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## INTERLOCKED MOLECULES CONTAINING QUATERNARY AZAAROMATIC MOIETIES

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**Abstract-** In the first part of the review examples of rotaxanes bearing quaternary azaaromatic moieties are presented, followed by examples of catenanes, shown in the second part. Among rotaxanes those containing tetracationic cyclophane, crown ether unit or other rings, such as cyclodextrins, cucurbiturils and calixarenes are described.

### INTRODUCTION

In a continuation of our reviews dealing with rotaxanes<sup>1,2</sup> and of our research concerning quaternary azaaromatic salts,<sup>3,4</sup> in the paper interlocked systems containing quaternary azaaromatics are presented. Interlocked molecules are a topic of a number of reports<sup>5-10</sup> due to their properties promising for construction of molecular machines<sup>11-17</sup> and switches.<sup>18-25</sup>

Among interlocked molecules a large group are those containing quaternary azaaromatic moieties.<sup>26-32</sup> Having in view enormous number of these species, in the present review only selected examples of interlocked molecules containing quaternary azaaromatic moieties will be described.

Supramolecular systems<sup>33-35</sup> and quaternary azaaromatics<sup>3,4,36</sup> are a topic of our research group. Quaternary azaaromatics have interesting properties allowing their application in many fields, for example as ionic liquids,<sup>37,38</sup> hydrogelators<sup>39,40</sup> and catalysts;<sup>41</sup> they may serve as carriers for DNA delivery<sup>42</sup> or as gene-transfer agents.<sup>43</sup> These compounds are promising in the study of artificial photosynthesis,<sup>44,45</sup> and viologens are interesting for their redox and electrochromic properties.<sup>46</sup> Quaternary azaaromatics<sup>47</sup> and related ylides<sup>48</sup> are used as synthons in chemical reactions.

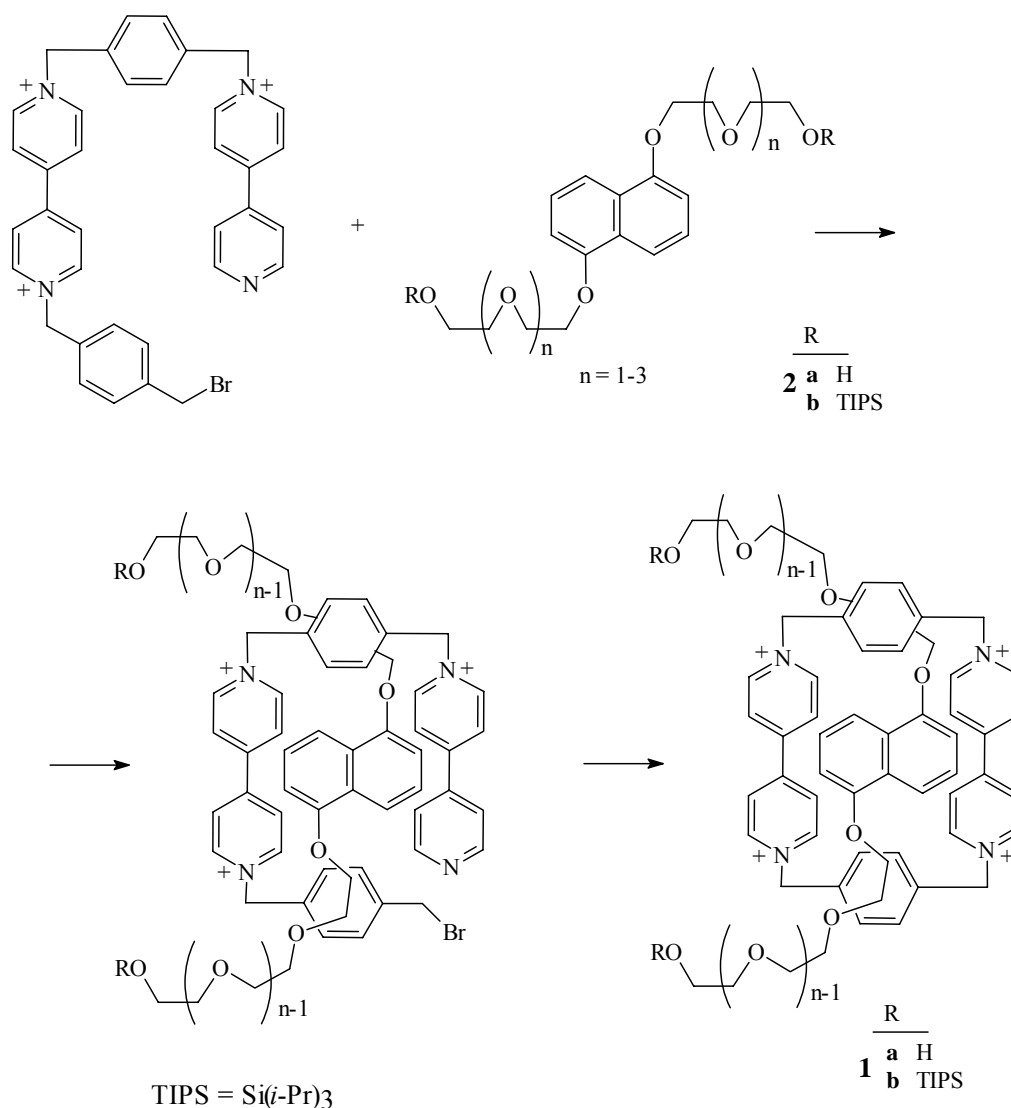
The first part of the review deals with rotaxanes and pseudorotaxanes bearing quaternary azaaromatic moieties; at the beginning those containing tetracationic cyclophane and crown ether units as rings have

been presented, followed by species containing cyclodextrin, cucurbituril and calixarene rings. In the second part catenanes are briefly described. Application possibilities of presented rotaxanes and catenanes are characterized. References are cited of works appeared during 2002-2004 years.

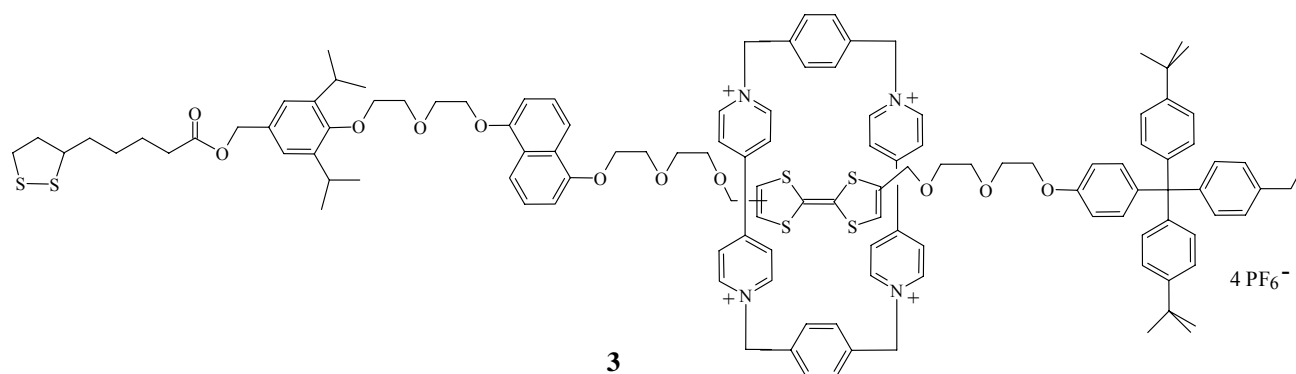
## 1. ROTAXANES BEARING QUATERNARY AZAAROMATIC MOIETIES

### a. Rotaxanes with tetracationic cyclophane as a ring

The UV/VIS spectroscopy investigation has shown that the self-assembly of [2]pseudorotaxane (**1a**) and [2]rotaxane (**1b**) depends on the bulkiness of stoppers and on the length of the polyethereal chains in the thread (**2**).<sup>49</sup> It was established that the template effect of **2** is lowered by the presence of large stoppers, especially when the chain is short, this behavior being due to steric hindrance.



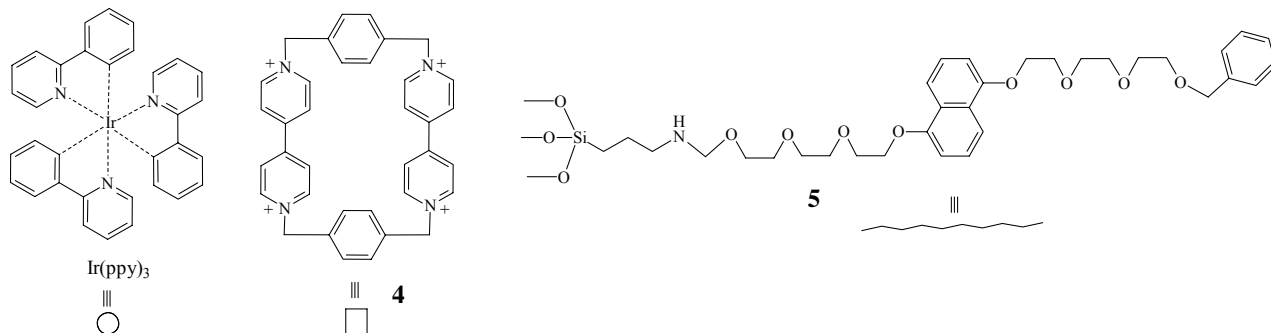
The redox-switching process of the bistable [2]rotaxane (**3**) has been investigated.<sup>19</sup> The appended disulfide group immobilizes **3** on gold surfaces as self-assembled monolayers (SAMs).



The presence of two unequally populated (*ca.* 1:9) translational isomers has been observed – the major isomer, in which the tetracationic cyclophane (**4**) encircles the tetrathiafulvalene (TTF) unit, and the minor one, in which **4** encircles the 1,5-dioxynaphthalene (DNP) unit. Amphiphilic bistable [2]rotaxanes can be transferred as molecular monolayers into a device using Langmuir-Blodgett (LB) technique. Sandwiching of self-organized LB monolayers between a bottom Si electrode and a top Ti/Al electrode affords a molecular switch tunnel junction.

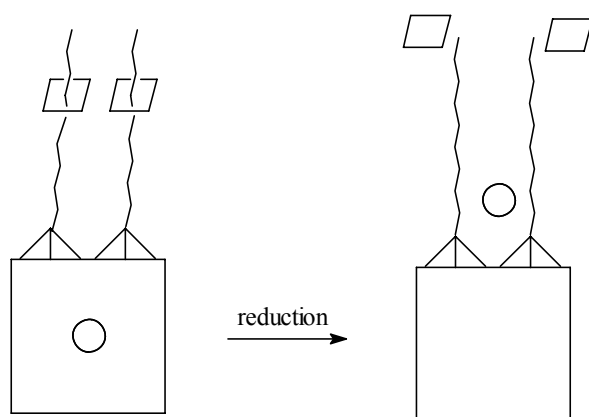
The ground state, when **4** encircles the TTF unit, represents the switch off (low conductance) state. When a + 2V bias is applied, **4** moves to DNP as a result of oxidation of TTF unit to its radical cation. However, when the bias is removed, and the neutrality of TTF is restored, **4** continues to reside on DNP forming the slow-decaying metastable state, *i.e.* switch-on (high conductance) state.<sup>22,50,51</sup> The above electrochemical investigation of **3**, serving as a model for solid-state molecular switch tunnel junctions (MSTJ) is promising in the design of nanoelectromechanical (NEM) systems.<sup>19</sup>

Pseudorotaxanes can thread and dethread in solution, however, when they are intended to serve as molecular machines, their attachment to solid support is required. For this purpose pseudorotaxane consisting of a thread (**5**) and the ring (**4**) has been tethered at the cylindrical nanopores in mesostructured silica; in this way a nanovalve able to trap guest molecules and to release them on demand has been created.<sup>52</sup>

