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Main-Chain and Pendant Poly([2]catenane)s Incorporating Complementary π-Electron-Rich and -Deficient Components

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A main-chain poly([2]catenane), incorporating an average of 25 repeating [2]catenane units and having an M_n value of 35 kg mol^{-1}, was synthesized by the polyesterification of a [2]catenane monomer composed of a bipyridinium-based tetracationic cyclophane mechanically interlocked with a 1,5-dioxynaphthalene-based macrocyclic polyether. Similarly, two main-chain poly(bis[2]catenane)s, both incorporating an average of 15 repeating bis[2]catenane units and both having M_n values of 45 kg mol^{-1}, were prepared by the copolymerizations of a bis[2]catenane monomer, possessing two hydroxymethyl functions with an appropriate bis(isocyanate). The same copolymerization was employed in order to produce a pendant poly([2]catenane), incorporating an average of 20 repeating [2]catenane units and having an M_n value of 27 kg mol^{-1}, from a [2]catenane monomer possessing two hydroxymethyl groups on its macrocyclic polyether component.

Introduction

The construction of polymers held together by a combination of covalent and "mechanical" bonds, i.e., polycatenanes[1], is not only an intriguing synthetic challenge but it also offers the opportunity of generating novel materials with unusual properties. Indeed, it has been demonstrated that the physical properties of interpenetrating polymer networks[2] are dictated by the mechanical entanglement of the polymeric chains, suggesting that the dynamic, mechanical, and rheological properties of polycatenanes should also be determined by their "mechanical" bonds. Intrigued by these potential properties, we have devised (Figures 1a, 1b, and 1c, respectively) synthetic approaches to main-chain poly([2]catenane)s,[3] main-chain poly(bis[2]catenane)s,[4] and pendant poly([2]catenane)s. In all cases, an appropriate [2]catenane or bis[2]catenane monomer, possessing two reactive functional groups on the same or on different macrocyclic components, is first of all synthesized and then it is polymerized (Figure 1a) or copolymerized (Figures 1b and 1c). In order to self-assemble[5] the catenated monomers, we have employed our well-established[6][7][8] donor/acceptor template-directed approach, which is based on the complementarity of π-electron-deficient bipyridinium-based and π-electron-rich dioxyarene-based macrocyclic components. Here, we report the synthesis and the characterization of two [2]catenanes and three bis[2]catenanes and their polymerization or copolymerization to afford one main-chain poly([2]catenane), two main-chain poly(bis[2]catenane)s, and one pendant poly([2]catenane).

Results and Discussion

Main-Chain Poly([2]catenane)s

The synthetic approach depicted schematically in Figure 1a involves the use of a [2]catenane monomer possessing two complementary functional groups − one on each macrocyclic component − which can be coupled, under appropriate conditions, to afford a main-chain poly([2]catenane). With this objective in mind, we synthesized[3d] the [2]catenane **1**·4PF$_6$ which incorporates one hydroxymethyl group and one carboxylic acid function. However, the direct polyesterification of the [2]catenane **1**·4PF$_6$ was not successful[3d] using a variety of conditions and coupling methods. As a result, we decided to employ an alternative route involving (i) the transformation of the CH$_2$OH group of **1**·4PF$_6$ into a CH$_2$Cl function, (ii) the subsequent conversion of the CH$_2$Cl into a CH$_2$Br group, and (iii) the polyesterification of the resulting [2]catenane in situ. The [2]catenane **1**·4PF$_6$ was treated (Scheme 1) with aqueous HCl to afford the [2]catenane **2**·4PF$_6$, after counterion exchange. Heating an MeCN solution of the [2]catenane **2**·4PF$_6$ in the presence of LiBr and 2,6-lutidine gave the poly([2]catenane) **3**·*n*(4PF$_6$), after counterion exchange. The chloride salt **3**·*n*(4Cl) of this poly([2]catenane) was analyzed in aqueous solution by gel permeation chromatography (GPC), which

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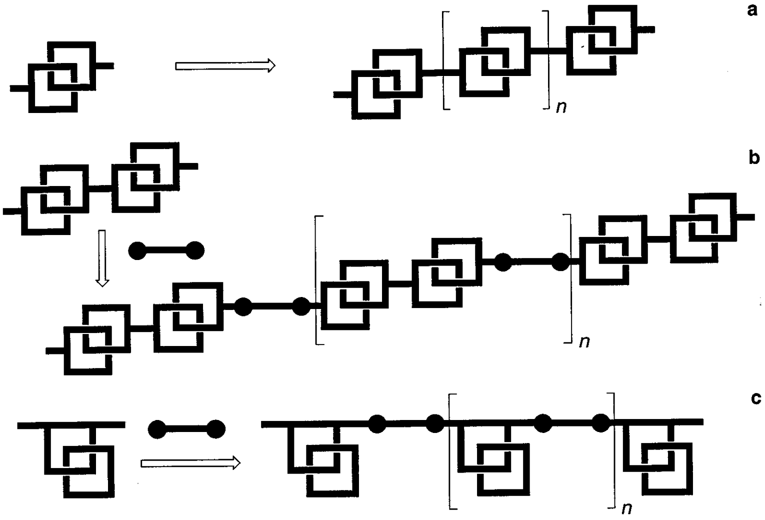
Figure 1. Synthetic approaches to (a) a main-chain poly([2]catenane), (b) a main-chain poly(bis[2]catenane), and (c) a pendant poly([2]catenane)

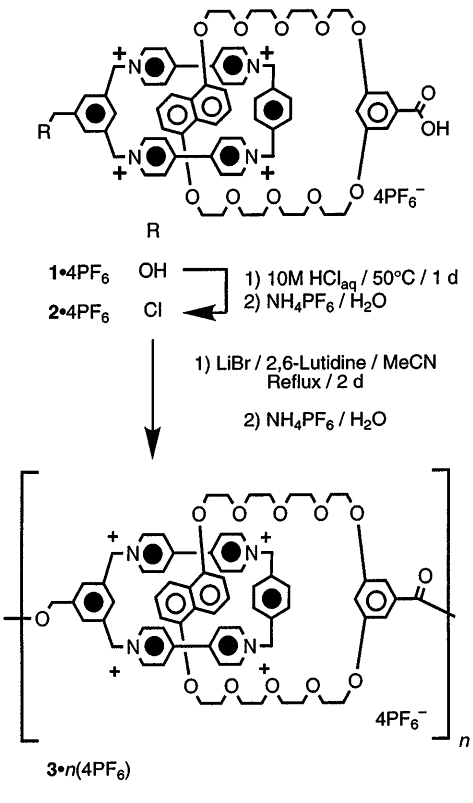


revealed a number-average molecular weight (M_n) of 35 kg mol^{-1}, corresponding to a degree of polymerization of 25 – i.e., the poly([2]catenane) **3**·n(4Cl) incorporates an average of 25 repeating [2]catenane units. Comparison of the ^1H-NMR spectra, recorded in CD_3CN at 25°C, of the [2]catenane **2**·$4PF_6$ and of the poly([2]catenane) **3**·$n(4PF_6)$ revealed significant differences. In particular, the CH_2Cl protons of the [2]catenane **2**·$4PF_6$ give rise to a singlet centered on $\delta = 4.55$ in the ^1H-NMR spectrum. By contrast, a multiplet at $\delta = 4.65-4.67$ is observed for the CH_2OCO protons of the poly([2]catenane) **3**·$n(4PF_6)$ in the ^1H-NMR spectrum.

