Molecular Meccano, 51[+]
Diastereoselective Self-Assembly of [2]Catenanes

Peter R. Ashton,[a] Aaron M. Heiss,[a][++] Dario Pasini,[a] Françisco M. Raymo,[a][++] Andrew N. Shipway,[a] J. Fraser Stoddart,*[a][++] and Neil Spencer[a]

Keywords: Catenanes / Diastereoselectivity / Molecular Recognition / Self-Assembly / Template-Directed Synthesis

Two chiral π-electron-rich crown ethers incorporating either a binaphthol or two D-mannitol units have been synthesized and their abilities to bind bipyridinium guests demonstrated. Both crown ethers could be interlocked mechanically with cyclobis(paraquat-*p*-phenylene) to afford two chiral [2]catenanes. Furthermore, these crown ethers were also mechanically interlocked with a tetracationic cyclophane incorporating a 2,2′-dihydroxy-1,1′-binaphthyl spacer to afford mixtures of diastereoisomeric [2]catenanes. The composition of these mixtures was determined by ^{1}H-NMR-spectroscopic and HPLC analyses which revealed that modest diastereoselection (56:44–67:33) occurs during the kinetically controlled self-assembly of the catenanes. The free energy barriers (12.8–16.8 kcal mol^{-1}) associated with the circumrotation of one macrocyclic component through the cavity of the other and vice versa were determined by variable-temperature ^{1}H-NMR spectroscopy. In addition, another dynamic process involving the "rocking" of the mean planes of the mechanically interlocked macrocycles with respect to each other was also identified and the associated free energy barriers (10.3–10.4 kcal mol^{-1}) determined.

Introduction

Catenanes[1] incorporating complementary π-electron-rich and π-electron-deficient macrocyclic components self-assemble[2] under kinetic control from appropriate precursors. In this process, intermediate complexes self-assemble under the guidance of [C−H···O] hydrogen bonds, [π···π] stacking, and [C−H···π] interactions after the formation of one covalent bond. The subsequent formation of a second covalent bond interlocks mechanically the components, converting the supramolecular complex into a molecular compound − namely, a catenane. Competition experiments have demonstrated[3] that the relative rates of formation of the second covalent bond "select" the components which will be integral parts of the interlocked molecules in the final product. In order to gain some further insight into the mechanisms of these self-assembly processes, we have investigated the formation of diastereoisomeric [2]catenanes,[4] starting from racemic mixtures of one component, or its precursors, and the pure enantiomer of the other component. Diastereoselection should occur if the rates of covalent bond formation are influenced by the different stereochemistries of the intermediate diastereoisomeric complexes. Here, we report the syntheses of (i) two *chiral* π-electron-rich crown ethers incorporating either an element of axial chirality or chiral centers, (ii) two *chiral* [2]catenanes, each incorporating one or other, of the *chiral* crown ethers and an *achiral* tetracationic cyclophane, (iii) the mechanical interlocking of the *chiral* crown ethers with a *chiral* tetracationic cyclophane to afford diastereoisomeric mixtures of *chiral* [2]catenanes, and (iv) the investigation of the dynamic processes associated with the relative movements of the ring components within these [2]catenanes in solution.

Results and Discussion

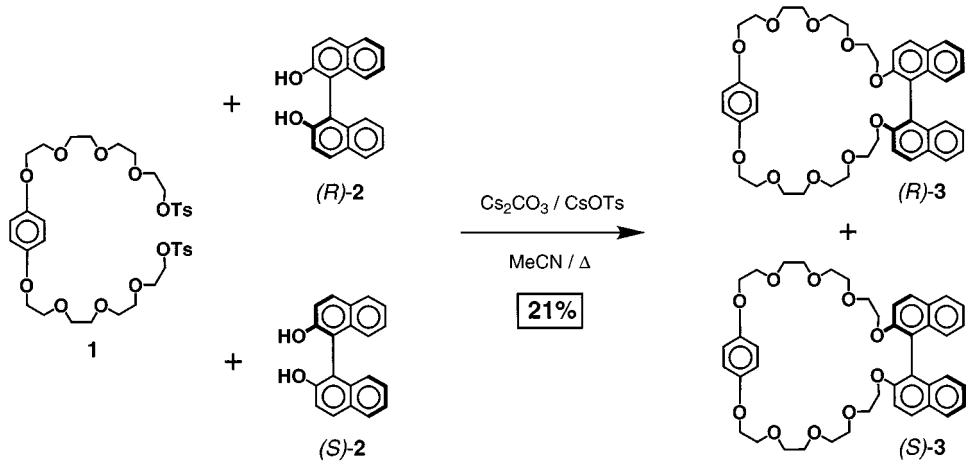
Synthesis

Reaction of **1** with (*RS*)-**2** under high-dilution conditions gave (Scheme 1) (*RS*)-**3** in an overall yield of 21%. The enantiomerically pure (*R*)-**3** was obtained by allowing **1** to react with (*R*)-**2** under otherwise identical conditions. High-performance liquid-chromatographic (HPLC) analysis of (*R*)-**3** revealed an enantiomeric purity higher than 98%. Upon mixing (Scheme 2) (*RS*)-**3** with **4**·2PF$_6$ in MeCN, an orange color appears, indicating complex formation. Spectrophotometric titrations revealed an association constant (K_a) of 23 M^{-1} at 25°C, corresponding to a free energy of association ($\Delta G°$) of −1.9 kcal mol^{-1}. Reaction of **5**·2PF$_6$ and **6** in the presence of (*RS*)-**3** gave (Scheme 3) (*RS*)-**7**·4PF$_6$ in an overall yield of 20%, after counterion exchange.

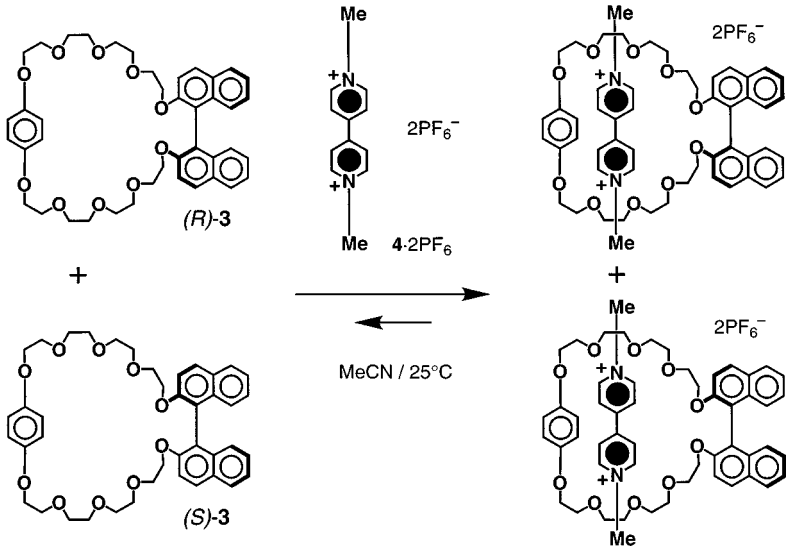
Alkylation (Scheme 4) of (D)-**8** with **9**, followed by the removal of the tetrahydropyranyl protecting group, afforded (D)-**10** in a yield of 57%. Tosylation of (D)-**10** gave (D)-**11**, which was allowed to react with 4-benzyloxyphenol, before

[a] School of Chemistry, University of Birmingham, Edgbaston, Birmingham B15 2TT, UK
[+] Part 50: P. R. Ashton, S. E. Boyd, A. Brindle, S. J. Langford, S. Menzer, L. Pérez-García, J. A. Preece, F. M. Raymo, N. Spencer, J. F. Stoddart, A. J. P. White, D. J. Williams, *New J. Chem.*, in press.
[++] Current address: Department of Chemistry and Biochemistry, University of California, Los Angeles, 405 Hilgard Avenue, Los Angeles, California, 90095-1569, USA
Fax: (internat.) +1-310/206-1843
E-mail: stoddart@chem.ucla.edu

