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A Photoswitchable Rotaxane with an Unfolded Molecular Thread

Sebastian Schmidt-Schäffer,[a] Lutz Grubert,[a] Ulrich W. Grummt,[b] Karin Buck,[a] and Werner Abraham*[a]

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Novel [2]rotaxanes containing the tetracationic cyclophane cyclobis(paraquat-4,4-biphenylene) and a dumbbell-shaped molecular thread incorporating a photoactive diarylcycloheptatriene station as well as a photo-inactive aryl station have been synthesized with yields of nearly 30% by the coupling of two halves of the molecular thread. Each half incorporates one of the two stations which are recognized by the tetracationic ring. The switch principle is based on photoheterolysis of a diarylcycloheptatriene bearing a suitable leaving group such as a methoxy substituent. The rotaxanes were transformed into the related rotaxanes incorporating a diaryl tropylium unit by electrochemical oxidation. The co-conformation of all rotaxanes was determined by ^{1}H NMR and UV/Vis spectroscopy. It has been shown that the occupation of the two different stations by the tetracationic ring depends both on the electron donor capacity of these stations and on the chain units between the stations. The desired preferred occupation of the diarylcycloheptatriene station was achieved by fine tuning both the stopper group at the end of the molecular thread and the number of oxygen atoms within the chain. By tuning the chain length it has also been achieved that both of the rotaxanes incorporating the diarylcycloheptatriene unit and the tropylium-containing rotaxanes adopt an unfolded structure in solution. The tetracationic ring resides exclusively on the second aryl station within the tropylium rotaxanes. Switching between co-conformations of the cycloheptatrienyl-containing rotaxanes and the tropylium-containing rotaxanes can be achieved by photoheterolysis of the methoxy-substituted diarylcycloheptatriene, yielding the tropylium rotaxane, which reacts thermally back to the cycloheptatriene rotaxane, and thus closes the switching cycle.

Introduction

Catenanes and rotaxanes are supramolecules, the components of which are mechanically interlocked. Nondegenerated rotaxanes consist of a ring and a threadlike component, incorporating two different recognition sites (stations). These stations control the interaction between the ring and the thread components.[1] Depending on the nature of the interaction, external stimuli can change the relative positions of the ring on the molecular thread by changing the interaction between the ring and the stations. This type of large-amplitude shuttling process can be triggered by chemical, electrochemical, and photochemical stimuli.[2] Photochemical and electrochemical energy, in particular, are of great interest as driving forces, because with them, no waste products are formed during the driving process. Such bistable rotaxanes can serve as archetypical molecules for the development of nano-, photo-, or electromechanical systems.[3] Nanoelectromechanical systems such as catenanes and rotaxanes have already been used in electronic devices.[4]

The tetracationic ring cyclo-bis(paraquat-*p*-phenylene) **1** is a widely-used ring component (see Scheme 3). We recently reported the synthesis and photochemical switching of a bistable rotaxane in which the ring component is **1** and the molecular thread contains a photoactive diarylcycloheptatriene (CHT) station and anisole as the second station.[5]

The noncovalent interactions between the ring and the two constitutionally different stations are of electrostatic, π-stacking, charge-transfer, and hydrogen-bonding nature.[6] Ring movement along the molecular thread stimulated by light or electron transfer is expected to occur against an activation barrier, since only very weak interactions between the ring and the thread are possible outside of the recognition stations.[7]

The different sets of noncovalent interactions are primarily determined by the electron donor capacity of the two recognition sites.[8] The ring therefore resides preferentially on the CHT station. However, NMR spectroscopic investigation has shown that the rotaxane adopts a folded conformation enabling a side-by-side π-π stacking interaction of the weaker electron donor station with the ring, thus optimizing binding energy. A nonfolded conformation is desirable for ring movement over a long distance.

[a] Humboldt-University, Institute of Chemistry,
Brook-Taylor-Str. 2, 12489 Berlin, Germany
Fax: +49-30-20937266
E-mail: abraham@chemie.hu-berlin.de
[b] Friedrich-Schiller-University, Institute of Physical Chemistry,
Helmholtzweg 4, 07743 Jena, Germany

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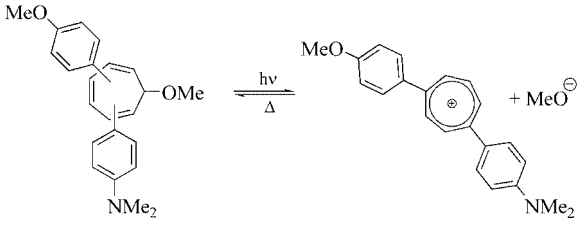
We therefore attempted to obtain new rotaxanes exhibiting this type of extended structure in solution.

In this paper, we describe the synthesis of several pairs of CHT-containing and related tropylium (Tr)-containing bistable rotaxanes, their characterization by NMR and UV/Vis spectroscopy, and their switching by light and by protons. Two pairs exhibited unfolded conformations in both the CHT-state and the Tr-state.



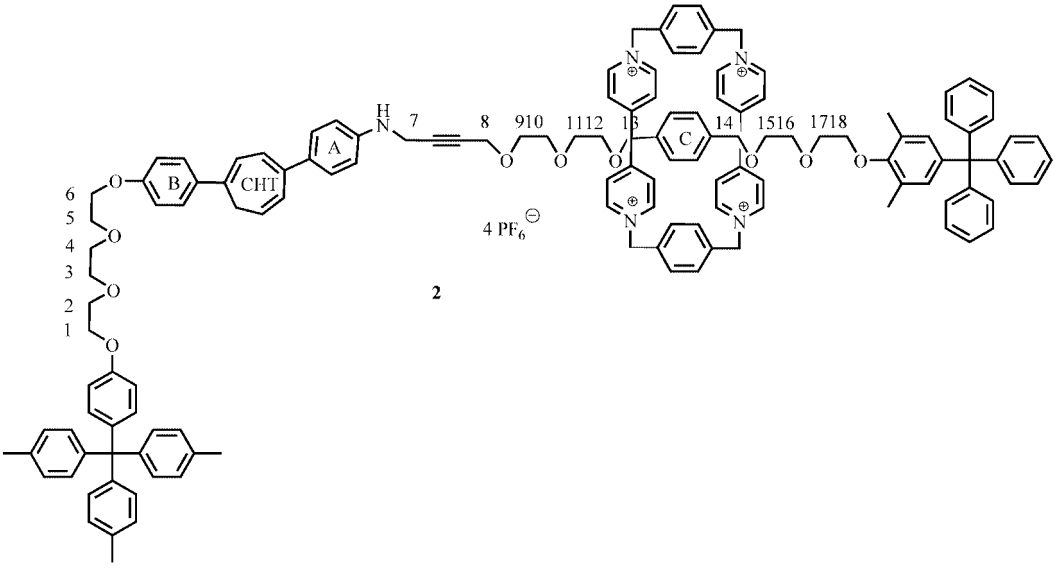
Scheme 1. Principle of photoheterolysis of a methoxy-diarylcycloheptatriene.

Results and Discussion

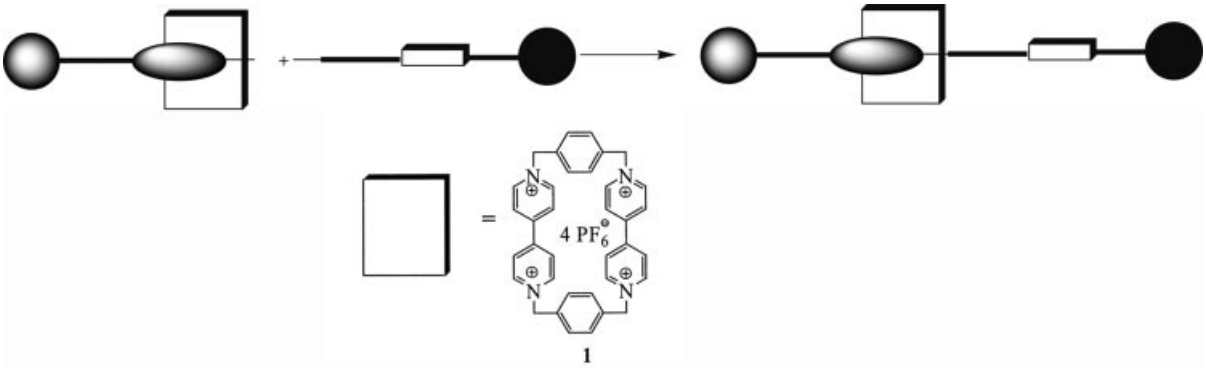
The switch principle is based on photoheterolysis of a diarylcycloheptatriene possessing a suitable leaving group such as a methoxy substituent (see Scheme 1).[9]

Photoheterolysis converts the electron-rich station into an electron-poor recognition site. Due to the generation of the positively charged tropylium ion, the tetracationic ring **1** will be repelled and will move to the weaker electron donor station present within the bistable rotaxane (see Scheme 2). By thermal recombination of the ions, the start conformation is restored, thus closing the switching cycle. The lifetime of the tropylium state must be long enough to allow movement of the ring. The rate constants of such shuttling processes in similar rotaxanes have been determined to be on the order of $10^3\,s^{-1}$.[1a,10] Furthermore, NMR studies of degenerated rotaxanes incorporating diaryl cycloheptatriene stations have revealed that the shuttling process is fast in relation to the timescale of NMR spectroscopy.[11]

In ideal bistable rotaxanes, the ring resides only on one of the two recognition sites. Both π-stacking and electrostatic interactions are controlled by the electron donor ca-



Scheme 2. Rotaxane **2** with numbering of some atoms.



Scheme 3. Principle of rotaxane synthesis.

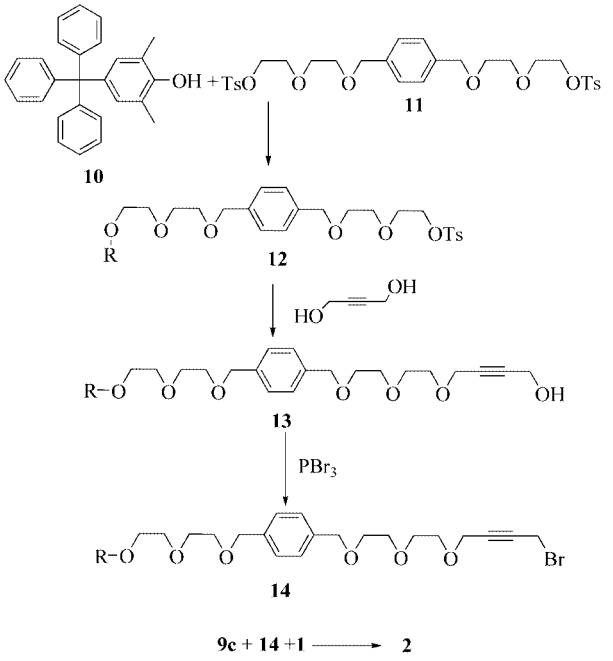
pacity of the stations, which is related to the oxidation potential. Therefore, the differences between the oxidation potentials of the diaryl cycloheptatriene station (A-CHT-B in Scheme 2) and station C should be large. Accordingly, we chose the xylyl station to be the photoinactive second station in a bistable rotaxane (see Scheme 2).

The syntheses of the new rotaxanes were carried out by a rather unusual pathway: two halves of the molecular thread, each having one recognition site and a bulky group at the end (see Scheme 2), were combined in the presence of ring **1**, as outlined in Scheme 3.

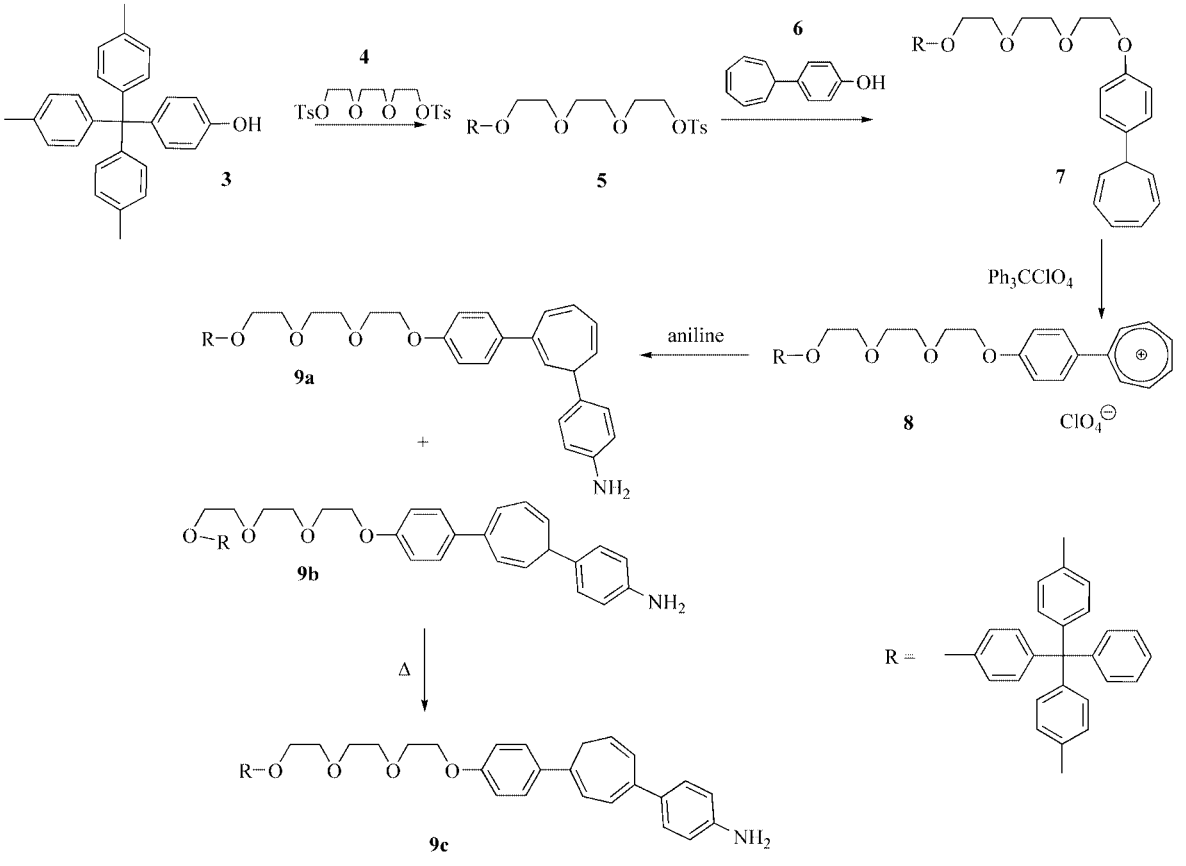
The two halves of the molecular thread of rotaxane **2** were synthesized as outlined in Scheme 4 and Scheme 5.

Rotaxane **2** was self-assembled using compounds **9c** and **14** as templates for the tetracationic ring **1** and binding together the two halves of the thread by alkylation of the amino group of compound **9c** in the presence of 2,6-di-*tert*-butyl-4-methylpyridine. Rotaxane **2** was isolated in 38% yield.

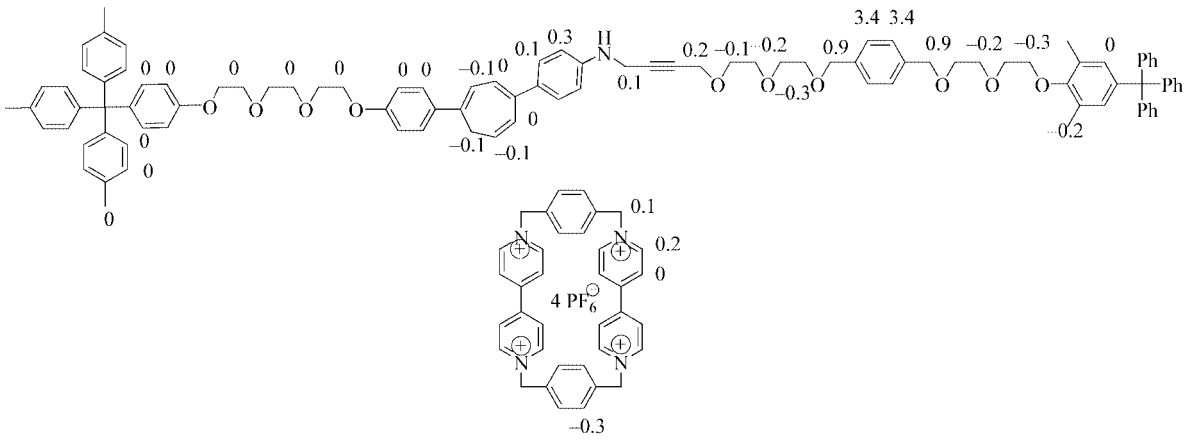
^{1}H NMR spectroscopy is useful for monitoring the distribution of the ring between the two recognition sites, i.e., diaryl cycloheptatriene (A-CHT-B in Scheme 2) and xylene (C). The chemically-induced shift values were calculated by comparison of the uncomplexed and complexed recognition stations, i.e., compounds **9c** and **14** vs. rotaxane **2**. The proton signals were attributed to the different aromatic groups with the aid of two-dimensional NMR spectroscopy, such as C–H-COSY, H–H-COSY, and ROESY. The chemically induced shift (CIS) values determined for rotaxane **2** are given in Scheme 6.



Scheme 5. Synthesis of the eastern half of the molecular thread.



Scheme 4. Synthesis of the western half of the molecular thread.

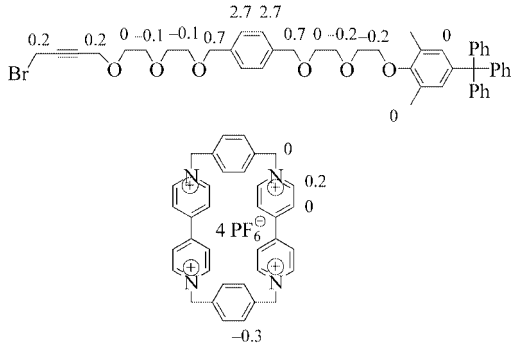


Scheme 6. Chemically-induced shift (CIS) of some proton resonances of rotaxane **2** calculated by comparison of related proton signals of fragments of the uncomplexed molecular thread and of rotaxane **2** (δ**9c**-δ**2** and δ**14**-δ**2**), and of the uncomplexed ring **1** and **2**.

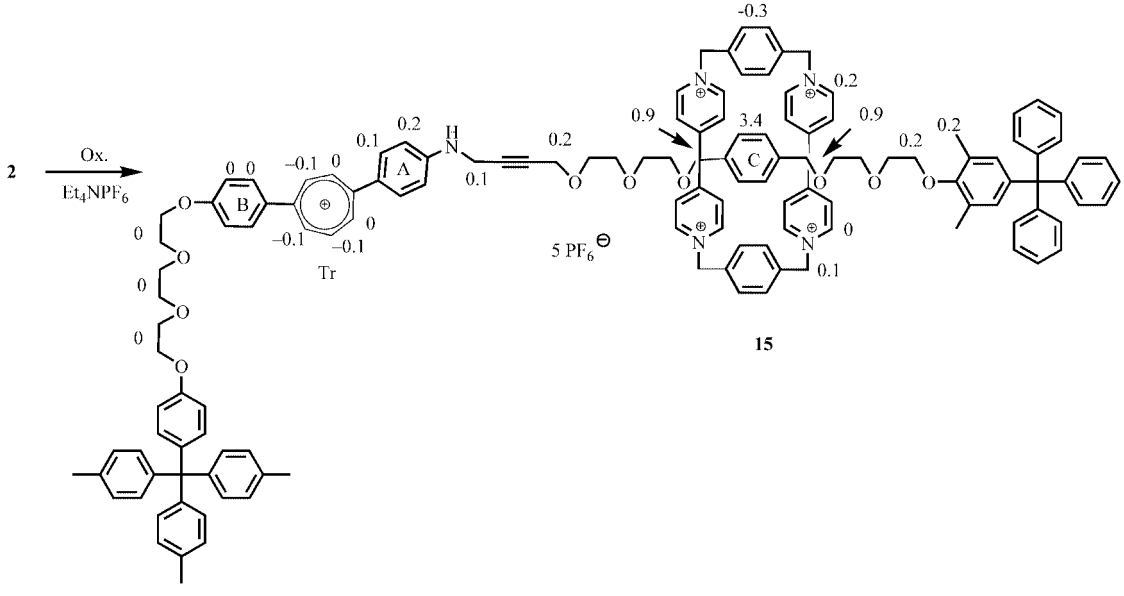
The strong upfield shift of the protons of station C clearly indicates that ring **1** preferentially encircles this recognition site. This behavior is surprising because the CHT station ($E_{1/2}^{ox}$ = 0.5 V[5]) is a much stronger electron donor than xylene ($E_{1/2}^{ox}$ = 1.3 V[12]). Indeed, it has recently been found with other rotaxanes that competition between dialkoxybenzene and xylene is decided in favor of the station derived from hydroquinone.[13]

In order to gain insight into the interaction between the xylene station and the tetracationic ring, we studied the pseudorotaxane formed in a 1:1 mixture (3×10^{-2} M) of compounds **14** and **1**. The results depicted in Scheme 7 confirmed the strong upfield shift of the xylene station.