Main-Chain Poly(bis[2]catenane)s

The synthetic approach depicted schematically in Figure 1b involves the use of a bis[2]catenane incorporating a reactive functional group on each of its two "terminal" macrocyclic components. The bis(macrocyclic polyether) **4** is a suitable precursor for such bis[2]catenanes. In order to test its ability to form catenanes, the bis(hexafluorophosphate) salt **5**·$2PF_6$ was allowed to react (Scheme 2) with the dibromide **6** in the presence of **4** under ultrahigh-pressure (12 kbar) conditions. Indeed, the resulting bis[2]catenane **8**·$8PF_6$ was isolated in a yield of 50%, after counterion exchange, and was characterized by liquid secondary-ion mass spectrometry (LSIMS), ^1H-NMR and ^{13}C-NMR spectroscopies, and elemental analysis. In particular, the LSIMS of **8**·$8PF_6$ revealed peaks at m/z values of 3539, 3394, and 3249 for $[M - PF_6]^+$, $[M - 2\,PF_6]^+$, and $[M - 3\,PF_6]^+$, respectively, corresponding to the consecutive loss of one, two, and three PF_6^- anions. Comparison of the ^1H-NMR spectra, recorded in CD_3CN at 25°C, of the bis(macrocyclic polyether) **4** and of the bis[2]catenane **8**·$8PF_6$ revealed significant upfield shifts in the resonances associated with the protons attached to the 1,5-dioxynaphthalene and resorcinol ring systems. In particular, the resonances of the protons in the positions 4 and 8 on the 1,5-dioxynaphthalene ring system shift by $\Delta\delta = -5.3$ ppm and appear at $\delta = 2.40-2.43$ in the ^1H-NMR spectrum of the bis[2]catenane **8**·$8PF_6$. The dramatic change in the δ values of these resonances is a result of shielding effects exerted by the sandwiching bipyridinium units and demonstrate that the 1,5-dioxynaphthalene ring systems are located inside the cavities of the tetracationic cyclophane components. Encouraged by this result, a similar template-directed procedure was employed (Scheme 2) to self-assemble the bis[2]catenane **9**·$8PF_6$ by allowing the bis(hexafluorophosphate) salt **5**·$2PF_6$ to react with the dibromide **7** under ul-

Scheme 1. Synthesis of the main-chain poly([2]catenane) **3**·$n(4PF_6)$

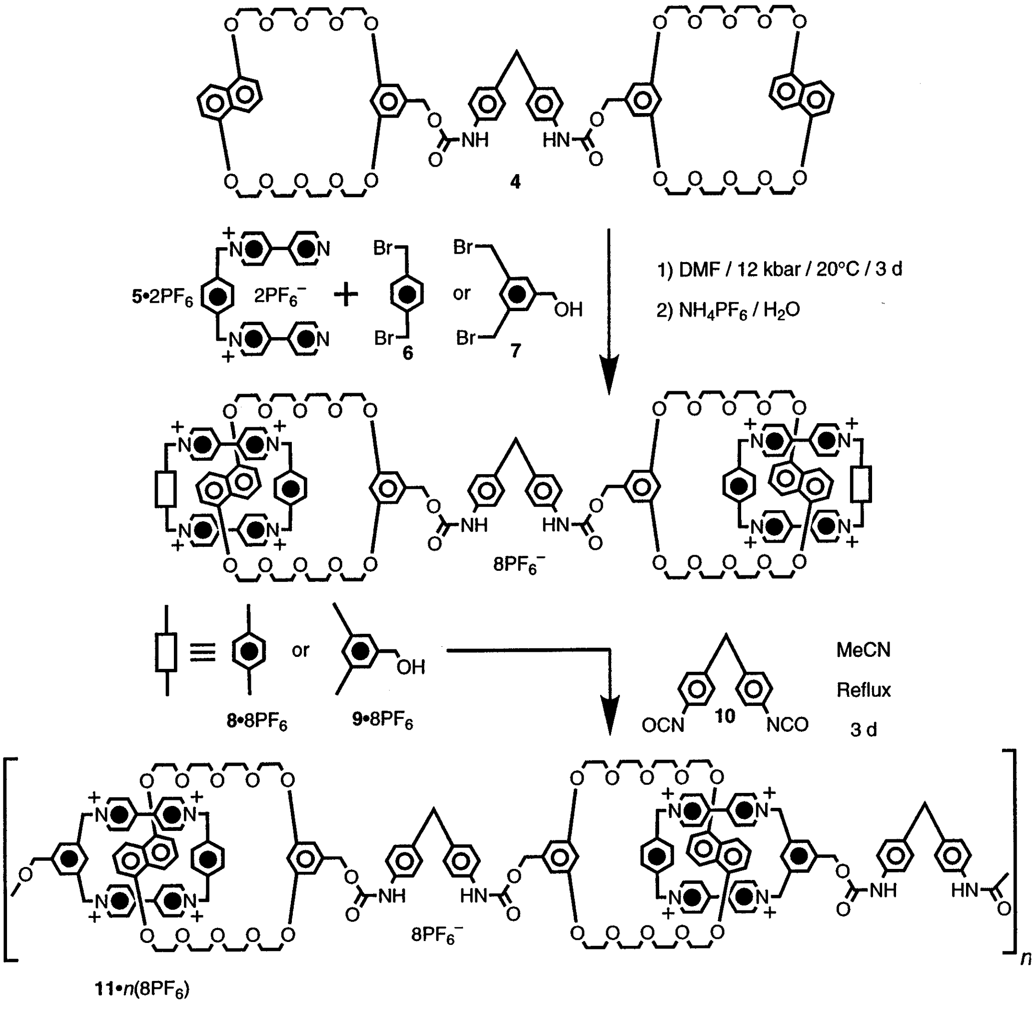


trahigh-pressure (12 kbar) conditions. The LSIMS of the resulting bis[2]catenane **9**·$8PF_6$ revealed peaks at *m/z* 3599, 3454, and 3309 for $[M - PF_6]^+$, $[M - 2\ PF_6]^+$, and $[M - 3\ PF_6]^+$, respectively, corresponding to the consecutive loss of one, two, and three PF_6^- anions. Furthermore, the ^{1}H-NMR spectrum, recorded in CD_3CN at 25°C, of the bis[2]catenane **9**·$8PF_6$ revealed the characteristic upfield shift ($\Delta\delta = -5.3$ ppm) of the resonances associated with the protons on the positions 4 and 8 of the 1,5-dioxynaphthalene ring system.

Since the bis[2]catenane **9**·$8PF_6$ incorporates one hydroxymethyl group on each of its two tetracationic cyclophane components, it is a suitable candidate for the synthesis of poly(bis[2]catenene)s such as those schematically depicted in Figure 1b. Indeed, reaction (Scheme 2) of the bis[2]catenane **9**·$8PF_6$ with the bis(isocyanate) **10** gave the poly(bis[2]catenane) **11**·*n*($8PF_6$). The chloride salt **11**·*n*(8Cl) of this poly(bis[2]catenane) was analyzed by GPC which revealed an M_n value of 45 kg mol^{-1} corresponding to a degree of polymerization of 15 – i.e., the poly(bis[2]catenane) **11**·*n*(8Cl) incorporates an average of 15 repeating units. Comparison of the ^{1}H-NMR spectra, recorded in CD_3CN at 25°C, of the bis[2]catenane **9**·$8PF_6$ and of the poly(bis[2]catenane) **11**·*n*($8PF_6$) revealed significant differences. In particular, the two singlets ($\delta = 4.90$ and 5.05) observed for the protons of the two $ArCH_2O$ groups of the bis[2]catenane **9**·$8PF_6$ merge into a broad signal centered on $\delta = 5.02$ in the ^{1}H-NMR spectrum of the poly(bis[2]catenane) **11**·*n*($8PF_6$).