  1434−193X/99/0505−0995 $ 17.50+.50/0



Scheme 1. Synthesis of the crown ethers (*R*)-**3** and (*S*)-**3**

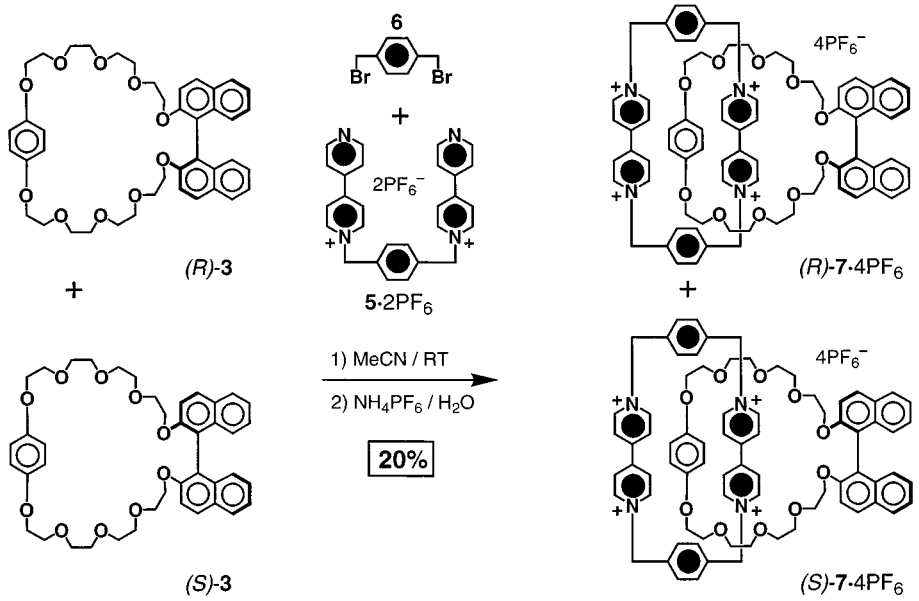


Scheme 2. Complexation of **4**·2PF_6 by (*R*)-**3** and (*S*)-**3**

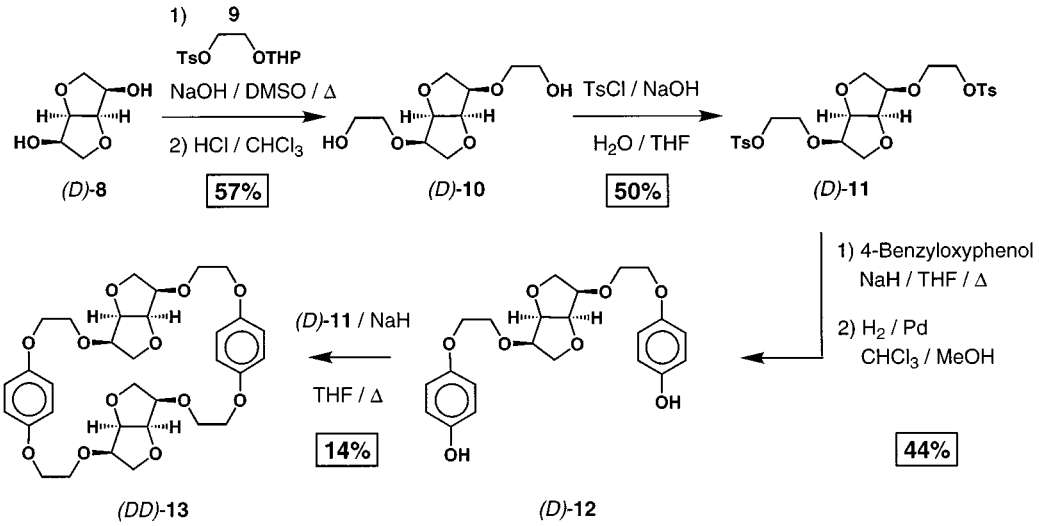
being subjected to hydrogenolysis. The resulting diol (D)-**12** was treated with (D)-**11** to yield the crown ether (DD)-**13** in a yield of 14%. Upon mixing the π-electron-rich crown ether (DD)-**13** and the π-electron-deficient guest **4**·2PF_6 in MeCN, an orange color appears spontaneously indicating the formation of a complex. Spectrophotometric titrations revealed an association constant (K_a) of 41 M^{-1} at 25°C, corresponding to a free energy of association ($\Delta G°$) of −2.2 kcal mol^{-1}. Reaction of **5**·2PF_6 and **6** in the presence of (DD)-**13** afforded (Scheme 5) the [2]catenane (DD)-**14**·4PF_6 in a yield of 17%, after counterion exchange.

Two pairs of enantiomers are associated (Figure 1) with the [2]catenane **15**·4PF_6. The diastereoisomers can be distinguished by ^{1}H-NMR spectroscopy and by HPLC while the enantiomers, of course, have identical ^{1}H-NMR spectra and retention times. The diastereoisomeric ratios for mixtures of these isomers, obtained following routes **A** and **B** (Scheme 6) under the conditions listed in Table 1, could be determined by ^{1}H-NMR spectroscopy and HPLC. When route **A** is employed (Entry 1 in Table 1) using racemic mixtures of the crown ether **3** and of the dibromide **16**, all four isomers self-assemble and no diastereoselectivity is observed. However, (*R*/*R*)-**15**·4PF_6 can be obtained exclusively when (*R*)-**3** and (*R*)-**16** are used (Entry 2 in Table 1) under similar conditions. When route **B** is employed (Entry 3 in Table 1) using (*R*)-**3** and a racemic mixture of the salt **17**·4PF_6, (*R*/*R*)-**15**·4PF_6 and (*R*/*S*)-**15**·4PF_6 are obtained in an overall yield of 33% and with a diastereoisomeric ratio of ca. 54:46 in favor of (*R*/*R*)-**15**·4PF_6. When similar conditions are employed (Entry 4 in Table 1) using a racemic mixure of the crown ether **3** and (*R*)-**17**·4PF_6, (*R*/*R*)-**15**·4PF_6 and (*R*/*S*)-**15**·4PF_6 are obtained in an overall yield of 23% and with a diastereoisomeric ratio of ca. 66:34 in favor of (*R*/*R*)-**15**·4PF_6.

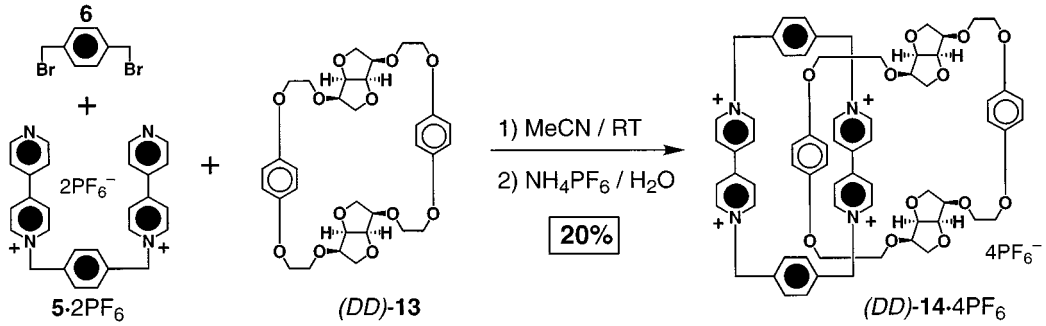
Mixtures of the diastereoisomeric [2]catenanes (*R*/DD)-**18**·4PF_6 and (*S*/DD)-**18**·4PF_6 (Figure 3) were obtained following routes **A** and **B** under the conditions listed in Table 2. When route **A** was employed (Entry 1 in Table 2) using (DD)-**13** and a racemic mixture of the dibromide **16**, (*R*/DD)-**18**·4PF_6 and (*S*/DD)-**18**·4PF_6 were obtained in an overall



Scheme 3. Template-directed synthesis of the [2]catenanes (*R*)-**7**·4PF_6 and (*S*)-**7**·4PF_6



Scheme 4. Synthesis of the crown ether (DD)-**13**



Scheme 5. Template-directed synthesis of the [2]catenane (DD)-**14**·4PF_6

yield of 25% with a diastereoisomeric ratio of 57:43 in favor of (*R*/DD)-**18**·4PF_6. By employing (DD)-**13** and (*R*)-**16** under similar conditions (Entry 2 in Table 2), (*R*/DD)-**18**·4PF_6 was obtained exclusively in a yield of 27%. When route **B** was employed (Entry 3 in Table 2), using (DD)-**13** and a racemic mixture of the salt **17**·2PF_6, (*R*/DD)-**18**·4PF_6 and (*S*/DD)-**18**·4PF_6 were obtained in an overall yield of 28% with a diastereoisomeric ratio of 58:42 in favor of (*R*/DD)-**18**·4PF_6.

