Pseudorotaxanes and Rotaxanes Incorporating Diarylcycloheptatriene Stations

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The nature of the interaction between the tetracationic cyclophane cyclobis(paraquat-4,4′-biphenylene) and molecular threads incorporating arylcycloheptatriene units as stations was studied through the differences between the proton resonances observed in the NMR spectra of free molecular threads and in those of corresponding pseudorotaxanes and rotaxanes (CIS values). Molecular threads of different lengths possessing one or two recognition stations and incorporating two different isomeric arylcycloheptatriene units were used for pseudorotaxanes and rotaxanes. The main contribution to the driving forces behind the complexation of pseudorotaxanes and the co-conformation of rotaxanes was deduced from the CIS values of distinct parts of the molecular threads. The unusual signal dispersion of the cyclophane proton resonances is attributed to the asymmetry caused by the molecular thread incorporating the asymmetric cycloheptatriene ring.

Introduction

The electron-deficient tetracationic cyclophane cyclobis(paraquat-*p*-phenylene) (**1**) has been widely used by the Stoddart group[1] and others[2] as a fundamental building block of rotaxanes and catenanes. Rotaxanes of host **1** are designed with molecular threads incorporating electron-rich aromatic subunits: stations on which the cyclophane should reside due to non-covalent interaction. The driving forces involved in thread-binding include electrostatic interaction, hydrogen bonding, and solvation effects, rather than charge-transfer interaction.[3−5] With pseudorotaxanes it has been found that both oxygen functionalities along the chain between donor stations and an aromatic core are necessary in order to position the guest in the cavity of **1**. On the other hand, there is no strong correlation between the binding constants measured for pseudorotaxanes based on **1** with various threads containing aromatic donors and the co-conformation of rotaxanes or catenanes,[4,5] and so a trial and error approach to the rotaxane design is often necessary. The oxidation potential of the electron donor station of the molecular thread may serve as a first approach towards the design of such subunits that would be expected to interact with **1**.

We have recently reported on rotaxanes containing two equivalent diarylcycloheptatriene stations[6] and on a photoswitchable rotaxane with one diarylcycloheptatriene station together with a second electron donor station,[7] and the question arises as to which forces govern the co-conformation of the rotaxanes formed with the cyclophane **1**.

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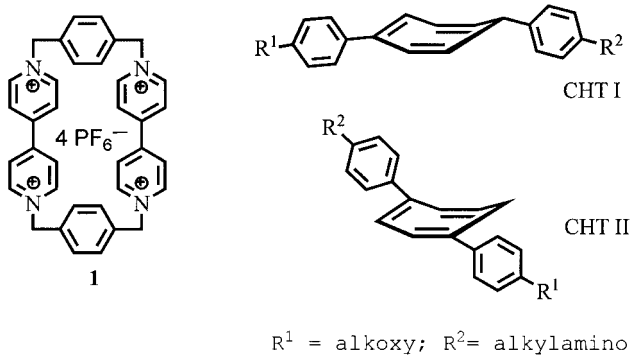
In contrast with other molecular threads previously used for rotaxanes and catenanes, the cycloheptatriene ring as donor station has two interesting properties: *firstly*, it is a nonplanar, boat-shaped ring, and *secondly*, two aryl substituents can be arranged in various positions along the π-system of the seven-membered ring, as shown in Scheme 1.



Scheme 1

In this paper we report the co-conformation of pseudorotaxanes and rotaxanes incorporating the substructures I and II (see Scheme 1).

Structure I is characterized by two aryl substituents, not conjugated to each other. Therefore, two separated subunits, namely the 3-aryl-cycloheptatriene and aniline, might interact separately with the tetracationic ring. Furthermore, this structure exists as two enantiomers. Structure II is available from I through the thermal hydrogen shift reaction and corresponds to an entire interaction unit. While the recognition units of the investigated molecular threads were varied, the length of the chain attached to the recognition stations was kept constant, so that differences observed in

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the complexation of the molecular threads with the host **1** could be attributed to the properties of these subunits.

Results and Discussion

Synthesis of Molecular Threads

Compound **3** was obtained as outlined in Scheme 2, by alkylation of 7-(4-hydroxyphenyl)-1,3,5-cycloheptatriene and subsequent acylation. The aniline substituent was introduced by nucleophilic attack of aniline on the tropylium salt to afford the two isomers **6** and **7**, which could be separated by column chromatography. Only isomer **6** was used for further studies. The isomeric molecular thread **8** of the structure type II was easily obtained through a thermal hydrogen shift. Compounds **6** and **8** were used to study pseudorotaxanes and rotaxanes incorporating only one station for the interaction with the cyclophane **1**. The synthesis of the molecular threads **10**−**13** was reported recently.[6,7]

Pseudorotaxanes and Rotaxanes

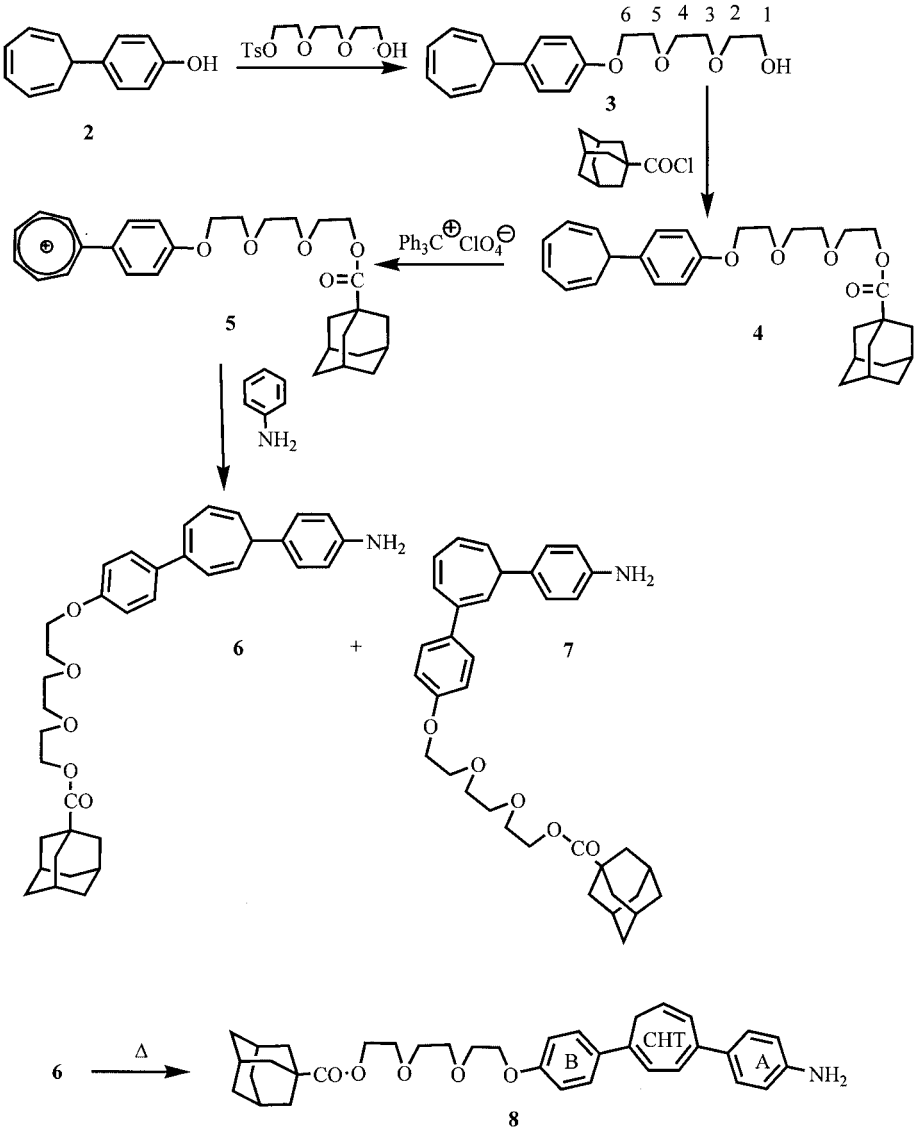
The molecular threads studied can be divided into three types:

− those containing only the diarylcycloheptatriene station with varying extents of π-conjugation (compounds **6** and **8**),

− those incorporating two competing donor stations (compounds **9** and **10**),

− compounds with shortened threads, used for comparison (compounds **11**−**13** are included here).

The interaction of different parts of the molecular threads with the cyclophane **1** was not studied by means of the association constants,[4] but rather by use of the chemically induced shifts (CISs), determined by the differences

