Mechanically Linked Polyrotaxanes: A Stepwise Approach

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Received April 23, 2003; Revised Manuscript Received July 21, 2003

ABSTRACT: A new synthetic approach for the preparation of mechanically linked polyrotaxanes was developed. Two variations of rotaxane monomers were synthesized, based on diphenylmethane and tetraphenylmethane blocking groups. Both rotaxanes bear a protected phenol functionality in the dumbbell-shaped part and a protected carboxylic acid functionality in the cyclic component. Via a "stepwise" polymerization, a rotaxane dimer and a rotaxane tetramer have been obtained. The procedure involves selective deprotection of the two functional groups in separate batches and a subsequent coupling reaction of the produced monofunctional/monoprotected monomers so that a dimer is formed. Longer and monodisperse oligomers can easily be obtained by repetition of this procedure. In addition, deprotection of both functionalities in the dimer and subsequent esterification resulted in the formation of a polymer with a molecular weight of ca. 400 000. The molecules obtained were isolated and characterized by ^{1}H NMR and mass spectrometry.

Introduction

The past few years, the interest in new topological structures based on rotaxanes and catenanes has strongly increased. Starting from "simple" assemblies, more and more complex structures, such as [5]catenanes[1] or tris-[2]rotaxanes[2] have been synthesized. Because of their unique characteristics, rotaxanes and catenanes have been proposed as potential candidates in the area of molecular machineries[3] (shuttles, piston/cylinder systems, switches and logical gates). For example, pH-driven,[4,5] light-driven,[6] or redox-driven[5] shuttle-type systems have been synthesized. An important contribution toward this direction has been realized by the group of Sauvage and co-workers.[7]

In the field of polymers, a number of fascinating polyrotaxane structures has been presented.[8] The properties of these compounds are in many cases very different compared to the "naked" polymers.[9] Among the various structures, one of the most interesting ones concerns polymers with mechanically linked repeating units. A significant progress has only been achieved for mechanically linked polycatenanes.[10] In contrast, in the case of polyrotaxanes, various attempts[11] have been made, but the results in the synthesis of these "daisy chain" molecules are less spectacular and mainly concern small oligomers (dimers)[2,11b] and polypseudorotaxanes.[12]

Here, we present a new approach for the synthesis of mechanically linked polyrotaxanes.[13] The synthesis is based on a new step-by-step approach, consisting of sequential deprotection−coupling steps. The method has been successfully applied in the synthesis of monodisperse oligomers of various sizes and for two different types of rotaxanes.

Three possible strategies that can lead to polyrotaxanes with mechanically linked repeating units are depicted in Scheme 1. The first method is based on the "clipping" procedure, and the second is based on the "threading" of the linear part through the cyclic part of the monomer and subsequent blocking. For both methods, the polymerization is not effective because (a) the complexation yield of cyclophane tetracation with polyether-based dumbbells is very low and (b) there is a significant risk of intermolecular reactions, yielding cyclic monomers, dimers and trimers. This has been found by Stoddart et al. for both crown ether−pyridylpyridinium[14] and crown ether−dibenzylammonium salt[15] systems.

Finally, in the third method (Scheme 1), a rotaxane monomer bearing two functional groups is prepared which is subsequently polymerized in a more "classical" way. In this approach the low-yielding step of the rotaxane-complex formation is eliminated, since the rotaxane functionality is permanently present in the monomer. However, attempts based on this approach did not give any polyrotaxanes;[11b] the main reason was the high percentage of intermolecular instead of intramolecular connection leading as before to cyclic monomers and dimers.

Recently, we have reported[16] a new procedure to prepare both mechanically linked rotaxane oligomers and polymers that eliminates the problem of intermolecular reactions that was present in all the previous cases. Although, basically the general scheme of the third strategy (Scheme 1) is followed, now the functionalities **X** and **Y** of the molecule are both orthogonally[17] protected. In particular, in this "stepwise polymerization" , a rotaxane bearing two protected functional groups $\mathbf{XP_1}$ and $\mathbf{YP_2}$, is used as the starting material (Scheme 2). The synthesis is based on a step-by-step approach consisting of sequential deprotection−coupling steps. The two functional groups in the bifunctional rotaxane are deprotected selectively in separate batches, leading to two monofunctional rotaxane monomers, one bearing

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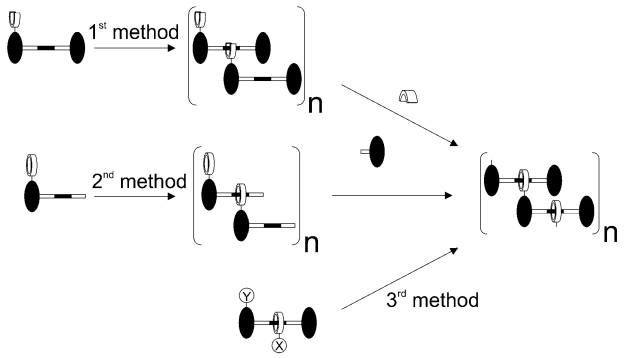
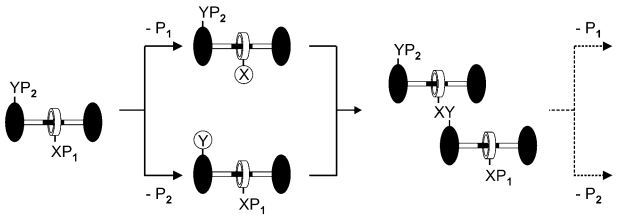
10.1021/ma034521t CCC: $25.00
Published on Web 08/26/2003

Scheme 1. Synthetic Approaches for the Preparation of a Mechanically Linked Polyrotaxane



Scheme 2. Schematic Presentation of the Stepwise "Polymerization" Procedure[a]



[a] In each step, which consists of two deprotection reactions and one coupling reaction, the number of repeating units in the oligomer is doubled.

the functional group **Y** in the dumbbell and one bearing the functional group **X** in the cyclic unit. A coupling reaction between these two products gives a rotaxane dimer[18] as the sole product. This dimer again contains the same two protected functional groups $\mathbf{XP_1}$ and $\mathbf{YP_2}$; therefore, the deprotection−coupling sequence can be repeated to obtain a tetramer. In this way, any size of oligomer can be obtained by just continuing the same deprotection−coupling procedure.[19]

Results and Discussion

Design of the Rotaxane Monomer. As a basis for the rotaxane, we have chosen the cyclophane-polyether system because it is well-known from literature that cyclophanes can be functionalized without losing their complexing properties.[20] The cyclophane contains an allyl-protected carboxylic acid, linked via a butyl spacer. The dumbbell contains either diphenylmethane or tetraphenylmethane end groups. One of them is functionalized with a *tert*-butyldiphenylsilyl- (TBDPS-) protected phenol. Selective deprotection is carried out with $Pd(PPh_3)_4$ and Bu_4NF, respectively. A more detailed description of the selection of the specific groups and deprotection conditions can be found in the Supporting Information. The final structures of the two proposed rotaxane monomers are depicted in Figure 1.

Synthesis of the Rotaxane Monomers. The "clipping" method was applied for the synthesis of both rotaxane monomers **1a**·$4PF_6^-$ and **1b**·$4PF_6^-$. The following molecules required for this method were initially prepared: (a) the dumbbell-shaped molecules, (b) the bis(pyridylpyridinium) dicationic salt **26**·$2PF_6^-$, and (c) the functionalized and protected *p*-bis(bromomethyl)-benzene **19**.

(a) Dumbbell-Shaped Molecules. On the basis of the same synthetic approach, two different dumbbell-shaped molecules bearing diphenylmethane **14a** and

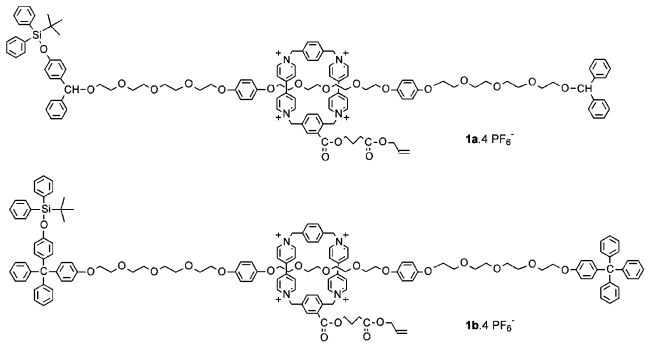
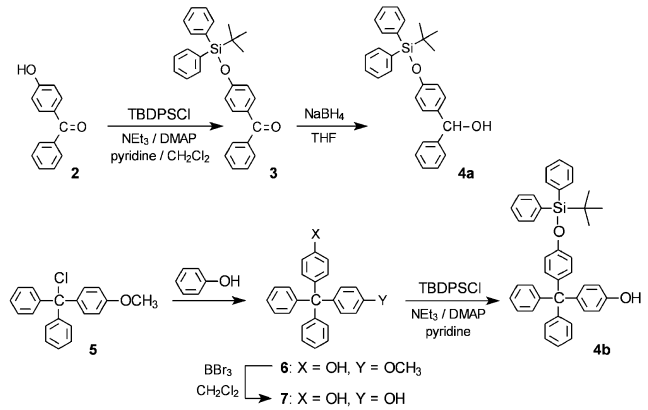


Figure 1. Proposed rotaxane monomers for the preparation of oligorotaxanes via the stepwise "polymerization" procedure.

