Pseudorotaxanes and Rotaxanes Incorporating Cycloheptatrienyl Stations − Synthesis and Co-Conformation

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Keywords: Cycloheptatriene / Diastereomer / Molecular recognition / Rotaxanes / Template synthesis

Novel [2]rotaxanes containing the tetracationic cyclophane cyclobis(paraquat-4,4′-biphenylene), linked mechanically to a dumbbell-shaped molecular thread incorporating a pair of diaryl cycloheptatriene units, have been synthesised in moderate yields of up to 35% by the acylative endcapping method, with the use of either bulky acyl chlorides or isocyanates. The pseudorotaxanes formed by the threading of the electron-rich molecular threads through the tetracationic ring were characterised by ^{1}H NMR and UV/Vis spectroscopy. The nonplanar, boat-shaped cycloheptatriene rings do not hamper the threading process. According to the ^{1}H NMR spectra, the tetracationic ring undergoes a fast shuttling process between the two cycloheptatriene stations in the rotaxanes. The unexpected signal dispersion of the cyclophane proton resonances is attributable to the existence of two diastereomeric rotaxanes. It was shown that interaction between the recognition sites is strongly influenced by the substitution pattern on the seven-membered ring; the interaction between the electron-deficient ring and a 1,3-diaryl-2,4,6-cycloheptatriene unit is much stronger than that with the regioisomeric 1,4-disubstituted pendant moiety.

Introduction

Switchable supermolecules consisting of mechanically joined molecules, as seen in rotaxanes and catenanes, are a big challenge in the field of supramolecular chemistry and could be considered as being the first steps towards molecular machines.[1,2] Rotaxanes consist of a threadlike molecule containing recognition sites and a macrocycle that encircles the molecular thread. In order to prevent dethreading of the ring, the threadlike molecule is terminated by bulky groups. The recognition sites present in both the molecular thread and the ring promote the formation of the supermolecule through several types of noncovalent bonding interaction and control the arrangement of the two components within the rotaxane.[3] The relative positions of the components of the rotaxane can be influenced by external stimuli − such as chemical, electrical, or light energy − that are able to switch the noncovalent interaction between the recognition sites on and off. Provided that two or more different recognition sites exist within the rotaxane, the switching of the intramolecular interaction is accompanied by a mechanical movement along the molecular thread. The conversion of light energy into mechanical energy is of particular interest and requires the incorporation of light-sensitive components into one of the rotaxane fragments. The photoinduced *cis-trans* isomerisation of azo groups has been used to modify the geometry and the properties of rotaxanes.[4] However, the question arises as to whether the geometry changes associated with *cis-trans* isomerisation of an azo unit incorporated in the molecular thread are sufficient to induce a change in the location at which the ring resides.

Stoddart and Balzani[5] have very recently a light-controlled rotaxane. It only works, however, reported in the presence of external redox compounds. It therefore seems necessary to look for further photoactive compounds suitable for a switching process. We have chosen the 2,4,6-cycloheptatriene ring as a photoactive building block for three reasons:

1. Substituted cycloheptatrienes undergo two types of photoreactions: namely 1,7-hydrogen shifts and intramolecular cyclisation.[6] Both reactions can be expected to induce drastic changes in the geometry of the molecular thread. The regioselectivity and the reversibility of photoreactions may be controlled by substituents in the seven-membered ring.[7,8]

2. Aryl-substituted cycloheptatrienes can be converted photochemically into the related tropylium ions, replacing an electron donor by an electron acceptor.[9,10]

3. 1,*x*-disubstituted cyclohepta-2,4,6-trienes contain a chiral centre.

Here we report on the synthesis and properties of rotaxanes consisting of a molecular thread with two cycloheptatriene units and the tetracationic cyclophane cyclobis(paraquat-4,4′-biphenylene) (**3**), which has been extensively used by Stoddart et al. as a component of catenanes and rotaxanes.[1] Pseudorotaxanes, precursors of rotaxanes, were also studied.

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Results and Discussion

Pseudorotaxanes

Pseudorotaxanes formed between the molecular threads (**1** or **2**) and the ring (**3**) serve as precursors for the rotaxanes described in this paper (see Scheme 1). The symmetrical compound **1** consists of a racemic mixture of three geometrical isomers: one pair of enantiomers (*SS* and *RR*) and the *meso* compound (*RS* = *SR*). Nevertheless, both the ^{1}H NMR and the ^{13}C NMR spectra exhibited only one resonance set for each subunit. The asymmetrical compound **2** consists of two diastereomeric pairs of enantiomers, but the diastereomers did not give rise to different NMR spectra; only one proton resonance set appears for each diaryl cycloheptatriene subunit. It would therefore be interesting to explore whether the diastereomers can be recognised by their different interactions with the ring **3**.

Complexation of the molecular thread **1** by the ring **3** results in the formation of three pseudorotaxanes (*SS*, *RR*, and *RS* = *SR*), and only the two diastereomeric pseudorotaxanes should be expected to exhibit differing interaction with the ring **3**.

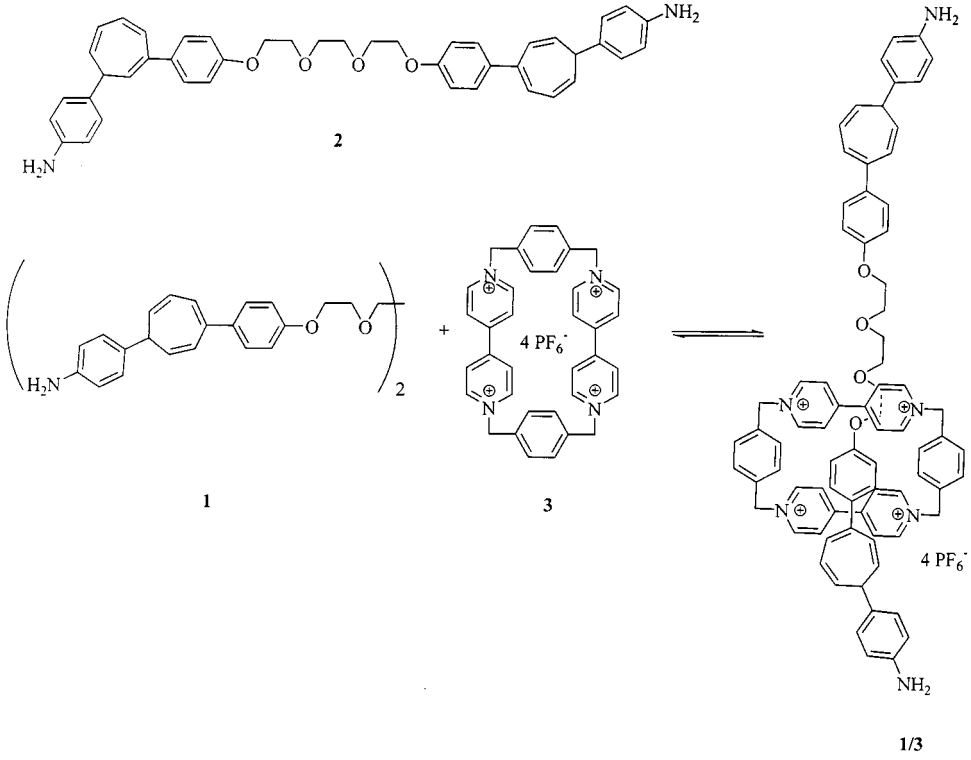
In order to evaluate the complexation behaviour qualitatively, the NMR spectra of equimolar mixtures of the guests **1** or **2** and the host **3** in the mixed solvent $CD_3CN/CDCl_3$ (4:1, concentration approx. 10^{-3} M) were recorded. This solvent mixture provided the best conditions for dissolving both the tetracationic ring **3** and the guests.

Noncovalent interactions between host and guest can be inferred from the significant shifts of the proton resonances, relative to those of the respective uncomplexed compounds, in the solution ^{1}H NMR spectra, and by the appearance of a charge transfer (CT) absorption band on the long wavelength side of the UV/Vis absorption spectrum. It is noteworthy that two different CT absorption bands appear, at 410 and 550 nm, when the spectrum of **1** is subtracted from the spectrum of the pseudorotaxane. These CT bands may be attributed to interactions between the electron-deficient ring **3** and distinct parts of **1** (the alkoxyphenylcycloheptatriene and aniline moieties, respectively). It is also remarkable that the regioisomeric thread **2** exhibits a shorter wavelength CT absorption band than **1** at 470 nm when it is complexed with **3**.

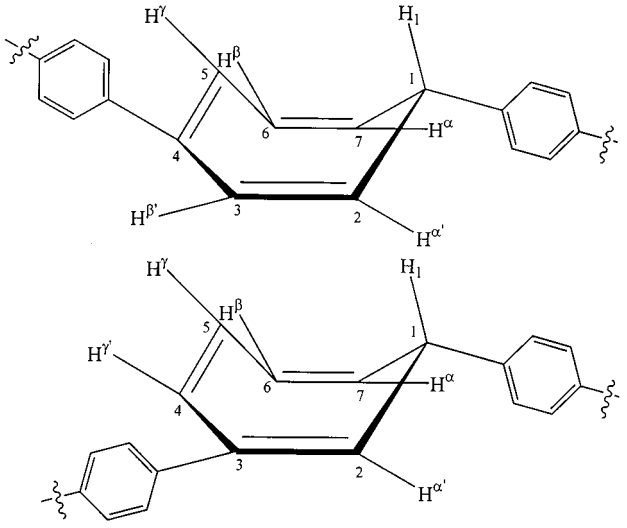
^{1}H NMR Spectroscopy

The protons of the seven-membered ring marked in Scheme 2 resonate in the ^{1}H NMR spectra with chemical shifts well separated from each other and from the other resonances of both the donor and acceptor systems. They can hence serve as useful ^{1}H NMR probes.

