Molecular Meccano, 45[◇]

High Yielding Template-Directed Syntheses of [2]Rotaxanes

José A. Bravo[a], Françisco M. Raymo[a], J. Fraser Stoddart*[a], Andrew J. P. White[b], and David J. Williams*[b]

Department of Chemistry and Biochemistry, University of California, Los Angeles[a],
405 Hilgard Avenue, Los Angeles, CA 90095-1569 (USA)
Fax: (internat.) + 1-310/206-1843
E-mail: stoddart@chem.ucla.edu

Department of Chemistry, Imperial College[b],
South Kensington, London SW7 2AY, UK
Fax: (internat.) + 44-171/594-5835

Received June 8, 1998

Keywords: Molecular recognition / Rotaxanes / Self-assembly / Template-directed synthesis

Three dumbbell-shaped compounds incorporating terminal triisopropylsilyl stoppers, connected to a central 1,5-dioxynaphthalene recognition site by $[-CH_2CH_2O-]_n$ spacers (n = 1–3), have been synthesized. These compounds have been employed as templates for the synthesis of [2]rotaxanes incorporating cyclobis(paraquat-*p*-phenylene) as the ring component. It was found that the length of the polyether chains of the templates influences the efficiencies of the template-directed syntheses. Rotaxane formation occurs only if $n > 1$ and, when $n = 3$ the corresponding [2]rotaxane can be isolated in a yield as high as 72 %. This remarkable yield is the highest ever obtained for the template-directed syntheses of [2]rotaxanes incorporating donor/acceptor interactions.

Introduction

Rotaxanes[1] are molecules composed of one or more macrocycles encircling one or more linear components which are terminated by bulky stoppers at their ends. Efficient template-directed syntheses[2] of rotaxanes have been devised and realized by relying upon the supramolecular assistance provided by metal coordination[3] or by hydrogen bonds.[4] The ability of cyclodextrins to bind organic molecules with pseudorotaxane geometries in aqueous solution has been also exploited[5] to self-assemble rotaxanes. We have devised two donor/acceptor template-directed approaches[6] to rotaxanes, each utilizing the π-electron-deficient bipyridinium-based tetracationic cyclophane, cyclobis(paraquat-*p*-phenylene), as their macrocyclic component. In one instance, cyclobis(paraquat-*p*-phenylene) self-assembles from appropriate precursors around a π-electron-rich recognition site incorporated within a preformed dumbbell-shaped polyether template. In the other case, the self-assembly of a pseudorotaxane complex from the preformed cyclobis(paraquat-*p*-phenylene) and an appropriate π-electron-rich acyclic polyether is followed by the covalent attachment of bulky stoppers at both ends of the guest. A number of cooperative noncovalent bonding interactions (i.e., [C−H···O] hydrogen bonds, [π···π] stacking, and [C−H···π] interactions) between the complementary recognition sites control[7] these self-assembly processes. For the π-electron-rich recognition sites of the dumbbell-shaped templates, we and others have employed 1,3-dioxybenzene,[8] 1,4-dioxybenzene,[8][9] 1,4-diaminobenzene,[10] 4,4′-biphenol,[11] 4,4′-benzidine,[10][11] indole,[12] and tetrathiafulvalene derivatives.[12] The yields of the resulting [2]rotaxanes range from 5 to 43% and are related to the nature and substitution pattern of the π-electron-rich aromatic unit incorporated in the template. Recently, we found[13] that 1,5-dioxynaphthalene-based acyclic polyethers are bound strongly ($K_a > 5000\ M^{-1}$ in MeCN at 25°C) by cyclobis(paraquat-*p*-phenylene) with pseudorotaxane geometries. Thus, in order to improve the yields in these template-directed syntheses, we decided to employ a 1,5-dioxynaphthalene ring system as the π-electron-rich unit of the template. Here, we report *(i)* the synthesis of three 1,5-dioxynaphthalene-based dumbbell-shaped compounds, and *(ii)* the efficient template-directed syntheses of two [2]rotaxanes, together with *(iii)* their X-ray crystallographic and *(iv)* ^{1}H-NMR spectroscopic analyses.

Results and Discussion

Synthesis

Reaction (Scheme 1) of the 1,5-dioxynaphthalene-based acyclic polyethers **1**−**3** with triisopropylsilyl triflate, in the presence of 2,6-dimethylpyridine, gave the dumbbell-shaped compounds **4**−**6** in yields of 74, 62, and 81%, respectively.

[d6] Part 44: M. Asakawa, P. R. Ashton, V. Balzani, C. L. Brown, A. Credi, O. A. Matthews, S. P. Newton, F. M. Raymo, A. N. Shipway, N. Spencer, A. Quick, J. F. Stoddart, A. J. P. White, D. J. Williams, *Chem. Eur. J.*, in press.

