Controlling Ring Translation of Rotaxanes†

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Novel rotaxanes containing two 9-aryl-9-methoxy-10-methyl-9,10-dihydroacridine moieties (acridanes) at both ends of the molecular axle as recognition stations for the tetracationic ring **CBQT**$^{4+}$ were synthesized together with their acridinium counterparts. A new concept of controlling the ring movement within rotaxanes has been realized with these rotaxanes. Owing to Brownian molecular movement, the ring shuttles from one end of the axle to the other one in acridane rotaxanes. The shuttle process is stopped by converting two or one of the acridane stations into the corresponding acridinium unit. If both acridanes are transformed by addition of an acid, the ring resides on evasive stations present in the center of the axle. Photons convert only the unoccupied acridane station, thus the ring remains on the unchanged acridane station. The shuttle process can be switched on by addition of a base and by the thermal reaction of the methoxide with the formed acridinium ion, respectively.

Introduction

Rotaxanes are mechanically coupled molecules consisting of two parts, the wheel and the extended molecular axle, which are freely movable relative to each other. They are promising candidates for the development of molecular machines.[1] The position of the wheel is governed by the interaction between the so called recognition stations present both in the wheel and the axle. If at least two stations are present within the axle, the dynamics of the ring translation along the axle depend on the presence of identical or different stations. Due to Brownian motion, the wheel shuttles between two identical stations in degenerate rotaxanes. The activation energy of this shuttle movement depends both on the chemical structure of the station and the distance between the two stations.[1d,1f] If the energy of the interaction between the two different stations and the wheel is sufficiently large, the wheel will predominantly reside on that station which supplies the highest energy gain for the wheel-axle-interaction. In switchable rotaxanes, the energy of interaction for the recognition station and the wheel is drastically weakened by an external stimulus. Accordingly, the interaction with the second, unchanged station is favored and the ring moves to this station and the so-called co-conformatio[2] is completely rearranged by Brownian motion. Solvents,[3] chemicals,[4] electrons,[5] and photons[1d,e] are able to act as stimuli. Using light is advantageous because no side products of the switching process are evolved and because light action is addressable.

Until now, efforts were directed mainly toward safeguarding the integrity of the co-conformers in both states. In contrast, only a few means for controlling the dynamics of the shuttle process by external stimuli are known. The addition of a base, an acid, or Zn^{2+},[6] a change of solvent,[7] or the structure of the axle[8] have influenced the rate of the ring motion.

A reduction in the size of the ring component due to photochemical electrocyclization resulted in a reduced shuttling motion.[9] The coordinative binding of metal ions stopped the shuttling process completely.[6a]

A photoreaction that switches the shuttling process off and on in a two station degenerate rotaxane may be an alternative means to control the movement of the wheel upon the axle. If we assume that only one of the two identical stations can be transformed so that the interaction energy between the wheel and this station is drastically reduced, the wheel will reside mainly on the unchanged station. Then, the reset would restart the shuttling process between the two now identical stations. How, then, can different photoreactivities of two identical moieties be achieved? Rotaxanes with charge transfer interaction between wheel and axle may be suitable. A real drawback of each photoresponsive system based on charge transfer interaction is the strongly diminished quantum yield of the photoprocess due to the increased thermal deactivation of the photoexcited state.[10] With two identical stations, only one station can be occupied at a time, and the free station must retain the natural, higher photoreactivity, completely unaffected by the charge transfer interaction. In this way, the necessary differentiation would be established.

Recently we have presented bistable rotaxanes which have the photoactive station 9-aryl-9-alkoxy-acridane which interacts with the tetracationic ring cyclobis(paraquat-*p*-phenylene)[11] (**CBQT**$^{4+}$).[12] The acridane is transformed into the acridinium alkoxide by photolysis. Therefore, the ring moves to a second evasive station present within the axle. As expected, the efficiency of the photolysis of the acridane occupied by the ring is decreased by more than a factor of five compared with an acridane compound, which is in the range of 50% if not in complex with **CBQT**$^{4+}$.[12,13] This differentiation appears to be sufficient to switch the shuttling process. Therefore, it is expected that the shuttling of the ring can be controlled by dependence on alternative stations present in the molecular thread of the rotaxanes.

Furthermore, acridanes are pseudo-bases. Accordingly, protons should be able to control the ring movement.[12b]

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Results and discussion

Synthesis of rotaxanes

A template directed threading-followed by connecting two half-axles approach was employed to generate different types of rotaxanes (Scheme 1). All of them include two acridinium/acridane-stations at the ends of the axle and with **CBQT**$^{4+}$ as the wheel. They differ from each other by kind and number of evasive stations in the middle of the axle. Protons should be able to transform the two acridane stations into two acridinium units. Addition of a base would result in restoring the starting acridane rotaxane. Photons are expected to transform only one of the acridane stations into the acridinium unit. The thermal back reaction between the released methoxide ion and the formed acridinium ion reverses the reaction. The lifetime of the acridinium methoxide is between seconds and hours, depending on the alcohol content of the solvent mixture.[12]

[2]Rotaxanes, molecules which consist of an axle and one macrocycle, were prepared by reaction of the western half of the molecular axle containing the acridane recognition station with the eastern half containing the acridinium unit in the presence of the tetracationic ring. Both an esterification and a "click" reaction were used to connect both parts of the molecular axle (see Schemes 2–4). Esterification of the alcohol **1** with the acid **2** results in the four station rotaxane **3**. Surprisingly, despite various ratios of **CBQT(PF$_6$)$_4$** and **1** and **2**, in one case both [2]rotaxane **3** and [3]rotaxane **4**, containing two macrocycles, were formed.

The three-station-rotaxane **10** is available by "click"-chemistry, whereby the question arises as to whether the triazole moiety is able to act as recognition station of **CBQT**$^{4+}$ (Scheme 4). "Click"-chemistry also is the basis of the synthesis of **14** and **19** (see Schemes 5 and 6). The reaction of the acridinium rotaxanes with methanol in acetonitrile solution in the presence of $NaHCO_3$ affords the related acridane rotaxanes **6**, **7**, **12**, **16** and **21** (Schemes 3–6)

For comparison, the acridinium axles **11**, **15** and **20** were also converted into the corresponding acridane axles **22–24** (Scheme 7).

Co-conformation

Acridinium rotaxanes. The mutual conversion of the acridane rotaxanes and their acridinium counterparts can be controlled by the alternate addition of acid and base. It is important, therefore, to determine the co-conformation of the two counterparts. In order to probe the solution-state structures of rotaxanes NMR-spectroscopy was employed. Complexation induced shifts (CIS) of proton signals of the rotaxanes compared to those of the wheel-free axles are equivalent to the interaction between the recognition stations and the wheel **CBQT**$^{4+}$. Although none of the molecular axles is symmetrical the two acridinium or acridane stoppers have almost identical NMR-signals (see for examples Schemes S10, S13, S14, ESI†). The assignment of proton signals of the axle is possible with the aid of two- dimensional techniques such as H,H-COSY, C,H-COSY and ROESY.

Rotaxane 3. CIS-values reveal that stations B and C are complexed by the ring **CBQT**$^{4+}$ (Scheme S5, ESI†). The proton resonances of both station B and station C are upfield shifted by 2–3 ppm compared with the axle **5**. In contrast, proton signals of the 9-aryl-acridinium units are not affected by the presence of the ring. Accordingly, the ring component shuttles between stations B and C as depicted in Scheme 1. NOE-Cross peaks between ring proton signals and the stations B and C reveal the proximity of **CBQT**$^{4+}$ and B and C. Due to the shuttling of the ring between stations B and C, the proton signals of B and C and of the chain between these stations are very broad but visible.

Rotaxane 4. In [3]rotaxane **4**, the second ring **CBQT**$^{4+}$ resides on the second evasive station. Like rotaxane **3**, both stations B and C are shielded. In contrast to the spectrum of **3**, the proton signals of stations B and C and the chain between them are well resolved. Apparently ring shuttling is restricted in the [3]rotaxane **4**. Proton resonances of stations A are not influenced by the presence of the two rings. (Scheme S6, ESI†).

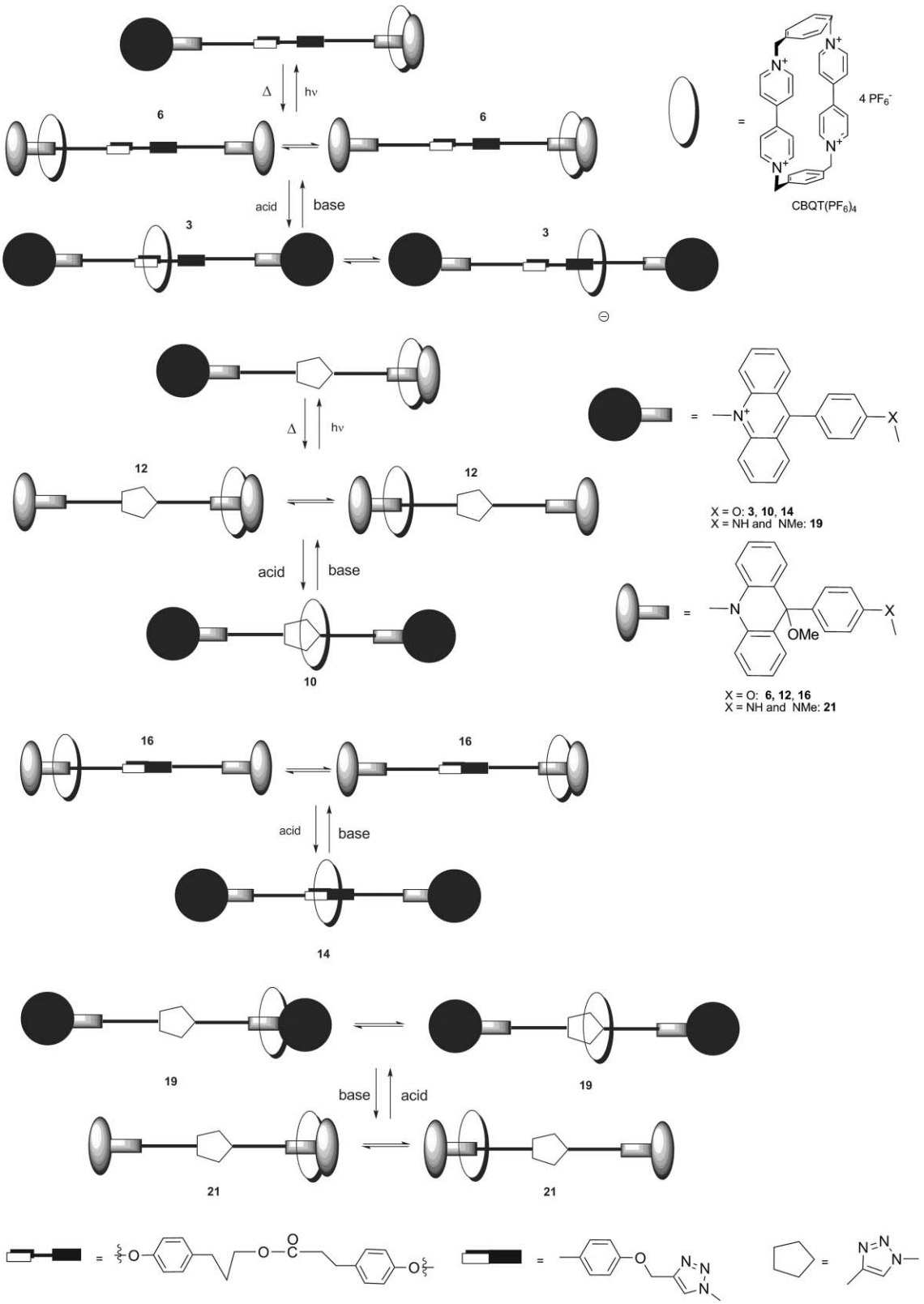
Rotaxane 10. In acridinium rotaxanes without an evasive station, the aryl substituent in the 9-position of the acridinium unit is able to accomodate **CBQT**$^{4+}$.[12b] However, the triazole moiety (T) present in rotaxane **10** competes with the acridinium stations. Indeed, the wheel resides mainly on the triazole station. Therefore, in the spectrum of **10**, the CH- resonance of the triazole unit is upfield shifted by 3.4 ppm. The methylene units adjacent to the triazole unit are considerably upfield shifted also (Scheme S9, ESI†). The small CIS-values observed for the 9-aryl protons indicate that the ring occupies the acridinium units only to a small extent.

Rotaxane 14. Besides the triazole moiety T, rotaxane **14** also contains station B, which is expected to be the superior recognition station. Indeed, station B is occupied predominantly by **CBQT**$^{4+}$ (Scheme S12, ESI†).

