HETEROCYCLES, Vol. 71, No. 8, 2007, pp. 1685 – 1713. © The Japan Institute of Heterocyclic Chemistry
Received, 20th December, 2006, Accepted, 11th May, 2007, Published online, 15th May, 2007. REV-06-615

INCLUSION COMPLEXES CONTAINING QUATERNARY AZAAROMATIC MOIETIES

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Abstract- In the paper inclusion complexes of cyclodextrins, cucurbiturils and calixarenes containing quaternary azaaromatic moieties are described, followed by complexes of crown ethers, tweezers and clips.

INTRODUCTION

Supramolecular chemistry is developing rapidly, the number of works concerning this field of science is enormous. Many papers describing interlocked species[1-5] as well as inclusion complexes of cavitands[6-8] and of calixarene-based capsules[9-11] appear. It should be pointed out that research dealing with the design of molecular machines attracts now a considerable attention.[12-14]

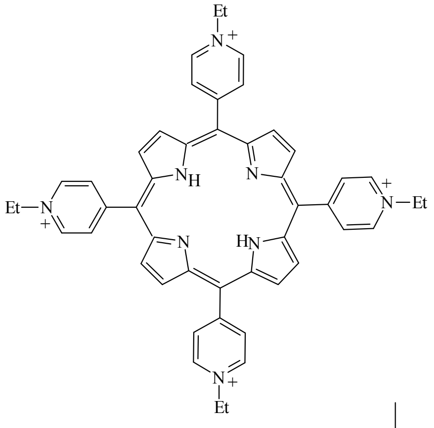
The present review is a continuation of our former papers on quaternary azaaromatics,[15-19] supramolecular spieces of a quaternary azaaromatic character,[20-22] as well as on cyclodextrins[23-25] and calixarenes.[8,11,26] Quaternary azaaromatics are a topic of a number of reports; due to their interesting properties and application possibilities[17] inclusion complexes containing these species are important, for example in the construction of molecular machines and switches.[13]

In first chapters of the review inclusion complexes of cyclodextrins, cucurbiturils and calixarenes are characterized. In next chapters some examples of complexes of crown ethers, tweezers and clips are presented. Since the number of supramolecular species containing quaternary azaaromatic moieties is very large, covering rotaxanes[27-32] and catenanes,[33-36] along with inclusion complexes of cyclodextrins,[37,38] cucurbiturils,[39] calixarenes,[40] cryptands,[41] tweezers[42] and clips,[43] in the paper only their chosen examples are described. References of works appeared in years 2005 and 2006 are cited.

1. INCLUSION COMPLEXES OF CYCLODEXTRINS

Cyclodextrins are a topic of an intense research due to their complexing properties; many works concerning these compounds are reported.[44-46] In the study of porphyrins bearing quaternary azaaromatic groups[47-49] it was observed that porphyrin (**1**) forms 1:1 inclusion complexes with β-CD, HP-β-CD and SBE-β-CD in basic aqueous solution (β-CD denotes cyclodextrin, HP-β-CD is hydroxypropyl-β-CD; SBE-β-CD is sulfobutylether-β-CD). The association constants of these complexes decrease in the order SBE-β-CD > HP-β-CD >> β-CD. Since HP-β-CD and SBE-β-CD bear functional groups, their solubility and flexibility are higher than in the case of native β-CD. The strong inclusion capacity of SBE-β-CD results from the fact that it is negatively charged, *i.e.*charged oppositely to porphyrin (**1**).[50]

The complex formation of porphyrin (**2**) with EDTA tethered β-CD dimer (**3**) was investigated by isothermal titration calorimetry (EDTA= ethylenediamine-*N*,*N*,*N*,*N*'-tetracetate).[51] It was observed that **2** forms with the dimer (**3**) the 1:2 complex, *i.e.* **2** is bound by four CD units. The affinity of **2** to calcium and europium complexes (**4**) and (**5**) of **3** is weaker than to negatively charged **3**, since the metal chelation restricts the tether flexibility.



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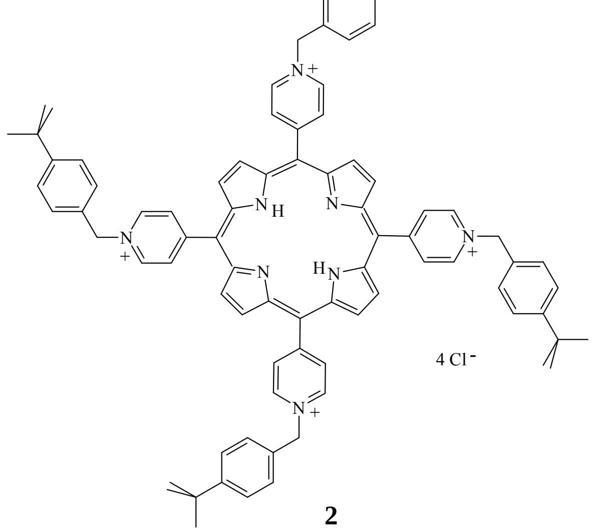

