

HETEROCYCLES, Vol 68, No. 7, 2006, pp. 1467 - 1500. © The Japan Institute of Heterocyclic Chemistry
Received, 11th April, 2006, Accepted, 12th May, 2005, Published online, 16th May, 2006. REV-06-606

SUPRAMOLECULAR SPECIES BEARING QUATERNARY AZAAROMATIC MOIETIES

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Abstract- In the paper at first rotaxanes are presented; these species are divided into three classes, *i.e.* those containing electron donor, electron acceptor and cyclodextrin molecules as rings. In following parts examples of catenanes, pretzelanes and molecular clips are described.

INTRODUCTION

Supramolecular chemistry is a rapidly developing research area¹⁻³ promising for application in nanotechnology. Rotaxanes,⁴⁻⁶ catenanes,⁷⁻⁹ knots¹⁰⁻¹² and cage complexes¹³ attract today a growing attention due to their interesting properties and a fascinating shape; they are used in the design of molecular machines, switches and various electronic devices.

In a continuation of our work concerning quaternary azaaromatics,^{14,15} rotaxanes¹⁶ and catenanes¹⁷ of quaternary azaaromatic character, as well as cyclodextrins¹⁸⁻²⁰ and calixarenes,²¹ we describe here selected examples of supramolecular species bearing quaternary azaaromatic moieties.

The first part of the paper deals with rotaxanes, divided into three kinds of species containing as a ring electron donor, electron acceptor and cyclodextrin molecules. In following parts examples of catenanes, pretzelanes and molecular clips are presented.

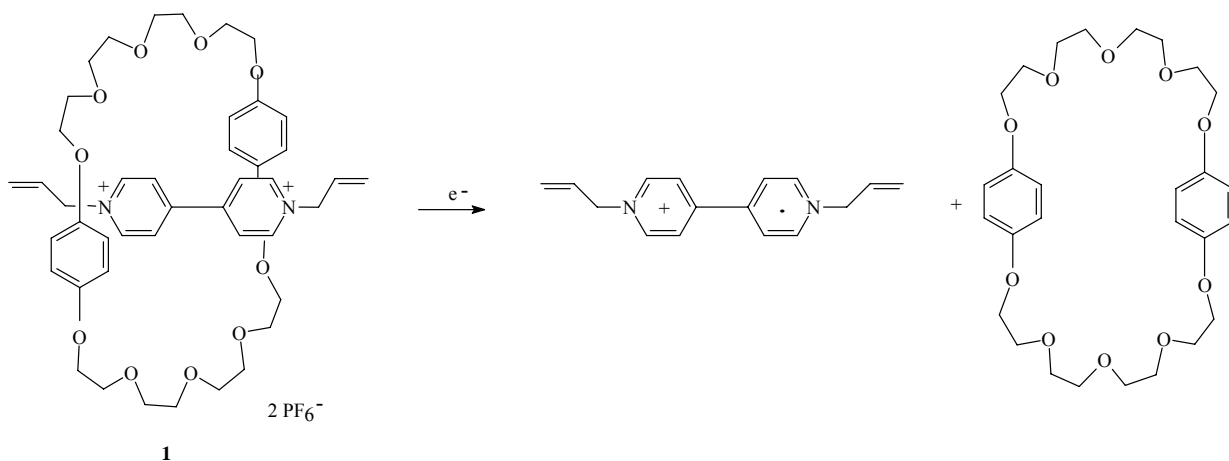
Since the number of supramolecular species bearing quaternary azaaromatic moieties is very large,²²⁻³⁰ inclusion complexes with host molecules such as crown ethers,³¹ cyclodextrins,³²⁻³⁶ cucurbiturils^{37,38} and calixarenes,^{39,40} as well as examples of molecular elevators,⁴¹ taco complexes⁴² and cryptand-based pseudorotaxanes⁴³⁻⁴⁵ are not described here. The references are cited starting from 2005.

1. ROTAXANES

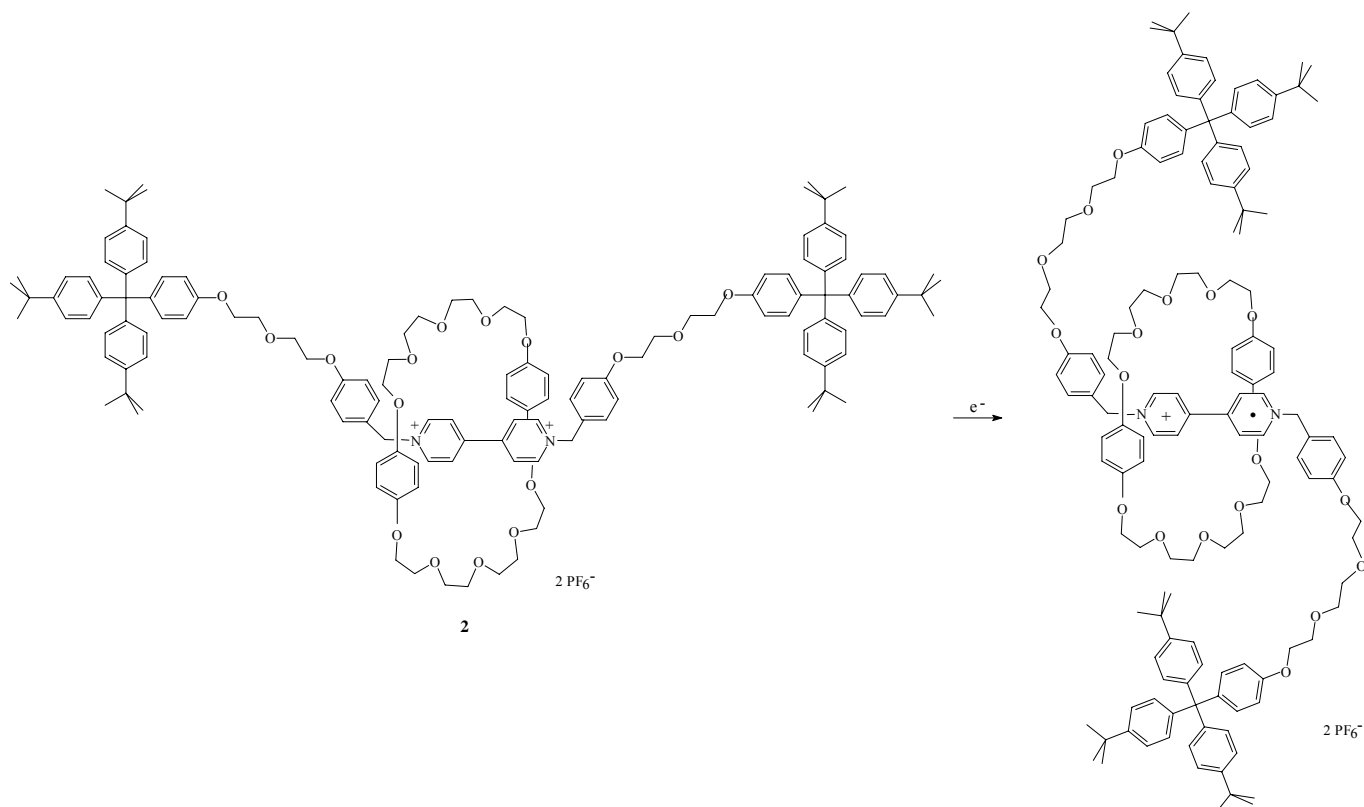
Rotaxanes are a topic of numerous reports,⁴⁶⁻⁵⁰ these species being of interest in the design of nano-systems such as switches, sensors and molecular machines.

Rotaxanes containing an electron donor ring

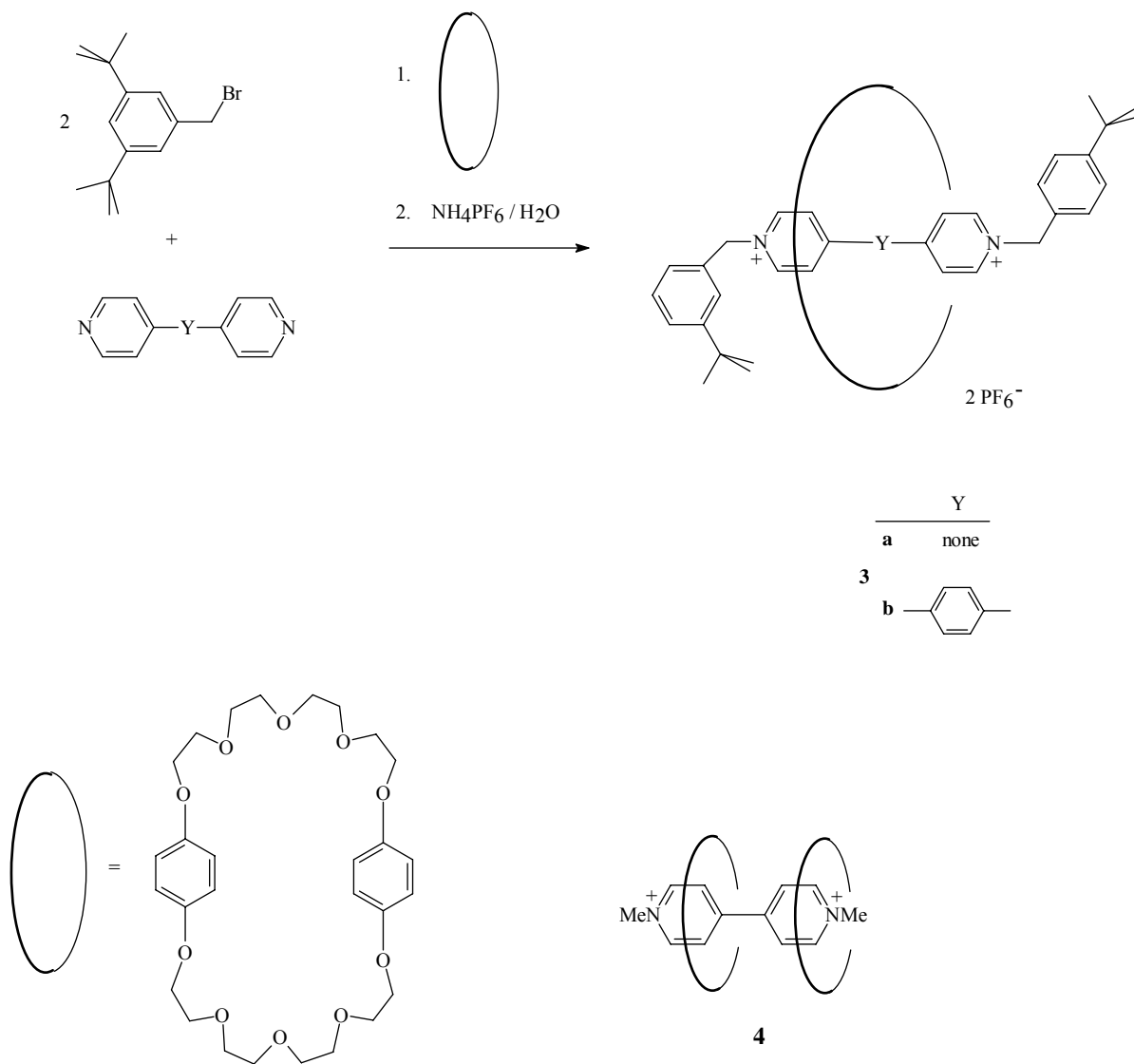
Examples of rotaxanes containing an electron donor ring are **1** and **2**. The oxidation state dependent conformations of **1** and **2** have been investigated by paramagnetic suppression spectroscopy (PASSY) technique.⁵¹ It was shown that the one electron reduction of the [2]pseudorotaxane (**1**) in solution leads to dissociation.



The one-electron reduction of the [2]rotaxane (**2**), however, does not result in the dissociation since its thread adopts a folded conformation in solution and does not enable the translational motion of the ring.

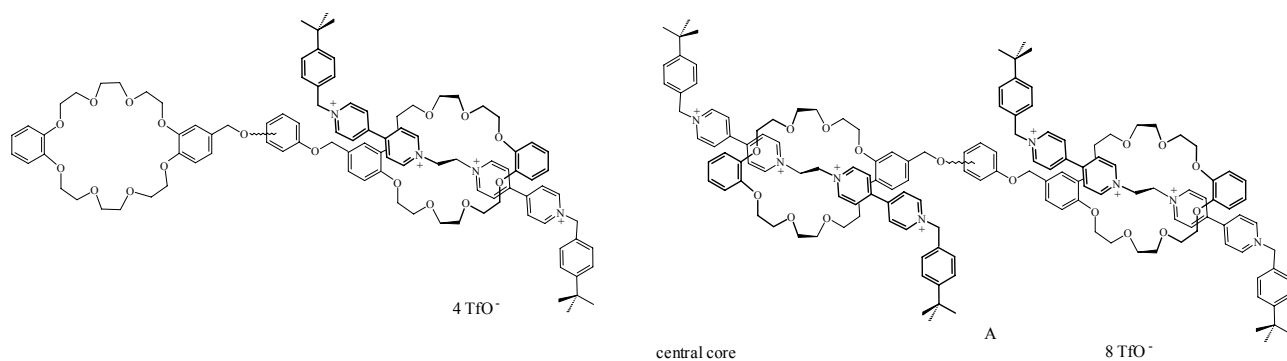


A facile one-pot synthesis of [2]rotaxanes (**3a,b**) is shown below.⁵² It was found that the [3]pseudorotaxane-like complex (**4**) forms both in solution and in the solid state.⁵²

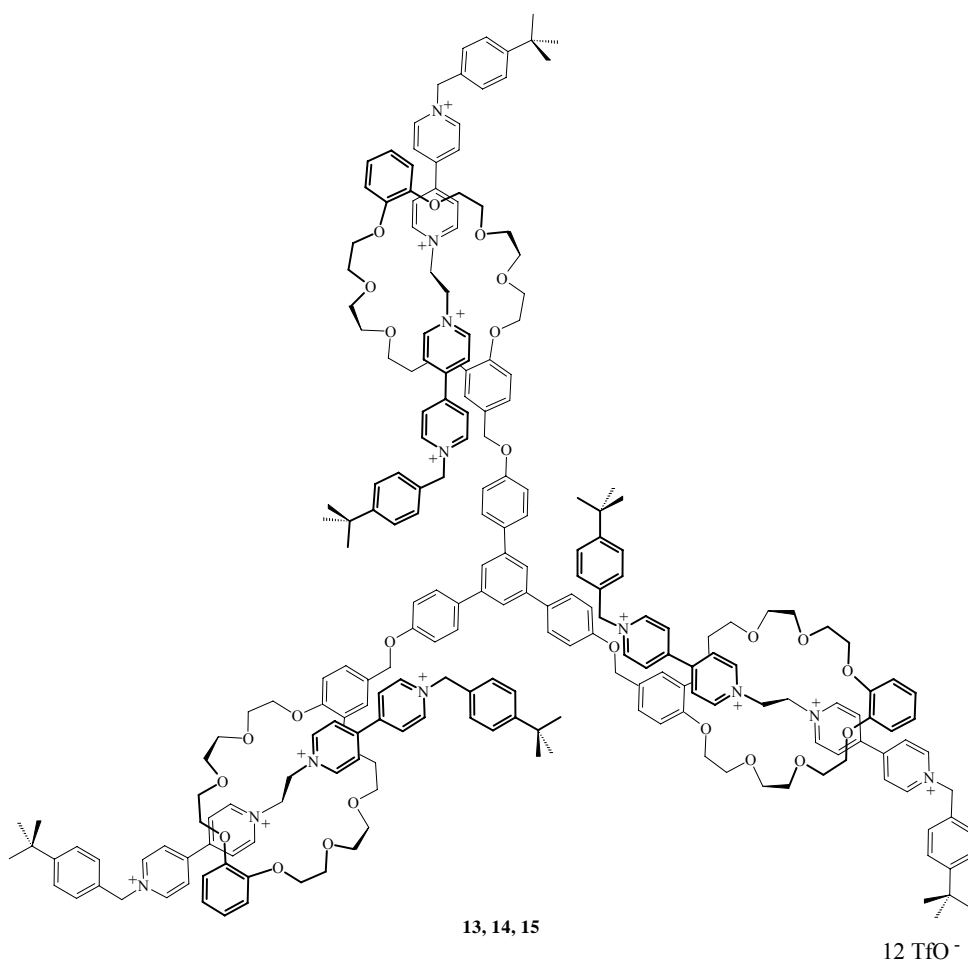
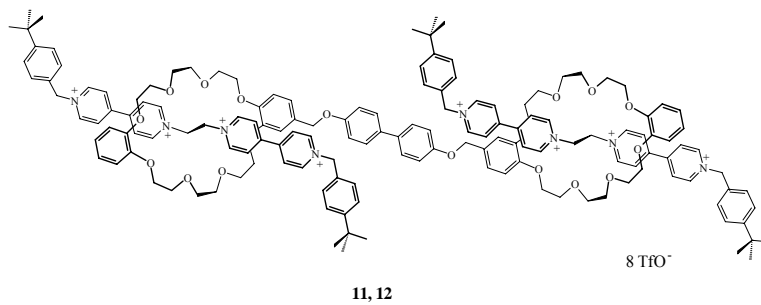
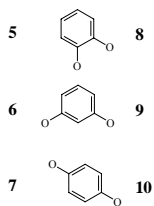


In the study of branched rotaxanes, following species have been obtained: based on bis(crown)ethers [2]rotaxanes (**5-7**), [3]rotaxanes (**8-10**) (with the second thread); [2]rotaxane (**11**) and [3]rotaxane (**12**) (with the second thread), as well as based on tris(crown)ether [2]rotaxane (**13**), along with [3]rotaxane (**14**) and [4]rotaxane (**15**) (bearing second and third threads, respectively).⁵³

In the case of *ortho* positions of oxygen atoms of the central benzene core, the formation of [2]rotaxane (**5**) and [3]rotaxane (**8**) is more difficult than in the case of *meta* and *para* positions of oxygen atoms of central benzene core, this behavior is due to steric hindrance and has its reflection in lower yields of [2]- and [3]rotaxanes (**5**) and (**8**), respectively, as compared with those of [2]rotaxanes (**6, 7**) and of [3]rotaxanes (**9, 10**).