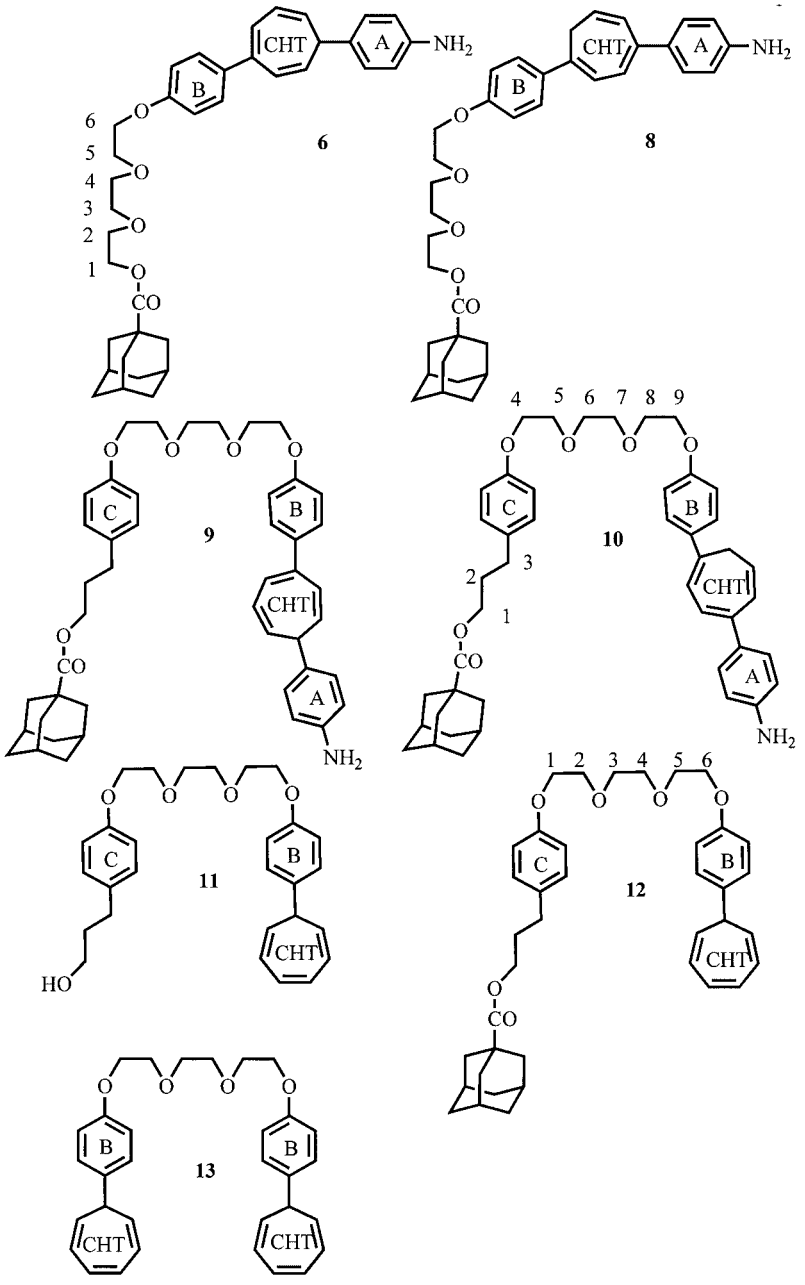


Scheme 2

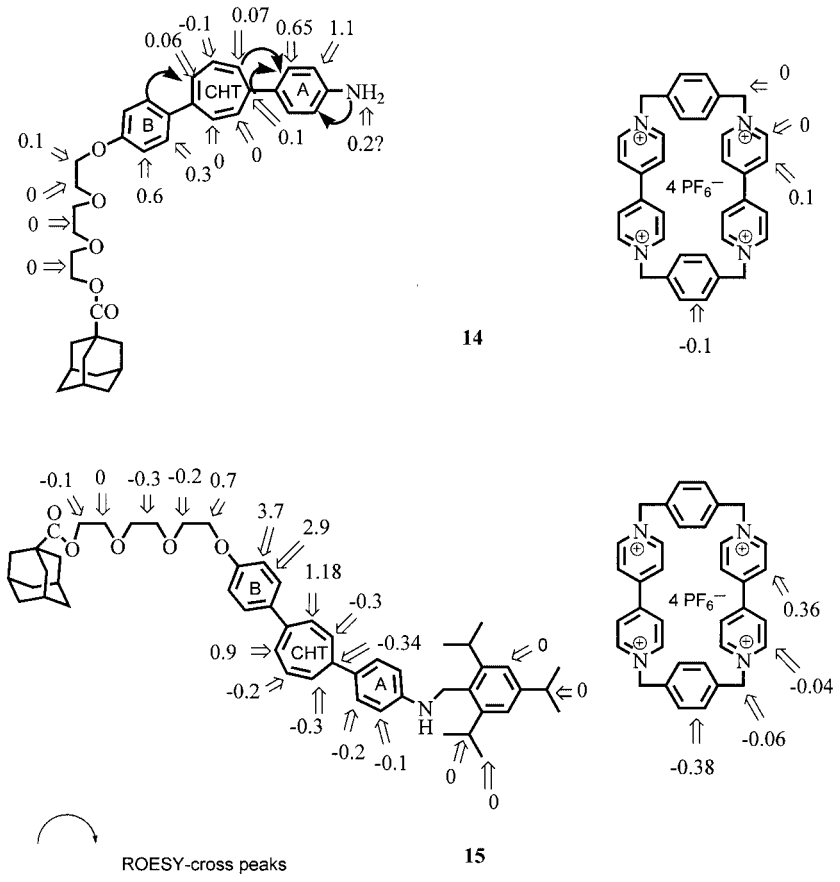
between the proton resonances of uncomplexed **1** and the threads and the related proton resonances within the pseudorotaxane formed by 1:1 mixtures (0.01 M) of the two components ($\delta_{uncomplexed} - \delta_{complexed}$). It was checked that the CIS values do not vary significantly in the concentration range used, because these values are similar to the maximal observable difference between the chemical shifts of uncomplexed and complexed components. The association constants can only supply information about the overall interaction of the components, but we were interested in the interaction of specific regions of the thread with the ring. Each cycloheptatriene station consists of three interaction units: the CHT ring and the two donor substituents B and C (see Scheme 3). Use of of the CIS values of the different protons of the subunits seems to be adequate for detection of the region of the strongest interaction for such related molecular threads.

One-Station Pseudorotaxanes and Rotaxanes

The molecular threads **6** and **8** serve as standards for the structures I and II (Scheme 1) to explore the interaction of these two different diarylcycloheptatriene stations with **1**. The CIS values of the pseudorotaxanes **14** and **16**, together with those of the related rotaxanes **15** and **17**, are given in Scheme 4 and Scheme 5. The assignment of different resonances of the aromatic protons to the rings A and B is possible with the help of NOEs (ROESY spectra).



Scheme 3



Scheme 4. Proton CIS values ($\delta_{free\ component} - \delta_{pseudorotaxane/rotaxane}$) of the components of **14** and **15**

With regard to the CIS values of the type I and II pseudorotaxanes (see Scheme 1), two findings are remarkable.

Firstly, the strongest interaction in both types of pseudorotaxane is found between **1** and the aniline part A of the diarylcycloheptatriene station. The observed upfield shift of the proton resonances indicates the sandwich-like arrangement of the aromatic substituents A and B between the bipyridinium units of the cyclophane **1**. In contrast, the upfield shift of the proton resonances of the CHT unit playing the role of a link between A and B is very small.

Secondly, it is obvious that the cycloheptatriene ring in structure II, enabling a conjugative connection between the aromatic substituents, is more strongly involved than in structure I; the strongest interaction of the cyclophane **1** occurs with the stronger electron donor A of the CHT station. The link between the two aryl groups represented by the CHT subunit is mostly affected at the positions adjacent to the aryl substituents. Because A is rather far from the ethyleneoxy units of the chain, it can be concluded that it is not the interaction of **1** with the chain that plays the dominant role, but rather electrostatic and charge transfer interactions.

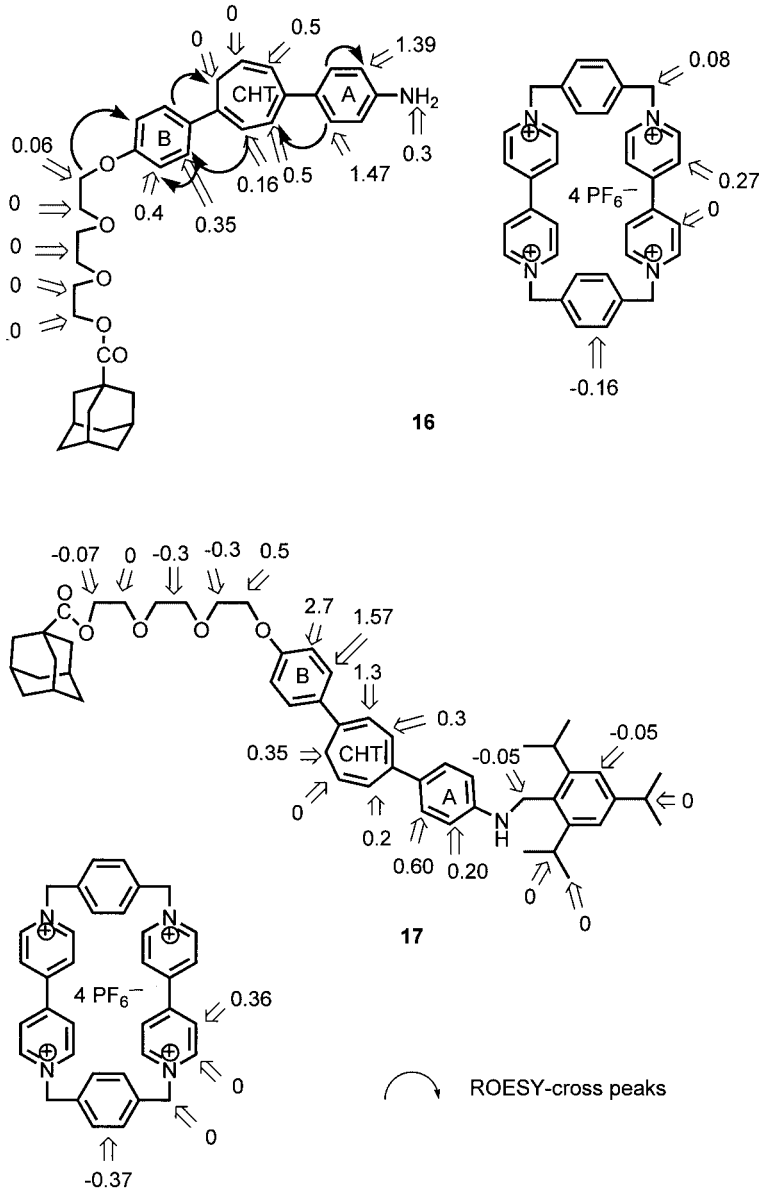
The aryl protons of the substituent A appear as fairly sharp doublets in the pseudorotaxane **14**. In contrast, the proton resonances of B are broad (see Supporting Information). The dynamic process giving rise to the signal broadening is therefore unlikely to be due to the exchange process between the complexed and non-complexed components. We consider the restricted internal rotation of the aryl group B due to interaction with **1** to be responsible for this effect. The proton resonances of the glycol chain are not shifted upon complexation.

