

# Rotaxanes and pseudorotaxanes with threads containing pyridinium units

Malgorzata Deska, Jolanta Kozłowska, and Wanda Sliwa\*

Jan Długosz University, Institute of Chemistry, Environmental Protection and Biotechnology,  
42-200 Częstochowa, Armii Krajowej 13/15 Street, Poland

E-mail: [w.sliwa@ajd.czest.pl](mailto:w.sliwa@ajd.czest.pl)

DOI: <http://dx.doi.org/10.3998/ark.5550190.p007.774>

---

## Abstract

In this review, a continuation of an earlier one concerning rotaxanes with threads containing viologen units, the syntheses and properties of rotaxanes with threads bearing quaternary pyridinium units are described, along with their possible applications. In the first part rotaxanes containing bis(dipyridiniumyl)ethane unit in the thread are presented; they include species with stoppers incorporating metal complexes. The second part concerns rotaxanes formed by anion templation, they are divided into those involving the Grubbs RCM procedure for construction of a ring, and those employing rings built by condensation reactions. Then rotaxanes synthesized with the use of previously prepared rings are described. The third part deals with rotaxane molecular machines, especially those bearing mannosyl moieties. In the last part pseudorotaxanes containing crown ether based cryptands as rings, are shown.

**Keywords:** Association constants; crown ether; cryptand; interlocked structure; templation

---

## Table of Contents

1. Introduction
  2. Rotaxanes containing bis(dipyridiniumyl)ethane unit in the thread
    - 2.1. Rotaxanes with conventional stoppers
    - 2.2. Rotaxanes with stoppers incorporating metal complexes
  3. Rotaxanes formed by anion templation
    - 3.1. Rotaxanes with rings built by Grubbs RCM procedure
    - 3.2. Rotaxanes with rings built by condensation reactions
    - 3.3. Rotaxanes with previously prepared rings
  4. Rotaxane-based molecular machines
  5. Pseudorotaxanes containing cryptands as rings
  6. Conclusions
  7. Acknowledgements
- References

## 1. Introduction

Rotaxanes,<sup>1-4</sup> as well as catenanes,<sup>5-7</sup> daisy chains,<sup>8,9</sup> and molecular knots,<sup>10,11</sup> belong to mechanically interlocked molecules;<sup>12,13</sup> in recent years investigation of these species has developed rapidly due to their valuable properties and applications in molecular electronics and in design of smart novel materials.

Rotaxanes are of interest in the nanotechnology field for the construction of molecular machines and devices;<sup>14,15</sup> also pseudorotaxanes,<sup>16-18</sup> polypseudorotaxanes<sup>19,20</sup> and

polyrotaxanes<sup>21-23</sup> deserve an attention. Rotaxanes based on cyclodextrins,<sup>24-27</sup> calixarenes,<sup>28,29</sup> and cucurbiturils<sup>30,31</sup> are also a topic of many recent reports; the CD-based rotaxanes<sup>32,33</sup> and CD-based polyrotaxanes<sup>34-36</sup> are now intensively studied (CD stands for cyclodextrin).

New species, *i.e.* rotaxanes and pseudorotaxanes containing pillararene units as rings, have recently been developed. Pillararenes<sup>8,37-41</sup> belong to a new class of cyclophanes, they are [1<sub>*n*</sub>]paracyclophanes composed of 1,4-hydroquinones linked by methylene bridges in their 2,5-positions; formally they are similar to calixarenes. It has been found that pillararenes may form rotaxanes and pseudorotaxanes,<sup>42,43</sup> in which threads may be *e.g.* viologen derivatives<sup>37,39</sup>

This review is a continuation of an earlier review dealing with rotaxanes with threads containing viologen units<sup>44</sup> and of our former papers dealing with interlocked structures of quaternary azaaromatics.<sup>45,46</sup> In view of our interest in quaternary azaaromatics, and moreover taking into account the enormous amount of reports on rotaxanes with threads containing pyridinium units, in the present review we describe only their selected examples.

## 2. Rotaxanes containing bis(dipyridiniumyl)ethane unit in the thread

### 2.1 Rotaxanes with conventional stoppers

Syntheses of two classes of rotaxanes, namely those with *t*-butylbenzyl stoppers and those with *t*-butylbenzoate stoppers have been performed. Pseudorotaxanes **1** and **2** containing crown ethers **A**, **B** or **N** were converted into rotaxanes **3** and **4**, respectively, using two methods of stoppering: for **1** the alkylation of terminal pyridine units by *t*-butylbenzyl groups, and for **2** the esterification of terminal benzyl alcohol by *p*-(*t*-butyl)benzoate groups (Scheme 1).<sup>47</sup>

- For **1**: the thread **5** was treated with crown ethers **A**, **B** or **N** affording pseudorotaxanes **1** which upon alkylation with 4-(*t*-butyl)benzyl bromide, followed by Br<sup>-</sup> → CF<sub>3</sub>SO<sub>3</sub><sup>-</sup> ion exchange yielded rotaxanes **3**.<sup>48</sup>

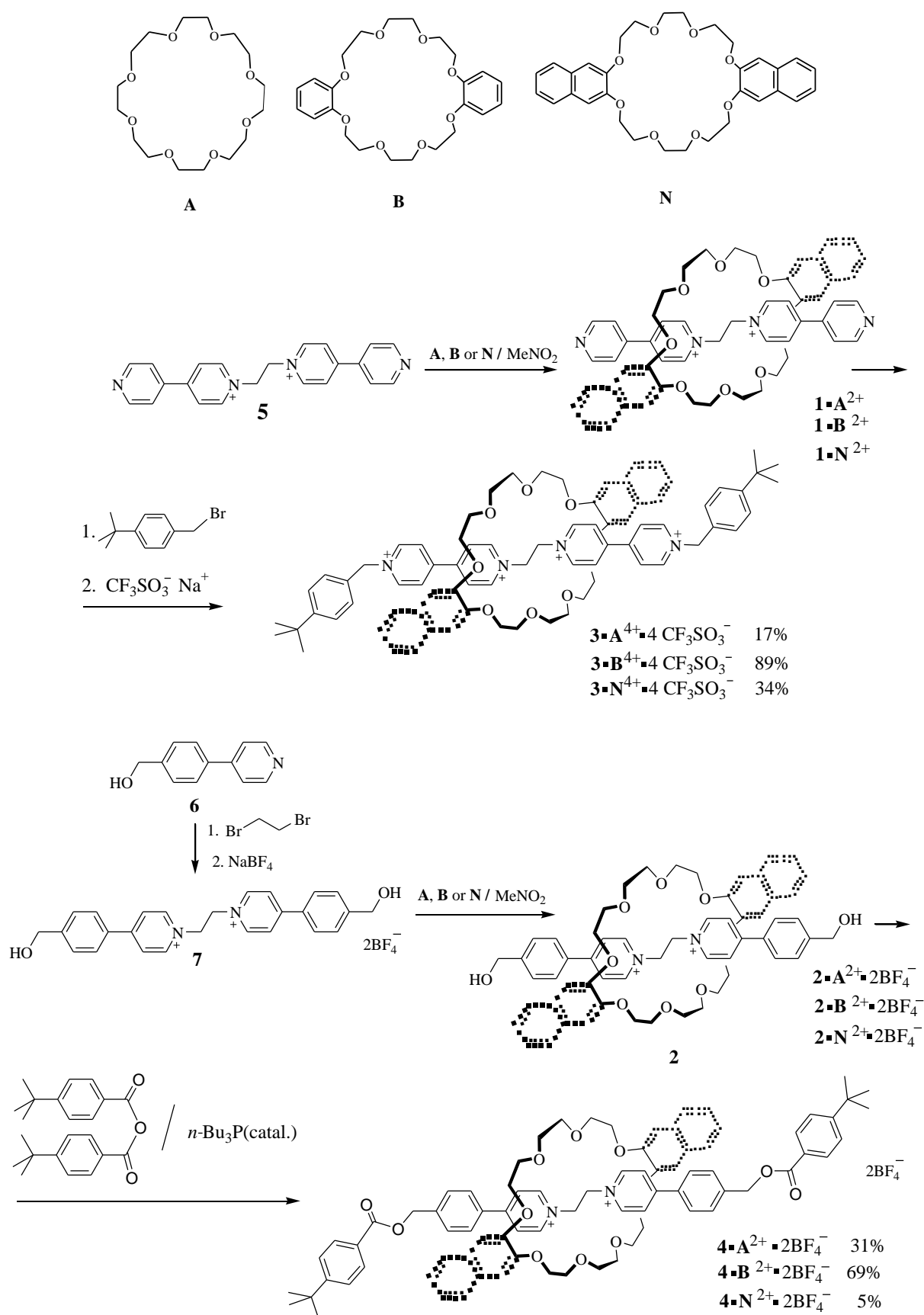
- For **2**: pyridine **6** was treated with 1,2-dibromoethane, followed by NaBF<sub>4</sub>, to give the thread **7** which with crown ethers afforded pseudorotaxanes **2**. The subsequent reaction of **2** with 4-(*t*-butyl)benzoic anhydride gave rise to rotaxanes **4**.<sup>49</sup>

The results of X-ray crystallography have shown that in rotaxanes **3·B**, **3·N** and **4·B** the threads exist in the low energy *anti* conformation, and the crown ethers adopt the S-shaped conformation.

The acid-base driven molecular shuttle consisting of two [2]rotaxanes **8**<sup>2+</sup> and H·**8**<sup>3+</sup> has been synthesized (Scheme 2). Both rotaxanes contain benzylianium and 1,2-bis(dipyridiniumyl) ethane recognition sites.<sup>50</sup>

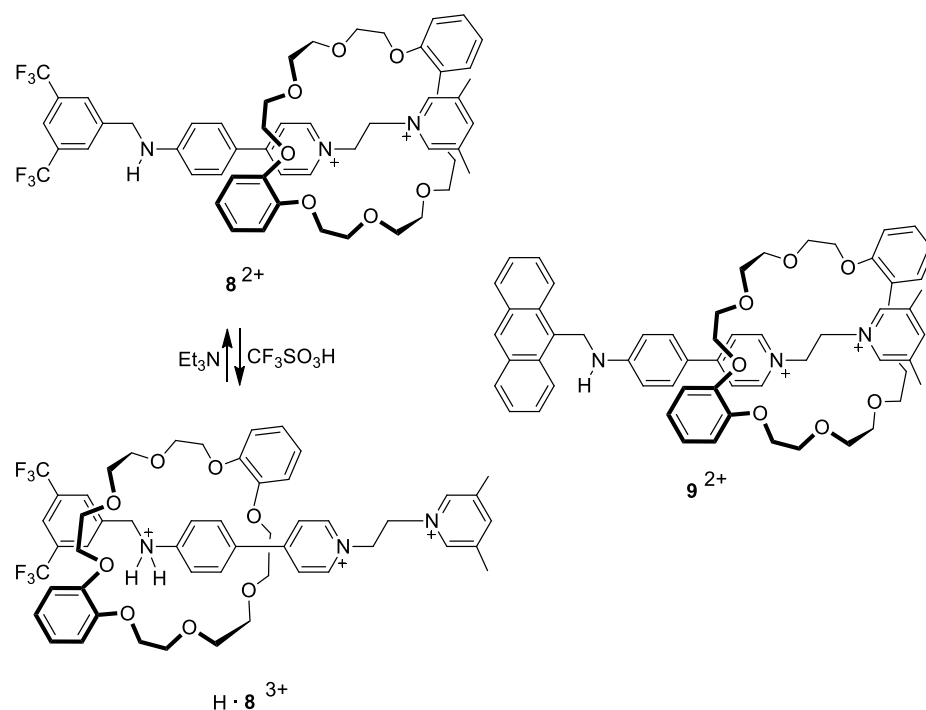
In **8**<sup>2+</sup>, in CD<sub>2</sub>Cl<sub>2</sub> the ring resides at the bis(dipyridiniumyl)ethane site. The protonation of **8**<sup>2+</sup> into H·**8**<sup>3+</sup> results in the moving of the ring to the benzylianium recognition site. This behavior shows that this molecular shuttle acts as a bistable ON/OFF switch.

The addition of a base such as Et<sub>3</sub>N results in the return of the ring to the bis(dipyridiniumyl)ethane site affording the original rotaxane **8**<sup>2+</sup>, and the subsequent addition of an acid CF<sub>3</sub>SO<sub>3</sub>H brings about a repetition of the process. The switching between **8**<sup>2+</sup> and H·**8**<sup>3+</sup> is accompanied by a visible color change.



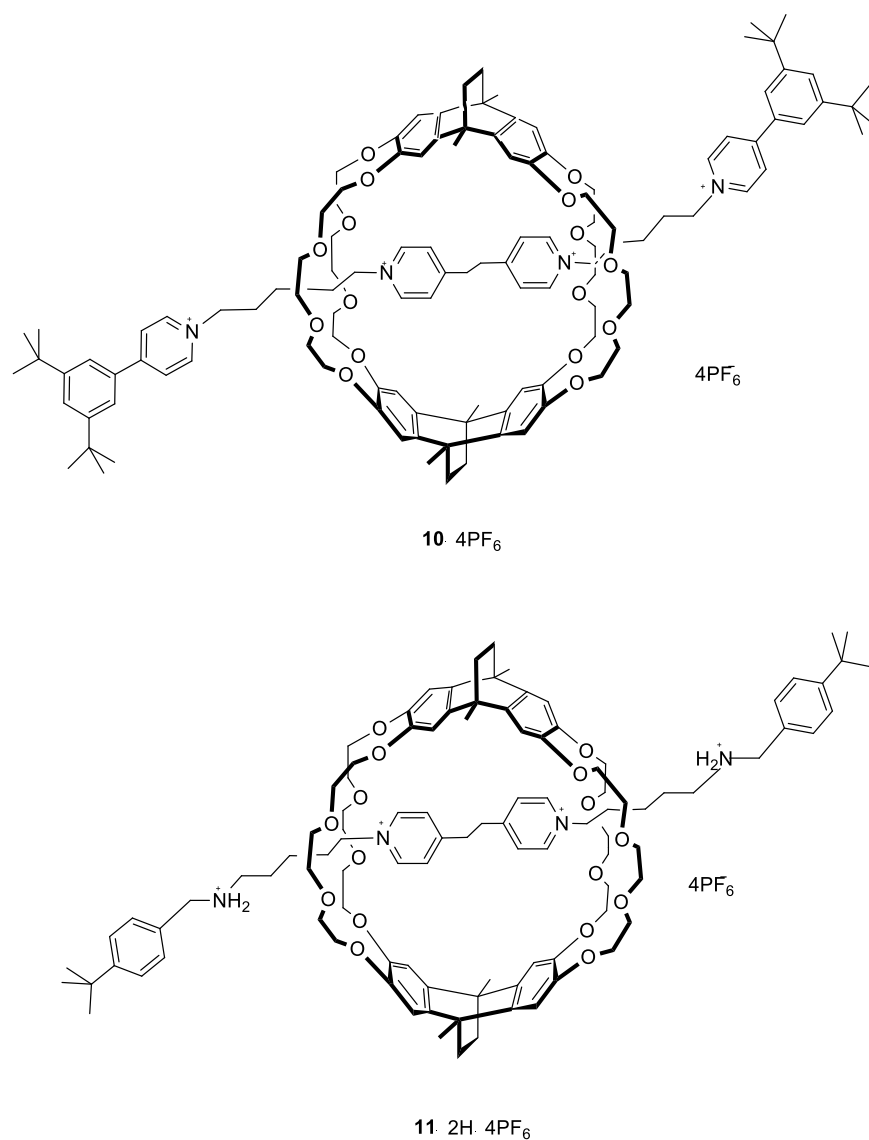
### Scheme 1

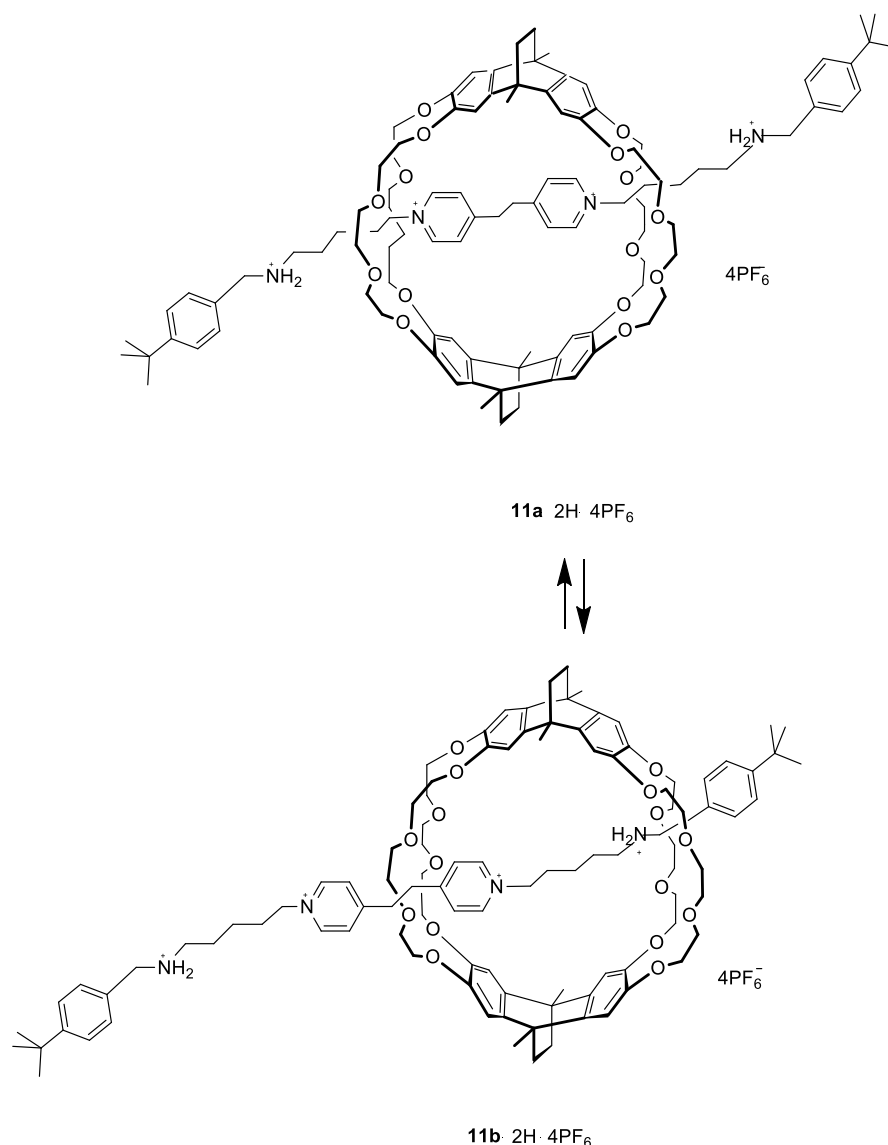
The molecular shuttle **9**<sup>2+</sup> similarly acting as **8**<sup>2+</sup> contains a 9-methylantracenylyl group instead of the 3,5-bis(trifluoromethyl)benzyl group; this shuttling can be monitored by a change in fluorescence intensity.<sup>50</sup>



Scheme 2

In the study of rotaxanes with large macrocyclic rings,<sup>51,52</sup> the [2]rotaxanes **10**·4PF<sub>6</sub> and **11**·2H·4PF<sub>6</sub> have been synthesized using threading-followed-by-stoppering procedure. In **10**·4PF<sub>6</sub> the thread contains four pyridinium stations and in **11**·2H·4PF<sub>6</sub> the thread contains two dialkylammonium and two pyridinium stations (Scheme 3).<sup>53</sup>





Scheme 3

The  $^1\text{H}$ NMR results have shown that rotaxane  $\mathbf{11}\cdot 2\text{H}\cdot 4\text{PF}_6$  in  $\text{CD}_3\text{NO}_2$  is a 1:4 mixture of translational isomers **a** and **b**. It was found that the ratio of translational isomers **a** and **b** depends on the solvent polarity. In polar solvents, such as  $\text{CD}_3\text{CN}$ , the  $\pi$ -stacking is favored over hydrogen-bonding interactions, and the symmetrical translational isomer **a** exists exclusively. However, in  $\text{CD}_3\text{NO}_2$ , which is less disruptive of hydrogen bonds than  $\text{CD}_3\text{CN}$ , the unsymmetrical isomer **b** is predominant. Conversion **a**→**b** may also take place upon treatment with TFA; the process is reversible, addition of  $\text{Et}_3\text{N}$  leads to the inverse, *i.e.* **b**→**a** process.