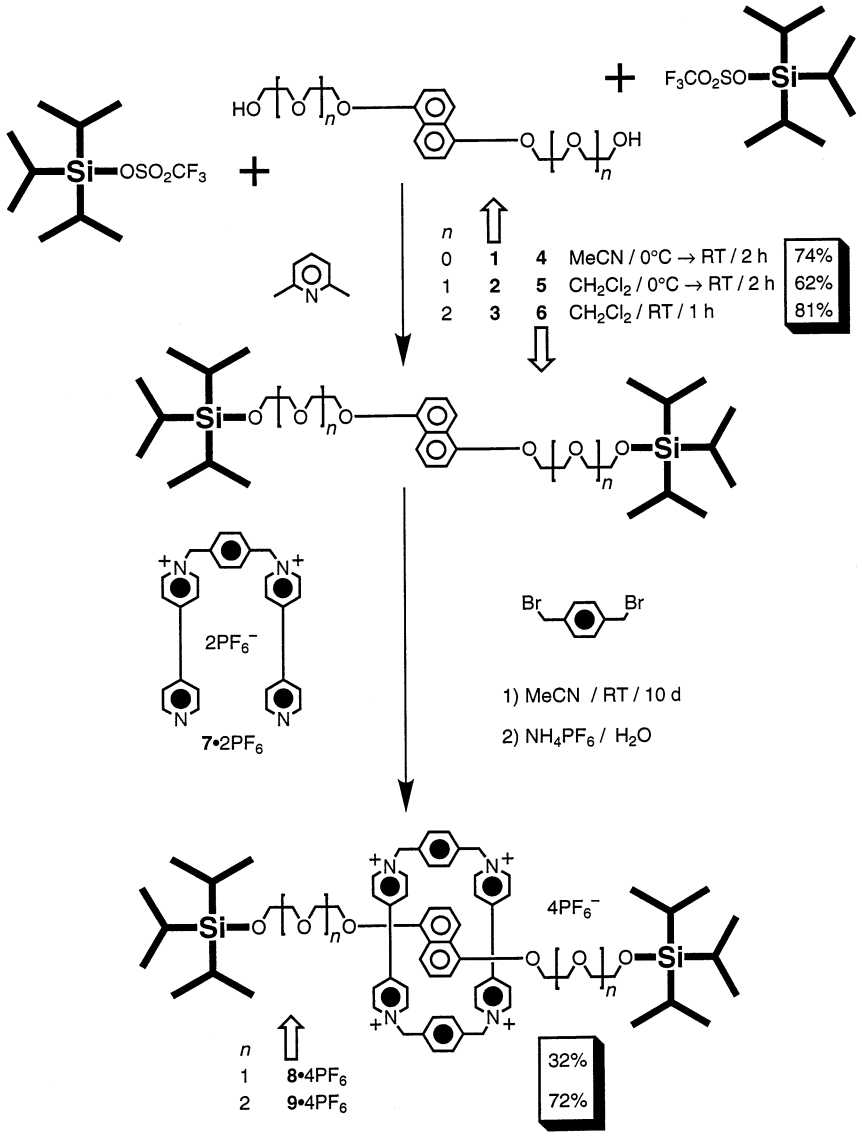
  1434−193X/98/1111−2565 $ 17.50+.50/0

Reaction of the bis(hexafluorophosphate) salt **7**·2 PF_6 with 1,4-bis(bromomethyl)benzene, in the presence of either **5** or **6**, afforded the corresponding [2]rotaxanes **8**·4 PF_6 and **9**·4 PF_6 in yields of 32 and 72%, respectively, after counterion exchange. By contrast, when the same reaction was performed in the presence of the dumbbell-shaped compound **4**, under otherwise identical conditions, *no* [2]rotaxane was isolated or indeed even detected in the reaction mixture. Thus, the efficiencies of these template-directed syntheses are affected by the number of [$-CH_2CH_2O-$] linkages incorporated within the polyether chains of the dumbbell-shaped templates. Indeed, it would appear that elongating the polyether chains makes the 1,5-dioxynaphthalene recognition site more accessible by isolating the bulky stoppers more distant from it. Furthermore, increasing the number of [$-CH_2CH_2O-$] linkages reinforces[7] the [C−H···O] interactions between the α-bipyridinium hydrogen atoms and the polyether oxygen atoms.

X-Ray Crystallography

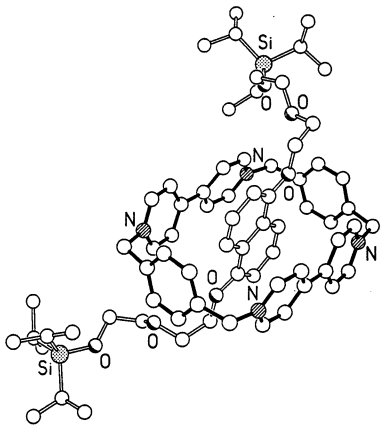
The X-ray structural analysis of the [2]rotaxane **8**·4 PF_6 shows (Figure 1) the dumbbell-shaped component to be threaded asymmetrically through the center of the tetracationic cyclophane such that the two triisopropylsilyl stoppers both lie on the same side of one of the bipyridinium units. With the exception of the two terminal [iPr_3SiO-] units, the molecule has approximate C_2 symmetry about an axis passing through the center of the bonds linking the pyridinium rings of the bipyridinium units. The [2]rotaxane is stabilized by *(i)* [π···π] stacking interactions between the 1,5-dioxynaphthalene and bipyridinium ring systems (mean interplanar separations, 3.37 and 3.47 Å), *(ii)* edge-to-face [C−H···π] interactions between the *peri*-hydrogen atoms of the 1,5-dioxynaphthalene ring system and the *p*-xylylene units ([H···π] distances of 2.56 and 2.53 Å, [C−H···π] angles of 147 and 151°, respectively), and *(iii)* [C−H···O] hydro-

Scheme 1. Synthesis of the dumbbell-shaped compounds **4**−**6** and of the [2]rotaxanes **8**·4 PF_6 and **9**·4 PF_6



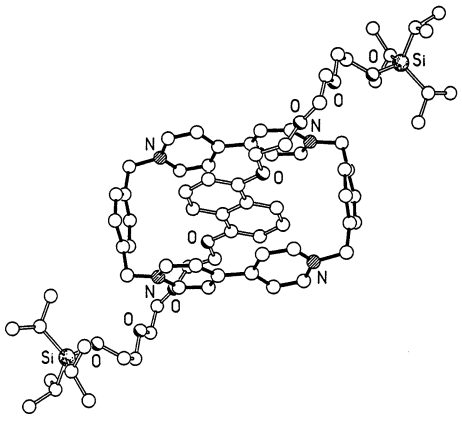
gen bonds between diametrically opposite α-bipyridinium hydrogen atoms − within the same unit − and the central oxygen atoms of each polyether chain in the dumbbell-shaped component (the respective [C···O], [H···O], [C−H···O] geometries are 3.24, 2.36 Å, 153° and 3.22, 2.32, 156°). There are no additional inter[2]rotaxane interactions of note.

