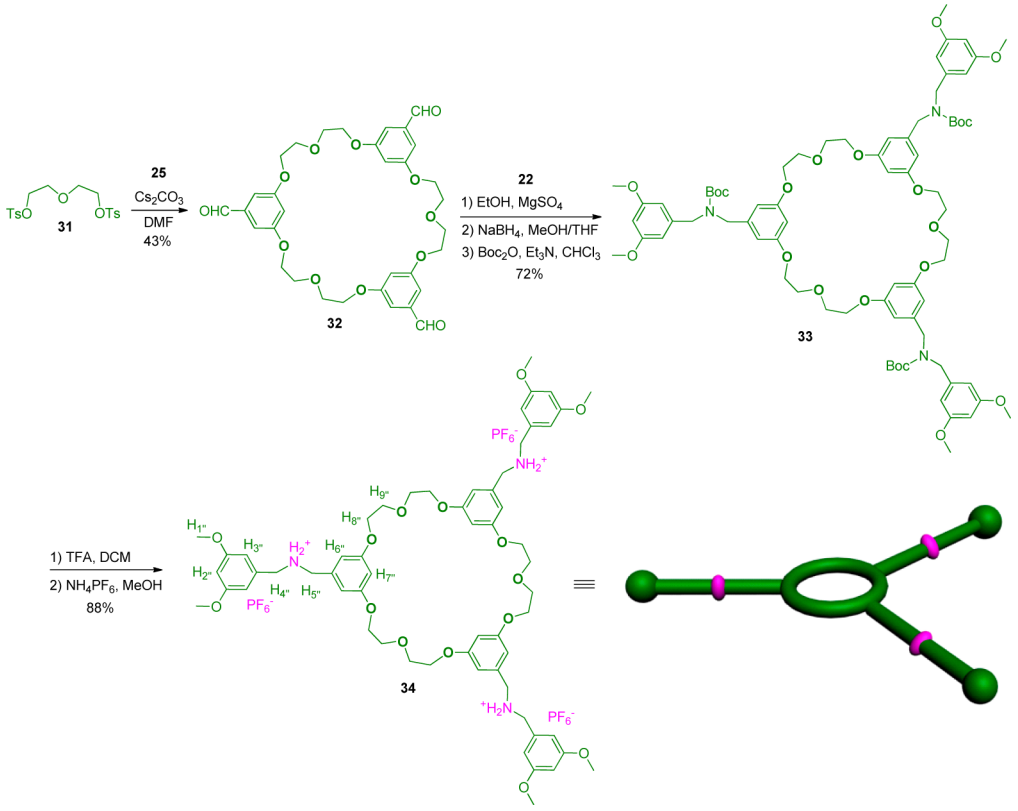
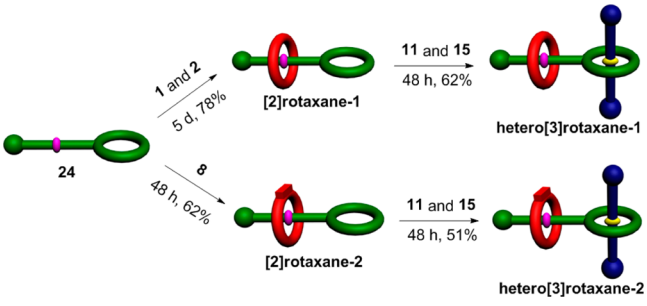
**Scheme 5. Synthesis of Dual-Functional Crown Ether 30**




**Scheme 6. Synthesis of Dual-Functional Crown Ether 34**




**Scheme 7. Synthesis of Hetero[3]rotaxane-1 and Hetero[3]rotaxane-2**




The resonance for ammonium protons in the $^1$H NMR spectrum of [2]rotaxane-1 is upfield-shifted (singlet at 8.31 ppm) compared to those of its bisimine-containing precursor. In addition, resonance of protons on the stopper units ($H_2$ and $H_3$, $H_6$ and $H_7$) of [2]rotaxane-1 (Figure 1C; see Scheme 4 for proton numbering) also display upfield shifts in comparison to those in the dual-functional molecule **24** (Figure 1B) as a result of shielding effects associated with the encircling crown ether macrocyclic ring. In contrast, the resonances for the methylene protons ($H_4$ and $H_5$) adjacent to the ammonium nitrogen are downfield-shifted. In addition, the proton ($H_b$) on the hetero-crown ether ring in [2]rotaxane-1 is downfield-shifted relative to the related proton in the model compound **4** (Figure 1A). The observed shifts in proton resonances, which are in good agreement with those noted in previous studies,[19,26] suggest that the newly installed crown ether ring system in [2]rotaxane-1 encircles the ammonium moiety of the dual-functional molecule. Additional evidence supporting this conclusion comes from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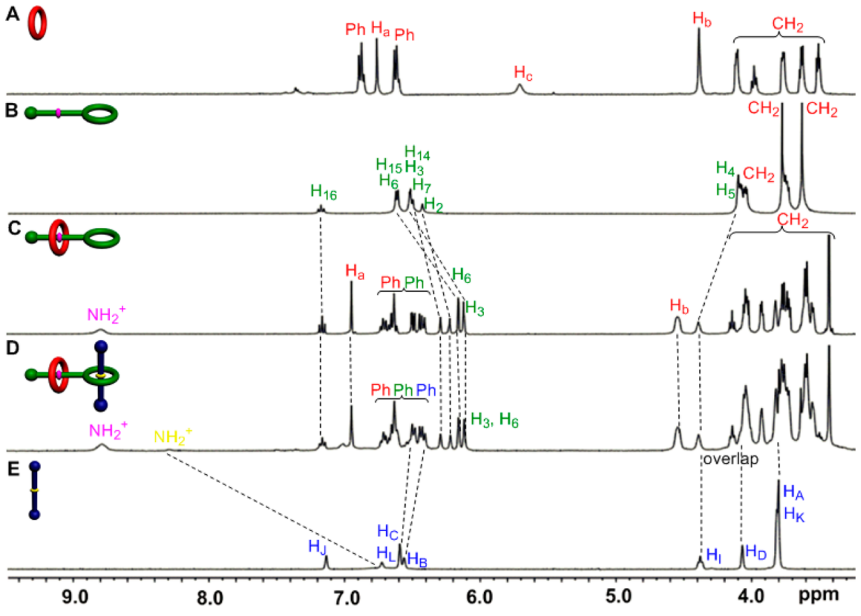


**Figure 1.** Partial $^1$H NMR spectra (400 MHz, $CD_3CN$, 298 K) of (A) **4**, (B) **24**, (C) [2]rotaxane-1, (D) hetero[3]rotaxane-1, and (E) **16**.

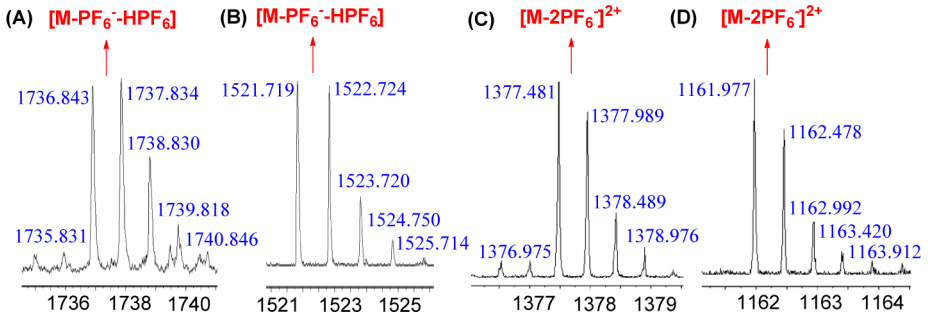


**Figure 2.** MALDI-TOF mass spectra of (A) hetero[3]rotaxane-1, (B) hetero[3]rotaxane-2, (C) hetero[4]rotaxane-3, and (D) hetero[4]rotaxane-4.

analysis of the electrospray ionization mass spectrum (ESI-MS), which contains a peak at $m/z$ 1320.3 that corresponds to the -$PF_6^-$ salt of [2]rotaxane-1 (see Supporting Information).

