Novel photoswitchable rotaxanes†

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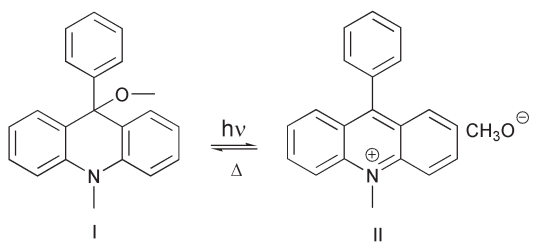
A photoresponsive rotaxane based on the photoheterolysis of an acridane unit which is at the same time a bulky end group has been developed.

Biological machines are able to transform chemical energy into linear or rotational motion. In order to simulate a linear motion with synthetic systems, bistable rotaxanes having two recognition stations of differing interaction strengths with the ring which may be an appropriate starting point.[1] An outer stimulus causes a shift of the ring from one station to the next. Chemical energy, or optimally, light energy, weakens the noncovalent interaction between the ring component and the first station on which the ring resides,[2] and thus, the second station comes into play. The original equilibrium, the so-called co-conformation,[3] is altered and the ring moves due to Brownian motion toward the station that now has the stronger affinity for the ring. The reset can take place either photochemically or thermally.[4]

Here we present a novel photoswitch based on bond fission for changing the co-conformation of a rotaxane.

Photoexcited *N*-methyl-9-phenyl-9-methoxy-9,10-dihydroacridine (*N*-methyl-9-phenyl-9-methoxyacridane) I forms an acridinium ion II (Scheme 1),[5] thus drastically changing both the electronic properties and the shape of the molecule. The acridane compound is reformed by the thermal attack of the leaving group methoxide upon the acridinium compound.

The rate constant of the thermal reaction II → I depends strongly on the solvent polarity.[5]



Scheme 1

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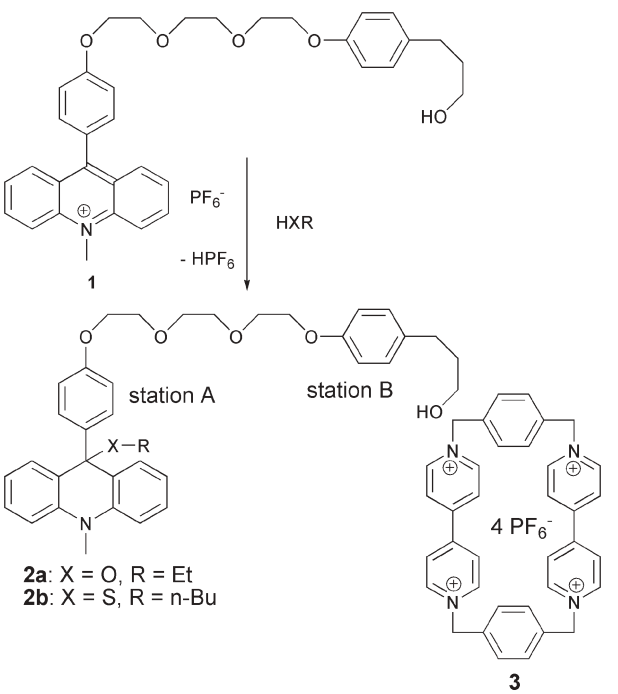
† Electronic supplementary information (ESI) available: Full synthetic details pertaining to the preparations of new compounds. UV-vis and NMR spectra of selected compounds. Assignment of protons of rotaxanes **4** and **6a**. Transient decay curves and absorption spectra. See DOI: 10.1039/b702737k

To introduce this photoswitch into rotaxanes, we have synthesized the molecular axle **2** (Scheme 2) (see ESI†). The tetracationic cyclophane cyclobis(paraquat-4,4′-bisphenylene) **3** was used as a ring component of the rotaxanes. Therefore, the differing electron donor strengths of the recognition stations within the axle will play a role. These two stations are the acridane which is, at the same time, the endcap group. A second photoinactive station is represented by anisole which is a relatively weak electron donor. An anisole unit is present both in station A (acridane) of **2** and as a substituent in compound **1**. Accordingly, the question arises as to whether there are sufficient differences of the interaction energies between **3** and the two stations.