Scheme 3. Synthesis of the Two Blocking Groups, Based on Diphenylmethane (4a) and Tetraphenylmethane (4b)



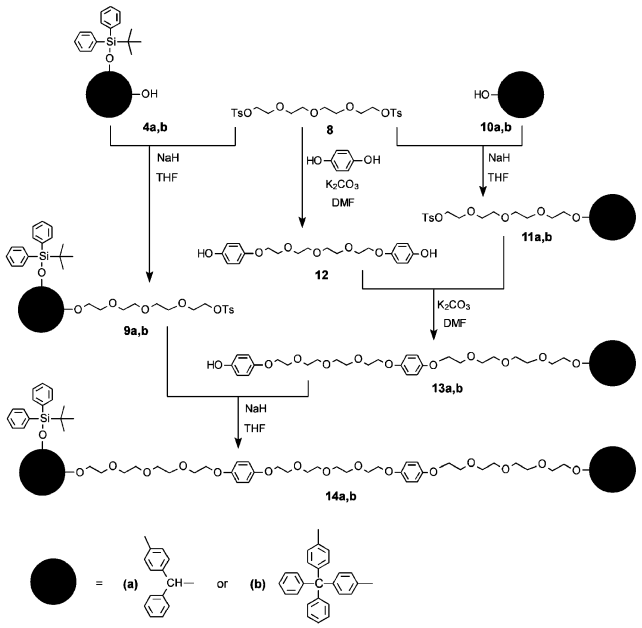
tetraphenylmethane **14b** blocking groups, respectively, were synthesized. In particular, the blocking groups (either functionalized or nonfunctionalized) were first prepared and connected to an ethylene glycol chain. Next, the middle part **12**, which is the same for both **14a** and **14b**, was synthesized. Its reaction with the ethylene glycol-extended blocking groups in two steps yielded the dumbbells.

The preparation of the diphenylmethane and tetraphenylmethane blocking groups, bearing the TBDPS-protected phenol moiety is depicted in Scheme 3.

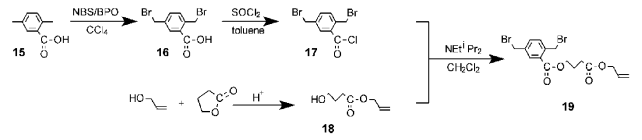
4-Hydroxybenzophenone (**2**) was reacted with *tert*-butyldiphenylchlorosilane as described in the literature.[21] To prevent deprotection, a mild reducing agent was used ($NaBH_4$) to yield the TBDPS-protected diphenylmethane blocking group **4a** (79%). On the other hand, the tetraphenylmethane-based blocking group was prepared by reaction of phenol with *p*-anisyldiphenylchloromethane (**5**). Demethylation of the methoxy group in **6** with BBr_3 yielded 4,4′-dihydroxytetraphenylmethane (**7**). Protection of one of the phenol groups produced the desired blocking group **4b**.[22]

Both unsubstituted blocking groups **10a** and **10b** were prepared according to literature methods.[23,24] These blocking groups were further reacted to give the final dumbbell molecules according to the procedure shown in Scheme 4. Most of the steps are based on the same general type of reaction, namely etherification of an alcohol or phenol with a tosylate derivative. NaH/THF and K_2CO_3/DMF were used since their efficiency for these etherifications is well-known.[25] For the synthesis of the diphenylmethane-based dumbbell **14a**, the two blocking groups **4a** and **10a** were reacted with the bis(tosylate) **8**. The middle part **12** was prepared via the

Scheme 4. Synthesis of the Dumbbell-shaped Molecules 14a and 14b, Bearing the TBDPS-Protected Phenol Functionalities



Scheme 5. Synthesis of the Dibromide 19 Bearing the Allyl-Protected Carboxylic Acid Functionality



reaction of the bis(tosylate) **8** with an excess of hydroquinone in the presence of potassium carbonate and subsequently reacted with **11a** to yield **13a**. Because of bisubstitution, the symmetric dumbbell is formed as a byproduct. Finally, the dumbbell-shaped molecule **14a** was produced in a 36% yield by reacting the functionalized blocking groups **9a** with **13a**. The relatively low yield can be attributed to silyl migration[26] of the silyl group. Following the same procedure, we have prepared the tetraphenylmethane-based dumbbell **14b** in similar yields.

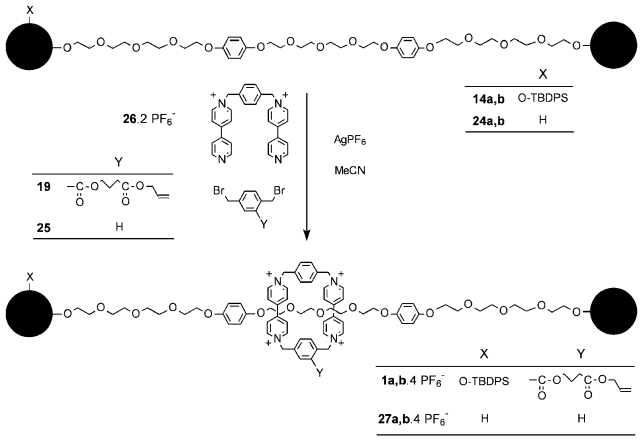
(b) Bis(pyridylpyridinium) Dicationic Salt 26·2PF$_6^-$. This compound was prepared according to a literature procedure[30] by the reaction of α,α′-dibromoxylene with 4,4′-bipyridyl.

(c) Functionalized and Protected *p*-Bis(bromomethyl)benzene 19. The synthesis of compound **19** is presented in Scheme 5. This molecule was essential for the preparation of a functionalized cyclophane since it contains three structural components: (a) two reactive bromine atoms necessary for the cyclophane formation, (b) a carboxylic acid function protected as allyl ester, and (c) a butyric acid extension for minimization of steric and electronic effects.

Bis(bromomethyl)benzoic acid **16** was prepared via the bromination of 2,5-dimethylbenzoic acid with NBS/BPO.[28] A detailed description of the byproducts formed during the bromination is given in the Supporting Information. The acid was converted quantitatively to the acid chloride **17** by reaction with thionyl chloride.

Compound **18** was prepared[29] by reacting γ-butyrolactone with an excess of allyl alcohol in the presence of sulfuric acid. Subsequent reaction with the acid chloride **17** gave allyl-4-butanoate-2,5-di(bromomethyl)-benzoate **19** in a 49% yield.

Scheme 6. Synthesis of the Bifunctional Rotaxanes 1a,b·4PF$_6^-$ and the Symmetric Rotaxanes 27a,b·4PF$_6^-$ [a]



[a] Key: a = Diphenylmethane, b = Tetraphenylmethane.

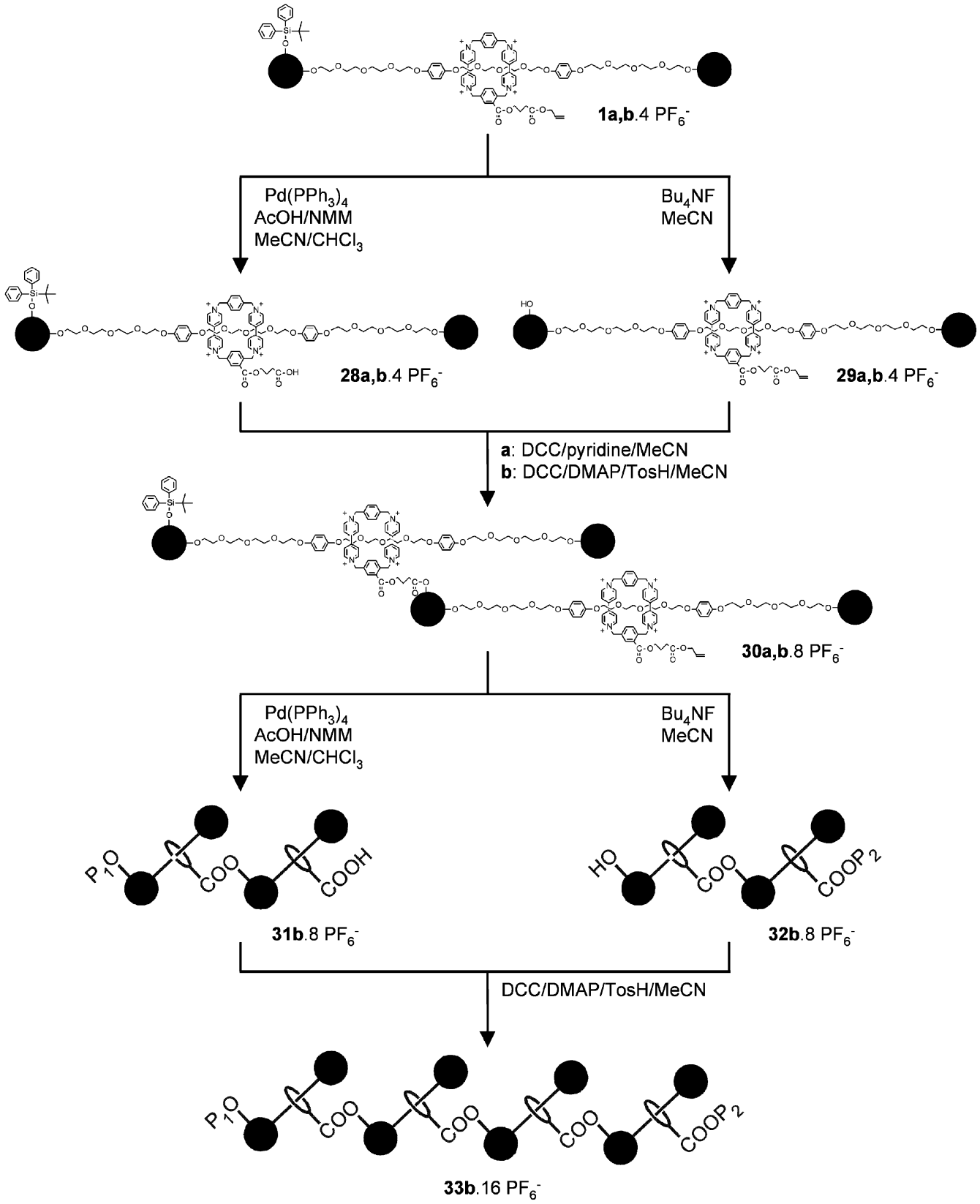
The rotaxane monomers were produced (Scheme 6) by reaction of the three components described above (dumbbells **14a** or **14b**, the bis(pyridylpyridinium) dicationic salt **26**·2PF$_6^-$ and the dibromide **19**) in the presence of AgPF$_6$. After 7 days, any polymeric byproducts as well as uncomplexed cyclophane were precipitated with $CHCl_3$ and removed by centrifugation. By the addition of Et_2O to the redissolved rotaxanes in CH_2Cl_2, the diphenylmethane- and tetraphenylmethane-based rotaxanes **1a**·4PF$_6^-$ and **1b**·4PF$_6^-$ were precipitated as red solids in 4.0% and 5.4% yields, respectively. The uncomplexed dumbbell was recovered from the supernatant liquids by silica column chromatography and reused. The solubility of the rotaxanes is largely depended on the counterion salts. The hexafluorophosphate salts are soluble in organic solvents of medium-high polarity such as CH_2Cl_2, acetone, CH_3CN, and DMF, while the chlorine salts are soluble in H_2O and H_2O−MeOH mixtures.