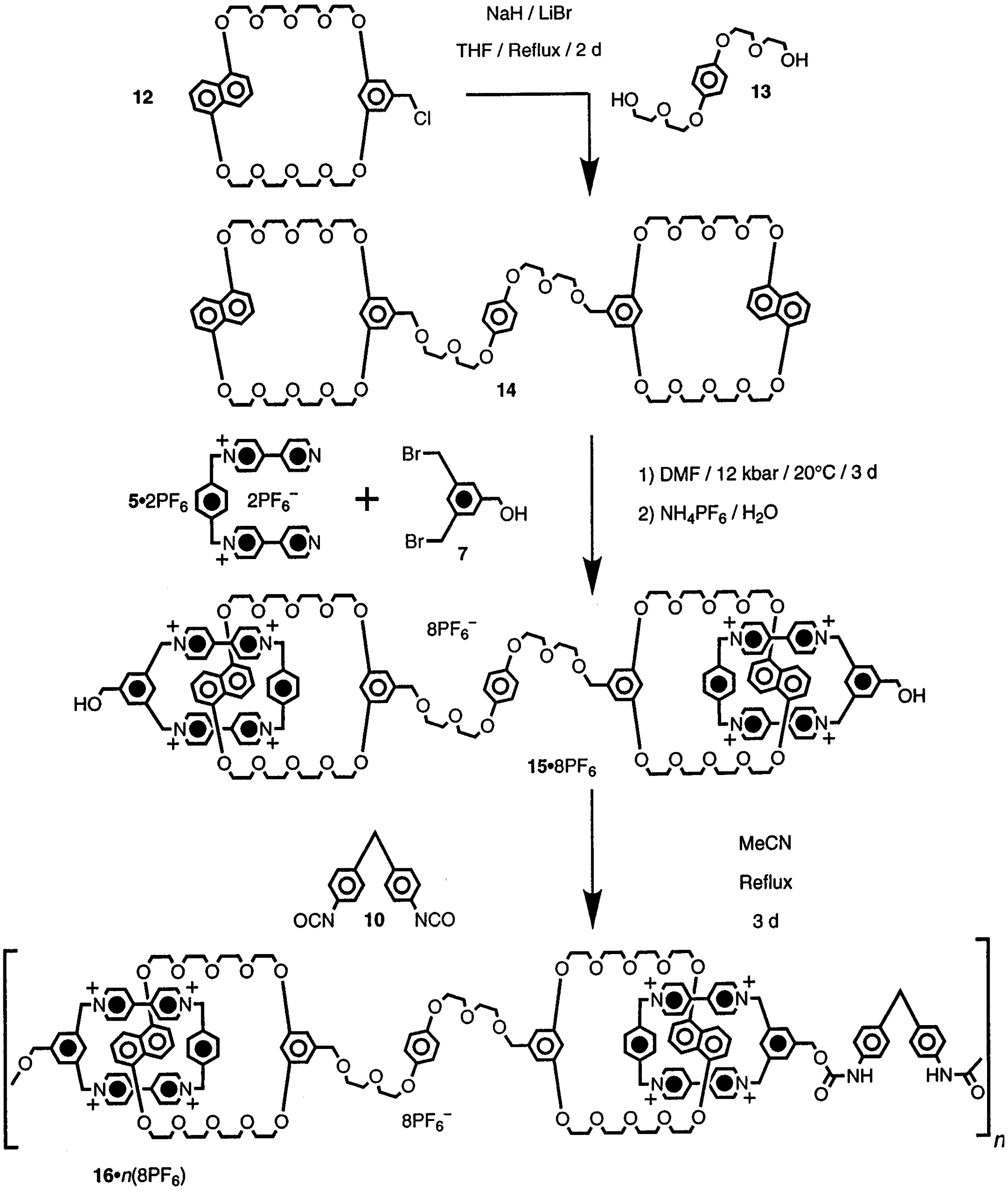
The bis(macrocyclic polyether) **14** was synthesized (Scheme 3) by allowing the macrocyclic polyether **12** to react with the diol **13**. Subsequent reaction of the bis(hexafluorophosphate salt) **5**·$2PF_6$ with the dibromide **7** in the presence of **14** and under ultrahigh-pressure (12 kbar) conditions gave the bis[2]catenane **15**·$2PF_6$ in a yield of 16%, after counterion exchange. The LSIMS of the bis[2]catenane **15**·$8PF_6$ revealed peaks at *m/z* values of 3688, 3543, and 3398 for $[M - PF_6]^+$, $[M - 2\ PF_6]^+$, and $[M - 3\ PF_6]^+$, respectively, corresponding to the consecutive loss of one, two, and three PF_6^- anions. In addition, the ^{1}H-NMR spectrum, recorded in CD_3CN at 25°C, of the bis[2]catenane **15**·$8PF_6$ showed the characteristic upfield shift ($\Delta\delta = -5.3$ ppm) of the resonances associated with the protons on the positions 4 and 8 of the 1,5-dioxynaphthalene ring system. Reaction of the bis[2]catenane **15**·$8PF_6$ with bis(isocyanate) **10** gave the polybis[2]catenane **16**·*n*($8PF_6$). The

Scheme 2. Synthesis of the main-chain poly(bis[2]catenane) **11**·*n*($8PF_6$)



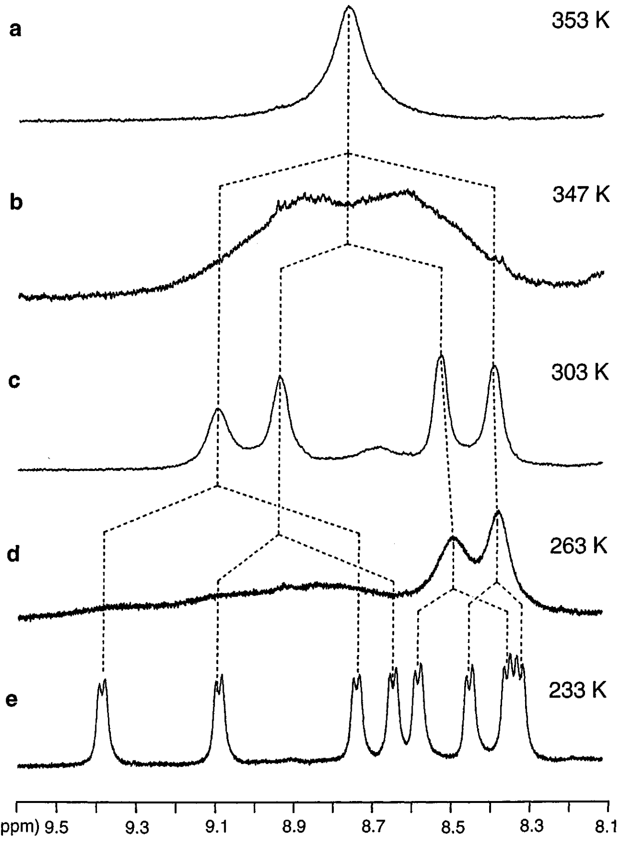
chloride salt **16**·*n*(8Cl) of this poly(bis[2]catenane) was analyzed by GPC which revealed an M_n value of 45 kg mol^{-1} corresponding to a degree of polymerization of 15 – i.e., the poly(bis[2]catenane) **16**·*n*(8Cl) incorporates an average of 15 repeating units. The infrared (IR) spectrum of the poly(bis[2]catenane) **16**·*n*($8PF_6$) showed the presence of two bands centered on 3375 and 1734 cm^{-1} which are characteristic of the NH and CO groups, respectively, of urethane linkages: these bands are not observed in the IR spectrum of the bis[2]catenane **15**·$8PF_6$.

