Translational Isomerism in Some Two- and Three-Station [2]Rotaxanes†

David B. Amabilino, Peter R. Ashton, Sue E. Boyd, Marcos Gómez-López, Wayne Hayes, and J. Fraser Stoddart*

School of Chemistry, University of Birmingham, Edgbaston, Birmingham B15 2TT, U.K.

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The template-directed syntheses of three [2]rotaxanes are described. They all have dumbbell components, with both hydroquinone and resorcinol rings inserted into polyether chains terminated by tetraarylmethane stoppers, that become encircled during the key self-assembly processes by the tetracationic cyclophane, cyclobis(paraquat-*p*-phenylene), with its two π-electron deficient bipyridinium units. It has been demonstrated by low-temperature ^{1}H NMR spectroscopy that the π-electron deficient tetracationic cyclophane has a remarkably high preference to reside around the hydroquinone ring in these molecular shuttles. This observation illustrates how a very small constitutional difference—hydroquinone *versus* resorcinol recognition sites—can lead to the overwhelming preference for one translational isomer over another in this particular range of [2]rotaxanes.

Introduction

Supramolecular chemists[1] employ the very same noncovalent bonding interactions—*e.g.*, π-π stacking interactions[2] and hydrogen bonds[3]—which regulate biological systems and processes in order to construct a series of fascinating unnatural interlocked molecular compounds,[4] such as the catenanes and rotaxanes.[5] In recent times, the supramolecular chemist has adopted concepts such as self-assembly,[6] self-replication,[7] and self-organization[8] that are prolific in biology and applied them successfully into the artificial world of synthetic chemistry. The first inefficient syntheses[9] of catenanes and rotaxanes relied upon the statistical threading of a linear component through a cyclic one. However, it has been possible to design and synthesize well-defined compatible and complementary molecular components with the ability to recognize each other and then to self-assemble them spontaneously into molecular assemblies by employing noncovalent bonding interactions. Notable examples, which illustrate the potential of the self-assembly strategy, have been described by Sauvage and co-workers,[10] who have designed and prepared an impressive array of catenanes, rotaxanes, and knots using a copper(I)-based template procedure. Hydrogen bonding has been employed more recently to self-assemble another class of catenanes and rotaxanes.[11] The ability of macrocyclic polyethers to form pseudorotaxane-like inclusion com-

† Molecular Meccano. 17. For Part 16, see: Asakawa, M.; Ashton, P. R.; Boyd, S. E.; Brown, C. L.; Menzer, S.; Pasini, D.; Stoddart, J. F.; Tolley, M. S.; White, A. J. P.; Williams, D. J.; Wyatt, P. G. *Chem. Eur. J.* **1997**, *3*, 463−481.

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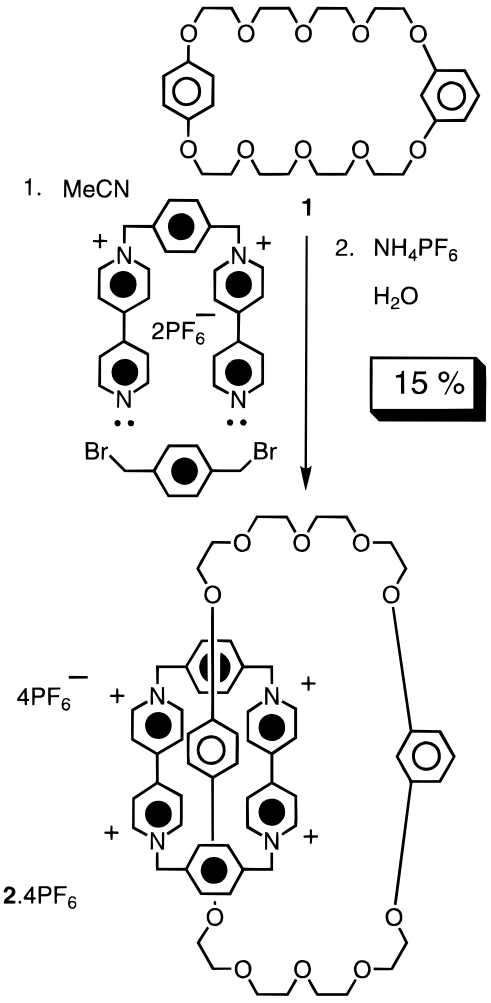
plexes with linear secondary dialkylammoniun salts[12] provides supramolecular chemists with further alternative building blocks for the construction of mechanically-interlocked molecular assemblies and supramolecular arrays.[13]

Rotaxanes, although lacking the topological appeal of the catenanes, have been the subject of intense research because of their abacus-like geometry which makes them an obvious initial starting point for the investigation of switching phenomena in molecular systems.[14] They can also be incorporated into polymers, *i.e.*, polyrotaxanes,[15] bringing together the scientific disciplines of supramolecular and macromolecular chemistry.

Our own research has concentrated on the investigations of interlocked and intertwined superstructures formed by the self-assembly of π-electron rich (*e.g.*, hydroquinone rings) and π-electron deficient *(e.g.*, 4,4′-bipyridinium units) components.[16] The molecular recognition that promotes the formation of these catenanes and rotaxanes containing these building blocks remains intact in the final interlocked molecules and intertwined

Scheme 1



supermolecules, making them ideal for studying the role of constitutional change upon the nature of noncovalent bonding interactions.[17]

Translational isomerism[17] has been observed previously in both catenanes and rotaxanes. In the latter case, a series of desymmetrized molecular shuttles[18]—*i.e.*, [2]rotaxanes, in which, for example, the π-electron deficient tetracationic cyclophane moves between two degenerate π-electron rich stations—have been designed and synthesized. It has been possible to modify the dumbbell component in such a way that it incorporates

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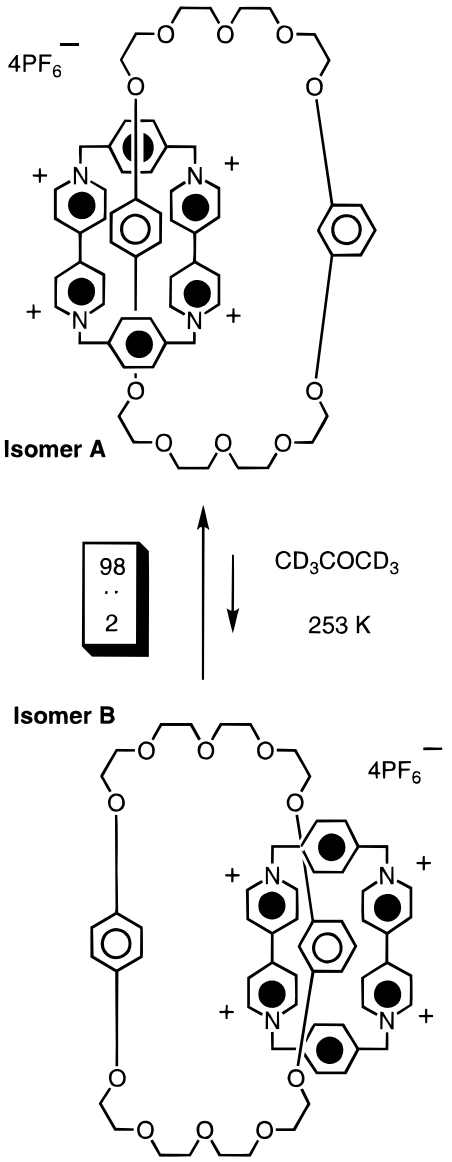
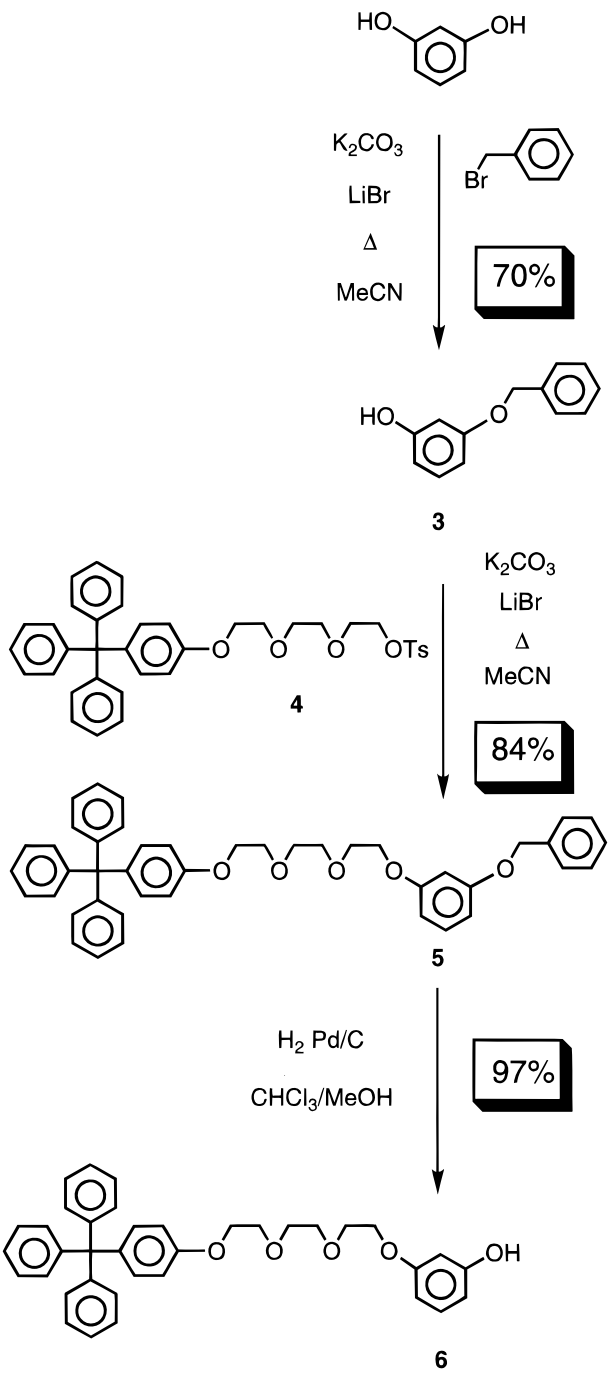
Scheme 2



two nondegenerate π-electron rich stations, one of them a hydroquinone ring and the other a *p*-xylene,[19] an indole,[20] or a tetrathiafulvalene unit.[21] Furthermore, a molecular switch,[22] inspired by the translational isomerism displayed in these desymmetrized [2]rotaxanes, has been constructed in which one of the π-electron rich stations is a benzidine unit and the other one is a biphenol unit. In the case of this particular molecular shuttle, the control of the movement of the tetracationic cyclophane can be effected either chemically or electrochemically.

A [2]catenane, **2**·4PF_6, incorporating a resorcinol unit (1,3-dihydroxybenzene) in the macrocyclic polyether component, namely, (*p*-phenylene)(*m*-phenylene)-33-crown-10 (**1**), with the tetracationic cyclophane cyclobis(paraquat-*p*-phenylene) as the π-electron deficient component, has been self-assembled[23] previously in 15% yield (Scheme 1). It was observed that changing the constitution of the macrocyclic polyether not only affects drastically the efficiency of the self-assembly process but it also alters the nature of the dynamic motion of the two interlocked rings with respect to each other. Variable temperature ^{1}H NMR spectroscopic studies carried out on a CD_3COCD_3 solution of **2**·4PF_6 revealed the existence (Scheme 2) of two translational isomers, A and B.[23] The translational isomer ratio A:B was found to be 98:2 at 253 K. It is noteworthy that this remarkable preference for the