Table 1. Reaction conditions[a] and diastereoselectivities observed for the kinetically controlled self-assembly of the [2]catenane **15**·4PF_6

Entry	Reagents	Reagents ratio	Time [d]	Yield[b] (%)	Diastereoselectivity ^{1}H NMR	HPLC
1	(*RS*)-**3**	1	14	16	50:50[c]	48:52[c]
	5·2PF_6	1				
	(*RS*)-**16**	1.2				
2	(*R*)-**3**	2	14	21	–	–
	7·2PF_6	1				
	(*R*)-**16**	1.2				
3	(*R*)-**3**	2	14	33	56:44[c]	54:46[c]
	6	1.2				
	(*RS*)-**17**·2PF_6	1				
4	(*RS*)-**3**	1	4	23	67:33[d]	66:34[d]
	6	6				
	(*R*)-**17**·2PF_6	7.2				

[a] All reactions were carried out in MeCN. – [b] Overall yield determined after column chromatography and counterion exchange. – [c] Ratio between (*R*/*R*)-**15**·4PF_6 and (*R*/*S*)-**15**·4PF_6. – [d] Ratio between (*R*/*R*)-**15**·4PF_6 and (*S*/*R*)-**15**·4PF_6.

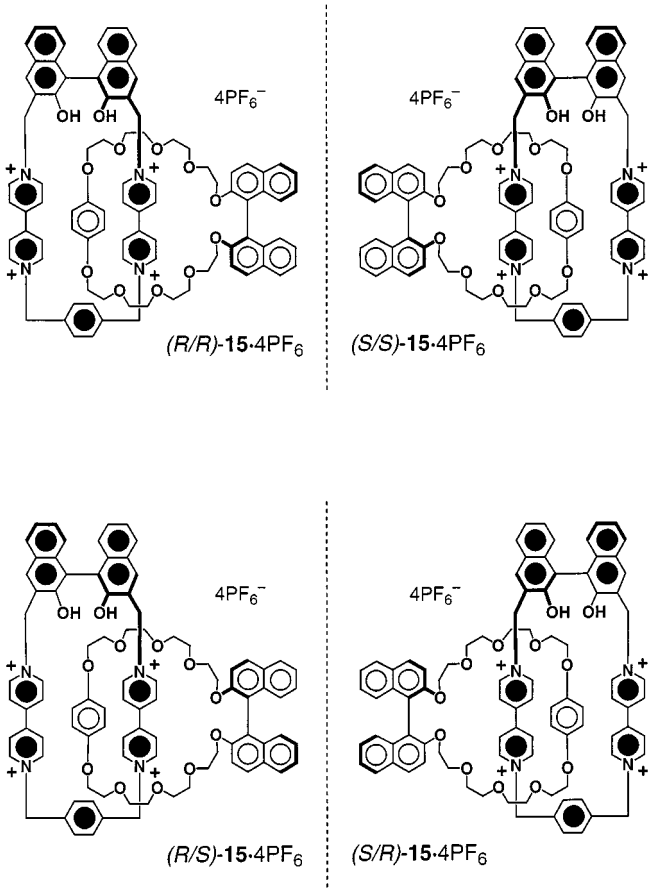


Figure 1. The two pairs of enantiomers associated with the [2]catenanes **15**·4PF_6

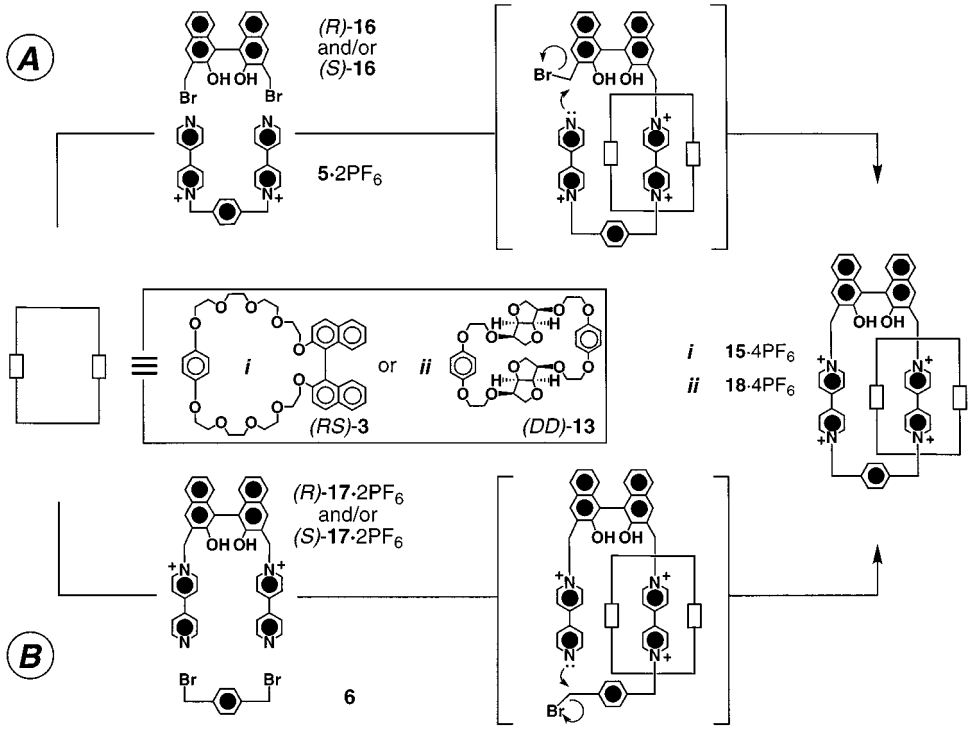
^{1}H-NMR Spectroscopy

The dynamic processes I–III illustrated in Figure 3 are associated with the [2]catenanes in solution. Process I involves the circumrotation of the crown ether component through the cavity of the tetracationic cyclophane. Process II corresponds to the circumrotation of the tetracationic cyclophane through the cavity of the macrocyclic polyether. Process III involves the "rocking" of the [O···O] axis of one 1,4-dioxybenzene unit with respect to the mean plane of the tetracationic cyclophane in which it is inserted.

In (*RS*)-**7**·4PF_6, process I cannot occur since the binaphthol unit is too large to pass through the cavity of the tetracationic cyclophane. At ambient temperature, process II is fast on the ^{1}H-NMR timescale and the bipyridinium units located inside and outside the cavity of the crown ether component cannot be distinguished. On cooling a $(CD_3)_2CO$ solution of (*RS*)-**7**·4PF_6 down, process II becomes slow and the set of signals associated with the α-bipyridinium protons separate into two sets. By employing the approximate coalescence treatment,[5] a free energy barrier of 12.8 kcal mol^{-1} at a coalescence temperature of 260 K was determined (Table 3) for process II. On further cooling, process III becomes slow and the two sets of signals for the α-bipyridinium protons separate into four sets. in addidtion, the 1,4-dioxybenzene protons H_a and H_b (Figure 3) can be distinguished since they resonate as two distinct singlets at δ = 2.18 and 5.80, respectively. Again, by employing the approximate coalescence treatment, a free energy barrier of 10.3 kcal mol^{-1} at a coalescence temperature of 217 K was determined (Table 3) for process III.

In (DD)-**14**·4PF_6, process I is slow on the ^{1}H-NMR timescale at ambient temperature in $(CD_3)_2CO$ and the "inside" and "outside" 1,4-dioxybenzene protons resonate at δ = 3.30 and 6.30, respectively. Upon warming the solution, broadening of the signals occurs as process I becomes fast. Line-broadening analysis[6] revealed (Table 3) a free energy barrier of 16.8 kcal mol^{-1} at a temperature of 335 K for process I. Upon cooling the solution down, processes II and III become slow. As a result, the set of signals observed for the α-bipyridinium protons separates into two sets and then into four. By employing the approximate coalescence treatment, free energy barriers of 12.8 and 10.4 kcal mol^{-1} at coalescence temperatures of 269 and 221 K, respectively, were determined (Table 3) for processes II and III, respectively.

In (*R*/*R*)-**15**·4PF_6, process I cannot occur since the binaphthol unit is too large to pass through the cavity of the tetracationic cyclophane, cf. the case of **7**·4PF_6. At 323 K,

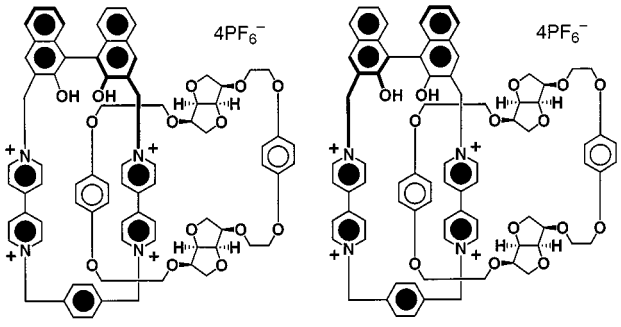


Scheme 6. The routes **A** and **B** used to synthesize the [2]catenanes **15**·4PF$_6$ and **18**·4PF$_6$

Table 2. Reaction conditions[a] and diastereoselectivities observed for the kinetically controlled self-assembly of the [2]catenane **18**·4PF$_6$

Entry	Reagents	Reagents ratio	Yield[b] (%)	Diastereoselectivity[c] ^{1}H NMR
1	**5**·2PF$_6$	1	25	57:43
	(DD)-**13**	1.5		
	(*RS*)-**16**	1		
2	**5**·2PF$_6$	1	27	–
	(DD)-**13**	2		
	(*R*)-**16**	1.2		
3	**6**	1.2	28	58:42
	(DD)-**13**	1.5		
	(*RS*)-**17**·2PF$_6$	1		

[a] All reactions were carried out in MeCN for 14 d. – [b] Overall yield determined after column chromatography and counterion exchange. – [c] Ratio between (*R*/DD)-**18**·4PF$_6$ and (*S*/DD)-**18**·4PF$_6$.