Scheme 3. Synthesis of the main-chain poly(bis[2]catenane) **16**·*n*($8PF_6$)



In solution, the tetracationic cyclophane components of the bis[2]catenanes **8**·$8PF_6$, **9**·$8PF_6$, and **15**·$8PF_6$ circumrotate through the cavities of the macrocyclic polyether components with which they are mechanically interlocked. The partial ^{1}H-NMR spectra shown in Figure 2 illustrate the effect of these dynamic processes on the resonances associated with the protons H_α in the α positions, with respect to the nitrogen atoms, on the bipyridinium units of the bis[2]catenane **15**·$8PF_6$. At 233 K in CD_3CN, the circumrotation of the tetracationic cyclophane components through the cavities of the macrocyclic polyether components is slow on the ^{1}H-NMR time scale and eight resonances are observed (Figure 2e) for the protons H_α. Four of these resonances correspond to the protons H_α of the bipyridinium units located "inside" the cavities of the macrocyclic polyether components and the other four signals are associated with the protons H_α of the bipyridinium units residing "alongside". On increasing the temperature, the circumrotation process becomes fast on the ^{1}H-NMR time scale and the resonances associated with the protons H_α of the "inside" and "alongside" bipyridinium units coalesce giving rise (Figure 2c) to four sets of signals only. By employing the approximate coalescence treatment,[9] the free energy barriers ($\Delta G_c^{\ddagger}$) for this dynamic process were determined at the coalescence temperatures (T_c). In **8**·8PF$_6$, **9**·8PF$_6$, and **15**·8PF$_6$, the $\Delta G_c^{\ddagger}$ values are 11.5, 12.3, and 12.3 kcal mol^{-1}, respectively, at T_c's of 249, 267, and 262 K, respectively.[10] By increasing the temperature further, the local C_{2h} symmetry imposed by the 1,5-dioxynaphthalene rings located "inside" the cavity of the tetracationic cyclophanes is lost[11] and the four sets of resonances coalesce (Figures 2a–2c) into two signals which are accidentally almost equivalent. Again by employing the approximate coalescence treatment, $\Delta G_c^{\ddagger}$ values of 16.0, 16.2, and 16.2 kcal mol^{-1} at T_c's of 344, 344, and 343 K, respectively, were determined for **8**·8PF$_6$, **9**·8PF$_6$, and **15**·8PF$_6$, respectively.

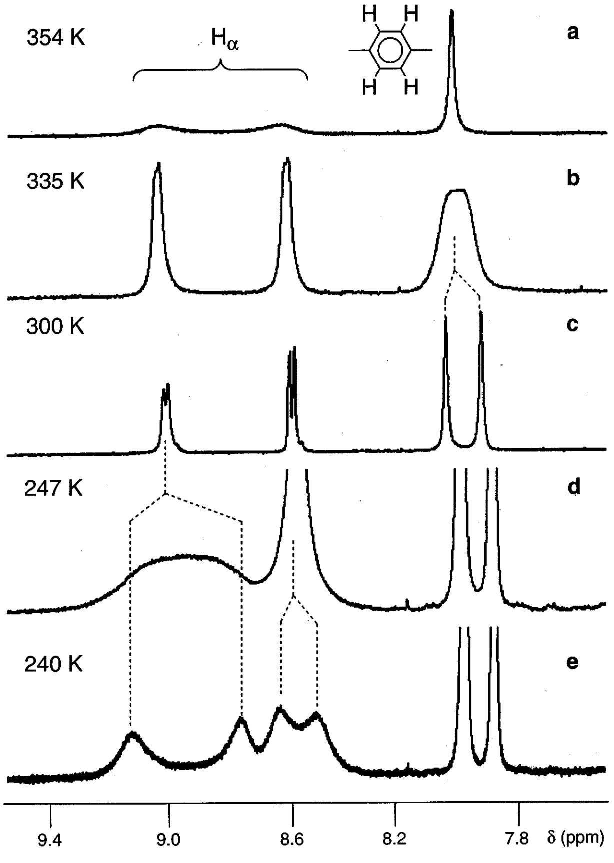
Figure 2. Partial ^{1}H-NMR spectra of the bis[2]catenane of **15**·8PF$_6$ recorded in CD$_3$CN at (a) 353, (b) 347, (c) 303, (d) 263, and (e) 233 K



Pendant Poly([2]catenane)s

In order to synthesize a pendant poly([2]catenane) according to the synthetic route depicted schematically in Figure 1c, a [2]catenane incorporating two reactive functional groups on one of its two macrocyclic components has to be used. As a result, the macrocyclic polyether **19** was synthesized (Scheme 4) by allowing the dibromide **17** to react with the diol **18** under high-dilution conditions. Acetylation of the two hydroxymethyl groups of **19** afforded the macrocyclic polyether **20** which was employed to self-assemble the [2]catenane **21**·4PF$_6$ by allowing the bis(hexafluorophosphate) salt **5**·2PF$_6$ to react with the dibromide **6** in the presence of **20**, followed by hydrolysis of the acetate groups and counterion exchange. The protection/deprotection of the two hydroxymethyl groups was dictated by the fact that, surprisingly, the [2]catenane **21**·4PF$_6$ was not obtained when the macrocyclic polyether **19** was employed instead of **20** under otherwise identical conditions. The LSIMS of the [2]catenane **21**·4PF$_6$ revealed peaks at *m/z* values of 1599, 1454, and 1309 for [M − PF$_6$]$^+$, [M − 2 PF$_6$]$^+$, and [M − 3 PF$_6$]$^+$, respectively, corresponding to the consecutive loss of one, two, and three PF$_6^-$ anions. Furthermore, the ^{1}H-NMR spectrum, recorded in CD$_3$CN at 25°C, of the [2]catenane **21**·4PF$_6$ showed the characteristic upfield shift ($\Delta\delta = -5.3$ ppm) of the resonances associated with the protons in the positions 4 and 8 on the 1,5-dioxynaphthalene ring system. At 240 K in CD$_3$CN, the circumrotation of the tetracationic cyclophane component through the cavity of the macrocyclic polyether component is slow on the ^{1}H-NMR time scale and the protons H_α in the α positions, with respect to the nitrogen atoms, on the bipyridinium units give rise (Figure 3e) to four sets of signals. On increasing the temperature, these resonances coalesce (Figures 3c–3d) into two sets of signals, as the circumro-

Figure 3. Partial ^{1}H-NMR spectra of the [2]catenane of **21**·4PF$_6$ recorded in CD$_3$CN at (a) 354, (b) 335, (c) 300, (d) 247, and (e) 240 K