The CT absorption band of the two pseudorotaxanes at 400−680 nm is centered at 450 nm and corresponds to the alkoxyarylcycloheptatriene part; the CT absorption caused by the interaction between the aniline substituent and **1** is expected to appear at 570 nm, and is hidden under the long-wavelength tail of the first CT band (see Supporting Information).

The formation of pseudorotaxanes is attested to the typical CIS values observed for the protons of the cyclophane **1**.[8] In particular, the upfield shift of the β-protons of the bipyridinium rings and the downfield shift of the protons of the benzylic spacer units are characteristic for such types of host-guest complexes.

Rotaxanes were obtained by alkylation of the amino groups of the molecular threads with the voluminous tris-*i*Pr-benzyl group in the presence of **1** (see Scheme 6).

The alkylated molecular threads that were obtained in addition to the rotaxanes were used to determine the CIS values of the related rotaxanes. The compounds **15** and **17** represent the prototypes of rotaxanes incorporating the diarylcycloheptatriene recognition station with different ar-



Scheme 5. Proton CIS values ($\delta_{free\ component} - \delta_{pseudorotaxane/rotaxane}$) of the components of **16** and **17**

rangements of the π-system of the seven-membered ring with respect to the aryl groups. Because only one station exists, the observed CIS values given in Scheme 4 and Scheme 5 represent the maximal shift of the protons that can be expected if the cyclophane **1** resides exclusively on the diarylcycloheptatriene station. There are remarkable differences between the pseudorotaxanes and the related rotaxanes.

The co-conformation of the rotaxane **15** differs from that of **14** in two ways.

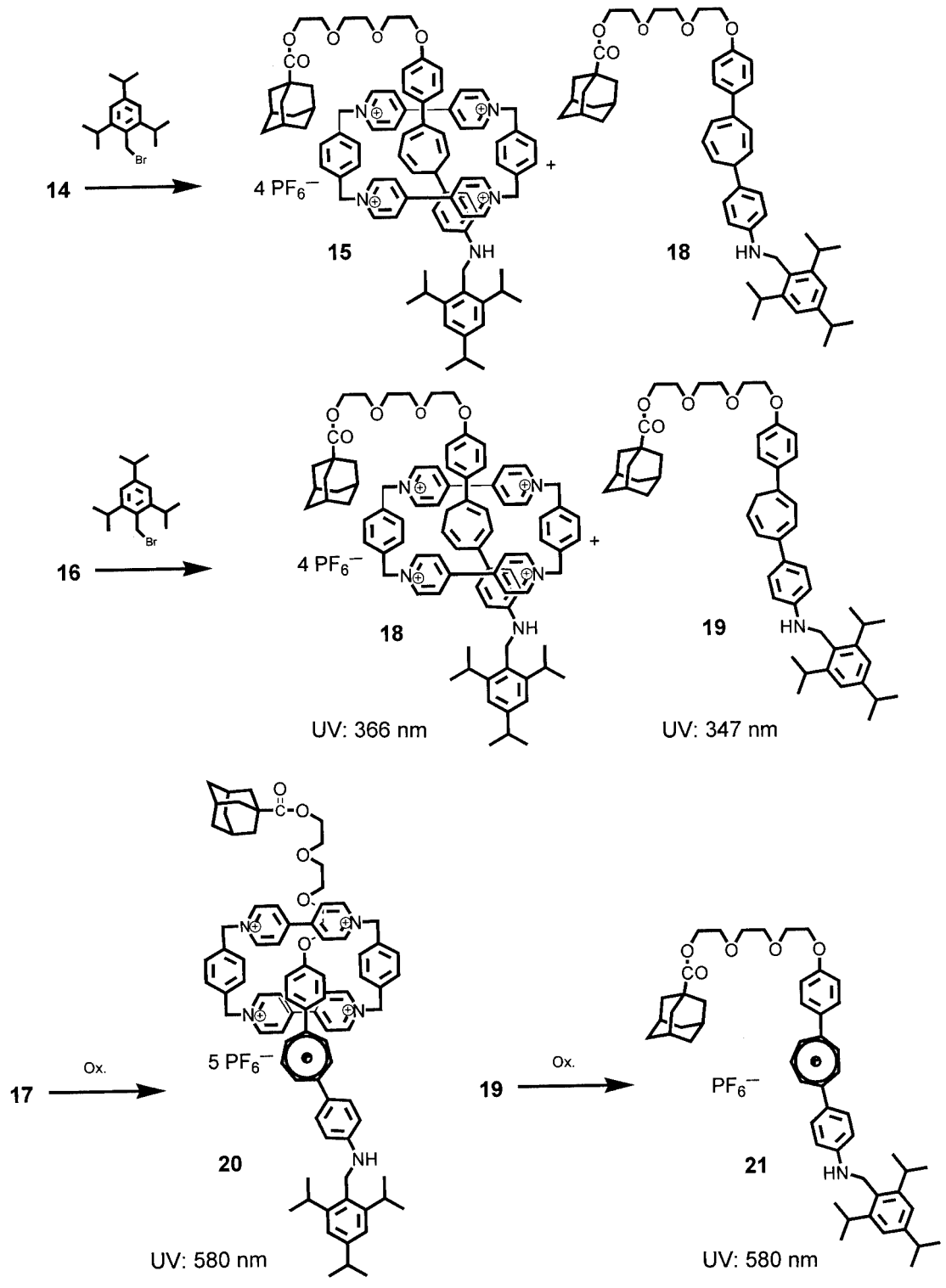
Firstly, the cyclophane **1** resides exclusively on the CHT and B subunits, resulting in strong upfield shifts of these protons (see Scheme 5). The parts of the CHT subunit adjacent to B are deeply involved. Both the aniline substituent and the adjacent parts of CHT lie outside the cyclophane cavity in the plane of the bipyridinium units, resulting in a downfield shift of the proton resonances.

Note that there is a large twisting angle between the main plane of CHT and the aniline ring A.

The change of residence of the cyclophane **1** within the rotaxane compared with the pseudorotaxane is obviously due to the steric hindrance of the bulky benzylic triisopropylphenyl group, which does not allow the occupation of A.

Secondly, the protons of the cyclophane are anisochronous, resulting in signal broadening or even splitting (see Supporting Information). This effect is especially pronounced in the rotaxanes, including the structure element I, and it can be attributed to the asymmetry caused by the entire thread, especially by the seven-membered ring (see Figure 1).

Therefore, two different bipyridinium units exist, provided that the internal rotation of these subunits is restricted. The splitting into several singlets is especially pronounced for the benzylic protons (b in Figure 1). These pro-



Scheme 6

tons cannot exchange places by internal rotation, and fast exchange by rotation of the entire ring **1** around the molecular thread is obviously prevented. Signal splitting of the resonances of the benzylic protons is also observed in the rotaxane **17**. However, the α- and β-proton resonances are only broadened (see Supporting Information).

The CT absorption band of the rotaxane **15** resembles that of the pseudorotaxane and is centered at 430 nm.

The conjugative arrangement of A and B across the seven-membered ring in the rotaxane **17** results in delocalization of the cyclophane over the entire CHT station, while the greater shielding of the aryl group B indicates that it

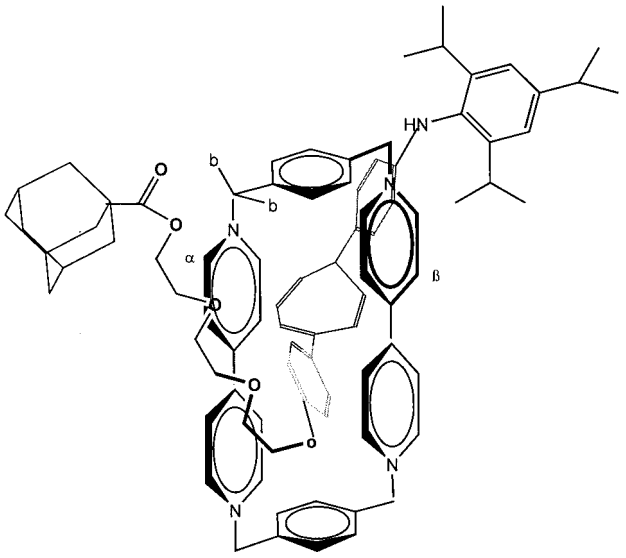
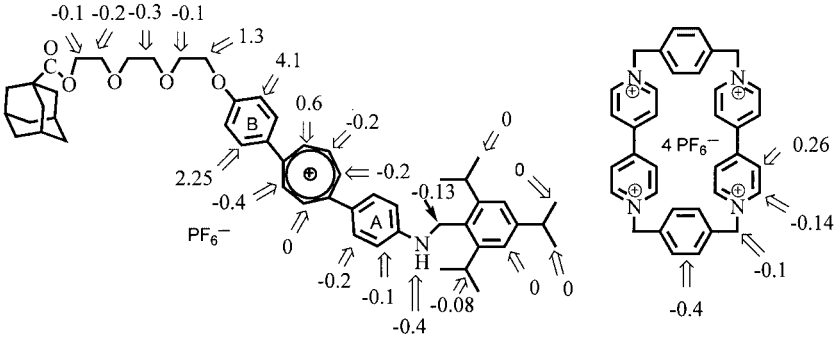


Figure 1. Structure of the rotaxane **15**

spends more time on this subunit. The greater upfield shift of B observed in the rotaxane **15** in relation to that in compound **17** indicates that the delocalization of the cyclophane over the CHT station in the rotaxane **17** gives rise to a diminished shielding of the entire station. Unlike in compound **15**, the steric hindrance does not fully prevent the interaction of **1** with the A ring, because this interaction is stronger than in the situation found in rotaxane **15**. However, it can also be inferred in this case that the co-conformation is changed on going from the pseudorotaxane **16** to the rotaxane **17**. It is worth noting that the absorption maximum of the CHT station in the rotaxane **17** is bathochromically shifted by 18 nm (1250 cm^{-1}) from the absorption maximum of the non-complexed molecular thread **19**. This strong shift can be attributed to the polar environment formed around the CHT station by the cyclophane.[7]

Because of the long-wavelength absorption edge of the molecular thread at 440 nm, no CT band could been detected in this region, only a CT band at 575 nm being visible. This long-wavelength absorption band is consistent with the co-conformation derived from the CIS values with the cyclophane also residing on the aniline substituent A.

