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Pseudorotaxanes and rotaxanes from macrocyclic rings incorporating acridinone, 9-phenylacridinium and 9-phenyl-9-methoxy-acridane moieties

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Abstract

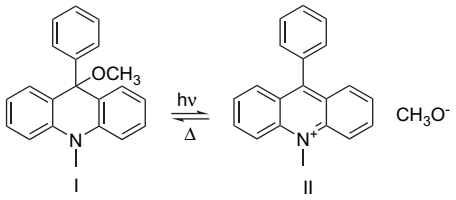
Two novel crown ethers incorporating the acridinone and the 9-phenyl-9-methoxy-acridane unit were used to form pseudorotaxanes with the 1,2-bis(4,4′dipyridinium)ethane axle, which are stoppered by the alkylative method to form rotaxanes. The pseudorotaxane formed from the acridane-containing crown was photochemically converted to the corresponding acridinium methoxide thereby releasing the guest. The acridane-containing rotaxane could not be isolated because the preparation conditions formed the acridinium salt.

Keywords: Pseudorotaxane; Acridane; Acridinium; Photochemistry

1. Introduction

Control over the relative position and motions of components in pseudorotaxanes supramolecules may impart machine-like properties on this supramolecules. Many examples of threading and unthreading of a [2]pseudorotaxane have been developed over the last few years.[1] Pseudorotaxanes based on 1,2-bis(4,4′dipyridinium)ethane as the axle and a dibenzo-24-crown-8 (**DB24C8**) as the wheel have been previously reported.[2] The interaction between these two components occurs by ion–dipole attraction between the pyridinium–N and the oxygen atoms of the crown ether, by hydrogen bonds between the α-N^+ hydrogen atoms and the oxygen atoms of the crown ether, and by π-stacking between the electron-poor pyridinium rings of the axle and the electron-rich catechol subunits of the wheel. Recently, a switchable pseudorotaxane was presented, which controls threading electronically by switching on/off the intramolecular charge transfer by addition of acid and base.[3] Photochemical switching of such pseudorotaxanes offers the advantage of generating no waste products during the switch cycles. To initiate the switching cycle, the interaction between wheel and axle must be changed by a suitable photoreaction. The conversion of an electron donor into an electron acceptor by photochemical means should allow interaction changes comparable to those performed by protonation/deprotonation. Therefore, we proposed to introduce the 9-alkoxy-9-phenyl-dihydroacridine (acridane) moiety into the catechol unit of the **DB24C8** crown ether.

9-Alkoxy-acridanes of the type **I** are known to yield the acridinium alkoxide **II** by photoexcitation. The reset of the system occurs thermally by the attack of the alkoxide ion on the acridinium ion (Scheme 1).[4–6]



Scheme 1. The structure of 9-alkoxy-acridane (**I**) and its corresponding acridinium alkoxide (**II**).

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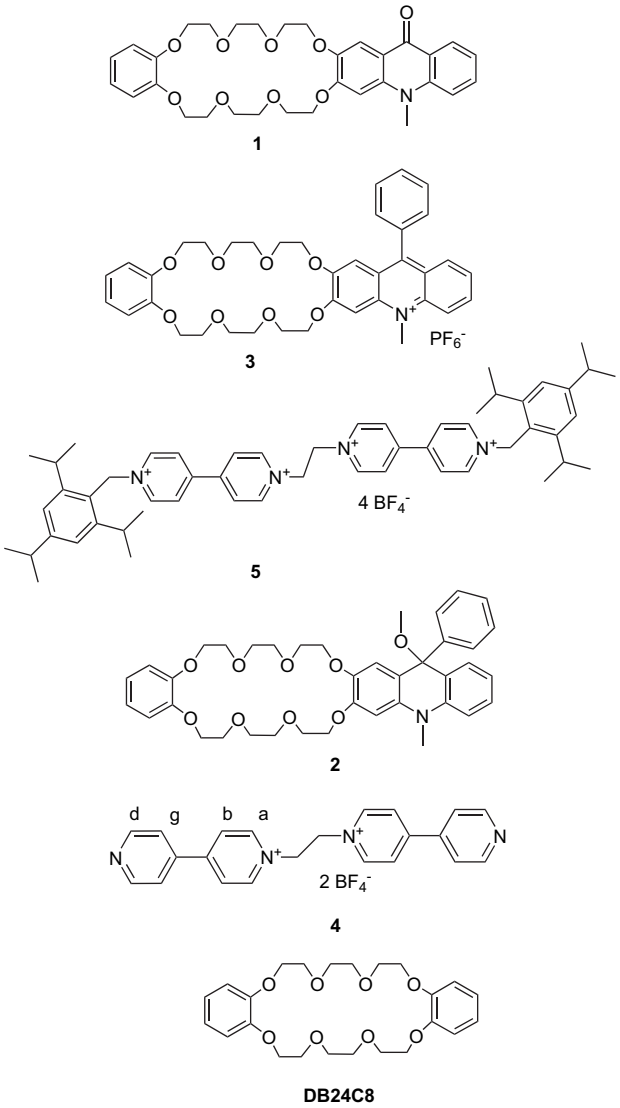
Here we report the complexation of modified crown ethers with the bipyridinium axle, the photochemically induced dethreading of a pseudorotaxane, and the synthesis of a novel rotaxane containing the acridinium moiety within the crown ether.