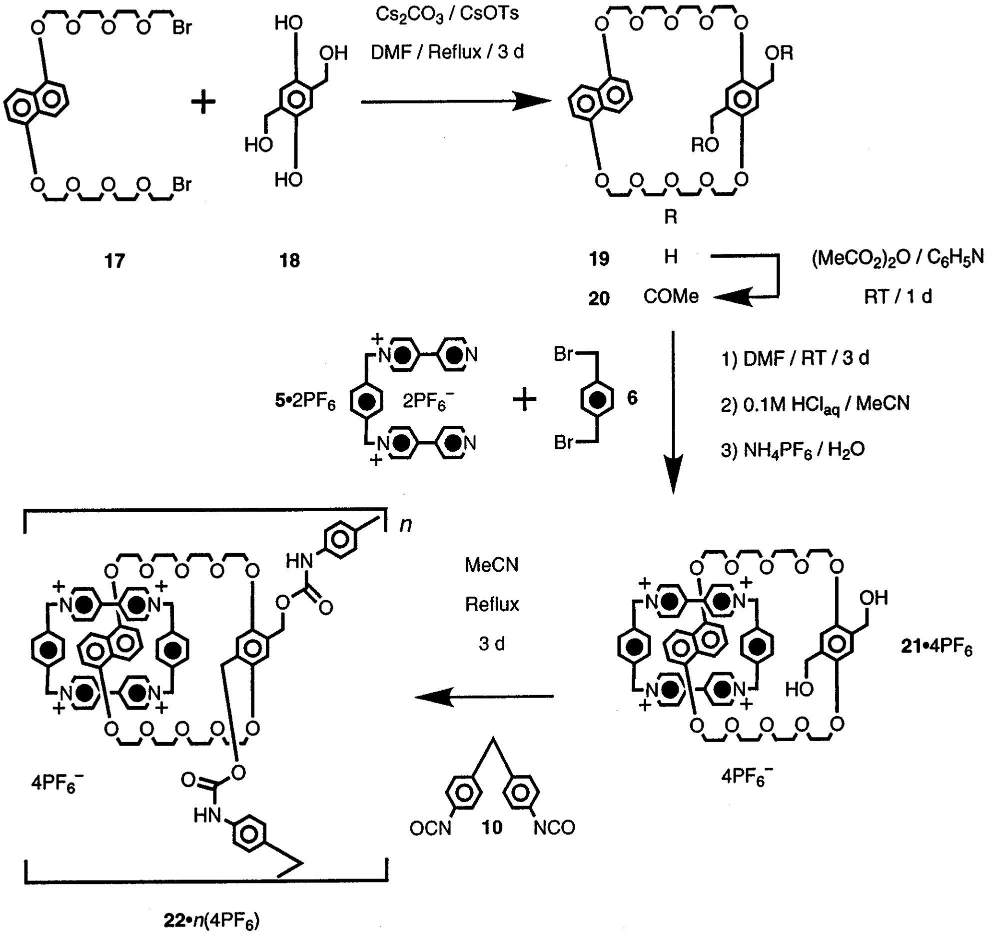
tation of the tetracationic cyclophane component becomes fast on the ^{1}H-NMR time scale. By employing the approximate coalescence treatment, a $\Delta G_c^{\ddagger}$ value of 11.5 kcal mol^{-1} at a T_c of 246 K was derived. By increasing the temperature further, the local C_{2h} symmetry imposed by the 1,5-dioxynaphthalene ring system located inside the cavity of the tetracationic cyclophane is lost.[11] As a result, the resonances associated with the protons H_α become (Figures 3a and 3b) broad and the two sets of signals associated with the *p*-phenylene protons coalesce into one only. Again, by employing the approximate coalescence treatment, a $\Delta G_c^{\ddagger}$ value of 16.6 kcal mol^{-1} at a T_c of 335 K was determined.

The presence of two hydroxymethyl groups on the macrocyclic polyether component of **21**·4PF$_6$ makes this [2]catenane a suitable candidate for the synthesis of pendant poly([2]catenane)s such as the one schematically depicted in Figure 1c. Indeed, reaction of the [2]catenane **21**·4PF$_6$ with the bis(isocyanate) **10** gave (Scheme 4) the pendant poly([2]catenane) **22**·*n*(4PF$_6$). The chloride salt **22**·*n*(4Cl) of this poly([2]catenane) was analyzed by GPC, which revealed an M_n value of 27 kg mol^{-1} corresponding to a degree of polymerization of 20 – i.e., the poly(bis[2]catenane) **22**·*n*(4Cl) incorporates an average of 120 repeating [2]catenane units. The IR spectrum of the poly([2]catenane) **22**·*n*(4PF$_6$) showed the presence of two bands centered at 3375 and 1734 cm^{-1} which are characteristic of the NH and CO groups, respectively, of urethane linkages: these bands are not observed in the IR spectrum of the [2]catenane **21**·4PF$_6$.

Conclusions

We have devised three synthetic approaches to polycatenanes incorporating bipyridinium-based tetracationic cyclophane components mechanically interlocked with 1,5-dioxynaphthalene-based macrocyclic polyethers. These procedures involve the use of appropriate [2]catenane or bis[2]catenane monomers incorporating two reactive functional groups on the same or on different macrocyclic components. Their subsequent polymerization or copolymerization with appropiate bridging units affords main-chain or pendant polycatenanes. By employing these synthetic methodologies, we have prepared one main-chain poly([2]catenane), two main-chain poly(bis[2]catenane)s, and one pendant poly([2]catenane) incorporating from 15 up to as many as 25 repeating units on average and having number-average molecular weights ranging from 27 to 45 kg mol^{-1}.

Scheme 4. Synthesis of the pendant poly([2]catenane) **22**·*n*(4PF$_6$)



RT: room temp.

Experimental Section

General Methods: Chemicals were purchased from Aldrich and used as received. Solvents were dried according to procedures described in the literature.[12] The compounds **1**·4PF$_6$,[3d] **4**,[4] **5**·2PF$_6$,[13] **7**,[3d] **12**,[14] **13**,[4] **17**,[8c] and **20**[15] were prepared according to literature procedures. − The reactions performed under ultrahigh-pressure conditions were carried out in Teflon vessels using a custom-built ultrahigh-pressure reactor manufactured by PSIKA Pressure Systems Limited of Glossop, UK. − Thin-layer chromatography (TLC) was carried out using aluminum 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). − Gel permeation chromatography (GPC) was carried out using a 420 Kontrun HPLC instrument, equipped with a Knauer Differential Refractometer No 98. Aqueous solutions (1 ml) of the chloride salts (10 mg) of the polycatenanes were analyzed by GPC, employing an aqueous solution of NaCl (1 M) as the eluant (flow rate 0.5 ml min^{-1}) in conjunction with a Sephadex G-150 column (length 100 cm, diameter 1 cm) calibrated using ribonuclease A (13.7 kg mol^{-1}), chymotrynogen A (25.0 kg mol^{-1}), ovalbumin (43.0 kg mol^{-1}), albumin (67.0 kg mol^{-1}), blue dextran 2000 (300.0 kg mol^{-1}), and lactose (180 g mol^{-1}) as standards.[16] The chloride salts of the polycatenanes were obtained as precipitates from MeCN solutions of the corresponding hexafluorophosphate salts, after the addition of *t*Bu$_4$NCl. − IR spectra were recorded with a Paragon 1000 Perkin-Elmer FTIR spectrometer using a Nujol mull and NaCl disks. − Melting points were determined using an Electrothermal 9200 apparatus and are not corrected. − Electron-impact mass spectra (EIMS) were recorded using a Kratos Profile spectrometer. Liquid secondary ion mass spectra (LSIMS) were obtained using 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 either a Bruker AC300 (300 MHz) or a Bruker AMX400 (400 MHz) spectrometer, also using either the solvent or TMS as internal standards. ^{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 and the coupling constants are expressed in Hertz (Hz). − Microanalyses were performed by the University of North London Microanalytical Service.

