Molecular Shuttles by the Protecting Group Approach†

Jianguo Cao, Matthew C. T. Fyfe, and J. Fraser Stoddart*

Department of Chemistry and Biochemistry, University of California, Los Angeles, California 90095

Graham R. L. Cousins and Peter T. Glink

School of Chemistry, University of Birmingham, Edgbaston, Birmingham B15 2TT, UK

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Two new [2]rotaxane-based molecular shuttles, in which a mechanically bound dibenzo[24]crown-8 (DB24C8) macroring shunts back and forth between two dialkylammonium recognition sites situated on a chemical dumbbell, have been constructed by a novel synthetic strategy that relies upon the use of the *tert*-butoxycarbonyl (Boc) protecting group. During the syntheses of both molecular shuttles, this protecting group masks a dialkylammonium recognition center which is liberated only *after* the [2]rotaxane constitution is established. In both cases, the molecular shuttles' other dialkylammonium center is essential for the rotaxane-forming reactions and it ensures that DB24C8 is interpenetrated by threadlike precursors, as a result of noncovalent bonding interactions, to produce [2]pseudorotaxanes which are stoppered subsequently through 1,3-dipolar cycloadditions between azides and bulky acetylenedicarboxylates. The new molecular shuttles have been examined by means of dynamic ^{1}H NMR spectroscopy, which reveals that the movements of the DB24C8 macroring are very highly dependent both on solvent properties and on the nature of the spacer unit linking the two dialkylammonium centers. Thus, DB24C8 shunts facilely between the dialkylammonium centers when the shuttles are dissolved in solvents that readily donate their nonbonding electrons into noncovalent bonds, e.g., DMF, and when spacer units that do not offer much steric resistance to shuttling, e.g., hexamethylene, are used. On the other hand, shuttling is difficult in solvents that are less inclined to donate their electrons into noncovalent bonds, e.g., $(CDCl_2)_2$, and when relatively bulky benzenoid spacer units, e.g., *p*-xylylene, link the two dialkylammonium centers. It has been proposed that the DB24C8 might act as a "ferry" which carries a proton between dialkylammonium and dialkylamine moieties in a singly protonated [2]rotaxane by means of ion−dipole interactions.

Introduction

The so-called rotaxanes have fascinated chemists for some years now,[1] not only because of their unique, mechanically interlocked, "bead on a dumbbell" structure, but also because of their potential to form the basis of functioning nanoscale devices,[2] e.g., molecular shuttles and switches,[3] in the future. In the simplest rotaxane-based molecular shuttle[4] (Figure 1), a macrocyclic "bead" travels back and forth between two identical "stations", i.e., molecular recognition sites, located on a chemical "dumbbell". The bead interacts with each of the stations through noncovalent bonding interactions[5] and is constrained to be bound mechanically to the dumbbell whose bulky terminal stopper groups it cannot traverse.

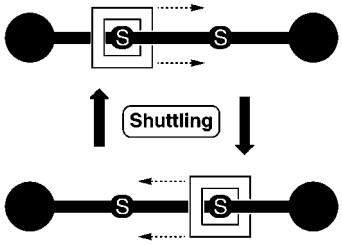

Figure 1. Elementary rotaxane-based molecular shuttle. The macrocyclic bead (open square) moves back and forth, like a shuttle, between two identical molecular recognition sites (S) with which it interacts through noncovalent bonds.

The present investigation addresses an irregularity that stems from our studies on rotaxane synthesis by a protocol relying on (1) the binding[6] of dialkylammonium ions by the crown ether dibenzo[24]crown-8 (DB24C8)

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* To whom correspondence should be addressed. Tel: (310) 206-7078. Fax: (310) 206-1843. E-mail: stoddart@chem.ucla.edu.

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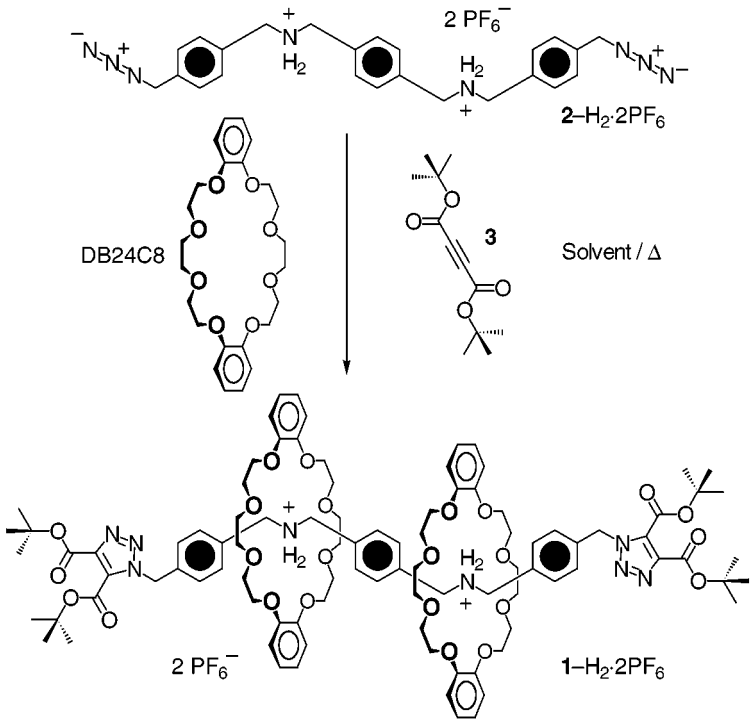
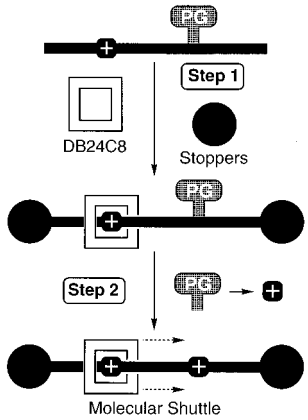
Scheme 1. The Only Rotaxane Isolated following Reaction of DB24C8, 2−H_2·2PF_6, and 3 Was the [3]Rotaxane 1−H_2·2PF_6



and (2) the 1,3-dipolar cycloaddition between azides and bulky acetylenedicarboxylates to form 1,2,3-triazoles that act as terminal stopper units. It was found[7] that the [3]rotaxane **1**−H_2·2PF_6 was the *only* rotaxane isolated (Scheme 1) when 1 equiv of DB24C8 was reacted with bisazide **2**−H_2·2PF_6 and di-*tert*-butyl acetylenedicarboxylate (**3**) in a range of organic solvents. Under no circumstances was the corresponding "two-station" [2]rotaxane **4**−H_2·2PF_6 (Figure 2), i.e., a potential DB24C8−bis(dialkylammonium) molecular shuttle, isolated from the reaction mixture. This compound was not formed presumably because the solubility of threadlike bis(dialkylammonium) dications in organic solvents is reliant upon the complexation of *both* of their dialkylammonium centers by DB24C8. Thus, the [2]pseudorotaxane[8] precursors of **4**−H_2·2PF_6 are practically insoluble in organic solvents and either precipitate out from solution during the reaction or are complexed by another DB24C8 molecule to generate the corresponding [3]pseudorotaxanes. On the other hand, the [3]pseudorotaxane[8] intermediates created during the reaction are soluble in organic solvents and therefore undergo stoppering reactions which produce **1**−H_2·2PF_6. Following on from these observations, we have devised a new protecting group approach for the syntheses of the degenerate DB24C8−bis(dialkylammonium) molecular shuttles **5a**−H_2·2PF_6

Scheme 2. Protecting Group Approach for the Synthesis of DB24C8−Bis(dialkylammonium) Molecular Shuttles[a]



[a] The key element of this approach is the use of a latent dialkylammonium center, formed by the attachment of a protecting group (PG) to a dialkylamine, which is maintained throughout the rotaxane-forming reaction (Step 1) between DB24C8 and another, "real" dialkylammonium unit. The synthetic approach concludes when the latent dialkylammonium center is transformed into its active counterpart by deprotection and protonation (Step 2).