In order to construct the topologically novel hetero[3]-rotaxane-1, [2]rotaxane-1 was treated with the ammonium salt **15** and the resulting threaded complex was subjected to a tributylphosphine-catalyzed end-capping reaction with 3,5-dimethylbenzoic anhydride (**11**). Evidence for the formation of hetero[3]rotaxane-1 in this process comes from analysis of its $^1$H NMR spectrum. As shown in Figure 1D, an obvious downfield shift of the resonance for ammonium protons and upfield shifts for benzene ring protons ($H_B$ and $H_C$) in the comparative spectra of [2]rotaxane-1 and hetero[3]rotaxane-1 show that the crown ether unit in the former substance is threaded by the ammonium template (modeled by **16**) (Figure 1E). The results of a two-dimensional rotating Overhauser effect spectroscopy (ROESY) experiment enabled the identification of changes occurring in resonances associated with dual-functional and hetero crown ether and dumbbell-shaped components upon formation of hetero[3]rotaxane-1. For example, the benzene ring prtotons of the dual-functional molecular component are strongly shielded by the hetero crown ether component in hetero[3]rotaxane-1. In addition, obvious correlations exist between the benzene ring ($H_3$ and $H_6$) and methylene ($H_b$) protons and between protons in the dumbbell-shaped and dual-functional molecular components of hetero[3]rotaxane-1 (Figure S3, Supporting Information). Finally, inspection of the matrix-assisted laser desorption ionization time-of flight (MALDI-TOF) mass spectrum (Figure 2A) shows the presence of a peak at $m/z$ 1736.84 that is assigned to $[M - PF_6^- - HPF_6]^+$ of hetero[3]rotaxane-1 (Figure 2A).

Another method used to generate a heterorotaxane from **24** involves the use of an olefin metathesis process. In this approach, the complex formed by treatment of **24** with the bisolefin-containing crown ether **8** was reacted in the presence of Grubbs' catalyst to form [2]rotaxane-2 (67%) (Scheme 7). Subsequent threading of [2]rotaxane-2 by the ammonium ion **15** followed by end-capping reaction with 3,5-dimethylbenzoic anhydride (**11**) produced hetero[3]rotaxane-2 in 51% yield. In the $^1$H NMR spectrum, protons in the two side methylene groups ($H_4$ and $H_5$) adjacent to the ammonium residue in [2]rotaxane-2 display similar downfield shifts as seen in the spectrum of [2]rotaxane-1, while the corresponding benzene ring protons ($H_2$, $H_3$ and $H_6$, $H_7$) display similar upfield shifts owing to the shielding effect of the encircling naphthalene-based crown ether ring system (Figure 3B,C). In the $^1$H NMR spectrum of hetero[3]rotaxane-2, the resonances associated with ammonium protons on the dumbbell component are shifted downfield relative to those in the model compound **16**, suggesting that that this moiety is encircled by a crown ether group of the dual-functional component. In addition, resonances of protons $H_B$ and $H_C$ also display upfield shifts in a manner that


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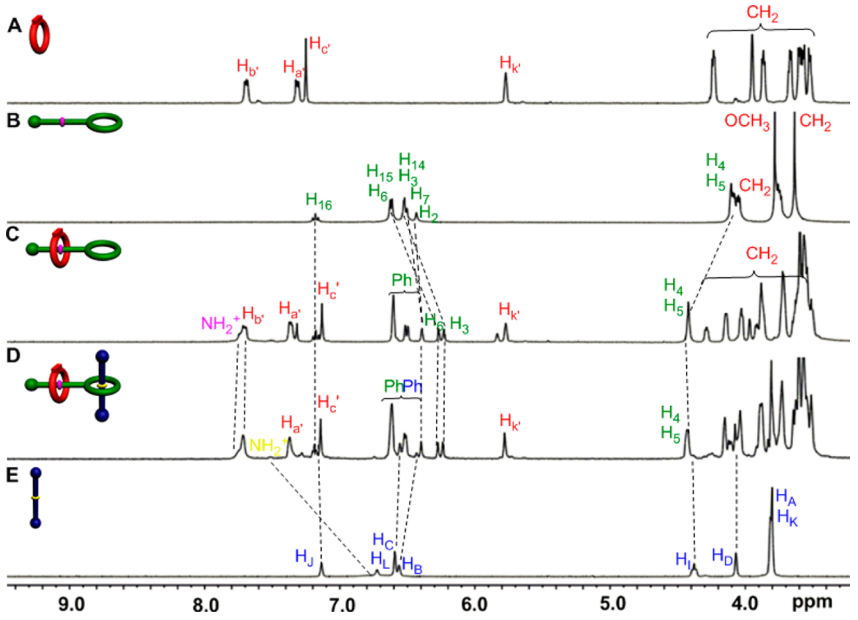
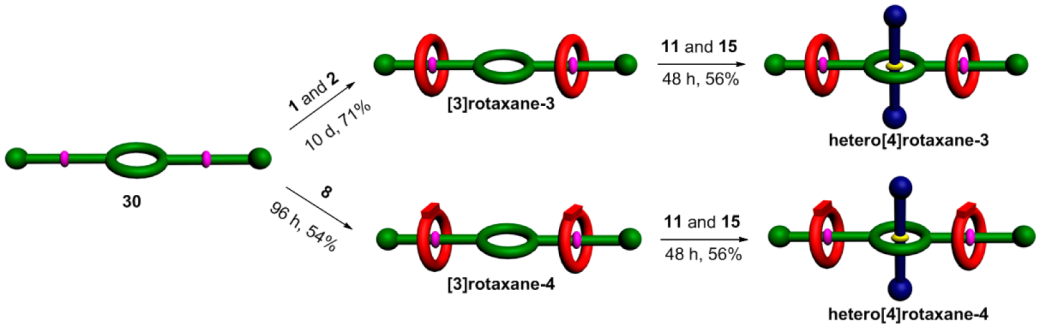



**Figure 3.** Partial $^1$H NMR spectra (400 MHz, $CD_3CN$, 298 K) of (A) **9**, (B) **24**, (C) [2]rotaxane-2, (D) hetero[3]rotaxane-2, and (E) **16**.

**Scheme 8. Synthesis of Hetero[4]rotaxane-3 and Hetero[4]rotaxane-4**




is similar to the corresponding protons in the spectrum of hetero[3]rotaxane-1 (Figure 3D,E).

The results of ESI MALDI-TOF mass spectrometric analysis support the assigned structures of [2]rotaxane-2 and hetero[3]-rotaxane-1. Specifically, the peak at $m/z$ 1105.1 in the spectrum of [2]rotaxane-2 is assigned to the $[M - PF_6^-]^+$ species, while the spectrum of hetero[3]rotaxane-2 contains a peak at $m/z$ 1521.72 for the $[M - PF_6^- - HPF_6]^+$ species (Figure 2B and Supporting Information). Finally, the two-dimensional ROESY spectrum of hetero[3]rotaxane-2 contains significant cross peaks associated with the existence of interactions between the host and guest components (Figure S4, Supporting Information).

An investigation was conducted to determine if hetero[4]-rotaxanes can be generated by use of appropriate polyfunctional substrates. The crown ether **30** was selected for this purpose because, in addition to a host component, it contains two ammonium units that can serve as templates for stitching processes that introduce crown ether rings. Template-directed clipping reaction of **30** and 2 equiv of dialdehyde **1** and diamine **2** in $CH_3CN$ was employed to generate a bisimine, which upon treatment with $BH_3$·THF produced [3]rotaxane-3 in a high yield (Scheme 8). In addition, the analogous [3]rotaxane-4 was prepared from **30** by olefin metathesis reaction of diene **8**. Both [3]rotaxanes were then subjected to threading with **15** and end-capping reactions with anhydride **15**. The overall sequences afforded hetero[4]rotaxane-3 and hetero[4]rotaxane-4 in high yields.

The steps in these assembly sequences were followed by $^1$H NMR spectroscopy. As can be seen by inspection of Figure 4 and Figure S5 (Supporting Information), the resonance of protons ($H_{2'}$, $H_{3'}$ and $H_{6'}$, $H_{7'}$) on the benzene rings of **30** are downfield-shifted in [3]rotaxane-3 and [3]rotaxane-4, while two side methylenes ($H_{4'}$ and $H_{5'}$) adjacent to the ammonium nitrogens are also downfield-shifted. The results clearly show that the template-directed clipping reaction leads to incorporation of crown ether components wrapped around the ammonium ion centers. In contrast to those of the dumbbell-shaped molecule **16**, the ammonium protons of hetero[4]-rotaxane-3 and hetero[4]rotaxane-4 are also downfield-shifted, while the resonances of benzene ring protons are upfield-shifted relative to those in **16**. Morover, the 2D ROESY spectra of both hetero[4]rotaxanes display some important correlations expected for their assigned structures (Figures S6 and S7, Supporting Information). Finally, the mass spectra of both substances contain peaks at expected $m/z$ ratios (as shown in Supporting Information and Figure 2C,D).