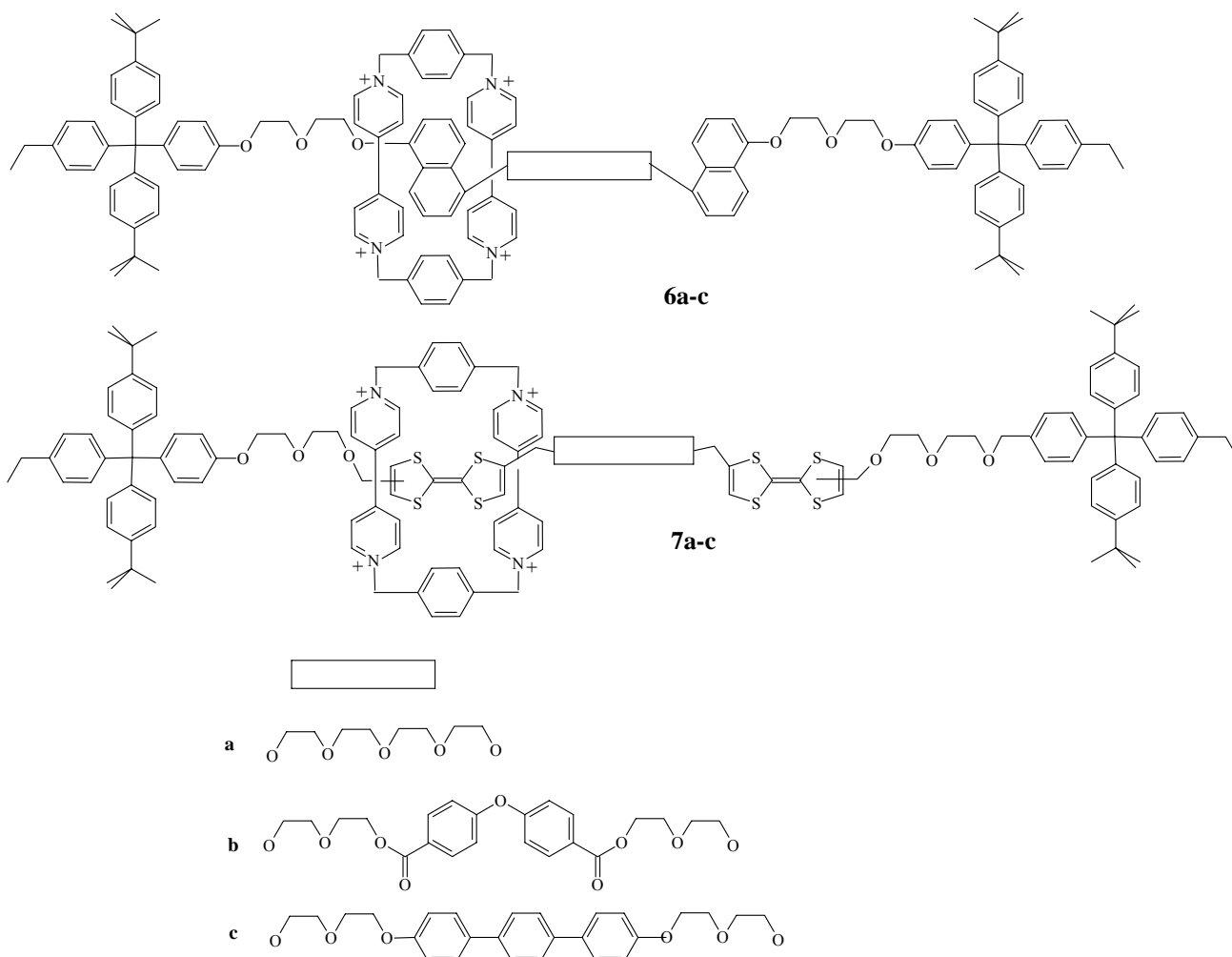


The tetracationic cyclophane (**4**) serves as a gate controlling access of guest molecules to nanopores and their escape out of nanopores. The Ir(ppy)<sub>3</sub> guest molecules were used; they are fluorescent, therefore their escape from nanopores may be followed by fluorescence spectroscopy.

When orifices of nanopores are covered with pseudorotaxanes, the  $\text{Ir}(\text{ppy})_3$  molecules are trapped inside. Upon reduction of **4** into its bisradical dicationic form with  $\text{NaCNBF}_4$ , the noncovalent bonding of **4** with thread (**5**) exists no more, therefore  $\mathbf{4}^{2+}$  units will be dethreaded and  $\text{Ir}(\text{ppy})_3$  molecules may escape (schematic representation is given below). Such nanovalve may be also operated by means of photochemistry.

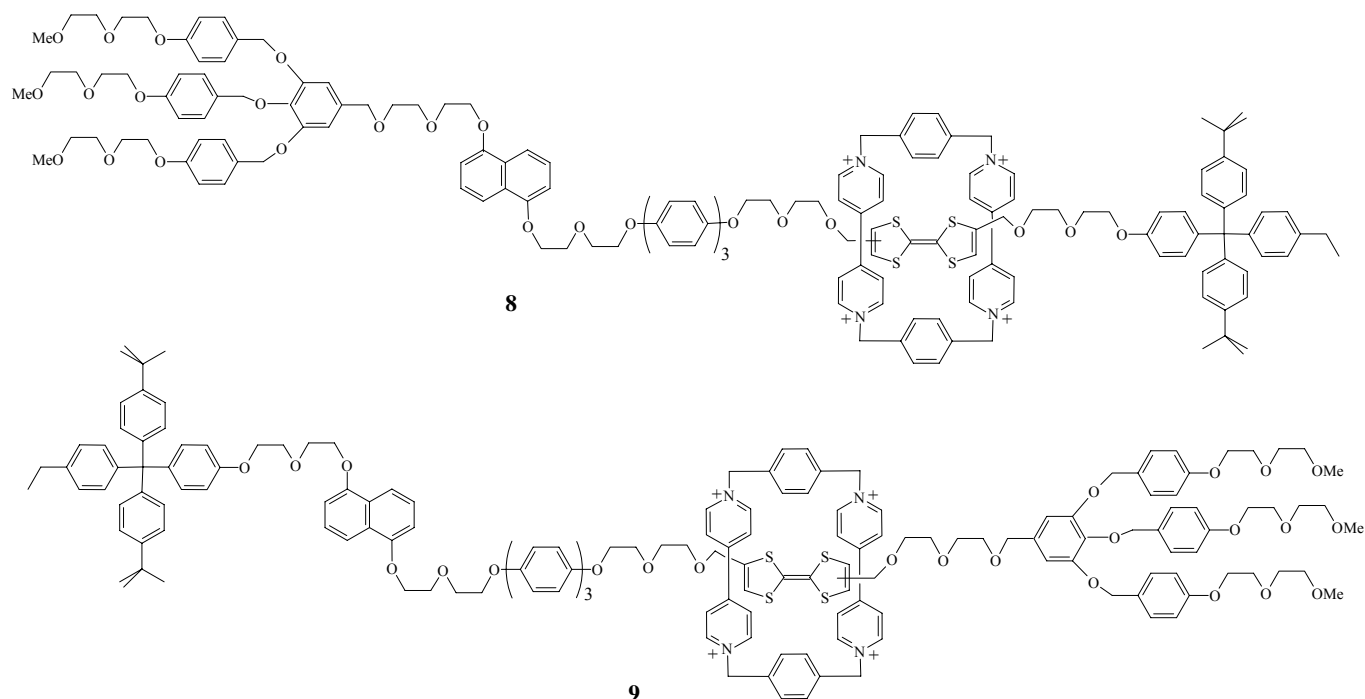


Rotaxanes (**6**) and (**7**) containing different spacers have been synthesized. Their shuttling process is dependent on the nature of spacers, this fact being promising in design of nanoelectromechanical (NEM) devices.<sup>53</sup>

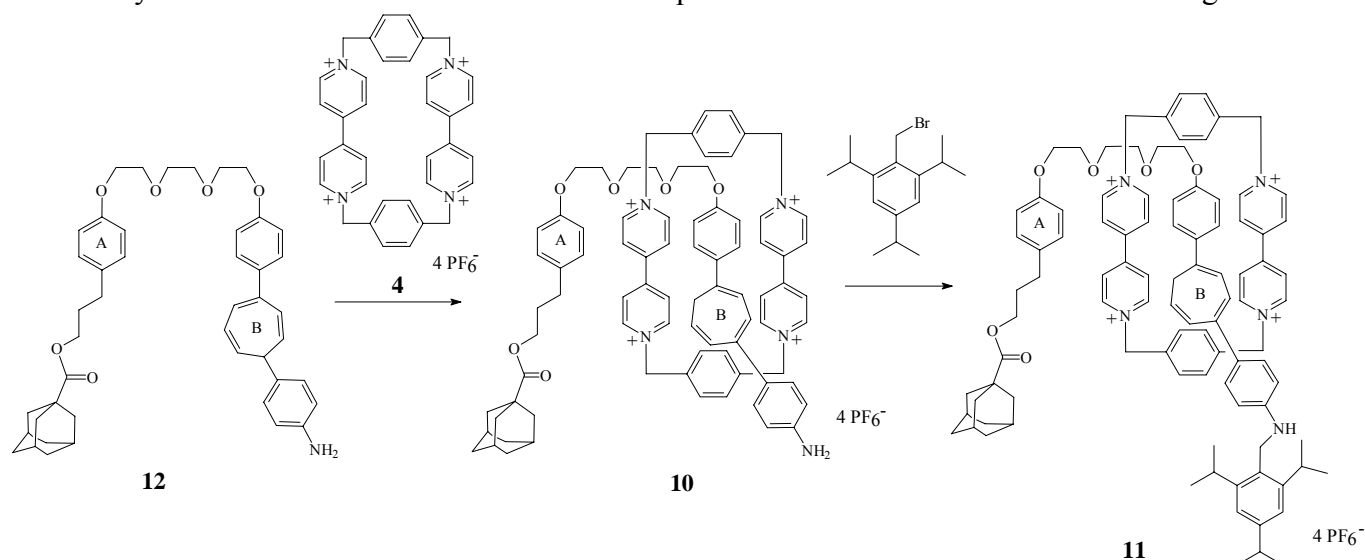


Two redox-controllable amphiphilic rotaxanes (**8**) and (**9**), bearing hydrophobic tetraarylmethane and hydrophilic dendritic stoppers have been synthesized.<sup>1,21,54</sup> In **8** the TTF unit is near the hydrophobic stopper, and in **9** – near the hydrophilic stopper. The tetracationic cyclophane (**4**) resides predominantly on the TTF unit.

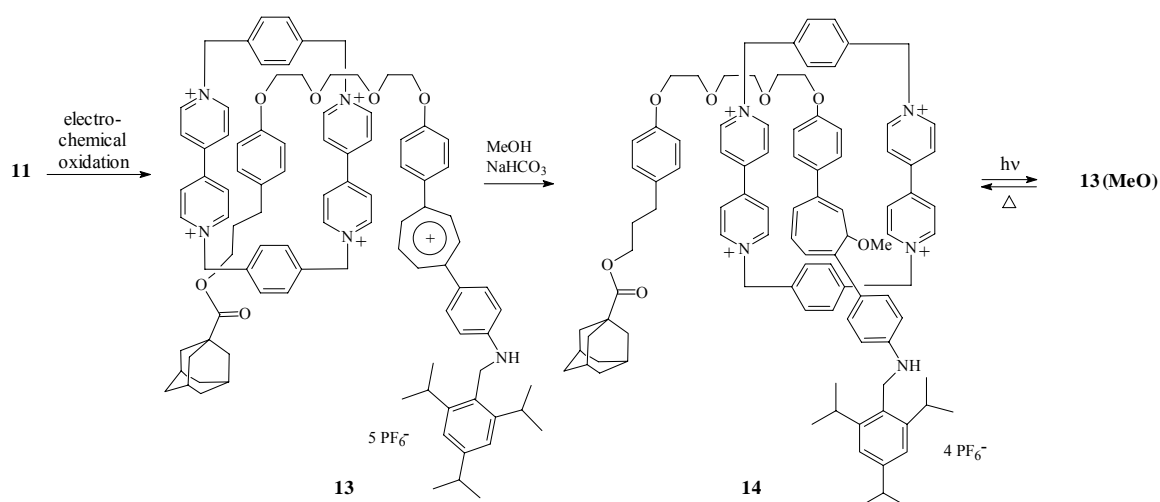
The ox/red stimulation of the TTF results in the shuttling of **4** between TTF and DNP units, however the ox/red stimulation of the cyclophane (**4**) initiates the unfolding/folding processes, in which **4** interacts with  $\pi$ -donating groups of stoppers.<sup>1,21,54</sup>