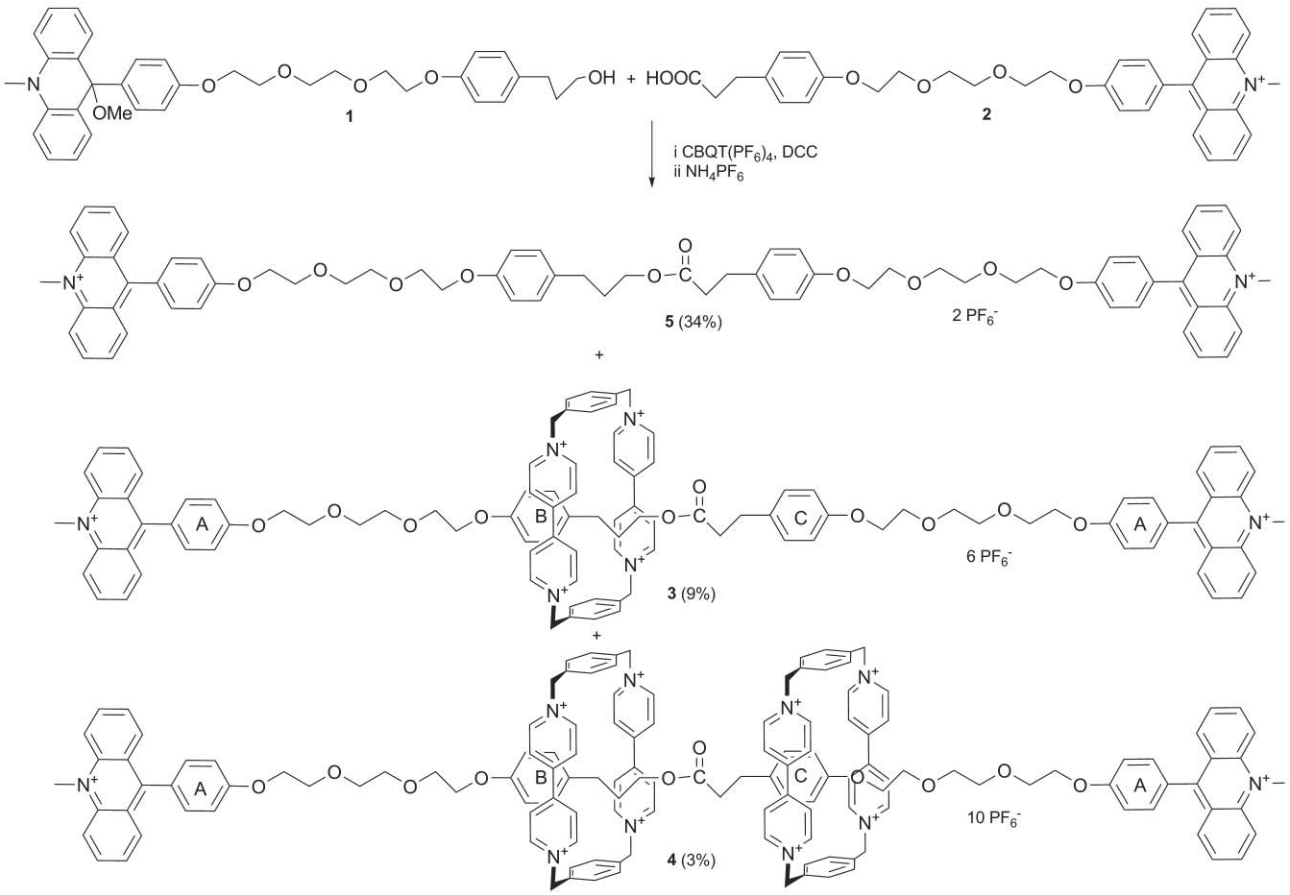
Rotaxane 19. A different situation is observed with rotaxane **19**. Despite the positively charged acridinium subunit, the aminophenyl group in the 9-position is a better recognition station than the triazole moiety (Fig. S5 and Scheme S14, ESI†) and the aryl protons are most strongly upfield shifted. However, to a smaller extent, the triazole unit is also occupied by the ring and we can therefore conclude that **CBQT**$^{4+}$ shuttles between these two stations.

It is worth noting that the second aminophenyl group, A′ of **19** (Scheme 6), which differs from A only by the presence of a methyl substituent, does not interact with the ring. The preferential location of the ring at the aminophenyl acridinium station instead of at the triazole station or the *N*-methylaminophenyl acridinium station may be attributed to the increased electron donor capability of the aminophenyl group compared to the alkoxypheny group of **10** on the one hand and steric interference due to the methyl group at the amino group of the other hand.

Acridane rotaxanes. Next we studied the shuttling process of the ring **CBQT**$^{4+}$ between the two acridane stations at the ends of the molecular axle. In general, the NMR-spectra of acridinium rotaxanes exhibit sharp, easy-to-assign proton signals. In contrast, ring rotations[12a] at room temperature lead to broad or even merged baseline proton signals of **CBQT**$^{4+}$ and the 9-aryl group of the acridane rotaxanes (compare Fig. S1 and S2, ESI†). Even proton signals of unoccupied evasive stations often are not visible at room temperature, possibly due to rotations of the aryl ring within the axle.[12]



Scheme 1 Types of novel rotaxanes possessing two acridane/acridinium stations.



Scheme 2 The synthesis of the four station rotaxanes: generation of [2]rotaxane 3 and [3] rotaxane 4. Axle 5 is also illustrated.

In a first approximation, the proton resonances of those methylene units directly bound to evasive stations B, C or T can be used as probe signals.[12a] If the probe signals are not upfield shifted, the ring **CBQT**$^{4+}$ does not interact with stations B, C or T.

By lowering the temperature, both the proton signals of the ring and of the stations A and B, C appear or become sharper and hence assignable (Fig. S3, ESI†).

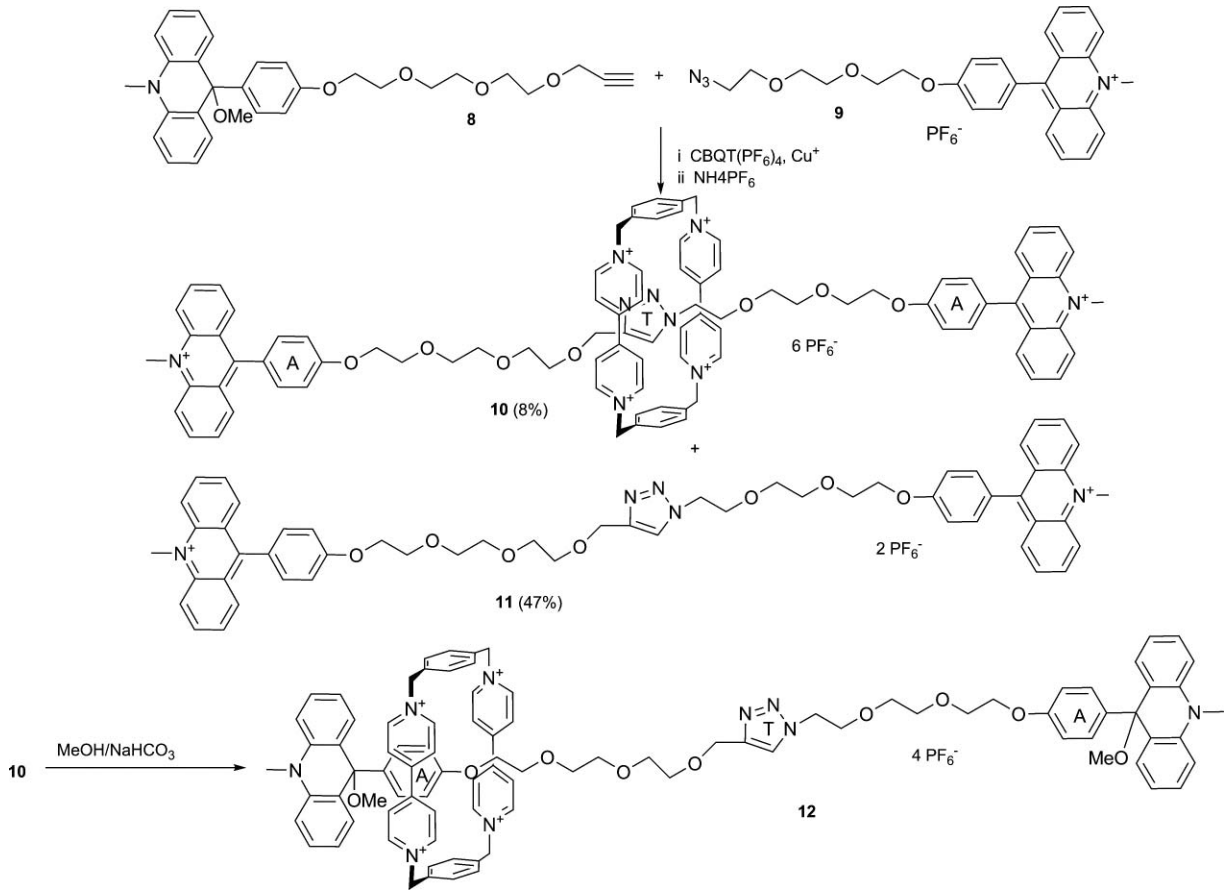
A priori, one may assume that the ring in degenerate acridane rotaxanes will reside alternately on both stations. Previous studies have revealed that evasive stations B or C are not able to compete with the acridane moiety for the interaction with **CBQT**$^{4+}$.[12]

Rotaxane 6. Neither proton signals of **CBQT**$^{4+}$ nor proton signals of aryl groups are visible in the NMR spectra at room temperature. Only the probe protons of the methylene groups between stations B and C appear at the same position as in the axle molecule **5** indicating that the ring does not reside on the stations B and C. However, at 233 K in CDOD/CD_3CN (2 : 1) solution, two sets of aryl protons related to A appear and can be assigned by H–H- and C–H-COSY cross peaks. One set is strongly upfield shifted; the other is only slightly upfield shifted (Scheme S6, ESI†). Protons of the stations B and C appear in the normal aromatic region. Two sets of aryl protons associated with A also appear at 233 K in acetone-d_6 solution and can be assigned by COSY and ROESY cross peaks. This way, in addition to NOE cross peaks, exchange cross peaks that correspond to the two different A stations can be observed in acetone-d_6, thus directly revealing the movement of CBQT^{4+} between the two acridane stations. The rotational movements of the aromatic rings of **CBQT**$^{4+}$ are frozen at low temperature and the proton resonances of **CBQT**$^{4+}$ are split into at least three sets, as usually found for acridane rotaxanes.[12]

Rotaxane 7. Proton resonances of both **CBQT**$^{4+}$ are very broad both in CD_3CN and in acetone-d_6 solution. NMR spectra in MeOD solution exhibit two broad singlets assignable in each case to the 8 α-protons of the pyridinium rings of the two **CBQT**$^{4+}$ wheels. Also, aryl protons of stations A–C are not visible. However, using the methylene groups of the chain between B and C as a probe, it is clear that B and C are not occupied by the rings. These proton resonances are in accord with those found in the axle **5** (Scheme S8, ESI†). Accordingly, the **CBQT**$^{4+}$-rings must reside on both the acridane stations. Shuttling does not occur because the two rings would interfere with each other.

Rotaxane 12. Only a weak evasive recognition station (triazole T) exists besides the powerful acridane recognition stations. *A priori*, one can assume that the ring will reside alternately on both stations A. However, only the proton signals of the occupied aryl group at the 9-position of the acridane ring appear in the ^{1}H-NMR spectrum of **12**. Due to the shielding effect exerted by **CBQT**$^{4+}$, the signals are upfield shifted by 4.4 and 2.3 ppm (Scheme S10, ESI†).

These resonances are not averaged values, but are consistent with an occupied acridane station of rotaxanes with one acridane



Scheme 3 The formation of acridane rotaxanes from acridinium rotaxanes by the addition of base and methanol.

station only.[12] Therefore, room temperature shuttling is slow on the NMR-time scale. Again at 233 K two sets of aryl protons are visible. One set is strongly upfield shifted further on; the second set is in the region normally indicative of an uncomplexed acridane station (Scheme S11, ESI†). The assignment of the proton signals is possible with the help of two-dimensional NMR-methods (HH-, CH-COSY and ROESY). The ROESY spectrum recorded at 233 K exhibits not only NOE cross peaks between the upfield shifted aryl protons of the axle and the xylylene spacer of **CBQT**$^{4+}$ but also exchange peaks arising from complementary protons of the two aryl groups at the 9-position of the acridane moieties appear (Fig. S4, ESI†). These peaks verify the shuttling of the ring between the two acridane stations.