Unlike the rotaxane **15**, compound **17** can be quantitatively transformed into the tropylium rotaxane **20** by electrochemical oxidation. In this rotaxane, the former donor station is now an acceptor station, and it is interesting to explore how the tetracationic ring **1** behaves. Compound **21**, obtained by electrochemical oxidation of the thread **19**, was used in order to calculate the CIS values from which the co-conformation is determined. According to the proton resonances of **21** (see Scheme 7), the electron-deficient natures not only of the tropylium ring but also of rings A and ring B can be inferred. However, the cyclophane surprisingly remains on the tropylium station above B, which can be confirmed from the very large upfield shift of the proton resonances of the substituent B (see Scheme 7). NOEs show the contacts between the cyclophane **1** (β-protons) and B. The signal pattern of the proton resonances of



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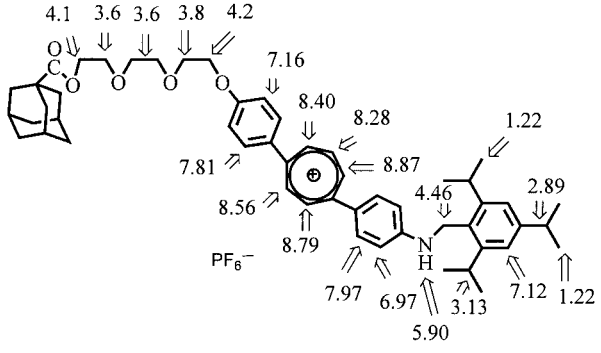

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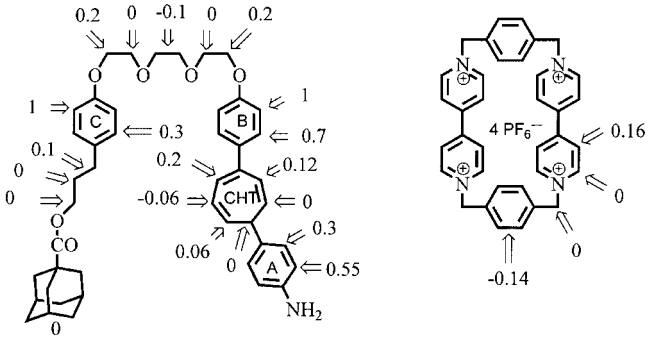
Scheme 7. Proton CIS values ($\delta_{free\ component} - \delta_{rotaxane}$) of the components of **20** and proton resonances (in ppm) of the molecular thread **21**

the cyclophane **1** is preserved on going from the cycloheptatrienyl rotaxane **17** to the rotaxane with the tropylium unit; broad signals of the α- and β-protons and the split resonance of the benzylic protons indicate the different sites of the thread seen by the cyclophane.

Two-Station Pseudorotaxanes and Rotaxanes

The pseudorotaxane **22** formed from thread **9** is an isomer of the pseudorotaxane formed with the molecular thread **10**, described recently.[7] The most important result for the pseudorotaxane **10/1** was the finding that the cyclophane resides exclusively on the cycloheptatriene station and that the strongest interaction occurs between ring A and **1**.

The situation is drastically changed for **22**: both station C and the diarylcycloheptatriene station interact with the cyclophane **1** (see Scheme 8). Unfortunately, the resonances of B and C in the pseudorotaxane **22** cannot be assigned because of the very broad signals of these aromatic protons (see Supporting Information). Nevertheless, it is clear that the signals for the ring protons of both B and of C are shifted upfield comparably in the pseudorotaxane **22**, because only strongly upfield-shifted resonances of aromatic protons are observed.



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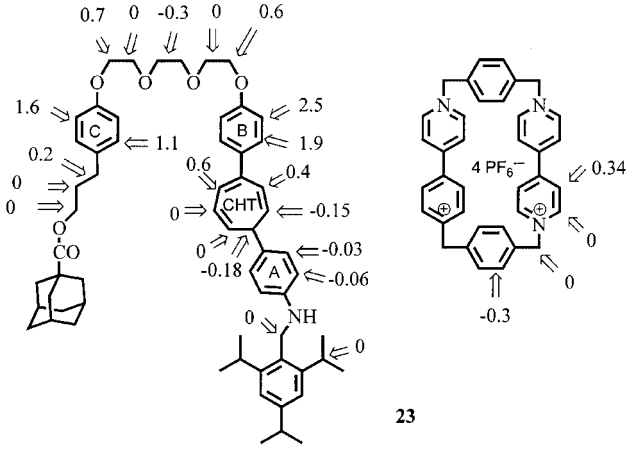

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Scheme 8. Proton CIS values ($\delta_{free\ component} - \delta_{pseudorotaxane/rotaxane}$) of the components of **22** and **23**

The relatively sharp signals of aromatic protons are attributed to the substituent A.

The molecular threads **11**, **12**, and **13** were involved in our studies of the complexation behavior in order to explore the "monoarylcycloheptatriene" interaction unit, as well as the influence of the bulky end-group on the interaction between the thread and the cyclophane **1**. Furthermore, compounds **11**−**13** have cycloheptatriene stations without conjugation between B and CHT, and the question arises as to whether this has consequences for the interaction strength.

In general, the assignment of proton resonances to the two alkoxyaryl groups B and C suffers from the broadening of the signals in the complexes **25** and **26**, preventing cross-peaks in the ROESY spectra. In contrast, all other proton resonances of the thread, and also of the host **1,** appear as sharp signals. We have learned from the other pseudorotaxanes and rotaxanes that the extent of the upfield shifts of the aromatic subunits of the thread is continued in the adjacent parts, such as the seven-membered ring or the aliphatic chain on the ester side of station C, and if this is taken into account, an assignment is possible according to this criterion (see Scheme 9).

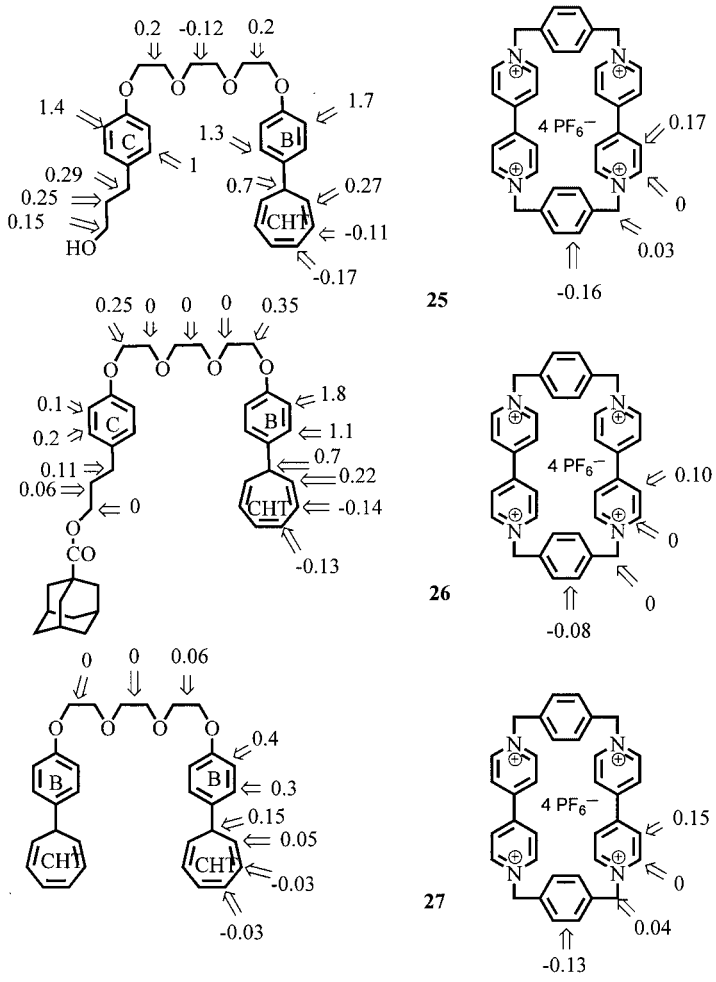
It is obvious that the interaction of B and C with **1** is comparable in the complex **25**. In contrast, there is a clear difference between B and C in the pseudorotaxane **26**. Unlike compound **12**, the thread **11** is accessible from two ends, giving rise to a shared interaction of the host **1** between B and C during threading and dethreading movements. Accordingly, station C is clearly much less involved in the interaction with the cyclophane **1** in the pseudorotaxane **26** (see Scheme 9). Furthermore, the diminished interaction of the two CHT stations, which can be inferred from the observed CIS values for the complex **27** (see Scheme 9), is explainable by the statistical distribution of the interaction possibilities on two equal recognition stations during the complexation and decomplexation processes.

The interruption of the conjugated π-system in the molecular threads **11** and **12** does not result in a decreased interaction of the aryl-CHT unit with the cyclophane. Obviously, the aromatic ring B, together with the adjacent ethyleneoxy bridge, is the decisive structure element.