Scheme 3



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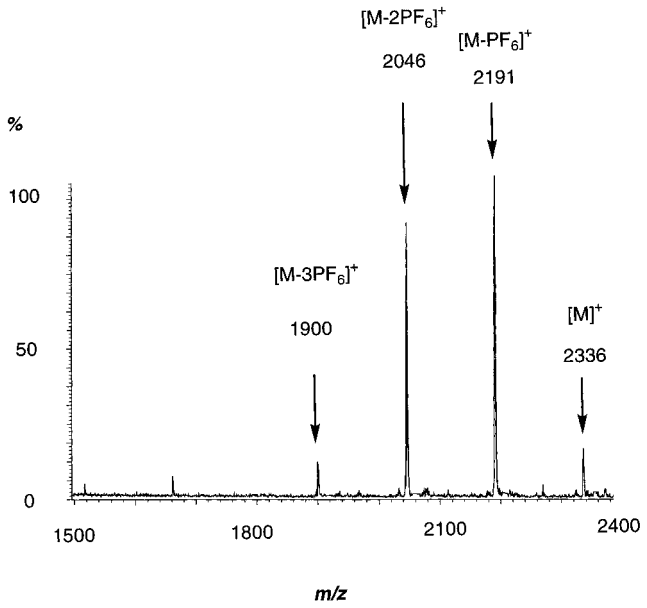
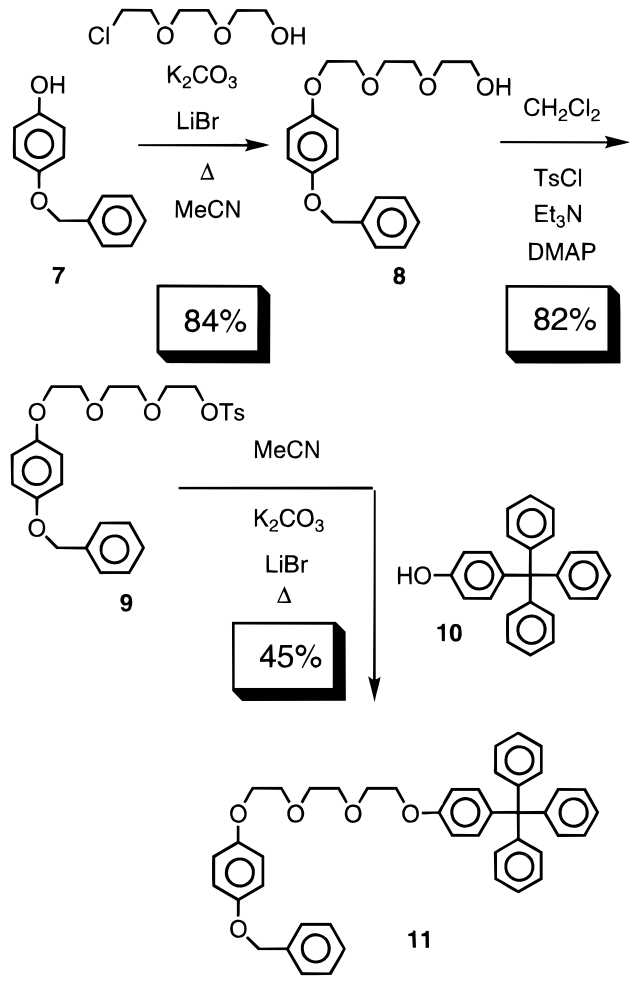


Figure 1. Mass spectrum of the two-station [2]rotaxane **23**·4PF_6.

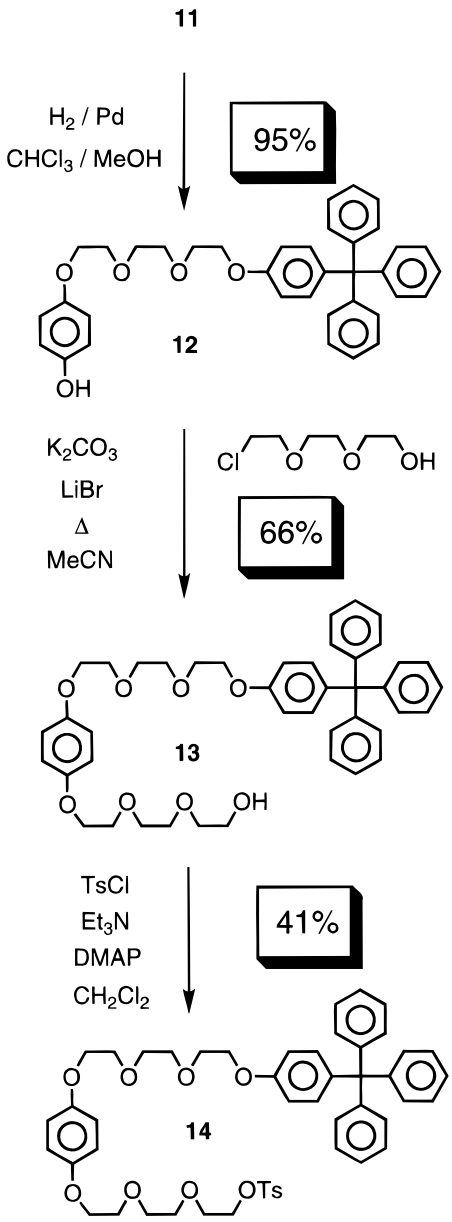
Scheme 4



inclusion of the hydroquinone ring within the cavity of the tetracationic cyclophane was exhibited for **2**·4PF_6—a very simple desymmetrized [2]catenane.

In this paper, we report on the self-assembly of three new [2]rotaxanes containing hydroquinone and resorcinol rings in their dumbbell components. We show how ^{1}H NMR spectroscopic studies provide information about the different translational isomers and how we are able to conclude that the high translational selectivity observed in the [2]catenane **2**·4PF_6 does translate into the analogous [2]rotaxanes. In addition, the translational selectivity displayed by the three new molecular shuttles gives information about the preferential sites of residence of the π-electron deficient tetracationic cyclophane, not only in relation to the stereoelectronic nature of the π-electron rich stations but also in respect to the symmetries of the π-electron rich dumbbell components. All of this information improves our understanding of the nature of the noncovalent bonding interactions which regulate the self-assembly processes, enabling the future construction of functioning molecular assemblies and supramolecular arrays.

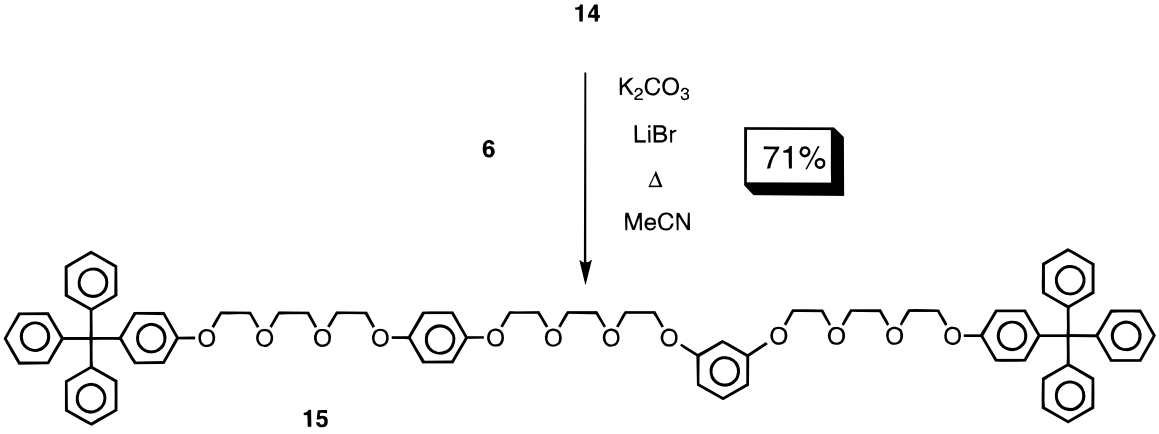
Scheme 5



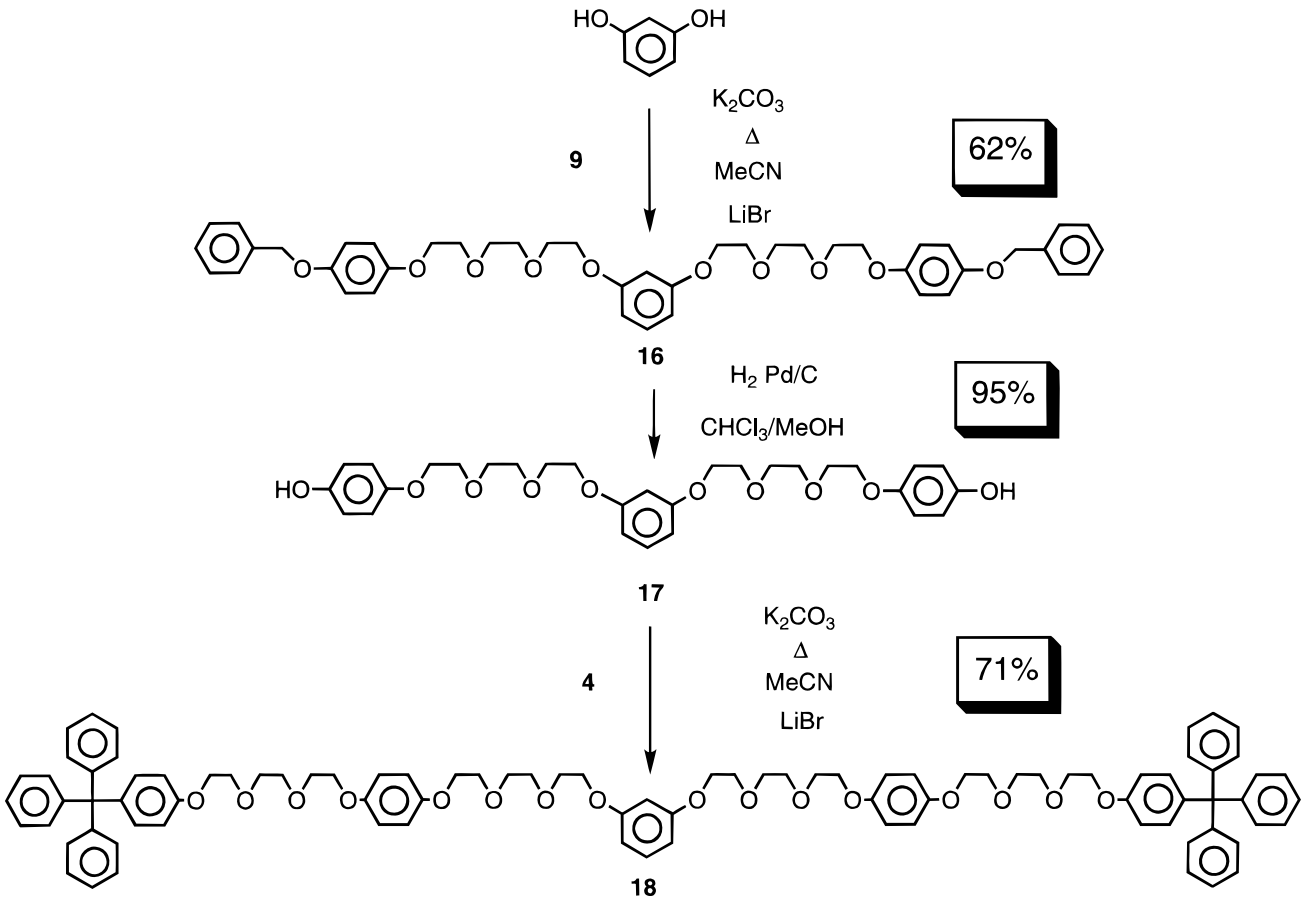
Results and Discussion

Synthesis. The first objective was to synthesize a desymmetrized dumbbell compound, comprising one resorcinol and one hydroquinone ring as the potential π-electron rich recognition sites. In order to achieve this

Scheme 6



Scheme 7



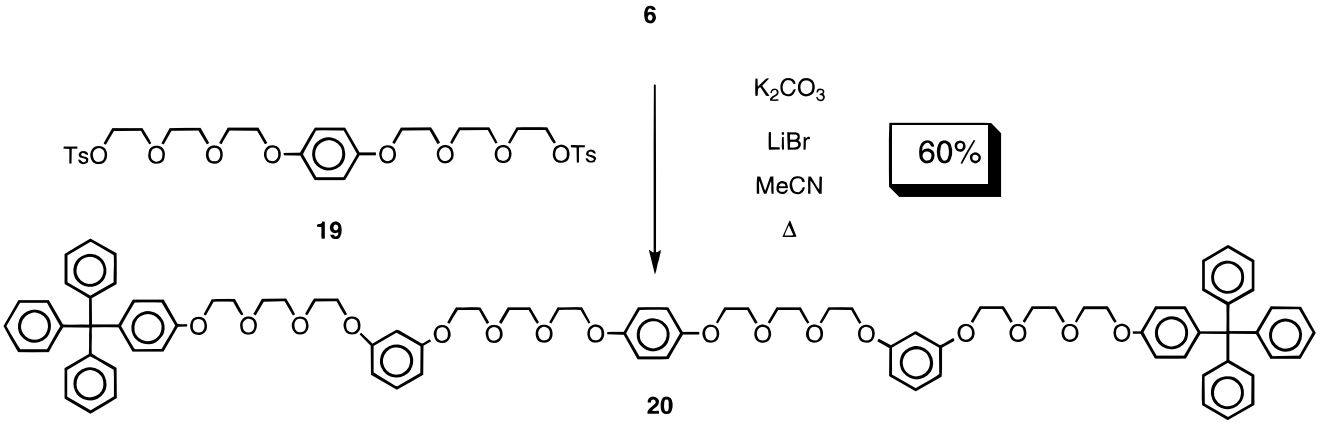
goal, the synthetic strategy outlined in Scheme 3 was applied in the first instance. An excess of resorcinol was reacted with benzyl bromide, under mildly basic conditions, to produce the phenol **3**.[24] Alkylation of the phenol **3** with the tosylate **4**[20] in the presence of base yielded the benzyl-protected phenol **5** in good yield. Hydrogenolysis of the *O*-benzyl groups in the masked phenol **5**, under standard conditions, afforded the phenol **6** in 97% yield.