The guests **1** and **2** contain two donor parts that, together with the oxygen atoms in the glycol chain between these donors, give rise to complexation by threading of the guest molecule through the cavity of the ring **3**.[11] The pseudorotaxane structure is indicated by the upfield shift in the proton resonances of the pyridinium ring of **3** and the downfield shift of the protons of the benzylic spacer unit.[12] Averaged signals of the different proton resonances were observed in each case, because both the exchange between



Scheme 1. Formation of the pseudorotaxane **1/3**, and the molecular thread **2**



Scheme 2

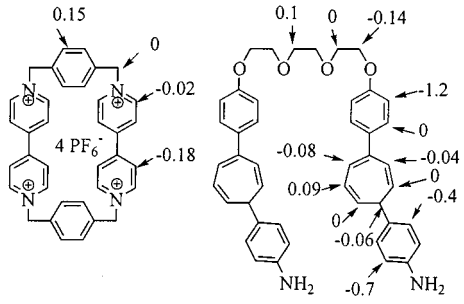


Figure 1. Observed chemical shifts of the proton resonances of the pseudorotaxane **1/3** relative to those in uncomplexed **1** and **3**, respectively

complexed and uncomplexed components and the shuttling processes of the ring along the molecular threads occur at a rate comparable to, or faster than, the 300 MHz ^{1}H NMR timescale at ambient temperatures.

The complex formation constant of the pseudorotaxane **1/3** in [D_3]acetonitrile/$CDCl_3$ (4:1) was determined by NMR titration to be 274±23 L·mol^{-1}.[13]

The donor stations of **1** are degenerate. Accordingly, only one set of proton resonances appears both for the molecular thread **1** and for the acceptor ring **3**, thus indicating that the exchange process between the two donor stations occurs rapidly. It is also remarkable that the asymmetry of the molecular thread, due to the differing configurations of the two seven-membered rings (*RS* vs. *RR*, *SS*) is not reflected in the NMR spectra of the pseudorotaxane.

In addition, the NMR spectra of the pseudorotaxane formed with compound **2** − the regioisomer of compound **1** − also exhibit only one set of proton resonances for **3**. These findings are in direct contrast to the behaviour of the rotaxanes, discussed later. Thus, it is reasonable to conclude that the fast exchange processes observed in the NMR spectra are dominated by threading and dethreading of both **1** and **2**. From the observed shifts in distinct proton resonances of the different subunits of **1** and **2**, it can be concluded that, in general, interaction between the flat aromatic units and the electron-deficient ring is stronger than that between the cycloheptatriene ring and **3** (see Figure 1). The smaller resonance shifts of the cycloheptatriene protons, in comparison to those of the aryl protons, may be due to the nonplanar structure of the seven-membered ring, which prevents close contact with the bipyridinium unit of the electron-deficient ring.

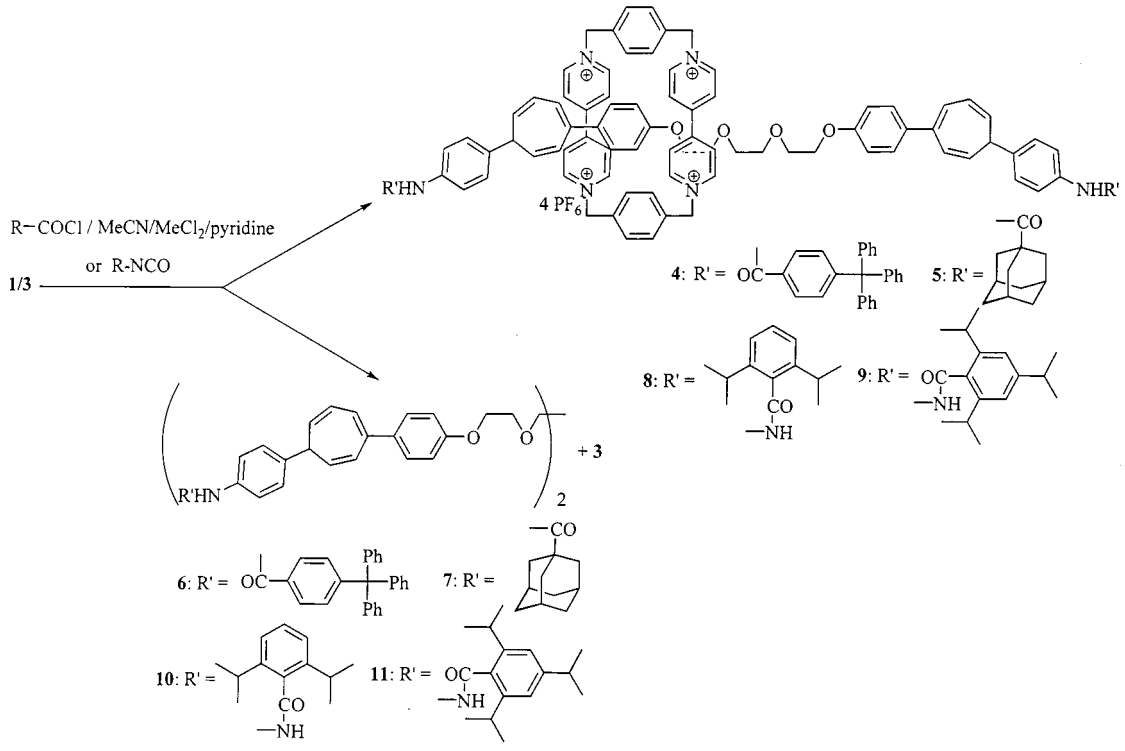
Nevertheless, it is noteworthy that the difference between the resonances of the cycloheptatriene protons is more pronounced under the influence of the cyclophane **3**. Vicinal β- and γ- protons (see Scheme 2) are shifted in the opposite direction, and whereas the resonance of the β-proton is shifted downfield, the resonance of the β′-proton on the other side of the cycloheptatriene ring is shifted upfield.

Oxygen atoms in the chain between the electron donor subunit support the complexation of the molecular threads containing aromatic units and cationic electron acceptors, such as paraquat, by wrapping back around the bipyridinium units to enable interaction between the chain oxygen and the α protons of the bipyridinium rings of the cyclophane.[12] Hydrogen bonds seem to be the favoured interaction. The resonances of the protons of the central ethyleneoxy group are slightly shifted slightly downfield (Δδ = 0.1 ppm). In contrast, the resonance of the methylene group next to the phenol unit is shifted upfield by 0.14 ppm. In this case, the shielding effect produced by the sandwiching of the bipyridinium units dominates. During the shuttling and dethreading processes, the tetracationic cyclophane interacts with each of the components of the molecular thread. It is worth noting that the signal of the NH protons, clearly detectable in the molecular thread, vanishes because of the interaction with **3**.

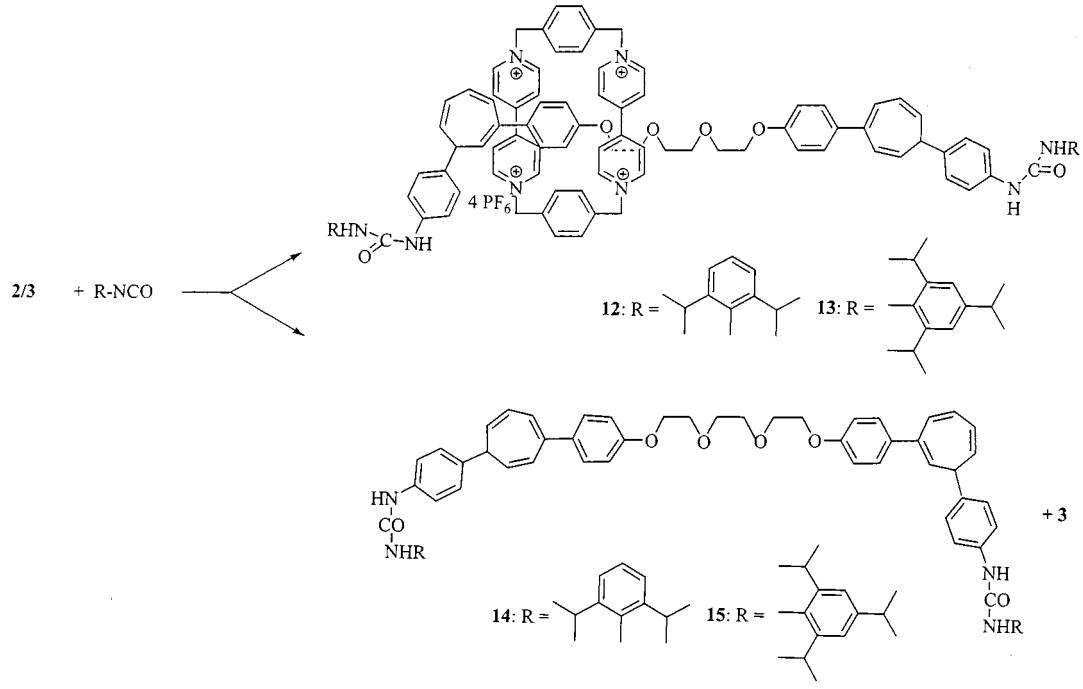
The molecular thread **2** differs from **1** in two properties: i) it contains two non-equivalent recognition sites and, ii) it has a more curved shape, due to the substitution pattern in one of the seven-membered rings. The question of the influence of the geometry on the stability of the complex therefore arises. Indeed, the complex formation constant of the pseudorotaxane **2/3** amounts to 156±18 L·mol^{-1} and is clearly smaller than that of **1/3**. One remarkable difference between **2/3** and **1/3** is the fact that it is in **2/3** that only one set of resonances of the aromatic ring protons is detectable. The other three resonance sets are assumed to be merged in with the base line.

Rotaxanes

Compounds **1** and **2** were used to prepare [2]rotaxanes by acylative end-capping. To this end, the pseudorotaxanes formed in the 1:1 mixtures of **3** and either **1** or **2** were treated with acyl chlorides and isocyanates, respectively; these reacted at the amino termini of the molecular threads (see Scheme 3 and Scheme 4) to provide rotaxanes **4**, **5**, **8**, **9**, **12**, and **13** as highly coloured compounds, in yields of up



Scheme 3. Synthesis of rotaxanes **4**, **5**, **8**, and **9**



Scheme 4. Synthesis of rotaxanes **12** and **13**

to 35%. Acylated molecular threads are the main products that can be used as reference compounds in order to compare the ^{1}H NMR resonances of the molecular thread protons with those of the rotaxane. The approach with isocyanates as capping reagents has an advantage over that with acyl chlorides in that no base (such as pyridine) is necessary for the reaction. The stopper units introduced are sufficiently bulky to prevent the tetracationic ring from slipping off the ends of the molecular thread, and ESI mass spectra accordingly revealed peaks corresponding to the molecular ion minus two, three, and four hexafluorophosphate counterions.