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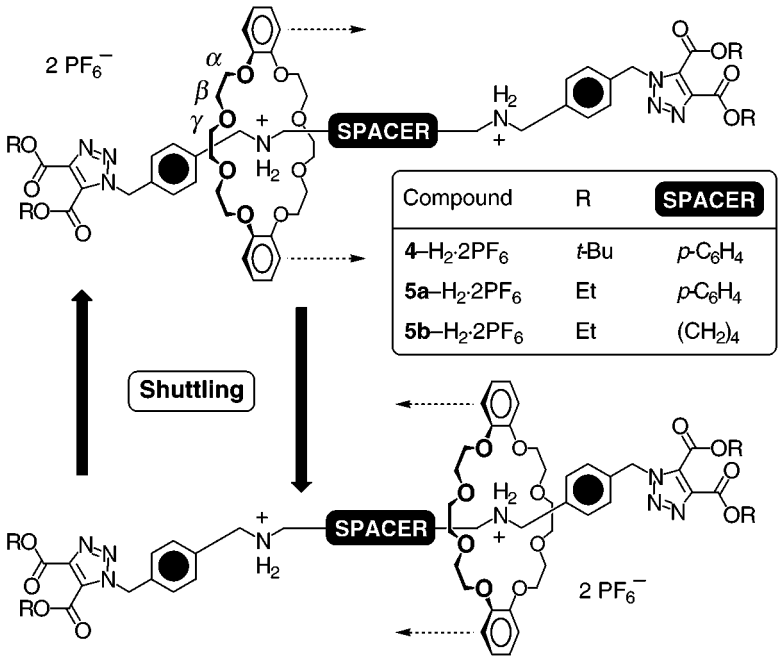

Figure 2. Potential molecular shuttles created by the interlocking of DB24C8 and bis(dialkylammonium) dumbbells.

and **5b**$-H_2\cdot 2PF_6$ (Figure 2). This approach relies (Scheme 2) on the employment of a latent dialkylammonium group that remains protected while another, "real" dialkylammonium center interacts, via noncovalent bonds, with DB24C8 during [2]rotaxane formation. Upon deprotection, the latent group is transformed into a further "real" dialkylammonium center, furnishing a two-station [2]rotaxane, i.e., a molecular shuttle with two sites for molecular recognition events between DB24C8 and a dialkylammonium unit, in the process. Here, we report the realization of the protecting group approach for the construction of molecular shuttles **5a**$-H_2\cdot 2PF_6$ and **5b**$-H_2\cdot 2PF_6$ and our subsequent investigation into the shuttling of the DB24C8 macroring in these two new compounds by variable temperature ^{1}H NMR spectroscopy.

Results and Discussion

Design Logic. We decided to utilize a Boc-protected dialkylamine as the latent dialkylammonium center necessary for our novel synthetic strategy. The Boc (*tert*-butoxycarbonyl) moiety was chosen as the protecting group because (1) we had employed it previously[7a,9] with much success for the syntheses of dialkylammonium-containing compounds; (2) of its facile introduction/removal;[10] (3) the byproducts following removal of this group—viz., CO_2 and 2-methylpropene—are volatile, as well as being unreactive in this instance; and (4) its *tert*-butyl moiety resonates as a characteristic singlet in the ^{1}H NMR spectrum, allowing the protected rotaxane and its precursors to be characterized unambiguously, thus making it easy to follow the deprotection step by ^{1}H NMR spectroscopy. However, the weakly acidic reagents generally employed to remove the Boc group, e.g., CF_3CO_2H, are incompatible with the *tert*-butyl ester groups present in the products of the original[7] rotaxane synthesis. Cleavage of these *tert*-butyl ester moieties would decrease the size of the stoppers, possibly rendering them incapable of preventing dissociation of the macrocycle from the dumbbell. We therefore investigated the employment of esters that were not as acid sensitive for the rotaxane syntheses.

Synthesis. After an inspection of the original crystal structures[7] and CPK space-filling models, we concluded that ethyl ester groups would be sufficiently bulky to make the terminal stopper groups large enough to ensure dumbbell−macrocycle interlocking. In fact, we found that the [2]rotaxane **6**$-H\cdot PF_6$—with ethoxycarbonyl groups appended to its triazole termini—could be isolated in 77% yield when **7**$-H\cdot PF_6$ was reacted (Scheme 3) with a large excess of DB24C8 and diethyl acetylenedicarboxylate (**8**). Without a doubt, the dumbbell and macrocycle components of this rotaxane are mechanically interlocked with one another, since (1) the compound survives column chromatography, (2) the LSI mass spectrum of **6**$-H\cdot PF_6$ displays a strong base peak at $m/z = 1096$ corresponding to [**6**-H]$^+$, and (3) the ^{1}H NMR spectrum of **6**$-H\cdot PF_6$ is similar to that of its congener with *tert*-butyl ester groups and also shows that DB24C8 and the dumbbell component are present in a 1:1 ratio. The fact that the ethyl esters make the termini of a dumbbell bulky enough to

(8) Pseudorotaxanes[1a,6] are complexes wherein one or more macrocycles encircle one or more threadlike species by virtue of noncovalent bonding interactions. The fundamental difference between pseudorotaxanes and their mechanically interlocked congeners, the rotaxanes, is that either one or both of their termini do not possess stopper groups that are bulky enough to prevent dissociation of the thread(s) from the macrocycle(s). The number of components, *n*, of which a pseudorotaxane is comprised is indicated by the descriptor [*n*]. Three [2]pseudorotaxanes could reasonably be formed en route to the [2]rotaxane **4**$-H_2\cdot 2PF_6$, viz., the "unstoppered" complex [DB24C8·**2**$-H_2][PF_6]_2$ and the two complexes in which one DB24C8 molecule is pierced by the singly stoppered thread (SST) produced by reaction of one of the azido groups of **2**$-H_2\cdot 2PF_6$ with **3**. By the same token, there are two [3]pseudorotaxanes that could be produced during the assembly of [3]rotaxane **1**$-H_2\cdot 2PF_6$, viz., "unstoppered" $[(DB24C8)_2\cdot$**2**$-H_2][PF_6]_2$ and the complex where the SST interpenetrates two DB24C8s.

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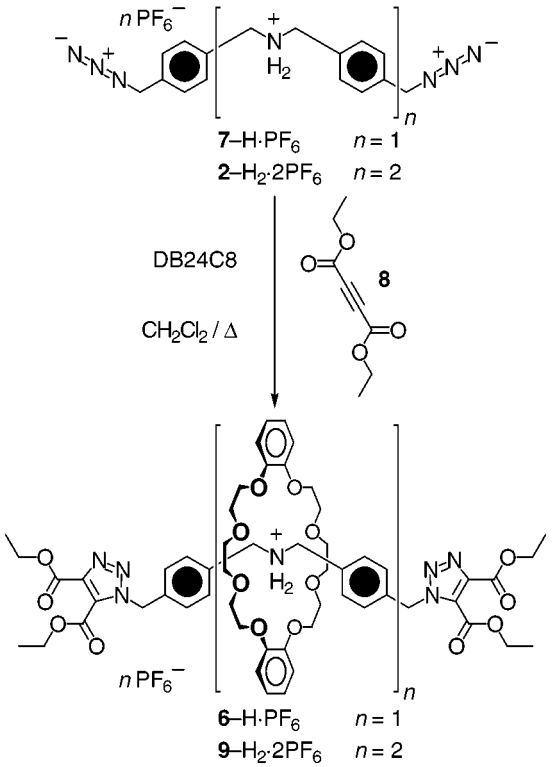
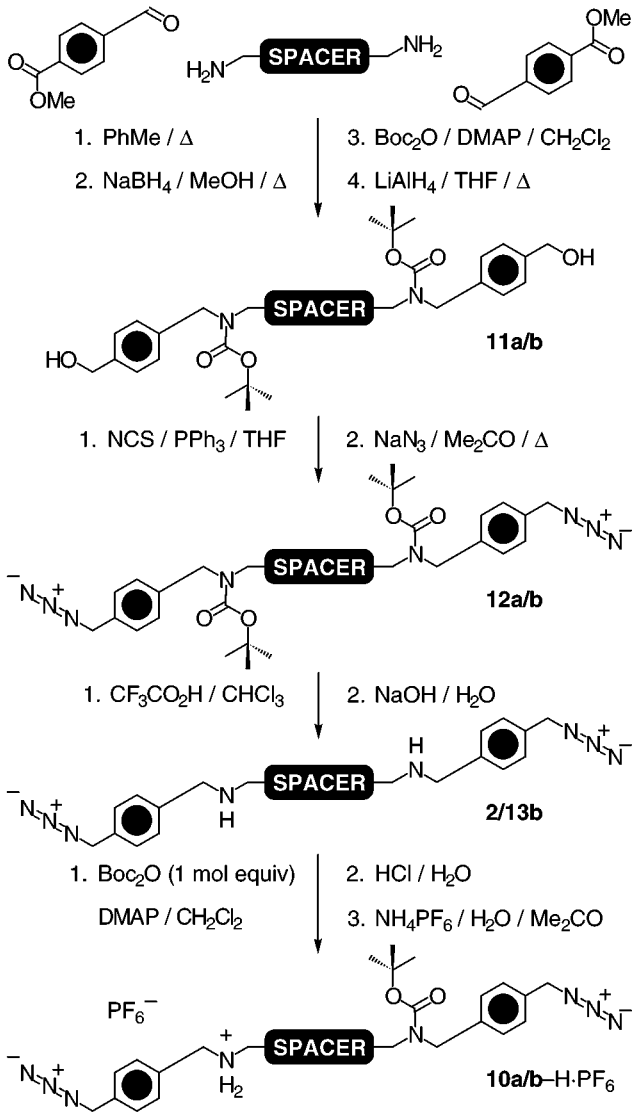
Scheme 3. Synthesis of the Rotaxanes 6−H·PF_6 and 9−H_2·2PF_6, Wherein Either One or Two DB24C8 Macrorings Are Constrained To Be Bound Mechanically on Dialkylammonium-Bearing Dumbbells by the Diethyl 1,2,3-Triazole-4,5-dicarboxylate Moiety