The other half of the dumbbell compound, comprising the π-electron rich hydroquinone ring, was synthesized according to the route outlined in Schemes 4 and 5. Commercially available 4-(benzyloxy)phenol (**7**) was alkylated with 2-(2-(2-chloroethoxy)ethoxy)ethanol in the presence of base to afford the alcohol **8**. Tosylation of the alcohol **8** yielded the corresponding tosylate **9**, which was then reacted with the phenol **10**[20] under basic conditions to produce the protected phenol **11**. Subsequent deprotection using standard procedures gave a 95% yield of the phenol **12**, which was further alkylated with 2-(2-(2-chloroethoxy)ethoxy)ethanol to produce the alcohol **13**, which was then reacted with tosyl chloride in the presence of triethylamine and DMAP to give the tosylate **14**.

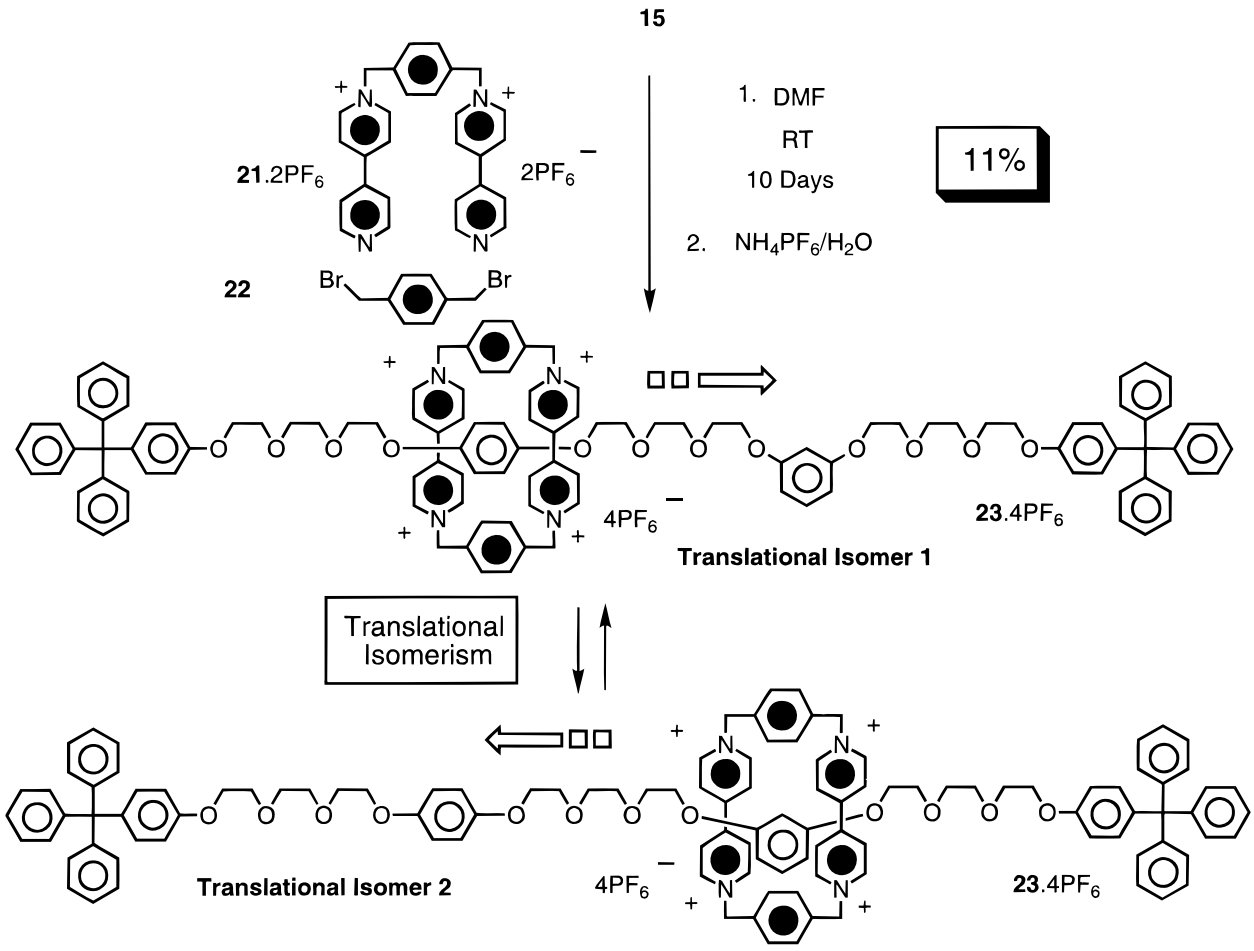
The unsymmetrical dumbbell compound **15**, comprising one hydroquinone ring and one resorcinol ring as the π-electron-donating recognition sites, was constructed (Scheme 6) by coupling the phenol **6** and the monotosylate **14** under mildly basic conditions.

(24) Fitton, A. O.; Ramage, G. R. *J. Chem. Soc.* **1962**, 4870−4874

Scheme 8



Scheme 9

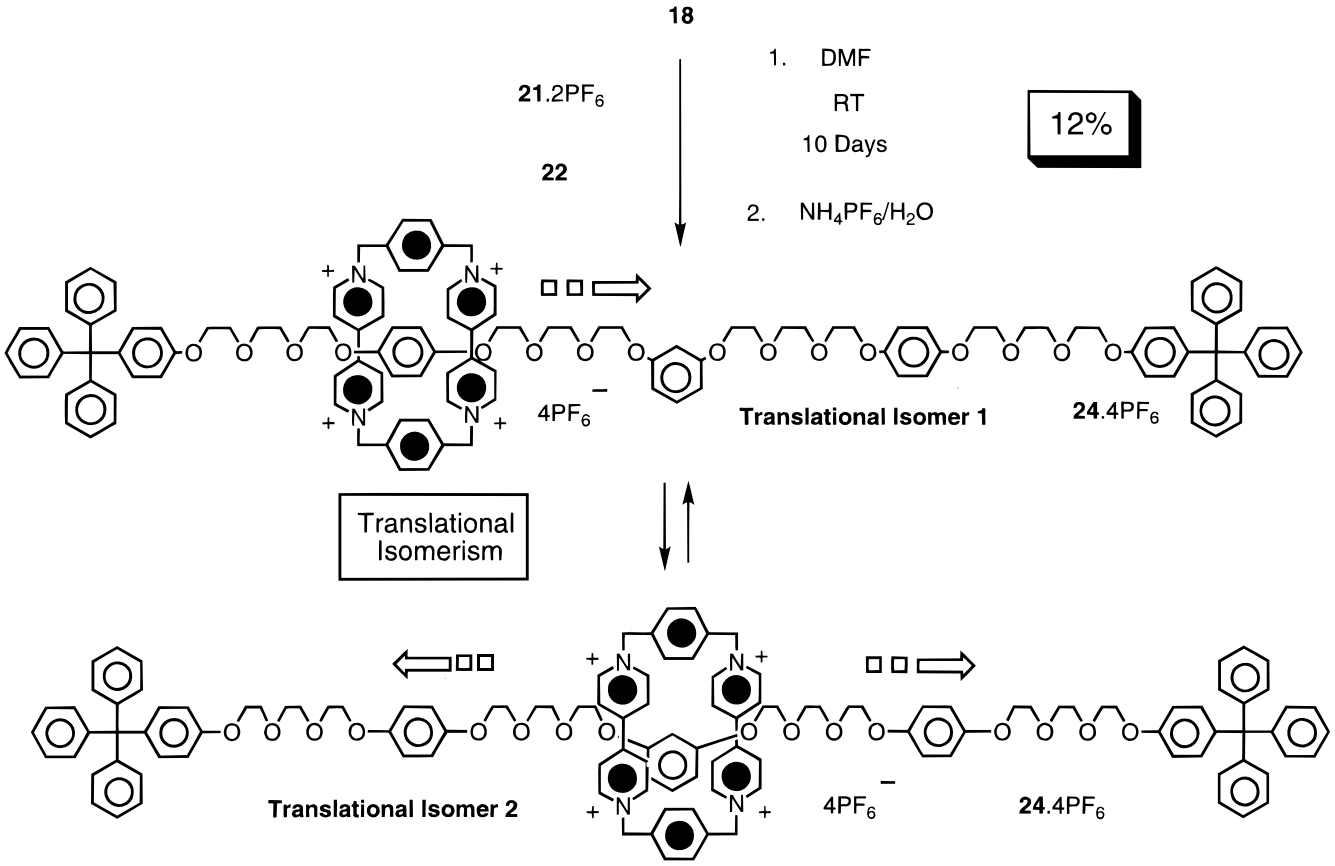


The syntheses of the symmetrical dumbbell compounds were achieved by following a similar synthetic strategy: it is outlined in Schemes 7 and 8. Resorcinol was dialkylated with tosylate **9** under basic conditions to yield the protected bisphenol **16**. Deprotection by hydrogenolysis of both benzyloxy groups afforded the corresponding bisphenol **17** which was then reacted with 2 molar equiv of the tosylate **4** in the presence of base to produce (Scheme 7) the symmetrical dumbbell compound **18** containing one resorcinol ring sandwiched between two hydroquinone rings within a polyether chain.

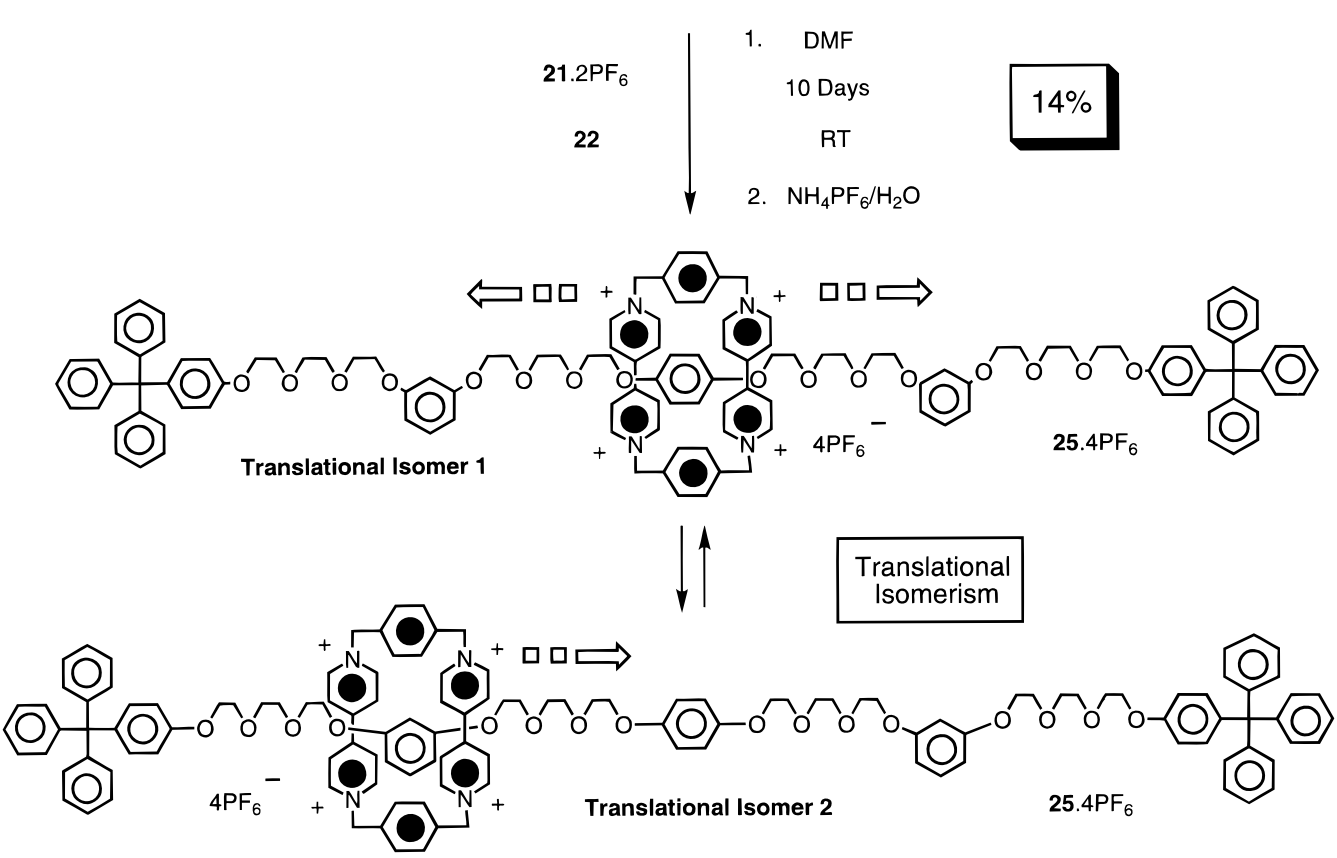
The analogous symmetrical dumbbell compound **20**, comprised of two resorcinol rings sandwiching one hydroquinone ring within a polyether chain, was synthesized (Scheme 8) in 60% by reaction under basic conditions of 2 molar equiv of the phenol **6** with the bistosylate **19** to produce the symmetrical dumbbell compound **20**.