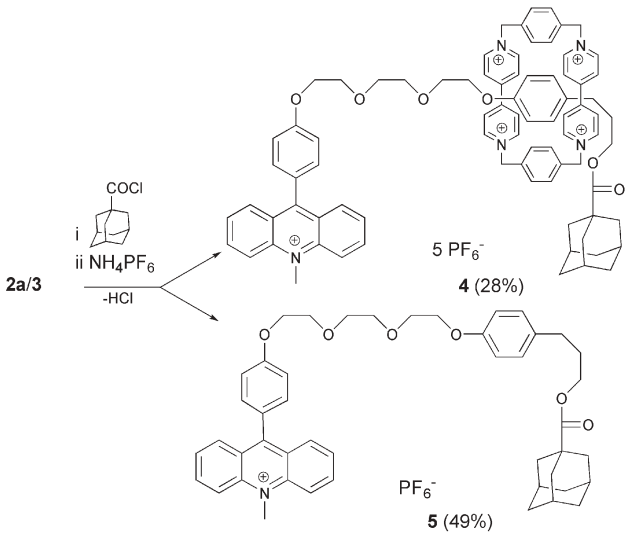
The rotaxane **4** was formed by the esterification of the OH-group of the pseudorotaxane **1/3** (Scheme 3). The synthesis route leads in only three steps to a rotaxane with a 1.8 nm distance between the two recognition stations.

According to the ^{1}H NMR spectrum of **4**, ring **3** resides exclusively on station B. The proton resonances of station B are strongly upfield shifted by 2.5 and 3.9 ppm.

Two-dimensional spectra (ROESY) show cross peaks between ring protons and protons of station B. It is noteworthy that the protons of the adjacent propoxy group are also upfield shifted by



Scheme 2 Components for rotaxane synthesis.

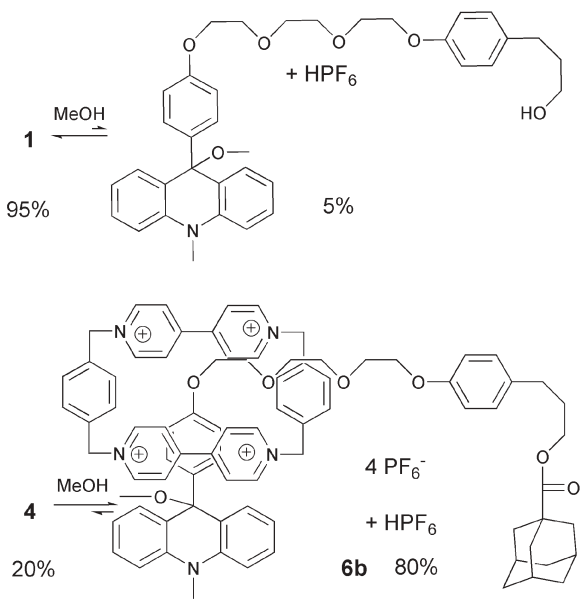


Scheme 3 Rotaxane synthesis.

0.5 and 0.2 ppm. Thus, these protons may serve as probes of the interaction between the ring and station B.

To generate the photoactive rotaxane, compound **4** must react with nucleophiles such as methanol. This can be easily accomplished by using methanol as the solvent because acridane compounds are ionogen compounds in methanol. Thus far, however, this equilibrium has never been studied. The equilibrium between the acridinium rotaxane **4** and the acridane rotaxane **6** favors **6** (80%) in diluted solution (10^{-4}…10^{-5} M) (Scheme 4). In contrast, the corresponding equilibrium of the molecular thread **1** is poised toward the acridinium compound (95%).

Evidently the rotaxane **4** gains free energy by conversion into the rotaxane **6** due to the interaction of the ring with station A instead of station B. This surprising finding can be explained by an additional edge-to-face interaction of **3** with the acridane ring.



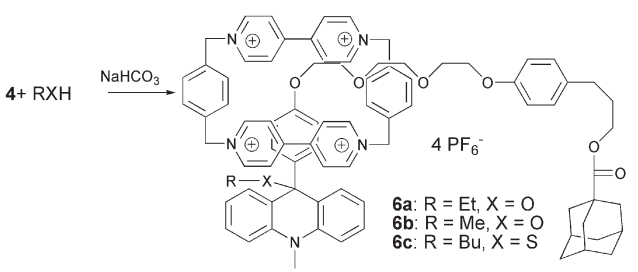
Scheme 4 Equilibria of ionogen compounds.

Accordingly, the proton resonances both of the acridane protons and the methoxy substituent are downfield shifted, leading to the conclusion that the ring occupies station A in the acridane rotaxane. To shift the equilibrium toward the photoactive rotaxane **6** in concentrated solutions, a base such as $NaHCO_3$ or Pr^i_2EtN should be added along with the nucleophile (Scheme 5). On a preparative scale, rotaxanes **6** are obtained in excess, with less than 15% **4**.