Because of the interaction of the electron-deficient macrocyclic ring and the electron-rich units incorporated within the molecular threads, an absorption band around 450 nm is observed in the UV/Vis spectrum of all rotaxanes.

^{1}H NMR Spectroscopy

The rotaxanes were characterised by ^{1}H NMR spectroscopy, including ^{1}H-^{1}H COSY and ^{1}H-^{13}C COSY spectra for full assignments in order to gain an insight into their co-conformation.[14]

Chemical-induced shifts (CIS) in the solution ^{1}H NMR spectra were calculated by comparison with the resonances in dichloromethane of the uncomplexed acylated molecular threads (these are only poorly soluble in the acetonitrile and acetone used to record the NMR spectra of the rotaxanes). It has been established that the resonances of the protons of the nonacylated threads do not vary significantly in solvents such as dichloromethane and acetonitrile. The ^{1}H NMR spectra recorded for the [2]rotaxanes exhibited marked differences both in comparison to those of the uncomplexed dumbbell-shaped acylated molecular threads and in comparison to those of the pseudorotaxanes described above:

i) Resonances of the Electron-Deficient Ring

The resonances of the α-dipyridinium protons (α relative pf N^+) are influenced to a smaller extent than the β-protons. This was also found with other pseudorotaxames[11] and rotaxanes.[15] Both proton resonances are shifted to higher fields as a result of this unit lying above the faces of the donor units of the thread (i.e. the cycloheptatrienylphenoxy unit and the aniline moiety). For example, the C-H-COSY spectrum of the rotaxane **9** in acetonitrile solution, displayed in Figure 2, demonstrates the CIS of different protons. The protons of the bridging phenyl rings of the tetracationic ring experience downfield shifts as a result of the edge-to-face arrangement of these rings in relation to the included donor units. The resonances of the α-bipyridinium protons depend on the solvent: they are shifted downfield relative to uncomplexed **3** in [D_6]acetone solution and upfield in [D_3]acetonitrile solution.

The signal pattern of the α-protons is remarkable. In general, these proton resonances have been observed to appear as one doublet in symmetrical two-station-rotaxanes; this is due to the fast shuttling of the ring along the molecular thread, so that all α-protons are isochronous.[16] This feature is not observed with the rotaxanes described here. In particular, the resonances of the α-protons clearly appear in the 600 MHz NMR spectrum as three doublets in the ratio 1:2:1, illustrated in Figure 3. Irradiation at a frequency ($\delta = 8.3$) corresponding to the β-protons gives rise to three singlets in the ratio of 1:2:1. In contrast, the resonances of the β-protons are not well resolved; however, the structure of the signal is similar to that of the α-proton signal. The splitting into three signal sets in 1:2:1 ratio can also be deduced from the signal pattern of the protons of the bridging benzyl units. In this case, however, the observed multiplets consist of overlapping spectra of a higher order. In general, the resolution of the resonances of the ring protons is lower in the more polar solvents such as acetonitrile and DMSO than it is in acetone solution.

The signal pattern is also dependent on the temperature, thus indicating that dynamic processes are involved. This can be demonstrated by increasing the temperature of an acetonitrile solution; the signal dispersion increases at first and decreases later (see supporting material). In principle, the signal pattern observed in DMSO is similarly dependent on the temperature. Even at 100 °C no doublet structure can be recognised.

ii) Resonances of the Molecular Thread

According to the resonance of 1-H of the cyclohepta-2,4,6-trienyl rings, only one isomer of the threadlike molecule exists, with the aryl substituent at the equatorial position on the seven-membered ring.[17]

Only one set is observed for all protons in the molecular thread, indicating fast shuttling of the tetracationic ring. Different parts of the cycloheptatriene ring interact with the cyclophane in different ways; this results in opposite chemical shifts being observed for the protons adjacent to the phenoxy substituent and for the other protons adjacent to C-1 of the seven-membered ring (see Figures 2 and 4). According to the different CIS values of the protons, shown in Figure 4, the two seven-membered ring protons adjacent to the phenoxy unit interact with the electron-deficient ring in the same way as the protons of the phenoxy ring do: they are shielded by the π-cloud of the bipyridinium ring. The other cycloheptatriene proton resonances experience downfield shifts by virtue of their lying in the plane of the bipyridinium rings.

The three resonances of the different methylene groups of the bridging glycol units are shifted in opposite directions. Whereas the singlet of the central methylene groups appears at the highest field in the pseudorotaxanes, the sequence is reversed in the rotaxanes. The methylene protons adjacent to the phenol units resonate with a significant upfield shift, implying that, on a time-averaged basis, these protons are oriented directly below the bipyridinium unit of **3**. In contrast, the methylene protons of the central part of the chain must be lying in the plane of the bipyridinium unit of **3**, thus enabling the formation of hydrogen bonds between the α-protons of the bipyridinium unit and the central oxygen atoms. This could be taken to indicate folding of the glycol chain. NOE effects between the β-pyridinium protons and the central methylene protons of the glycol chain, seen in ROESY spectra recorded for rotaxane **9** in acetonitrile, reveal that these parts of the cyclophane and the molecular thread are close together.

At ambient temperatures in CD_3CN solution, the signals of the phenol ring protons are merged in with the base line between $\delta = 6$ and 4. On warming the acetonitrile solution up to 343 K, two broad doublets appear, as illustrated in Figure 5.

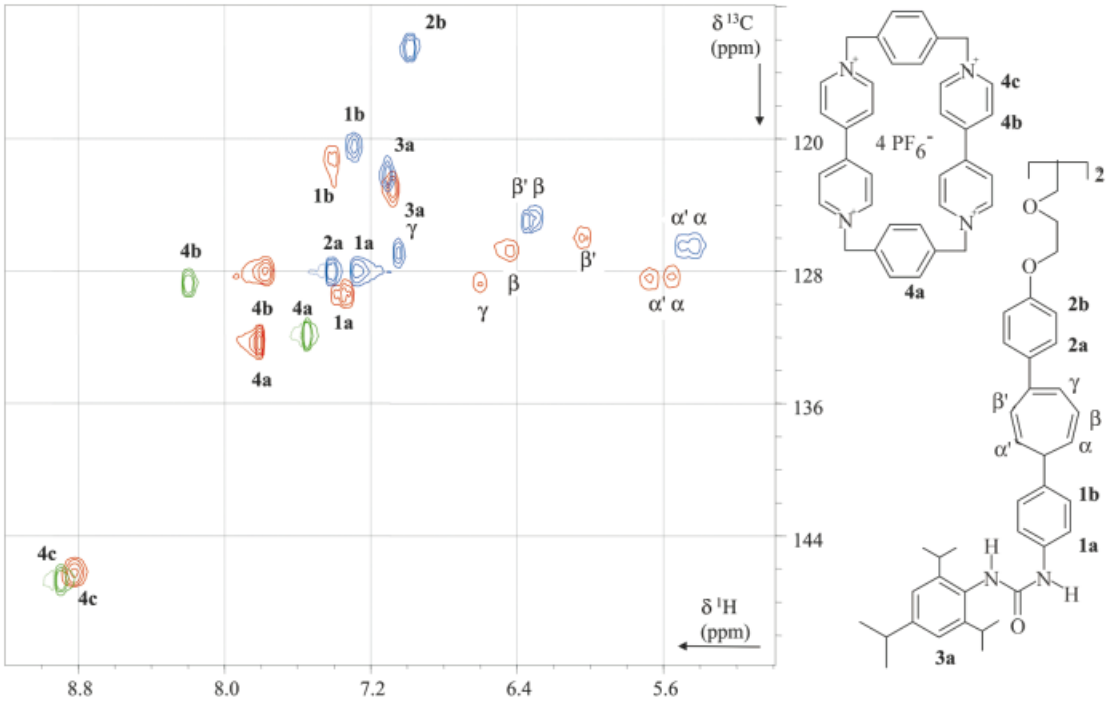


Figure 2. C-H COSY cross-peaks of the rotaxane **9** and its uncomplexed components recorded in [D_3]acetonitrile solution (green: uncomplexed ring; blue: uncomplexed molecular thread; red: rotaxane)

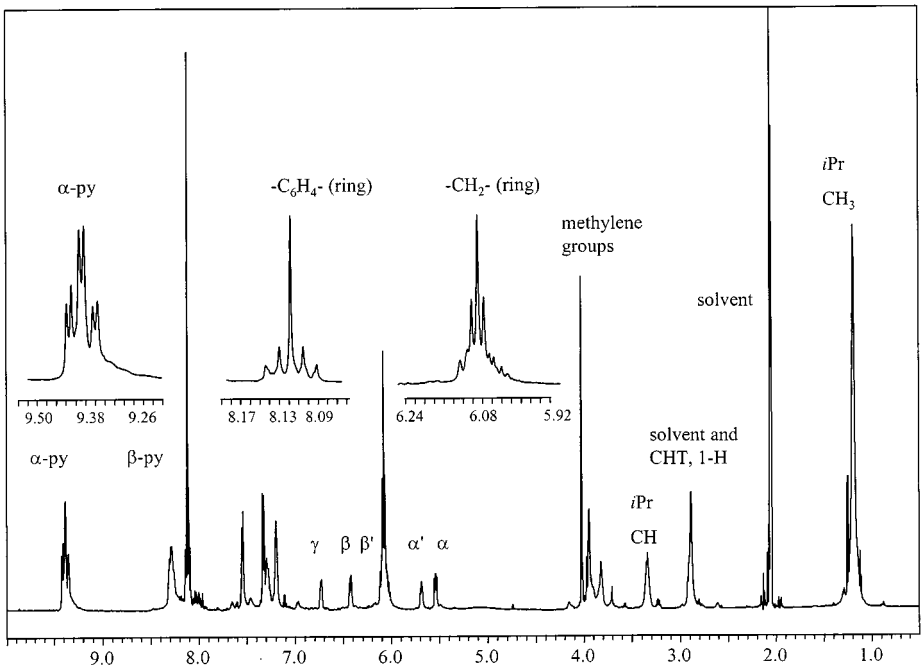


Figure 3. Signal pattern of the proton resonances of the cyclophane (α-py, β-py, -C_6H_4-$_{ring}$; -CH_2-$_{ring}$) observed with the rotaxane **9** ([D_6]acetone, 600 MHz ^{1}H NMR)

iii) Co-Conformation

The conformations of the [2]rotaxanes exist in a state of flux and only the averaged signals can be observed. However, not all dynamic processes are detectable by NMR spectroscopy. The observed three proton resonance sets of **3** could be explained in terms of three concepts. Firstly, the different stereoisomers of the molecular thread give rise to anisochronous protons in the ring. Secondly, the ring itself might become asymmetric. Thirdly, the ring might oscillate between several distinct environments of conformers of the molecular thread, such as conformers incorporating two cycloheptatriene boats with the same and the opposite ori-