prevent DB24C8 expulsion is also highlighted by the synthesis of the corresponding [3]rotaxane **9**−H_2·2PF_6 in 54% yield from the reaction (Scheme 3) of an excess of DB24C8 with **2**−H_2·2PF_6 and **8**. It should be noted that the isolated yields obtained for **6**−H·PF_6 and **9**−H_2·2PF_6 are very much larger than those reported[7] for the corresponding rotaxanes constructed with di-*tert*-butyl 1,2,3-triazole-4,5-dicarboxylates, e.g., **1**−H_2·2PF_6. This increase in efficiency arises presumably because of the enhanced stability of diethyl 1,2,3-triazole-4,5-dicarboxylates compared to their di-*tert*-butyl-containing congeners.[11]

Compounds **10a**−H·PF_6 and **10b**−H·PF_6 (Scheme 4) were selected as suitable threadlike precursors of the DB24C8−bis(dialkylammonium) molecular shuttles **5a**−H_2·2PF_6 and **5b**−H_2·2PF_6 (Figure 2), whose two dialkylammonium centers are separated by *p*-xylylene and 1,6-hexamethylene spacers, respectively. These compounds possess both an active dialkylammonium center, thus permitting rotaxane formation with DB24C8, and a latent dialkylammonium group in the form of a Boc-protected dialkylamine. Two approaches were envisaged for the syntheses of the respective conjugate bases of these compounds, i.e., **10a** and **10b**. The first of these approaches involved treating the doubly Boc-protected compounds **12a** and **12b**—synthesized in several steps from methyl 4-formylbenzoate and either *p*-xylylenediamine or 1,6-hexanediamine, respectively—with 1 mol equiv of CF_3CO_2H. Unfortunately, however, the yields obtained for this monodeprotection reaction were extremely inconsistent. Therefore, we preferred a second, more reliable approach in which one of the amino groups from bis(dialkylamines) **2** and **13b** was protected with the Boc moiety by reaction with 1 mol equiv of Boc_2O. In all instances, **10a** and **10b** were obtained in yields close to the theoretical maximum (50%) using this procedure. Fortunately, **10a** and **10b** could be transformed into their conjugate acids, viz., **10a**−H·PF_6 and **10b**−H·PF_6, without significant cleavage of the Boc protecting groups occurring. These transformations took advantage of the fact that the salts **10a**−H·Cl and **10b**−H·Cl are CH_2Cl_2 soluble and remained in the organic phase when their respective conjugate bases were dissolved in CH_2Cl_2 and shaken with aqueous HCl.

Scheme 4. Synthesis of the Precursor Threadlike Compounds 10a−H·PF_6 and 10b−H·PF_6[a]



[a] As defined previously in Figure 2, the units labeled SPACER are *p*-C_6H_4 and $(CH_2)_4$ for the compounds in series **a** and **b**, respectively.

The ^{1}H NMR spectrum (300.1 MHz, CD_2Cl_2, 293 K) of a 1:1 mixture of DB24C8 and the threadlike salt **10a**−H·PF_6 revealed that both components are complexed to greater than 95%. Armed with this information, we then carried out the rotaxane-forming reactions depicted in Scheme 5. The "protected" [2]rotaxanes **14a**−H·PF_6 and

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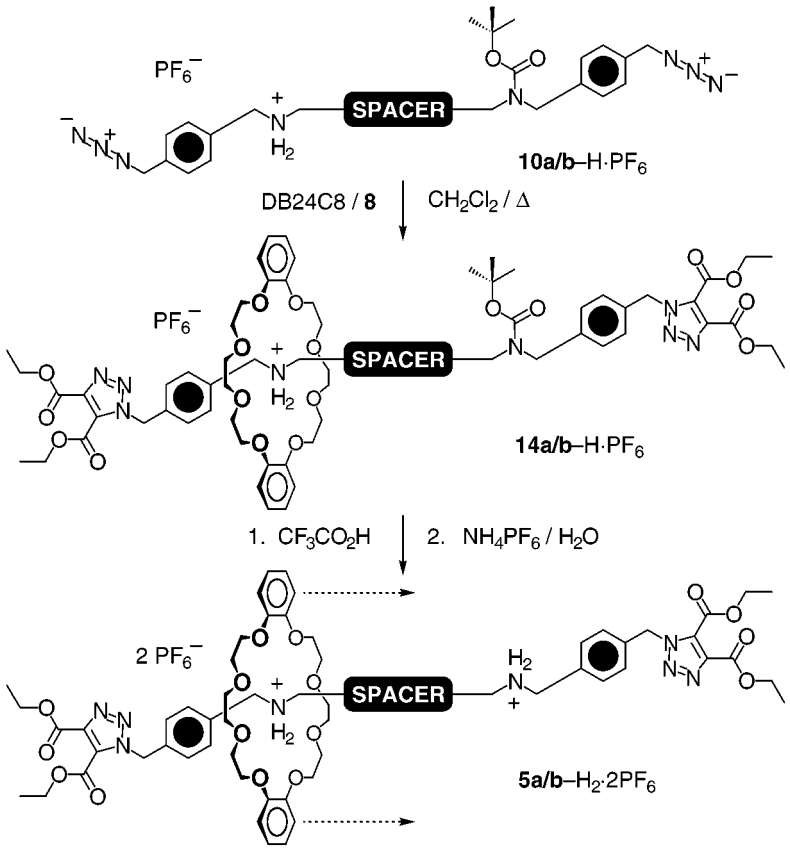
Scheme 5. Synthesis of the DB248C8−Bis(dialkylammonium) Molecular Shuttles 5a−H_2·2PF_6 and 5b−H_2·2PF_6 by Way of the "Protected" Rotaxanes 14a−H·PF_6 and 14b−H·PF_6[a]



[a] As indicated in Figure 2, the units marked SPACER are *p*-C_6H_4 and $(CH_2)_4$ in the series **a** and **b**, respectively.

14b−H·PF_6 were procured in reasonable yields when their respective [2]pseudorotaxane precursors—i.e., the complexes [DB24C8·**10a**−H][PF_6] and [DB24C8·**10b**−H][PF_6]—were doubly stoppered by reaction with diethyl acetylenedicarboxylate (**8**). To complete the fulfillment of the protecting group approach, the Boc-protected amino moieties of **14a**−H·PF_6 and **14b**−H·PF_6 were transformed into ammonium centers, via deprotection and protonation, leading to the formation of the molecular shuttles **5a**−H_2·2PF_6 and **5b**−H_2·2PF_6.

Shuttle Characterization by ^{1}H NMR Spectroscopy. As was the case with the first degenerate molecular shuttle to be reported,[4] the ^{1}H NMR spectra of both **5a**−H_2·2PF_6 and **5b**−H_2·2PF_6 display temperature-dependent behavior in a range of solvents. By using the data obtained from variable temperature ^{1}H NMR spectroscopic studies, we have been able to determine the free energies of activation for shuttling ($\Delta G_c^{\ddagger}$) of the DB24C8 macroring in the rotaxanes **5a**−H_2·2PF_6 and **5b**−H_2·2PF_6.