The ratio of translational isomers **a** and **b** is also influenced by the kind of counterions. When the  $\text{CD}_3\text{NO}_2$  solution of  $\mathbf{11}\cdot 2\text{H}\cdot 4\text{PF}_6$  was treated with  $\text{Bu}_4\text{NCl}$ , the ring was shifted to the centre of the rotaxane, to give  $\mathbf{11a}\cdot 2\text{H}\cdot 4\text{Cl}$ . The subsequent addition of  $\text{AgPF}_6$  in order to remove the chloride anions from the solution affords the original 1:4 mixture of **a** and **b**, *i.e.*  $\mathbf{11b}\cdot 2\text{H}\cdot 4\text{PF}_6$  is formed and the translational isomer **b** prevails.

The obtained results show that the above molecular switch can be controlled by three ways: by changing solvent polarity, by addition acid/basic reagents (TFA/ $\text{Et}_3\text{N}$ ) or by exchange of counterions ( $\text{PF}_6^- \rightarrow \text{Cl}^-$ ).

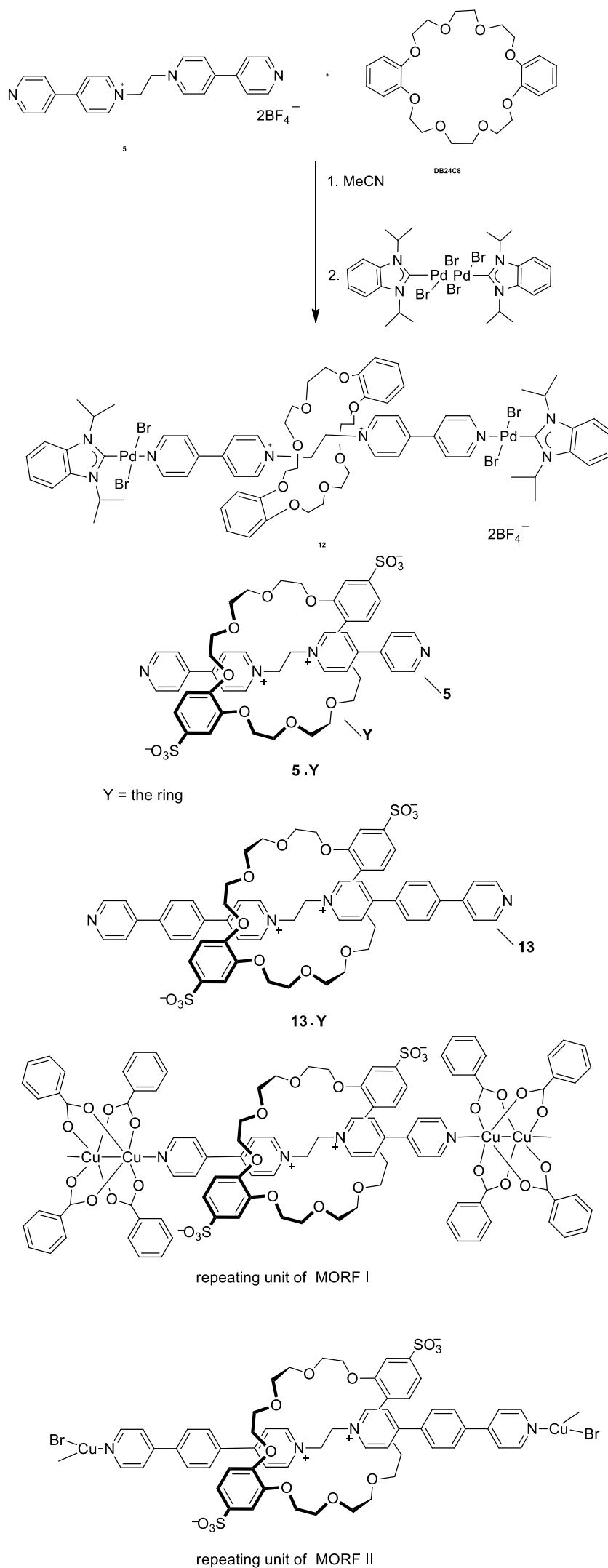
## 2.2. Rotaxanes with stoppers incorporating metal complexes

Recently *N*-heterocyclic carbenes have been widely investigated; they are used in construction of three-dimensional structures<sup>54,55</sup> and of metalla-macrocycles.<sup>56,57</sup>

As an example of rotaxanes stoppered by palladium *N*-heterocyclic carbene may serve [2]rotaxane **12**, obtained from bis(dipyridiniumyl)ethane **5** and dibenzo[24]crown-8 (DB24C8) in the presence of dimeric Pd(II)benzimidazol-2-ylidene complex  $[\text{PdBr}_2(i\text{-Pr}_2\text{-bimy})]_2$ .<sup>58,59</sup>

The X-ray analysis of **12** shows a crystallographically imposed inversion symmetry; the  $\pi$ - $\pi$  stacking interactions between the electron deficient pyridinium units of the thread and electron-

rich catechol units of the ring result in the bending of the ring into the S-shape conformation (Scheme 4).



Scheme 4

It was found that metal-organic rotaxane frameworks MORFs (*i.e.* MOFs containing [2]rotaxane as one of the organic linkers) may be constructed without the need for independent counterions. The elimination of counterions in MORFs is possible by combining neutral linkers with neutral metal nodes.

As examples may serve the neutral [2]pseudorotaxanes composed of bis(dipyridiniumyl)ethane as a thread and of disulfonated dibenzo-24 crown-8 ether **Y** as a ring. When they are combined with neutral metallic units such as Cu(II) benzoate paddlewheel or Cu(I)Br, the linear coordination polymers are formed; they are neutral MORFs.<sup>60</sup>

The interaction of a dicationic thread with a dianionic ring not only affords a neutral linker, but strongly enhances the binding between the thread and the ring due to electrostatic attraction of pyridinium units with sulfonate groups. Such structure connected with a neutral metal complex able to propagate a polymeric framework yields an overall neutral MORF.

Two [2]pseudorotaxane ligands containing dications **5** and **13** as threads and dianion **Y** as a ring were obtained; they are **5·Y** and **13·Y**, respectively; the thread **13** is an extended version of **5**, differing from **5** by the presence of two inserted *p*-phenylene units.

Crystals of [2]pseudorotaxane {[**5·Y**](MeOH)<sub>7</sub>(DMF)} were grown from a mixture of **5**[BF<sub>4</sub>]<sub>2</sub> and [Me<sub>4</sub>N]<sub>2</sub>[**Y**] in MeOH/DMF. In **5·Y** the electron-deficient pyridinium units of **5** are  $\pi$ -stacked with the electron-rich aromatic units of **Y**; the resulting charge transfer absorption is visible by the appearance of the yellow color. The obtained [2]pseudorotaxane can act as a neutral linker for binding metal units to give MORFs.

For preparation of MORF, the Cu paddlewheel, *i.e.* copper(II) benzoate [Cu<sub>2</sub>(BzO)<sub>4</sub>] was used as a neutral metal node able for linear propagation.<sup>61</sup> Combining **5**[BF<sub>4</sub>]<sub>2</sub> with [Me<sub>4</sub>N]<sub>2</sub>[**Y**] and [Cu<sub>2</sub>(BzO)<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>] in MeOH/DMF afforded turquoise crystals of {[Cu<sub>2</sub>(BzO)<sub>4</sub>(**5·Y**)](MeOH)<sub>2</sub>(DMF)}<sub>x</sub>, *i.e.* MORF I. In this MORF the terminal pyridine groups of pseudorotaxane **5·Y** bind to the two coordination sites of the Cu(II) paddlewheel. The linear coordination polymer MORF I so formed is overall neutral.

In {[Cu<sub>2</sub>(BzO)<sub>4</sub>(**5·Y**)]}<sub>x</sub> the sulfonate groups of **Y** are localized close to one of the benzene rings of the Cu(II) paddlewheel; this close neighborhood may result in hydrogen bonding which would disturb the arrangement of the whole system. In order to overcome this inconvenience, the thread **13**, longer than **5** was used to prepare MORF II. Such experiment combining **13**[BF<sub>4</sub>]<sub>2</sub> with [Me<sub>4</sub>N]<sub>2</sub>[**Y**] and CuBr in MeOH/H<sub>2</sub>O afforded yellow crystals of {[CuBr(**13·Y**)](H<sub>2</sub>O)<sub>10</sub>}<sub>x</sub>, *i.e.* MORF II. In this MORF the terminal pyridine groups of pseudorotaxane **13·Y** bind to the two trigonal planar Cu(I) centres.

The above results are promising for the preparation of robust materials with interlocked components.

### 3. Rotaxanes formed by anion templation

In the study of rotaxanes the anion recognition attracts today a growing attention due to the crucial role of anions in biological and environmental processes, therefore many reports concerning this topic appear.<sup>62,63</sup> It is important that for selective recognition of guests the rotaxanes should contain an appropriate reporter group providing their electrochemical or optical response.

The anion templation method, widely used for the synthesis of rotaxanes, will be described below. Syntheses of selected rotaxanes, performed by this method are divided here into three classes:

- 1) syntheses of rotaxanes with rings built by Grubbs RCM procedure,
- 2) syntheses of rotaxanes with rings built by condensation reactions, and
- 3) syntheses of rotaxanes with previously prepared rings.

### 3.1. Rotaxanes with rings built by Grubbs RCM procedure

In the Grubbs ring closing metathesis (RCM) procedure the divinyl precursor of the ring of rotaxane is cyclized with the use of Grubbs second generation catalyst. Three examples A-C of this method are shown below.

#### Example A

The redox-active rotaxane **14**·PF<sub>6</sub> containing two ferrocene derivative units appended to the thread was synthesized with the aim to investigate its electrochemical sensing of anions in solution, having in view the redox-active properties of ferrocenes for the detection of anions.<sup>64,65</sup> In this rotaxane the ferrocene pentaphenyl derivative units serve as redox-active species, and moreover they are stoppers.

The rotaxane **14**·PF<sub>6</sub> was synthesized using the chloride template clipping, which was performed by treatment of **15**·Cl with bis-vinyl isophthalamide **16** serving as a precursor of the ring. This RCM process was carried out in the presence of Grubbs second generation catalyst. The formed rotaxane **14**·Cl upon anion exchange was converted into **14**·PF<sub>6</sub>.<sup>66</sup>

The results of X-ray analysis of **14**·Cl and **14**·PF<sub>6</sub> have shown that:

In the structure of **14**·Cl the chloride anion is situated in the cavity of the rotaxane, and is held in place by hydrogen bonding to the pyridinium and isophthalamide clefts. Between the pyridinium unit and hydroquinone rings the  $\pi$ - $\pi$  stacking exists.

In the structure of **14**·PF<sub>6</sub>, formed after the removal of the chloride template from the rotaxane cavity, the PF<sub>6</sub><sup>-</sup> counteranion is situated outside the rotaxane cavity and does not interact with the rotaxane structure. The anion exchange (Cl<sup>-</sup> → PF<sub>6</sub><sup>-</sup>) did not influence the  $\pi$ - $\pi$  stacking between the pyridinium unit and hydroquinone rings, this  $\pi$ - $\pi$  stacking still remains in **14**·PF<sub>6</sub>.

The anion recognition properties of rotaxane **14**·PF<sub>6</sub> were examined by <sup>1</sup>HNMR titration experiments with tetrabutylammonium (TBA) salts of Cl<sup>-</sup>, H<sub>2</sub>PO<sub>4</sub><sup>-</sup>, PhCOO<sup>-</sup>, HSO<sub>4</sub><sup>-</sup> and NO<sub>3</sub><sup>-</sup> anions. It was shown that upon removal of the chloride anion template, the rotaxane exhibits not only enhanced binding of chloride, but also the higher selectivity for chloride over the more basic oxoanions in the competitive solvent system CDCl<sub>3</sub>/CD<sub>3</sub>OD (1:1). This behavior results from the fact that only chloride can bind inside the cavity of rotaxane; polyatomic oxoanions are too large for such penetration and therefore they are situated at the periphery of the cavity.

The investigation of electrochemical anion recognition by rotaxane **14**·PF<sub>6</sub> has shown that it gave a characteristic electrochemical response with chloride in contrast to oxoanions H<sub>2</sub>PO<sub>4</sub><sup>-</sup>, PhCOO<sup>-</sup>, HSO<sub>4</sub><sup>-</sup> and NO<sub>3</sub><sup>-</sup>; for addition of chloride to rotaxane **14**·PF<sub>6</sub> the maximum cathodic shift of the pentaphenylferrocene/pentaphenylferrocenium<sup>+</sup> Pf/Pf<sup>+</sup> redox couple occurred at one equivalent of Cl<sup>-</sup>, whereas for other anions the maximum shift was observed at more equivalents of anions added (Scheme 5). This fact results from the strong binding of chloride anion inside the interlocked cavity of rotaxane.<sup>66</sup>

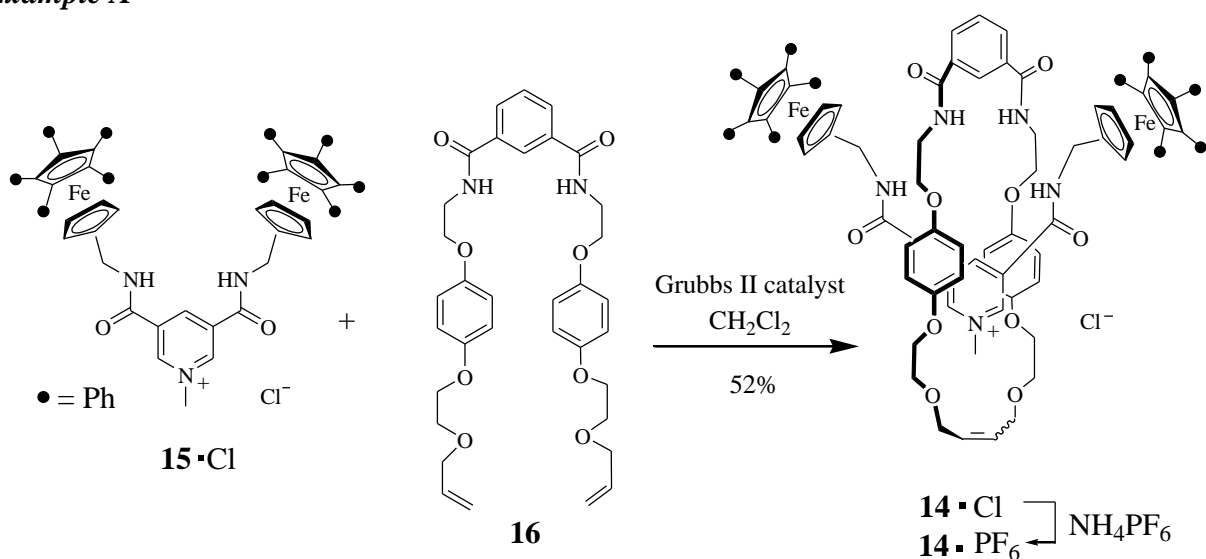
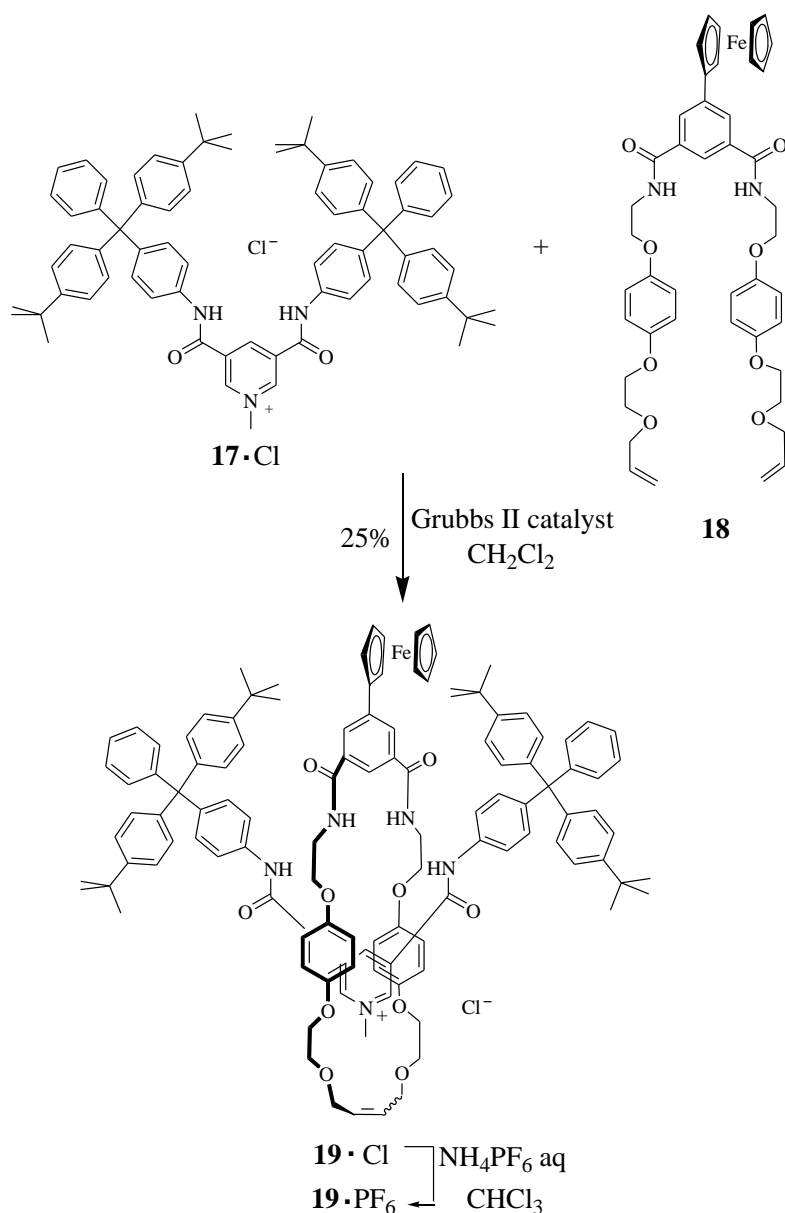
#### Example B

Another example of rotaxane formation by chloride anion templation and RCM is the synthesis of rotaxane **19**·PF<sub>6</sub> bearing ferrocene moiety on the ring. The synthesis of **19**·Cl involves the reaction of the thread **17**·Cl with **18**, being a precursor of the ring; the process is carried out in the presence of Grubbs II catalyst in CH<sub>2</sub>Cl<sub>2</sub>. The ion exchange by treatment of **19**·Cl with NH<sub>4</sub>PF<sub>6</sub> afforded the desired rotaxane **19**·PF<sub>6</sub>.<sup>67</sup>

The <sup>1</sup>HNMR titration results have shown that **19**·PF<sub>6</sub> is selective for chloride anion over more basic oxoanions H<sub>2</sub>PO<sub>4</sub><sup>-</sup>, PhCOO<sup>-</sup> and HSO<sub>4</sub><sup>-</sup>. Very strong binding was found for **19**·PF<sub>6</sub> and TBACl in CD<sub>3</sub>CN, ( $K > 10^4$  M<sup>-1</sup>).

It was observed that **19**·PF<sub>6</sub> displays electrochemical recognition of Cl<sup>-</sup>; it was evidenced by a maximum cathodic shift response of the ferrocene/ferrocenium<sup>+</sup> Fc/Fc<sup>+</sup> redox couple observed at equimolar concentrations of rotaxane and Cl<sup>-</sup> ion, while in the case of oxoanions an excess of their equivalents is necessary.