(*R*/*DD*)-**18**·4PF$_6$ (*S*/*DD*)-**18**·4PF$_6$

Figure 2. The two diastereoisomers (*R*/DD)-**18**·4PF$_6$ and (*S*/DD)-**18**·4PF$_6$

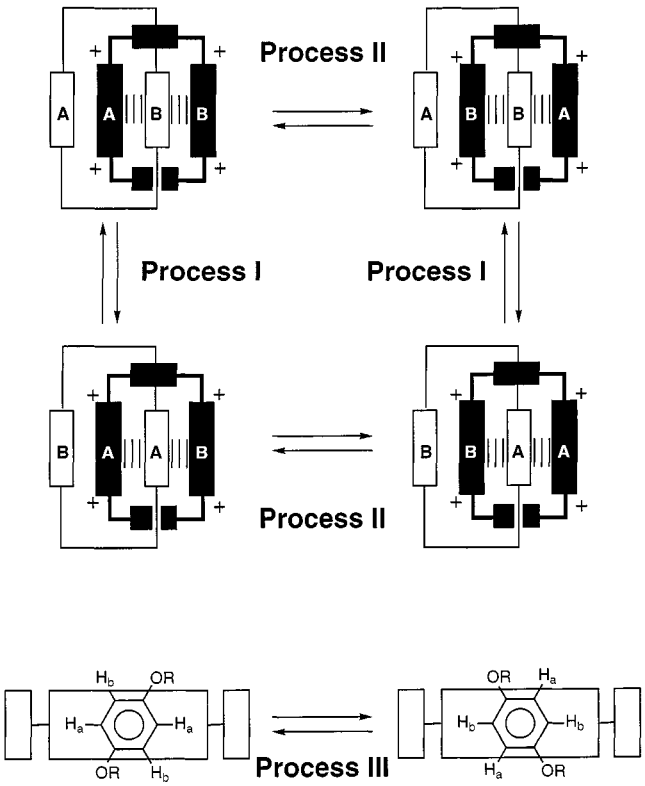


Figure 3. The dynamic processes associated with the [2]catenanes in solution

the ^{1}H-NMR spectrum of a $(CD_3)_2CO$ solution of (*R*/*R*)-**15**·4PF$_6$ shows (Figure 4) one set of signals for the α-bipyridinium protons adjacent to the binaphthol spacer and one

Table 3. Kinetic parameters for the dynamic processes associated with the [2]catenanes (*RS*)-**7**·4PF_6, (DD)-**14**·4PF_6, and (*R*/DD)-**18**·4PF_6 in $(CD_3)_2CO$

Compound	Probe protons	$\Delta\nu$[a] [Hz]	k[b] [s^{-1}]	T[c] [K]	$\Delta G^{\neq}$[d]·[kcal mol^{-1}]	Process
(*RS*)-**7**·4PF_6	α-bipyridinium	40	89	260	12.8	II[e]
	α-bipyridinium	117	260	217	10.3	III[e]
(DD)-**14**·4PF_6	"outside" [OC_6H_4O]	26	82	335	16.8	I[f]
	α-bipyridinium	101	224	269	12.8	II[e]
	α-bipyridinium	103	229	221	10.4	III[e]
(*R*/DD)-**19**·4PF_6	mannitol H^3 and H^4	116	258	294	14.6	I[e]

[a] Error ± 1 Hz. – [b] Error ± 5 s^{-1}. – [c] Error ± 1 K. – [d] Error ± 0.2 kcal mol^{-1}. – [e] The coalescence method was employed to determine the kinetic parameters. – [f] The exchange method was employed to determine the kinetic parameters.

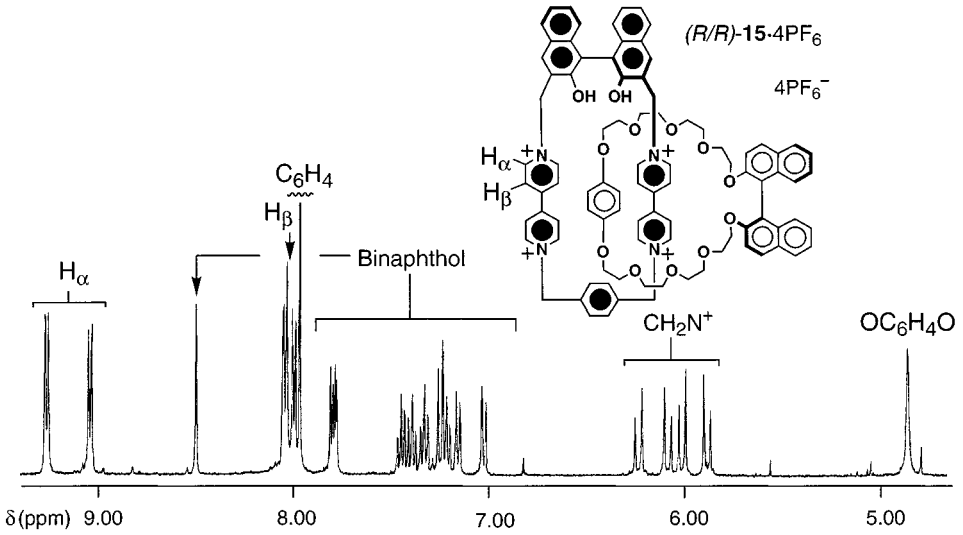


Figure 4. Partial ^{1}H-NMR spectrum of the [2]catenane (*R*/*R*)-**15**·4PF_6 recorded in $(CD_3)_2CO$ at 323 K

set of signals for α-bipyridinium protons close to the *p*-phenylene spacer. Similarly, one AB system (δ = 6.06−6.30) is observed for the [CH_2N^+] protons adjacent to the binaphthol spacer and another (δ = 5.84−6.04) is associated to the [CH_2N^+] protons close to the *p*-phenylene spacer. The 1,4-dioxybenzene protons resonate as a singlet at δ = 4.86. On cooling the solution down, processes II and III become slow, giving rise to very complex ^{1}H-NMR spectra which we have not been able to assign fully.

In (*R*/DD)-**18**·4PF_6, process I is slow on the ^{1}H-NMR timescale at 253 K in $(CD_3)_2CO$. As a result, the H^3 and H^4 protons of the mannitol units give rise (Figure 5) to two sets of signals at δ = 4.84 and 4.55 which coalesce into one on warming the solution up to 295 K. By employing the coalescence treatment, a free energy barrier of 14.6 kcal mol^{-1} at a coalescence temperature of 294 K was determined (Table 3) for process I. At low temperatures, processes II and III become slow, giving rise to very complex ^{1}H-NMR spectra which we have not been able to assign fully.

The diastereoisomeric mixtures of the [2]catenanes **15**·4PF_6 and **18**·4PF_6 were analyzed by ^{1}H-NMR spectroscopy in order to evaluate the diastereoisomeric ratios. Even although the ^{1}H-NMR spectra are very complex, unique resonances for the diastereoisomers can be identified and their relative intensities measured. As an example, the partial ^{1}H-NMR spectrum of a mixture of (*R*/*R*)-**15**·4PF_6 and (*R*/*S*)-**15**·4PF_6 is shown in Figure 6. The resonances associated with the 1,4-dioxybenzene protons of the two diastereoisomers appear as two distinct singlets at δ = 4.87 and 4.81.

Conclusions

Complementary components, incorporating either elements of axial chirality or chiral centers, were allowed to react under competitive conditions. Their diastereoselective self-assembly into [2]catenanes occurs through the formation of intermediate diastereoisomeric complexes. The relative stereochemistries of the interlocked components of the intermediate complexes govern the rates of ring closure (Scheme 6) determining the outcome of the kinetically controlled self-assembly processes and imposing diastereoselection. Variable-temperature ^{1}H-NMR-spectroscopic analyses of some of the [2]catenanes enabled the determination of the free energy barriers associated with the dynamic processes involving the circumrotation of one macrocyclic component through the cavity of the other and vice versa and the "rocking" of the mean planes of the mechanically interlocked macrocycles with respect to each other.