[2]Catenane **2**·4PF$_6$: A solution of **1**·4PF$_6$ (100 mg, 0.06 mmol) in aqueous HCl (10 M, 100 ml) was stirred for 1 d at 50°C. After cooling down to room temperature, H$_2$O (300 ml) and then NH$_4$PF$_6$ were added to afford the [2]catenane **2**·4PF$_6$ (101 mg, 100%) as a purple precipitate. − M. p. > 250°C. − LSIMS: *m/z* = 1633 [M − PF$_6$]$^+$, 1470 [M − 2 PF$_6$]$^+$. − ^{1}H NMR (CD$_3$CN): δ = 2.40−2.43 (2 H, m), 3.09−4.33 (32 H, m), 4.55 (2 H, s), 5.30−5.34 (4 H, m), 5.66−6.09 (6 H, m), 6.23−6.27 (4 H, m), 6.99−7.02 (2 H, m), 7.13−7.20 (6 H, m), 7.25−7.27 (2 H, m), 7.50−7.52 (2 H, m), 7.91−7.94 (2 H, m), 8.01−8.04 (2 H, m), 8.40−8.44 (2 H, m), 8.48−8.51 (2 H, m), 8.95−8.99 (2 H, m), 9.08−9.11 (2 H, m). − ^{13}C NMR (CD$_3$CN): δ = 32.8, 64.9, 65.5, 66.1, 68.9, 69.2, 69.4, 70.4, 70.6, 71.0, 71.1, 71.4, 71.7, 71.9, 104.9, 105.6, 106.1, 109.3, 109.7, 109.9, 110.8, 125.3, 125.5, 126.7, 127.0, 127.7, 128.1, 128.5, 129.6, 131.4, 132.3, 132.6, 133.7, 135.1, 135.6, 137.5, 143.1, 145.5, 145.8, 146.1, 146.2, 146.7, 166.7. − C$_{70}$H$_{75}$ClF$_{24}$N$_{10}$O$_{12}$P$_4$: calcd. C 47.24, H 4.21, N 7.87; found C 47.17, H 4.16, N 7.80.

Poly([2]catenane) **3**·*n*(4PF$_6$): A solution of **2**·4PF$_6$ (100 mg, 0.05 mmol), LiBr (20 mg), and 2,6-lutidine (100 mg) in MeCN (20 ml) was heated under reflux for 2 d. After cooling down to room temperature, *t*Bu$_4$NCl was added to afford a purple precipitate which was filtered off, washed with Me$_2$CO, and dissolved in H$_2$O. Addition of KPF$_6$ gave **3**·*n*(4PF$_6$) (33 mg) as a purple precipitate. − M. p. > 250°C. − ^{1}H NMR (CD$_3$CN): δ = 2.40−2.43 (2 H, m), 3.30-4.40 (32 H, m), 4.65−4.67 (2 H, m), 5.40−6.20 (14 H, m), 6.60−8.10 (16 H, m), 8.20−9.20 (8 H, m). − ^{13}C NMR (CD$_3$CN) δ = 66.0, 69.0, 71.4, 105.45, 109.6, 114.1, 125.4, 126.7, 128.5, 131.4, 132.3, 137.1, 145.6, 166.3. − GPC: M_n = 35 kg mol^{-1}; DP(M_n) = 25.

Bis[2]catenane **8**·8PF$_6$: A solution of the bis(macrocyclic polyether) **4** (100.0 mg, 0.06 mmol), the bis(hexafluorophosphate) salt **5**·2PF$_6$ (119.0 mg, 0.17 mmol), and the dibromide **6** (44.5 mg, 0.17 mmol) in dry DMF (8 ml) was subjected to a pressure of 12 kbar for 3 d at 20°C. The solvent was removed under reduced pressure and the residue was purified by column chromatography (SiO$_2$, MeOH/2 M NH$_4$Cl$_{aq}$/MeNO$_2$, 7:2:1) to afford a purple solid which was dissolved in H$_2$O. After the addition of NH$_4$PF$_6$, the bis[2]catenane **8**·8PF$_6$ (124.0 mg, 50%) precipitated out of the solution as a purple crystalline solid. − Mp > 250°C. − LSIMS: *m/z* = 3539 [M − PF$_6$]$^+$, 3394 [M − 2 PF$_6$]$^+$, 3249 [M − 3 PF$_6$]$^+$. − ^{1}H NMR (CD$_3$CN): δ = 2.40−2.43 (4 H, m), 3.14−3.16 (8 H, m), 3.43−3.46 (8 H, m), 3.57−3.62 (8 H, m), 3.76−3.77 (8 H, m), 3.87−3.88 (10 H, m), 3.95−3.97 (8 H, m), 4.05−4.07 (8 H, m), 4.14−4.15 (8 H, m), 5.05 (4 H, s), 5.18−5.21 (2 H, m), 5.62 (8 H, d, ^2J = 12 Hz), 5.72 (8 H, d, ^2J = 12 Hz), 5.84−5.87 (4 H, m), 6.10−6.13 (8 H, m), 7.03−7.06 (16 H, m), 7.33−7.36 (4 H, m), 7.47−7.50 (4 H, m), 7.85−7.90 (8 H, m), 7.93 (2 H, s), 7.97−8.03 (8 H, m) 8.44−8.47 (8 H, m), 8.94−8.97 (8 H, m). − ^{13}C NMR (CD$_3$CN): δ = 41.6, 66.0, 66.5, 68.7, 69.2, 70.3, 70.6, 71.2, 71.5, 71.6, 72.0, 100.3, 105.0, 106.8, 109.2, 120.2, 125.2, 126.3, 126.7, 129.2, 129.6, 130.4, 132.0, 132.4, 137.6, 138.0, 141.4, 145.4, 152.0, 155.0, 160.1. − C$_{153}$H$_{162}$F$_{48}$N$_{10}$O$_{24}$P$_8$: calcd. C 49.86, H 4.45, N 3.80; found C 49.96, H 4.35, N 3.71.