2. Results and discussion

2.1. Pseudorotaxanes

Recently, we described the preparation of macrocycles incorporating the acridane moiety.[7] From this study, crown ethers **1**–**3** were selected in order to investigate the complexation behavior with the short molecular thread **4** used as a component of the pseudorotaxanes (Scheme 2).[2]

The question arises as to whether the complexation of **4** is influenced by replacing one catechol unit in **DB24C8** by the dihydroacridinone (**1**) and the acridane unit (**2**). The guest **4** is arranged in between the two catechol units in the pseudorotaxane formed with **DB24C8**.[8] Therefore, the complex strength would be governed by both of the ring systems attached to the oxyethylene bridges.



Scheme 2. Compounds used as wheels and axles.

The complexation can easily be monitored with ^{1}H NMR spectroscopy because there is a slow exchange on the NMR time scale. The appearance of two signal sets indicates complex formation; the binding constant can be determined by integration of suitable proton resonances of free and complexed components of the pseudorotaxanes. We studied the complexation of **4** with the hosts **DB24C8**, **1**, and **2** in nitromethane[D_3] solution and determined association constants of 650, 1800 and 160 M^{-1}, respectively, using the single point method. Even in polar solvents, the influence of ion pairs cannot be completely excluded.[9] However, since the same concentration of the guest **4** was used in the complexation studies the order of the obtained association constants should not be corrupted by ion pairs formed by **4**. From these data we drew two conclusions. First, the larger π-system of the dihydroacridinone (host **1** vs **DB24C8**) contributes to a stronger complexation. An X-ray crystal structure determination verified the sandwich-like arrangement of the aryl groups (see the ORTEP diagram, Fig. 1). The arrangement of the guest within the host **1** corresponds to that of the complex **DB24C8** with **4**.[8]

The pseudorotaxane formed in solution is characterized by the highfield shift of the resonances of the β-, γ-, and δ-protons (with respect to N^+) of the pyridinium units of compound **4**. The resonances of the α-proton and the N^+–CH_2 proton form hydrogen bonds to the oxygen atoms of the crown ether and are, therefore, downfield shifted. Similar behavior was observed in the pseudorotaxane **4/DB24C8**.[8]

Secondly, the acridane-containing host **2** binds the guest **4**. However, the complexation constant is diminished compared with host **1**, most probably due to steric interference. Unfortunately, we were not able to get suitable crystals to determine the structure of the complex. However, the shifts of the proton signals in the ^{1}H NMR spectra of the pseudorotaxane **2/4** observed in nitromethane[D_3] solution (Fig. 3) correspond to

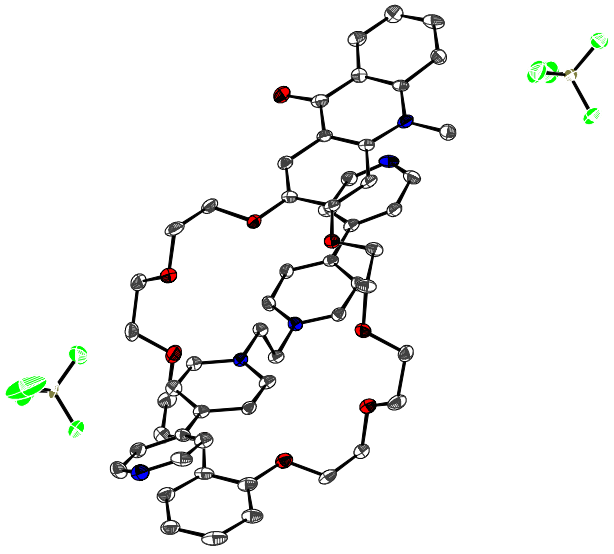


Figure 1. Crystal structure of the pseudorotaxane **1/4**; the distance between the dihydroacridinone and the pyridinium moieties is 3.75 Å. Hydrogen atoms and crystal water are omitted for clarity.

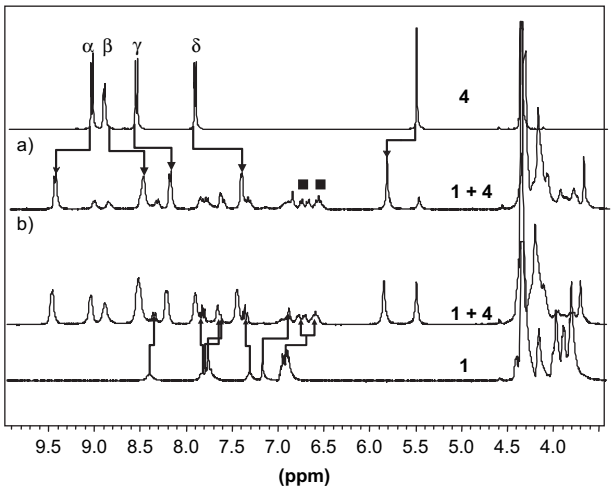


Figure 2. ^{1}H NMR spectra of the pseudorotaxane **1/4** (a) **1**: 7.4×10^{-3} M; **4**: 6.7×10^{-3} M and (b) **1**: 7.0×10^{-3} M; **4**: 1.2×10^{-2} M and its components in nitromethane[D_3] solution. The association constants obtained by the single point method using the signals of the α-proton and of the protons of the ethane bridge are: (a) 1700 M^{-1} and (b) 1900 M^{-1}.

