Rotaxanes and pseudorotaxanes with threads containing viologen units

Malgorzata Deska, Jolanta Kozlowska, and Wanda Sliwa*

Jan Dlugosz University, Institute of Chemistry, Environmental Protection and Biotechnology, 42-200 Czestochowa, Armii Krajowej 13/15 Street, Poland
E-mail: w.sliwa@ajd.czest.pl

Abstract
In the present review rotaxanes and pseudorotaxanes with threads containing viologen units are described. First the rotaxanes and pseudorotaxanes in which the crown ether serves as a ring are presented, they are followed by rotaxanes and pseudorotaxanes containing the crown-based cryptand as a ring. For the above interlocked species the synthetic approaches and properties, especially those promising for their use in sensors and switches are shown.

Keywords: Catenane, crown ether, cryptand, rotaxane, viologen

Table of Contents

1. Introduction
2. Rotaxanes and Pseudorotaxanes Containing Crown Ether as a Ring
   2.1. Rotaxanes
   2.2. Pseudorotaxanes
3. Rotaxanes and Pseudorotaxanes Containing the Crown-based Cryptand as a Ring
   3.1 Rotaxanes
   3.2 Pseudorotaxanes
4. Conclusions
5. Acknowledgements
6. References

1. Introduction

Rotaxanes\textsuperscript{1-5} and pseudorotaxanes\textsuperscript{6-9} are examples of mechanically interlocked species\textsuperscript{10,11}, besides them, to interlocked architectures belong also catenanes\textsuperscript{12-15} as well as more complex structures such as trefoil knots\textsuperscript{16}, Solomon knots\textsuperscript{17}, Borromean rings\textsuperscript{18}, daisy chains\textsuperscript{19} or ravels\textsuperscript{20}.
Rotaxanes are a topic of enormous number of reports due to their valuable properties, interesting in the construction of molecular machines and supramolecular polymers. Pseudorotaxanes are also intensively studied, they are prototypes of molecular machines and serve as building blocks for interlocked supramolecular assemblies, some of them are promising in preparation of molecular sensors and in drug delivery.

There should be mentioned here also rotaxanes and pseudorotaxanes containing cyclodextrins, calixarenes or cucurbiturils. Today many works concerning viologen-based rotaxanes and pseudorotaxanes appear, in these systems viologens are components of a thread or are present as parts of the tetracationic cyclophane serving as a ring. Moreover viologens find a variety of applications due to their redox properties, they are promising for design of molecular machines and switches and construction of new materials, the rapid development of viologen chemistry has its reflection in many reports concerning these compounds.

In the paper rotaxanes and pseudorotaxanes with threads containing viologen units are described. They are divided into two classes: those containing crown ether as a ring, presented in the first part, and those containing the crown-based cryptand as a ring, shown in the second part. The review is a continuation of our former papers dealing with supramolecular structures with quaternary azaaromatic character.

Taking into account the great number of reports concerning rotaxanes and pseudorotaxanes with threads containing viologen units, in the review only selected examples of such species are presented.

2. Rotaxanes and Pseudorotaxanes Containing Crown Ether as a Ring

2.1. Rotaxanes

From among a great number of rotaxanes built from a thread containing viologen, and having crown ether as a ring, some examples will be presented. Design of molecular machines is today a great challenge on the scientific field, below selected works concerning this topic are described.

The operation mechanism of bistable rotaxane 1+ which acts as a molecular shuttle driven by visible light was studied by computational calculations. The shuttling free energy and shuttling relaxation time were calculated and the experimental estimations for the relative stability of the different molecular co-conformations were reproduced.

It was established that the rotaxane 1+ undergoes photoinduced ring shuttling in solution, its thread contains ruthenium (II) complex [Ru(bpy)3]2+ (P2+) serving as a photosensitizer and as a stopper, the second stopper is T. The electron-accepting stations are 4,4’-bipyridinium unit, i.e. V1 2+ and 3,3’-dimethyl-4,4’-bipyridinium unit, i.e. V2 2+. The rigid spacer S consists of three p-phenylene units, and the π-electron-donating ring is bis-p-phenylene[34]crown-10. The V1 unit is a stronger electron-acceptor station than V2, therefore the ring encircles V1 unit, and it is the stable translational isomer of 1 in the ground state.
Scheme 1

Step 1

$e^-$

Step 2

$a = \text{electron transfer from } P^{2+} \text{ to } V_{1}^{2+}$

Step 3

$b = \text{ring displacement from } V_{1}^{*} \text{ to } V_{2}^{2+}$

Step 4

$e^-$

$c = \text{electron transfer from } V_{1}^{*} \text{ to } P^{3+}$

Step 5

$d = \text{return from } V_{2}^{2+} \text{ to } V_{1}^{2+}$
The working mechanism of rotaxane 1 involves the “four-stroke” (a-d) molecular shuttle driven by visible light. Excitation of P$^{2+}$ by light (step 1) results in the electron transfer from P$^{2+}$ to V$_{1}^{2+}$ (step 2), this process competes with the intrinsic decay of the P$^{2+}$ excited state (step 3). Upon reduction of V$_{1}^{2+}$, deactivating V$_{1}^{2+}$ by formation of V$_{1}^{+}$, the ring moves to V$_{2}^{2+}$ (step 4), this step competes with the back electron transfer from V$_{1}^{+}$ to the oxidized unit P$^{3+}$ (step 5).