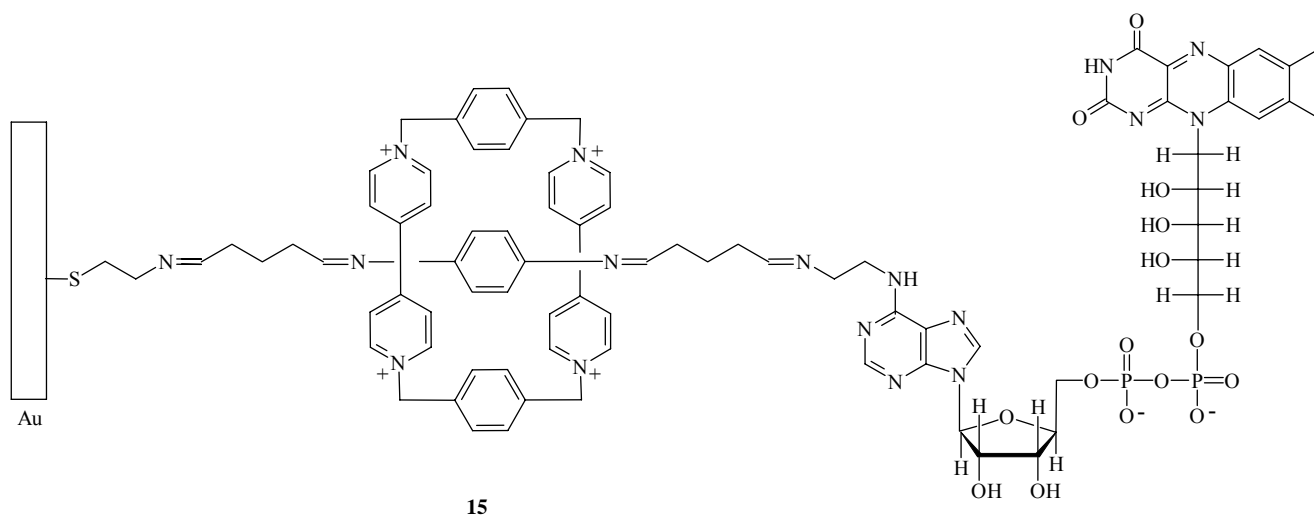
Pseudorotaxane (**10**) and rotaxane (**11**) have been synthesized.<sup>55</sup> Molecular thread (**12**) binds the tetracationic cyclophane (**4**) by CT and electrostatic interactions with aromatic ring A and the cycloheptatriene B unit situated between two aromatic rings. The cyclophane (**4**) resides in **10** and **11** exclusively on the B unit due to the lower oxidation potential of the B unit than that of the ring A.



The electrochemical oxidation of **11** affords the [2]rotaxane (**13**) in which the formed tropylium ion repulses **4**, therefore **4** encircles the ring A. By dissolving the rotaxane (**13**) in methanol in the presence of  $\text{NaHCO}_3$ , the attack of the  $\text{MeO}^-$  nucleophile on the tropylium ion transforms it into cycloheptatriene. Since tropylium ion exists no more, **4** again moves to the B unit and encircles it, forming rotaxane (**14**). The photochemical excitation of **14** gives **13(MeO)** in which the tropylium ion is present, therefore **4** encircles A. The thermal back reaction results in the return of **13(MeO)** into **14** in which **4** encircles the unit B. In this way the molecular machine, driven by light and thermal energy has been made.<sup>55</sup>



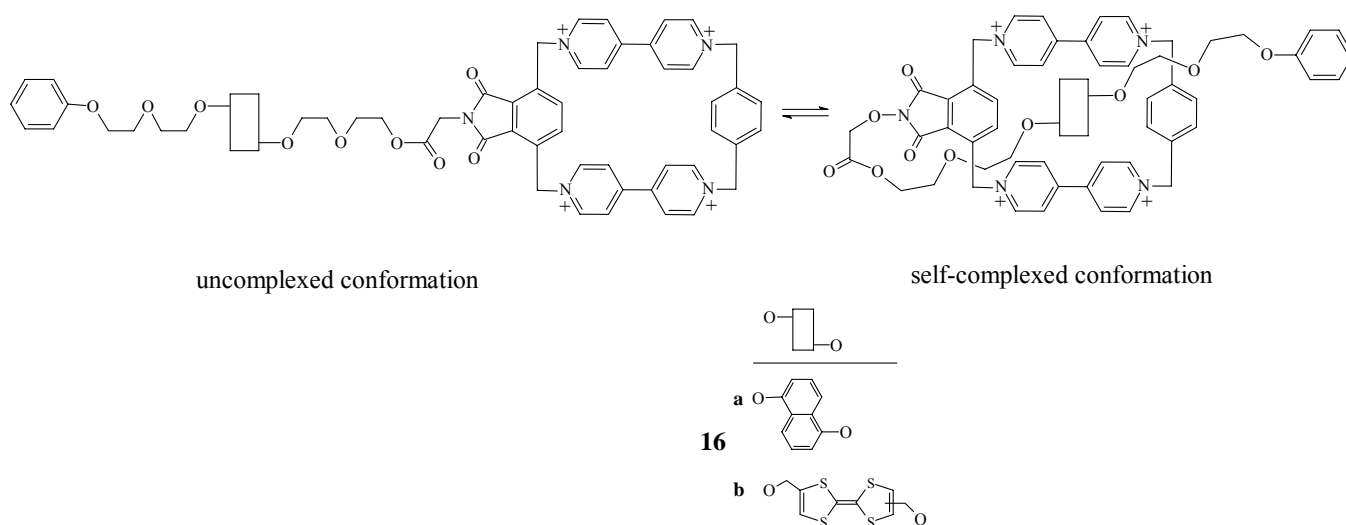
The electrical contacting of redox enzymes, *e.g.* glucose oxidase, with electrodes is very important for the design of biofuel cells.<sup>56,57</sup> A method for the electrical contacting of glucose oxidase with electrode by using the redox-active FAD stoppered rotaxane (**15**) as an electron-transfer mediator connecting the enzyme to the electrode has been reported.<sup>58</sup> (FAD = flavine adenine dinucleotide).



It should be pointed out that the bioelectrocatalyzed oxidation of glucose by glucose oxidase occurs at a very low redox potential (*ca.*  $-0.4\text{V}$ , this value being very close to the thermodynamic redox potential of the FAD cofactor).<sup>58</sup>

Self-complexing molecules are promising as thermally and electrothermally controllable molecular switches. They usually have an arm component covalently linked to a macrocycle; the flexible link enables its entrance into the macrocycle cavity. Self-complexing compounds may undergo a reversible movement of the arm into and out of the macrocycle cavity by a particular stimulus, therefore they may serve as molecular machines.<sup>59,60</sup>

Compounds (**16a,b**) are examples of self-complexing molecular switch, thermally and electrochemically controllable.<sup>61</sup> They exist in an equilibrium between straight (uncomplexed) and folded (self-complexed) conformations. By a fine-tuning of their structure, **16a,b** can be made highly sensitive to temperature and applied voltages, in this way becoming thermosensors or electroswitches.



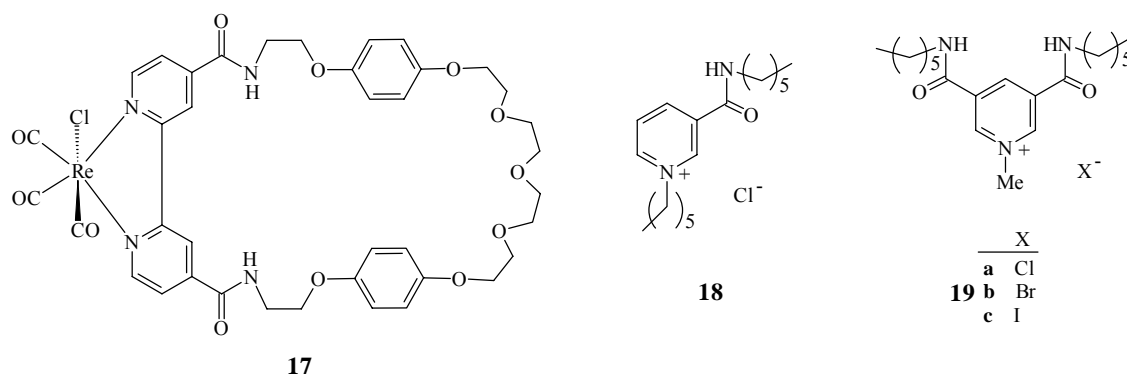
The results of variable UV/Vis spectroscopy have shown that the equilibrium of **16a** in acetonitrile solution is highly sensitive to temperature; the color change appears. Such temperature-dependent color change is reversible and may be recycled many times.

The molecular recognition between TTF (donor) and **4** (acceptor) can be turned “off” by the oxidation of the TTF to  $\text{TTF}^{+}$  or  $\text{TTF}^{2+}$ , and “on” by their reduction back to the neutral form. Upon the addition of tris(*p*-bromophenyl)ammonium hexachloroantimonate<sup>21</sup> to the  $\text{CD}_3\text{COCD}_3$  solution of **16b**, the obtained  $\text{TTF}^{2+}$  dication no longer resides inside **4** cavity and the straight conformation appears. However, when zinc dust is added, the formed neutral TTF enters back the **4** cavity to give the folded conformation.<sup>61</sup>

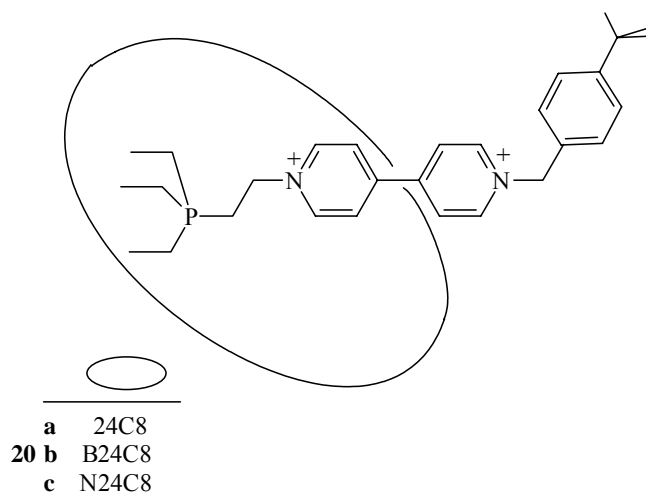
## b. Rotaxanes with crown ether unit as a ring

In the study of pseudorotaxanes<sup>62</sup> and rotaxanes<sup>63</sup> formed by templation of a chloride anion, it was found that the macrocycle (**17**) may give with azaaromatic salts (**18**) and (**19**) pseudorotaxanes by a halide ion templation in  $\text{CD}_3\text{COCD}_3$ .<sup>64</sup> The macrocycle (**17**) strongly binds halide anions, especially chloride and bromide.

Since the pyridinium cation is strongly ion-paired to the chloride or bromide counterion, the chloride recognition by **17** results in the threading of the azaaromatic cation through the macrocycle (**17**). The addition of **18** or **19a** to **17** considerably enhances its luminescence intensity due to the formation of pseudorotaxane which increases the rigidity of **17** and disfavours nonradiative decay processes.



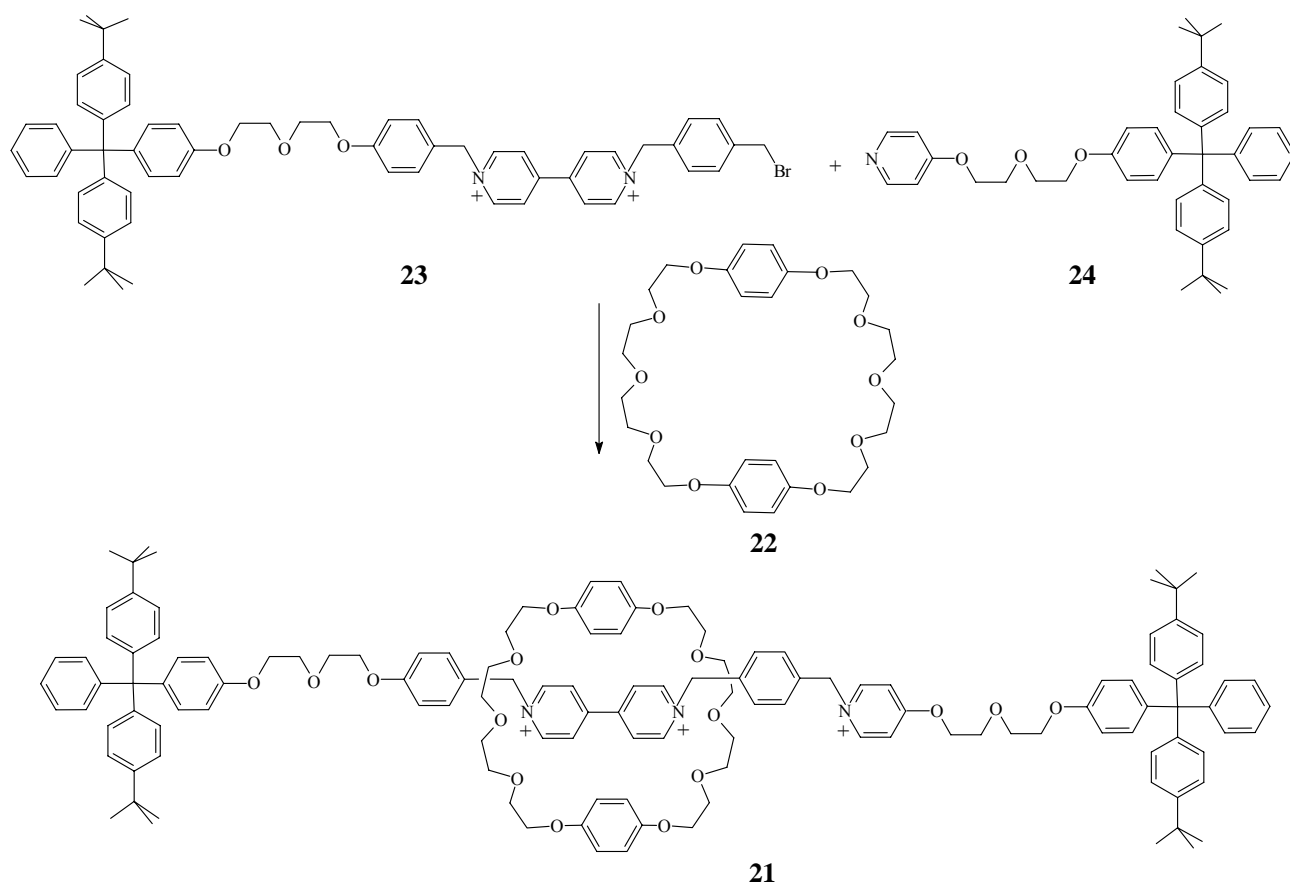
Rotaxanes (**20a-c**) have been synthesized.<sup>65</sup> Rotaxanes (**20b**) and (**20c**) consist of the unsymmetrical thread and an unsymmetrical ring, therefore either of them may exist as two conformers.