The final phase of this effort focused on the star-shaped dual-functional crown ether **34**, bearing three ammonium units linked to a central crown ether core (Scheme 9). Treatment of **34** with 3 equiv of dialdehyde **1** and diamine **2** in $CH_3CN$ led to formation of [4]rotaxane-5 in 62% yield. The structure of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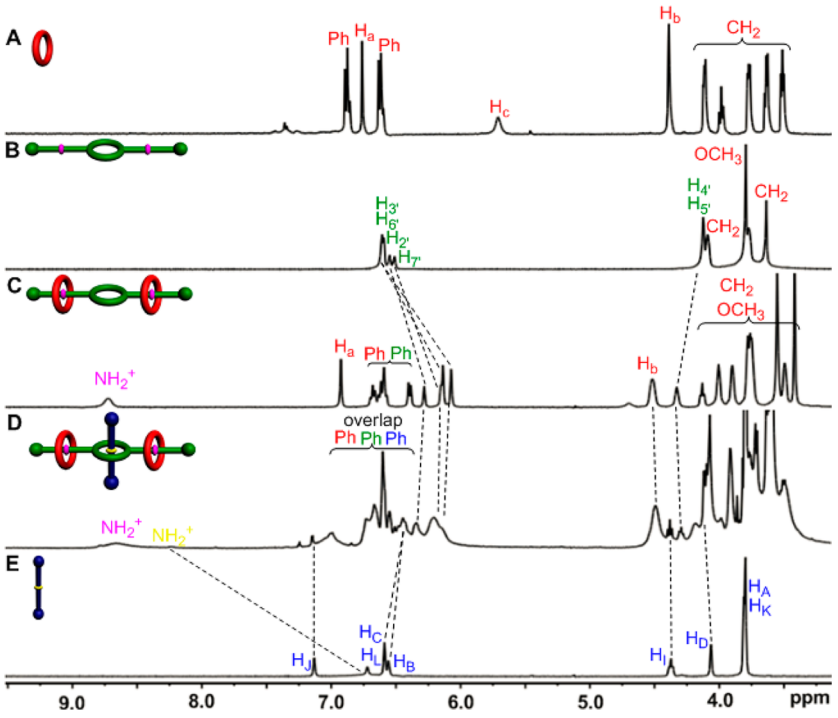
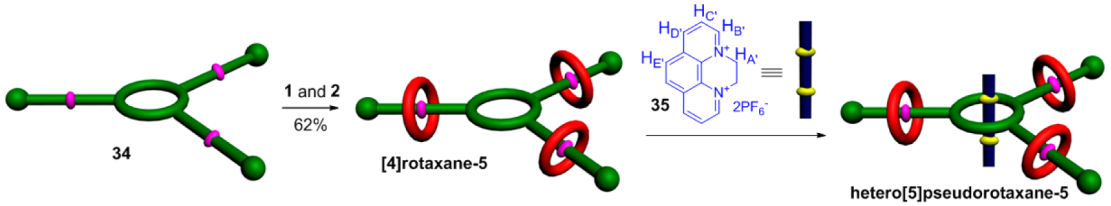



**Figure 4.** Partial $^1$H NMR spectra (400 MHz, $CD_3CN$, 298 K) of (A) **4**, (B) **30**, (C) [3]rotaxane-3, (D) hetero[4]rotaxane-3, and (E) **16**.

**Scheme 9. Synthesis of [4]Rotaxane-5 and Hetero[5]pseudorotaxane-5**



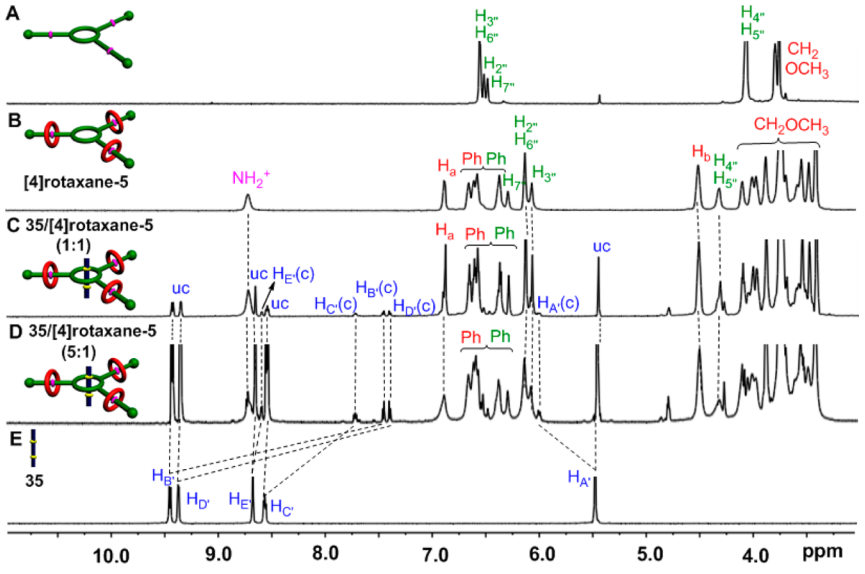




**Figure 5.** Partial $^1$H NMR spectra (400 MHz, $CD_3CN$, 298 K) of (A) **34**, (B) [4]rotaxane-5, (C) [4]rotaxane-5/**35** = 1:1, (D) [4]rotaxane-5/**35** = 1:5, and (E) phenanthroline-based ammonium **35** (E). Complexed and uncomplexed species are denoted by (c) and uc, respectively.

this substance was assigned by using $^1$H NMR spectroscopy and mass spectrometry (Figure 5A and Supporting Information). In addition, further studies revealed that [4]rotaxane-5 reacts to form hetero[5]pseudorotaxane when treated with the rod-type, phenanthroline-based ammonium ion **35**. As can be seen by viewing the $^1$H NMR spectra contained in Figure 5B,D, obvious shifts in key resonance of protons take place in this process. For instance, the aromatic protons ($H_{B'}$, $H_{C'}$, $H_{D'}$, $H_{E'}$) display obvious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upfield shifts, and protons in the nitrogen-bonded methylene groups display downfield shifts upon the addition of 1 equiv of ammonium **35** to [4]rotaxane-5. These changes are in agreement with those made in previous studies.[27] Addition of 5 equiv of **35** to [4]rotaxane-5 led to formation of more hetero[5]pseudorotaxane. On the basis of an analysis of the **35** concentration dependence of this process, an association constants for the equilibrium reaction of [4]rotaxane-5 with **35** to form hetero[5]pseudorotaxane is estimated to be $2.42 \times 10^2$ $M^{-1}$.

## CONCLUSION

In the study describe above, three polyfunctional building blocks possessing crown ether host and ammonium guest components were synthesized and used to construct new types of topologically novel hetero[*n*]rotaxanes. In the routes for preparation of the target hetero[*n*]rotaxanes, the guest ammonium units serve as templates to direct construction of encircling crown ether ring systems by use of template-directed clipping reaction or olefin metathesis reactions as key stitching processes. In these processes, the host crown ether units guide introduction of dumbbell-shaped molecules by use of a threading-followed-by stoppering strategy. The results of this effort demonstrate the feasibility of the self-assembly strategy relying on the use of polyfunctional substrates. In addition, by using this approach a number of topologically unique heterorotaxane structures have been prepared. Finally, this investigation provides a foundation for future studies aimed at constructing more complicated heterorotaxane architectures, such as switchable systems, self-assembling polymers, and functional molecular machines.

## EXPERIMENTAL SECTION

**General Methods.** All reactions and assembly processes were carried out under an argon atmosphere by using standard Schlenk techniques, unless otherwise stated. Tetrahydrofuran (THF) was distilled under nitrogen from sodium benzophenone. EtOH and MeOH were distilled under a drying pipe from magnesium−iodine. *N*,*N*-Dimethylformamide (DMF) was dried with magnesum sulfate and then distilled under vacuum. Oxybis(ethane-2,1-diyl) bis(4-methylbenzenesulfonate) **31**,[24] the 3,5-dimethoxybenzoic anhydride (**11**),[28] and the phenanthroline-based ammonium **35**[29] were prepared by using literature methods or modifications therof. All other starting materials were obtained commercially as analytical grade and used without further purification. $^1$H and $^{13}$C NMR spectra were collected with either a 400 or 600 MHz spectrometer. Mass spectra were measured in the ESI or MALDI mode.