Figure 1. Ball-and-stick representation of the solid-state structure of the [2]rotaxane $\mathbf{8}^{4+}$



The solid-state structure (Figure 2) of the higher-order homologue **9**·4 PF_6, containing four oxygen atoms within each of the polyether chains of the dumbbell-shaped component, has crystallographic C_i symmetry. The 1,5-dioxynaphthalene ring system is sandwiched symmetrically between the bipyridinium ring systems of the tetracationic cyclophane (the mean interplanar separations are 3.44 Å). The only additional intramolecular stabilization interactions are edge-to-face [C−H···π] in nature, between the *peri*-hydrogen atoms of the 1,5-dioxynaphthalene ring system and the *p*-xylylene units of the tetracationic cyclophane (the [H···π] distances are 2.56 Å with associated [C−H···π] angles of 146°). There are no intra[2]rotaxane [H···O] contacts of less than 2.58 Å. As in the case of **8**·4 PF_6, there are no inter[2]rotaxane interactions of note.

Figure 2. Ball-and-stick representation of the solid-state structure of the [2]rotaxane $\mathbf{9}^{4+}$



^{1}H-NMR Spectroscopy

The ^{1}H-NMR spectra (CD_3CN, 25°C) of the dumbbell-shaped compounds **5** and **6** show (Table 1) sharp and well-resolved signals for the 1,5-dioxynaphthalene protons $H_{2/6}$, $H_{3/7}$, and $H_{4/8}$ at δ ≈ 6.9, 7.4, and 7.8, respectively. In the ^{1}H-NMR spectra (CD_3CN, 25°C) of the [2]rotaxanes **8**·4 PF_6 and **9**· 4 PF_6, the resonances of the 1,5-dioxynaphthalene protons $H_{2/6}$, $H_{3/7}$, and $H_{4/8}$ shift to δ ≈ 6.3, 6.0, and 2.4, respectively. These significant chemical shift changes are a result of shielding effects exerted by the sandwiching bipyridinium units and are particularly evident for the resonances of the protons $H_{4/8}$ which shift by Δδ = −5.37 and −5.34 in **8**·4 PF_6 and **9**·4 PF_6, respectively.

The ^{1}H-NMR spectrum (CD_3CN, 25°C) of the tetracationic cyclophane **10**·4 PF_6 (Table 1) shows two sets of signals at δ = 8.89 and 8.17 for the α- and β-bipyridinium protons, respectively. In the [2]rotaxanes **8**·4 PF_6 and **9**·4 PF_6, the local C_{2h} symmetry of the 1,5-dioxynaphthalene unit imposes (Figure 3) two different environments (sites A and B) on the α-bipyridinum protons and likewise two different environments (sites C and D) on the β-bipyridinium

Table 1. Chemical shift values[a] for the bipyridinium and the 1,5-dioxynaphthalene protons of the [2]rotaxanes **8**·4 PF_6 and **9**·4 PF_6 and their separate components **5**, **6**, and **10**·4 PF_6

Compound	H_α/H'_α[b]	H_β/H'_β[c]	$H_{2/6}$[d]	$H_{3/7}$[e]	$H_{4/8}$[f]
5	–	–	6.91	7.34	7.78
6	–	–	6.92	7.36	7.78
8·4PF_6	8.92 and 8.65	7.39 and 7.20	6.27	5.99	2.41
9·4PF_6	9.02 and 8.65	7.30 and 7.22	6.26	5.97	2.44
10·4PF_6	8.89	8.17	–	–	–

[a] The chemical shift values (δ, ppm) reported in the Table correspond to the center of each set of signals associated with the protons listed and were determined in CD_3CN at 25°C. − [b] Hydrogen atoms in the α positions (Figure 3), with respect to the nitrogen atoms, on the bipyridinium units. − [c] Hydrogen atoms in the β positions (Figure 3), with respect to the nitrogen atoms, on the bipyridinium units. − [d] Hydrogen atoms in the positions 2 and 6 on the 1,5-dioxynaphthalene unit. − [e] Hydrogen atoms in the positions 3 and 7 on the 1,5-dioxynaphthalene unit. − [f] Hydrogen atoms in the positions 4 and 8 on the 1,5-dioxynaphthalene unit.

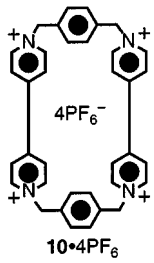


Table 2. Kinetic parameters[a] associated with the degenerate site exchange processes in the [2]rotaxanes **8**·4 PF_6 and **9**·4 PF_6.

[2]Rotaxane	Probe Protons	Δν[b] [Hz]	k_c[c] [s^{-1}]	T_c[d] [K]	$\Delta G_c^{\ddagger}$[e] [kcal mol^{-1}]
8·4 PF_6	H_α	104	231	330	15.8
	H_β	76	168	325	15.8
9·4 PF_6	H_α	157	349	319	15.0
	H_β	77	170	310	15.0

[a] Determined by variable-temperature ^{1}H-NMR spectroscopy (400 MHz) in CD_3CN. − [b] Limiting frequency separation. − [c] Rate constant at the coalescence temperature. − [d] Coalescence temperature. − [e] Free energy barrier at the coalescence temperature.

protons. As a result, the four bipyridinium protons H_α, H'_α, H_β, and H'_β give rise (Table 1 and Figure 4c) to four distinct resonances in the ^{1}H-NMR spectrum recorded in CD_3CN at 25°C. However, *(i)* dislodgment of the 1,5-dioxynaphthalene unit from the cavity of the tetracationic cyclophane, followed *(ii)* by its 180° rotation around the [O···O] axis or by a 180° rotation of the tetracationic cyclophane around an axis passing through its center of inversion and perpendicular to its mean plane (defined by its four methylene carbon atoms), and *(iii)* by its reinsertion inside the cavity of the tetracationic cyclophane (Process I in Figure 3) exchanges the protons H_α and H'_α between sites A and B, as well as H_β and H'_β between C and D. Similarly, *(i)* dislodgment of the 1,5-dioxynaphthalene ring system from the cavity of the tetracationic cyclophane, followed *(ii)* by 180° rotation of the bipyridinium units around their [N···N] axes, and *(iii)* by reinsertion of the 1,5-dioxynaphthalene ring system inside the cavity of the tetracationic cyclophane (Process II in Figure 3) exchanges protons H_α and H'_α between sites A and B, as well as H_β and H'_β between C and D. Thus, when Process I and/or Process II are fast on the ^{1}H-NMR timescale, fast site exchange occurs and protons H_α and H_β cannot be distinguished from H'_α and H'_β, respectively. Indeed, on warming a CD_3CN solution of either **8**·4 PF_6 or **9**·4 PF_6, Process I and/or Process II become fast on the ^{1}H-NMR timescale and the resonances of H_α and H'_α, as well as those of H_β and H'_β, coalesce (Figure 4a and 4b) into one signal only in each case. By employing the approximate coalescence method,[14] the kinetic parameters (Table 2) associated with the degenerate site-exchange processes − i.e., Process I and/or Process II − were determined.[15]