The back electron transfer from the reduced station V$_{1}^{+}$ to the oxidized unit P$^{3+}$ (step 6) restores the electron-acceptor ability of V$_{1}^{+}$ by formation of V$_{1}^{2+}$. As a result, a back movement of the ring from V$_{2}^{2+}$ occurs (step 7). The above forward and backward movement of the ring presents a full “four-stroke” mechanical cycle (Scheme 1).

![Scheme 2](image-url)
The quantitative comparison of calculations with experimental findings can be achieved by calculating the MM (molecular mechanical) free-energy profile and then the shuttling relaxation time by solving the Fokker-Planck equation.

The role of counterions is very important and should be taken into account for the computational reproduction of the observed shuttling kinetics. Anions are strongly bound to the thread, it was shown that the shuttling is almost barrierless in the absence of counterions. If the interaction between the positively charged rotaxane and its counteranions could be weakened, either by changing the counterion or by changing the solvent, such system would be able to work as a fast-switching molecular machine.

Another structure interesting in building molecular machines is the bistable system 26+ based on a two-component [c2]daisy chain stoppered at both ends. Each component consists of the crown ether ring bound with the thread containing two stations, i.e. viologen and NH2+ units (Scheme 2).52

In this system, in CD3CN solution the two crown ether rings move between two recognition sites under acid-base control; during this process the length of the whole system (i.e. the distance between two stoppers) undergoes contraction by treatment with a base (A→B) and expansion by treatment with acid (B→A). Such behavior is similar to the action of a muscle.

In A the rings encircle the -NH2+- units; the rings are close by, i.e. the system is expanded, the distance between two stoppers is a. Upon addition of phosphazene P1-tBu base the -NH2+- units undergo deprotonation, resulting in shift of both rings to viologen units, this motion leads to formation of B, where rings are far away from each other, i.e. the system is contracted, the distance between two stoppers is b. Since a>b, the system behaves as a muscle. The addition of trifluoroacetic acid causes the reprotonation of -NH- groups to-NH2+- and return to original expanded system A. The above reversible muscle-like structures are promising for design of molecular machines.

In daisy chains the molecules are linked together by mechanical bonds; the mechanically interlocked molecules (MIMs) attract today a growing attention.10,63 One should point out that the polymers in which repeating units are connected by mechanical bond, i.e. mechanically interlocked polymers are promising for use in nanotechnology and material science.64-70

Below the synthesis of polymer daisy chain 3 using “threading-followed-by-polymerization” method is described.71 It is noteworthy that in this procedure the tedious syntheses of monomers are avoided. The synthesis begins with the treatment of acid 4 containing crown ether unit with thionyl chloride affording acid chloride 5 which directly, without purification was mixed with viologen derivative 6 in acetonitrile at –70 °C, this low temperature was employed to minimize the esterification and maximize the complexation of 6 with 5 affording the pseudorotaxane-type monomer 6•5. The temperature was allowed next to rise slowly to – 50 °C and triethylamine was added to catalyze esterification, then the reaction mixture was warmed to room temperature.

The in situ generated 6•5 underwent polymerization to give the polymer daisy chain 3. After the exchange of Cl– into PF6– ions, the side products were removed by precipitation with DMSO.
Scheme 3
It was established that 45 repeating units exist in a single polymer chain of 3, the molecular weight of 3 is 64 kDa.\(^\text{72}\)

The above results show that the dynamic supramolecular monomers, \textit{i.e.} monomers with different parts linked by noncovalent bonds may serve for convenient construction of mechanically interlocked polymers (Scheme 3).

In order to perform a quantitative conformational study of redox-active [2]rotaxanes, at first the conformational analysis of [2]rotaxane \(8^{2+}\) serving as a model and of its radical cation \(8^{+}\) was made. Rotaxane \(8^{2+}\) consists of the viologen \(V^{2+}\), the ring 9 and stoppers A and B. The stopper A is rigidly connected with viologen, while the stopper B is attached to viologen by a flexible polyether chain. In this investigation the combined electrochemical techniques and NMR spectroscopic methods such as COSY, NOESY and PASSY (paramagnetic line-broadening and suppression) were used (Scheme 4).