**Synthesis of 8.** A mixture of **5** (1.60 g, 10.0 mmol), **6** (6.10 g, 20 mmol), and $K_2CO_3$ (4.20 g, 30.0 mmol) in anhydrous DMF (50 mL) was stirred for 24 h at 50 °C. The resulting mixture was cooled to room temperature and concentrated in vacuo, giving a residue that was extracted by ethyl acetate. The organic layer was then dried over anhydrous sodium sulfate and concentrated in vacuo, giving a residue was dissolved in dry THF (40 mL). To the solution was added NaH (4.00 g, 0.1 mol, 60% dispersion in mineral oil). After being stirred for 2 h, allyl bromide (2.42 g, 20.0 mmol) was added and the mixture was stirred for 36 h and then quenched by addition of saturated ammonium chloride (aq). Concentration in vacuo gave a residue that was extracted with $CH_2Cl_2$. The organic layer was dried over anhydrous sodium sulfate and concentrated in vacuo, giving a residue that was subjected to silica gel column chromatography with petroleum ether/ethyl acetate (1:1) as the eluent to form **8** as a brown liquid; yield 3.38 g, 67%. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.66 (dd, $J$ = 5.7, 3.2 Hz, 2H), 7.32 (dd, $J$ = 5.9, 3.1 Hz, 2H), 7.15 (s, 2H), 5.90 (ddd, $J$ = 16.2, 10.7, 5.4 Hz, 2H), 5.22 (dd, $J$ = 38.3, 13.7 Hz, 4H), 4.28 (t, $J$ = 4.9 Hz, 4H), 4.01 (d, $J$ = 5.4 Hz, 4H), 3.95 (t, $J$ = 4.9 Hz, 4H), 3.83−3.74 (m, 4H), 3.74−3.64 (m, 8H), 3.64−3.54 (m, 4H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 148.9, 134.7, 129.3, 126.3, 124.2, 117.1, 108.5, 72.2, 70.9, 70.7, 70.6, 69.5, 69.4, 68.3. ESI MS $m/z$ = 527.3 [M + $Na^+$], 543.3 [M + $K^+$]; calcd exact mass 504.27. Anal. Calcd for $C_{28}H_{40}O_8$: C, 66.65; H, 7.99. Found: C, 66.72; H, 7.91.

**Synthesis of 9.** To a solution of **8** (505 mg, 1.0 mmol) in dry dichloromethane (DCM, 20 mL) was added Grubbs catalyst (2nd generation) (85 mg, 0.1 mmol). After being stirred at reflux for 48 h, the mixture was diluted with ethyl vinyl ether. Concentration in vacuo gave a residue that was subjected to silica gel column chromatography with petroleum ether/ethyl acetate (1:1) as the eluent to obtain macrocycle **9** as a brown viscous liquid; yield 197 mg, 41%. $^1$H NMR (400 MHz, $CD_3CN$) $\delta$ 7.71 (dd, $J$ = 5.9, 3.3 Hz, 2H), 7.33 (dd, $J$ = 6.1, 3.2 Hz, 2H), 7.27 (s, 2H), 5.79 (s, 2H), 4.28−4.19 (m, 4H), 3.97 (s, 4H), 3.92−3.83 (m, 4H), 3.73−3.65 (m, 4H), 3.66−3.56 (m, 8H), 3.54 (d, $J$ = 5.2 Hz, 4H). $^{13}$C NMR (100 MHz, $CD_3CN$) $\delta$ 149.6, 130.0, 129.8, 126.9, 124.8, 108.6, 71.3, 71.1, 71.0, 70.9, 70.0, 69.0. ESI MS $m/z$ = 499.3 [M + $Na^+$], 515.3 [M + $K^+$]; calcd exact mass 476.24. Anal. Calcd for $C_{26}H_{36}O_8$: C, 65.53; H, 7.61. Found: C, 65.60; H, 7.67.

**Synthesis of 14.** A solution of **12** (830 mg, 5.0 mmol) and **13** (520 mg, 5.0 mmol) was stirred at reflux for 24 h in MeOH (40 mL) under an argon atmosphere. After the reaction mixture was cooled to ambient temperature, $NaBH_4$ (3.40 g, 90.0 mmol) was added portionwise to the stirring solution. After being stirred overnight, the mixture was diluted with saturated ammonium chloride (aq). Concentration in vacuo gave a residue that was extracted by ethyl acetate. The organic layer was dried over anhydrous sodium sulfate and concentrated in vacuo, giving a residue that was subjected to silica gel column chromatography with ethyl acetate as the eluent to give **14** as a viscous liquid; yield 1.05 g, 83%. $^1$H NMR (600 MHz, $CDCl_3$) $\delta$ 6.49 (s, 2H), 6.36 (s, 1H), 3.79 (s, 6H), 3.73 (s, 2H), 3.62 (t, $J$ = 5.7 Hz, 2H), 2.64 (t, $J$ = 6.5 Hz, 2H), 2.12 (s, 2H), 1.58−1.52 (m, 4H), 1.45−1.36 (m, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 160.7, 142.2, 105.9, 98.9, 62.2, 55.2, 53.9, 48.9, 32.3, 29.4, 23.3. ESI MS $m/z$ = 254.2 [M + $H^+$]; calcd exact mass 253.17. Anal. Calcd for $C_{14}H_{23}NO_3$: C, 66.37; H, 9.15; N, 5.53. Found: C, 66.43; H, 9.08, N, 5.49.

**Synthesis of 15.** To a solution of **14** (253 mg, 1.0 mmol) in dry DCM (20 mL) was added TFA (0.32 mL, 5.0 mmol) at room temperature. After being stirred for 2 h, the solution was concentrated in vacuo, giving a residue that was dissolved in MeOH (2 mL). To this solution was added saturated $NH_4PF_6$ (4 mL, aq) to yield a white precipitate, which was collected by filtration, washed with $H_2O$, and dried under vacuum to give **15**; yield 363 mg, 91%. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 6.76 (s, 2H), 6.56 (d, $J$ = 6.2 Hz, 2H), 6.47 (s, 1H), 4.31 (t, $J$ = 6.4 Hz, 2H), 4.14 (s, 2H), 3.77 (s, 6H), 3.02 (s, 2H), 2.18 (s, 2H), 1.75 (s, 4H), 1.49−1.38 (m, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 161.6, 130.9, 107.3, 102.3, 67.4, 55.4, 52.5, 47.2, 27.3, 25.2, 22.2. ESI MS $m/z$ = 252.8 [M − $PF_6^-$]; calcd exact mass 399.14. Anal. Calcd for $C_{14}H_{24}F_6NO_3P$: C, 42.11; H, 6.06; N, 3.51. Found: C, 42.05; H, 5.99; N, 3.60.

**Synthesis of 16.** To a solution of **15** (800 mg, 2.0 mmol) in acetone (5 mL) were added **11** (1.00 g, 3.0 mmol) and tributylphosphine (75 $\mu$L, 0.3 mmol). The mixture was stirred for 12 h. Conentration in vacuo gave a residue that was subjected to silica gel column chromatography with dichloromethane as the eluent to give **16** as a viscous solid; yield 620 mg, 55%. $^1$H NMR (400 MHz, $CD_3CN$) $\delta$ 7.14 (s, 1H), 6.73 (s, 1H), 6.58 (d, $J$ = 12.0 Hz, 4H), 4.38 (t, $J$ = 6.1 Hz, 2H), 4.07 (s, 2H), 3.81 (d, $J$ = 5.1 Hz, 12H), 3.03 (d, $J$ = 7.2 Hz, 2H), 1.81−1.66 (m, 4H), 1.45 (d, $J$ = 7.3 Hz, 2H). $^{13}$C NMR (100 MHz, $CD_3CN$) $\delta$ 161.8, 161.6, 161.2, 132.8, 108.2, 108.0, 107.4, 105.4, 101.4, 68.3, 55.7, 55.5, 51.7, 47.9, 27.3, 25.2, 22.4. ESI MS $m/z$ = 418.4 [M − $PF_6^-$]; calcd exact mass 563.19. Anal. Calcd for $C_{23}H_{32}F_6NO_6P$: C, 49.03; H, 5.72; N, 2.49. Found: C, 49.11; H, 5.81; N, 2.41.