Starting from the unfunctionalized dumbbells **24a** and **24b** (byproducts in the synthesis of **13**) and using α,α′-dibromo-*p*-xylene instead of the intermediate **19**, one can form the "symmetric" analogues **27a**·4PF$_6^-$ and **27b**·4PF$_6^-$ in a 19% yield for both cases. The large difference in yields between the functionalized and nonfunctionalized rotaxanes can be attributed to steric hindrance due to the carboxylic acid functionality in the cyclophane.[11a]

Rotaxane Oligomers. Both rotaxanes **1a**·4PF$_6^-$ and **1b**·4PF$_6^-$ bear at appropriate positions two protected functional groups so that oligomers and/or polymers with mechanically linked repeating units can be formed. According to Scheme 3, three steps are necessary to obtain the dimer, selective deprotection of the carboxylic acid and phenol group in two separate batches and subsequent coupling of the produced monofunctional rotaxane monomers.

In one batch, the phenol moiety was deprotected by cleavage of the silyl ether bond with Bu_4NF in MeCN (Scheme 7). Counterion exchange with aqueous NH_4PF_6 gave the monomer−OH **29**·4PF$_6^-$ in a quantitative yield. In another batch, the carboxylic acid functionality of the rotaxane monomer was deprotected

Scheme 7. Synthesis of Rotaxane Dimers 30a,b·8PF$_6^-$ and the Rotaxane Tetramer 33b·16PF$_6^-$ [a]



[a] Key: a = Diphenylmethane, b = Tetraphenylmethane.

with $Pd(PPh_3)_4$ in $MeCN/CHCl_3$/NMM/AcOH. Under these conditions, the monomer−COOH **28**·4PF$_6^-$ was formed in 3 h. The deprotections were performed on both the diphenylmethane- and tetraphenylmethane-based rotaxanes. All the four monofunctional monomers obtained (**28a**·4PF$_6^-$, **28b**·4PF$_6^-$, **29a**·4PF$_6^-$, and **29b**·4PF$_6^-$) were characterized by ^{1}H NMR spectroscopy and MALDI−TOF mass spectrometry, indicating complete removal of the protective groups and the absence of side reactions. Thus, it was confirmed that the func-

tional groups on the rotaxane monomers were indeed orthogonally protected. Because of stability problems in the diphenylmethane rotaxanes (see Supporting Information), oligomers were only prepared with the tetraphenylmethane-based compounds.

In the next step, the monomer−COOH **28b**·4PF_6^- and the monomer−OH **29b**·4PF_6^-, both bearing tetraphenylmethane blocking groups, were esterified in CH_2Cl_2 in the presence of DCC and pyridine. After 7 days at room temperature, DHU was filtered off and the rotaxanes precipitated with Et_2O. Column chromatography and subsequent counterion exchange with aqueous NH_4PF_6 yielded the rotaxane dimer **30b**·8PF_6^- in a 30% yield. The low yield can be attributed to the conversion of monomer−COOH **28**·4PF_6^- to the stable *N*-acylurea derivative during the reaction, as was revealed by mass spectrometry. This conversion is a known problem in esterifications with DCC[30] and has also been observed in the esterification of catenanes.[10d] Undoubtedly, a low yielding coupling step would cause severe limitations in the preparation of longer oligorotaxanes and/or polyrotaxanes. Therefore, on model compounds as well as on the rotaxanes, several modifications of the esterification procedure were tried in order to improve the yield of this step. The major side-reaction concerns rearrangement of the *O*-acylurea intermediate to an *N*-acylurea. It was found that this reaction can almost completely be prevented if pyridine is replaced by a more powerful catalyst like DMAP in combination with *p*-toluenesulfonic acid (ratio compound/DMAP/*p*-toluenesulfonic acid 1.0/2.0/1.9). The small excess of DMAP compared to the acid is enough to permit a rapid esterification while the presence of the acid strongly suppresses the rearrangement of the *O*-acylurea to the *N*-acylurea. These results are slightly different from those reported by the group of Stupp[31] where it is mentioned that, in the best conditions, the ratio DMAP/acid should be exactly one. Use of the optimal conditions, raised the isolated yield for the rotaxane dimer **30b**·8PF_6^- from 30% to 80% without any observable amount of *N*-acylurea.

To prove that the stepwise "polymerization" of Scheme 3 can be used for oligomers longer than dimers, the deprotection and coupling steps were repeated in the presence of the newly formed ester link. So, next the synthesis of the rotaxane tetramer was performed. The phenol and carboxylic acid functionality in the tetraphenyl-based rotaxane dimer **30b**·8PF_6^- were deprotected in two separate batches. Esterification of the two monofunctional dimers gave a mixture of unreacted dimer−OH, some *N*-acylurea of the dimer−COOH and the tetramer **33b**·16PF_6^-. The reaction mixture was eluted over a silica column with MeCN/MeOH. By the addition of NH_4PF_6 at a concentration from 0 to 1.5% (v/v) we were able to isolate the rotaxane tetramer in a 35% yield. The low yield can be attributed to the difficult separation of the products.

In Figure 2, the ^{1}H NMR spectra of the rotaxane monomer **1b**·4PF_6^-, dimer **30b**·8PF_6^- and tetramer **33b**·16PF_6^- are presented. All show typical signals corresponding to the cyclophane (8.32−8.42 ppm and 9.44−9.60 ppm) and the dumbbell (3.75−4.15 ppm and 7.31−7.45 ppm). Their ratios are the same in each case. In contrast, the peaks assigned to the protective groups (allyl at 5.35−5.50 and 6.12 ppm, TBDPS at 7.53−7.63 and 7.87 ppm) decrease, as expected, with a factor of 2 each time since the number of repeating units doubles.

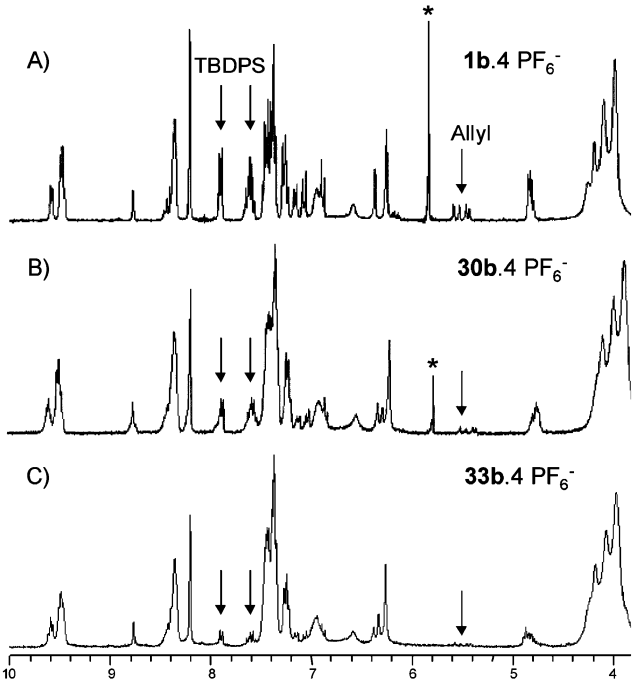


Figure 2. ^{1}H NMR spectra of the tetraphenylmethane-based rotaxanes: (a) monomer **1b**·4PF_6^-; (b) dimer **30b**·8PF_6^-; (c) tetramer **33b**·16PF_6^-. The asterisk marks a signal due to residual solvent.

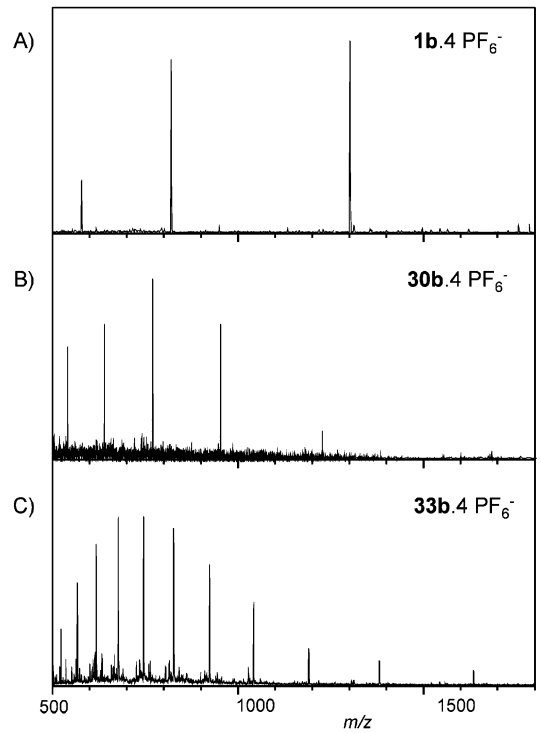


Figure 3. Electron spray mass spectra of the tetraphenylmethane-based rotaxanes: (a) monomer **1b**·4PF_6^-; (b) dimer 30b·8PF_6^-; (c) tetramer **33b**·16PF_6^-.