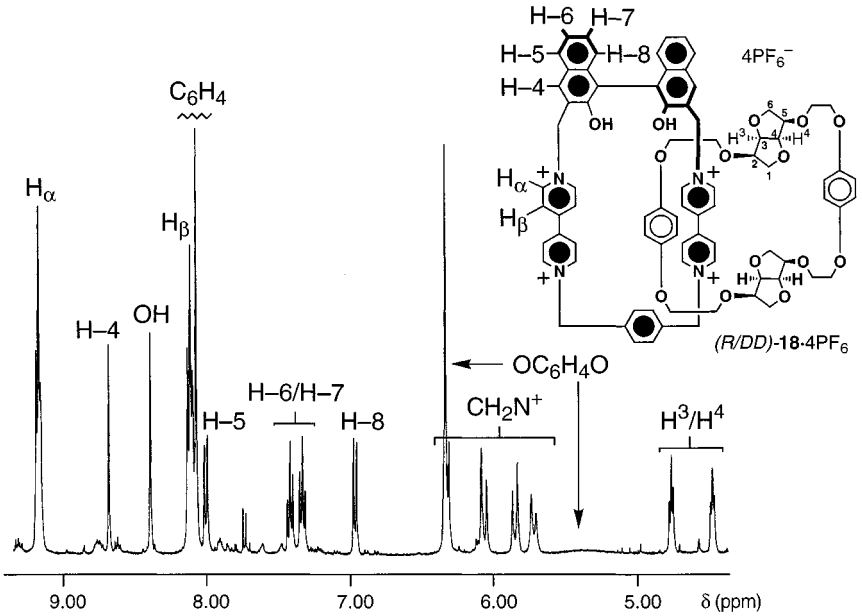


Figure 5. Partial ^{1}H-NMR spectrum of the [2]catenane (*R*/DD)-**18**·4PF$_6$ recorded in $(CD_3)_2CO$ at 253 K

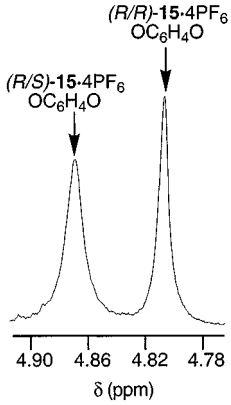


Figure 6. Partial ^{1}H-NMR spectrum of a mixture of (*R*/*S*)-**15**·4PF$_6$ of (*R*/*R*)-**15**·4PF$_6$ recorded in $(CD_3)_2CO$ at 323 K

Experimental Section

General Methods: Chemicals were purchased from Aldrich and used as received. Solvents were dried according to procedures described in the literature.[7] The compounds **1**,[8] **5**·2PF$_6$,[7] **15**,[9] **17**·2PF$_6$[9] were prepared according to procedures described in the literature. − Thin-layer chromatography (TLC) was carried out using aluminium 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). − High-performance liquid chromatography (HPLC) was performed using a Gilson 714 system fitted with a UV/Vis detector. − Melting points were determined with an Elecrothermal 9200 apparatus and are not corrected. − UV/Vis spectra were recorded with a Perkin-Elmer Lambda 2 using HPLC-quality solvents. − Electron-impact mass spectra (EIMS) were performed using a Kratos Profile spectrometer. − Liquid secondary-ion mass spectra (LSIMS) were obtained from 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 onto a stainless steel probe tip. High-resolution mass spectra (LSIMS) were obtained with the VG Zabspec operating at a resolution of 6000 and using voltage scanning with CsI as a reference. − ^{1}H-Nuclear Magnetic Resonance (^{1}H-NMR) spectra were recorded either with a Bruker AC300 (300 MHz) spectrometer or with a Bruker AMX400 (400 MHz) spectrometer using either the solvent or TMS as internal standards. − ^{13}C-Nuclear Magnetic Resonance (^{13}C-NMR) spectra were recorded with either a Bruker AC300 (75.5 MHz) spectrometer 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. − Microanalyses were performed by the University of Birmingham Microanalytical Service and by the University of North London Microanalytical Service.

Crown Ether 3: A solution of **1** (2.7 g, 3.5 mmol) in dry MeCN (50 mL) was added to a suspension of Cs_2CO_3 (11.5 g, 35 mmol) and CsOTs (3 g, 9.8 mmol) in dry MeCN (400 mL). The mixture was heated under reflux and (*RS*)-**2** (1 g, 3.5 mmol) in dry MeCN (200 mL) was added dropwise over a period of 6 h. Heating under reflux was continued for 3 d. The reaction mixture was filtered, the solvent was removed under reduced pressure, and the residue partitioned between H_2O (400 mL) and $CHCl_3$ (400 mL). The aqueous layer was extracted with $CHCl_3$ (3 × 400 mL). The combined organic layers were washed with H_2O (3 × 300 mL) and dried ($MgSO_4$). The solvent was removed under reduced pressure and the residue was purified by column chromatography (SiO_2: hexane/$MeCO_2Et$, 50:50 and then 20:80, v/v) to afford (*RS*)-**3** (520 mg, 21%) as a white glass. − LSIMS; *m*/*z*: 712 [M]$^+$. − ^{1}H NMR (300 MHz, $CDCl_3$, 25°C): δ = 7.90 (2 H, d, *J* = 7 Hz), 7.83 (2 H, d, *J* = 7 Hz), 7.40 (2 H, d, *J* = 7 Hz), 7.31 (2 H, m), 7.19 (2 H, m), 7.15 (2 H, d, *J* = 7 Hz), 6.81 (4 H, s), 4.05 (8 H, m), 3.78 (4 H, m), 3.62 (4 H, m), 3.50 (4 H, m), 3.42 (4 H, m), 3.28 (4 H, m), 3.11 (4 H, m). − ^{13}C NMR (75.5 MHz, $CDCl_3$, 25°C): δ = 154.4, 153.2, 134.1, 129.4, 129.3, 127.8, 126.2, 125.6, 123.6, 120.5, 116.0, 115.8, 70.9, 70.5, 70.4, 69.8, 69.7, 69.6, 68.5, 29.7. − $C_{42}H_{48}O_{10}$ (712.84): calcd. C 70.77, H 6.78; found C 70.49, H 6.75. − The enantiomerically pure crown ether (*R*)-**3** was obtained by employing enantiomerically pure (*R*)-**2** instead of (*RS*)-**2** under otherwise identical conditions. − $[\alpha]^{20}_{589}$ = +34 (*c* = 0.08 in $CHCl_3$).

[2]Catenane 7·4PF$_6$: (*RS*)-**3** (180 mg, 0.25 mmol), **5**·2PF$_6$ (176 mg, 0.30 mmol), and **6** (66 mg, 0.26 mmol) in dry MeCN (30 mL) was stirred for 10 d at ambient temp. The solvent was removed under reduced pressure and the residue was purified by column chromatography (SiO$_2$: MeOH/2 M aq. NH$_4$Cl/MeNO$_2$, 7:2:1, v/v/v). The resulting solid was dissolved in H$_2$O and a saturated aqueous solution of NH$_4$PF$_6$ was added until no further precipitation occurred. The red precipitate was filtered and air-dried to afford (*RS*)-**7**·4PF$_6$ (90 mg, 20%) as a red solid. − LSIMS; *m*/*z*: 1812 [M]$^+$, 1667 [M − PF$_6$]$^+$, 1522 [M − 2PF$_6$]$^+$, 1377 [M − 3PF$_6$]$^+$. − ^{1}H NMR [400 MHz, (CD$_3$)$_2$CO, 25°C]: δ = 9.31 (8 H, d, *J* = 7 Hz), 8.18 (8 H, d, *J* = 7 Hz), 8.03 (8 H, s), 7.92 (2 H, d, *J* = 7 Hz), 7.85 (2 H, d, *J* = 7 Hz), 7.35 (2 H, m), 7.24 (2 H, m), 7.07 (2 H, d, *J* = 7 Hz), 6.03 (4 H, d, *J* = 13 Hz), 5.93 (4 H, d, *J* = 13 Hz), 4.20−3.15 (36 H, m). − ^{13}C NMR [75.5 MHz, (CD$_3$)$_2$CO, 25°C]: δ = 155.2, 151.1, 147.7, 147.6, 145.8, 137.7, 134.5, 131.8, 130.7, 128.8, 127.3, 126.8, 125.8, 125.1, 122.0, 118.2, 113.9, 71.7, 71.1, 70.7, 70.6, 70.4, 70.1, 69.1, 67.9, 65.7. − C$_{78}$H$_{80}$N$_4$O$_{10}$P$_4$F$_{24}$ (1813.31): calcd. C 51.66, H 4.45 N 3.09; found C 51.60, H 4.42, N 2.88.