![Scheme 4](image)

\textbf{Scheme 4}

It was observed that in the rotaxane \(8^{2+}\) in its dicationic \(V^{2+}\) state in solution the thread is folded, the B stopper being directed back to the centre of the molecule, the crown ether 9 encircles the viologen site. Upon one-electron reduction of viologen, affording the radical cation \(V^{+}\), the thread retains its folded conformation and 9 remains localized at the \(V^{+}\), although \(V^{+}\) has lower affinity than \(V^{2+}\) for 9. It was found that even in the case of the fully reduced viologen \(V^{0}\), the ring 9 still resides at the viologen unit.\(^\text{73}\)

The above study of the simple [2]rotaxane 8 \textit{i.e.} containing one viologen unit was followed by conformational study in solution of two bistable rotaxanes 10 and 11, \textit{i.e.} containing two viologen units.\(^\text{74}\) The investigation of both rotaxanes 10 and 11 in their parent and reduced states was made using the same electrochemical and NMR spectroscopic methods as in the former experiment.\(^\text{73}\)
Rotaxanes 10 and 11 have been synthesized, they both have two stations, $V_1$ and $V_2$, the links $L_1$ and $L_2$ (in 10 and 11, respectively) between two recognition sites, and stoppers A and B; the crown ether 9 is a ring.

Scheme 5

Tripodal stopper A serves in rotaxanes 10 and 11 for attachment of the thread to the surface of semiconductors or metals; in experiments the attachment to the surface of TiO$_2$ nanoparticles
and nanostructured electrodes was made. Both rotaxanes 10 and 11 contain flexible polyether PE units connecting V₂ with the stopper B while their links between stations V₁ and V₂ have different rigidity. In rotaxane 10 the viologen units V₁ and V₂ are bound by a flexible trimethylene chain L₁, while in rotaxane 11 the viologen units V₁ and V₂ are linked by a rigid terphenylene chain L₂ (Scheme 5). It should be pointed out that the flexibility of the chains L₁ and L₂ influences the shuttling of the ring. In 10 the trimethylene link L₁ is flexible and may be folded, therefore the shuttling of the ring is limited, while in 11 the terphenylene link L₂ is rigid and the shuttling proceeds without limitations.

In 10 and 11, in the parent state the ring resides at V₁, since V₁ is more electron deficient and less sterically hindered than V₂. At the beginning the behavior of 10 and 11 was investigated when V₁ was reduced to the first reduced state. It was possible to selectively reduce V₁ (without the reduction of V₂), since V₁ and V₂ have sufficiently different reduction potentials. The reduction of V₁ in 10 and 11 may be performed by applying an appropriate negative potential or by using Zn metal, under these conditions the stations V₂ do not undergo reduction; as a result 10•3PF₆ and 11•3PF₆ in singly reduced radical cation states are formed.

The given above NMR methods enable the monitoring of structural and conformational changes of [2]rotaxane molecule at different oxidation states. It was found that in radical cations of reduced viologens the unpaired electron density causes a measurable PRE (paramagnetic relaxation enhancement). The PRE values allow to characterize the localization of the ring and to estimate the conformation of the thread of the [2]rotaxane in the reduced states.

In 10•3PF₆ the viologen V₂ is folded back toward V₁, so that methyl groups of V₂ can approach V₁. The analysis of PRE has shown that the stopper B starts to be in the vicinity of V₁ due to the folding of L₁ and of the PE chain. In 10•3PF₆ the ring still predominantly resides at V₁⁺⁺, although the interaction of the ring with V₁⁺⁺ is weakened since V₁⁺⁺ has higher electron density than had V₁. Even after a second reduction (i.e. for 10•2PF₆) the ring still encircles V₁. At last, after the third reduction (i.e. for 10•PF₆), the ring shuttles to V₂.

In 11•3PF₆ however, V₂ cannot approach to V₁; the ring mainly resides at V₂ which is a weaker recognition site than V₁. The folding of L₂ in 11 is impossible in all reduction states. The shuttling occurs after the first reduction (i.e. for 11•3PF₆), in this time the ring encircles V₂, which is a weaker recognition site than V₁, and also after the second reduction (i.e. for 11•2PF₆) and after the third reduction (i.e. for 11•PF₆) the ring always encircles V₂.

The above investigation of tripodal rotaxanes 10 and 11 shows that the nature of the link between stations V₁ and V₂ is crucial for their switching ability.

In order to explain how electrostatic attraction may help to control the shuttling process, [2]rotaxanes and related [2]pseudorotaxanes containing oppositely charged threads and rings have been investigated. In these systems, referred to as ion-paired [2]rotaxanes and ion-paired [2]pseudorotaxanes, the positive and negative charges are compensated and the mutual molecular recognition is considerably increased by electrostatic attraction between components, which are
not only mechanically interlocked, but also strongly electrostatically attached. The studied rotaxanes and pseudorotaxanes contain doubly positively charged viologen threads which go through doubly negatively charged crown ether rings.