Despite the rather large differences in the CIS values observed with the molecular threads of the pseudorotaxanes **25**−**27**, the CIS values of the cyclophane **1** are very similar in all pseudorotaxanes. This supports the assumption that the differences are products of the interaction mode and not of different stability constants of the complexes.

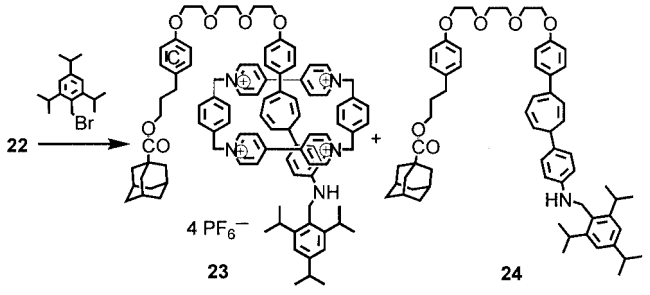
The influence of the conjugative connection of A and B through the CHT-ring in the thread **10** can be inferred by comparison of the different CIS values caused by the interaction of compounds **9** (Scheme 8) and **10**[7] with **1**: the increased donor strength of the CHT structure II causes preferential residence of the cyclophane on this station.

Like those of the one-station pseudorotaxanes, the CT absorption of **22** is centered at 450 nm and differs from the CT band of the rotaxane (see below). Consistently with the increased interaction of the conjugated CHT station in compound **10,** the CT absorption band of **10/1** now appears at 580 nm.



Scheme 9. Proton CIS values ($\delta_{free\ component} - \delta_{pseudorotaxane/rotaxane}$) of the components of **25**–**27**

The rotaxane **23**, which is related to the pseudorotaxane **22**, was synthesized similarly to rotaxanes **15** and **17** (see Scheme 10).



Scheme 10

In contrast with the pseudorotaxane, only the proton resonances of A can be observed at room temperature in the rotaxane **23**. However, at 343 K the doublets of the protons at B and C appear (see Supporting Information) and can be assigned through NOEs (ROESY spectra at 343 K). According to the CIS values shown in Scheme 8, there are changes of the co-conformation on going from the pseudorotaxane **22** to the rotaxane **23**.

Again, the introduction of the bulky group at the amino end of the molecular thread prevents residence of **1** on the substituent A of the CHT station. Instead, the interaction of **1** with the aryl group B and the CHT ring itself is increased in relation to **22**. The CIS values of the proton resonances of the parts B and CHT are comparable with those observed with the one-station rotaxane **15**.

Furthermore, the interaction with the station C is increased. We interpret this finding in terms of a folded conformation of the thread resulting in contacts between station C and the cyclophane **1**. This assumption is supported by different CIS values of the protons of the ethyleneoxy chain. Unlike the protons adjacent to the aryl groups B and C, the central part is shifted downfield. At the same time, NOEs between these protons and α- and β-protons of **1** (relative to the N atom in the bipyridinium units) confirm the contacts. This behavior resembles that of the isomeric rotaxane with conjugation between the substituents A and B.[7] Whereas the CIS values observed for compound **23** and the related isomeric rotaxane are com-

parable, the yield of the synthesis of **23** is only half of that of the isomeric rotaxane.[7]

The observation of two CT absorption bands at 430 and 570 nm corresponds to the interaction of the cyclophane **1** both with B−CHT and A.

Conclusions

The degrees of occupation of the different stations in both pseudorotaxanes and rotaxanes by the tetracationic ring are determined mainly by the strength of the electrostatic and charge-transfer interactions. The oxidation potentials of the stations can be used to estimate the strength of such interactions, assisting the design of the molecular thread. As expected, the substitution pattern of the seven-membered ring strongly influences the interaction between this recognition station and the cyclophane.

Steric interference between the ring and the end-group of the thread may hinder the interaction. In the design of the bulky stopper group to be introduced at the ends of the molecular thread it has to be taken into account that the stopper group must not overlap with the recognition station.

Experimental Section

General Methods: MeCN was distilled from over CaH_2. Silica gel 60 (0.040−0.063 mm) (Fluka) was used for column chromatography (CC). Melting points (m.p.s) were determined with a Boetius heating microscope.

NMR spectra were recorded on Bruker DPX 300 (300 MHz), Bruker Advance 400 (400 MHz) or Bruker AMX 600 (600 MHz) instruments. UV/Vis spectra were recorded with a Shimadzu UV 2101 PC spectrometer.

Molecular Threads

Compounds **9**, **10**, and **13** were available from earlier studies.[6,7,9]

Compound 6: Preparation as indicated in Scheme 3, 7-(4-hydroxyphenyl)cyclohepta-1,3,5-triene (**2**; 3.02 g, 16.4 mmol) and NaOEt (2.2 g, 32.8 mmol) in MeCN (50 mL) were stirred for 30 min at room temperature. After that time the solution was heated under reflux and triethylene glycol monotosylate (5 g, 16.4 mmol) in MeCN (40 mL) was added dropwise. Heating at reflux was continued for 4 h. After filtration of a precipitate, the solvent was removed under reduced pressure and the remaining mixture was worked up by CC (silica gel, cyclohexane/acetone 4:1.5) to provide **3** as an oil, 3.4 g (65%). ^{1}H NMR (300 MHz, CD_3CN, TMS): 2.63 (t, $J_{H,H}$ = 6 Hz, 1 H; CHT, 7-H), 2.79 (t, $J_{H,H}$ = 5 Hz, 1 H; OH), 3.49 (m, 2 H, 1-H), 3.63 (m, 6 H; 2-H, 3-H, 4-H), 3.81 (m, 2 H; 5-H), 4.11 (m, 2 H; 6-H), 5.40 (m, 2 H; CHT, 1-H, 6-H), 6.28 (m, 2 H; CHT, 2-H, 5-H), 6.29 (m, 1 H, CHT, 5-H), 6.77 (m, 2 H; CHT, 3-H, 4-H), 6.96 (d, $J_{H,H}$ = 8 Hz, 2 H; phenyl), 7.32 ppm (d, $J_{H,H}$ = 8 Hz; phenyl). $C_{19}H_{24}O_4$ (316.1675): calcd. (%): calcd. C 72.13, H 7.65; found (%) C 72.35, H 7.43.

Compound **3** (3.17 g, 10.03 mmol) was treated with adamantane-1-carbonyl chloride (2.18 g, 11.03 mmol) in pyridine (25 mL) for 4 h at 75 °C. The reaction mixture was poured into dilute HCl (30 mL). The aqueous solution was extracted several times with dichloromethane as solvent, the organic phases were washed with a saturated aqueous solution of NaCl and dried (Na_2SO_4), and the solvents were evaporated. The ester **4** (4.64 g, 91%) was purified by CC (silica gel, cyclohexane/acetone 4:1), yielding an oil (3.7 g, 70%). ^{1}H NMR (300 MHz, CD_3CN, TMS): δ = 1.69, 1.86, 1.93 (br. m, 15 H, adamantane), 2.62 (t, $J_{H,H}$ = 6 Hz, 1 H; CHT, 7-H), 3.61 (m, 6 H; 3-H, 4-H, 5-H), 3.78 (m, 2 H; 1-H), 4.11 (m, 4 H; 2-H, 6-H), 5.36 (m, 2 H; CHT, 1-H, 6-H), 6.24 (m, 2 H, CHT, 2-H, 5-H), 6.75 (m, 2 H; CHT, 3-H, 4-H), 6.93 (d, $J_{H,H}$ = 9 Hz, 2 H; phenyl), 7.29 ppm (d, $J_{H,H}$ = 9 Hz, 2 H; phenyl). $C_{30}H_{38}O_5$ (478.6197): calcd. (%): calcd. C 75.28, H 8.00; found (%) C 74.97, H 8.11.

The ester **4** (3.7 g, 7.7.mmol) was oxidized by treatment with trityl tetrafluoroborate (2.64 g, 7.7 mmol) in dichloromethane (20 mL), affording the tropylium salt **5** as a red foam (2.97 g, 67%) after the reaction mixture had been poured into methyl-*tert*-butyl ether (MTBE) and the resulting oil treated with MTBE and $CHCl_3$. ^{1}H NMR (300 MHz, CD_3CN, TMS): δ = 1.70, 1.86, 1.94 (br. m, 15 H, adamantane), 3.64 (m, 6 H; 2-H, 3-H, 4-H), 3.86 (m, 2 H; 5-H), 4.11 (m, 2 H; 1-H), 4.26 (m, 2 H; 6-H), 7.25 (d, $J_{H,H}$ = 9 Hz, 2 H; phenyl), 8.00 (d, $J_{H,H}$ = 9 Hz, 2 H; phenyl), 8.90 (m, 4 H, tropylium), 9.25 ppm (d, $J_{H,H}$ = 11 Hz, 2 H; tropylium). $C_{30}H_{37}ClO_9$ (577.066): calcd. (%): calcd. C 62.44, H 6.64, Cl 6.14; found (%) C 62.32, H 6.51, Cl 5.83.

The tropylium salt **4** (3.0 g, 5.2 mmol), dissolved in dichloromethane (20 mL) and acetonitrile (10 mL), was added to aniline (1.94 g, 20.8 mmol) in acetonitrile (1 mL). After having been stirred for 5 h at room temperature, the solution was washed with a $NaHCO_3$ solution, the organic phase was dried (Na_2SO_4), and the solvent was removed under reduced pressure. The excess of aniline was removed by use of *n*-hexane. The isomer **6** was separated from **7** by CC (silica gel, toluene/ethyl acetate 10:1) (oil, 593 mg, 20%). ^{1}H NMR (300 MHz, CD_3CN, TMS): δ = 1.67, 1.84, 1.943 (br. m, 15 H, adamantane), 2.68 (t, $J_{H,H}$ = 6 Hz, 1 H; CHT, 7-H), 3.64 (m, 4 H; 3-H, 4-H), 3.77 (m, 2 H; 1-H), 4.06 (br., 1 H, NH), 4.1 (m, 6 H; 2-H, 5-H, 6-H), 5.44 (m, 1 H; CHT, 6-H), 5.51 (m, 1 H; CHT, 1-H), 6.28 (m, 1 H, CHT, 5-H), 6.33 [d, J(H,H = 10 Hz, 1 H; CHT, 2-H), 6.64 (d, $J_{H,H}$ = 9 Hz, 2 H; A), 6.93 (d, $J_{H,H}$ = 9 Hz, 2 H; B), 7.10 (d, $J_{H,H}$ = 9 Hz, 2 H; A), 7.44 ppm (d, $J_{H,H}$ = 9 Hz, 2 H; B). $C_{36}H_{43}NO_5$ (569.7303): calcd. (%): calcd. C 75.89, H 7.61, N 2.46; found (%) C 75.92, H 7.66, N 2.74.

