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ROTAXANES CONTAINING QUATERNAR AZAAROMATIC MOIETIES

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Abstract- In the paper at first rotaxanes are briefly described, then rotaxanes bearing quaternary azaaromatic moiety in the thread are presented followed by those containing quaternary azaaromatic moiety in the ring.

INTRODUCTION

In recent years the rapid development of research concerning supramolecular chemistry is observed.[1-3] Interlocked systems such as rotaxanes,[4-10] catenanes[11-14] and knots[15] are a topic of numerous works; their classification is proposed.[16] Research of rotaxanes and catenanes[3,17] is made in the aspect of their use in the fabrication of molecular machines[18,19] and electronic devices.[20-22]

The present review concerns rotaxanes; many different protocols, involving self-assembly[23] have been developed for the template-directed syntheses of these species.[24-27] External stimuli of two-station [2]rotaxanes, such as light[24] or electrical[28] excitation, redox reactions[29] and pH changes[25] may alter the preferential recognition site of the ring; this results in its shuttling between two stations[30,31] which is useful for mechanical and switching functions.

Rotaxanes are promising in the construction of chemically, photochemically and electrochemically driven molecular machines[1,3,32] performing shuttling[30,31] or muscle-like contractions and elongations,[5] they serve for the design of molecular cables[33] and information processors[34] and are able to switch a chiral optical response “on” or “off”.[35] Rotaxanes synthesized on surfaces may form two-dimensional crossbar circuits for logic applications.[28]

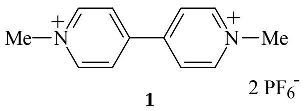
As the number of rotaxanes and pseudorotaxanes reported is enormous, only those containing quaternary azaaromatic moieties will be presented. Supramolecular species[36,37] and quaternary azaaromatics[38-41] are a topic of our research group. Quaternary azaaromatics are of interest for their reactivity,[42,43] biological activities[44-49] and various applications[50,51] – as dyes,[52-54] surfactants,[55] antifoulants[56,57] and catalysts;[58] they may serve for construction of luminescence[59] and NLO (nonlinear optical)[60,61] materials and unimolecular electrical rectifiers.[62-65] Some quaternary azaaromatics are DNA intercalators[66-68] or have character of alkaloids.[69] One should also mention viologens[70-73] and porphyrins bearing quaternary azaaromatic groups.[74,75]

In the first part of the review rotaxanes bearing quaternary azaaromatic moiety in the thread will be presented, and in the second one those containing quaternary azaaromatic moiety in the ring. References are cited of works appeared in years 2002 and 2003, examples which are shown were reported mainly in 2003.

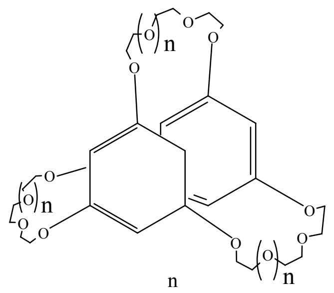
1. ROTAXANES CONTAINING QUATERNARY AZAAROMATIC MOIETY IN THE THREAD

In the study of inclusion complexes it was established that cryptands are powerful receptors for viologen derivatives; the formed host-guest systems have much higher association constants than host-guest complexes of analogous crown ethers.[76-79]

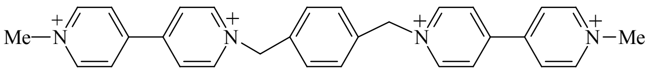
The complex formation of viologens (**1-3**) with cryptands (**4, 5**) and crown ethers (**6-8**) was investigated. Acetone solutions of **2** with cryptand (**5**) and of **2** with crown ether (**8**) are orange and yellow, respectively, due to the charge-transfer interactions. In acetone solution **2** forms with **5** the 1:2 complex (**2·5**$_2$), while with **8** the 1:1 complex (**2·8**) is obtained, this difference being due to the rigidity of **5**. The (**2·5**$_2$) complex has a structure of the cryptand-based [3]pseudorotaxane, stabilized by hydrogen bonding and face-to face π-stacking interactions.[80]



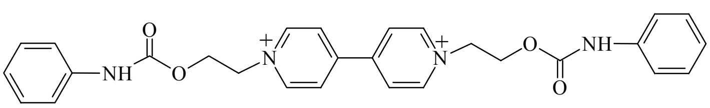
1 2 PF_6^-



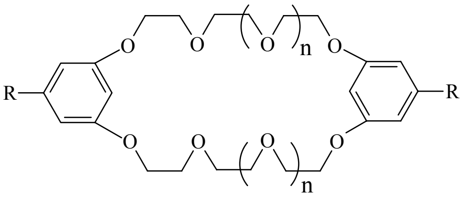
	n
4	1
5	2



2 4 PF_6^-



3 2 PF_6^-



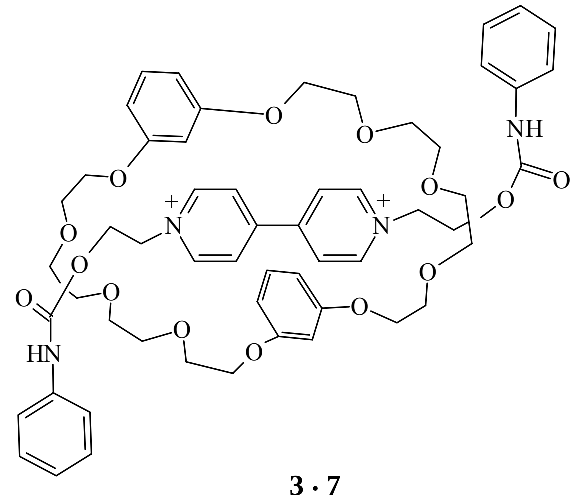
	n	R
6	1	H
7	2	H
8	2	CH_2OH

In cryptand complexes, the different stoichiometries are possible for the same host-guest pair,[81] for example **1** forms with **4** and with **5** the 1:1 complexes in solution, while in the solid state 1:2 complexes have been obtained.

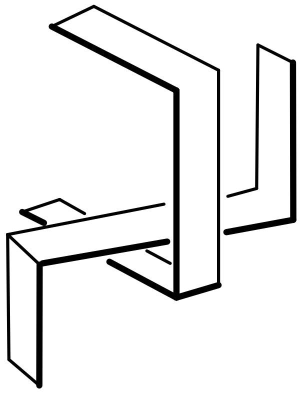
Three CD_3COCD_3 solutions containing equimolar amounts of **1** with **4**, **5** and **6** were investigated by ^{1}H NMR spectrometry. The association constants of **1·4** and **1·5** are higher than that of **1·6**.[82] In all three solutions the yellow color was observed as a result of CT interactions between the electron poor guest (**1**) and the electron-rich aromatic rings of hosts (**4-6**), stronger in **1·4** and **1·5** than in **1·6**.

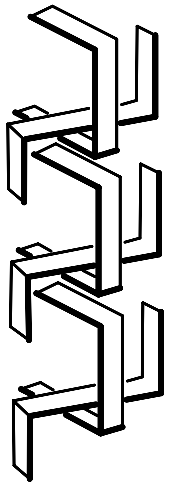
In 1:1 complexes the cryptand cavity is fully occupied by the guest, while in 1:2 complexes the guest occupies parts of cavities of two cryptand molecules. The cavity of **4** is smaller than that of **5**, therefore in **1·4**$_2$ the guest (**1**) protrudes out from the cavities of two molecules (**4**) forming a pseudorotaxane, while for the complex (**1·5**$_2$) this is not the case.

Many works concern supramolecular, *i.e.* noncovalent polymers,[83,84] among them species of a pseudorotaxane character[85] are the subject of intense study. One should mention here supramolecular poly(taco complex) of **3** with crown ether (**7**) (taco is a folded sandwich type as shown below). Single crystals of **3·7**, grown from a mixture of acetone and chloroform are stabilized by C-H...O and face-to face π-stacking interactions between pyridinium rings of **3** and both phenylene rings of **7**. Four hydrogen bonds among six ones between **3** and **7** involve *N*-methylene hydrogen atoms, this behavior being rather uncommon in host-guest hydrogen bonding. In the solid state the complex is arranged linearly to form supramolecular poly(taco complex), in which hydrogen bonding of the PF_6^- counterions with the urethane linkages of the guest (**3**) plays a crucial role.[86]

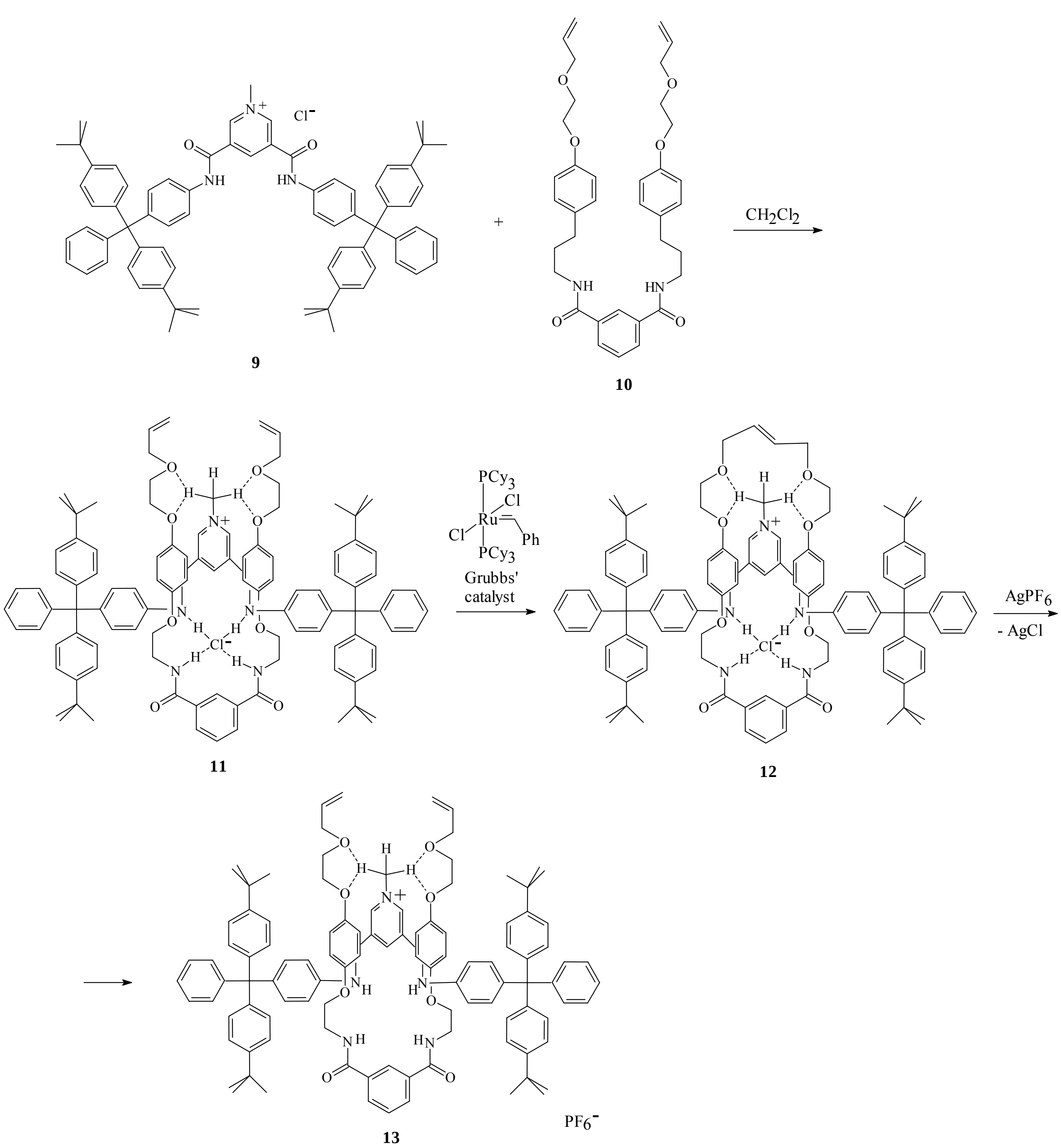


3 · 7



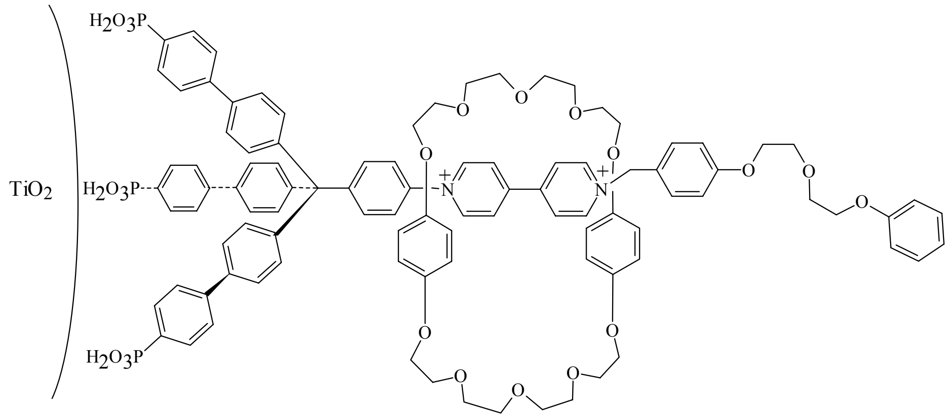


The following reaction is an example of the anion-templated rotaxane preparation by a clipping procedure.

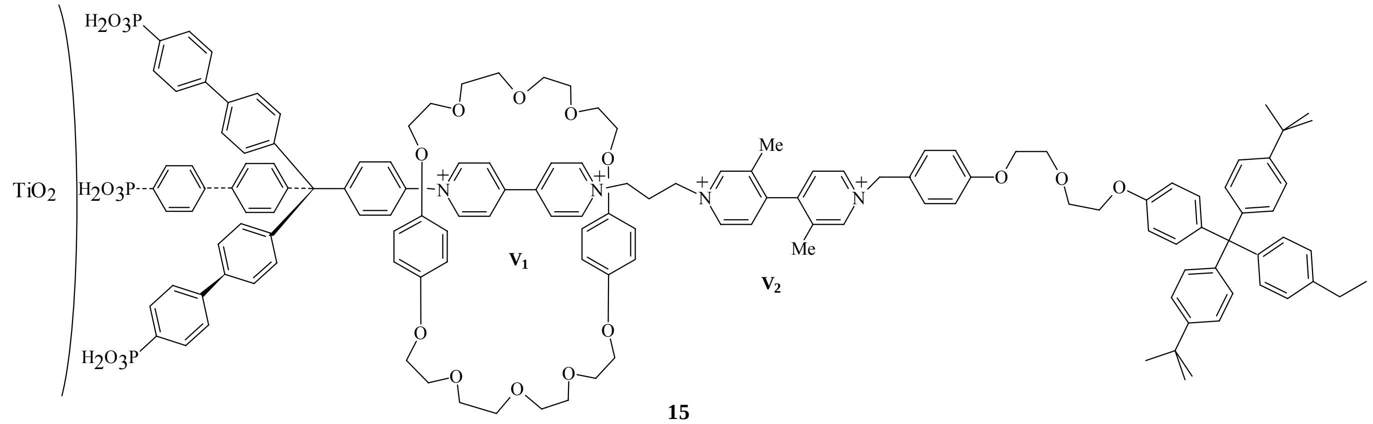


The ion pair (**9**) serving as a dumbbell forms with diamide (**10**) the complex (**11**), which was submitted to Grubbs' ring-closing metathesis leading to rotaxane (**12**) stabilized by hydrogen bonds. Only *trans* isomer was produced in this reaction. The removal of chloride anion template from **12** by treatment with $AgPF_6$ affords rotaxane (**13**). It was established that pyridinium cation in **13** shows higher selectivity for chloride anions than the noninterlocked pyridinium cation in the ion pair (**9**).[87]

Pseudorotaxane (**14**)[88] and rotaxane (**15**),[89] adsorbed at the surface of a titanium dioxide nanoparticle have been reported.