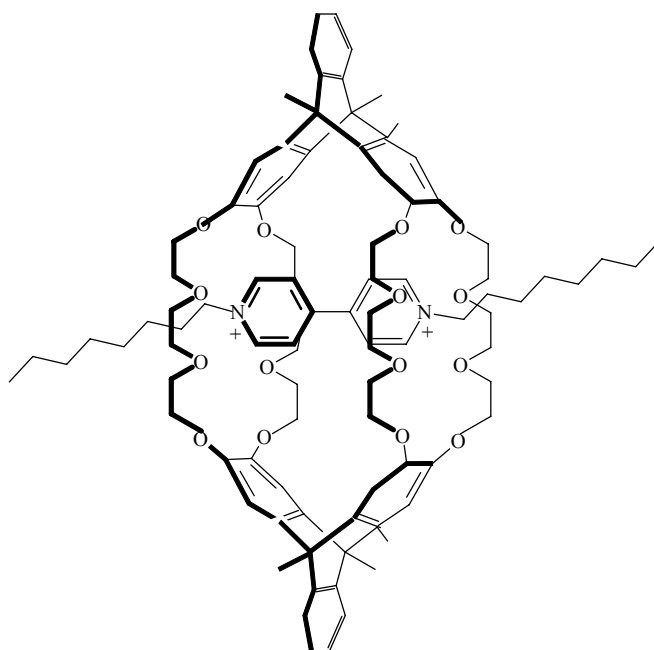


central core



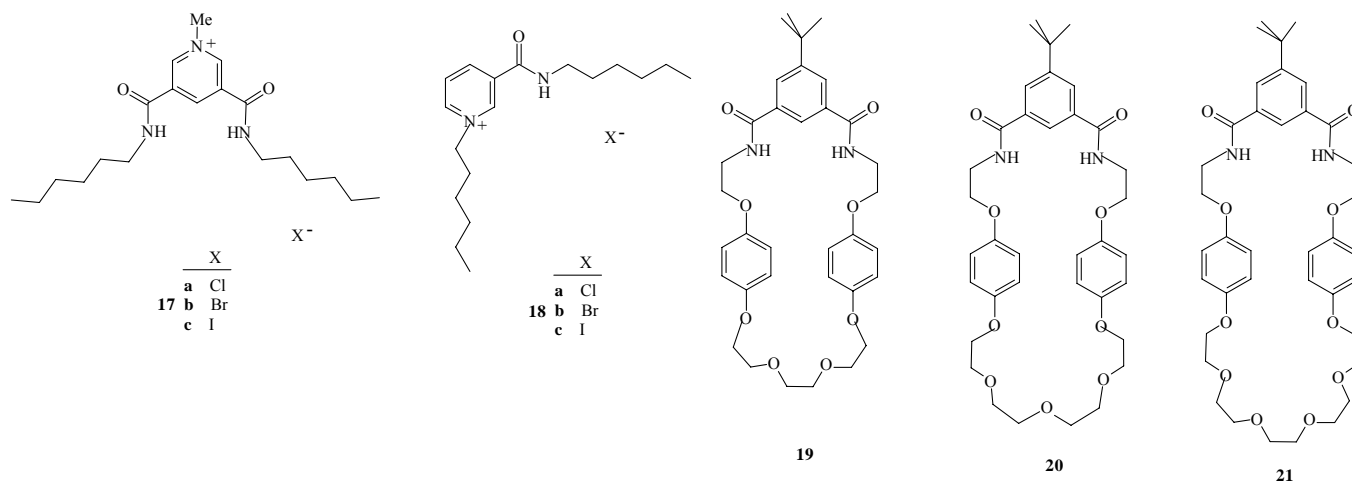
The efficiency of the formation of rotaxanes, lowering with the successive threading, results from electrostatic repulsion between an existing rotaxane thread and the new incoming thread as well as from steric interaction between already complexed crown ether and the new incoming thread.

The synthesis of the very stable pseudorotaxane (**16**) containing the triptycene based polyether has been made.⁵⁴

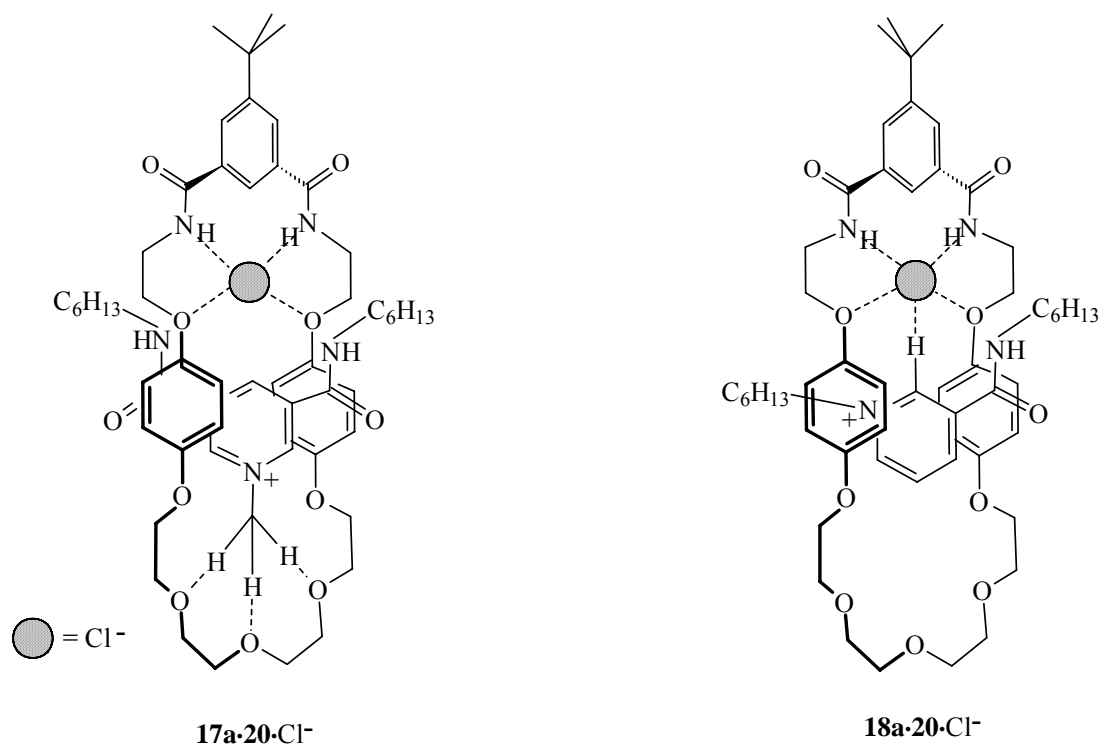


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Pseudorotaxanes consisting of pyridinium species (**17**, **18**) as threads and macrocyclic isophthalamide polyethers (**19-21**) as rings have been obtained by halide anion templation.⁵



Pseudorotaxanes (**17a·20·Cl⁻**) and (**18a·20·Cl⁻**) are shown below.



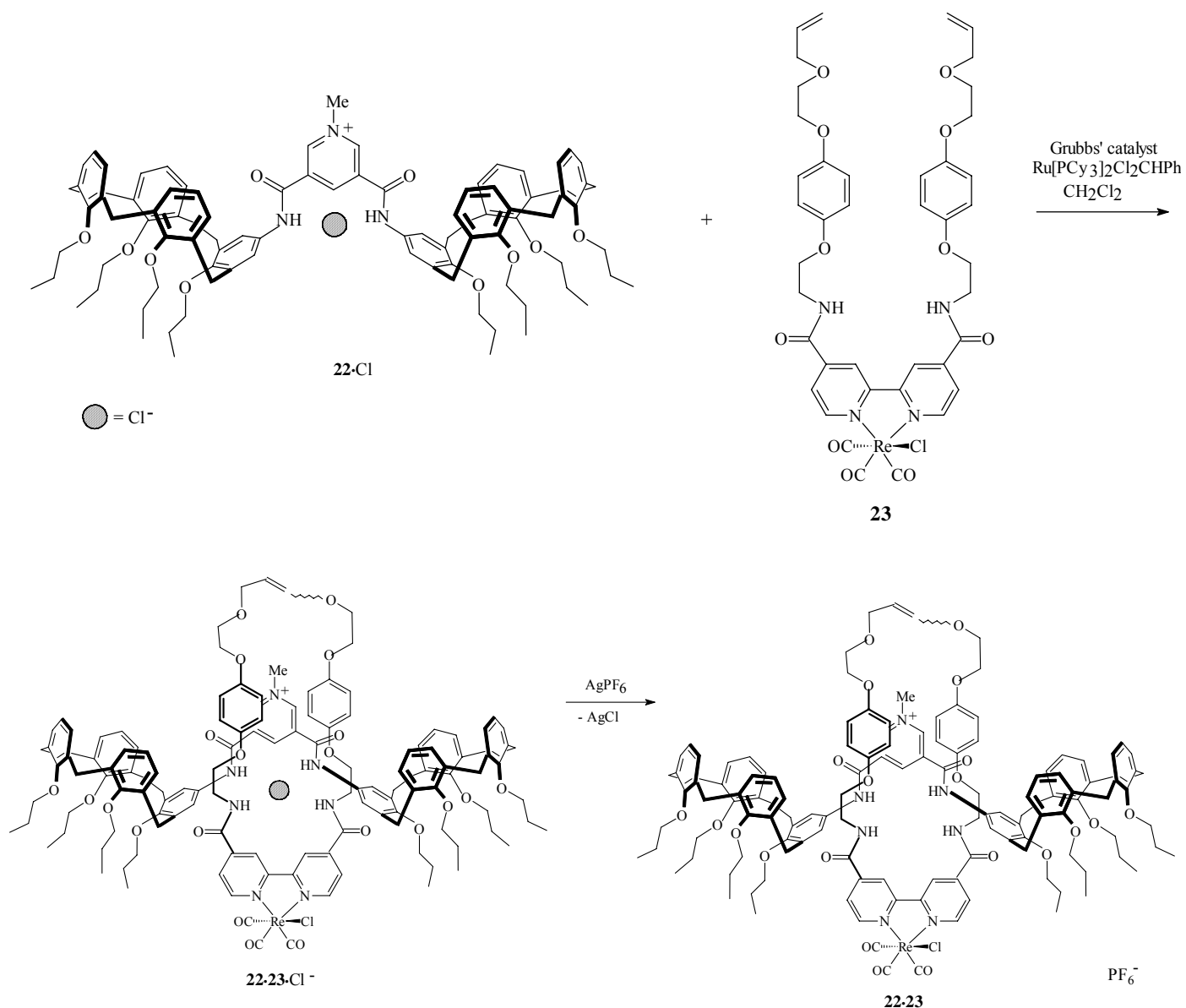
It was established that the strength of halide binding of **17** and **18** decreases in the order $\text{Cl}^- > \text{Br}^- > \text{I}^-$ ions, due to the highest hydrogen bond acceptor ability and the best size match fitting of Cl^- over Br^- and I^- .

The association constant values for pseudorotaxanes formed by **17a** and **18a** decrease in the order **19** > **20** > **21**, since for **19** the π - π stacking and hydrogen bonding as well as size complementarity with the thread are stronger than in the case of **20** and **21**.

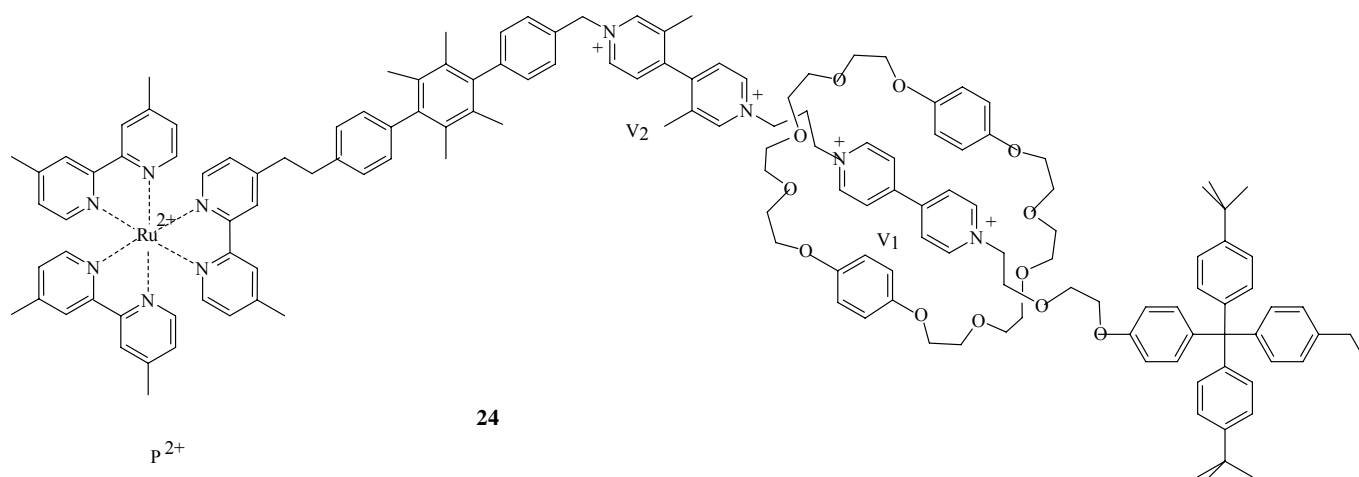
The association constant values are higher for pseudorotaxanes containing threads (**17**) than for those containing threads (**18**) due to the stronger stability of the former, resulting from the hydrogen bonds of N^+CH_3 group with polyether.

In the study of anion-templated reactions, the synthesis of the rotaxane (**22·23**) selectively sensing hydrogensulfate anion has been made.⁵⁶ In this process the compound **22·Cl⁻**, *i.e.* the thread stoppered by calixarene units reacts with rhenium derivative (**23**), a precursor of the ring to give [2]rotaxane (**22·23·Cl⁻**) which upon the exchange of the templating Cl^- ion for the noncoordinating PF_6^- ion affords rotaxane (**22·23**).

It was found that **22·23** may serve as a luminescent anion sensor, its selectivity decreasing in the order $\text{HSO}_4^- > \text{NO}_3^- > \text{Cl}^-$. The preferential binding of HSO_4^- by **22·23** is due to the shape of its cavity, fitting well to the structure of tetrahedral HSO_4^- anion.



In the search for artificial molecular machines⁵⁷⁻⁶¹, rotaxane (**24**) has been designed; it is an autonomous linear motor powered only by sunlight, without generation of waste products.⁶² Rotaxane (**24**) bears two electron poor stations V_1 and V_2 , the former among them being the better electron acceptor.



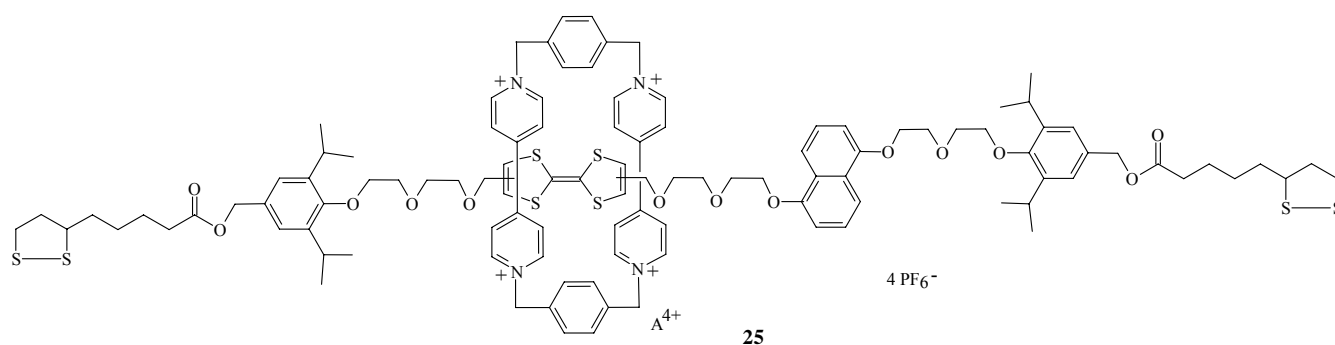
Rotaxane (**24**) behaves like a “four stroke” motor. In the stable conformation of **24** the ring encircles the station (V_1^{2+}). Light excitation of the photosensitizer (P^{2+}) followed by the transfer of an electron from $^*P^{2+}$ to V_1^{2+} to give V_1^+ results in the movement of the ring to V_2^{2+} station. The back electron transfer from V_1^+ to P^{3+} restores the electron acceptor power of V^{2+} , the ring returns from V_2^{2+} to V_1^{2+} and the process is repeated.