The self-assembly of the unsymmetrical [2]rotaxane **23**·4PF_6 was achieved (Scheme 9) in 11% yield by stirring 1 molar equiv of the π-electron rich dumbbell compound **15** in the presence of 3 molar equiv of the bipyridinium salt **21**·2PF_6 and 1.2 molar equiv of 1,4-bis(bromomethyl)benzene (**22**) in a DMF solution at room temperature and ambient pressure (Scheme 9), followed by counterion exchange with NH_4PF_6/H_2O to yield the hexafluorophosphate salt **23**·4PF_6. The mass spectrum (Figure 1) of **23**·4PF_6 reveals peaks corresponding to the molecular ion

Scheme 10



Scheme 11



and the molecular ion less one, two, and three hexafluorophosphate counterions.

The symmetrical [2]rotaxanes **24**·4PF_6 and **25**·4PF_6, comprising the dumbbell components **18** and **20**, respec-

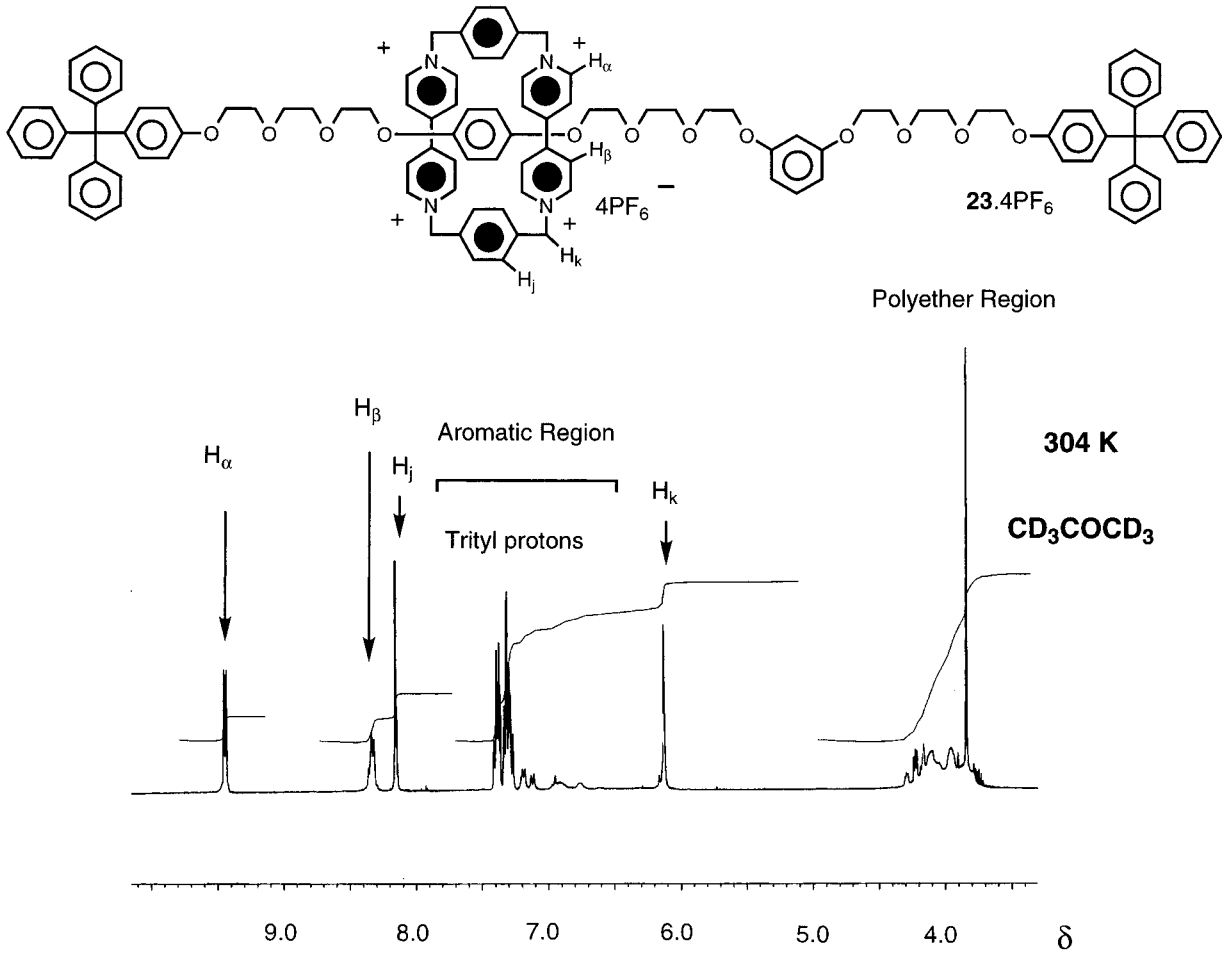


Figure 2. Partial ^{1}H NMR spectrum of **23**·4PF$_6$ in CD_3COCD_3 at 304 K.

tively, were self-assembled in 12% and 14% yields, employing conditions identical to those used for the self-assembly of the [2]rotaxane **23**·4PF$_6$ (Schemes 10 and 11).

The yields of the [2]rotaxanes are relatively low in comparision to the 32% yield reported for the self-assembly of the prototypical molecular shuttle[18] in which the symmetrical linear dumbbell component contains two π-electron rich hydroquinone rings. Nonetheless, the yields of **23**·4PF$_6$, **24**·4PF$_6$, and **25**·4PF$_6$ seem to be of similar magnitudes to those reported for the self-assembly of other molecular shuttles in which one of the hydroquinone rings is replaced by a different π-electron rich unit.

It can be concluded that the presence of the meta-substituted resorcinol ring in the linear polyether chain undermines the efficiency of the self-assembly processes when compared to the reference situation where only para-substituted hydroquinone rings are present in the dumbbell components. Nevertheless, the decrease in the efficiency of the self-assembly process is not as dramatic as that observed for the related [2]catenanes. This difference undoubtedly reflects the inclusion of a meta-substituted benzene ring in the macrocyclic polyether component which forces the crown ether to adopt a conformation that disrupts the molecular recognition between the individual molecular precursors, thus hindering the self-assembly process. On the other hand, the dumbbell component possesses much more conformational freedom than do the macrocyclic polyether analogs, and so the inclusion of meta-substituted benzenoid rings in a linear system does not affect the self-assembly processes as much as that in the case of a [2]catenane.

^{1}H NMR Spectroscopy. The ^{1}H NMR spectra recorded for the [2]rotaxanes **23**·4PF$_6$, **24**·4PF$_6$, and **25**·4PF$_6$ exhibit marked temperature dependencies in accordance with the highly fluxional solution state structures expected for mechanically-interlocked compounds.

The ^{1}H NMR spectrum (400 MHz, CD_3COCD_3) of **23**·4PF$_6$ at room temperature (Figure 2) shows largely broadened or averaged signals. In particular, only one resonance is observed for each of the α and β protons on the bipyridinium units of the tetracationic cyclophane. Process 1, *i.e.*, the shuttling of the tetracationic cyclophane back and forth between the nondegenerate π-electron rich recognition sites (Scheme 9), is therefore occurring at a rate comparable to or greater than that of the 400 MHz ^{1}H NMR time scale at ambient temperatures. Upon cooling of the solution, the spectra sharpen (Figure 3) initially such that, at 240 K, resonances attributable to the major translational isomer 1, *i.e.*, the species in which the tetracationic cyclophane resides on the hydroquinone station, are well resolved. The assignment of the resonances was assisted by two-dimensional COSY and NOESY experiments. The corresponding resonances expected for the minor translational isomer 2 are, however, broad and indistinct by comparison. The reason for this phenomenom is probably associated in part with a further site-exchange process occurring as a result of the included resorcinol ring departing from the cavity of the tetracationic cyclophane, re-orienting itself, and re-entering the cavity.

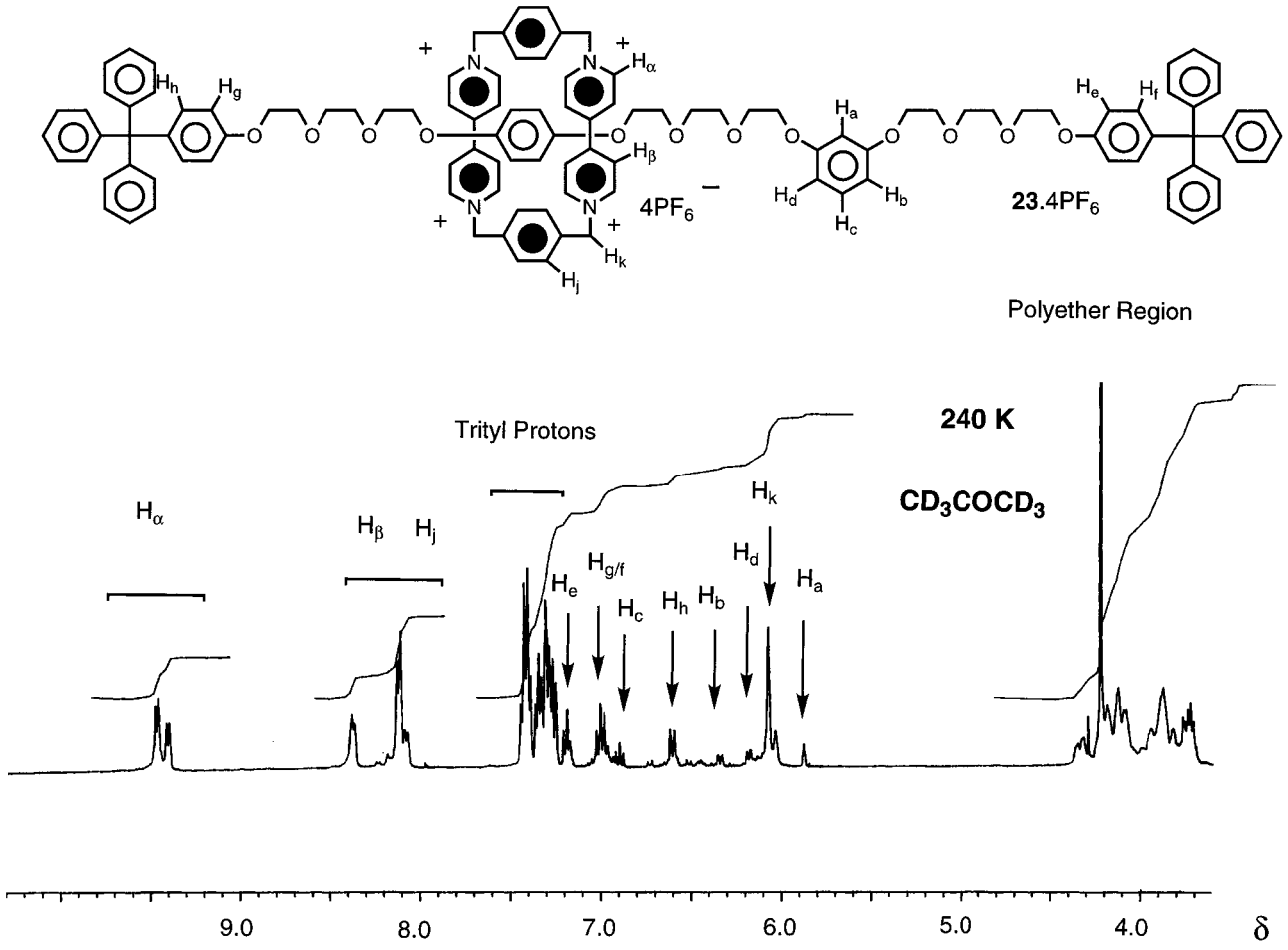


Figure 3. Partial ^{1}H NMR spectrum of **23**·4PF_6 in CD_3COCD_3 at 240 K.