As examples served the ion-paired [2]rotaxanes and ion-paired [2]pseudorotaxanes consisting of the thread incorporating cationic viologen unit and of bis-\(p\)-phenylene-34-crown-10 rings with anionic groups \(-\text{COO}^-\) and \(-\text{SO}_3^-\), 12 and 13, respectively, the neutral crown ethers 9 and 14 served for comparison purposes. It was observed that the association constants of viologens 15 and 16 with anionic crown ethers 12 and 13 are higher than those with neutral crown ethers 9 and 14; the affinity of the investigated crown ethers toward viologens decreases in the order: 13 > 12 ≥ 14 > 9 (Scheme 6).

![Diagram](image)

**Scheme 6**

**Synthesis of ion-paired [2]rotaxanes** was made using the reaction of monocation precursor 17 with the crown ether 18 and the stopper component 19, the formed [2]rotaxane 20 was converted by sodium bicarbonate into ion-paired [2]rotaxane 21 (Scheme 7).
It was found that the reaction of 17 with the mixture of syn- and anti- isomers of the crown ether 13 (in form of the Bu$_4$N$^+$ salt) and with 19 affords in 50%, two syn- and anti- isomers of ion–paired rotaxanes 22 and 23, respectively, due to the presence of equal amounts of syn- and anti- isomers in the starting material 13. One should point out that, contrary to the starting 13, the isomers 22 and 23 could be separated; it was observed that the anti- rotaxane 23 shows cycloenantiomerism (Scheme 8).
**Scheme 8**

**Synthesis of ion-paired [2]pseudorotaxanes** involves the reaction of viologen 16 with crown ethers 12 and 13 (in form of Me₄N⁺ and Bu₄N⁺ salts, respectively) in aqueous ethanol affording...
[2]pseudorotaxanes 24 and 25. One should note that 24 and 25 are considerably stable, they exist in solution and in the solid state (Scheme 9).

Scheme 9

The crystal structures of hydrated pseudorotaxanes 24 and 25 have been examined: In pseudorotaxane 24, the viologen cationic nitrogen atoms and the anionic carboxylate groups of the ring 12 are far from each other, and the carboxylates point away from the viologen unit into layers of hydrating water molecules. The hydration shell of water molecules (twelve water molecules per each ion-paired [2]rotaxane molecule) forms layers separating adjacent ion-paired [2]pseudorotaxane units. Such hydration prevents the direct contacts of positively charged nitrogen atoms with carboxylate groups.

In pseudorotaxane 25, however, the viologen cationic nitrogen atoms are more close to anionic sulfonate groups of the ring 13 than in the case of 24. Moreover, the number of hydrating water molecules is lower than for 24 (it is only two per each ion-paired [2]pseudorotaxane molecule), and as a result, in the solid 25 the viologen cationic nitrogen atoms and anionic sulfonate groups are not separated from each other by layers of water molecules, therefore $K_a$ of 25 is higher than $K_a$ of 24. The above observations show that the sulfonate groups provide a better charge delocalization than the carboxylate groups, and enhance the stability of ion-paired [2]pseudorotaxane.

One should point out that the behavior of ion-paired [2]rotaxanes and ion-paired [2]pseudorotaxanes is different from common [2]rotaxanes and [2]pseudorotaxanes since in the ion-paired systems the electrostatic attraction between components exists. It is noteworthy that carboxylate groups of ion-paired [2]rotaxanes can be reversibly protonated, in the contrary to sulfonate groups which cannot be protonated, due to this property rotaxanes containing sulfonated rings can maintain their charges in media of a wider acidity range. One should also note that ion-paired [2]pseudorotaxanes are considerably stable even in aqueous solutions.
The above described ion-paired [2]rotaxanes and ion-paired [2]pseudorotaxanes, consisting of oppositely charged interlocked components are promising for design of molecular electronic devices driven by electrostatic attraction forces.  

2.2. Pseudorotaxanes

Pseudorotaxanes are building blocks for interlocked supramolecular systems; due to their interesting properties they are widely investigated. Below selected examples of pseudorotaxanes with threads containing viologen units are presented.

Pseudorotaxanes consisting of the thread containing viologen and a terpyridine group with its transition metal complexes and of rings 24-crown-8(A), dibenzo-24-crown-8(B) or dinaphtho-24-crown-8(N) were studied in view of their ON/OFF behavior (Scheme 10).  

\[
\text{Scheme 10}
\]

First, the association of the thread \(26^{3+}\) containing the square planar complex \([\text{PtMe}(26)]^{4+}\) and the octahedral complex \([\text{Ru(terpy)}(26)]^{5+}\) with crown ethers A, B and N yielding pseudorotaxanes was made. The Pt(II) and Ru(II) ions were selected since they afford robust, inert complexes with terpyridine ligand. The results of experiments show that the \(K_a\) values for
[2]pseudorotaxanes containing rings A and B increase with higher $\pi$-stacking in order $A < B$, and no significant difference exists in the association between free $26^{3+}$, square planar complex or octahedral complex. However, when crown ether N is used as the ring, the above typical trend exists no more, and the observed differences depend on the coordination geometry of the complex (Scheme 11).