The ^{1}H NMR spectrum of **5a**−H_2·2PF_6 in CD_2Cl_2 at ambient temperature shows (Figure 3) that the dumbbell has two distinct halves, as highlighted by the observance of two peaks for both (1) the CH_2 protons linking the triazole units to the terminal *p*-xylylenyl rings and (2) the C$H_2$$NH_2^+$ protons. In one of these halves, the dialkylammonium center is encircled, in characteristic[6] fashion, by the DB24C8 macroring, while, in the other, the dialkylammonium moiety is free, i.e., not complexed. The two halves are interconverting very slowly with one another on the ^{1}H NMR time scale, as evidenced by the two different sets of peaks for occupied and unoccupied dialkylammonium sites. We then decided to study the shuttle's dynamic properties in $(CD_3)_2SO$, a solvent with

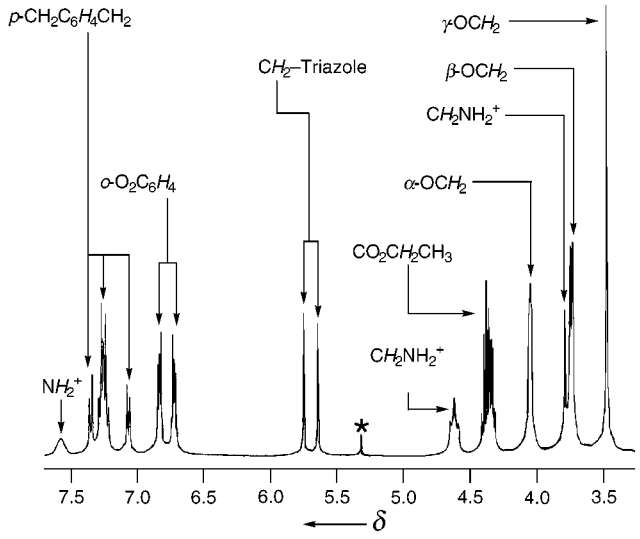


Figure 3. Partial ^{1}H NMR spectrum (400.1 MHz, CD_2Cl_2, 300 K) of **5a**−H_2·2PF_6. The descriptors α, *β* and *γ*—used to classify DB24C8's OCH_2 protons—are defined in Figure 2. The signals labeled C$H_2$$NH_2^+$ (ocpd) and C$H_2$$NH_2^+$ (unocpd) refer to the CH_2 protons whose neighboring NH_2^+ groups are and are not encircled by the DB24C8 macroring, respectively. The resonance labeled with an asterisk results from residual protons in the solvent.

Table 1. ^{1}H NMR Spectroscopic,[a] Kinetic, and Thermodynamic Data Associated with the Shuttling of the DB24C8 Macroring in Compounds 5a−H_2·2PF_6 and 5b−H_2·2PF_6 Side by Side with Solvent Properties and Stability Constants for the [DB24C8·DBA−H][PF_6] Complex at 298 K

compound	solvent	$\Delta\nu$ (Hz)	k_c[b] (s^{-1})	T_c (K)	$\Delta G_c^{\ddagger}$[c] (kcal mol^{-1})	DN[d]	K_a[e] (M^{-1})
5a−H_2·2PF_6	$(CD_3)_2SO$	44	98	424	21.3	29.8	0[f]
5b−H_2·2PF_6	$(CDCl_2)_2$	28	62	353	17.9	0.0	>25000
5b−H_2·2PF_6	CD_3NO_2	69	155	303	14.7	2.7	22000
5b−H_2·2PF_6	CD_3CN	81	182	286	13.8	14.1	420[f]
5b−H_2·2PF_6	$(CD_3)_2CO$	47	106	275	13.5	17.0	360[f]
5b−H_2·2PF_6	$(CD_3)_2NCDO$	49	108	217	10.5	26.6	0

[a] The CH_2 protons attached to the triazole unit were used to probe the dynamic processes in all examples. [b] Estimated by using the coalescence method as described in Sutherland, I. O. *Annu. Rep. NMR Spectrosc.* **1971**, *4*, 71−235. Thus, the rate constants for shuttling (k_c) at the coalescence temperature (T_c) were evaluated by employing the approximate expression $k_c = \pi(\Delta\nu)/(2)^{1/2}$, where $\Delta\nu$ is the chemical shift difference between coalescing signals in the absence of exchange. [c] The relationship $\Delta G_c^{\ddagger} = -RT_c \ln(k_c h/k_B T_c)$—where R, h and k_B correspond, respectively, to the gas, Planck and Boltzmann constants—was used to obtain values for the free energy of activation for shuttling ($\Delta G_c^{\ddagger}$) at T_c. [d] Values for the Gutmann donor numbers (DN) were taken from ref 12. [e] Stability constants for the complex formed between DB24C8 and dibenzylammonium hexafluorophosphate (DBA−H·PF_6) at 298 K. Unless noted otherwise, the values were obtained by the single-point method[6] (percentage errors < 10%). [f] The values were acquired from ref 6a.

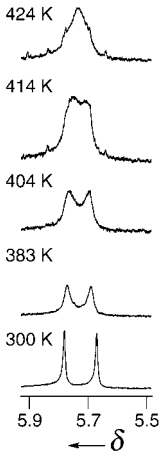


Figure 4. Partial variable temperature ^{1}H NMR spectra (400.1 MHz, $(CD_3)_2SO$) of **5a**−H_2·2PF_6 which highlight the two signals associated with the CH_2−triazole protons. These signals are well-separated at ambient temperature but gradually merge together at higher temperatures, coalescing ultimately at 424 K.

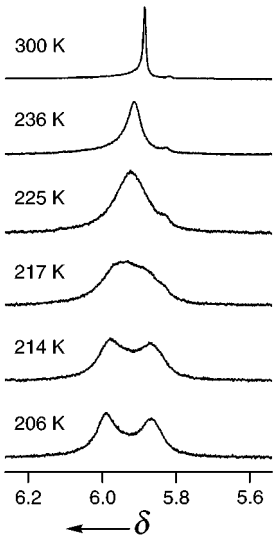


Figure 5. Partial variable temperature ^{1}H NMR spectra (400.1 MHz, $(CD_3)_2NCDO$) of **5b**−H_2·2PF_6 which highlight the CH_2−triazole resonance(s). The resonances for the two CH_2−triazole units coalesce at 217 K in this case. These resonances coalesce at much higher temperatures in solvents with lower DNs.

a relatively high boiling point (462 K), thus permitting ^{1}H NMR spectra to be recorded at elevated temperatures, and a strong propensity to enter into hydrogen-bonding interactions with dialkylammonium centers, thereby weakening the DB24C8−dialkylammonium interactions and making it easier for the DB24C8 macroring to travel back and forth between the dialkylammonium centers. The ^{1}H NMR spectrum of **5a**−H_2·2PF_6 in $(CD_3)_2SO$ at ambient temperature shows, like the corresponding spectrum recorded in CD_2Cl_2, two distinct singlets for the CH_2 protons located between the triazole stoppers and the terminal *p*-xylylenyl rings. However, these two signals coalesce (Figure 4) at elevated temperatures because the shuttling process speeds up and occurs at a rate similar to the ^{1}H NMR time scale. By using the data from the dynamic ^{1}H NMR spectroscopic studies in $(CD_3)_2SO$, we were able to determine a $\Delta G_c^{\ddagger}$ value for the shuttling process associated with **5a**−H_2·2PF_6. The value obtained (Table 1) is very much larger than the values we have observed for other molecular shuttles[3a] and highlights the difficulty associated with passing a benzenoid ring—which originates, in this case, from the *p*-xylylenyl spacer—through the cavity of the DB24C8 macroring.[6]

Table 2. Effect of Added *i*-Pr_2NEt on the ^{1}H NMR Spectroscopic,[a] Kinetic, and Thermodynamic Data Associated with the Shuttling of the DB24C8 Macroring in 5b−H_2·2PF_6[b]

i-Pr_2NEt (mol equiv)	$\Delta\nu$ (Hz)	k_c[c] (s^{-1})	T_c (K)	$\Delta G_c^{\ddagger}$[c] (kcal mol^{-1})
0	49	108	217	10.5
1	43	97	257	12.6
2	42	94	269	13.3
3	42	94	275	13.6
4	42	94	275	13.6

[a] Probe protons = CH_2−triazole. [b] Concentration = 6.7×10^{-3} M in $(CD_3)_2NCDO$. [c] Determined as described in the Footnotes to Table 1.

We hoped that the reduced steric bulk of the hexamethylene spacer in **5b**−H_2·2PF_6 would make it easier for DB24C8 to pass between the two dialkylammonium stations. If this conjecture did indeed hold true, we would be able to determine $\Delta G_c^{\ddagger}$ values at less elevated temperatures, making it possible to study the shuttling processes in a much wider range of solvents. Gratifyingly, the ^{1}H NMR spectrum of **5b**−H_2·2PF_6 in $(CD_3)_2NCDO$ at ambient temperature reveals that, in this instance,