Compound 8: A solution of **6** (1 g, 1.7 mmol) in toluene (150 mL) was heated under reflux for 11 h. After removal of the solvent the isomer **8** was obtained as an oil, which was purified by CC (silica gel, toluene/ethyl acetate 10:1) (yellow solid, 0.8 g, 80%), m.p. 82−84.5. ^{1}H NMR (300 MHz, CD_3CN, TMS): δ = 1.70, 1.85, 1.93 (br. m, 15 H, adamantane), 2.76 (d, $J_{H,H}$ = 7 Hz, 2 H; CHT, 7-H), 3.60 (m, 6 H; 3-H, 4-H, 5-H), 3.8 (m, 2 H; 1-H), 4.1 (m, 4 H; 2-H, 6-H), 4.2 (br., 1 H; NH), 5.61 (m, 1 H; CHT, 6-H), 6.40 (d, $J_{H,H}$ = 10 Hz,1 H; CHT, 5-H), 6.53 (d, $J_{H,H}$ = 7 Hz, 1 H; CHT, 2-H), 6.66 (d, $J_{H,H}$ = 9 Hz, 2 H; A), 6.92 (d, $J_{H,H}$ = 9 Hz, 2 H; B), 6.98 (d, $J_{H,H}$ = 7 Hz, 1 H; CHT, 3-H), 7.29 (d, $J_{H,H}$ = 9 Hz, 2 H; A), 7.51 ppm (d, $J_{H,H}$ = 9 Hz; B). $C_{36}H_{43}NO_5$ (569.73): calcd. (%): calcd. C 75.89, H 7.61, N 2.46; found (%) C 75.66, H 7.81, N 2.84.

Compounds 11 and 12: Compound **2** (3.9 g, 21.6 mmol), 3-(4-hydroxyphenyl)propanol (3.28 g, 21.6 mmol), and NaOEt (4.4 g, 64.8 mmol) in MeCN (250 mL) were stirred for 30 min at room temperature, as in the procedure used for the synthesis of **9**.[7] After that period, the solution was heated under reflux, and triethylene glycol bistosylate (9.8 g, 21.8 mmol) in MeCN (50 mL) was added dropwise to the solution. Heating at reflux was continued for 6 h. The solvent was removed under reduced pressure and the remain-

ing mixture was worked up by CC (silica gel, cyclohexane/acetone 3:1) thus separating **11** from the symmetric substitution products (oil, 4.45 g, 50%). ^{1}H NMR (300 MHz, CD_3CN, TMS): δ = 1.85 (m, 2 H; 2-H), 2.6 (m, 3 H; 3-H, CHT, 7-H), 3.66 (t, $J_{H,H}$ = 6 Hz, 2 H; 1-H), 3.76 (s, 4 H; 6-H, 7-H), 3.86 (m, 4 H; 5-H, 8-H), 4.12 (m, 4 H; 4-H, 9-H), 5.40 (m, 2 H; CHT, 1-H, 6-H), 6.25 (m, 2 H, CHT, 2-H, 5-H), 6.74 (m, 2 H; CHT, 3-H, 4-H), 6.84 (d, $J_{H,H}$ = 9 Hz, 2 H; C), 6.93 (d, $J_{H,H}$ = 9 Hz, 2 H; B), 7.10 (d, $J_{H,H}$ = 9 Hz; C), 7.27 ppm (d, $J_{H,H}$ = 9 Hz, B). $C_{28}H_{34}O_5$ (450.57): calcd. (%): calcd. C 74.64, H 7.61; found (%) C 74.45, H 7.74.

Compound **11** (3.76 g, 8.34 mmol) was treated with adamantane-1-carbonyl chloride (1.82 g, 9.17 mmol) in pyridine (9 mL) for 4 h at 75 °C. The reaction mixture was poured into dilute HCl (15 mL). The aqueous solution was extracted several times with dichloromethane as solvent, the organic phases were washed with a saturated aqueous solution of NaCl and dried (Na_2SO_4), and the solvents were evaporated. The remaining oil was purified by CC (silica gel, cyclohexane/acetone 5:2) to afford **12** (2.9 g, 57%). ^{1}H NMR (300 MHz, CD_3CN, TMS): δ = 1.71, 1.85, 1.98 (m, 17 H; adamantane, 2-H), 2.61 (m, 3 H; 3-H, CHT, 7-H), 3.65 (s, 4 H; 6-H, 7-H), 3.77 (m, 4 H; 5-H, 8-H), 3.97 (t, $J_{H,H}$ = 6 Hz, 2 H; 1-H), 4.1 (m, 4 H; 4-H, 9-H), 5.37 (m, 2 H; CHT, 1-H, 6-H), 6.24 (m, 2 H, CHT, 2-H, 5-H), 6.75 (m, 2 H; CHT, 3-H, 4-H), 6.83 (d, $J_{H,H}$ = 8 Hz, 2 H; C), 6.93 (d, $J_{H,H}$ = 8 Hz, 2 H; B), 7.10 (d, $J_{H,H}$ = 8 Hz; C), 7.27 ppm (d, $J_{H,H}$ = 8 Hz, B). $C_{39}H_{48}O_6$ (612.80): calcd. (%): calcd. C 76.44, H 7.90; found (%) C 76.57, H 7.98.

Pseudorotaxanes

The pseudorotaxane NMR spectra were recorded with mixtures of the cyclophane **1** and the molecular threads in CD_3CN (1 mL). The concentrations of the two components were about 10^{-2} M.

Compound 14: [8 mg **1** (0.0073 M), 4.2 mg **6** (0.0073 M)]. ^{1}H NMR (400 MHz, CD_3CN, TMS): δ = 1.70, 1.85, 1.9 (br. m, 15 H; adamantane), 2.56 (t, $J_{H,H}$ = 6 Hz, 1 H; CHT, 7-H), 3.66 (m, 6 H; 3-H, 4-H, 5-H), 3.8 (m, 2 H; 2-H), 4.0 (m, 2 H; 1-H), 4.13 (m, 2 H; 6-H), 5.37 (m, 1 H; CHT, 6-H), 5.47 (m, 1 H; CHT, 1-H), 5.56 (d, $J_{H,H}$ = 8 Hz, 2 H; A), 5.75 (br. s, 8 H; cyclophane), 6.31 (d, $J_{H,H}$ = 9 Hz,1 H; CHT, 2-H), 6.39 (m, 1 H; CHT, 5-H), 6.45 (d, $J_{H,H}$ = 8 Hz, 2 H; A), 6.5 (br., 2 H, B), 6.97 (d, $J_{H,H}$ = 6 Hz, 1 H; CHT, 4-H), 7.1 (br. s, 2 H; B), 7.62 (s, 8 H; cyclophane), 8.08 (br. s, 8 H; cyclophane), 8.86 ppm (br. s, 8 H; cyclophane).

Compound 16: [11.1 mg **1** (0.01 M), 6.5 mg **8** (0.0114 M)]. ^{1}H NMR (400 MHz, CD_3CN, TMS): δ = 1.69, 1.84, 1.9 (br. m, 15 H; adamantane), 2.77 (d, $J_{H,H}$ = 7 Hz, 2 H; CHT, 7-H), 3.6 (m, 6 H; 3-H, 4-H, 5-H), 3.8 (m, 2 H; 2-H), 3.99 (br. s, 2 H; NH), 4.0 (m, 2 H; 1-H), 4.12 (m, 2 H; 6-H), 5.27 (d, $J_{H,H}$ = 8 Hz, 2 H; A), 5.66 (m, 1 H; CHT, 6-H), 5.7 (br. s, 8 H; cyclophane), 5.84 (d, $J_{H,H}$ = 8 Hz, 2 H; A), 5.93 (d, $J_{H,H}$ = 10 Hz, 1 H; CHT, 5-H), 6.37 (d, $J_{H,H}$ = 6 Hz,1 H; CHT, 2-H), 6.48 (d, $J_{H,H}$ = 6 Hz,1 H; CHT, 3-H), 6.53 (d, $J_{H,H}$ = 8 Hz, 2 H; B), 7.15 (d, $J_{H,H}$ = 6 Hz, 2 H; B), 7.66 (s, 8 H; cyclophane), 7.98 (br. s, 8 H; cyclophane), 8.85 ppm (br. s, 8 H; cyclophane).