The tetraphenylmethane-based monomer, dimer and tetramer rotaxanes were characterized by electron spray mass spectrometry (Figure 3). The monomer **1b**·4PF_6^- shows three peaks at 578 $[M - 4PF_6^-]^{4+}$, 819 $[M - 3PF_6^-]^{3+}$, and 1302 $[M - 2PF_6^-]^{2+}$. For the dimer **30b**·8PF_6^- six peaks are observed from 541 $[M - 8PF_6^-]^{8+}$ to 1689 $[M - 3PF_6^-]^{3+}$, and finally for the

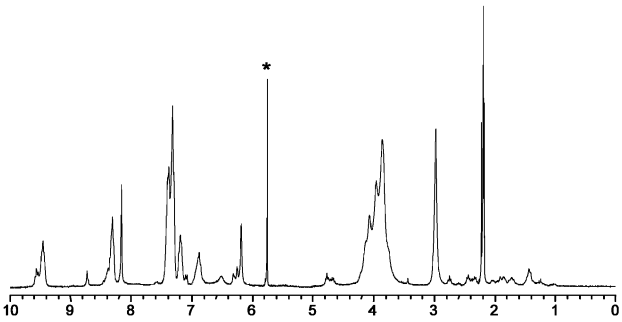
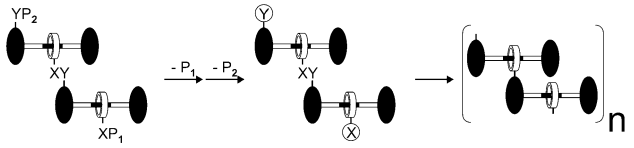


Figure 4. ^{1}H NMR spectrum of the polyrotaxane **35b**·$n$$PF_6^-$. The asterisk marks a signal due to residual solvent.

Scheme 8. Schematic Presentation of the Synthesis of the Polyrotaxane 35b·4*n*PF_6^-.



tetramer **33b**·16PF_6^-, 11 peaks from 523 [M − 16PF_6^-]$^{16+}$ to 1635 [M − 6PF_6^-]$^{6+}$ are visible.

Rotaxane Polymer. Although the molecular weight of the tetramer is as high as 10 000, it cannot be considered to be a polymer. Theoretically, polymerization can take place when both functional groups **X** and **Y** of the rotaxane monomer **1b**·4PF_6^- are deprotected. However, from the literature[11b] it is known that this leads mainly to low molecular weight cyclic products instead of a polymer. By using the dimer **30b**·8PF_6^- as starting material, the two functional groups are more separated in space, hereby decreasing the possibility of intramolecular reactions, and thus a high molecular weight polymer can be obtained.

The synthesis of the polymer **35b**·4$n$$PF_6^-$ is depicted in Scheme 8. Initially, the two functional groups were deprotected in two sequential steps. The produced bifunctional dimer **34b**·8PF_6^- was polymerized under the optimal conditions used for the preparation of the tetramer. After 5 days the polyrotaxane **35b**·4$n$$PF_6^-$ was precipitated from CH_2Cl_2/Et_2O.

The ^{1}H NMR spectrum of the polyrotaxane **35b**·4$n$$PF_6^-$ shows broad peaks as is expected for high molecular weight compounds, due to slight differences in the chemical environment for the separate monomer units.

Attempts have been made to determine the molecular weight by gel permeation chromatography. As calibration standards, the monomer, dimer, and tetramer could be used. Despite our efforts, no appropriate gel system was found. Different materials used were silica, Sephandex, LH-20, and Styragel. Pure solvents or solutions with salts[25b] were tested. In all cases, the separation is dominated by absorption of the rotaxanes on the column material, instead of separation due to differences in size. Finally, the molecular weight of the polyrotaxane **35b**·4$n$$PF_6^-$ was measured with static light scattering. A Zimm plot of the results, obtained in CH_2Cl_2 is shown in Figure 5. A molecular weight M_w of 400 000 and a mean-square radius of gyration of 80 ± 10 nm was found. Assuming a polydispersity of 2 for a polycondensation, the average degree of polymerization is 75 monomer units.

We believe that one of the main reasons for the high molecular weight is related to the configuration of the

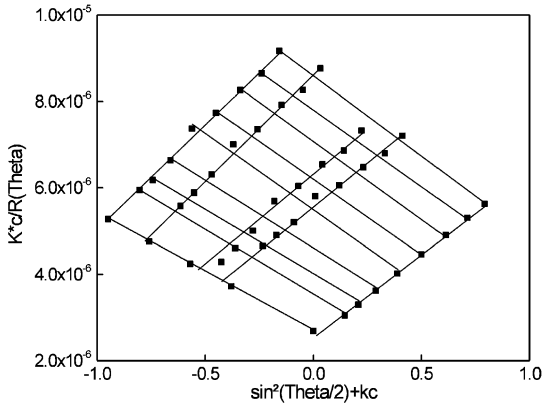


Figure 5. Zimm plot for the light scattering of the polyrotaxane **35b**·$n$$PF_6^-$ in CH_2Cl_2.

rotaxane dimer. In the monomer, the rotaxane "spends" some time in an arrangement in which the cyclophane is located close to the blocking groups. As a result, the two functional groups are close in space and therefore easy to couple. In contrast, in the dimer an arrangement in which the cyclophane is close to the blocking groups, does not lead to a close proximity of the two functional groups and therefore the two functions are free to react intramolecularly. The close spatial proximity of the cyclophane to the blocking groups is not surprisingly, taking into account that (i) the tetraphenylmethane system is rich in electrons (especially the functionalized one) and (ii) the energy barrier to move from the hydroquinone group to the blocking group is similar to the energy barrier to move between the two hydroquinone groups.

Conclusions

The preparation of five new rotaxanes is described in the present article. In particular, two rotaxane monomers, one rotaxane dimer, one tetramer, and a polymer were obtained. The structure of these rotaxanes was based on the polyether−cyclophane system. For the preparation of monodisperse oligorotaxanes, consisting of either two or four repeating units, we have developed a new synthetic route, based on a step-by-step approach. The procedure requires rotaxanes, bearing two functions orthogonally protected at appropriate positions. Two rotaxane monomers have been designed, which bear one protected phenol moiety in the dumbbell part of the rotaxane and one protected carboxylic acid moiety in the cyclophane component. As blocking groups, both diphenylmethane and tetraphenylmethane have been used.

By sequential deprotection and coupling of the carboxylic acid and phenol functionalities it was possible to synthesize the tetraphenylmethane-based rotaxane dimer in high yield (80%). The same procedure was repeated with dimer to obtain in this way the rotaxane tetramer. The advantage of this approach is the synthesis of monodisperse oligomers, and by repetition of the deprotection−coupling steps, any number of repeating units can be obtained, which can be used for the studies of the dynamic properties of mechanically linked molecules.

The polycondensation of the bisdeprotected rotaxane dimer gave for the first time a high molecular weight mechanically linked polyrotaxane with on average 75 mechanically linked repeating units per polymer chain.

Experimental Section

Materials. Chemicals were used as received from their commercial sources. All reactions were carried out under a nitrogen atmosphere. Solvents were dried over molecular sieves except for THF, which was distilled from NaH and sodium (benzophenon) and DMF which was distilled twice from P_2O_5 under reduced pressure. Benzhydrol (**10a**),[23] 4-hydroxytetraphenylmethane (**10b**),[24] and **26**·$2PF_6^-$[27] were prepared according to literature procedures.

Characterization. ^{1}H NMR spectra were recorded on a 300 MHz Varian (VXR 300) spectrometer or a 500 MHz Varian (Unity 500) spectrometer. Chloroform-d_1 was used as an internal standard, unless stated otherwise. MALDI−TOF spectra were taken on a Micromass TofSpec E mass spectrometer using 2,5-dihydroxybenzoic acid (DHB) as matrix. Electron spray mass spectra were recorded on a Sciex API3000 triple/quadruple mass spectrometer. High-resolution mass spectra (HRMS) were obtained from a JEOL MS Route JMS-600H. Elemental analyses were carried out at the Microanalytical Department of the University of Groningen.

Dihydroquinone Tetraethylene Glycol (12). Hydroquinone (11.0 g, 100 mmol) and **8** (5.03 g, 10 mmol) were dissolved in dry DMF (50 mL). After the addition of K_2CO_3 (2.90 g, 21 mmol), the reaction mixture was stirred for 15 h at 80 °C. The solvent was removed in vacuo and the resultant brown oil was dissolved in CH_2Cl_2 and extracted with water. The organic layer was dried over Na_2SO_4 and the solvent was removed in vacuo. The resulting oil was dissolved in warm chloroform, and after cooling, the excess hydroquinone was filtered off. Column chromatography [SiO_2, Et_2O:CH_2Cl_2 (2:1)], yielded a clear oil (2.1 g, 55%). ^{1}H NMR: δ 3.67 (s, 8H), 3.75 (t, 4H), 3.92 (t, 4H), 6.67 (d, 8H).

4-(Diphenyl-*tert*-butylsiloxy)benzophenone (3). Pyridine (8.4 mL, 100 mmol) was added to a solution of *tert*-butyldiphenylsilyl chloride (7.2 mL, 28 mmol) in dry THF (15 mL) and stirred for 15 min. This solution was added dropwise to a solution of 4-hydroxybenzophenon (5.0 g, 25 mmol), NEt_3 (3.8 mL, 28 mmol), and DMAP (0.15 g, 1.25 mmol) in dry THF (35 mL) at 0 °C over a period of 0.5 h. After being stirred for 5 h at room temperature, the solution was concentrated, Et_2O was added, and the resulting solution was extracted with 0.1 M HCl and water. The organic layer was dried over $MgSO_4$, the solvent removed in vacuo, and the product recrystallized from hexane as white crystals (10.0 g, 92%). ^{1}H NMR: δ 1.11 (s, 9H), 6.81 (d, 2H), 7.33−7.54 (m, 9H), 7.63 (d, 2H), 7.67−7.74 (m, 6H). Anal. Calcd for $C_{29}H_{28}O_2Si$: C, 79.78; H, 6.47. Found: C, 79.89; H, 6.57.