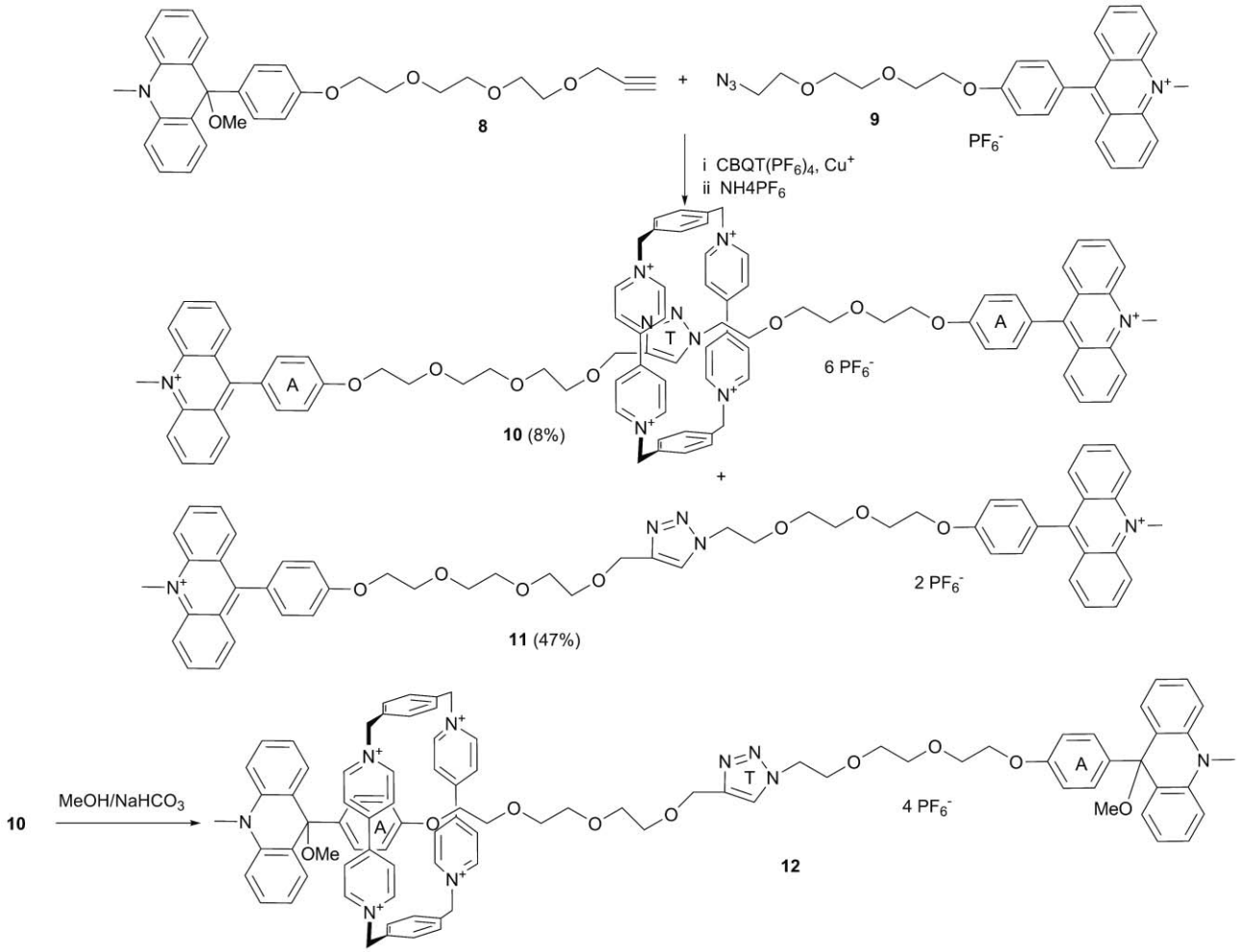
Rotaxane 16. Only one set of aryl protons for the occupied upfield shifted 9-aryl acridane moiety (Scheme S13, ESI†) appears at 233 K in CD_3CN/CD_3OD solution (1 : 1). Therefore, not even at low temperature can shuttling of **CBQT**$^{4+}$ between the two acridane stations be detected.

Rotaxane 21. The two acridane stations of the rotaxane **21** are not exactly identical (see Scheme 6). At room temperature, two sets of aryl protons for A and A′ are present. While the aryl protons of station A appear at 1.9 and 4.5 ppm, those for A′ are very broad and appear at 6.5 and 7.0 ppm. Again, the assignment was made with the help of CH-COSY und ROESY spectra (Fig. S6 and Scheme S15, ESI†). Ring movement is recognizable by the fact that the equilibrium between the acridinium moiety and the acridane unit (as an ionogenic compound) within the rotaxane **21** favors the acridane moiety in solvents containing methanol, *e.g.*, residual acridinium rotaxane **19** is transformed into the corresponding acridane rotaxane **21**. This finding is typical for an acridane unit occupied by **CBQT**$^{4+}$.[12] In contrast, the molecular axle **24** reacts with methanol to give 50% acridinium compound (Scheme S16, ESI†).

The equilibrium between **19** and **21** is determined easily by UV-Vis-spectroscopy, because only the acridinium compound absorbs visible light (compare spectra given in Fig. S7, ESI†). These differences in the behaviors of the rotaxane and the molecular axle are only explicable if the two acridane units are alternately protected by the ring from conversion into the acridinium form.

Switching

Switching by protons. The addition of an acid such as $HClO_4$ or HPF_6 converts the acridane rotaxanes in methanol solution to their related acridinium counterparts. Because **CBQT**$^{4+}$ now resides on the evasive stations (*e.g.* B and C in rotaxane **3**; T in rotaxane **10**; B in rotaxane **14** and A and T in rotaxane **19**), the large amplitude movement of the ring is stopped. The addition of a base such as ethyl-di(isopropyl)amine re-establishes the acridane rotaxanes. The switching process can easily be followed by UV-Vis-spectroscopy (see Fig. 1 for an example). Acridane rotaxanes absorb light below 350 nm; acridinium rotaxanes exhibit the



Scheme 4 Click-chemistry used to connect the two halves of the axle.

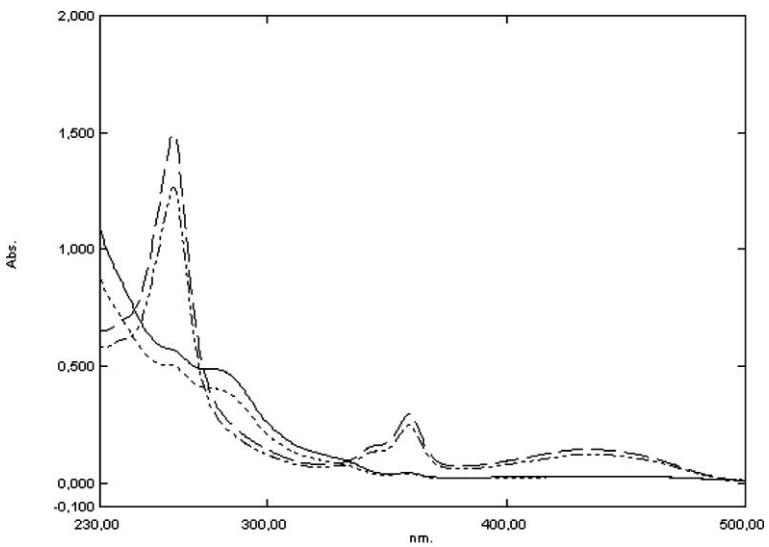
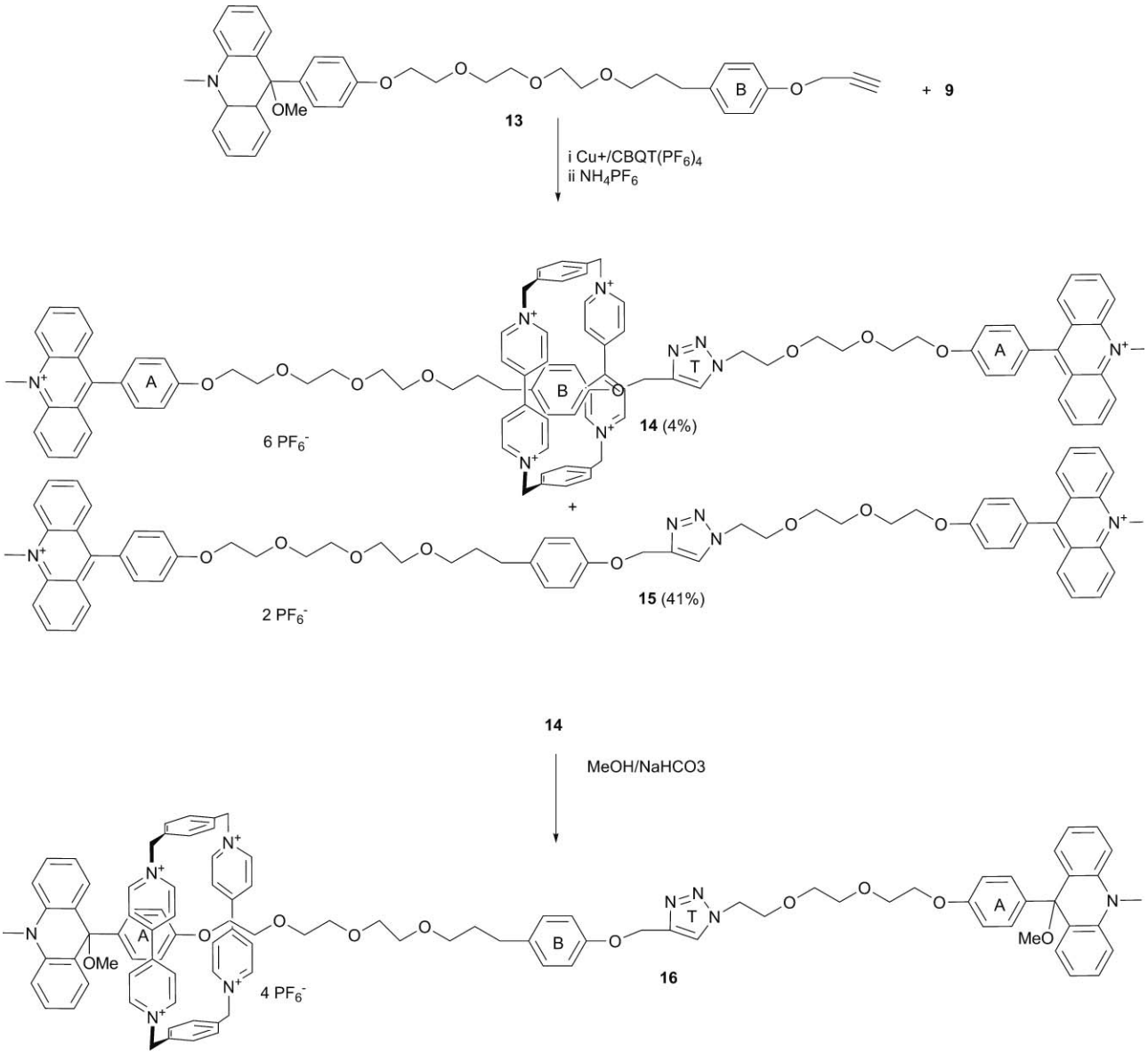


Fig. 1 UV/Vis spectra (MeCN–MeOH 4 : 1, 1×10^{-5} M) of **12** (——) after addition of 1 equiv of $HClO_4$ (— — —); after addition of 10×5 equiv of ethyl-di-isopropylamine (– – –) after addition of 10×5 equiv of $HClO_4$ (– - - –).



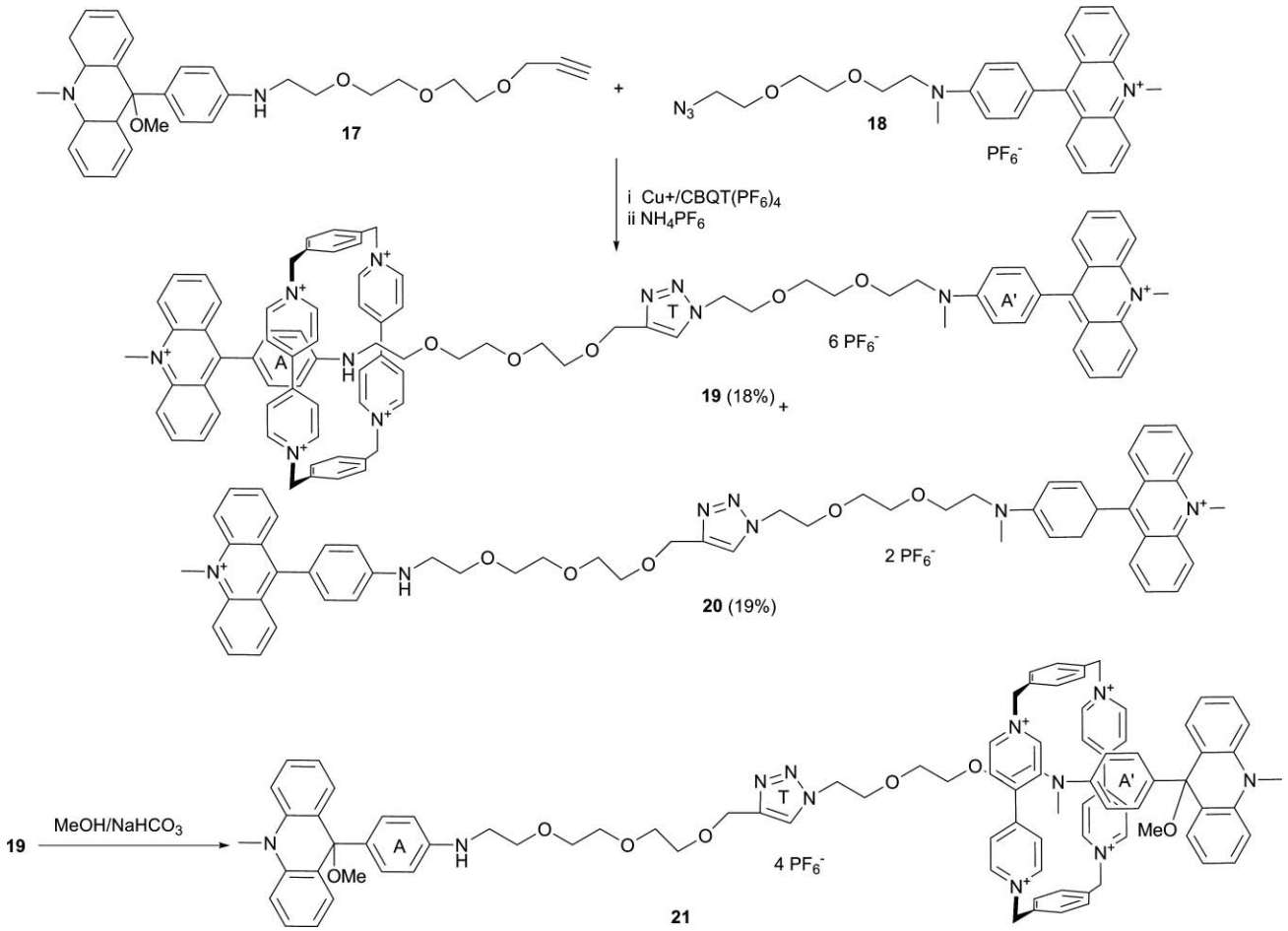
Scheme 5 Formation of the three-station-rotaxane **14** by click-chemistry and the conversion from acridinium **14** to acridane **16** by addition of base.

characteristic absorption spectra of the acridinium salts (around 440 nm for **3**, **10** and **14** and around 550 nm for **19**).