The CIS values observed with rotaxane **2** and the pseudorotaxane in Scheme 7 are very similar, indicating the rela-



Scheme 7. CIS values of the protons of the pseudorotaxane **1/14** calculated by comparison of the uncomplexed and complexed components.



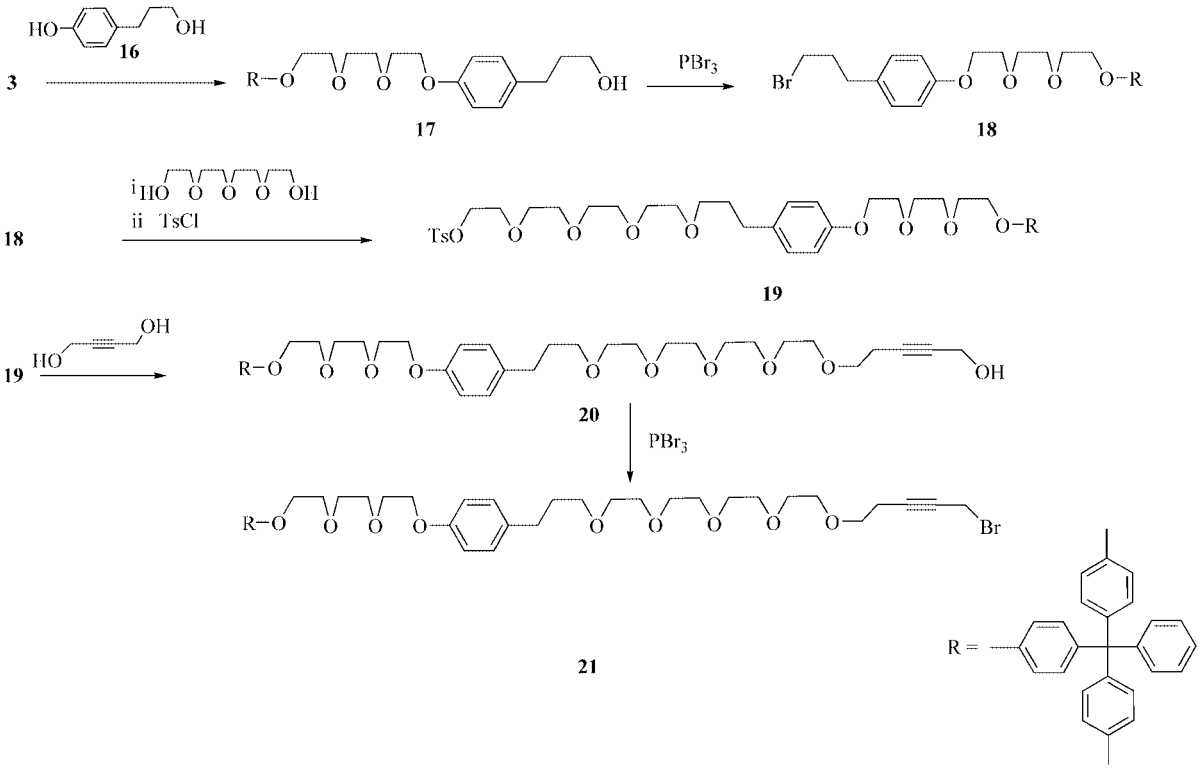
Scheme 8. CIS values of some protons of rotaxane **15** calculated by comparison of related protons of molecular thread **41** (for the tropylium ion region) and of **14** (for the region of station C).

tively strong interaction of the xylene station with the tetracationic ring. This finding emphasizes that not only the electrostatic, π-stacking, and CT-interaction forces control recognition, but that the hydrogen bonds formed between the oxygen atoms of the oxyethylene chains and the acidic protons of ring **1** play an important role in it as well.[14]

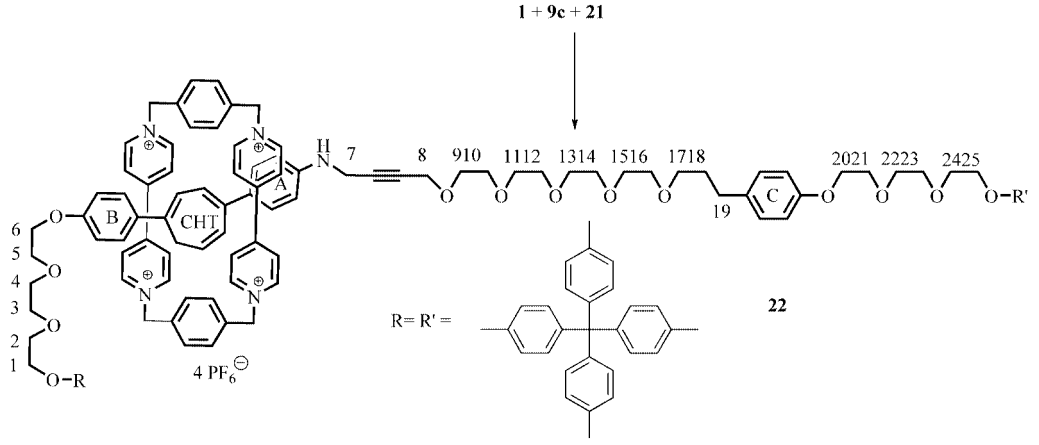
The rotaxane was electrochemically oxidized, providing the violet tropylium rotaxane **15** (Scheme 8).

The CIS values of the protons of station C given in Scheme 8 are identical to those in Scheme 6. Accordingly, the position of the ring within the rotaxane is not changed by traversal from **2** to **15**, and this pair of rotaxanes is therefore useless for any switching process.

For this reason, a photo inactive station had to be chosen, with an oxidation potential also considerably lower than that of the A–CHT–B station, but avoiding the neighboring of this station by two oxyethylene chains. We decided to incorporate an anisole station bearing an alkyl chain on one side instead of the oxyethylene chain. For this purpose, the eastern half of the molecular thread had to



Scheme 9. Synthesis of the eastern half of the molecular thread of rotaxane **22**.



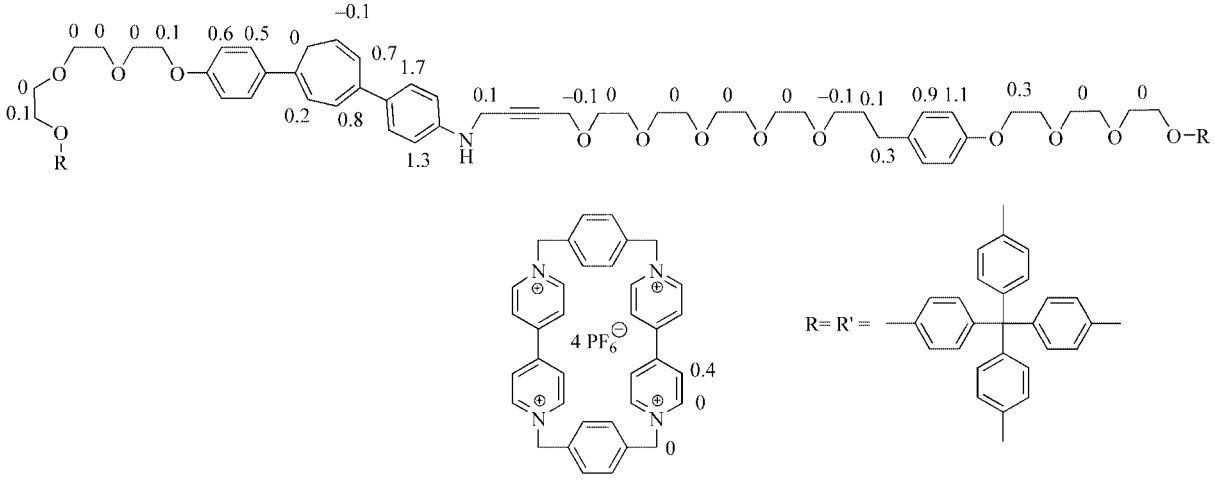
Scheme 10. Synthesis of rotaxane **22**.

be newly designed (see Scheme 9). The rotaxane synthesis following the reaction sequence to **2** (Scheme 10) provides compound **22** in 27% yield.

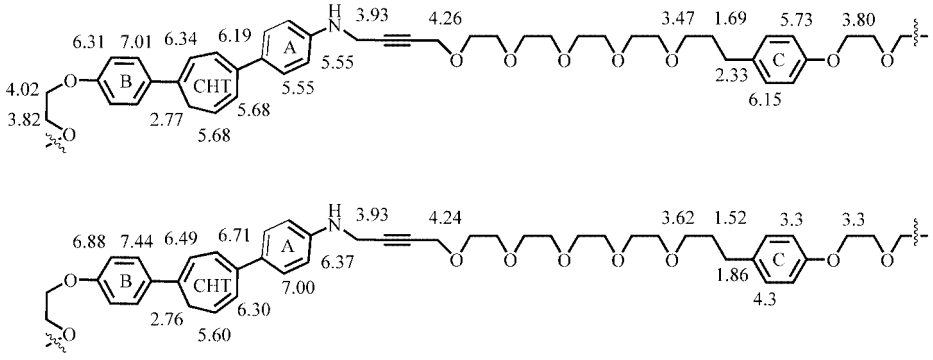
Assignment of the proton resonances observed for **22** in acetonitrile solution to the different aromatic groups is difficult because, due to dynamic processes, not all proton resonances appear at room temperature. However, at 343 K, the most important proton resonances appear and can be attributed to the two stations involved, with the help of two-dimensional methods such as determination of H–H-, C–H- and NOE-cross peaks. Assignment of the strongly upfield-shifted resonances of aromatic protons to the substituents A and B is possible based on C–H-COSY cross peaks because, unlike the ^{1}H signals, the ^{13}C resonances are only marginally shifted due to interaction with ring **1**. The assignments were further confirmed by NOE effects (ROESY spectra). The extent of participation of station C in the interaction of the molecular thread with **1** can be deduced from the resonances of the protons at positions 18 and 19 (Scheme 10). These protons are shifted upfield together with the protons of C, provided that station C is occupied by the tetracationic ring. The resonances of 18- and 19-H are easy to identify, because these signals are separated from other proton resonances.

The CIS values calculated by comparison of the NMR spectra of compound **22** and those of compounds **20** and **9c** are given in Scheme 11.

The expected preferred occupation of the CHT station can be determined based on CIS values. In addition, however, station C interacts with the ring component by a fast shuttling process of the ring between the two stations or an interaction of C alongside the outer bipyridinium units of the ring due to folding of the thread. The differences in shielding effects found for protons 7 and 8 and 17 and 18, respectively (see Scheme 10), are most likely related to folding of the glycol chain between the two stations, thus bringing the two stations within the vicinity of the tetracationic ring.[5] This interpretation is supported by the observation of additional sets of signals (with portion of 40%) for protons 17–19 and aromatic protons of C. These protons are shifted strongly upfield, indicating a strong interaction with ring **1**. Because the integrity of compound **22** is guaranteed by mass spectra and elemental analysis, only isomers and conformers are possible as origins of the additional signal sets. However, isomers of the cycloheptatriene could not be detected. Instead, a second set of CHT-protons was observed, less upfield-shifted than that of the main conformer. Further, isomers of the CHT fragment cannot explain the



Scheme 11. CIS values obtained for rotaxane **22**.



Scheme 12. Proton resonances of the two conformers of rotaxane **22** (δ, [D_6]acetone solutions).

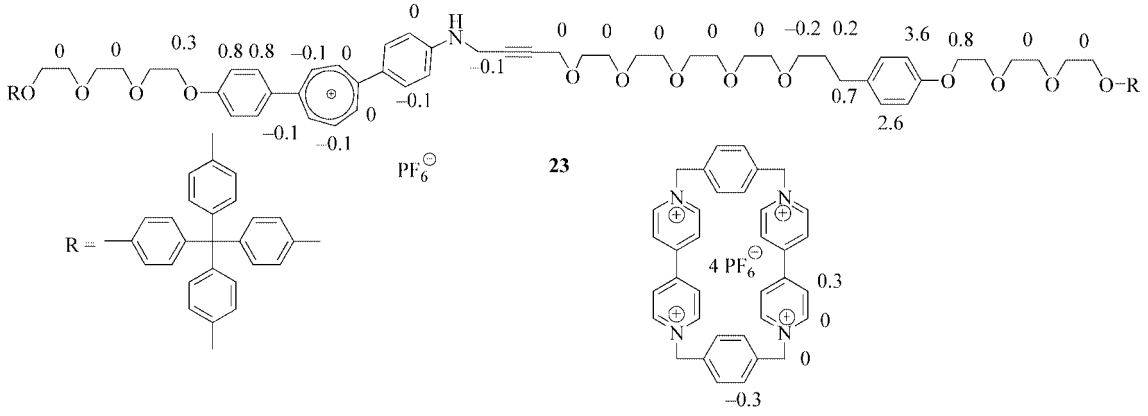
additional sets of signals in the region of the proton resonances of C. Therefore, additional co-conformers with ring **1** residing on station C are most likely present. The proton resonances of two co-conformers are depicted in Scheme 12.

Surprisingly, the exchange between these conformers is slow, on the time scale of NMR spectroscopy, even at 65 °C. The temperature-dependent spectra measured between 5 °C and 65 °C (see Supporting Information) reveal a downfield-shift of the protons of station C with increasing temperature and an upfield-shift of the protons of phenyl group A; however, the ratio of the signals remains constant. Obviously, the forces driving the interaction between ring **1** and the anisole station are not weak enough to yield exclusive occupation of the diaryl cycloheptatriene station. Again, the electron donor capacity of the station is not the only property governing interaction with the tetracationic ring.

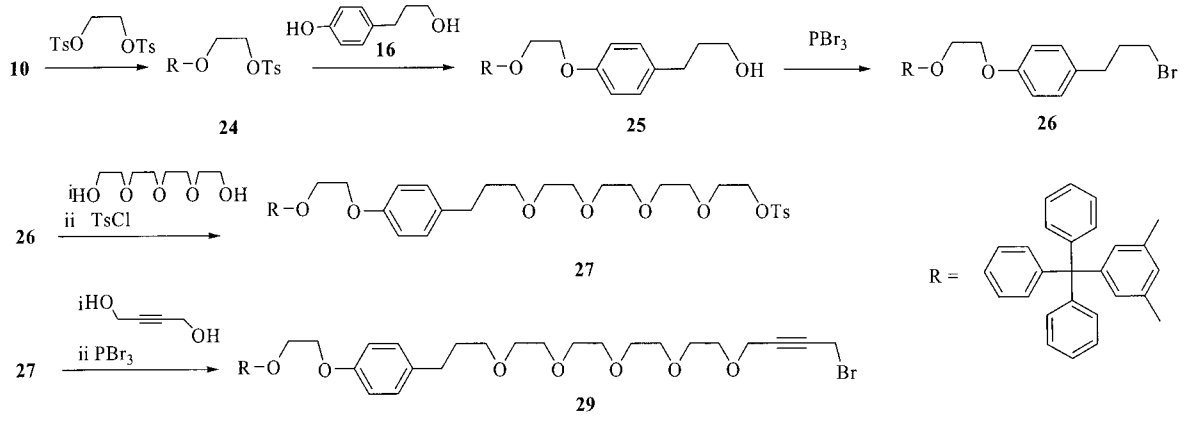
The oxidation of rotaxane **22** provides the tropylium rotaxane **23**, consisting of only one conformer. As expected, the calculated CIS-values confirmed that ring **1** resides on station C (see Scheme 13). However, because in rotaxane **22** only 60% of the desired co-conformer exists with ring **1** residing on the CHT station, studies of rotaxane pair **22/23** were not continued.

We expected that the driving forces leading to the interaction of station C with the ring could be weakened by shortening of the oxyethylene chain between the phenol oxygen and the bulky stopper group. The trityl stopper should additionally hinder any interaction between the oxygen atoms of the chain with the acidic protons of **1** by incorporation of methyl groups in the phenol fragment bearing the trityl group. For this purpose, the eastern half of the molecular thread was newly designed. The sequence of synthesis is analogous to that for the molecular thread of rotaxane **22** (see Scheme 14).

The western half of the molecular thread incorporating the CHT station was modified in relation to the stopper fragment. Compound **33c** (Scheme 15) was used for the synthesis of rotaxane **34** (Scheme 16). Compound **33c**, with the trityl-dimethylphenol fragment, has more steric requirements than the adamantoyl group present in the western half of thread **36** (see Scheme 17). However, it was found (see below) that the stopper fragment on this side of the molecular thread does not affect the co-conformation of the rotaxanes. Indeed, it was found that modification of the linker at station C was decisive. Both rotaxane **34** and rotaxane **37** exhibit exclusive occupation of the CHT station. Additionally, there are no hints of a folded structure of the



Scheme 13. CIS values obtained for the tropylium rotaxane **23** by comparison of compound **41**, molecular thread **20**, uncomplexed ring **1**, and rotaxane **23**.

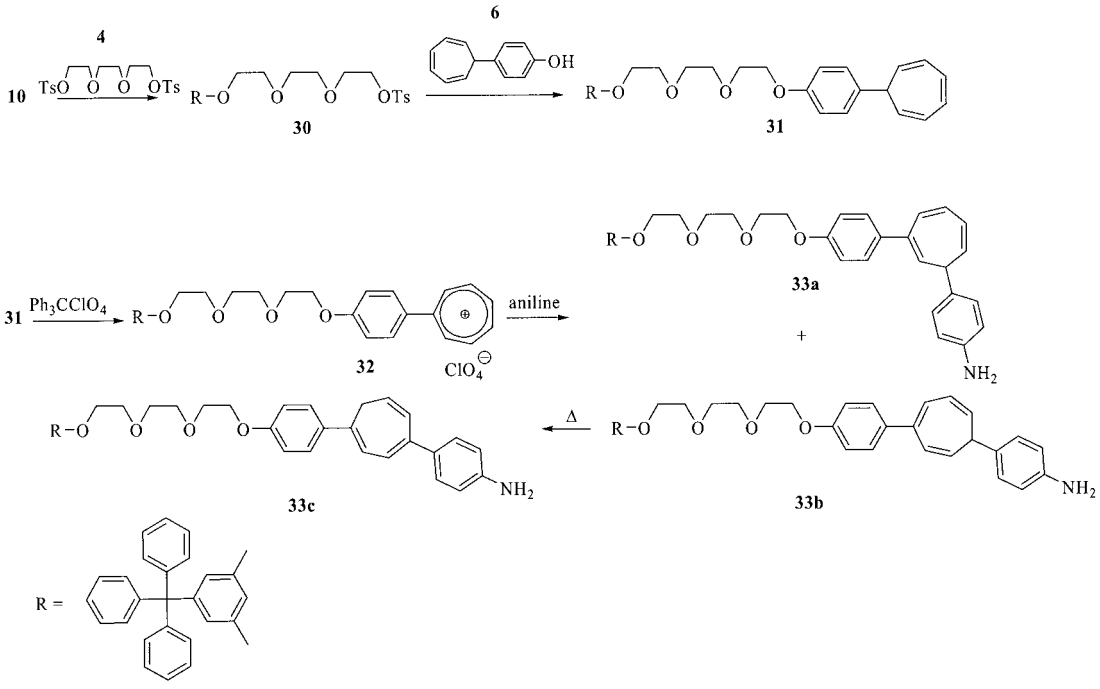


Scheme 14. Synthesis of the eastern half of the molecular thread of rotaxane **34**.