**Synthesis of 21.** A mixture of **19** (680 mg, 1.0 mmol) and **20** (140 mg, 1.0 mmol) in dry DMF (400 mL) was added dropwise over a period of 24 h to a stirred suspension of $Cs_2CO_3$ (1300 mg, 4.0 mmol) in DMF (200 mL) at 80 °C. The mixture was stirred for 48 h, cooled to room temperature, and filtered. The filtrate was concentrated in vacuo, giving a residue that was extracted by ethyl acetate. The organic layer was dried over anhydrous sodium sulfate. Concentration in vacuo gave a residue that was subjected to silica gel column chromatography with DCM/ethyl acetate (5:1) as the eluent to give **21** as a white solid;


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yield 219 mg, 46%. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 9.84 (s, 1H), 7.10 (d, $J$ = 7.7 Hz, 1H), 6.99 (d, $J$ = 1.8 Hz, 2H), 6.76 (s, 1H), 6.48 (d, $J$ = 7.1 Hz, 3H), 4.17−4.09 (m, 4H), 4.10−4.01 (m, 4H), 3.85 (dd, $J$ = 10.8, 6.4 Hz, 8H), 3.78−3.69 (m, 8H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 191.7, 160.3, 159.8, 138.1, 129.6, 108.3, 107.8, 106.8, 101.8, 70.8, 69.5, 69.3, 67.6, 67.2. ESI MS $m/z$ = 499.3 [M + $Na^+$], 515.3 [M + $K^+$]; calcd exact mass 476.2. Anal. Calcd for $C_{25}H_{32}O_9$: C, 63.01; H, 6.77. Found: C, 63.09; H, 6.69.

**Synthesis of 23.** To a solution of **21** (480 mg, 1.0 mmol) in anhydrous EtOH (20 mL) was added **22** (170 mg, 1.0 mmol), with anhydrous magnesium sulfate acting as drying agent. The mixture was stirred at reflux for 24 h. Concentration in vacuo gave a residue that was dissolved in THF (15 mL) and MeOH (15 mL). To this solution was added $NaBH_4$ (150 mg, 4.0 mmol) slowly in 10 portions. After being stirred overnight, the mixture was diluted with saturated ammonium chloride (aq). Concentration in vacuo gave a residue that was extracted with absolute ethyl ether. The organic layer was dried over anhydrous sodium sulfat and concentrated in vacuo, giving a residue that was dissolved in dry chloroform (20 mL). To this solution were added $Boc_2O$ (440 mg, 2.0 mmol) and triethylamine (0.43 mL). The mixture was stirred for 24 h at room temperature and concentrated in vacuo, giving a residue that was subjected to silica gel column chromatography with petroleum ether/ethyl acetate (1:2) as the eluent to give the Boc-protected **23** as a white solid; yield 546 mg, 75%. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.13 (t, $J$ = 8.1 Hz, 1H), 6.50 (d, $J$ = 8.4 Hz, 3H), 6.40 (d, $J$ = 11.6 Hz, 3H), 6.34 (d, $J$ = 8.7 Hz, 3H), 4.33 (s, 2H), 4.25 (s, 2H), 4.18−4.07 (m, 4H), 4.05 (s, 4H), 3.95−3.79 (m, 8H), 3.78 (d, $J$ = 10.3 Hz, 6H), 3.72 (d, $J$ = 14.3 Hz, 8H), 1.49 (s, 9H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 162.5, 160.8, 159.9, 140.5, 140.2, 129.6, 106.9, 106.8, 106.1, 105.3, 101.8, 100.3, 98.9, 80.0, 70.8, 69.5, 69.5, 67.2, 63.5, 55.2, 49.4, 36.4, 28.4. ESI MS $m/z$ = 750.5 [M + $Na^+$], 766.4 [M + $K^+$]; calcd exact mass 727.36. Anal. Calcd for $C_{39}H_{53}NO_{12}$: C, 64.36; H, 7.34; N, 1.92. Found: C, 64.42; H, 7.28; N, 1.98.

**Synthesis of 24.** To a solution of **23** (730 mg, 1.0 mmol) in dry DCM (30 mL) was added TFA (0.32 mL, 5.0 mmol) at room temperature. After being stirred for 2 h, the mixture was concentrated in vacuo, giving a residue that was dissolved in MeOH (5 mL). To this solution was added saturated $NH_4PF_6$ (10 mL, aq) to give a white precipitate, which was isolated by filtration, washed with $H_2O$, and dried under vacuum to give **24**; yield 665 mg, 86%. $^1$H NMR (400 MHz, $CD_3CN$) $\delta$ 7.18 (t, $J$ = 8.2 Hz, 1H), 6.62 (m, 4H), 6.52 (m, 4H), 6.43 (s, 1H), 4.13−4.03 (m, 12H), 3.82−3.73 (m, 14H), 3.64 (s, 8H). $^{13}$C NMR (100 MHz, $CD_3CN$) $\delta$ 161.7, 160.6, 160.4, 133.6, 130.8, 108.3, 106.4, 102.9, 101.4, 70.8, 69.7, 68.1, 67.8, 55.7. ESI MS $m/z$ = 628.0 [M − $PF_6^-$]; calcd exact mass 773.28. Anal. Calcd for $C_{34}H_{46}F_6NO_{10}P$: C, 52.78; H, 5.99; N, 1.81. Found: C, 52.69; H, 6.06; N, 1.73.

**Synthesis of 27.** A mixture of **25** (138 mg, 1.0 mmol), **6** (610 mg, 2.0 mmol), and $K_2CO_3$ (420 mg, 3.0 mmol) in anhydrous DMF (50 mL) was stirred for 24 h at 50 °C. The resulting mixture was cooled to room temperature and concentrated in vacuo, giving a residue that was extracted with ethyl acetate. The organic layer was dried over anhydrous sodium sulfate and concentrated in vacuo, giving a residue that was dissolved in dry DCM (20 mL) To this solution at 0 °C were sequentially added $Et_3N$ (1.5 mL) and $p$-tosyl chloride (950 mg, 5.0 mmol) in dry DCM (30 mL) . After the mixture was stirred at ambient temperature overnight, 5 N HCl (4 mL) was added. The separated organic phase was washed with saturated brine (30 mL) and dried over $MgSO_4$, giving a residue that was concentrated in vacuo and then subjected to silica gel column chromatography with petroleum ether/ethyl acetate (1:1) as the eluent to give **27** as a brown liquid; yield 455 mg, 64%. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 9.88 (s, 1H), 7.79 (d, $J$ = 7.9 Hz, 4H), 7.34 (d, $J$ = 7.9 Hz, 4H), 7.02 (s, 2H), 6.76 (s, 1H), 4.15 (s, 8H), 3.86 (d, $J$ = 15.6 Hz, 4H), 3.73−3.61 (m, 12H), 2.43 (s, 6H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 191.9, 160.2, 144.8, 138.1, 132.7, 129.7, 127.8, 108.0, 107.8, 70.6, 69.4, 69.2, 68.6, 67.6, 21.5. ESI MS $m/z$ = 733.3 [M + $Na^+$], 749.3 [M + $K^+$]; calcd exact mass 710.21. Anal. Calcd for $C_{33}H_{42}O_{13}S_2$: C, 55.76; H, 5.96. Found: C, 55.71; H, 6.04.

**Synthesis of 28.** Compound **28** was prepared via an analogous method to that used for **21**; yield 272 mg, 54%. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 9.84 (s, 2H), 6.98 (d, $J$ = 1.8 Hz, 4H), 6.74 (s, 2H), 4.27−4.06 (m, 8H), 4.00−3.81 (m, 8H), 3.75 (s, 8H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 191.9, 160.2, 138.1, 108.4, 107.7, 70.8, 69.4, 67.6. ESI MS $m/z$ = 527.3 [M + $Na^+$], 543.2 [M + $K^+$]; calcd exact mass 504.20. Anal. Calcd for $C_{26}H_{32}O_{10}$: C, 61.90; H, 6.39. Found: C, 61.82; H, 6.46.