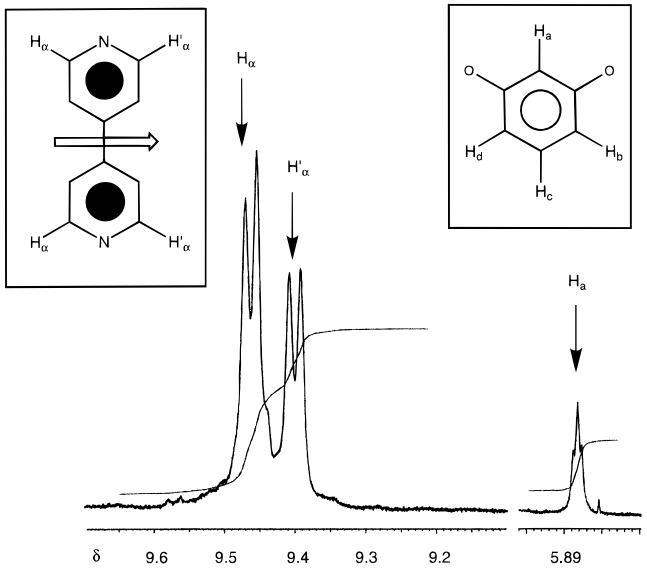
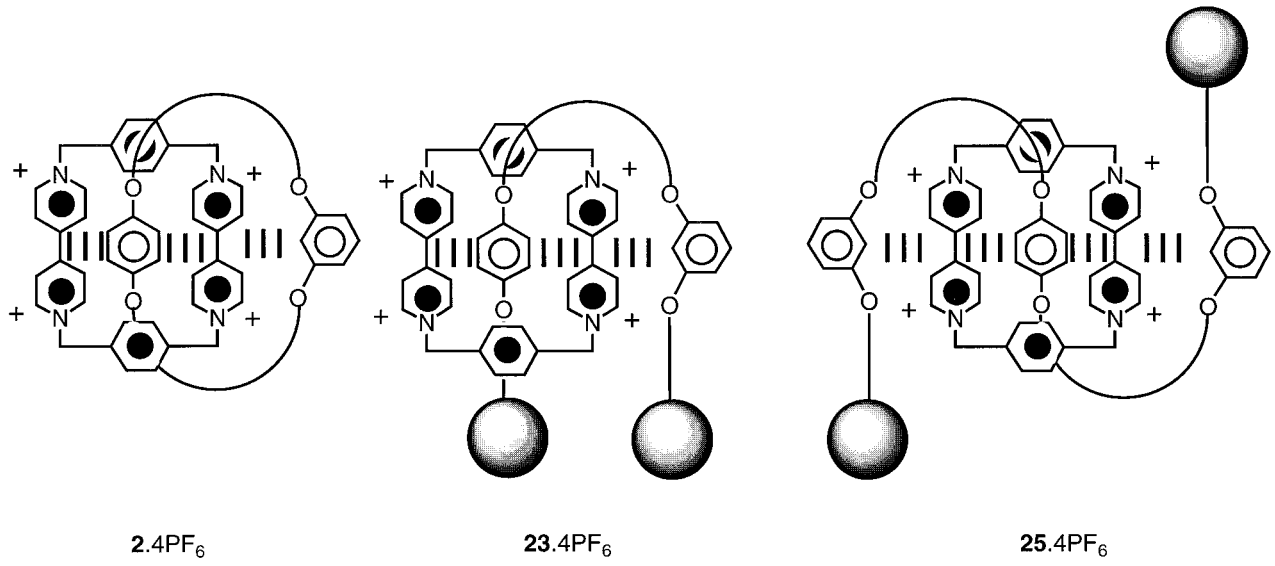


Figure 4. Partial ^{1}H NMR spectrum of **23**·4PF_6 in CD_3COCD_3 at 240 K depicting the shift region of the α-bipyridinium protons and the region for the resorcinol H_a proton.

Relative recognition-site occupancies were calculated by comparison of the net integral intensities of the isolated resonances observed for the major translational isomer with the total integral intensity of the characteristic chemical shift region for the α-protons on the bipyridinium units (Figure 4). Specifically, the signals corresponding to the *unoccupied* resorcinol station show the expected apparent triplet (H_a), two double doublets (H_b and H_d), and a further apparent triplet (H_c) resonating at δ 5.87 ($J \approx 1$ Hz), δ 6.15 and 6.35, and δ 6.85 ($J \approx 7$ Hz), respectively. Similarly, resonances corresponding to the protons of the linking phenylene rings within the tetraarylmethane stoppers appear as two different AA′XX′ systems, resonating at δ 6.58 and 6.97 and δ 6.97 and 7.20, respectively. The isolated resonances were compared to the overlapping resonances for the α-protons of the bipyridinium units, as illustrated in Figure 4. This region shows the two doublets expected for the chemically nonequivalent α-protons of the bipyridinium units in the desymmetrized tetracationic cyclophane associated with the major translational isomer, resonating on top of a broad signal attributable to the minor translational isomer. As this region must account for all the tetracationic cyclophane present in both translational isomers of the [2]rotaxane, a not unreasonable estimate of the relative concentration of the minor translational isomer present in the solution at this temperature can be obtained by simple subtraction of the appropriately-weighted integral intensity. Thus, the relative recognition-site occupancy for the tetracationic cyclophane of the [2]rotaxane **23**·4PF_6 in CD_3COCD_3 solution at 240 K was calculated as 2:1 in favor of hydroquinone occupancy over that of resorcinol occupancy.

Unfortunately, further cooling of the solution resulted in only further broadening of the resonances to the extent that, at temperatures around 200 K (400 MHz), no signals were clearly resolved. The increasing complexity of the spectra with decreasing temperature could result from the system folding itself (Scheme 12) in order to

Scheme 12



maximize the effectiveness of the "alongside" interaction between the tetracationic cyclophane and the unoccupied π-electron rich recognition site. Resolution of this issue could only be accomplished using much higher field strengths and has not been explored further here. It is noteworthy, however, that the relative site occupancy observed for the analogous [2]catenane[23]—a system in which the two π-electron rich components are incorporated into a crown ether ring and are thus preorganized for efficient "inside" and "alongside" complexation of the tetracationic cyclophane—is much more strongly weighted in favor of hydroquinone occupation at the expense of resorcinol occupation.

The behavior of the three-station [2]rotaxane **24**·4PF_6 is very similar to that of **23**·4PF_6. The main difference comes from the symmetrical nature of the dumbbell component of **24**·4PF_6, comprising two degenerate hydroquinone stations. The shuttling of the tetracationic cyclophane gives rise to two different translational isomers, 1 and 2, as depicted in Scheme 10. The ^{1}H NMR spectrum (400 MHz, CD_3COCD_3) of **24**·4PF_6 at 240 K (Figure 5) shows well-resolved resonances attributable to the major translational isomer 1. The signals corresponding to the protons of the unoccupied resorcinol ring can also be observed: they are an apparent triplet (H_a) at δ 5.70 ($J \approx 1$ Hz), two overlapping double doublets ($H_{b/d}$) centered on δ 6.25, and another apparent triplet (H_c) centered on δ 6.84 ($J \approx 7$ Hz). The signals for the protons corresponding to the linking phenylene rings within the tetraarylmethane stoppers resonate as two different AA′XX′ ($H_{e/f}$ and $H_{g/h}$) systems with δ 7.15 and 6.91 and δ 6.96 and 6.57. These two AA′XX′ systems correspond to the major translational isomer 1, where the tetracationic cyclophane is residing on one of the degenerate hydroquinone rings. No isolated resonances for the minor translational isomer 2 can be observed. The relative recognition-site occupancy for the tetracationic cyclophane in **24**·4PF_6 in CD_3COCD_3 at 240 K was calculated in the same fashion as for that described in **23**·4PF_6. It revealed a 4:1 ratio in favor of translational isomer 1 over translational isomer 2.

The three-station [2]rotaxane **25**·4PF_6, in which a hydroquinone station is sandwiched between two resorcinol units, behaves in a manner similar to the [2]rotaxanes **23**·4PF_6 and **24**·4PF_6. The ^{1}H NMR spectrum recorded in CD_3COCD_3 at 220 K (400 MHz) shows well-resolved resonances for the protons corresponding to the alongside resorcinol rings. A broad apparent singlet (H_a) at δ 5.88, two double doublets ($H_{d/b}$) at δ 6.13 and 6.45, and an apparent triplet (H_c) at δ 7.18 ($J \approx 7$ Hz), corresponding to the major translational isomer 1 (Scheme 11), where the hydroquinone ring is included within the cavity of the tetracationic cyclophane, are observed. The signals corresponding to the linking phenylene rings within the tetraarylmethane stoppers resonate as a single AA′BB′ ($H_{e/f}$) system at δ 6.98 and 7.16 for the major translational isomer, indicating the presence of a symmetrical [2]rotaxane. The relative recognition-site occupancy calculated for **25**·4PF_6 in CD_3COCD_3 at 220 K was 8:1 in favor of translational isomer 1 over translational isomer 2. This high selectivity can be explained on the basis of the most favored geometry in solution (Scheme 12), wherein the tetracationic cyclophane resides around the central hydroquinone ring, leaving the two π-electron deficient bipyridinium units of the tetracationic cyclophane to interact in an "exo" fashion with the two alongside π-electron rich resorcinol rings, resulting in the tetracationic cyclophane being sandwiched by the two "free" resorcinol rings, as observed in other linear pseudorotaxane systems.[23b] By adopting this geometry, the rotaxane gains some extra stabilizing interactions.

Conclusions

The self-assembly of three novel [2]rotaxanes, **23**·4PF_6–**25**·4PF_6, containing resorcinol and hydroquinone stations, has been achieved in reasonable yields (11–12%). Although these yields are lower than that (32%) for the self-assembly of a [2]rotaxane comprising two hydroquinone rings in the dumbbell component,[18] they are similar to those obtained when one of the hydroquinone rings is replaced by another π-electron rich station.[19–21]

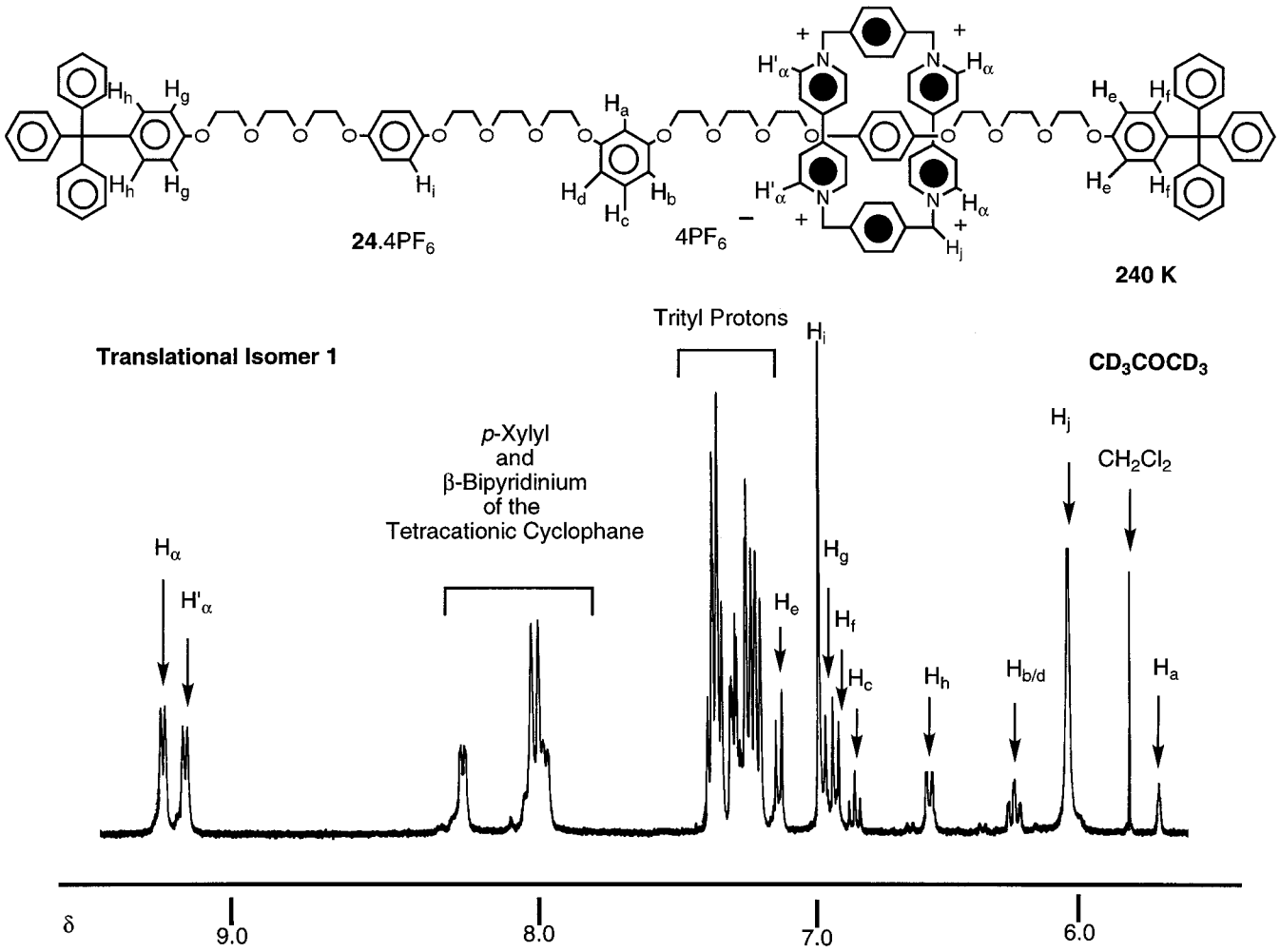


Figure 5. Partial ^{1}H NMR spectrum of the [2]rotaxane **24**·4PF$_6$ in CD_3COCD_3 at 240 K.