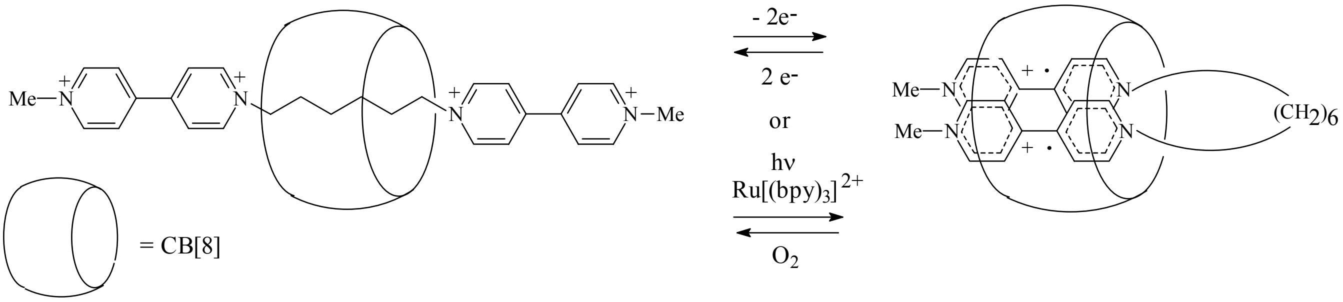
14



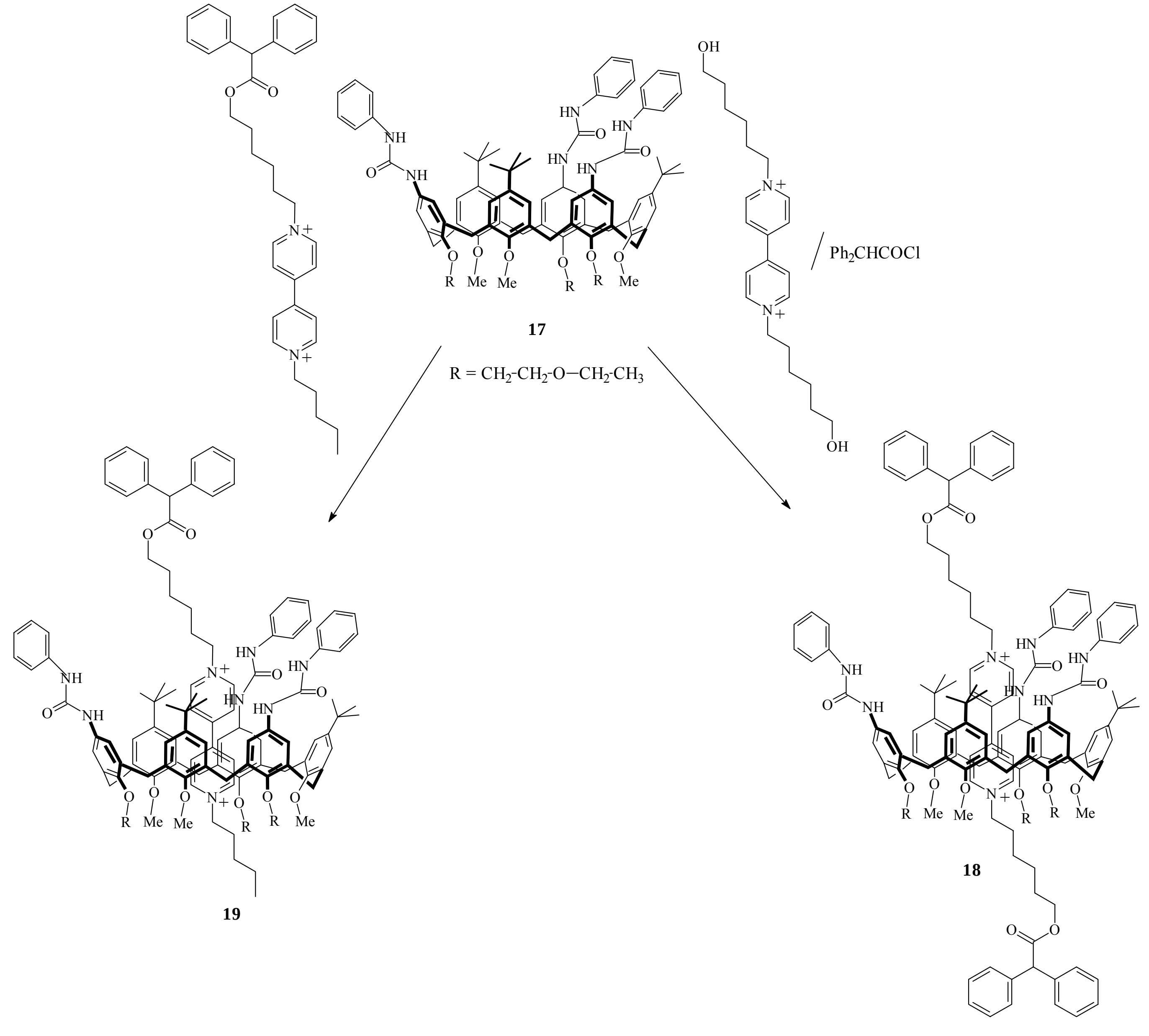
15

The rotaxane (**15**) is electronically switchable. By applying a suitable potential the bis-1,4-phenylene[34]crown-10 ring (**16**) may be localized at either $\mathbf{V_1}$ or $\mathbf{V_2}$ recognition sites. The ring is initially localized on the unit ($\mathbf{V_1}^{2+}$). The transfer of one electron to $\mathbf{V_1}^{2+}$ leads to the radical cation ($\mathbf{V_1}^{+\bullet}$), therefore the ring is not longer localized on $\mathbf{V_1}^{2+}$ but interacts with both $\mathbf{V_1}$ and $\mathbf{V_2}$. Transfer of a second electron to $\mathbf{V_1}$ results in the formation of the diradical ($\mathbf{V_1}^{\cdot\cdot}$) and the localization of the ring (**16**) on $\mathbf{V_2}^{2+}$. The further transfer of electrons causes the formation of fully reduced [2]rotaxane, accompanied by a conformational change – the fully reduced [2]rotaxane folds, enabling the stacking of diradicals ($\mathbf{V_1}^{\cdot\cdot}$) and ($\mathbf{V_2}^{\cdot\cdot}$). The subsequent removal of electrons causes the unfolding of the rotaxane and results in the localization of the ring (**16**) at first on $\mathbf{V_2}^{2+}$ and then on $\mathbf{V_1}^{2+}$, coming back to the starting point. The above electronically switchable rotaxane is promising in the design of functional nanoscale architectures.[89]

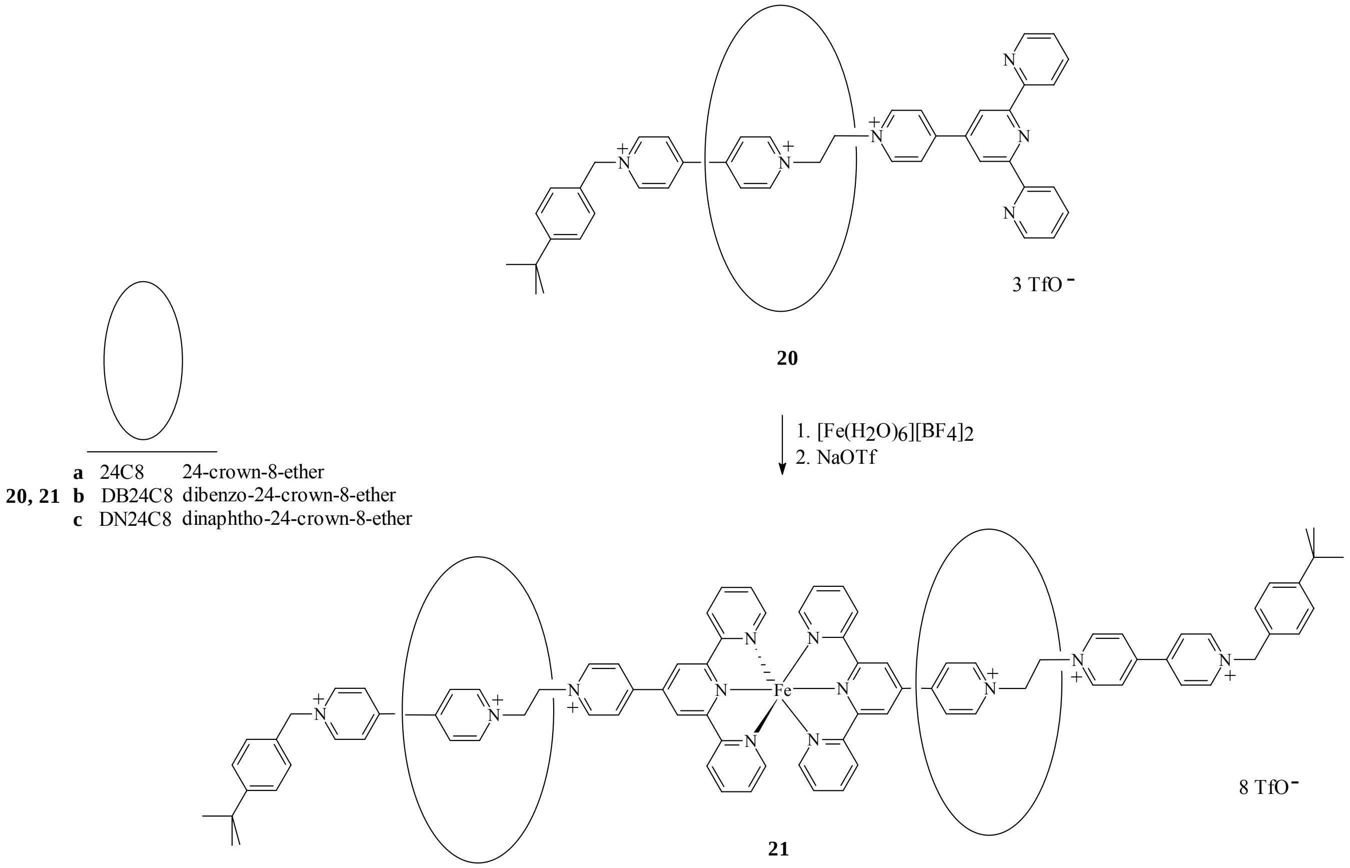
An example of a molecular machine is [2]pseudorotaxane consisting of hexamethylene-bridged bisviologen and cucurbit[8]uril, which reversibly forms a molecular loop by electrochemical or photochemical reduction, as shown below.[90]



Calixarene (**17**) may serve as a ring and viologen derivatives as threads in the construction of rotaxanes or pseudorotaxanes. It was established by ^{1}H NMR spectral study of rotaxane (**18**) and of pseudorotaxane (**19**) that the thread accesses the calixarene cavity only through the wide rim, although both rims are large enough for this purpose. Syntheses of **18** and **19** proceed as follows.[91]

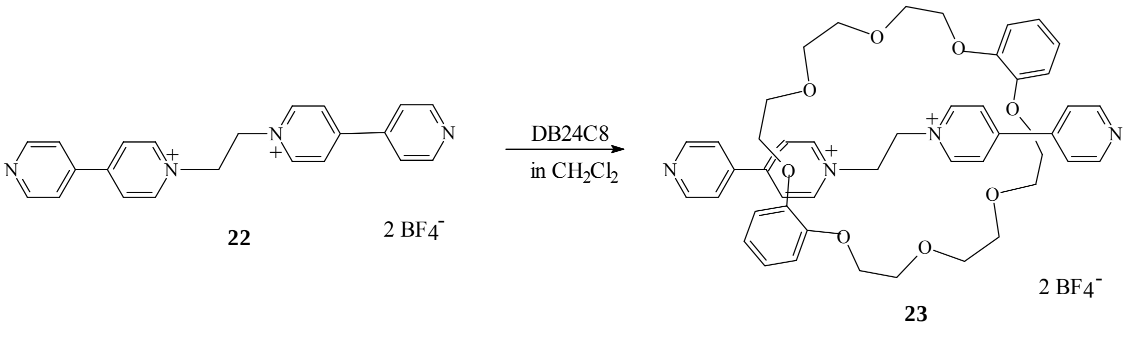


Terpyridine stoppered [2]rotaxanes (**20a-c**) have been synthesized by slipping procedure and used as ligands to form homoleptic Fe(II) complexes (**21a-c**).[92]

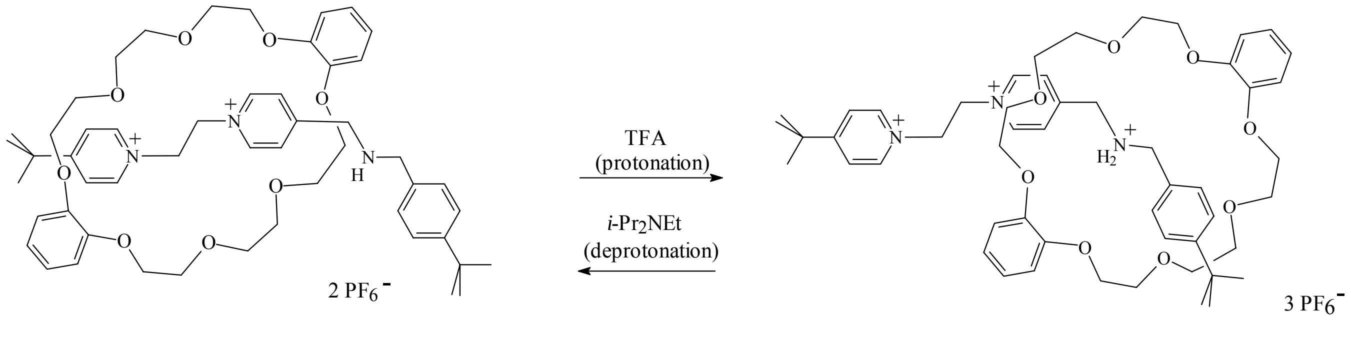


Polyrotaxanes may be obtained by metal-ligand self-assembly; in this way the formation of cavities and channels is possible.[93] The synthesis of metal-based polyrotaxanes consisting of pyridinium threads, crown ether rings and transition metal ion nodes has been reported. The cavity properties may be controlled by the modifications of crown ethers; the dynamic motion of the crown ether threaded onto a metal-ligand net is promising in the design of solid-state materials.

Dipyridinium salt (**22**) gives with DB24C8 the pseudorotaxane (**23**) which acts as a ligand to afford [2]rotaxanes stoppered by metal complexes. This procedure may serve for metal-ligand self-assembly reactions leading to linear 1D and square-grid 2D metal-based polyrotaxanes. When one equivalent of **22** is mixed with two equivalents of DB24C8 and one equivalent of $[M(H_2O)_6][BF_4]_2$ (M=Co, Zn) in MeCN, the formation of polyrotaxanes $\{[M(H_2O)_2(MeCN)_2(\mathbf{23})][BF_4]_4\cdot(MeCN)_2(H_2O)_2\}_x$ takes place.[94]



It was observed that [2]rotaxane (**24**) containing two recognition sites for the ring DB24C8 forms a pH-switching system, shown below.