Figure 3. The dynamic processes (Process I and Process II) associated with the [2]rotaxanes **8**·4 PF_6 and **9**·4 PF_6 in solution; A, B, C, and D indicate the different environments imposed on the bipyridinium protons H_α, H'_α, H_β, and H'_β by the local C_{2h} symmetry of the 1,5-dioxynaphthalene unit

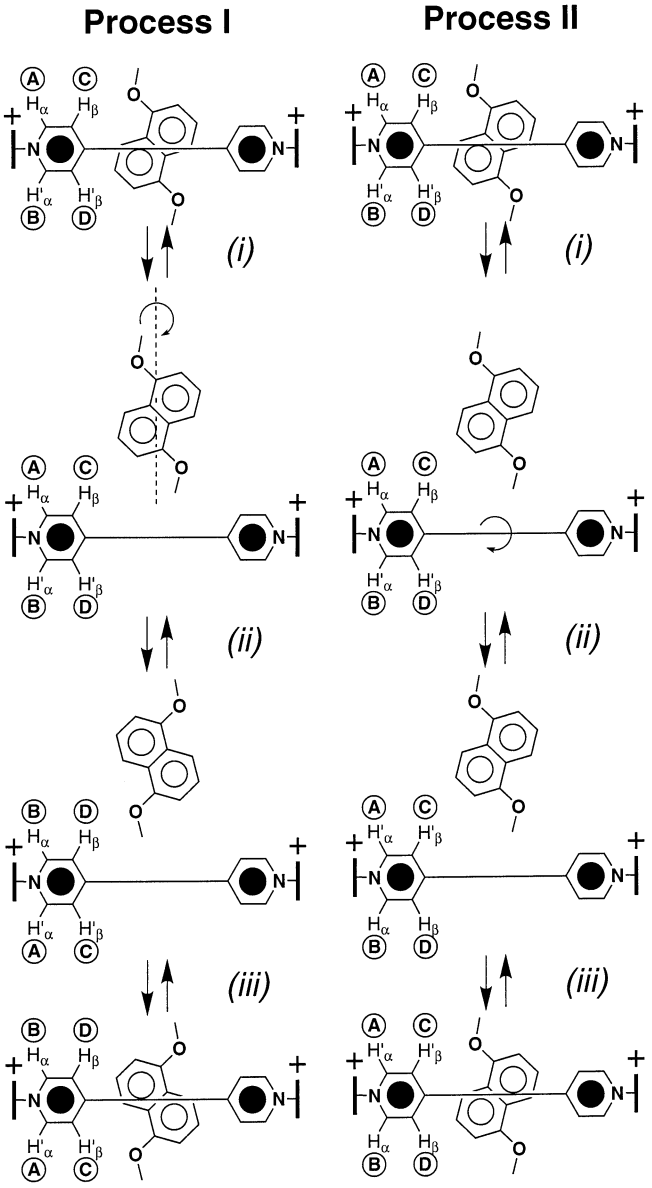
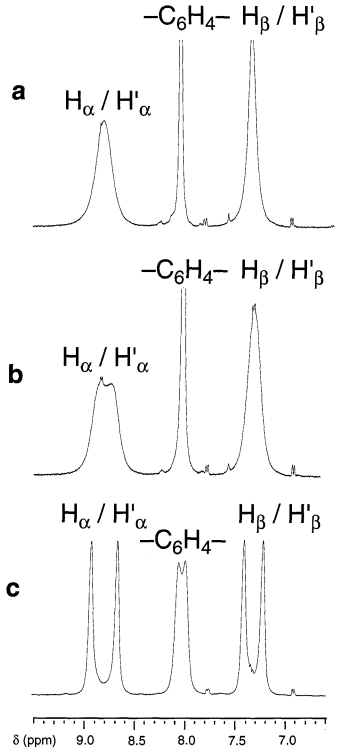


Figure 4. Partial ^{1}H-NMR spectra of the [2]rotaxane of **8**·4PF_6 recorded in CD_3CN at (**a**) 62, (**b**) 57, and (**c**) 25°C



Conclusions

Dumbbell-shaped compounds, composed of a polyether chain intercepted by a 1,5-dioxynaphthalene unit and terminated by triisopropylsilyl stoppers, have been employed to template the formation of cyclobis(paraquat-*p*-phenylene) around the π-electron-rich recognition site. The efficiency of the overall reactions is affected by the number of [−CH_2CH_2O−] linkages separating the stoppers from the 1,5-dioxynaphthalene recognition site. No rotaxane is

formed when only one [−CH_2CH_2O−] linkage separates stoppers and recognition site. Instead, when two or three [−CH_2CH_2O−] repeating units connect the stoppers to the recognition site, the [2]rotaxanes are obtained in yields of 32 or 72%, respectively. The mechanical bond holding the macrocyclic and dumbbell-shaped components together is evident in the solid-state structures of the two [2]rotaxanes, as revealed by single-crystal X-ray structural analyses. In solution, the insertion of the 1,5-dioxynaphthalene recognition site inside the cavity of cyclobis(paraquat-*p*-phenylene) is demonstrated by some dramatic chemical shift changes observed on rotaxane formation in the ^{1}H-NMR spectra. In addition, variable-temperature ^{1}H-NMR spectroscopic studies revealed the occurrence of degenerate site-exchange processes in both [2]rotaxanes. The free energy barriers ($\Delta G_c^{\neq}$ = 15−16 kcal mol^{-1}) associated with these dynamic processes were determined by employing the approximate coalescence method. The efficiency and ease of realization of these template-directed syntheses recommend their use for the construction of controllable "molecular shuttles"[16] able to perform logic operations at the molecular level.[17][18]