Table 1. Relative Site Occupancy for Resorcinol-Containing Molecular Assemblies As Determined by ^{1}H NMR Spectroscopy

compound	solvent	temperature (K)	site occupancy[a]
2·4PF$_6$	CD_3COCD_3	253	98:2
23·4PF$_6$	CD_3COCD_3	240	2:1
24·4PF$_6$	CD_3COCD_3	240	4:1
25·4PF$_6$	CD_3COCD_3	220	8:1

[a] The site occupancy is always such that the major translational isomer has the cyclobis(paraquat-*p*-phenylene) tetracationic component encircling the hydroquinone ring in the other component.

There is a decrease in the efficiency of the self-assembly process when one of the hydroquinone stations is replaced by a resorcinol one, but the effect is not as dramatic as that observed in the case of the corresponding [2]catenane system.

The variable temperature ^{1}H NMR spectroscopic studies reveal that [2]rotaxanes **23**·4PF$_6$–**25**·4PF$_6$ exist as two different translational isomers in all three cases. The two-station [2]rotaxane **23**·4PF$_6$ displays an approximately 2:1 selectivity for the major translational isomer 1 over the translational isomer 2. The three-station [2]rotaxane **24**·4PF$_6$ shows a selectivity of approximately 4:1. The difference in selectivity can be explained easily on the basis that the [2]rotaxane possesses two hydroquinone stations and only one resorcinol one. Finally, the three-station [2]rotaxane **25**·4PF$_6$ exhibits the highest selectivity of 8:1 as a result of folding in solution (Scheme 12) in order to maximize the alongside noncovalent bonding interactions (Table 1). The [2]rotaxane **25**·4PF$_6$ enjoys the highest selectivity of one translational isomer over the other, and therefore it represents the first step in the construction of abacus-like molecular structures with switching capabilities that could be controlled by external stimuli.

The isomer selectivities observed for the linear [2]rotaxanes are not nearly as high as that for the analogous [2]catenane **2**·4PF$_6$. This observation is an interesting one that merits further investigation by computational methods. These investigations are underway.

Experimental Section

General Procedures. Solvents were used as supplied, with the exception of the following: dimethylformamide (DMF) was distilled from calcium hydride under reduced pressure and acetonitrile (MeCN) was distilled under nitrogen from calcium hydride. Developed thin layer chromatography (TLC) plates were air-dried, scrutinized under a UV lamp, and, if necessary, then either sprayed with cerium(IV)sulfate–sulfuric acid reagent and heated to ca. 100 °C or developed in an iodine tank. Microanalyses were performed by the University of Sheffield Microanalytical Service. Melting points were determined in an open capillary tube and are uncorrected. ^{1}H nuclear magnetic resonance (NMR) spectra were recorded at either 300 or 400 MHz using the deuterated solvent as a lock and residual protonated solvent or tetramethylsilane as an internal reference. ^{13}C NMR spectra were recorded at either 75 or 100 MHz.

3-(Benzyloxy)phenol[24] (3). A solution of resorcinol (50 g, 450 mmol) and K_2CO_3 (6.21 g, 45 mmol) in dry MeCN (200

mL) was refluxed under nitrogen for 1 h. A solution of benzyl bromide (7.7 g, 0.045 mol) in dry MeCN (250 mL) was added dropwise over 1 h to the reaction mixture, the solution was allowed to reflux for 4 days under nitrogen with vigorous stirring. The solution was cooled down to room temperature and filtered, and the solvent was removed *in vacuo*. The residual oil was taken up in CH_2Cl_2 (200 mL) and washed with dilute aqueous HCl (pH 3, 2 × 200 mL) and then brine (2 × 200 mL). The organic phase was dried ($MgSO_4$) and the solvent removed *in vacuo*. Column chromatography (SiO_2, CH_2Cl_2) afforded the phenol **3** as a white solid (6.29 g, 70%): mp 51−51.8 °C (lit.[24] mp 50−51 °C); IR (NaCl) 3424, 3031, 2936, 2872, 2433, 1594, 1498, 1490, 1454, 1381, 1238, 1216, 1146, 1080, 1026, 940, 838, 764, 696 cm^{-1}; EIMS 200 (M^+); ^1H NMR ($CDCl_3$, 300 MHz, 25 °C) δ 5.01 (s, 2H), 6.12 (s, 1H), 6.49−6.47 (dd, 1H, J = 7, 1 Hz), 6.62−6.60 (dd, 1H, J = 7, 1 Hz), 7.15 (t, 1H, J = 7 Hz), 7.45−7.34 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 70.2, 102.7, 107.5, 108.4, 127.6, 128.1, 128.7, 130.3, 136.9, 156.8, 160.2.

1-[2-(2-(2-(Tritylphenoxy)ethoxy)ethoxy)ethoxy]-3-(benzyloxy)benzene (5). A solution of 3-(benzyloxy)phenol (**3**) (1.79 g, 8.9 mmol), K_2CO_3 (1.8 g, 13 mmol), and a catalytic amount of LiBr in dry MeCN (100 mL) was mixed and heated under reflux for 1 h in a nitrogen atmosphere. A solution of tosylate[20] **4** (5.58 g, 8.9 mmol) in dry MeCN (100 mL) was added dropwise over 30 min to the reaction mixture; the solution was heated under reflux for 4 days under nitrogen with vigorous stirring. The solution was allowed to cool to rt before it was filtered and the solvent removed *in vacuo*. The residual oil was dissolved in CH_2Cl_2 (200 mL) and washed with dilute HCl (pH 3, 2 × 200 mL) and brine (2 × 200 mL). The organic phase was dried ($MgSO_4$) and the solvent removed *in vacuo* to yield the protected phenol **5** as a yellow oil (4.82 g, 84%): IR (NaCl) 3056, 2924, 2873, 1594, 1508, 1491, 1448, 1250, 1182, 1154, 829, 748, 702 cm^{-1}; LSIMS *m/z* 650 (M^+); ^1H NMR ($CDCl_3$, 300 MHz, 25 °C) δ 3.78 (s, 4H), 3.90−3.86 (m, 4H), 4.15−4.12 (m, 4H), 5.06 (s, 2H), 6.57−6.54 (dd, 1H, J = 7, 1 Hz), 6.62−6.60 (m, 2H), 6.83−6.80 (AA′BB′ system, 2H, J = 8 Hz), 7.14−7.11 (AA′BB′ system, 2H, J = 8 Hz), 7.30−7.19 (m, 16H), 7.48−7.35 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 64.3, 67.3, 67.5, 69.8, 70.0, 70.8, 102.1, 107.2, 107.4, 113.4, 125.9, 127.4, 127.5, 127.9, 128.6, 129.9, 131.1, 132.2, 139.2, 147.1, 156.8, 160.0; HRMS calcd for $C_{44}H_{42}O_5$ $[M]^+$ 650.3032, found 650.3041 (err −1.3 ppm).

1-[2-(2-(2-(Tritylphenoxy)ethoxy)ethoxy)ethoxy]-3-hydroxybenzene (6). A solution of **5** (5.57 g, 8.7 mmol) in $CHCl_3$ (200 mL) was added to a suspension of Pd/C (5%, 1.5 g) in MeOH (200 mL). The suspension was stirred for 12 h as hydrogen gas was bubbled into the mixture. The suspension was filtered through Celite, and the solvent was removed *in vacuo* to produce phenol **6** as a white solid (4.66 g, 97%). Phenol **6** is prone to oxidation, and so the next reaction was carried out immediately using the crude product.

1-[2-(2-(2-Hydroxyethoxy)ethoxy)ethoxy]-4-(benzyloxy)benzene[20] (8). A stirred suspension of 4-(benzyloxy)phenol (15 g, 75 mmol) and K_2CO_3 (35 g, 250 mmol) in dry MeCN (250 mL) was brought to reflux under nitrogen. 2-(2-(2-Chloroethoxy)ethoxy)ethanol (22 mL) was added dropwise, and the resulting mixture was stirred at reflux under nitrogen for 3 days. The suspension was filtered and the solvent removed *in vacuo*. CH_2Cl_2 (200 mL) was added to the residue; the resultant mixture was washed with dilute HCl (pH 3, 3 × 250 mL) and then distilled H_2O (3 × 250 mL). The organic phase was dried ($MgSO_4$) and the solvent removed *in vacuo*, yielding product **8** as a white powder (21.05 g, 84%): mp 49−50 °C; IR (NaCl) 3298, 2935, 2879, 1511, 1452, 1237, 1115, 1066, 1029, 952, 833, 737 cm^{-1}; EIMS *m/z* 332 (M^+); ^1H NMR ($CDCl_3$, 300 MHz, 25 °C) δ 3.50−3.63 (m, 2H), 3.68−3.74 (m, 4H), 3.82−3.85 (t, 2H), 4.07−4.10 (m, 4H), 5.01 (s, 2H), 6.83−6.91 (m, 4H), 7.28−7.44 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 61.8, 68.1, 69.9, 70.4, 70.7, 70.8, 72.5, 115.7, 115.8, 127.5, 127.9, 128.5, 137.3, 153.1, 153.2; HRMS calcd for $C_{19}H_{24}O_5$ $[M]^+$ 332.1623, found 332.1616 (err 2.3).

1-[2-(2-(2-(*p*-Toluenesulfonyloxy)ethoxy)ethoxy)ethoxy]-4-(benzyloxy)benzene (9). A solution of the alcohol **8** (3 g, 9.2 mmol), Et_3N (3.78 mL, 37.4 mmol), and a catalytic amount of DMAP in dried CH_2Cl_2 was prepared and cooled to 0 °C under nitrogen. A solution of *p*-toluenesulfonyl chloride (2.07 g, 10 mmol) in dry CH_2Cl_2 (300 mL) was added dropwise with continuous stirring over 2 h to the reaction mixture; the solution was allowed to warm up to rt while being stirred under nitrogen for 4 h. The solution was filtered and the solvent removed *in vacuo*. CH_2Cl_2 (200 mL) was added to the residue, and the solution was washed with dilute HCl (pH 3, 2 × 250 mL) and distilled H_2O (2 × 250 mL). The organic layer was dried ($MgSO_4$) and the solvent was removed *in vacuo* to yield a yellow oil which was recrystallized from hexane:EtOAc (8:2) to give a pale yellow powder. This powder was washed thoroughly with hexane to give product **9** as a white powder (3.7 g, 82%): mp 52−52 °C; IR (NaCl) 2869, 2360, 1597, 1506, 1353, 1189, 1175, 1096, 920, 712, 662 cm^{-1}; LSIMS 486 (M^+); ^1H NMR ($CDCl_3$, 300 MHz, 25 °C) δ 2.43 (s, 3H), 3.59−3.62 (m, 2H), 3.64−3.71 (m, 6H), 3.78−3.81 (m, 2H), 4.04−4.07 (m, 2H), 5.01 (s, 2H), 6.82−6.92 (m, 4H), 7.31−7.44 (m, 7H), 7.79−7.81 (AA′BB′ system, 2H, J = 8 Hz); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 21.6, 68.1, 68.7, 69.2, 69.9, 70.7, 70.8, 70.8, 115.6, 115.8, 127.5, 127.9, 128.0, 128.5, 129.8, 133.1, 137.3, 144.8, 153.2; HRMS calcd for $C_{26}H_{30}O_7S$ $[M]^+$ 486.1712, found 486.1700 (err 2.5).