![Scheme 11](image)

As an explanation it was established that in the case of the pseudorotaxane $[\text{PtMe}(26\cdot\text{N})]^{4+}$, i.e. 27, the square planar Pt complex provides a large electron-deficient surface for $\pi$-stacking with the naphtho unit of N, therefore the interaction between thread and ring is enhanced and $K_a$ of pseudorotaxane 27 is higher than for the pseudorotaxane $[\text{Ru(terpy)}(26\cdot\text{N})]^{5+}$, i.e. 28. This difference results from the fact that the octahedral Ru complex, present in 28 creates a steric hindrance between the ancillary terpy ligand and the naphtho unit, the $\pi$-stacking is lower than in 27, therefore the $K_a$ of pseudorotaxane 28 is lower (Scheme 12).

In order to investigate this behavior with more labile metals, as an analogue of $[\text{PtMe}(26)]^{4+}$, the square planar complex $[\text{Ag(MeCN)}(26)]^{4+}$ was prepared, and as an analogue of $[\text{Ru(terpy)}(26)]^{5+}$ the bis-ligand octahedral complex $[\text{Cd}(26)_2]^{8+}$ was used. It was found that the $K_a$ values for formation of [2]pseudorotaxanes from square planar complexes of Pt(II) and Ag(I) with N (27 and 29), respectively) are higher than in the case of octahedral complexes of Ru(II) and Cd(II), (28 and 30, respectively).
This observation concerning the influence of coordination environment of the metal on $K_a$ of formed pseudorotaxanes gave an idea for the design of an ON/OFF system in which the conversion between ON and OFF states occurs by changing one type of metal coordination environment for another in a similar way as other systems are controlled by pH. For this purpose the Ag(I) (square planar) and Cd(II) (octahedral) complexes were used to construct a system of OFF/ON switching by exchanging metal ions, i.e. by changing coordination environment of the terpy site. The arbitrary thresholds of $K_a > 1300$ M$^{-1}$ and $K_a < 600$ M$^{-1}$ represent the requirements for the threaded state (ON) and unthreaded state (OFF), respectively. In this experiment the equilibrium mixture containing the free [2]pseudorotaxane ligand $[26\cdot N]^3+$ was reacted with AgBF$_4$ in CD$_3$CN to give pseudorotaxane $[29\cdot N]^{4+}$, designated as the ON state. Upon treatment of this complex with CdCl$_2$•6H$_2$O, the [2]pseudorotaxane $[30\cdot N]^{8+}$ was formed, it was designated as the OFF state. The subsequent treatment of the OFF state with cyclam resulted in the removal of the Cd$^{2+}$ ion and regeneration of the free ligand $[26\cdot N]^{3+}$ which by adding AgBF$_4$ could restore the ON state. This procedure leads to the ON/OFF system, controllable by the coordination environment of the metal ion.

The above results have shown that the geometry of the metal coordination site can be used to monitor the association constant $K_a$ for formation of [2]pseudorotaxanes; when the metal ions are exchangeable, and the ring is sufficiently large (as N), the control of ON/OFF threading is possible. It should be pointed out that such control involving coordination of metal ions is promising for design of molecular switches (Scheme 13).
Scheme 13

In the study of complexation of viologens 31-33 with crown ethers, it was established that this process can be considerably enhanced by introduction of ion-pair recognition via the presence of
urea units in the crown ether; this improvement is controlled by the nature of the viologen anions.\textsuperscript{79}

Due to the ion-pair recognition, the host can increase its binding affinity, and in some cases may even change its binding selectivity. One should point out the crucial role of ion-pair recognition in biological and analytical applications.\textsuperscript{80,81} It is noteworthy that the improvement of the binding affinity of viologens is very important for preparation of large supramolecular systems (Scheme 14).

In the experiments the heteroditopic receptor 34 was used as a ring, it contains the crown ether unit for binding the dicationic bipyridinium part of viologens 31-33 and two urea units for binding the two anions of these viologens. The complexation of 31-33 which have different anions with the crown ether 34 was investigated with the aim to improve the binding affinity of viologens. Crown ether 35 served here for comparative purposes.