The ring shuttling may occur by purely intramolecular mechanism, as shown above, or by intermolecular mechanism involving the assistance of phenothiazine, serving as an external electron relay.

Rotaxanes containing an electron acceptor ring

Compound (**25**) may serve as example of rotaxanes containing an electron receptor ring A^{4+} . In bistable [2]rotaxanes, the ring A^{4+} has a greater affinity for the tetrathiafulvalene (TTF) unit than for competing 1,5-dioxynaphthalene (DNP) unit. When TTF undergoes two electron oxidation, A^{4+} is electrostatically repelled from TTF^{2+} and moves to DNP station. Chemical or electrochemical reduction of the TTF^{2+} unit back to its neutral state results in the return of A^{4+} to its original favored position, *i.e.* to TTF.

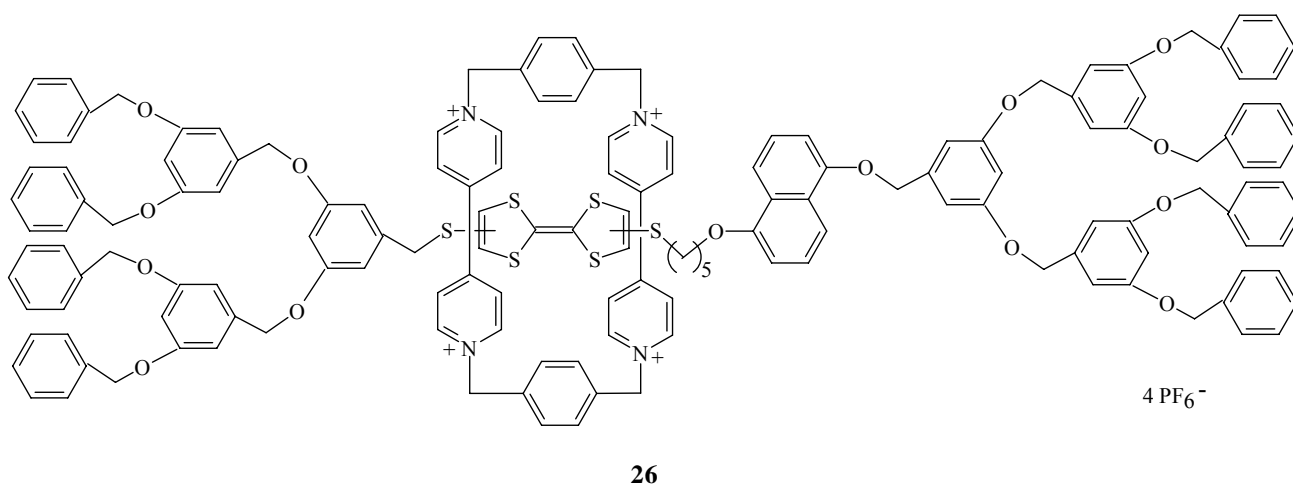
In the investigation of bistable rotaxanes, the self-assembled monolayer (SAM) structure of **25** has been studied. As a preliminary approach the SAM of the left half of **25**, *i.e.* of the model shuttle of the ring A^{4+} on the TTF station anchored to a gold surface was examined by molecular dynamics (MD) simulations.⁶³



Various coverages of SAM of the half of **25** on Au (111) surface have been used in order to determine the optimum packing density. It was found that the orientation of A^{4+} depends on the coverage, changing to obtain highly packed SAMs. At lower coverage the ring A^{4+} lies with its large hollow (*i.e.* its four positive charges) parallel to the surface. However, at higher coverages the ring A^{4+} occupies a smaller surface area by lying on one of its sides (viologen side or phenylene ring side) parallel to the surface.

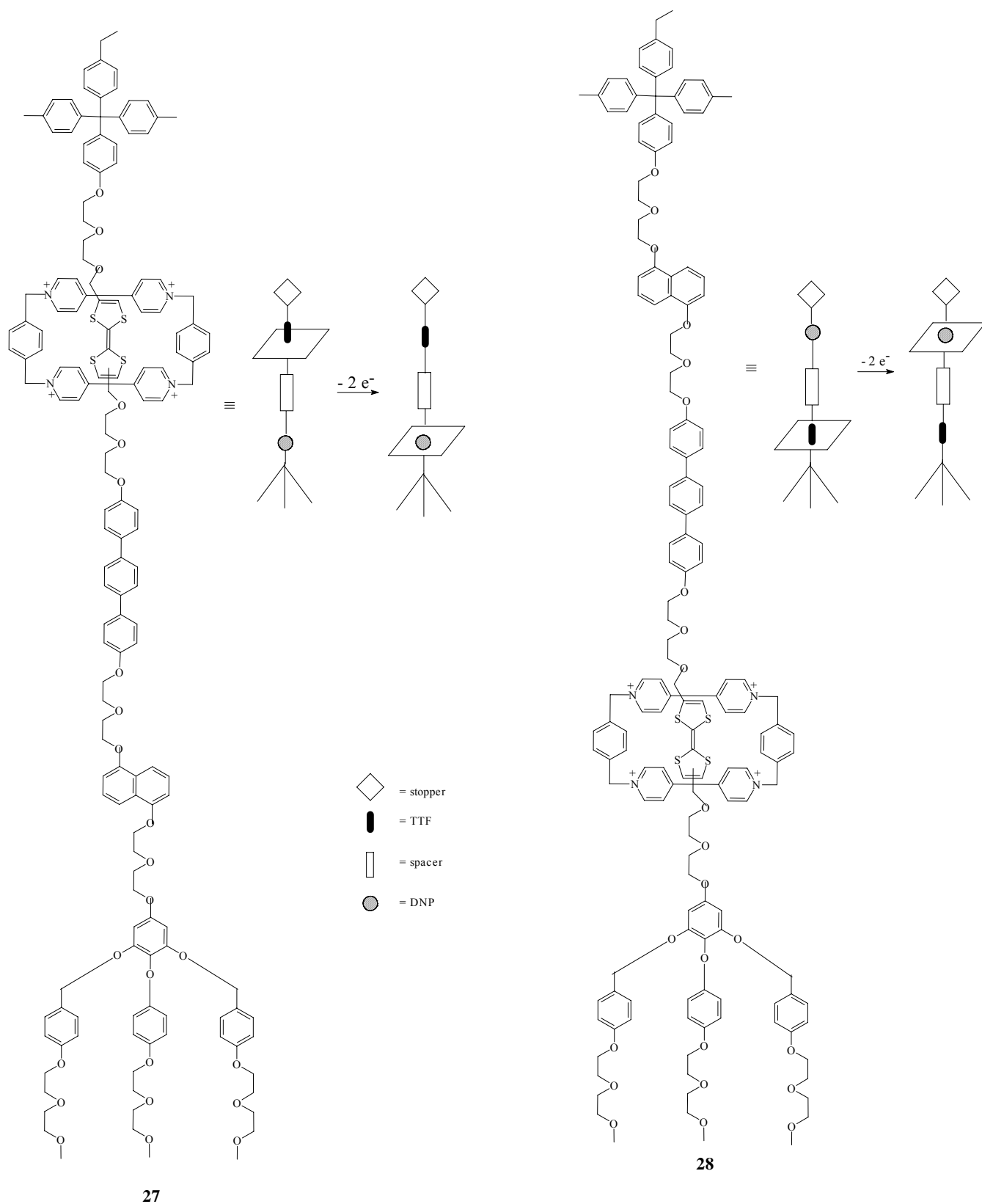
The stable conductance transitions in rotaxane (**26**) based LB (Langmuir-Blodgett) thin films have been reported. The films of **26** have been prepared on an ITO-coated glass substrate (ITO=

indium tin oxide). Reproducible nanometer-scale recording on these films has been achieved using scanning tunneling microscope (STM).⁶⁴



Rotaxane (**26**) shows reversible movement of the ring A^{4+} between TTF and DNP units, triggered by chemical stimuli. This fact results in the conductance switching of the film of **26**, which may be utilized for STM-based, stable, reproducible nanorecording.

The redox-controlled switching in condensed monolayers of amphiphilic, bistable [2]rotaxanes at the air/water interface has been investigated by surface-sensitive synchrotron X-Ray reflectometry (XR).⁶⁵ The bistable [2]rotaxane (**27**) and its model, the rotaxane (**28**) are shown below.



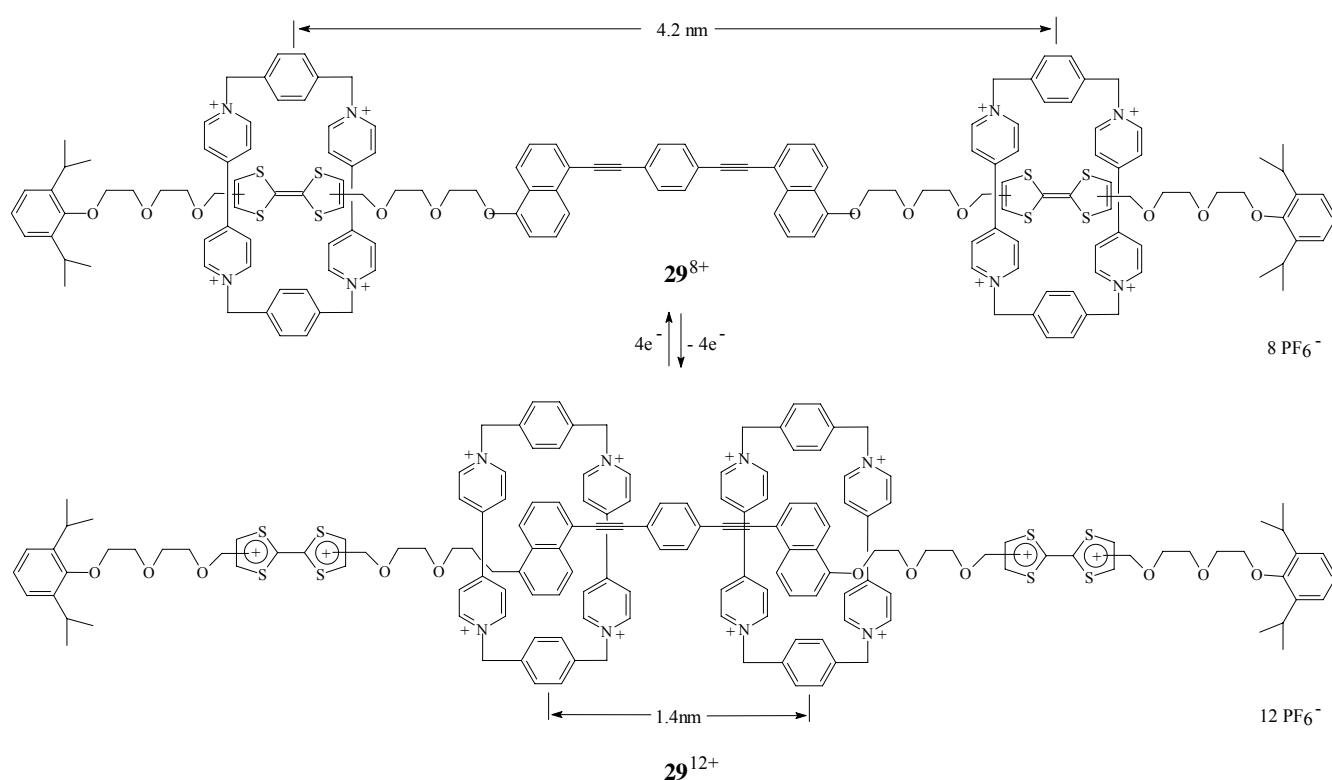
Since the stoppers are hydrophilic and hydrophobic, the molecules are amphiphilic and may form Langmuir monolayers when deposited at the air/water interface. Rotaxanes (**27**) and (**28**) are

constitutional isomers, containing TTF and DNP units at different positions with respect to the two stoppers, therefore upon oxidation the ring A^{4+} in **27** and in **28** moves in opposite directions.

Solutions of **27** and **28** in chloroform were spread onto the water surface, and the resulting monolayers were compressed. Oxidation of the monolayers was made by injecting an aqueous solution of $\text{Fe}(\text{ClO}_4)_3$ into the water subphase. In the initial state, the ring encircles the TTF station, while upon oxidation, the formed $\text{TTF}^{\bullet+}$ or TTF^{2+} electrostatically repels the tetracationic ring, therefore the ring moves to the DNP station.

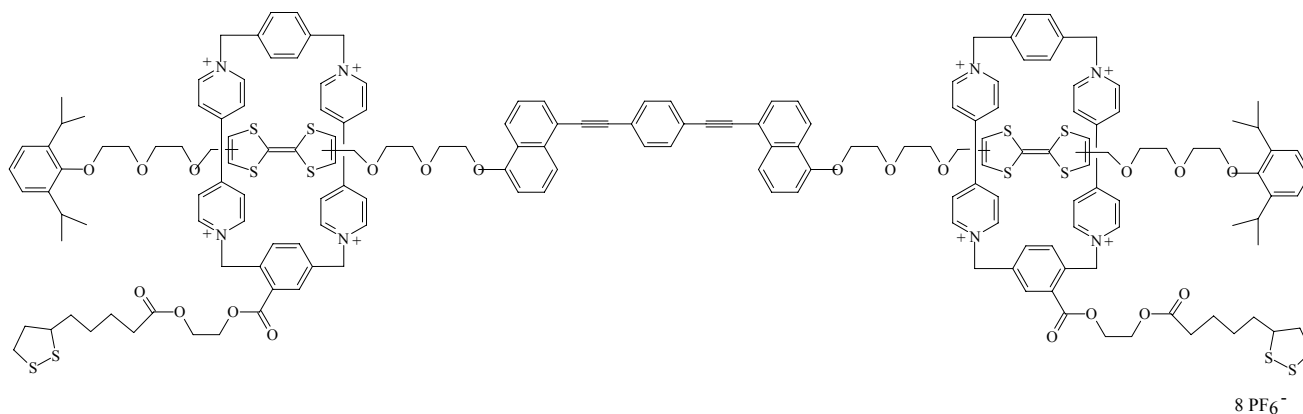
The in-plane structure of the rotaxane monolayers was investigated by grazing-incidence X-Ray diffraction. The fact that the total monolayer thickness is smaller than the thickness expected of fully extended rotaxane molecules is an evidence of their tilting and folding. These processes afford a disordered, fluidlike local environment within the monolayer, which enables movement of the ring without significant changes in the overall thickness of the film. Therefore, the switching may also be possible in films sandwiched between two solid surfaces, *e.g.* in crossbar memory devices. The results of the XR measurements have shown that the bistable rotaxanes retain their switching properties even in condensed monolayer phases.

Bistable rotaxanes and bistable catenanes are well suited for controllable nanomechanical work. The [3]rotaxane, *i.e.* the molecular muscle (**29**) was synthesized in order to mimic the contraction and extension of skeletal muscles.⁶⁶ In **29** two TTF and two DNP recognition stations are situated symmetrically along a thread which is encircled by two A^{4+} units.