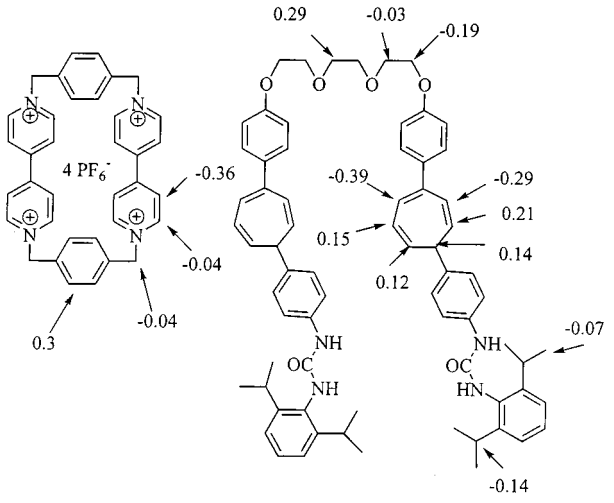


Figure 4. CIS values (ppm) of the proton resonances of the rotaxane **8**

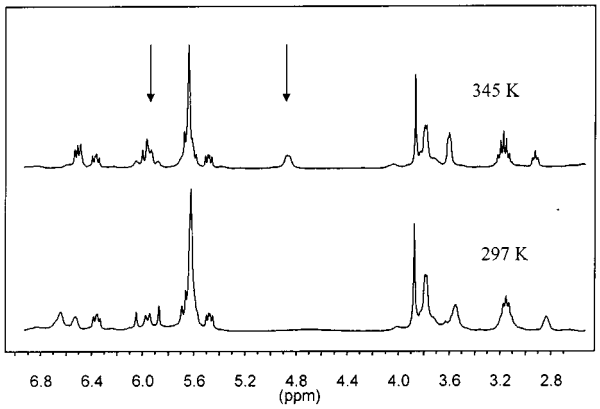
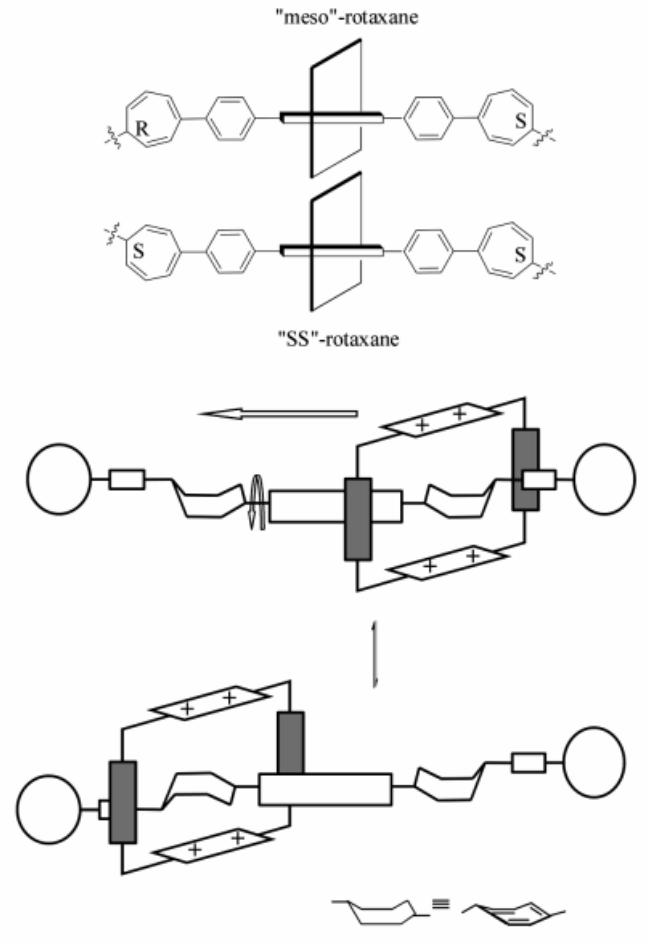


Figure 5. Partial ^{1}H NMR (300 MHz) spectra recorded for **8** at 297 and 345 K. Arrows denote the proton resonances of the phenoxy groups

entation with respect to the bipyridinium units of **3** (top or bottom, see Scheme 5).

Of the two diastereomeric rotaxanes that exist, the *meso* compound is a symmetrical, two-station rotaxane, whereas the other diastereomer is an asymmetrical, two-station rotaxane (see Scheme 5). The three doublets are therefore most likely to originate from two diastereomeric rotaxanes. The "*meso*" rotaxane gives rise to one doublet (both sites of **3** are equivalent, 8 isochronous protons), and the other two doublets are attributable to the two non-equivalent sites of **3** within the two enantiomeric "*SS*" and "*RR*" rotaxanes (two pairs of four isochronous protons).

Taking the inherent asymmetry of the boat-shaped cycloheptatriene rings into account, all protons of the tetracationic ring might become anisochronous (see Scheme 5). However, the fast shuttling process reduces the number of resonance sets. Nevertheless, considering the possible dispositions of the two boats of cycloheptatriene rings relative to each other and assuming a preferred arrangement of the boat within **3** (as illustrated in Scheme 5), a maximum of 16 resonances can be expected for the α-protons of the two



Scheme 5. Diastereomeric rotaxanes (top) and arrangements of the cycloheptatriene ring relative to the tetracationic cyclophane (bottom)

diastereomeric rotaxanes. Obviously, either most asymmetrical co-conformations must undergo rapid exchange, or the differences between the CIS values induced by those co-conformations are too small to be visible in the NMR spectra. The fast exchange may proceed both by rotation of the cyclophane about the thread and by rotation of the diaryl cycloheptatriene units within the molecular thread. In contrast, rotation of aromatic rings within the cyclophane would result in equivalent cyclophane protons and is obviously not observed.

The unexpected downfield shift of the resonances of the α-pyridinium protons in [D_6]acetone solution must originate from the presence of the cycloheptatriene rings within the thread. The protons of the latter are also shifted in opposite directions (see above).

Conversely, the ^{13}C NMR spectra do not reflect the signal dispersion observed with the proton spectra because the hydrogens, in contrast to the carbon atoms, are at the periphery of the interacting moieties (see also Figure 2).

Rotaxanes Incorporating Two Different Donor Stations

Two questions relating to unsymmetrical rotaxanes arise. Is there a difference in the interactions of the two stations

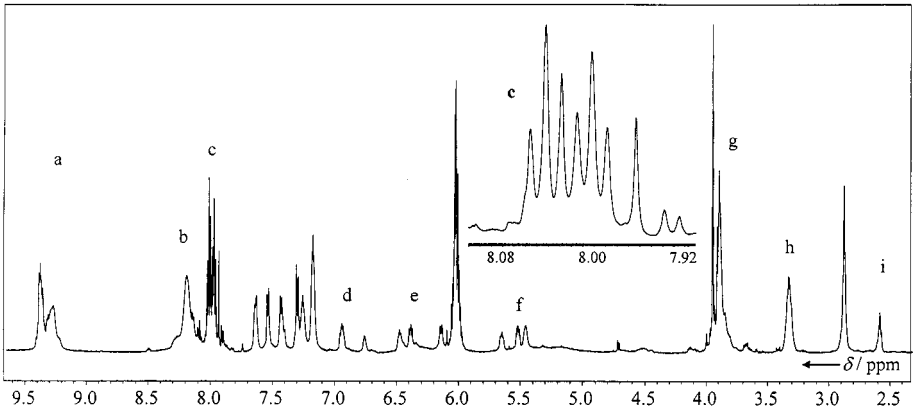


Figure 6. Partial ^{1}H NMR (600 MHz) spectrum recorded for **12** in [D_6]acetone solution (a,b,c: cyclophane protons; d−f,i: CHT γ-,β-, α-,1-H,g: glycol unit; h: isopropyl)

of the molecular thread with the tetracationic cyclophane? If so, does this different interaction result in a preference for one of the two stations?

The asymmetry of the rotaxanes **12** and **13** is attributable not only to the two diastereomers but also to the different substitution patterns in the two cycloheptatriene rings. This has the consequence of an additional splitting of the resonances both of the ring protons and of those of the two isomeric cycloheptatriene units. The resonances of the α-protons of the bipyridinium units of **3** clearly separate into two partly unresolved broad sets of signals (see Figure 6) and indicate that the two sites of the acceptor ring **3** are distinguishable, due to the two different aryl cycloheptatriene units of the molecular thread. However, the number of signal sets cannot be derived from the complex pattern.

Again, the resonances of the β-protons of **3** only appear as one broad signal. This finding reinforces the observations made with the symmetrical rotaxanes (see above).

A prochiral centre is generated at the methylene bridge of the tetracationic ring, due to the asymmetric thread. In contrast to the proton resonances in the 300 MHz spectrum, the protons both of the methylene groups and of the benzene rings in the benzylic bridges of **3** resonate as multiplets in the 600 MHz spectrum. The proton resonances of the glycol units of the chain are much less strongly separated but exhibit the same features as observed in the symmetrical rotaxane, indicating interaction between the central glycol unit and the cyclophane. Indeed, it is apparent from NOESY measurements recorded with **13** in [D_6]acetone that the α-, β-, and methylene protons of **3** show significant NOEs with the ethylene protons of the glycol unit.