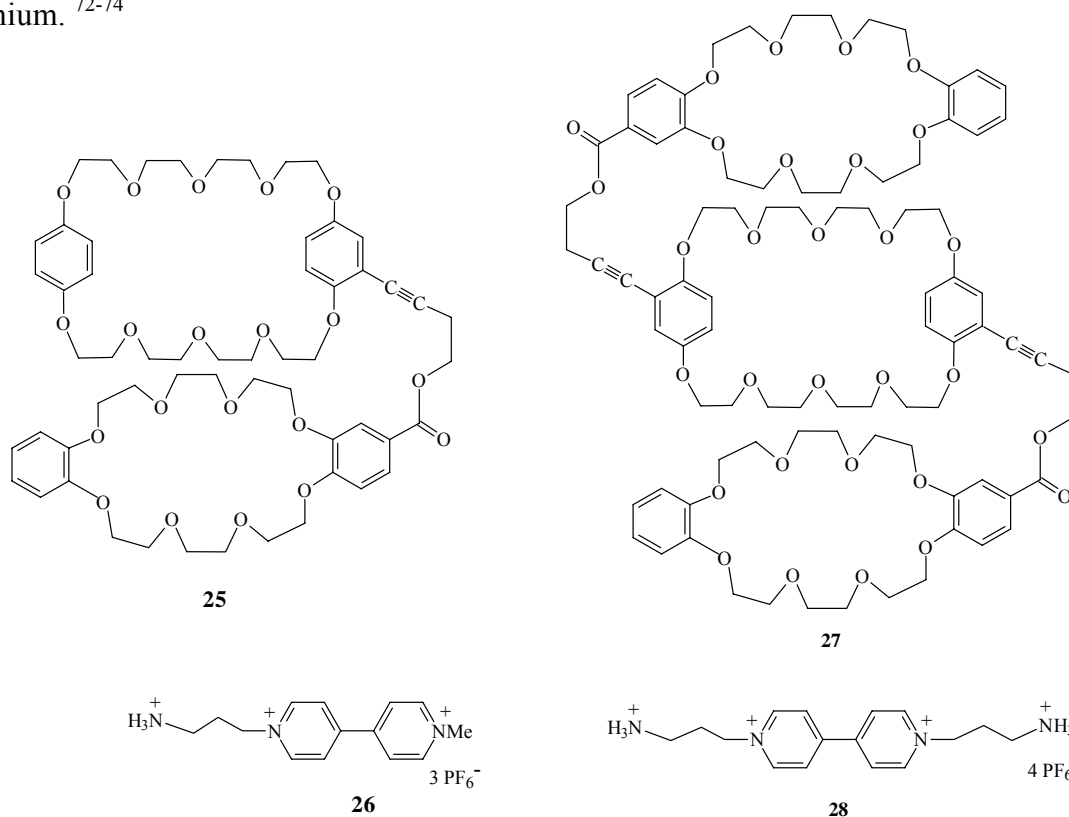
Many solventless reactions have been studied,<sup>66-69</sup> however, the rate acceleration may also be achieved by premixing of solid reactants in solution.<sup>70</sup> The subsequent evaporation affords an amalgam which is favorable for a solventless reaction. Such a molecular-level mixing, *i.e.* a premixing method accelerates reaction and increases its yield.

As an example may serve the synthesis of rotaxane (**21**) achieved by mixing reactants (**22-24**) in acetone/dichloromethane, followed by evaporation.<sup>70,71</sup>

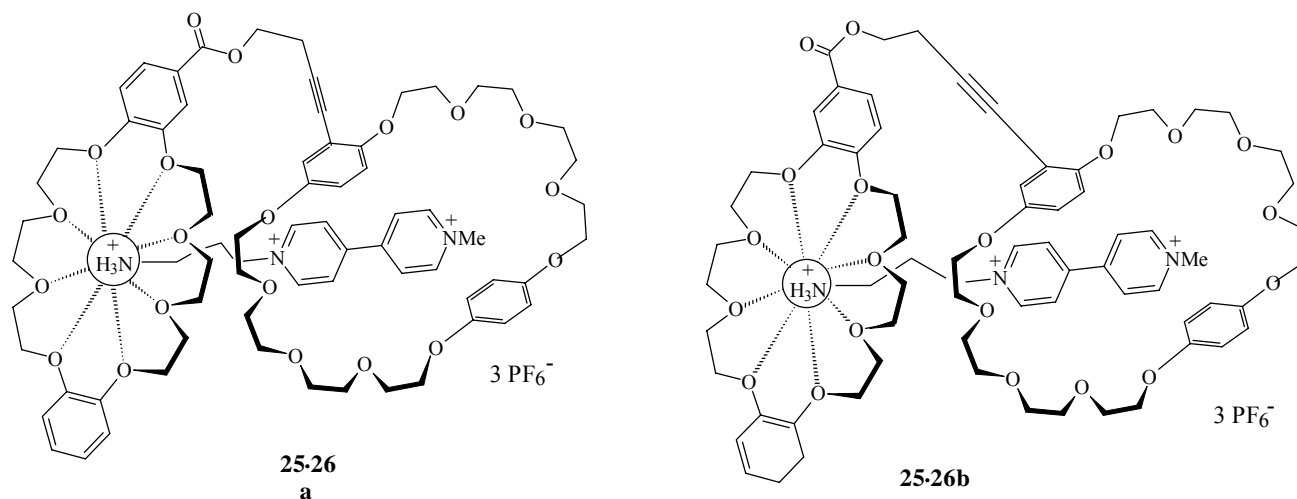




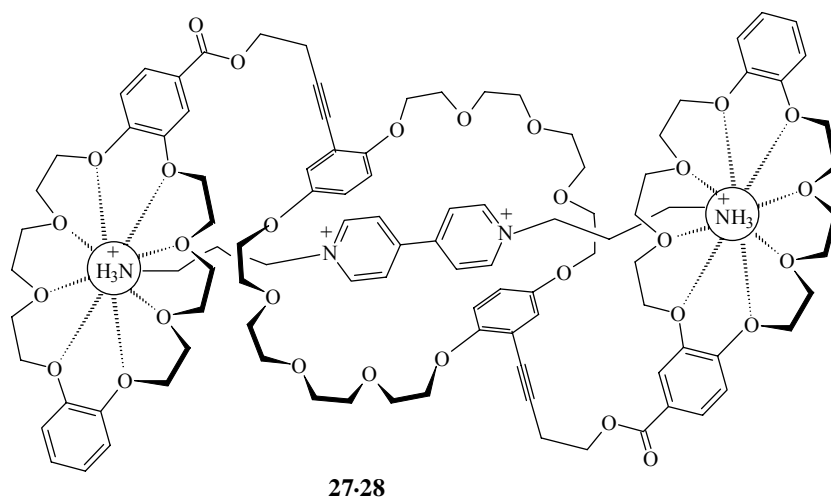
It was established that pseudorotaxanes (**25-26**) and (**27-28**) are very stable due to the cooperation of two different non-covalent interactions : the donor-acceptor interaction between bis-*p*-phenylene-34-crown-10 and 4,4'-dipyridinium and the electrostatic interaction between dibenzo[24]crown-8 and alkylammonium.<sup>72-74</sup>



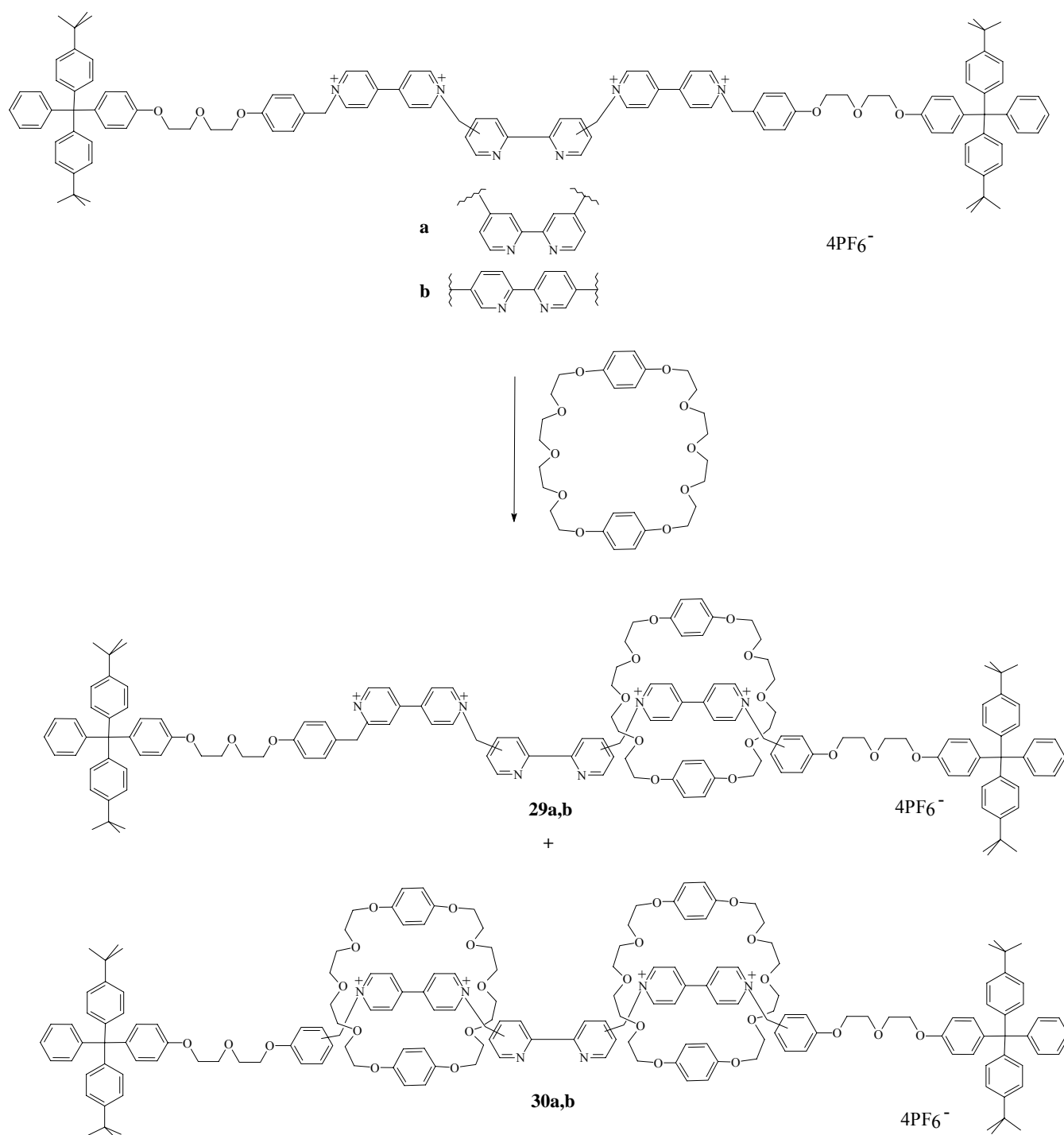
Compound (**25**) binds **26** by one donor-acceptor and one electrostatic interaction, whereas **27** binds **28** by one donor-acceptor and two electrostatic interactions. Mixing of **25** with **26** in acetonitrile affords two isomeric pseudo[2]rotaxanes (**25·26a**) and (**25·26b**), in which orientation of bis-*p*-phenylene[34]crown-10 unit relative to dibenzo[24]crown-8 is different.