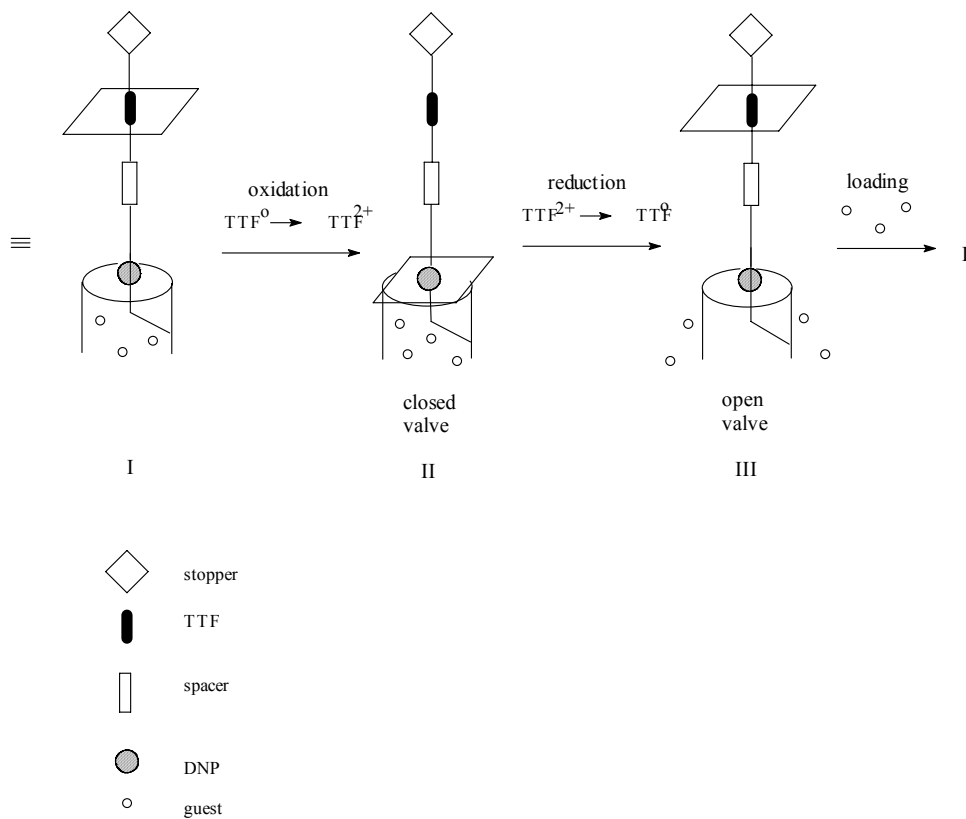
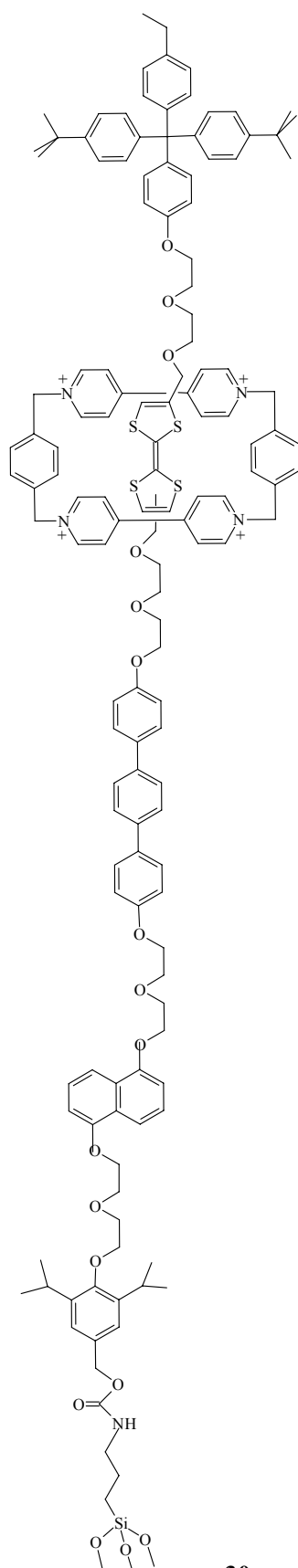
The solution of **29** in CD_3COCD_3 was oxidized with one-electron oxidant, tri(*p*-bromophenyl)-amminium hexafluoroantimonate. Both TTF units are completely oxidized to their TTF^{2+} forms, *i.e.* **29**⁸⁺ is oxidized to **29**¹²⁺. Addition of zinc powder leads to reduction of TTF^{2+} dications back to their neutral state and to the shuttling back of A^{4+} rings from DNP to TTF stations.

The distance of A^{4+} rings in **29**⁸⁺ is 4.2 nm, while in **29**¹²⁺ only 1.4 nm, *i.e.* the oxidation leads to the contraction of the inter-ring distance. The subsequent reduction of **29**¹²⁺ to **29**⁸⁺ results in the extension of this distance back to 1.4 nm. Such reversible process resembles the contraction and extension of a muscle. The shuttling of rings A^{4+} caused by external stimuli may be controlled by ¹H NMR and UV-Vis analysis, therefore such systems are of interest for construction of nanoelectromechanical devices. The attachment of both A^{4+} rings to gold surface is possible by disulfide tethers, as shown below.



The reversible switching of the distance between both A^{4+} rings from 4.2 to 1.4 nm may serve for the construction of a chemomechanical actuator utilizing **29**⁸⁺ self-assembled by Au-S bonds onto cantilever beams. The contraction of the distance between two A^{4+} rings caused by oxidation with $\text{Fe}(\text{ClO}_4)_3$ results in the bending of the beam. The reverse process, *i.e.* the extension of this distance caused by reduction with ascorbic acid, results in the return of the beam to its original equilibrium position. One may hope that such cumulative movements would lead to the larger-scale mechanical work.

The attachment of organic linear motor molecules to stable inorganic porous materials enables the construction of molecular valves. The reversibly operating nanovalve, controlled by redox chemistry has been designed.⁶⁷ Its action involves shuttling of the ring A^{4+} between two stations – TTF and DNP of the bistable [2]rotaxane (**30**) attached to mesoporous MCM-41 silica particles. At the start, A^{4+} encircles the TTF moiety. When TTF station is oxidized to TTF^{2+} , the ring A^{4+} moves to DNP due to Coulombic repulsion between A^{4+} and TTF^{2+} . The reduction of TTF^{2+} to TTF^0 results in the return of A^{4+} to TTF^0 . The closing and opening of the valve was accompanied by the loading and release of guest molecules; as those $\text{Ir}(\text{ppy})_3$ in EtOH/PhMe (1:1) solution and Rhodamine B in MeCN solution were used.



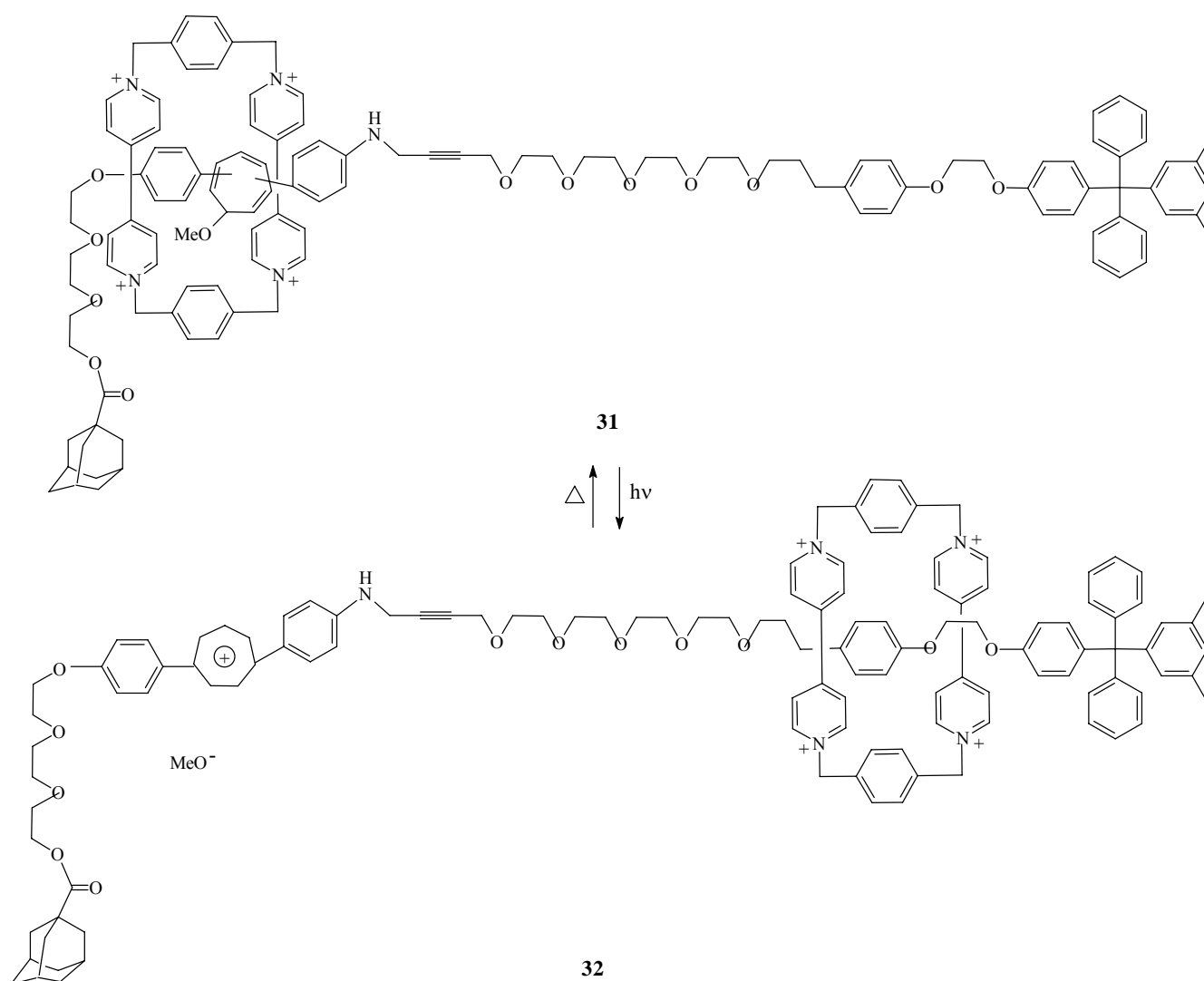
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To close the valve, (I), the oxidation of TTF^0 to TTF^{2+} by $\text{Fe}(\text{ClO}_4)_3$ was made. As a result, the ring A^{4+} moves to DNP, the valve is closed (II) and the DNP luminescence is quenched. To open the valve, the

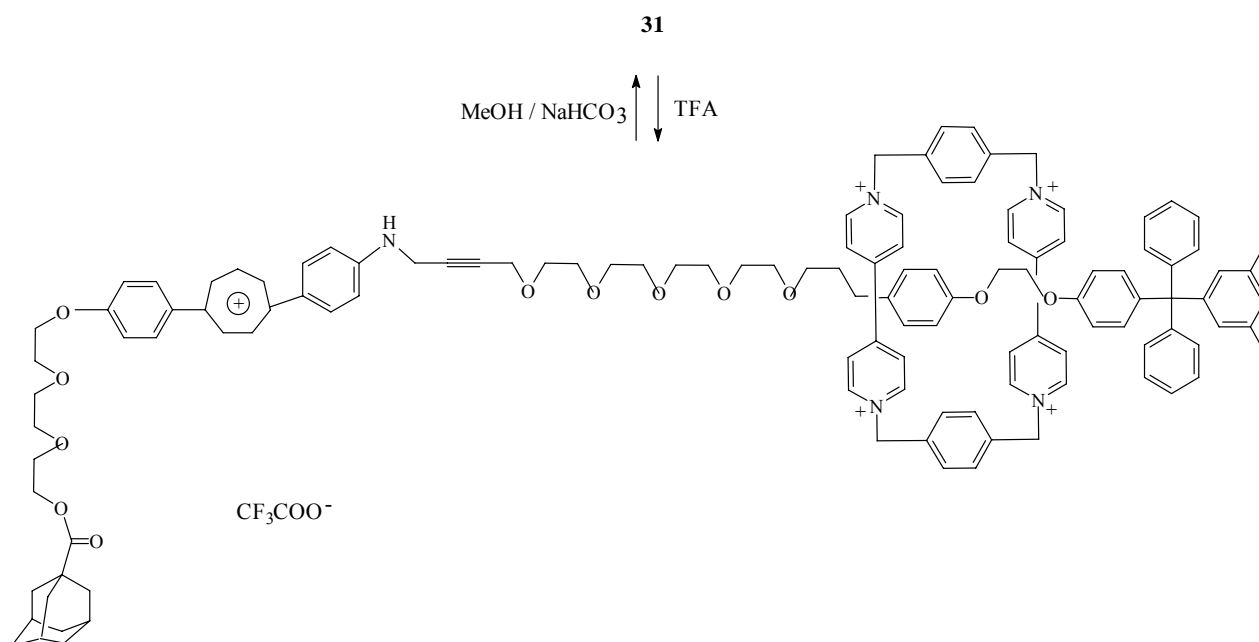
reduction of TTF^{2+} to TTF^0 by ascorbic acid was made. As a result, A^{4+} returns to TTF, the valve opens (III) and the DNP luminescence increases. When the valve is opened, the guest molecules are released and they escape into solution. This release of guest molecules results in their luminescence. The loading of the valve with guest molecules leads back to (I), and the process is repeated.

The operation of the valve is monitored by measurement of the DNP or guest's luminescence. One should point out that the action of a such nanovalve is fully reversible and the redox reagents used are mild.

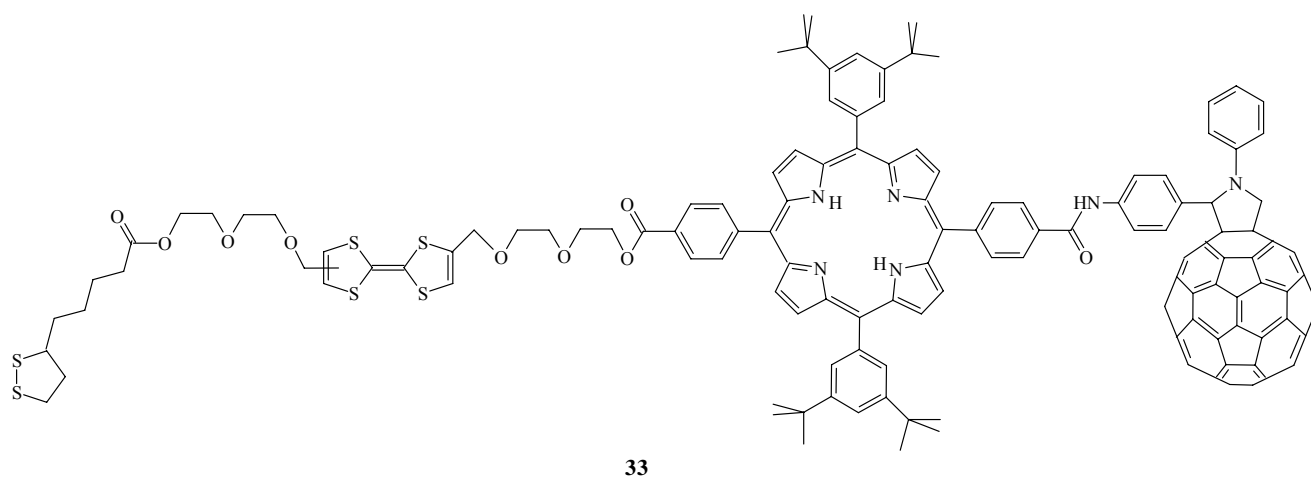
The bistable rotaxane (**31**) is an example of a molecular switch.⁶⁸



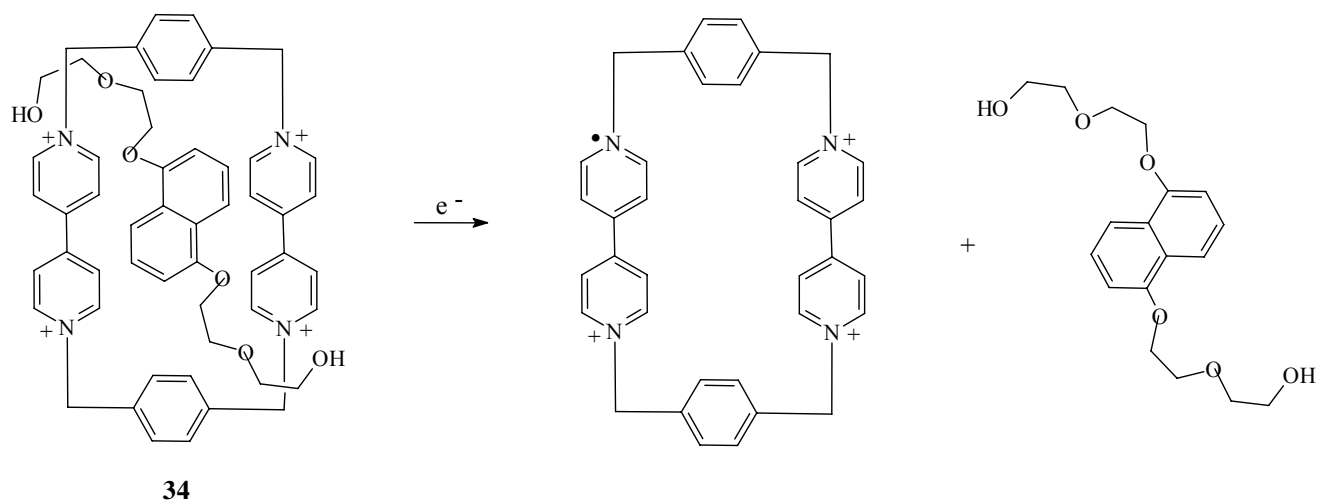
The ring A^{4+} is situated preferentially on the cycloheptatriene (CHT) station. The photoheterolysis of **31** resulting in the oxidation of CHT unit into tropylium ion which repels the ring to the weaker donor station, affords **32**. The reverse reaction, *i.e.* the shuttling of A^{4+} to CHT station proceeds thermally. The switching may also be acid-base triggered, as shown below.