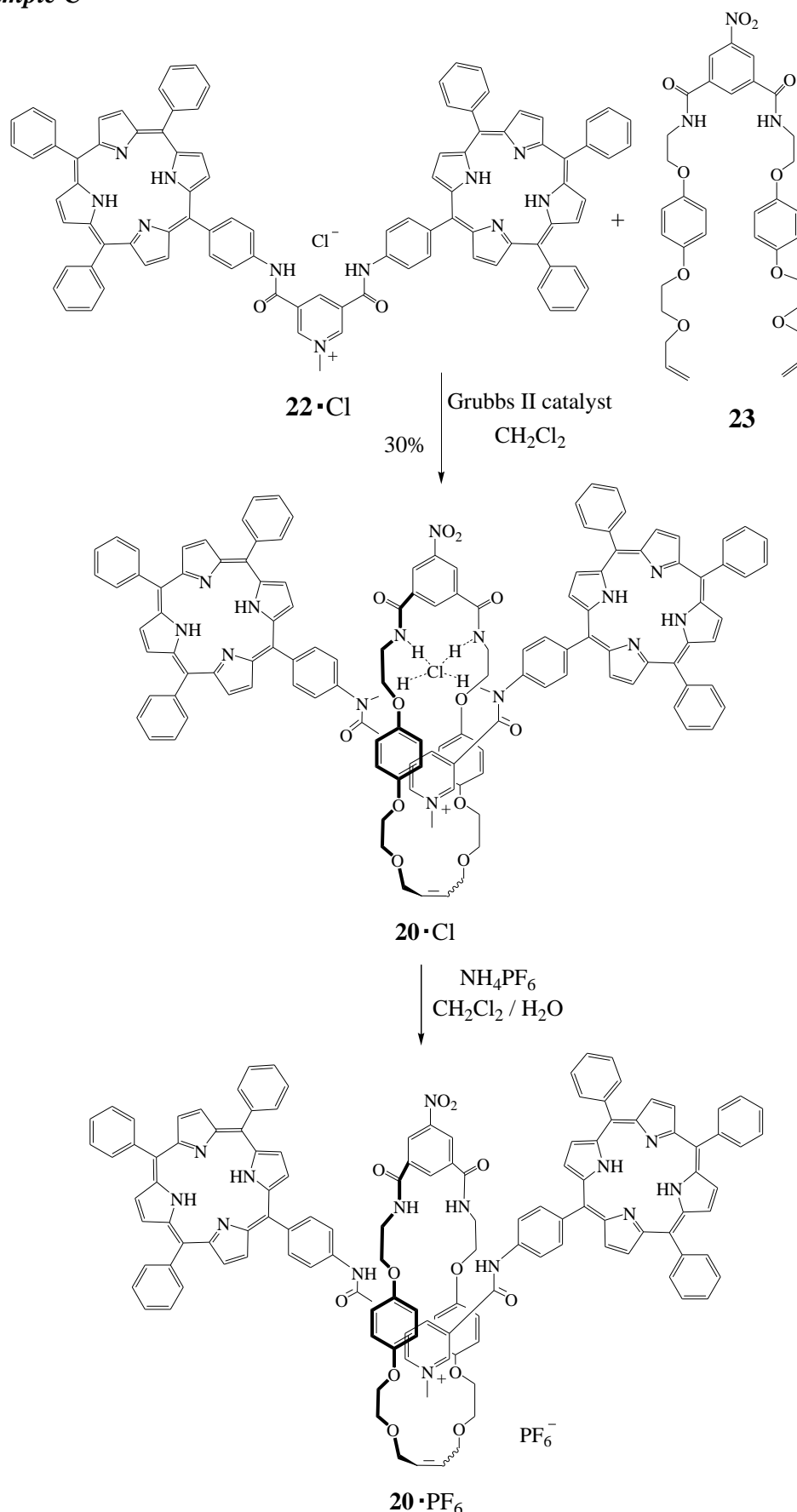


**Example A****Example B****Scheme 5****Example C**

Two porphyrin-functionalized rotaxanes **20**·PF<sub>6</sub><sup>-</sup> and **21**·PF<sub>6</sub><sup>-</sup> have been synthesized for investigation of their anion recognition abilities (Scheme 6).<sup>68</sup> One should point out that porphyrins are interesting as potential reporter species due to their redox and optical properties.<sup>69,70</sup>

For the synthesis of rotaxane **20**·PF<sub>6</sub>, in which two porphyrin units are appended to the thread, the compound **22**·Cl was treated with **23** as a bis-vinyl precursor of the ring in the presence of Grubbs second generation catalyst in CH<sub>2</sub>Cl<sub>2</sub>. The obtained rotaxane **20**·Cl upon ion exchange afforded rotaxane **20**·PF<sub>6</sub>. In both rotaxanes porphyrin units serve as large stoppers.

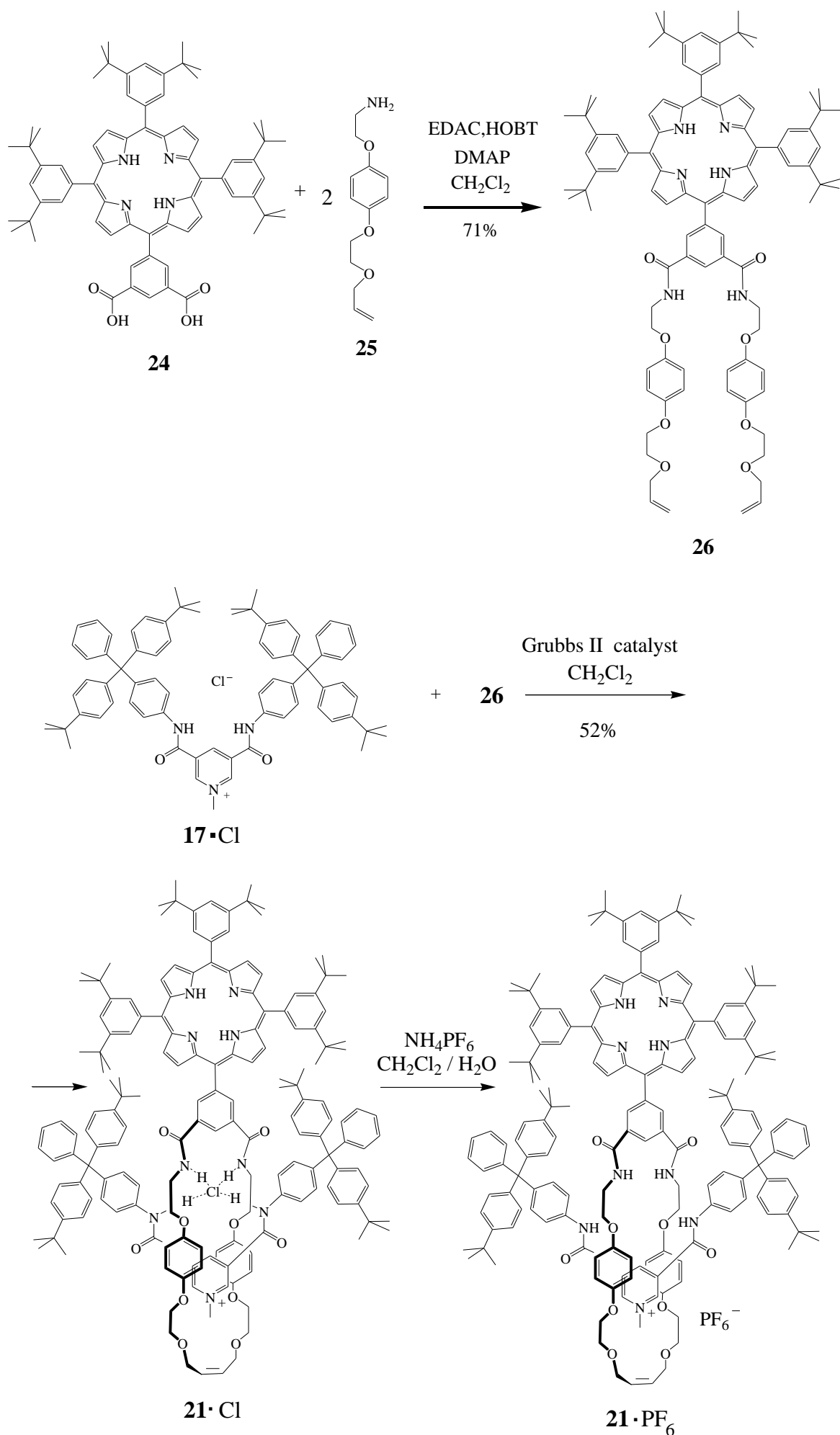
### Example C



**Scheme 6**

Synthesis of rotaxane **21**·PF<sub>6</sub>, in which one porphyrin unit is appended to the ring begins with the treatment of porphyrin **24** with amine **25** leading to the ring precursor **26**. The reaction of the thread **17**·Cl with **26** yielded rotaxane **21**·Cl, converted by ion exchange into **21**·PF<sub>6</sub> (Scheme 7).

It was established that rotaxanes **20**·PF<sub>6</sub><sup>-</sup> and **21**·PF<sub>6</sub><sup>-</sup> show high binding selectivities to Cl<sup>-</sup> over Br<sup>-</sup> and NO<sub>3</sub><sup>-</sup> anions; moreover **21**·PF<sub>6</sub><sup>-</sup> binds Cl<sup>-</sup> and Br<sup>-</sup> anions selectively over more basic H<sub>2</sub>PO<sub>4</sub><sup>-</sup> and AcO<sup>-</sup> anions. Despite these properties the rotaxanes **20**·PF<sub>6</sub><sup>-</sup> and **21**·PF<sub>6</sub><sup>-</sup> are ineffective as optical anion sensors, but are capable for detection of Cl<sup>-</sup> anions electrochemically *via* cathodic shifts in the porphyrin P/P<sup>+</sup> redox couples.



Scheme 7

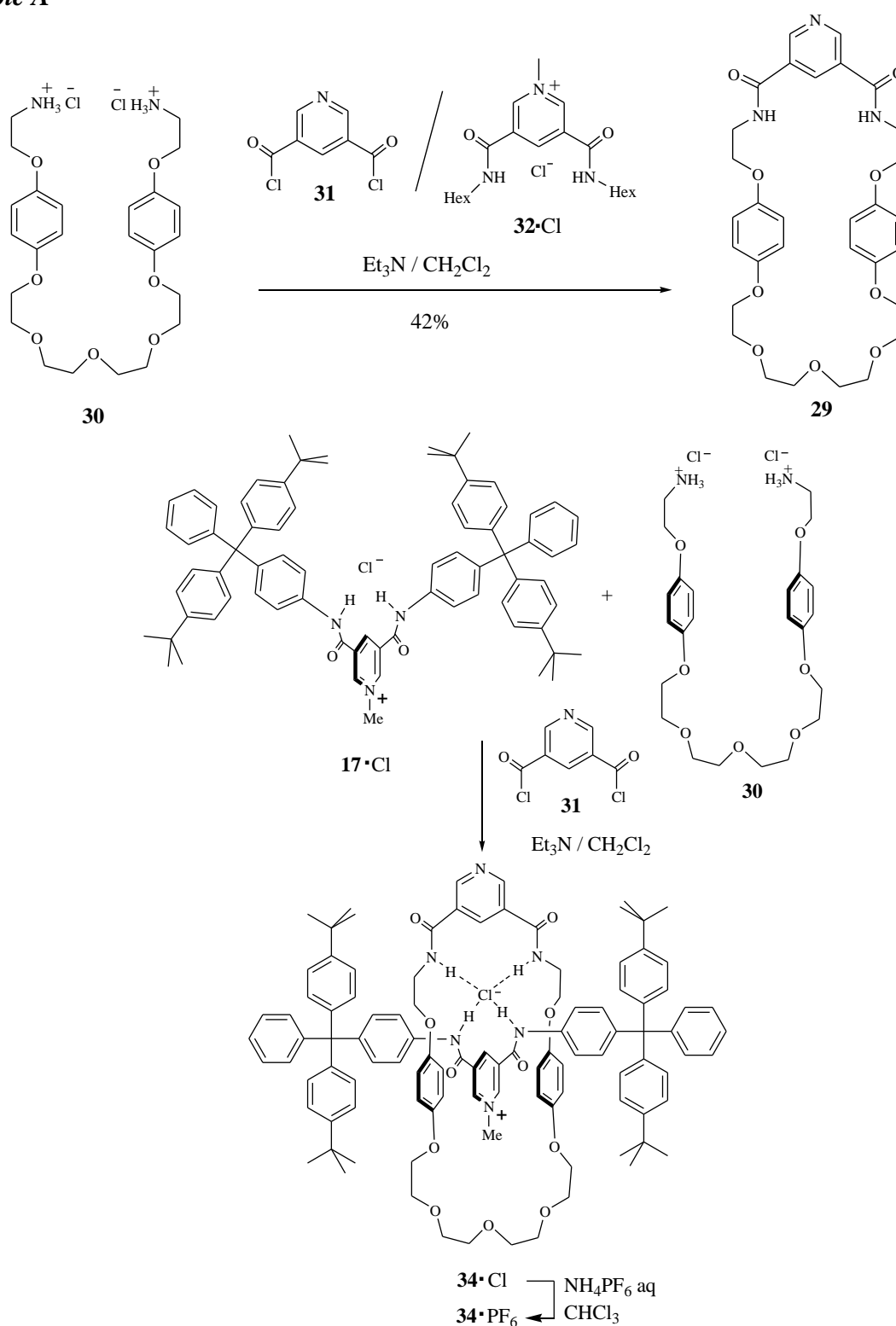
### 3.2. Rotaxanes with rings built by condensation reactions

In the synthesis of rotaxanes by chloride anion templation, an alternative method to that performed by RCM procedure, may be used. In this approach a diamine serving as a precursor of the ring undergoes cyclization by condensation reaction. Below two examples A and B of this method are presented.

#### Example A

The synthesis of [2]rotaxane composed of the thread **17**·Cl bearing pyridinium group and of the ring **29** containing crown ether unit was performed. The ring **29** was obtained by condensation of diamine **30** with pyridine **31** in CH<sub>2</sub>Cl<sub>2</sub>; it was found that the yield of this process increased when the reaction was carried out in the presence of pyridinium derivative **32**·Cl. This observation indicates the existence of Cl<sup>-</sup> anion templation and a  $\pi$ - $\pi$  stacking between the positively charged electron-deficient pyridinium group of **32**·Cl and the electron rich hydroquinone motifs of **30**, facilitating the cyclization (Scheme 8).

#### Example A



Scheme 8

Having the above result in mind, it was supposed that the replacement of the pyridinium **32**·Cl by pyridinium incorporated into the previously stoppered thread should afford a rotaxane. And indeed, the mixture of stoppered thread **17**·Cl and diamine **30** (in the form of hydrochloride) upon treatment with pyridine **31** yielded rotaxane **34**·Cl (Scheme 8).<sup>71</sup>

In order to assess the ability of rotaxane **34** to bind anions, the removal of the Cl<sup>-</sup> anion from the interlocked cavity was made. For this purpose the chloride anion was exchanged for the non-coordinating hexafluorophosphate anion by repeated washing of **34**·Cl solution in chloroform with NH<sub>4</sub>PF<sub>6</sub> aqueous solution to give **34**·PF<sub>6</sub>.

The anion binding properties of the rotaxane **34**·PF<sub>6</sub> were studied by titration with TBA salts of Cl<sup>-</sup>, Br<sup>-</sup>, H<sub>2</sub>PO<sub>4</sub><sup>-</sup> and AcO<sup>-</sup> in CDCl<sub>3</sub>/CD<sub>3</sub>OD (1:1) solution. The results indicate that the interlocked cavity of rotaxane **34**·PF<sub>6</sub> is selective for Cl<sup>-</sup> above oxoanions; it has a size and shape complementary for Cl<sup>-</sup>, while the larger oxoanions cannot penetrate this cavity.

The described experiments show that the obtained interlocked systems are promising for application as anion sensors.

### Example B

Using the above chloride anion templating method, syntheses of [2]rotaxanes able to recognize chloride anion in aqueous media were performed. Reactions of **17**·Cl with diamine **30** (n=1) or **30** (n=0) and appropriate bis(acid chloride) yielded two series of [2]rotaxanes, **33-35** and **36-38**, respectively (Scheme 9).<sup>72</sup>

For example, the reaction of **17**·Cl with diamine **30** (n=1) and 3,5-bis(chlorocarbonyl)pyridine afforded rotaxane **34**·Cl. This compound upon treatment with NH<sub>4</sub>PF<sub>6</sub> was converted into **34**·PF<sub>6</sub> which by methylation afforded the dicationic [2]rotaxane **39**·I·PF<sub>6</sub>. The reaction of **34**·Cl upon ion exchange gave **34**·PF<sub>6</sub> which was methylated and treated with NH<sub>4</sub>PF<sub>6</sub> to give rotaxane **39**·2PF<sub>6</sub> (not shown as a Scheme).

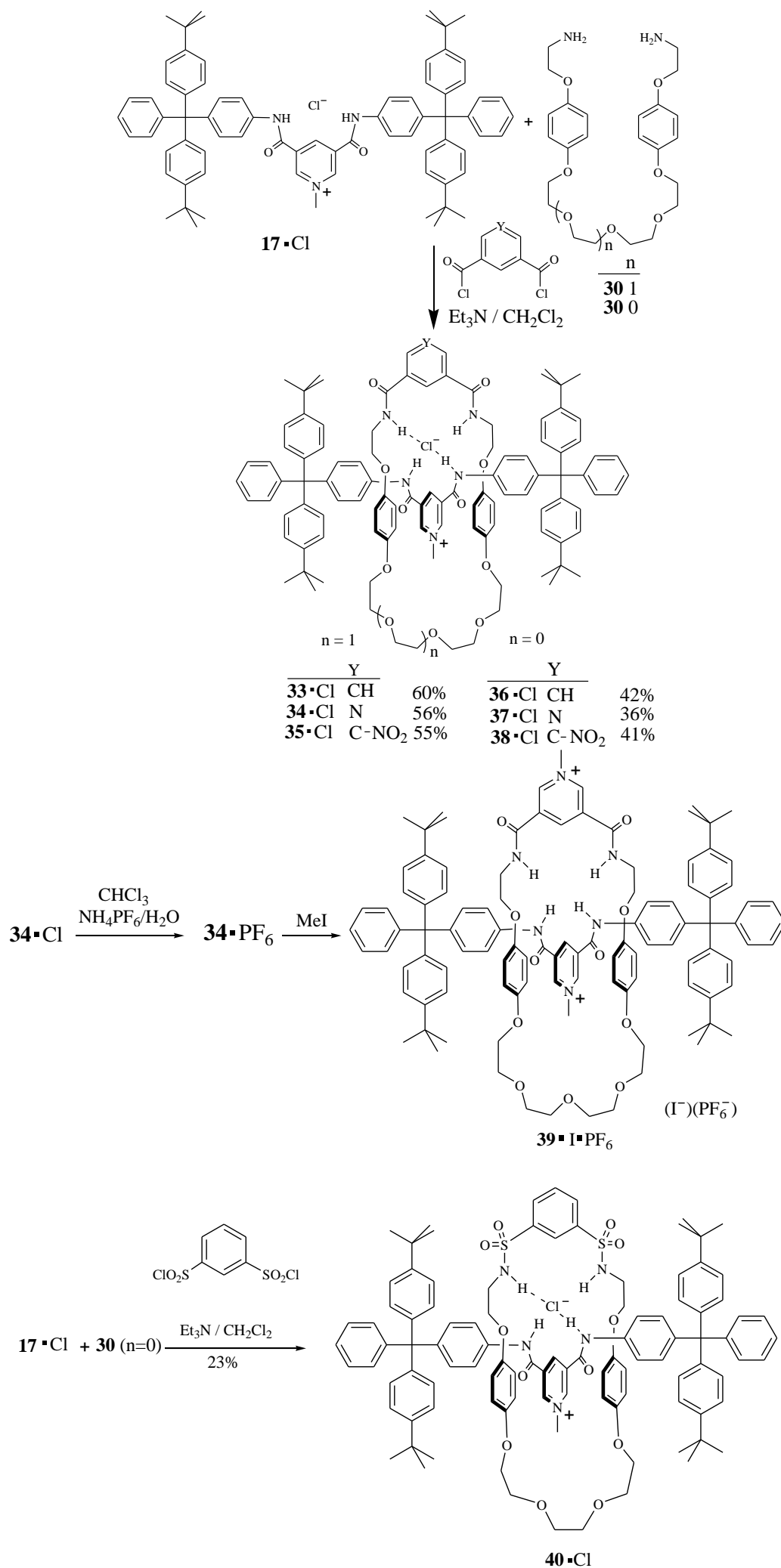
In a similar way **17**·Cl reacted with diamine **30** (n=0) and 1,3-benzenedisulfonyl chloride to give rotaxane **40**·Cl, containing sulfonamide groups; it is the first rotaxane bearing sulfonamide groups.