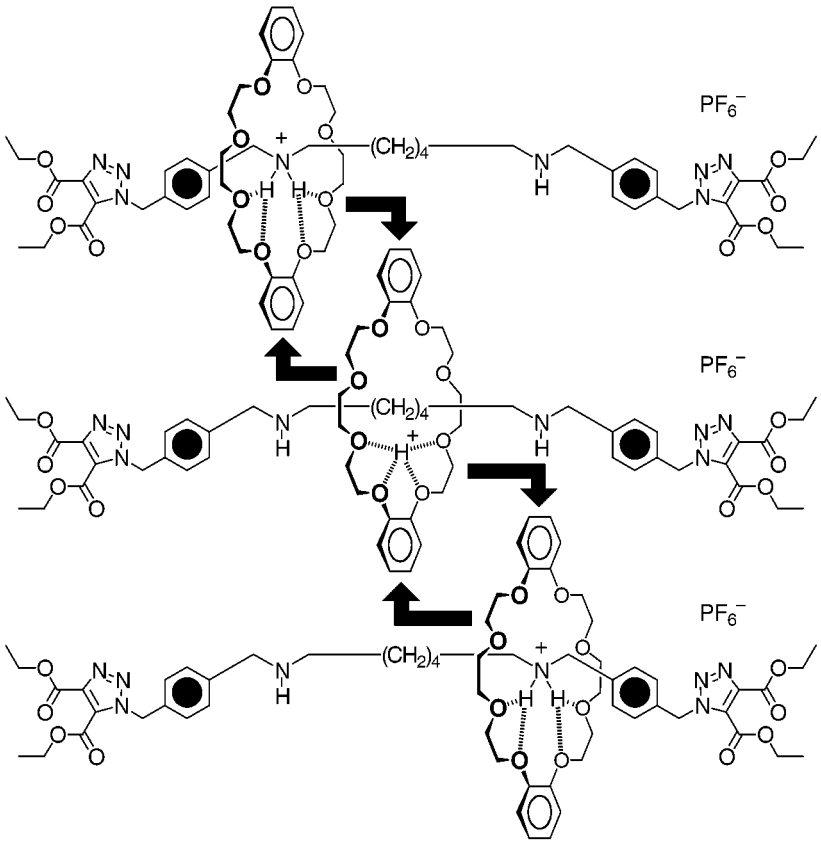


Figure 6. "Proton ferry" in which DB24C8 utilizes noncovalent bonds to transport a proton between two dialkylamine units in **5b**−H·PF_6. Also see ref 14.

shuttling is faster than the ^{1}H NMR time scale; only one signal is observed for the CH_2 protons located between the triazole unit and the terminal *p*-xylylenyl ring. This signal broadens out and splits into two separate signals at lower temperatures (Figure 5). The temperature at which the signals coalesce (T_c) varies drastically (Table 1) with the nature of the solvent employed for the studies. For example, T_c for **5b**−H_2·2PF_6 is 136 K higher in $(CDCl_2)_2$ than it is in $(CD_3)_2$NCDO. We noticed that both T_c and $\Delta G_c^{\ddagger}$ increase as the Gutmann donor number[12] (DN) decreases. Put another way, it becomes more difficult for the DB24C8 macroring to shuttle between the two dialkylammonium stations as the ability of the solvent to donate its electrons into noncovalent bonds decreases and the dialkylammonium centers become less solvated. Notably, the marked dependence of $\Delta G_c^{\ddagger}$ on the DN mirrors the reliance[6] of the stability constants (K_a) of the [2]pseudorotaxane complex created from DB24C8 and dibenzylammonium hexafluorophosphate (DBA−H·PF_6) on the same set of numbers.

Finally, we examined the effect of base on the shuttling of the DB24C8 macroring in **5b**−H_2·2PF_6. It was found that $\Delta G_c^{\ddagger}$ rises, i.e., it becomes more difficult for shuttling to occur, when the relative amount of *i*-Pr_2NEt present is increased (Table 2). Moreover, the $\Delta G_c^{\ddagger}$ values obtained do not change when the concentration of **5b**−H_2·2PF_6 is altered. If we assume that a proton is removed from only one[13] of the two dialkylammonium centers in **5b**−H_2·2PF_6, it is not inconceivable that—because the $\Delta G_c^{\ddagger}$ values are not concentration dependent—DB24C8 acts as a "proton ferry" (Figure 6) which transfers a proton intramolecularly[14] between dialkylammonium and dialkylamine moieties, at elevated temperatures in the singly deprotonated compound **5b**−H·PF_6, by harnessing ion−dipole interactions between the proton and some of the DB24C8 macroring's oxygen atoms.

Conclusions

Molecular shuttles, in the shape of two-station [2]rotaxanes constituted by DB24C8 and bis(dialkylammonium) dumbbells, cannot be acquired by the one-pot reaction between DB24C8, a bulky acetylenedicarboxylate, and a bis(dialkylammonium) thread with two azido groups. Consequently, a novel synthetic approach was developed for the construction of the molecular shuttles **5a**−H_2·2PF_6 and **5b**−H_2·2PF_6, compounds which show interesting solvent-dependent shuttling phenomena and highlight the steric issues that are important to the chemistry of DB24C8 and dialkylammonium ions. The key to the new synthetic approach was the use of the Boc protecting group, which masked latent dialkylammonium sites during rotaxane formation. We believe that protecting group approaches, such as the one delineated here,

(12) Gutmann, V. *Electrochim. Acta* **1976**, *21*, 661−670.

(13) Dibenzylammonium centers that are interlocked with DB24C8 in [2]rotaxanes are much less acidic than their noninterlocked counterparts (Cantrill, S. J.; Stoddart, J. F. Unpublished observations) and, thus, are extremely difficult to deprotonate.

(14) The intermediate illustrated in Figure 6 could be further stabilized by interactions of a "distal" nature to the "bound" proton from both the secondary amine centers simultaneously. Since these additional intramolecular interactions are attainable within the confines of a nine-membered ring, their involvement in an intramolecular proton ferrying mechanism is certainly plausible. This proposed mechanism will be the subject of further investigations in our laboratory.

should be generally applicable to problems in contemporary synthetic supramolecular chemistry,[5c] where specific molecular recognition interactions need to be turned on and off with precision during the construction of intricate molecular compounds using prior supramolecular assistance.

Experimental Section

General Procedures. Anhydrous CH_2Cl_2 and MeCN were obtained by distillation from CaH_2 under N_2. Anhydrous THF was obtained by distillation from Na−Ph_2CO under N_2. Column chromatography was carried out using silica gel 60F (Merck 9385, 0.040−0.063 mm). Melting points are uncorrected. ^{1}H NMR spectra were recorded at either 300.1, 360.1, or 400.1 MHz. The deuterated solvent was used as the lock, while either the solvent's residual protons or TMS was employed as the internal standard. ^{13}C NMR spectra were recorded at either 75.5, 90.6 or 100.6 MHz. Accurate mass measurements by liquid secondary ion (LSI) mass spectrometry were performed using a *m*-nitrobenzyl alcohol matrix and employing narrow range voltage scanning at a resolution of 6000 with either poly(ethylene glycol) or cesium iodide as reference compounds. Accurate mass measurements by fast atom bombardment (FAB) mass spectrometry were performed using a krypton primary atom beam in conjunction with a *m*-nitrobenzyl alcohol matrix.

{**[2]-[Bis(4-((4,5-bisethoxycarbonyl-1,2,3-triazo-1-yl)methyl)benzyl)ammonium][dibenzo[24]crown-8]rotaxane**} **Hexafluorophosphate (6−H·PF$_6$).** Bis(4-azidomethylbenzyl)ammonium hexafluorophosphate[7a] (**7**−H·PF_6, 0.22 g, 0.49 mmol) was dissolved in a CH_2Cl_2 (2 mL) solution of DB24C8 (0.70 g, 1.57 mmol), then the whole was treated with diethyl acetylenedicarboxylate (**8**, 0.28 g, 1.65 mmol) and heated under reflux for 4 d. After cooling to 20 °C and solvent evaporation under reduced pressure, the residue was subjected to column chromatography (SiO_2, Me_2CO−*n*-C_6H_{14}, 3:7 to 1:1), furnishing the title compound as a yellow oil (0.41 g, 77%): ^{1}H NMR (300.1 MHz, $CDCl_3$, 293 K) δ = 1.35 (t, J = 6 Hz, 6H), 1.40 (t, J = 6 Hz, 6H), 3.42 (s, 8H), 3.72 (m, 8H), 4.05 (m, 8H), 4.40 (q, J = 6 Hz, 4H), 4.43 (q, J = 6 Hz, 4H), 4.56 (m, 4H), 5.69 (s, 4H), 6.71 (m, 4H), 6.85 (m, 4H), 7.12 (d, J = 8 Hz, 4H), 7.23 (d, J = 8 Hz, 4H), 7.60 (br, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$, 293 K) δ = 13.9, 14.2, 52.1, 53.2, 62.1, 63.2, 68.1, 70.2, 70.6, 112.7, 121.8, 128.3, 129.8, 129.9, 132.1, 135.3, 140.5, 147.2, 158.2, 160.2; HRMS (LSI) $C_{56}H_{70}N_7O_{16}$ [M − PF_6]$^+$ calcd m/z = 1096.4879, found m/z = 1096.4886.