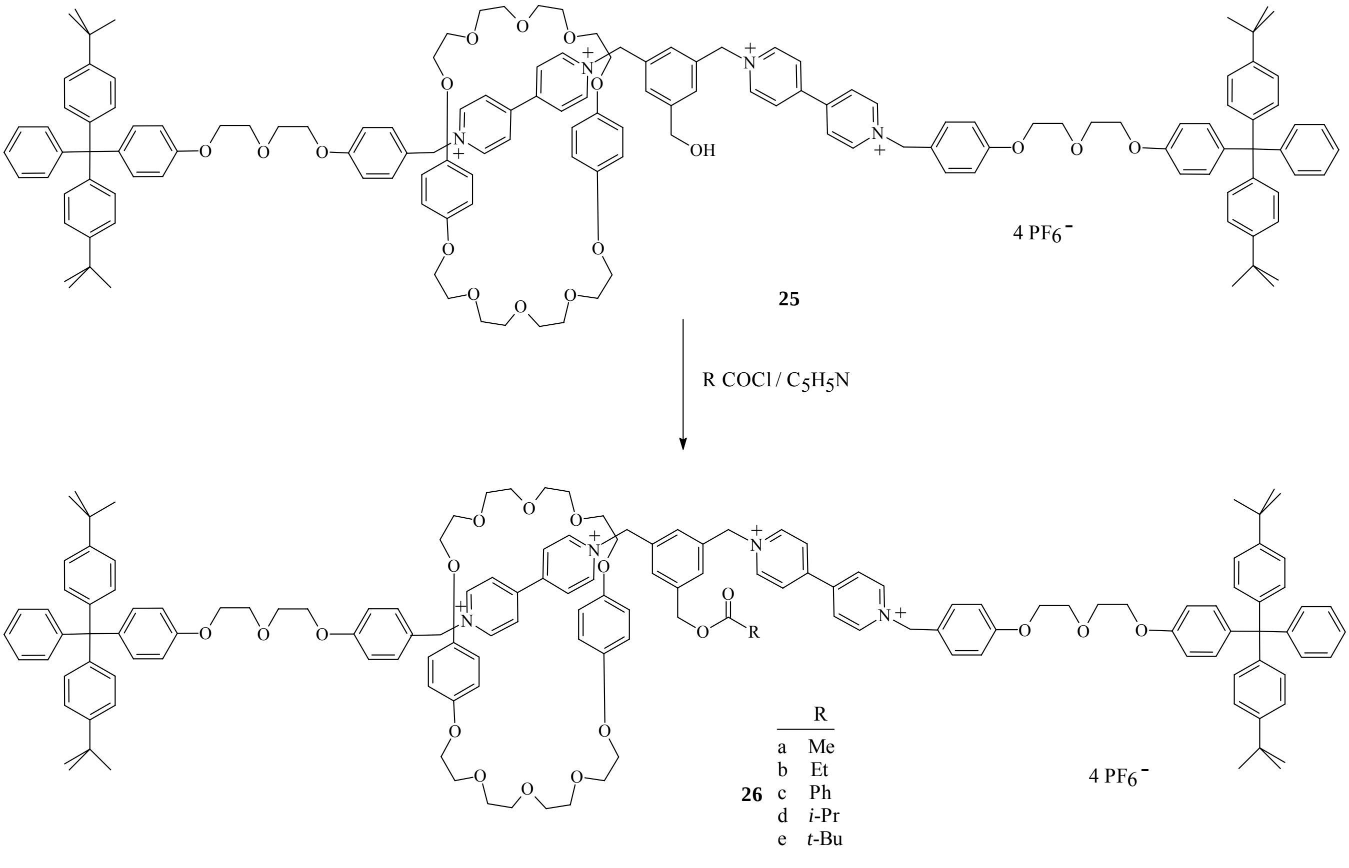


24

24·H

In $CDCl_3$ solution the ring encircles the 1,2-bis(pyridinium)ethane moiety; the protonation results in the movement of the ring to the $CH_2NH_2^+CH_2$ recognition site, *i.e.* in the formation of **24·H**. The process is completely reversible.[25]

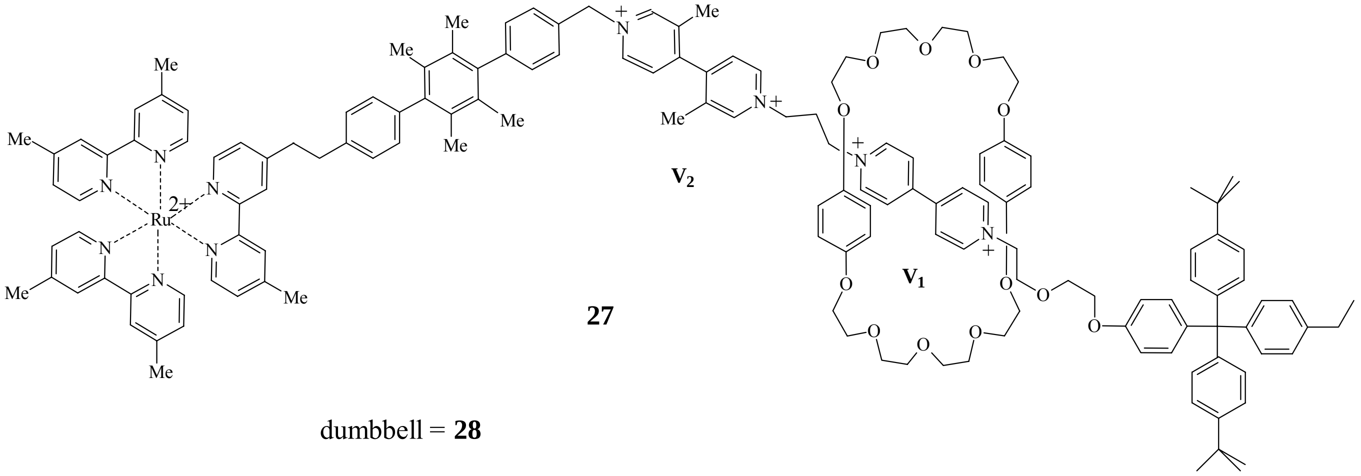
The two-station rotaxane (**25**) obtained by slipping procedure has been acylated to give rotaxanes (**26a-e**). The dynamic ^1H NMR spectroscopic analysis indicates that shuttling of the ring (**16**) in rotaxanes (**26a-d**) takes place, while in **26e** it does not occur since the steric barrier (*t*-Bu) is too high.[95] The above results show that shuttling in rotaxanes can be tuned by the modification of their structure.



In the study of electroactive films incorporating 4,4'-bipyridinium building blocks,[96] the use of amphiphilic rotaxane (**25**) for preparation of monolayers at the air/water interface was reported.

The rotaxane (**25**) has an amphiphilic character due to the presence of hydrophilic 4,4'-bipyridinium cations and hydrophobic tetraarylmethane stoppers;[28] it does not dissolve in aqueous solutions and may be compressed into organized monolayers at the air/water interface. The monolayer can be transferred from the air/water interface to electrode surface. The electrode/monolayer/electrode junction was formed combining the L-B (Langmuir-Blodgett) technique with electron beam evaporation, this result being promising in design of electronic devices.

Studies of supramolecular chemistry[97] have revealed that light excitation of molecular machines causes mechanical movement without the formation of waste products. The rotaxane (**27**) consists of the crown ether ring (**16**), threaded onto the dumbbell (**28**) bearing a ruthenium (II) photosensitizer (**29**) as one of stoppers and incorporating two different 4,4'-bipyridinium stations (**V$_1$**) and (**V$_2$**).[98]



27

dumbbell = **28**

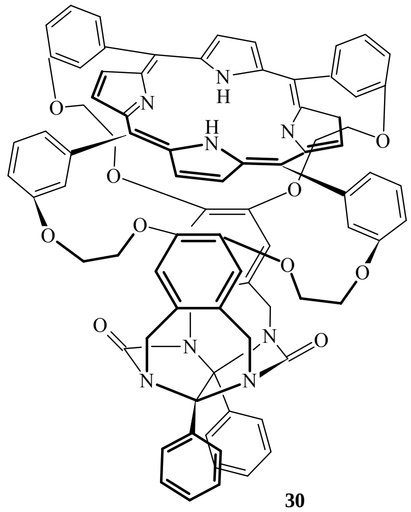
Due to the presence of two different electron accepting bipyridinium units, two translational isomers of **27** are possible, the more stable is this in which the ring encircles the stronger electron acceptor, *i.e.* **V$_1$**. Light excitation of the ruthenium photosensitizer causes the transfer of an electron from **29** to **V$_1$**, reducing it to the radical cation. When the back electron transfer from reduced **V$_1$** to oxidized **29** is slow, the ring moves to **V$_2$** and then returns to **V$_1$** due to the back electron-transfer, restoring the initial state.

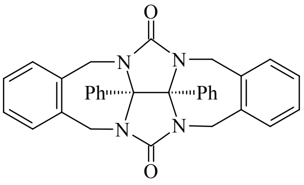
The operation of this molecular machine, *i.e.* the ring shuttling requires a long lifetime of the photoinduced electron transfer state; for this purpose the incorporation of **27** and **28** into Al/MCM-41 aluminosilicate was attempted.[98-100] However, rotaxane (**27**) undergoes dethreading under incorporation conditions, only dumbbell (**28**) could be incorporated into the aluminosilicate channels.

In the investigation of photochemistry of **28** hosted inside aluminosilicate mesopores it has been shown that the reduced **V$_1$** is long-lived, this behavior being promising for the operation of molecular machine. The coadsorption of an electron donor such as 1,4-dimethoxybenzene may significantly increase the lifetime of **V$_1$**, up to several milliseconds.

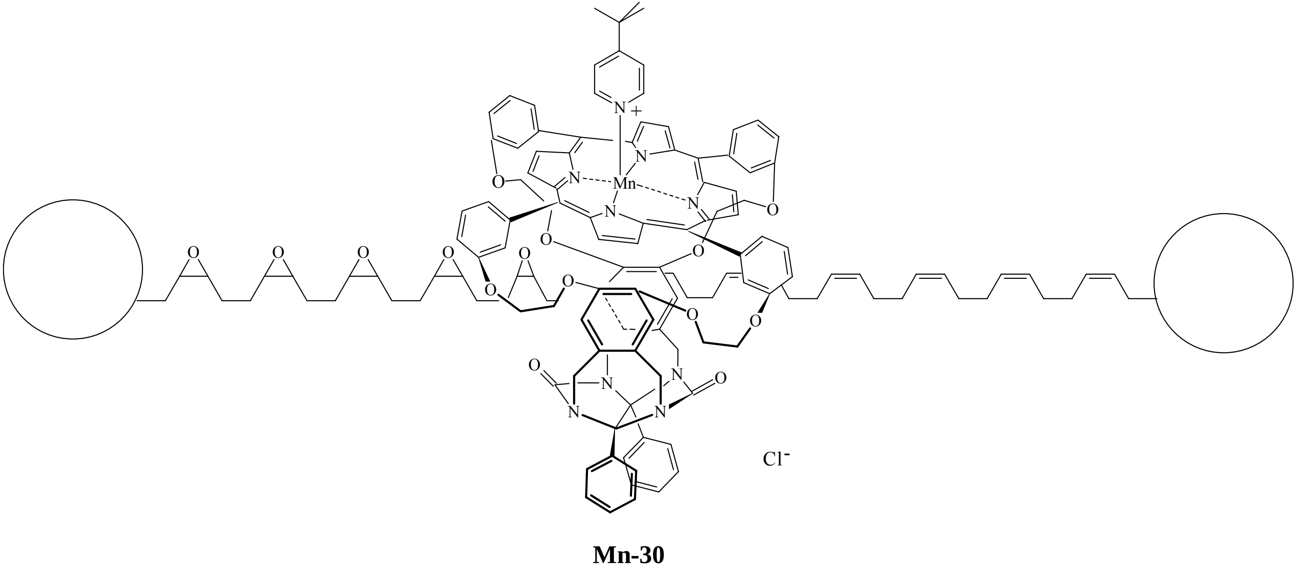
Rotaxanes and pseudorotaxanes are interesting not only for their application in molecular machines, but also because catalytically efficient pseudorotaxanes take part in DNA replication and degradation.[101] In such structures the enzyme (for example DNA polymerase III) completely encircles the DNA strand and acts catalytically on the macromolecular substrate before dissociating from it. Such processive enzymes are very efficient.

Porphyrin clip (**30**) containing porphyrin and diphenylglycoluril derivative (**31**) may serve for construction of synthetic analogues of processive enzymes; it forms very stable 1:1 host-guest complexes with viologens. [102]


30

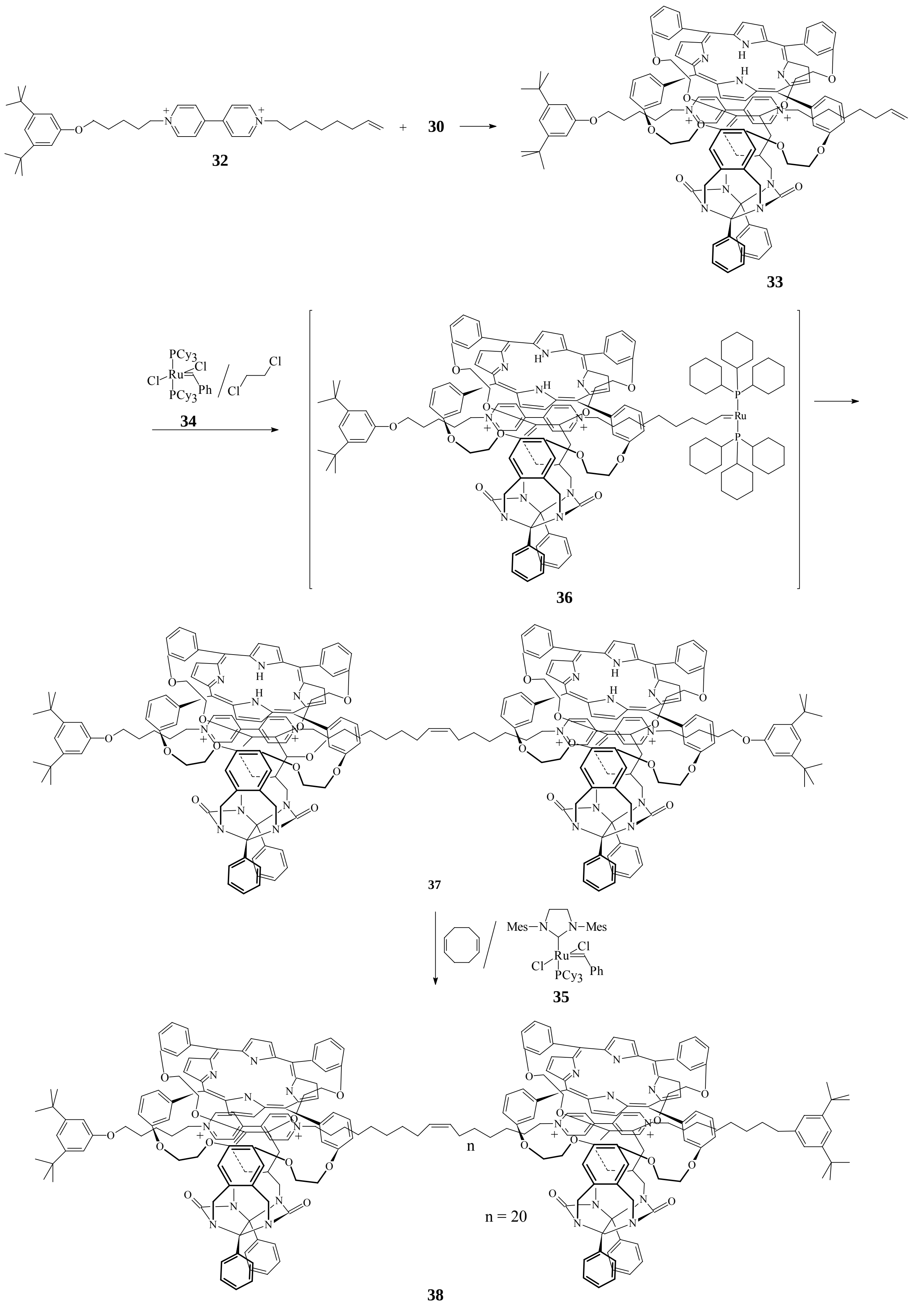

31

Mn-**30** is a very active epoxidation catalyst;[103] in the rotaxane serving as a processive mimic consisting from Mn-**30** and polymeric thread with double bonds Mn-**30** slides over the thread epoxidizing double bonds, as shown below.