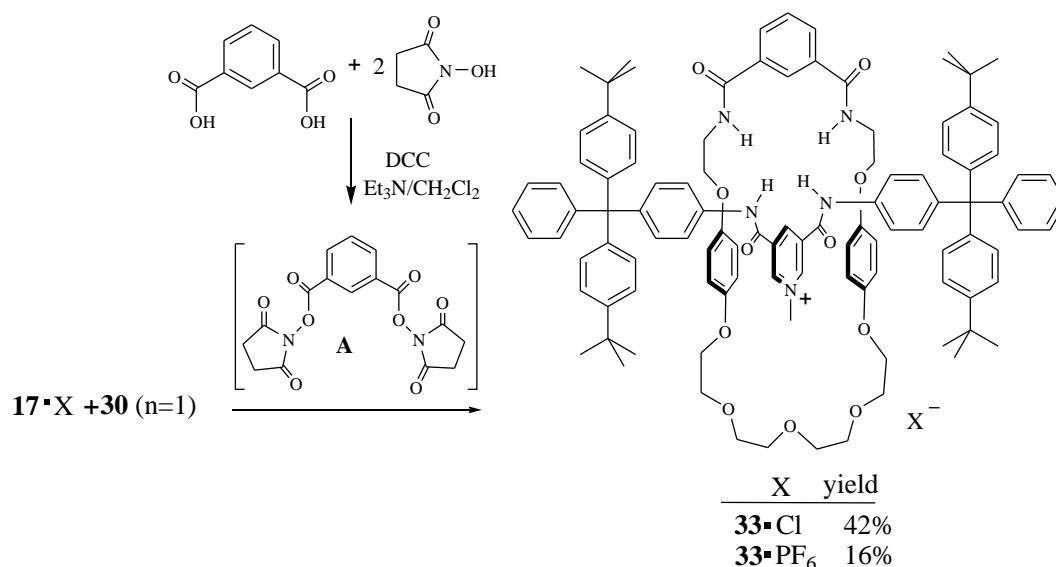
Reaction of **17**·X (X=Cl, PF<sub>6</sub>) with diamine **30** (n=1) and the activated ester **A**, (obtained *in situ* by treatment of isophthalic acid with *N*-hydroxysuccinimide in the presence of DCC) afforded rotaxanes **33**·Cl and **33**·PF<sub>6</sub>. It was observed that in the case of **17**·Cl used as a thread, the yield was higher than in the case of **17**·PF<sub>6</sub>; this fact indicates that chloride as a templating agent considerably enhances the rotaxane synthesis.<sup>72</sup>

For investigation of anion-binding properties of rotaxanes, the exchange of the chloride templating anion for the non-coordinating PF<sub>6</sub><sup>-</sup> was necessary. The anion-binding properties of rotaxanes (**33-38**)·PF<sub>6</sub> were examined by <sup>1</sup>HNMR titration using TBA salts of Cl<sup>-</sup>, H<sub>2</sub>PO<sub>4</sub><sup>-</sup> and AcO<sup>-</sup> anions in CDCl<sub>3</sub>/CD<sub>3</sub>OD (1:1) solution. It was found that rotaxanes (**33-38**)·PF<sub>6</sub> bind Cl<sup>-</sup> anion very strongly ( $K > 10^4 \text{ M}^{-1}$ ).

Therefore similar anion-binding titrations were performed in the presence of 10% water; the calculation of association constants shows that the monocationic rotaxanes (**33-38**)·PF<sub>6</sub> bind chloride anion strongly even in this competitive aqueous solvent mixture, while the binding of oxoanions H<sub>2</sub>PO<sub>4</sub><sup>-</sup> and OAc<sup>-</sup> is only weak, despite the greater basicity of these anions.

## Example B





Scheme 9

It has been established that the Cl<sup>-</sup> binding of rotaxanes can be increased by the attachment of electron withdrawing substituents to the isophthalamide unit. This was confirmed by observation that rotaxanes containing the electron-withdrawing pyridine and nitroisophthalamide units, **34**•PF<sub>6</sub> and **35**•PF<sub>6</sub>, respectively, show an enhanced affinity for Cl<sup>-</sup>. This fact is due to the increased acidity of amide protons, and as a result, their hydrogen-bonding ability to the anions.

It was found that the dicationic [2]rotaxane **39**•I•PF<sub>6</sub> binds Cl<sup>-</sup> with  $K_a$  equal to 3000 M<sup>-1</sup> in the 10% water solvent system. This high  $K_a$  value results from the increased charge electrostatics, and, as a consequence, the higher acidity of the cavity protons of rotaxane. Therefore, the anion-binding investigation was made in a solvent system containing a higher, 35% percentage of water.

The orthogonal cavity disposition of the two 3,5-bisamide-substituted pyridinium motifs of the dicationic rotaxane **39**•2PF<sub>6</sub> enhances the ability to selectively bind chloride even in 35% water, while no binding of oxoanions acetate or dihydrogen phosphate was observed, since they are too large to penetrate into the rotaxane pocket.

It is noteworthy that the strong binding of chloride anion by investigated rotaxanes is due to nearly total encapsulation of chloride in the isophthalamide cleft of the ring and due to the interaction with binding groups of the thread.

### 3.3. Rotaxanes with previously prepared rings

Two examples *A* and *B* for synthesis of rotaxanes, in which the rings were previously prepared, will be described here. Example *A* concerns the synthesis of products by slippage, with the use of anion templation, and the subsequent conversion of these structures into rotaxanes. Example *B* shows the procedure, which also may be presented here; it involves the use of the chloride-palladium coordination bond as a rotaxane-forming template.

#### Example A

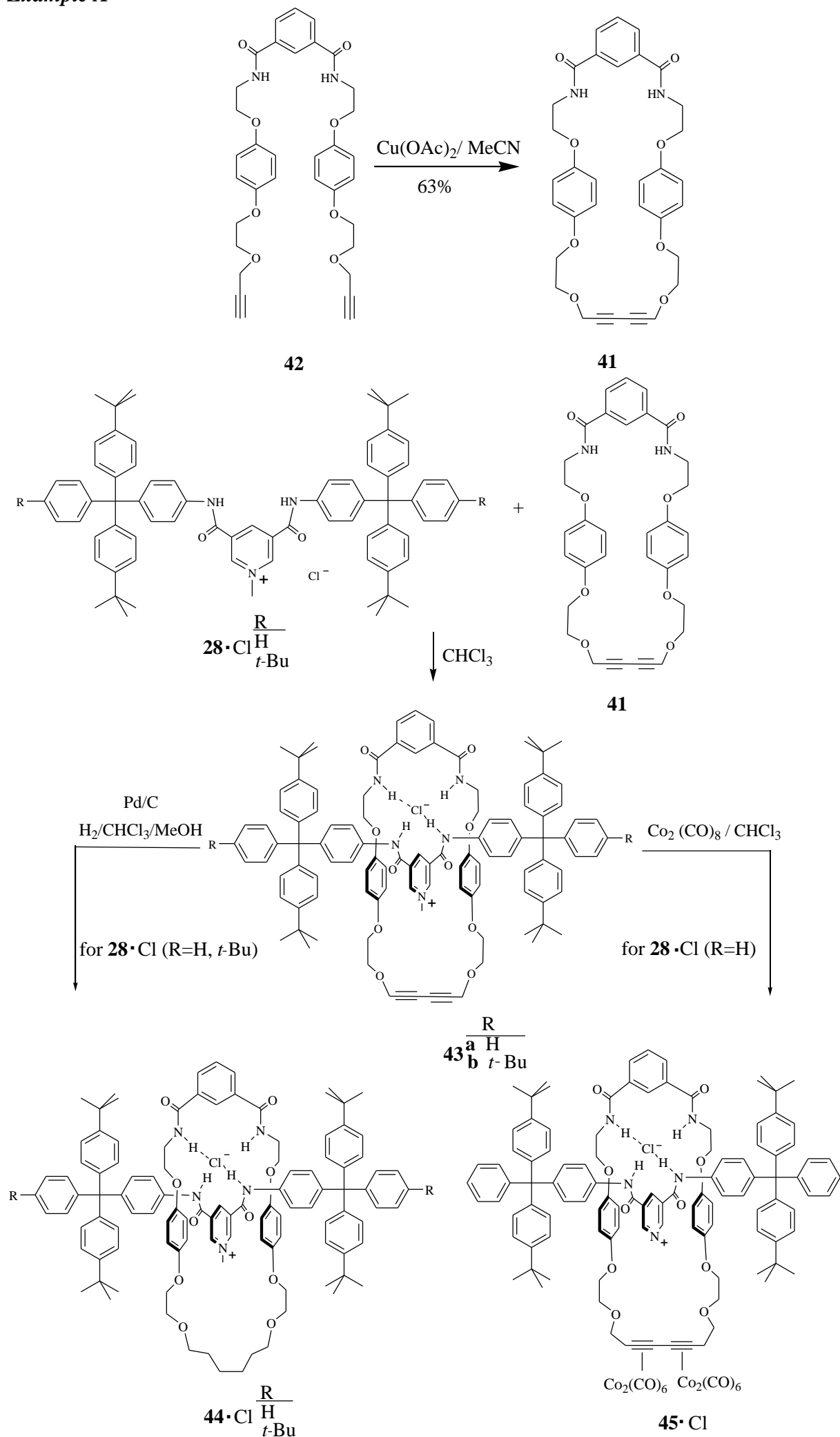
Rotaxanes may be obtained using various methods, such as stoppering,<sup>73,74</sup> or slipping;<sup>63,71</sup> however, the slippage, *i.e.* slipping of the ring over one of the stoppers is not so widely investigated. Below the formation of rotaxanes by using slippage and anion templation is described.

Slippage usually involves heating the thread and ring in order to overcome the energy barrier to slippage  $\Delta G_{on}$ . The resulting rotaxane structure can be kinetically trapped by cooling the equilibrated mixture to room temperature; in this process the barrier to slippage off ( $\Delta G_{off}$ ) cannot be overcome.<sup>75</sup>

The first examples of using slippage and anion templation to assemble rotaxanes, and investigate the role of the templating anion in the slippage process by kinetic methods, have been reported.<sup>76</sup> In these experiments the ring **41** was obtained from **42** by Eglinton coupling of the terminal alkyne groups with copper(II) acetate. The ring **41** has an isophthalamide anion binding

cavity and contains electron rich hydroquinone units for  $\pi$ - $\pi$  stacking interactions with the electron-deficient pyridinium unit of the thread (Scheme 10).

**Example A**



**Scheme 10**



It was found that the terphenyl stoppered threads **28**·Cl (R = H, *t*-Bu) form by equilibration with **41** in the presence of an anion template (here chloride), *via* slippage, the structures **43a,b**, which may be converted into rotaxanes by using two strategies: hydrogenation or complexation with cobalt carbonyl.

- Hydrogenation of the diyne group with the use of palladium on carbon under a hydrogen atmosphere in the presence of methanol affords rotaxanes **44**·Cl (R=H) and **44**·Cl (R=*t*-Bu).
- Complexation of the diyne group with cobalt carbonyl yields the rotaxane **45**·Cl.

### Example B

In the following experiment the synthesis of rotaxane is templated by formation of the anion-palladium coordination bond. It was also observed that chloride anion may induce shuttling of a rotaxane. One should point out that the use of anions to induce shuttling in rotaxanes<sup>77</sup> has not been so widely studied as the use of other stimuli; especially the ability of halides to form strong coordination bonds with transition metals up to now is rather seldom exploited. Below also the chloride-switchable molecular shuttle is described.

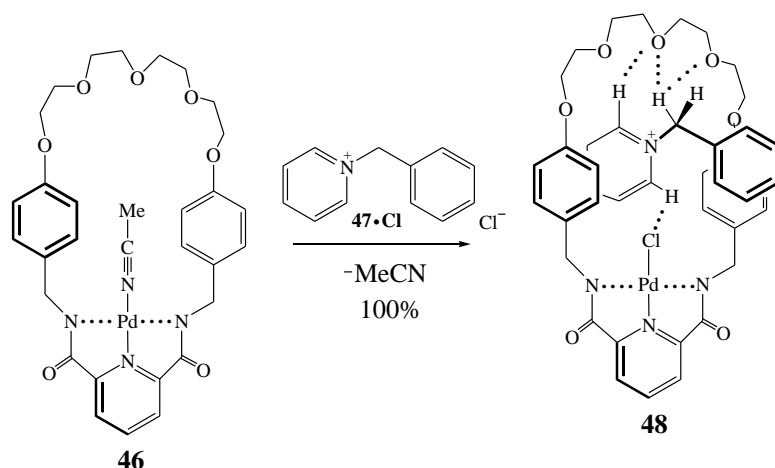
It was found that the displacement of the acetonitrile ligand from the complex **46** by the chloride ion of benzylpyridinium chloride **47**·Cl resulted in the encapsulation of the cationic **47**<sup>+</sup> by the anionic PdCl-coordinated ring to give pseudorotaxane **48**.<sup>78</sup> It is noteworthy that the chloride anion plays a crucial role in threading; this observation was confirmed by the fact that the use of **47**·PF<sub>6</sub> did not result in threading. The above described result is promising for design of anion selective triggers.

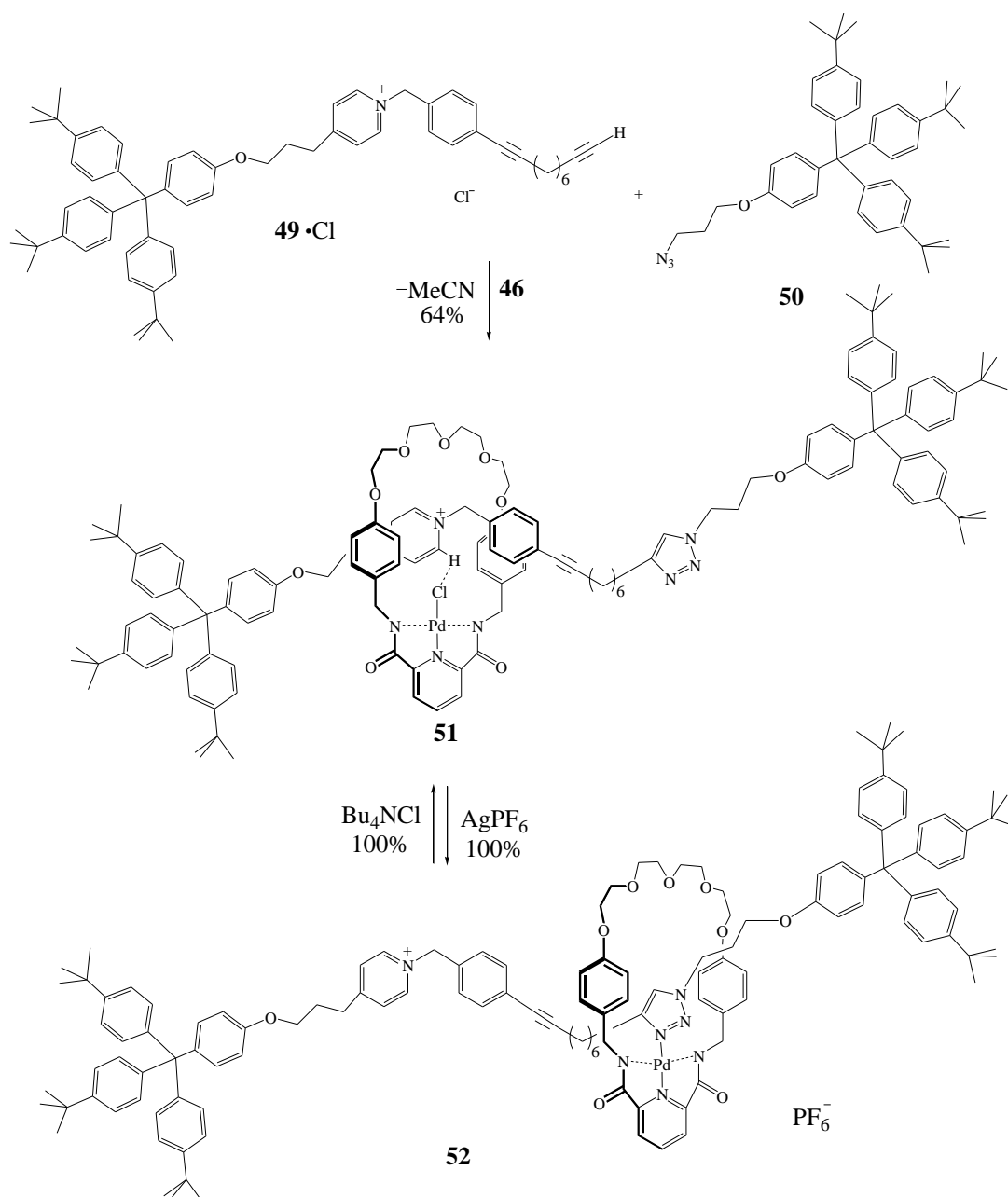
For investigation of chloride-switchable molecular shuttle, first the click reaction of **49**·Cl having the terminal alkynyl group with azide **50** and with complex **46** was made. In the formed rotaxane **51** the ring encircles the pyridinium station, and Cl<sup>-</sup> anion is a coordinating ligand.

In order to obtain a molecular shuttle, rotaxane **51** was treated with AgPF<sub>6</sub>; this reaction results in the precipitation of AgCl and shift of the ring to the second station, *i.e.* triazole unit; in this process the rotaxane **52** is formed. The triazole unit is now a coordination site, and the coordinating ligand Cl<sup>-</sup> is replaced by the noncoordinating PF<sub>6</sub><sup>-</sup> counterion. The addition of Bu<sub>4</sub>NCl to **52** restores the starting rotaxane **51** (Scheme 11).

One may conclude that the reported formation of the anion-palladium coordination bond may be used as an efficient rotaxane-forming template as well as the basis for a chloride-switchable molecular shuttle and is of interest for construction of sensors and molecular machines.

### Example B





Scheme 11

#### 4. Rotaxane-based molecular machines

Construction of molecular machines is a great challenge on the scientific field; a special attention is paid today to rotaxane-based molecular machines,<sup>79</sup> interesting in the area of novel materials<sup>80,81</sup> and medicine.<sup>82,83</sup>

Rotaxane **53**·2PF<sub>6</sub>, acting as molecular shuttle was synthesized in one-pot reaction from pyridine derivative **54**, dipyridyl dibromide **55** and crown ether **Z**.<sup>84</sup> In rotaxane **53**·2PF<sub>6</sub> the ring can reside either on the central 2,2'-bipyridine station **C** or on one of the two terminal monopyridinium stations **A** or **B** (here the ring residing on **A** is shown) and can shuttle between **A** and **B** by addition of simple reagents such as acid/base or metal ion/metal ion complexing ligand pairs (Scheme 12).