**Synthesis of 29.** Compound **29** was prepared by an analogous method to that used for **23**; yield 694 mg, 69%. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 6.42 (s, 4H), 6.38 (s, 2H), 6.35 (d, $J$ = 7.0 Hz, 6H), 4.34 (s, 4H), 4.26 (s, 4H), 4.07 (s, 8H), 3.85 (s, 8H), 3.76 (s, 12H), 3.74 (s, 8H), 1.49 (s, 18H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 160.8, 160.0, 155.8, 140.3, 106.5, 105.7, 105.1, 100.4, 98.9, 80.0, 70.8, 69.5, 67.2, 55.2, 49.4, 49.0, 28.4. ESI MS $m/z$ = 1029.6 [M + $Na^+$], 1045.9 [M + $K^+$]; calcd exact mass 1006.50. Anal. Calcd for $C_{54}H_{74}N_2O_{16}$: C, 64.40; H, 7.41; N, 2.78. Found: C, 64.46; H, 7.35; N, 2.73.

**Synthesis of 30.** Compound **30** was prepared by an analogous method to that used for **24**; yield 505 mg, 92%. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 6.60 (d, $J$ = 4.6 Hz, 8H), 6.54 (s, 2H), 6.51 (s, 2H), 4.12 (s, 8H), 4.08 (s, 8H), 3.79 (s, 12H), 3.77 (s, 8H), 3.63 (s, 8H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 161.8, 160.9, 133.2, 108.5, 108.4, 103.6, 101.6, 70.9, 69.6, 68.2, 55.8, 51.9, 51.8. ESI MS $m/z$ = 404.8 [M − $2PF_6^-$]$^{2+}$, 808.8 [M − $PF_6^-$ − $HPF_6$], 845.7 [M − $2PF_6^-$ + $K^+$]; calcd exact mass 1098.34. Anal. Calcd for $C_{44}H_{60}F_{12}N_2O_{12}P_2$: C, 48.09; H, 5.50; N, 2.55. Found: C, 48.03; H, 5.59; N, 2.62.

**Synthesis of 32.** A solution of **25** (138 mg, 1.0 mmol) and $Cs_2CO_3$ (1.30 g, 4.0 mmol) in dry DMF (50 mL) was stirred for 1 h at 50 °C under an argon atmosphere. Then **31** (420 mg, 1.0 mmol) in DMF (50 mL) was added dropwise over 1 h to a stirred solution. After further stirring for 24 h, the resulting mixture was allowed to cool to room temperature and filtered. After that, the solvent were removed under vacuum, and the residue was extracted by ethyl acetate and then dried over anhydrous sodium sulfate. Removal of solvent under reduced pressure and purification by silica gel column chromatography with petroleum ether/ethyl acetate (1:2) as the eluent obtained **32** as a white solid; yield 268 mg, 43%. $^1$H NMR (600 MHz, $CDCl_3$) $\delta$ 9.85 (s, 3H), 6.99 (s, 6H), 6.73 (s, 3H), 4.19−4.09 (m, 12H), 3.91 (s, 12H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 191.9, 160.2, 108.8, 107.8, 69.5, 67.8. ESI MS $m/z$ = 647.5 [M + $Na^+$], 663.5 [M + $K^+$]; calcd exact mass 624.22. Anal. Calcd for $C_{33}H_{36}O_{12}$: C, 63.45; H, 5.81. Found: C, 63.52; H, 5.75.

**Synthesis of 33.** Compound **33** was prepared by an analogous method to that used for **23**; yield 496 mg, 72%. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 6.48 (s, 3H), 6.40 (d, $J$ = 8.5 Hz, 6H), 6.34 (d, $J$ = 8.3 Hz, 9H), 4.34 (s, 6H), 4.26 (s, 6H), 4.11 (s, 12H), 3.88 (s, 12H), 3.75 (s, 18H), 1.51 (s, 27H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 160.8, 159.9, 155.9, 140.3, 106.5, 105.9, 105.7, 105.2, 100.8, 99.0, 80.0, 69.6, 67.4, 55.2, 49.4, 49.0, 28.4. ESI MS $m/z$ = 1400.8 [M + $Na^+$], 1416.8 [M + $K^+$]; calcd exact mass 1377.68. Anal. Calcd for $C_{75}H_{99}N_3O_{21}$: C, 65.34; H, 7.24; N, 3.05. Found: C, 65.41; H, 7.32, N, 2.94.

**Synthesis of 34.** Compound **34** was prepared by an analogous method to that used for **24**; yield 667 mg, 88%. $^1$H NMR (400 MHz, $CD_3CN$) $\delta$ 6.57 (d, $J$ = 2.4 Hz, 12H), 6.54 (s, 3H), 6.50 (s, 3H), 4.09 (s, 24H), 3.81 (s, 12H), 3.78 (s, 18H). $^{13}$C NMR (100 MHz, $CD_3CN$) $\delta$ 161.9, 160.9, 133.5, 133.4, 108.8, 108.4, 103.4, 101.5, 69.8, 68.4, 55.8, 51.8. ESI MS $m/z$ = 1078.46 [M − $PF_6^-$ − $2HPF_6$], 1090.46 [M − $3HPF_6$ + $Na^+$]; calcd exact mass 1515.44. Anal. Calcd for $C_{60}H_{78}F_{18}N_3O_{15}P_3$: C, 47.53; H, 5.19; N, 2.77. Found: C, 47.60; H, 5.24, N, 2.68.

**Synthesis of [2]Rotaxane-1.** A solution of **24** (77 mg, 0.1 mmol), **1** (35 mg, 0.1 mmol) and **2** (38 mg, 0.1 mmol) in dry $CH_3CN$ (10 mL) was stirred for 5 days at room temperature under an argon atmosphere. Then $BH_3$·THF (0.8 mL) was added and the solution was further stirred overnight. The solvents were removed under vacuum and the residue was purified by column chromatography (silica gel, DCM/MeCN/MeOH = 100:0:0−75:25:1) to obtain [2]rotaxane-1 as a light brown solid; yield 114 mg, 78%. $^1$H NMR (400 MHz, $CD_3CN$) $\delta$ 8.79 (s, 2H), 7.16 (t, $J$ = 8.2 Hz, 1H), 6.94 (s, 2H), 6.73−6.60 (m, 6H), 6.50 (d, $J$ = 2.4 Hz, 1H), 6.48 (d, $J$ = 2.4 Hz, 1H), 6.46−6.38 (m, 3H), 6.29 (t, $J$ = 2.2 Hz, 1H), 6.22 (d, $J$ = 2.1 Hz, 1H), 6.16

(d, $J$ = 2.2 Hz, 2H), 6.12 (d, $J$ = 2.2 Hz, 2H), 4.54 (s, 4H), 4.39 (s, 2H), 4.14 (t, $J$ = 6.6 Hz, 2H), 4.08−4.01 (m, 8H), 3.96−3.90 (m, 4H), 3.82 (s, 4H), 3.80−3.72 (m, 12H), 3.64 − 3.57 (m, 12H), 3.55 (d, $J$ = 5.3 Hz, 4H), 3.46 − 3.39 (m, 6H), 1.88−1.77 (m, 2H), 1.49 (m, 2H), 1.30 (br s, 20H), 0.89 (t, $J$ = 6.8 Hz, 3H). $^{13}$C NMR (100 MHz, $CD_3CN$) $\delta$ 161.8, 160.9, 160.7, 147.4, 137.8, 134.3, 134.2, 130.9, 122.7, 120.4, 115.9, 113.3, 112.0, 111.1, 108.0, 107.9, 107.0, 103.3, 102.8, 101.6, 71.5, 71.3, 71.1, 70.0, 69.9, 69.1, 68.5, 68.2, 56.0, 53.4, 32.4, 30.1, 29.8, 29.7, 29.1, 26.2, 23.1, 14.1. ESI MS $m/z$ = 1320.3 [M − $PF_6^-$]; calcd exact mass 1463.72. Anal. Calcd for $C_{75}H_{106}F_6N_4O_{16}P$: C, 61.50; H, 7.29; N, 3.83. Found: C, 61.33; H, 7.35; N, 3.76.