4-((Diphenyl-*tert*-butyl)siloxy)diphenylmethanol (4a). **3** (3.20 g, 7.33 mmol) was dissolved in dry THF (25 mL). $NaBH_4$ (83 mg, 2.20 mmol) was added, and the reaction mixture was refluxed for 7 h. After cooling, Et_2O was added, and the resulting solution was washed with water and dried over $MgSO_4$. Evaporation of the solvent in vacuo and column chromatography [SiO_2, hexane:Et_2O (3:1)] yielded the product as a clear oil (2.54 g, 79%). ^{1}H NMR: δ 1.13 (s, 9H), 2.19 (d, 1H), 5.74 (d, 1H), 6.76 (d, 2H), 7.11 (d, 2H), 7.24−7.50 (m, 11H), 7.74 (d, 4H). HRMS $C_{29}H_{30}O_2Si$: calcd, 438.2026; found, 438.2015.

2-(2-(2-(2-(4-((Diphenyl-*tert*-butyl)siloxy)diphenylmethoxy)ethoxy)ethoxy)ethoxy)ethoxy Tosylate (9a). A suspension of NaH (0.25 g, 6.3 mmol) in dry THF (10 mL) was added to a solution of **4a** (2.50 g, 5.7 mmol) in dry THF (15 mL). After stirring for 10 min, this solution was added to a refluxing solution of **8** (5.73 g, 11.4 mmol) in dry THF (40 mL) and refluxing was continued for 3 h. The reaction mixture was concentrated in vacuo, extracted with CH_2Cl_2/H_2O, and dried over $MgSO_4$. Concentration of the organic layer and column chromatography [SiO_2, $CHCl_3$:Et_2O (11:1)] yielded the product as a light-yellow oil (2.85 g, 65%). ^{1}H NMR: δ 1.13 (s, 9H), 2.41 (s, 3H), 3.54−3.65 (m, 14H), 4.12 (t, 2H), 5.27 (s, 1H), 6.68 (d, 2H), 7.10 (d, 2H), 7.22−7.40 (m, 13H), 7.68 (d, 4H), 7.77 (d, 2H).

2-(2-(2-(2-(Diphenylmethoxy)ethoxy)ethoxy)ethoxy)ethoxy Tosylate (11a). A solution of benzhydrol (1.47 g, 8 mmol) in THF (10 mL) was added to a suspension of NaH (0.35 g, 8.8 mmol) in THF (5 mL) and refluxed for 2 h after which it was added dropwise to a refluxing solution of **8** (6.03 g, 12 mmol) over a period of 0.5 h. After stirring for 2 h, the reaction mixture was concentrated, CH_2Cl_2 was added, and the resulting mixture was extracted with water. The organic phase was dried over $MgSO_4$ and the solvent evaporated in vacuo. After column chromatography [SiO_2, Et_2O] the product was isolated as a gray oil (1.60 g, 39%). ^{1}H NMR: δ 2.43 (s, 3H), 3.54−3.72 (m, 14H), 4.13 (t, 2H), 5.40 (s, 1H), 7.21−7.37 (m, 12H), 7.78 (d, 2H). HRMS $C_{28}H_{34}O_7S$: calcd, 514.2025; found, 514.2018.

1-{*p*-[2-(2-(2-(2-(Diphenylmethoxy)ethoxy)ethoxy)ethoxy)ethoxy]phenoxy}-13-{*p*-hydroxyphenoxy}-3,6,9-trioxaundecane (13a): A solution of **11a** (0.80 g, 1.5 mmol), **12** (1.14 g, 3 mmol), and K_2CO_3 (0.41 g, 3 mmol) in dry DMF (20 mL) was stirred for 20 h at 80 °C. The solvent was removed in vacuo, and the resulting brown oil was dissolved in CH_2Cl_2 and washed with water. The organic layer was dried over Na_2SO_4, and the solvent removed in vacuo. Column chromatography [SiO_2, CH_2Cl_2:acetone 9:1] yielded the product as a gray oil (0.48 g, 45%). ^{1}H NMR: δ 3.60−3.84 (m, 26H), 3.95−4.08 (m, 6H), 5.40 (s, 1H), 6.71 (s, 4H), 6.78 (d, 4H), 7.21−7.37 (m, 10H). The disubstituted product could be isolated in a 20% yield. ^{1}H NMR: δ 3.59−3.73 (m, 32H), 3.78−3.84 (m, 8H), 4.02−4.18 (m, 8H), 5.40 (s, 2H), 6.81 (s, 8H), 7.22−7.38 (m, 20H).

[1-{*p*-[2-(2-(2-(2-(Diphenylmethoxy)ethoxy)ethoxy)ethoxy)ethoxy]phenoxy}-13-{*p*-[2-(2-(2-(2-(4-((diphenyl-*tert*-butyl)siloxy)diphenylmethoxy)ethoxy)ethoxy)ethoxy]phenoxy}-3,6,9-trioxaundecane (14a): A suspension of NaH (75 mg, 1.87 mmol) in dry THF (8 mL) was added to a solution of **13a** (1.23 g, 1.7 mmol) in dry THF (20 mL). After being stirred at room temperature for 10 min, this solution was added to a refluxing solution of **9a** (1.31 g, 1.7 mmol) in dry THF (25 mL) and refluxing was continued for 2 h. The reaction mixture was concentrated, extracted with CH_2Cl_2/H_2O, and dried over $MgSO_4$. Concentration of the organic layer and column chromatography [SiO_2, CH_2Cl_2:acetone (9:1)] yielded the product as a light-yellow oil (0.80 g, 36%). ^{1}H NMR: δ 1.08 (s, 9H), 3.52−3.73 (m, 32H), 3.78−3.83 (m, 8H), 4.00−4.07 (m, 8H), 5.27 (s, 1H), 5.40 (s, 1H), 6.67 (d, 2H), 6.81 (s, 8H), 7.03 (d, 2H), 7.19−7.40 (m, 13H), 7.67 (d, 4H).

4-Hydroxy-4′-methoxytetraphenylmethane (6). *p*-Anisylchlorodiphenylmethane (0.79 g, 2.5 mmol) and phenol (5.1 g, 54 mmol) were stirred for 20 h at 60 °C, cooled, dissolved in CH_2Cl_2, and extracted twice with 1 M Na_2CO_3 and twice with H_2O. The solution was dried over $MgSO_4$ and the solvent removed in vacuo. Column chromatography [SiO_2, hexane:Et_2O (2:1)] yielded the product as a white solid (0.45 g, 68%). ^{1}H NMR: δ 3.80 (s, 3H), 5.20 (s, 1H), 6.71 (d, 2H), 6.81 (d, 2H), 7.08 (d, 2H), 7.12 (d, 2H), 7.18−7.30 (m, 10H).

4,4′-Dihydroxytetraphenylmethane (7): BBr_3 (0.85 g, 3.4 mmol) in dry CH_2Cl_2 (3 mL) was added to a solution of **6** (0.50 g, 1.4 mmol) in dry CH_2Cl_2 (15 mL). After being stirred for 1.5 h at room temperature, the reaction mixture was extracted with water and dried over $MgSO_4$, yielding the product as a white solid (0.5 g, ∼100%). ^{1}H NMR ($CDCl_3$/CD_3OD): δ 6.48 (s, 2H), 6.55 (d, 4H), 6.88 (d, 4H), 7.01−7.15 (m, 10H).

4-(Diphenyl-*tert*-butylsiloxy)-4′-hydroxytetraphenylmethane (4b). To a solution of **7** (0.82 g, 2.3 mmol) in triethylamine (7 mL) and pyridine (5 mL) were added DMAP (71 mg, 0.6 mmol) and *tert*-butylchlorodiphenylsilane (0.61 mL, 2.3 mmol), and the reaction was stirred overnight at room temperature. The solution was extracted with water and dried over $MgSO_4$, and the solvent was removed in vacuo. Column chromatography [SiO_2, hexane:Et_2O:CH_2Cl_2 (3:1:1)] yielded the product as a clear oil (0.76 g, 55%). ^{1}H NMR: δ 1.08 (s, 9H), 6.64 (d, 4H), 6.87 (d, 2H), 6.93 (d, 2H), 7.08−7.21 (m, 10H), 7.32−7.38 (m, 6H), 7.71 (dd, 4H). HRMS $C_{41}H_{38}O_2Si$: calcd, 590.2641; found, 590.2629.

2-(2-(2-(2-(4-[4-((Diphenyl-*tert*-butyl)siloxy)]tritylphenoxy)ethoxy)ethoxy)ethoxy)ethoxy Tosylate (9b). A suspension of NaH (15 mg, 0.39 mmol) in dry THF (0.5 mL) was

added to a solution of **4b** (0.20 g, 0.35 mmol) in dry THF (2 mL) This solution was added to a refluxing solution of **8** (0.70 g, 1.4 mmol) in dry THF (7 mL), and refluxing was continued for 2 h. The reaction mixture was concentrated in vacuo, extracted with CH_2Cl_2/H_2O, and dried over $MgSO_4$. Concentration of the organic layer and column chromatography [SiO_2, Et_2O:hexane:CH_2Cl_2 (2:1:1)] yielded the product as a clear oil (0.18 g, 55%). ^{1}H NMR: δ 1.08 (s, 9H), 6.58 (d, 2H), 6.69 (d, 2H), 6.81 (d, 2H), 6.94 (d, 2H), 7.04 (dd, 4H), 7.09−7.17 (m, 6H), 7.26−7.39 (m, 8H), 7.64 (d, 4H), 7.74 (d, 2H).

2-(2-(2-(2-(4-Tritylphenoxy)ethoxy)ethoxy)ethoxy)-ethoxytosylate (11b). A suspension of NaH (53 mg, 1.3 mmol) in dry THF (2 mL) was added to a solution of 4-hydroxytetraphenylmethane (0.40 g, 1.2 mmol) in dry THF (6 mL). After being stirred for 5 min, this solution was added to a refluxing solution of **8** (1.2 g, 2.4 mmol) in dry THF (10 mL), and refluxing was continued for 1.5 h. The reaction mixture was concentrated in vacuo, CH_2Cl_2 was added, and the reaction mixture was washed with water and dried over $MgSO_4$. Concentration of the organic layer and column chromatography [SiO_2, Et_2O:CH_2Cl_2:hexane (2:1:1)] yielded the product as a white solid (0.58 g, 72%). ^{1}H NMR: δ 2.41 (s, 3H), 3.58−3.70 (m, 10H), 3.81−3.88 (t, 2H), 4.06−4.20 (m, 4H), 6.80 (d, 2H), 7.12 (d, 2H), 7.17−7.26 (m, 15H), 7.33 (d, 2H), 7.81 (d, 2H).