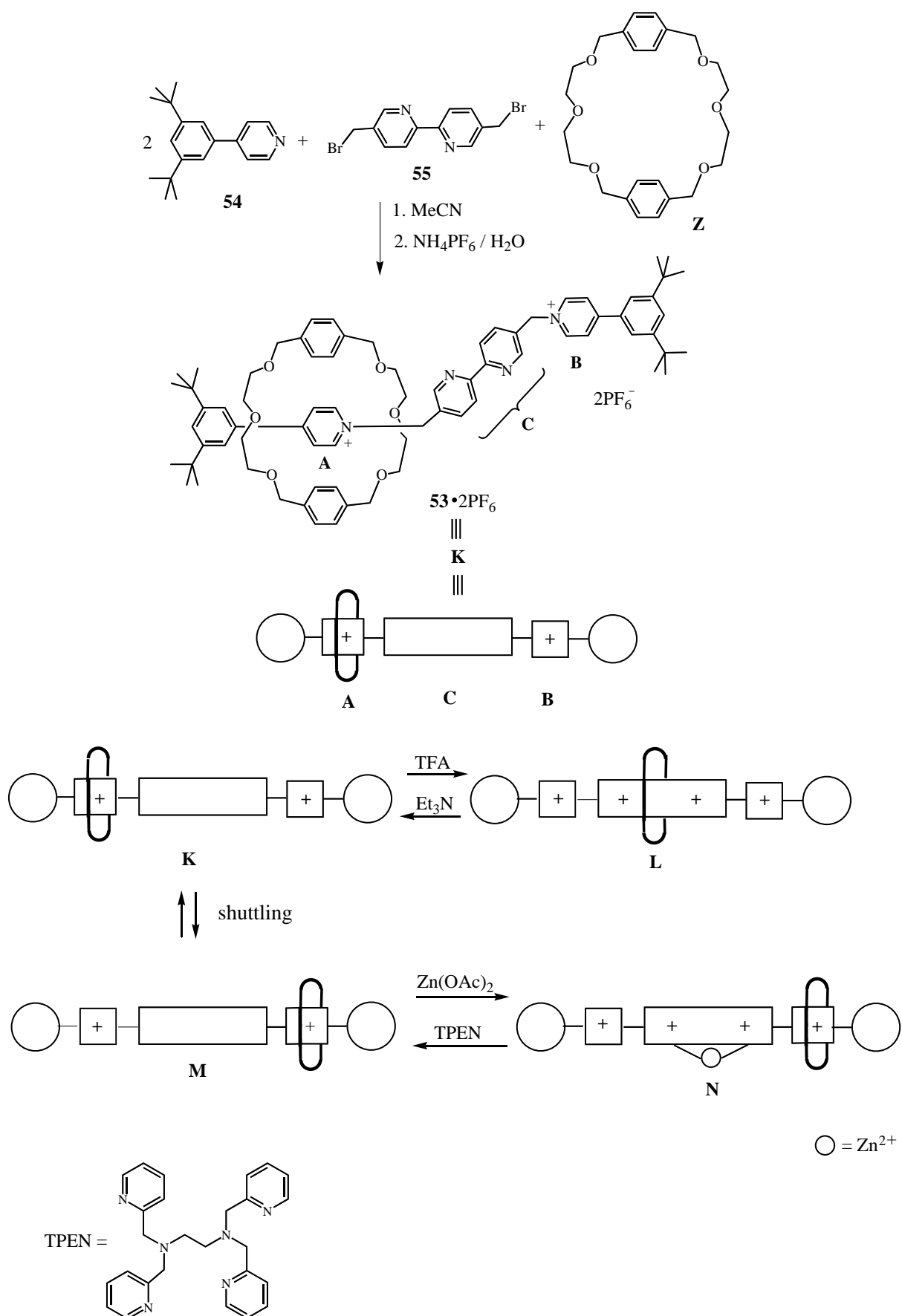
The X-ray crystallographic analysis of **53**·2PF<sub>6</sub> shows that the ring encircles one of the pyridinium units, **A** or **B**, affording rotaxanes **K** or **M**, respectively, which undergo a shuttling. It was observed that upon protonation of **K** the ring encircles stronger the doubly protonated 2,2'-bipyridinium ion **C** than monopyridinium ions **A** or **B** in CD<sub>3</sub>NO<sub>2</sub>, therefore upon addition of TFA to **K**, the ring moves from pyridinium ion **A** (shown here) or **B** to 2,2'-bipyridinium unit **C** to give **L**; this process is reversible, the treatment of **L** with Et<sub>3</sub>N restores **K**.

Since the ring is small, the coordination of a suitable metal ion or its associated ligands to the group **C** can stop the shuttling **K/M** and force the ring to reside on **A** or **B**. For this purpose Zn(OAc)<sub>2</sub> was added to the solution of **53**·2PF<sub>6</sub> in CD<sub>3</sub>NO<sub>2</sub>; as a result the compound **N** was

formed, in which the ring encircles one of the pyridinium stations (here **B**). The coordinated  $\text{Zn}^{2+}$  ion can be removed from the station **C** by addition of tetrapyrrolineethylenediamine (TPEN) which strongly binds  $\text{Zn}^{2+}$ . As a result, the compound **M** is recovered. In this way the shuttling of the ring between two monopyridinium units **A** and **B** was regenerated, *i.e.* the compounds **K** and **M** were restored.<sup>84</sup>

The above system mimics the behavior of a molecular machine in which the molecular motion can be stopped and restarted, and due to presence of three discrete states the design of molecular switches, sensors or logic gates is possible.

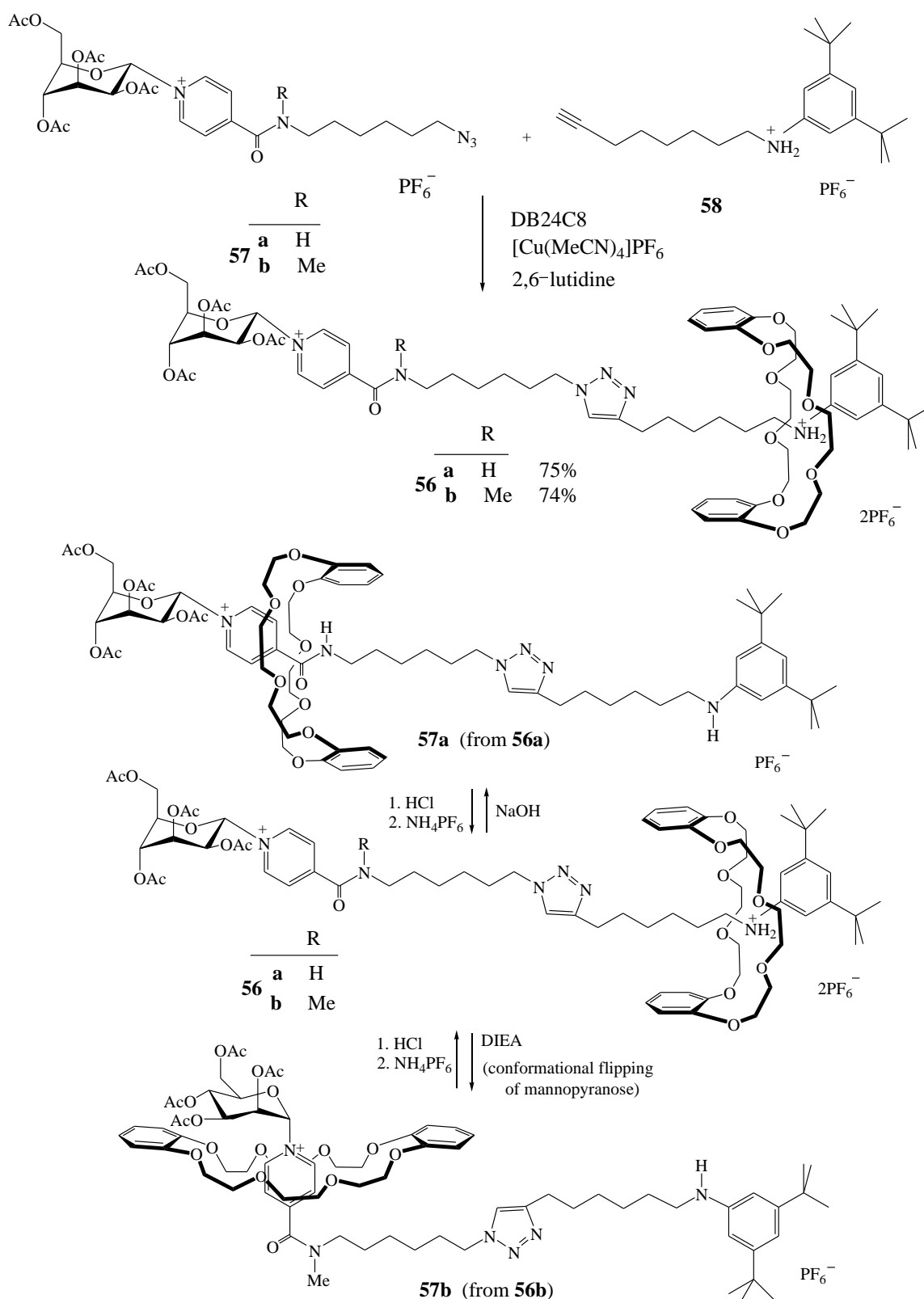
Other molecular machines were selected from investigations on mannosylrotaxanes; below three examples A-C are presented.



Scheme 12

**Example A**

In the study of glycorotaxanes as corresponding molecular muscles<sup>85</sup> and machines,<sup>86</sup> the two large amplitude mannosyl[2]rotaxane molecular machines **56a,b** have been synthesized from mannosylpyridinium azide **57a,b** and the alkyne **58** in the presence of dibenzo[24]crown-8 (DB24C8) by using click chemistry.<sup>87</sup> Their thread bears two stations: an anilinium and a mono- or disubstituted pyridinium amide, and the ring is DB24C8 (Scheme 13).

**Example A****Scheme 13**

Anilinium is much better station than the pyridinium amide. Upon deprotonation of the anilinium by diisopropylethylamine (DIEA) the ring shuttles toward the pyridinium amide station. It was found that the resulting interaction of the ring with pyridinium amide depends on its mono- or disubstitution.

- In the case of monosubstituted pyridinium amide in **56a**, the ring encircles the NH group to give rotaxane **57a**; the oxygen atoms of the ring form hydrogen bonds with the amide hydrogen NH and with the neighboring H $_{\beta}$  atoms of the pyridinium unit.

- In the case of the disubstituted pyridinium amide in **56b**, however, the ring is localized around the positive charge of pyridinium unit to give rotaxane **57b**; the ring forms hydrogen bonds with H $_{\alpha}$  atoms of pyridinium unit which are situated near the cationic nitrogen atom, and interacts by ion-dipole contacts with the cationic charge. This behavior results in the conformational flipping of the mannopyranose from  ${}^1C_4$  to  ${}^4C_1$ ; in **56a** and **57a** the chair conformation of mannopyranose is  ${}^1C_4$  while in **57b** it is  ${}^4C_1$ .<sup>87</sup>

The above observations show that rotaxanes **56b** and **57b** are examples of molecular machines able to cause conformational changes of a glucidic stopper by the ring shuttling which results from the pH variation.

It should be pointed out that this domino effect from one end of the molecule to the other, *i.e.* deprotonation of the anilinium station/translation of the ring/conformational isomerization of the mannosyl stopper is a molecular mimic of behavior of an allosteric biomacromolecule.

### Example B

The three-station glycorotaxanes **58a,b** acting as molecular machines have been synthesized from rotaxanes **56a,b**. In this process rotaxanes **56a,b** upon methylation of the triazole unit yield rotaxanes **58a,b** bearing three stations, *i.e.* anilinium, mono- or disubstituted pyridinium amide and *N*-methyltriazolium (Scheme 14).

The affinity of the ring for the stations at room temperature decreases in the order: anilinium > monosubstituted pyridinium amide  $\approx$  *N*-methyltriazolium > disubstituted pyridinium amide > aniline. The exchange between these three stations is fast on the NMR time-scale for temperatures 298-193K.<sup>88</sup>

Anilinium is the best station for the ring, therefore at low pH the ring resides exclusively at the anilinium station. Deprotonation of **58a,b** by diisopropylethylamine (DIEA) results in the displacement of the ring affording **59a** and **59b**, respectively.

Rotaxanes **58a/59a** and **58b/59b** act as molecular machines by acid-base reaction as described below.

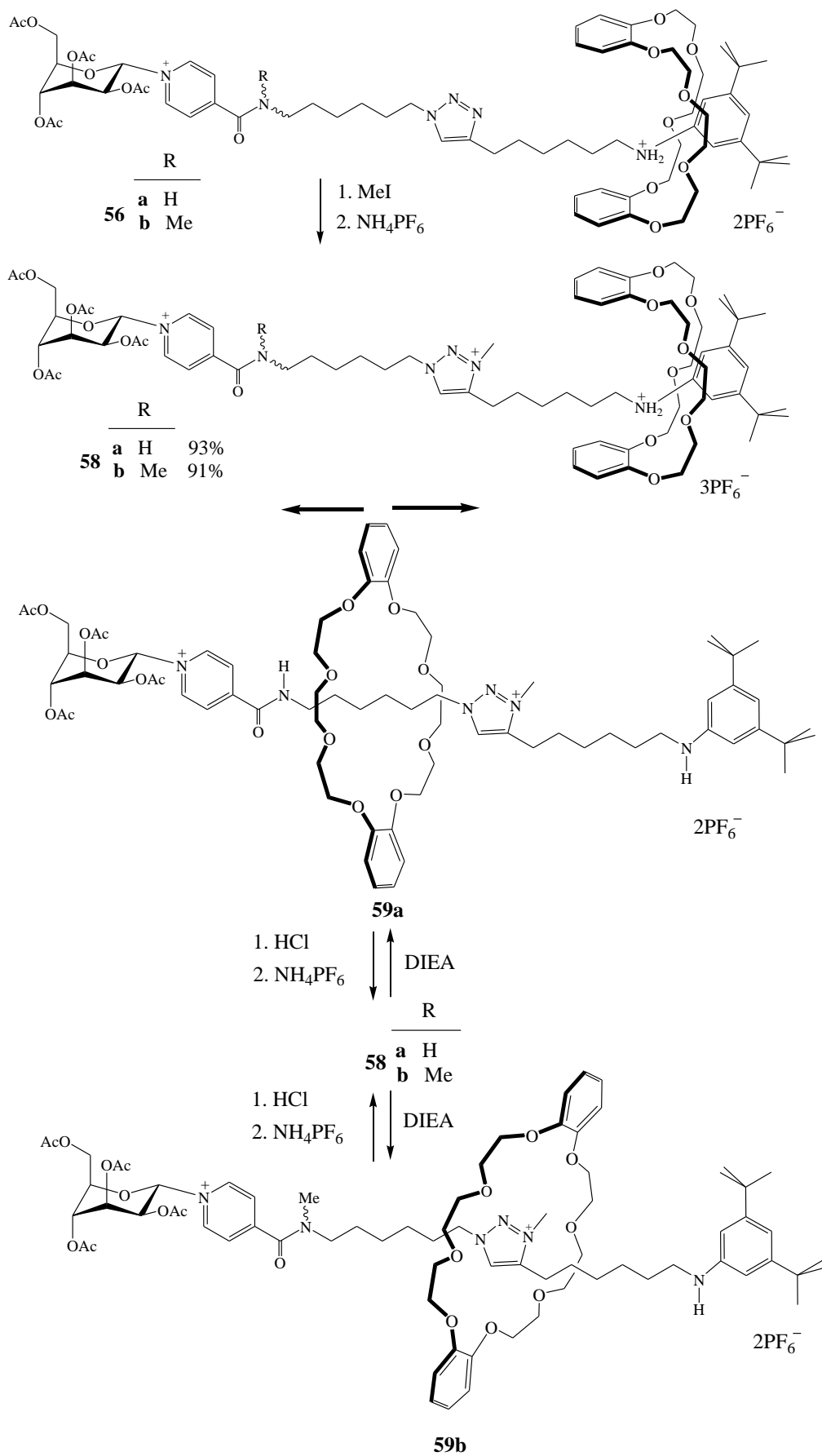
#### Action of rotaxanes **58a/59a** as molecular machines

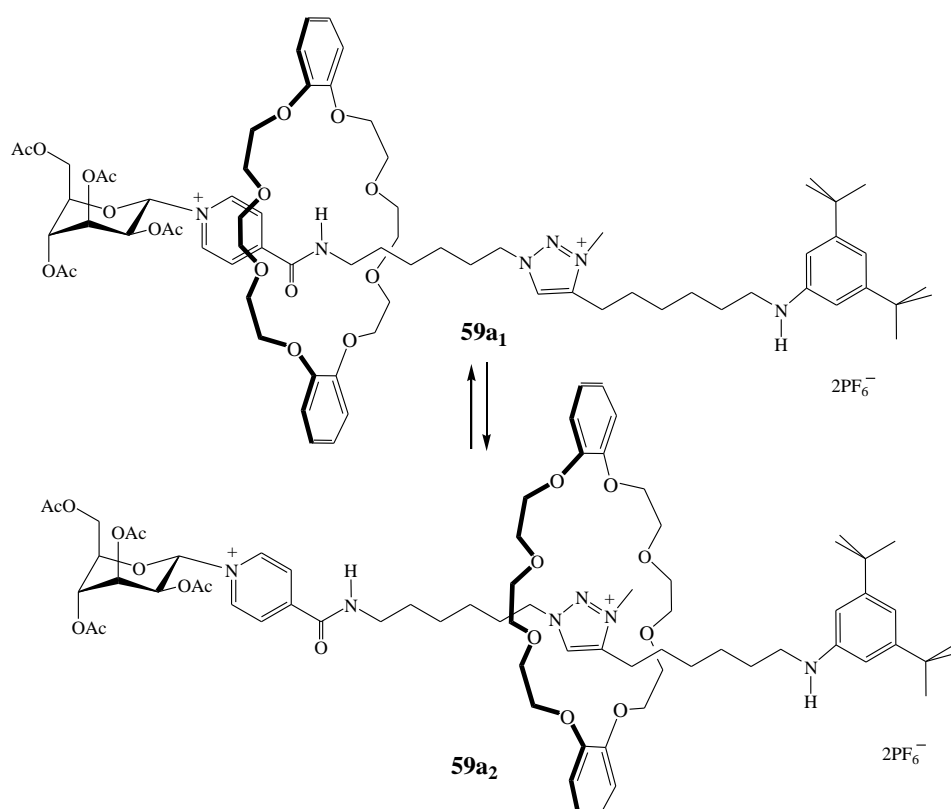
In the case of monosubstituted pyridinium amide in **58a** the ring resides at the best station, *i.e.* anilinium, but after deprotonation of anilinium, in **59a** the shuttling occurs as in a degenerate molecular machine; the ring oscillates between *N*-methyltriazolium and monosubstituted pyridinium amide. The exchange between two translational isomers **59a<sub>1</sub>** and **59a<sub>2</sub>** is fast on the NMR timescale.

At room temperature a slight preference for the pyridinium amide is observed. Lowering the temperature increases  $\Delta G$ , and as a result the ring resides more and more at pyridinium amide. Around 223K the oscillation between two stations stops, and the ring spends most of its time at pyridinium amide, like in a bistable molecular machine. Increasing the temperature restores the oscillation movement, while the reprotonation of the aniline station stops the oscillation, and as a result the ring resides exclusively at the anilinium station.

It is noteworthy that in **59a** the ring acts as a molecular brake of rotation of the covalent bond between the pyridinium and the amide carbonyl group. When the ring is located between pyridinium and amide, it interacts by hydrogen bonding with both the pyridinium hydrogen atoms and with the amide NH at the same time. The ring is anchored at the two H-bonding sites and in this way surrounds the pyridinium–amide linkage; as a result the ring disturbs rotation of this linkage.

## Example B





Scheme 14

#### Action of rotaxanes **58b/59b** as molecular machines

In the case of disubstituted pyridinium amide in **58b**, the ring resides at the best station, *i.e.* anilinium, but after deprotonation of anilinium, in **59b** the ring moves to *N*-methyltriazolium station (which is a better station for the ring than the disubstituted pyridinium amide) and resides at the *N*-methyltriazolium station. The molecular machine created in this way behaves as a pH-sensitive bistable [2]rotaxane in which the ring shuttles between the anilinium and *N*-methyltriazolium stations and is located at either anilinium or *N*-methyltriazolium station, depending on pH.<sup>88</sup>

#### Example C

To rotaxane-based molecular machines belong [c2]daisy chains acting as molecular muscles.<sup>89</sup> It is known that [c2]daisy chains containing two stations may adopt contracted or extended co-conformation, giving rise to their action as muscles.<sup>90</sup> The described below work is an interesting example of molecular machine built from [c2]daisy chains containing two and three stations.

Four mannosyl[c2]daisy chains containing two and three stations have been synthesized and their shuttling behavior was studied. These compounds act as molecular machines triggered by deprotonation/carbamoylation, temperature and solvent polarity.