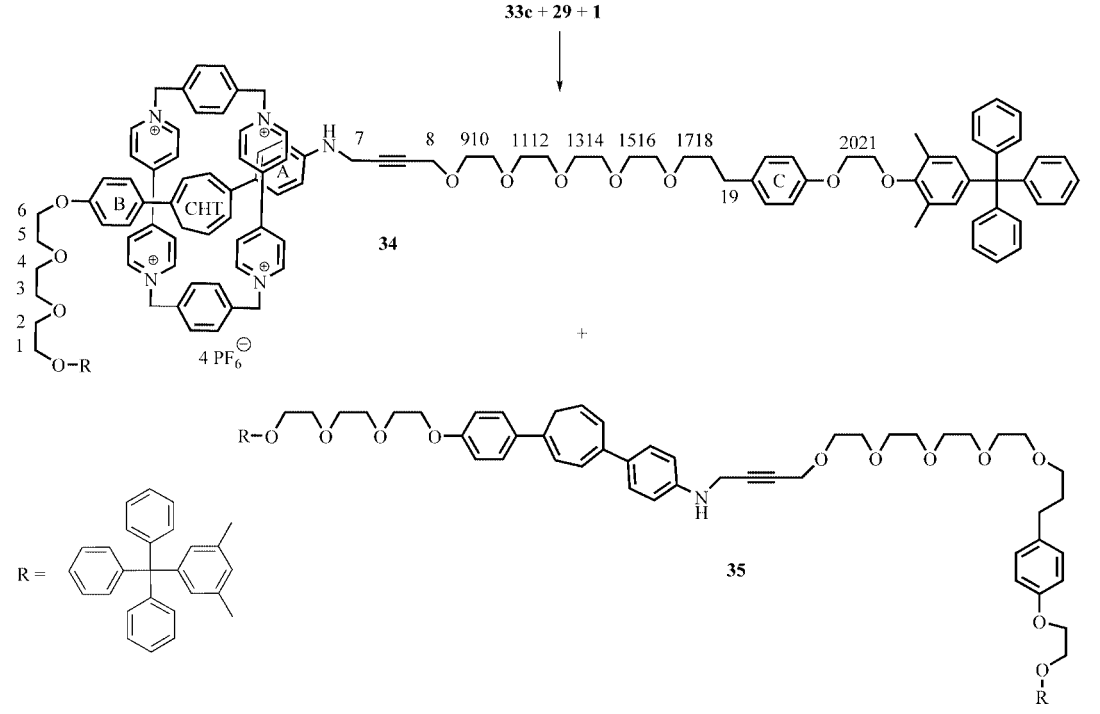
molecular thread resulting in an interaction of station C alongside the bipyridinium units of ring **1**. The CIS values of the protons both of the CHT ring and the aromatic substituents A, B, and C given in Scheme 18 reveal the desired residence of ring **1** on the CHT station with a clear preference for the A-substituent.

Assignment of the signals was performed by two-dimensional NMR spectroscopy, such as C–H-COSY, H–H-COSY and ROESY (see Supporting Information). Furthermore, marginal shifts of 18-H- and 19-H-proton resonances are a strong indication that interaction of station C with **1** fails.

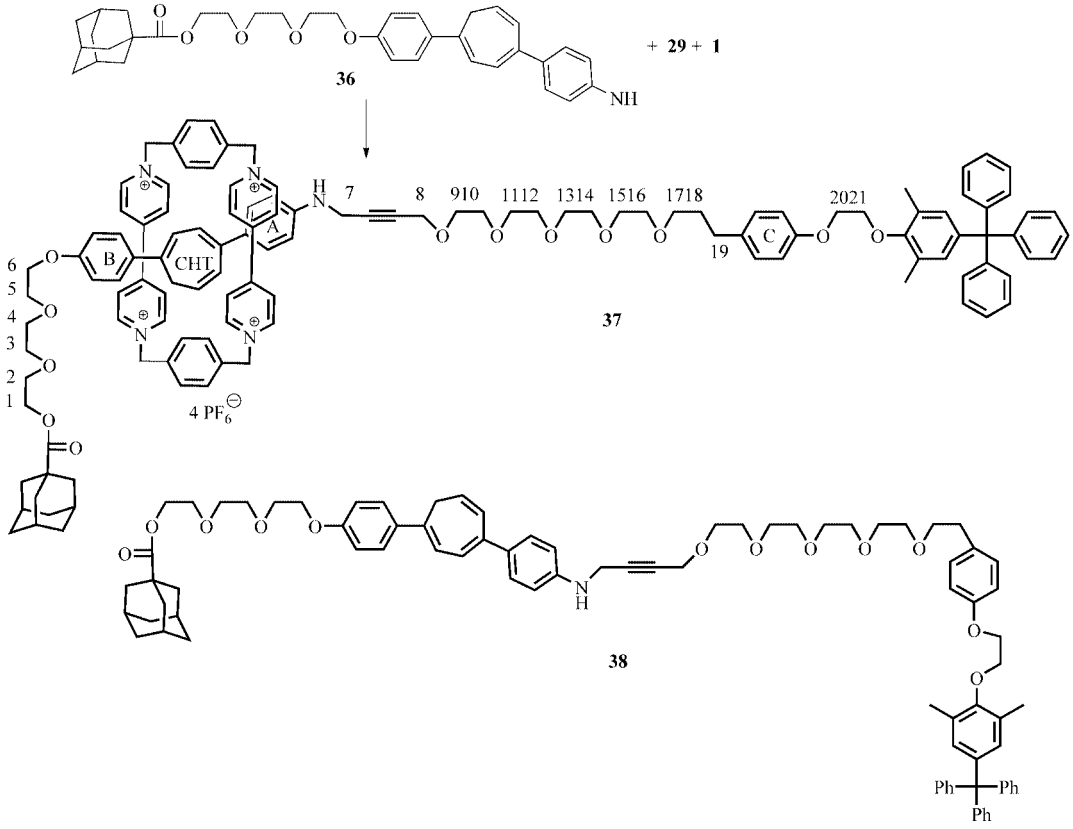
NOE effects observed in the ROESY spectra of rotaxane **37** are additionally marked by arrows in Scheme 18. Residence of ring **1** on the CHT station is indicated by contacts between both the ß-protons (in relation to N) of the bipyri-



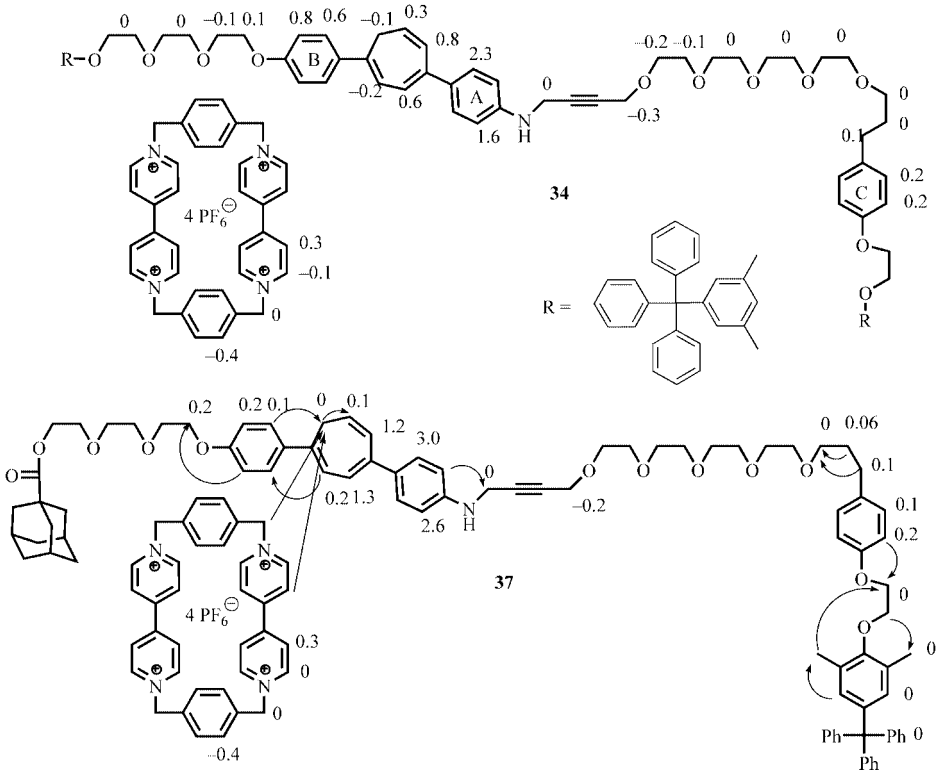
Scheme 15. Synthesis of the western half of the molecular thread of rotaxane **34**.



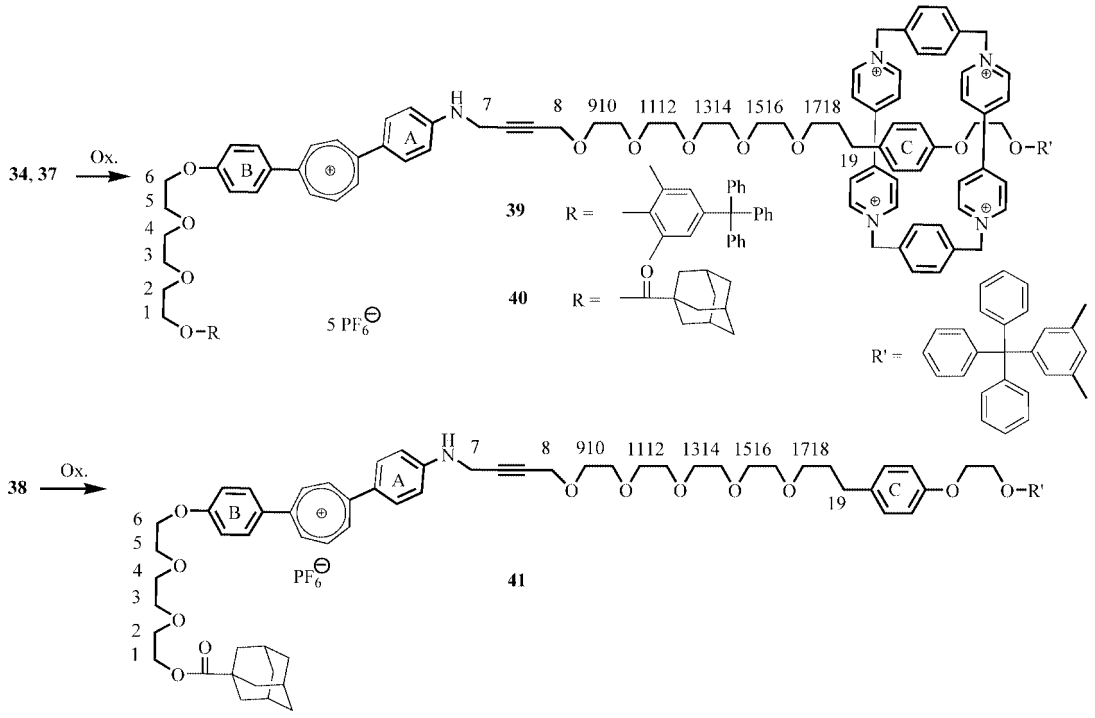
Scheme 16. Synthesis of rotaxane **34**.



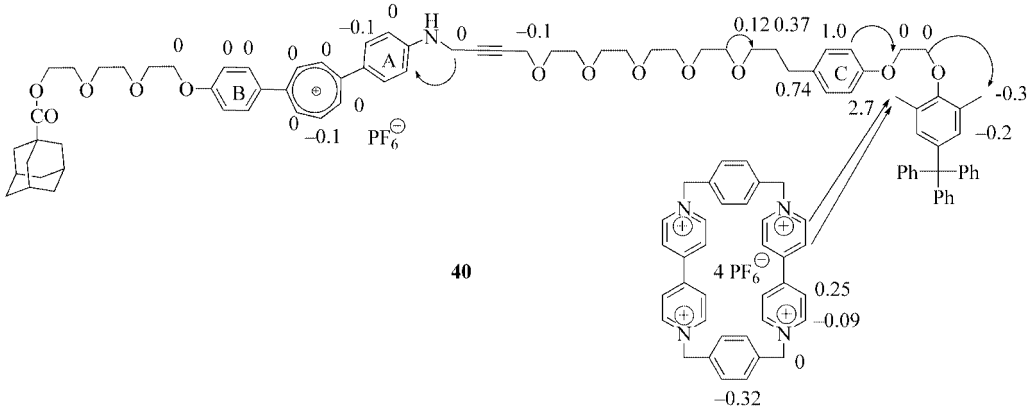
Scheme 17. Synthesis of rotaxane **37**.



Scheme 18. CIS values of proton resonances of rotaxanes **34** and **37** obtained by comparison of the proton resonances of uncomplexed molecular threads and compound **2** with related proton resonances measured in the rotaxanes. Arrows mark NOEs between protons observed by ROESY spectra.



Scheme 19. Electrochemical oxidation of rotaxanes **34** and **37** and molecular thread **38**.



Scheme 20. CIS values calculated for rotaxane **40**. Arrows mark NOEs between protons observed by ROESY spectra.

dinium unit and the benzylic protons of **1** (see Supporting Information).

Again, the corresponding tropylium rotaxanes **39** and **40** were obtained by electrochemical oxidation of compounds **34** and **37**. The molecular thread **38** was also oxidized in order to compare the proton resonances of rotaxane **37** with those of compound **41** (Scheme 19).

Strong upfield shifts of the proton resonances of station C (for compound **40**, see Scheme 20) confirm the change of location of **1** in the rotaxane, for example in traversal from **37** to **40** (Scheme 19). Thus, the proton resonances of 18-H and 19-H, separate from other signals, indicate where the ring resides. Further, occupation of station C is confirmed by ROESY-cross peaks between the α- and ß-protons of ring **1** and the methyl groups of the stopper fragment (see Scheme 20).

Switching Cycle

Introduction of the leaving group into the cycloheptatriene ring is very easy. Both the tropylium rotaxanes **39** and **40** and compound **41** have only to be dissolved in methanol. The long-wavelength absorption band at 550 nm disappears in solutions with concentrations up to 3×10^{-5} M (see Figure 1, a). For solutions of higher concentration, addition of a base such as $NaHCO_3$ to an acetonitrile solution containing 1 M methanol is necessary.

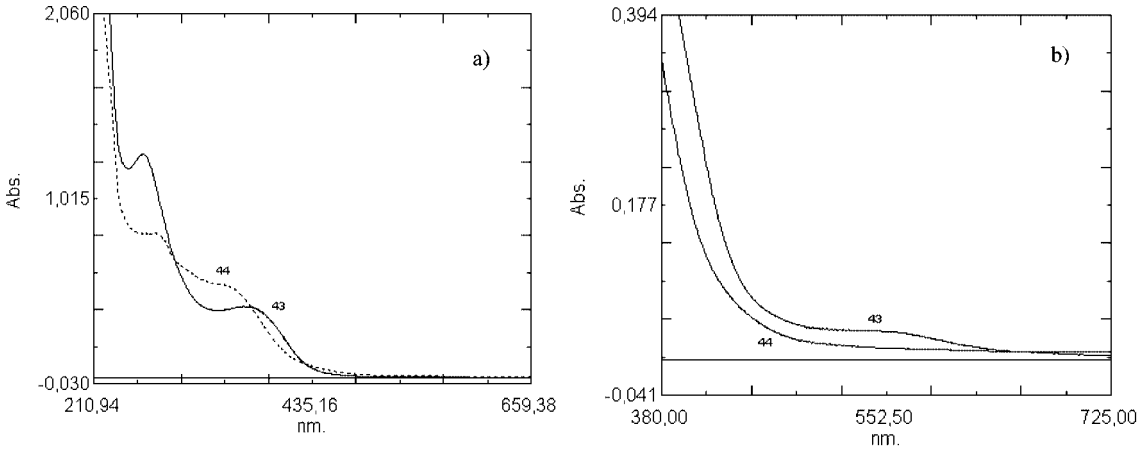
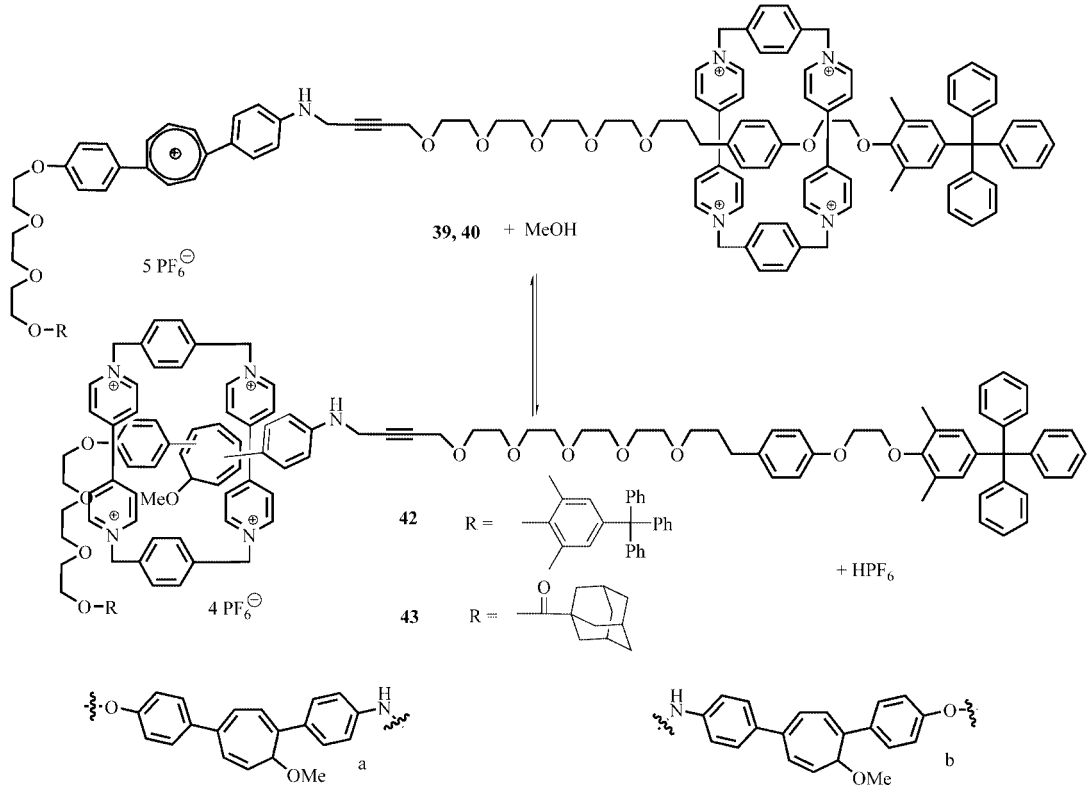


Figure 1. a) UV/Vis absorption spectra of rotaxane **43** (2.5×10^{-5} M) and molecular thread **44** (3×10^{-5} M) in acetonitrile solution containing methanol (1 M). b) Partial UV/Vis-absorption spectra of rotaxane **43** (5×10^{-4} M) and molecular thread **44** (5×10^{-4} M) in acetonitrile solution containing methanol (1 M).

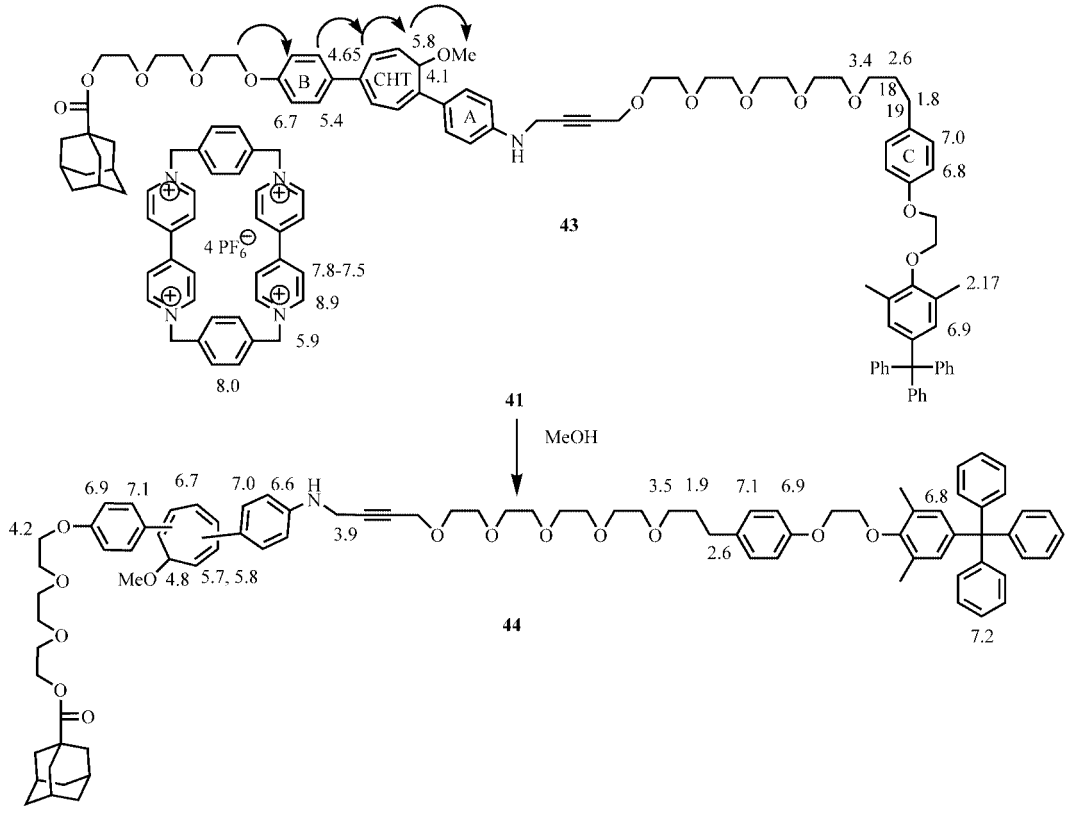
Several isomers of the newly-formed 7-methoxycycloheptatriene derivatives are possible. In the NMR spectra, at least three isomers are visible. However, the appearance of an absorption band around 370 nm (see Figure 1, a) corresponds to the formation of the two main isomers a and b which are thermodynamically favored (Scheme 21).[5]

There are two important differences between the absorption spectra of rotaxane **43** and the corresponding thread **44**. The shoulder at the long-wavelength site of compound **43**, which is due to the diarylcycloheptatriene chromophore, is bathochromically shifted by about 1800 cm^{-1} compared with **44**. Only rotaxane **43** exhibits a weak absorption band around 550 nm (see Figure 1, b), which is assigned to the charge-transfer absorption band of the rotaxane.