The photoactive molecular triad (**33**) composed of an electron-donating TTF unit, a chromophoric porphyrin and an electron-accepting C₆₀ molecule has been designed as a source of electrical current at the expense of light energy.⁶⁹



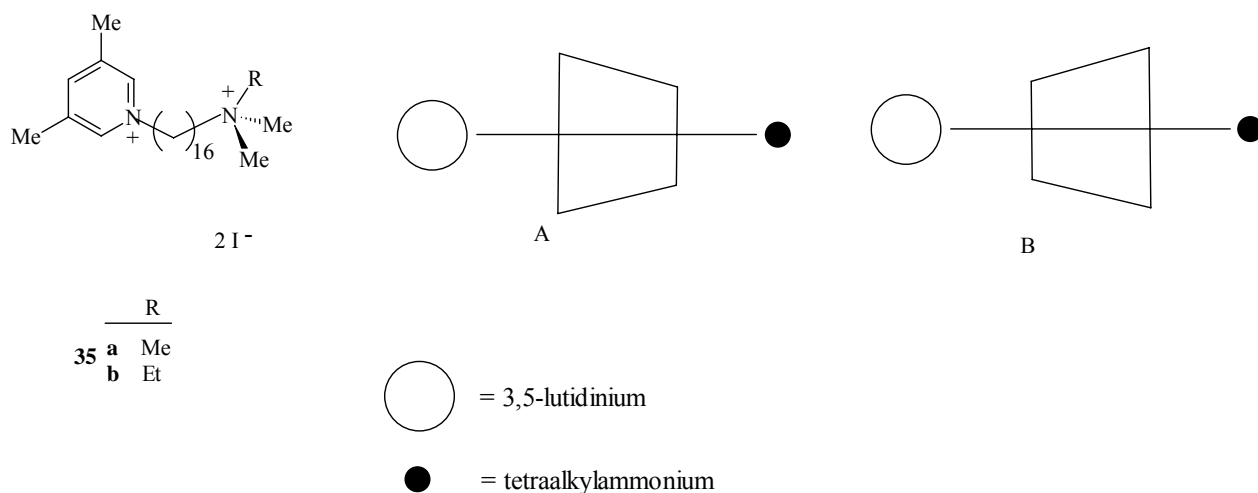
The above triad was self-assembled on gold electrodes by a disulfide anchoring group. In a closed circuit, a triad-SAM functionalized working electrode, when irradiated with a 413 nm Kr-laser (a wavelength close to the porphyrin absorption) generates photocurrent to drive the dethreading of a supramolecular machine; as such served [2]pseudorotaxane (**34**).



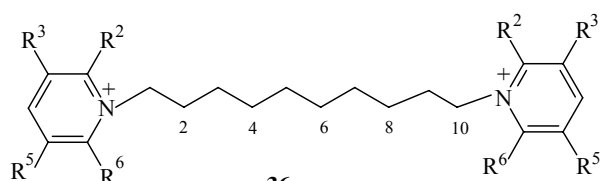
The electron is transferred to pseudorotaxane, resulting in the reduction of A^{4+} to $A^{\bullet 3+}$, leading to the dethreading due to the weaker CT interaction of $A^{\bullet 3+}$ with DNP. Since the dethreading is accompanied by the increase of fluorescence of DNP, this process can be monitored by measurement of fluorescence intensity. The development of the above supramolecular machine driven by triad (33) is promising for the construction of nanoscale light-harvesting systems.

Rotaxanes containing a cyclodextrin ring

In the study of rotaxanes containing a cyclodextrin ring,^{6,70,71} it was established that lutidinium bis-quaternary iodides (35) form with α -CD two semirotaxanes; they exist as orientational isomers A and B, among them B being more stable.⁷²

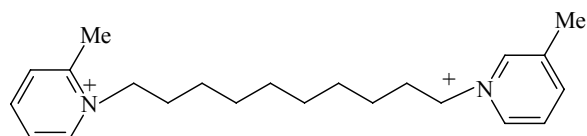


Threading of α -CD onto dipyrindinium dichloride (36a) and its symmetrically substituted derivatives (36b,c) and (37a-c) as well as unsymmetrically substituted derivatives (38) and (39) has been investigated.⁷³

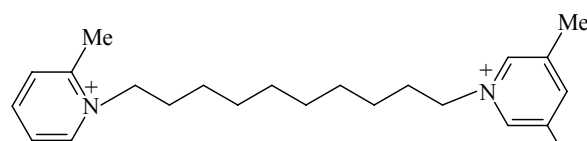


36a-c
37a-c

	R ²	R ³	R ⁵	R ⁶
36a	H	H	H	H
36b	H	Me	H	H
36c	Me	H	H	H
37a	Me	H	Me	H
37b	H	Me	Me	H
37c	Me	H	H	Me



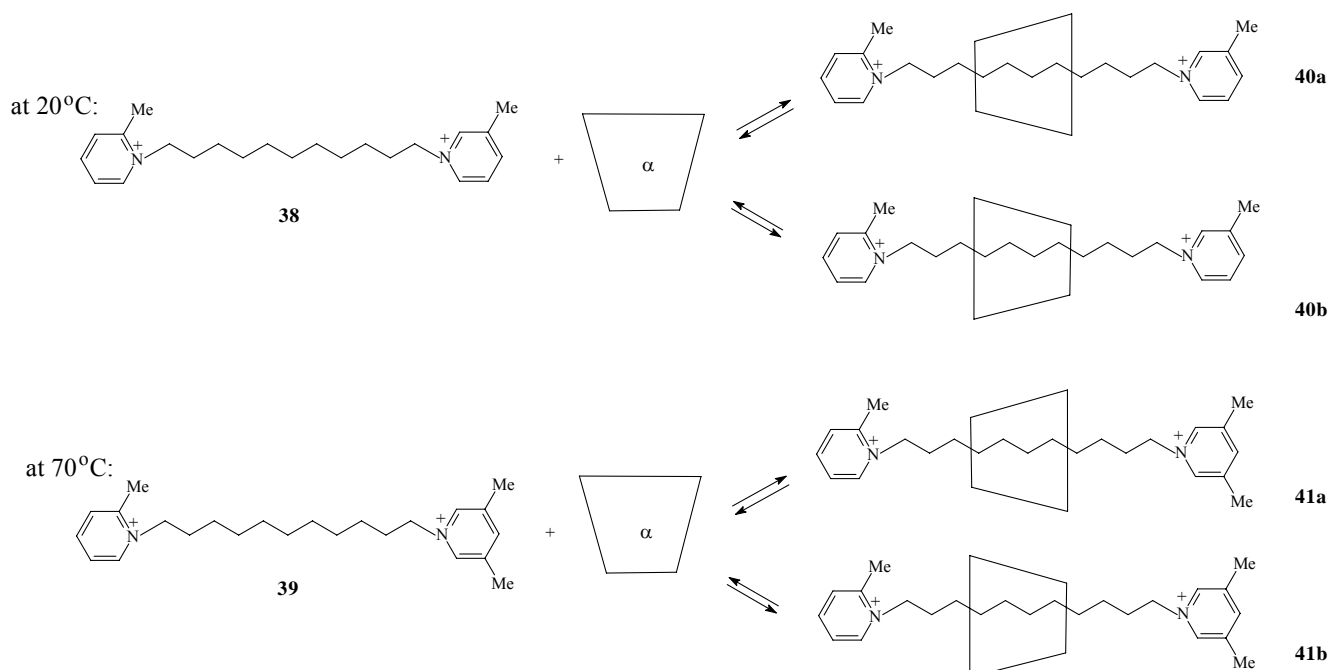
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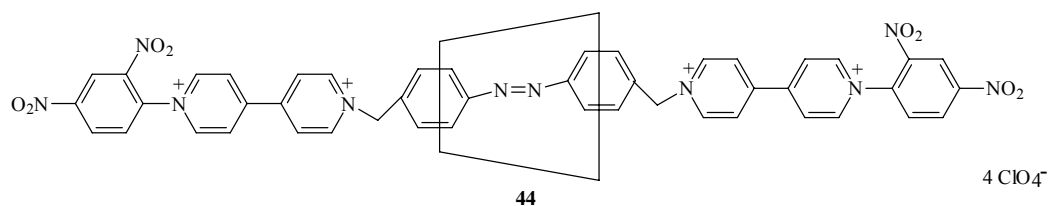
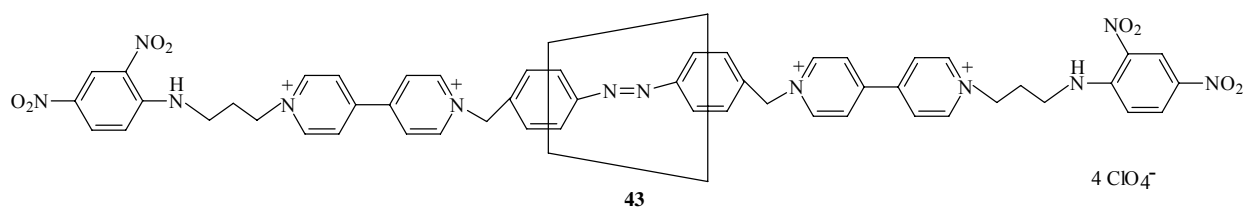
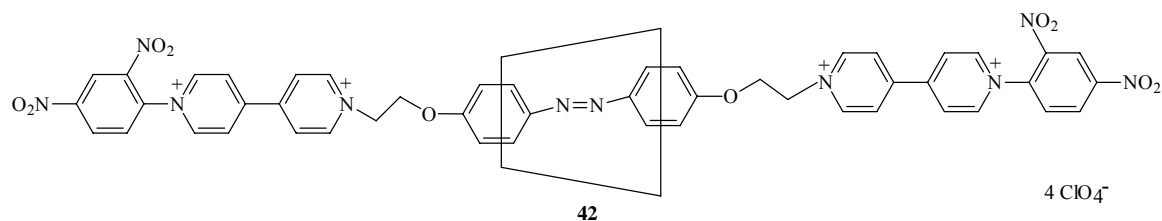
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It was observed that unsubstituted **36a** as well as **36b** (bearing two methyl groups at positions 3) are included into α -CD cavity completely. The complexation of **36c** (bearing two methyl groups at positions 2) and of **37a** (bearing four methyl groups in positions 2 and 5) is slower, *i.e.* the presence of methyl groups at positions 2 retards the complexation. Compounds (**37b**) (bearing four methyl groups at positions 3 and 5) and (**37c**) (bearing four methyl groups at positions 2 and 6) do not form complexes with α -CD.

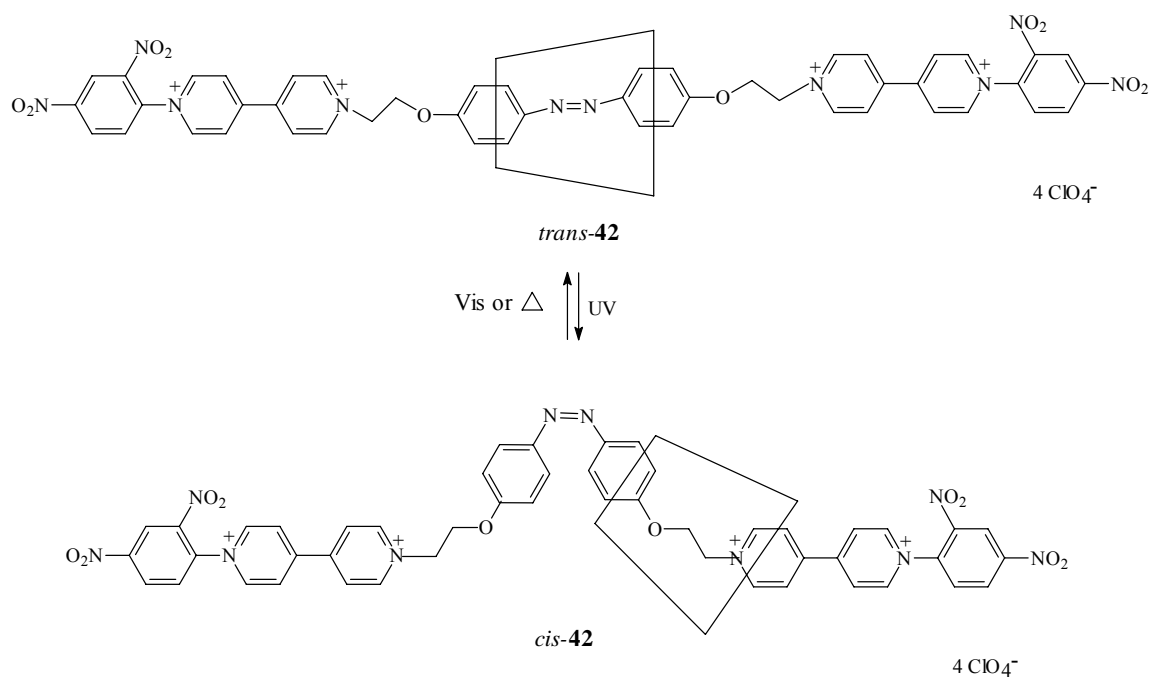
The treatment of **38** with α -CD at 20°C leads to the equilibrium of two pseudorotaxanes (**40a**) and (**40b**), *i.e.* complexes of **38** with α -CD are formed in the random face direction of α -CD. It should be pointed out that **39** at 20°C affords with α -CD only one pseudorotaxane (**41a**), while at 70°C the face selectivity of α -CD disappears, instead the equilibrium between isomers (**41a**) and (**41b**) is achieved.



Three rotaxanes (**42-44**) have been investigated by NMR and CD spectroscopies in the aspect of their shuttling processes.⁷⁴ The rotaxane (**42**) undergoes photoisomerization in water and in DMSO; **43**—only in DMSO, for **44** however no photoisomerization was observed in both water and DMSO.

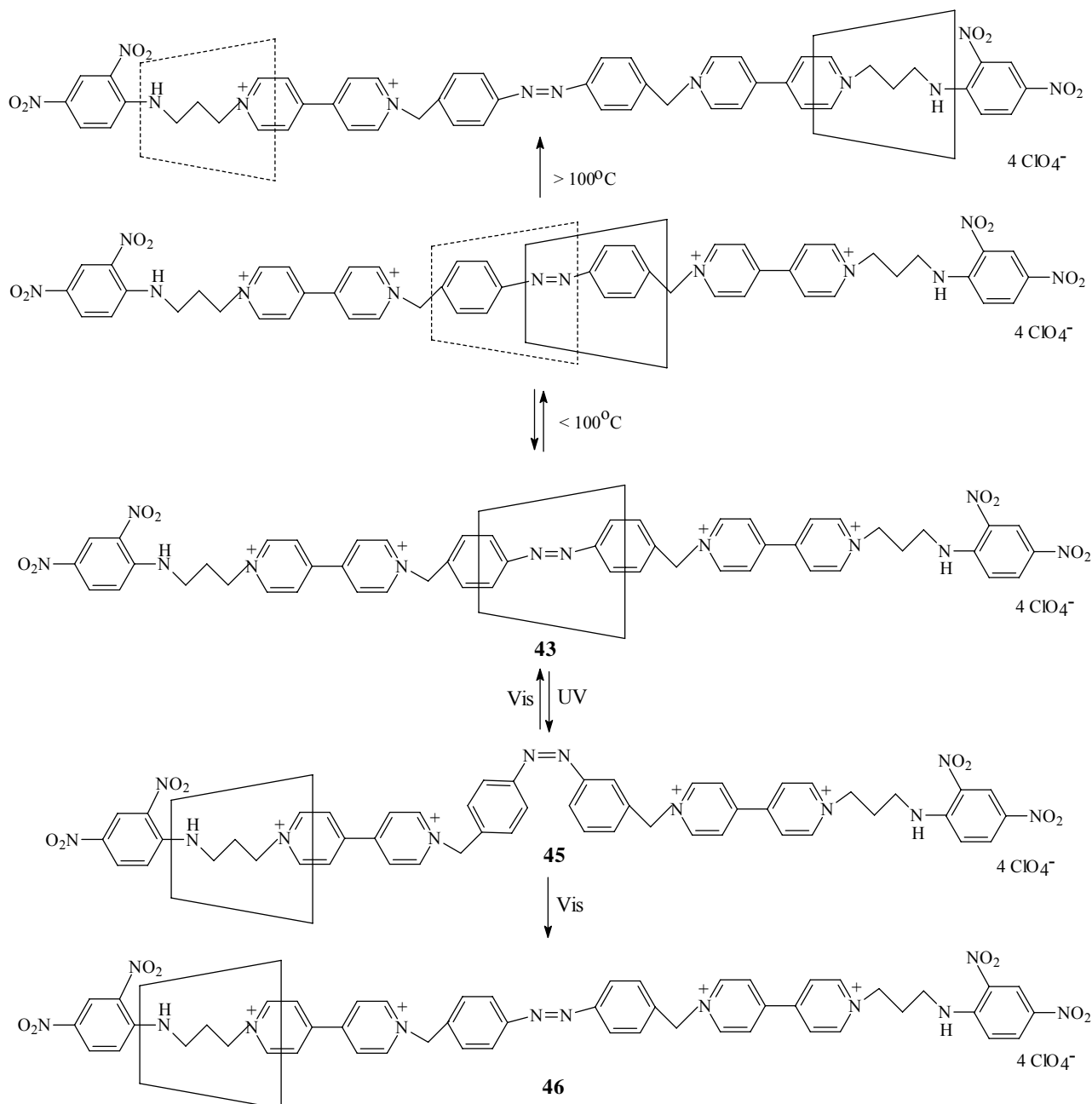


It was found that **42** undergoes reversible photoisomerization from *trans*-**42** to *cis*-**42** by UV irradiation and from *cis* to *trans* by visible light irradiation or heating. In this shuttling process the α -CD molecule reversibly moves between the azobenzene unit and ethylene spacer.