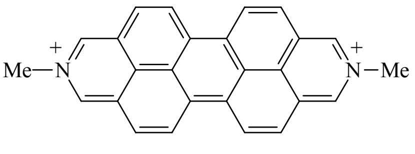


Mn-30

Rotaxane of this kind was synthesized by using olefin metathesis. The reaction of viologen (**32**) with **30** affords pseudorotaxane (**33**) which in the presence of Grubbs' catalyst (**34**), *via* a [2]rotaxane intermediate (**36**) leads to [3]rotaxane (**37**). The rotaxane (**37**) was used as a chain transfer agent in polymerization of 1,5-cyclooctadiene catalyzed by **35**, which affords [3]rotaxane (**38**).[102]


32
30
33
PCy3
Ru
Cl
Cl
Ph
PCy3
Cl
Cl
34
36
P
Ru
P
37
Mes
N
N
Mes
Ru
Cl
Cl
PCy3
Ph
35
n
n = 20
38

The rigid, π-accepting aromatic polycycle (**39**) forms with the electron-donating crown ether (**16**) in MeCN the 1:1 and 1:2 complexes, depending on concentration of **16**. In 1:1 complex the ring is located at the end of **39**. The 1:2 complex, in which two ring molecules are situated at both *N*-methylated aza ends of **39** is a [3]pseudorotaxane.[104]

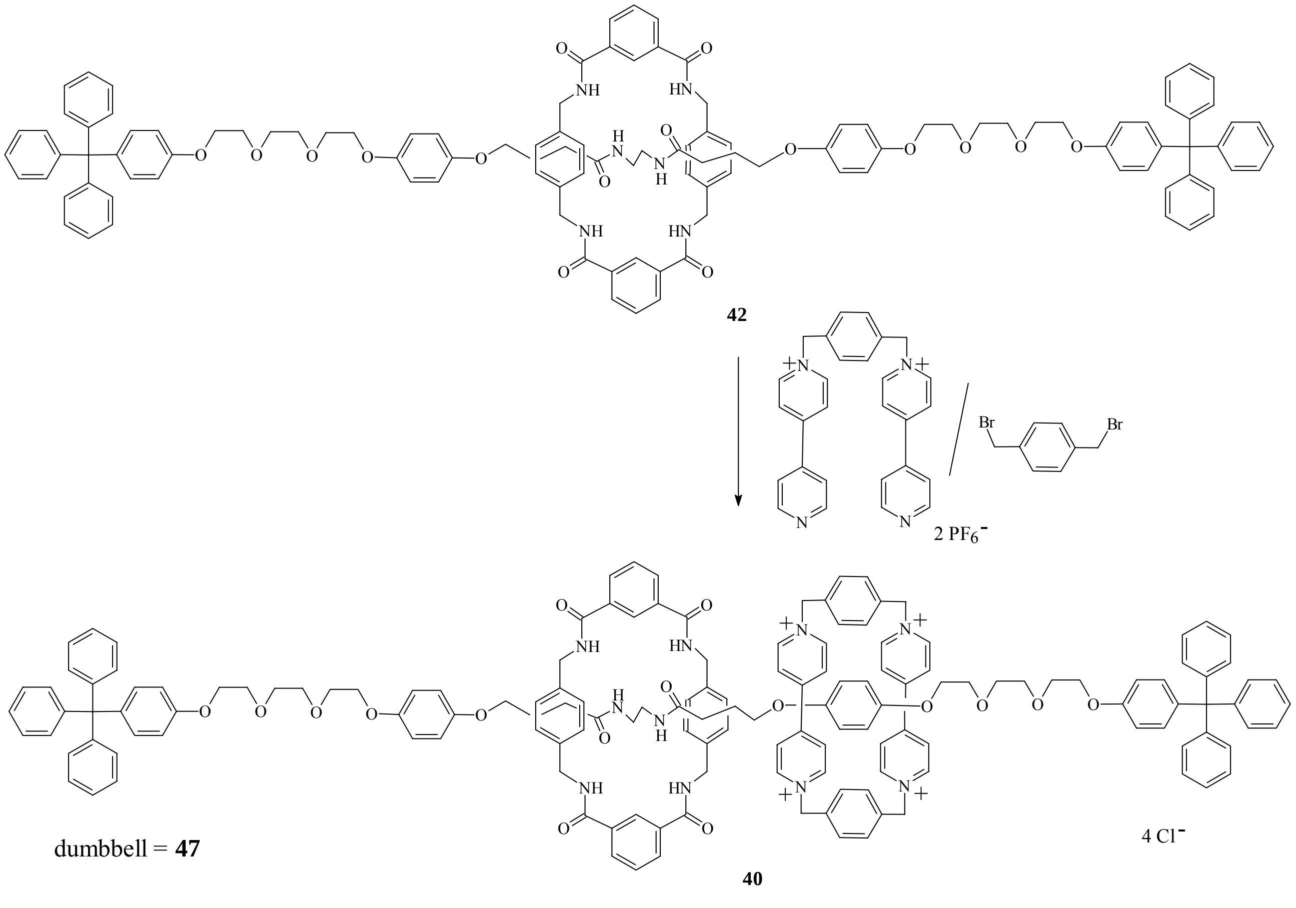


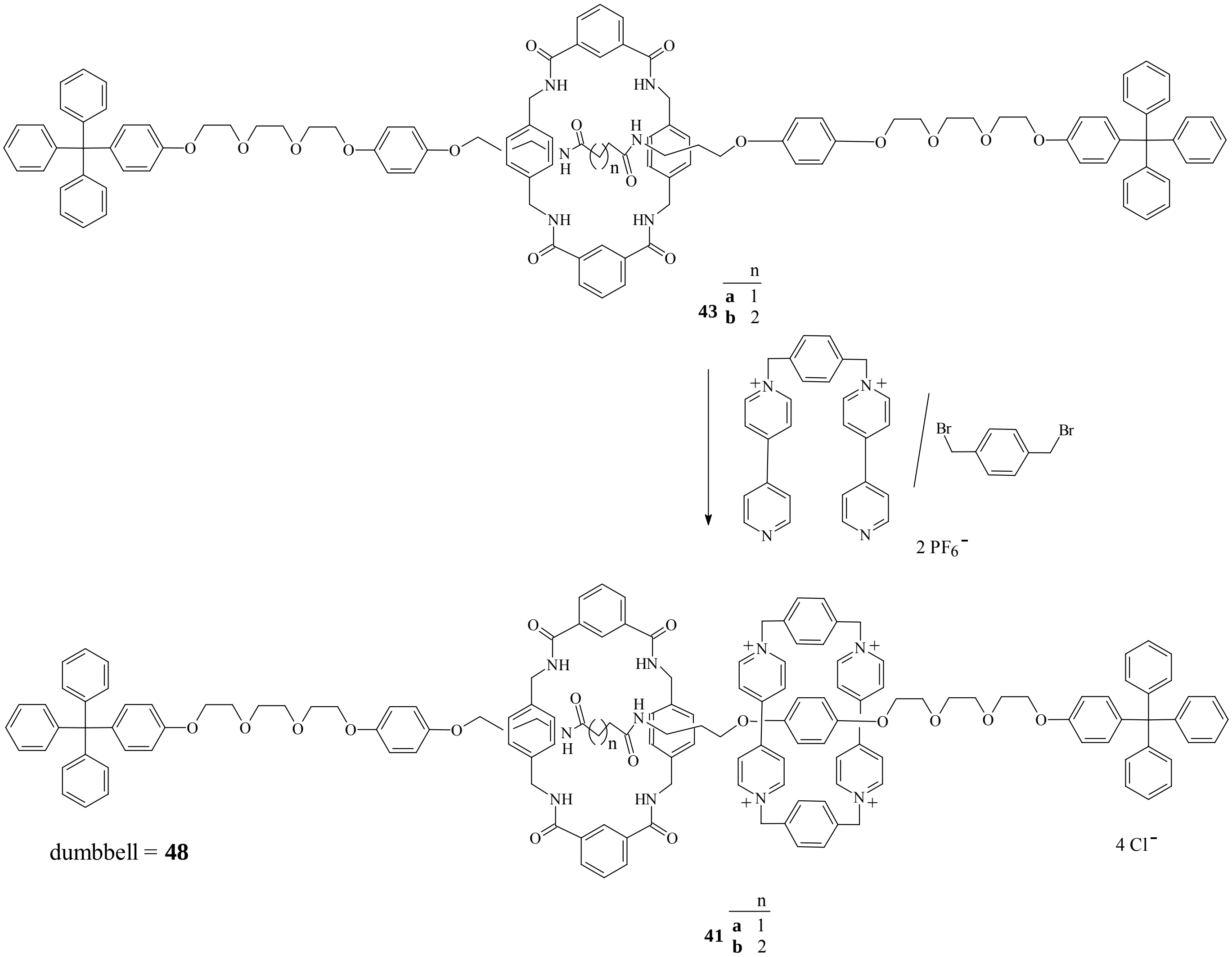
39

Binding causes the extinction of fluorescence from **39** and the appearance of a CT absorption band in the visible region. Illumination of this CT band promotes the formation of an intimate radical ion pair which does not separate into solvated ions. The subsequent charge recombination results in the enhanced population of the triplet state of **39**, much less energetic than the CT state.

2. ROTAXANES CONTAINING QUATERNARY AZAAROMATIC MOIETY IN THE RING

Hetero[3]rotaxanes (**40**) and (**41a,b**) were synthesized from neutral [2]rotaxanes (**42**) and (**43a,b**) which were obtained by clipping procedure, and their inter-ring behavior was compared with that of heterorotaxane (**44**). The above three heterorotaxanes comprise the neutral tetramide cyclophane (**45**) and the tetracationic cyclobis(dipyridinium) (**46**) as rings encircling the dumbbells (**47-49**).[105]

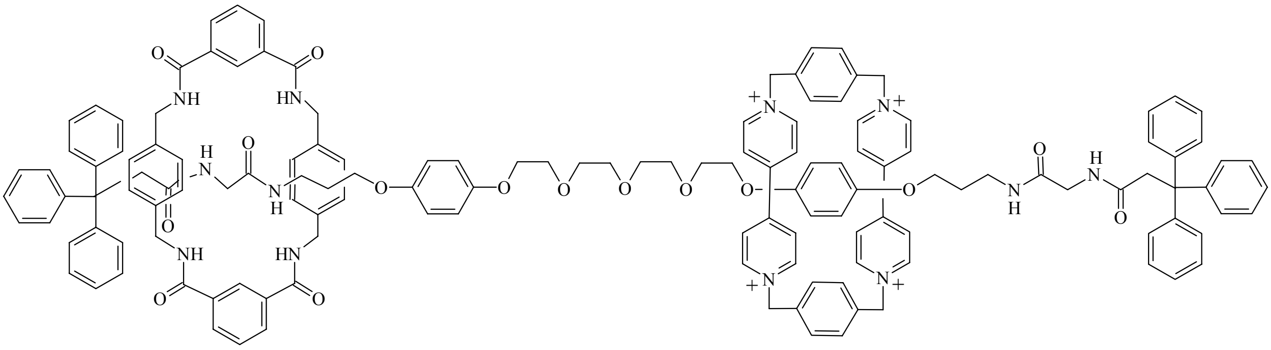




	n
43 **a**	1
b	2

dumbbell = **48**

	n
41 **a**	1
b	2



dumbbell = **49**

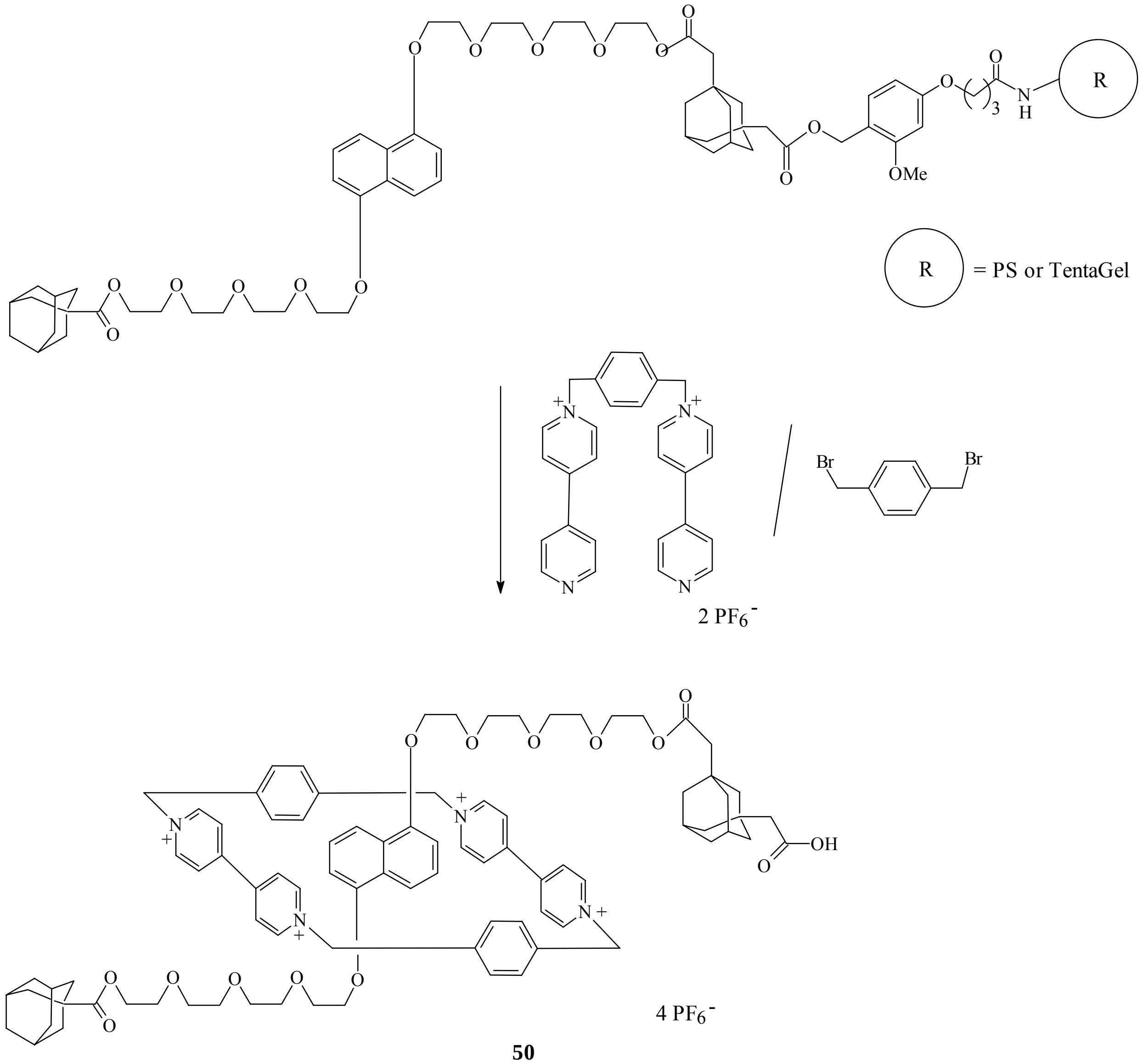
44

Two rotaxanes (**40**) and (**41a,b**) contain the ring (**45**) (the hydrogen-bonding template) at the center of the molecule, and the electron-rich hydroquinone moiety (the donor-acceptor interaction template) between **45** and the triphenylmethyl stopper, while in the third rotaxane (**44**) the ring (**45**) is situated between hydroquinone molecule and the stopper.