{**[3]-[Dibenzo[24]crown-8][*N*,*N*′-bis(4-((4,5-bisethoxycarbonyl-1,2,3-triazo-1-yl)methyl)benzyl)-*p*-xylylenediammonium][dibenzo[24]crown-8]rotaxane**} **Bis(hexafluorophosphate) (9−H$_2$·2PF$_6$).** *N*,*N*′-Bis(4-azidomethylbenzyl)-*p*-xylylenediammonium bis(hexafluorophosphate)[7a] (**2**−H_2·2PF_6, 0.20 g, 0.28 mmol) was dissolved in a MeCN (2 mL) solution of DB24C8 (0.63 g, 1.39 mmol). The solvents were removed under reduced pressure, and the residue was taken up in CH_2Cl_2. The resulting cloudy solution was treated with diethyl acetylenedicarboxylate (**8**, 0.24 g, 1.40 mmol), before being heated under reflux for 4 d. Upon cooling, the solvents were evaporated off in vacuo, and the residue was subjected to column chromatography (SiO_2, Me_2CO−*n*-C_6H_{14}, 1:1 to 4:1), furnishing the title compound as a white solid (0.29 g, 54%): ^{1}H NMR (300.1 MHz, $CDCl_3$, 293 K) δ = 1.28 (t, J = 6 Hz, 6H), 1.37 (t, J = 6 Hz, 6H), 3.48 (m, 8H), 3.73 (br, 24H), 3.90 (m, 8H), 4.07 (m, 8H), 4.29 (br m, 8H), 4.49 (m, 4H), 4.69 (m, 4H), 5.64 (s, 4H), 6.65 (m, 8H), 6.72 (m, 8H), 7.02 (s, 4H), 7.04 (d, J = 9 Hz, 4H), 7.26 (d, J = 9 Hz, 4H), 7.44 (br, 4H); ^{13}C NMR (75.5 MHz, $CDCl_3$, 293 K) δ = 13.8, 14.1, 51.8, 52.0, 53.1, 62.0, 63.0, 67.6, 70.2, 70.7, 112.3, 121.2, 128.0, 129.4, 129.8, 132.0, 132.6, 134.9, 139.5, 147.2, 158.1, 159.5; HRMS (LSI) $C_{88}H_{112}F_6N_8O_{24}P$ [M − PF_6]$^+$ calcd m/z = 1809.7431, found m/z = 1809.7401.

***N*-(4-Azidomethylbenzyl)-*N*-(4-(*N*′-(4-azidomethylbenzyl)-*N*′-(*tert*-butoxycarbonyl)aminomethyl)benzyl)ammonium Hexafluorophosphate (10a−H·PF$_6$).** A solution of *N*,*N*′-bis(4-azidomethylbenzyl)-*p*-xylylenediamine[7a] (**2**, 8.00 g, 19.0 mmol), Boc_2O (4.10 g, 19.0 mmol), and DMAP (0.10 g, 0.8 mmol) in CH_2Cl_2 (200 mL) was stirred at 20 °C for 3 h. The solvent was removed under reduced pressure and the residue chromatographed (SiO_2, EtOAc−*n*-C_6H_{14}, 1:4) to provide the amine **10a** as a thick oil (4.90 g, 50%): ^{1}H NMR (400.1 MHz, $CDCl_3$, 300 K) δ = 1.49 (s, 9H), 3.80 (s, 2H), 3.82 (s, 2H), 4.30−4.45 (br m, 8H), 7.14−7.49 (m, 12H); ^{13}C NMR (100.6 MHz, $CDCl_3$, 300 K) δ = 28.4, 49.0 (br), 52.8, 54.5, 80.1, 128.3, 128.4, 128.6, 134.0, 139.2, 140.4, 155.9; MS (FAB) m/z = 527 [M + H]$^+$. A solution of **10a** (0.90 g, 1.7 mmol) in CH_2Cl_2 (50 mL) was washed with 10% aqueous HCl. The organic phase was concentrated, then the residue was dissolved in Me_2CO−H_2O (1:1) and saturated aqueous NH_4PF_6 was added. The Me_2CO was evaporated off under reduced pressure, then the H_2O was decanted off from the oil formed. This oil was washed further with H_2O and vacuum-dried to provide the title compound (1.00 g, 87%): ^{1}H NMR (400.1 MHz, $CDCl_3$, 300 K) δ = 1.42 (s, 9H), 4.12−4.44 (br m, 12H), 6.95−7.60 (m, 12H); ^{13}C NMR (100.6 MHz, $CDCl_3$, 300 K) δ = 28.3, 49.2 (br), 51.4 (br), 53.9, 54.3, 81.2, 127.7, 128.0, 128.2, 128.5, 129.0, 129.2, 130.3, 134.5, 137.6, 156.2; HRMS (LSI) $C_{29}H_{35}N_8O_2$ [M − PF_6]$^+$ calcd m/z = 527.2911, found m/z = 527.2882.

{**[2]-[*N*-(4-((4,5-Bisethoxycarbonyl-1,2,3-triazo-1-yl)methyl)benzyl)-*N*-(4-(*N*′-(4-((4,5-bisethoxycarbonyl-1,2,3-triazo1-yl)methyl)benzyl)-*N*′-(*tert*-butoxycarbonyl)aminomethyl)benzyl)ammonium][dibenzo[24]crown-8]rotaxane**} **Hexafluorophosphate (14a−H·PF$_6$).** DB24C8 (0.55 g, 1.2 mmol), **10a**−H·PF_6 (0.41 g, 0.6 mmol), and diethyl acetylenedicarboxylate (**8**, 0.20 g, 1.2 mmol) were heated under reflux for 2 d in anhydrous CH_2Cl_2 (10 mL). The solvent was evaporated off in vacuo and the residue was chromatographed (SiO_2, Me_2CO−*n*-C_6H_{14}, 1:1), yielding the title compound as a white solid (0.30 g, 34%): ^{1}H NMR (360.1 MHz, CD_3CN, 300 K) δ = 1.22−1.33 (m, 12H), 1.38 (s, 9H), 3.54 (br s, 8H), 3.74 (br, 8H), 4.00 (br, 8H), 4.14−4.38 (m, 12H), 4.66 (br, 4H), 5.59 (s, 2H), 5.72 (s, 2H), 6.70−6.80 (m, 8H), 7.02 (d, J = 8 Hz, 4H), 7.18−7.25 (m, 4H), 7.30 (d, J = 8 Hz, 4H), 7.56 (br, 2H); ^{13}C NMR (90.6 MHz, CD_3CN, 300 K) δ = 13.4, 13.6, 14.1, 14.3, 14.8, 15.0, 28.5, 29.6, 30.9, 52.8, 53.0, 53.9, 54.2, 54.9, 62.7, 64.0, 68.7, 71.0, 71.4, 80.7, 113.2, 121.1, 122.0, 122.9, 123.0, 128.0, 128.9, 129.0, 129.9, 130.4, 130.8, 131.0, 131.4, 131.8, 133.2, 134.5, 136.3, 139.8, 140.1, 140.6, 141.0, 148.2, 156.4, 159.1, 159.4, 161.1, 161.2; HRMS (FAB) $C_{69}H_{87}N_8O_{18}$ [M − PF_6]$^+$ calcd m/z = 1315.6138, found m/z = 1315.6147.

{**[2]-[*N*,*N*′-Bis(4-((4,5-bisethoxycarbonyl-1,2,3-triazo-1-yl)methyl)benzyl)-*p*-xylylenediammonium][dibenzo[24]crown-8]rotaxane**} **Bis(hexafluorophosphate)(5a−H$_2$·2PF$_6$).** The "protected" rotaxane **14a**−H·PF_6 (0.30 g, 0.2 mmol) was dissolved in $CDCl_3$ (5 mL), before being treated with CF_3CO_2H (0.5 mL). The reaction was monitored by ^{1}H NMR spectroscopy, and after 3 h, the solution was concentrated and the residue dissolved in CH_2Cl_2. The organic extracts were washed with saturated aqueous NH_4PF_6, dried ($MgSO_4$), concentrated, and chromatographed (SiO_2, CH_2Cl_2−MeOH, 19:1) to furnish the title compound as a white foamlike solid (0.17 g, 55%): mp 69−72 °C; ^{1}H NMR (400.1 MHz, $CDCl_3$, 300 K) δ = 1.29−1.37 (m, 12H), 3.47 (s, 8H), 3.73−3.75 (m, 8H), 3.79 (s, 4H), 4.04 (br m, 8H), 4.33−4.39 (m, 8H), 4.56−4.70 (m, 4H), 5.64 (s, 2H), 5.75 (s, 2H), 6.71−6.74 (m, 4H), 6.83−6.86 (m, 4H), 7.07 (d, J = 8 Hz, 2H), 7.22−7.30 (m, 8H), 7.35 (d, J = 8 Hz, 2H), 7.48−7.66 (br, 4H); ^{13}C NMR (90.6 MHz, CD_3CN, 300 K) δ = 13.7, 14.0, 52.1, 52.4, 53.0, 53.4, 61.8, 61.9, 62.9, 63.1, 67.9, 70.0, 70.5, 112.5, 121.5, 128.0, 128.5, 128.7, 129.0, 129.6, 129.8, 130.3, 132.0, 132.9, 135.1, 140.0, 140.2, 140.3, 147.2, 158.0, 158.3, 160.0, 160.1; HRMS (FAB) $C_{64}H_{80}N_8O_{16}$ [M − 2PF_6]$^+$ calcd m/z = 1216.5692, found m/z = 1216.5673.