The shuttling between both acridane stations revealed for rotaxanes **6**, **12** and **16** is stopped if both acridane stations are transformed into the corresponding acridinium stations. Now shuttling of **CBQT**$^{4+}$ between B and **C** takes place as found for rotaxane **3** (see above); no shuttling occurs for **10** and **14**, because only the evasive stations T and B, respectively, are involved in the interaction between **CBQT**$^{4+}$ and the molecular axles (see Scheme 8 for two examples).

In the case of the rotaxane **21**, only about 30% of the acridane units can be converted to the acridinium units to prevent protonation of the amino groups of the acridane units (see Fig. S8, ESI†). Addition of ethyl-di(isopropyl)amine to the methanol solution starts movement of the ring forward and back along the whole length of the axle; protonation stops the shuttling process and the wheel shuttles between A and T.

Switching by photons. Contrary to proton switching, the strategy of photon control is based on the photolysis of only one, namely the unoccupied, acridane station. Therefore, by photolysis a rotaxane with one acridinium and one acridane station will be formed. At least 5% methanol must be present in the solution in order to perform a quantitative photoheterolysis.[12] Also the reverse reaction between the acridinium ion and the methoxide requires an alcohol (methanol or ethanol) because the latter reacts with the acridinium ion. The methoxide ion accepts the released proton. The thermal back reaction which occurs after photoexcitation is uniform as revealed by the appearance of two isosbestic points in consecutive UV-Vis-spectra (Fig. S9 and S10, ESI†). The rate of the thermal reaction depends on the nature of the alcohol. For example, the lifetime of the acridinium methoxide formed from the rotaxane **12** is 70 s in methanol and 600 s in ethanol solution. The use of ethanol results in the exchange of the leaving group without any detriment to the switching cycle.



Scheme 6 Synthesis of rotaxanes with 9-aminophenyl groups at the acridinium and acridane moieties.

The lifetime of the rotaxane containing one acridinium and one acridane unit is too short to analyze the co-conformation with NMR-spectroscopy. However, all studies have revealed that the acridinium moiety is not occupied by **CBQT**$^{4+}$, even if only a weakly interacting alternate station such as the alkoxyphenyl moiety is present.[12] Therefore, the acridinium station which is formed intermediately is not able to compete with the remaining acridane station.

As expected, the efficiency of the photoreaction of rotaxanes **6**, **12**, **16** and **21** is significantly higher than that of rotaxanes containing only one acridane station occupied by **CBQT**$^{4+}$.[12]

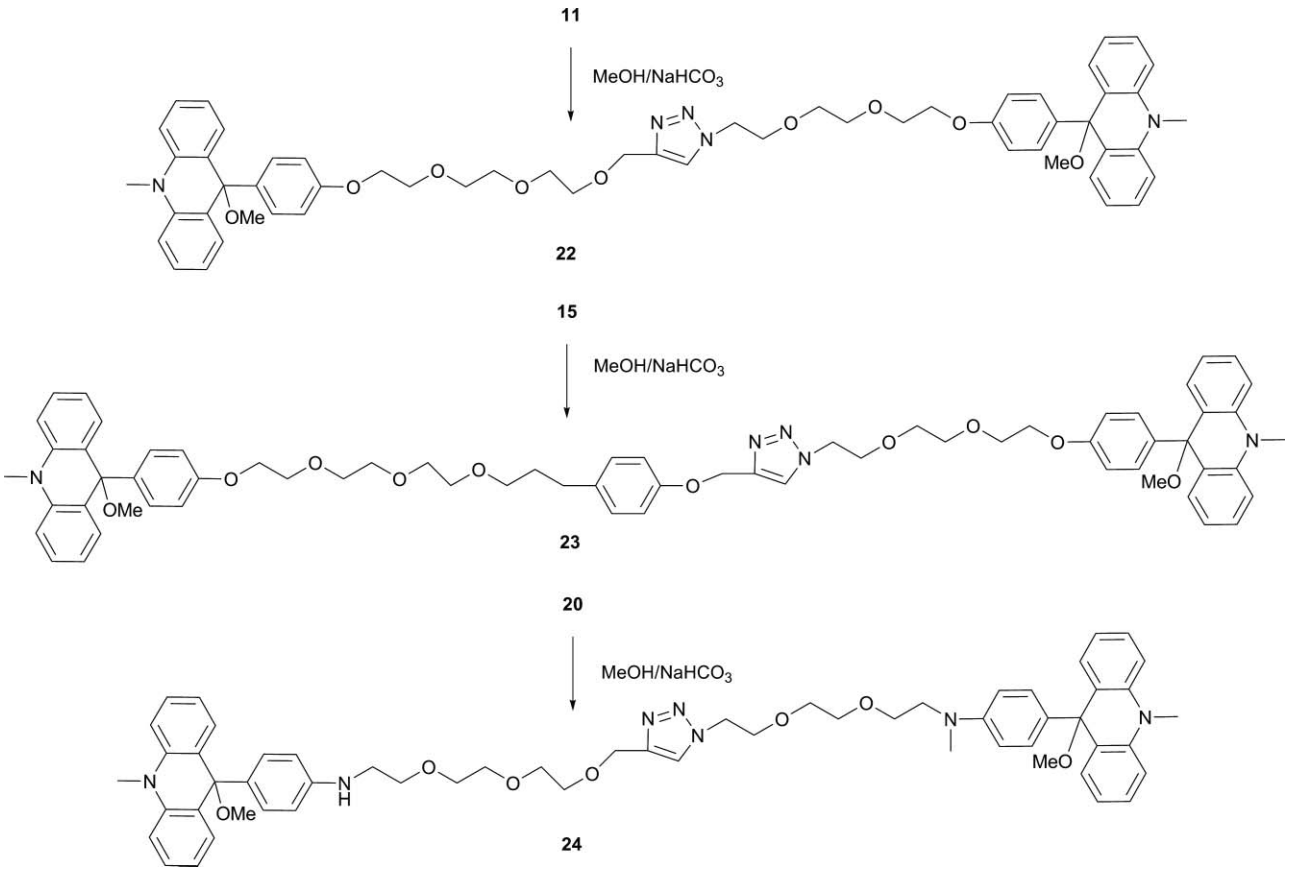
[3]Rotaxane **7** and [2]rotaxane **6** offer the opportunity to compare a rotaxane with two occupied acridane stations with a rotaxane with only one occupied acridane station. Under identical conditions of equal light intensity and absorbance at 330 nm, a turnover of 35% is obtained for **6** at 5 s irradiation time. In contrast, only 10% is obtained for **7**. As expected, the efficiency is significantly higher if an unoccupied acridane station can be excited. Also the transient absorption spectra given in Fig. 2 are slightly different as will be discussed below.

The photolytic behaviors of rotaxanes **12** and **21** are compared with those for the one station rotaxanes **25** and **26** having only one occupied acridane station and which were described in an earlier publication (Schemes 9 and 10).[12a]

The increase of the transient absorbance under comparable excitation conditions for the photolysis of **6**, **12**, **16** and **21** is at least ten times higher than the absorbance increase by the photolysis of the reference compounds **25** and **26** (see Fig. S11 and S12, ESI†). Upon photolysis of **12**, 50% of the increase of the transient absorbance of compound **22** is observed (Fig. S13, ESI†). We therefore conclude that the photolysis of the unoccupied acridane station occurred.

This conclusion is supported by the further finding that the photolysis of an occupied acridane station results in a side reaction that forms an acridinium ion by electron transfer. The characteristic absorption spectrum of the radical trication **CBQT**$^{\bullet 3+}$[14] is superimposed on the transient UV-Vis-spectrum of the acridinium ion. The radical cation decomposes and forms the acridinium ion and the methoxy radical.[15] **CBQT**$^{4+}$ is thereby regenerated by electron back-transfer from **CBQT**$^{\bullet 3+}$ to the methoxy radical. This behavior, typical for occupied acridane stations, is not observed in the cases of rotaxanes **6**, **12**, **16** and **21** (Fig. S14–S16, ESI†). Accordingly, only the transient absorption spectrum monitored with [3]rotaxane **7** (see Fig. 2) exhibits increased absorptions at 410 nm and >500 nm.

The nucleophilic reaction of the methoxide with the acridinium rotaxane reverts to rotaxanes with two acridane stations thus switching on the shuttle movement of the ring (Scheme 9). The switching cycle can be repeated at least ten times without relevant



Scheme 7 Syntheses of axles with two acridane stations.

changes of the UV-Vis-spectrum of the acridane rotaxanes. Notably, the acridane rotaxanes can be prepared *in situ* from the acridinium rotaxanes by addition of ethyl-di-isopropylamine. The switching cycle is not disturbed by the presence of the amine.

Conclusions

We have synthesised novel bistable rotaxanes with a 9-aryl-9-methoxy-acridane station at both ends of the axle. The ring **CBQT**$^{4+}$ shuttles from one acridane station to the other one along the entire axle molecule. This large amplitude movement between the acridane stations (about 2.5 nm for rotaxane **12** and 3.5 nm for rotaxane **6** assuming an extended linear structure of the axle) is stopped either by addition of protons or, more favorably, by light.

The principle of photo-switching is based on the much greater photoheterolysis efficiency of acridanes not occupied by the electron deficient ring compared to those of the occupied acridane station. The high photoreactivity is an important advantage over rotaxanes reported earlier by us.

After excitation of the non-occupied 9-methoxy-9-aryl-acridane station with light (>300 nm), the methoxide ion is released and an acridinium ion is formed. The remaining second acridane station has a considerably greater affinity for the ring than the generated acridinium and evasive stations present within the axle. Accordingly, the ring does not shuttle but remains on the unchanged acridane station.

In contrast, acid–base switching involves both acridane stations and the ring resides on the evasive stations in the middle of the axle.

Both variations of switching can be repeated at least ten times without fading.

Taken together, our results uncover novel principles for controlling the motion of rotaxanes, findings that may be exploited for the development of molecular machines.

Experimental

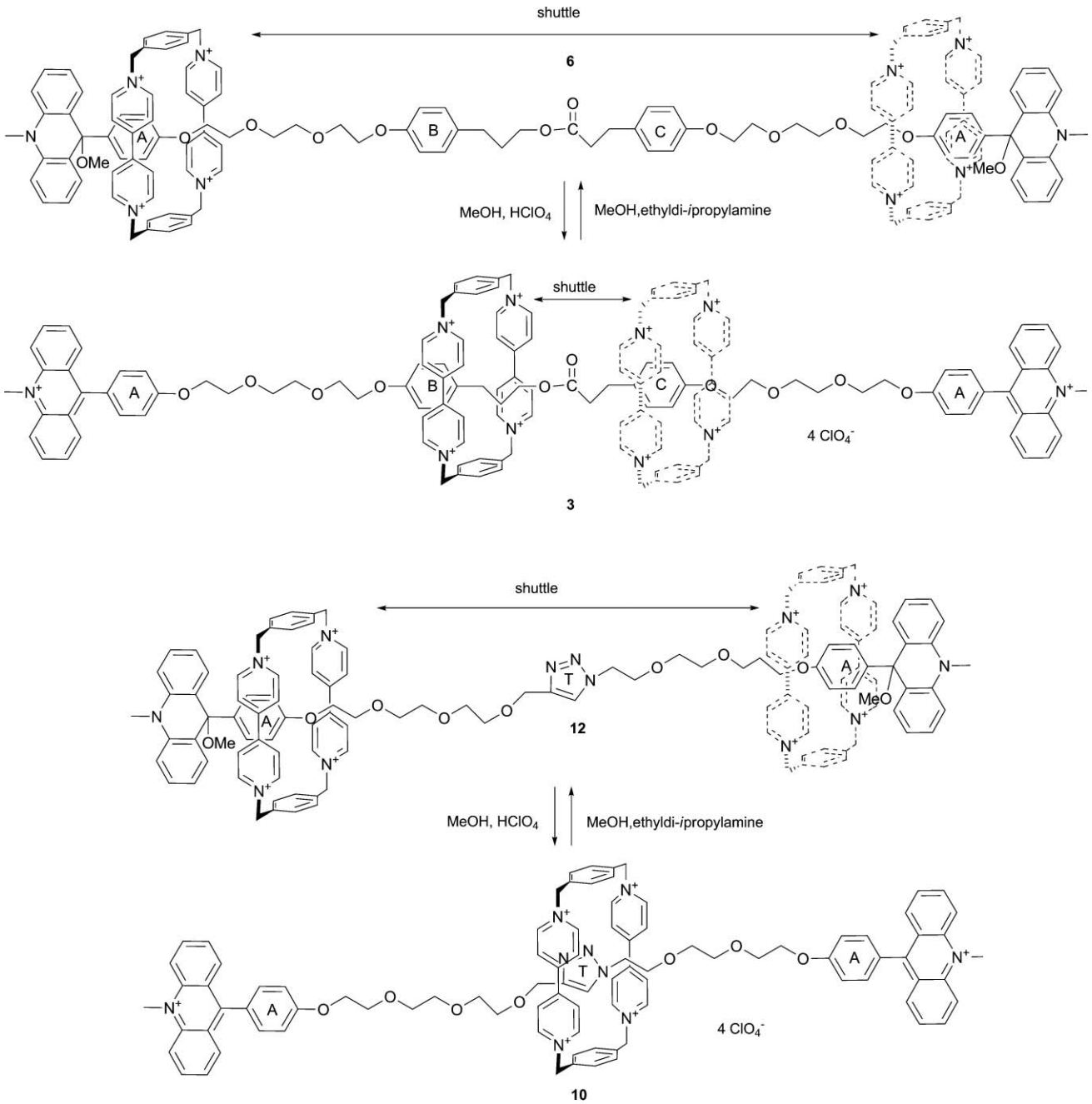
General methods

Commercially available chemicals and solvents (UVASOL, Merck) were used as received unless otherwise noted; solvents were dried according to standard procedures. Column chromatography (CC) was carried out on *200 mesh* silica gel (Merck). Melting points (m.p.) were determined with a Boetius heating microscope.