Hetero[3]rotaxanes have properties which are not available in homo[3]rotaxanes, for example the activation energy for the shuttling of **46** along the thread is lower in hetero[3]rotaxanes than in homo[3]rotaxanes due to the presence of the neutral tetramide cyclophane (**45**) in the former ones.

The ^{1}H NMR and UV spectral studies show that the different situation of the ring (**45**) in **40** and **41a,b** as compared with that of **44** results in the increased repulsion between the rings (**45**) and (**46**) in [3]rotaxanes (**40**) and (**41a,b**), and a lower donor-acceptor interaction between hydroquinone moieties and **46**; for the first time the NOE between rings (**45**) and (**46**) in [3]rotaxane (**40**) has been observed.[105]

A solid-phase synthesis of [2]rotaxane (**50**) stoppered by adamantyl groups has been performed by clipping procedure, as shown below.[106]

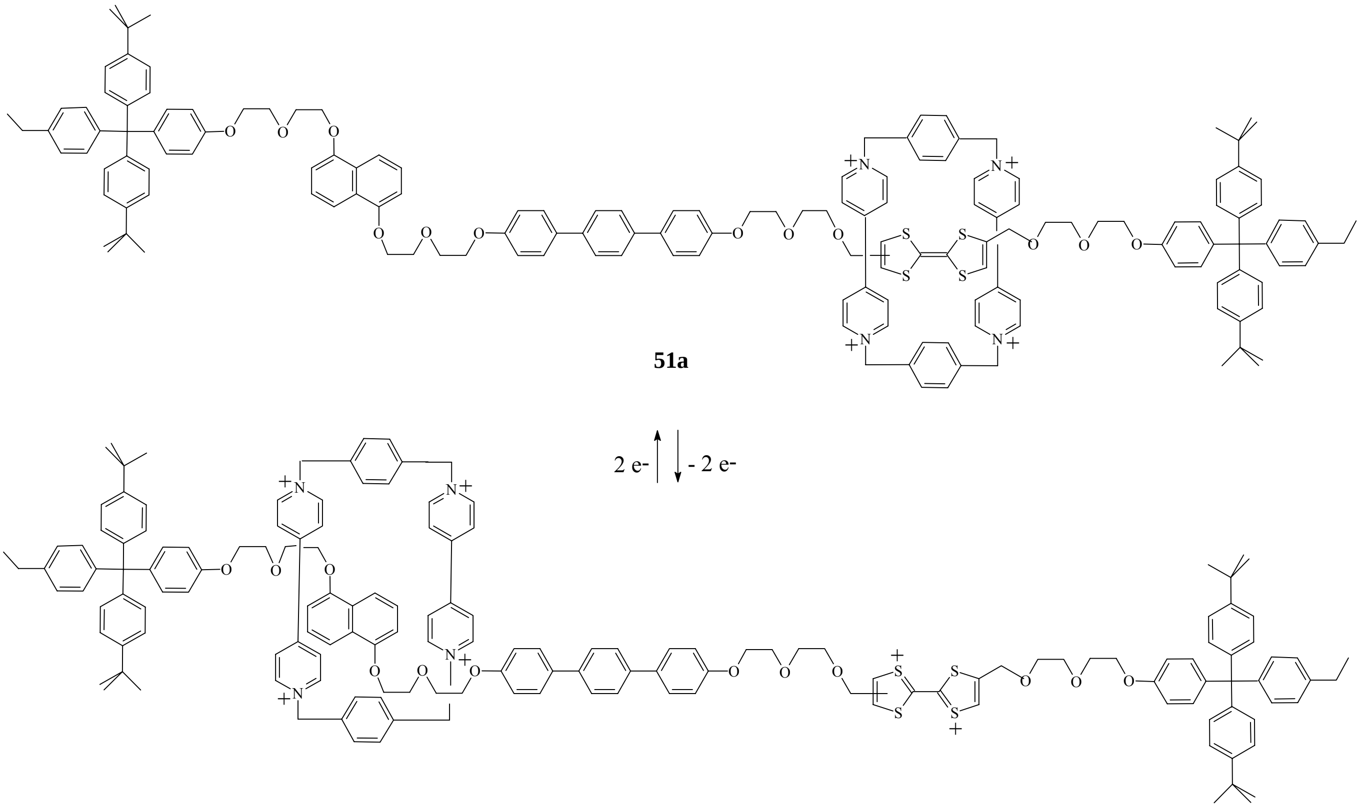


50

This reaction is advantageous, since the conversion is complete. It was found that PS (polystyrene) resin was superior to TentaGel (polystyrene-polyethylene glycol based resin) although the latter has better swelling properties in polar solvents.

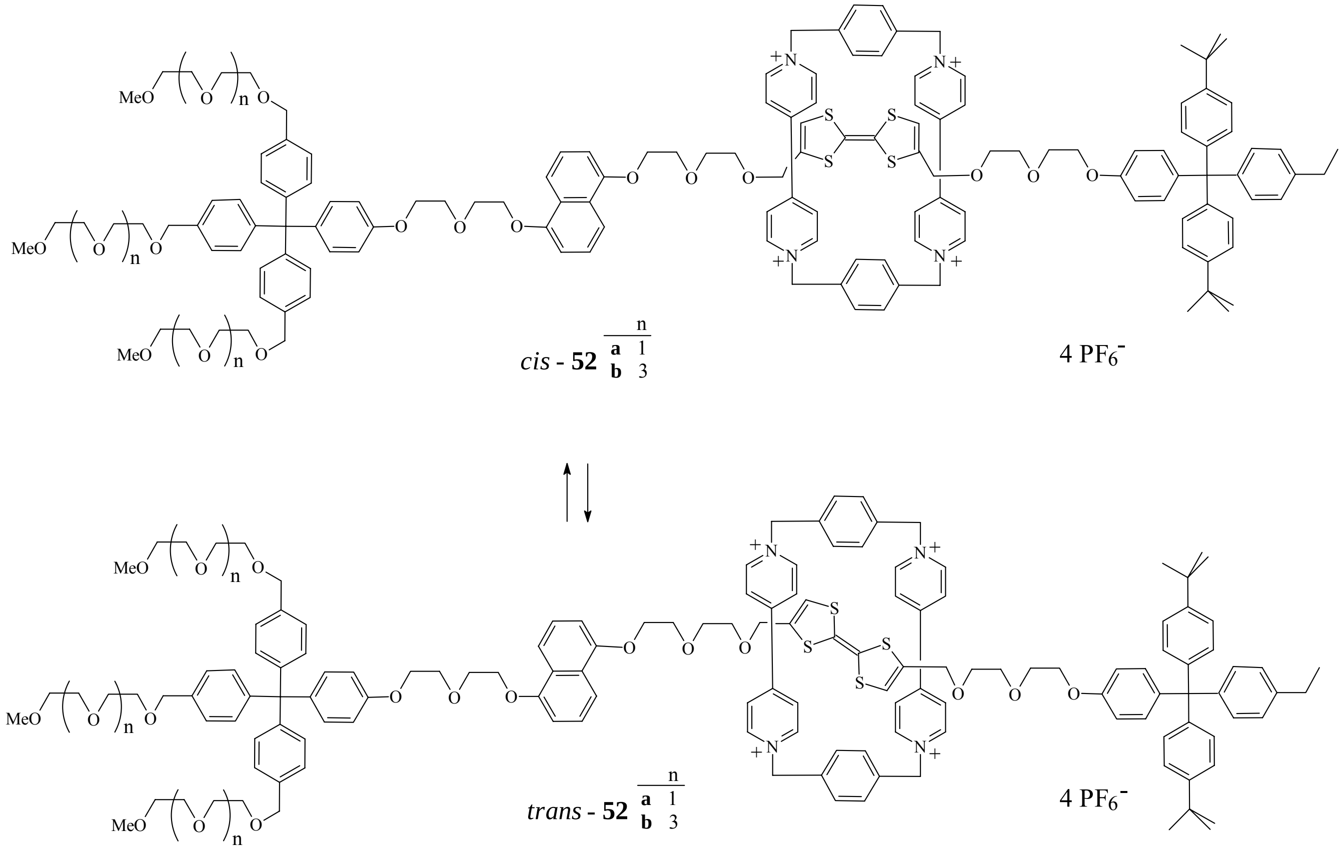
The [2]rotaxane (**51a**) contains the tetrathiafulvalene (TTF) and 1,5-dioxynaphthalene (DNP) recognition sites for **46**, separated by a rigid terphenylene spacer. TTF is a convenient redox-active unit due to its very good electron-donating properties; DNP is a somewhat weaker electron-donor.

The UV and ^{1}H NMR spectroscopy results show that [2]rotaxane (**51a**) is a translational isomer in which TTF is encircled by **46**. The oxidation of rotaxane (**51a**) with $Fe(ClO_4)_3$ results in the formation of other translational isomer (**51b**) due to the moving of **46** from TTF^{2+} to DNP (the distance is *ca.* 3,7 nm). Its reduction with ascorbic acid or zinc powder leads to transformation of TTF^{2+} into TTF^0 and movement of **46** from DNP back to much stronger π-electron-donating TTF unit; in this way the original translational isomer (**51a**) in which TTF is encircled by **46** is restored.[29]



51b

In the study of long and flexible two-station [2]rotaxanes,[29,107] the synthesis of **52a,b** consisting of the ring (**46**) as an electron-acceptor and of a thread containing TTF and DNP units as electron-donors, stoppered by tetraarylmethane hydrophilic and hydrophobic groups has been made.[27,108] UV-VIS and ^{1}H NMR spectra as well as electrochemical measurements indicate that **52a,b** exist in solution as translational isomers in which **46** surrounds the TTF unit, forming *ca.* 1:1 mixture of *cis* and *trans* species.

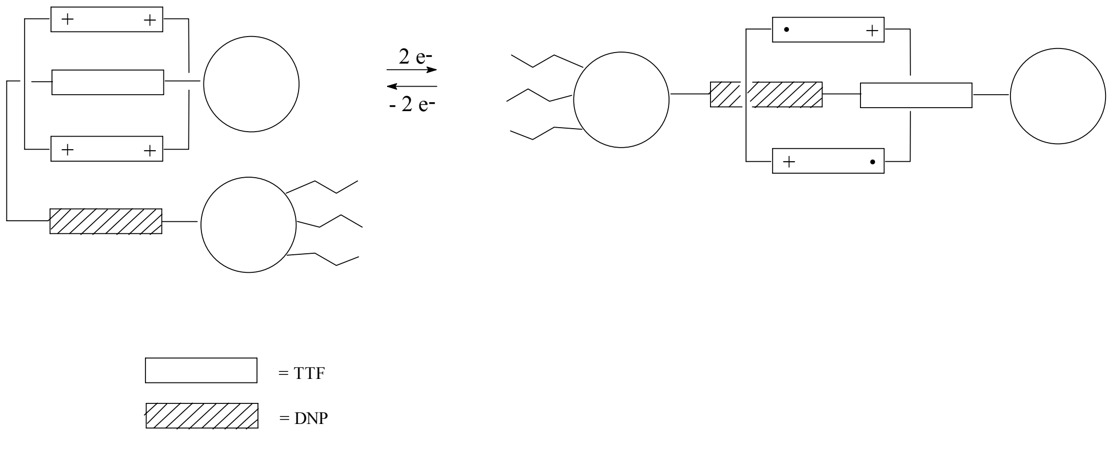


cis - **52** **a**, **b**

trans - **52** **a**, **b**

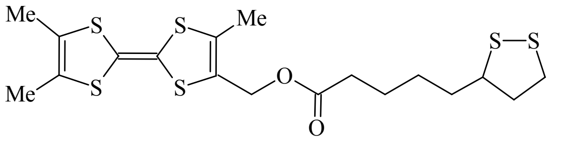
The electrochemical behavior of **52a,b** in MeCN solution was investigated. Upon ox/red (chemical or electrochemical) TTF-localized stimulation, **46** shuttles between TTF and DNP stations. The monoelectronic oxidation by addition of one equivalent of Fe(III) perchlorate causes the shift of **46** from TTF$^{+\cdot}$ to DNP. Reduction of the formed TTF $^{+\cdot}$**,** by adding 1,1'-dimethyl-4,4'-bipyridinium dication in its mono reduced form, moves the ring (**46**) back to the TTF unit, in this way restoring the original state.

It was established that **52a,b** may exist in solution as folded conformations of a pseudocatenane type, similarly as in the case of long and flexible rotaxanes and pseudorotaxanes.[29,107] Upon red/ox (electrochemical) ring (**46**) -localized stimulation, an unfolding/folding conformational change occurs. The first bielectronic reduction of $\mathbf{46}^{4+}$ in folded conformations of **52a,b** results in their unfolding, as shown below.

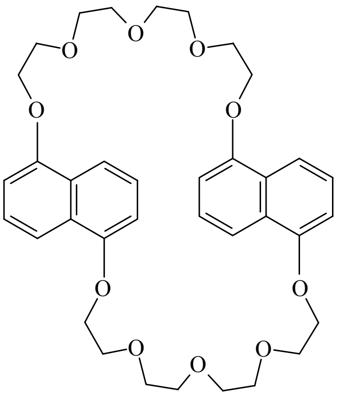


Amphiphilic rotaxanes having redox switching properties have been designed in order to obtain solid-state devices. These molecules should be incorporated in an oriented fashion in such devices, therefore they must be self-organized, for example in a two-dimensional fashion at the air-water interface as L-B films.[108]

The electrochemically controllable complexation of TTF derivative (**53**) with **46** and 1,5-dinaphtho[38]crown ether **54** has been studied.[109]



53

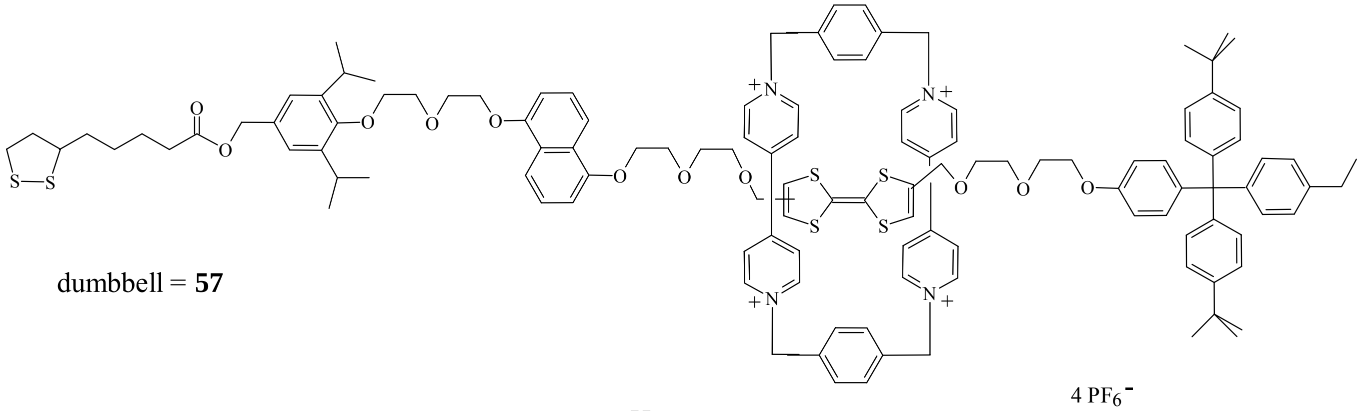


54

In order to investigate complexation at the solid-liquid interface, the mixed monolayers were made by immersing a gold wire in **53** and butyl disulfide. Due to the coassembling of butyl disulfide with **53** the isolation of the TTF units within the self-assembled monolayer is possible; in this way intermolecular electron- transfer reactions may be avoided.