1-[2-(2-(2-(Tritylphenoxy)ethoxy)ethoxy)ethoxy]-4-(benzyloxy)benzene (11). A stirred suspension of the vacuum-dried tritylphenol (**10**) (1.64 g, 5 mmol) and K_2CO_3 (2.86 g, 20.7 mmol) in dry MeCN (12 mL) was brought to reflux under nitrogen. A solution of tosylate **9** (2 g, 4.11 mmol) in dry MeCN (15 mL) was added dropwise over 30 min. The resulting mixture was stirred for 4 days at 80 °C under nitrogen. The cream-colored suspension was filtered and the solvent removed *in vacuo*. The residual oil was taken up in CH_2Cl_2 (100 mL) and washed with dilute HCl (pH 3, 3 × 100 mL) and distilled H_2O (3 × 100 mL). The organic phase was dried ($MgSO_4$) and the solvent removed *in vacuo* to yield a yellow oil. Column chromatography (SiO_2, CH_2Cl_2) afforded **11** as a white solid (2.19 g, 45%): mp 80.8−81 °C; IR (NaCl) 3056, 3030, 2920, 2871, 1507, 1452, 1229, 1125, 826, 747, 702 cm^{-1}; EIMS *m/z* 650 (M^+); ^1H NMR ($CDCl_3$, 300 MHz, 25 °C) δ 3.77 (s, 4H), 3.84−3.88 (m, 4H), 4.08−4.14 (m, 4H), 5.01 (s, 2H), 6.81−6.84 (AA′BB′ system, 2H, J = 8 Hz), 6.85−6.93 (m, 4H), 7.11−7.14 (AA′BB′ system, 2H, J = 8 Hz), 7.18−7.46 (m, 20H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 64.4, 67.3, 68.1, 69.9, 70.0, 70.7, 70.9, 113.4, 115.7, 115.9, 125.9, 126.2, 127.5, 127.5, 127.9, 128.6, 131.2, 132.2, 137.3, 139.2, 147.1, 153.2, 153.2, 156.8. Anal. Calcd for $C_{44}H_{42}O_5$: C, 81.20; H, 6.50. Found: C, 81.02; H, 6.70.

1-[2-(2-(2-(Tritylphenoxy)ethoxy)ethoxy)ethoxy]-4-hydroxybenzene (12). A solution of **11** (1.55 g, 2.38 mmol) in CH_2Cl_2 (125 mL) was added to a suspension of Pd/C (5%, 0.31 g) in MeOH (125 mL). H_2 gas was bubbled through the mixture with continuous stirring for 15 h. The solution was filtered through Celite. The solvent was removed *in vacuo* to yield **12** as a white solid (1.24 g, 95%). This product was unstable, and so the next reaction was carried out immediately using the crude product.

1-[2-(2-(2-(Tritylphenoxy)ethoxy)ethoxy)ethoxy]-4-[2-(2-(2-hydroxyethoxy)ethoxy)ethoxy]benzene[19] (13). A stirred suspension of **12** (1.24 g, 2.21 mmol) and K_2CO_3 (4.36 g, 31.5 mmol) in MeCN (40 mL) was brought to reflux under nitrogen with continuous stirring. 2-(2-(2-Chloroethoxy)-ethoxy)ethanol (2.74 mL, 14.8 mmol) was added dropwise, and the resulting mixture was heated under reflux under nitrogen for 3 days. The solution was cooled and filtered, and the solvent was removed *in vacuo*. CH_2Cl_2 (200 mL) was added to the residue, and the resultant mixture was washed with dilute HCl (pH 3, 2 × 250 mL) and then distilled H_2O (2 × 250 mL). The organic phase was dried ($MgSO_4$) and the solvent removed *in vacuo* to yield a yellow oil. Column chromatography [SiO_2, CH_2Cl_2:MeOH (98.5:1.5)] gave **13** as a yellow oil, which was crystallized from hexane and washed thoroughly with hexane:EtOAc (5:2) to yield the title compound as a pale yellow solid (1.2 g, 69%): mp 49−50 °C; IR (NaCl) 3420, 3057, 3029, 2874, 2360, 2340, 1508, 1490, 1234, 1183, 1123, 1066, 939, 750, 702 cm^{-1}; LSIMS *m/z* 692 (M^+); ^1H NMR δ ($CDCl_3$, 300 MHz, 25 °C) δ 3.61−3.67 (m, 6H), 3.70−3.76 (m, 6H), 3.82−3.88 (m, 6H), 4.06−4.12 (m, 6H), 6.77−6.8

(AA′BB′ system, 2H, $J = 8$ Hz), 6.83 (s, 4H), 7.07−7.10 (AA′BB′ system, 2H, $J = 8$ Hz), 7.18−7.26 (m, 15H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 42.7, 61.8, 64.3, 67.3, 68.2, 69.8, 69.9, 69.9, 70.4, 70.8, 70.9, 72.5, 113.4, 115.6, 125.9, 127.4, 131.1, 132.2, 139.2, 147.1, 153.1. Anal. Calcd for $C_{43}H_{48}O_8$: C, 74.54; H, 6.98. Found: C, 74.56; H, 6.94.

1-[2-(2-(2-(*p*-Toluenesulfonyloxy)ethoxy)ethoxy)ethoxy]-4-[2-(2-(2-(tritylphenoxy)ethoxy)ethoxy)ethoxy]-benzene (14). A stirred solution of the vacuum-dried **13** (0.4 g, 0.5 mmol), Et_3N (0.8 mL, 8 mmol), and a catalytic amount of DMAP in dry CH_2Cl_2 (20 mL) was cooled to 0 °C under a nitrogen atmosphere. A solution of *p*-toluenesulfonyl chloride (0.14 g, 0.55 mmol) in dry CH_2Cl_2 (10 mL) was added dropwise over 30 min. The resultant mixture was left stirring at 0 °C for 2 h. The solution was warmed up to room temperature and then filtered, and the solvent was removed *in vacuo* to give a yellow oil. This oil was dissolved in CH_2Cl_2 (100 mL) and washed with dilute HCl (pH 3, 2 × 100 mL) and distilled H_2O (2 × 100 mL). The organic phase was dried ($MgSO_4$) and the solvent removed *in vacuo* to yield a pale yellow oil. Column chromatography [SiO_2, CH_2Cl_2:MeOH (99:1)] afforded **14** as a yellow oil (0.1 g, 41%): IR (NaCl) 3055, 2923, 1598, 1508, 1453, 1356, 1232, 1176, 1124, 1010, 924, 816, 704 cm^{-1}; LSIMS *m/z* 846 (M^+); ^{1}H NMR ($CDCl_3$, 300 MHz, 25 °C) δ 2.41 (s, 3H), 3.59−3.81 (m, 18H), 4.02−4.17 (m, 8H), 6.76−6.79 (AA′BB′ system, 2H, $J = 8$ Hz), 6.81−6.83 (m, 4H), 7.07−7.10 (AA′BB′ system, 2H, $J = 8$ Hz), 7.13−7.25 (m, 15H), 7.29−7.31 (AA′BB′ system, 2H, $J = 6$ Hz), 7.58−7.61 (AA′BB′ system, 2H, $J = 6$ Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.6, 42.8, 61.8, 64.3, 67.3, 68.1, 68.8, 69.9, 70.4, 70.8, 70.8, 70.9, 71.4, 72.5, 113.4, 115.7, 125.9, 127.4, 128.0, 129.7, 129.8, 131.1, 132.2, 133.1, 139.2, 144.8, 147.1, 153.1, 153.2, 156.8. Anal. Calcd for $C_{50}H_{54}O_{10}S$: C, 70.90; H, 6.43; S, 3.78. Found: C, 71.02; H, 6.21; S, 3.90.

1-{*p*-[2-(2-(2-(4-Tritylphenoxy)ethoxy)ethoxy)-ethoxy]phenoxy}-10-{*m*-[2-(2-(2-(4-tritylphenoxy)-ethoxy)ethoxy)ethoxy]phenoxy}-3,6-dioxaoctane (15). A solution of phenol **6** (0.58 g, 1.04 mmol), K_2CO_3 (1g, 7.2 mmol), and a catalytic amount of LiBr in dry MeCN (100 mL) was heated under reflux over 1 h under a nitrogen atmosphere. A solution of tosylate **14** (0.88 g, 1.04 mmol) in dry MeCN (70 mL) was added dropwise over 30 min to the previous solution. The resulting mixture was heated under reflux for 5 days under nitrogen with vigorous stirring. The solution was cooled down to rt and then filtered, and the solvent was removed *in vacuo*. The residual oil was then dissolved in CH_2Cl_2 (200 mL) and washed with dilute HCl (pH 3, 2 × 200 mL) and brine (2 × 200 mL). The organic phase was dried ($MgSO_4$) and the solvent removed *in vacuo* to give a brown oil. Column chromatography [SiO_2, CH_2Cl_2:MeOH (99:1)] yielded dumbbell compound **15** as a brown oil (0.91 g, 71%): IR (NaCl) 3054, 3029, 2922, 2873, 1606, 1508, 1492, 1448, 1230, 1185, 1128, 1065, 948, 827, 748, 703 cm^{-1}; LSIMS *m/z* 1234 (M^+); ^{1}H NMR ($CDCl_3$, 300 MHz, 25 °C) δ 3.76 (s, 12H), 3.87−3.86 (m, 12H), 4.12−4.09 (m, 12H), 6.54−6.52 (m, 2H), 6.83−6.80 (AA′BB′ system, 4H, $J = 8$ Hz), 6.86−6.85 (m, 4H), 7.14−7.11 (AA′BB′ system, 4H, $J = 8$ Hz), 7.29−7.18 (m, 32 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 30.2, 64.1, 67.1, 67.2, 67.9, 69.6, 69.8, 70.7, 71.1, 72.3, 101.6, 106.9, 113.2, 115.4, 125.7, 127.3, 128.4, 129.7, 131.0, 132.0, 139.0, 146.9, 152.9, 153.4, 156.6, 159.8; HRMS calcd for $C_{80}H_{82}O_{12}$ $[M]^+$ 1234.5806, found 1234.5831 (err −2.0).

1,3-Bis[2-(2-(2-(4-((benzyloxy)phenoxy)-ethoxy)ethoxy)ethoxy]benzene (16). A solution of resorcinol (0.24 g, 2.2 mmol), K_2CO_3 (1.5 g, 10.8 mmol), and a catalytic amount of LiBr in dry MeCN (50 mL) was brought to reflux for 1 h in a nitrogen atmosphere. A solution of tosylate **9** (2.12 g, 4.4 mmol) in dry MeCN (150 mL) was added dropwise over 30 min to the reaction mixture; the solution was refluxed under nitrogen for 5 days with vigorous stirring. The solution was cooled to rt and filtered, and the solvent was removed *in vacuo*. The residual oil was dissolved in CH_2Cl_2 (200 mL) and washed with dilute HCl (pH 3, 2 × 200 mL) and brine (2 × 200 mL). The organic phase was dried ($MgSO_4$) and the solvent removed *in vacuo*. Column chromatography [SiO_2, EtOAc:hexane (40:60) and then CH_2Cl_2:MeOH (98:2)] yielded diprotected bisphenol **16** as a yellow oil (2.0 g, 62%): IR (NaCl) 3062, 3032, 2924, 2872, 1593, 1507, 1454, 1289, 1228, 1124, 924, 826, 741, 697 cm^{-1}; LSIMS *m/z* 738 (M^+); ^{1}H NMR ($CDCl_3$, 300 MHz, 25 °C) δ 3.73 (s, 8H), 3.84−3.80 (m, 8H), 4.09−4.04 (m, 8H), 4.98 (s, 4H), 6.51−6.49 (m, 3H), 6.86−6.84 (m, 8H), 7.13 (t, 1H, $J = 7$ Hz)), 7.42−7.24 (m, 10H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 61.8, 67.4, 68.1, 69.8, 69.9, 70.7, 70.9, 102.4, 106.9, 107.2, 108.1, 115.7, 115.9, 127.5, 127.9, 128.6, 130.0, 137.3, 153.2; HRMS calcd for $C_{44}H_{50}O_{10}$ $[M]^+$ 738.3440, found 738.3411 (err −1.0).

1,3-Bis[2-(2-(2-(4-hydroxyphenoxy)ethoxy)ethoxy)-ethoxy]benzene (17). A solution of compound **16** (0.580 g, 0.78 mmol) in $CHCl_3$ (100 mL) was added to a suspension of Pd/C (5%, 1 g) in MeOH (100 mL). The resulting suspension was stirred at rt for 10 h as H_2 gas was bubbled into the mixture. The suspension was then filtered through Celite and the solvent removed *in vacuo* to give the bisphenol **17** as a white solid (0.42 g, 95%). Since compound **17** is unstable, the next reaction was carried out immediately using the crude product.