1-{*p*-[2-(2-(2-(2-(4-Tritylphenoxy)ethoxy)ethoxy)ethoxy)-ethoxy]phenoxy}-13-{*p*-hydroxyphenoxy}-3,6,9-trioxaundecane (13b). 11b (0.40 g, 0.6 mmol) and **12** (0.15 g, 0.4 mmol) were dissolved in dry DMF (7 mL), and K_2CO_3 (0.09 g, 0.64 mmol) was added. After 20 h at 90 °C, CH_2Cl_2 was added, and the reaction mixture was extracted with 0.1 M HCl and water and dried over Na_2SO_4. Concentration of the organic layer and column chromatography [SiO_2, CH_2Cl_2:acetone (9:1)] yielded the product as a clear oil (0.20 g, 58%). ^{1}H NMR: δ 3.60−3.68 (m, 16H), 3.71−3.78 (m, 8H), 3.89−4.04 (m, 8H), 6.67 (d, 4H), 6.72 (d, 2H), 6.74 (s, 4H), 7.03 (d, 2H), 7.09−7.20 (m, 15H). The disubstituted product could be isolated in 22% yield. ^{1}H NMR: δ 3.60−3.68 (m, 24H), 3.71−3. 08 (m, 12H), 3.91−4.04 (m, 12H), 6.67 (d, 4H), 6.73 (s, 8H), 7.03 (d, 4H), 7.09−7.20 (m, 30H).

1-{*p*-[2-(2-(2-(2-(4-tritylphenoxy)ethoxy)ethoxy)ethoxy)-ethoxy]phenoxy-13-{*p*-[2-(2-(2-(2-(4-[4-((diphenyl-*tert*-butyl)siloxy)]tritylphenoxy)ethoxy)ethoxy)ethoxy)ethoxy]-phenoxy}-3,6,9-trioxaundecane (14b). A suspension of NaH (8 mg, 0.2 mmol) in dry THF (0.3 mL) was added to a solution of **13b** (0.16 g, 0.18 mmol) in dry THF (3 mL). This solution was added to a refluxing solution of **9b** (0.17 g, 0.18 mmol) in dry THF (4 mL), and the refluxing was continued for 2 h. The reaction mixture was concentrated in vacuo, CH_2Cl_2 was added, and the reaction mixture was washed with water and dried over $MgSO_4$. Concentration of the organic layer and column chromatography [SiO_2, CH_2Cl_2:acetone (9:1)] yielded the product as a clear oil (0.13 g, 45%). ^{1}H NMR: δ 1.07 (s, 9H), 3.60−3.68 (m, 16H), 3.72−3.80 (m, 8H), 3.98−4.08 (m, 8H), 6.58 (d, 2H), 6.69 (d, 2H), 6.73 (d, 2H), 6.77 (s, 8H), 6.81 (d, 2H), 6.94 (d, 2H), 7.04 (d, 6H), 7.10−7.21 (m, 21H), 7.27−7.39 (m, 6H), 7.64 (dd, 4H). Anal. Calcd for $C_{102}H_{112}O_{16}Si$: C, 75.50; H, 7.00. Found: C, 75.28; H, 7.18.

2,5-Bis(bromomethyl)benzoic Acid (16). 2,5-Dimethylbenzoic acid (5.00 g, 33.3 mmol), *N*-bromosuccinimide (2.52 g, 14.2 mmol), and benzoylperoxide (171 mg, 0.71 mmol) were dissolved in CCl_4 (100 mL) and refluxed. A red color appeared which disappeared again after 15 min. NBS (2.52 g) and BPO (171 mg) were added, and refluxing was continued. NBS (2.52 g) and BPO (171 mg) were added two more times after 15 and 45 min. Each time a red color appeared which disappeared before addition of the next portion. The reaction mixture was refluxed for 30 min after the last addition and then cooled fast. The solid was filtered off and the filtrate concentrated in vacuo. The solid was dissolved in CH_2Cl_2:acetone (3:1) and precipitated with hexane (30 mL). The precipitate was filtered off, dissolved in CH_2Cl_2:acetone (3:1) and again precipitated with hexane (40 mL). The product was filtered off as an off-white solid (2.6 g, 25%). ^{1}H NMR: δ 4.50 (s, 2H), 4.99 (s, 2H), 7.50 (d, 1H), 7.61 (dd, 1H), 8.16 (d, 1 H).

Allyl-4-hydroxybutanoate (18). Concentrated sulfuric acid (0.10 g, 1 mmol) was added to a mixture of butyrolactone (0.43 g, 5 mmol) and allyl alcohol (2.9 g, 50 mmol) and the reaction mixture stirred for 1 day at room temperature. $NaHCO_3$ (0.1 g, 1 mmol) was added and the reaction mixture stirred for another hour. Et_2O was added and extracted twice with 1 M Na_2CO_3 solution and water, the resulting solution dried over $MgSO_4$ and the solvent evaporated in vacuo. Kugelrohr distillation (73 °C, 0.04 mmHg) yielded the product as a clear liquid (0.21 g, 29%). ^{1}H NMR: δ 1.80 (quintet, 2H), 2.38 (t, 2H), 2.57 (s, 1H), 3.56 (t, 2H), 4.47 (d, 2H), 5.12 (d, 1H), 5.21 (d, 1H), 5.72−5.88 (m, 1H).

Allyl-4-butanoate-2,5-bis(bromomethyl)benzoate (19). 16 (0.21 g, 0.68 mmol) was suspended in dry toluene (10 mL). $SOCl_2$ (0.10 mL, 1.43 mmol) was added and the reaction mixture refluxed for 1 h. The reaction mixture was concentrated in vacuo, dissolved in dry CH_2Cl_2 (7 mL) and NEt^iPr_2 (0.13 mL, 0.82 mmol) and 18 (0.10 g, 0.68 mmol) were added. The reaction mixture was stirred overnight at room temperature, extracted with water and dried over $MgSO_4$. Concentration of the organic layer and column chromatography [SiO_2, hexane:$CHCl_3$:Et_2O (8:3:1)] yielded the product as a light-yellow oil (0.15 g, 49%). ^{1}H NMR: δ 2.08 (m, 2H), 2.46 (m, 2H), 4.34 (m, 2H), 4.47 (dd, 2H), 4.53 (d, 2H), 4.90 (dd, 2H), 5.16 (d, 1H), 5.24 (d, 1H), 5.77−5.90 (m, 1H), 7.36−7.49 (m, 2H), 7.88 (d, 1H).

{[1-{*p*-[2-(2-(2-(2-(diphenylmethoxy)ethoxy)ethoxy)ethoxy]phenoxy}-13-{*p*-[2-(2-(2-(2-[4-((diphenyl-*tert*-butyl)siloxy)phenyl]phenylmethoxy)ethoxy)ethoxy)ethoxy]phenoxy}-3,6,9-trioxaundecane][cyclo(2,5-(paraquat-*p*-phenyleneparaquat)(allyl-4-butanoate)benzoate)]rotaxane} Tetrakis(hexafluorophosphate) (1a·4PF$_6^-$): The dumbbell **14a** (158 mg, 0.12 mmol) and **19** (52 mg, 0.12 mmol) were dissolved in dry MeCN (0.3 mL). $AgPF_6$ (70 mg, 0.28 mmol) and **26**·2PF_6^- (85 mg, 0.12 mmol), dissolved in dry MeCN (0.3 mL), were added. After being stirred for 4 days at room temperature, the reaction mixture was centrifuged and the solution concentrated to 0.5 mL. By addition of $CHCl_3$ (4 mL), the paraquat dication and cyclophane precipitated. The solution was concentrated to 3 mL, and Et_2O (1 mL) was added. The red precipitate was subjected to column chromatography [SiO_2, MeOH:2 M NH_4Cl:$MeNO_2$ (7:2:1)] and after ion exchange with NH_4PF_6, the product was obtained as a red solid (10 mg, 5%). ^{1}H NMR (CD_3CN): δ 1.20 (s, 9H), 2.38 (quintet, 2H), 2.77 (t, 2H), 3.60−4.15 (m, 48H), 4.70−4.76 (m, 4H), 5.22 (d, 1H), 5.28−5.43 (m, 3H), 6.10 (m, 1H), 6.27 (s, 4H), 6.48 (s, 2H), 6.52 (s, 2H), 6.88 (d, 2H), 7.23 (d, 2H), 7.34−7.61 (m, 21H), 7.85 (d, 4H), 8.16 (s, 4H), 8.30−8.40 (m, 10H), 8.71 (s, 1H), 9.43−9.49 (m, 6H), 9.59 (d, 2H). MALDI−TOF (dihydroxybenzoic acid matrix): 2298 [M − 2PF_6]$^+$; 2153 [M − 3PF_6]$^+$; 2009 [M − 4PF_6]$^+$. UV/vis (solvent): λ_{max} [nm] (ϵ [M^{-1} cm^{-1}]) = 265 (36 000); 466 (650).