The two cycloheptatriene units within the rotaxanes interact with the electron-deficient ring in similar ways. Again, the seven-membered ring is separated into two sections (see Figure 7), due to an upfield shift of the protons adjacent to the phenoxy unit and a downfield shift of the other protons. This discrimination is preserved in acetonitrile solution even at temperatures up to 345 K.

Only two sets of protons belonging to aromatic subunits within the molecular thread are observed; the other two (probably the phenoxy groups) appear only at higher temperatures, as broad signals that cannot be assigned by COSY experiments. The remarkable difference between the two cycloheptatriene subunits is the much stronger upfield shift of the α′- and γ′-protons of the 1,3-disubstituted cycloheptatriene. Both the protons of the phenoxy units and the α′- and γ′-protons of the 1,3-substituted cycloheptatriene moiety (Scheme 2) are merged in the base line and appear only in NMR spectra recorded at 320 K or above. Taking the CIS values observed for the two different cycloheptatriene rings of the dumbbell-shaped compound into account, together with the extremely broad signals of the α′- and γ′-protons, a much stronger interaction between the

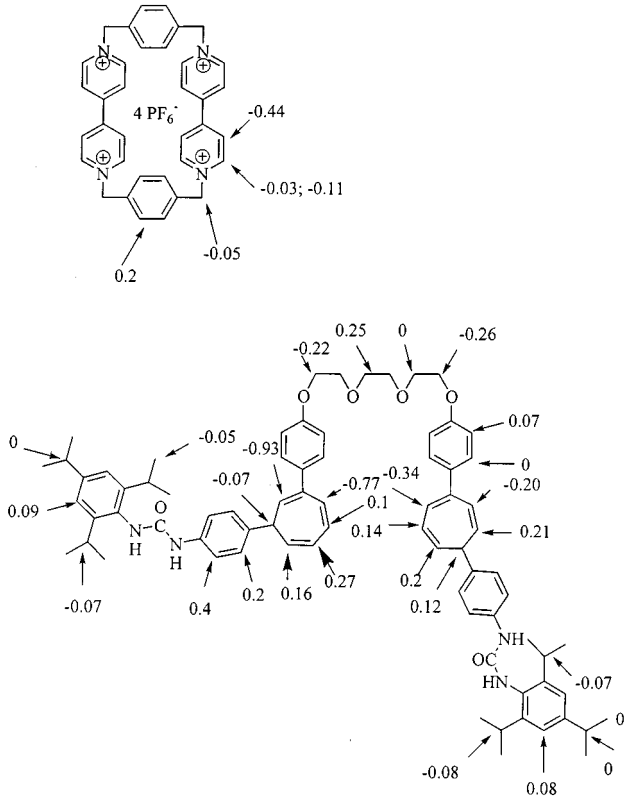


Figure 7. CIS-values (ppm) of the proton resonances of the rotaxane **13** observed in acetonitrile solution

1,3-disubstituted cycloheptatriene ring and the tetracationic ring can be inferred than in the case of the 1,4-regioisomer. On the other hand, no preference of the tetracationic ring for one of the two stations can be deduced from the NMR spectra recorded at low temperature. When the [D_6]acetone solution is cooled to 193 K, the ^{1}H NMR spectrum is exceedingly broad, and so provides little useful information. In particular, the occupied and unoccupied cycloheptatriene stations could not be distinguished.

The features of the ^{1}H NMR spectra are not generally changed on going from a CD_3CN solution to a [D_6]acetone to a [D_6]DMSO solution. It can therefore be concluded that hydrogen bonds do not play a significant role in the dynamic processes of the rotaxane. The only effect of DMSO as solvent is extensive line-broadening of the resonances of the bipyridinium protons.

Conclusions

For the first time, rotaxanes incorporating the photolabile cycloheptatriene group have been synthesised, utilising the acylating end-capping method with moderate yields. On the basis of their ^{1}H NMR spectra, the structural features of these [2]rotaxanes have been derived. The tetracationic cyclophane preferentially resides over the diaryl cycloheptatriene unit of the molecular thread, regardless of the boat-shaped conformation of the seven-membered ring. The protons of the cycloheptatriene ring are shifted both to higher and to lower fields, due to interaction with the tetracationic ring. These protons can therefore serve as sensitive probes with which to study the co-conformation of the rotaxanes in solution. The substitution pattern of the seven-membered ring strongly dictates the interaction with the tetracationic ring of the rotaxane.

Whereas diastereomeric molecular threads do not give rise to separate resonances either in the ^{1}H or ^{13}C NMR spectra, the differences between the diastereomers are amplified by interaction of the diastereomers with the tetracationic ring in the rotaxanes.

From the signal pattern observed for the cyclophane protons, it is not possible to infer a folded structure of the [2]rotaxanes, bringing the unoccupied cycloheptatriene unit into close contact with the exterior of the cyclophane. Nevertheless, fast equilibria between folded rotaxane structures may exist, as indicated by NOE effects between the protons of the glycol chain and the cyclophane protons.

The cyclophane migrates between the two diaryl cycloheptatriene units. The shuttling process is rapid on an NMR timescale, in the cases both of the symmetrical and of the asymmetrical rotaxane.

Knowledge of the probable co-conformation in solution is of importance for gaining understanding of the photochemical processes that occur in the rotaxanes. Investigations to establish the possibility of switching the properties of the rotaxanes both by photochemical and by electrochemical methods are in progress.

Experimental Section

General Methods: Reagents and solvents were purchased from the Aldrich Chemical Company and were used as supplied, with the exception of tetrahydrofuran (THF), which was distilled under argon from sodium benzophenone ketyl.

Analytical TLC was performed on Merck DC-Alufolien Kieselgel 60 F_{254} (0.2 mm). Column chromatography was performed on Merck Kieselgel 60 (0.040−0.063 mm, 230−400 mesh). Analytical HPLC was performed with Shimadzu equipment (LC-6A, SPD 6A, SCL 6B, C-R4 AX) using a reversed phase column.

ESI mass spectrometry was carried out on a triple quadrupole instrument (TSQ 700, Finnigan MAT, Bremen, Germany) equipped with an electrospray ion source (API-ESI) operating in the positive mode with a capillary temperature of 200 °C and a high voltage of 4.5 kV. The samples were dissolved in acetonitrile (concentration 10−50 pmol μL^{-1}. Nitrogen was used as sheath gas at a pressure of 3.4 bar. The spectra were composed of an average of 64 scans. NMR spectra were recorded on a Bruker DPX 300 (300 MHz) or a Bruker AMX 600 (600 MHz) with either the solvent or TMS as the internal standard. Chemical shifts are given in ppm relative to TMS. UV/Vis spectra were recorded with a Shimadzu UV 2101 PC spectrometer.

Materials: The molecular threads **1** and **2** were prepared according to ref.[18] using an improved procedure.

2,4,6-Triisopropylphenyl Isocyanate. − A) 2,4,6-Triisopropylaniline: Zn dust (9 g) was slowly added to stirred 1-nitro-2,4,6-triisopropylbenzene (4.14 g, 56 mmol)[19] dissolved in acetic acid (150 mL) and concd. HCl (40 mL), maintaining the temperature at about 100 °C. After this had cooled to ambient temperature, KOH was added to the solution so as to produce a pH between 8 and 9. The solution was extracted with diethyl ether. The organic phase was separated, and the solvent was removed under vacuum. The residue was treated with concd. HCl (150 mL). The precipitate was collected and washed with diethyl ether. The amine was obtained by treatment with aqueous KOH and dissolved in diethyl ether. The solution was dried ($MgSO_4$) and then evaporated. The remaining amine was purified by distillation, b.p. 64 °C (10^{-2} mbar) affording 9.5 g (87%) 2,4,6-triisopropylaniline. − ^{1}H NMR ($CDCl_3$): δ = 1.27 (d, J = 7.0 Hz, 12 H, CH_3), 1.29 (d, J = 7.0 Hz, 6 H, CH_3), 2.82 (sep, J = 7.0 Hz, 1 H, -$CHMe_2$), 2.93 (sep, J = 7.0 Hz, 2 H, -$CHMe_2$), 3.61 (s, 2 H, NH_2), 6.91 (s, 2 H, CH arom.). − ^{13}C NMR ($CDCl_3$): δ = 22.3 (2 C, CH_3), 24.2 (CH_3), 27.9 (2 C, -$CHMe_2$), 33.6 (−$CHMe_2$), 120.5 (2 C, phenyl C^3), 132.2 (2 C, phenyl C^2), 136.0 (phenyl C^1), 137.0 (phenyl C^4).

B) 2,4,6-Triisopropylphenyl Isocyanate: Diphosgene (4.7 g, 23.7 mmol) was added to 2,4,6-triisopropylaniline (5.2 g, 23.7 mmol) dissolved in dry dioxane (100 mL). The reaction mixture was refluxed for 3 h. After the mixture had cooled to ambient temperature, the solvent and excess diphosgene were removed under vacuum. The remaining 2,4,6-triisopropylphenyl isocyanate was purified by vacuum distillation. b.p. 110 °C ($2{\cdot}10^{-4}$ mbar), yield 5.76 g (99%), colourless oil. − ^{1}H NMR ($CDCl_3$): δ = 1.22/1.24 (d, J = 7.0 Hz, 12 H, CH_3), 1.27 (d, J = 7.0 Hz, 6 H, CH_3), 2.89 (sept, J = 7.0 Hz, 1 H, -$CHMe_2$), 3.19 (sept, J = 7.0 Hz, 2 H, -$CHMe_2$), 6.96 (2 H, CH, phenyl). − ^{13}C NMR ($CDCl_3$): δ = 22.9 (CH_3), 24.0/24.1 (2 C, -CH_3), 29.6 (2 C, -$CHMe_2$), 34.2 (-$CHMe_2$), 121.3 (2 C, CH phenyl), 126.3 (C−NCO), 142.7 (2 C-*ortho*), 146.6 (C-*para*). − FT-IR: $\tilde{\nu}$ = 2201.2 cm^{-1}.