The addition of **46** and **54** was followed by the cyclic voltammetry study. It was shown that the immobilized guest (**53**) interchanges between two ring units (**46**) and (**54**) upon altering its oxidation state from 0 (when encircled by electron-deficient **46**) to 2^+ (when encircled by electron rich **54**).[109]

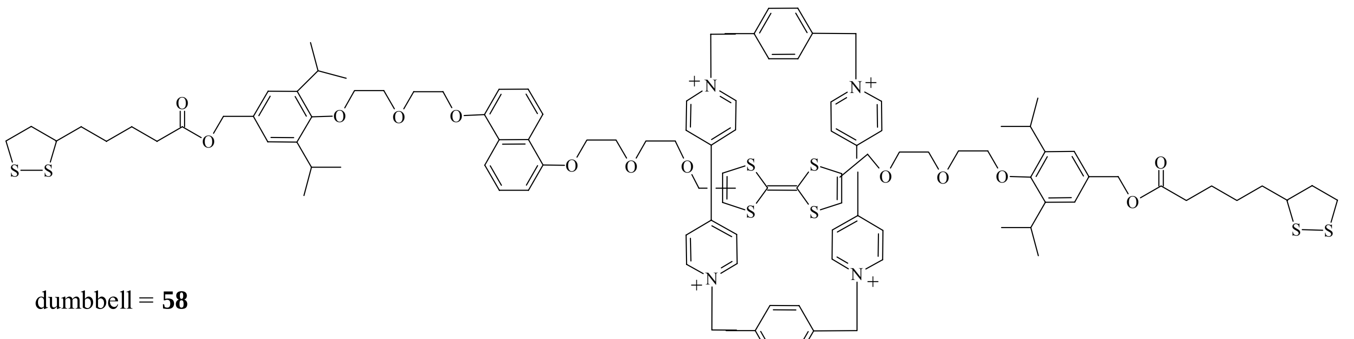
The investigation of [2]rotaxanes (**55**) and (**56**) obtained from corresponding dumbbells (**57**) and (**58**) by clipping procedure[27] has been made in the aspect of their application in single-molecule transistors.[110]



dumbbell = **57**

4 PF_6^-

55



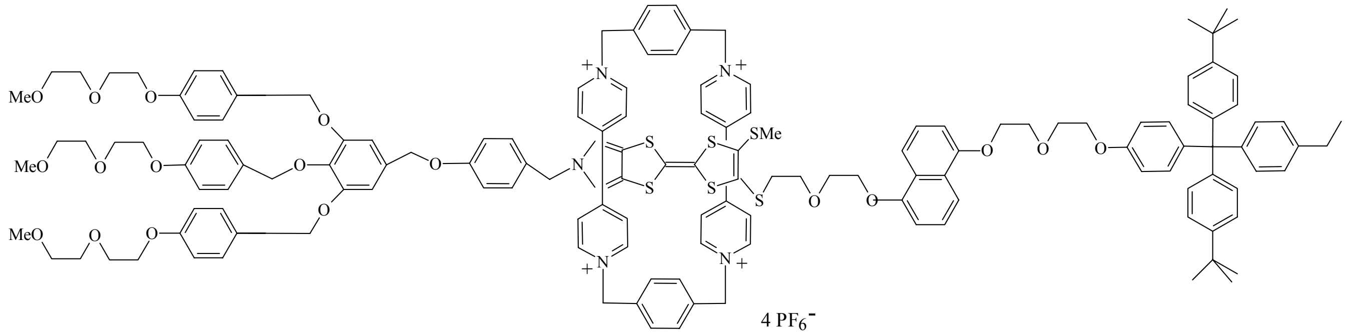
dumbbell = **58**

56

4 PF_6^-

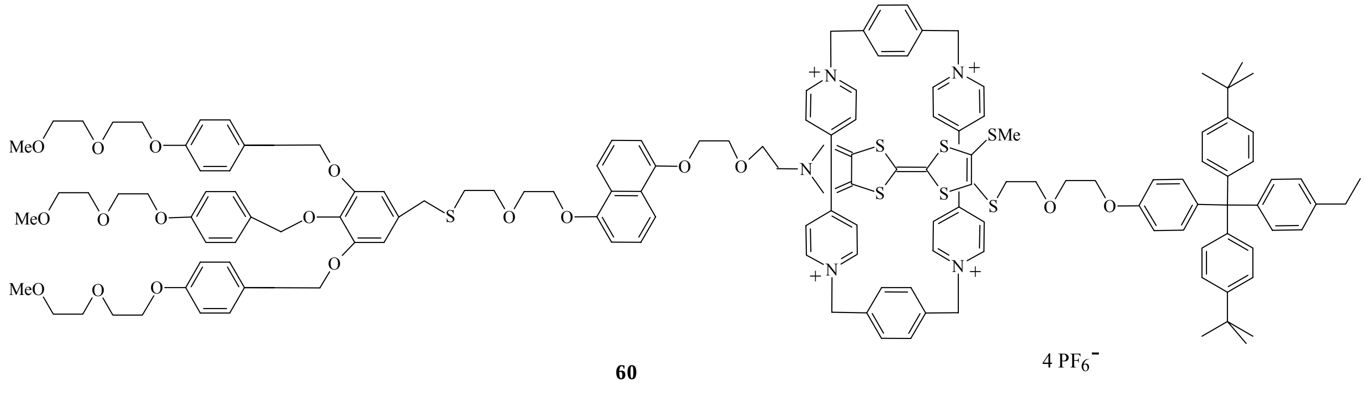
In these experiments single-molecule 3TDs (three-terminal devices) with a Pt break-junction source and drain electrodes have been used.[111] The conductance spectra of rotaxane (**55**) and of its dumbbell (**57**) are asymmetric due to the presence of only one terminal five-membered disulfide ring which is chemisorbed to one electrode, while those of rotaxane (**56**) and of its dumbbell (**58**) are symmetric, since **56** and **58** are terminated at both ends by five-membered disulfide rings chemisorbed to both electrodes. As a result, in devices containing **55** the current decreased at lower temperature than in the case of **56**.

For the design of electronic devices from redox-controllable amphiphilic [2]rotaxanes,[22,28] they should have redox-active units situated along the thread and should bear both hydrophobic and hydrophilic groups as stoppers. Amphiphilic [2]rotaxanes (**59**) and (**60**) contain two π-electron-rich recognition sites for **46** – a monopyrrolotetrathiafulvalene (PTTF) and DNP units, and are terminated by a hydrophobic tetraarylmethane and a hydrophilic, dendritic stoppers.[107] Rotaxanes (**59**) and (**60**) have been obtained by clipping procedure and isolated as mixtures of two possible translational isomers.



4 PF_6^-

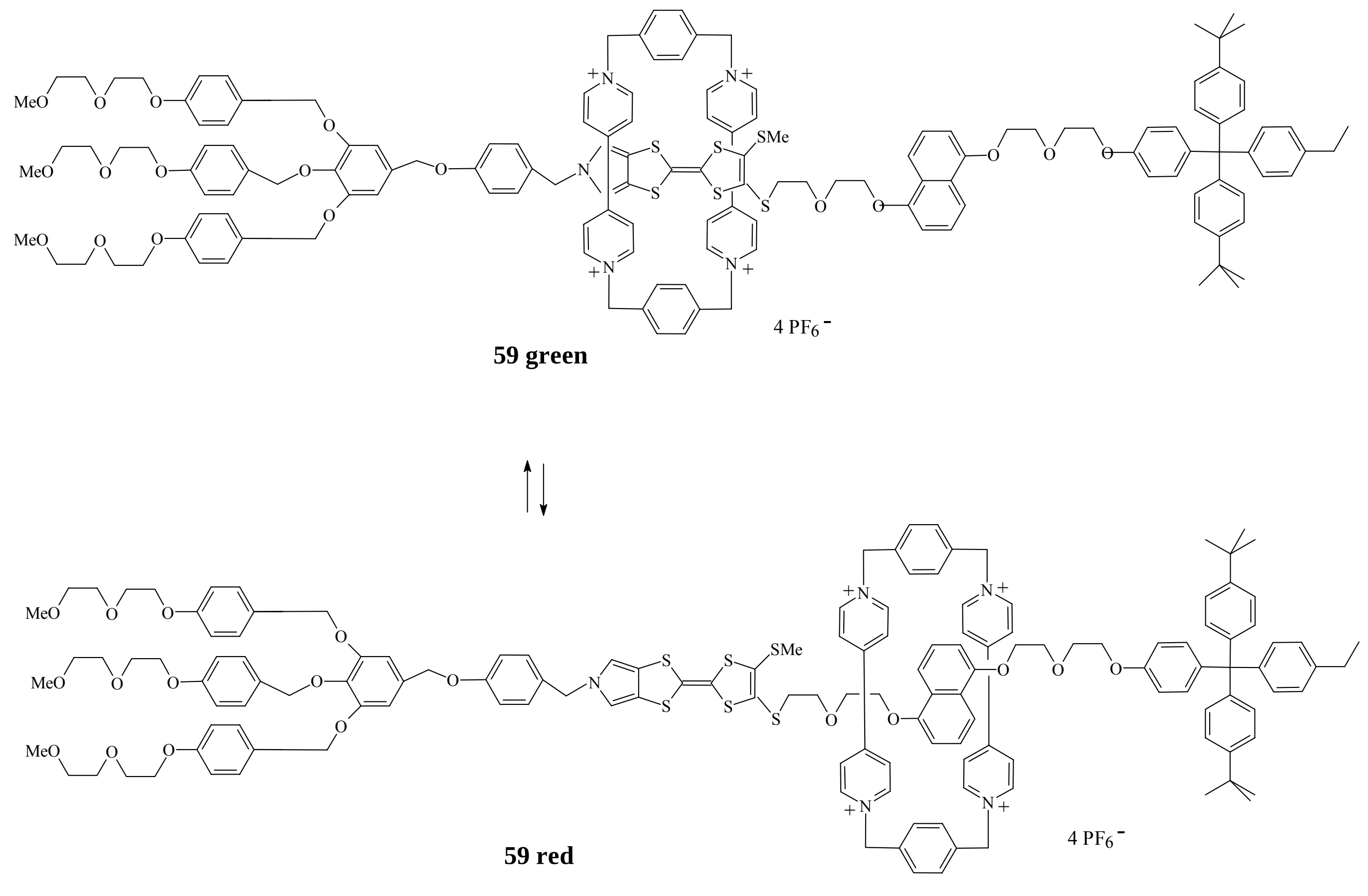
59



60

4 PF_6^-

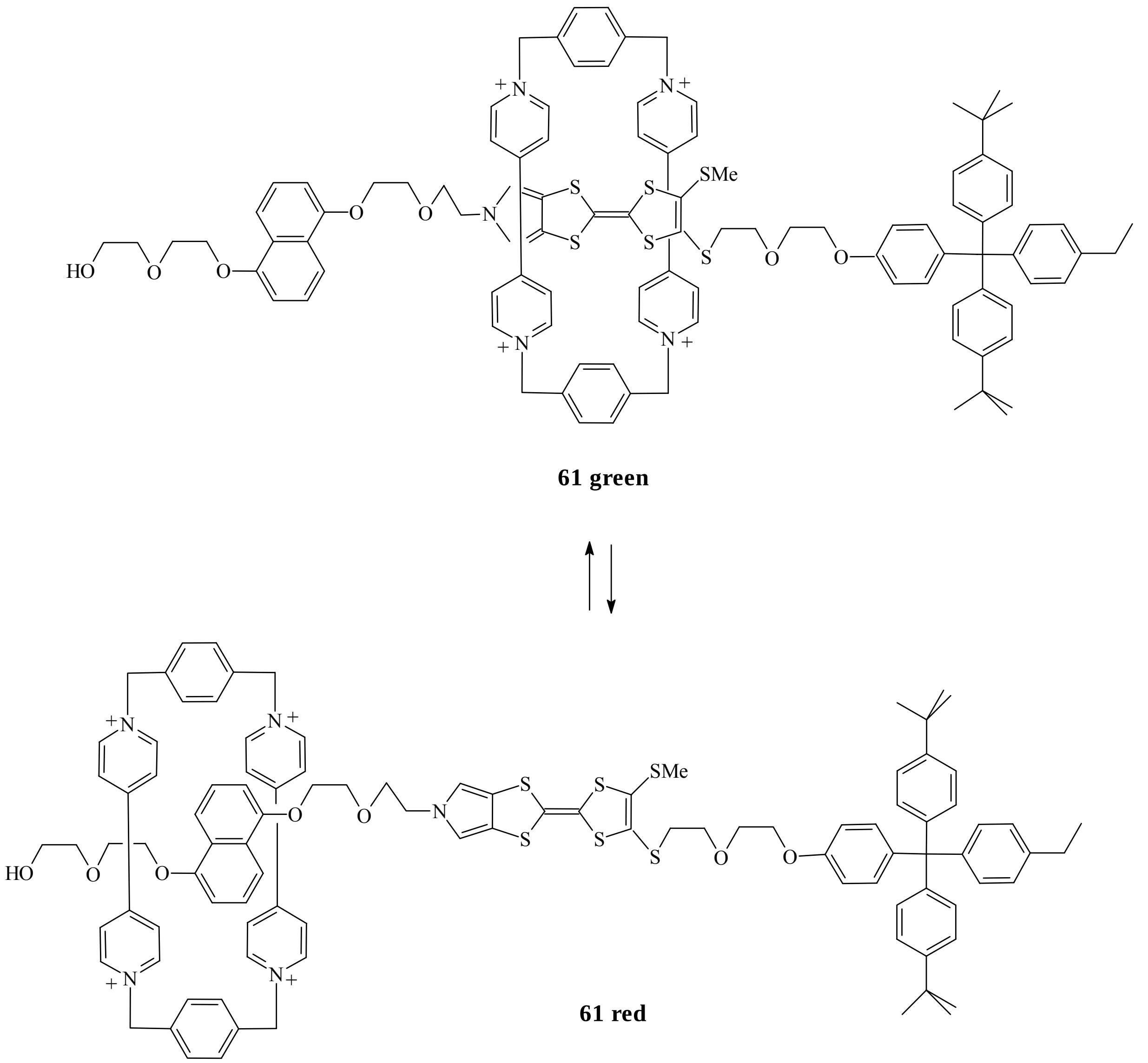
In **59** the SMe group is situated between PTTF and DNP, hindering fast interconversion between both translational isomers; this enables isolation of both translational isomers: **59** green (in which **46** encircles PTTF) and **59** red (in which **46** encircles DNP). The shuttling of **46** accompanied by color changes can be investigated by ^{1}H NMR and UV-VIS spectroscopies. In **60** no SMe group is present between two recognition sites – PTTF and DNP, therefore the shuttling of **46** between these two sites is faster, making the separation of the two translational isomers of **60** impossible. It should be pointed out that solid-state switches fabricated from TTF-based amphiphilic [2]rotaxanes are better than switches prepared from TTF-based catenanes.[22,112]



59 green

59 red

The [2]pseudorotaxane (**61**) containing PTTF and DNP recognition sites has been obtained from appropriate semidumbbell by slipping procedure; it exists as a mixture of two translational isomers: **61** green (in which **46** encircles PTTF) and **61** red (in which **46** encircles DNP).