***N*,*N*′-Bis(*tert*-butoxycarbonyl)-*N*,*N*′-bis(4-hydroxymethylbenzyl)-1,6-hexanediamine (11b).** 1,6-Hexanediamine (2.20 g, 18.6 mmol) and methyl 4-formylbenzoate (6.10 g, 37.2 mmol) were heated together in refluxing PhMe (250 mL) for 30 min. The reaction mixture was cooled to 20 °C and the solvent was evaporated off in vacuo to yield 1,6-bis(4-methoxycarbonylbenzylidene)hexanediamine as a white solid (7.74 g, 100%): mp 102−104 °C; ^{1}H NMR (360.1 MHz, $CDCl_3$, 300

K) δ = 1.28−1.32 (m, 4H), 1.58−1.68 (m, 4H), 3.52 (t, J = 8 Hz, 4H), 3.81 (s, 6H), 7.66 (d, J = 8 Hz, 4H), 7.95 (d, J = 8 Hz, 4H), 8.19 (s, 2H); ^{13}C NMR (90.6 MHz, $CDCl_3$, 300 K) δ = 27.1, 30.7, 52.2, 61.8, 127.8, 129.8, 131.6, 140.2, 159.8, 166.6; MS (FAB) m/z = 409 $[M + H]^+$. This solid was suspended in MeOH (300 mL), then the mixture was heated under reflux and treated with $NaBH_4$ (4 × 1.40 g, 4 × 37.0 mmol) over 1 h. The reaction mixture was cooled to 20 °C and treated cautiously with 2 M HCl. The solvents were evaporated off under reduced pressure, then the residue was partitioned between CH_2Cl_2 and 3 M NaOH. The aqueous phase was extracted with additional portions of CH_2Cl_2, then the combined organic extracts were dried ($MgSO_4$), filtered, and concentrated to yield *N*,*N*′-bis(4-methoxycarbonylbenzyl)-1,6-hexanediamine as a white solid (7.30 g, 93%): mp 99−100 °C; ^{1}H NMR (360.1 MHz, $CDCl_3$, 300 K) δ = 1.28−1.46 (m, 8H), 2.56 (t, J = 7 Hz, 4H), 3.79 (s, 4H), 3.86 (s, 6H), 7.34 (d, J = 8 Hz, 4H), 7.94 (d, J = 8 Hz, 4H); ^{13}C NMR (90.6 MHz, $CDCl_3$, 300 K) δ = 27.1, 30.0, 49.3, 51.9, 53.6, 127.8, 128.7, 129.6, 145.9, 166.9; MS (FAB) m/z = 413 $[M + H]^+$. A solution of this diamine (7.00 g, 17.0 mmol), Boc_2O (7.50 g, 34.4 mmol), and DMAP (0.10 g, 0.9 mmol) in CH_2Cl_2 (300 mL) was stirred for 3 h at 20 °C. The solution was washed successively with 10% aqueous HCl and saturated aqueous $NaHCO_3$ and dried ($MgSO_4$). Filtration, solvent evaporation and column chromatography (SiO_2, EtOAc−*n*-C_6H_{14}, 3:7) furnished *N*,*N*′-bis(*tert*-butoxycarbonyl)-*N*,*N*′-bis-(4-methoxycarbonylbenzyl)-1,6-hexanediamine as a thick oil that eventually solidified (10.40 g, 100%): mp 98−99 °C; ^{1}H NMR (360.1 MHz, $CDCl_3$, 300 K) δ = 1.12−1.24 (br, 4H), 1.30−1.55 (br m, 22H), 3.07−3.20 (br m, 4H), 3.87 (s, 6H), 4.37−4.49 (br, 4H), 7.16−7.27 (br, 4H), 7.95 (d, J = 8 Hz, 4H); ^{13}C NMR (90.6 MHz, $CDCl_3$, 300 K) δ = 14.1, 21.0, 26.5, 27.7, 28.0, 28.3, 29.1, 46.9, 49.7, 50.5, 51.2, 52.0, 52.8, 60.3, 79.7, 126.7, 127.3, 128.9, 129.7, 130.6, 144.2, 156.8, 166.8; MS (FAB) m/z = 514 $[M - Boc]^+$. $LiAlH_4$ (3 × 0.80 g, 3 × 20.0 mmol) was added to an anhydrous THF (300 mL) solution of this oil, then the mixture was heated under reflux for a further 30 min. When the reaction mixture had cooled to 20 °C, 2 M HCl was added to adjust the pH to less than 2. The solvents were removed in vacuo, and the residue was partitioned between H_2O and CH_2Cl_2. After further extraction of the aqueous phase with CH_2Cl_2, the combined organic extracts were dried ($MgSO_4$), filtered, and concentrated to afford **11b** as a thick oil that eventually solidified (8.10 g, 86%): mp 69−70 °C; ^{1}H NMR (360.1 MHz, $CDCl_3$, 300 K) δ = 1.14 (br s, 4H), 1.34−1.52 (br, 22H), 2.63 (br s, 2H), 2.99−3.15 (br, 4H), 4.35 (s, 4H), 4.61 (s, 4H), 7.15 (d, J = 8 Hz, 4H), 7.26 (d, J = 8 Hz, 4H); ^{13}C NMR (90.6 MHz, $CDCl_3$, 300 K) δ = 26.5, 27.7, 28.4, 29.1, 46.4, 49.5, 50.1, 53.4, 64.7, 79.6, 126.2, 127.0, 127.2, 127.7, 127.9, 137.7, 140.0, 155.6, 156.0; MS (FAB) m/z = 558 $[M + H]^+$.

***N*,*N*′-Bis(*tert*-butoxycarbonyl)-*N*,*N*′-bis(4-azidomethylbenzyl)-1,6-hexanediamine (12b).** NCS (7.70 g, 58.0 mmol) and PPh_3 (15.00 g, 58.0 mmol) were stirred in anhydrous THF (300 mL) for 15 min, then the whole was treated with a THF (100 mL) solution of **11b** (8.00 g, 14.0 mmol). The reaction mixture was stirred at 20 °C overnight, then the white solid generated was collected and washed with THF. The combined THF solutions were evaporated, and the residue was chromatographed (SiO_2, EtOAc−*n*-C_6H_{14}, 1:4), affording *N*,*N*′-bis-(*tert*-butoxycarbonyl)-*N*,*N*′-bis(4-chloromethylbenzyl)-1,6-hexanediamine as a thick oil (4.80 g, 56%): ^{1}H NMR (360.1 MHz, $CDCl_3$, 300 K) δ = 1.17−1.27 (br m, 4H), 1.32−1.49 (br, 22H), 3.02−3.19 (br m, 4H), 4.32−4.44 (br, 4H), 4.55 (s, 4H), 7.15−7.23 (br, 4H), 7.31 (d, J = 8 Hz, 4H); ^{13}C NMR (90.6 MHz, $CDCl_3$, 300 K) δ = 14.1, 21.0, 22.6, 26.6, 28.4, 31.5, 46.0, 46.5, 49.5, 50.1, 79.6, 127.4, 127.9, 128.7, 136.3, 138.8, 156.0; MS (FAB) m/z = 594 $[M]^+$; $C_{32}H_{46}Cl_2N_2O_4$ (593.6) calcd: C, 64.75; H, 7.81; N, 4.72. Found: C, 64.79; H, 7.87; N, 4.57. This dichloride was heated under reflux with NaN_3 (1.00 g, 15.4 mmol) in Me_2CO (200 mL). After 20 h, an additional portion of NaN_3 (1.00 g, 15.4 mmol) was added and refluxing was continued for another 24 h. After cooling to 20 °C, the residual salts were filtered off and washed with CH_2Cl_2. The combined solutions were evaporated to dryness, and the residue was chromatographed (SiO_2, EtOAc−*n*-C_6H_{14}, 3:7) to provide **12b** as a colorless oil (4.80 g, 98%): ^{1}H NMR (360.1 MHz, $CDCl_3$, 300 K) δ = 1.15−1.26 (br, 4H), 1.38−1.52 (br m, 22H), 3.03−3.22 (br, 4H), 4.30 (s, 4H), 4.40 (br, 4H), 7.21−7.28 (m, 8H); ^{13}C NMR (90.6 MHz, $CDCl_3$, 300 K) δ = 14.1, 21.0, 26.5, 28.4, 46.6, 49.5, 50.1, 60.3, 79.6, 127.4, 128.0, 128.3, 134.1, 139.0, 156.2; MS (FAB) m/z = 607 $[M + H]^+$; $C_{32}H_{46}N_8O_4$ (606.8) calcd: C, 63.34; H, 7.64; N, 18.47. Found: C, 63.20; H, 7.58; N, 18.20.