Experimental Section

General Methods: Chemicals were purchased from Aldrich and used as received. Solvents were dried according to procedures described in the literature.[19] The compounds **1**,[20] **2**,[21] **3**,[22] and **7**·2 PF_6[9c] were prepared according to literature procedures. − Thin layer chromatography (TLC) was carried out using aluminum or plastic sheets precoated with silica gel 60 F (Merck 5554). The plates were inspected by UV light and developed with iodine vapor. Column chromatography was carried out using silica gel 60 F (Merck 9385, 230−400 mesh). − Melting points were determined with an Electrothermal 9200 apparatus and are not corrected. − Liquid secondary ion mass spectra (LSIMS) were obtained with a VG Zabspec mass spectrometer, equipped with a 35 keV cesium ion gun. Samples were dissolved in either a 3-nitrobenzyl alcohol or 2-nitrophenyl octyl ether matrix, previously coated on to a stainless steel probe tip. − ^{1}H-NMR spectra were recorded with a Bruker AC200 (200 MHz), a Bruker AC300 (300 MHz), or a Bruker AMX400 (400 MHz) spectrometer, using either the solvent or TMS as internal standards. ^{13}C-NMR spectra were recorded with a Bruker AC200 (50.3 MHz), a Bruker AC300 (75.5 MHz) or a Bruker AMX400 (100.6 MHz) spectrometer, using either the solvent or TMS as internal standards. All chemical shifts are quoted in ppm on the δ scale and the coupling constants are expressed in Hertz (Hz). − Microanalyses were performed by the University of North London Microanalytical Service or by Quantitative Technologies Inc.

1,5-Bis[2-(triisopropylsilyloxy)ethoxy]napthalene (**4**): Triisopropylsilyl triflate (3.33 g, 11 mmol) and 2,6-dimethylpyridine (1.16 g, 11 mmol) were added to an H_2O/ice-cooled solution of **1** (0.90 g, 3.60 mmol) in dry MeCN (30 ml) under N_2. The solution was allowed to warm up to ambient temperature. After 2 h, it was extracted with 1 M HCl and then with H_2O. The organic layer was dried ($MgSO_4$) and the solvent was removed under reduced pressure. The residue was purified by flash column chromatography [SiO_2: hexane/PhMe (1:1)] to yield **4** (0.60 g, 74%) as yellow solid after recrystallization from $MeCO_2Et$. − M. p. 92°C. − LSIMS: *m/z* = 560 [M]$^+$. − ^{1}H NMR (200 MHz, $CDCl_3$, 25°C): δ = 7.87 (2 H, d, *J* = 8 Hz), 7.29−7.37 (2 H, m), 6.86 (2 H, d, *J* = 8 Hz), 4.09−4.26 (8 H, m), 1.00−1.30 (42 H, m). − ^{13}C NMR (50.3 MHz, $CDCl_3$, 25°C): δ = 154.6, 126.9, 125.0, 114.6, 105.7, 69.8, 62.3, 18.0, 12.1. − $C_{32}H_{56}O_4Si_2$·0.5 H_2O (578.98): calcd. C 67.50, H 10.09; found C 67.64, H 9.61.

1,5-Bis{2-[2-(triisopropylsilyloxy)ethoxy]ethoxy}napthalene (**5**): Triisopropylsilyl triflate (1.14 g, 3.7 mmol) and 2,6-dimethylpyridine (0.40 g, 3.7 mmol) were added to a H_2O/ice-cooled solution of **2** (0.50 g, 1.18 mmol) in dry CH_2Cl_2 (20 ml) under N_2. The solution was allowed to warm up to ambient temperature. After 2 h, it was extracted with 1 M HCl and then with H_2O. The organic layer was dried ($MgSO_4$) and the solvent was removed under reduced pressure. The residue was purified by flash column chromatography [SiO_2: $MeCO_2Et$/CH_2Cl_2 (1:3)] to yield **5** (0.60 g, 62%) as an oil. − LSIMS: *m/z* = 649 [M]$^+$. − ^{1}H NMR (300 MHz, $CDCl_3$, 25°C): δ = 7.79 (2 H, d, *J* = 8 Hz), 7.16−7.29 (2 H, m), 6.75 (2 H, d, *J* = 8 Hz), 4.00−4.36 (4 H, m), 3.73−3.98 (8 H, m), 3.56−3.70 (4 H, m), 0.86−1.16 (42 H, m). − ^{13}C NMR (75 MHz, CD_3CN, 25°C): δ = 154.4, 126.9, 125.0, 114.7, 105.6, 73.2, 70.0, 68.0, 63.2, 18.0, 17.7, 12.3. − $C_{36}H_{64}O_6Si_2$ (649.07): calcd. C 66.62, H 9.94; found C 66.73, H 9.75.

1,5-Bis(2-{2-[2-(triisopropylsilyloxy)ethoxy]ethoxy}-ethoxy)naphthalene (**6**): Triisopropylsilyl triflate (0.90 g, 2.9 mmol) and 2,6-dimethylpyridine (0.31 g, 2.9 mmol) were added to a solution of **3** (0.50 g, 1.17 mmol) in dry CH_2Cl_2 (15 ml) under N_2. After stirring at room temperature for 1 h, the organic layer was washed with H_2O and dried ($MgSO_4$). The solvent was removed under reduced pressure to afford **6** (0.70 g, 81%) as an oil. − LSIMS: *m/z* = 736 [M]$^+$. − ^{1}H NMR (300 MHz, $CDCl_3$, 25°C): δ = 7.83 (2 H, d, *J* = 8 Hz), 7.30−7.37 (2 H, m), 6.83 (2 H, d, *J* = 8 Hz), 4.26−4.30 (4 H, m), 3.97−4.02 (4 H, m), 3.57−3.87 (16 H, m), 0.95−1.15 (42 H, m). − ^{13}C NMR (75 MHz, CD_3CN, 25°C): δ = 154.4, 126.8, 125.0, 114.7, 105.7, 72.8, 71.1, 71.0, 69.9, 68.0, 63.0, 18.0, 12.0. − $C_{40}H_{72}O_8Si_2$ (737.18): calcd. C 65.17, H 9.89; found C 65.42, H 9.68.