ESI mass spectroscopy was carried out on LTQ FT, Finnigan MAT, Bremen, Germany) equipped with an electrospray ion source (Thermo Electron).

NMR spectra were recorded on a Bruker DPX 300 (300 MHz) and a Bruker Advance 400 (400 MHz). The proton signals were attributed to the different subunits with the aid of two-dimensional NMR spectroscopy, such as C–H-COSY, H–H-COSY, and ROESY.

UV/Vis measurements were performed with a Shimadzu UV 2101 PC spectrometer.



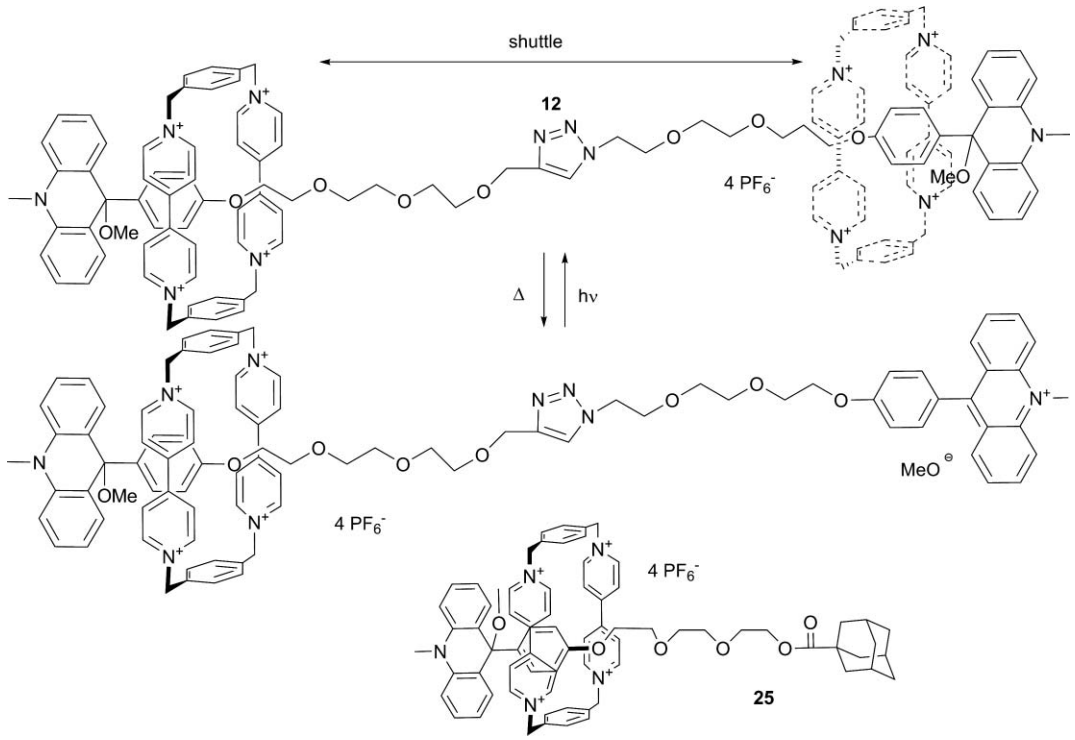
Scheme 8 Examples for controlling the wheel movement by protons.

Irradiation of the rotaxane solutions were carried out with a conventional mercury arc (HBO 500 or HBO 200) combined with a cut-off filter of 300 nm. Transient absorption spectra between 240 and 500 nm were recorded with the UV 2101 PC spectrometer using the fastest scan mode. The transient UV-Vis-absorption spectrum of photoexcited **CBQT**$^{4+}$ in methanol solution was recorded with the help of a flash photolysis apparatus.[16] We thank A. Jacobi and Prof. U.-W. Grummt, University Jena, for these measurements.

Turnover of acridinium ions generated by photolysis was determined by comparing the absorbance at 360 nm with the absorbance obtained upon addition of $HClO_4$.

Rotaxanes 3 and 4

1[12a] (0.299 g, 0.50 mmol) and **CBQT(PF$_6$)$_4$**[11] (0.617 g, 0.56 mmol) in DMF (0.7 mL) were stirred under an argon atmosphere for 0.5 h. A mixture of **2** (ESI†) (0.391 g, 0.55 mmol), dicyclohexylcarbodiimide (0.113 g, 0.55 mmol), and DMAP (0.007 g, 0.06 mmol) was added within 0.5 h. The suspension was stirred for 48 h. The resulting solution was diluted with dichloromethane (50 mL). The precipitate was washed with dichloromethane until the solution is colorless. The solid was treated with a mixture (2 mL) of acetonitrile (40 mL), ethylacetate (20 mL), cyclohexane (10 mL), and NH_4PF_6 (0.7 g). **CBQT(PF$_6$)$_4$** was filtered off. The



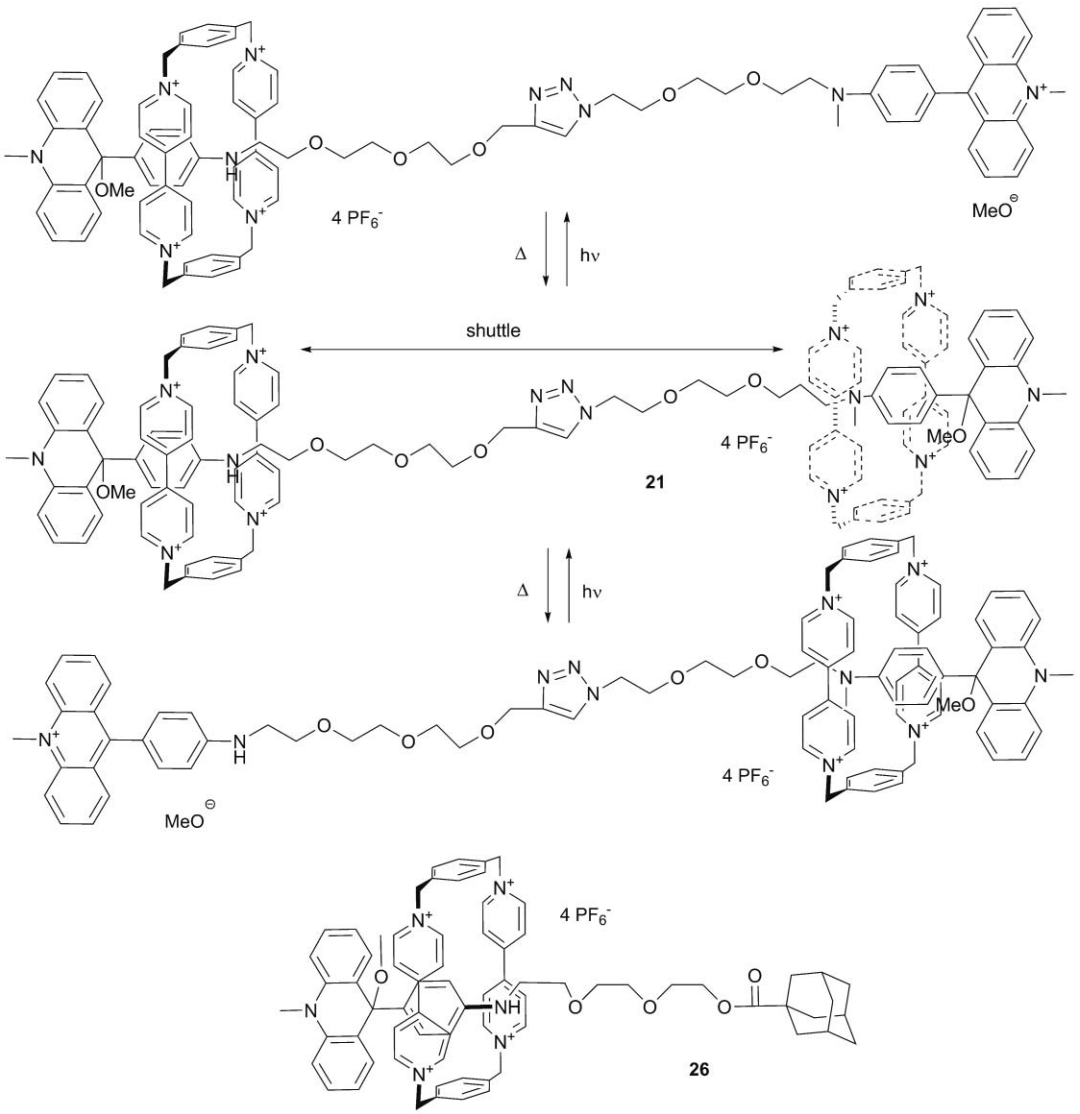
Scheme 9 Switching of rotaxane **12** by photons and rotaxane **25** for comparison.

solution was subjected to column chromatography (CC) (silica gel, acetonitrile (40 mL), ethylacetate (20 mL), cyclohexane (10 mL) and NH_4PF_6 (0.7 g). The yellow fractions were collected and evaporated to give a mixture of **3** and **4**. The two rotaxanes were separated by preparative TLC (silica gel, acetonitrile (40 mL), ethylacetate (20 mL), cyclohexane (10 mL) and NH_4PF_6 (0.4 g) affording **3** (R_f 0.63, 0.115 g, 9%), m.p. 168 °C and **4** (R_f 0.46–0.34, 0.059 g, 3%), m.p. 214 °C as orange solids after washing with water.

Rotaxane **3**, ^{1}H NMR (400 MHz, CD_3CN, TMS) (^{13}C, 100 MHz): δ = 1.83 (30) (m, 2 H; CH_2), 2.0 (30) (m, 2 H; CH_2), 2.3 (30) (m, 2 H; CH_2), 2.5 (29) (m, 2 H; CH_2), 2.9 (112) (s br, 2 H; Ar), 3.0 (112) (s br, 2 H; Ar), 3.1 (67) (s br, 2 H; ethyleneoxy), 3.5 (68) (s br, 2 H; ethyleneoxy), 3.8–3.9 (67.4–71.06) (m br, 10 H; ethyleneoxy), 3.96 (69.7) (s br, 4 H; ethyleneoxy), 4.02 (69.8) (s br, 2 H; ethyleneoxy), 4.16 (64.2) (t, J = 9 Hz, 2 H; CH_2OC=O), 4.3 (65.0) (s br, 4 H; ethyleneoxy), 4.5 (127), 4.6 (128) (s br, 2 H; Ar), 4.79 (s, 6 H; N$^+$Me), 5.77 (65) (m, 8 H; CBQT^{4+}), 6.95 (115) (d, J = 8 Hz, 1 H; aryl), 7.1 (115) (d br, 2 H; aryl), 7.39 (132.2) (d, J = 8 Hz, 2 H; aryl); 7.4 (132) (d, J = 8 Hz, 1 H; aryl), 7.25 (115) (d, J = 8 Hz, 1 H; aryl), 7.3 (132) (d br, 1 H; aryl), 7.82–7.85 (128, 131) (m, 11 H; acridinium, H-2,7, CBQT^{4+}); 7.94 (126.8) (d, J = 7 Hz, 8 H; CBQT^{4+}), 8.07 (130.4) (d, J = 9 Hz, 2 H; acridinium, H-1,8); 8.12 (130) (d, J = 9 Hz, 1 H; acridinium, H-1) 8.35 (138.7) ((m, 4 H; acridinium, H-3,6); 8.57 (118.7) (d, J = 8 Hz, 4 H; acridinium, H-4,5); 8.93 (145.0) (d, J = 7 Hz, 8 H; CBQT^{4+}); HRMS (ESI): m/z: found: 685.2240; calcd for [M – $3PF_6^-$] $[C_{106}H_{104}F_{18}N_6O_{10}P_3]^{3+}$: 685.2241; found: 477.6771; calcd for [M – $4PF_6^-$] $[C_{106}H_{104}F_{12}N_6O_{10}P_2]^{4+}$: 477.6769; found: 353.1484; calcd for [M – $5PF_6^-$] $[C_{106}H_{104}F_6N_6O_{10}P]^{5+}$: 353.1486; found: 270.1293; calcd for [M – $6PF_6^-$] $[C_{106}H_{104}N_6O_{10}]^{6+}$; 270.1297.