{[1-{*p*-[2-(2-(2-(2-(4-tritylphenoxy)ethoxy)ethoxy)-ethoxy)ethoxy]phenoxy-13-{*p*-[2-(2-(2-(2-(4-[4-((diphenyl-*tert*-butyl)siloxy)]tritylphenoxy)ethoxy)ethoxy)ethoxy]phenoxy}-3,6,9-trioxaundecane][cyclo-(2,5-(paraquat-*p*-phenyleneparaquat)(allyl-4-butanoate) benzoate)]rotaxane} Tetrakis(hexafluorophosphate) (1b·4PF$_6^-$). The dumbbell **14b** (157 mg, 0.1 mmol) and **26**·2PF_6^- (68 mg, 0.1 mmol) were dissolved in dry DMF (0.3 mL). $AgPF_6$ (61 mg, 0.25 mmol) in MeCN (0.4 mL) and allyl-4-butanoate-2,5-di(bromomethyl) benzoate **19** (42 mg, 0.1 mmol) in MeCN (0.5 mL) were added. After being for 7 days at room temperature, the reaction mixture was centrifuged and the solution concentrated to 1 mL. By addition of $CHCl_3$ (5 mL), the free cyclophane precipitated. The solution was concentrated to 1 mL and the rotaxane precipitated by the addition of Et_2O (3 mL). The solid was dissolved in $CHCl_3$ (1 mL) and again precipitated with Et_2O (1 mL), yielding the product as a red solid (18.6 mg, 6.6%). ^{1}H NMR (acetone-d_6): δ 1.25 (s, 9H), 2.36 (quintet, 2H), 2.75 (t, 2H), 3.75−4.15 (m, 48H), 4.67−4.77 (m, 4H), 5.36 (d, 1H), 5.47 (d, 1H), 6.12 (m, 1H), 6.21 (s, 4H), 6.32 (s, 2H), 6.52 (s, 2H), 6.82−6.98 (m, 6H), 7.03 (d, 2H), 7.12 (d, 2H), 7.18−7.25 (m, 6H), 7.31−7.45 (m, 21H), 7.53−7.63 (m, 6H), 7.87 (d, 4H), 8.18 (s, 4H), 8.32−8.42

(m, 10H), 8.74 (s, 1H), 9.44−9.50 (m, 6H), 9.60 (d, 2H). MALDI−TOF: *m*/*z* 2603 ($M - 2PF_6$)$^+$, 2458 ($M - 3PF_6$)$^+$, 2313 ($M - 4PF_6$)$^+$. Anal. Calcd for $C_{146}H_{154}F_{24}N_4O_{20}P_4Si$: C, 60.62; H, 5.37; N, 1.94. Found: C, 60.25; H, 5.38; N, 2.02. Thus, 95% of the unthreaded dumbbell could be recovered by column chromatography of the ether phase [SiO_2, CH_2Cl_2:acetone (9:1)].

{**[1-{*p*-[2-(2-(2-(2-(Diphenylmethoxy)ethoxy)ethoxy)ethoxy)ethoxy] phenoxy}-13-{*p*-[2-(2-(2-(2-[4-((diphenyl-*tert*-butyl)siloxy)phenyl]phenylmethoxy)ethoxy)-ethoxy)ethoxy)ethoxy]phenoxy}-3,6,9-trioxaundecane]-[cyclo(2,5-(paraquat-*p*-phenyleneparaquat)-4-carboxybutylbenzoate)]rotaxane} Tetrakis(hexafluorophosphate) (28a·4PF$_6^-$).** To a solution of **1a**·4PF_6^- (10 mg, 3.9 μmol) in $CHCl_3$ (0.4 mL) were added acetic acid (13 μL, 230 μmol) and NMM (13 μL, 115 μmol). A solution of $Pd(PPh_3)_4$ (9 mg, 7.7 μmol) in $CHCl_3$ (0.1 mL) was added, and the reaction mixture was stirred for 3 h at room temperature. After addition of $CHCl_3$ (3 mL), the rotaxane was precipitated with Et_2O (1 mL). The solid was extracted with CH_2Cl_2/H_2O and the solvent evaporated in vacuo, yielding the product as a red solid (7.8 mg, 80%). ^{1}H NMR (CD_3CN): δ 1.20 (s, 9H), 2.38 (quintet, 2H), 2.77 (t, 2H), 3.60−4.15 (m, 48H), 4.71 (t, 2H), 5.43 (s, 1H), 5.54 (s, 1H), 6.27 (s, 4H), 6.48 (s, 2H), 6.52 (s, 2H), 6.88 (d, 2H), 7.23 (d, 2H), 7.34−7.61 (m, 21H), 7.85 (d, 4H), 8.16 (s, 4H), 8.30−8.40 (m, 10H), 8.71 (s, 1H), 9.43−9.49 (m, 6H), 9.59 (d, 2H).

{**[1-{*p*-[2-(2-(2-(2-(Diphenylmethoxy)ethoxy)ethoxy)ethoxy]phenoxy}-13-{*p*-[2-(2-(2-(2-[4-hydroxyphenyl]phenylmethoxy)ethoxy)ethoxy)ethoxy)-ethoxy]phenoxy}-3,6,9-trioxaundecane][cyclo(2,5-(paraquat-*p*-phenyleneparaquat)(allyl-4-butanoate)-benzoate)]rotaxane} Tetrakis(hexafluorophosphate) (29a·4PF$_6^-$).** *o*-Nitrophenol (0.6 mg, 4.3 μmol) and Bu_4NF (9.5 μL, 9.5 μmol) were added to a solution of **1a**·4PF_6^- (10 mg, 3.9 μmol) in MeCN (0.2 mL). After 30 min, the rotaxane was precipitated with water and centrifuged. The solid was dissolved in $CHCl_3$ (2 mL) and precipitated with Et_2O (1 mL) twice, yielding the product as a red solid (6.4 mg, 70%). ^{1}H NMR (CD_3CN): δ 2.38 (quintet, 2H), 2.77 (t, 2H), 3.60−4.15 (m, 48H), 4.70−4.76 (m, 4H), 5.22 (d, 1H), 5.28−5.43 (m, 3H), 6.10 (m, 1H), 6.27 (s, 4H), 6.48 (s, 2H), 6.52 (s, 2H), 6.90 (d, 2H), 7.25 (d, 2H), 7.34−7.49 (m, 15H), 8.16 (s, 4H), 8.30−8.40 (m, 9H), 8.61 (s, 1H), 8.71 (s, 1H), 9.43−9.49 (m, 6H), 9.59 (d, 2H).

{**[1-{*p*-[2-(2-(2-(2-(4-Tritylphenoxy)ethoxy)ethoxy)-ethoxy)ethoxy]phenoxy}-13-{*p*-[2-(2-(2-(2-(4-[4-((diphenyl-*tert*-butyl)siloxy)]tritylphenoxy)ethoxy)eth-oxy)ethoxy)ethoxy]phenoxy}-3,6,9-trioxaundecane][cyclo(2,5-(paraquat-*p*-phenyleneparaquat)-4-carboxybutylbenzoate)]rotaxane} Tetrakis(hexafluorophosphate) (28b·4PF$_6^-$)**: To a solution of **1b**·4PF_6^- (64 mg, 22 μmol) in $CHCl_3$ (0.5 mL), were added acetone (0.2 mL), acetic acid (76 μL, 1.33 mmol), and NMM (73 μL, 0.66 mmol). A solution of $Pd(PPh_3)_4$ (51 mg, 44 μmol) in $CHCl_3$ (0.5 mL) was added, and the reaction mixture was stirred for 3 h at room temperature. After addition of $CHCl_3$ (3 mL), the rotaxane was precipitated with Et_2O (1 mL). PPh_3 was removed by precipitation with acetone. Evaporation of the solvent in vacuo yielded the product as a red solid (50 mg, 80%). ^{1}H NMR (acetone-d_6): δ 1.24 (s, 9H), 2.33 (quintet, 2H), 2.71 (t, 2H), 3.78−4.21 (m, 48H), 4.71 (t, 2H), 6.20 (s, 4H), 6.31 (s, 2H), 6.54 (s, 2H), 6.82−6.93 (m, 6H), 7.02 (d, 2H), 7.11 (d, 2H), 7.18−7.23 (m, 6H), 7.30−7.44 (m, 21H), 7.52−7.61 (m, 6H), 7.86 (d, 4H), 8.17 (s, 4H), 8.31−8.41 (m, 10H), 8.73 (s, 1H), 9.46−9.53 (m, 6H), 9.58 (d, 2H). MALDI−TOF (dihydroxybenzoic acid matrix): *m*/*z* 2563 ($M - 2PF_6$)$^+$, 2418 ($M - 3PF_6$)$^+$, 2273 ($M - 4PF_6$)$^+$.

{**[1-{*p*-[2-(2-(2-(2-(Diphenylmethoxy)ethoxy)eth-oxy)ethoxy)ethoxy]phenoxy}-13-{*p*-[2-(2-(2-(2-(4-[4-hydroxytritylphenoxy)ethoxy)ethoxy)ethoxy]-phenoxy}-3,6,9-trioxaundecane][cyclo(2,5-(paraquat-*p*-phenyleneparaquat)(allyl-4-butanoate)benzoate)]rotax-ane} Tetrakis(hexafluorophosphate) (29b·4PF$_6^-$).** *o*-Nitrophenol (4.2 mg, 0.03 mmol) and Bu_4NF (27 μL, 0.03 mmol) were added to a solution of **1b**·4PF_6^- (61 mg, 0.02121 mmol) in MeCN (0.7 mL). After 30 min at room temperature, CH_2Cl_2 was added, and the resulting solution was extracted twice with H_2O/NH_4PF_6 and twice with water. The rotaxane was precipitated from the organic phase with Et_2O, yielding the product as a red solid (42 mg, 75%). ^{1}H NMR (acetone-d_6): δ 2.34 (quintet, 2H), 2.76 (t, 2H), 3.75−4.15 (m, 48H), 4.69−4.75 (m, 4H), 5.35 (d, 1H), 5.47 (d, 1H), 6.10 (m, 1H), 6.20 (s, 4H), 6.31 (s, 2H), 6.52 (s, 2H), 6.85−6.98 (m, 6H), 7.10 (d, 2H), 7.16−7.21 (m, 6H), 7.28−7.45 (m, 21H), 8.18 (s, 4H), 8.32−8.42 (m, 10H), 8.74 (s, 1H), 9.44−9.50 (m, 6H), 9.60 (d, 2H). MALDI−TOF (dihydroxybenzoic acid matrix): *m*/*z* 2365 ($M - 2PF_6$)$^+$, 2220 ($M - 3PF_6$)$^+$, 2075 ($M - 4PF_6$)$^+$.