{[2]-[1,5-Bis{2-[2-(triisopropylsilyloxy)ethoxy]ethoxy}-napthalene]-[9,18,29,38-tetraazonia[1.1.0.1.1.0]paracyclophane]-Rotaxane} Tetrakis(hexafluorophosphate) (**8**·4 PF_6): A solution of **7**·2 PF_6 (1.01g, 1.4 mmol), 1,4-bis(bromomethyl)benzene (0.38 g, 1.4 mmol), and **5** (0.31 g, 0.5 mmol) in dry MeCN (15 ml) was stirred at ambient temperature for 10 d. The solvent was removed under reduced pressure and the residue was washed with Et_2O and dissolved in Me_2CO. After filtration, the solvent was removed under reduced pressure and the residue was purified by column chromatography [SiO_2: MeOH/2 M NH_4Cl_{aq}/$MeNO_2$ (7:2:1)] to afford a purple solid. The solid was dissolved in H_2O and NH_4PF_6 added to the resulting solution to afford **8**·4 PF_6 (0.27 g, 32%) as a purple solid. − M. p. > 300°C. − LSIMS: *m/z* = 1603 [M − PF_6]$^+$, 1458 [M − 2 PF_6]$^+$, 1313 [M −3 PF_6]$^+$, 1168 [M − 4 PF_6]$^+$. − ^{1}H NMR (400 MHz, CD_3CN, 25°C): δ = 8.92 (4 H, br. s), 8.65 (4 H, br. s), 8.07 (4 H, br. s), 7.95 (4 H, br. s), 7.39 (4 H, br. s), 7.20 (4 H, br. s), 6.27 (2 H, d, *J* = 8 Hz), 5.97−6.01 (2 H, m), 5.71 (8 H, s), 4.00−4.32 (16 H, m), 2.41 (2 H, d, *J* = 8 Hz), 1.00−1.30 (42 H, s). − ^{13}C NMR (75 MHz, CD_3CN, 25°C): δ = 152.0, 146.3, 145.9, 144.9, 137.5, 132.3, 132.3, 129.1, 127.2, 125.8, 125.3, 109.3, 105.4, 74.4, 70.7, 69.3, 66.3, 64.4, 18.4, 12.8. − $C_{72}H_{96}F_{24}N_4O_6P_4Si_2$ (1749.60): calcd. C 49.43, H 5.53, N 3.20; found C 49.66, H 5.59, N 3.27. − Single crystals suitable for X-ray analysis were grown by vapor diffusion of *i*Pr_2O into an Me_2CO solution of **8**·4 PF_6. X-ray data: [$C_{72}H_{96}N_4O_6Si_2$][PF_6]$_4$·2 Me_2CO, *M* = 1865.7, monoclinic, $P2_1/n$ (no. 14), *a* = 19.874(1), *b* =

12.517(1), c = 36.480(2) Å, β = 96.19(1)°, V = 9022(1) Å^3, Z = 4, D_c = 1.374 g cm^{-3}, μ(Cu-K_α) = 19.3 cm^{-1}, F(000) = 3888, T = 173 K; red prisms, 0.53 × 0.30 × 0.27 mm, Siemens P4/RA diffractometer, ω-scans, 13220 independent reflections. The structure was solved by direct methods. Disorder was found in one of the terminal triisopropylsilyl groups of the thread, and this was resolved into two partial occupancy orientations with only the atoms of the major occupancy orientation being refined anisotropically. The remaining non-hydrogen atoms were all refined anisotropically. Refinement was by full-matrix least-squares based on F^2 to give R_1 = 0.072, wR_2 = 0.167 for 8912 independent observed reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta \leq 120°$] and 1122 parameters. Crystallographic data (excluding structure factors) for this structure have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC-101765. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK [fax: (internat.) + 44-1223/336-033; e-mail: deposit@ccdc.cam.ac.uk].