1,8-Bis{4-[5-(4-aminophenyl)cyclohepta-1,3,6-trienyl]phenoxy}-3,6-dioxaoctane (1) and 1-{4-[4-(4-Aminophenyl)cyclohepta-1,3,6-trienyl]phenoxy}-8-{4-[3-(4-aminophenyl)cyclohepta-1,4,6-trienyl]-phenoxy}-3,6-dioxaoctane (2): 1,8-Bis[4-tropylium)phenoxy]-3,6,-dioxaoctane bisperchlorate (3 g, 4.4 mmol) dissolved in acetonitrile (100 mL) was slowly dropped into a solution (3 mL acetonitrile) of freshly distilled aniline (6.2 g, 66.7 mmol). The reaction mixture was stirred at room temperature for 3 h and the solvent was removed under reduced pressure. The residue was treated with 1 M NaOH (100 mL) and extracted with dichloromethane. The organic phase was washed with water and dried (Na_2SO_4). After evaporation of the solvent, the remaining oily mixture was removed from aniline by dropping the mixture into *n*-hexane. The resulting solid (2 g, 67%), consisting of the regioisomers **1** and **2**, was separated by column chromatography (*n*-hexane/ethyl acetate, 1.5:1). The progress of chromatography was followed by analytical HPLC (acetonitrile/water) in order to identify fractions containing **2**, which was eluted earlier, and **1**. Chromatographic separation of 1 g of the crude solid afforded 0.28 g **2** (28%), m.p. 54−57 °C, and 0.20 g **1** (20%), m.p. 103−107 °C (ref.[18] 88 °C).

Compound 1: ^{1}H NMR ($CDCl_3$): δ = 7.43 (d, *J* = 9.0 Hz, 4 H, phenyl), 7.18 (d, *J* = 8.0 Hz, 4 H, phenyl), 7.01 (d, *J* = 6.0 Hz, 2 H, CHT, 2-H), 6.93 (d, *J* = 9.0 Hz, 4 H, phenyl), 6.72 (d, *J* = 9.0 Hz, 4 H, phenyl), 6.35 (d, *J* = 10.0 Hz, 2 H, CHT, 7-H), 6.28 (m, CHT, 2 H, 3-H), 5.51 (m, 2 H, CHT, 6-H), 5.42 (m, 2 H, CHT, 4-H), 4.15 (m, 4 H, OCH_2, phenoxy), 3.89 (m, 4 H, CH_2O), 3.77 (s, 4 H, OCH_2), 4.09 (br, 4 H, NH_2), 2.68 (t, *J* = 6.0 Hz, 2 H, CHT, 5-H). − ^{13}C NMR ([D$_6$]acetone): δ = 159.5 (phenyl), 147.8 (phenyl), 143.1 (C-1), 135.2 (phenyl), 132.6 (phenyl), 128.8 (phenyl), 128.2/128.1 /127.4 (C-2,3,7), 125.4/125.3 (C-4,6), 115.5 (phenyl), 115.4 (phenyl), 71.4 (O−C), 70.3 (C−O), 68.3 (O−C), 45.4 (C-5). − $C_{44}H_{44}N_2O_4$ (664.85): calcd.C 79.49, H 6.67, N 4.21; found C 79.12 H 6.79 N 3.89.

Compound 2: ^{1}H NMR ($CDCl_3$): δ = 7.40 (d, *J* = 9.0 Hz, 2 H, phenyl), 7.30 (d, *J* = 9.0 Hz, 2 H, phenyl), 7.17 (dd, 4 H, phenyl), 7.00 (d, *J* = 6.0 Hz, 1 H, CHT, 2-H), 6.92 (d, *J* = 9.0 Hz, 2 H, phenyl), 6.84 (m, 4 H, phenyl, CHT, 6,7-H), 6.65 (d, *J* = 8.0 Hz, 4 H, phenyl), 6.33 (d, *J* = 10.0 Hz, 1 H, CHT, 7-H), 6.30 (m, 1 H, CHT, 3-H), 6.23 (d, 1 H, CHT, 5-H), 5.52 (m, 1 H, CHT, 6-H), 5.43 (m, 1 H, CHT, 4-H), 5.34 (m, 2 H, CHT, 2,4-H), 4.13 (m, 4 H, OCH_2, phenoxy), 3.87 (m, 4 H, CH_2O), 3.76 (s, 4 H, OCH_2), 3.64 (br. s, 4 H, NH), 2.69 (t, *J* = 6.0 Hz, 1 H, CHT, 5-H), 2.54 (t, *J* = 6.0 Hz, 1 H, CHT, 3-H). − $C_{44}H_{44}N_2O_4$ (664.85): calcd. C 79.49, H 6.67, N 4.21; found C 78.92, H 6.91, N 4.09.

Rotaxanes. − General Procedure: A solution of cyclobis[paraquat-*p*-phenylene tetrakis(hexafluorophospate)] (**3**)[20] (165 mg, 0.15 mmol) in dry acetonitrile (6.4 mL) was mixed with a solution of **1** or **2** (99.6 mg, 0.15 mmol) in dry dichloromethane (1.6 mL) under an argon atmosphere. The acyl chloride or the isocyanate (0.3 mmol), respectively, was added to the red solution of the pseudorotaxane. In the case of the acyl chlorides, dry pyridine (1 mmol) was added in order to trap HCl. The reaction mixture was stirred in the dark for 7 days at room temperature. After evaporation of the solvent under vacuum, the residue was treated with acetonitrile (5 mL). The insoluble acylated free molecular thread was filtered off and the solution was evaporated. The residue was dissolved in the solvent mixture used for column chromatography (acetonitrile/ethyl acetate/cyclohexane/acetonitrile saturated with ammonium hexafluorophosphate 3.5:2:1:0.5) to precipitate insoluble **7**, which was filtered off. The solution was subjected to column chromatography on silica gel. The first yellow fraction contained a further proportion of the molecular thread. The red fractions were collected and the solvents were evaporated. The residue was washed with water, dried, and washed with dichloromethane in order to remove the soluble acylated thread. The combined fractions containing the acylated molecular thread were subjected to column chromatography (ethyl acetate/*n*-hexane between 2:1 and 4:1).

[2]Rotaxane 4 × 4 PF_6: This compound was prepared according to the general procedure, by use of **1** and *p*-tritylbenzoyl chloride (112 mg, 0.30 mM). Yield 74 mg (20%), red solid, m.p. 200−202 °C. − ^{1}H NMR (CD_3CN): δ = 8.80 (m, 8 H, **7**), 8.76 (s, 2 H, NH), 7.83 (s, 8 H, **7**), 7.75 (m, 8 H, **7**), 7.64 (d, *J* = 8.0 Hz, 4 H, phenyl), 7.43 (d, *J* = 8.0 Hz, 4 H, phenyl), 7.36 (d, *J* = 8.0 Hz, 4 H, phenyl), 7.28 (m, 15 H, phenyl), 7.22 (d, *J* = 8.0 Hz, 4 H, phenyl), 6.61 (br. d, 2 H, CHT, 5-H), 6.48−6.43 (m, 2 H, CHT, 6-H), 6.08 (d, *J* = 10.0 Hz, 2 H, CHT, 3-H), 5.70 (br. s 10 H, **7** and CHT, 2-H), 5.61-5.56 (m, 2 H, CHT, 7-H), 3.92 (s, 4 H, CH_2O), 3.83 (m, 4 H, OCH_2), 3.63 (br. s, 4 H, OCH_2), 3.01 (br. t, 2 H, CHT, 1-H). − ^{13}C NMR (CD_3CN): δ = 166.2, 157.3, 151.8, 147.6, 147.3, 145.4, 122.1, 141.5, 139.7, 138.1, 137.8, 133.1, 131.6, 128.7, 128.2, 128.0, 127.4, 125.5, 126.3, 127.6, 70.4, 69.3, 67.1, 65.5, 45.0. − ESIMS: *m*/*z* = 1084.2 $[M - 2\ PF_6]^{2+}$, 1011.2 $[M - 3\ PF_6 - H^+]^{2+}$, 938.2 $[M - 4\ PF_6 - 2\ H^+]^{2+}$, 674.5 $[M - 3\ PF_6]^{3+}$, 625.8 $[M - 4\ PF_6 - H^+]^{3+}$, 469.6 $[M - 4\ PF_6]^{4+}$. − MS MALDI-TOF (DHB) cald. for $C_{132}H_{112}N_6O_6$ $[M - 4\,PF_6]^+$ 1876.90 found 1876.78. − $C_{132}H_{112}F_{24}N_6O_6P_4$ (2458.26): calcd. C 64.50, H 4.59, N 3.42; found C 64.32, H 4.73, N 3.31.

Molecular Thread 6: This compound was prepared as described above. The acylated molecular thread **6** (153 mg, 75%) was isolated as a colourless solid, m.p. 162 °C. − ^{1}H NMR (CD_2Cl_2): δ = 7.94 (s, 2 H, NH), 7.76 (d, *J* = 9.0 Hz, 4 H, phenyl), 7.62 (d, *J* = 9.0 Hz, 4 H, phenyl), 7.45 (d, *J* = 9.0 Hz, 4 H, phenyl), 7.41 (d, *J* = 9.0 Hz, 4 H, phenyl), 7.48 (d, *J* = 9.0 Hz, 4 H, phenyl), 7.26 (s, 15 H, phenyl), 7.03 (d, 2 H, CHT, 5-H), 6.93 (d, *J* = 9.0 Hz, 4 H, phenyl), 6.40−6.31 (m, 4 H, CHT, 3-H and 6-H), 5.58 (m, 2 H, CHT, 2-H), 5.50 (m, 2 H, CHT, 7-H), 4.13 (m, 4 H, OCH_2), 3.84 (m, 4 H, OCH_2), 3.72 (s, 4 H, CH_2O), 2.89 (t, *J* = 6.0 Hz, 2 H, CHT, 1-H). − ESIMS calcd. for $[C_{96}H_{81}N_2O_6]^+$ 1358.7 found 1358.6. − $C_{96}H_{80}N_2O_6$ (1357.7): calcd. C 84.93, H 5.94, N 2.06; found C 79.72, H 7.23.