Bis[2]catenane **9**·8PF$_6$: A solution of the bis(macrocyclic polyether) **4** (100.0 mg, 0.06 mmol), the bis(hexafluorophosphate) salt **5**·2PF$_6$ (100.0 mg, 0.14 mmol), and the dibromide **7** (41.0 mg, 0.14 mmol) in dry DMF (8 ml) was subjected to a pressure of 12 kbar for 3 d at 20°C. The solvent was removed under reduced pressure and the residue was purified by column chromatography (SiO$_2$, MeOH/2 M NH$_4$Cl$_{aq}$/MeNO$_2$, 7:2:1) to afford a purple solid which was dissolved in H$_2$O. After the addition of NH$_4$PF$_6$, the bis[2]catenane **9**·8PF$_6$ (32.0 mg, 13%) precipitated out of the solution as a purple crystalline solid. − Mp > 250°C. − LSIMS: *m/z* = 3599 [M − PF$_6$]$^+$, 3454 [M − 2 PF$_6$]$^+$, 3309 [M − 3 PF$_6$]$^+$. − ^{1}H NMR (CD$_3$CN): δ = 2.40−2.43 (4 H, m), 3.10−4.40 (66 H, m), 4.90 (4 H, s), 5.05 (4 H, s), 5.37−5.40 (2 H, m), 5.60−6.20 (28 H, m), 6.95−6.99 (4 H, m), 7.09−7.19 (12 H, m), 7.35−7.38 (4 H, m), 7.47−7.50 (4 H, m), 7.71 (2 H, s), 7.82−7.85 (4 H, m), 7.90−7.94 (4 H, m), 8.01−8.04 (4 H, m), 8.32−8.36 (4 H, m), 8.47−8.51 (4 H, m), 8.70−8.74 (4 H, m), 9.03−9.06 (4 H, m). − ^{13}C NMR (CD$_3$CN): δ = 41.6, 62.9, 63.8, 64.0, 65.8, 66.1, 68.9, 70.4, 71.4, 71.8, 100.3, 105.1, 106.8, 109.5, 109.8, 110.9, 118.3, 120.1, 124.4, 125.2, 126.6, 128.4, 128.6, 130.2, 130.5, 131.5, 132.2, 134.4, 137.5, 137.7, 138.0, 141.3, 145.5, 145.8, 146.5, 147.3, 151.2, 152.1, 155.0, 160.7. − C$_{155}$H$_{164}$F$_{48}$N$_{10}$O$_{26}$P$_8$: calcd. C 49.70, H 4.27, N 3.74; found C 49.79, H 4.35, N 3.87

Poly(bis[2]catenane) **11**·*n*(8PF$_6$): A solution of the bis[2]catenane **9**·8PF$_6$ (100.0 mg, 0.03 mmol) and the bis(isocyanate) **10** (6.7 mg, 0.03 mmol) in dry MeCN (8 ml) was heated under reflux for

3 d. After cooling down to room temperature, *t*Bu_4NCl was added to afford a purple precipitate which was washed with Me_2CO and dissolved in H_2O. Addition of KPF_6 gave **11**·*n*(8PF_6) (107 mg) as a purple precipitate. − Mp > 250°C. − ^1H NMR (CD_3CN): δ = 2.40−2.43 (4 H, m), 3.19−3.23 (4 H, m), 3.39−3.42 (4 H, m), 2.59−4.10 (54 H, m), 4.27−4.31 (4 H, m), 4.97−5.07 (8 H, m), 5.37−5.40 (2 H, m), 5.60−6.20 (28 H, m), 6.80−7.50 (32 H, m), 7.70−7.71 (2 H, m), 7.80−8.00 (12 H, m), 8.32−8.36 (4 H, m), 8.47−8.51 (4 H, m), 8.70−8.74 (4 H, m), 9.03−9.06 (4 H, m). − ^{13}C NMR (CD_3CN): δ = 40.9, 65.4, 65.3, 66.4, 68.5, 68.8, 70.2, 71.2, 71.7, 99.9, 104.7, 105.3, 106.4, 109.4, 110.9, 118.2, 118.5, 119.8, 124.9, 125.1, 126.3, 127.8, 129.4, 130.1, 132.4, 133.1, 133.8, 134.5, 137.5, 145.3, 146.3, 151.9, 154.4, 154.8, 160.5. − GPC: M_n = 45 kg mol^{-1}; DP(M_n) = 15.

Bis(macrocyclic polyether) **14**: A mixture of **13** (107 mg, 0.28 mmol) and NaH (40 mg, 0.6 mmol) in THF (20 ml) was heated under reflux and Ar for 1h. Then, a solution of **12** (400 mg, 0.6 mmol) and LiBr (100 mg, 1.1 mmol) in THF (10 ml) was added to the mixture which was heated under reflux and Ar for a further 2 d. After cooling down to room temperature, the solvent was removed under reduced pressure and the residue was purified by column chromatography (SiO_2, $MeCO_2Et$) to give **14** (0.27 g, 60%) as a colorless oil. − LSIMS: *m/z* = 1570 $[M]^+$. − ^1H NMR ($CDCl_3$): δ = 3.50−3.87 (72 H, m), 3.93−4.07 (8 H, m), 4.30−4.35 (8 H, m), 4.41 (4 H, s), 6.16 (2 H, s), 6.42−6.45 (4 H, m), 6.72−6.78 (8 H, m), 7.24−7.27 (4 H, m), 7.81−7.83 (4 H, m). − ^{13}C NMR ($CDCl_3$): δ = 67.2, 67.9, 68.0, 69.2, 69.5, 69.6, 70.4, 70.5, 70.7, 70.8, 72.9, 100.2, 105.7, 106.2, 114.5, 115.4, 125.0, 126.7, 140.4, 153.0, 154.5, 159.8. − $C_{84}H_{114}O_{28}$: calcd. C 64.20, H 7.26, found C 66.10, H 7.03.

Bis[2]catenane **15**·8PF_6: A solution of the bis(macrocyclic polyether) **14** (251 mg, 0.16 mmol), the bis(hexafluorophosphate) salt **5**·2PF_6 (248 mg, 0.35 mmol), and the dibromide **7** (100 mg, 0.35 mmol) in dry DMF (8 ml) was subjected to a pressure of 12 kbar for 3 d at 20°C. 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 which was dissolved in H_2O. After the addition of NH_4PF_6, the bis[2]catenane **15**·8PF_6(100 mg, 16%) precipitated out of the solution as a purple crystalline solid. − M. p. > 250°C. − LSIMS: *m/z* = 3688 $[M - PF_6]^+$, 3543 $[M - 2\ PF_6]^+$, 3398 $[M - 3\ PF_6]^+$. − ^1H NMR (CD_3CN): δ = 2.40−2.43 (4 H, m), 3.50−4.30 (88 H, m), 4.40−4.42 (4 H, m), 4.90−4.93 (4 H, m), 5.51−5.53 (2 H, m), 5.55−5.80 (16 H, m), 5.87−6.89 (4 H, m), 6.01−6.04 (4 H, m), 6.20−6.23 (4 H, m), 6.70−6.71 (4 H, m), 6.92−6.94 (4 H, m), 7.09−7.20 (12 H, m), 7.61−7.62 (2 H, m), 7.86−8.03 (12 H, m), 8.25−8.29 (4 H, m), 8.50−8.54 (4 H, m), 8.85−8.89 (4 H, m), 9.08−9.12 (4 H, m). − ^{13}C NMR (CD_3CN): δ = 63.6, 65.7, 65.9, 68.7, 68.8, 69.0, 69.2, 70.1, 70.4, 70.8, 70.9, 71.2, 71.5, 71.7, 104.9, 105.5, 106.0, 109.1, 109.7, 110.9, 125.0, 125.3, 126.3, 126.8, 127.7, 129.4, 132.1, 132.2, 132.4, 132.7, 133.2, 134.3, 137.4, 145.2, 145.4, 145.7, 146.4, 146.6, 146.9. − $C_{158}H_{182}F_{48}N_8O_{30}P_8$: calcd. C 49.50, H 4.75, N 2.92; found C 49.61, H 4.74, N 2.91