Unfortunately, assignment of all the proton signals of the aryl groups is not possible. However, the occupation of the methoxy-substituted CHT station can be determined from two findings: first, the resonances of 18-H and 19-H are not upfield-shifted but are equal to those of molecular thread **41** (Scheme 22, see also Supporting Information). Second,



Scheme 21. Reaction of the tropylium rotaxanes with methanol and the most probable isomers.



Scheme 22. Some proton resonances of rotaxane **43** and thread **44**. Arrows mark NOEs between protons observed by ROESY spectra.

the long-wavelength absorption bands of rotaxanes **42** and **43** are bathochromically shifted compared with the absorption band of molecular thread **44** due to the polar environment induced by tetracationic ring **1**[5] (see Scheme 22 and Figure 1, a).

Photoheterolysis of Rotaxanes 42, 43 and Molecular Thread 44

These three compounds undergo a photoreaction in methanol solution by excitation at a wavelength between 330 and 370 nm, resulting in the formation of the corresponding tropylium methoxides, as monitored by the appearance of intermediates at the absorption band around 570 nm (see Figure 2). Because the co-conformation of the tropylium rotaxanes consists of occupation of station C by ring **1**, movement of the ring from the CHT station to C is initiated by the photoreaction (see Scheme 23).

The lifetime of the rotaxanes in their "tropylium state" is limited by the thermal nucleophilic attack of the solvent on the tropylium in a pseudo-first-order reaction ion-assisted by the methoxide base. In the absence of a base, the reaction of methanol with the tropylium rotaxanes occurs within minutes. For rotaxanes **42** and **43**, the lifetime of the ionic state is 3 s. The reaction of the solvent with the tropylium ion is not hindered by the cationic ring because the latter resides on station C far from the tropylium ring. On the other hand, the ionic state of compound **44** has a longer lifetime of 7 s; the positively charged ring in **42** and **43** may accelerate the nucleophilic attack of the methoxide ion on the tropylium ion.

Quantum yields of photoheterolysis were not determined. However, it is obvious that the quantum efficiency of the photoreaction of molecular thread **44** is about one order of magnitude greater than that of the rotaxanes by comparing the recorded signal intensity observed with equal excitation conditions (compare parts a and b in Figure 2). This is due to the higher rate of non-radiative deactivation of the excited state of the rotaxanes resulting from the existence of a low-lying charge transfer state within the rotaxanes. The quantum yields of the photoheterolysis reaction of model compounds such as shown in Scheme 1 were determined to be in the range of 0.1.[9]

On the other hand, competing photoreactions such as the sigmatropic hydrogen shift observed in molecular thread **44** are quenched in the rotaxanes, allowing more switching cycles of the rotaxanes compared with the thread. The irradiation of the model compound and the molecular thread **44** with 10 laser flashes reduces the intensity of the transient optical absorption due to the related tropylium ions by a factor of about 2. A similar result was obtained by stationary irradiation of diluted solutions of the molecular thread with the unfiltered light of a high pressure mercury lamp. In this case only the absorption band of the diaryl

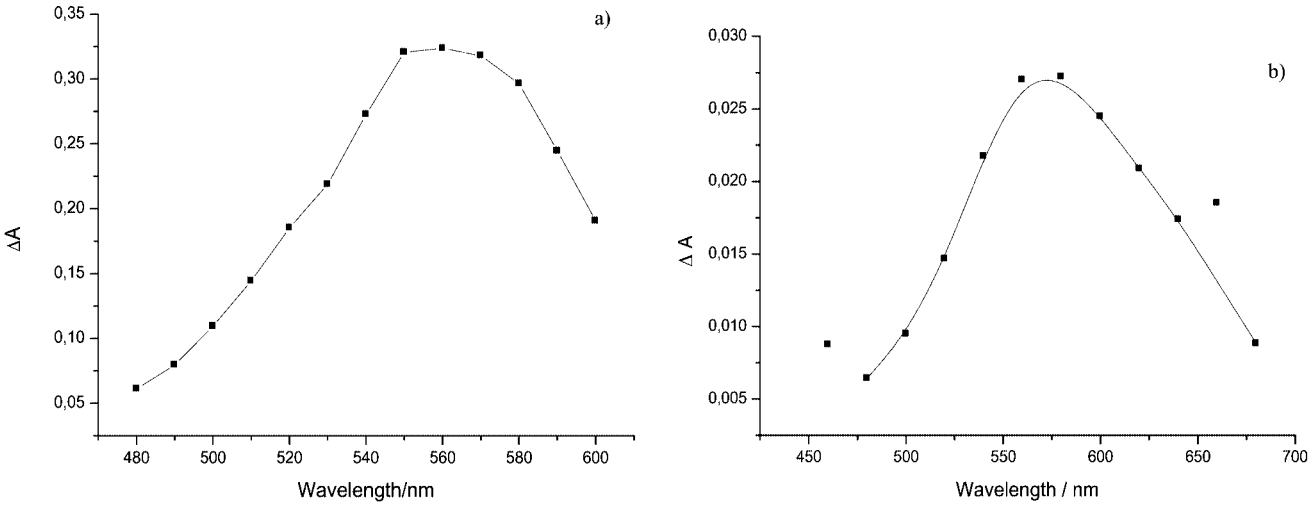
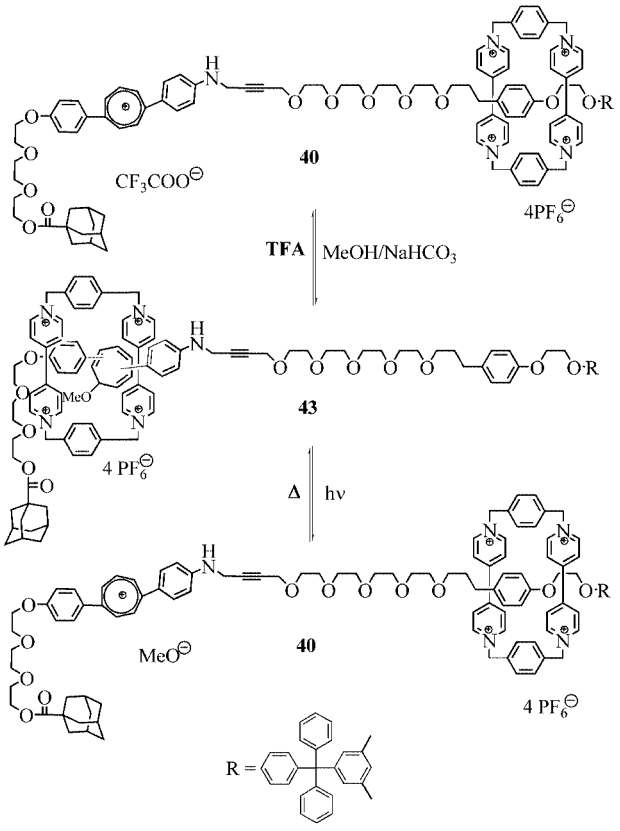


Figure 2. a) Transient absorption spectra observed during flash photolysis of molecular thread **44**. b) Transient absorption spectra observed during flash photolysis of rotaxane **43**.



Scheme 23.

methoxycycloheptatriene chromophore can be monitored, indicating the irreversible degradation of the photoactive subunit (see Supporting Information). The observed spectral changes support the assumption that a sigmatropic hydrogen shift is the competing photoreaction. However, in the case of the rotaxanes, both the flash and the stationary irradiation using equal excitation conditions as mentioned above did not reduce the transient intensity and the intensity of the cycloheptatriene chromophore, respectively, by more than 5%. Accordingly, transient absorption spectra of tropylium rotaxanes could be obtained point by point from consecutively recorded kinetic traces. The same signal intensity monitored at 570 nm was observed after the first and the fifteenth flash.

Besides the light-driven formation of the tropylium rotaxane **40** (with methoxide as anion) from **43**, this reaction can also be initiated by protons. Addition of trifluoroacetic acid (TFA) to rotaxanes **42** and **43** in methanol-containing solutions generates the tropylium rotaxane, and addition of a base such as solid $NaHCO_3$ yields back **42** or **43** (Scheme 23). The chemically-driven cycle can be followed by UV/Vis spectroscopy (see Figure 3).

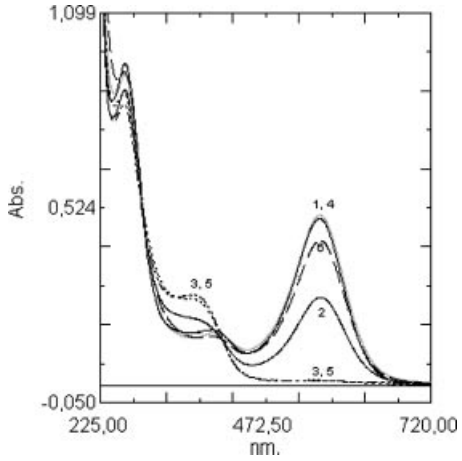


Figure 3. UV/Vis absorption spectra of rotaxane **42**: 1 – rotaxane **39** in acetonitrile solution; 2 – after addition of methanol (0.5 mL/9.5 mL); 3 – after addition of $NaHCO_3$; 4 – addition of TFA; 5 – addition of $NaHCO_3$; 6 – after addition of TFA.

Conclusions

We have demonstrated that the conformation of a rotaxane incorporating a photoactive electron donor station and a second photo-inactive and weaker electron donor station can be fine-tuned in such a way that only one station interacts with the tetracationic cyclophane used as the wheel. Both the electron-donor capability and the adjacent chain units govern the strength of the interaction between the electron-poor ring and the electron-rich photoinactive station. In these rotaxanes, reversible switching between two states is based on the photoheterolysis of methoxycycloheptatrienes incorporated in the molecular thread. The thermal reaction of the solvent methanol with the tropylium ions assisted by the methoxide ion generated by photoheterolysis closes the cycle. The switching cycle can be repeated several times without fading the photoactive unit of the rotaxanes. A switching cycle can also be obtained using acids and bases. The actual state of the system can conveniently be determined by UV/Vis-spectroscopic monitoring of the tropylium absorption band around 550 nm. Due to the extended conformation of the rotaxanes, shuttle movements of large amplitude are initiated by light and thermal energy. Work is in progress to fix these types of switchable rotaxanes onto surfaces.

Experimental Section

General Methods: MeCN was distilled over CaH_2. Silica gel 60 (0.040–0.063 mm) (Fluka) was used for column chromatography (CC). Melting points (m.p.) were determined with a Boetius heating microscope. NMR spectra were recorded on a Bruker DPX 300 (300 MHz), a Bruker Advance 400 (400 MHz) or a Bruker AMX 600 (600 MHz) spectrometer. UV/Vis spectra were recorded with a Shimadzu UV- 2500 PC spectrometer. The flash photolysis apparatus used is of conventional design. Briefly, a cylindrical cell of 10 cm length and 10 mm diameter is positioned in the common focal line of a double elliptical reflector with two flash-lamps. The electrical energy of the flashes was about 900 J (20 μF capacitor, 6.7 kV) the flash duration amounts to 14 μs. Glass filters are inserted between the sample and the flash lamps. In the particular cases, Schott UG2 (maximal transmission at 365 nm) and Schott UG11 (maximal transmission at 330 nm) were used. A Xe high-pressure arc lamp (100 W) serves as the measuring source. The electrical output of the photomultiplier is recorded with the help of a digital oscilloscope and transferred to a personal computer. Data evaluation was performed by non-linear regression using the ALAU program.[15] Transient absorption spectra were obtained point by point from consecutively recorded kinetic traces. Stationary absorption spectra of the solutions were recorded before and after repeated flashing in order to detect irreversible degradation. Steady state photolysis experiments were carried out with acetonitrile solutions by using a 500-W high-pressure mercury lamp. The solutions were irradiated in 1-cm quartz cuvettes. Thermal switching between tropylium rotaxanes and methoxycycloheptatrienyl rotaxanes was done by alternate addition of solid $NaHCO_3$ and acetonitrile solution of trifluoroacetic acid (TFA). Rapid scan (1 to 50 V/s) cyclic voltammetry was performed using a PG 285 IEV potentiostat (HEKA Elektronik). ESI mass spectrometry was carried out with a Finnigan LTQ equipment (Thermo Electron).

Syntheses

Rotaxane 2

a: 4-[Tris(*p*-tolyl)methyl]phenol (3): Tris(*p*-tolyl)methyl chloride[16] (10 g, 17.9 mmol) and phenol (10 g, 106 mmol) were heated at 80 °C for 16 h. The reaction mixture was recrystallized from ethanol after cooling down to room temperature, yielding **3** (9.4 g, 80%) as a white solid, m.p. 213 °C. ^{1}H NMR (300 MHz, [D_6]acetone, TMS): δ = 2.30 (s, 9 H, CH_3), 4.70 (s, 1 H, OH), 6.69 [d, 2 H, *J*(H,H) = 8 Hz, phenyl], 7.01–7.07 (m, 12 H, phenyl), 7.07 [d, *J*(H,H) = 8 Hz, 2 H, phenyl] ppm. $C_{28}H_{26}O$ (378.52): calcd. C 88.95, H 6.92; found C 88.62, H 7.03.

b: 2-{2-[2-(4-Tris(*p*-tolyl)methylphenoxy)ethoxy]ethoxy}ethyl *p*-Toluenesulfonate (5): NaOEt (0.55 g, 8.13 mmol) was added to triethylene glycol bis(tosylate) **4** (16.0 g, 34.9 mmol) and **3** (2.20 g, 5.81 mmol) dissolved in acetonitrile (150 mL). The solution was refluxed for 6 h. After cooling and filtration, the solvent was removed under vacuum. The crude product was dissolved in acetone, and the excess of **4** was precipitated by adding diethyl ether. The filtrate was evaporated and the residue was purified by CC (cyclohexane/acetone, 10:1). **5** (3.19 g, 83%) was obtained as colorless oil. ^{1}H NMR (300 MHz, [D_6]acetone, TMS): δ = 2.28 (s, 9 H, methyl), 2.42 (s, 3 H, tosyl), 3.53 (m, 2 H, oxyethylene), 3.58 (m, 2 H, oxyethylene), 3.66 [t, *J*(H,H) = 5 Hz, 2 H, oxyethylene], 3.76 [t, *J*(H,H) = 5 Hz, 2 H, oxyethylene], 4.08 [t, *J*(H,H) = 5 Hz, 2 H, oxyethylene], 4.15 [t, *J*(H,H) = 5 Hz, 2 H, oxyethylene], 6.82 [d, *J*(H,H) = 9 Hz, 2 H, phenyl], 7.00–7.08 (m, 12 H, phenyl), 7.08 [d, *J*(H,H) = 9 Hz, 2 H, phenyl], 7.44 [d, *J*(H,H) = 8 Hz, 2 H, phenyl], 7.80 [d, *J*(H,H) = 9 Hz, 2 H, phenyl] ppm. MS: $[C_{41}H_{44}NaO_6S]^+$ calcd. 687.2751; found 687.2764 [M + Na]. $C_{41}H_{44}SO_6$ (664.86): calcd. C 74.07, H 6.67, S 4.82; found C 74.17, H 6.72, S 4.55.

c: 7-[4-(2-{2-[2-(4-Tris(*p*-tolyl)methylphenoxy)ethoxy]ethoxy}-ethoxy)phenyl]cyclohepta-1,3,5-triene (7): 7-(4-Hydroxyphenyl)-1,3,5-cycloheptatriene (**6**)[17] was synthesized according to a modified procedure: phenol (5.50 g, 58.5 mmol) and 7-methoxy-1,3,5-cycloheptatriene (4,0 g, 32.7 mmol) were mixed. The mixture was immediately cooled to –30 °C. The temperature was held at –30 °C for 72 h. The excess phenol was removed by washing with warm water (200 mL, 50 °C). The residue was digested with water (200 mL, 90 °C, ten times). Compound **6** crystallized from the collected aqueous solutions as white crystals (2.89 g, 48%), m.p. 84–85 °C, ref.[17] 61.5–62.5 °C.

Compounds **6** (0.79 g (4.26 mmol), **5** (2.70 g, 4.06 mmol), and NaOEt (0.333 g, 4.90 mmol) in acetonitrile (150 mL) were stirred at room temperature for 15 min and heated to reflux for 5 h. After cooling, the solution was filtered and the solvents were evaporated. Purification of the crude product by CC (cyclohexane/acetone, 10:1) afforded **6** (2.30 g, 84%) as an oil. ^{1}H NMR (300 MHz, [D_6]-acetone, TMS): δ = 2.28 (s, 9 H, methyl), 2.59 [t, *J*(H,H) = 5 Hz, 2 H, CHT, 7-H], 3.68 (s, 4 H, oxyethylene), 3.82 (m, 4 H, oxyethylene), 4.09 (m, 2 H, oxyethylene), 4.12 (m, 2 H, oxyethylene), 5.35 (m, 2 H, CHT, 1-H, 6-H), 6.22 (m, 2 H, CHT, 2-H, 5-H), 6.73 [t, *J*(H,H) = 3 Hz, 2 H, CHT, 3-H, 4-H], 6.82 [d, *J*(H,H) = 9 Hz, 2 H, phenyl], 6.94 [d, *J*(H,H) = 9 Hz, 2 H, phenyl], 7.01–7.09 (m, 14 H, phenyl), 7.27 [d, *J*(H,H) = 9 Hz, 2 H, phenyl] ppm. MS: $[C_{47}H_{48}Na\ O_4]^+$ calcd. 699.35; found 699.27 [M + Na]. $C_{47}H_{48}O_4$ (676.90): calcd. C 83.40, H 7.15; found C 83.59, H 6.93.

d: [4-(2-{2-[2-(4-Tris(*p*-tolyl)methylphenoxy)ethoxy]ethoxy}ethoxy)-phenyl]tropylium Perchlorate (8): Compound **7** (2.20 g, 3.25 mmol) in dichloromethane (50 mL) was treated with trityl perchlorate (1.46 g, 3.90 mmol). After stirring for 18 h, the precipitate was filtered off and methyl-*tert*-butyl ether (MTBE, 400 mL) was added

to the filtrate. After 1 d the red oily precipitate was separated. The oil was washed with MTBE and dried under vacuum affording **8** as a yellow foam (2.40 g, 95%), m.p. 80–82 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.26 (s, 9 H, methyl), 3.74 (s, 4 H, oxyethylene), 3.80–3.89 (m, 4 H, oxyethylene), 4.02–4.07 (m, 2 H, oxyethylene), 4.10–4.14 (m, 2 H, oxyethylene), 6.68 [d, *J*(H,H) = 9 Hz, 2 H, phenyl], 6.95 [d, *J*(H,H) = 9 Hz, 2 H, phenyl] 6.97–7.10 (m, 14 H, phenyl), 7.82 [d, *J*(H,H) = 9 Hz, 2 H, phenyl], 6.97–7.10 (m, 14 H, phenyl), 8.76–8.73 (m, 2 H, tropylium), 8.77–8.85 (m, 2 H, tropylium), 9.04 [d, *J*(H,H) = 10 Hz, 2 H, tropylium] ppm. MS: $[C_{47}H_{47}O_4]^+$ calcd. 675.3469; found 675.3494 (M – ClO_4).

e) 4-{3-[4-(2-{2-[2-(4-Tris(*p*-tolyl)methylphenoxy)ethoxy]ethoxy}-ethoxy)phenyl]cyclohepta-2,4,6-trienyl}phenylamine (9a) and 4-{4-[4-(2-{2-[2-(4-Tris(*p*-tolyl)methylphenoxy)ethoxy]ethoxy}ethoxy-phenyl]cyclohepta-2,4,6-trienylphenylamine (9b): Aniline (1.20 g, 12.9 mmol) in acetonitrile (5 mL) was added to **8** (2.00 g, 2.57 mmol) dissolved in acetonitrile (25 mL). An oily precipitate was immediately formed. After 20 min the solution was separated from the oil and evaporated under reduced pressure. The crude product was purified by CC (toluene/ethyl acetate, 12:1) affording **9a** and **9b** (975 mg, 49%). The isomers were separated by repeating CC.