It was found that complexes of 31-33 with 34 have the 1:1 stoichiometry in solution and they have higher \( K_a \) values than corresponding complexes with 35; this behavior results from the ion-pair recognition. One should note that the \( K_a \) values for complexes of 31-33 with 34 are different, this fact indicates the different binding strengths of different anions of 31-33 with the urea groups of 34.\textsuperscript{79}

The experiments show that the complexes of 31 and 32 with 34 are in the solid state the taco complexes, in which the bipyridinium part of 31 or 32 is sandwiched between two aromatic rings of the crown ether moiety in 34. However, 33•34 is not a taco complex in the solid state, but is a pseudorotaxane, in which the bipyridinium part of 33 is encircled by the crown ether 34. This result was unexpected, since 31•34 and 32•34, as well as previously reported host-guest complexes consisting of viologens and BMP32C10\textsuperscript{82} have the taco structure in the solid state.

The above described viologen/crown ether complexation, easily controlled by changing viologen anions is promising in design of molecular machines.

The crown-based lariat ethers are widely used in preparation of membranes and cation-conducting channels,\textsuperscript{83-88} however their complexation with viologens has been only rarely reported. It was found that viologens 31 and 36 form pseudorotaxanes with lariat ether 37 in the solid state. One should note that viologen 31 affords with lariat ether 37 more stable pseudorotaxane than with the corresponding crown ether 38, \textit{i.e.} BMP26C8; the \( K_a \) value for 31•37 \textit{i.e.} A is ca 13 times higher than \( K_a \) for 31•38 in solution, due to the presence of two benzyloxy groups in 37.

On the other side, comparing the association constant values of different viologens 31 and 36 with crown ethers, it was observed that 31 forms with 37 stronger pseudorotaxane 31•37=A than 36 does, forming 36•37, \textit{i.e.} pseudorotaxane B (Scheme 15).\textsuperscript{89}
Scheme 14
Scheme 15

Studying the crystal structures of both pseudorotaxanes, 31•37 (A) and 36•37 (B) it was found that in A and B the two pyridinium rings are coplanar, this behavior being not observed in other complexes of 31 with various crown ethers.90,91 The solid-state structures of A and B are stabilized by face-to-face π-stacking and charge transfer interactions between the four phenylene rings of 37 and the two pyridinium rings of 31 or 36. It was established that the benzyloxy groups in 37 enable an efficient face-to-face interactions with the pyridinium rings of viologens 31 and 36.

In the packing structure of A two pseudorotaxanes A are linked by a bridge consisting of two PF$_6^-$ ions and one water molecule. In the packing structure of B, however, four pseudorotaxanes B are linked by a PF$_6^-$ anion, each pair of pseudorotaxanes B being connected by hydrogen bonds of hydroxyethyl groups between two molecules of viologen 36, each included in the cavity of 37.

It was observed that lariat ether 37 can include the K$^+$ ions. The addition of KPF$_6$ to A resulted in its dissociation, since K$^+$ replaced the viologen 31 as the guest of 37. However, the subsequent addition of crown ether DB18C6 caused the inclusion of K$^+$ into DB18C6, followed by restoration of pseudorotaxane A. Due to this fact the K$^+$ ions and DB18C6 may be used as a switch to control the association of viologen 31 with lariat ether 37, it is noteworthy that the dissociation percentage depends on the concentration of added K$^+$ ions.

The same process with the use of pseudorotaxane B has shown that for dissociation of B a smaller amount of KPF$_6$ was required than for dissociation of A, because $K_a$ of B is lower than $K_a$
of A. The obtained experimental results reveal that the \(N\)-substitution of viologens strongly influences the association strength between viologens 31 or 36 with lariat ether 37.

3. Rotaxanes and pseudorotaxanes containing crown-based cryptand as a ring

3.1. Rotaxanes

It is known that compounds serving as threads, containing viologen units form with crown-based cryptands the rotaxanes of higher association constants than rotaxanes formed with crown ethers. It should be pointed out that rotaxanes with crown-based cryptands as rings, are not so thoroughly studied as those containing crown ether rings. Below rotaxanes with crown-based cryptands as rings will be described.

The synthesis of [2]rotaxanes 39 and 40 consisting of viologens 41 and bis(\(m\)-phenylene)-32-crown-10-based cryptands 42 and 43, respectively, was performed using a threading-followed-by-stoppering method. For rotaxane 39, as stoppers the tris(4-methoxyphenyl)phosphine groups were used, however, for rotaxane 40 the triphenylphosphine groups showed to be big enough to serve as stoppers (Scheme 16a).
Syntheses of 39 and 40 were carried out by reacting viologen derivative 41 with cryptands 42 and 43 and tris(4-methoxyphenyl)phosphine or triphenylphosphine, respectively, in MeNO₂. It should be pointed out that association constants between viologens and cryptands are high, therefore even in dilute solutions high yields of rotaxanes were achieved (Scheme 16b).²²

\[
\begin{align*}
\text{Br} & \quad \text{N} \quad \text{N} \quad \text{N} \quad \text{N} \\
\text{C} & \quad \text{C} \quad \text{C} \quad \text{C} \\
\text{Br} & \quad \text{Br} \\
\end{align*}
\]

\[
\begin{align*}
\text{Br} & \quad \text{N} \quad \text{N} \quad \text{N} \quad \text{N} \\
\text{C} & \quad \text{C} \quad \text{C} \quad \text{C} \\
\text{Br} & \quad \text{Br} \\
\end{align*}
\]