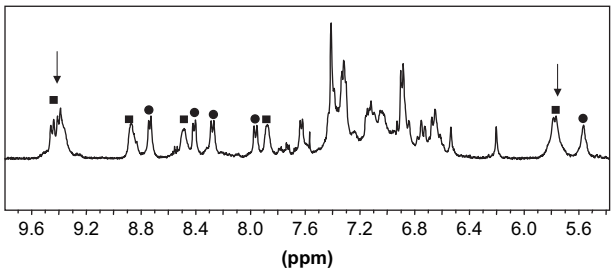


Figure 3. Part of the ^{1}H NMR spectrum of the pseudorotaxane **2/4** in nitromethane[D_3] solution (10^{-2} M). Marks denote the free (circle) and the complexed (square) components. Arrows denote peak splitting due to asymmetry of the crown ether.

those of the complex **1/4** (Fig. 2). Significant downfield shifts (ppm) for α (0.3) and N^+-CH_2 (0.3) protons are indicative of C–H···O hydrogen bonds to crown ether O-atoms. Upfield shifts observed for the β (0.3), γ (0.3), δ (0.4), and crown aromatic protons indicate π-stacking between the aromatic units of the macrocycle and the pyridinium protons of the axle **4**. Due to the asymmetry of the crown ether, the α-proton and N^+-CH_2 proton signals are split (arrows in Fig. 3).

In contrast, the crown **3** containing the acridinium subunit does not interact with the cationic guest **4**. The proton resonances of **4** were not shifted in the presence of **3**. Thus, the prerequisite for a photoswitchable pseudorotaxane was attained.

2.2. Photoreaction

The macrocycle **2** with the acridane subunit underwent a photoreaction upon excitation with 300 nm light to form the corresponding acridinium containing macrocycle **3** both in acetonitrile and alcoholic solutions. The thermal recovery of the acridane compound is slow in acetonitrile solution. The back reaction in alcoholic solution was accomplished within 2 h to give the acridane with the alkoxy group of the alcohol used as solvent, e.g., the methoxy leaving group is

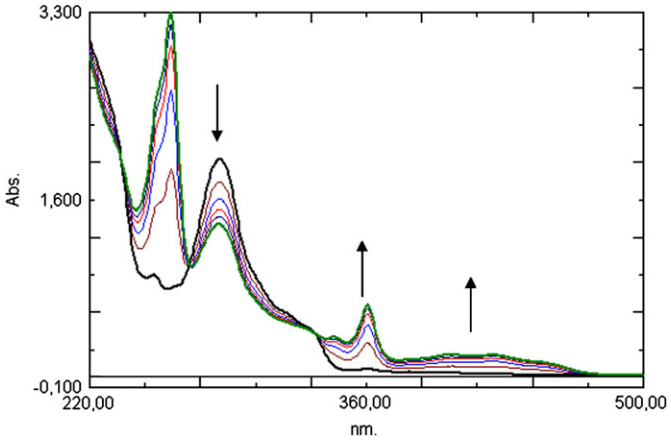


Figure 4. UV–vis spectra of compound **2** in methanol solution (6.8×10^{-5} M) recorded after consecutive irradiations (λ_{exc}=313 nm) for 0, 3, 5, 9, 15, 18 min.

replaced by the propoxy group in *n*-propanol solution. The switching cycle could be repeated several times without decay of the systems. The individual photoreactions and thermal reactions could be followed by UV–vis spectroscopy (see Fig. 4) because the longest wavelength absorption maximum of the acridinium compounds is around 440 nm while that of the acridanes is around 310 nm. Because of the thermal back reaction, the photoreaction results in the formation of the acridinium compound until the equilibrium with the back reaction has become established.

According to the photoreaction in diluted solutions, irradiation of compound **2** on a preparative scale also yields the acridinium methanolate. Therefore, the irradiation of the pseudorotaxane **2/4** is expected to result in the release of the compound **4**. Indeed, the ^{1}H NMR spectra revealed the release of **4** upon irradiation followed by the uptake of **4** during the thermal back reaction of the formed acridinium compound **3** with the methoxide counter ion (see Fig. 5).

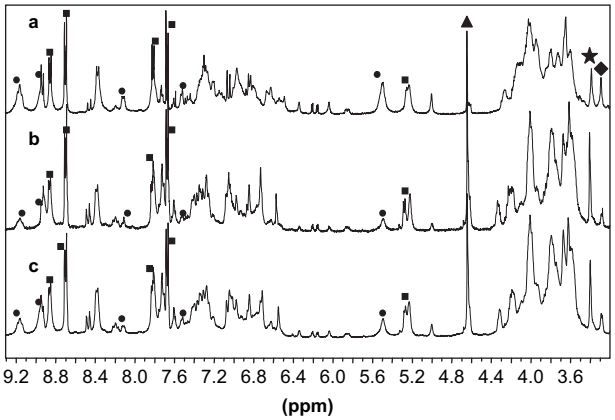
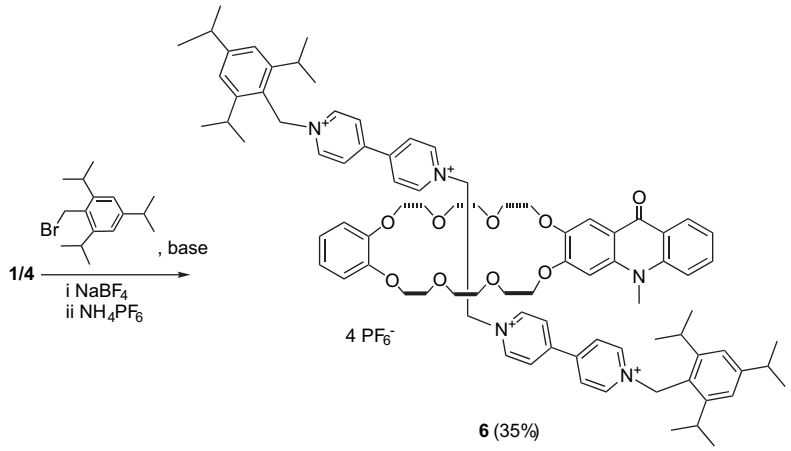


Figure 5. ^{1}H NMR spectra of the pseudorotaxane **2/4** in acetonitrile[D_3] solution (**2**=1.1×10^{-2} M, **4**=9.7×10^{-3} M). (a) Before the irradiation; the ratio between the free and complexed components is 0.9 (squares denote free components and circles denote the complex; the triangle marks the signal of the *N*-methyl group of the acridinium compound, the star and rhombus denote the *N*-methyl group and methoxy group, respectively, of compound **2**). (b) Irradiation at 300 nm for 20 min; the ratio of free (squares) and complexed (circles) components is 3.3. (c) Thermal back reaction after 24 h; the ratio of free (squares) and complexed (circles) components is diminished to 2.