2,5-Di-*O*-2′-(hydroxyethoxy)-1,4:3,6-dianhydro-D-mannitol [(D)-10]: A suspension of finely ground NaOH (6.6 g, 165 mmol) in DMSO (100mL) was stirred mechanically for 15 min at 50°C. (D)-**8** (3 g, 21 mmol) was added to the mixture and stirring and heating were maintained for 1 h. A solution of **9** (18.5 g, 62 mmol) in DMSO (30 mL) was added and the resulting mixture was heated for 18 h at 80°C with stirring. After cooling down to ambient temperature, the solvent was removed under reduced pressure by trap-to-trap distillation and the solid residue was treated with a 1:1 (v/v) mixture of CHCl$_3$/H$_2$O (800 mL). The organic layer was washed with H$_2$O and dried (MgSO$_4$). The solvent was removed under reduced pressure and the residue was purified by column chromatography (SiO$_2$: EtOAc) to yield (R_f = 0.20) 2,5-di-*O*-[2′-(tetrahydropyranyloxy)ethoxy]-1,4:3,6-dianhydro-D-mannitol (5 g, 61%) as a yellow oil. − ^{1}H NMR (300 MHz, CDCl$_3$, 25°C): δ = 4.65−4.58 (4 H, m), 4.17−3.95 (4 H, m), 3.90−3.40 (16 H, m), 1.85−1.35 (12 H, m). − ^{13}C NMR (75.5 MHz, CDCl$_3$, 25°C): δ = 99.1, 98.8, 80.9, 80.5, 71.1, 70.0, 66.9, 66.7, 62.3, 62.1, 60.4, 30.6, 25.4, 19.6, 19.4. − Concentrated HCl (0.5 mL) was added to a solution of 2,5-di-*O*-[2′-(tetrahydropyranyloxy)ethoxy]-1,4:3,6-dianhydro-D-mannitol (4 g, 12.4 mmol) in MeOH (30 mL). The solution was stirred for 3 h at ambient temp., after which time no traces of starting material were present by TLC (SiO$_2$: CHCl$_3$/MeOH, 100:1, v/v). The solution was filtered, concentrated and the residue was dissolved in CHCl$_3$ and dried (K$_2$CO$_3$) to yield (D)-**10** (2.7 g, 93%) as a colourless oil. − ^{1}H NMR (300 MHz, CDCl$_3$, 25°C): δ = 4.58 (2 H, m), 4.08 (4 H, m), 3.72 (10 H, m), 3.15 (2 H, br. s). − ^{13}C NMR (75.5 MHz, CDCl$_3$, 25°C): δ = 80.7, 80.5, 72.5, 71.5, 61.9.

2,5-Di-*O*-[2′-(*p*-tolylsulfonyloxy)ethoxy]-1,4:3,6-dianhydro-D-mannitol (D)-11: A solution of NaOH (2 g, 50 mmol) in H$_2$O (50 mL) was added to a solution of (D)-**10** (2.6 g, 11 mmol) in THF (50 mL). The reaction mixture was cooled down to 0°C with stirring and a solution of *p*-toluenesulfonyl chloride (5.1 g, 27 mmol) in THF (80 mL) was added dropwise over a period of 1 h. The reaction mixture was stirred for 3 h and then was poured into 400 mL of a 1:1 ice/water mixture. The aqueous layer was extracted with CH$_2$Cl$_2$ (3 × 500 mL), the combined organic layers were dried (MgSO$_4$), and concentrated under reduced pressure.·The residue was purified by column chromatography (SiO$_2$, CH$_2$Cl$_2$ and then CH$_2$Cl$_2$/MeOH, 98:2, v/v) to yield (D)-**11** (3.0 g, 50%) as a brown oil. − $[\alpha]_{589}^{20}$ = +59 (*c* = 0.03 in CHCl$_3$). − LSIMS; *m*/*z*: 543 [M + H]$^+$. − ^{1}H NMR (300 MHz, CDCl$_3$, 25°C): δ = 7.80 (4 H, d, *J* = 8 Hz), 7.35 (4 H, d, *J* = 8 Hz), 4.48 (2 H, m), 4.18 (4 H, m), 3.98−3.55 (10 H, m), 2.45 (6 H, s). − ^{13}C NMR (75.5 MHz, CDCl$_3$, 25°C): 144.9, 129.9, 128.0, 99.2, 80.7, 80.6, 71.2, 69.3, 68.1, 21.7. − C$_{24}$H$_{30}$O$_{10}$S$_2$ (542.43): calcd. C 53.12, H 5.57, S 11.82; found C 53.26, H 5.65, S 12.10.

2,5-Di-*O*-[2′-(*p*-hydroxyphenoxy)ethoxy]-1,4:3,6-dianhydro-D-mannitol (D)-12: A solution of 4-benzyloxyphenol (8.9 g, 44.2 mmol) was added to a suspension of 3.7 g of NaH (93 mmol, 60% in mineral oil) in dry DMF (300 mL). The reaction mixture was heated at 80°C for 2 h and then a solution of (D)-**11** (8 g, 15 mmol) in dry DMF (100 mL) was added under N$_2$. The reaction mixture was maintained at 90°C for 4 d and then H$_2$O and 10% aqueous H$_2$SO$_4$ were added. The solvent was removed under reduced pressure and the residue was partitioned between H$_2$O (300 mL) and CH$_2$Cl$_2$ (300 mL). The aqueous layer was extracted with CH$_2$Cl$_2$ (3 × 400 mL). The combined organic layers were washed with an aqueous solution of 1M NaOH (3 × 400 mL), H$_2$O (3 × 300 mL), and dried (MgSO$_4$). The solvent was removed under reduced pressure and the residue was purified by column chromatography (SiO$_2$: hexane/MeCO$_2$Et, 20:80 and then 50:50, v/v) to yield 2,5-di-*O*-[2′-(*p*-benzyloxyphenoxy)ethoxy]-1,4:3,6-dianhydro-D-mannitol as a white solid (4 g, 45%). − $[\alpha_{589}]^{20}$ = +61 (*c* = 0.07 in CHCl$_3$). − EIMS; *m*/*z* (%): 598 (65) [M]$^+$. − ^{1}H NMR (300 MHz, CDCl$_3$, 25°C): δ = 7.45 (10 H, m), 6.95 (8 H, m), 5.02 (4 H, s), 4.61 (2 H, m), 4.22−3.75 (14 H, m). − ^{13}C NMR (75.5 MHz, CDCl$_3$, 25°C): δ = 153.2, 153.0, 137.3, 128.6, 127.5, 116.1, 115.8, 115.6, 81.0, 80.6, 71.2, 70.6, 69.3, 68.2. − C$_{36}$H$_{38}$O$_8$ (598.65): calcd. C 72.22, H 6.40; found C 72.21, H 6.45. − A solution of 2,5-di-*O*-[2′-(*p*-benzyloxyphenoxy)ethoxy]-1,4:3,6-dianhydro-D-mannitol (4 g, 6.6 mmol) in CHCl$_3$/MeOH (9:1, v/v, 70 mL) was subjected to hydrogenolysis for 8 h at ambient temp. in the presence of 10% palladium on charcoal (0.5 g). The mixture was filtered and the solvent was removed under reduced pressure to afford (D)-**12** (2.7 g, 98%) as a white solid which was used in the following step without further purification. − LSIMS; *m*/*z*: 441 [M + Na]$^+$, 418 [M]$^+$. − ^{1}H NMR [300 MHz, (CD$_3$)$_2$CO, 25°C]: δ = 7.85 (2 H, br. s), 6.88 (8 H, m), 4.62 (2 H, m), 4.15 (2 H, m), 4.04 (4 H, m), 3.95−3.6 (8 H, m). − ^{13}C NMR [75.5 MHz, (CD$_3$)$_2$CO, 25°C]: δ = 153.0, 152.1, 116.4, 116.3, 81.4, 81.3, 71.7, 69.4, 68.9.