Compound 22: [11.8 mg **1** (0.011 M), 8.0 mg **9** (0.013 M)]. ^{1}H NMR (400 MHz, CD_3CN, 303 K, TMS): 1.73, 1.88, 1.95 (br. m, 17 H; adamantane; 2-H), 2.51 (t, $J_{H,H}$ = 8 Hz, 2 H; 3-H), 2.67 (d, $J_{H,H}$ = 6 Hz, 2 H; CHT, 7-H), 3.8−3.9 (m, 12 H; 4-H, 9-H), 3.96 (t, $J_{H,H}$ = 6 Hz, 2 H; 1-H), 5.46 (m, 1 H; CHT, 6-H), 5.55 (m, 1 H; CHT, 2-H), 5.7 (br. s, 8 H; cyclophane), 5.9 (br., A, B or C), 6.1 (br. d, 2 H; A, B, or C), 6.23 (d, $J_{H,H}$ = 9 Hz,1 H; CHT, 2-H), 6.38 (m, 1 H; CHT; 5-H), 6.7 (br.,); A, B or C), 6.8 (d, $J_{H,H}$ = 8 Hz, 2 H; A, B or C), 6.85 (d, $J_{H,H}$ = 7 Hz, 1 H; CHT, 4-H), 7.66 (s, 8 H; cyclophane), 8.0 (br. d, 8 H; cyclophane), 8.84 ppm (br. d, 9 H; cyclophane).

Compound 25: [25.0 mg **1** (0.023 M), 10.3 mg **11** (0.023 M)]. ^{1}H NMR (400 MHz, CD_3CN, 303 K, TMS): 1.60 (m, 2 H; 2-H), 1.9 (1 H; CHT, 7-H), 2.31 (t, $J_{H,H}$ = 7 Hz, 2 H; 3-H), 2.64 (t, $J_{H,H}$ = 5 Hz, 1 H; OH), 3.51 (m, 2 H; 1-H), 3.78 (m, 4 H; 5-H, 8-H), 3.85 (m, 4 H; 4-H, 9-H), 3.89 (s, 4 H; 6-H, 7-H), 5.1 (br., B or C), 5.13 (m, 2 H; CHT, 1-H, 6-H), 5.5 (br., B or C), 5.7 (br. s, 8 H; cyclophane), 5.8 (br., B or C), 6.2 (br., B or C), 6.36 (m, 2 H; CHT, 2-H, 5-H), 6.90 (m, 2 H; CHT, 3-H, 4-H), 7.68 (s, 8 H; cyclophane), 7.99 (d, $J_{H,H}$ = 7 Hz, 8 H; cyclophane), 8.86 ppm (d, $J_{H,H}$ = 7 Hz, 8 H; cyclophane).

Compound 26: [11 mg **1** (0.01 M), 6.7 mg **12** (0.016 M)]. ^{1}H NMR (400 MHz, CD_3CN, 303 K, TMS): 1.73, 1.88, 1.95 (br. m, 17 H; adamantane; H-2), 1.9 (1 H; CHT, 7-H), 2.48 (t, $J_{H,H}$ = 7 Hz, 2 H; 3-H), 3.75−3.85 (m, 12 H, 4-H −9-H), 3.95 (t, $J_{H,H}$ = 6 Hz, 2 H; 1-H), 5.0 (br., B or C), 5.16 (br., 2 H; CHT, 1-H, 6-H), 5.7 (s, 8 H; cyclophane), 6.1 (br., B or C), 6.2 (br., B or C), 6.4 (m, 2 H; CHT, 2-H, 5-H), 6.7 (br., B or C), 6.90 (br. s, 2 H; CHT, 3-H, 4-H), 7 (br., B or C), 7.62 (s, 8 H; cyclophane), 8.06 (d, $J_{H,H}$ = 7 Hz, 8 H; cyclophane), 8.86 ppm (d, $J_{H,H}$ = 7 Hz, 8 H; cyclophane).

Compound 27: [22.2 mg **1** (0.02 M), 2.9 mg **13** (0.006 M)]. ^{1}H NMR (300 MHz, CD_3CN, TMS): δ = 2.46 (t, $J_{H,H}$ = 6 Hz, 2 H; CHT, 7-H), 3.77 (s, 4 H; 4-H, 3-H), 3.8 (m, 4 H; 2-H, 5-H), 4.0 (m, 4 H; 1-H, 6-H), 5.31 (m, 4 H; CHT, 1-H, 6-H), 5.47 (m, 1 H; CHT, 1-H), 5.56 (d, $J_{H,H}$ = 8 Hz, 2 H; A), 5.70 (s, 8 H; cyclophane), 6.26 (m, 4 H; CHT, 2-H, 5-H), 6.53 (br. s, 4 H; B), 6.77 (m, 4 H; CHT, 3-H, 4-H), 6.9 (br. s, 4 H; B), 7.65 (s, 8 H; cyclophane), 8.01 (br. s, 8 H; cyclophane), 8.85 ppm (br. s, 8 H; cyclophane).

Rotaxane 15: Compound **6** (0.15 g, 0.27 mmol), dissolved in MeCN (1 mL), was added to **1** (0.5 g, 0.45 mmol) in acetonitrile solution (1 mL). The solution was purged with argon for 0.5 h, and 2,4,6-tris(isopropyl)benzyl bromide (0.080 g, 0.27 mmol), together with 2,6-di-*tert*-butyl-4-methylpyridine (0.055 g, 0.27 mmol), dissolved in acetonitrile (2 mL), was added to the green solution of the pseudorotaxane. The reaction solution was stirred under an argon atmosphere for 96 h at room temperature. The precipitate was filtered off, the solution was evaporated, and the residue was extracted with MTBE (75 mL). The thread **18** was obtained from the filtrate as an oil and was purified by CC (silica gel, *n*-hexane/ethyl acetate 2:1) (0.13 g, 61%). ^{1}H NMR (300 MHz, CD_3CN, TMS): δ = 1.23 (d, $J_{H,H}$ = 7 Hz, 18 H; *i*Pr), 1.68, 1.84, 1.9 (br. m, 15 H; adamantane), 2.72 (t, $J_{H,H}$ = 6 Hz, 1 H; CHT, 7-H), 2.88 (sept, $J_{H,H}$ = 7 Hz, 1 H; *i*Pr), 3.21 (sept, $J_{H,H}$ = 7 Hz, 2 H; *i*Pr), 3.6 (m, 6 H; 3-H, 4-H, 5-H), 3.76 (m, 2 H; 1-H), 4.19 (s, 2 H; *N*-benzyl), 5.47 (m, 1 H; CHT, 6-H), 5.57 (m, 1 H; CHT, 1-H), 6.34 (m, 2 H; CHT, 2-H, 5-H), 6.72 (d, $J_{H,H}$ = 8 Hz, 2 H: A), 6.94 (d, $J_{H,H}$ = 9 Hz, 2 H; B), 7.04 (d, $J_{H,H}$ = 6 Hz, 1 H; CHT, 4-H) 7.09 (s, 2 H; *i*Pr-Ph), 7.19 (d, $J_{H,H}$ = 8 Hz, 2 H; A), 7.46 ppm (d, $J_{H,H}$ = 9 Hz, 2 H; B), $C_{52}H_{67}NO_5$ (786.10): calcd. (%): calcd. C 79.45, H 8.59, N 1.78; found (%) C 78.99, H 8.44, N 1.84.

The solid, insoluble in MTBE, was purified by column chromatography on neutral Al_2O_3 (Fluka) with a solvent mixture of acetonitrile (400 mL), ethyl acetate (200 mL), and cyclohexane (100 mL) and containing ammonium hexafluorophosphate (7 g). The red fraction was concentrated under reduced pressure and the resulting solid was washed with water (350 mL). Compound **15** was obtained as a red solid (mp 202−206 °C, 0.071 g, 14%). ^{1}H NMR (400 MHz, CD_3CN, 333 K, TMS): δ = 1.23 (d, $J_{H,H}$ = 7 Hz, 6 H; *i*Pr), 1.25 (d, $J_{H,H}$ = 7 Hz, 12 H; *i*Pr), 1.67, 1.71, 1.81, 1.9 (br. m, 15 H; adamantane), 2.87 (sept, $J_{H,H}$ = 7 Hz, 1 H, *i*Pr), 3.06 (t, $J_{H,H}$ =

6 Hz, 1 H; CHT, 7-H), 3.14 (m, 2 H; *i*Pr), 3.27 (d, $J_{H,H}$ = 9 Hz,2 H: B), 3.37 (br. m, 2 H; 6-H), 3.8 (m, 4 H; 2-H, 5-H), 3.9 (s, 4 H; 3-H, 4-H), 4.2 (m, 4 H; H-1; *N*-benzyl), 4.62 (d, $J_{H,H}$ = 9 Hz, 2 H; B), 5.69−5.85 (m, 11 H; CHT, 1-H, 2-H, 6-H; cyclophane), 6.17 (d, $J_{H,H}$ = 6 Hz,1 H; CHT, 4-H), 6.55 (m, 1 H; CHT, 5-H), 6.79 (d, $J_{H,H}$ = 8 Hz, 2 H; A), 7.10 (s, 2 H; *i*Pr-Ph), 7.37 (d, $J_{H,H}$ = 8 Hz, 2 H; A), 7.85 (m, 16 H, cyclophane), 8.86−8.93 ppm (m, 8 H; cyclophane). MS (ESI): 1740.6522^{+} (M − PF_6^-, $[C_{88}H_{99}F_{18}N_5O_5P_3]^+$), calcd. 1740.656; 797.8473^{2+} (M − 2PF_6^-, $[C_{88}H_{99}F_{12}N_5O_5P_2]^{2+}$), calcd. 797.8456. $C_{88}H_{99}F_{24}N_5O_5P_4$ (1886.61): calcd. (%): calcd. C 56.02, H 5.29, N 3.71; found (%) C 56.04, H 5.50, N 3.47.