9a: Yield 390 mg (20 %), m.p. 72–74 °C. ^{1}H NMR (300 MHz, [D$_6$]-acetone, TMS): δ = 2.26 (s, 9 H, methyl), 2.54 [t, *J*(H,H) = 6 Hz, 1 H, CHT, 1-H], 3.65 (s, 4 H, oxyethylene), 3.75–3.81 (m, 4 H, oxyethylene), 4.03–4.11 (m, 4 H, oxyethylene), 4.55 (br. s, 2 H, NH_2), 5.35 (m, 1 H, CHT, 7-H), 5.37 [d, *J*(H,H) = 6 Hz, 1 H, CHT, 2-H], 6.22 (m, 1 H, CHT, 6-H), 6.70 [d, *J*(H,H) = 9 Hz, 2 H, phenyl], 6.79 [d, *J*(H,H) = 9 Hz, 2 H, phenyl], 6.84 (m, 1 H, CHT, 5-H), 6.88 [d, *J*(H,H) = 9 Hz, 2 H, phenyl], 6.92 [d, *J*(H,H) = 6 Hz, 1 H, CHT, 4-H], 7.01–7.07 (m, 12 H, phenyl), 7.06 [d, *J*(H,H) = 9 Hz, 2 H, phenyl], 7.11 [d, *J*(H,H) = 9 Hz, 2 H, phenyl], 7.27 [d, *J*(H,H) = 9 Hz, 2 H, phenyl] ppm. MS: $[C_{53}H_{54}NO_4]^+$ calcd. 768.4047; found 768.4063 [M + H]$^+$. $C_{53}H_{53}NO_4$ (767.99): calcd. C 82.89, H 6.96, N 1.82; found C 82.56, H 6.90, N 1.64.

9b: 585 mg (19%), m.p. 70–72 °C. ^{1}H NMR (300 MHz, [D$_6$]acetone, TMS): δ = 2.28 (s, 9 H, methyl), 2.67 [t *J*(H,H) = 5 Hz, 1 H, CHT, 1-H], 2.84 (s, 2 H, NH_2), 3.69 (s, 4 H, oxyethylene), 3.78–3.85 (m, 4 H, oxyethylene), 4.11 [t, *J*(H,H) = 5 Hz, 2 H, oxyethylene], 4.16 [t, *J*(H,H) = 5 Hz, 2 H, oxyethylene], 5.43 (m, 1 H, CHT, 7-H), 5.23 (m, 1 H, CHT, 2-H), 6.28 (m, 1 H, CHT, 6-H), 6.34 [d, *J*(H,H) = 9 Hz, 1 H, CHT, 3-H], 6.70 [d, *J*(H,H) = 9 Hz, 2 H, phenyl], 6.83 [d, *J*(H,H) = 9 Hz, 2 H, phenyl], 6.97 [d, *J*(H,H) = 8 Hz, 2 H, phenyl], 7.02–7.06 (m, 12 H, phenyl), 7.04 (CHT, 5-H), 7.07 [d, *J*(H,H) = 9 Hz, 2 H, phenyl], 7.10 [d, *J*(H,H) = 8 Hz, 2 H, phenyl], 7.46 [d, *J*(H,H) = 9 Hz, 2 H, phenyl] ppm. MS: $[C_{53}H_{54}NO_4]^+$ calcd. 768.4047; found 768.4044 [M + H]$^+$. $C_{53}H_{53}NO_4$ (767.99): calcd. C 82.89, H 6.96, N 1.82; found C 82.52, H 7.10, N 1.80.

4-{4-[4-(2-{2-[2-(4-Tris(*p*-tolylmethyl)phenoxy)ethoxy]-ethoxy}ethoxy)phenyl]cyclohepta-1,3,6-trienyl}phenylamine (9c): Compound **9b** (0.22 g, 0.286 mmol) in toluene (30 mL) was heated at reflux for 30 h. After removal of the solvent, the residue was purified by CC (toluene/ethyl acetate, 12:1), and a greenish-yellow solid (0.165 g, 75%) resulted, m.p. 77–78 °C. ^{1}H NMR (300 MHz, [D$_6$]acetone, TMS): δ = 2.27 (s, 9 H, methyl). 2.77 [d, *J*(H,H) = 8 Hz, 2 H, CHT, 5-H], 3.67 (s, 4 H, oxyethylene), 3.78–3.84 (m, 4 H, oxyethylene), 4.09 [t, *J*(H,H) = 5 Hz, 2 H, oxyethylene], 4.14 [t, *J*(H,H) = 5 Hz, 2 H, oxyethylene], 5.53–5.62 (m, 1 H, CHT, 6-H), 6.38 [d, *J*(H,H) = 9 Hz, 1 H, CHT, 7-H], 6.51 [d, *J*(H,H) = 6 Hz, 1 H, CHT, 3-H], 6.70 [d, *J*(H,H) = 9 Hz, 2 H, phenyl], 6.82 [d, *J*(H,H) = 9 Hz, 2 H, phenyl], 6.92 [d, *J*(H,H) = 9 Hz, 2 H, phenyl], 6.95 [d, *J*(H,H) = 6 Hz, 1 H, CHT, 2-H], 7.00–7.10 (m, 14 H, phenyl), 7.27 [d, *J*(H,H) = 9 Hz, 2 H, phenyl], 7.49 [d, *J*(H,H) = 9 Hz, 2 H, phenyl] ppm. MS: $[C_{53}H_{53}NNaO_4]^+$ calcd. 790.3867; found 790.3855 [M + Na]$^+$. $C_{53}H_{53}NO_4$ (767.99): calcd. C 82.89, H 6.69, N 1.82; found C 82.89, H 7.11, N 1.93.

2,6-Dimethyl-4-tritylphenol (10): Triphenylmethyl chloride (22 g, 78.9 mmol) and 2,6-dimethylphenol (40 g, 327 mmol) were heated at 170 °C for 2 h. After cooling to room temperature, the reaction mixture was recrystallized from ethanol, yielding **10** as a white solid (22.1 g, 77%), m.p. 164 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.13 (s, 6 H, methyl), 4.51 (s, 1 H, OH), 6.79 (s, 2 H, phenyl), 7.13–7.27 (m, 15 H, phenyl) ppm. $C_{27}H_{24}O$ (364.49): calcd.C 88.97, H 6.65; found C 88.63, H 6.96.

2-(2-{4-[2-(2-Tosylethoxy)ethoxymethyl]benzyloxy}ethoxy)ethyl Toluene-4-sulfonate (11): 2-(2-{4-[2-(2-Hydroxyethoxy)ethoxymethyl]-benzyloxy}ethoxy)ethanol[18] (27.0 g, 85.9 mmol) and *p*-toluenesulfonyl chloride (33.6 g, 176 mmol) in dichloromethane (400 mL) were treated with solid NaOH at 0 °C for 1 h. After stirring for 20 h at room temperature, the precipitate was filtered off. The solvent was removed under reduced pressure and the remaining product was purified by CC (cyclohexane/acetone, 4:1) affording **11** as white solid (41.7 g, 76%), m.p. 50 °C. ^{1}H NMR (300 MHz, [D$_6$]-acetone, TMS): δ = 2.43 (s, 6 H, methyl), 3.56 (s, 8 H, oxyethylene), 3.68 [t, *J*(H,H) = 5 Hz, 4 H, oxyethylene], 4.17 [t, *J*(H,H) = 5 Hz, 4 H, oxyethylene], 4.50 (s, 4 H, H-10),. 7.31 (s, 4 H, phenyl), 7.45 [d, *J*(H,H) = 8 Hz, 4 H, phenyl], 7.80 [d, *J*(H,H) = 8 Hz, 4 H, phenyl] ppm. $C_{30}H_{38}S_2O_{10}$ (622.75): calcd. C 57.86, H 6.15; S 10.30; found C 57.67, H 6.19, S 10.23.

2-[2-(4-{2-[2-(2,6-Dimethyl-4-tritylphenoxy)ethoxy]ethoxy-methyl}benzyloxy)ethoxy]ethyl Toluene-4-sulfonate (12): Compound **11** (49.2 g, 79 mmol) in acetonitrile solution (300 mL) was added to **10** (6.00 g, 15.8 mmol) and NaOEt (1.53 g, 22.5 mmol) dissolved in acetonitrile (100 mL). The reaction mixture was heated at reflux for 4 h. After cooling and filtration, the solvent was removed under reduced pressure. The remaining residue was purified by CC (cyclohexane/acetone, 8:1) yielding an oil (6.05 g, 76%). ^{1}H NMR (300 MHz, [D$_6$]acetone, TMS): δ = 2.17 (s, 6 H, methyl), 2.42 (s, 3 H, methyl), 3.54 (m, 2 H, oxyethylene), 3.59 (m, 2 H, oxyethylene), 3.66 (m, 4 H, oxyethylene), 3.69 (m, 2 H, oxyethylene), 3.82 [t, *J*(H,H) = 5 Hz, 2 H, oxyethylene], 3.96 [t, *J*(H,H) = 5 Hz, 2 H, oxyethylene], 4.16 [t, *J*(H,H) = 5 Hz, 2 H, oxyethylene], 4.49 (s, 2 H, benzyl), 4.55 (s, 2 H, benzyl), 6.86 (s, 2 H, phenyl), 7.15–7.35 (m, 15 H, phenyl), 7.30 (s, 2 H, phenyl), 7.32 (s, 3 H, phenyl), 7.44 [d, *J*(H,H) = 8 Hz, 2 H, phenyl], 7.80 [d, *J*(H,H) = 8 Hz, 2 H, phenyl] ppm. $C_{50}H_{54}SO_8$ (815.02): calcd. C 73.68, H 6.68, S 3.93; found C 73.57, H 6.52, S 3.84.

4-{2-[2-(4-{2-[2-(2,6-Dimethyl-4-tritylphenoxy)ethoxy]ethoxy-methyl}benzyloxy)ethoxy]ethoxy}but-2-yn-1-ol (13): 1,4-Butyndiol (1.90 g, 22.1 mmol) and NaOEt (0.30 g, 4.42 mmol) were dissolved in DMSO (30 mL), and then slightly concentrated under vacuum (15 mbar, 50 °C). Compound **12** (3.00 g, 3.68 mmol) in DMSO (20 mL) was added, and the solution was warmed to 90 °C. The solvent was removed under reduced pressure, and the remaining residue was distributed between water (200 mL) and dichloromethane (200 mL). The aqueous layer was extracted with dichloromethane (3×100 mL). The combined organic phases were dried (Na_2SO_4) and evaporated, yielding a crude oil that was purified by CC (cyclohexane/acetone, 4:1) to give **13** (1.75 g, 65%). ^{1}H NMR (300 MHz, [D$_6$]acetone, TMS): δ = 2.17 (s, 6 H, methyl), 3.58–3.67 (m, 10 H, oxyethylene), 3.69–3.74 (m, 2 H, oxyethylene), 3.77–3.81 (m, 2 H, oxyethylene), 3.93–3.98 (m, 2 H, oxyethylene), 4.18 [t, *J*(H,H) = 2 Hz, 2 H, propargyl], 4.19- 4.23 (m, 2 H, propargyl), 4.52 (s, 2 H, benzyl), 4.55 (s, 2 H, benzyl), 6.86 (s, 2 H, phenyl), 7.16–7.31 (m,

15 H, phenyl), 7.33 (s, 4 H, phenyl) ppm. $C_{47}H_{52}O_7$ (728.37): calcd. C 77.44, H 7.19; found C 77.06, H 7.38.

2-{2-[2-(4-{2-[2-(4-Bromobut-2-ynyloxy)ethoxy]ethoxymethyl}benzyloxy)ethoxy]ethoxy}-1,3-dimethyl-5-tritylbenzol (14): Compound **13** (0.40 g, 0.549 mmol) and 2,6-di-*tert*-butyl-4-methylpyridine (0.10 g, 1.37 mmol) were dissolved in dry dichloromethane (50 mL). The solution was cooled to –30 °C. PBr_3 (0.30 g, 1.11 mmol) and 2,6-di-*tert*-butyl-4-methylpyridine (0.20 g, 2.74 mmol) in dichloromethane (10 mL) were added. The solution was kept at –30 °C for 1 h, followed by addition of DMF (2 mL). After warming to room temperature and stirring for 2 h, water (200 mL) was added. The organic layer was separated, and the solvent was removed. The crude product was purified by CC (cyclohexane/acetone, 6:1) to give an oil (0.242 g, 56%). ^{1}H NMR (300 MHz, [D$_6$]-acetone, TMS): δ = 2.17 (s, 6 H, methyl), 3.61 (s, 8 H, oxyethylene), 3.62–3.67 (m, 2 H, oxyethylene), 3.69–3.73 (m, 2 H, oxyethylene), 3.76–3.81 (m, 2 H, oxyethylene), 3.93–3.98 (m, 2 H, oxyethylene), 4.15 (m, 2 H, propargyl), 4.22–4.25 (m, 2 H, propargyl), 4.52 (s, 2 H, benzyl), 4.55 (s, 2 H, benzyl), 6.86 (s, 2 H, phenyl), 7.15–7.30 (m, 15 H, phenyl), 7.33 (s, 4 H, phenyl) ppm. $C_{47}H_{51}BrO_6$ (791.81): calcd. C 71.29, H 6.49, Br 10.09; found C 70.78, H 6.35, Br 10.22.

Rotaxane 2

Compounds **9c** (0.19 g, 0.247 mmol), **1** (0.27 g, 0.247 mmol) and 2,6-di-*tert*-butyl-4-methylpyridine (0.06 g, 0.297 mmol) were dissolved in DMF (1.9 mL). After 45 min, **14** (0.196 g, 0.247 mmol) was added. The solution was stirred at room temperature for 2 d. Dichloromethane (8 mL) was added in order to precipitate **1**. Cyclohexane (50 mL) was added to the red filtrate. The filtrate was concentrated under reduced pressure at 30 °C. The resulting precipitate was purified by CC (methanol/nitromethane/2 M aqueous NH_4Cl, 4:4:1). The violet fraction was concentrated and the rotaxane precipitated. The precipitate was dissolved in a mixture of acetone (20 mL) and water (100 mL). NH_4PF_6 (0.50 g) was added in order to precipitate **2**. The precipitate was washed with water and dried, affording pure **2** (0.243 g, 38%), m.p. 150–157 °C. ^{1}H NMR (300 MHz, [D$_6$]acetone, TMS): δ = 2.12 (s, 6 H, methyl), 2.28 (s, 9 H, methyl), 2.76 [d, *J*(H,H) = 8 Hz, 1 H, CHT, 7-H], 3.69 (s, 4 H, 3-H, 4-H), 3.73–4.17 (m, 32 H, oxyethylene), 4.41 (br. s, 2 H, phenyl, C), 4.45 (br. s, 2 H, phenyl, C), 5.16 (br. s, 1 H, NH), 5.61 (m, 1 H, CHT, 6-H), 6.02–6.10 (m, 8 H, cyclophane **1**), 6.27 [d, *J*(H,H) = 9 Hz, 1 H, CHT, 5-H], 6.44 (br. s, 2 H, phenyl, A), 6.47 [d, *J*(H,H) = 7 Hz, 1 H, CHT, 2-H], 6.85 (1 H, CHT, 3-H), 6.85 [d, *J*(H,H) = 9 Hz, 2 H, phenyl], 6.85 (s, 2 H, phenyl), 7.02–7.09 (m, 16 H, phenyl, A), 7.14–7.30 (m, 15 H, phenyl), 7.43 [d, *J*(H,H) = 9 Hz, 2 H, phenyl, B], 8.12 (s, 8 H, **1**), 8.32 [d, *J*(H,H) = 6 Hz, 8 H, **1**], 9.39 [d, *J*(H,H) = 6 Hz, 8 H, **1**] ppm. $C_{136}H_{135}N_5O_{10}P_4F_{24}$ (2579.51): calcd. C 63.33, H 5.28, N 2.72; found C 62.74, H 5,23, N 2.64. UV/Vis: λ_{max} (ε) = 254 (59300), 352 (25900), 555 nm (380).

Rotaxane 15

Rotaxane **2** (0.100 g, 0.039 mmol) dissolved in 0.1 *m* Et_4NPF_6/MeCN solution (50 mL) was oxidized by a controlled potential electrolysis (E_A = 0.9–1.3 V [SCE], HEKA PG285) at a Pt-electrode in the anode region of an H cell until a charge output of 0.078 F had been consumed. After evaporating the solvent and washing with water, the remaining solid was purified by column chromatography (silica gel, acetonitrile (400 mL), ethyl acetate (200 mL), cyclohexane (100 mL) containing ammonium hexafluorophosphate (7 g)). The violet fraction was evaporated and the remaining solid was washed with water yielding **6** (0.10 g, 70%) as a violet solid, m.p. 152–161 °C. ^{1}H NMR (400 MHz, CD_3CN, TMS): δ = 2.08 (s, 6 H, methyl), 2.26 (s, 9 H, methyl), 3.61 (s, 2 H, benzyl, C), 3.66 (benzyl, C), 3.65–3.93 (m, 20 H, oxyethylene), 3.91 (m, 2 H, propargyloxy), 3.92 (m, 2 H, propargyloxy), 4.00 (m, 2 H, oxyethylene), 4.00–4.03 (m, 6 H, oxyethylene), 4.04 (m, 2 H, 1-H), 4.23 [t, *J*(H,H) = 5 Hz, 2 H, 6-H], 5.67 (m, 8 H, **1**), 6.76 (br. d, 2 H, phenyl), 6.79 [d, *J*(H,H) = 9 Hz, 2 H, phenyl, A], 6.87 (s, 2 H, phenyl), 7.01–7.10 (m, 14 H, phenyl), 7.16–7.27 (m, 17 H, phenyl), 7.81 (s, 8 H, **1**), 7.82 (m, 2 H, phenyl, B), 7.84 [d, *J*(H,H) = 9 Hz, 2 H, phenyl, A], 7.92 [d, *J*(H,H) = 7 Hz, 8 H, **1**], 8.39 (m, 1 H, Tr, 6-H), *8.54* (m, 1 H, Tr, 5-H), 8.67 [d, *J*(H,H) = 12 Hz, 1 H, Tr, 3-H], 8.69 [d, *J*(H,H) = 12 Hz, 1 H, Tr, 7-H], 8.78 [d, *J*(H,H) = 12 Hz, 1 H, Tr 2-H], 8.87 [d, *J*(H,H) = 7 Hz, 8 H, **1**] ppm. ^{13}C NMR (100 MHz, CD_3CN, TMS): 164.5, 163.5, 162.0, 157.6 (phenyl), 154.2 (phenyl), 153.9, 149.0, 148.5, 148.0 (phenyl), 147.3, 146.7, 146.1, 145.5 (**1**), 145.4 (C–R1), 145.3, 143.5, 138.0 (**1**), 136.3 (phenyl), 133.5 (phenyl, B), 132.7 (phenyl), 132.7, 132.2 (phenyl), 132.2, 131.6 (**1**), 131.6 (phenyl), 131.5 (phenyl, A), 131.4 (phenyl), 130.6 (phenyl), 129.1 (phenyl), 128.5 (Tr, 5-C), 127.9 (**1**), 127.7 (phenyl, C), 127.5, 126.8 (phenyl), 117.0 (phenyl, B), 115.1 (phenyl, A), 114.2 (phenyl), 83.0, 80.0, 72.5 (17-C, 18-C), 72.4 (benzyl), 71.4, 71.3, 71.3, 71.2, 71.1, 71.0, 71.0, 70.2, 70.0, 69.0, 68.2 (oxyethylene), 65.5 (**1**), 65.3 (tetraphenylmethyl), 64.1 (tetraphenylmethyl), 58.6 (8-C), 33.1 (7-C), 20.8 (methyl), 16.9 (methyl) ppm. $C_{136}H_{134}F_{30}N_5O_{10}P_5$ (2723.47): calcd. C 59.98, H 4.96, N 2.57; found C 60.38, H 5.41, N 2.48. UV/Vis (MeCN): λ_{max} (ε) = 258 (63900), 400 (9400), 533.5 nm (34500).