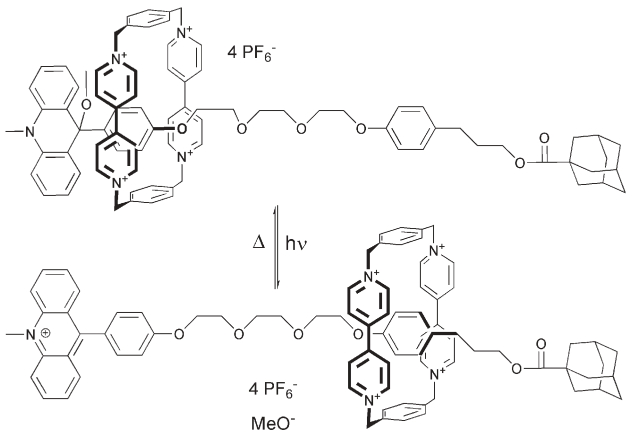
In contrast to the rotaxane **4**, the proton signals in the ^1H NMR spectra of the ring **3** and of the aryl protons of stations A and B of rotaxanes **6** are broad or are even merged in the baseline at room temperature. However, the proton signals of the propoxy chain of station B are sharp, and therefore assignable. These proton resonances are low-field shifted compared to those of rotaxane **4** and are identical with the proton resonances of compound **5**. On the other hand, the protons of the RX-group are low-field shifted due to their location at the edge of the ring. Both findings, taken together, clearly demonstrate the occupancy of station A by the ring. ^1H NMR spectra recorded at lower temperature reveal that the tetracationic cyclophane **3** encircles station A. At 333 K, signals are much sharper; the aryl protons of the two stations appear and can be assigned by ROESY spectra. The protons of station A are upfield shifted by 2.7 and 5.5 ppm (ESI†). Due to the asymmetry of the axle, the bipyridinium protons appear as four broad singlets and the protons of the methylene groups of **3** are split into two doublets of the AB-system (ESI†).[6]

Rotaxanes **6** in dilute solutions are able to repair themselves. The proportion of the acridinium rotaxane **4** remaining after the synthesis is decreased when **4** is dissolved in methanol because the equilibrium favors the acridane. In contrast, preparation of methanol solutions of the acridane compounds **2a** and **2b** forms 40 and 55% acridinium ions **1** by dissociation. These differences in behavior of rotaxanes and free axles are caused by the additional free energy attained by the interaction of the tetracationic ring and the phenyl substituent of the acridane moiety.

The photoexcitation of the molecular axle **2a** results in the corresponding acridinium ethoxide in solutions of both acetonitrile and alcohols. Three isosbestic points of UV-vis spectra recorded after consecutive irradiations of the solution indicate a simple uniform photoreaction. The quantum yield is 0.5 in acetonitrile solution. In alcoholic solutions, the thermal back reaction is pseudo-first order. The lifetime of the acridinium alkoxide depends strongly on the nature of the solvent. In a mixture of ethanol–acetonitrile (5 : 1), the lifetime is 1200 s, 170 s in ethanol, and 97 s in methanol solution. Also, the rotaxanes **6** undergo photoreaction by excitation with 313 nm light. In each case, a transient exhibiting the UV-vis spectrum of the acridinium ion was detected (ESI†).



Scheme 5 Synthesis of acridane rotaxanes.



Scheme 6 Molecular shuttle **6b**.

The lifetime of the transient of rotaxane **6a** in ethanol solution is 1200 s. The acridinium methoxide intermediate formed from rotaxane **6b** possesses a lifetime of 130 s, while irradiation of a methanol solution of the acridane rotaxane **6c** with the thiolate leaving group generates the acridinium thiolate which has a 180 s lifetime. Analysis of the ^{1}H NMR spectra of the rotaxanes **4** and **6**, respectively, has revealed that in the conversion from the acridane to the acridinium rotaxane, a complete change of the location of the ring occurs. Accordingly, the photoreaction of **6** leads to a change of the site of the ring within the rotaxane. In other words, a shuttle process is induced by irradiation (see Scheme 6). The reset of the system occurs thermally and the lifetime of the intermediate state of the rotaxanes can be controlled by the solvent properties.

The lifetime of the rotaxanes in their acridinium state is long enough to allow the ring movement along the molecular axle.[7] Therefore it is reasonable to conclude that both the forward and the back reaction is accompanied by ring motion.

However, the efficiency of the photoreaction suffers due to two problems. The charge transfer interaction between ring **3** and station A is connected with a charge transfer state which opens additional channels for decay of the excited state of the rotaxane **6**. Secondly, the ring component **3** also absorbs light at the excitation wavelength of 313 nm. This inner filter absorbs 50% of the incoming light. A comparison of the absorbance at 360 nm observed after the excitation of **2a** and **6a** results in a decrease of the quantum yield to 20% of that of the **2a** axle alone. Thus, based on a quantum yield 0.5 (see above) for **2a**, the efficiency of the rotaxane photoheterolysis is in the range of 0.1. Ten switch cycles do not result in any irreversible degradation of the acridane rotaxane.

In summary, we have described a new class of tunable rotaxanes incorporating an acridane moiety. The complete change of the ring position following the photochemical and thermal reactions are an advantage of the new system. Both ends of the rotaxanes can easily be modified to introduce functional groups which are able to immobilize such rotaxanes on surfaces and nanoparticles. Work is currently in progress to realize these functionalities.

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