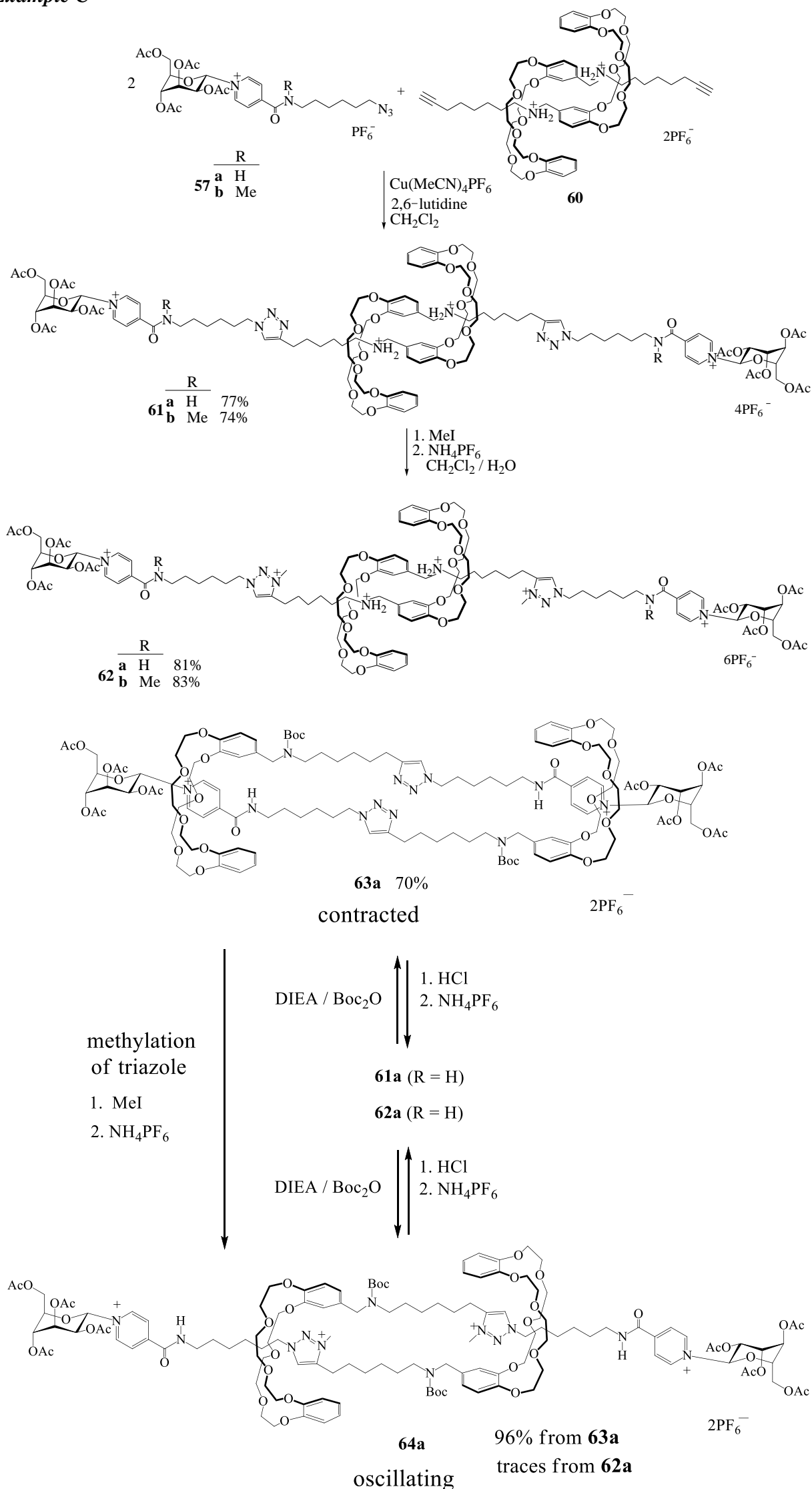
The synthesis begins with the click reaction of mannosyl pyridinium azide **57a,b** with alkyne **60** leading to rotaxanes **61a,b** containing two stations: ammonium and mono- or disubstituted pyridinium amide. These compounds upon methylation of the triazole unit afford rotaxanes **62a,b** bearing three stations; *i.e.* ammonium, substituted pyridinium amide and *N*-methyltriazolium.<sup>91</sup> It was found that in the case of protonated ammonium stations the daisy chains adopt the extended co-conformation (Scheme 15).

The deprotonation/carbamoylation process of **61a,b** and **62a,b** was performed by using diisopropylethylamine (DIEA) and di-*t*-butyl dicarbonate (Boc<sub>2</sub>O).

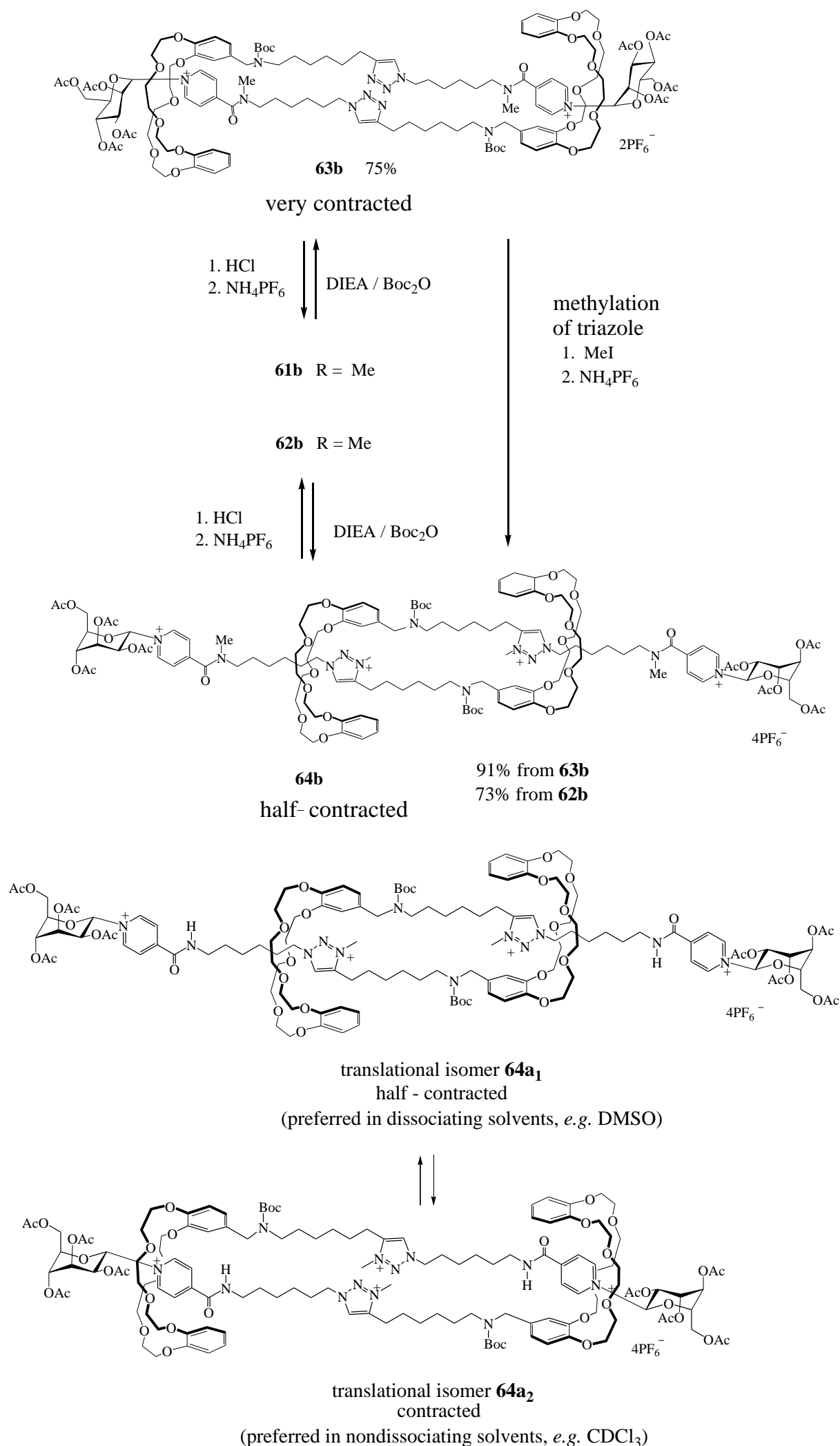
#### Deprotonation/carbamoylation of rotaxanes **61a,b**

Upon deprotonation/carbamoylation of rotaxanes **61a,b** having extended co-conformation they shift the both rings along the thread to both ends, affording **63a** (in a contracted co-conformation) and **63b** (in a very contracted co-conformation). In contracted co-conformation the distance between both mannosyl groups is smaller than in extended co-conformation. It is interesting that in the synthesis of **63b** the conformational flipping of the mannopyranose molecules from <sup>1</sup>C<sub>4</sub> to <sup>4</sup>C<sub>1</sub> occurs.

## Example C







Scheme 15

*Deprotonation/carbamoylation of rotaxanes 62a,b*

Rotaxanes **62a,b** have been subjected to similar deprotonation/carbamoylation procedure, it was found however, that **62a** gives only traces of **64a**, whereas the reaction of **62b** affords **64b** in

73% yield. To overcome this difficulty concerning the low yield of **64a**, the rotaxanes **63a,b** were methylated at the triazole rings to give **64a,b** in *ca* 90% yields.

Upon deprotonation/carbamoylation of rotaxane **62a**, the formed **64a** adopts an alternating co-conformation between a half-contracted and contracted co-conformation, the both rings shuttle between triazolium and monosubstituted pyridinium amide stations, since each ring has similar affinity to these two stations. In this way the oscillating molecular muscle was formed. It is noteworthy that the above continuous oscillation of both rings between *N*-methyltriazolium and monosubstituted pyridinium amide stations may be controlled by the variation of the solvent polarity. In dissociating solvents like DMSO the half-contracted translational co-conformer **64a1** is preferred, whereas in nondissociating solvents like CDCl<sub>3</sub> the contracted translational isomer **64a2** is preferred.

Upon deprotonation/carbamoylation of rotaxane **62b**, however, the formed **64b** adopts a half-contracted co-conformation. The both rings become situated at *N*-methyltriazolium stations, since each ring has higher affinity to *N*-methyltriazolium than to the disubstituted pyridinium amide station.<sup>91</sup>

## 5. Pseudorotaxanes containing cryptands as rings

Pseudorotaxanes containing crown ether based cryptands (further named cryptands) as rings were not so widely investigated as those containing crown ethers. One should note that pseudorotaxanes formed from viologens and cryptands are bound more strongly than pseudorotaxanes formed from viologens and crown ethers.<sup>92</sup> From among many syntheses of pseudorotaxanes built from viologens and cryptands,<sup>93-95</sup> below three selected examples 1-3 are given.

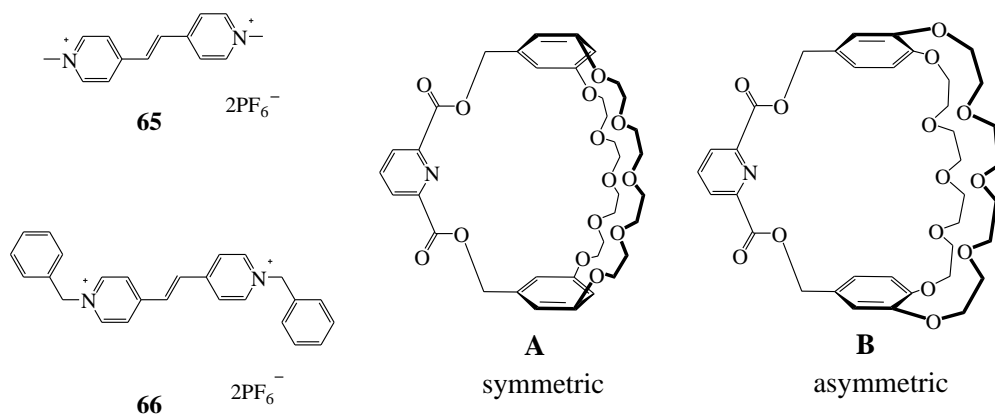
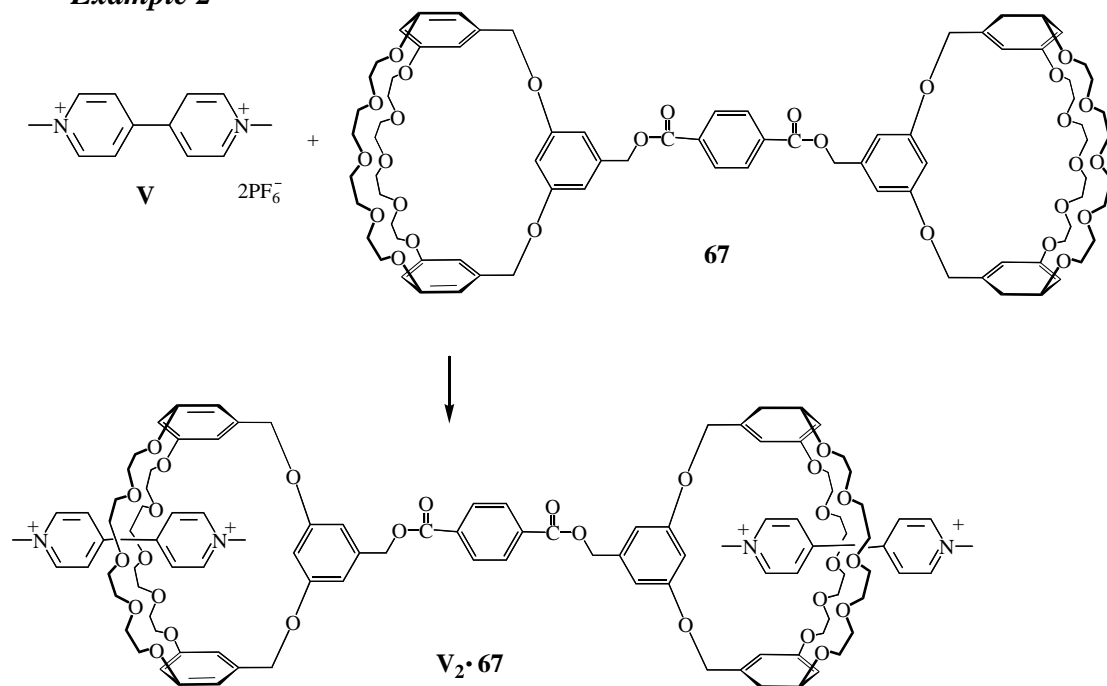
### Example 1

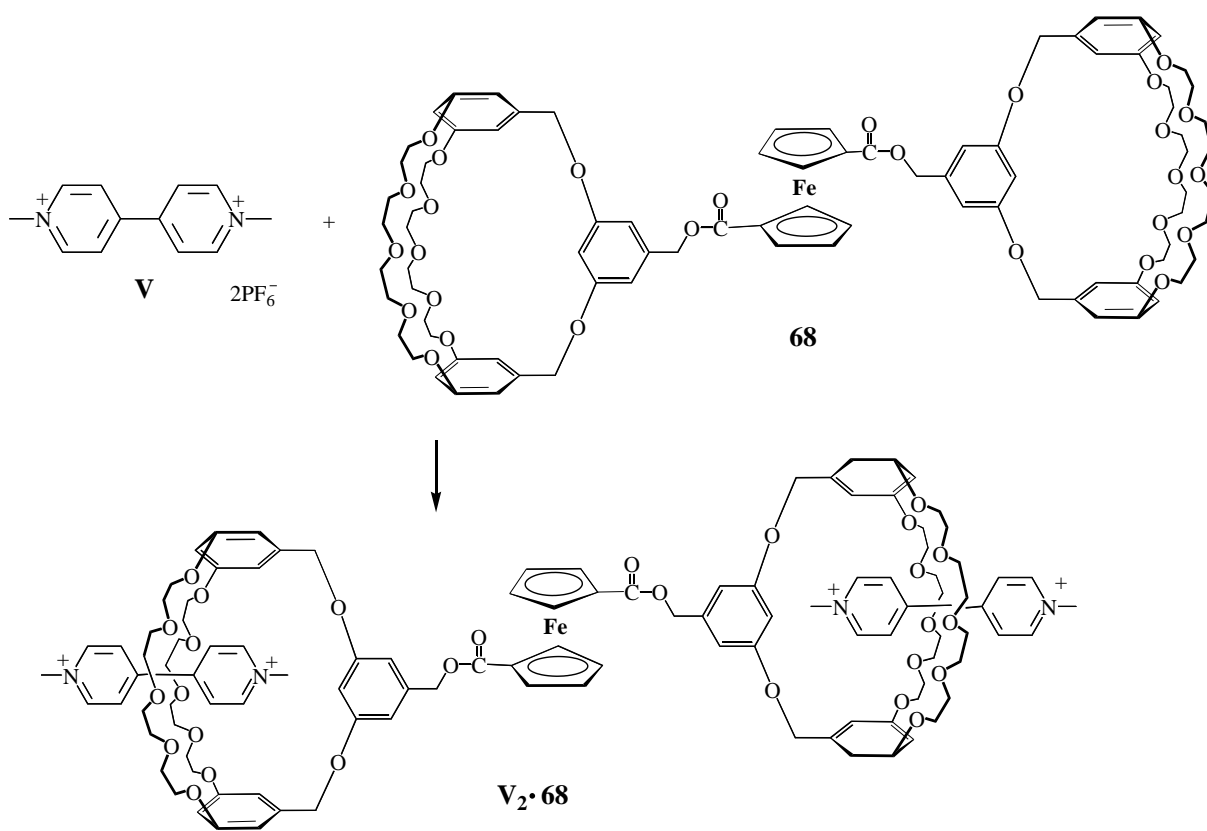
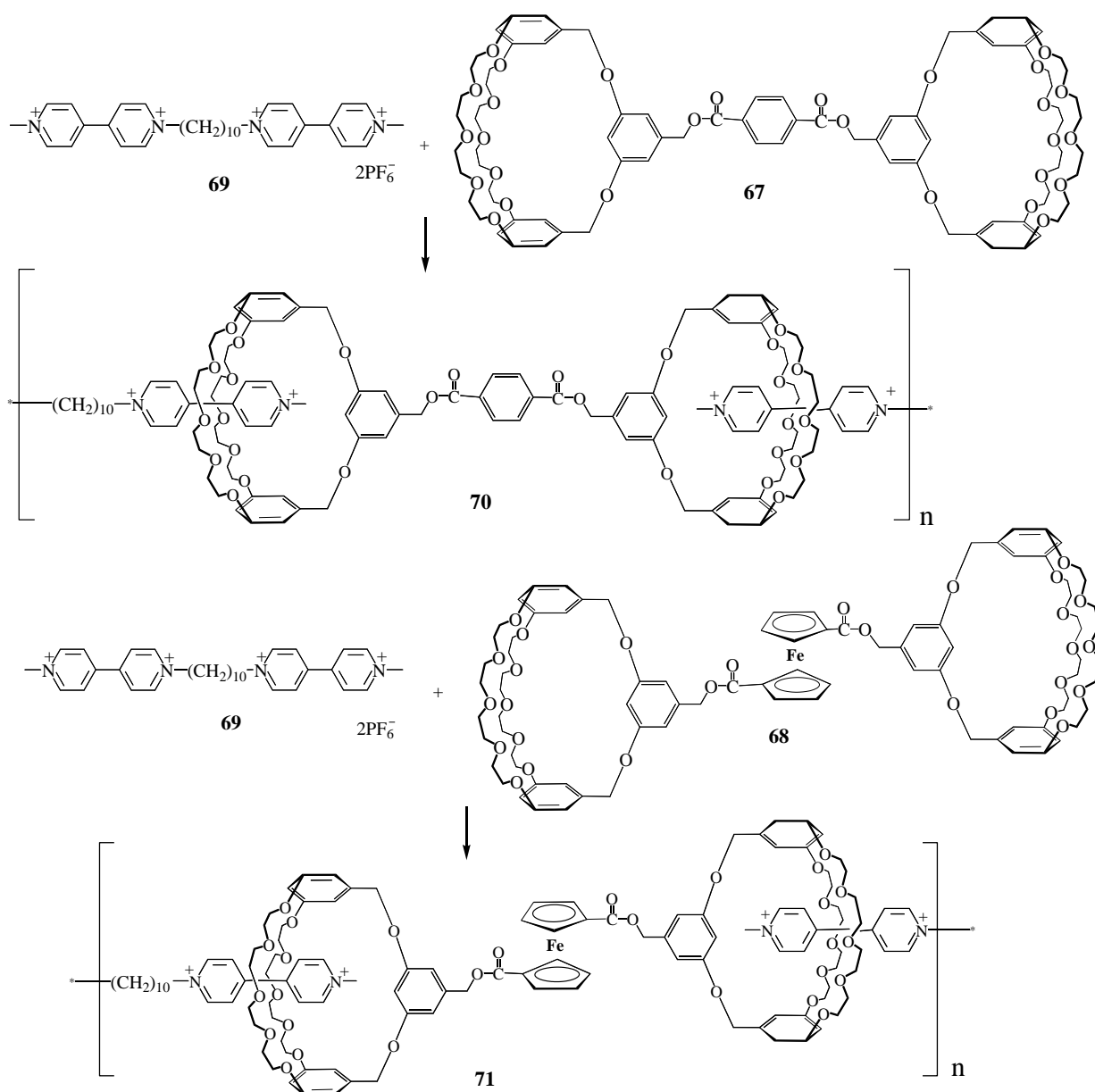
Basing on the recognition of vinylogous viologens **65** and **66** with symmetric **A** and asymmetric **B** cryptands, four [2]pseudorotaxanes were obtained. It should be pointed out that vinylogous viologens, *i.e.*  $\pi$ -extended viologens enlarge the properties of viologens, such as fluorescence and photocontrolled isomerisations, however, they are not so often as viologens used for construction of mechanically interlocked structures.<sup>96</sup>

The  $K_a$  values of investigated [2]pseudorotaxanes are high, and are comparable to the corresponding host-guest systems viologen/cryptand; they decrease in the order **65·A**>**66·A**>**65·B**>**66·B**.<sup>97</sup> The structure of pseudorotaxane **66·B** is shown. The X-ray analysis of the crystal structure of [2]pseudorotaxanes **65·A** and **66·B** indicates that they are stabilized by hydrogen bonding and face-to-face  $\pi$ -stacking interactions. The [2]pseudorotaxane **65·A** has the highest  $K_a$  value (of the 10<sup>6</sup> range) among investigated species; it forms a supramolecular poly[2]pseudorotaxane structure in the solid state.