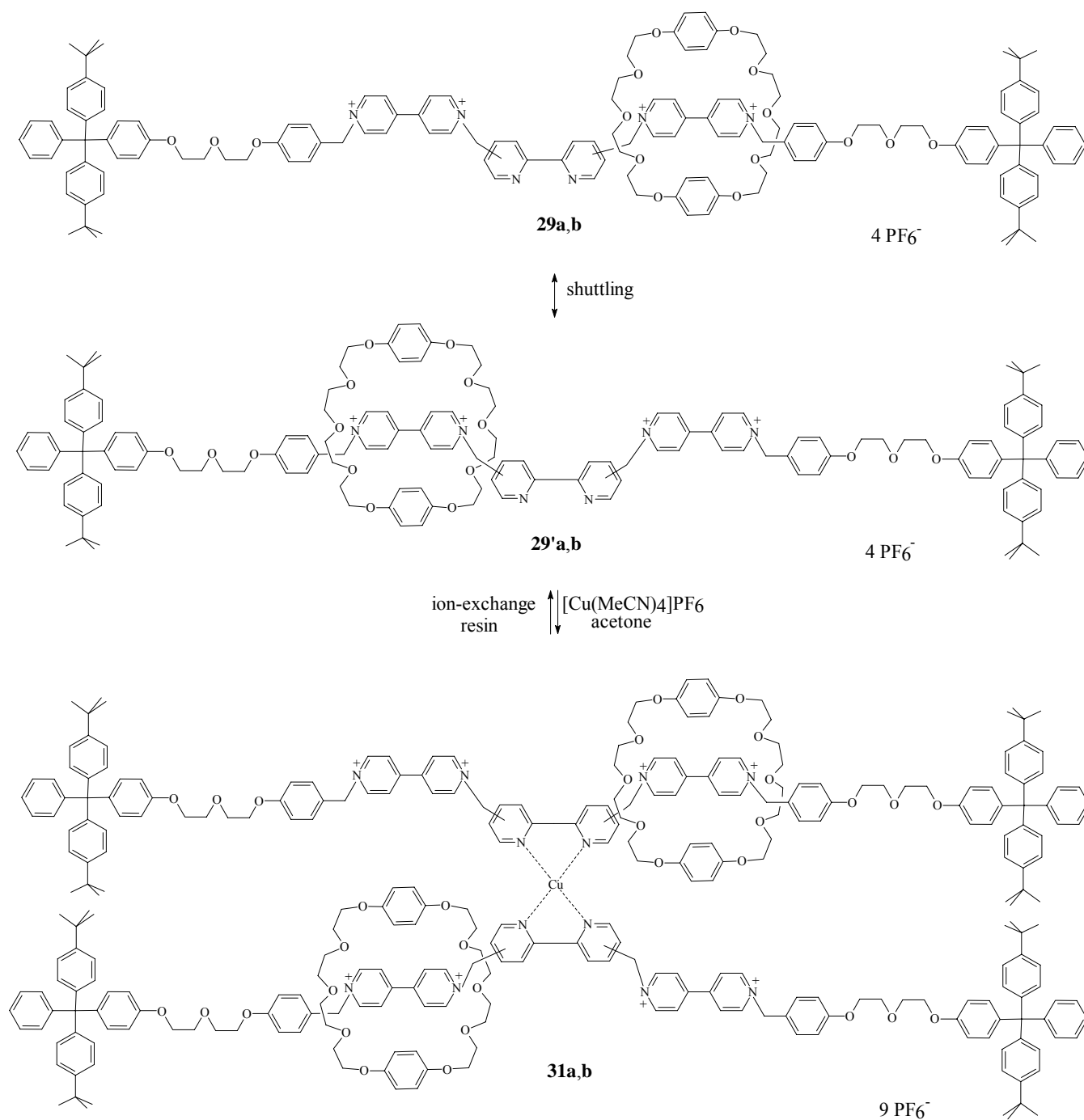
Mixing of **27** with **28** in acetonitrile affords pseudorotaxane (**27·28**) ; one isomer is shown. For this pseudorotaxane three isomers are possible, depending of the different orientation of bis-*p*-phenylene-[34]-crown-10 relative to two dibenzo[24]crown-8 units.<sup>72</sup>



In the search for molecular switches,<sup>24,75,76</sup> [2]rotaxane (**29a,b**) containing chelating sites has been obtained, along with [3]rotaxane (**30a,b**).<sup>77</sup>

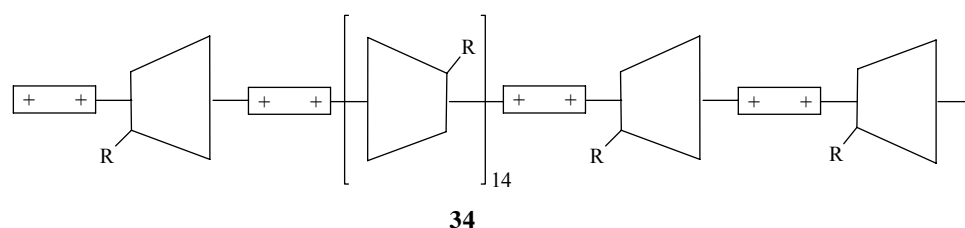
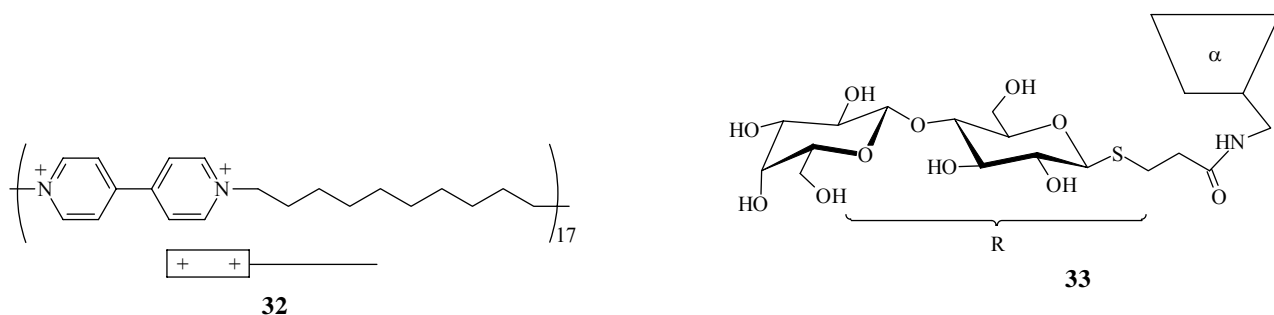


Rotaxanes (**29a,b**) and (**29'a,b**) form a shuttling system; the crown ether ring moves forward and back between the two equivalent bipyridinium units at the rate impossible to follow by NMR spectrometry. When this shuttling system reacts with  $[Cu(MeCN)_4]PF_6$ , the interruption of shuttling occurs due to the formation of complex (**31a,b**). Treatment of **31a,b** with ion-exchange resin (Murochelate B-1), which is equivalent to Dowex A-1 results in the decomplexation, and the shuttling appears again.<sup>77,78</sup> In this way a switching system was created.



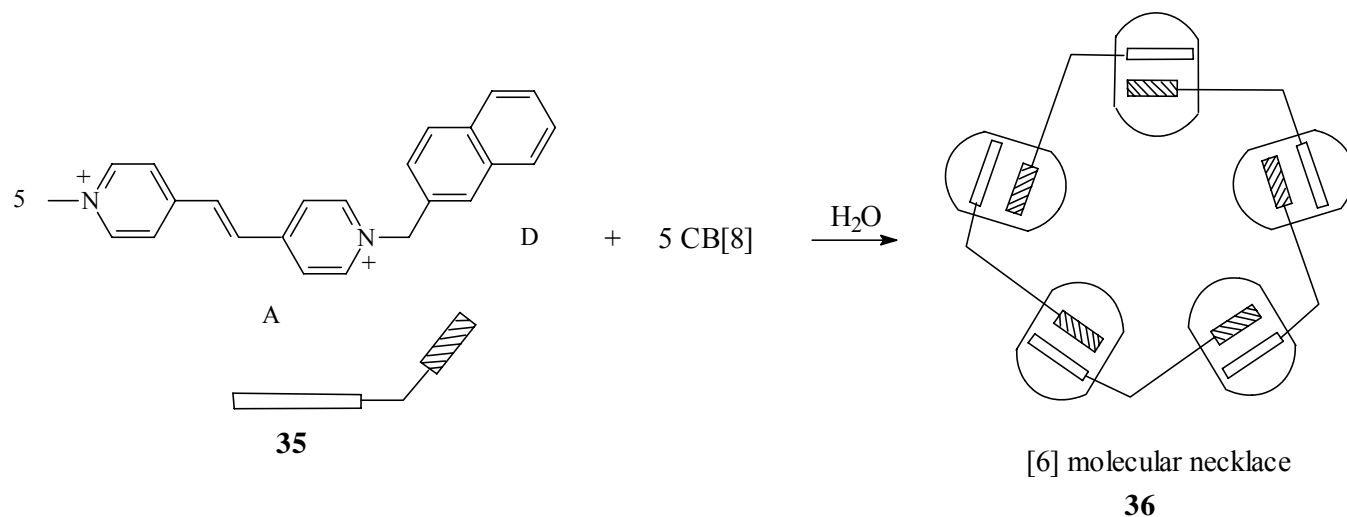
### c. Rotaxanes with cyclodextrin, cucurbituril and calixarene units as rings

Polyviologen (**32**) and lactoside-bearing  $\alpha$ -CD (**33**) self-assemble to give stable multivalent pseudorotaxane (**34**). In **34** the CD units are able to rotate around and to shuttle along the polyviologen chain possessing flexible decamethylene units; these properties afford supramolecular structure with the fluidity of cellular membranes.