Crown Ether (DD)-13: A solution of (D)-**12** (500 mg, 1.20 mmol) was added to a suspension of of NaH (155 mg, 3.90 mmol, 60% suspension in mineral oil) and CsOTs (20 mg) in dry DMF (120 mL). The mixture was heated for 1 h at 80°C and a solution of (D)-**11** (650 mg, 1.20 mmol) in dry DMF (80 mL) was added dropwise over a period of 6 h under N$_2$. The mixture was maintained for 14 d at 90°C. After cooling down to ambient temp., H$_2$O (50 mL) and aqueous 10% H$_2$SO$_4$ (20 mL) were added. The solvent was removed under reduced pressure and the residue was partitioned between H$_2$O (300 mL) and CHCl$_3$ (300 mL). The aqueous layer was extracted with CHCl$_3$ (3 × 400 mL). The combined organic layers were washed with H$_2$O (3 × 300 mL) and dried (MgSO$_4$). The solvent was removed under reduced pressure and the residue was purified by column chromatography (SiO$_2$, MeCO$_2$Et and then CH$_2$Cl$_2$/MeOH, 95:5) to yield (DD)-**13** (100 mg, 14%) as a white solid. − $[\alpha]_{589}^{20}$ = +45 (*c* = 0.023 in CHCl$_3$). − LSIMS; *m*/*z*: 616 [M]$^+$. − ^{1}H NMR (300 MHz, CDCl$_3$, 25°C): δ = 6.81 (8 H, s), 4.53 (4 H, m), 4.20−3.95 (20 H, m), 3.90−3.70 (8 H, m). − ^{13}C NMR (75.5 MHz, CDCl$_3$, 25°C): 153.0, 115.8, 80.8, 80.7, 71.5, 69.6, 68.6. − C$_{32}$H$_{40}$O$_{12}$ (616.60): calcd. C 62.33, H 6.54; found C 62.44, H 6.45.

[2]Catenane (DD)-14·4PF$_6$: A solution of **5**·2PF$_6$ (55 mg, 0.078 mmol), **6** (25 mg, 0.095 mmol), and (DD)-**13** (70 mg, 0.114 mmol) in dry MeCN (30 mL) was stirred for 12 d at ambient temp. The solvent was removed under reduced pressure and the residue was

purified by column chromatography (SiO_2: MeOH/2 M aq. NH_4Cl/$MeNO_2$, 7:2:1, v/v/v). The resulting solid was dissolved in H_2O and a saturated aqueous solution of NH_4PF_6 was added until no further precipitation occurred. The red precipitate was washed several times with $MeNO_2/H_2O$ to yield (DD)-**14**·4PF_6 (25 mg, 17%) as a red solid. − $[\alpha]^{25}_{578} = -78$ ($c = 0.003$ in Me_2CO). − LSIMS; *m/z*: 1735 $[M + H_2O]^+$, 1571 $[M - PF_6]^+$, 1427 $[M - 2PF_6]^+$, 1282 $[M - 3PF_6]^+$. − ^{1}H NMR [400 MHz, $(CD_3)_2SO$, 25°C]: δ = 9.20 (8 H, d, J = 7 Hz), 8.10 (8 H, bs), 7.92 (8 H, s), 6.28 (4 H, s), 5.74 (4 H, d, J = 13 Hz), 5.64 (4 H, d, J = 13 Hz), 4.90 (2 H, m), 4.60 (2 H, m), 4.3−3.5 (28 H, m), 3.30 (4 H, s). − ^{13}C NMR [75.5 MHz, $(CD_3)_2SO$, 25°C]: δ = 153.4, 151.6, 147.5, 145.9, 137.9, 132.1, 127.0, 115.9, 114.3, 85.7, 82.1, 81.2, 80.7, 74.6, 72.6, 71.2, 70.8, 69.1, 68.7. − $C_{68}H_{72}F_{24}N_4O_{12}P_4$ (1717.13): calcd. C 47.56, H 4.23, N 3.26; found C 47.67, H 4.14, N 3.26.

[2]Catenane (*R*/*R*)-15·4PF$_6$: A solution of (*R*)-**3** (200 mg, 0.28 mmol), **5**·2PF_6 (100 mg, 0.14 mmol), and (*R*)-**16** (80 mg, 0.17 mmol) in dry MeCN (30 mL) was stirred for 14 d at ambient temp. The solvent was removed under reduced pressure and the residue was purified by column chromatography (SiO_2: MeOH/2 M aq. NH_4Cl/$MeNO_2$, 7:2:1, v/v/v and then MeOH/1 M aq. NH_4Cl, 7:3, v/v). The resulting solid was dissolved in H_2O and a saturated aqueous solution of NH_4PF_6 was added until no further precipitation occurred. The red precipitate was filtered and air dried to yield (*R*/*R*)-**15**·4PF_6 (57 mg, 24%) as a red solid. − $[\alpha]_{589}^{25} = +131$ ($c = 0.002$ in MeCN). − LSIMS; *m/z*: 1876 $[M - PF_6]^+$, 1731 $[M - 2PF_6]^+$, 1586 $[M - 3PF_6]^+$. − HRLSIMS; *m/z* calcd. for $[M - 2PF_6]^+$ ($C_{92}H_{88}F_{12}N_4O_{12}P_2$) 1730.5686, found 1730.5609. − ^{1}H NMR [400 MHz, $(CD_3)_2CO$, 0°C]: δ = 9.33 (4 H, d, J = 7 Hz), 9.13 (4 H, d, J = 7 Hz), 8.53 (2 H, s), 8.37 (2 H, bs), 8.08 (2 H, d, J = 7 Hz), 8.02 (4 H, d, J = 7 Hz), 7.98 (4 H, s), 7.96 (4 H, d, J = 7 Hz), 7.78−7.71 (4 H, m), 7.47 (2 H, m), 7.43 (2 H, m), 7.33 (2 H, m), 7.23 (2 H, m), 7.18 (2 H, d, J = 7 Hz), 7.02 (2 H, d, J = 8 Hz), 6.27 (2 H, d, J = 14 Hz), 6.10 (2 H, d, J = 14 Hz), 6.00 (2 H, d, J = 13 Hz), 5.87 (2 H, d, J = 13 Hz), 4.83 (4 H, br. s), 4.2−3.5 (32 H, m). − ^{13}C NMR [75.5 MHz, $(CD_3)_2CO$, 25°C]: δ = 155.4, 153.9, 151.8, 148.0, 147.9, 146.8, 146.0, 137.6, 135.8, 134.6, 134.4, 131.6, 130.7, 130.6, 129.9, 129.6, 129.1, 128.7, 127.4, 126.7, 125.9, 125.8, 125.2, 125.1, 124.8, 122.9, 121.6, 118.0, 114.7, 113.7, 71.5, 71.3, 70.9 ,70.7, 70.6, 70.3, 69.8, 67.7, 65.6, 63.6.

[2]Catenane (*R*/DD)-18·4PF$_6$: A solution of **5**·2PF_6 (55 mg, 0.08 mmol), (DD)-**13** (70 mg, 0.11 mmol), and (*R*)-**16** (43 mg, 0.09 mmol) in dry MeCN (30 mL) was stirred for 14 d at ambient temp. The solvent was removed under reduced pressure and the residue was purified by column chromatography (SiO_2: MeOH/2 M aq. NH_4Cl/$MeNO_2$, 7:2:1, v/v/v and then MeOH/1 M aq. NH_4Cl, 7:3, v/v). The resulting solid was dissolved in H_2O and a saturated aqueous solution of NH_4PF_6 was added until no further precipitation occurred. The red precipitate obtained was washed several times with $MeNO_2/H_2O$ to yield (*R*/DD)-**18**·4PF_6 (40 mg, 26%) as a red solid. − $[\alpha]_{589}^{25} = +80$ ($c = 0.008$ in MeCN). − LSIMS; *m/z*: 1947 $[M + Na]^+$, 1778 $[M - PF_6]^+$, 1635 $[M - 2PF_6]^+$, 1490 $[M - 3PF_6]^+$. − ^{1}H NMR (400 MHz, CD_3COCD_3, 31°C): δ = 9.27 (4 H, d, J = 7 Hz), 9.20 (4 H, d, J = 7 Hz), 8.51 (2 H, s), 8.30 (2 H, s), 8.17 (4 H, d, J = 7 Hz), 8.13 (4 H, d, J = 7 Hz), 8.11 (4 H, s), 8.08 (2 H, d, J = 8 Hz), 7.50 (2 H, dt, J = 1.5, 8 Hz), 7.41 (2 H, dt, J = 1.5, 8 Hz), 7.12 (2 H, d), 6.34 (2 H, d, J = 14 Hz), 6.13 (2 H, d, J = 14 Hz), 6.05 (2 H, d, J = 13 Hz), 5.98 (2 H, d, J = 13 Hz), 5.50 (8 H, br. s), 4.68 (4 H, br. s), 4.21−3.55 (28 H, m). − ^{13}C NMR (75.5 MHz, CD_3COCD_3, 25°C): δ = 153.9, 153.8, 148.7, 148.2, 146.4, 145.7, 137.8, 136.2, 135.6, 131.9, 129.9, 129.7, 129.3, 127.6, 126.5, 125.4, 124.9, 122.1, 115.5, 114.0, 81.1, 81.0, 73.0, 70.4, 68.7, 65.8, 63.5. − $C_{82}H_{80}F_{24}N_4O_{14}P_4$ (1925.40): calcd. C 51.15, H 4.19; found C 51.35, H 4.26.