Rotaxane **4**: ^{1}H NMR (400 MHz, CD_3CN, TMS) (^{13}C, 100 MHz): δ = 1.8 (29.8) (m, 2 H; CH_2), 2.0 (28.6) (m, 2 H; CH_2), 2.45 (33.0) (t, J = 8 Hz, 2 H; CH_2), 2.73 (28.2) (t, J = 8 Hz, 2 H; CH_2), 2.9 (66.8) (s,br, 2H; ethyleneoxy) 2.95 (111.6) (d, J = 8 Hz, 2 H; Ar), 3.05 (111.8) (d, J = 8 Hz, 2 H; Ar), 3.1 (66.8) (s br, 2 H; ethyleneoxy), 3.75 (69.2) (m br, 4 H; ethyleneoxy), 3.89–4.05 (68, 70) (m br, 12 H; ethyleneoxy), 4.3 (70.6) (s br; 4 H; ethyleneoxy), 4.34 (64.5) (t, J = 7 Hz, 2 H; CH_2OC=O), 4.61 (128.1) (d, J = 9 Hz, 2 H; Ar), 4.8 (38.6, 128.1) (m, 8 H; NMe, Ar), 5.76 (64.9) (m, 16 H; CBQT^{4+}), 7.0 (114.8) (m, 4 H; aryl), 7.37 (132.0) (m, 4 H; aryl), 7.86, 7.87 (130.9, 131.0) (ds, 16 H; CBQT^{4+}), 7.8 (130.4) (m, 4 H; acridinium, H-2,7), 7.95–7.99 (126.6) (m, 20 H; acridinium, H-1,8, CBQT^{4+}), 8.35 (138.1) ((m, 4 H; acridinium, H-3,6); 8.55 (118.7) (d, J = 9 Hz, 4 H; acridinium, H-4,5), 8.95 (145.0) (m, 16 H; CBQT^{4+}); HRMS (ESI): m/z: found: 1051.9301; calcd for [M – $3PF_6^-$] $[C_{142}H_{136}F_{42}N_{10}O_{10}P_7]^{3+}$: 1051.9306; found: 752.7045; calcd for [M – $4PF_6^-$] $[C_{142}H_{136}F_{36}N_{10}O_{10}P_6]^{4+}$: 752.7036; found: 573.1709; calcd for [M – $5PF_6^-$] $[C_{142}H_{136}F_{30}N_{10}O_{10}P_5]^{5+}$: 573.1699; found: 453.4821; calcd for [M – $6PF_6^-$] $[C_{142}H_{136}F_{24}N_{10}O_{10}P_4]^{6+}$: 453.4829; found 367.9898; calcd for [M – $7PF_6^-$] $[C_{142}H_{136}F_{18}N_{10}O_{10}P_3]^{7+}$: 367.9904; found 303.8706; calcd for [M – $8PF_6^-$] $[C_{142}H_{136}F_{12}N_{10}O_{10}P_2]^{8+}$: 303.8710.

10-methyl-9-(4-(2-(2-(2-(4-(3-(3-(4-(2-(2-(2-(4-(10-methylacridinium-9-yl)phenoxy)ethoxy)ethoxy)ethoxy)phenyl)propanoyloxy)propyl)phenoxy)ethoxy)ethoxy)ethoxy)-phenyl)acridinium hexafluorophosphate (**5**). The collected dichloromethane solutions obtained during the procedure to isolate rotaxanes 3 and 4 contained the molecular axle 5. The solvent was removed and the residue was purified by CC (silica gel, acetone (400 mL)/cyclohexane (40 mL)/NH_4PF_6 (0.5 g). The yellow fractions were collected and the solvent was removed



Scheme 10 Switching of rotaxane **21** by photons and rotaxane **26** for comparison.

in vacuo. The residue was treated with water (30 mL) and dichloromethane (30 mL). The organic phase was separated and the aqueous phase was extracted with dichloromethane (2 × 30 mL). The combined organic phases were dried ($MgSO_4$). The solvent was evaporated to give 5 as an orange solid (0.232 g, 34%).

^{1}H NMR (400 MHz, CD_3CN, TMS) (^{13}C, 100 MHz): δ = 1.8 (31.9) (m, 2 H; CH2), 2.5–2.55 (29.9, 35.9) (m, 4 H; CH2), 2.77 (29.8) (t, J = 7 Hz, 2 H; CH_2), 3.68–3.70 (70.4, 70.5) (m, 8 H; ethyleneoxy), 3.78 (69.4) (t, J = 5 Hz, 4 H; ethyleneoxy); 3.89 (69.2) (t, J = 5 Hz, 4 H; ethyleneoxy), 4.02 (60.0) (m, 2 H; CH_2OC=O), 4.06 (&(: = 9 (T, J = 5 Hz, 4 H; ethyleneoxy), 4.28 (67.4) (t, J = 5 Hz, 4 H; ethyleneoxy), 4.7 (38.7) (s, 6 H; NMe), 6.8 (114.3) (d, J = 9 Hz, 4 H; aryl), 7.07 (132.0) (d, J = 9 Hz, 4 H; aryl), 7.26 (114.9) (d, J = 9 Hz, 4 H; Ar), 7.44 (130.4) (d J = 9 Hz, 4 H; Ar), 7.82 (130.6) (m, 4 H; acridinium, H-2,7); 8.11 (127.6) (d, J = 8 Hz, 4 H; acridinium, H-1,8), 8.37 (138.5) (m, 4 H; acridinium, H-3,6), 8.58 (d, J = 9 Hz, 4 H; acridinium, H-4,5); HRMS (ESI): m/z: found: 550.2585; calcd for $[M - 2PF_6^-]$ $[C_{70}H_{72}N_2O_{10}]^{2+}$: 550.2588.

Rotaxane 6

$NaHCO_3$ (0.2 g) was added to the acridinium rotaxane **3** (0.05 g, 0.020 mmol) dissolved in acetonitrile (5 mL) followed by addition of methanol (0.1 mL). The suspension was stirred for 36 h. $NaHCO_3$ was filtered off. The dark brown solution was evaporated. The remaining oily solid was extracted with chloroform (3 × 5 mL). The remaining solid (0.040 g, 89%) was used without further purification.^{1}H-NMR (400 MHz, acetone-d_6) (^{13}C 100 MHz): δ = 1.8 (30.6) (s br, 2 H; CH_2), 2.4 (110.0) (s br, 2 H; Ar), 2.5 (30) (s br, 2 H; CH_2), 2.6 (30) (s br, 2 H; CH_2), 2.8 (30.2) (s br, 2 H; CH_2), 3.0 (66.7) (s, br, 2 H; ethyleneoxy), 3.40 (52) (s, 6 H; CH_3, OMe), 3.5–3.7 (66.2, 69.3, 70.0, 70.3) (m br, 14 H; ethyleneoxy), 3.9 (32.8, 69.8) (m, 8 H; ethyleneoxy, NMe), 3.95 (69.8) (s br, 2 H; OCH_2), 4.02 (70.4) (s br, 2 H; CH_2OC=O), 4.2 (69.8) (s br 2 H; OCH_2), 4.66 (127.7) (s br, 2 H; Ar), 6.0 (64, 113.6) (m br, 10 H; $CBQT^{4+}$, Ar), 6.8 (129.8) (s br, 2 H; Ar), 7.4–7.7 (m br, 18 H; acridane, $CBQT^{4+}$), 8.5 (126,9) (s br, 4 H; $CBQT^{4+}$), 8.6 (126.4)

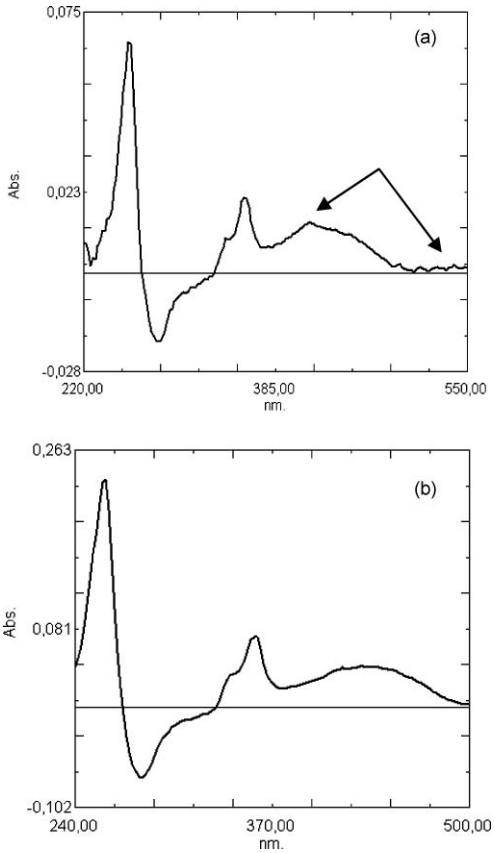


Fig. 2 Transient absorbance monitored with the [3]rotaxane **7** (3×10^{-5} M, arrows denote the increased absorption by the radical ion) (a) and the [2]rotaxane **6** (3×10^{-5} M) in methanol solution (b).

(s br, 2 H; $CBQT^{4+}$), 9.1 (143.7) (s br, 2 H; $CBQT^{4+}$), 9.4 (144.3) (s br, 2 H; $CBQT^{4+}$), 9.6 (144.7) (s br, 4 H; $CBQT^{4+}$. ^{1}H-NMR (400 MHz, CD_3OD/CD_3CN 2 : 1, 243 K) (^{13}C 100 MHz): $\delta = 1.8$ (31.2) (s br, 2 H; CH_2), 2.1 (111) (s, br, 2 H; Ar), 2.5 (31.4) (s br, 2 H; CH_2), 2.6 (37) (s br, 2 H; CH_2), 2.8 (30.1) (s br, 2 H; CH_2), 2.7(68) (s br, 2 H; ethyleneoxy), 3.4 (34) (s, 3 H; NMe), 3.5–3.8 (34, 70) (m br, 25 H; ethyleneoxy, NMe), 4.4 (129) (s br, 2 H; Ar), 5.6 (65) (m br, 8 H; $CBQT^{4+}$), 5.9 (114) (s br, 2 H; Ar), 6.7 (127) (s br, 2 H; Ar), 6.9 (121, 126.8) (s br, 6 H; $CBQT^{4+}$, acridane, H-2,7), 7.0 (114) (s br, 4 H; acridane, H-4,5), 7.2 (129) (s br, 4 H; acridane, H-3,6), 7.6 (130) (s br, 4H; acridane, H-1,8), 8.1 (128) (s br, 2 H; $CBQT^{4+}$), 8.3 (127.0) (s br, 4 H; $CBQT^{4+}$), 8.5 (144) (s br, 4 H; $CBQT^{4+}$), 8.9 (145) s br, 4 H; $CBQT^{4+}$). ^{1}H-NMR (400 MHz, aceton-d_6, 233 K) (^{13}C 100 MHz): $\delta = 1.8$ (30.6) (s br, 2 H; CH_2, 2.4 (110) (s, br, 2 H; Ar), 2.5 (30) (s br, 2 H; CH_2), 2.6 (30) (s br, 2 H; CH_2), 2.8 (30.2) (s br, 2 H; CH_2), 3.0 (66.7) (s br, 2 H; ethyleneoxy), 3.4 (52) (s, 6 H; OMe), 3.5–3.8 (66) (m br, 16 H; ethyleneoxy), 3.9 (32.8, 69.8) (m, 8 H; ethyleneoxy, NMe), 3.95 (69.8) (m, 2 H; ethyleneoxy), 4.02 (70.4) (s br, 2 H; $CH_2OC{=}O$), 4.2 (69.8) (m, 2 H; ethyleneoxy), 4.7 (127.7) (s br, 2 H; Ar), 5.98 (65, 113.6) (m br, 10 H; CBQT4+, Ar), 6.7 (114) (s br, 2 H; Ar), 6.8 (129.8) (s br, 4 H; Ar), 6.9 (121, 126.8) (s br, 6 H; $CBQT^{4+}$, acridane, H-2,7), 7.0 (114) (s br, 4 H; acridane, H-4,5), 7.1 (114) (s br, 2 H; Ar), 7.2 (129) (s br, 4 H; acridane, H-3,6), 7.3 (131) (s br, 2 H; Ar), 7.6 (130) (s br, 4H; acridane, H-1,8), 8.0–8.2 (130.4) (s br, 8 H; $CBQT^{4+}$), 8.5 (126.9) (s br, 2 H; $CBQT^{4+}$), 8.6 (126.4) (s br, 4 H; $CBQT^{4+}$), 9.1 (143.7) (s br, 2 H; $CBQT^{4+}$), 9.4 (144.3) s br, 2 H; $CBQT^{4+}$), 9.6 (144.7) (s br, 4 H; $CBQT^{4+}$); HRMS (ESI): *m/z*: found 986.3737 calcd. for (M – $2PF_6^-$), $[C_{108}H_{110}F_{12}N_6O_{12}P_2]^{2+}$: 986.3727; found 609.2610; calcd. for (M – $3PF_6^-$), $[C_{108}H_{110}F_6N_6O_{12}P]^{3+}$: 609.2602; found 420.7046 calcd. for (M – $4PF_6^-$), $[C_{108}H_{110}N_6O_{12}]^{4+}$): 420.7040.

Rotaxane 7

$NaHCO_3$ (0.2 g) was added to the acridinium rotaxane **4** (0.05 g, 0.014 mmol) dissolved in acetonitrile (5 mL) followed by addition of methanol (0.1 mL). The suspension was stirred for 36 h. $NaHCO_3$ was filtered off. The dark brown solution was evaporated. The remaining oily solid was extracted with chloroform (3×5 mL). The remaining solid (0.042 g, 89%) was used without further purification.^{1}H NMR (400 MHz, CD_3CN, TMS) (^{13}C, 100 MHz): $\delta = 1.9$ (29.5) (s br, 2 H; CH_2), 2.5 (38) (s br, 2 H; CH_2), 2.6 (35.7) (s br, 2 H; CH_2), 2.8 (30.9) (s br, 2 H; CH_2), 2.9 (67.2) (s, br, 2 H; ethyleneoxy), 3.30 (52.2) (s, 6 H; CH_3, OMe), 3.5–3.8 (m br, 14 H; ethyleneoxy), 4.13 (64.0) (s br, 2 H; $CH_2OC{=}O$), 9.1 (144.3) (s br, 16 H; $CBQT^{4+}$); HRMS (ESI): found 975.9666 calcd. for (M – $3PF_6^-$), $[C_{144}H_{142}F_{30}N_{10}O_{12}P_5]^{3+}$: 975.9667; found 695.7339; calcd. for (M – $4PF_6^-$), $[C_{144}H_{142}F_{24}N_{10}O_{12}P_4]^{4+}$: 695.7337; found 527.5944 calcd. for (M – $5PF_6^-$), $[C_{144}H_{142}N_{10}O_{12}P_3]^{5+}$): 527.5940.