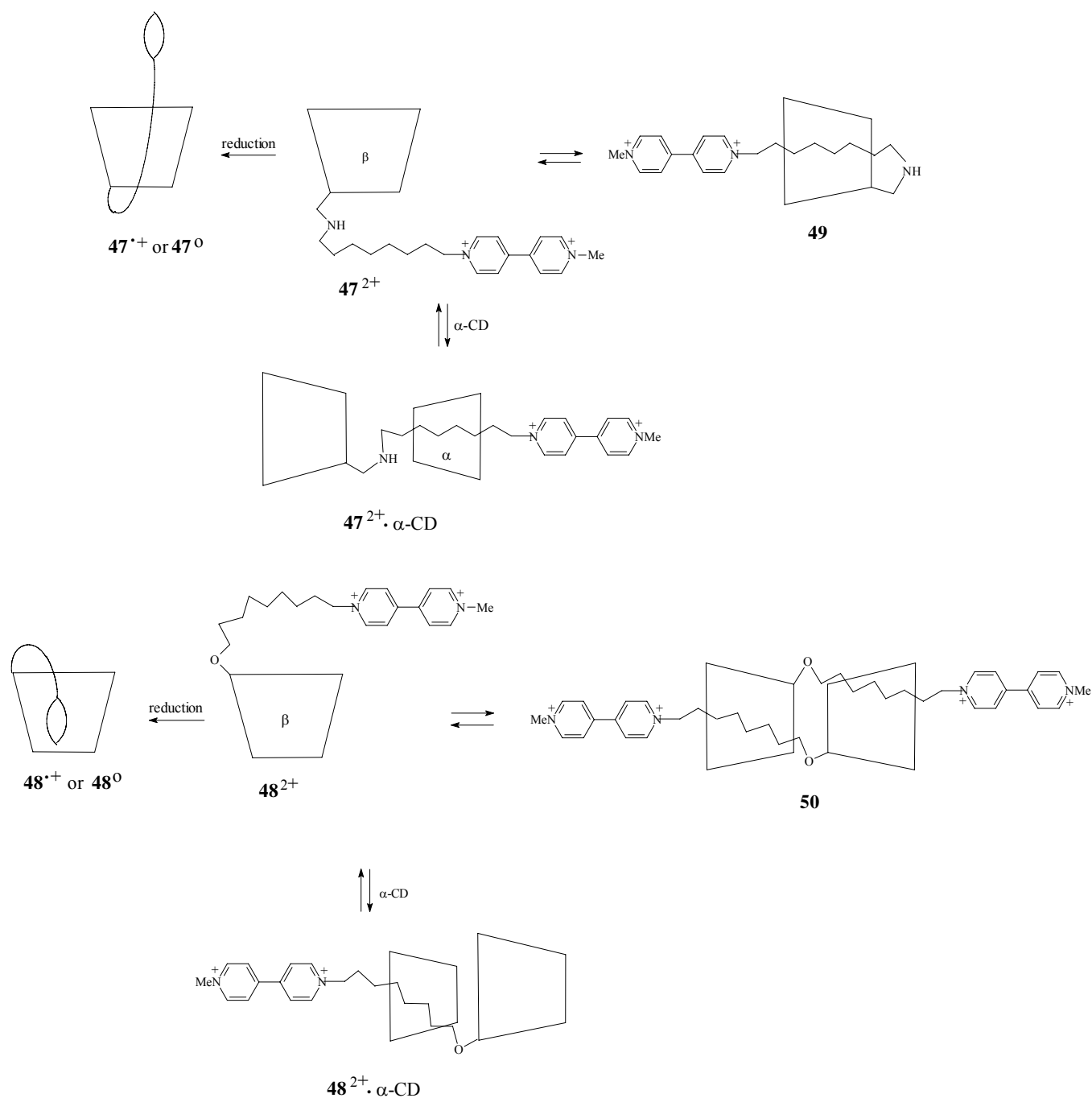


In rotaxane (**43**) upon heating, the α -CD molecule shuttles within the azobenzene unit below 100°C, and between two stoppers at temperatures above 100°C.

The UV irradiation of **43** results in the *trans-cis* isomerization, accompanied by the movement of α -CD molecule towards the stopper affording **45**; the visible light irradiation of **45** results in the *cis-trans* photoisomerization to give the rotaxane (**46**), this process however being irreversible.



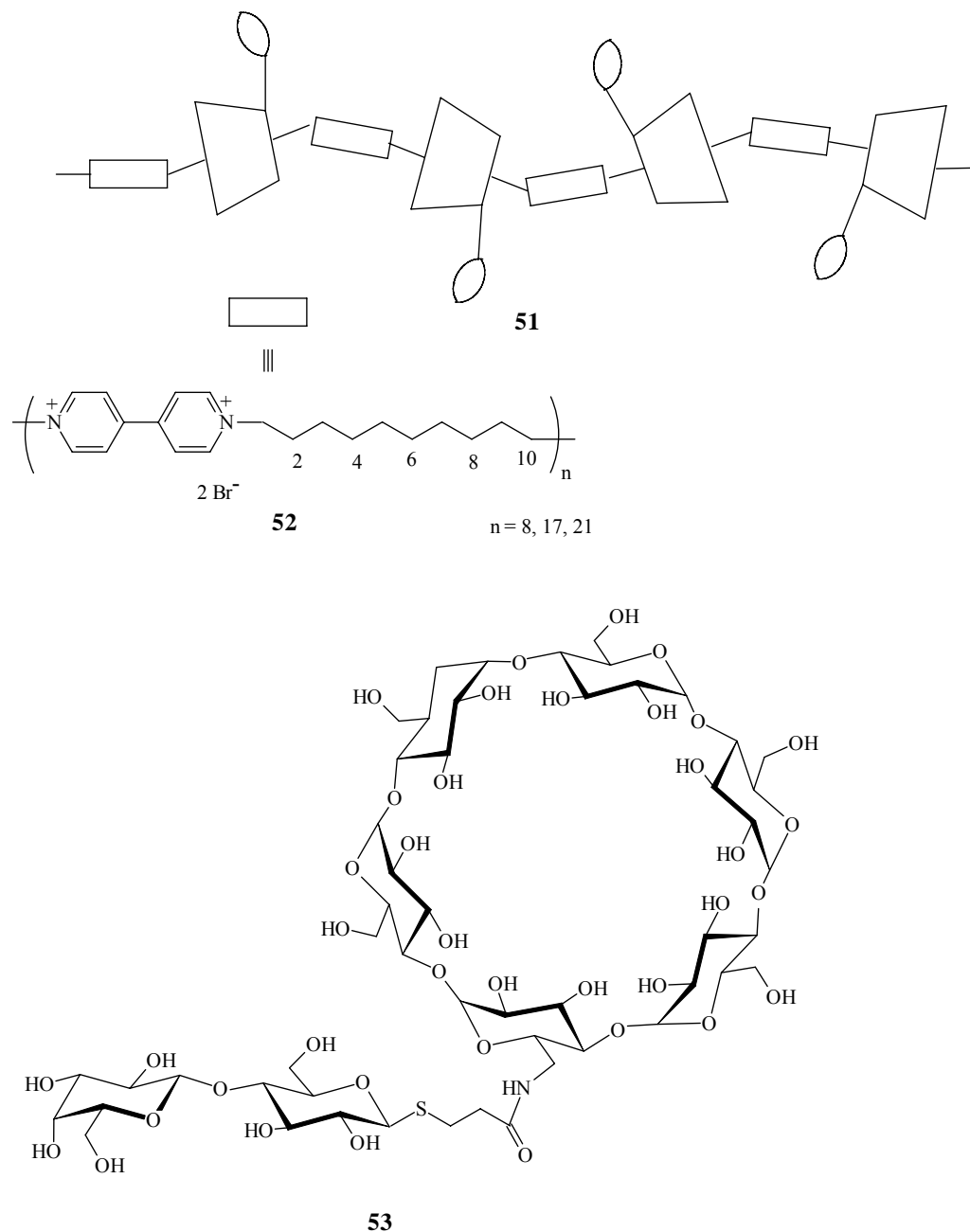
The self-inclusion behavior of two β -CD derivatives (**47**²⁺) and (**48**²⁺), in which the viologen group is tethered at the narrow and large rim, respectively, has been investigated using ¹H NMR and circular dichroism spectroscopic methods.⁷⁵ It was found that **47** forms an intramolecular self-inclusion complex (**49**), whereas **48** forms the head-to-head dimer (**50**).



The reduction of 47^{2+} leads to $47^{\bullet+}$ or 47^0 intramolecular complexes in which the viologen unit protrudes outside the β -CD molecule. The reduction of 48^{2+} leads also to $48^{\bullet+}$ or 48^0 intramolecular complexes, however with viologen unit inside the β -CD cavity. These results indicate the preference of viologen units for the large rim of β -CD, so for oxidized as for reduced viologen forms.

In the study of complexation of 47^{2+} and 48^{2+} with α -CD it was observed that they form [2]pseudorotaxanes ($47^{2+} \cdot \alpha$ -CD) and ($48^{2+} \cdot \alpha$ -CD), respectively, in both of them the viologen unit being situated in the vicinity of the large rim of α -CD molecule.

Pseudorotaxanes (**51**) consisting of linear polyviologen polymers (**52**) as threads and lactoside-bearing α -CD molecules (**53**) as rings have been synthesized.⁷⁶

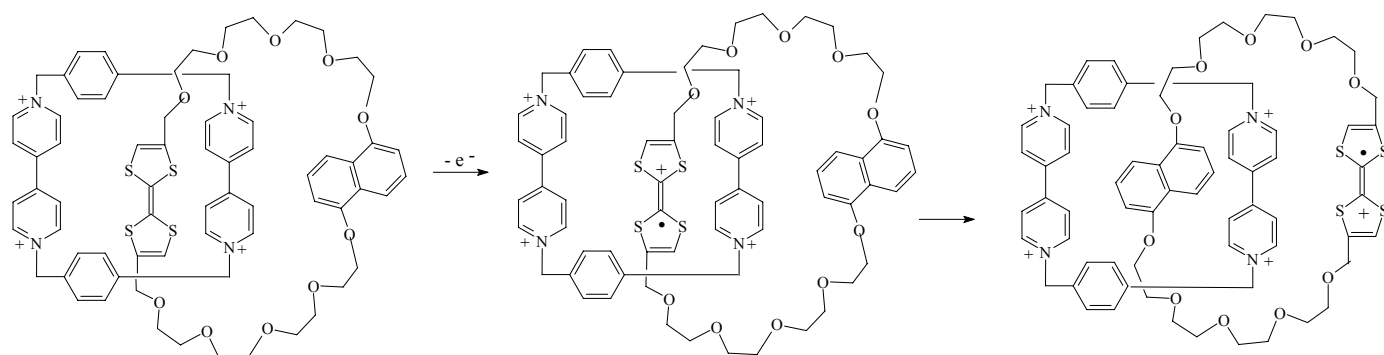


It was found that polyviologens are responsive to the Bradford assay. This response indicates the degree of threading of CD rings of the polypseudorotaxanes and shows the utility of biochemical assays in solving supramolecular chemistry problems.

2. CATENANES

Catenanes are today a topic of intense research; many reports concerning this theme appear.^{1,7-9} The numerical simulation at an all-atom level has been applied for investigation of the microscopic switching mechanism of the [2]catenane (**54**), which is a prototype of a molecular machine.⁷⁷ Upon external stimuli

action this system switches reversibly between two different stable states, however the switching time scale ranges from microseconds up to milliseconds, this region lying well over typical time scales of standard molecular dynamics (MD) simulations.

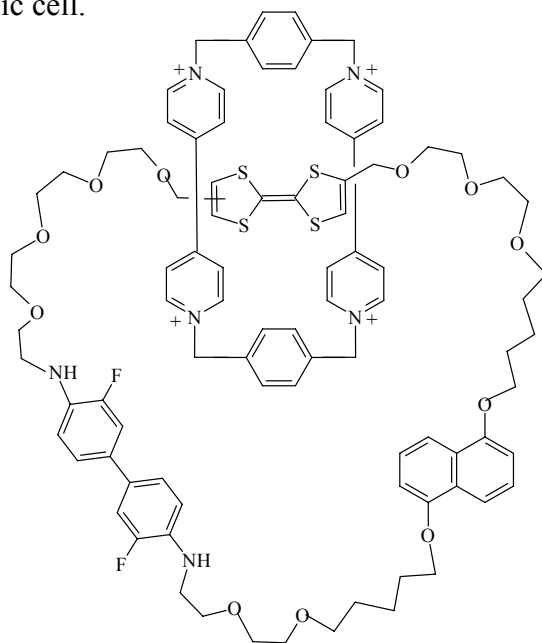


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To overcome this problem, the combining of action-derived dynamics (ADD) and dynamical trajectories instead of using the alternative transition path sampling (TPS) showed to be advantageous. The long reactive trajectory for the conformational rearrangement occurring in the switching process of **54** enabled the detailed analysis of its microscopic mechanism.

Along the trajectory connecting the reactant and product states, several intermediates resulting from the combination of π - π and electrostatic interactions have been found; in these investigations the dynamic effects have been taken into account. It was found that counterions interact strongly with the positively charged system; they compete with the TTF and DNP units to stay close to the ring A^{4+} .

In the search for pixel components of electronic paper displays, the electrochemical color-switchable tristable [2]catenane (**55**) has been designed.⁷⁸ This dye may generate green, blue and red colors under different voltages, in a single basic cell.



55

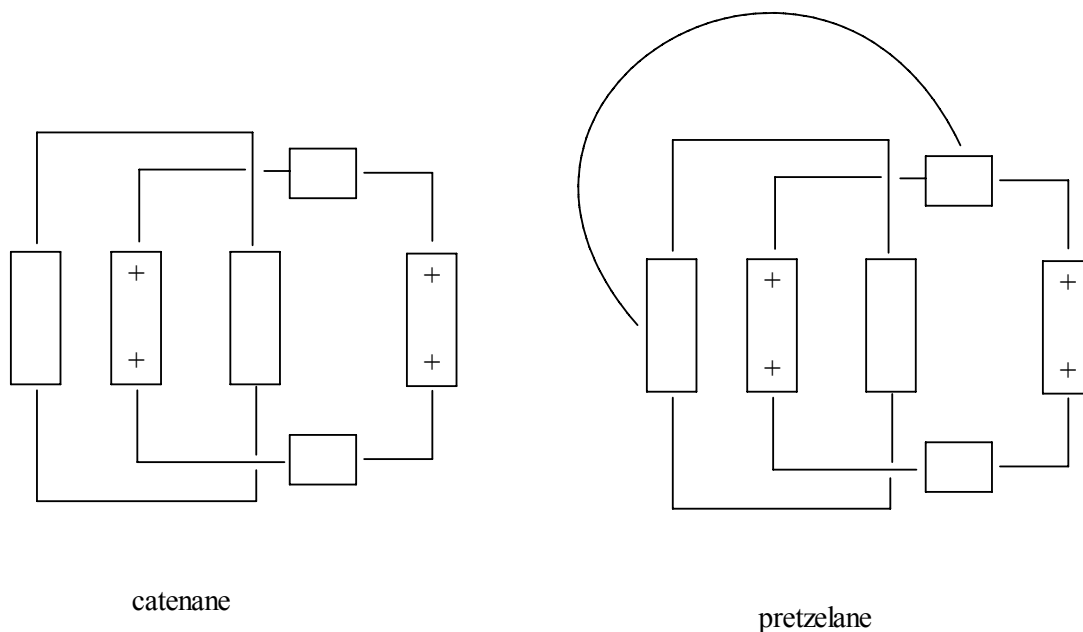
The dye (**55**) consists of three electron donor units linked by crown-etheral spacers, which are subsequently encircled by the ring A^{4+} , which is an electron acceptor. The donors, *i.e.* TTF, substituted benzidine (BZD) and DNP units, generate green, blue and red colors, respectively.