General Procedure for the Competition Experiments: Known amounts (0.04−0.20 mmol) of the reagents (Tables 1 and 2) were stirred in MeCN (20−30 mL) at ambient temp. The mixtures were then purified by column chromatography (SiO_2: MeOH/2 M aq. NH_4Cl/$MeNO_2$, 7:2:1, v/v/v and then MeOH/1 M aq. NH_4Cl, 7:3, v/v). We estimate an error of 2% as a result of instrumentation and sample manipulation.

Association Constants: A series of solutions with constant concentration (1.15×10^{-3} M) of either (*RS*)-**3** or of (DD)-**13** and containing different amounts of **4**·2PF_6 (10^{-4}−10^{-1} M) in MeCN were prepared. The absorbance at the wavelength (λ_{max}) corresponding to the maximum of the charge-transfer band for the 1:1 complex was measured for all the solutions at 25°C. The correlations between the absorbance and the guest concentration was used[10] to evaluate the association constant (K_a) by non-linear curve fitting.

High-Performance Liquid Chromatography: (*RS*)-**3** was analyzed at ambient temperature by employing a Chiralcel OD-H column flow rate = 1.0 mL/min; mobile phase heptane/EtOH, 80:20, v/v; detector wavelength = 230 nm]. The retention times of (*S*)-**3** and (*R*)-**3** were 14 and 16 min, respectively. The diasteroisomeric mixtures of the [2]catenanes **15**·4PF_6 and **18**·4PF_6 were analyzed at ambient temperature by employing a Hypersil BDS C18 column {flow rate = 1.0 mL/min; mobile phase: pump A = 0.1% CF_3CO_2H in H_2O, pump B = (0.1% CF_3CO_2H in MeCN)/(0.1% CF_3CO_2H in H_2O), 95:5, v/v; time [min]/pump A (%) = 0/50, 0.10/50, 5/60, 12/100, 40/100, 45/50; detector wavelength = 260 nm}.

Acknowledgments

The Glaxo Chromatography Department is gratefully acknowledged for the HPLC analysis of the crown ether **3** and for financial support along with the Engineering and Physical Sciences Research Council in the United Kingdom.

[1] For accounts, books, and reviews on catenanes, see: [1a] G. Schill, *Catenanes, Rotaxanes and Knots*, Academic Press, New York, **1971**. − [1b] D. M. Walba, *Tetrahedron* **1985**, *41*, 3161−3212. − [1c] C. O. Dietrich-Buchecker, J.-P. Sauvage, *Chem. Rev.* **1987**, *87*, 795−810. − [1d] J.-P. Sauvage, *Acc. Chem. Res.* **1990**, *23*, 319−327. − [1e] C. O. Dietrich-Buchecker, J.-P. Sauvage, *Bioorg. Chem. Front.*,**1991**, *2*, 195−248. − [1f] J.-C. Chambron, C. O. Dietrich-Buchecker, J.-P. Sauvage, *Top. Curr. Chem.* **1993**, *165*, 131−162. − [1g] F. Bickelhaupt, *J. Organomet. Chem.* **1994**, *475*, 1−14. − [1h] D. B. Amabilino, J. F. Stoddart, *Chem. Rev.* **1995**, *95*, 2725−2828. − [1i] F. Vögtle, T. Dünnwald, T. Schmidt, *Acc. Chem. Res.* **1996**, *29*, 451−460. − [1j] A. C. Benniston, *Chem. Soc. Rev.* **1996**, *25*, 427−435. − [1k] M. Fujita, K. Ogura, *Coord. Chem. Rev.* **1996**, *148*, 249−264. − [1l] R. Jäger R., F. Vögtle, *Angew. Chem. Int. Ed. Engl.*, **1997**, *36*, 930−944. − [1m] M. Belohradsky, F. M. Raymo, J. F. Stoddart, *Collect. Czech. Chem. Commun.* **1997**, *62*, 527−557. − [1n] S. A. Nepogodiev, J. F. Stoddart, *Chem. Rev.* **1998**, *98*, 1959−1976. − [1o] D. G. Hamilton, J. E. Davies, L. Prodi, J. K. M. Sanders, *Chem. Eur. J.* **1998**, *4*, 608−620. − [1p] J.-C. Chambron, J.-P. Sauvage, *Chem. Eur. J.* **1998**, *4*, 1362−1366.

[2] For accounts and reviews on the kinetically controlled self-assembly of catenanes, see: [2a] D. Philp, J. F. Stoddart, *Synlett* **1991**, 445−458. − [2b] D. Pasini, F. M. Raymo, J. F. Stoddart, *Gazz. Chim. Ital.* **1995**, *125*, 431−443. − [2c] 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. − [2d] F. M. Raymo, J. F. Stoddart, *Pure Appl. Chem.* **1996**, *68*, 313−322. − [2e] R. E. Gillard, F. M. Raymo, J. F. Stoddart, *Chem. Eur. J.* **1997**, *3*, 1933−1940. − [2f] F. M. Raymo, J. F. Stoddart, *Pure Appl. Chem.* **1997**, *69*,

1987−1997. − [2g] F. M. Raymo, J. F. Stoddart, *Chemtracts* **1998**, *11*, 491−511.
[3] D. B. Amabilino, P. R. Ashton, L. Pérez-García, J. F. Stoddart, *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2378−2380.
[4] For examples of chiral catenanes, see: [4a] D. K. Mitchell, J.-P. Sauvage, *Angew. Chem. Int. Ed. Engl.*, **1988**, *27*, 930−931. − [4b] J.-C. Chambron, D. K. Mitchell, J.-P. Sauvage, *J. Am. Chem. Soc.* **1992**, *114*, 4625−4631. − [4c] Y. Kaida, Y. Okamoto, J.-C. Chambron, D. K. Mithcell, J.-P. Sauvage, *Tetrathedron Lett.* **1993**, *34*, 1019−1022. − [4d] J.-C. Chambron, C. O. Dietrich-Buchecker, G. Rapenne, J.-P. Sauvage, *Chirality* **1998**, *10*, 125−133. − [4e] S. Ottens-Hildebrandt, T. Schmidt, F. Vögtle, *Liebigs Ann.* **1995**, 1855−1860. − [4f] R. Jäger, F. Vögtle, *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 930−944. − [4g] C. Yamamoto, Y. Okamoto, T. Schmidt, R. Jäger, F. Vögtle, *J. Am. Chem. Soc.* **1997**, *119*, 10547−10548. − [4h] P. R. Ashton, A. S. Reder, N. Spencer, J. F. Stoddart, *J. Am. Chem. Soc.* **1993**, *115*, 5286−5287. − [4i] P. R. Ashton, I. Iriepa, M. V. Reddington, N. Spencer, A. M. Z. Slawin, J. F. Stoddart, D. J. Williams, *Tetrahedron Lett.* **1994**, *35*, 4835−4838. − [4j] M. Asakawa, P. R. Ashton, S. E. Boyd, C. L. Brown, S. Menzer, D. Pasini, J. F. Stoddart, M. S. Tolley, A. J. P. White, D. J. Williams, P. G. Wyatt, *Chem. Eur. J.* **1997**, *3*, 463−481. − [4l] P. R. Ashton, S. E. Boyd, S. Menzer, D. Pasini, F. M. Raymo, N. Spencer, J. F. Stoddart, A. J. P. White, D. J. Williams, P. G. Wyatt, *Chem. Eur. J.* **1998**, *4*, 299−310.
[5] I. O. Sutherland, *Annu. Rep. NMR Spectrosc.* **1971**, *4*, 71−235.
[6] J. Sandström, *Dynamic NMR Spectroscopy*; Academic Press, London, **1982**, chapter 6.
[7] B. S. Furniss, A. J. Hannaford, P. W. G. Smith, A. R. Tatchell, *Practical Organic Chemistry*, Longman, New York, **1989**.
[8] 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*, 193−218
[9] M. Asakawa, P. R. Ashton, S. E. Boyd, C. L. Brown, S. Menzer, D. Pasini, J. F. Stoddart, A. J. P. White, D. J. Williams, P. G. Wyatt, *Chem. Eur. J.* **1997**, *3*, 463−481.
[10] K. A. Connors, *Binding Constants*, Wiley, New York, **1987**.

Received November 30, 1998
[O98539]