Poly(bis[2]catenane) **16**·*n*(8PF_6): A solution of the bis[2]catenane **15**·8PF_6 (100.0 mg, 0.02 mmol) and the bis(isocyanate) **10** (5.0 mg, 0.02 mmol) in dry MeCN (8 ml) was heated under reflux for 3 d. After cooling down to room temperature, *t*Bu_4NCl was added to afford a purple precipitate which was washed with Me_2CO and dissolved in H_2O. Addition of KPF_6 gave **16**·*n*(8PF_6) (104 mg) as a purple precipitate. − M. p. > 250°C. − ^1H NMR (CD_3CN): δ = 2.40−2.43 (4 H, m), 3.50−4.50 (88 H, m), 4.80 (2 H, s), 4.98−5.03 (4 H, m), 5.52 (2 H, s), 5.51−5.53 (2 H, m), 5.55−6.33 (28 H, m), 6.50−6.84 (8 H, m), 6.95−8.10 (34 H, m), 8.45−8.48 (4 H, m), 8.55−8.58 (4 H, m), 8.88−8.91 (4 H, m), 9.08−9.12 (4 H, m). − ^{13}C NMR (CD_3CN): δ = 40.3, 63.6, 65.6, 65.9, 68.7, 68.8, 69.0, 69.2, 70.1, 70.4, 70.8, 70.9, 71.3, 71.6, 71.8, 104.9, 105.5, 106.0, 109.3, 109.8, 110.9, 125.0, 125.3, 126.3, 126.8, 127.8, 129.4, 132.2, 132.2, 132.4, 132.7, 133.2, 134.3, 137.4, 145.2, 145.4, 145.7, 146.4, 146.6, 146.9, 155.3. − GPC: M_n = 45 kg mol^{-1}; DP(M_n) = 15.

Macrocyclic Polyether **19**: A solution of **17** (6.38 g, 10.0 mmol) in dry DMF (240 ml) was added to a solution of **18** (1.70 g, 10.0 mmol) in dry DMF (300 ml), containing Cs_2CO_3 (4.10 g, 30.0 mmol) and CsOTs (800 mg, 3.0 mmol), over 20 h at room temperature. The resulting mixture was heated at 110°C for 24 h and, after cooling down to room temperature, it was filtered. The organic solution was concentrated under vacuum and the residue was purified by column chromatography (SiO_2, CH_2Cl_2/$MeCO_2Et$/MeOH 20:5:2) to afford **19** (1.94 g, 30%) as a colorless oil. − LSIMS: *m/z* = 646 $[M]^+$. − ^1H NMR ($CDCl_3$): δ = 3.66−3.82 (20 H, m), 3.89−3.92 (4 H, m), 3.97−4.02 (4 H, m), 4.17−4.20 (4 H, m), 5.03 (4 H, s), 6.61−6.64 (2 H, m), 7.19−7.23 (2 H, m), 7.26−7.30 (2 H, m), 7.76−7.79 (2 H, m). − ^{13}C NMR ($CDCl_3$): δ = 61.1, 67.6, 68.4, 69.3, 69.3, 70.4, 70.5, 105.2, 133.4, 144.2, 124.6, 124.9, 126.3, 150.2, 153.9. − $C_{34}H_{46}O_{12}$: calcd. C 63.14, H 7.17; found C 63.10, H 7.18.

[2]Catenane **21**·4PF_6: A solution of the macrocyclic polyether **20** (330.0 mg, 0.44 mmol), the bis(hexafluorophosphate) salt **5**·2PF_6 (159.0 mg, 0.25 mmol), and the dibromide **6** (59.0 mg, 0.25 mmol) in dry DMF (8 ml) was stirred at room temperature for 3 d. 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 which was dissolved in a mixture of MeCN and aqueous HCl (0.1 M). The mixture was stirred at room temperature for 1 d and then the solvent was removed under reduced pressure. The residue was dissolved in H_2O and NH_4PF_6 was added to afford the [2]catenane **21**·4PF_6 (250 mg, 61%) as a purple precipitate. − M. p. > 250°C. − LSIMS: *m/z* = 1599 $[M - PF_6]^+$, 1454 $[M - 2\ PF_6]^+$, 1309 $[M - 3\ PF_6]^+$. − ^1H NMR (CD_3CN): δ = 2.36−2.38 (2 H, m), 3.59−3.62 (4 H, m), 3.70−3.75 (4 H, m), 3.79−3.83 (4 H, m), 3.90−3.93 (4 H, m), 4.00−4.05 (4 H, m), 4.08−4.11 (4 H, m), 4.13−4.16 (4 H, m), 4.22−4.25 (4 H, m), 4.28−4.31 (4 H, m), 5.66 (4 H, d, ^2J = 12 Hz), 5.80 (4 H, d, ^2J = 12 Hz), 5.90−5.92 (2 H, m), 6.16−6.19 (4 H, m), 7.04−7.08 (8 H, m), 7.90−7.94 (4 H, m), 8.02−8.04 (4 H, m), 8.54−8.56 (4 H, m), 8.92−8.93 (4 H, m). − ^{13}C NMR (CD_3CN): δ = 66.0, 66.7, 69.0, 69.3, 70.4, 70.8, 71.0, 71.1, 71.3, 71.6, 71.7, 72.1, 73.4, 100.5, 105.1, 108.1, 109.3, 116.5, 118.3, 125.3, 126.5, 129.2, 131.4, 132.4, 137.6, 142.7, 145.5, 152.1, 160.6. − $C_{70}H_{78}F_{24}N_4O_{12}P_4$: calcd. C 47.35, H 4.39, N 3.15; found C 47.44, H 4.27, N 3.18.

Poly([2]catenane) **22**·*n*(4PF_6): A solution of the [2]catenane **21**·4PF_6 (30 mg, 0.02 mmol) and the bis(isocyanate) **10** (5 mg, 0.02 mmol) in dry MeCN (8 ml) was heated under reflux for 3 d. After cooling down to room temperature, *t*Bu_4NCl was added to afford a purple precipitate which was washed with Me_2CO and dissolved in H_2O. Addition of an excess of KPF_6 gave **22**·*n*(4PF_6) (35 mg) as a purple precipitate. − M. p. > 250°C. − ^1H NMR (CD_3CN): δ = 2.40−2.43 (2 H, m) 3.59−3.99 (32 H, m), 4.27 (4 H, s), 4.29 (2 H, s), 5.50−5.88 (8 H, m), 5.90−5.92 (2 H, m), 6.14−6.16 (2 H, m), 6.60 (2 H, s), 6.86−7.50 (18 H, m), 7.90−7.93 (4 H, m), 8.01−8.04 (4 H, m), 8.40−9.00 (8 H, m). − ^{13}C NMR (CD_3CN): δ = 39.7, 51.8, 65.7, 68.9, 70.3, 70.5, 70.9, 71.6, 71.7, 72.1, 104.5, 109.2, 129.0, 129.8, 131.8, 137.4, 151.9. − GPC: M_n = 27 kg mol^{-1}; DP(M_n) = 20.

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[11] The loss of the local C_{2h} symmetry imposed by the "inside" 1,5-dioxynaphthalene ring systems can occur after (i) dislodgement of the 1,5-dioxynaphthalene ring system from the cavity of the tetracationic cyclophane, (ii) 180° rotation of the 1,5-dioxynaphthalene ring system about its [O···O] axis and/or a 180° rotation of the bipyridinium units with respect to their [N···N] axes, and (iii) reinsertion of the 1,5-dioxynaphthalene ring system into the cavity of the tetracationic cyclophane. However, it is not possible to determine the pathway of this process by variable-temperature ^{1}H-NMR spectroscopy. 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.

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