It was observed that the formation of [2]pseudorotaxanes **65·B** and **66·B** can be controlled by adding and removing of potassium ion. Upon addition of KPF<sub>6</sub>, cryptand **B** forms a more stable complex with K<sup>+</sup> than with **66**, and as a result the complex **66·B** disassembles. However, when DB18C6 is added to trap the added K<sup>+</sup>, the complex **66·B** is recovered, *i.e.* the process is reversible. Due to this behavior, the formation of pseudorotaxane **66·B** can be switched off and on by addition of KPF<sub>6</sub>, followed by DB18C6; in this way a cation-responsive host-guest pair for design of stimuli-responsive molecular shuttles and machines was created.

The  $K_a$  value for **65·B** (of the 10<sup>5</sup> range) is higher than that for **66·B** (of the 10<sup>4</sup> range), therefore the reversible switch in **65·B** is more difficult than that in **66·B**. This observed cation-responsive binding of vinylogous viologens **65** and **66** with **B** is promising for design of controllable molecular shuttles (Scheme 16).

**Example 1****Example 2**

**Example 3****Scheme 16**

### Example 2

Pseudorotaxanes<sup>98</sup> are important building blocks for rotaxanes, catenanes, as well as polyrotaxanes and polycatenanes.<sup>99,100</sup> Syntheses of pseudorotaxanes from viologens and crown ethers are a topic of numerous reports,<sup>101-104</sup> however those concerning pseudorotaxanes built from viologens and cryptands are not so largely investigated. It was found that the self-assembly of viologen **V** with biscryptand **67** having covalent (terephthalate) linkage and biscryptand **68** having metal-complex (ferrocene ester) linkage affords [3]pseudorotaxanes **V2·67** and **V2·68** formed statistically and anticooperatively, respectively.<sup>105</sup>

The individual solutions of viologen **V** and of biscryptand **67** in CDCl<sub>3</sub>/(CD<sub>3</sub>)<sub>2</sub>CO (1:3) are colorless, however the solution of viologen **V** with **67** is yellow due to charge transfer between the electron deficient viologen **V** and electron rich aromatic rings of biscryptand **67**. The self-assembly of viologen **V** with **67** affords the [3]pseudorotaxane **V2·67**.

In a similar manner the complex **V2·68** was obtained. The biscryptand **68** is red, therefore color change resulting from charge transfer between viologen **V** and **68** in CDCl<sub>3</sub>/(CD<sub>3</sub>)<sub>2</sub>CO (1:3) could not be seen. One should point out that the anticooperative formation of [3]pseudorotaxane **V2·68** was observed in complexations of viologens with biscryptands for the first time.

### Example 3

Supramolecular polymers attract recently a growing attention. In contrast to covalent polymers, they are noncovalent, mechanically interlocked structures of promising properties.<sup>106-112</sup> The crown ether-based, pseudorotaxane type supramolecular polymers are used in preparation of interesting structures. However it should be taken into account that for preparation of large supramolecular polymers, the monomers with high association constants are necessary.

Cryptands are much better receptors for viologens than crown ethers, therefore they have promising properties to form supramolecular polymers. It is also noteworthy that viologens, in contrast to complexation with crown ethers, leading often to taco systems,<sup>113</sup> form with cryptands the threaded, pseudorotaxane-products.<sup>101,114</sup>

It was found that bisviologen **69** (as a BB monomer) forms with biscryptands **67** and **68** (as AA monomers) the linear noncovalent supramolecular polymers **70** and **71**, respectively, of a well defined pseudorotaxane structure, having covalent (terephthalate) or metal-complex (ferrocene ester) linkages. They are of a AA-BB type and have relatively high molecular weights.<sup>99</sup>

The equimolar solution of bisviologen **69** and biscryptand **67** in chloroform/acetonitrile (1:1) is yellow due to charge transfer interaction of electron deficient pyridinium rings of **69** with electron rich aromatic rings of biscryptand **67**; this fact confirms the complexation. The equimolar solution of **69** with **67** shows high specific viscosity, indicating the high association constant in this system. One should note that it is the highest specific viscosity reported for a pseudorotaxane supramolecular polymer. It was found that long thin fibers could be drawn from concentrated equimolar solutions of **69** with **67**, this observation also confirms formation of supramolecular polymer **70**. Similarly, from concentrated solution of **69** with **68** also thin fibers of supramolecular polymer **71** could be drawn. The obtained pseudorotaxane supramolecular polymers **70** and **71** may be converted into irreversibly mechanically linked rotaxane polymers by attachment of bulky stoppers at the ends of bisviologen **69**.

## 6. Conclusions

Interlocked systems, mainly rotaxanes<sup>115-118</sup> and catenanes<sup>119-122</sup> as well as polyrotaxanes<sup>123-126</sup> and polycatenanes<sup>127-130</sup> are today intensively studied. Due to the multiplicity of works, the above described reports on rotaxanes and pseudorotaxanes with threads containing

pyridinium units are only selected examples, however, one should hope that some light will be shed on this important area of chemistry and related sciences.

Among studies concerning this topic, a wide research leading to design of molecular machines<sup>131,132</sup> exists, therefore development of this field may be expected.<sup>133,134</sup> Worth noting are here rotacatenanes<sup>133</sup> which are a combination of rotaxanes and catenanes, promising for construction of molecular machines.

Taking into account a rapid progress of supramolecular chemistry research, one should point out a growing attention paid today to foldamers.<sup>134-136</sup> They are helical receptors for rod-like guest molecules. It was found that double helical foldamers coiled around rod-shaped guest molecules can perform a screw-type motion, which does not occur in other molecular machines.<sup>137,138</sup>

Foldamer-based rotaxanes named foldaxanes<sup>139</sup> may form stable, double-helical structures *via* hydrogen-bonding and  $\pi$ -stacking interactions. Foldaxanes are obtained by unfolding/refolding mechanism of a high kinetic barrier, therefore they have relatively high stability.

It has been observed that in foldaxanes, in which rods have different helix-binding sites, the shuttling proceeds faster than the disassembly of the foldaxane.<sup>140</sup> In other words, it has been established that the action of these nanomachines is much faster than their assembly/disassembly process, similarly as in the case of “biomachines”. One may believe that the above results will be useful in future for construction of molecular machines.<sup>134,135</sup>

## 7. 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 of this project.

## References

1. Dasgupta, S.; Huang, K.-W.; Wu, J. *Chem. Commun.* **2012**, 48, 4821.  
<http://dx.doi.org/10.1039/c2cc31009k>  
PMid:22498508
2. Zhu, K.; Vukotic, V. N.; Loeb, S. J. *Angew. Chem. Int. Ed.* **2012**, 51, 2168.  
<http://dx.doi.org/10.1002/anie.201108488>  
PMid:22259027
3. Joosten, A.; Trolez, Y.; Collin, J.-P.; Heitz, V.; Sauvage, J.-P. *J. Am. Chem. Soc.* **2012**, 134, 1802.  
<http://dx.doi.org/10.1021/ja210113y>  
PMid:22236438
4. Yamada, Y.; Okamoto, M.; Furukawa, K.; Kato, T.; Tanaka, K. *Angew. Chem. Int. Ed.* **2012**, 51, 709.  
<http://dx.doi.org/10.1002/anie.201107104>  
PMid:22134904
5. Evans, N. H.; Beer, P. D. In *Supramolecular Chem. From Molecules to Nanomaterials*, Eds. Gale, P.; Steed, J. John Wiley: New York, 2012; p 2225.
6. Ayme, J.-F.; Lux, J.; Sauvage, J.-P.; Sour, A. *Chem. Eur. J.* **2012**, 18, 5565.  
<http://dx.doi.org/10.1002/chem.201104061>  
PMid:22431359
7. Elbaz, J.; Wang, Z.-G.; Wang, F.; Willner, I. *Angew. Chem. Int. Ed.* **2012**, 51, 2349.  
<http://dx.doi.org/10.1002/anie.201107591>  
PMid:22287100

8. Strutt, N. L.; Zhang, H.; Giesener, M. A.; Lei, J.; Stoddart, J. F. *Chem. Commun.* **2012**, 48, 1647.  
<http://dx.doi.org/10.1039/c2cc16030g>  
PMid:22187005
9. Zheng, B.; Zhang, M.; Dong, S.; Liu, J.; Huang, F.; *Org. Letters* **2012**, 14, 306.  
<http://dx.doi.org/10.1021/ol203062w>  
PMid:22148951
10. Beves, J. E. *Chimia* **2012**, 66, 170.  
<http://dx.doi.org/10.2533/chimia.2012.170>  
PMid:22613142
11. Keene, F. R. In *Supramolecular Chemistry; From Molecules to Nanomaterials*, Eds. P. Gale, P.; Steed, J. Wiley: New York, 2012; pp 217. PMid:22413819.
12. Venturi, M.; Marchi, E.; Balzani, V. *Top. Curr. Chem.* **2012**, 323, 73.  
[http://dx.doi.org/10.1007/128\\_2011\\_293](http://dx.doi.org/10.1007/128_2011_293)  
PMid:22076080
13. Hänni, K. D.; Leigh, D. A. *Chem. Soc. Rev.* **2010**, 39, 1240.  
<http://dx.doi.org/10.1039/b901974j>  
PMid:20309484
14. Vukotic, V. N.; Harris, K. J.; Zhu, K.; Schurko, R. W.; Loeb, S. J. *Nature Chem.* **2012**, 4, 456.  
<http://dx.doi.org/10.1038/nchem.1354>  
PMid:22614379.
15. Took, C.; Frey, J.; Sauvage, J. P. In *Molecular Switches*, Eds. Feringa, B. L.; Browne, W. R.; Wiley: New York, Vol. 1, 2011; p 97.  
<http://dx.doi.org/10.1002/9783527634408.ch4>
16. Noujeim, N.; Zhu, K.; Vukotic, V. N.; Loeb, S. J. *Org. Letters* **2012**, 14, 2484.  
<http://dx.doi.org/10.1021/ol300761q>  
PMid:22551383.
17. Yan, X.; Wei, P.; Xia, B.; Huang, F.; Zhou, Q. *Chem. Commun.* **2012**, 48, 4968.  
<http://dx.doi.org/10.1039/c2cc31374j>  
PMid:22497011
18. Loew, N. L.; Dzyuba, E. V.; Brusilowskij, B.; Kaufmann, L.; Franzmann, E.; Maison, W.; Brandt, E.; Aicher, D.; Wiehe, A.; Schalley, C. A. *Beilstein J. Org. Chem.* **2012**, 8, 234.  
<http://dx.doi.org/10.3762/bjoc.8.24>  
PMid:22423290 PMCID:3302084
19. Mlika, R.; Hbaieb, S.; Ben Chaabene, R.; Chevalier, Y.; Kalfat, R.; Ben Quada, H. *Synthetic Met.* **2012**, 162, 186.  
<http://dx.doi.org/10.1016/j.synthmet.2011.11.029>
20. Fu, Q.; Ren, J. M.; Qiao, G. G. *Polym. Chem.* **2012**, 3, 343.  
<http://dx.doi.org/10.1039/c1py00362c>
21. Bang, E.-K.; Lista, M.; Sforzini, G.; Sakai, N.; Matile, S. *Chem. Sci.* **2012**, 3, 1752.  
<http://dx.doi.org/10.1039/c2sc20098h>
22. Yui, N. In *Supramolecular Polymer Chemistry*, Ed. Harada, A. Wiley – VCH: New York, 2012; p 195.  
<http://dx.doi.org/10.1002/9783527639786.ch9>
23. Yamada, Y.; Nomura, T.; Harashima, H.; Yamashita, A.; Yui, N. *Biomaterials* **2012**, 33, 3952.  
<http://dx.doi.org/10.1016/j.biomaterials.2012.01.049>  
PMid:22386920.
24. Deligkiozi, I.; Papadakis, R.; Tsolomitis, A. *Supramol. Chem.* **2012**, 24, 333.  
<http://dx.doi.org/10.1080/10610278.2012.660529>
25. Akae, Y.; Okamura, H.; Koyama, Y.; Arai, T.; Takata, T. *Org. Letters* **2012**, 14, 2226.  
<http://dx.doi.org/10.1021/ol300578q>  
PMid:22519824

26. Zhu, L.; Yan, H.; Nguyen, K. T.; Tian, H.; Zhao, Y. *Chem. Commun.* **2012**, 48, 4290.  
<http://dx.doi.org/10.1039/c2cc17114g>  
PMid:22301771
27. Girek T. J. *Incl. Phenom. Macrocycl. Chem.* **2012**, 74, 1.  
<http://dx.doi.org/10.1007/s10847-012-0112-1>
28. Talotta, C.; Gaeta, C.; Neri, P. *Org. Lett.* **2012**, 14, 3104.  
<http://dx.doi.org/10.1021/ol3011997>  
PMid:22668501
29. Wu, S.-F.; Ma, X. *Tetradron. Lett.* **2011**, 52, 5960.  
<http://dx.doi.org/10.1016/j.tetlet.2011.08.129>
30. Sinha, M.K.; Reany, O.; Yefet, M.; Botoshansky, M.; Keinan, E. *Chem. Eur. J.* **2012**, 18, 5589.  
<http://dx.doi.org/10.1002/chem.201103434>  
PMid:22434704.
31. Kolman, V.; Khan, M. S. A.; Babinsky, M.; Marek, R.; Sindelar, V. *Org. Lett.* **2011**, 13, 6148.  
<http://dx.doi.org/10.1021/ol2023888>  
PMid:22066799.
32. Liu, P.; Chipot, C.; Shao, X.; Cai, W. *J. Phys. Chem. C* **2012**, 116, 4471.
33. Kiguchi, M.; Nakashima, S.; Tada, T.; Watanabe, S.; Tsuda, S.; Tsuji, Y.; Terao, J. *Small* **2012**, 8, 726.  
<http://dx.doi.org/10.1002/smll.201102075>  
PMid:22223591
34. Przybylski, C.; Bonnet, V.; Jarroux, N. *Macro Lett.* **2012**, 1, 533.  
<http://dx.doi.org/10.1021/mz3000607>
35. Zhou, Y.; Wang, H.; Wang, Ch.; Li, Y.; Lu, W.; Chen, S.; Luo, J.; Jiang, Y.; Chen, J. *Molecular Pharm.* **2012**, 9, 1067.
36. Albuzat, T.; Keil, M.; Ellis, J.; Alexander, C.; Wenz, G. *J. Mater. Chem.* **2012**, 22, 8558.  
<http://dx.doi.org/10.1039/c2jm16425f>
37. Cragg, P. J.; Sharma, K. *Chem. Soc. Rev.* **2012**, 41, 597.  
<http://dx.doi.org/10.1039/c1cs15164a>  
PMid:21804967
38. Ogoshi, T.; Kitajima, K.; Aoki, T.; Yamagishi, T. A.; Nakamoto, Y. *J. Phys. Chem. Lett.* **2010**, 1, 817.  
<http://dx.doi.org/10.1021/jz900437r>
39. Ogoshi, T.; Nishida, Y.; Yamagishi, T. A.; Nakamoto, Y. *Macromolecules* **2010**, 43, 7068.  
<http://dx.doi.org/10.1021/ma101320z>
40. Ma, Y.; Chi, X.; Yan, X.; Liu, J.; Yao, Y.; Chen, W.; Huang, F.; Hou, J.-L. *Org. Lett.* **2012**, 14, 1532.  
<http://dx.doi.org/10.1021/ol300263z>  
PMid:22401142.
41. Xue, M.; Yang, Y.; Chi, X.; Zhang, Z.; Huang, F. *Acc. Chem. Res.* **2012**, 45, 1294.  
<http://dx.doi.org/10.1021/ar2003418>  
PMid:22551015
42. Li, C.; Xu, Q.; Li, J.; Yao, F.; Jia, X. *Org. Biomol. Chem.* **2010**, 8, 1568.  
<http://dx.doi.org/10.1039/b920146g>  
PMid:20336850
43. Li, C. J.; Zhao, L.; Li, J. A.; Ding, X.; Chen, S. H.; Zhang, Q. L.; Yu, Y. H.; Jia, X. S. *Chem. Commun.* 2010, 46, 9016.  
<http://dx.doi.org/10.1039/c0cc03575k>  
PMid:21057678.
44. Deska, M.; Kozłowska, J.; Sliwa, W. *Arkivoc*, in press.
45. Sliwa, W.; Bachowska, B.; Girek, T. *Curr. Org. Chem.* **2012**, 16, 1332.  
<http://dx.doi.org/10.2174/138527212800564240>



46. Sliwa, W.; Chrzastek, L. *Curr. Org. Chem.* **2009**, *13*, 339.  
<http://dx.doi.org/10.2174/138527209787582295>
47. Mercer, D. J.; Vella, S. J.; Guertin, L.; Suhan, N. D.; Tiburcio, J.; Vukotic, V. N.; Wisner, J. A.; Loeb, S. J. *Eur. J. Org. Chem.* **2011**, 1763.  
<http://dx.doi.org/10.1002/ejoc.201001616>
48. Tramontozzi, D. A.; Suhan, N. D.; Eichhorn, S. H.; Loeb, S. J. *Chem. Eur. J.* **2010**, *16*, 4466.  
<http://dx.doi.org/10.1002/chem.200903174>  
PMid:20352637.
49. Suzuki, S.; Nakazono, K.; Takata, T. *Org. Lett.* **2010**, *12*, 712.  
<http://dx.doi.org/10.1021/ol902719m>  
PMid:20088538
50. Vella, S. J.; Tiburcio, J.; Loeb, S. J. *Chem. Commun.* **2007**, 4752.  
<http://dx.doi.org/10.1039/b710708k>  
PMid:18004430
51. Zhao, J.-M.; Zong, Q.-S.; Han, T.; Xiang, G.-F.; Chen, C.-F. *J. Org. Chem.* **2008**, *73*, 6800.  
<http://dx.doi.org/10.1021/jo801170t>  
PMid:18672935
52. Zhang, C.; Chen, C.-F. *J. Org. Chem.* **2007**, *72*, 9339.  
<http://dx.doi.org/10.1021/jo7017526>  
PMid:17958375
53. Lin, C.-F.; Lai, C.-C.; Liu, Y.-H.; Peng, S.-M.; Chiu, S.-H. *Chem. Eur. J.* **2007**, *13*, 350.  
<http://dx.doi.org/10.1002/chem.200601432>  
PMid:17323386
54. Rit, A.; Pape, T.; Hepp, A.; Hahn, F.E. *Organometallics* **2011**, *30*, 334.  
<http://dx.doi.org/10.1021/om101102j>
55. Rit, A.; Pape, T.; Hahn, F. E. *J. Am. Chem. Soc.* **2010**, *132*, 4572.  
<http://dx.doi.org/10.1021/ja101490d>  
PMid:20222710
56. Conrady, F. M.; Fröhlich, R.; Schulte to Brinke, C.; Pape, T.; Hahn, F. E. *J. Am. Chem. Soc.* **2011**, *133*, 11496.  
<http://dx.doi.org/10.1021/ja205021p>  
PMid:21728329
57. Yuan, D. Y.; Huynh, H. V. *Organometallics* **2010**, *29*, 6020.  
<http://dx.doi.org/10.1021/om1008023>
58. Huynh, H. V.; Sim, W.; Chin, C. F. *Dalton Trans.* **2011**, *40*, 11/690.
59. Han, Y.; Huynh, H. V.; Tan, G. K. *J. Organomet. Chem.* **2007**, *26*, 6447.  
<http://dx.doi.org/10.1021/om700753d>
60. Knight L. K.; Vukotic, V. N.; Viljoen, E.; Caputo, C.; Loeb, S. J. *Chem. Commun.* **2009**, 5585.  
<http://dx.doi.org/10.1039/b911889f>  
PMid:19753365
61. Mohamadin, M. I; Abdullah, N. *Int. J. Phys. Sci.* **2011**, *6*, 2526.
62. Gassensmith, J. J.; Matthys, S.; Lee, J. J.; Wojcik, A.; Karnat, P. V.; Smith, B. D. *Chem. Eur. J.* **2010**, *16*, 2916.  
<http://dx.doi.org/10.1002/chem.200902547>  
PMid:20082394
63. McConnell, A. J.; Serpell, C. J.; Thompson, A. L.; Allan, D. R.; Beer, P. D. *Chem. Eur. J.* **2010**, *16*, 1256  
<http://dx.doi.org/10.1002/chem.200902659>  
PMid:19950342
64. Zapata, F.; Caballero, A.; Tarraga, A.; Molina, P. *J. Org. Chem.* **2010**, *75*, 162.  
<http://dx.doi.org/10.1021/jo9023446>  
PMid:19968276