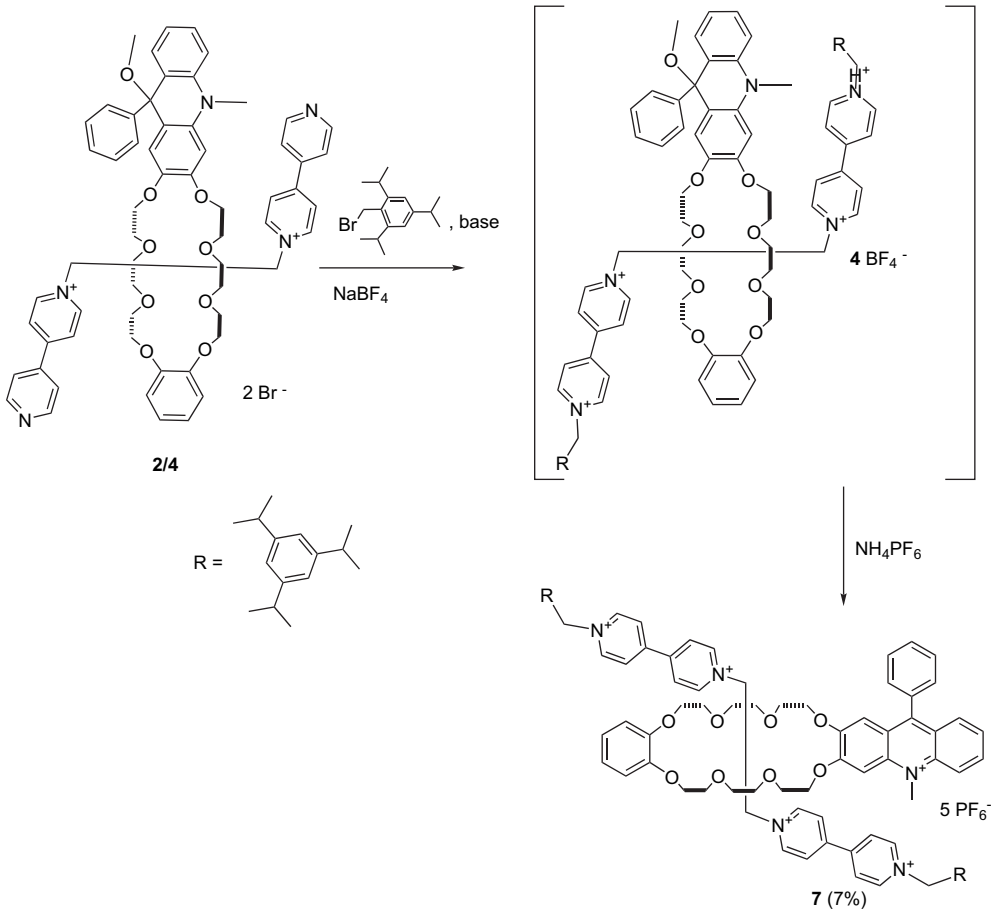


Scheme 3. Synthesis of rotaxane **6**.

2.3. Rotaxane synthesis

The pseudorotaxanes **1/4** and **2/4** were used to obtain rotaxanes by the alkylative end-capping protocol (Schemes 3 and 4).[10] The rotaxane **8** was synthesized in order to compare its NMR spectrum with **6** and **7**.

The association constant of the pseudorotaxane **2/4** is less than that of **1/4** (see above). Accordingly, the yield of the rotaxane **7** is much smaller (see Scheme 4). Moreover, we were not able to obtain the primarily formed acridane rotaxane because under the conditions of separation and purification, only the corresponding acridinium rotaxane **7** could be isolated, even under neutral conditions. It was not possible to convert the acridinium rotaxane to the acridane rotaxane because the basic conditions necessary for the reaction of the acridinium salt with methanol destroyed the axle molecule **5**.[11]



Scheme 4. Synthesis of rotaxane **7**.

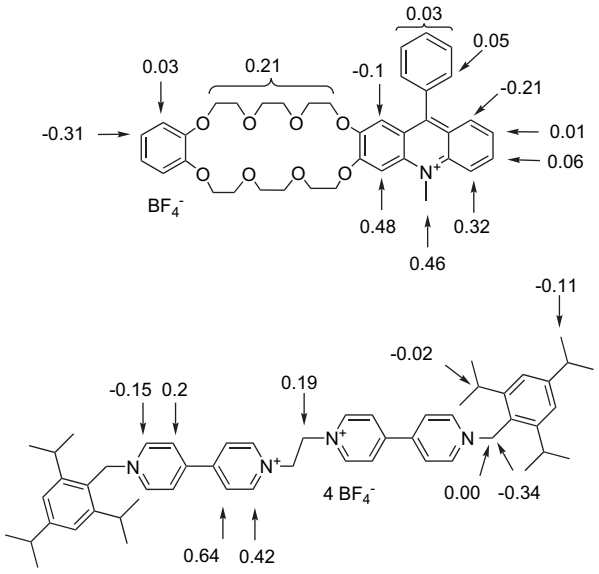


Figure 6. Chemical shift differences of proton resonances of rotaxane **7** obtained by comparison of the proton resonances of the free axle **5** and the free crown ether **3** ($\delta_{\text{free component}}-\delta_{\text{rotaxane}}$) in acetonitrile[$D_3$] solution.