Rotaxane 22

3-[4-(2-{2-[2-(4-[Tris(*p*-tolyl)methyl]phenoxy)ethoxy]ethoxy)phenyl]-propane-1-ol (17): Compounds **3** (3.40 g, 5.11 mmol), **16** (0.94 g, 6.18 mmol) and NaOEt (0.42 g, 6.17 mmol) were dissolved in acetonitrile (150 mL). The solution was heated to reflux for 6 h, filtered, and evaporated to give the crude product that was purified by CC (cyclohexane/acetone, 4:1) to yield a colourless oil (3.20 g, 97%). ^{1}H NMR (300 MHz, [D$_6$]acetone, TMS): δ = 1.76 (m, 2 H, propane), 2.28 (s, 9 H, methyl), 2.60 [t, *J*(H,H) = 7 Hz, 2 H, benzyl], 2.87 (br. s, 1 H, OH), 3.54 (m, 2 H, oxypropyl), 3.67 (s, 4 H, oxyethylene), 3.79 (m, 2 H, oxyethylene), 3.81 (m, 2 H, oxyethylene), 4.07 (m, 2 H, oxyethylene), 4.09 (m, 2 H, oxyethylene), 6.82 [d, *J*(H,H) = 9 Hz, 2 H, phenyl], 6.83 [d, *J*(H,H) = 9 Hz, 2 H, phenyl],7.09 [d, *J*(H,H) = 9 Hz, 2 H, phenyl], 7.07 [d, *J*(H,H) = 9 Hz, 2 H, phenyl], 7.06 (s, 12 H, phenyl) ppm. MS (ESI): *m*/*z* = 667.5 [M + Na$^+$]$^+$ calcd. 667.83. $C_{43}H_{48}O_5$ (667.83): calcd. C 80.09, H 7.50; found C 80.10, H 7.56.

1-Bromo-3-[4-(2-[2-(2-[4-tris(*p*-tolyl)methyl]phenoxy)ethoxy]-ethoxy)phenyl]propane (18): Compound **17** (1.10 g, 1.71 mmol) and 2,6-di-*tert*-butyl-4-methylpyridine (0.41 g, 2.00 mmol) dissolved in dichloromethane (30 mL) were cooled to –30 °C. PBr_3 (0.90 g, 3.3 mmol) in dichloromethane (10 mL) was added. After stirring for 2 h at –30 °C, DMF (2 mL) was added. The solution was kept at room temperature for 18 h. After that period the solution was poured into ice-water (100 mL). The organic phase was separated, washed with water, and dried (Na_2SO_4). The solvent was removed, and the residue was purified by CC (cyclohexane/acetone, 10:1), affording a colourless oil (0.71 g, 59%). ^{1}H NMR (300 MHz, [D$_6$]-acetone, TMS): δ = 2.10 (m, 2 H, propane), 2.29 (s, 9 H, methyl),2.69 [t, *J*(H,H) = 8 Hz, 2 H, benzyl], 3.44 (m, 2 H, oxypropyl), 3.67 (s, 4 H, oxyethylene), 3.80 (m, 2 H, oxyethylene), 3.81 (m, 2 H, oxyethylene), 4.08 (m, 2 H, oxyethylene), 4.10 (m, 2 H, oxyethylene), 6.83 [d, *J*(H,H) = 9 Hz, 2 H, phenyl], 6.86 [d, *J*(H,H) = 9 Hz, 2 H, phenyl], 7.06 (s, 12 H, phenyl), 7.07 [d, *J*(H,H) = 9 Hz, 2 H, phenyl], 7.12 [d, *J*(H,H) = 9 Hz, 2 H, H-19] ppm. $C_{43}H_{47}BrO_4$ (723.73): calcd. C 72.97, H 6.69, Br 11.29; found C 72.81, H 6.90, Br 11.50.

2-{2-[2-(2-{3-[4-(2-{2-[2-(4-tris(*p*-tolyl)phenoxy)ethoxy]-ethoxy}ethoxy)phenyl]propoxy}ethoxy)ethoxy]ethoxy}ethyl Toluene-4-sulfonate (19)

a: A solution of tetraethylene glycol (1.94 g, 10.0 mmol) and NaOEt (0.38 g, 5.58 mmol) in DMSO (8 mL) was stirred for 15 min at 70 °C. Compound **37** (0.50 g, 0.71 mmol) was added, and the solution was stirred at 95 °C for 5 h. The solution was concentrated to 10 mL under reduced pressure, and the remaining mixture was distributed between dichloromethane (250 mL) and water (200 mL) containing NaCl (2 M). The aqueous phase was washed with dichloromethane (3 × 200 mL).The collected organic phases were dried and concentrated. The remaining residue was purified by CC (cyclohexane/acetone, 3:1) to give 2-{2-[2-(2-{3-[4-(2-{2-[2-(4-tris(*p*-tolyl)methylphenoxy)ethoxy]ethoxy}ethoxy)phenyl]-propoxy}ethoxy)ethoxy]ethoxy}ethanol as a colourless oil (0.31 g, 53%). ^{1}H NMR (300 MHz, [D$_6$]acetone, TMS): δ = 1.79 (m, 2 H, propyl), 2.29 (s, 9 H, methyl), 2.60 [t, *J*(H,H) = 8 Hz, 2 H, benzyl], 2.83 (t, 1 H, OH), 3.41 (m, 2 H, propoxy), 3.51–3.52 (m, 4 H, oxyethylene), 3.58–3.60 (m, 12 H, oxyethylene), 3.67 (s, 4 H, oxyethylene), 3.79 (m, 2 H, oxyethylene), 3.81 (m, 2 H, oxyethylene), 4.08 (m, 2 H, oxyethylene), 4.10 (m, 2 H, oxyethylene), 6.83 [d, *J*(H,H) = 9 Hz, 2 H, phenyl], 6.84 [d, *J*(H,H) = 9 Hz, 2 H, phenyl], 7.06 (s, 12 H, phenyl), 7.07 [d, *J*(H,H) = 9 Hz, 2 H, phenyl], 7.10 [d, *J*(H,H) = 9 Hz, 2 H, phenyl] ppm. MS (ESI): *m*/*z* = 843.6 [M + Na$^+$]$^+$, calcd. 844.04. $C_{51}H_{64}O_9$ (821.05): calcd. C 74.61, H 7.86; found C 74.84, H 7.88.

b: NaOH (in powder form, 1.50 g, 3.75 mmol) was added to the alcohol described above (1.39 g, 1.71 mmol) and *p*-toluenesulfonyl chloride (1.90 g, 9.97 mmol) dissolved in dichloromethane (30 mL). After stirring for 1 h at room temperature, the solution was heated to reflux for 1 h. The solution was poured into ice-water (100 mL) and extracted with dichloromethane (3 × 50 mL). The organic phases were evaporated and the remaining residue was purified by CC (cyclohexane/acetone, 5:1) affording **19** as an oil (1.37 g, 82%). ^{1}H NMR (300 MHz, [D$_6$]acetone, TMS): δ = 1.79 (m, 2 H, propyl), 2.29 (s, 9 H, methyl), 2.45 (s, 3 H, methyl), 2.60 [t, *J*(H,H) = 8 Hz, 2 H, benzyl], 3.40 (m, 2 H, propoxy), 3.51 (m, 6 H, oxyethylene), 3.56–3.57 (m, 6 H, oxyethylene), 3.65 (m, 2 H, oxyethylene), 3.67 (s, 4 H, oxyethylene), 3.79 (m, 2 H, oxyethylene), 3.81 (m, 2 H, oxyethylene), 4.10 (m, 2 H, oxyethylene), 4.08 (m, 2 H), 4.15 (m, 2 H, oxyethylene), 6.83 [d, *J*(H,H) = 9 Hz, 2 H, phenyl], 6.84 [d, *J*(H,H) = 9 Hz, 2 H, phenyl], 7.06 (s, 12 H, phenyl), 7.07 [d, *J*(H,H) = 9 Hz, 2 H, phenyl], 7.10 [d, *J*(H,H) = 9 Hz, 2 H, phenyl], 7.47 [d, *J*(H,H) = 8 Hz, 2 H, phenyl], 7.81 [d, *J*(H,H) = 8 Hz, 2 H, phenyl] ppm. MS (ESI): *m*/*z* = 997.6 [M + Na$^+$]$^+$, calcd. $C_{58}H_{70}NaO_{11}S$ 998.22. $C_{58}H_{70}SO_{11}$ (975.23): calcd. C 71.43, H 7.24, S 3.29; found C 71.17, H 7.35, S 3.07.

4-(2-{2-[2-(2-{3-[4-(2-{2-[2-(4-Tris(*p*-tolyl)methylphenoxy)-ethoxy]ethoxy}phenyl]propoxy}ethoxy)ethoxy]ethoxy}ethoxy)but-2-yne-1-ol (20): NaOEt (0.11 g, 1.54 mmol) and but-2-yne-1,4-diol (3.0 g, 35 mmol) in DMSO (20 mL) were heated to 70 °C for 1 h. Compound **19** (1.05 g, 1.03 mmol) dissolved in DMSO (10 mL) was added, and the mixture was heated to 90 °C for 1.5 h. The solvent was removed at 95 °C (15 mbar). The residue was distributed between water (200 mL) and dichloromethane (200 mL), the aqueous phase was washed with dichloromethane (3 × 100 mL), and the combined organic phases were dried (Na_2SO_4). After removal of the solvent, the residue was purified by CC (cyclohexane/acetone, 4:1; 3:1; 2:1) to yield an oil (0.89 g, 93%). ^{1}H NMR (300 MHz, [D$_6$]acetone, TMS): δ = 1.79 (m, 2 H, propyl), 2.28 (s, 9 H, methyl), 2.60 [t, *J*(H,H) = 8 Hz, 2 H, benzyl], 2.86 (br. s., 1 H, OH), 3.41 (m, 2 H, propoxy), 3.52 (m, 2 H, oxyethylene), 3.58–3.59 (m, 14 H, oxyethylene), 3.67 (s, 4 H, oxyethylene), 3.79 (m, 2 H, oxyethylene), 3.81 (m, 2 H, oxyethylene), 4.08 (m, 2 H, oxyethylene), 4.10 (m, 2 H, oxyethylene), 4.17 (s, 2 H, OCH_2-but-2-yne), 4.20 (s, 2 H, OCH_2-but-2-yne), 6.83 [d, *J*(H,H) = 9 Hz, 2 H, phenyl], 6.84 [d, *J*(H,H) = 9 Hz, 2 H, phenyl], 7.06 (s, 12 H, phenyl), 7.07 [d, *J*(H,H) = 9 Hz, 2 H, phenyl], 7.10 [d, *J*(H,H) = 9 Hz, 2 H, phenyl] ppm. MS (ESI): *m*/*z* = 911.6 [M + Na]$^+$, calcd. $C_{55}H_{68}NaO_{10}$, 912.11. $C_{55}H_{68}O_{10}$ (889.15): calcd. C 74.30, H 7.71; found C 73.77, H 7.72.

1-Bromo-4-(2-{2-[2-(2-{3-[4-(2-{2-[2-(4-tris(*p*-tolyl)methylphenoxy)-ethoxy]ethoxy}phenyl]propoxy}ethoxy)ethoxy]ethoxy}ethoxy)but-2-yne (21): Compound **20** (0.68 g, 0.77 mmol) dissolved in dry dichloromethane (30 mL) was cooled to –18 °C. PBr_3 (2.0 g, 7.40 mmol) and 2,6-di-*tert*-butyl-4-methylpyridine (0.16 g, 0.78 mmol) dissolved in dichloromethane (10 mL) were added. The reaction mixture was kept at –30 °C for 30 min, then DMF (2 mL) was added. The mixture was stirred at room temperature for 3 h, and water (200 mL) was added. The organic phase was separated, dried, and evaporated to give the crude product that was purified by CC (cyclohexane/acetone (6:1) to yield an oil (0.52 g, 71%). ^{1}H NMR (300 MHz, [D$_6$]acetone, TMS): δ = 1.79 (m, 2 H, propyl), 2.23 (s, 9 H, methyl), 2.60 [t, *J*(H,H) = 8 Hz, 2 H, benzyl], 3.41 (m, 2 H, propoxy), 3.52 (m, 2 H, oxyethylene), 3.58–3.60 (m, 14 H, oxyethylene), 3.67 (s, 4 H, oxyethylene), 3.79 (m, 2 H, oxyethylene), 3.81 (m, 2 H, oxyethylene), 4.08 (m, 2 H, oxyethylene), 4.10 (m, 2 H, oxyethylene), 4.16 (s, 2 H, bromomethyl), 4.23 (s, 2 H, oxyethylene), 6.83 [d, *J*(H,H) = 9 Hz, 2 H, phenyl], 6.84 [d, *J*(H,H) = 9 Hz, 2 H, phenyl], 7.06 (s, 12 H, phenyl), 7.07 [d, *J*(H,H) = 9 Hz, 2 H, phenyl], 7.10 [d, *J*(H,H) = 9 Hz, 2 H, phenyl] ppm. MS (ESI): *m*/*z* = 975.3845 [M + Na$^+$]$^+$; calcd. $C_{55}H_{67}BrNaO_9$, 975.3846.

Compound **21** (0.16 g, 0.163 mmol) in DMF solution (0.3 mL) was added to the green solution of **9c** (0.76 g, 0.10 mmol), **1** (0.12 g, 0.110 mmol) and 2,6-di-*tert*-butyl-4-methylpyridine (0.050 g, 0.24 mmol)) in DMF (1.5 mL). The reaction mixture was kept at 0 °C for 14 d, followed by addition of dichloromethane (10 mL). Precipitated **1** was filtered from the solution and the filtrate was poured into MTBE (100 mL). The oily precipitate was separated and purified by CC (methanol/2 M/NH_4Cl(aq)/nitromethane (4:1:4). The green fraction was evaporated and the rotaxane was dissolved in water and a small amount of acetone. The rotaxane was then precipitated by addition of several equivalents of NH_4PF_6(aq). The resulting green solid was washed with water several times and dried (0.072 g, 27%), m.p. 133–140 °C. ^{1}H NMR (300 MHz, [D$_6$]acetone, TMS): δ = 1.69 (m, 2 H, 18-H), 2.23 [t, *J*(H,H) = 8 Hz, 2 H, 19-H], 2.27 (s, 18 H, methyl), 2.76 [d, 7 Hz, 2 H, CHT, 7-H], 3.41–3.89 (m, 36 H, oxyethylene), 3.93 (s, 2 H, 7-H), 4.00–4.15 (m, 6 H, oxyethylene), 4.26 (s, 2 H, 8-H), 5.63–5.78 (m, 12 H, **1**, CHT, 1-H, 2-H, phenyl, C), 6.16 [d, *J*(H,H) = 6 Hz, 1 H, CHT, 4-H], 6.19 (br. s, 2 H, phenyl, A), 6.31 [d, *J*(H,H) = 9 Hz, 2 H, phenyl, B], 6.34 [d, *J*(H,H) = 6 Hz, 1 H, CHT, 5-H], 6.64 [d, *J* = 9 Hz, 2 H], 6.70 [d, *J*(H,H) = 9 Hz, 2 H], 6.75 [d, *J*(H,H) = 9 Hz, 2 H], 7.01 [d, *J*(H,H) = 9 Hz, 2 H, phenyl, B], 7.02–7.07 (m, 28 H, phenyl), 7.79–7.82 (m, 8 H, **1**), 7.86 (s, 8 H, **1**), 8.85–8.89 (m, 8 H, **1**) ppm. MS: *m*/*z* = 1224.5315, 768.0323; calcd. $C_{144}H_{151}N_5O_{13}P_2F_{12}$ (M – 2PF$_6^-$)$^{2+}$, 1224.5313, $C_{144}H_{151}N_5O_{13}PF_6$ (M – 3PF$_6$)$^{3-}$ 768.0328. $C_{144}H_{151}N_5O_{13}P_4F_{24}$ (2739.72): calcd. C 63.13, H 5.56, N 2.56; found C 63.00, H 5.98, N 2.49.

Rotaxane 23: Rotaxane **22** (0.063 g, 0.022 mmol), dissolved in 0.1 M Et_4NPF_6 MeCN solution (50 mL), was oxidized by a controlled potential electrolysis (E_A = 1.3 V [SCE], HEKA PG285) at a Pt-electrode in the anode region of an H cell until a charge output of 4420 mC had been consumed. After evaporating the solution and washing with water, the remaining solid was purified by column chromatography [silica gel, acetonitrile (400 mL), ethyl acetate (200 mL), cyclohexane (100 mL) containing ammonium hexafluorophosphate (7 g)]. Rotaxane **23** (0.042 g, 67%) was obtained as a

violet solid, m.p. 124–134 °C. ^{1}H NMR (400 MHz, CD_3CN, TMS): δ = 1.54 (m, 2 H, 18-H), 1.82 (t, J(H,H) = 8 Hz, 2 H, 19-H), 2.26 (s, 9 H, methyl), 2.28 (s, 9 H, methyl), 3.30 (m, 2 H, oxyethylene), 3.99–4.04 (m, 4 H, oxyethylene), 4.12 (m, 2 H, 8-H), 4.21 (m, 2 H, oxyethylene), 4.32 (br. d, 2 H, phenyl, C), 4.16 (m, 2 H, oxyethylene), 4.22 [d, J(H,H) = 8 Hz, 2 H, phenyl, C], 5.58–5.72 (m, 8 H, **1**), 6.27 [d, J(H,H) = 9 Hz, 2 H, phenyl, B], 6.67–6.77 (m, 4 H, phenyl), 6.90 [d, J(H,H) = 9 Hz, 2 H, phenyl, A], 7.04 (s, 2 H, phenyl), 7.13–7.33 (m, 30 H, phenyl), 7.53 [d, J(H,H) = 9 Hz, 2 H, phenyl, B], 7.78 [d, J(H,H) = 9 Hz, 2 H, phenyl, A], 6.97 [d, J(H,H) = 9 Hz, 2 H, phenyl, B], 7.01–7.09, (m, 30 H, phenyl), 7.77–7.82 (m, 16 H, **1**), 7.89 [d, J(H,H) = 9 Hz, 2 H, Phenyl, A], 8.37 (m, 1 H, Tr, 6-H), 8.50 [d, J(H,H) = 10 Hz, 1 H, Tr, 5-H], 8.64 [d, J(H,H) = 12 Hz, 1 H, Tr, 3-H], 8.72 [d, J(H,H) = 11 Hz, 1 H, Tr 7-H], 8.80 (m, 1 H, Tr, 2-H), 8.83 [d, J(H,H) = 6 Hz, 8 H, **1**] ppm.