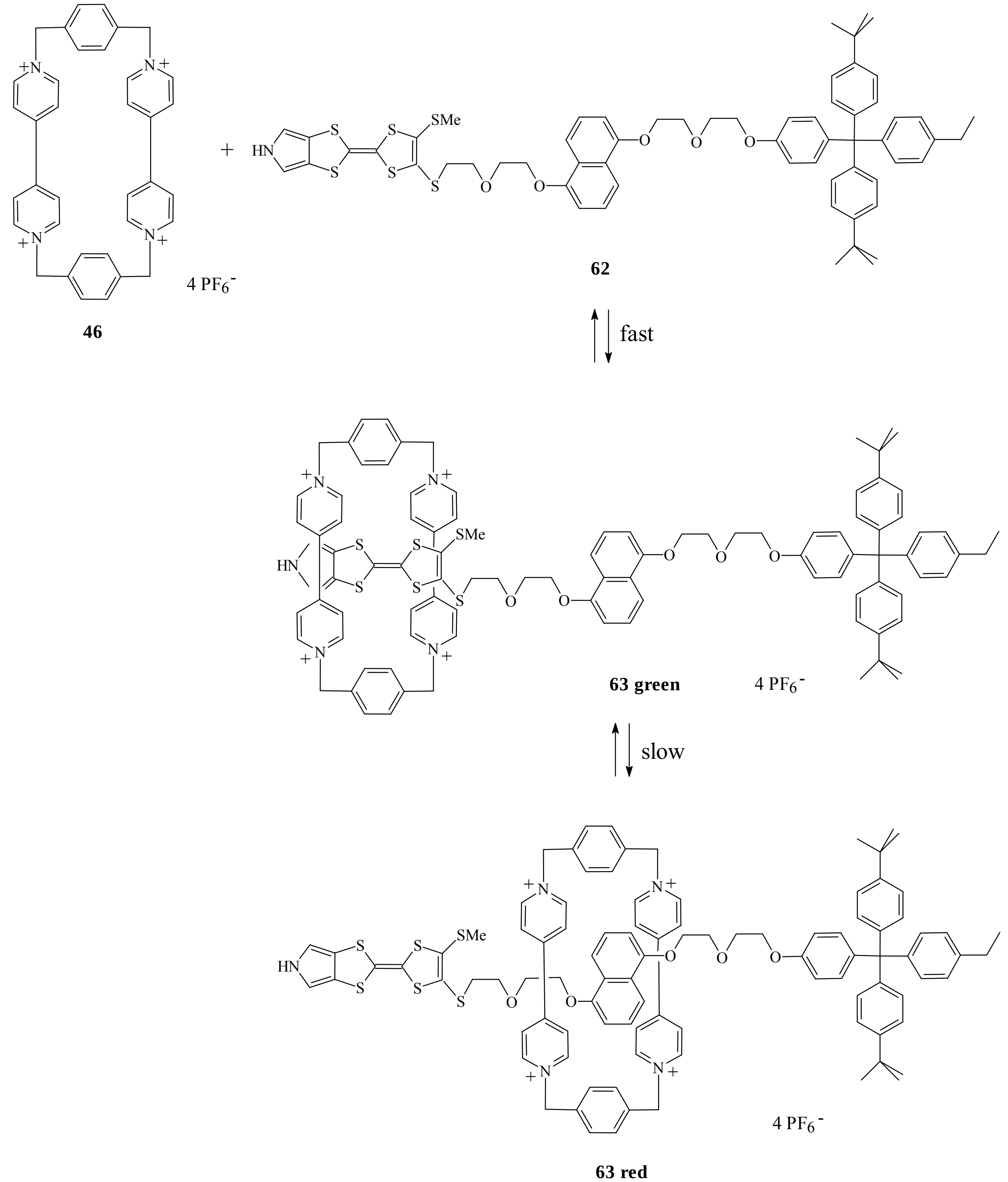
61 green

61 red

In rotaxanes (**59**) and (**60**) shuttling of **46** can be driven by electrochemical oxidation of PTTF unit, in [2]pseudorotaxane (**61**) however, the electrochemical oxidation causes dethreading.

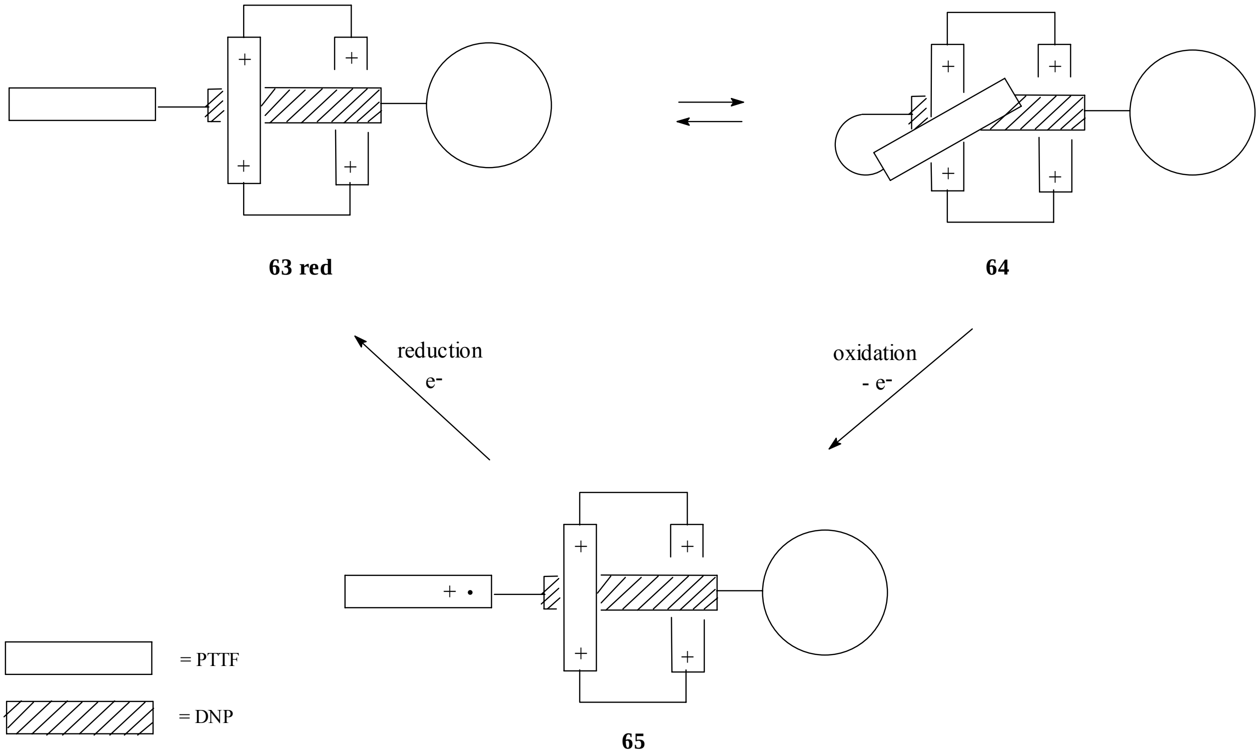
It is suggested that a well-defined distinction between rotaxanes and pseudorotaxanes does not exist.[113] When the ring and stoppers have nearly the same size, rotaxanes achieve a character of pseudorotaxanes and may undergo dethreading under appropriate conditions. In some cases, a rotaxane at room temperature may be a pseudorotaxane at higher temperatures.

Semidumbbell **62** contains two recognition sites – PTTF with SMe group and DNP, the SMe group being situated between them. Mixing equimolar amounts of **46** with **62** in acetone affords (fast) kinetically labile **63** green (in which **46** encircles PTTF). When **63** green was left in acetone for 24 h at room temperature, its partial (slow) interconversion into kinetically stable **63** red (in which **46** encircles DNP) took place. The isolation of **63** red by TLC as a rotaxane-like complex is possible, while **63** (green) undergoes dethreading, *i.e.* **63** green has a pseudorotaxane character. When the solution of **63** red stands for 24h at room temperature, the shuttling of **46** from DNP back to TTF recognition site occurs, *i.e.* **63** green is recovered.



The presence of SMe group allows to isolate **63** red suggesting that is has some [2]rotaxane character and allows to study the kinetics of the shuttling of **46**; it was established that the shuttling of **46** between PTTF and DNP is an unimolecular first order reaction.[113]

The electrochemical and photophysical studies have shown that **63** red does not exist exclusively as a linear translational isomer. Due to the length and flexibility of the semidumbbell (**62**), the PTTF unit may arrange itself near one of the bipyridinium units of **46** in a folded conformation (**64**) allowing the donor-acceptor interactions; **63** red is in equilibrium with **64**. The electrochemical study of **63** red, made in MeCN solution has revealed that the removal of one electron ($\mathrm{PTTF}\rightarrow\mathrm{PTTF}^{+\cdot}$) from the folded conformation (**64**) results in the breaking of donor-acceptor interactions between PTTF and **46**, leading to linear **65**. The subsequent reduction of **65** ($\mathrm{TTF}^{+\cdot}\rightarrow\mathrm{TTF}$) regenerates the original linear conformation of **63** red, which is in equilibrium with its folded conformation (**64**). These unique properties of **63** red are promising for its use in artificial molecular machines.[113]



The AMBER force field with RESP charges has been used for study of structures and energetics of two pseudorotaxanes consisting of **46** and 4,4'-biphenol and of **46** and benzidine[114] (AMBER = Assisted Model Building and Energy Refinement; RESP = Restrained Electrostatic Potential). The ring (**46**) serves as an electron-deficient receptor, while biphenol and benzidine are electron-rich donors.

CONCLUSION

The chemistry of rotaxanes containing quaternary azaaromatic moieties is developing rapidly. Since numerous works concerning this theme are reported,[115] in the present review only chosen examples have been described.

An attention should be paid to fullerene-based rotaxanes,[116] rotaxanes containing cucurbituril[117] and cyclodextrin[118] rings, as well as to rotaxane dendrimers;[119] of a special interest is the use of rotaxanes as molecular-scale logic gates.[120]

REFERENCES

1. V. Balzani, M. Venturi, and A. Credi, *Molecular Devices and Machines – A Journey into the Nanoworld,* Wiley-VCH, Weinheim, 2003.
2. J.-M. Lehn, *Science*, 2002, **295**, 2400.
3. V. Balzani, A. Credi, and M. Venturi, *Chem. Eur. J.,* 2002, **8**, 5524.
4. A. Altieri, F. G. Gatti, E. R. Kay, D. A. Leigh, D. Martel, F. Paolucci, A. M. Z. Slawin, and J. K. Y. Wong, *J. Am. Chem. Soc.*, 2003, **125**, 8644.
5. M. C. Jimenez-Molero, C. Dietrich-Buchecker, and J.-P. Sauvage, *Chem. Commun.,* 2003, 1613.
6. W. Reckien and S. D. Peyerimhoff, *J. Phys. Chem.*, 2003, **107A**, 9634.
7. X. Zheng and K. Sohlberg, *J. Phys. Chem.*, 2003, **107A**, 1207.
8. P. N. Taylor, A. J. Hagan, and H. L. Anderson, *Org. Biomol. Chem.,* 2003, **1**, 3851.
9. O. Lukin, T. Kubota, Y. Okamoto, F. Schelhase, A. Yoneva, W. M. Müller, U. Müller, and F. Vögtle, *Angew. Chem., Int. Ed.,* 2003, **42**, 4542.
10. G. Cooke, *Angew. Chem., Int. Ed.,* 2003, **42**, 4860.
11. X. Li, J. Illigen, M. Nieger, S. Michel, and C. A. Schalley, *Chem. Eur. J.,* 2003, **9**,1332.
12. H.-R. Tseng, S. A. Vignon, P. C. Celestre, J. F. Stoddart, A. J. P. White, and D. J. Williams, *Chem. Eur. J.,* 2003, **9**, 543.
13. L. Flamigni, A. M. Talarico, S. Serroni, F. Puntoriero, M. J. Gunter, M. R. Johnston, and T. P. Jeynes, *Chem. Eur. J.,* 2003, **9**, 2649.
14. M. J. Gunter, S. M. Farquhar, and T. P. Jeynes, *Org. Biomol. Chem.,* 2003, **1**, 4097.
15. O. Lukin, W. M. Müller, U. Müller, A. Kaufmann, C. Schmidt, J. Leszczynski, and F. Vögtle, *Chem. Eur. J.,* 2003, **9**, 3507.
16. J. C. Dobrowolski, *Croat. Chem. Acta,* 2003, **76**, 145.
17. B. X. Colasson, C. Dietrich-Buchecker, M. C. Jimenez-Molero, and J. P. Sauvage, *J. Phys. Org. Chem.,* 2002, **15**, 476.
18. C. A. Stanier, S. J. Alderman, T. D. W. Claridge, and H. L. Anderson, *Angew. Chem., Int. Ed.,* 2002, **41**, 1769.
19. N. Koumura, E. M. Geertsema, M. B. van Gelder, A. Meetsma, and B. L. Feringa, *J. Am. Chem. Soc.,* 2002, **124**, 5037.
20. Y. Chen, G.-Y. Jung, D. A. A. Ohlberg, X. Li, D. R. Stewart, J. O. Jeppesen, K. A. Nielsen, J. F. Stoddart, and R. S. Williams, *Nanotechnology,* 2003, **14**, 462.
21. Y. Chen, D. A. A. Ohlberg, X. Li, D. R. Stewart, R. S. Williams, J. O. Jeppesen, K. A. Nielsen, J. F. Stoddart, D. L. Olynick, and E. Anderson, *Appl. Phys. Lett.,* 2003, **82**, 1610.