2.4. Rotaxane conformation

The transformation of the pseudorotaxane into the rotaxane is associated with the additional generation of positive charges in the axle **5** due to the introduction of the stopper units. We used the tri-*iso*-propylbenzyl group as the stopper fragment on the assumption that the interaction between the axle and **DB24C8** would be the same as that of the pseudorotaxane (hydrogen bonds and π-stacking).[8] However, according to the observed shifts of the proton resonances of rotaxanes **6** and **7**, the interaction is changed upon conversion from pseudorotaxanes to rotaxanes. The general trend of the proton resonances in the bipyridinium axle is the significant downfield shift of most of the proton resonances. Only the δ proton resonances are slightly upfield shifted. The chemical shift differences of the rotaxane **7** (Fig. 6) clearly indicate that π-stacking cannot be an important interaction mode between the crown and the

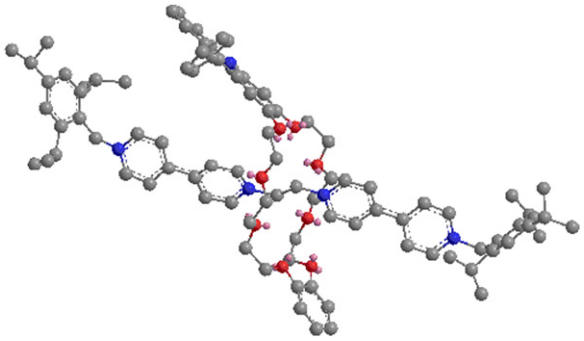
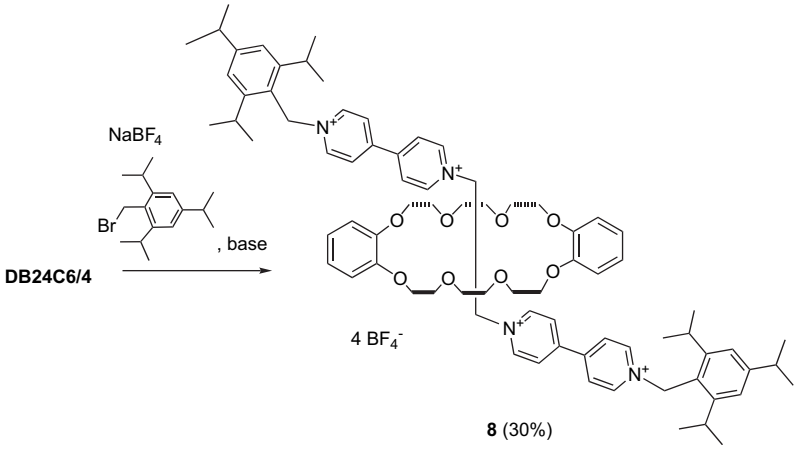


Figure 7. Molecular model at MM2 level of the rotaxane **7** (hydrogen and anions omitted for clarity).

axle of the rotaxanes **6** and **7**. Also in the rotaxane **8** (see Scheme 5), the proton resonances correspond to those of **6** and **7**. This finding is contradictory to the known rotaxane, which contains 4-*tert*-butylbenzyl stoppers instead of the tri-*iso*-propylbenzyl stopper.[8] Therefore we concluded that the steric hindrance between the *iso*-propyl groups of the stopper and the crown ether prevents formation of a folded conformation of the crown ether necessary for π-stacking. The lowfield shifts of the α-proton and N^+-CH_2 proton of the bipyridinium axle are in accord with hydrogen bonds to oxygen of the crown.[8] Assuming a more elongated, nonfolded conformation of the crown, an edge-to-face interaction between the bipyridinium rings of the axle and the acridinium unit of the crown ether may give rise to the observed downfield shift of the proton resonances. A possible co-conformation of the rotaxane **7** is illustrated in Figure 7.

In contrast to the rotaxanes **6** and **8**, the benzylic protons of the stopper unit in rotaxane **7** are split into two doublets, which couple with each other. This finding indicates that the rotation about the $C-N^+$ bond is slow on the time scale of NMR spectroscopy.

On the other hand, both the axle and the asymmetric crown ether exhibit only one set of proton signals indicating that both bipyridinium units exchange their places by shuttling within the crown. At the same time, the conformation of the crown has to adapt to the changed axle position (Fig. 7).



Scheme 5. Synthesis of the rotaxane **8** used as reference.

3. Conclusions

In summary, we have designed two novel rotaxanes based on modified crown ethers incorporating the dihydroacridinone and acridinium unit. The 1,2-bis(4,4′dipyridinium)ethane axle was used to form pseudorotaxanes, which were transformed into rotaxanes by the alkylative end-capping method. The binding motif is drastically changed in going from pseudorotaxanes to rotaxanes.

4. Experimental

4.1. 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 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.