65. Willener, Y.; Joly, K. A.; Moody, C. J.; Tucker, J. H. R. *J. Org. Chem.* **2008**, *73*, 1225  
<http://dx.doi.org/10.1021/jo701809b>  
PMid:18205379
66. Evans, N. H.; Serpell, C. J.; White, N. G.; Beer, P. D. *Chem. Eur. J.* **2011**, *17*, 12347.  
<http://dx.doi.org/10.1002/chem.201101811>  
PMid:21953676
67. Evans, N. H.; Beer, P. D. *Org. Biomol. Chem.* **2011**, *9*, 92.  
<http://dx.doi.org/10.1039/c0ob00458h>  
PMid:21063586
68. Brown, A.; Beer, P. D. *Dalton Trans.* **2012**, *41*, 118.  
<http://dx.doi.org/10.1039/c1dt11372k>  
PMid:22075843
69. Lee, C. H.; Yoon, H.; Kim, P.; Cho, S.; Kim, D.; Jang, W. D. *Chem. Commun.* **2011**, *47*, 4246.  
<http://dx.doi.org/10.1039/c1cc00112d>  
PMid:21350745
70. Lee, C. H.; Yoon, H.; Jang, W. D. *Chem. Eur. J.* **2009**, *15*, 9972.  
<http://dx.doi.org/10.1002/chem.200901988>  
PMid:19722242
71. Hancock, L. M.; Beer, P. D. *Chem. Eur. J.* **2009**, *15*, 42.  
<http://dx.doi.org/10.1002/chem.200802029>  
PMid:19040231
72. Hancock, L. M.; Gilday, L. C.; Carvalho, S.; Costa, P. J.; Félix, V.; Serpell, C. J.; Kilah, N. L.; Beer, P. D. *Chem. Eur. J.* **2010**, *16*, 13082.  
<http://dx.doi.org/10.1002/chem.201002076>  
PMid:21031371
73. Collin, J.-P.; Frey, J.; Heitz, V.; Sauvage, J.-P.; Tock, C.; Allouche, L. *J. Am. Chem. Soc.* **2009**, *131*, 5609.  
<http://dx.doi.org/10.1021/ja900565p>  
PMid:19334735
74. Brown, A.; Mullen, K. M.; Ryu, J.; Chmielewski, M. J.; Santos, S. M.; Félix, V.; Thompson, A. L.; Warren, J. E.; Pascu, S. I.; Beer, P. D. *J. Am. Chem. Soc.* **2009**, *131*, 4937.  
<http://dx.doi.org/10.1021/ja809905x>  
PMid:19296631
75. Gibson, H. W.; Yamaguchi, N.; Niu, Z.; Jones, J. W.; Slebodnick, C.; Rheingold, A. L.; Zakharov, L. N. *J. Polym. Sci. Part. A; Polym. Chem.* **2010**, *48*, 975.  
<http://dx.doi.org/10.1002/pola.23861>
76. McConnell, A. J.; Beer, P. D. *Chem. Eur. J.* **2011**, *17*, 2724.  
<http://dx.doi.org/10.1002/chem.201002528>  
PMid:21264965
77. Ng, K.-Y.; Félix, V.; Santos, S. M.; Reesa, N. H.; Beer, P. D. *Chem. Commun.* **2008**, 1281.  
<http://dx.doi.org/10.1039/b719304a>  
PMid:18389107
78. Barrel, M. J.; Leigh, D. A.; Lusby, P. J.; Slavin, A. M. Z. *Angew. Chem. Int. Ed.* **2008**, *47*, 8036.  
<http://dx.doi.org/10.1002/anie.200802745>  
PMid:18792909
79. Griffiths, K. E.; Stoddart, J. F. *Pure Appl. Chem.* **2008**, *80*, 485.  
<http://dx.doi.org/10.1351/pac200880030485>
80. Juluri, B. K.; Kumar, A. S.; Liu, Y.; Ye, T.; Yang, Y.-W.; Flood, A. H.; Stoddart, J. F.; Weiss, P. S.; Huang, T. J. *ACS Nano* **2009**, *3*, 291.  
<http://dx.doi.org/10.1021/nn8002373>  
PMid:19236063

81. Li, D.; Paxton, W. F.; Baughman, R. H.; Huang, T. J.; Stoddart, J. F.; Weiss, P. S. *MR Bull.* **2009**, *34*, 671.  
<http://dx.doi.org/10.1557/mrs2009.179>
82. Du, L.; Liao, S. J.; Khatib, H. A.; Stoddart, J. F.; Zink, J. I. *J. Am. Chem. Soc.* **2009**, *131*, 15136.  
<http://dx.doi.org/10.1021/ja904982j>  
PMid:19799420
83. Chwalek, M.; Auzély, R.; Fort, S. *Org. Biomol. Chem.* **2009**, *7*, 1680.  
<http://dx.doi.org/10.1039/b822976g>  
PMid:19343257
84. Chen, N.-C.; Lai, C.-C.; Liu, Y.-H.; Peng, S.-M.; Chiu, S.-H. *Chem. Eur. J.* **2008**, *14*, 2904.  
<http://dx.doi.org/10.1002/chem.200701854>  
PMid:18213659
85. Coutrot, F.; Romuald C.; Busseron E. *Org. Lett.* **2008**, *10*, 3741.  
<http://dx.doi.org/10.1021/ol801390h>  
PMid:18666774
86. Coutrot, F.; Busseron E. *Chem. Eur. J.* **2008**, *14*, 4784.  
<http://dx.doi.org/10.1002/chem.200800480>  
PMid:18409178
87. Coutrot F.; Busseron E. *Chem. Eur. J.* **2009**, *15*, 5186.  
<http://dx.doi.org/10.1002/chem.200900076>  
PMid:19229918
88. Busseron, E.; Romuald, C.; Coutrot F. *Chem. Eur. J.* **2010**, *16*, 10062.  
<http://dx.doi.org/10.1002/chem.201000777>  
PMid:20607770
89. Ueng, S. H.; Hsueh, S. Y.; Lai, C. C.; Liu, Y. H.; Peng, S. M.; Chiu, S. H. *Chem. Commun.* **2008**, 817.  
<http://dx.doi.org/10.1039/b716331b>  
PMid:18253514
90. Dawson, R. E.; Lincoln, S. F.; Easton, C. J. *Chem. Commun.* **2008**, 3980.  
<http://dx.doi.org/10.1039/b809014a>  
PMid:18758599
91. Romuald C.; Busseron E.; Coutrot, F. *J. Org. Chem.* **2010**, *75*, 6516.  
<http://dx.doi.org/10.1021/jo101234u>  
PMid:20815375
92. Wang, F.; Zhou, Q.; Zhu, K.; Li, S.; Wang, C.; Liu, M.; Li, N.; Fronczek, F. R.; Huang, F. *Tetrahedron* **2009**, *65*, 1488.  
<http://dx.doi.org/10.1016/j.tet.2008.11.081>
93. Liu, M.; Li, S.; Hu, M.; Wang, F.; Huang, F. *Org. Lett.* **2010**, *12*, 760.  
<http://dx.doi.org/10.1021/ol9028463>  
PMid:20092356
94. Zhu, K.; Wu, L.; Yan, X.; Zheng, B.; Zhang, M.; Huang, F. *Chem. Eur. J.* **2010**, *16*, 6088.  
PMid:20391577.
95. Liu, M.; Yan, X.; Hu, M.; Chen, X.; Zhang, M.; Zheng, B.; Hu, X.; Shao, S.; Huang, F. *Org. Lett.* **2010**, *12*, 2558.  
<http://dx.doi.org/10.1021/ol100770j>  
PMid:20465232
96. Yan, X.; Zhang, M.; Wei, P.; Zheng, B.; Chi, X.; Ji, X.; Huang, F. *Chem. Commun.* **2011**, 47, 9840.  
<http://dx.doi.org/10.1039/c1cc13472h>  
PMid:21808783
97. Yan, X.; Wei, P.; Zhang, M.; Chi, X.; Liu, J.; Huang, F. *Org. Lett.* **2011**, *13*, 6370.  
<http://dx.doi.org/10.1021/ol202657s>  
PMid:22077161

98. Durola, F.; Sauvage, J.-P.; Wenger, O. S. *Coord. Chem. Rev.* **2010**, *254*, 1748.  
<http://dx.doi.org/10.1016/j.ccr.2009.09.034>
99. Niu, Z.; Huang, F.; Gibson, H. W. *J. Am. Chem. Soc.* **2011**, *133*, 2836.  
<http://dx.doi.org/10.1021/ja110384v>  
PMid:21309571
100. Fang, L.; Olson, M. A.; Benitez, D.; Tkatchouk, E.; Goddard III, W. A.; Stoddart, J. F. *Chem. Soc. Rev.* **2010**, *39*, 17.  
<http://dx.doi.org/10.1039/b917901a>  
PMid:20023833
101. Zhang, M.; Zhu, K.; Huang, F. *Chem. Commun.* **2010**, *46*, 8131.  
<http://dx.doi.org/10.1039/c0cc02717k>  
PMid:20830438
102. Wang, C.; Olson, M. A.; Fang, L.; Benitez, D.; Tkatchouk, E.; Basu, S.; Basuray, A. N.; Zhang, D.; Zhu, D.; Goddard, W. A.; Stoddart, J. F. *Proc. Natl. Acad. Sci. U.S.A.* **2010**, *107*, 13991.  
<http://dx.doi.org/10.1073/pnas.1009302107>  
PMid:20663950 PMCID:2922539
103. Trabolsi, A.; Fahrenbach, A. C.; Dey, S. K.; Share, A. I.; Friedman, D. C.; Basu, S.; Gasa, T. B.; Khashab, N. M.; Saha, S.; Aprahamian, I.; Khatib, H. A.; Flood, A. H.; Stoddart, J. F. *Chem. Commun.* **2010**, *46*, 871.  
<http://dx.doi.org/10.1039/b918321c>  
PMid:20107634
104. Jiang, Y.; Cao, J.; Zhao, J.-M.; Xiang, J.-F.; Chen, C.-F. *J. Org. Chem.* **2010**, *75*, 1767.  
<http://dx.doi.org/10.1021/jo902571n>  
PMid:20136155
105. Niu, Z.; Gibson, H. W. *Org. Biomol. Chem.* **2011**, *9*, 6909.  
<http://dx.doi.org/10.1039/c1ob06299a>  
PMid:21870005
106. Xu, D.; Hawk, J. L.; Loveless, D. M.; Jeon, S. L.; Craig, S. L. *Macromolecules* **2010**, *43*, 3556.  
<http://dx.doi.org/10.1021/ma100093b>  
PMid:20479956 PMCID:2869658
107. Pensec, S.; Nouvel, N.; Guilleman, A.; Creton, C.; Boué, F. O.; Bouteiller, L. *Macromolecules* **2010**, *43*, 2529.  
<http://dx.doi.org/10.1021/ma901709e>
108. Burattini, S.; Greenland, B. W.; Merino, D. H.; Weng, W.; Seppala, J.; Colquhoun, H. M.; Hayes, W.; Mackay, M. E.; Hamley, I. W.; Rowan, S. J. *J. Am. Chem. Soc.* **2010**, *132*, 12051.  
<http://dx.doi.org/10.1021/ja104446r>  
PMid:20698543
109. Rancatore, B. J.; Mauldin, C. E.; Tung, S.-H.; Wang, C.; Hexemer, A.; Strzalka, J.; Fréchet, J. M. J.; Xu, T. *ACS Nano* **2010**, *4*, 2721.  
<http://dx.doi.org/10.1021/nn100521f>  
PMid:20402495
110. Tancini, F.; Yebeutchou, R. M.; Pirondini, L.; De Zorzi, R.; Geremia, S.; Scherman, O. A.; Dalcanale, E. *Chem. Eur. J.* **2010**, *16*, 14313.  
<http://dx.doi.org/10.1002/chem.201002237>  
PMid:21125623
111. Greuel, J. R.; Andrews, T. E.; Wichman, J. J.; Tessner, J. D.; Wiegel, K. N. *Liq. Cryst.* **2010**, *37*, 1515.  
<http://dx.doi.org/10.1080/02678292.2010.531404>
112. Li, S.; Zheng, B.; Chen, J.; Dong, S.; Ma, Z.; Huang, F.; Gibson, H. W. *J. Polym. Sci. Part A; Polym. Chem.* **2010**, *48*, 4067.  
<http://dx.doi.org/10.1002/pola.24192>

113. Li, S.; Liu, M.; Zheng, B.; Zhu, K.; Wang, F.; Li, N.; Zhao, X.-L.; Huang, F. *Org. Lett.* **2009**, *11*, 3350.  
<http://dx.doi.org/10.1021/ol9012052>  
PMid:19572601
114. Li, S.; Zheng, B.; Huang, F.; Zakharov, L.; Slebodnick, C.; Rheingold, A.; Gibson, H. W. *Sci. China Chem.* **2010**, *53*, 858.  
<http://dx.doi.org/10.1007/s11426-010-0120-1>
115. Chen, N.-C.; Chuang, C.-J.; Wang, L.-Y.; Lai, C.-C.; Chiu, S.-H. *Chem. Eur. J.* **2012**, *18*, 1896.  
<http://dx.doi.org/10.1002/chem.201103464>  
PMid:22249948
116. Coskun, A.; Hmadeh, M.; Barin, G.; Gándara, F.; Li, Q.; Choi, E.; Strutt, N. L.; Cordes, D. B.; Slawin, A. M. Z.; Stoddart, J. F.; Sauvage, J.-P.; Yaghi, O. M. *Angew. Chem. Inter. Ed.* **2012**, *51*, 2160.
117. Gibson, H. W.; Wang, H.; Niu, Z.; Slebodnick, C.; Zhakharov, L. N.; Rheingold, A. L. *Macromolecules* **2012**, *45*, 1270.  
<http://dx.doi.org/10.1021/ma202373x>
118. Avellini, T.; Li, H.; Coskun, A.; Barin, G.; Trabolsi, A.; Basuray, A. N.; Dey, S. K.; Credi, A.; Silvi, S.; Stoddart, J. F.; Venturi, M. *Angew. Chem. Inter. Ed.* **2012**, *51*, 1611.
119. Capdevila-Cortada, M.; Novoa, J. J. *Chem. Eur. J.* **2012**, *18*, 5335.  
<http://dx.doi.org/10.1002/chem.201103550>  
PMid:22431244
120. Yamaguchi, H.; Harada, A. in *Supramolecular Polymer Chemistry*, Ed. Harada, A. Wiley – VCH: New York, 2012; p 127.  
<http://dx.doi.org/10.1002/9783527639786.ch6>
121. Xiao, T.; Li, S.-L.; Zhang, Y.; Lin, C.; Hu, B.; Guan, X.; Yu, Y.; Jiang, J.; Wang, L. *Chem. Sci.* **2012**, *3*, 1417.  
<http://dx.doi.org/10.1039/c2sc01004f>
122. Sannohe, Y.; Sugiyama, H. *Bioorg. Med. Chem.* **2012**, *20*, 2030.  
<http://dx.doi.org/10.1016/j.bmc.2012.01.040>  
PMid:22364954
123. Ito, K. *Polymer J.* **2012**, *44*, 38.  
<http://dx.doi.org/10.1038/pj.2011.85>
124. Inoue, Y.; Ye, L.; Ishihara, K.; Yui, N. *Colloids Surfaces B* **2012**, *89*, 223.  
<http://dx.doi.org/10.1016/j.colsurfb.2011.09.020>  
PMid:21974908
125. Yamada, Y.; Hashida, M.; Nomura, T.; Harashima, H.; Yamasaki, Y.; Kataoka, K.; Yamashita, A.; Katoono, R.; Yui, N. *Chem. Phys. Chem.* **2012**, *13*, 1161.  
<http://dx.doi.org/10.1002/cphc.201100800>  
PMid:22383277
126. Wang, P.-J.; Wang, J.; Ye, L.; Zhang, A.-Y.; Feng, Z.-G. *Polymer* **2012**, *53*, 2361.  
<http://dx.doi.org/10.1016/j.polymer.2012.03.060>
127. Hagiwara, T.; Murano, Y.; Watanabe, Y.; Hoshi, T.; Sawaguchi, T. *Tetrahedron Lett.* **2012**, *53*, 2805.
128. Hagiwara, T.; Yamazaki, M.; Suzuki, T.; Sawaguchi, T.; Yano, S. *Polymer* **2011**, *52*, 5426.  
<http://dx.doi.org/10.1016/j.polymer.2011.10.022>
129. Heine, J.; Schmedt auf der Gunne, J.; Dehnen, S. *J. Am. Chem. Soc.* **2011**, *133*, 10018.  
<http://dx.doi.org/10.1021/ja2030273>  
PMid:21657228
130. Bunha, A.; Tria, M. C.; Advincula, R. *Chem. Commun.* **2011**, *47*, 9173.  
<http://dx.doi.org/10.1039/c1cc13162a>  
PMid:21748185
131. Fioravanti, G. *Current Org. Synth.* **2012**, *9*, 199.  
<http://dx.doi.org/10.2174/157017912799828996>

132. Balzani, V.; Credi, A.; Venturi, M. In *From Non-Covalent Assemblies to Molecular Machines*, Eds. Sauvage, J. P.; Gaspard, P. Wiley-VCH: New York, 2011; p 159.
133. Barin, G.; Coskun, A.; Friedman, D. C.; Olson, M. A.; Colvin, M. T.; Carmielli, R.; Dey, S. K.; Bozdemir, O. A.; Wasielewski, M. R.; Stoddart, J. F. *Chem. Eur. J.* **2011**, *17*, 213.  
<http://dx.doi.org/10.1002/chem.201002152>  
PMid:21207618
134. Prabhakaran, P.; Priya, G.; Sanjayan, G. J. *Angew. Chem. Int. Ed.* **2012**, *51*, 4006.  
<http://dx.doi.org/10.1002/anie.201107521>  
PMid:22374711
135. Li, Z.-T.; Zhang, K.-D.; Shi, Z.-M.; Wang, L.; Zhou, C.; Lu, B.-Y. *Pure Appl. Chem.* **2012**, *84*, 965.  
<http://dx.doi.org/10.1351/PAC-CON-11-08-20>
136. Zhang, K.-D.; Zhao, X.; Wang, G. T.; Liu, Y.; Zhang, Y.; Lu, H. J.; Jiang, X. K.; Li, Z. T. *Angew. Chem. Int. Ed.* **2011**, *50*, 9866.  
<http://dx.doi.org/10.1002/anie.201104099>  
PMid:21887826
137. Silvi, S.; Venturi, M.; Credi, A. *Chem. Commun.* **2011**, *47*, 2483.  
<http://dx.doi.org/10.1039/c0cc03829f>  
PMid:21135934
138. Ruangsupapichat, N.; Pollard, M. M.; Harutyunyan, S. R.; Feringa, B. L. *Nat. Chem.* **2011**, *3*, 53.  
<http://dx.doi.org/10.1038/nchem.872>  
PMid:21160518
139. Ferrand, Y.; Gan, Q.; Kauffmann, B.; Jiang, H.; Huc, I. *Angew. Chem. Int. Ed.* **2011**, *50*, 7572.  
<http://dx.doi.org/10.1002/anie.201101697>  
PMid:21717537
140. Gan, Q.; Ferrand, Y.; Bao, C.; Kauffmann, B.; Grelard, A.; Jiang, H.; Huc, I. *Science* **2011**, *331*, 1172.  
<http://dx.doi.org/10.1126/science.1200143>  
PMid:21385710

## 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 à Toulouse, France, she moved to Jan Długosz University of Czestochowa, 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 Dlugosz University (formerly Pedagogical University) of Czestochowa, in Institute of Chemistry, Environment Protection and Biotechnology. Dr. Jolanta Kozłowska obtained PhD at Technical University of Wroclaw; 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.