Rotaxane 10

A solution of **8** (ESI†) (0.33 g, 0.69 mmol), **9** (ESI†) (0.41 g, 0.69 mmol) and **CBQT(PF$_6$)$_4$** [11] (0.76 g, 0.69 mmol) in dry DMF (2 mL) was stirred for 30 min under an argon atmosphere. A solution of $CuSO_4{\times}5H_2O$ (0.11 g, 0.41 mmol) and sodium ascorbate (0.14 g, 0.72 mmol) in water (0.8 mL) was added within 15 min.. The resulting suspension was stirred at room temperature for 2 days. The reaction mixture was evaporated *in vacuo* at 90 °C. The resulting residue was treated with MeCN (10 mL) and NH_4PF_6 (5% in MeCN). The precipitate was filtered and the filtrate was evaporated. The resulting oil was extracted with dichloromethane (3×10 mL) in order to dissolve compound **9**. The insoluble residue was treated with 8 mL of a solution of NH_4PF_6 (7 g) in MeCN (400 mL), ethyl acetate (200 mL) and cyclohexane (100 mL). Free **CBQT(PF$_6$)$_4$** was filtered off. The solution was chromatographed (NH_4PF_6 (7 g) in MeCN (400 mL)/ethylacetate (200 mL)/cyclohexane (100 mL). The yellow fractions were collected and the solvents were removed. The resulting yellow solid was washed with water and dried in vacuum to give **10** (0.13 g, 8%), m.p. 219 °C. UV-Vis (λ_{max}/nm (ε/$M^{-1}cm^{-1}$): 260 (138000), 359.5 (27600), 432 (13500). ^{1}H NMR (400 MHz, CD_3CN, TMS) (^{13}C, 100 MHz): $\delta = 2.58$ (62.7) (s, 2 H; OCH_2), 3.28–3.25 (m, 2 H; OCH_2), 3.55–3.52 (m, 2 H; OCH_2), 3.8 (50.4) (m, 2 H; NCH_2) 3.86–3.73 (m, 14 H; ethyleneoxy), 3.9 (67.9, 69.3) (m 4 H; ethyleneoxy), 4.06 (t, $J = 5$ Hz, 2 H, OCH_2), 4.66 (121.9) (s, 1H;, triazole), 4.80 (s, 6 H; N^+Me), 5.73 (s, 8 H; $CBQT^{4+}$), 6.83 (114.9) (d, $J = 8$ Hz, 2 H; aryl), 6.90 (114.8) (d, $J = 8$ Hz, 2 H; aryl), 7.35 (132.2) (d, $J = 8$ Hz, 4 H; aryl); 7.70 (s, 8 H; $CBQT^{4+}$); 7.88–7.82 (127.9) (m, 4 H; acridinium, H-2,7), 8.00 (130.4) (m, 4 H; acridinium, H-1,8); 8.08 (127.3) (d, $J = 7$ Hz, 8 H; $CBQT^{4+}$); 8.36 (138.8) (m, 4 H; acridinium, H-3,6); 8.56 (118.7) (d, $J = 8$ Hz, 4 H; acridinium, H-4,5); 8.92 (145.1) (d, $J = 7$ Hz, 8 H; $CBQT^{4+}$); HRMS (ESI): *m/z*: found: 999.7720; calcd for [M – $2PF_6^-$] $[C_{91}H_{89}F_{24}N_9O_7P_4]^{2+}$: 999.7721; found: 618.1945; calcd for [M – $3PF_6^-$] $[C_{91}H_{89}F_{18}N_9O_7P_3]^{3+}$: 618.1931; found: 427.4050 calcd

for [M – 4PF_6^-] [$C_{91}H_{89}F_{12}N_9O_7P_2$]$^{4+}$: 427.4037; found: 312.9308; calcd for [M – 5PF_6^-] [$C_{91}H_{89}F_6N_9O_7P$]$^{5+}$; 312.9300.

The dichloromethane solution containing the axle **11** was evaporated. The remaining residue was purified by column chromatography (NH_4PF_6 (7 g) in MeCN (400 mL)/ethylacetate (200 mL)/cyclohexane (100 mL) to give pure **11** (0.16 g, 47%) as an orange, resinous compound. ^{1}H NMR (400 MHz, CD_3CN, TMS) (^{13}C, 100 MHz): δ = 3.66–3.63 (m, 8 H; ethyleneoxy), 3.73–3.68 (m, 4 H; ethyleneoxy); 3.84 (69.1) (t, J = 5 Hz, 2 H; OCH_2), 3.92–3.89 (m, 4 H; ethyleneoxy), 4.28–4.24 (m, 4 H; ethyleneoxy), 4.62 (51.8) (t, J = 5 Hz, 2 H; NCH_2), 4.69 (62.6) (s, 2 H; OCH_2); 4.79 (s, 6 H; N+Me), 7.23, 7.25 (114.4) (m 4 H; aryl), 7.44, 7.45 (131.3) (dd, J = 9 Hz, 4 H; aryl), 7.84 (127.4) (m, 4 H; acridinium, H-2,7), 8.11 (130.0) (m, 4 H; acridinium, H-1,8), 8.35 (138.5) (m, 4 H; acridinium, H-3,6), 8.58 (d, J = 9 Hz, 4 H; acridinium, H-4,5); HRMS (ESI): m/z: found: 1044.3886; calcd for [M – PF_6^-] [$C_{55}H_{57}F_6N_5O_7P$]$^+$: 1044.3894; found: 449.7122; calcd for [M – 2PF_6^-] [$C_{55}H_{57}N_5O_7$]$^{2+}$: 449.7124.

Rotaxane 12

$NaHCO_3$ (0.2 g) was added to the acridinium rotaxane **10** (0.05 g, 0.022 mmol) dissolved in acetonitrile (5 mL) followed by addition of methanol (0.1 mL). The suspension was stirred for 36 h. $NaHCO_3$ was filtered off. The dark brown solution was evaporated. The remaining oily solid was extracted with chloroform (3 × 5 mL). The remaining solid (0.040 g, 89%) was used without further purification. UV-Vis (MeCN), λ/nm (ε/$M^{-1}cm^{-1}$): 262 (45000), 277 (sh); (38800), 331 (sh) 8100.^{1}H-NMR (400 MHz, MeOD/CD_3CN 3 : 1) (^{13}C 100 MHz): δ = 2.3 (110.8) (d, J(H,H) = 8.3 Hz, 4 H; Ar), 2.7 (67.4) (s, br, 4 H; ethyleneoxy), 3.40 (49.3) (s, 6 H; CH_3, methoxy), 3.5–3.8(33.2, 69.3,69.6,70.0, 70.3,70.4) (m, 24 H; NMe, ethyleneoxy), 4.1 (63.5) (s br, 2 H; OCH_2), 4.3 (50.4) (t, J(H,H) = 6.6 Hz, 2 H; NCH_2), 4.87 (128.0) (d, J(H,H) = 8.4 Hz, 4 H; Ar), 5.7 (64) (s br, 8 H; $CBQT^{4+}$), 7.3–7.9 (m br, 32 H; acridane, $CBQT^{4+}$), 9.0 (145) (s br, 8 H; $CBQT^{4+}$). ^{1}H-NMR (400 MHz, CD_3OD/CD_3CN 3 : 1, 233 K) (^{13}C 100 MHz): δ = 2.2 (s, br, 2 H; Ar), 2.8 (68) (s, br, 2 H; ethyleneoxy), 3.0 (70) (s br, 2 H; ethyleneoxy), 3.3–3.8 (32, 49, 70 (m br, 30 H; NMe, OMe, ethyleneoxy), 4.2 (s br, 2 H; OCH_2), 4.5 (50.0, 127.4) (s br, 4 H; NCH_2, Ar), 5.7 (64) (d br, 8 H; $CBQT^{4+}$), 6.7 (113.4) (s br, 2 H; Ar), 6.9 (120.4) (s br, 4 H; acridane, H-2,7), 7.1 (112.6, 113.4, 126) (s br, 6 H; Ar, acridane, H-4,5), 7.2 (128) (s br, 4 H; $CBQT^{4+}$) 7.3 (128) (s br, 4H; acridane, H-3,6), 7.5 (132) (s br, 4H; acridane, H-1,8), 7.7 (128) (s br, 8 H; $CBQT^{4+}$) 8.2 (127.7) (s br, 4H; $CBQT^{4+}$), 8.7 (145) (s br, 4 H; $CBQT^{4+}$), 9.0 (145) s br, 4 H; $CBQT^{4+}$); HRMS (ESI): m/z: found 885.8261 calcd. for (M – 2PF_6^-), [$C_{93}H_{95}F_{12}N_9O_9P_2$]$^{2+}$: 885.8268; found 542.2242; calcd. for (M – 3PF_6^-), [$C_{93}H_{95}F_6N_9O_9P$]$^{3+}$: 542.2230; found 370.4323 calcd. for (M – 4PF_6^-), [$C_{93}H_{95}N_9O_9$]$^{4+}$): 370.4313.

Rotaxane 14

A solution of **9** (0.188 g, 0.32 mmol), **13** (ESI†) (0.199 g, 0.32 mmol) and **CBQT(PF$_6$)$_4$** (0.352 g, 0.32 mmol) in dry DMF (2 mL) was stirred for 30 min under an argon atmosphere. A solution of $CuSO_4$×$5H_2O$ (0.047 g, 0.19 mmol) and sodium ascorbate (0.065 g, 0.33 mmol) in water (0.8 mL) was added within 15 min. The resulting suspension was stirred at room temperature for 2 days. The reaction mixture was evaporated *in vacuo* at 90 °C. The resulting residue was treated with MeCN (10 mL) and NH_4PF_6 (5% in MeCN). The precipitate was filtered and the filtrate was evaporated. The resulting oil was extracted with dichloromethane (3 × 10 mL) in order to dissolve compound **15**. The insoluble residue was treated with 8 mL of a solution of NH_4PF_6 (7 g) in MeCN (400 mL), ethyl acetate (200 mL), and cyclohexane (100 mL). Free **CBQT(PF$_6$)$_4$** was filtered off. The solution was chromatographed (NH_4PF_6 (7 g) in MeCN (400 mL)/ethylacetate (200 mL)/cyclohexane (100 mL). The yellow fractions were collected and the solvents were removed. The resulting yellow solid was washed with water and dried in vacuum to give **14** (0.035 g, 4%), m.p. 160 °C. ^{1}H NMR (400 MHz, CD_3CN, TMS) (^{13}C, 100 MHz): δ = 1.4 (30.3) (m, 2 H; CH_2), 1.7 (31) (m, 2 H; CH_2),3.61 (70.8) (t, J = 6 Hz; 2 H; OCH_2), 3.66 (111.6) (d, J = 9 Hz, 2 H; Ar), 3.72–3.76 (m, 12 H; ethyleneoxy), 3.9 (m 4 H; ethyleneoxy), 3.99 (127.9) (d, J = 9 Hz, 2 H; Ar), 4.12 (t, J = 5 Hz, 2 H; OCH_2), 4.20 (68.0) (t, J = 4 Hz, 2 H; ethyleneoxy), 4.27 (68.0) (t, J = 4 Hz, 2 H; ethyleneoxy), 4.59 (60) (s, 2 H; OCH_2), 4.80 (50.6, 39.0) (m, 8 H; NCH_2, N^+Me), 5.73 (m, 8 H; $CBQT^{4+}$), 7.19 (114.5) (d, J = 9 Hz, 2 H; aryl), 7.25 (114.5) (d, J = 9 Hz, 2 H; aryl), 7.45 (132.2) (m, 4 H; aryl), 7.70(131) (s, 8 H; $CBQT^{4+}$); 7.85 (127.8) (m, 4 H; acridinium, H-2,7), 7.95 (127.3) (d, J = 7 Hz, 8 H; $CBQT^{4+}$), 8.10 (130.2) (m, 4 H; acridinium, H-1,8), 8.21 (125.4) (s, 1 H; triazol), 8.36 (138.5) (m, 4 H; acridinium, H-3,6), 8.56 (118.4) (d, J = 10 Hz, 4 H; acridinium, H-4,5), 8.92 (145.1) (d, J = 7 Hz, 8 H; $CBQT^{4+}$); HRMS (ESI): m/z: found: 1066.8073; calcd for [M – 2PF_6^-] [$C_{100}H_{99}F_{24}N_9O_8P_4$]$^{2+}$: 1066.8086; found: 662.8846; calcd for [M – 3PF_6^-] [$C_{100}H_{99}F_{18}N_9O_8P_3$]$^{3+}$: 662.8842; found: 460.9224 calcd for [M – 4PF_6^-] [$C_{100}H_{99}F_{12}N_9O_8P_2$]$^{4+}$: 460.9220; found: 339.7449; calcd for [M – 5PF_6^-] [$C_{100}H9_{99}F_6N_9O_8P$]$^{5+}$; 339.7446.