4.1.1. Pseudorotaxane self assembly

Association constants were determined according to Eq. 1 using the single point method.

$$H + \mathbf{4} \rightleftharpoons H\cdot\mathbf{4}$$

$$K_{a,exp} = \frac{|H\cdot\mathbf{4}|}{|H||\mathbf{4}|} \quad (1)$$

The fresh pseudorotaxanes solutions were obtained by dissolution of the guest **4** in 0.7 mL of the solvent. The solution was given into a NMR tube. **DB24C8**, **1**, **2**, and **4** were precisely weighed out and were dissolved in the solution of **4**. The determination of the association constants are based on at least three independent runs. The single point method was based on the integration of proton signals (α-protons and protons of the ethane bridge) of complexed and uncomplexed guest **4**. The major source of error in calculated *K* values results from errors in weights and volumes and can be estimated to ±10%.

4.1.2. X-ray crystallographic studies

The pseudorotaxane **1/4** was obtained in monocrystalline form by slow cooling of the warm methanol solution. Data were collected with a STOE-diffractometer using graphite-monochromated Mo Kα radiation. The structures were solved by direct methods (SHELXS-97) and refined by full-matrix least squares techniques against F^2 (SHELXL-97).[12] The hydrogen atoms were included at calculated positions. All other nonhydrogen atoms were refined anisotropically. The X-STEP-Program was used for structure representations. Crystallographic data (excluding structure factors) for the structure in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no CCDC 661659. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, (fax: +44-(0)1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).

UV–vis measurements were performed with a Shimadzu UV 2101 PC spectrometer.

Photochemical reactions were carried out by the irradiation of the methanol solution contained in a quartz cuvette 1×1 cm. A high pressure mercury lamp with metal interference filter was used as the irradiation source.

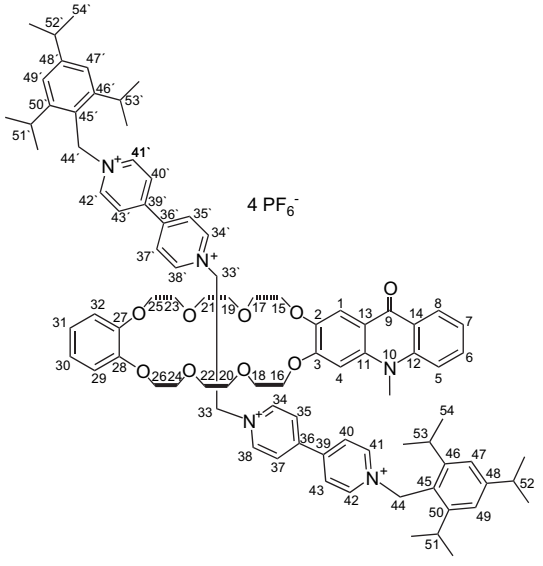
A Rayonet reactor equipped with lamps of 3000 Å was used for the irradiations on a preparative scale.

4.2. Materials

The syntheses of compounds **1**–**3** were described recently.[7] Compound **4** was obtained according to the literature.[13]

4.3. Rotaxane *6*

Compound **4** (as dibromide, 0.1 g, 0.19 mmol) dissolved in water (6 mL) was mixed with **1** (0.1 g, 0.17 mmol) in nitromethane solution (6 mL). $NaBF_4$ (0.18 g, 1.6 mmol) was added. After stirring for 1 h, 1,3,5-tri-*iso*-propylbenzyl bromide (0.36 g, 1.2 mmol) was added. The reaction mixture was stirred for 4 days. The solvents were evaporated in vacuo. The remaining residue was treated with chloroform. The insoluble solid was filtered and the organic phase was evaporated. The remaining solid was washed with *tert*-butylmethyl ether (MTBE) and recrystallized from water to give the red rotaxane (0.1 g, 35%). The BF_4^- anion was replaced by PF_6^- upon adding NH_4PF_6 to a solution of the rotaxane in acetonitrile solution, mp 159–163 °C. Anal. $C_{86}H_{107}F_{24}N_5O_9P_4$ (1933.6636); HRMS (ESI): $[M-2PF_6^-]^{2+}$ calcd for $C_{86}H_{107}F_{12}N_5O_9P_2$: 821.8676, found 821.8653.

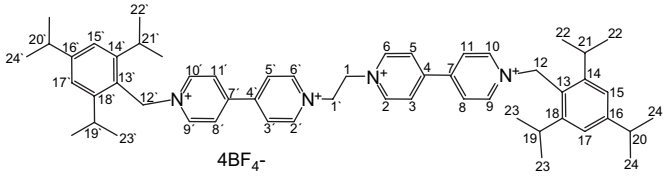


^{1}H NMR (300 MHz, CD_3CN, TMS): δ=9.33 (d, J=6.8 Hz, 4H, H-34,34′,38,38′), 8.46 (d, J=6.8 Hz, 4H, H-41,41′,42,42′), 8.31 (m, 1H, H-8), 8.20 (d, J=6.8 Hz, 4H, H-35,35′,37,37′), 8.02 (d, J=6.8 Hz, 4H, H-40, 40′, 43, 43′), 7.88 (m, 1H, H-7), 7.76 (d, J=9.4 Hz, H-5), 7.41 (s, 1H, H-1), 7.39 (m, 1H, H-6), 7.29 (s, 4H, H-47, 47′, 49, 49′), 6.95 (s, 1H, H-4), 6.59 (m, 2H, H-29, 32), 6.41 (m, 2H, H-30, 31), 5.70 (s, 4H, H-44, 44′), 5.62 (s, 4H, H-33,33′), 4.06 (m, 24H, H-15,16,17,18,19,20,21,22,23,24,25,26), 3.97 (s, 3H, N−CH_3), 2.97 (m, 6H, H-51, 51′, 52, 52′, 53, 53′), 1.17 (m, 36H, CH_3).

The axle **5** can be isolated from the MTBE-phase (0.9 g, 40%), mp>360 °C.