**Synthesis of [2]Rotaxane-2.** Compounds **24** (193 mg, 0.25 mmol) and **8** (126 mg, 0.25 mmol) were dissolved in anhydrous $CH_2Cl_2$ (50 mL) and stirred for 2 h at room temperature under an argon atmosphere. Then Grubbs catalyst (2nd generation) (9 mg, 0.01 mmol) was added and the resulting mixture was refluxed for 48 h. The reaction was allowed to cool to room temperature and quenched by addition of ethyl vinyl ether. The reaction was stirred for an additional 1 h. The excess solvent was removed in vacuo and purified on a silica gel column with DCM/MeOH = 100:0−50:1 as the eluent to obtain [2]rotaxane-2 as a brown solid; yield 209 mg, 67%. $^1$H NMR (400 MHz, $CD_3CN$) $\delta$ 7.70 (dd, $J$ = 6.0, 3.3 Hz, 4H), 7.36 (dd, $J$ = 6.0, 3.1 Hz, 2H), 7.18 (t, $J$ = 8.3 Hz, 1H), 7.13 (s, 2H), 6.60 (s, 4H), 6.50 (d, $J$ = 8.2 Hz, 2H), 6.39 (s, 1H), 6.25 (d, $J$ = 14.9 Hz, 2H), 5.77 (s, 2H), 4.42 (s, 4H), 4.13 (s, 4H), 4.02 (d, $J$ = 4.2 Hz, 4H), 3.88 (s, 8H), 3.72 (d, $J$ = 3.1 Hz, 8H), 3.60 (t, $J$ = 6.6 Hz, 16H), 3.61−3.51 (m, 18H). $^{13}$C NMR (100 MHz, $CD_3CN$) $\delta$ 161.5, 160.6, 160.5, 148.8, 147.7, 134.0, 139.0, 130.7, 129.8, 129.6, 126.9, 125.1, 124.9, 108.6, 108.4, 108.2, 107.9, 106.7, 103.0, 102.6, 100.9, 71.4, 71.1, 70.8, 70.6, 70.4, 70.4, 70.0, 69.8, 69.7, 69.5, 68.9, 68.5, 68.0, 67.9, 55.6. ESI MS $m/z$ = 1105.1 [M − $PF_6^-$]; calcd exact mass 1249.52. Anal. Calcd for $C_{60}H_{82}F_6NO_{18}P$: C, 57.64; H, 6.61; N, 1.12. Found: C, 57.71; H, 6.52; N, 1.18.

**Synthesis of Hetero[3]rotaxane-1.** To a solution of [2]rotaxane-1 (146 mg, 0.1 mmol) and **15** (40 mg, 0.1 mmol) in dichloromethane (3 mL) were added **11** (52 mg, 0.15 mmol) and tributylphosphine (7.0 $\mu$L, 0.03 mmol). After the reaction mixture was stirred for 48 h at room temperature under an argon atmosphere, water was added and the reaction mixture was stirred for an additional 1 h. After filtration, the filtrate was washed with 5% sodium carbonate solution and then saturated ammonium hexafluorophosphate solution and dried over anhydrous magnesium sulfate. The solvents were removed under vacuum and the residue was purified by column chromatography (silica gel, DCM/MeOH = 100:0−50:1) to obtain the hetero[3]-rotaxane-1 as a viscous solid; yield 126 mg, 62%. $^1$H NMR (600 MHz, $CD_3CN$) $\delta$ 8.79 (s, 4H), 7.14−7.18 (m, 2H), 6.95 (s, 2H), 6.72−6.70 (t, $J$ = 6.0 Hz, 2H), 6.66−6.61 (m, 6H), 6.53 (s, 2H), 6.50−6.48 (m, 2H), 6.43 (d, $J$ = 12 Hz, 2H), 6.40 (s, 1H), 6.29 (s, 1H), 6.21 (s, 1H), 6.15 (s, 2H), 6.11 (s, 2H), 4.54 (s, 4H), 4.40 (s, 2H), 4.14 (t, $J$ = 6.0 Hz, 2H), 4.08−4.02 (m, 10H), 3.92 (t, $J$ = 6.0 Hz, 4H), 3.81 (t, $J$ = 6.0 Hz, 6H), 3.80−3.76 (m, 10H), 3.75 (d, $J$ = 6.0 Hz, 4H), 3.72 (t, $J$ = 6.0 Hz, 4H), 3.63−3.58 (m, 12H), 3.53 (d, $J$ = 6.0 Hz, 4H), 3.49 (t, $J$ = 6.0 Hz, 4H), 3.42 (s, 6H), 3.00 (t, $J$ = 12 Hz, 2H), 1.84−1.81 (m, 2H), 1.72−1.67 (m, 2H), 1.50−1.47 (m, 4H), 1.42−1.37 (m, 2H), 1.29 (br s, 20H), 0.89 (t, $J$ = 6.0 Hz, 3H). $^{13}$C NMR (100 MHz, $CD_3CN$) $\delta$ 167.3, 161.9, 161.8, 161.6, 161.4, 160.9, 160.7, 160.9, 147.2, 137.5, 135.5, 134.9, 130.7, 129.2, 122.0, 120.0, 112.8, 110.7, 109.3, 108.3, 108.1, 107.6, 107.5, 107.0, 106.3, 105.7, 104.0, 103.4, 103.0, 102.7, 101.6, 101.2, 71.9, 71.8, 71.0, 69.8, 69.6, 69.1, 68.1, 61.7, 55.9, 55.8, 55.6, 53.2, 51.8, 50.4, 48.1, 32.3, 30.0, 29.7, 29.2, 26.3, 26.0, 24.1, 23.0, 14.0, 13.5. MALDI-TOF MS: $m/z$ = 1736.84 [M − $PF_6^-$ − $HPF_6$], $m/z$ = 1882.76 [M − $PF_6^-$]; calcd exact mass 2027.92. Anal. Calcd for $C_{98}H_{139}F_{12}N_5O_{22}P_2$: C, 58.01; H, 6.90; N, 3.45. Found: C, 58.11; H, 6.83; N, 3.52.

**Synthesis of Hetero[3]rotaxane-2.** Hetero[3]rotaxane-2 was prepared by an analogous method to that used for hetero[3]rotaxane-1; yield 92 mg, 51%. $^1$H NMR (600 MHz, $CD_3CN$) $\delta$ 7.71 (s, 4H), 7.37 (s, 2H), 7.19 (t, $J$ = 12.0 Hz, 2H), 7.14 (s, 2H), 6.61 (br s, 6H), 6.55 (s, 1H), 6.52 (d, $J$ = 6.0 Hz, 3H), 6.41 (s, 2H), 6.27 (s, 1H), 6.24 (s, 1H), 5.78 (s, 2H), 4.43 (s, 4H), 4.24 (s, 2H), 4.15−4.10 (m, 6H), 4.07−4.04 (m, 6H), 3.88 (br s, 8H), 3.83 (br s, 8H), 3.73 (s, 8H), 3.64−3.51 (m, 36H), 3.03 (t, $J$ = 6.0 Hz, 2H), 1.51−1.30 (m, 6H), 0.95−0.91 (m, 2H). $^{13}$C NMR (100 MHz, $CD_3CN$) $\delta$ 161.9, 161.6, 161.0, 160.7, 160.7, 147.9, 134.1, 134.0, 133.4, 130.7, 129.9, 126.9, 125.1, 124.9, 108.6, 108.4, 108.3, 108.0, 107.7, 107.0, 103.1, 102.7, 101.6, 101.0, 71.2, 70.9, 70.5, 70.1, 70.0, 69.8, 69.6, 69.0, 68.2, 68.0, 61.7, 55.8, 55.8, 55.6, 53.2, 51.8, 48.2, 32.0, 25.9, 23.0, 13.0. MALDI-TOF MS $m/z$ = 1521.72 [M − $PF_6^-$ − $HPF_6$]; calcd exact mass 1812.70. Anal. Calcd for $C_{83}H_{114}F_{12}N_2O_{24}P_2$: C, 54.96; H, 6.34; N, 1.54. Found: C, 54.89; H, 6.39; N, 1.61.