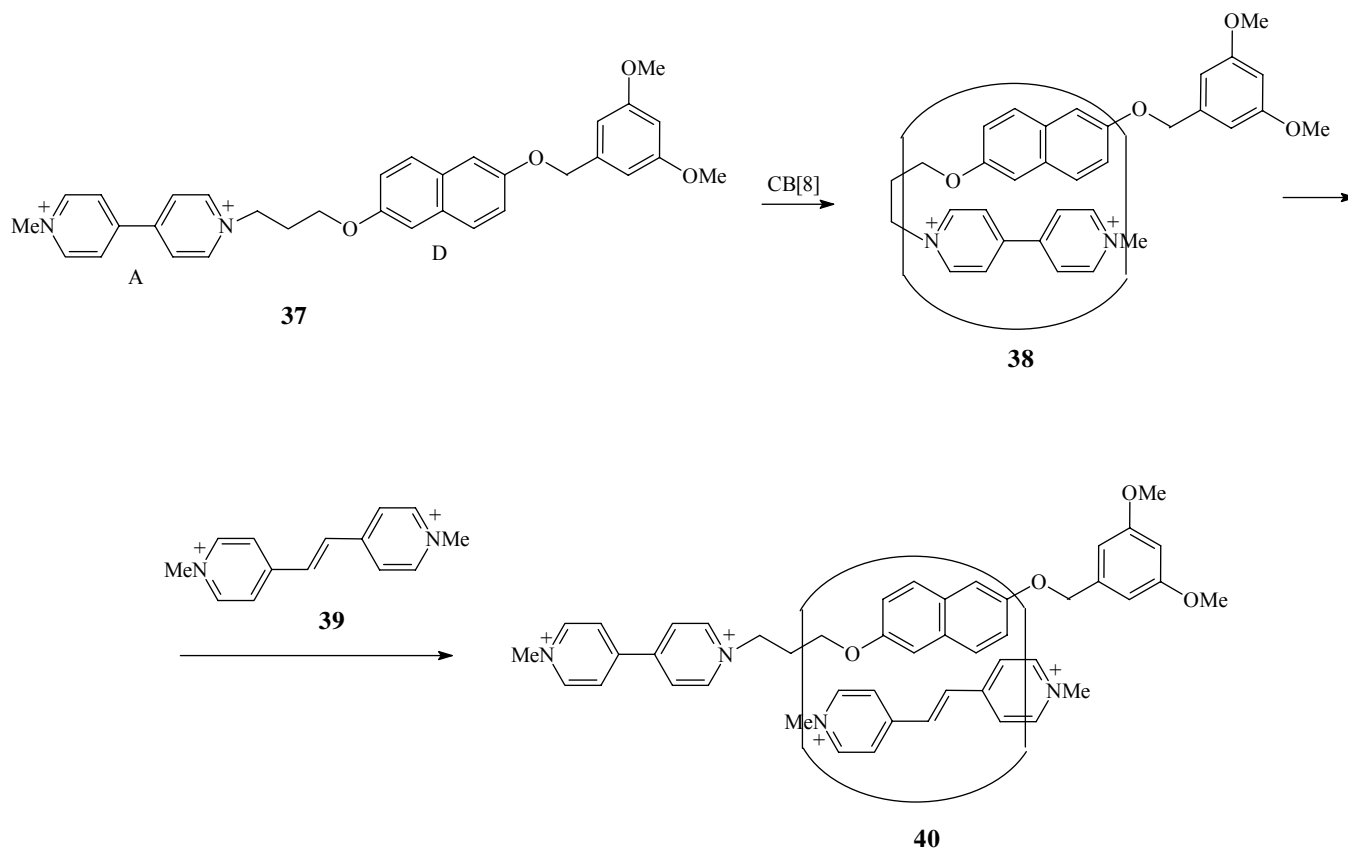


Using **34** a successful inhibition of galectin-1-mediated T-cell agglutination was achieved.<sup>79,80</sup> Since galectin-1 plays an important role in cancer diseases<sup>81,82</sup> the investigation of its binding is promising in therapeutics.<sup>83</sup> The above results are important for the study of protein-carbohydrate interactions.

In the investigation of cucurbiturils<sup>84,85</sup> the self-assembly of a bent molecule (**35**) comprising electron acceptor (A) and electron donor (D) moieties, with CB[8], leading to a cyclic pentamer (**36**) has been achieved. The formed **36**, *i.e.* the [6]molecular necklace, [6]MN is held by host-stabilized intermolecular CT interactions.<sup>86</sup> Using such stabilized CT interactions, the supramolecular assemblies, *e.g.* molecular loops<sup>87,88</sup> and redox-controllable vesicles<sup>89</sup> could be synthesized.



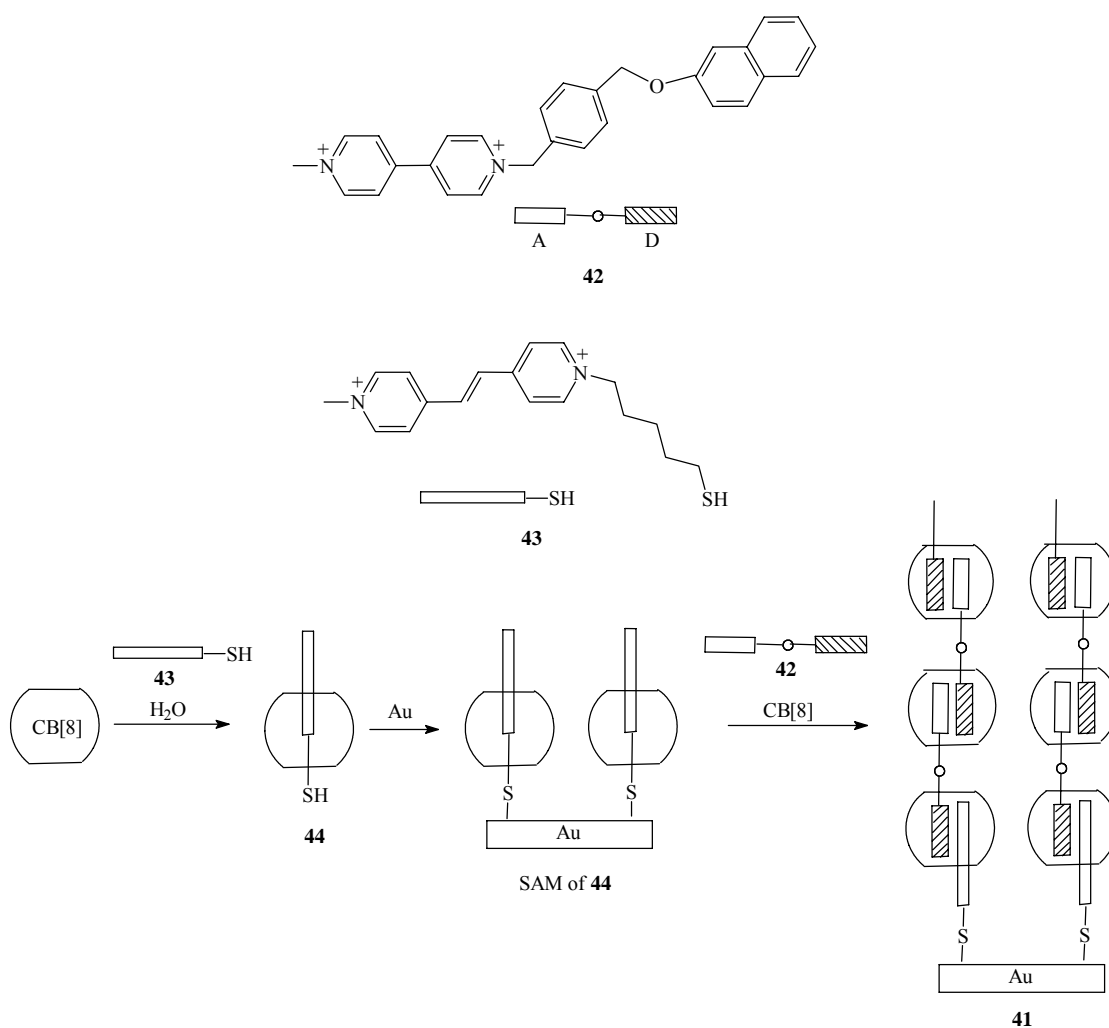
It was observed that the guest molecule (**37**) consisting of electron acceptor and electron donor gives with CB[8] the 1:1 CT complex (**38**)<sup>88</sup> of a folded structure, in which CT interaction is host-stabilized. The addition of the dipyridinium ethylene (**39**) leads to the ternary complex (**40**), since **39** is a stronger electron acceptor than bipyridinium unit.



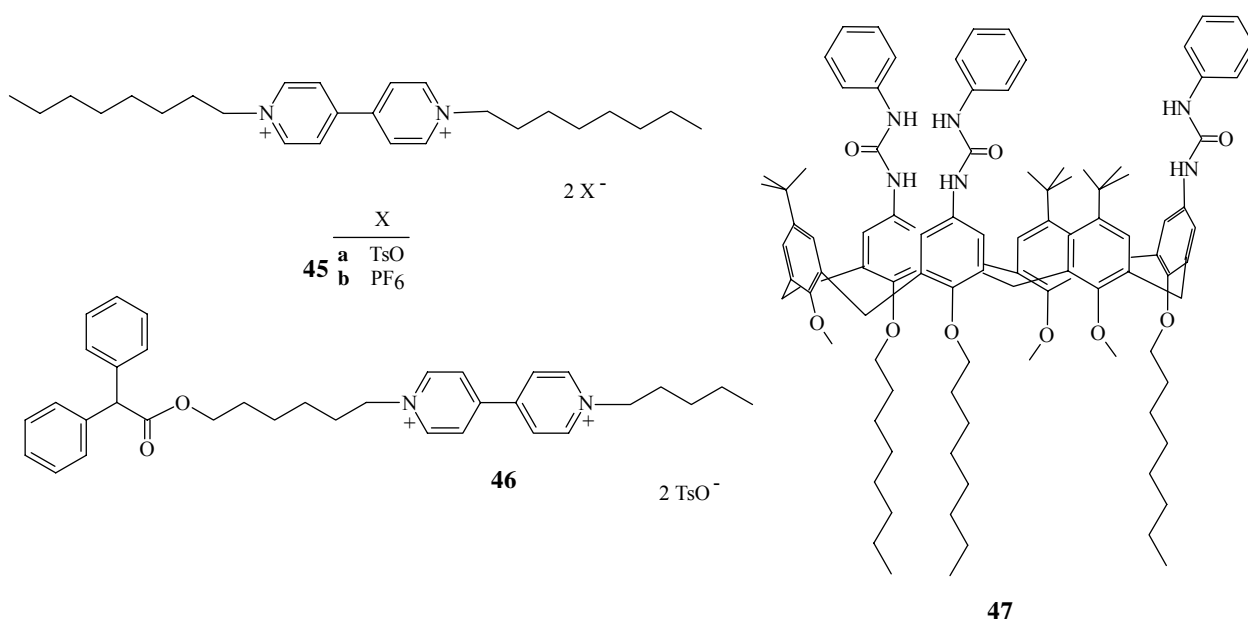
Supramolecular polymers in which monomers are noncovalently linked, *e.g.* by hydrogen bonding, metal-ligand, CT,  $\pi$ - $\pi$  stacking or host-guest interactions are intensively studied.<sup>90</sup> Due to reversibility of noncovalent interactions, properties of such polymers may be controlled.

Poly(pseudorotaxane) (**41**) consisting of the guest-molecule (**42**) and CB[8] has been obtained.<sup>91</sup> The guest molecule (**42**) contains electron-acceptor A (4,4'-bipyridinium) and electron-donor D ( $\beta$ -naphthol) units connected by a rigid linker (*p*-xylylene) to avoid the intramolecular CT complex formation inside CB cavity.

CB[8] and **43** bearing dipyridinium ethylene unit and a terminal thiol group form in water the complex (**44**). The gold substrate was immersed in the aqueous solution of **44** *in situ* to give the SAM of **44**. The subsequent soaking of the formed SAM on gold in an aqueous solution containing **42** and CB[8] resulted in the growth of the poly(pseudorotaxane) (**41**) of a polymerization degree *ca.* 4, promising for the preparation of molecular sensors.



Pseudorotaxanes consisting of viologens (**45a,b**) and (**46**) as threads and calixarene (**47**) bearing ureido groups<sup>92</sup> as a ring have been investigated in view of their threading-dethreading process,<sup>93</sup> promising in the design of molecular machines.



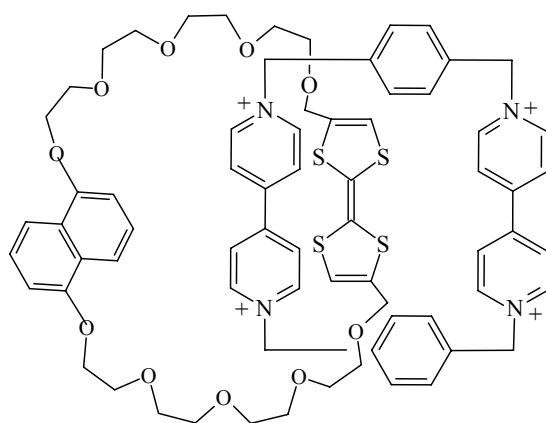
The nature of counteranions of bipyridinium threads strongly influences the formation of pseudorotaxanes. The coordination of these counteranions by NH ureido groups of the calixarene (**47**) via hydrogen bonding is important for the breaking of tight ion pairs prior to threading. In apolar solvents which are used for the self-assembly process, the bipyridinium cations form tight ion pairs with their anions. The separation of the dicationic thread from its counteranions should occur before the inclusion into the calixarene cavity.

The self-assembly of viologens (**45a**) and (**46**) with calixarene (**47**) has been made in CH<sub>2</sub>Cl<sub>2</sub> solution. The threading and dethreading rate constants are dependent on the nature of the counteranion of the thread, for example when **45a** is used instead of **45b**, the threading and dethreading rate constants increase.