4.4. 1,1′-Bis(4,4′-dipyridinium-1′methyl-14,16,18-tri-isopropylbenzol)ethane tetrafluoroborate ***5***

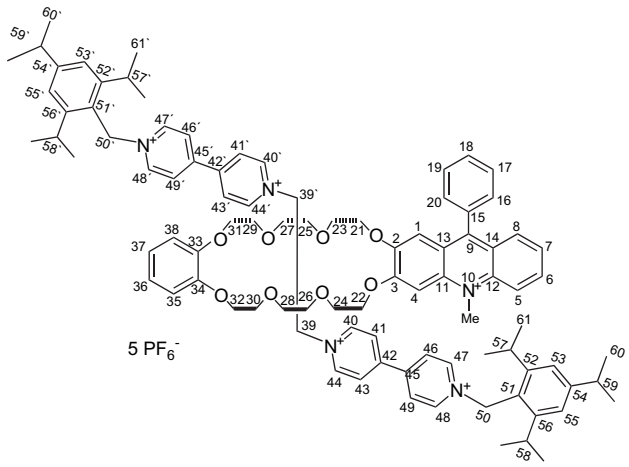
Anal. Calcd for $C_{54}H_{70}B_4F_{16}N_4$ (1122.38): C, 57.79; H, 6.29; N, 4.99. Found: C, 57.36; H, 6.02; N, 4.65.



^{1}H NMR (400 MHz, CD_3OD, TMS): δ=9.10 (d, 4H, J=6.8 Hz, H-2,2′,6,6′), 8.86 (d, 4H, J=6.8 Hz, H-9,9′,10,10′), 8.57 (d, 4H, J=6.8 Hz, H-3,3′,5,5′), 8.53 (d, 4H, J=6.8 Hz, H-8,8′,11,11′), 7.20 (s, 4H, H-15,15′,17,17′), 6.05 (s, 4H, H-12,12′), 5.39 (s, 4H, H-1,1′), 2.94 (m, 6H, H-19,19′,20,20′,21,21′), 1.22 (d, J=9.6 Hz, 12H, H-24,24′), 1.13 (d, J=9.0 Hz, 24H, H-22,22′,23,23′). ^{13}C NMR (75 MHz, CD_3OD): 150.1 (C_q, C-4,4′,7,7′), 146.5 (CH, C-2,2′,6,6′), 144.9 (CH, C-9,9′,10,10′), 141.9 (C_q, C-14,14′,16,16′,18,18′), 138.2 (C_q, C-13,13′), 128.2 (CH, C-3,3′,5,5′), 127.7 (CH, C-8,8′,11,11′), 120.9 (CH, C-15,15′,17,17′), 72.31 (CH_2, C-12,12′), 60.5 (CH_2, C-1,1′), 30.9, 30.3 (CH, C-19,19′,20,20′,21,21′), 23.6 (CH_3, C-22,22′,23,23′,24,24′).

4.5. Rotaxane ***7***

Compound **2** (0.1 g, 0.15 mmol) dissolved in nitromethane (1 mL) was added to **4** (as dibromide, 0.23 g, 0.46 mmol) in water/nitromethane solution (2 mL, 1:1). After addition of $NaBF_4$ (0.18 g, 1.6 mmol) the reaction mixture was stirred for 1 h. 1,3,5-Tri-*iso*-propylbenzyl bromide (0.27 g, 0.9 mmol) was added and the reaction solution was stirred for 4 days. The solvents were removed in vacuo. The remaining solid was washed with MTBE (2×50 mL). The suspension was filtered and the solid was treated with boiling water. Upon cooling, a solid was separated and purified by column chromatography (silica gel, acetonitrile/methanol/water saturated with NH_4Cl, 4:4:1) to give **7** as tetra chloride (0.05 g, 7%). The obtained solid was dissolved in acetonitrile and treated with NH_4PF_6 to exchange the counter ion, mp 150−156 °C. Anal. $C_{92}H_{112}F_{30}N_5O_8P_5$ (2139.6720); HRMS (ESI): $[M-2PF_6^-]^{2+}$ calcd for $C_{92}H_{112}F_{18}N_5O_8P_3$: 924.8712, found 924.8711; $[M-4PF_6^-]^{4+}$ calcd for $C_{92}H_{112}F_6N_5O_8P$: 389.9538, found 389.9534.