Scheme 16b

Two [2]rotaxanes 44 and 45 have been synthesized using the immediate solvent evaporation method (ISEM).²³ It was observed that this procedure considerably accelerates organic reactions as compared to the conventional solution conditions, since the acceleration is due to enhancement of molecule-to-molecule contacts between reactants. One should point out that the yields of reactions performed by ISEM method are not lower than those obtained in conventional processes.

Syntheses of rotaxanes 44 and 45 are based on acylation reactions, i.e. the urethane formation and the esterification, respectively.²⁴ For this purpose viologen 36 was mixed in acetonitrile with cryptand 46 and with 3,5-dimethylphenyl isocyanate used to form stoppers, and a catalytic amount of dibutyltin dilaureate was added, the subsequent evaporation yielded a film, which after purification by flash column chromatography afforded rotaxane 44. By the same procedure, using 3,5-dimethylbenzoic anhydride to form stoppers, and a catalytic amount of trimethylphosphine as a base, the rotaxane 45 was prepared (Scheme 17).
Two [3]rotaxanes, 47 and 48 consisting of the thread 49 containing two viologen units and of bis(\(m\)-phenylene)-32-crown-10-based cryptands 42 and 43, respectively, have been obtained using the threading-followed-by-stoppering procedure.\(^{95}\) The reaction of bisviologen derivative 49 with cryptand 42 and tris(4-methoxyphenyl)phosphine afforded [3]rotaxane 47, whereas the same procedure, but with cryptand 43 and triphenylphosphine gave rise to [3]rotaxane 48 (Scheme 18).
One should mention that the synthesis of [3]rotaxanes is more difficult than synthesis of [2]rotaxanes. It is known that in the case of cooperative complexation between components, existing in formation of [3]rotaxanes or higher order rotaxanes, the yields of [2]rotaxanes are very low, this fact is advantageous for the synthesis of higher order rotaxanes. In the preparation of [3]rotaxanes 47 and 48 even in dilute solutions, the strong association and the cooperative complexation between the thread 49 and two cryptands exist, therefore no [2]rotaxanes are formed, and as a result, the [3]rotaxanes 47 and 48 are obtained in high yields (Scheme 19).
3.2. Pseudorotaxanes
Pseudorotaxanes with threads containing viologen units and crown-based cryptand as a ring are, similarly as corresponding rotaxanes, more strongly bound than pseudorotaxanes with crown ether rings; some examples are shown below.

In the study of interaction of viologens 31, 50 and 36 with cryptand 51 it was found that 31 and 50 which are methyl substituted, form with 51 the inclusion complexes of T-shape 31•51 and 50•51, while 36 which is not methyl substituted forms with 51 the symmetrically threaded pseudorotaxane 36•51 (Scheme 20).

In methyl substituted viologens 31 and 50, the hydrogen bonding with the electron rich oxygen atoms of 51 exists, therefore inclusion complexes 31•51 and 50•51 are stronger than the pseudorotaxane 36•51, in which no hydrogen bonds with oxygen atoms of 51 are present. It was found that the $K_a$ values decrease in the order 31•51 $\geq$ 50•51 $\geq$ 36•51. The experimental results were confirmed by theoretical calculations.\textsuperscript{96}

Describing pseudorotaxanes in which the cryptand serves as a ring, one should also pay an attention to those containing pseudocryptands,\textsuperscript{30-97,98} an example of such species is presented below.\textsuperscript{99} In this study there was performed the synthesis of pseudocryptand–type [2]pseudorotaxane involving self-assembly of viologen 31 with crown ether 52 bearing two pyridyl units. In the product, 52 is folded and the two pyridyl units interact via off-set face-to-face $\pi$-stacking. The two nitrogen atoms of pyridyl units are pointed to the central cavity.

Scheme 19
forming a pseudocryptand. Viologen 31 is threaded through the cavity of pseudocryptand affording pseudocryptand-type [2]pseudorotaxane 31•52.

Scheme 20

This pseudorotaxane is stabilized by hydrogen bonds of hydrogen atoms of 31 with oxygen and nitrogen atoms of 52 and by off-set face-to-face π-stacking between pyridinium rings of 31 and phenylene rings of 52.