The dichloromethane solution containing the axle **15** was evaporated. The remaining residue was purified by CC (NH_4PF_6 (0.5 g) in acetone (400 mL)/cyclohexane (40 mL). After evaporating the solvents the residue wetre treated with water (30 mL) and dichloromethane (30 mL). The aqueous phase was extracted with dichloromethane (2 × 30 mL) The combined organic phases were dried ($MgSO_4$). The solvent was evaporated *in vacuo* to give pure **15** (0.158 g, 41%) as an orange, resinous compound. ^{1}H NMR (400 MHz, CD_3CN, TMS) (^{13}C, 100 MHz): δ = 1.64 (31.6) (m, 2 H; CH_2), 2.44 (31.2) (t, J = 9 Hz, 2 H; CH_2), 3.34 (69.5) (t, J = 6 Hz, 2 H; OCH_2), 3.55–3.58 (m, 4 H; ethyleneoxy), 3.60–3.63 (m, 10 H; ethyleneoxy); 3.67–3.69 (m, 2 H; ethyleneoxy), 3.82 (70) (t, J = 5 Hz, 2 H; ethyleneoxy), 4.23 (68) (t, J = 5 Hz, 2 H; ethyleneoxy), 4.26 (68) (t, J = 5 Hz, 2 H; ethyleneoxy), 4.51 (50.3) (t, J = 5 Hz, 2 H; NCH_2), 4.80 (38.9) (s, 6 H; N^+Me), 4.95 (61.6) (s, 2 H; OCH_2), 6.77 (114.7) (d, J = 7 Hz, 2 H; Ar), 6.97 (127.9) (d, J = 7 Hz, 2 H; Ar), 7.2 (115.1) (m, 4 H; Ar), 7.4 (132.2) (m, 4 H; Ar), 7.79 (127.9) (m, 4 H; acridinium, H-2,7), 7.92 (125.4) (s, 1 H; triazol), 8.05 (127.9) (m, 4 H; acridinium, H-1,8), 8.33 (138.8) (m, 4 H; acridinium, H-3,6), 8.57 (m, 4 H; acridinium, H-4,5); HRMS (ESI): m/z: found: 516.7490; calcd for [M – 2PF_6^-] [$C_{64}H_{67}N_5O_8$]$^{2+}$: 516.7489.

Rotaxane 16

$NaHCO_3$ (0.2 g) was added to the acridinium rotaxane **10** (0.05 g, 0.022 mmol) dissolved in acetonitrile (5 mL) followed by addition of methanol (0.1 mL). The suspension was stirred

for 36 h. $NaHCO_3$ was filtered off. The dark brown solution was evaporated. The remaining oily solid was extracted with chloroform (3 × 5 mL). The remaining solid (0.039 g, 81%) was used without further purification. ^{1}H-NMR (400 MHz, MeOD/CD_3CN 1 : 1, 233 K) (^{13}C 100 MHz): δ = 1.7 (32.5) (s br, 2 H; CH_2), 2.2 (109.7) (s br, 2 H; Ar), 2,5 (30.8) (s br, 2 H; CH_2), 2.7 (67.4) (s br, 2 H; ethyleneoxy), 3.3 (51, 64) (s, 8 H; OCH_2, OMe), 3.4 (32.5) (s, 6 H; NMe), 3.5–3.8 (m br, 16 H; ethyleneoxy), 3.7 (74) (s br, 2 H; ethyleneoxy), 4.2 (67.4) (s br, 2 H; OCH_2), 4.4 (127.8) (s br, 2 H; Ar), 4.5 (48.7) (m, br, 2 H; NCH_2), 5.6–5.7 (64.1) (m br, 8 H; $CBQT^{4+}$), 6.7 (113.7) (d, J = 9 Hz, 2 H; aryl), 6.8 (120) (m, br, 4 H; acridane, H-2,7), 7.03 (d, J = 9 Hz, 2 H; aryl), 7.2–7.6 (m br, 20 H; acridane, $CBQT^{4+}$), 8.1 (127) (s br, 4 H; $CBQT^{4+}$), 8.3 (127) (s br, 4 H; $CBQT^{4+}$), 8.6 (144.3) (s br, 4 H; $CBQT^{4+}$), 8.9 (145.1) (s br, 4 H; $CBQT^{4+}$); HRMS (ESI): m/z: found 952.8625 calcd. for (M – $2PF_6^-$), $[C_{102}H_{105}F_{12}N_9O_{10}P_2]^{2+}$: 952.8629; found 586.9198; calcd. for (M – $3PF_6^-$), $[C_{102}H_{105}F_6N_9O_{10}P]^{3+}$: 586.9203; found 403.9497 calcd. for (M – $4PF_6^-$), $[C_{93}H_{95}N_9O_9]^{4+}$): 403.9491.

Rotaxane 19

A solution of **17** (ESI†) (0.35 g, 0.72 mmol), **18** (ESI†) (0.44 g, 0.72 mmol) and **CBQT(PF$_6$)$_4$** (0.79 g, 0.72 mmol) in dry DMF (2 mL) was stirred for 30 min under an argon atmosphere. A solution of $CuSO_4$×$5H_2O$ (0.10 g, 0.37 mmol) and sodium ascorbate (0.14 g, 0.72 mmol) in water (0.8 mL) was added within 15 min. The resulting suspension was stirred at room temperature for 2 days. The reaction mixture was evaporated *in vacuo* at 90 °C. The resulting residue was treated with MeCN (10 mL) and NH_4PF_6 (5% in MeCN). The precipitate was filtered and the filtrate was evaporated. The resulting oil was extracted with dichloromethane in order to dissolve compound **20**. The insoluble residue was treated with 8 mL of a solution of NH_4PF_6 (7 g) in MeCN (400 mL), ethyl acetate (200 mL), and cyclohexane (100 mL). Free **CBQT(PF$_6$)$_4$** was filtered off. The solution was chromatographed (NH_4PF_6 (7 g) in MeCN (400 mL)/ethylacetate (200 mL)/cyclohexane (100 mL). The violet fractions were collected and the solvents were removed. The resulting dark violet solid was washed with water and dried in vacuum to give **19** (0.295 g, 18%), m.p. 185 °C. UV-Vis (λ_{max}/nm (ε/$M^{-1}cm^{-1}$): 257.5 (180700), 343.5 (14400), 358.5 (27000), 412 (6000), 530 (16400); ^{1}H NMR (400 MHz, CD_3CN, TMS) (13C, 100 MHz): δ = 1.24 (43.3) (s, br, 2 H; $NHCH_2$), 3.03 (38.9) (s, br, 3 H; NMe), 3.5 (67.8) (m, 2 H; OCH_2), 3.5 (69.5) (m, 2 H; ethyleneoxy), 3.6 (51.8) (m, 2 H; $NMeCH_2$), 3.6–3.8 (70.3, 70.5) (m, 16 H; ethyleneoxy), 4.08 (109.3) (d, J = 9 Hz, 2 H; aryl), 4.21 (49.7) (t, J = 5 Hz, 2 H; NCH_2), 4.73 (38.6) (s, 3 H; N+Me), 4.82 (38.6) (s, 3 H; N+Me), 5.73 (64.9) (m, 8 H; $CBQT^{4+}$), 6.57(124.1) (s, 1 H; triazole), 6.67 (133.2) (d, J = 9 Hz, 2 H; aryl), 6.97 (111.4) (d, J = 8 Hz, 2 H; aryl), 7.37 (133.2) (d, J = 8 Hz, 4 H; aryl), 7.73 (131.1) (s, 8 H; $CBQT^{4+}$), 7.80 (127.9) (m, 2 H, acridinium, H-2,7), 7.85 (130.4) (d, J = 9 Hz, 2 H; acridinium, H-1,8), 8.07 (127.3) (d, J = 7 Hz, 8 H; $CBQT^{4+}$); 8.1 (127.9) (m, 2 H; acridinium, H-2,7), 8.20 (130.4) (d, J = 9 Hz, 2 H; acridinium, H-1,8), 8.31 (138.8) (m, 2 H; acridinium, H-3,6), 8.44 (138.8) (m, 2 H; acridinium, H-3,6), 8.51 (118.7) (d, J = 9 Hz, 2 H; acridinium, H-4,5), 8.62 (118.9) (d, J = 9 Hz, 2 H; acridinium, H-4,5), 8.94 (145.5) (d, J = 7 Hz, 8 H; $CBQT^{4+}$); HRMS (ESI): m/z: found: 1005.7961; calcd for [M – $2PF_6^-$] $[C_{92}H_{93}F_{24}N_{11}O_5P_4]^{2+}$: 1005.7959; found: 622.2094; calcd for [M – $3PF_6^-$] $[C_{92}H_{93}F_{18}N_{11}O_5P_3]^{3+}$: 622.2090;); found: 430.4160 calcd for [M – $4PF_6^-$] $[C_{92}H_{93}F_{12}N_{11}O_5P_2]^{4+}$: 430.4156.

The dichloromethane solution containing the free axle was evaporated. The remaining residue was purified by column chromatography (NH_4PF_6 (7 g) in MeCN (400 mL)/ethylacetate (200 mL)/cyclohexane (100 mL) to give pure **20** (0.15 g, 19%) as an orange, resinous compound. ^{1}H NMR (400 MHz, CD_3CN, TMS) (^{13}C 100 MHz): δ = 3.1 (38.6) (s, 3 H; NMe), 3.36 (43.2) (t, J(H,H) = 5.5 Hz, 2 H; NH–CH_2), 3.5–3.7 (68.4, 69.1, 69.3, 69.6, 70.2, 70.3, 70.4) (m, 16 H; ethyleneoxy), 3.85 (t, J(H,H) = 5.3 Hz, 2 H; OCH_2), 4.47 (50.1) (t, J(H,H) = 5.0 Hz, 2 H; NCH_2), 4.58 (63.9) (s, 2 H; OCH2), 4.71, 4.72 (38.8) (ds, 6 H; N^+Me), 6.92 (112.2) (d, J(H,H) = 8.5 Hz, 2 H; Ar), 7.02 (111.7) (d, J(H,H) = 8.8 Hz, 2 H; Ar), 7.29 (132.8) (d, J(H,H) = 8.7 Hz, 2 H; Ar), 7.36 (132.8) (d, J(H,H) = 9.0 Hz, 2 H; Ar), 7.8 (127.2) (m, 4H; acridinium, H-2,7), 8.21 (130.9) (d, J(H,H) = 8.7 Hz, 2 H; acridinium, H-1,8), 8.28 (m, 2 H; acridinium, H-3,6), 8.49 (d, J(H,H) = 9.3 Hz, 2 H; acridinium, H-4,5); HRMS (ESI): m/z: found 1056.4355; calcd for [M – PF_6^-] $[C_{56}H_{61}F_6O_5N_7P]^+$: 1056.4371;]; found 455.7365; calcd for [M – $2PF_6^-$] $[C_{56}H_{61}O_5N_7]^{2+}$: 455.7362.

Rotaxane 21

$NaHCO_3$ (0.2 g) was added to the acridinium rotaxane **19** (0.150 g, 0.065 mmol) dissolved in acetonitrile (5 mL) under addition of methanol (0.1 mL). The suspension was stirred for 36 h. $NaHCO_3$ was filtered off. The dark blue solution was evaporated. The remaining oily solid was extracted with chloroform (3 × 5 mL). The remaining solid (0.130 g, 96%) was used without further purification. UV-Vis (λ_{max}/nm (ε/$M^{-1}cm^{-1}$): 265 (68900); ^{1}H-NMR (400 MHz, MeOD/CD_3CN 2 : 1) (^{13}C 100 MHz): δ = 1.9 (108.2) (s br, 2 H; Ar), 2.0 (43.9) (s br, 2 H; NCH_2), 2.7 (38.2) (s, 3 H; NMe), 3.2 (48.8) (s, 3 H; OMe), 3.3 (52.3) (s, 3 H; OMe), 3.6–3.8 (32.5, 70.0) (m, 24 H; NMe, ethyleneoxy), 4.1 (63.0) (s, 2 H; OCH_2), 4.3 (49.9) (t, J(H,H) = 5.1 Hz, 2 H; NCH_2), 4.4 (49.9) (m, 2 H; NCH_2), 4.45 (128.5) (s, br, 2 H; Ar), 5.7 (63.7) (s br, 8 H; $CBQT^{4+}$), 6.5 (111) (s br, 2 H, Ar), 6.8 (120.0) (s br, 4 H; acridane, H-2,7), 7.1–7.4 (113, 128.7, 128.9) (m br, 12 H; acridane) 7.6 (127, 130) (s br 16 H; $CBQT^{4+}$), 8.7 (s br, 8 H; $CBQT^{4+}$). HRMS (ESI): m/z: found 948.8233; calcd. for (M – MeO^- – PF_6^-), $[C_{93}H_{96}F_{18}N_{11}O_6P_3]^{2+}$: 948.8235; found 891.8501; calcd for [M–2 PF_6^-], $[C_{94}H_{99}F_{12}N_{11}O_7P_2]^2$: 891.8501; found 584.2276; calcd for [M – MeO^- – $2PF_6^-$], $[C_{93}H_{96}F_{12}N_{11}O_6P_2]^{3+}$:584.2276; found 546.2464; calcd for [M – $3PF_6^-$], $[C_{94}H_{99}F_6N_{11}O_7P]^{3+}$: 546.2451; found 401.9294 calcd for [M – MeO^- – $3PF_6^-$] $[C_{93}H_{96}F_6N_{11}O_6P]^{4+}$: 401.9297.

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