It was also established that the electrochemical reduction of viologens (**45**) and (**46**) results in the fast dethreading of the pseudorotaxane. The electron-transfer kinetics for the reduction of the thread unit is slower when it is encapsulated in the calixarene cavity.<sup>93</sup>

## 2. CATENANES BEARING QUATERNARY AZAAROMATIC MOIETIES

Electrochemically switchable bistable catenane (**48**) served for computational procedure, explaining switching mechanism. Semiempirical AM1 electronic structure calculations for a large ensemble of chemically reasonable configurations are consistent with experimental results. The analysis of charge distribution has indicated that the co-conformational switching upon oxidation is initiated by electrostatic repulsion between tetracationic cyclophane and TTF<sup>+</sup>.<sup>94-96</sup>

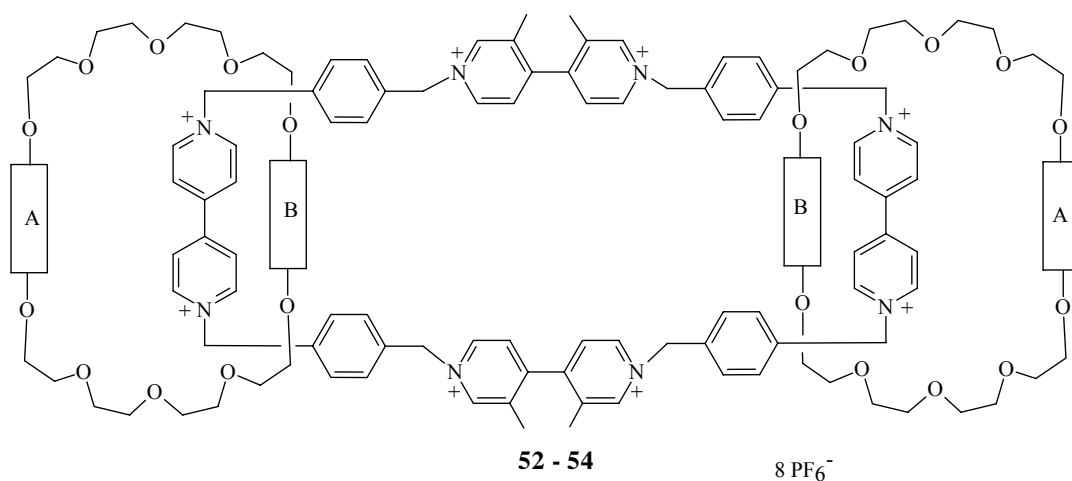
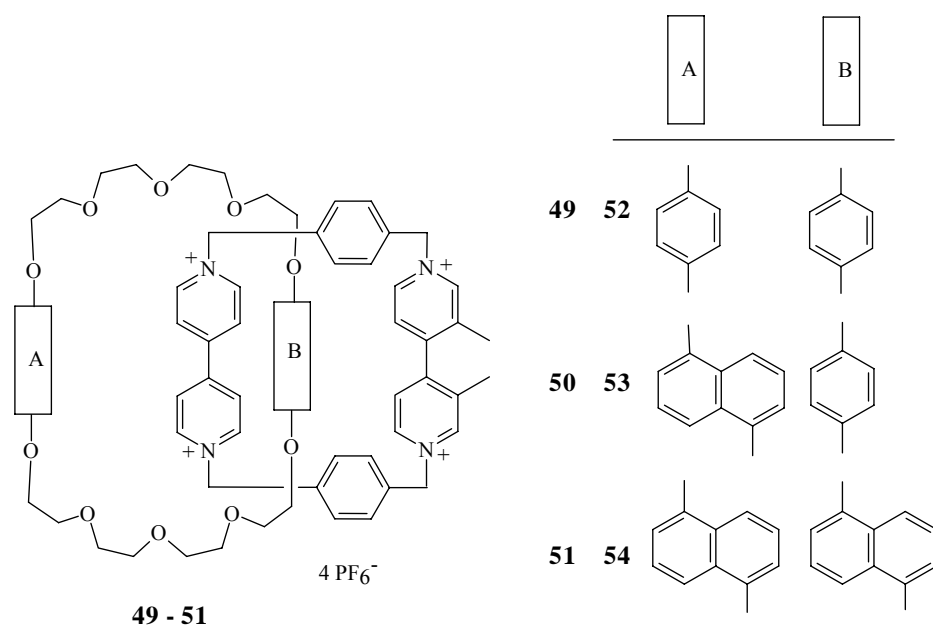


**48**

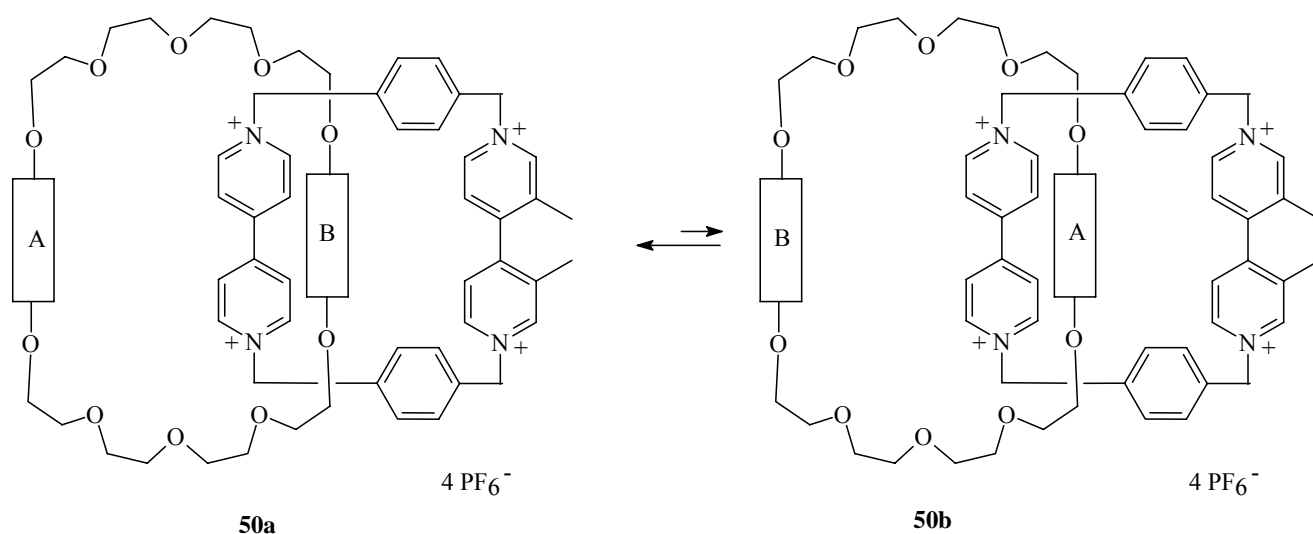
The template-directed syntheses of [2]catenanes (**49-51**) in which one of bipyridinium units is replaced by picolinium unit have been made.<sup>97</sup> As minor products of these reactions the [3]catenanes (**52-54**) have been obtained. In [2]catenanes (**49-51**) the crown ether ring can circumrotate between two recognition sites upon chemical or electrochemical stimulation. Such mechanical movement allows to use these [2]catenanes as controllable, bistable molecular switches.



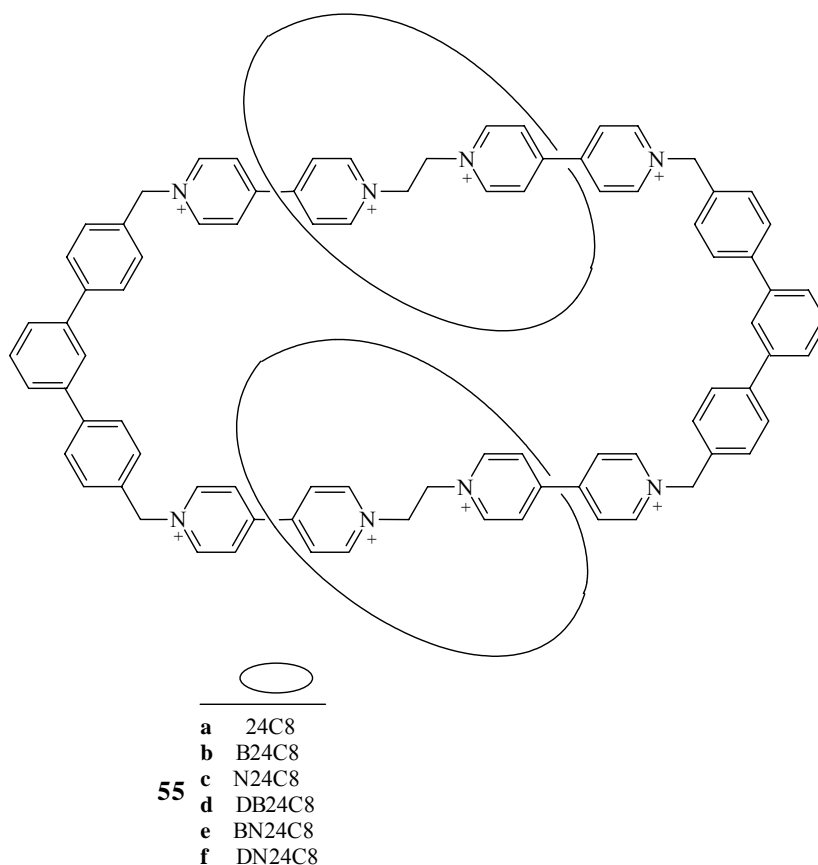
It was shown that the stable translational isomer of (**49-51**) is the one in which the crown ether ring encircles the electronically and sterically more attractive planar bipyridinium rather than the nonplanar bipycolinium unit. Similarly as in the case of (**49-51**), in (**52-54**) both crown ether rings encircle bipyridinium, and not bipycolinium units.



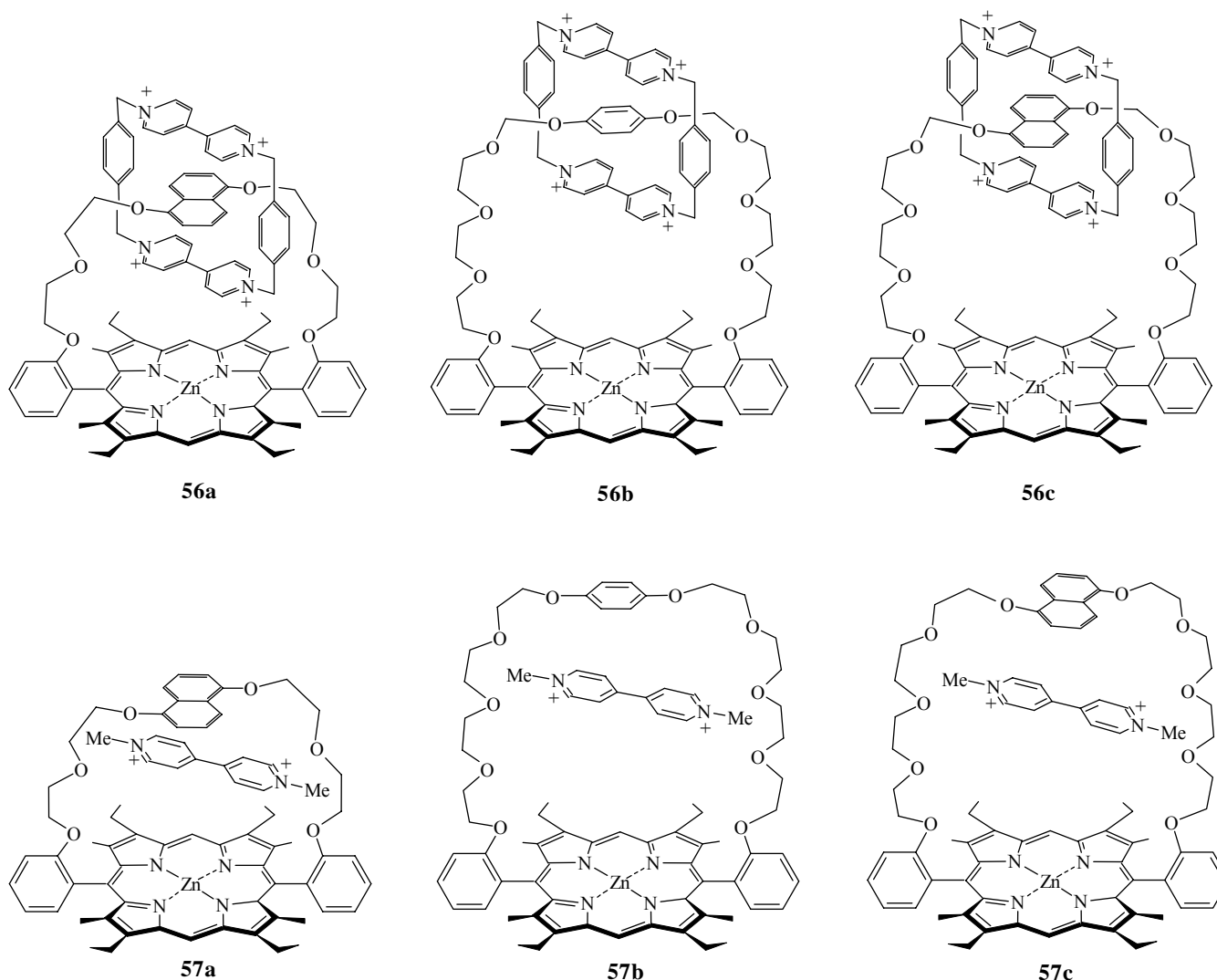
For [2]catenane (**50**) the circumrotation of the crown ether ring through the cavity of tetracationic cyclophane results in the equilibrium of translational isomers (**50a**) and (**50b**); the isomer (**50a**) with hydroquinone unit residing inside the cyclophane cavity prevails.<sup>97</sup>



The synthesis of [3]catenanes (**55a-f**) has been reported.<sup>98</sup> It was found that the formation of [3]catenane (**57d**) affords the highest yield among **55a-f**, due to the effective activity of DB24C8 as a template.