Rotaxane 18: Compound **8** (0.114 g, 0.20 mmol), dissolved in MeCN (1 mL), was added to **1** (0.44 g, 0.40 mmol) in acetonitrile solution (1 mL). The solution was purged with argon for 0.5 h, and 2,4,6-tris(isopropyl)benzyl bromide (0.060 g, 0.20 mmol), together with 2,6-di-*tert*-butyl-4-methylpyridine (0.041 g, 0.20 mmol), dissolved in acetonitrile (2 mL) was added to the green solution of the pseudorotaxane. The reaction solution was stirred under an argon atmosphere for 96 h at room temperature. The precipitate was filtered off, the solution was evaporated, and the residue was extracted with MTBE (75 mL). The thread **19** was obtained from the filtrate as oil and purified by CC (silica gel, *n*-hexane/ethyl acetate 2:1) (0.096 g, 61%). ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ = 1.26 (d, $J_{H,H}$ = 7 Hz, 18 H; *i*Pr), 1.7, 1.9, 2.0 (br. m, 15 H; adamantane), 2.83 (d, $J_{H,H}$ = 7 Hz, 2 H; CHT, 2-H), 2.91 (sept, $J_{H,H}$ = 7 Hz, 1 H; *i*Pr), 3.23 (sept, $J_{H,H}$ = 7 Hz, 2 H; *i*Pr), 3.7 (m, 6 H; 2-H, 3-H, 4-H), 3.9 (m, 2 H; 5-H), 4.1 (m, 2 H, 6-H), 4.2 (m, 2 H, 1-H), 4.3 (s, 2 H; *N*-benzyl), 5.61 (m, 1 H; CHT, 5-H), 6.43 (d, $J_{H,H}$ = 9 Hz, 1 H; CHT, 6-H), 6.52 (d, $J_{H,H}$ = 6 Hz, 1 H: CHT, 2-H), 6.98 (d, $J_{H,H}$ = 6 Hz, 1 H; CHT, 3-H), 6.69 (d, $J_{H,H}$ = 9 Hz, 2 H; A), 6.91 (d, $J_{H,H}$ = 9 Hz, 2 H; B), 7.07 (s, 2 H; *i*Pr-Ph), 7.44 (d, $J_{H,H}$ = 9 Hz, 2 H; A), 7.45 ppm (d, $J_{H,H}$ = 9 Hz, 2 H; B), $C_{52}H_{67}NO_5$ (786.09): calcd. (%): calcd. C 79.45, H 8.59, N 1.78; found (%) C 79.32, H 8.84, N 1.67.

The solid, insoluble in MTBE, was purified by column chromatography on neutral Al_2O_3 (Fluka) with a solvent mixture of acetonitrile (400 mL), ethyl acetate (200 mL), and cyclohexane (100 mL), and containing ammonium hexafluorophosphate (7 g). The red fraction was concentrated under reduced pressure and the resulting solid was washed with water (350 mL). Compound **15** was obtained as a red solid (mp 202−206 °C, 0.085 g, 22.5%). ^{1}H NMR (400 MHz, CD_3CN, TMS): δ = 1.25 (d, $J_{H,H}$ = 7 Hz, 6 H; *i*Pr), 1.28 (d, $J_{H,H}$ = 7 Hz, 12 H; *i*Pr), 1.7, 1.8, 1.9 (br. m, 15 H; adamantane), 2.43 (d, $J_{H,H}$ = 8 Hz, 2 H; CHT, 7-H), 2.91 (sept, $J_{H,H}$ = 7 Hz, 1 H; *i*Pr), 3.24 (sept, $J_{H,H}$ = 7 Hz, 2 H; *i*Pr), 3.6 (m, 2 H; 6-H), 3.7 (m, 2 H; 2-H), 3.8 (m, 6 H, 3-H, 4-H, 5-H), 4.2 (m 4 H, 1-H, B), 4.3 (s, 2 H; *N*-benzyl), 4.91 (d, $J_{H,H}$ = 8 Hz, B), 5.20 (d, $J_{H,H}$ = 7 Hz, 1 H; CHT, 2-H), 5.63−5.79 (m, 9 H; CHT, 6-H, cyclophane), 6.23 (d, $J_{H,H}$ = 10 Hz,1 H; CHT, 5-H), 6.71 (d, $J_{H,H}$ = 7 Hz, 1 H; CHT, 3-H), 6.55 (d, $J_{H,H}$ = 8 Hz, 2 H; A), 6.80 (d, $J_{H,H}$ = 8 Hz, 2 H; A), 7.10 (s, 2 H; *i*Pr-Ph), 7.8 (br., 8 H, cyclophane), 7.89 (s, 8 H; cyclophane), 8.88 ppm (br., 8 H, cyclophane). $C_{52}H_{66}F_6NO_5P$ (930.05): calcd. (%): calcd. C 67.15, H 7.15, N 1.51; found (%) C 66.89, H 7.43, N 1.78, MS: found 784.4229 (M − PF_6, $[C_{52}H_{66}NO_5]^+$), calcd. 784.4936.

Rotaxane 20: The rotaxane **18** (0.08 g, 0.05 mmol) in Et_4NPF_6 MeCN solution (0.1 M, 50 mL) was oxidized by controlled potential electrolysis (E_A= 0.9−1.4 V [SCE], HEKA PG285) on a Pt electrode in the anode region of a H cell until a charge output of 2 Fmol^{-1} had been consumed. After evaporation and washing with water, the remaining blue solid was purified by column chromatography (silica gel, acetonitrile (400 mL), ethyl acetate (200 mL), cyclohexane (100 mL) containing ammonium hexafluorophosphate (7 g)). Compound **20** (0.05 g, 65%) was obtained as a blue solid, m.p. 202−204 °C. ^{1}H NMR (600 MHz, CD_3CN, TMS): δ = 1.25 (d, $J_{H,H}$ = 7 Hz, 18 H; *i*Pr), 1.7, 1.9 (br. m, 15 H; adamantane), 2.86 (br. m, 2 H; 6-H), 2.93 (sept, $J_{H,H}$ = 7 Hz, 1 H; *i*Pr), 3.00 (d, $J_{H,H}$ = 9 Hz, 2 H; B), 3.13 (sept, $J_{H,H}$ = 7 Hz, 2 H; *i*Pr), 3.7, 3.8, 3.9, 4.2 (br., 10 H; 5-H, 3-H, 4-H, 2-H, 1-H), 4.6 (br. d, 2 H; *N*-benzyl), 5.56 (d, $J_{H,H}$ = 9 Hz, B), 5.76, 5.77, 5.78, 5.83, 5.88 (m, 8 H; cyclophane), 6.27 (br., 1 H; NH), 7.07 (d, $J_{H,H}$ = 8 Hz, 2 H; A), 7.17 (s, 2 H; *i*Pr-Ph), 7.79−7.96 (m, 9 H, cyclophane, tropylium), 7.90 (s, 8 H; cyclophane), 8.2 (m, 3 H; A, tropylium), 8.45 (m, 1 H, tropylium), 8.8 (br., 1 H; tropylium), 8.9 (m, 1 H; tropylium) 8.9 ppm (br., 8 H, cyclophane). UV/Vis (acetonitrile): λ_{max}/nm (ε) 583 (43800 mol^{-1}dm^{3}cm^{-1}), 350 (10900 mol^{-1}dm^{3}cm^{-1}), 261.5 nm (57500 mol^{-1}dm^{3}cm^{-1}). $C_{88}H_{98}F_{30}N_5O_5P_5$ (2030.56): calcd. (%): calcd. C 52.05, H 4.86, N 3.45; found (%) C 51.87, H 5.03, N 3.65.

Molecular Thread 21: Compound **19** (0.096 g, 0.15 mmol) in Et_4NPF_6 MeCN solution (0.1 M, 50 mL) was oxidized by controlled potential electrolysis (E_A= 0.8−1.2 V [SCE], HEKA PG285) at a Pt-electrode in the anode region of a H cell until a charge output of 2 Fmol^{-1} had been consumed. After evaporation and washing with water, the remaining blue solid was purified by column chromatography [silica gel, acetonitrile (400 mL), ethyl acetate (200 mL), cyclohexane (100 mL) containing ammonium hexafluorophosphate (7 g)] to afford the tropylium thread (0.088 g 78%), the NMR spectrum of which is necessary in order to calculate the CIS values of **20**, m.p. 97−99 °C. ^{1}H NMR (600 MHz, CD_3CN, TMS): δ = 1.23 (d, $J_{H,H}$ = 7 Hz, 18 H, *i*Pr), 1.7 (m, 2 H; 2-H), 1.7, 1.8 (br., 15 H; adamantane), 2.90 (sept, $J_{H,H}$ = 7 Hz, 1 H, *i*Pr), 3.14 (sept, $J_{H,H}$ = 7 Hz, 2 H; *i*Pr), 3.6 (m, 6 H; 2-H, 3-H, 4-H), 3.8 (m, 2 H; 5-H), 4.1 (m, 2 H; 1-H), 4.2 (m, 2 H; 6-H), 4.44 (br., 2 H; *N*-benzyl), 5.91 (t, $J_{H,H}$ = 4 Hz, 1 H; NH), 6.94 (d, $J_{H,H}$ = 9 Hz, 2 H; A), 7.12 (s, 2 H; *i*Pr-Ph), 7.15 (d, $J_{H,H}$ = 9 Hz, 2 H; B), 7.80 (d, $J_{H,H}$ = 9 Hz, 2 H; B), 7.95 (d, $J_{H,H}$ = 9 Hz, 2 H; A), 8.28 (m, 1 H; tropylium), 8.40 (m, 1 H; tropylium), 8.57 (m, 1 H; tropylium), 8.67 (m, 1 H; tropylium), 8.78 ppm (m, 1 H; tropylium). UV/Vis (acetonitrile): λ_{max}/nm (ε) 575 (41400 mol^{-1}dm^{3}cm^{-1}), 403 (10100 mol^{-1}dm^{3}cm^{-1}), 270.5 nm (22100 mol^{-1}dm^{3}cm^{-1}). $C_{52}H_{66}F_6NO_5P$ (930.05): calcd. (%): calcd. C 57.15, H 7.15, N 1.51; found (%) C 57.37, H 7.09, N 1.76.

Supporting Information (see also the footnote on the first page of this article): Selected ^{1}H NMR spectra of pseudorotaxanes and rotaxanes, UV/Vis spectrum of **14**.

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