{[2]-[1,5-Bis(2-{2-[2-(triisopropylsilyloxy)ethoxy]ethoxy}-ethoxy)naphthalene]-[9.18,29,38-tetraazonia[1.1.0.1.1.0]-paracyclophane]-Rotaxane} Tetrakis(hexafluorophosphate) (**9**·4 PF_6): A solution of **7**·2 PF_6 (0.52 g, 0.7 mmol), 1,4-bis(bromomethyl)benzene (0.19 g, 0.74 mmol), and **6** (0.20 g, 0.27 mmol) in dry MeCN (8 ml) was stirred at ambient temperature for 10 d. The solvent was removed under reduced pressure and the residue was washed with Et_2O and dissolved in Me_2CO. After filtration, the solvent was removed under reduced pressure and the residue was purified by column chromatography [SiO_2: MeOH/2 M NH_4Cl_{aq}/$MeNO_2$ (7:2:1)] to afford a purple solid. The solid was dissolved in H_2O and NH_4PF_6 added to the resulting solution to afford **9**·4 PF_6 (0.36 g, 72%) as a purple solid. – M. p. > 300°C. – LSIMS: m/z = 1692 [M − PF_6]$^+$, 1547 [M − 2 PF_6]$^+$, 1402 [M − 3 PF_6]$^+$, 1257 [M − 4 PF_6]$^+$. – ^{1}H NMR (300 MHz, CD_3CN, 25°C): δ = 9.02 (4 H, br. s), 8.65 (4 H, br. s), 7.97−8.01 (8 H, m), 7.22−7.34 (8 H, m), 6.26 (2 H, d, J = 8 Hz), 5.94−6.00 (2 H, m), 5.72−5.74 (8 H, m), 3.66−4.30 (24 H, m), 2.44 (2 H, d, J = 8 Hz), 1.00−1.30 (42 H, s). – ^{13}C NMR (75 MHz, CD_3CN, 25°C): δ = 152.5. 146.0, 145.6, 145.0, 137.4, 132.1, 129.0, 127.0, 125.5, 125.2, 109.1, 105.1, 73.5, 72.0, 71.7, 70.5, 69.1, 65.8, 63.5, 18.1, 12.5. – $C_{76}H_{104}F_{24}N_4O_8P_4Si_2$ (1837.71): calcd. C 49.67, H 5.70, N 3.05; found C 50.87, H 5.58, N 2.97. – Single crystals suitable for X-ray analysis were grown by vapor diffusion of iPr$_2$O into a MeCN solution of **9**·4 PF_6. X-ray data: $[C_{76}H_{104}N_4O_8Si_2][PF_6]_4$, M = 1837.7, triclinic, $P\bar{1}$ (no. 2), a = 10.541(3), b = 12.209(2), c = 19.142(4) Å, α = 91.59(1), β = 104.26(2), γ = 111.42(1)°, V = 2203.6(8) Å^3, Z = 1 (the molecule has crystallographic C_i symmetry), D_c = 1.385 g cm^{-3}, μ(Mo-K_α) = 2.17 cm^{-1}, F(000) = 956, T = 293 K; orange prisms, 0.90 × 0.50 × 0.27 mm, Siemens P4/PC diffractometer, ω-scans, 5739 independent reflections. The structure was solved by direct methods. Disorder was found in one of the PF_6^- anions, and this was resolved into two partial occupancy orientations with only the atoms of the major occupancy orientation being refined anisotropically. The remaining non-hydrogen atoms were all refined anisotropically. Refinement was by full-matrix least-squares based on F^2 to give R_1 = 0.068, wR_2 = 0.158 for 3519 independent observed reflections [$F_o > 4\sigma(F_o)$, $2\theta \leq 45°$] and 556 parameters. Crystallographic data (excluding structure factors) for this structure have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC-101764. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK [fax: (internat.) + 44-1223/336-033; e-mail: deposit@ccdc.cam.ac.uk].

[1] For reviews and accounts on rotaxanes, see: [1a] C. O. Dietrich-Buchecker, J.-P. Sauvage, *Bioorg. Chem. Front.* **1991**, *2*, 195−248. – [1b] J.-C. Chambron, C. O. Dietrich-Buchecker, J.-P. Sauvage, *Top. Curr. Chem.* **1993**, *165*, 131−162. – [1c] H. W. Gibson, H. Marand, *Adv. Mater.* **1993**, *5*, 11−21. – [1d] H. W. Gibson, M. C. Bheda, P. T. Engen, *Prog. Polym. Sci.* **1994**, *19*, 843−945. – [1e] F. Vögtle, T. Dünnwald, T. Schmidt, *Acc. Chem. Res.* **1996**, *29*, 451−460. – [1f] R. Jäger, F. Vögtle, *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 930−944. – [1g] D. B. Amabilino, J. F. Stoddart, *Chem. Rev.* **1995**, *95*, 2725−2828. – [1h] M. Belohradsky, F. M. Raymo, J. F. Stoddart, *Collect. Czech. Chem. Commun.* **1996**, *61*, 1−43.

[2] For reviews and accounts on template-directed syntheses, see: [2a] D. H. Busch, N. A. Stephenson, *Coord. Chem. Rev.* **1990**, *100*, 119−154. – [2b] J. S. Lindsey, *New J Chem* **1991**, *15*, 153−180. – [2c] D. H. Busch *J. Inclusion Phenom.* **1992**, *12*, 389−395. – [2d] S. Anderson, H. L. Anderson, J. K. M. Sanders, *Acc. Chem. Res.* **1993**, *26*, 469−475. – [2e] R. Cacciapaglia, L. Mandolini, *Chem. Soc. Rev.* **1993**, *22*, 221−231. – [2f] R. Hoss, F. Vögtle, *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 375−384. – [2g] J. P. Schneider, J. W. Kelly, *Chem. Rev.* **1995**, *95*, 2169−2187. – [2h] D. Philp, J. F. Stoddart, *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1155−1196. – [2i] F. M. Raymo, J. F. Stoddart, *Pure Appl. Chem.* **1996**, *68*, 313−322. – [2j] M. C. T. Fyfe, J. F. Stoddart, *Acc. Chem. Res.* **1997**, *30*, 393−401.

[3] [3a] J.-C. Chambron, S. Chardon-Noblat, A. Harriman, V. Heitz, J.-P. Sauvage, *Pure Appl. Chem.* **1993**, *65*, 2343−2349. – [3b] J.-C. Chambron, C. O. Dietrich-Buchecker, V. Heitz, J.-F. Nierengarten, J.-P. Sauvage, C. Pascard, J. Guilhem, *Pure Appl. Chem.* **1995**, *67*, 233−240.

[4] [4a] F. Vögtle, R. Jäger, M. Händel, S. Ottens-Hildebrandt, *Pure Appl. Chem.* **1996**, *68*, 225−232. – [4b] A. S. Lane, D. A. Leigh, A. Murphy, *J. Am. Chem. Soc.* **1997**, *119*, 11092−11093.

[5] [5a] H. Ogino, *New J. Chem.* **1993**, *17*, 683−688. – [5b] R. Isnin, A. E. Kaifer, *Pure Appl. Chem.* **1993**, *65*, 495−498. – [5c] A. Harada, *Coord. Chem. Rev.* **1996**, *148*, 115−133. – [5d] S. A. Nepogodiev, J. F. Stoddart, *Chem. Rev.*, **1998**, *98*, 1959−1976.