***N*,*N*′-Bis(4-azidomethylbenzyl)-1,6-hexanediamine (13b).** CF_3CO_2H (5 mL) was added to a $CHCl_3$ (100 mL) solution of **12b** (4.70 g, 7.8 mmol) and the whole was stirred at 20 °C for 20 h. The solution was concentrated in vacuo and the residue was partitioned between 3 M NaOH and $CHCl_3$. The aqueous phase was extracted further with $CHCl_3$, then the combined organic extracts were dried, filtered, and concentrated to afford **13b** as a colorless oil (3.10 g, 99%): ^{1}H NMR (360.1 MHz, $CDCl_3$, 300 K) δ = 1.29−1.33 (m, 4H), 1.45−1.52 (m, 4H), 2.59 (t, J = 7 Hz, 4H), 3.76 (s, 4H), 4.29 (s, 4H), 7.24 (d, J = 8 Hz, 4H), 7.31 (d, J = 8 Hz, 4H); ^{13}C NMR (90.6 MHz, $CDCl_3$, 300 K) δ = 27.2, 30.0, 49.4, 53.6, 54.5, 128.2, 128.5, 133.8, 140.8; MS (FAB) m/z = 407 $[M + H]^+$.

***N*-(4-Azidomethylbenzyl)-*N*-(6-(*N*′-(4-azidomethylbenzyl)-*N*′-(*tert*-butoxycarbonyl)aminohexyl))ammonium Hexafluorophosphate (10b−H·PF$_6$).** By employing a procedure similar to that described above for **10a**, **13b** (3.10 g, 7.6 mmol), Boc_2O (1.60 g, 7.6 mmol), and DMAP (0.05 g, 0.4 mmol) were reacted together to provide, after column chromatography (SiO_2, EtOAc), **10b** as a thick oil (1.70 g, 44%): ^{1}H NMR (360.1 MHz, $CDCl_3$, 300 K) δ = 1.19−1.28 (m, 6H), 1.34−1.49 (m, 11H), 2.57 (t, J = 7 Hz, 2H), 3.05−3.20 (br m, 2H), 3.76 (s, 2H), 4.29 (s, 4H), 4.40 (br, 2H), 7.24 (m, 6H), 7.31 (d, J = 8 Hz, 2H); ^{13}C NMR (90.6 MHz, $CDCl_3$, 300 K) δ = 26.7, 27.0, 28.4, 30.0, 48.3 (br), 49.4, 53.7, 54.4, 54.5, 128.3, 128.4, 128.5, 133.8, 134.1, 140.8, 155.4; MS (FAB) m/z = 507 $[M + H]^+$; $C_{27}H_{38}N_8O_2$ (506.6) calcd: C, 64.01; H, 7.56; N, 22.12. Found: C, 63.81; H, 7.34; N, 21.84. By using the protocol described above for the synthesis of **10a**−H·PF_6, **10b**−H·PF_6 was obtained as an oil (1.67 g, 100%) from **10b** (1.30 g, 2.6 mmol): ^{1}H NMR (360.1 MHz, $CDCl_3$, 300 K) δ = 1.11−1.45 (m, 15H), 1.66 (br, 2H), 2.98 (br, 2H), 3.07 (t, J = 7 Hz, 2H), 4.18 (s, 2H), 4.28−4.34 (m, 6H), 7.16−7.26 (m, 4H), 7.32 (d, J = 8 Hz, 2H), 7.43 (d, J = 8 Hz, 2H); ^{13}C NMR (90.6 MHz, $CDCl_3$, 300 K) δ = 25.3, 25.7, 25.8, 27.0, 28.3, 30.9, 47.6, 50.3, 51.7, 54.0, 54.4, 80.4, 115.0, 127.5, 128.5, 129.0, 129.3, 130.5, 134.3, 137.6, 138.5, 156.2; MS (FAB) m/z = 507 $[M - PF_6]^+$; $C_{27}H_{39}F_6N_8O_2P$ (652.6) calcd: C, 49.69; H, 6.02; N, 17.17. Found: C, 49.12; H, 6.00; N, 16.75.

{[2]-[*N*-(4-((4,5-bisethoxycarbonyl-1,2,3-triazo-1-yl)methyl)benzyl)-*N*-(6-(*N*′-(4-((4,5-bisethoxycarbonyl-1,2,3-triazo-1-yl)-methyl)benzyl)-*N*′-(*tert*-butoxycarbonyl)aminohexyl))ammonium][dibenzo[24]crown-8]rotaxane} Hexafluorophosphate (14b−H·PF$_6$). DB24C8 (0.70 g, 1.5 mmol), **10b**−H·PF_6 (0.50 g, 0.7 mmol), and diethyl acetylenedicarboxylate (**8**, 0.40 g, 2.3 mmol) were heated under reflux for 3 d in anhydrous CH_2Cl_2 (10 mL). The solution was concentrated in vacuo and the residue chromatographed (SiO_2, Me_2CO−*n*-C_6H_{14}, 7:3) to yield the title compound as white solid (0.32 g, 29%): mp 62−64 °C; ^{1}H NMR (360.1 MHz, $CDCl_3$, 300 K) δ = 0.89 (br s, 4H), 1.17−1.45 (m, 25H), 2.85−3.02 (br m, 4H), 3.30−3.36 (m, 4H), 3.50−3.57 (m, 4H), 3.75 (s, 8H), 3.94−4.04 (m, 4H), 4.06−4.16 (m, 4H), 4.22−4.41 (m, 10H), 4.53−4.62 (br m, 2H), 5.65 (s, 2H), 5.72 (s, 2H), 6.73−6.82 (m, 8H), 7.00−7.21 (m, 8H), 7.29 (d, J = 8 Hz, 2H); ^{13}C NMR (90.6 MHz, $CDCl_3$, 300 K) δ = 13.5, 13.8, 25.7, 28.0, 30.5, 46.1, 48.6, 51.3, 52.9, 53.1, 61.5, 61.6, 62.7, 62.9, 67.8, 69.8, 70.3, 79.3, 112.4, 121.4, 127.8, 129.7, 130.0, 132.6, 132.7, 134.9, 139.9, 140.0, 147.0, 157.8, 158.0, 159.9; HRMS (FAB) $C_{67}H_{91}N_8O_{18}$ $[M - PF_6]^+$ calcd m/z = 1295.6451, found m/z = 1295.6494.

{[2]-[*N*,*N*′-Bis(4-((4,5-bisethoxycarbonyl-1,2,3-triazo-1-yl)methyl)benzyl)-1,6-hexanediammonium][dibenzo[24]crown-8]rotaxane} Bis(hexafluorophosphate) (5b−H$_2$·2PF$_6$). By employing a procedure similar to that described for the synthesis of **5a**−H_2·2PF_6, **14b**−H·PF_6 (0.30 g, 0.2 mmol) was reacted with CF_3CO_2H (0.5 mL) in $CDCl_3$ (5 mL) over 5 h. Following a comparable workup and chromatography (SiO_2,

CH_2Cl_2−MeOH, 94:6), the title compound was obtained as a white solid (0.07 g, 23%): mp 65−67 °C; ^{1}H NMR (400.1 MHz, $CDCl_3$, 300 K) δ = 0.89 (br m, 2H), 1.01 (br m, 2H), 1.20−1.49 (m, 16H), 2.79−2.84 (br m, 2H), 2.89−2.98 (br, 2H), 3.29−3.31 (m, 4H), 3.53−3.56 (m, 4H), 3.74 (s, 8H), 3.96−4.00 (m, 4H), 4.14−4.19 (m, 4H), 4.27−4.41 (m, 8H), 4.57 (br, 2H), 4.98 (br, 2H), 5.66 (s, 2H), 5.71 (s, 2H), 6.77−6.83 (m, 8H), 7.10−7.18 (br m, 4H), 7.21 (d, J = 8 Hz, 2H), 7.38−7.42 (m, 4H); ^{13}C NMR (90.6 MHz, $CDCl_3$, 300 K) δ = 13.7, 14.0, 21.4, 24.3, 25.4, 25.5, 26.0, 26.1, 48.5, 48.9, 51.5, 53.2, 53.4, 61.8, 62.0, 63.0, 68.1, 70.0, 70.5, 112.7, 121.7, 128.0, 128.5, 129.7, 130.0, 130.3, 132.6, 133.1, 135.0, 140.1, 140.4, 147.2, 158.0, 158.2, 160.0, 160.1; HRMS (FAB) $C_{62}H_{84}N_8O_{18}$ $[M - 2PF_6]^+$ calcd m/z = 1196.6005, found m/z = 1196.5976.

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