It was found that the opening and closing of the pseudocryptand noncovalent linkage (i.e. the third pseudo-bridge) in 31•52 can be controlled owing to the basicity of pyridine units. The addition of TFA results in the opening of the pseudocryptand and formation of the taco complex 31•52 (TFA)₂, whereas the addition of triethylamine causes the recovery of the pseudocryptand-type [2]pseudorotaxane 31•52. These experiments indicate that the opening and closing of the linkage of pyridyl units acts under acid-base control (Scheme 21).99

It should be pointed out that the formation of the third pseudo-bridge of pseudocryptand via the H-bonding of 31 with pyridyl units of 52 and the π-stacking increases the association constant of the pseudocryptand-type [2]pseudorotaxane 31•52 nearly threefold as compared to association constant of complexation of 31 with unsubstituted BMP32Cl0. An interesting feature of the pseudocryptand-type [2]pseudorotaxane 31•52 is the fact that it has the acid-base
adjustable association constant; this for the first time observed behavior is possible due to the basicity of pyridyl groups, which form the third pseudo-bridge.

![Diagram](attachment:image.png)

Scheme 21

Studying the interaction of viologens 53a,f with the large triptycene-based macrotricyclic host 54 it was established that the kind of obtained stable pseudorotaxane-type complexes depends on the structure of viologens.

Among investigated species, the viologens 53 a-d bearing alkyl groups are threading both lateral crown units of 54 to give 1:1 pseudorotaxane-type complexes A; here the complex 53c•54 is shown. However viologens 53e,f bearing β-hydroxyethyl and γ-hydroxypropyl groups, respectively, thread (as two molecules 53e or 53f) the central cavity of 54 to give 2:1 pseudorotaxane-type complexes B, here the complex (53e)2•54 is shown. It is noteworthy that complexes A and B are formed in solution and in solid state and are stable (Scheme 22).100
Scheme 22
4. Conclusions

Today investigations concerning mechanically interlocked structures are rapidly developing. Having in view a multitude of works dealing with rotaxanes\textsuperscript{101-103} and pseudorotaxanes,\textsuperscript{104,105} as well as works concerning these both structures,\textsuperscript{106,107} in the present paper only selected examples are described.

Among a great number of applications of rotaxanes, such as construction of molecular devices or sensors, one should point out the possibility to use these species in the design of molecular machines.\textsuperscript{108-110}

Recently an intense research of cyclodextrin-based rotaxanes is observed.\textsuperscript{111-114} One should mention here also pillarene-based pseudorotaxanes,\textsuperscript{115,116} they are a new class of supramolecular structures yet not so thoroughly studied as other, longer known species.

A growing attention is paid now to polyrotaxanes\textsuperscript{117,118} and polypseudorotaxanes\textsuperscript{119,120} which are a topic of increasing number of reports.

5. Acknowledgements

The work is a part of the project no. N N209 441539. The authors gratefully acknowledge Polish Ministry of Science along with Higher Education and National Science Centre for financial support.

6. References

<table>
<thead>
<tr>
<th>No.</th>
<th>Authors</th>
<th>Journal</th>
<th>Year(s)</th>
<th>Pages</th>
</tr>
</thead>
</table>
Authors’ Biographies

Wanda Sliwa graduated from Wrocław University of Technology, Poland where she became an associate professor. After a year research at Université Paul Sabatier a Toulouse, France, she moved to Jan Długosz University of Częstochowa, Poland, where she has been Professor of Chemistry since 1990, as well as being a vice-rector, head of the Organic Chemistry Department and director of the Institute of Chemistry. She is author or coauthor of four books and 16 monographs, around 350 papers and ten patents, and has received several awards for scientific and pedagogical achievements. Her research concerns azaaromatic compounds and supramolecular chemistry.

Malgorzata Deska graduated from Pedagogical University of Częstochowa, Poland, she received there M.Sc. degree in 1990. Since this time she works at Jan Długosz University (formerly Pedagogical University) of Częstochowa in Organic Chemistry Department and in
Biochemistry Department. In 2004 she obtained her PhD at Technical University of Krakow, the
doctor thesis concerned physicochemical properties of diazaphenanthrenes. She has published 15
papers in refereed journals, 5 communications to scientific meetings and is a coauthor of a book.
The research interests of Dr Malgorzata Deska are connected with chemistry of heterocyclic
compounds, cyclodextrins and calixarenes.

Jolanta Kozłowska graduated from Pedagogical University of Czestochowa, Poland and
received there the Chemistry M.Sc. degree in 1997. In 2000 she obtained the Mathematics M.Sc.
degree at Opole University (Poland). She works at Jan Długosz University (formerly Pedagogical
University) of Czestochowa, in Institute of Chemistry, Environment Protection and
Biotechnology. Dr. Jolanta Kozłowska obtained PhD at Technical University of Wrocław; her
doctor theme concerned membrane processes with the use of macrocycles. She is coauthor of 16
papers in refereed journals, and of 20 conference communications. Her research is connected
with application of membrane technics in separation of metal ions.