Catenanes (**56a-c**) consisting of tetracationic cyclophane (**4**) and polyether-strapped porphyrins have been spectroscopically and electrochemically characterized.<sup>99,100</sup> The porphyrin subunit is a very convenient molecule for control of their dynamics and can be accessed by chemical, electrochemical or photochemical stimuli. The electron transfer rates in catenanes (**56a-c**) were compared with those of corresponding host-guest complexes (**57a-c**).<sup>101</sup>



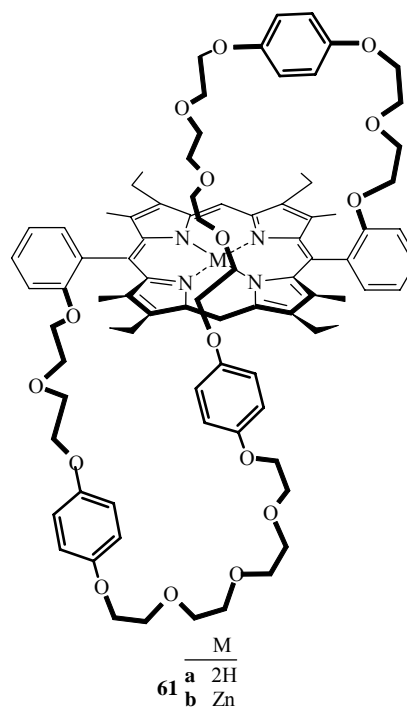
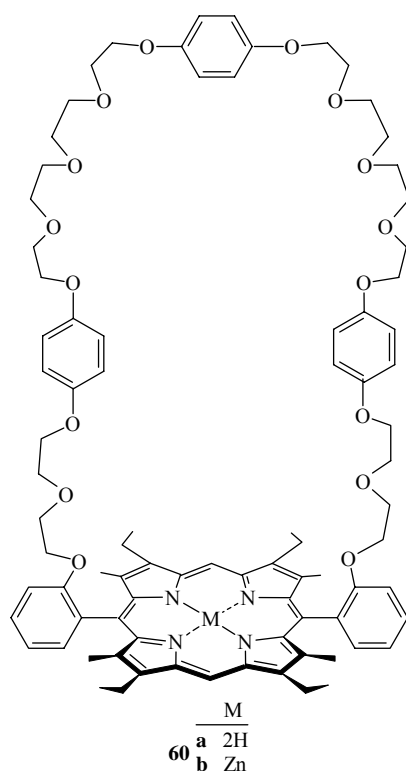
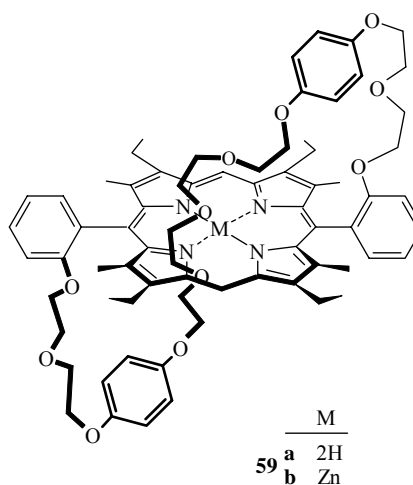
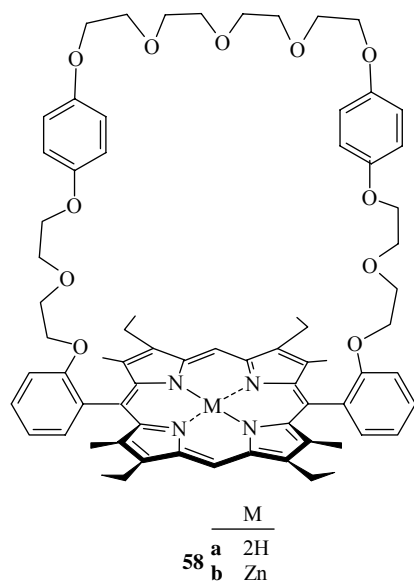
In catenanes the luminescence is quenched as compared to that of porphyrin. The quenching is due to the electron-transfer reaction from the singlet excited state of the porphyrin to the electron acceptor (**4**), *i.e.* to the charge separation (CS). The CS reactions of **56b** and **56c** are slower than in the case of **56a**, similarly as in the case of **57a-c**.

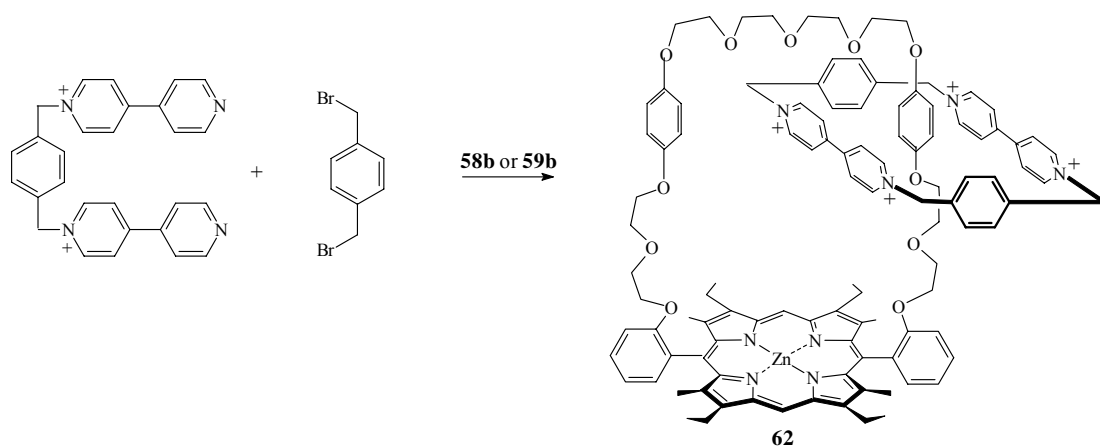
Catenanes (**56a-c**) show very rich redox behavior due to the presence of several different and interacting electro-active subunits. Oxidation processes involve porphyrin and substituted dimethoxybenzene (DMB) or substituted dimethoxynaphthalene (DMN), and the reduction processes – the tetracationic cyclophane (**4**).

Tetracationic cyclophane (**4**) undergoes two bielectronic reduction processes of two equivalent bipyridinium units. However, in catenane two bipyridinium subunits of **4** are not equivalent, they have different (inside and outside) environment. The first reduction involves the outer bipyridinium subunit, and the second reduction involves the inner one. The inner bipyridinium unit is more difficult to reduce than the outer one, since it interacts with two electron donor moieties: porphyrin and DMB or DMN subunits.

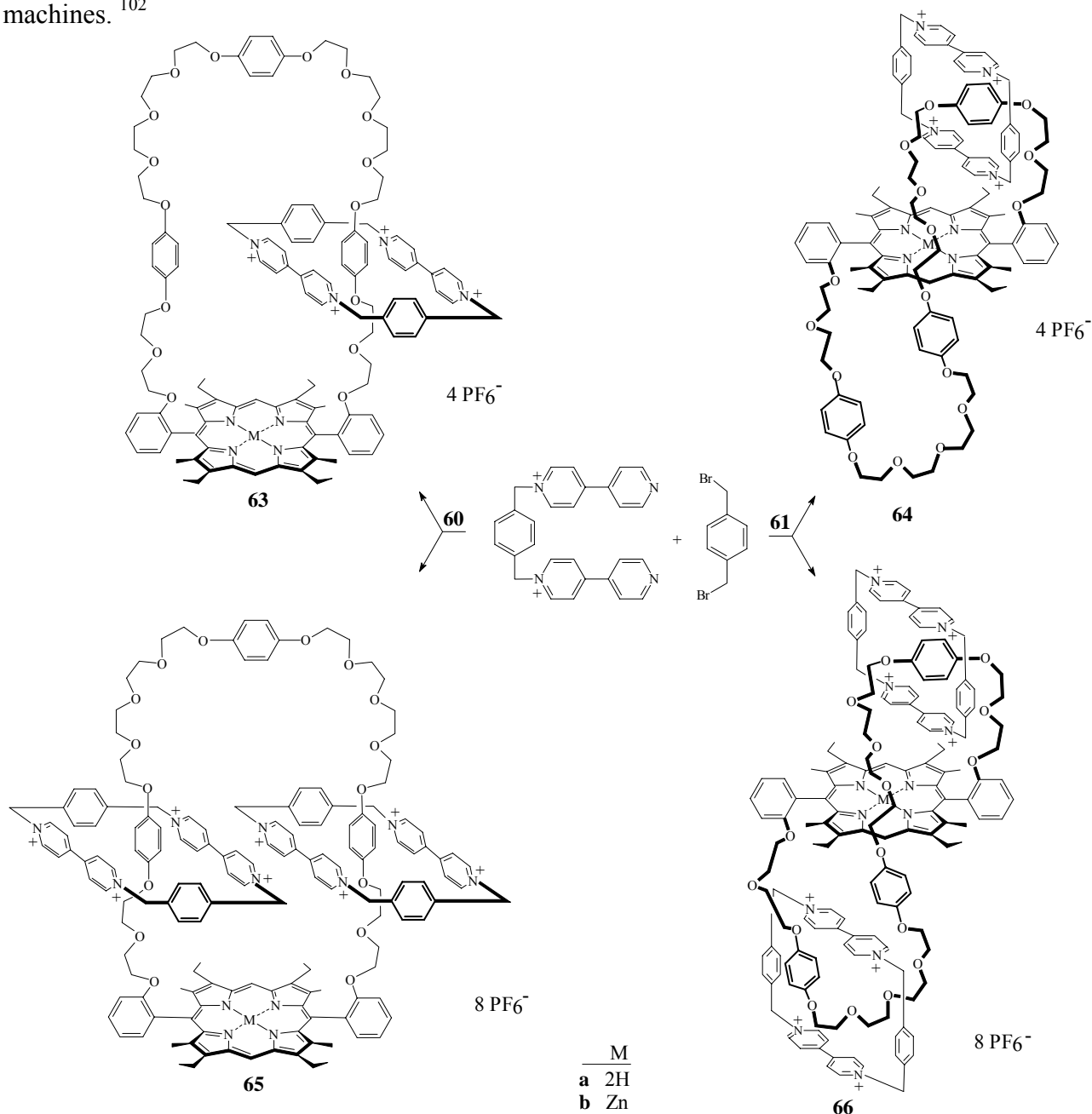
The porphyrin-centered oxidation processes in **56a** occur at more positive potentials than in **56b,c**. This fact shows that the CT interactions in **56a** are stronger than in **56b** and **56c**. It was established that catenanes (**56a-c**) display a slower electron transfer than complexes (**57a-c**) both in CS and CR (charge recombination) processes.<sup>100</sup>

Porphyrins strapped with polyether chains containing two and three 1,4-dioxybenzene units (**58,59**) and (**60,61**), respectively, have been subjected to catenation.<sup>102</sup> The catenation of **58b** and **59b** at high pressure (12 kbar) affords only one [2]catenane (**62**).





Catenation of **60** and **61** performed under similar conditions affords two [2]catenanes (**63**) and (**64**) and two [3]catenanes (**65**) and (**66**), respectively. The above catenanes may be considered as molecular machines.<sup>102</sup>



## CONCLUSION

The rapid development of interlocked molecules chemistry has its reflection in the variety of papers, so experimental works<sup>103-112</sup> as reviews<sup>113-116</sup> concerning this topic. Numerous works deal with the design of molecular machines<sup>117</sup> and switches,<sup>118</sup> the improvement of properties of constructed molecular devices being a considerable challenge.<sup>119,120</sup>

It seems that in the future a special attention will be paid to interlocked molecules useful for investigations in the field of enzymatic chemistry<sup>58</sup> and in the study of biological systems<sup>79</sup> leading to better effectiveness of therapeutic treatments.<sup>83</sup>

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