[6] For reviews and accounts on donor/acceptor template-directed syntheses of catenanes and rotaxanes, see: [6a] D. Philp, J. F. Stoddart, *Synlett* **1991**, 445−458. – [6b] D. Pasini, F. M. Raymo, J. F. Stoddart, *Gazz. Chim. Ital.* **1995**, *125*, 431−443. – [6c] D. B. Amabilino, F. M. Raymo, J. F. Stoddart, *Comprehensive Supramolecular Chemistry*, vol. 9 (Eds.: M. W. Hosseini, J.-P. Sauvage), Pergamon, Oxford, **1996**, p. 85−130. – [6d] F. M. Raymo, J. F. Stoddart, *Chemtracts*, **1998**, *11*, 491−511.

[7] R. E. Gillard, F. M. Raymo, J. F. Stoddart, *Chem. Eur. J.* **1997**, *3*, 1933−1940.

[8] D. B. Amabilino, P. R. Ashton, S. E. Boyd, M. Gómez-López, W. Hayes, J. F. Stoddart, *J. Org. Chem.* **1997**, *62*, 3062−3075.

[9] [9a] P.-L. Anelli, N. Spencer, J. F. Stoddart, *J. Am. Chem. Soc.* **1991**, *113*, 5131−5133. – [9b] P. R. Ashton, M. Grognuz, A. M. Z. Slawin, J. F. Stoddart, D. J. Williams, *Tetrahedron Lett.* **1991**, *32*, 6235−6238. – [9c] P.-L. Anelli, P. R. Ashton, R. Ballardini, V. Balzani, M. Delgado, M. T. Gandolfi, T. T. Goodnow, A. E. Kaifer, D. Philp, M. Pietraszkiewicz, L. Prodi, M. V. Reddington, A. M. Z. Slawin, N. Spencer, J. F. Stoddart, C. Vicent, D. J. Williams, *J. Am. Chem. Soc.* **1992**, *114*, 198−213. – [9d] P. R. Ashton, M. R. Johnston, J. F. Stoddart, M. S. Tolley, J. W. Wheeler, *J. Chem. Soc., Chem. Commun.* **1992**, 1128−1131. – [9e] M. Asakawa, P. R. Ashton, S. Iqbal, J. F. Stoddart, N. D. Tinker, A. J. P. White, D. J. Williams, *Chem. Commun.* **1996**, 483−486. – [9f] P. R. Ashton, S. R. L. Everitt, M. Gómez-López, N. Jayamaran, J. F. Stoddart, *Tetrahedron Lett.* **1997**, *38*, 5691−5694. – [9g] A. C. Benniston, A. Harriman, V. M. Lynch, *J. Am. Chem. Soc.* **1995**, *117*, 5275−5291. – [9h] A. Archut, W. M. Müller, S. Baumann, M. Habel, F. Vögtle, *Liebigs Ann.* **1997**, 495−499.

[10] E. Córdova, R. A. Bissell, A. E. Kaifer, *J. Org. Chem.* **1995**, *60*, 1033−1035.

[11] E. Córdova, R. A. Bissell, N. Spencer, P. R. Ashton, J. F. Stoddart, A. E. Kaifer, *J. Org. Chem.* **1993**, *58*, 6550−6552.

[12] P.-L. Anelli, M. Asakawa, P. R. Ashton, R. A. Bissell, G. Clavier, R. Górski, A. E. Kaifer, S. J. Langford, G. Mattersteig, S. Menzer, D. Philp, A. M. Z. Slawin, N. Spencer, J. F. Stoddart, M. S. Tolley, D. J. Williams, *Chem. Eur. J.* **1997**, *3*, 1113−1135.

[13] M. Asakawa, W. Dehaen, G. L′abbé, S. Menzer, J. Nouwen, F. M. Raymo, J. F. Stoddart, D. J. Williams, *J. Org. Chem.* **1996**, *61*, 9561−9595.

[14] J. Sandström, *Dynamic NMR Spectroscopy*, Academic Press, London, **1982**.
[15] It is not possible to establish by variable-temperature ^{1}H-NMR spectroscopy if only one or both Processes I and II are occurring in solution. For related examples, see: M. Asakawa, P. R. Ashton, S. E. Boyd, C. L. Brown, R. E. Gillard, O. Kocian, F. M. Raymo, J. F. Stoddart, M. S. Tolley, A. J. P. White, D. J. Williams, *J. Org. Chem*. **1997**, *62*, 26−37.
[16] For a definition of the term "molecular shuttle", see ref.[9a].
[17] For examples of controllable "molecular shuttles", see: [17a] R. A. Bissell, E. Córdova, A. E. Kaifer, J. F. Stoddart, *Nature* **1994**, *369*, 133−137. − [17b] M.-V. Martínez-Díaz, N. Spencer, J. F. Stoddart, *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1904−1907. − [17c] H. Murakami, A. Kawabuchi, K. Kotoo, M. Kunitake, N. Nakashima, *J. Am. Chem. Soc.* **1997**, 119, 7605−7606.
[18] For reviews on "molecular machines", see: [18a] M. Gómez-López, J. A. Preece, J. F. Stoddart, *Nanotechnology* **1996**, *7*, 183−192. − [18b] M. Gómez-López, J. F. Stoddart, *Bull. Soc. Chim. Belg.* **1997**, *106*, 491−500. − [18c] V. Balzani, M. Gómez-López, J. F. Stoddart, *Acc. Chem. Res.* **1998**, *31*, 405−414. − [18d] J.-C. Chambron, J.-P. Sauvage, *Chem. Eur. J.* **1998**, *4*, 1362−1366.
[19] B. S. Furniss, A. J. Hannaford, P. W. G. Smith, A. R. Tatchell, *Practical Organic Chemistry*, Longman, New York, **1989**.
[20] P. R. Ashton, A. Chemin, C. G. Claessens, S. Menzer, J. F. Stoddart, A. J. P. White, D. J. Williams, *Eur. J. Org. Chem*. **1998**, 969−981.
[21] C. L. Brown, D. Philp, N. Spencer, J. F. Stoddart, *Isr. J. Chem*. **1992**, *32*, 61−67.
[22] P. R. Ashton, J. Huff, S. Menzer, I. W. Parsons, J. A. Preece, J. F. Stoddart, M. S. Tolley, A. J. P. White, D. J. Williams, *Chem. Eur. J.* **1996**, *2*, 31−44.

[98256]