1-[2-(4-{3-[2-(2-{2[2-(4-Bromobut-2-ynyloxy)ethoxy]ethoxy}ethoxy)-ethoxy]propyl}phenoxy)ethoxy]-2,6-dimethyl-4-tritylbenzene (29)

a: 2-(2,6-Dimethyl-4-tritylphenoxy)ethyl Toluene-4-sulfonate (24): Compound **10** (10 g, 27.4 mmol) and ethylene glycol bis(tosylate)[19] (38 g, 102 mmol), dissolved in acetonitrile (300 mL) were treated with NaOEt (2.42 g, 35.6 mmol). The mixture was heated to reflux for 16 h. After cooling, the solution was concentrated. The precipitate was filtered, and the excess \tosylate was precipitated by adding diethyl ether and hexane. The filtrate was concentrated and the remaining residue was purified by CC (cyclohexane/acetone, 10:1). A white solid resulted by slow evaporation of the hexane/diethyl ether solution, 13.3 g (86%), m.p. 133 °C. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ = 2.09 (s, 6 H, methyl), 2.44 (s, 3 H, methyl), 3.98 [t, J(H,H) = 5 Hz, 2 H, oxyethylene], 4.33 [t, J(H,H) = 5 Hz, 2 H, oxyethylene], 6.79 (s, 2 H, phenyl), 7.14–7.25 (m, 15 H, phenyl), 7.34 [d, J(H,H) = 8 Hz, 2 H, phenyl], 7.83 [d, J(H,H) = 8 Hz, 2 H, phenyl] ppm. $C_{36}H_{34}SO_4$ (562.73): calcd. C 76.84, H 6.09, S 5.70; found C 76.59, H 6.18, S 5.69.

b: 3-{4-[2-(2,6-Dimethyl-4-tritylphenoxy)ethoxy]phenyl}propan-1-ol (25): Compounds **24** (2.5 g, 4.44 mmol), **16** (0.68 g, 4.44 mmol) and NaOEt (0.36 g, 5.33 mmol) in acetonitrile were heated to reflux for 6 h. The solution was filtered and evaporated, and the residue was purified by CC (cyclohexane/acetone, 4:1), affording **25** as viscous oil (2.4 g, 99%). ^{1}H NMR (300 MHz, [D$_6$]acetone, TMS): δ = 1.78 (m, 2 H, methylene), 2.19 (s, 6 H, methyl), 2.63 [t, J(H,H) = 8 Hz, 2 H, benzyl], 2.84 (br. s, 1 H, OH), 3.54 (m, 2 H, oxymethylene), 4.16 (m, 2 H, oxyethylene), 4.29 (m, 2 H, oxyethylene), 6.88 (s, 2 H, phenyl), 6.89 [d, J(H,H) = 9 Hz, 2 H, phenyl], 7.14 [d, J(H,H) = 9 Hz, 2 H, phenyl], 7.16–7.30 (m, 15 H, phenyl) ppm. $C_{38}H_{38}O_3$ (542.71): calcd. C 84.10, H 7.06; found C 84.29, H 7.35.

c: 2-{2-[4-(3-Bromopropyl)phenoxy]ethoxy}-1,3-dimethyl-5-tritylbenzene (26): Compound **25** (2.07 g, 3.81 mmol) and 2,6-di-*tert*-butyl-4-methylpyridine (0.45 g, 2.2 mmol) were dissolved in dichloromethane (30 mL) and cooled to –30 °C. PBr_3 (2.70 g, 10 mmol) was added, and the solution was kept at –30 °C for 2 h. After that period, DMF (2 mL) was added and the solution was stirred at room temperature for 18 h. The solution was poured into ice water (100 mL). The organic layer was dried (Na_2SO_4) and the solvents were evaporated. The residue was purified by CC (cyclohexane/acetone, 10:1) affording a white solid (2.06 g, 87%), m.p. 139 °C. ^{1}H NMR (300 MHz, [D$_6$]acetone, TMS): δ = 2.12 (m, 2 H, methylene), 2.20 (s, 6 H, methyl), 2.71 [t, J(H,H) = 8 Hz, 2 H, benzyl], 3.43 (m, 2 H, hydroxymethyl), 4.16 (m, 2 H, oxyethylene), 4.29 (m, 2 H, oxyethylene), 6.86 (s, 2 H, phenyl), 6.90 [d, J(H,H) = 9 Hz, 2 H, phenyl], 7.14 [d, J(H,H) = 9 Hz, 2 H, phenyl], 7.16–7.30 (m, 15 H, phenyl) ppm. $C_{38}H_{37}BrO_2$ (605.61): calcd. C 75.37, H 6.16, Br 13.19; found C 75.32, H 6.43, Br 13.48.

d: 2-(2-{2-[2-(3-{4-[2-(2,6-Dimethyl-4-tritylphenoxy)ethoxy]-phenyl}propoxy)ethoxy]ethoxy}ethoxy)ethyl Toluene-4-sulfonate (27)

a: Tetraethylene glycol (5 g, 26 mmol) and NaOEt (0.60 g, 8,82 mmol) dissolved in DMSO (70 mL) were heated to 70 °C for 15 min. Compound **26** (1.65 g, 7.7 mmol) in DMSO (15 mL) was added. The mixture was heated to 90 °C for 90 min. The solvent was removed under reduced pressure, and the residue was distributed between dichloromethane (250 mL) and an aqueous NaCl solution (2 M, 200 mL). The organic layer was dried and concentrated. The residue was purified by CC (cyclohexane/acetone, 3:1) affording 2-(2-{2-[2-(3-{4-[2-(2.6-Dimethyl-4-tritylphenoxy)ethoxy]phenyl}propoxy)ethoxy]ethoxy}ethoxy)ethanol (1.33 g, 68%) as an oil. ^{1}H NMR (300 MHz, [D$_6$]acetone, TMS): δ = 1.81 (m, 2 H, methylene), 2.20 (s, 6 H, methyl), 2.62 [t, J(H,H) = 8 Hz, 2 H, benzyl], 2.84 (br. s., 1H, OH), 3.39 (m, 2 H, oxymethylene), 3.43 (m, 2 H, hydroxymethylene), 3.52 (m, 2 H, oxyethylene), 3.58–3.59 (m, 5 H, oxyethylene), 4.17 (m, 2 H, oxyethylene), 4.30 (m, 2 H, oxyethylene), 6.88 (s, 2 H, phenyl), 6.90 [d, J(H,H) = 9 Hz, 2 H, phenyl], 7.15 [d, J(H,H) = 9 Hz, 2 H, phenyl], 7.17–7.32 (m, 15 H, phenyl) ppm. $C_{46}H_{54}O_7$ (718.92): calcd. C 76.85, H 7.57; found C 76.69, H 7.69.

b: 2-(2-{2-[2-(3-{4-[2-(2,6-Dimethyl-4-tritylphenoxy)ethoxy]-phenyl}propoxy)ethoxy]ethoxy}ethoxy)ethanol (1.10 g, 1.53 mmol) and tosyl chloride (1.50 g, 7.87 mmol) dissolved in dichloromethane (30 mL) were treated with NaOH (1.50 g, 37.5 mmol). The solution was kept at room temperature for 1 h, then heated to reflux for 30 min. The resulting solution was distributed between ice-water (100 mL) and dichloromethane (50 mL). The aqueous solution was extracted several times with dichloromethane. The combined organic layers were dried, and the solvents were evaporated. The remaining oil was purified by CC (cyclohexane/acetone, 5:1) to yield **27** (1.27 g, 95%) as an oil. ^{1}H NMR (300 MHz, [D$_6$]acetone, TMS): δ = 1.80 (m, 2 H, methylene), 2.20 (s, 6 H, methyl), 2.45 (s, 3 H, methyl), 2.62 [t, J(H,H) = 8 Hz, 2 H, benzyl], 3.42 (m, 2 H, oxymethylene), 3.52 (m, 6 H, oxyethylene), 3.57 (m, 6 H, oxyethylene), 3.65 (m, 2 H, oxyethylene), 4.15 (m, 2 H, oxyethylene), 4.17 (m, 2 H, oxyethylene), 4.30 (m, 2 H, oxyethylene), 6.88 (s, 2 H, phenyl), 6.90 [d, J(H,H) = 9 Hz, 2 H, phenyl], 7.14 [d, J(H,H) = 9 Hz, 2 H, phenyl], 7.17–7.31 (m, 15 H, phenyl) ppm. $C_{53}H_{60}SO_9$ (873.10): calcd. C 72.91, H 6.93, S 3.67; found C 72.28, H 6.82, S 3.46.

e: 4-[2-(2-{2-[2-(3-{4-[2-(2,6-Dimethyl-4-tritylphenoxy)ethoxy]-phenyl}propoxy)ethoxy]ethoxy)ethoxy]but-2-yn-1-ol (28): But-2-yne-1,4-diol (3 g, 35 mmol) and NaOEt (0.28 g, 2.1 mmol) were dissolved in DMSO (100 mL).The solution was concentrated to 2/3 of the volume under reduced pressure at 90 °C. Compound **27** (1.00 g, 1.15 mmol) in DMSO (20 mL) was added, and the solution was concentrated at 90 °C and 45 mbar for 45 min. Most of the solvent was removed at 95 °C and 15 mbar. The remaining residue was distributed between dichloromethane (200 mL) and water (200 mL). The aqueous solution was extracted with dichloromethane (3 × 150 mL). The combined organic phases were dried and concentrated. The remaining oil was purified several times by CC (cyclohexane/acetone, 4:1, 3:1, 2:1) affording colourless oil (0.86 g, 96%). ^{1}H NMR (300 MHz, [D$_6$]acetone, TMS): δ = 1.81 (m, 2 H, methylene), 2.20 (s, 6 H, methyl), 2.63 [t, J(H,H) = 8 Hz, 2 H, benzyl], 3.43 (m, 2 H, oxymethylene), 3.53 (m, 2 H, oxyethylene), 3.56 (m, 2 H, oxyethylene), 3.58–3.60 (m, 12 H: oxyethylene), 4.17 (m, 4 H, oxyethylene), 4.18 (s, 2 H, oxyethylene), 4.30 (m, 2 H, oxyethylene), 6.88 (s, 2 H, phenyl), 6.90 [d, J(H,H) = 9 Hz, 2 H, phenyl], 7.14 [d, J(H,H) = 9 Hz, 2 H, phenyl], 7.17–7.32 (m, 15 H, phenyl) ppm. MS (ESI): m/z = 809.4 [M + Na]$^+$.

1-[2-(4-{3-[2-(2-{2[2-(4-Bromo-but-2-ynyloxy)ethoxy]ethoxy}-ethoxy)ethoxy]propyl}phenoxy)ethoxy]-2,6-dimethyl-4-tritylbenzol (29): Compound **28** (0.76 g, 0.97 mmol) and 2,6-di-*tert*-butyl-4-methylpyridine (0.40 g, 1.95 mmol) were dissolved in dichloromethane (30 mL) and the solution was cooled to –18 °C. PBr_3 (3.0 g, 270 mmol) and 2,6-di-*tert*-butyl-4-methylpyridine (0.20 g, 0.95 mmol) dissolved in dry dichloromethane (10 mL) were added, and the solution was kept at –30 °C for 15 min. After adding DMF (5 mL), the solution was warmed to room temperature and stirred for 2 h. Water (100 mL) was added to the reaction solution, the organic phase was dried (Na_2SO_4), and the solvents evaporated. The remaining oil was purified by CC (cyclohexane/acetone, 6:1) affording colourless oil (0.71 g, 86%). ^{1}H NMR (300 MHz, [D$_6$]acetone, TMS): δ = 1.81 (m, 2 H, methylene), 2.19 (s, 6 H, methyl), 2.62 [t, *J*(H,H) = 8 Hz, 2 H, benzyl], 3.42 (m, 2 H, oxymethylene), 3.52 (m, 2 H, oxyethylene), 3.58–3.59 (m, 14 H, oxyethylene), 4.13 (m, 2 H, bromomethyl), 4.15 (m, 2 H, oxyethylene), 4.22 (s, 2 H, oxyethylene), 4.28 (m, 2 H, oxyethylene), 6.88 (s, 2 H, phenyl), 6.89 [d, *J*(H,H) = 9 Hz, 2 H, phenyl], 7.13 [d, *J*(H,H) = 9 Hz, 2 H, phenyl], 7.16–7.29 (m, 15 H, phenyl) ppm. $C_{50}H_{57}BrO_7$ (849.88): calcd. C 70.66, H 6.76, Br 9.40; found C 70.93, H 6.79, Br 9.72.

f: 2-{2-[2-(2,6-Dimethyl-4-tritylphenoxy)ethoxy]ethoxy}ethyl Toluene-4-sulfonate (30): NaOEt (0.80 g, 11.8 mmol) was added to triethylene glycol bis(tosylate) **4** (30.0 g, 65.4 mmol) and **10** (3.00 g, 8.21 mmol) dissolved in acetonitrile (200 mL). The solution was refluxed for 16 h. After cooling and filtration, the solvent was removed under reduced pressure. The crude product was dissolved in acetone, and excess **4** was precipitated by adding diethyl ether. The filtrate was evaporated, and the remaining mixture was purified by CC (cyclohexane/acetone, 10:1). Compound **30** (4.40 g, 82%) was obtained as colourless oil. Slow evaporation of diethyl ether from a solution of **30** in hexane/diethyl ether afforded white crystals, m.p. 75 °C. ^{1}H NMR (300 MHz, [D$_6$]acetone, TMS): δ = 2.15 (s, 9 H, methyl), 2.41 (s, 3 H, tosyl), 3.61 (m, 2 H, oxyethylene), 3.66 (m, 2 H, oxyethylene), 3.70 [t, *J*(H,H) = 5 Hz, 2 H, oxyethylene], 3.77 [t, *J*(H,H) = 5 Hz, 2 H, oxyethylene], 3.92 [t, *J*(H,H) = 5 Hz, 2 H, oxyethylene], 4.16 [t, *J*(H,H) = 5 Hz, 2 H, oxyethylene], 6.81 (s, 2 H, phenyl), 7.13–7.27 (m, 15 H, phenyl), 7.30 [d, *J*(H,H) = 8 Hz, 2 H, phenyl], 7.79 [d, *J*(H,H) = 8 Hz, 2 H, phenyl] ppm. $C_{40}H_{42}SO_6$ (650.82): calcd. (%): C 73.82, H 6.50, S 4.93; found C 73.87, H 6.73, S 5.00.

g: 7-[4-(2-{2-[2-(2,6-Dimethyl-4-tritylphenoxy)ethoxy]-ethoxy}ethoxy)phenyl]cyclohepta-1,3,5-triene (31): 7-(4-Hydroxyphenyl)-1,3,5-cycloheptatriene[2] (**6**), (1.40 g, 7.60 mmol), **30** (3.35 g, 5.15 mmol), and NaOEt (0.77 g, 11.00 mmol) were dissolved in acetonitrile (200 mL), and the solution was stirred at room temperature for 15 min. The solution was heated to reflux for 5 h. After cooling, the solution was filtered and the solvents were evaporated. Purification of the crude product by CC (cyclohexane/acetone, 6:1) afforded **31** (4.20 g, 94%) as an oil. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ = 2.17 (s, 9 H, methyl), 2.65 [t, *J*(H,H) = 6 Hz, 2 H, CHT, 7-H], 3.77 (s, 4 H, oxyethylene), 3.82 [t, *J*(H,H) = 5 Hz, 4 H, oxyethylene], 3.88 [t, *J*(H,H) = 5 Hz, 2 H, oxyethylene], 3.96 [t, *J*(H,H) = 5 Hz, 2 H, oxyethylene], 4.14 [t, *J*(H,H) = 5 Hz, 2 H, oxyethylene], 5.38 (m, 2 H, CHT, 1-H, 6-H), 6.22 (m, 2 H, CHT, 2-H, 5-H), 6.73 [t, *J*(H,H) = 3 Hz, 2 H, CHT, 3-H, 4-H], 6.80 (s, 2 H, phenyl), 6.91 [d, *J*(H,H) = 9 Hz, 2 H, phenyl], 7.25 [d, *J*(H,H) = 9 Hz, 2 H, phenyl], 7.13–7.30 (m, 15 H, phenyl) ppm. MS: *m*/*z* = 685.3287 [M + Na], [$C_{46}H_{46}$Na O_4]$^+$, calcd. 685.3294. $C_{46}H_{46}O_4$ (662.84): calcd. C 83.35, H 7.00; found C 83.45, H 7.25.

h: [4-(2-{2-[2-(2,6-Dimethyl-4-tritylphenoxy)ethoxy]ethoxy}ethoxy)-phenyl]tropylium Perchlorate (32): Compound **31** (2.70 g, 4.07 mmol) dissolved in dichloromethane (50 mL) was treated with trityl perchlorate (2.44 g, 6.51 mmol). After stirring for 18 h, the red mixture was filtered and. MTBE (400 mL) was added to the filtrate. After 1 d the red oily precipitate was separated. The oil was washed with MTBE and dried under vacuum affording **32** as a yellow foam (2.64 g, 88%), m.p. 78–86 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.15 (s, 6 H, methyl), 3.78 (s, 4 H, oxyethylene), 3.82 [t, *J*(H,H) = 5 Hz, 2 H, oxyethylene], 3.91 [t, *J*(H,H) = 5 Hz, 2 H, oxyethylene], 3.95 [t, *J*(H,H) = 5 Hz, 2 H, oxyethylene], 4.21 [t, *J*(H,H) = 5 Hz, 2 H, oxyethylene], 6.80 (s, 2 H, phenyl), 7.06 [d, *J*(H,H) = 9 Hz, 2 H, phenyl], 7.12–7.25 (m, 15 H, phenyl), 7.89 [d, *J*(H,H) = 9 Hz, 2 H, phenyl], 8.71 (m, 2 H, tropylium), 8.81–8.91 (m, 2 H, tropylium), 9.11 [d, *J*(H,H) = 11 Hz, 2 H, tropylium] ppm. $C_{46}H_{45}ClO_8$ (761.30): calcd. C 72.57, H 5.96; found C 72.36, H 6.04.

i: 4-{3-[4-(2-{2-[2-(2,6-Dimethyl-4-tritylphenoxy)ethoxy]ethoxy}-ethoxy)phenyl]cyclohepta-2,4,6-trienyl}phenylamine (33a) and 4-{4-[4-(2-{2-[2-(2,6-Dimethyl-4-tritylphenoxy)ethoxy]ethoxy}ethoxy)-phenyl]cyclohepta-2,4,6-trienyl}phenylamine (33b): Aniline (3.47 g, 37.3 mmol) in acetonitrile (10 mL) was added to **32** (2.46 g, 3.23 mmol) dissolved in acetonitrile (10 mL). After 30 min, the solution was evaporated under vacuum. The crude product was purified by CC (cyclohexane/acetone, 4:1). A second CC (toluene/ethyl acetate) afforded **33a** (0.47 g, 19%) and **33b** (0.65 g, 27%). **33a**: m.p. 79–83 °C. ^{1}H NMR (300 MHz, [D$_6$]acetone, TMS): δ = 2.16 (s, 6 H, methyl), 2.65 [t, *J*(H,H) = 6 Hz, 1 H, CHT, 1-H], 3.69 (s, 4 H, oxyethylene), 3.77 (m, 2 H, oxyethylene), 3.82 (m, 2 H, oxyethylene), 3.94 (m, 2 H, oxyethylene), 4.13 (m, 2 H, oxyethylene), 5.37 (m, 1 H, CHT, 7-H), 5.38 [d, *J*(H,H) = 6 Hz, 1 H, CHT, 2-H], 6.29 (m, 1 H, CHT, 6-H), 6.72 [d, *J*(H,H) = 9 Hz, 2 H, phenyl], 6.85 (s, 2 H, phenyl), 6.85 (m, 1 H, CHT, 5-H), 6.90 [d, *J*(H,H) = 9 Hz, 2 H, phenyl], 6.94 [d, *J*(H,H) = 6 Hz, 1 H, CHT, 4-H], 7.10–7.27 (m, 15 H, phenyl), 7.29 [d, *J*(H,H) = 9 Hz, 2 H, phenyl], 7.37 [d, *J*(H,H) = 9 Hz, 2 H, phenyl] ppm. MS: *m*/*z* = 754.3894 [M + H]$^+$, [$C_{52}H_{52}NO_4$]$^+$, calcd. 754.3896. $C_{52}H_{51}NO_4$ (753.97): calcd. C 82.84, H 6.82, N 1.86; found C 82.49, H 6.86, N 1.86.

33b: M.p. 70–73 °C, ^{1}H NMR (300 MHz, [D$_6$]acetone, TMS): δ = 2.17 (s, 6 H, methyl), 2.67 [t, *J*(H,H) = 6 Hz, 1 H, CHT, 1-H], 2.84 (s, 2 H, NH_2), 3.70 (s, 4 H, oxyethylene), 3.79 [t, *J*(H,H) = 5 Hz, 2 H, oxyethylene], 3.85 [t, *J*(H,H) = 5 Hz, 2 H, oxyethylene], 3.96 [t, *J*(H,H) = 5 Hz, 2 H, oxyethylene], 4.17 [t, *J*(H,H) = 5 Hz, 2 H, oxyethylene], 5.44 (m, 1 H, CHT, 7-H), 5.53 (m, 1 H, CHT, 2-H), 6.29 (m, 1 H, CHT, 6-H), 6.34 [d, *J*(H,H) = 9 Hz, 1 H, CHT, 3-H], 6.70 [d, *J*(H,H) = 9 Hz, 2 H, phenyl], 6.86 [d, *J*(H,H) = 9 Hz, 2 H, phenyl], 6.97 [d, *J*(H,H) = 8 Hz, 2 H, phenyl], 7.05 [d, *J*(H,H) = 6 Hz, 1 H, CHT, 5-H], 7.11 [d, *J*(H,H) = 9 Hz, 2 H, phenyl], 7.16–7.30 (m, 15 H, phenyl), 7.46 [d, *J*(H,H) = 9 Hz, 2 H, phenyl] ppm. MS: *m*/*z* = 754.3896 [M + H]$^+$, [$C_{52}H_{52}NO_4$]$^+$, calcd. 754.3896. $C_{53}H_{53}NO_4$ (754.27): calcd. C 82.84, H 6.82, N 1.86; found C 82.85, H 6.81, N 1.86.

j: 4-{4-[4-(2-{2-[2-(2,6-Dimethyl-4-tritylphenoxy)ethoxy]ethoxy}-ethoxy)phenyl]cyclohepta-1,3,6-trienyl}phenylamine (33c): Compound **33b** (0.24 g, 0.312 mmol) in toluene (20 mL) was heated to reflux for 30 h. After the solvents were evaporated, the residue was purified by CC (toluene/ethyl acetate, 12:1), and a greenish-yellow solid (0.165 g, 70%) resulted, m.p. 69–71 °C. ^{1}H NMR (300 MHz, [D$_6$]acetone, TMS): δ = 2.17 (s, 6 H, methyl). 2.84 [d, *J*(H,H) = 6 Hz, 2 H, CHT, 5-H], 3.70 (s, 4 H, oxyethylene), 3.79 (m, 2 H, oxyethylene), 3.84 (m, 2 H, oxyethylene), 3.95 (m, 2 H, oxyethylene), 4.16 (m, 2 H, oxyethylene), 5.60 (m, 1 H, CHT, 6-H), 6.39 [d, *J*(H,H) = 9 Hz, 1 H, CHT, 7-H], 6.51 [d, *J*(H,H) = 7 Hz, 1 H, CHT, 3-H], 6.70 [d, *J*(H,H) = 9 Hz, 2 H, phenyl], 6.86 (s, 2 H, phenyl), 6.93 [d, *J*(H,H) = 9 Hz, 2 H, phenyl], 6.98 [d, *J*(H,H) = 7

Hz, 1 H, CHT, 2-H], 7.17–7.30 (m, 17 H, phenyl), 7.50 [d, *J*(H,H) = 9 Hz, 2 H, phenyl] ppm. MS: *m*/*z* = 776.3700 $[M + Na]^+$, $[C_{52}H_{51}NNaO_4]^+$ calcd., 776.3716. $C_{52}H_{51}NO_4$ (753.97): calcd. C 82.84, H 6.82, N 1.86; found C 82.52, H 6.97, N 1.80.