[2]Rotaxane 5 × 4 PF_6: This compound was prepared from **1** and adamantoyl chloride (56 mg). Compound **5** (56 mg, 28 mg, 12%) was obtained as a red solid, m.p. 175−177 °C. − ^{1}H NMR (CD_3CN): δ = 8.82 (m, 8 H, **7**), 7.95 (s, 2 H, NH), 7.81 (s, 8 H, **7**), 7.76 (m, 8 H, **7**), 7.54 (d, *J* = 8.0 Hz, 4 H, phenyl), 7.33 (d, *J* = 8.0 Hz, 4 H, phenyl), 6.61 (br, 2 H, CHT, 5-H), 6.45 (m, 2 H, CHT, 6-H), 6.09 (br. d, 2 H, CHT, 3-H), 5.71 (br. s 10 H, **7** and CHT, 2-H), 5.57 (m, 2 H, CHT, 7-H), 3.94 (s, 4 H, CH_2O), 3.85 (m, 4 H, OCH_2), 3.65 (br. s, 4 H, OCH_2), 2.98 (br. t, 2 H, CHT, 1-H), 1.92 (br. s, 6 H, adamantane), 1.75 (br. s, 24 H, adamantane). − ^{13}C NMR ([D$_6$]acetone): δ = 176.8, 157.7, 148.0, 145.9, 139.1, 139.0, 138.3, 131.8, 128.3, 127.9, 127.6, 127.4, 127.2, 126.1, 125.5, 121.5, 70.7, 71.7, 68.1, 65.7, 45.2, 42.1, 38.9, 36.8, 29.1. − ESIMS: *m*/*z* = 899.8 $[M - 2\ PF_6]^{2+}$, 826.9 $[M - 3\ PF_6 - H^+]^{2+}$, 551.5 $[M - 3\ PF_6]^{3+}$. − $C_{102}H_{102}F_{24}N_6O_6P_4$ (2087.85): calcd. C 58.68, H 4.92, N 4.03; found C 58.87, H 5.01, N 3.81.

Molecular Thread 7: The synthesis of **5** afforded 89 mg (60%) **7** as a yellowish solid, insoluble in acetonitrile, m.p. 100 °C. − ^{1}H NMR (CD_2Cl_2): δ = 7.56 (d, *J* = 9.0 Hz, 4 H, phenyl), 7.62 (d, *J* = 9.0 Hz, 4 H, phenyl), 7.48 (s 1 H, NH), 7.44 (d, *J* = 9.0 Hz, 4 H, phenyl), 7.32 (d, *J* = 8.0 Hz, 4 H, phenyl), 7.02 (d, *J* = 6.0 Hz, 2 H, CHT, 5-H), 6.93 (d, *J* = 9.0 Hz, 4 H, phenyl), 6.39−6.30 (m, 4 H, CHT, 3-H and 6-H), 5.56 (m, 2 H, CHT, 2-H), 5.48 (m, 2 H,

CHT, 7-H), 4.13 (m, 4 H, OCH_2), 3.83 (m, 4 H, OCH_2), 3.71 (s, 4 H, CH_2O), 2.86 (t, J = 6.0 Hz, 2 H, CHT, 1-H), 2.07 (br. s, 6 H, adamantane), 1.96 (br. s, 12 H, adamantane), 1.76 (br. s, 12 H, adamantane). − ^{13}C NMR (CD_2Cl_2): δ =176.3, 158.9, 142.8, 139.7, 137.3, 134.9, 128.4, 128.2, 127.2, 126.9, 126.8, 125.5, 125.3.120.9, 114.9.45.1, 41.8, 39.6, 36.8, 28.7. − $C_{66}H_{70}N_2O_6$ (987.30): calcd. C 80.30, H 7.15, N 2.84; found C 79.98, H 7.27, N 2.72.

[2]Rotaxane 8 × 4 PF_6: This compound was prepared from **1** according to the general procedure, by use of 2,6-diisopropylphenyl isocyanate (61 mg). Yield 97 mg (30%), red solid, m.p. 210−212 °C. − ^{1}H NMR (CD_3CN): δ = 8.84−8.78 (m, 8 H, **7**), 7.81 (s, 8 H, **7**), 7.76 (br. m, 8 H, **7**), 7.81−7.18 (m, 14 H, phenyl), 6.46 (br. s, 2 H, NH), 6.60 (br. s, 2 H, CHT, 5-H), 6.64−6.59 (m, 2 H, CHT, 6-H), 6.09 (s, 1 H, NH), 6.03 (br. d, 2 H, CHT, 3-H), 5.91, (s, 1 H, NH), 5.70 (br. s 10 H, **7** and CHT, 2-H), 5.60- 5.55 (m, 2 H, CHT, 7-H), 3.95 (s, 4 H, CH_2O), 3.86 (br. s, 4 H, OCH_2), 3.63 (br. s, 4 H, OCH_2), 3.22 [sept, J = 7.0 Hz, 4 H, CH(CH_3)$_2$], 2.93 (br. t, 2 H, CHT, 1-H), 1.17 [d, J = 7.0 Hz, 24 H, CH(CH_3)$_2$]. − ^{13}C NMR (CD_3CN): δ = 157.4, 155.9, 148.5, 148.0, 145.6, 144.0, 131.6, 128.7, 128.1, 127.8, 127.7, 127.3, 126.1, 125.3, 71.3, 70.6, 68.4, 65.5, 45.2, 29.3, 23.7. − ESIMS: m/z = 940.8 [M − 2 PF_6]$^{2+}$, 867.9 [M − 3 PF_6 − H^+]$^{2+}$, 579.0 [M − 3 PF_6]$^{3+}$. − $C_{106}H_{110}F_{24}N_6O_6P_4$ (2143.96): calcd. C 59.38, H 5.17, N 3.92; found C 59.18, H 4.93, N 3.71.

Molecular Thread 10: The synthesis of **8** provided **10** (88 mg, 55%) as a yellowish solid, insoluble in acetonitrile, m.p. 183−185 °C. − ^{1}H NMR ($CDCl_3$): δ = 7.42 (d, J = 9.0 Hz, 4 H, phenyl), 7.42 (d, J = 9.0 Hz, 4 H, phenyl), 7.25 (br. s, 14 H, phenyl), 6.99 (d, J = 6.0 Hz, 2 H, CHT, 5-H), 6.91 (d, J = 9.0 Hz, 4 H, phenyl), 6.3−6.2 (br. m, 4 H, CHT, 3-H and 6-H), 5.49 (m, 4 H, CHT, 2-H), 5.41 (m, 4 H, CHT, 7-H), 4.13 (s, 4 H, OCH_2), 3.88 (m, 4 H, OCH_2), 3.77 (m, 4 H, CH_2O), 3.36 [br. s, 4 H, CH(CH_3)$_2$], 2.79 (br. s, 2 H, CHT, 1-H), 1.22 [br. s, 24 H, CH(CH_3)$_2$]. − ^{13}C NMR ($CDCl_3$): δ = 158.3, 155.1, 142.4, 134.6, 128.1, 128.0, 126.9, 126.6, 125.1, 124.8, 124.3 (br), 120.5, 114.6, 70.9, 69.8, 67.5, 44.6, 28.5, 24.1/23.3 (br). − $C_{70}H_{78}N_4O_6$ (1071.42): calcd. C 78.47, H 7.34, N 5.23; found C 78.33, H 7.51, N 4.95.

[2]Rotaxane 9 × 4 PF_6: This compound was prepared from **1** according to the general procedure, by use of 2,4,6-triisopropylphenyl isocyanate (74 mg). Yield 117 mg (35%), red solid, m.p. 215−219 °C. − ^{1}H NMR (CD_3CN): δ = 8.84−8.78 (m, 8 H, **7**), 7.81 (s, 8 H, **7**), 7.77 (br. m, 8 H, **7**), 7.46 (d, J = 9.0 Hz, 4 H, phenyl), 7.36 (d, J = 9.0 Hz, 2 H, phenyl), 7.08 (s, 4 H, phenyl), 6.58, 6.55 (br. m, 3 H, CHT, 5-H and NH), 6.43 (m, 2 H, CHT, 6-H), 6.04 (d, J = 9.0 Hz, 2 H, CHT, 3-H), 5.70 (br. s 10 H, **7** and CHT, 2-H), 5.59 (m, 2 H, CHT, 7-H), 3.95 (s, 4 H, CH_2O), 3.85 (br. s, 4 H, OCH_2), 3.62 (br. s, 4 H, OCH_2), 3.20 [sept, J = 7.0 Hz, 4 H, CH(CH_3)$_2$], 2.92 [m, 4 H, CH(CH_3)$_2$ and CHT, 1-H], 1.23 [d, J = 7.0 Hz, 12 H, CH(CH_3)$_2$], 1.17 [d, J = 7.0 Hz, 24 H, CH(CH_3)$_2$]. − ^{13}C NMR (CD_3CN): δ = 157.2, 147.9, 147.5, 145.3, 143.5, 137.7, 133.8, 131.4, 128.5, 127.9, 127.6, 127.5, 127.2, 125.9, 125.1, 120.5, 71.5, 70.4, 68.0, 65.3, 45.0, 28.5, 24.3, 24.0. − ESIMS: m/z = 983.6 [M − 2 PF_6]$^{2+}$, 606.9 [M − 3 PF_6]$^{3+}$, 558.6 [M − H^+]$^{3+}$, 418.9 [M − 4 PF_6^-]$^{4+}$. − $C_{112}H_{122}F_{24}N_6O_6P_4$ (2228.12): calcd. C 60.38, H 5.52, N 3.77; found C 60.10 H 5.36, N 3.48.