Three different voltages V_0 , V_1 and V_2 control the color. At V_0 all three donor units are neutral, the ring A^{4+} encircles the TTF unit, the color is green; at V_1 voltage the TTF unit is oxidized, it repels the ring A^{4+} which moves to BZD, generating the blue color. Change of the voltage to V_2 results in the oxidation of BZD donor station, therefore A^{4+} moves to DNP, generating the red color. The return of the voltage to V_0 leads to the back movement of A^{4+} to TTF unit, accompanied by the generation of green color.

The dye (**55**) is easily embedded in polymer matrices; its use in the simple package processing, such as ink-jet printing technology is promising for paper-like electronic displays.

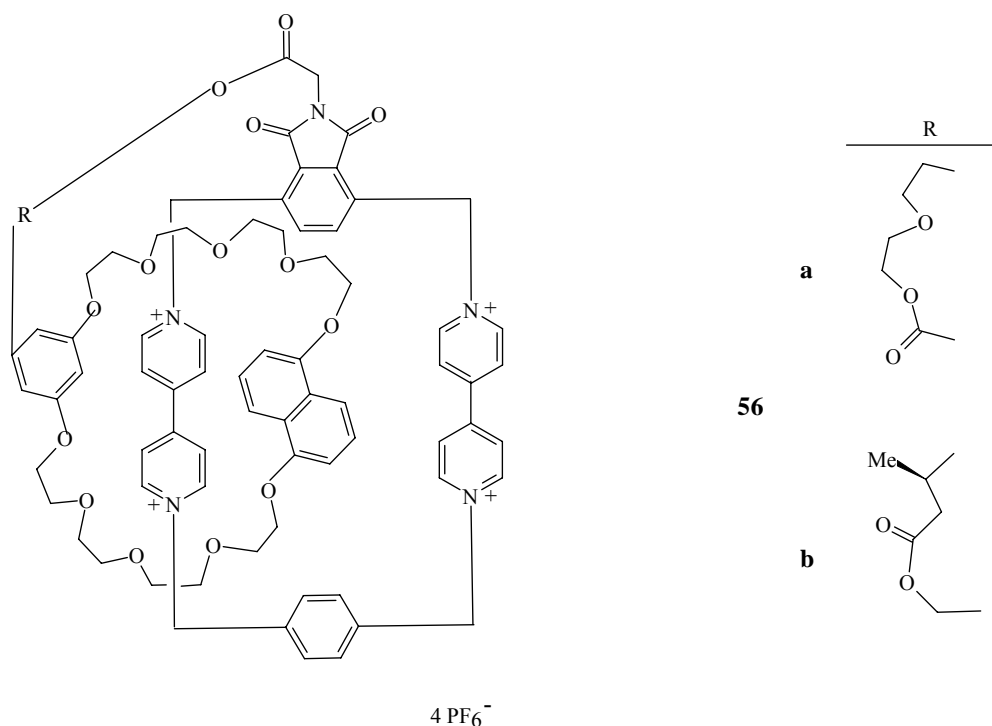
3. PRETZELANES

Pretzelanes may be considered as bridged catenanes, as shown below.⁷⁹

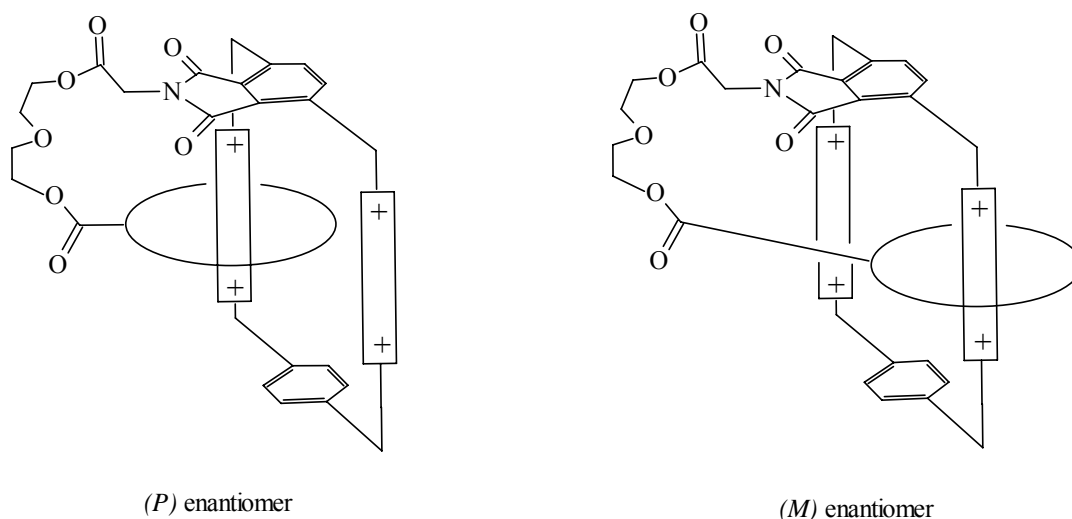


Donor-acceptor pretzelanes are obtained by template - directed procedures on the basis of the donor-acceptor interactions occurring between π -electron poor (*e.g.* bipyridinium, diazapyrenium) and π -electron rich (*e.g.* 1,5-dioxynaphthalene, hydroquinone) units.⁸⁰

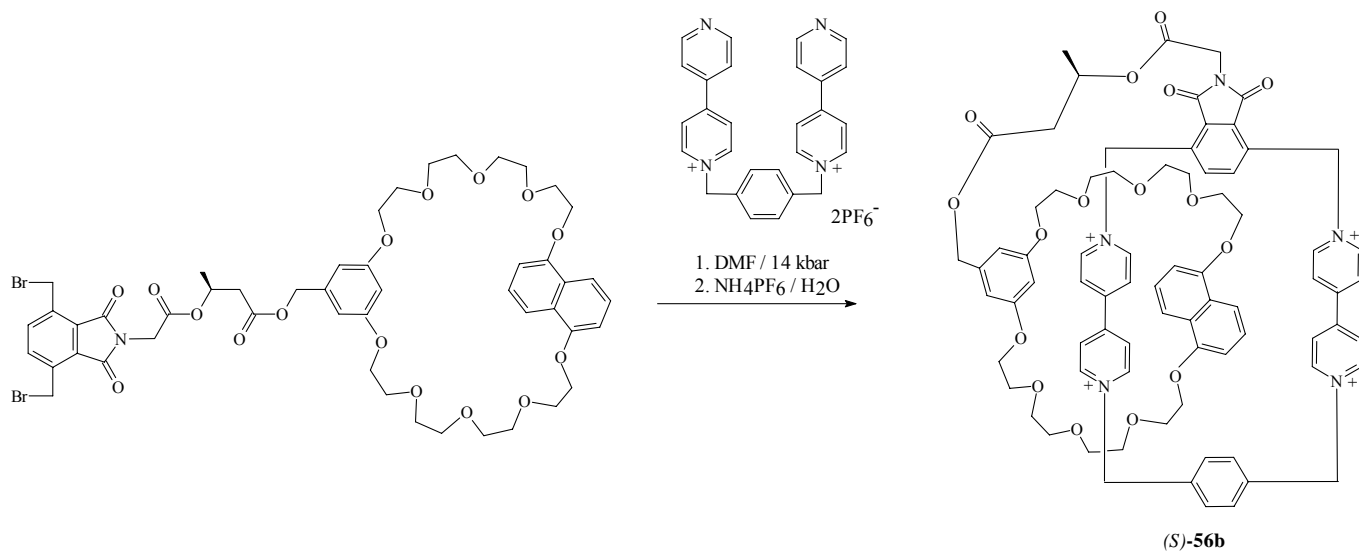
The synthesis of pretzelanes (**56a,b**) has been reported.⁸⁰



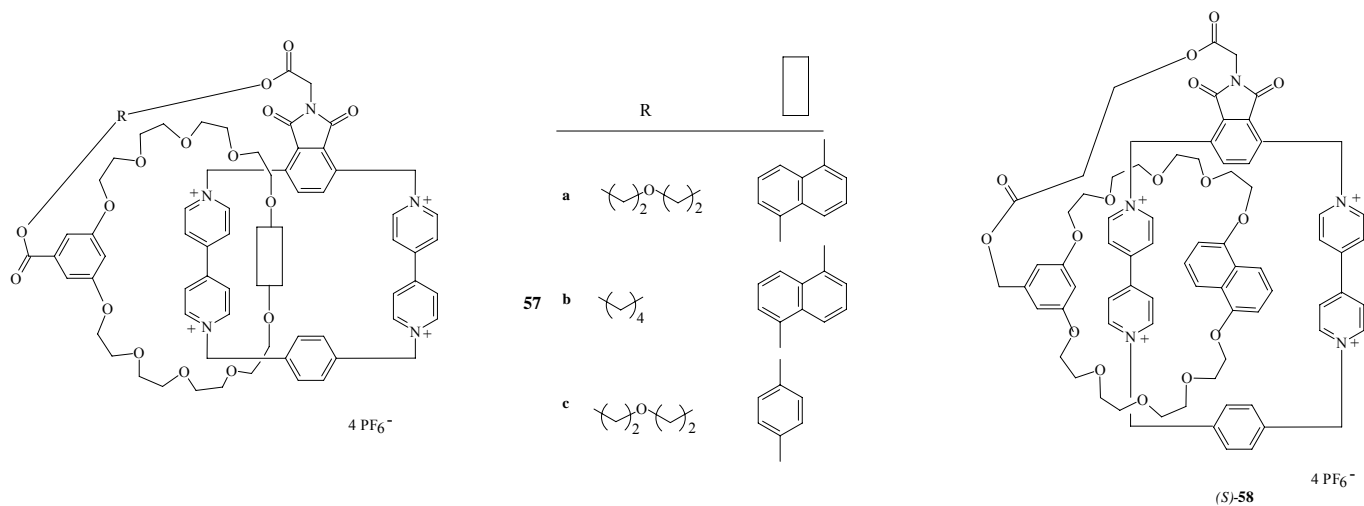
The stereochemistry of pretzelanes is connected with the relative spatial arrangements of the two interlocked rings. The helical chirality of **56a** involves the localization of the crown ether on one from among two bipyridinium units of the ring A^{4+} ; as a result, a pair of (*P*) and (*M*) enantiomers exists.



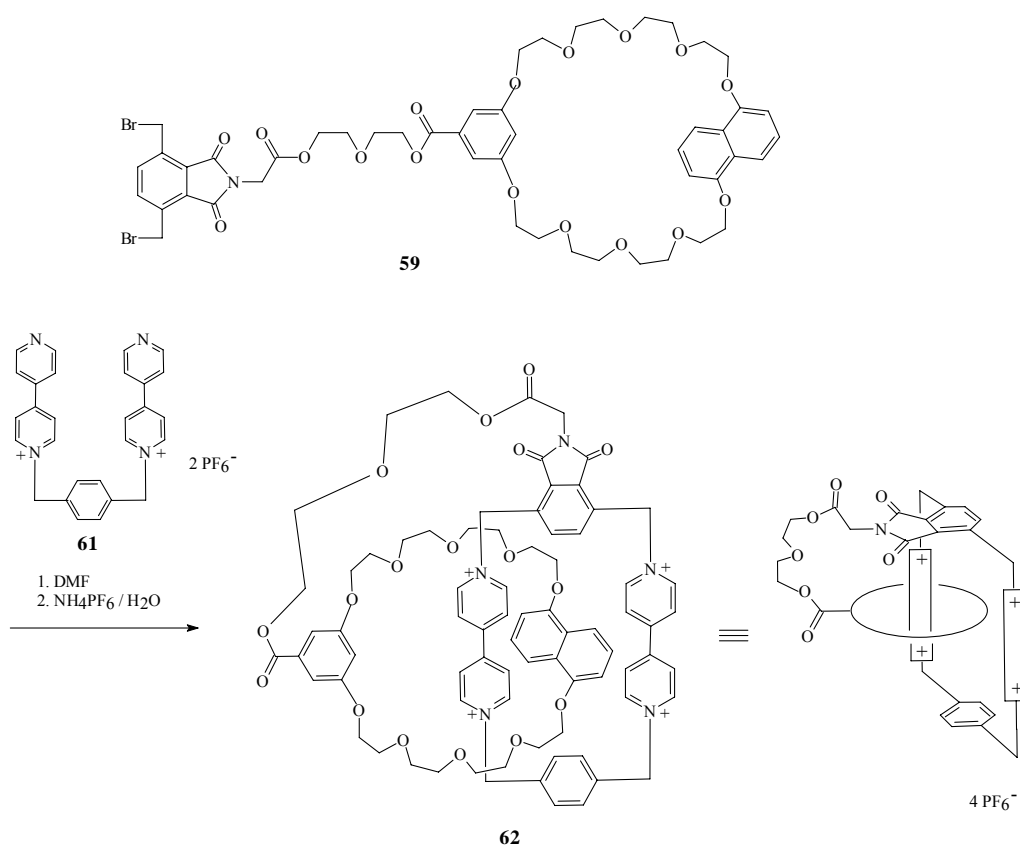
The effect of the presence of a stereogenic center leading to a preference of one conformational diastereoisomer in the synthesis of (*S*)-*PM*-**56b** bearing a methyl group was studied by dynamic ^1H NMR spectroscopy, circular dichroism and molecular modelling. The obtained results indicate that the (*S*)-(*M*)-**56b** is more stable than the (*S*)-(*P*)-**56b**. This observation is explained by the fact that the conformations adopted by the linkers are different in both diastereoisomers. In (*S*)-(*M*)-**56b** the methyl group of the linker points away from the cavity, whereas in (*S*)-(*P*)-**56b** it points towards the cavity, in this way causing the steric hindrance which results in lower stability of (*S*)-(*P*)-**56b**.



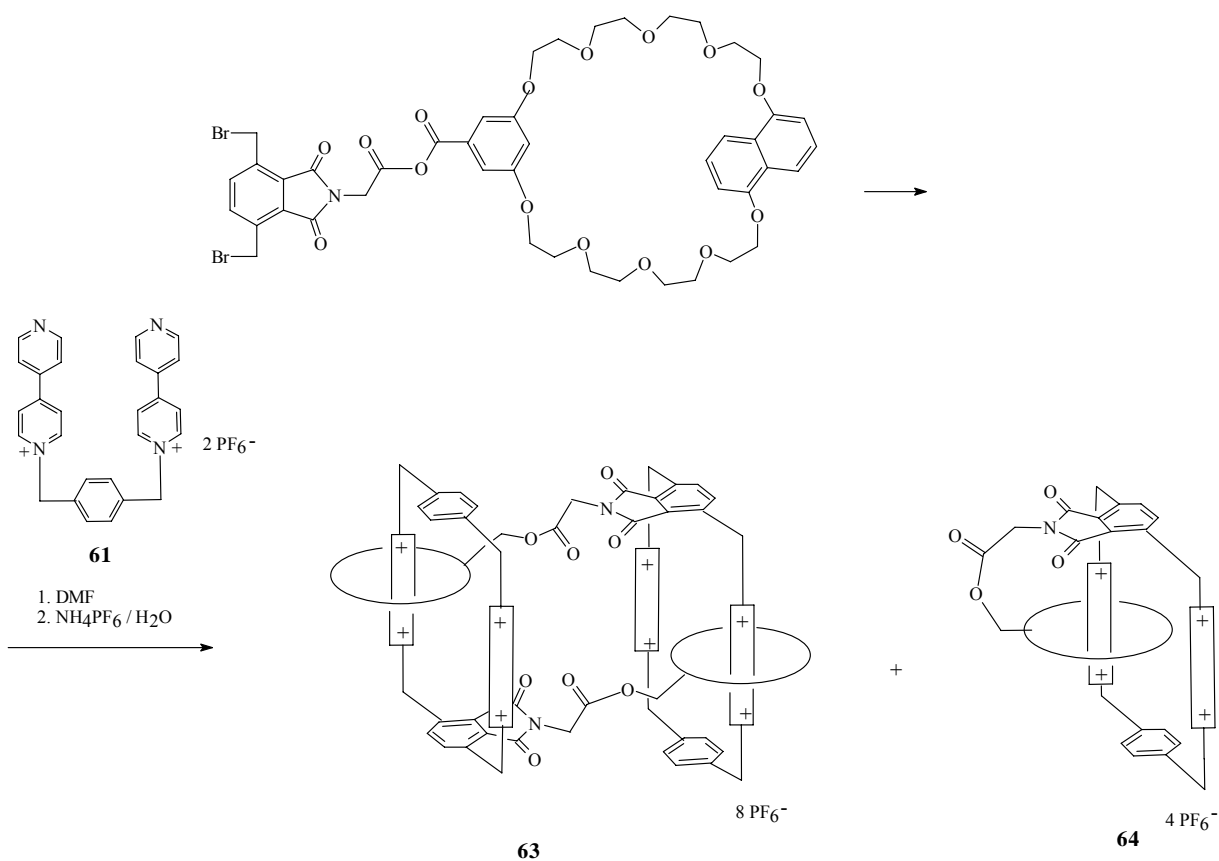
Pretzelanes (**57**) and (**58**) have been synthesized and their dynamic interconversions have been investigated.⁷⁹



Reactions of dibromides (**59**) and (**60**) with compound (**61**) have been studied.⁸¹ In the case of **59**, having a long and flexible linker the intramolecular cyclization leading to pretzelane (**62**) occurs.