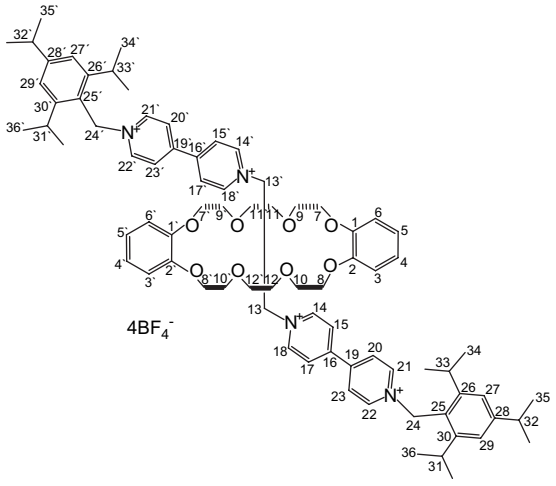


^{1}H NMR (400 MHz, CD_3CN, TMS): δ=9.47 (d, 4H, J=5.3 Hz, H-40,40′,44,44′), 9.14 (d, 4H, J=4.5 Hz, H-41,41′,43,43′), 8.90 (d, 8H, J=8.6 Hz, H-46,46′,47,47′, 48,48′,49,49′), 8.79 (d, 1H, J=9.0 Hz, H-5), 8.23 (t, 1H, J=7.5 Hz, H-6), 8.10 (s, 1H, H-4), 7.71 (m, 5H, H-7,17,18,19), 7.58 (s, 1H, H-8), 7.41 (br s, 2H, H-16,20), 7.21 (s, 4H, H-53,53′,55,55′), 6.88 (s, 1H, H-1), 6.70 (m, 2H, H-35,38), 6.38 (br m, 2H, H-36,37), 5.99 (d, 2H, J=15.8 Hz, H-50,50′), 5.64 (d, 2H, J=16.3 Hz, H-50,50′), 5.45 (br m, 4H, H-39,39′), 5.10 (s, 3H, N−CH_3), 5.03 (br s, 2H, H-22), 4.20 (br s, 4H, H-31,32), 4.05 (br s, 2H, H-21), 3.97 (s, 16H, H-23,24,25,26,27,28,29,30), 2.95 (m, 6H, H-57,57′,58, 58′,59,59′), 1.08 (m, 36H, CH_3). ^{13}C NMR (75 MHz, CD_3CN): δ=153.8 (C_q, C-33,34), 151.4 (C_q, C-45,45′), 150.2 (C_q, C-42,42′), 148.8 (C_q, C-2,3) 148.2 (CH, C-40,40′,44,44′), 148.2 (CH, C-47,47′,48,48′), 145.9 (CH, C-5), 132.9 (C_q, C-11), 132.3 (C_q, C-12), 131.7 (CH, C-17,18,19), 130.9 (CH, C-16,20), 129.2 (C_q, C-13), 129.0 128.9 (CH, C-41,41′,43,43′), 127.7 (C_q, C-14), 127.5 (CH, C-46,46′,49,49′), 124.2 (CH, C-53,53′,55,55′), 123.5 (CH, C-6), 122.9 (CH, C-7), 120.9 (CH, C-36,37), 117.0 (CH, C-35,38), 105.7 (CH, C-1), 101.3 (CH, C-4), 80.0 (CH, C-8), 72.5 (CH_2, C-22), 71.7 (CH_2, C-25,26,27,28), 69.4 (CH_2, C-23,24,29,30), 66.0 (CH_2, C-3,21,31), 59.9 (CH_2, C-50,50′), 58.7 (CH_2, C-39,39′), 41.5 (CH_3, N−CH_3), 33.8 (CH, C-59,59′), 31.4 (CH, C-57,57′,58,58′), 25.3 (CH_3, C-61,61′), 24.7 (CH_3, C-60,60′).

4.6. Rotaxane ***8***

Compound **4** (as dibromide, 0.1 g, 0.19 mmol) in water solution (5 mL) was mixed with **DB24C8** (0.15 g, 0.33 mmol) in nitromethane solution (5 mL). $NaBF_4$ (0.18 g, 1.6 mmol) was added. The mixture was stirred for 10 min. 1,3,5-Tri-*iso*-propylbenzyl bromide (0.36 g, 1.2 mmol) was then added and the reaction mixture was stirred for 2 days. After evaporation

of the solvents in vacuo the residue was successively extracted with MTBE, chloroform, and water. The insoluble residue was separated, dried, and recrystallized from water to give **7** as a red solid (0.09 g, 30%), mp 152–159 °C. Anal. $C_{78}H_{102}B_4F_{30}N_5O_8$ (1570.7814); HRMS (ESI): $[M-2BF_4^-]^{2+}$ calcd for $C_{78}H_{102}B_2F_8N_4O_8$: 698.3872, found 698.3892.



^{1}H NMR (300 MHz, CD_3CN, TMS): δ=9.33 (d, 4H, J=6.8 Hz, H-14,14′,18,18′), 8.67 (d, 4H, J=6.0 Hz, H-21,21′,22,22′), 8.20 (d, 4H, J=6.4 Hz, H-20,20′,23,23′), 8.15 (d, 4H, J=6.8 Hz, H-15,15′,17,17′), 7.32 (s, 4H, H-27,27′,29,29′), 6.65 (m, 4H, H-3,3′,6,6′), 6.45 (m, 4H, H-4,4′,5,5′), 5.98 (s, 4H, H-24,24′), 5.62 (s, 4H, H-13,13′), 4.02 (m, 24H, H-7,7′,8,8′,9,9′,10,10′11,11′,12,12′), 3.01 (m, 6H, H-31,31′,32,32′,33,33′), 1.22 (m, 36H, CH_3). ^{13}C NMR (75 MHz, CD_3CN): 154.1 (C_q, C-1,1′,2,2′), 151.5 (C_q, C-19, 19′), 150.7 (C_q, C-16,16′), 150.5 (C_q, C-26,26′,28,28′, 30,30′), 148.7 (C_q, C-25,25′), 148.3, (CH, C-14,14′,18,18′), 145.9 (CH, C-21,21′,22,22′), 128.6 (CH, C-15,15′,17,17′), 127.4 (CH, C-20,20′,23,23′), 124.3 (CH, C-27,27′,29,29′), 122.9 (CH, C-4,4′,5,5′), 114.1 (CH, C-3,3′,6,6′), 72.7 (CH_2, C-11,11′,12,12′), 71.1 (CH_2, C-9,9′,10,10′), 69.2 (CH_2, C-7, 7′,8,8′), 59.9 (CH_2, C-24,24′), 58.7 (CH_2, C-13,13′), 35.9 (CH, C-32,32′), 31.4 (CH, C-31,31′,33,33′), 25.0 (CH_3, C-34, 34′,36,36′), 24.7 (CH_3, C-35,35′).

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