Molecular Thread 11: The synthesis of **9** afforded **11** (104 mg, 60%) as a yellowish solid (83 mg, 48%), which was purified by column chromatography, m.p. 153−155 °C. − ^{1}H NMR ($CDCl_3$): δ = 7.42 (d, J = 9.0 Hz, 4 H, phenyl), 7.26 (br. s, 8 H, phenyl), 7.10 (s, 4 H, phenyl), 6.99 (d, J = 6.0 Hz, 2 H, CHT, 5-H), 6.91 (d, J = 9.0 Hz, 4 H, phenyl), 6.34−6.27 (br. m, 4 H, CHT, 3-H and 6-H), 6.3 and 6.0 (br. s, NH), 5.51−5.39 (m, 4 H, CHT, 2-H and 7-H), 4.14 (m, 4 H, OCH_2), 3.88 (m, 4 H, OCH_2), 3.77 (s, 4 H, CH_2O), 3.34 [sept, J = 7.0 Hz, 4 H, CH(CH_3)$_2$], 2.93 [sept, J = 7.0 Hz, 4 H, CH(CH_3)$_2$], 2.80 (br. t, 2 H, CHT, 1-H), 1.27 [d, J = 6.0 Hz, 12 H, CH(CH_3)$_2$], 1.22 [br. s, 24 H, CH(CH_3)$_2$]. − ^{13}C NMR ($CDCl_3$): δ = 158.4, 155.5, 147.7, 142.5, 134.7, 128.1, 128.0, 126.9, 126.7, 125.1, 124.9, 122.3, 120.5, 114.6, 70.9, 69.8, 67.5, 44.7, 34.3, 28.6, 24.0. − $C_{76}H_{90}N_4O_6$ (1155.58): calcd. C 78.99, H 7.85, N 4.85; found C 78.83, H 7.73, N 4.71.

[2]Rotaxane 12 × 4 PF_6: This compound was prepared from **2** according to the general procedure, by use of 2,6-diisopropylphenyl isocyanate (61 mg). Yield 77 mg (24%), red solid, m.p. 211−214 °C. − ^{1}H NMR ([D_6]acetone, 600 MHz): δ = 9.4−9.2 (m, 8 H, **7**), 8.23 (br. s, 8 H, **7**), 8.06−7.97 (m, 8 H, **7**), 7.67 (d, J = 8.0 Hz, 2 H, phenyl), 7.57 (d, J = 8.0 Hz, 2 H, phenyl), 7.46 (d, J = 8.0 Hz, 2 H, phenyl), 7.33 (d, J = 8.0 Hz, 2 H, phenyl) 7.29 (br. s, 2 H, phenyl), 7.21 (br. s, 4 H, phenyl), 6.97 (m, 1 H, CHT, 5-H), 6.78 (br. s, 1 H, CHT, 5-H), 6.51 (br. m, 1 H, CHT, 6-H), 6.42 (br. m 1 H, CHT, 6-H), 6.18 (d, J = 9.0 Hz, 1 H, CHT, 3-H), 6.09−6.02 (m, 8 H, **7**, CH_2-benzyl), 5.68 (br. m, CHT, 2-H), 5.55 (m, 1 H, CHT, 7-H), 5.49 (br. m, 1 H, CHT, 7-H), 3.98 (s, 4 H, CH_2O), 3.92 (br. m, 8 H, OCH_2), 3.34 [br. m, 4 H, CH(CH_3)$_2$], 2.90 (br. s, 1 H, CHT, 1-H), 2.61 (br. m, 1 H, CHT, 1-H), 1.20 [br. s, 24 H, CH(CH_3)$_2$]. − ESIMS: m/z = 983.6 [M − 2 PF_6]$^{2+}$, 606.9 [M − 3 PF_6]$^{3+}$, 558.6 [M − H^+]$^{3+}$, 418.9 [M − 4 PF_6^-]$^{4+}$. − $C_{106}H_{110}F_{24}N_6O_6P_4$ (2143.96): calcd. C 59.38, H 5.17, N 3.92; found C 59.21, H 5.00, N 3.69.

Molecular Thread 14: The synthesis of **12** afforded 95 mg **14** (59 %) as a yellowish solid, insoluble in acetonitrile, m.p. 139−144 °C. − ^{1}H NMR (CD_2Cl_2): δ = 7.41 (d, J = 9.0 Hz, 2 H, phenyl), 7.2 (br. m, 14 H, phenyl), 6.99 (d, J = 6.0 Hz, 1 H, CHT, 5-H), 6.91−6.82, (m, 8 H, phenyl and CHT, 4-H, 5-H), 6.33−6.21 (br. m, 3 H, CHT, 3-H and 6-H), 5.46−5.25 (m, 4 H, CHT, 2-H and 7-H), 4.11 (m, 2 H, OCH_2), 4.06 (m, 2 H, OCH_2), 3.82 (m, 4 H, OCH_2), 3.70 (s, 4 H, CH_2O), 3.28 [br. s, 4 H, CH(CH_3)$_2$], 2.75 (br. s, 1 H, CHT, 1-H), 2.61 (br. s, 1 H, CHT, 1-H), 1.18 [br. s, 24 H, CH(CH_3)$_2$]. − ^{13}C NMR (CD_3CN): δ = 158.9, 158.6, 155.6, 155.5, 148.2, 142.8, 136.6, 135.0, 133.9, 131.7, 131.0, 129.3, 128.7, 128.4, 128.3, 128.2, 128.1, 127.2, 127.0, 126.9, 125.4, 125.2, 124.7, 121.0, 120.9, 116.7, 114.9, 114.6, 71.2, 70.1, 67.9, 45.1, 43.7, 43.6, 28.9, 24.3, 23.5. − $C_{70}H_{78}N_4O_6$ (1071.42): calcd. C 78.47, H 7.34, N 5.23; found C 78.55, H 7.56, N 5.09.

[2]Rotaxane 13 × 4 PF_6: This compound was prepared from **2** according to the general procedure, by use of 2,4,6-triisopropylphenyl isocyanate (74 mg). Yield 100 mg (30%), red solid, m.p. 225−227 °C. − ^{1}H NMR ([D_6]acetone, 600 MHz): δ = 9.4−9.1 (m, 8 H, **7**), 8.21 (br. s, 8 H, **7**), 8.05−7.96 (m, 8 H, **7**), 7.67 (d, J = 8.0 Hz, 2 H, phenyl), 7.56 (d, J = 8.0 Hz, 2 H, phenyl), 7.46 (d, J = 8.0 Hz, phenyl), 7.32 (d, J = 8.0 Hz, 2 H, phenyl), 7.28 (br. s, 2 H, phenyl), 7.21 (br. s, 4 H, phenyl), 7.09 (br. s, 4 H, phenyl), 6.97 (m, 1 H, CHT, 5-H), 6.79 (br. s, 1 H, CHT, 5-H), 6.51 (br. m, 1 H, CHT, 6-H), 6.41 (br. m 1 H, CHT, 6-H), 6.18 (d, J = 8.0 Hz, 1 H, CHT, 3-H), 6.18−6.01 (m, 8 H, **7**, CH_2-benzyl), 5.67 (br. m, CHT, 2-H), 5.55 (m, 1 H, CHT, 7-H), 5.50 (br. m, 1 H, CHT, 7-H), 3.97 (s, 4 H, CH_2O), 3.92 (br. m, 8 H, OCH_2), 3.33 [br. m, 4 H, CH(CH_3)$_2$], 2.91 [m, 3 H, CH(CH_3)$_2$ and CHT, 1-H], 2.61 (br. m, 1 H, CHT, 1-H), 1.25 [d, J = 7.0 Hz, 12 H, CH(CH_3)$_2$], 1.20 [br. s, 24 H, CH(CH_3)$_2$]. − ^{13}C NMR (CD_3CN): δ = 158.2, 158.0, 148.2, 147.9, 145.6, 145.5, 138.0, 137.9, 133.2, 131.7, 131.6, 130.7, 130.1, 128.8, 128.4, 128.0, 127.8, 127.5, 127.4, 126.1, 125.8, 125.4, 122.3, 71.7, 70.6, 68.3, 65.6, 45.3, 43.6, 35.1, 29.5, 24.3, 23.7. − ESIMS: m/z =

982.5 [M − 2 PF_6]$^{2+}$, 607.2 [M − 3 PF_6]$^{3+}$, 557.9 [M − H^+]$^{3+}$, 418.7 [M − 4 PF_6^-]$^{4+}$. − $C_{112}H_{122}F_{24}N_6O_6P_4$ (2228.12): calcd. C 60.38, H 5.52, N 3.77; found C 60.13, H 5.77, N 3.87.

Molecular Thread 15: The synthesis of **12** afforded **15** (53 mg, 33%) as a yellowish solid, insoluble in acetonitrile, m.p. 154−156 °C. − ^{1}H NMR (CD_2Cl_2): δ = 7.41 (d, 2 H, phenyl), 7.24 (br. s, 8 H, phenyl), 7.09 (br. s, 4 H, phenyl), 7.02−6.81, (m, 9 H, phenyl and CHT, 4-H, 5-H), 6.34−6.23 (br. m, 3 H, CHT, 3-H and 6-H), 5.49 (m, 2 H, CHT, 2-H), 5.40 (m, 2 H, CHT, 7-H), 5.30 (m, 4 H, CHT, 2-H, 7-H), 4.11 (m, 2 H, OCH_2), 4.06 (m, 2 H, OCH_2), 3.82 (m, 4 H, OCH_2), 3.70 (s, 4 H, CH_2O), 3.29 [br. s, 4 H, C*H*(CH_3)$_2$], 2.91 [sept, 2 H, C*H*(CH_3)$_2$], 2.78 (br. s, 1 H, CHT, 1-H), 2.64 (br. t, 1 H, CHT, 1-H), 1.25, 1.20 [d, br s, 36 H, CH(C*H*$_3$)$_2$]. − ^{13}C NMR (CD_3CN): δ = 158.4, 158.1, 155.4, 147.4, 142.3, 136.1, 134.5, 133.4, 131.2, 130.5, 128.8, 128.2, 127.9, 127.8, 127.7, 126.7, 126.5, 124.9, 124.7, 124.2, 120.4, 116.3, 114.4, 114.1.70.7, 69.6, 67.5, 44.6, 43.1, 34.3, 28.5, 23.7, 23.1. − $C_{70}H_{78}N_4O_6$ (1071.42: calcd. C 78.47, H 7.34, N 5.23; found C 78.23, H 7.44, N 5.17.

Acknowledgments

Financial support provided by Deutsche Forschungsgemeinschaft and Fonds der Chemischen Industrie is gratefully acknowledged. We warmly thank S. Lutze for the determination of the complexation constants of pseudorotaxanes and Dr. A. Martin for the support related to the synthesis of rotaxanes.

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Received March 20, 2001
[O01130]