Rotaxane 34: Compound **29** (0.230 g, 0.271 mmol) dissolved in DMF (0.3 mL) was added to a solution of **33c** (0.180 g, 0.239 mmol), **1** (0.342 g, 0.311 mmol) and 2,6-di-*tert*-butyl-4-methylpyridine (0.100 g, 0.488 mmol) in DMF (2.8 mL). The reaction mixture was stirred at 0 °C for 14 d, then dichloromethane (10 mL) was added to the solution. Precipitated **1** was filtered off. The filtrate was poured into cyclohexane (40 mL), and. the oily precipitate was separated. Evaporation of the filtrate, and purification by CC (cyclohexane/acetone, 6:1), afforded the molecular thread **35** (0.07 g, 18%), m.p. 63–65 °C. ^{1}H NMR (300 MHz, CD_3CN, TMS): δ = 1.79 (m, 2 H, 18-H), 2.16 (s, 6 H, methyl), 2.18 (s, 6 H, methyl), 2.58 [t, *J*(H,H) = 8 Hz, 2 H, 19-H], 2.74 [d, *J*(H,H) = 7 Hz, 2 H, CHT, 7-H], 3.40 [t, *J*(H,H) = 6 Hz, 2 H, 17-H], 3.52 (m, 2 H, 16-H), 3.55–3.58 (m, 14 H, 9-H–15-H), 3.69 (s, 4 H, 3-H, 4-H), 3.78 (m, 2 H, 2-H), 3.83 (m, 2 H, 5-H), 3.93 (m, 2 H, 1-H), 4.01 (m, 2 H, 7-H), 4.13 (s, 2 H, 8-H), 4.14 (m, 2 H, 16-H), 4.15 (m, 2 H, 21-H), 4.26 (m, 2 H, 20-H), 5.59 (m, 1 H, CHT, 6-H), 6.40 (m, 1 H, CHT, 5-H), 6.51 [d, *J*(H,H) = 6 Hz, 1 H, CHT, 2-H], 6.75 [d, *J*(H,H) = 9 Hz, 2 H, phenyl, A], 6.86 (s, 2 H, phenyl), 6.88 [d, *J*(H,H) = 8Hz, 2 H, phenyl, C], 6.89 (s, 2 H, phenyl), 6.91 (br. s, 2 H, phenyl, B), 6.99 [d, *J*(H,H) = 6 Hz, 1 H, CHT, 3-H], 7.13 [d, *J*(H,H) = 8 Hz, 2 H, phenyl, C], 7.15–7.30 (m, 30 H, phenyl), 7.35 [d, *J*(H,H) = 9 Hz, 2 H, phenyl, A], 7.48 [d, *J*(H,H) = 9 Hz, 2 H, phenyl, B] ppm. MS: *m*/*z* = 1544.7764 $[M + Na^+]^+$,1522.7813 $[M + H^+]^+$; calcd. $C_{102}H_{107}NNaO_{11}$ 1544.7736, $C_{102}H_{108}NO_{11}$ 1522.7917.

The oily precipitate, insoluble in hexane, was purified by CC (methanol/nitromethane/water (4:4:1) containing NH_4Cl (2 M). The green fraction was concentrated under reduced pressure, and the resulting oil was dissolved in water/acetone. Rotaxane **34** was precipitated by addition of excess saturated aqueous NH_4PF_6. The green solid was filtered, washed with water, and dried under reduced pressure (0.175 g, 28%), m.p. 135–143 °C. ^{1}H NMR (400 MHz, [D$_6$]acetone, TMS): δ = 1.7 (m, 2 H, 18-H), 2.18 (s, 6 H, methyl), 2.22 (s, 6 H, methyl), 2.6 [t, *J*(H,H) = 8Hz, 2 H, 19-H], 2.84 [d, *J*(H,H) = 7 Hz, 2 H, CHT, 7-H], 3.40–3.66 (m, 16 H, 10-H–17-H), 3.73 (m, 2 H, 6-H), 3.79–3.95 (m, 8 H, 2-H–5-H), 3.98 (s, 2 H, 7-H), 3.99 (m, 2 H, 1-H), 4.08 (m, 2 H, 6-H), 4.17 (m, 2 H, 20-H), 4.26 (m, 2 H, 21-H), 4.39 (s, 2 H, 8-H), 5.03 [d, *J*(H,H) = 8 Hz, 2 H, phenyl, A], 5.23 [d, *J*(H,H) = 8 Hz, 2 H, phenyl, A], 5.63 [d, *J*(H,H) = 9 Hz, 1 H, CHT, 5-H], 5.82 (m, 1 H, CHT, 6-H), 6.21–6.07 (m, 11 H, **1**, benzyl), 6.40 [d, *J*(H,H) = 7 Hz, 1 H, CHT, 3-H], 6.67 (br. d, 2 H, phenyl, C), 6.87 (s, 2 H, phenyl), 6.90 (s, 2 H, phenyl), 6.90–6.92 (m, 4 H, phenyl, B; C), 7.16–7.34 (m, 30 H, phenyl), 8.19 (s, 8 H, **1**), 8.30 [d, *J*(H,H) = 7 Hz, 2 H, **1**], 9.45 [d, *J*(H,H) = 7 Hz, 8 H, **1**] ppm.

Rotaxane 37: 2-[2-(2-{4-[4-(4-Aminophenyl)cyclohepta-1,3,5-trienyl]phenoxy}ethoxy)ethoxy]ethyl adamantane-1-carboxylate[5] (**36**) (0.215 g, 0.377 mmol), **1** (0.621 g, 0.566 mmol) and 2,6-di-*tert*-butyl-4-methylpyridine (0.077 g, 0.377 mmol) in DMF solution (0.6 mL) were stirred for 30 min at room temperature. Compound **29** (0.320 g, 0.377 mmol) in DMF (0.6 mL) was added, and the solution was stirred for 20 min at room temperature, then the reaction mixture was kept at 0 °C for 16 d. The green solution was evaporated, and the remaining residue was treated with MTBE (50 mL). From the solution the molecular thread **38** was isolated as an oily solid (0.110 g, 22%). ^{1}H NMR (300 MHz, CD_3CN, TMS): δ = 1.7 (m, 7 H, adamantane), 1.8 (m, 2 H, 18-H), 2.2 (s, 6 H, methyl), 2.58 (m, 2 H, 19-H), 2.76 (dd, 2 H, CHT, 7-H), 3.40 (m, 2 H, 17-H), 3.5 (m, 26 H, 1-H–5-H, 9-H–16-H), 4.0 (br. s, 2 H, 7-H), 4.2–4.3 (m, 8 H, 6-H, 8-H, 20-H, 21-H), 5.59 (m, 1 H, CHT, 6-H), 6.40 [d, *J*(H,H) = 8 Hz, 1 H, CHT, 5-H], 6.51 [d, *J*(H,H) = 6 Hz, 1 H, CHT, 2-H], 6.70 [d, *J*(H,H) = 9 Hz, 2 H, phenyl, A], 6.9 (m, 6 H, phenyl, phenyl, B, phenyl,C), 7.0 [d, *J*(H,H) = 6 Hz, 1 H, CHT, 3-H], 7.13 [d, *J*(H,H) = 9 Hz, 2 H, phenyl, C], 7.3 (m, 17 H, phenyl, phenyl, C), 7.35 [d, *J*(H,H) = 9 Hz, 2 H, phenyl, A], 7.50 [d, *J*(H,H) = 9 Hz, 2 H, phenyl, B] ppm. The NMR resonances were used to determine the CIS values of the protons of **37**.

The precipitate, insoluble in MTBE, was treated with the solvent mixture [acetonitrile (400 mL)/ethyl acetate (200 mL)/cyclohexane (100 mL) containing NH_4PF_6 (7 g)] that was used for the purification of **37** by CC. The excess of **1** (insoluble in this solvent mixture) was filtered (0.36 g) and the filtrate was used for CC. The evaporation of the green fraction afforded a green solid (0.190 g, 21%), which was washed with water and dried, m.p. 136–142 °C. ^{1}H NMR (400 MHz, CD_3CN, TMS): δ = 1.7 (m, 8 H, adamantane), 1.7 (m, 2 H, 18-H), 1.9 (m, 7 H, adamantane), 2.09 (s, 6 H, methyl), 2.52 [t, *J*(H,H) = 8 Hz, 2 H, 18-H], 2.80 [d, *J*(H,H) = 7 Hz, 2 H, CHT, 7-H], 3.4 (m, 8 H, oxyethylene), 3.4–3.6 (m, 6 H, oxyethylene), 3.6 (m, 8 H, oxyethylene), 3.8 (m, 2 H, 5-H), 3.92 (br. s, 2 H, 7-H), 4.1 (m, 4 H, 5-H, oxyethylene), 4.1 (m, 4 H, 6-H, 21-H), 4.2 (m, 2 H, 20-H), 4.3 (br. d, 2 H, phenyl, A), 4.34 (s, 2 H, 8-H), 4.75 [d, *J*(H,H) = 9 Hz, 2 H, phenyl, A], 5.18 [d, *J*(H,H) = 10 Hz, 1 H, CHT, 5-H], 5.66 [d, *J*(H,H) = 7 Hz, 1 H, CHT, 3-H], 5.7 (1 H, CHT, 6-H), 5.8 (m, 9 H, **1**, benzyl), 6.34 [d, *J*(H,H) = 7 Hz, 1 H, CHT, 2-H], 6.41 [br. d, *J*(H,H) = 8 Hz, 2 H, phenyl, B], 6.70 [br. d, *J*(H,H) = 8 Hz, 2 H, phenyl, C], 6.92 (s, 2 H, phenyl), 6.97 [br. d, *J*(H,H) = 8 Hz, 2 H, phenyl, C], 7.10 [br. d, *J*(H,H) = 8 Hz, 2 H, phenyl, B], 7.2–7.3 (m, 15 H, phenyl), 7.78 [d, *J*(H,H) = 7 Hz, 8 H, **1**], 7.9 (m, 8 H, **1**), 8.90 [d, *J*(H,H) = 7 Hz, 8 H, **1**] ppm. UV/Vis (MeCN): λ (ε) = 260 (43150), 360,5 (16930), 554 nm (764). $C_{122}H_{131}F_{24}N_5O_{12}P_4$ (2439.23): calcd. C 60.07, H 5.41, N 2.67; found C 59.82, H 5.67, N 2.80.

Rotaxane 39: Rotaxane **34** (0.135 g, 0.052 mmol) dissolved in 0.1 M Et_4NPF_6 MeCN solution (50 mL) was oxidized by a controlled potential electrolysis (E_A = 0.9–1.2 V [SCE], HEKA PG285) at a Pt-electrode in the anode region of an H cell until a charge output of 9920 mC had been consumed. After evaporating and washing with water, the remaining solid was purified by column chromatography [silica gel, acetonitrile (400 mL), ethyl acetate (200 mL), cyclohexane (100 mL) containing ammonium hexafluorophosphate (7 g)]. Rotaxane **39** (0.10 g, 70%) was obtained as a violet solid, m.p. 160–167 °C. ^{1}H NMR (400 MHz, CD_3CN, 343 K, TMS): δ = 1.41 (m, 2 H, 18-H), 1.92 (m, 2 H, 19-H), 2.12 (s, 6 H, methyl), 2.38 (s, 6 H, methyl), 3.44–3.59 (m, 12 H, oxyethylene), 3.63–3.70 (m, 4 H, oxyethylene), 3.71 (s, 4 H, oxyethylene), 3.78 (m, 2 H, oxyethylene), 3.83 (m, 2 H, oxyethylene), 3.92 (m, 2 H, oxyethylene), 4.04 (m, 2 H, oxyethylene), 4.09 (s, 2 H, 7-H), 4.14 (s, 2 H, 8-H), 4.16 (m, 2 H, oxyethylene), 4.22 [d, *J*(H,H) = 8Hz, 2 H, phenyl, C], 4.86 [d, *J*(H,H) = 8 Hz, 2 H, phenyl, C], 5.77 (s, 8 H, **1**), 6.58 (br. d, 2 H, phenyl, B), 6.71 [d, *J*(H,H) = 9 Hz, 2 H, phenyl, A], 6.85 (s, 2 H, phenyl), 7.04 (s, 2 H, phenyl), 7.13–7.33 (m, 30 H, phenyl), 7.53 [d, *J*(H,H) = 9 Hz, 2 H, phenyl, B], 7.78 [d, *J*(H,H) = 9 Hz, 2 H, phenyl, A], 7.85 (s, 8 H, **1**), 7.92 [d, *J*(H,H) = 7 Hz, 8 H, **1**], 8.43 (m, 1 H, Tr, 6-H), 8.46 (m, 1 H, Tr, 7-H), 8.60 [d, *J*(H,H) = 12 Hz, 1 H, Tr, 2-H], 8.70 [d, *J*(H,H) = 12 Hz, 1 H, Tr, 5-H], 8.80 [d, *J*(H,H) = 12 Hz, 1 H, Tr 3-H], 8.93 [d, *J*(H,H) = 7 Hz, 8 H, **1**] ppm.

Rotaxane 40: Rotaxane **37** (0.09 g) was oxidized as in the procedure used for the synthesis of **39**, providing a violet solid (0.05 g, 42%),

m.p. 138–41 °C. ^{1}H NMR (400 MHz, CD_3CN, TMS): δ = 1.4 (m, 2 H, 18-H), 1.7 (m, 9 H, adamantane), 1.8 (m, 7 H, adamantane, 19-H), 2.4 (s, 6 H, methyl), 3.4–3.7 (m, 28 H, oxyethylene, phenyl, C), 3.9 (m, 2 H, 5-H), 4.1 (m, 10 H, 6-H, 7,8-H, 20,21-H), 4.5 (br. d, 2 H, phenyl, C), 5.75 (m, 8 H, **1**), 6.58 (br. d, 2 H, phenyl, B), 6.76 [d, *J*(H,H) = 9 Hz, 2 H, phenyl, A], 6.9 (br., 2 H, phenyl, B), 7.1 (s, 2 H, phenyl), 7.2–7.3 (m, 15 H, phenyl), 7.7–7.9 (m, 20 H, **1**, phenyl, A, B), 8.45 (m, 1 H, Tr, 6-H), 8.54 (m, 1 H, Tr, 7-H), 8.67 [d, *J*(H,H) = 12 Hz, 1 H, Tr, 2-H], 8.73 [d, *J*(H,H) = 12 Hz, 1 H, Tr, 5-H], 8.77 [d, *J*(H,H) = 12 Hz, 1 H, Tr, 3-H], 8.93 (m, 8 H, **1**) ppm. UV/Vis (MeCN): λ (ε) = 262 (55200), 401.5 (9700), 552 nm (33500). $C_{122}H_{130}F_{30}N_5O_{12}P_5$ (2581.79): calcd. C 56.72, H 5.07, N 2.71; found C 56.92, H 4.77, N 2.90. MS (ESI): *m*/*z* = 1145.5956 ($[C_{122}H_{130}F_{12}N_5O_{12}P_3]^{2+}$) calcd. 1145.9321 $(M - 2PF_6)^{2+}$, 715.6386 ($[C_{122}H_{130}F_{12}N_5O_{12}P_2]^{3+}$) calcd. 715.6333 $(M - 3PF_6)^{3+}$.

Molecular Thread 41: Compound **38** (0.045 g) was oxidized as in the procedure used for the synthesis of compound **39**, providing a violet solid (0.05 g, 42%), m.p. 62–65 °C. ^{1}H NMR (400 MHz, CD_3CN, TMS): 1.7 (m, 7 H, adamantane), 1.76 (m, 2 H, 18-H), 1.8 (m, 8-H, adamantane), 2.12 (s, 6 H, methyl), 2.54 [t, *J*(H,H) = 8 Hz, 2 H, 19-H], 3.38 [t, *J*(H,H) = 7 Hz, 2 H, 17-H], 3.5 (m, 14 H, oxyethylene), 3.6 (m, 8 H, oxyethylene), 3.8 (m, 2 H, 5-H), 4.0 (m, 2 H, 21-H), 4.1 (m, 6 H, 6-H, 7-H, 8-H), 4.2 (m, 4 H, 20-H, oxyethylene), 6.21 (br. t, 1 H, NH), 6.81 [d, *J*(H,H) = 9 Hz, 2 H, phenyl, C], 6.9 (m, 4 H, phenyl, phenyl, A), 7.08 [d, *J*(H,H) = 9 Hz, 2 H, phenyl, C], 7.13–7.17 (m, 17 H, phenyl, phenyl B), 7.80 [d, *J*(H,H) = 9 Hz, 2 H, phenyl, B], 7.88 [d, *J*(H,H) = 7 Hz, 2 H, phenyl, A], 8.3 (m, 1 H, Tr, 6-H), 8.45 [dd, 1 H, Tr, 7-H], 8.60 dd, 1 H, Tr, 2-H), 8.65 (dd, 1 H, Tr, 5-H), 8.76 (dd, 1 H, Tr, 3-H) ppm. UV/Vis (MeCN): λ (ε) = 273 (16830), 398 (7270), 555 nm (22930). $C_{86}H_{98}F_6NO_{12}P$ (1482.66): calcd. C 69.67, H 6.66, N 0.94; found C 69.92, H 5.73, N 0.90. MS (ESI): *m*/*z* = 1336.7088 ($[C_{86}H_{98}NO_{12}]^+$) calcd. 1336.7089 $(M - PF_6)^+$.

Methoxy-Substituted Rotaxanes 42 and 43: The isomeric mixture of methoxy derivatives **42** and **43** were obtained by addition of methanol (0.1 mL) to a solution of **39** or **40** (0.02 g) in MeCN (2 mL) containing $NaHCO_3$ (0.02 g). After stirring for 4 h, the violet color disappeared. After filtration, the solvent was removed under reduced pressure. In order to record the NMR spectra, the solid was dissolved with CD_3CN (0.6 mL). The spectra (^{1}H NMR (see Supporting Information), H–H-COSY and ROESY) show the presence of the main isomer **42a** or **43a**.

43a: $C_{123}H_{133}F_{24}N_5O_{13}P_4$ (2467.8467). MS (ESI): *m*/*z* = 1088.9586 ($[C_{123}H_{133}F_{12}N_5O_{13}P_2]^{2+}$) $(M - 2PF_6)^+$, calcd. 1088.9592; 677.6508 ($[C_{123}H_{133}F_6N_5O_{13}P]^{3+}$) $(M - 3PF_6)^+$, calcd. 677.6514. UV/Vis (MeCN): λ (ε) = 265 (57130), 365 nm (sh) (15680).

Methoxy-Substituted Molecular Thread 44: The mixture of isomers of compound **44** was obtained by addition of methanol (0.1 mL) to a solution of compound **41** (0.03 g) in MeCN (2 mL) containing $NaHCO_3$ (0.02 g). The suspension was stirred until the violet color disappeared. In order to record the NMR spectra, the solution was filtered, evaporated, and the residue was dissolved in CD_3CN (0.2 mL) and CD_3OH (0.4 mL).

Supporting Information: (see footnote on the first page of this article): NMR spectra of rotaxanes **22** and **42**, 2D-NMR spectra of rotaxane **34**, UV/Vis spectra of rotaxanes **37**, **40** and **43**, UV spectra monitored after irradiation of the molecular thread **44**.

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