22. M. Jacoby, *Chem. Eng. News,* 2002, **80**, 38.
23. G. M. Whitesides and B. Grzybowski, *Science,* 2002, **295**, 2418.
24. F. G. Gatti, S. León, J. K. Y. Wong, G. Bottari, A. Altieri, M. A. F. Morales, S. J. Teat, C. Frochot, D. A. Leigh, A. M. Brouwer, and F. Zerbetto, *Proc. Natl. Acad. Sci. USA,* 2003, **100**, 10.
25. A. M. Elizarov, T. Chang, H. -S. Chiu, and J. F. Stoddart, *J. Org. Chem.,* 2002, **67**, 9175.
26. S.-H. Chiu and J. F. Stoddart, *J. Am. Chem. Soc.,* 2002, **124**, 4174.
27. J. F. Stoddart and H.-R. Tseng, *Proc. Natl. Acad. Sci. USA,* 2002, **99**, 4797.
28. Y. Luo, C. P. Collier, J. O. Jeppesen, K. A. Nielsen, E. Delonno, G. Ho, J. Perkins, H.-R. Tseng, T. Yamamoto, J. F. Stoddart, and J. R. Heath, *Chem. Phys. Chem.,* 2002, **3**, 519.
29. H.-R. Tseng, S. A. Vignon, and J. F. Stoddart, *Angew. Chem., Int. Ed.,* 2003, **42**, 1491.
30. J. M. Mahoney, R. Shukla, R. A. Marshall, A. M. Beatty, J. Zajicek, and B. D. Smith, *J. Org.Chem.,* 2002, **67**, 1436.
31. S.-H. Chiu, S. J. Rowan, S. J. Cantrill, J. F. Stoddart, A. J. P. White, and D. J. Williams, *Chem. Eur. J.,* 2002, **24**, 5170.
32. T. Hugel, N. B. Holland, A. Cattani, L. Moroder, M. Seitz, and H. E. Gaub, *Science,* 2002, **296**, 1103.
33. R. Ballardini, V. Balzani, M. Clemente-León, A. Credi, M. T. Gandolfi, E. Ishow, J. Perkins, J. F. Stoddart, H.-R. Tseng, and S. Wenger, *J. Am. Chem. Soc.,* 2002, **124**,12786.
34. D. R. Stewart, D. A. A. Ohlberg, P. Beck, Y. Chen, R. S. Williams, J. O. Jeppesen, K. A. Nielsen, and J. F. Stoddart, *Nanotechnology,* 2003, **14**, 462.
35. M. Asakawa, G. Brancato, M. Fanti, D. A. Leigh, T. Shimizu, A. M. Z. Slavin, J. K. Y. Wong, F. Zerbetto, and S. Zhang, *J. Am. Chem. Soc.,* 2002, **124**, 2939.
36. W. Śliwa and T. Girek, *Heterocycles,* 2003, **60**, 2147.
37. J.-K. Choi, T. Girek, D.-H. Shin, and S.-T. Lim, *Carbohydrate Polymers,* 2002, **49**, 289.
38. W. Śliwa, *Current Org. Chem.,* 2003, **7**, 995.
39. J. Peszke and W. Śliwa, *Spectrochim. Acta A,* 2002, **58**, 2127.
40. B. Bachowska and T. Zujewska, *Aust. J. Chem.,* 2001, **54**, 105.
41. B. Marciniak, V. Pavlyuk, and M. Deska, *Acta Cryst.,* 2002, **E58**, 489.
42. V. K. Aggarwal, R. S. Grainger, G. K. Newton, P. L. Spargo, A. D. Hobson, and H. Adams, *Org. Biomol. Chem.,* 2003, **1**, 1884.
43. S. Alunni, V. Laureti, L. Ottavi, and R. Ruzziconi, *J. Org. Chem.,* 2003, **68**, 718.
44. P. Allevi and M. Anastasia, *Tetrahedron: Asymmetry,* 2003, **14**, 2005.
45. M. A. Ilies, W. A. Seitz, M. T. Caproiu, M. Wentz, R. E. Garfield, and A. T. Balaban, *Eur. J. Org.*

Chem., 2003, 2645.

46. P. Fatheree, M. S. Linsell, D. D. Long, D. Marquess, E. J. Moran, M. B. Nodwell, S. D. Turner, and J. Aggen, PCT Int. Appl. WO 03 31,449 (2003) (*Chem. Abstr*., 2003, **138**, 321580).
47. A. Conejo-Garcia, J. M. Campos, R. M. Sanchez-Martin, M. A. Gallo, and A. Espinosa, *J. Med. Chem.,* 2003, **46**, 3754.
48. Y. Kumar, N. Tewari, H. Nizar, B. P. Rai, and S. K. Singh, *Org. Process Research Developm.,* 2003, **7**, 758.
49. A. Sankaranarayanan, U.S. Pat. Appl. Publ. US 2003 32,660 (2003) (*Chem. Abstr.,* 2003, **138**, 153445).
50. T. Okada and M. Ogawa, *Chem. Commun.,* 2003, 1378.
51. W. Bonrath, J.-M. Leveque, J.-L. Luche, and C. Petrier, PCT Int. Appl. WO 03 48,078 (2003) (*Chem. Abstr.,* 2003, **139**, 36083).
52. J. W. Lee, M. Jung, G. R. Rosania, and Y.-T. Chang, *Chem. Commun.,* 2003, 1852.
53. Q. Zheng, G. S. He, T.-C. Lin, and P. N. Prasad, *J. Mater. Chem.,* 2003, **13**, 2499.
54. F. Y. Li, X. R. Zou, and C. H. Huang, *Chin. Chem. Lett.,* 2003, **14**, 641.
55. P. Quagliotto, G. Viscardi, C. Barolo, E. Barni, S. Bellinvia, E. Fisicaro, and C. Compari, *J. Org. Chem.,* 2003, **68**, 7651.
56. M. Faimali, K. Sepčič, T. Turk, and S. Geraci, *Biofouling,* 2003, **19**, 47.
57. I. Omae, *Chem. Rev.,* 2003, **103**, 3431.
58. K. Suga, K. Ohkubo, and S. Fukuzumi, *J. Phys. Chem.,* 2003, **107A**, 4339.
59. T. Yamashita, Jpn. Kokai Tokkyo Koho JP 2003 261,564 (2003) (*Chem. Abstr.,* 2003, **139**, 261283).
60. B. J. Coe, J. A. Harris, I. Asselberghs, K. Wostyn, K. Clays, A. Persoons, B. S. Brunschwig, S. J. Coles, T. Gelbrich, M. E. Light, M. B. Hursthouse, and K. Nakatani, *Adv. Functional Mater.,* 2003, **13**, 347.
61. D. Laage, W. H. Thompson, M. Blanchard-Desce, and J. T. Hynes, *J. Phys. Chem.,* 2003, **107A**, 6032.
62. R. M. Metzger, *Chem. Rev.,* 2003, **103**, 3803.
63. M. Sakomura, T. Oono, R. Sakon, and M. Fujihira, *Ultramicroscopy,* 2002, **91**, 215.
64. G. J. Ashwell, D. S. Gandolfo, and R. Hamilton, *J. Mater. Chem.,* 2002, **12**, 416.
65. J. W. Baldwin, R. R. Amaresh, I. R. Peterson, W. J. Shumate, M. P. Cava, M. A. Amiri, R. Hamilton, G. J. Ashwell, and R. M. Metzger, *J. Phys. Chem.,* 2002, **106B**, 12158.
66. H.-P. Xie, X. Chu, J.-H. Jiang, H. Cui, G.-L. Shen, and R.-Q. Yu, *Spectrochim. Acta,* 2003, **59A**, 743.

67. B. Juskowiak, E. Gałęzowska, and S. Takenaka, *Spectrochim. Acta,* 2003, **59A**, 1083.
68. S. Fukuzumi, M. Nishimine, K. Ohkubo, N. V. Tkachenko, and H. Lemmetyinen, *J. Phys. Chem.,* 2003, **107B**, 12511.
69. C. A. Volk and M. Köck, *Org. Lett.,* 2003, **5**, 3567.
70. T. C. Singh, P. V. Rao, T. Veeraiah, and G. Venkateshwarlu, *Indian J. Chem., Sect. A,* 2003, **42A**, 1666.
71. N. Tamaoki and T. Kidowaki, Jpn. Kokai Tokkyo Koho JP 2003 261,489 (2003) (*Chem. Abstr.,* 2003, **139**, 245906).
72. S. Fukuzumi, Y. Endo, Y. Kashiwagi, Y. Araki, O. Ito, and H. Imahori, *J. Phys. Chem.,* 2003, **107B**, 11979.
73. R. Solarska, R. Morand, and J. Augustynski, *Coll. Czech. Chem. Commun.,* 2003, **68**, 1596.
74. S. Santra, D. Kumaresan, N. Agarwal, and M. Ravikanth, *Tetrahedron,* 2003, **59**, 2353.
75. A. Maraval, S. Franco, C. Vialas, G. Pratviel, M. A. Blasco, and B. Meunier, *Org. Biomol. Chem.,* 2003, **1**, 921.
76. F. Huang, J. W. Jones, C. Slebodnick, and H. W. Gibson, *J. Am. Chem. Soc.,* 2003, **125**, 14458.
77. T. Nabeshima, Y. Yoshihira, T. Saiki, S. Akine, and E. Horn, *J. Am. Chem. Soc.,* 2003, **125**, 28.
78. H. Romain, D. Florence, and M. Alain, *Chemistry,* 2002, **8**, 2438.
79. J. W. Jones, L. N. Zakharov, A. L. Rheingold, and H. W. Gibson, *J. Am. Chem. Soc.,* 2002, **124**, 13378.
80. F. Huang, F. R. Fronczek, and H. W. Gibson, *J. Am. Chem. Soc.,* 2003, **125**, 9272.
81. F. Huang, H. W. Gibson, W. S. Bryant, D. S. Nagvekar, and F. R. Fronczek, *J. Am. Chem. Soc.,* 2003, **125**, 9367.
82. J. W. Jones and H. W. Gibson, *J. Am. Chem. Soc.,* 2003, **125**, 7001.
83. J. H. K. K. Hirschberg, A. Ramzi, R. P. Sijbesma, and E. W. Meijer, *Macromolecules,* 2003, **36**, 1429.
84. J.-M. Lehn, *Polym. Int.,* 2002, **51**, 825.
85. H. W. Gibson, N. Yamaguchi, and J. W. Jones, *J. Am. Chem. Soc.,* 2003, **125**, 3522.
86. F. Huang, F. R. Fronczek, and H. W. Gibson, *Chem. Commun.,* 2003, 1480.
87. J. A. Wisner, P. D. Beer, M. G. B. Drew, and M. R. Sambrook, *J. Am. Chem. Soc.,* 2002, **124**,12469.
88. B. Long, K. Nikitin, and D. Fitzmaurice, *J. Am. Chem. Soc.,* 2003, **125**, 5152.
89. B. Long, K. Nikitin, and D. Fitzmaurice, *J. Am. Chem. Soc.,* 2003, **125**, 15490.
90. W. S. Jeon, A. Y. Ziganshina, J. W. Lee, Y. H. Ko, J.-K. Kang, C. Lee, and K. Kim, *Angew. Chem., Int. Ed.,* 2003, **42**, 4097.

91. A. Arduini, F. Calzavacca, A. Pochini, and A. Secchi, *Chem. Eur. J.,* 2003, **9**, 793.

92. G. J. E. Davidson and S. J. Loeb, *J. Chem. Soc., Dalton Trans.,* 2003, 4319.

93. K. -M. Park, D. Whang, E. Lee, J. Heo, and K. Kim, *Chem. Eur. J.,* 2002, **8**, 498.

94. G. J. E. Davidson and S. J. Loeb, *Angew. Chem., Int. Ed.,* 2003, **42**, 74.

95. M. Bělohradský, A. M. Elizarov, and J. F. Stoddart, *Coll. Czech., Chem. Commun.,* 2002, **67**, 1719.

96. F. M. Raymo, R. J. Alvarado, and E. J. Pacsial, *J. Supramol. Chem.,* 2002, **2**, 63.

97. A. Credi, *Handbook of Photochemistry and Photobiology,* ed. by H. S. Nalwa and M. S. A. Abdel-Mottaleb, American Scientific Publishers: Stevenson Ranch, 2003, Vol. 3, p. 319.

98. M. Alvaro, B. Ferrer, H. García, E. J. Palomares, V. Balzani, A. Credi, M. Venturi, J. F. Stoddart, and S. Wenger, *J. Phys. Chem.,* 2003, **107B**, 14319.

99. Y. S. Park, E. J. Lee, Y. S. Chun, Y. D. Yoon, and K. B. Yoon, *J. Am. Chem. Soc.,* 2002, **124**, 7123.

100. M. Alvaro, B. Ferrer, V. Fornés, H. García, and J. C. Scaiano, *J. Phys. Chem.,* 2002, **106B**, 6815.

101. S. J. Benkovic, A. M. Valentine, and F. Salinas, *Annu. Rev. Biochem.,* 2001, **70**, 181.

102. R. G. E. Coumans, J. A. A. W. Elemans, P. Thordarson, R. J. M. Nolte, and A. E. Rowan, *Angew. Chem., Int. Ed.,* 2003, **42**, 650.

103. J. A. A. W. Elemans, E. J. A. Bijsterveld, A. E. Rowan, and R. J. M. Nolte, *Chem. Commun.,* 2000, 2443.

104. A. C. Benniston, M. Davies, A. Harriman, and C. Sams, *J. Phys. Chem.,* 2003, **107A**, 4669.

105. L. Chen, X. Zhao, Y. Chen, C.-X. Zhao, X.-K. Jiang, and Z.-T. Li, *J. Org. Chem.,* 2003, **68**, 2704.

106. J. A. Bravo, D. Orain, and M. Bradley, *Chem. Commun.,* 2002, 194.

107. J. O. Jeppesen, K. A. Nielsen, J. Perkins, S. A. Vignon, A. Di Fabio, R. Ballardini, M. T. Gandolfi, M. Venturi, V. Balzani, J. Becher, and J. F. Stoddart, *Chem. Eur. J.,* 2003, **9**, 2982.

108. T. Yamamoto, H. -R. Tseng, J. F. Stoddart, V. Balzani, A. Credi, F. Marchioni, and M. Venturi, *Coll. Czech. Chem. Commun.,* 2003, **68**, 1488.

109. M. R. Bryce, G. Cooke, F. M. A. Duclairoir, P. John, D. F. Perepichka, N. Polwart, V. M. Rotello, J. F. Stoddart, and H.-R. Tseng, *J. Mater. Chem.,* 2003, **13**, 2111.

110. H. Yu, Y. Luo, K. Beverly, J. F. Stoddart, H.-R. Tseng, and J. R. Heath, *Angew. Chem., Int. Ed.,* 2003, **42**, 5706.

111. W. Liang, M. P. Shores, M. Bockrath, J. R. Long, and H. Park, *Nature,* 2002, **417**, 725.

112. J. Becher, J. O. Jeppesen, and K. Nielsen, *Synthetic Met.,* 2003, **133-134**, 309.

113. J. O. Jeppesen, S. A. Vignon, and J. F. Stoddart, *Chem. Eur. J.,* 2003, **9**, 4611.

114. X. Grabuleda, P. Ivanov, and C. Jaime, *J. Org. Chem.,* 2003, **68**, 1539.

115. H.-R. Tseng, S. A. Vignon, P. C. Celestre, J. Perkins, J. O. Jeppesen, A. Di Fabio, R. Ballardini, M. T. Gandolfi, M. Venturi, V. Balzani, and J. F. Stoddart, *Chem. Eur. J.,* 2004, **10**, 155.

116. Y. Nakamura, S. Minami, K. Iizuka, and J. Nishimura, *Angew. Chem., Int. Ed.,* 2003, **42**, 3158.

117. K. Kim, *Chem. Soc. Rev.,* 2002, **31**, 96.

118. H. Onagi, C. J. Blake, C. J. Easton, and S. F. Lincoln, *Chem. Eur. J.,* 2003, **9**, 5978.

119. J. W. Lee and K. Kim, *Top. Curr. Chem.,* 2003, **228**, 111.

120. A. P. de Silva and N. D. McClenaghan, *Chem. Eur. J.,* 2004, **10**, 574.