1,3-Bis{2-(2-(2-[4-tritylphenoxy)ethoxy)ethoxy)-ethoxy]phenoxy]ethoxy)ethoxy)ethoxy}benzene (18). A solution of the biphenol **17** (0.41 g, 0.73 mmol), K_2CO_3 (1 g, 7.2 mmol), and a catalytic amount of LiBr in dry MeCN (70 mL) was refluxed for 1 h under nitrogen. A solution of tosylate **4** (1.14 g, 1.84 mmol) in dry MeCN (100 mL) was added dropwise over 30 min to the reaction mixture; the solution was heated under reflux for 5 days in a nitrogen atmosphere with vigorous stirring. The solution was then allowed to cool down to rt before it was filtered and the solvent removed *in vacuo*. The residual oil was dissolved in CH_2Cl_2 (200 mL) before being washed with dilute HCl (pH 3, 2 × 200 mL) and brine (2 × 200 mL). The organic phase was dried ($MgSO_4$) and the solvent removed *in vacuo*. Column chromatography [SiO_2, CH_2Cl_2:MeOH (98:2)] afforded the dumbbell compound **18** as a brown oil (1.07 g, 71%): IR (NaCl) 3054, 3030, 2874, 1597, 1510, 1452, 1240, 1183, 1136, 949, 827, 740, 700 cm^{-1}; LSIMS *m/z* 1460 $(M + H)^+$; ^{1}H NMR ($CDCl_3$, 300 MHz, 25 °C) δ 3.72 (s, 16H), 3.89−3.85 (m, 16H), 4.14−4.08 (m, 16H), 6.55−6.52 (m, 3H), 6.83−6.80 (AA′BB′ system, 4H, $J = 8$ Hz), 6.86−6.85 (m, 8H), 7.14−7.11 (AA′BB′ system, 4H, $J = 8$ Hz), 7.29−7.19 (m, 31H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 53.5, 61.8, 64.3, 67.3, 67.4, 68.1, 69.8, 69.9, 70.9, 72.5, 101.8, 107.1, 113.4, 115.6, 123.4, 125.9, 127.5, 128.6, 129.9, 131.1, 132.2, 139.2, 147.1, 153.1, 156.7, 160.0. Anal. Calcd for $C_{92}H_{98}O_{16}$: C, 75.68; H, 6.77. Found: C, 75.62; H, 6.87.

1,4-Bis{2-(2-(2-[3-[2-(2-(2-(4-tritylphenoxy)ethoxy)-ethoxy)ethoxy]phenoxy]ethoxy)ethoxy)ethoxy}-benzene (20). A solution of the phenol **6** (4.29 g, 7.6 mmol), K_2CO_3 (3 g, 21 mmol), and a catalytic amount of LiBr in dry MeCN (150 mL) was heated under reflux for 1 h in a nitrogen atmosphere. A solution of the bistosylate **19** (2.61 g, 3.8 mmol) in dry MeCN (150 mL) was added dropwise over 30 min to the reaction mixture; the solution was refluxed under nitrogen for 7 days with vigorous stirring. The solution was then allowed to cool down to rt before it was filtered and the solvent removed *in vacuo*. The residual oil was dissolved in CH_2Cl_2 and washed with dilute HCl (pH 3, 2 × 200 mL) and then brine (2 × 200 mL). The organic phase was dried ($MgSO_4$) and the solvent removed *in vacuo*. Column chromatography [(SiO_2, CH_2Cl_2:MeOH (99:1) and then CH_2Cl_2:MeOH (98:2)] afforded the dumbbell compound **20** as a brown oil (3.33 g, 60%): IR (NaCl) 3054, 3029, 2923, 2873, 1594, 1507, 1492, 1448, 1233, 1185, 1126, 946, 827, 748, 703 cm^{-1}; LSIMS *m/z* 1460 $(M + H)^+$; ^{1}H NMR ($CDCl_3$, 300 MHz, 25 °C) δ 3.72 (s, 16H), 3.89−3.84 (m, 16H), 4.14−4.07 (m, 16H), 6.53−6.51 (m, 6H), 6.83−6.80 (AA′BB′ system, 4H, $J = 8$ Hz), 6.86−6.85 (m, 4H), 7.13−7.10 (AA′BB′ system, 4H, $J = 8$ Hz), 7.29−7.19 (m, 32H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 30.4, 42.8, 64.4, 67.3, 67.5, 68.1, 69.8, 70.0, 70.1, 70.1, 71.3, 71.4, 101.9, 107.2, 113.4, 115.7, 125.9, 127.5, 129.9, 131.2, 132.2, 139.2, 147.1, 153.2, 156.8, 160.0. Anal. Calcd for $C_{92}H_{98}O_{16}$: C, 75.68; H, 6.77. Found: C, 75.67; H, 6.68.

{[2]-[1-{*p*-[2-(2-(2-(4-Tritylphenoxy)ethoxy)ethoxy)-ethoxy]phenoxy}-10-{*m*-[2-(2-(2-(4-tritylphenoxy)ethoxy-)ethoxy)ethoxy]phenoxy}-3,6-dioxaoctane][9,18,29,38-tetraazonia[1.1.0.1.1.0]paracyclophane]rotaxane} Tetrakis(hexafluorophosphate) (23·4PF$_6$). A solution of the

dumbbell compound **15** (0.503 g, 0.4 mmol), the bipyridinium salt **21**·2PF_6 (0.086 g, 1.2 mmol), and the dibromide **22** (0.38 g, 1.4 mmol) in dry DMF (10 mL) was stirred for 10 days at room temperature and pressure. Thereafter, Et_2O (50 mL) was added to the reaction mixture in order to precipitate all the charged species. The orange precipitate was filtered and washed with Et_2O (50 mL) and CH_2Cl_2 (50 mL). Column chromatography [SiO_2, MeOH:NH_4Cl (2 M):$MeNO_2$ (7:2:1)] afforded the rotaxane **23**·4PF_6 as a red solid in the form of the chloride salt. The red solid was dissolved in H_2O, and a saturated aqueous solution of NH_4PF_6 was added dropwise until no further precipitation was observed. The red precipitate was filtered off and washed thoroughly with H_2O to yield rotaxane **23**·4PF_6 as a red powder (100 mg, 11%) after vacuum drying: mp > 250 °C dec; IR (NaCl) 3055, 2921, 2360, 1636, 1594, 1508, 1452, 1247, 1183, 1151, 841, 699 cm^{-1}; UV/vis λ_{max} (ϵ) 252 nm (37500), 463 nm (328); LSIMS *m*/*z* 2336 (M^+), 2191 $(M - PF_6)^+$, 2046 $(M - 2PF_6)^+$, 1900 $(M - 3PF_6)^+$; ^1H NMR (CD_3COCD_3, 300 MHz, 25 °C) δ 4.15−3.64 (m, 40H), 5.99 (s, 8H), 6.81−6.49 (bm, approximately 3H,), 6.99−6.96 (AA′BB′ system, 4H, J = 8 Hz), 7.07−7.04 (AA′BB′ system, 4H, J = 8 Hz), 7.26−7.19 (m, 31H), 8.02 (s, 8H), 8.19−8.17 (d, 8H, J = 6 Hz), 9.31−9.29 (d, 8H, J = 6 Hz); HRMS calcd for $C_{116}H_{114}F_{18}N_4P_3O_{12}$ $[M - PF_6]^+$ 2189.7359, found 2189.7323 (err 1.7).

{**[2]-[1,3-Bis**{**2-(2-(2-[4-[2-(2-(2-(4-tritylphenoxy)-ethoxy)ethoxy)ethoxy]phenoxy]ethoxy)ethoxy)-ethoxy**}**phenyl][9,18,29,38-tetraazonia[1.1.0.1.1.0]-paracyclophane]rotaxane**} **Tetrakis(hexafluorophosphate) (24·4PF_6).** A solution of the dumbbell compound **18** (0.50 mg, 0.4 mmol), the bipyridinium salt **21**·2PF_6 (0.086 g, 1.2 mmol), and the dibromide **22** (0.38 g, 1.4 mmol) in dry DMF (10 mL) was stirred for 10 days at room temperature and pressure. Thereafter, Et_2O (50 mL) was added to the reaction mixture in order to precipitate all the charged species. The orange precipitate was filtered and washed with Et_2O (50 mL) and CH_2Cl_2 (50 mL). Column chromatography [SiO_2, MeOH:NH_4Cl (2 M):$MeNO_2$ (7:2:1)] afforded the rotaxane **24**·4PF_6 as a red solid in the form of the chloride salt. The red solid was dissolved in H_2O, and a saturated aqueous solution of NH_4PF_6 was added dropwise until no further precipitation was observed. The red precipitate was filtered off and washed thoroughly with H_2O to yield rotaxane **24**·4PF_6 as a red powder (0.11 g, 12%) after vacuum drying: mp > 250 °C dec; IR (NaCl) 3054, 2921, 1636, 1508, 1452, 1248, 1136, 1056, 842, 702 cm^{-1}; UV/vis λ_{max} (ϵ) 244 nm (38700), 445 nm (320); LSIMS *m*/*z* 2560 (M^+), 2415 $(M - PF_6)^+$, 2270 $(M - 2PF_6)^+$, 2125 $(M - 3PF_6)^+$; ^1H NMR (CD_3COCD_3, 300 MHz, 25 °C) δ 4.07−3.65 (bm, approximately 52H), 6.00 (s, 8H), 6.82 (bm, approximately 4H), 7.02 (bm, approximately 2H), 7.28−7.16 (m, 34H), 8.02 (s, 8H), 8.21−8.19 (d, 8H, J = 6 Hz), 9.34−9.32 (d, 8H, J = 6 Hz); HRMS calcd for $^{12}C_{127}{}^{13}C_1H_{130}F_{18}N_4O_{16}P_3$ $[M - PF_6]^+$ 2414.8440, found 2414.8352 (err 3.7).

{**[2]-[1,4-Bis**{**2-(2-(2-[3-[2-(2-(2-(4-tritylphenoxy)-ethoxy)ethoxy]phenoxy]ethoxy)ethoxy)-ethoxy**}**phenyl][9,18,29,38-tetraazonia[1.1.0.1.1.0]-paracyclophane]rotaxane**} **Tetrakis(hexafluorophosphate) (25·4PF_6).** A solution of the dumbbell compound **20** (0.83 g, 0.5 mmol), the bipyridinium salt **21**·2PF_6 (1.2 g, 1.7 mmol), and the dibromide **22** (0.18 mg, 0.6 mmol) in dry DMF (10 mL) was stirred for 10 days at room temperature and pressure. Thereafter, Et_2O (50 mL) was added to the reaction mixture in order to precipitate all the charged species. The orange precipitate was filtered and washed with Et_2O (50 mL) and CH_2Cl_2 (50 mL). Column chromatography [SiO_2, MeOH: NH_4Cl (2 M):$MeNO_2$ (7:2:1)] afforded the rotaxane **25**·4PF_6 as a red solid in the form of the chloride salt. The red solid was dissolved in H_2O, and a saturated aqueous solution of NH_4PF_6 was added dropwise until no further precipitation was observed. The red precipitate was filtered and washed thoroughly with H_2O to yield the rotaxane **25**·4PF_6 as a red powder (0.20 g, 14%) after vacuum drying: mp > 250 °C dec; IR (NaCl) 3056, 2922, 2360, 1635, 1507, 1411, 1134, 836, 790, 702 cm^{-1}; UV/vis λ_{max} (ϵ) 242 nm (38 100), 442 nm (315); LSIMS *m*/*z* 2415 $(M - PF_6)^+$, 2270 $(M - 2PF_6)^+$, 2125 $(M - 3PF_6)^+$; ^1H NMR (CD_3COCD_3, 300 MHz, 25 °C) δ 4.10−3.64 (m, 52H), 5.99 (s, 8H), 6.82 (bs, approximately 6H), 7.07−7.04 (AA′BB′, system, 4H, J = 8 Hz), 7.29−7.15 (m, 34H), 8.02 (s, 8H), 8.24−8.21 (d, 8H, J = 6 Hz), 9.33−9.31 (d, 8H, J = 6 Hz); HRMS calcd for $^{12}C_{127}{}^{13}C_1H_{130}F_{18}N_4O_{16}P_3$ $[M - PF_6]^+$ 2414.8440, found 2414.8486 (err −1.9).

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Supporting Information Available: Copies of NMR spectra (8 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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