Dimer (30b·8PF$_6^-$). 29b·4PF_6^- (17 mg, 6.3 μmol), **28b**·4PF_6^- (18 mg, 6.3 μmol), DMAP (1.6 mg, 13 μmol), and TosH (2.2 mg, 11 μmol) were dissolved in MeCN (0.2 mL), and DCC (4 mg, 19 μmol) was added. After the reaction was stirred for 1 day at room temperature, DHU was removed by centrifugation and the product precipitated with CH_2Cl_2/Et_2O. Column chromatography [SiO_2, MeOH:2 M NH_4Cl:$MeNO_2$ (7:2:1) → MeOH:H_2O (7:2) → MeCN + 0.5% NH_4PF_6] yielded the product as a red solid (27 mg, 78%). ^{1}H NMR (acetone-d_6): δ 1.23 (s, 9H), 2.31−2.46 (m, 4H), 2.75 (t, 4H), 3.75−4.22 (m, 96H), 4.67−4.79 (m, 6H), 5.35 (d, 1H), 5.47 (d, 1H), 6.12 (m, 1H), 6.19 (s, 8H), 6.26 (s, 2H), 6.32 (s, 2H), 6.53 (s, 4H), 6.81−6.97 (m, 12H), 7.01 (d, 4H), 7.10 (d, 4H), 7.18−7.23 (m, 12H), 7.31−7.45 (m, 42H), 7.52−7.63 (m, 6H), 7.86 (d, 4H), 8.17 (s, 8H), 8.30−8.42 (m, 20H), 8.74 (s, 2H), 9.44−9.50 (m, 12H), 9.56−9.60 (m, 4H). MALDI−TOF: *m*/*z* 4923 ($M - 4PF_6$)$^+$, 4778 ($M - 5\ PF_6$)$^+$, 4633 ($M - 6PF_6$)$^+$, 4488 ($M - 7\ PF_6$)$^+$, 4343 ($M - 8PF_6$)$^+$.

Dimer—COOH (31b·8PF$_6^-$): To a solution of **30b**·8PF_6^- (27 mg, 4.9 μmol) in $CHCl_3$ (0.1 mL) were added acetone (0.1 mL), acetic acid (17 μL, 0.30 mmol), and NMM (16 μL, 0.15 mmol). A solution of $Pd(PPh_3)_4$ (11 mg, 10 μmol) in $CHCl_3$ (0.1 mL) was added, and the reaction mixture was stirred for 7 h at room temperature. After addition of CH_2Cl_2 (2 mL), the rotaxane was precipitated with Et_2O (1 mL). PPh_3 was removed by precipitation with acetone. The solution was extracted twice with CH_2Cl_2/NH_4PF_6 and twice with CH_2Cl_2/H_2O. Column chromatography [SiO_2, MeCN:MeOH:NH_4PF_6 (9:1:0% → 9:1:1%)] yielded the product as a red solid (11 mg, 40%). ^{1}H NMR (acetone-d_6): δ 1.23 (s, 9H), 2.31−2.46 (m, 4H), 2.75 (t, 4H), 3.75−4.22 (m, 96H), 4.67−4.79 (m, 4H), 6.19 (s, 8H), 6.26 (s, 2H), 6.32 (s, 2H), 6.53 (s, 4H), 6.81−6.97 (m, 12H), 7.01 (d, 4H), 7.10 (d, 4H), 7.18−7.23 (m, 12H), 7.31−7.45 (m, 42H), 7.52−7.63 (m, 6H), 7.86 (d, 4H), 8.17 (s, 8H), 8.30−8.42 (m, 20H), 8.74 (s, 2H), 9.44−9.50 (m, 12H), 9.56−9.60 (m, 4H). MALDI−TOF (dihydroxybenzoic acid matrix): *m*/*z* 4738 ($M - 5\ PF_6$)$^+$, 4593 ($M - 6PF_6$)$^+$, 4448 ($M - 7\ PF_6$)$^+$;

Dimer—OH (32b·8PF$_6^-$): *o*-Nitrophenol (0.9 mg, 7 μmol) and Bu_4NF (6 μL, 6 μmol) were added to a solution of **30b**·8PF_6^- (27 mg, 4.8 μmol) in MeCN (0.2 mL). After 30 min, CH_2Cl_2 was added and extracted twice with H_2O/NH_4PF_6 and twice with water. The rotaxane was precipitated from the organic phase with Et_2O, yielding the product as a red solid (22 mg, 85%). ^{1}H NMR (acetone-d_6): δ 2.31−2.46 (m, 4H), 2.75 (t, 4H), 3.75−4.22 (m, 96H), 4.67−4.79 (m, 6H), 5.35 (d, 1H), 5.47 (d, 1H), 6.12 (m, 1H), 6.19 (s, 8H), 6.26 (s, 2H), 6.32 (s, 2H), 6.53 (s, 4H), 6.81−6.97 (m, 12H), 7.01 (d, 4H), 7.10 (d, 4H), 7.18−7.23 (m, 12H), 7.31−7.45 (m, 42H), 8.17 (s, 8H), 8.30−8.42 (m, 20H), 8.74 (s, 2H), 9.44−9.50 (m, 12H), 9.56−9.60 (m, 4H). MALDI−TOF (dihydroxybenzoic acid matrix): *m*/*z* 4540 ($M - 5\ PF_6$)$^+$, 4395 ($M - 6PF_6$)$^+$, 4250 ($M - 7\ PF_6$)$^+$.

Tetramer (33b·16PF$_6^-$): Dimer−COOH **31b**·8PF_6^- (6.9 mg, 1.3 μmol) and Dimer−OH **32b**·8PF_6^- (5.6 mg, 1.1 μmol) were dissolved in dry MeCN (0.15 mL). DMAP (0.26 mg, 2.1 μmol) in MeCN (10 μL), TosH (0.4 mg, 2.0 μmol) in MeCN (10 μL), and DCC (0.9 mg, 4.2 μmol) in MeCN (10 μL) were added. After 4 days at room temperature, DCC (2 mg) was added. After 7 days the reaction mixture was extracted with CH_2Cl_2/NH_4PF_6 and twice with CH_2Cl_2/H_2O, and the product subsequently precipitated from CH_2Cl_2/Et_2O. Column chromatography [SiO_2, MeCN:MeOH:NH_4PF_6 (9:1:0% → 9:1:1.5%)] yielded the pure tetramer as a red solid (4.0 mg, 35%). ^{1}H NMR (acetone-d_6): δ 1.23 (s, 9H), 2.31−2.46 (m, 8H), 2.75 (t, 8H), 3.75−4.22 (m, 192H), 4.67−4.79 (m, 10H), 5.35 (d, 1H), 5.47

(d, 1H), 6.12 (m, 1H), 6.19 (s, 16H), 6.26 (s, 4H), 6.32 (s, 4H), 6.53 (s, 8H), 6.81−6.97 (m, 28H), 7.01 (d, 4H), 7.10 (d, 4H), 7.18−7.23 (m, 28H), 7.31−7.45 (m, 84H), 7.52−7.63 (m, 6H), 7.86 (d, 4H), 8.17 (s, 16H), 8.30−8.42 (m, 40H), 8.74 (s, 4H), 9.44−9.50 (m, 24H), 9.56−9.60 (m, 8H).

HO—Dimer—COOH (34b·8PF_6^-): To a solution of the dimer−OH **32b**·8PF_6^- (22 mg, 4.2 μmol) in $CHCl_3$ (0.1 mL) were added acetone (0.1 mL), acetic acid (14 μL, 0.25 mmol), and NMM (14 μL, 0.13 mmol). A solution of $Pd(PPh_3)_4$ (10 mg, 8 μmol) in $CHCl_3$ (0.1 mL) was added, and the reaction mixture was stirred for 3 h. After addition of CH_2Cl_2 (2 mL), the rotaxane was precipitated with Et_2O (1 mL). PPh_3 was removed by precipitation with acetone. Precipitation from $CHCl_3/Et_2O$ yielded the product as a red solid (20 mg, 91%). ^{1}H NMR (acetone-d_6): δ 2.31−2.46 (m, 4H), 2.75 (t, 4H), 3.75−4.22 (m, 96H), 4.67−4.79 (m, 4H), 6.19 (s, 8H), 6.26 (s, 2H), 6.32 (s, 2H), 6.53 (s, 4H), 6.81−6.97 (m, 14H), 7.01 (d, 2H), 7.10 (d, 2H), 7.18−7.23 (m, 14H), 7.31−7.45 (m, 42H), 8.17 (s, 8H), 8.30−8.42 (m, 20H), 8.74 (s, 2H), 9.44−9.50 (m, 12H), 9.56−9.60 (m, 4H). MALDI−TOF: *m*/*z* 4051 [M − 8PF_6]$^+$, 4196 [M − 7 PF_6]$^+$, 4341 [M − 6PF_6]$^+$, 4486 [M − 5 PF_6]$^+$, 4631 [M − 4PF_6]$^+$.

Polymer (35b·*n*PF_6^-). The difunctional dimer **34b**·8PF_6^- (20 mg, 3.8 μmol), DMAP (0.9 mg, 8 μmol), and TosH (1.3 mg, 7 μmol) were dissolved in dry MeCN (0.05 mL). DCC (2.4 mg, 12 μmol) was added and was again added after 2 days (1.6 mg). After 7 days, the product was precipitated twice from CH_2Cl_2/Et_2O and subsequently extracted with CH_2Cl_2/NH_4PF_6 and twice with CH_2Cl_2/H_2O to yield the polymer as a red solid (16 mg, 80%).

Acknowledgment. The authors thank B. Kwant and J. Drakopoulou for their assistance in the synthetic work, M. Jeronimus-Stratingh for performing the electron spray MS experiments, and A. Kiewiet for the high-resolution MS measurements. This work was financially supported by the Netherlands Foundation for Chemical Research (NWO−CW).

Supporting Information Available: Text discussing the design of the rotaxane monomer, bromination of bis(bromomethyl)benzoic acid, and stability of the rotaxane monomers, a table giving ^{1}H NMR data for the byproducts formed in the synthesis of **16**, and figures showing the structures of the byproducts formed in the synthesis of **16** and a MALDI-TOF spectrum of **1a**·4PF_6^-. This material is available free of charge via the Internet at http://pubs.acs.org.

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MA034521T