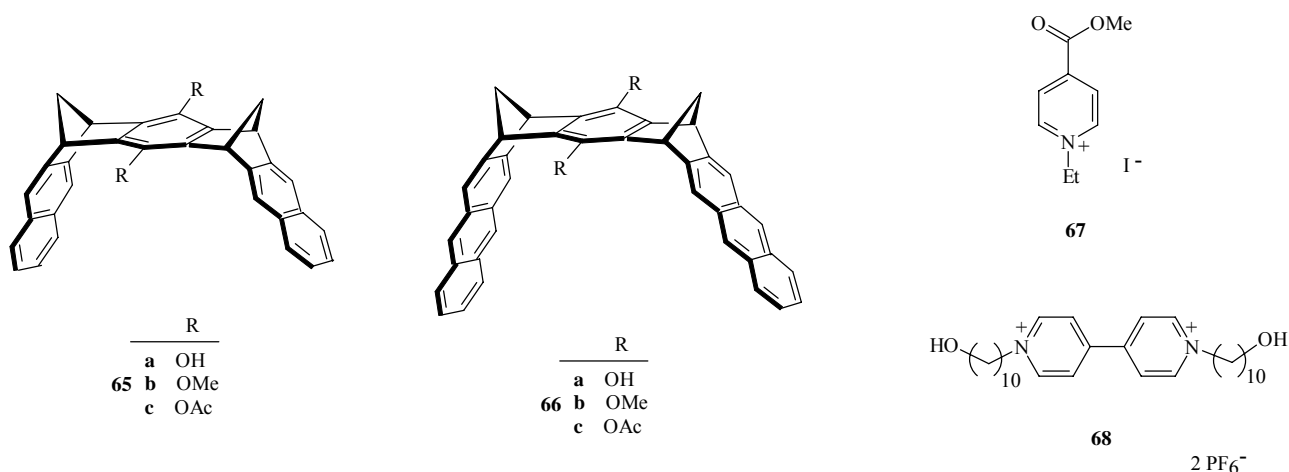


However, in the case of **60**, having a shorter and less flexible linker the intermolecular cyclization prevails, affording the cyclic bis[2]catenane (**63**) as a major product, whereas the intramolecular cyclization leads to pretzelane (**64**) as a minor product.



4. MOLECULAR CLIPS

It was found that naphthalene and anthracene clips (**65a-c**) and (**66a-c**) form stable host-guest complexes with electron poor molecules, such as **67** and **68**.⁸²

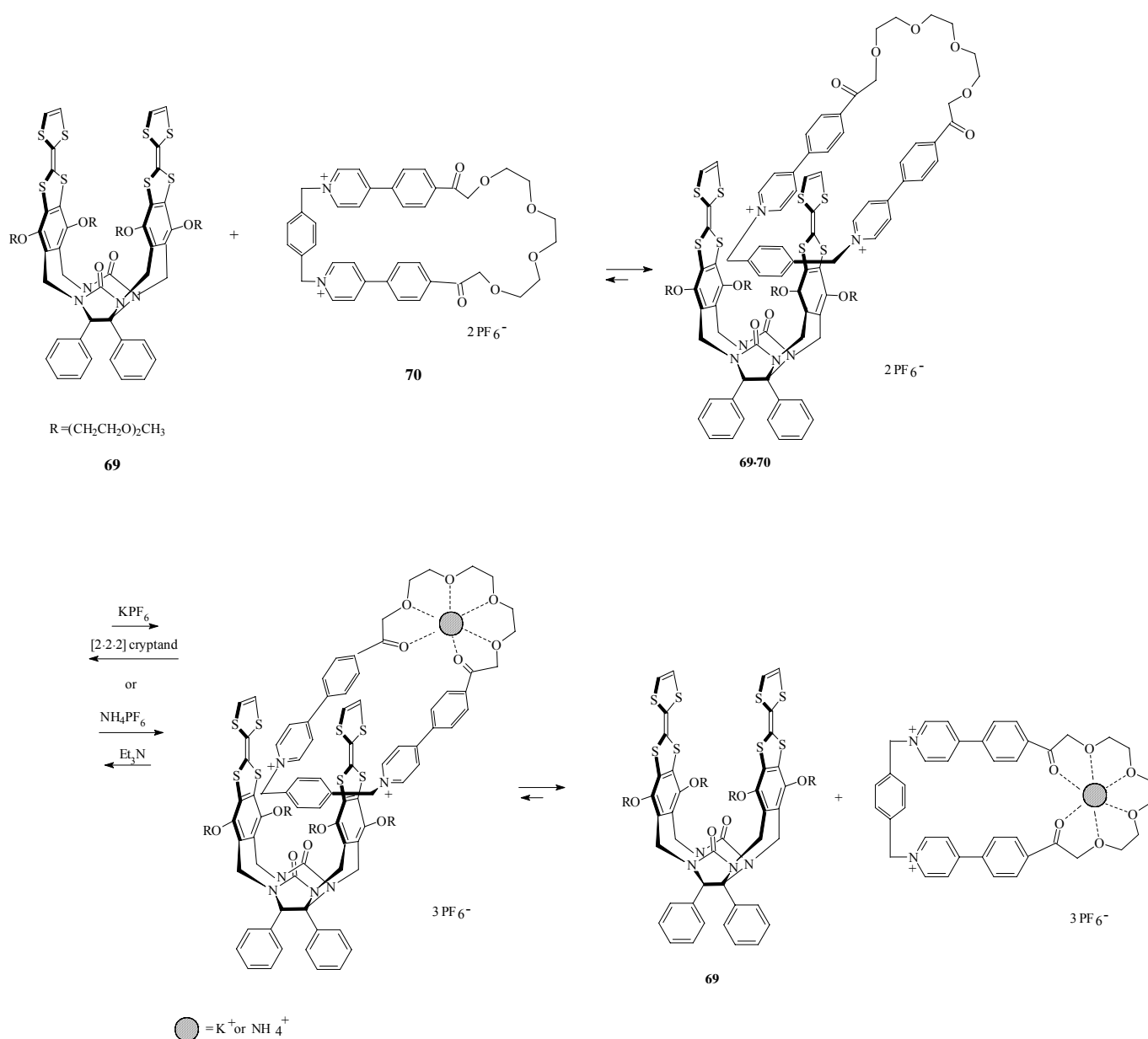


Complexes of clips (**65**) are weaker than those of clips (**66**), since **66** have larger van der Waals contact surfaces of the anthracene sidewalls as compared with naphthalene sidewalls of **65**. In the case of **65** and **66** the complex stabilities decrease in the order **a** > **c** > **b** due to the smaller steric demand of hydroxyl group as compared to OMe and OAc groups, as well as due to the function of OH group as both donor and acceptor of hydrogen bonds with guest molecules.

In a study of clips, the molecular switch consisting of glycoluril-based molecular clip (**69**) and macrocycle (**70**) has been synthesized. The macrocycle (**70**) consists of an π -electron rich, ring-expanded [18]crown 6, *i.e.* 18C6 unit able to bind alkali metal and NH_4^+ ions and of a π -electron poor aromatic system able to bind π -electron rich units, such as TTF.⁸³

The interaction of the clip (**69**) with **70** in MeCN leads to the formation of the complex (**69**·**70**), changing the yellow color of the MeCN solution of **69** from yellow to brown. The addition of KPF_6 to the brown solution results in the recovery of the original yellow color, due to the dissociation of the complex (**69**·**70**).

The addition of [2.2.2]cryptand which has a strong affinity to K^+ ions removes the K^+ ion from the macrocycle (**70**) causing the regeneration of the complex (**69**·**70**), and the appearance of the brown color. This threading-dethreading process can be repeated several times adding K^+ ion and [2.2.2]cryptand sequentially; the reversible color changes allow to monitor the switching process by the naked eye.



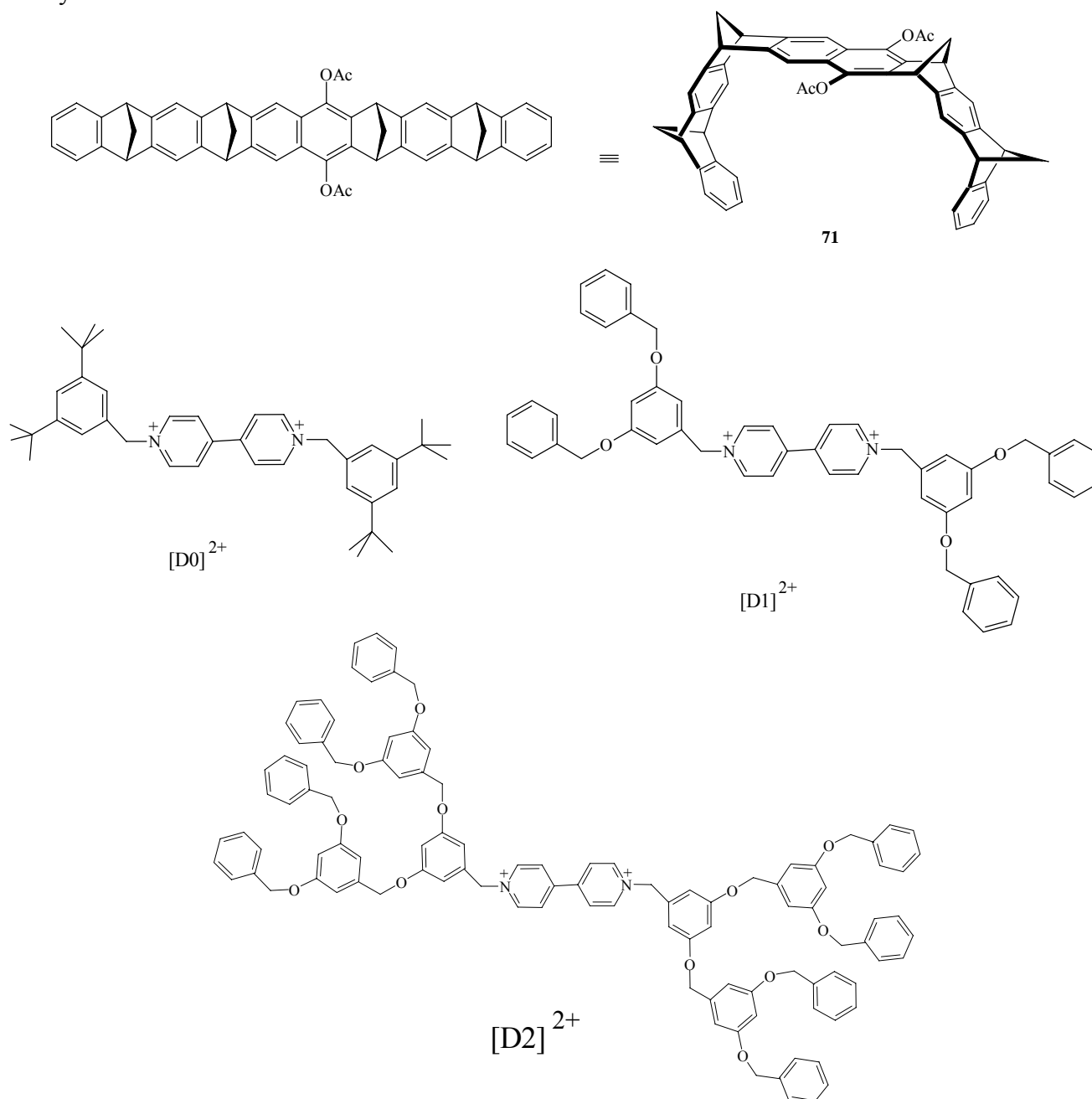
The above [2]pseudorotaxane-like molecular switch can also be controlled using $\text{NH}_4^+/\text{Et}_3\text{N}$ system, since NH_4^+ ion has similar size and binding affinity toward 18C6 as K^+ ion. The addition of NH_4PF_6 causes the dissociation of the complex (**69·70**); the addition of Et_3N results in the formation of Et_3NH^+ ion and of NH_3 , which do not bind to 18C6, and therefore the complex (**69·70**) is regenerated.

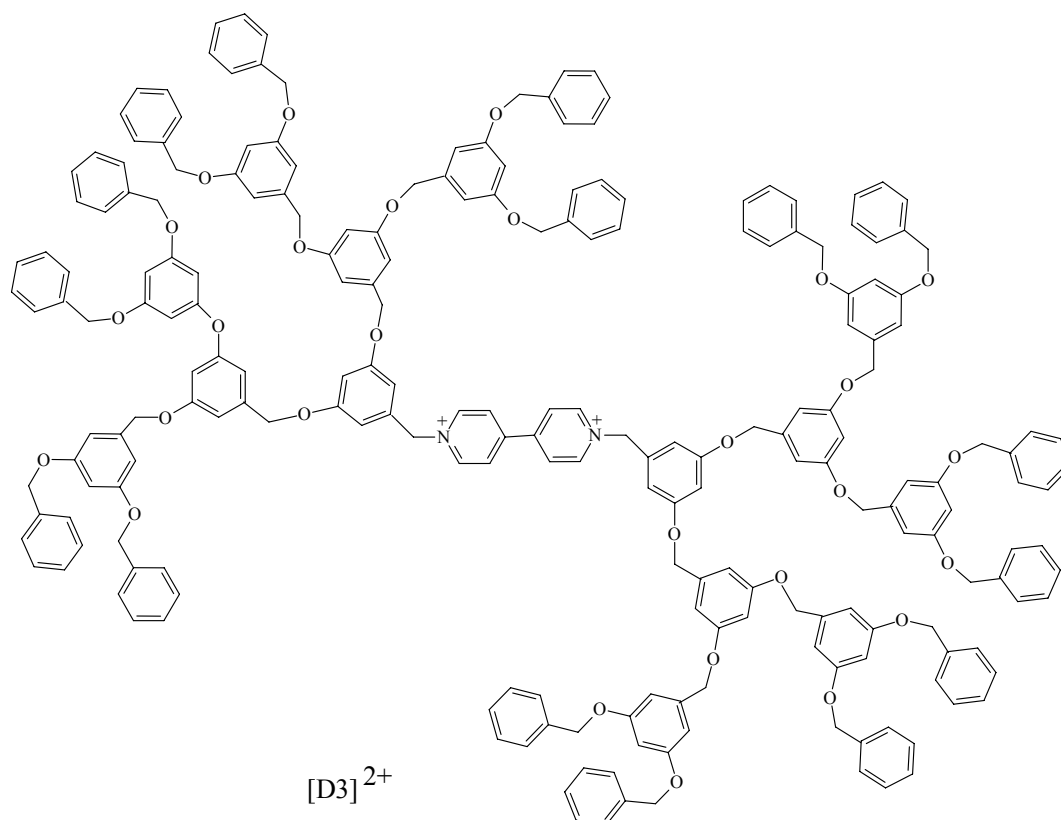
It was observed that the complex (**69·70**) shows thermochromism since its reversible color changes can be triggered thermally.⁸⁴ The switching behavior of the complex (**69·70**) may be also controlled by oxidation/reduction procedure. The addition of $(p\text{-BrPh})_3\text{NSbCl}_6$ to a mixture of **69** and **70** results in the oxidation of TTF units into $\text{TTF}^{\bullet+}$ radical cations and the dissociation of the complex (**69·70**), caused by electrostatic repulsion between positively charged pyridinium units of **70** and radical cations $\text{TTF}^{\bullet+}$ of **69**. The addition of zinc to the solution reduces $\text{TTF}^{\bullet+}$ back to TTF molecules and regenerates the complex (**69·70**). As above, the color changes are observable by the naked eye.

Taking the intensity of the absorbance in UV spectrum of complex (**69-70**) as the output, and K^+ , NH_4^+ and the heat as the inputs, this molecular clip/macrocyclic system can be considered as a three-input molecular NOR logic gate.

In investigation of tweezers enclosing the dendritic core, it was established that the electron rich tweezer (**71**) forms adducts with first-, second- and third-generation dendrimers $[Dn]^{2+}$ ($n=1,2,3$).^{85,86} The association constant values of adducts ($71 \cdot [Dn]^{2+}$) decrease with the higher dendrimer generation. This behavior is due to the fact that bipyridinium core is stabilized by „intramolecular solvation”, resulting from the back-folding of the electron-donor branches; this process increases with dendrimer generation.

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It was established that adducts are formed by charge transfer interaction, and they dissociate upon one-electron reduction of the dendritic core.

CONCLUSION

The rapid development of supramolecular chemistry has its reflexion in a variety of works. Among them, the number of supramolecular species bearing quaternary azaaromatic moieties⁸⁷⁻⁸⁹ is large, therefore in the present paper only chosen examples have been described.

The current investigations concern design of miniaturized electronic devices. In recent times an intense study dealing with construction of sunlight-powered molecular machines is to be seen, and a widespread attention is paid today to this new, promising research area.^{26,57,58,90}

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