**Synthesis of [3]Rotaxane-3.** [3]Rotaxane-3 was prepared by an analogous method to that used for [2]rotaxane-1; yield 178 mg, 71%. $^1$H NMR (400 MHz, $CD_3CN$) $\delta$ 8.73 (s, 4H), 6.93 (s, 4H), 6.69 (t, $J$ = 7.1 Hz, 4H), 6.64−6.58 (m, 8H), 6.40 (d, $J$ = 7.5 Hz, 4H), 6.29 (s, 2H), 6.15 (d, $J$ = 6.0 Hz, 6H), 6.08 (s, 4H), 4.53 (s, 8H), 4.34 (s, 4H), 4.14 (t, $J$ = 6.3 Hz, 4H), 4.01 (s, 8H), 3.91 (s, 8H), 3.79−3.76 (m, 24H), 3.56 (s, 16H), 3.50 (s, 8H), 3.43 (s, 12H), 1.86−1.79 (m, 4H), 1.53−1.48 (m, 4H), 1.30 (s, 40H), 0.89 (t, $J$ = 8.0 Hz, 6H). $^{13}$C NMR (100 MHz, $CD_3CN$) $\delta$ 167.4, 161.6, 160.6, 147.2, 137.5, 135.0, 134.9, 122.1, 120.0, 112.7, 110.7, 109.4, 107.5, 103.0, 101.5, 72.0, 71.8, 71.0, 69.6, 69.2, 68.1, 68.0, 55.6, 53.4, 50.5, 32.3, 30.1, 29.8, 26.4, 23.1, 14.1. MALDI-TOF MS $m/z$ = 2191.73 [M − $PF_6^-$ − $HPF_6$]; calcd exact mass 2481.26. Anal. Calcd for $C_{126}H_{182}F_{12}N_8O_{24}P_2$: C, 60.95; H, 7.39; N, 4.51. Found: C, 61.04; H, 7.25; N, 4.66.

**Synthesis of [3]Rotaxane-4.** [3]Rotaxane-4 was prepared by an analogous method to that used for [2]rotaxane-2; yield 112 mg, 54%. $^1$H NMR (600 MHz, $CD_3CN$): $\delta$ 7.71 (s, 8H), 7.37 (s, 4H), 7.17 (s, 1H), 7.13 (s, 2H), 7.08 (s, 1H), 6.63 (s, 2H), 6.59 (d, $J$ = 9.6 Hz, 6H), 6.28−6.14 (m, 4H), 6.04 (s, 2H), 5.77 (s, 2H), 4.50 (s, 4H), 4.43 (s, 4H), 4.24 (s, 4H), 4.15 (s, 4H), 4.10 (s, 2H), 4.07 (s, 4H), 4.03 (s, 4H), 3.89 (s, 4H), 3.83 (s, 6H), 3.80 (s, 6H), 3.75 (s, 6H), 3.71−3.55 (m, 36H), 3.53 (s, 12H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 161.1, 160.9, 160.1, 147.1, 147.0, 132.9, 129.1, 126.5, 124.7, 108.0, 107.5, 107.2, 102.4, 70.7, 70.4, 70.2, 70.0, 69.4, 69.1, 68.6, 68.4, 67.4, 55.5, 55.2, 52.6. MALDI-TOF MS $m/z$ = 1760.41 [M − $PF_6^-$ − $HPF_6$]; calcd exact mass 2050.83. Anal. Calcd for $C_{96}H_{132}F_{12}N_2O_{28}P_2$: C, 56.19; H, 6.48; N, 1.37. Found: C, 56.26; H, 6.55; N, 1.32.

**Synthesis of Hetero[4]rotaxane-3.** Hetero[4]rotaxane-3 was prepared by an analogous method to that used for hetero[3]rotaxane-1; yield 170 mg, 56%. $^1$H NMR (400 MHz, $CD_3CN$) $\delta$ 8.65 (s, 1H), 7.15−6.99 (m, 4H), 6.73−6.67 (m, 8H), 6.60 (br s, 8H), 6.58−6.55 (m, 2H), 6.51−6.44 (m, 4H), 6.34 (br s, 4H), 6.20 (br s, 8H), 4.49 (s, 8H), 4.38 (t, $J$ = 6.4 Hz, 2H), 4.29 (s, 2H), 4.18 (s, 4H), 4.12 (d, $J$ = 4.0 Hz, 4H), 4.10−4.07 (m, 12H), 3.92 (s, 8H), 3.82−3.79 (m, 18H), 3.77−3.71 (m, 12H), 3.64−3.58 (m, 28H), 3.51−3.49 (m, 6H), 3.02 (t, $J$ = 8.0 Hz, 2H), 1.83−1.85 (m, 4H), 1.79−1.69 (m, 4H), 1.50−1.47 (m, 6H), 1.29 (br s, 40H), 0.90 (t, $J$ = 8.0 Hz,6H). The $^{13}$C NMR spectrum was not collected due to the poor solubility of hetero[4]-rotaxane-3. MALDI-TOF MS $m/z$ = 1377.48 [M − 2$PF_6^-$]$^{2+}$; calcd exact mass 3044.44. Anal. Calcd for $C_{149}H_{214}F_{18}N_9O_{30}P_3$: C, 58.75; H, 7.08; N, 4.14. Found: C, 58.82; H, 7.05; N, 4.08.

**Synthesis of Hetero[4]rotaxane-4.** Hetero[4]rotaxane-4 was prepared by an analogous method to that used for hetero[3]rotaxane-1; yield 128 mg, 49%. $^1$H NMR (600 MHz, $CD_3CN$) $\delta$ 7.75−7.70 (m, 8H), 7.37 (dd, $J$ = 6.1, 3.2 Hz, 4H), 7.31 (s, 4H), 7.16−7.14 (m, 2H), 6.89 (s, 4H), 6.63−6.60 (m, 12H), 6.58−6.56 (m, 2H), 6.52 (d, $J$ = 2.0 Hz, 2H), 6.27 (d, $J$ = 2.2 Hz, 2H), 5.77 (s, 2H), 4.45−4.43 (m, 4H), 4.39 (t, $J$ = 6.0 Hz, 2H), 4.32−4.28 (m, 4H), 4.13 (s, 8H), 4.10−4.06 (m, 8H), 3.92−3.89 (m, 8H), 3.83 (s, 4H), 3.82 (s, 8H), 3.80 (s, 12H), 3.78−3.76 (dd, $J$ = 5.4, 3.4 Hz, 8H), 3.72−3.70 (m, 6H), 3.66−3.63 (m, 12H), 3.62−3.60 (m, 12H), 3.58 (br s, 12H), 3.54 (br, 8H), 3.04 (s, 2H), 1.75−1.70 (m, 6H). The $^{13}$C NMR spectrum was not collected due to the poor solubility of hetero[4]rotaxane-4. MALDI-TOF MS $m/z$ = 1162.05 [M − $PF_6^-$]$^{2+}$; calcd exact mass 2614.01. Anal. Calcd for $C_{119}H_{164}F_{18}N_3O_{34}P_3$: C, 54.65; H, 6.32; N, 1.61. Found: C, 54.60; H, 6.26; N, 1.66.

**Synthesis of [4]Rotaxane-5.** [4]Rotaxane-5 was prepared by an analogous method to that used for [2]rotaxane-1; yield 223 mg, 62%. $^1$H NMR (400 MHz, $CD_3CN$) $\delta$ 8.74 (s, 6H), 6.89 (s, 6H), 6.70−6.57 (m, 18H), 6.39 (s, 6H), 6.30 (s, 3H), 6.15 (s, 9H), 6.09 (s, 6H), 4.53 (s, 12H), 4.33 (s, 6H), 4.11 (s, 6H), 3.99 (s, 12H), 3.89 (s, 12H), 3.75


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(s, 36H), 3.56 (s, 12H), 3.50 (s, 6H), 3.43 (s, 18H), 1.81 (s, 6H), 1.45 (s, 6H), 1.28 (s, 60H), 0.89 (s, 9H). $^{13}$C NMR (100 MHz, $CD_3CN$) $\delta$ 167.3, 161.7, 161.5, 160.6, 147.2, 137.5, 134.9, 122.0, 120.0, 112.8, 110.7, 109.3, 107.5, 107.0, 103.6, 101.5, 72.0, 71.8, 71.1, 69.8, 69.2, 68.1, 55.7, 53.3, 50.5, 32.4, 30.1, 29.8, 29.3, 26.4, 23.1, 14.2. MALDI-TOF MS $m/z$ = 3152.89 [M − $PF_6^-$ − 2HP$F_6$]; calcd exact mass 3152.90. Anal. Calcd for $C_{183}H_{261}F_{18}N_{12}O_{33}P_3$: C, 61.19; H, 7.32; N, 4.68. Found: C, 61.33; H, 7.15; N, 4.76.

## ■ ASSOCIATED CONTENT

### Supporting Information

Crystal structure and data for compound **30**; $^1$H NMR, $^{13}$C NMR, ROESY, and MS spectra of all the new interminates, [*n*]rotaxanes and hetero[*n*]rotaxanes. This material is available free of charge via the Internet at http://pubs.acs.org.

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### Notes

The authors declare no competing financial interest.

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