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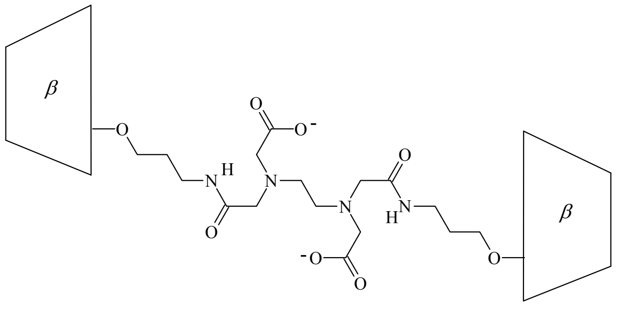

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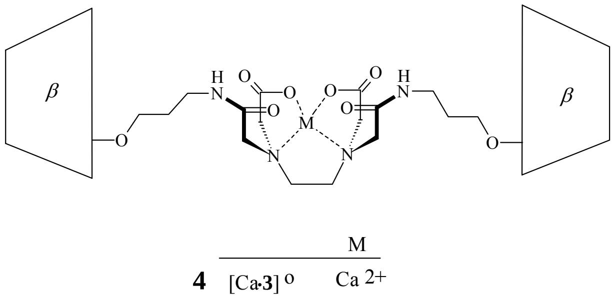
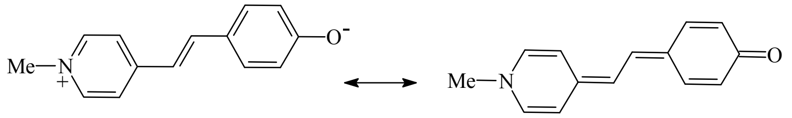


		M
4	[Ca·**3**] ^{o}	Ca $^{2+}$
5	[Eu·**3**] $^{+}$	Eu $^{3+}$

The UV spectra of dyes (**6**) and (**7**) were investigated in solutions of Me-β-CD, using hydroxylic and dipolar non-protic solvents.[52] In aqueous solutions of **6** the addition of Me-β-CD results in a red shift, indicating formation of the **6**/Me-β-CD 1:1 inclusion complex, due to the transfer of the probe to a microenvironment of lower polarity. For **6** in alcohols blue shifts were observed, they decrease in the order BuOH>i-PrOH>EtOH>MeOH indicating dye-solvent interactions through hydrogen bonding. If dye-solvent interactions are strong, the dye-CD interactions are consequently weak and vice versa.

In the case of hydrogen-bond accepting solvents, **6** and **7** show blue shifts decreasing in the order MeCN>acetone>DMF>DMA>DMSO. It should be noted that it is the order of increasing basicity of the medium.



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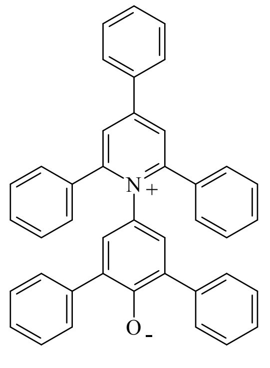

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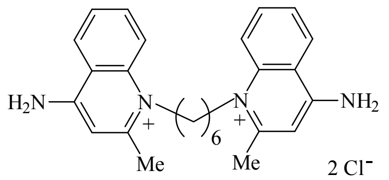
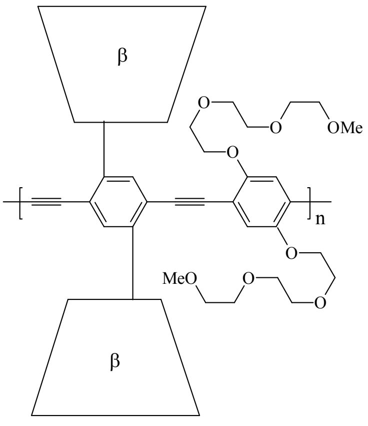


8

When aqueous solution of dequalinium chloride (**8**), which is an antibacterial drug is treated with β-CD, a strong increase of fluorescence intensity occurs due to the formation of 1:1 host-guest complex; this behavior enables the determination of **8** in bulk aqueous solutions in the presence of β-CD by flow injection spectrofluorometric method.[53]

In the study of supramolecular polymers bearing CD moieties,[54] it was established that water-soluble polymer (**9**) shows fluorescence quenching upon formation of inclusion complexes with viologens. The water solubility of polymer (**9**) results from the presence of hydrophilic CD moieties.[55]

The quenching of fluorescence of **9** by viologens (**10**) and (**11**) is due to their electron accepting character. The addition of **10** leading to inclusion complex (**12**) results in strong fluorescence quenching, in the case of viologen (**11**) however only low fluorescence quenching was observed, since the formation of an inclusion complex of **11** with CD is difficult.[56]



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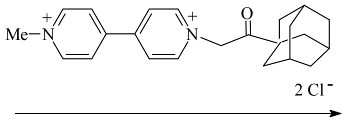

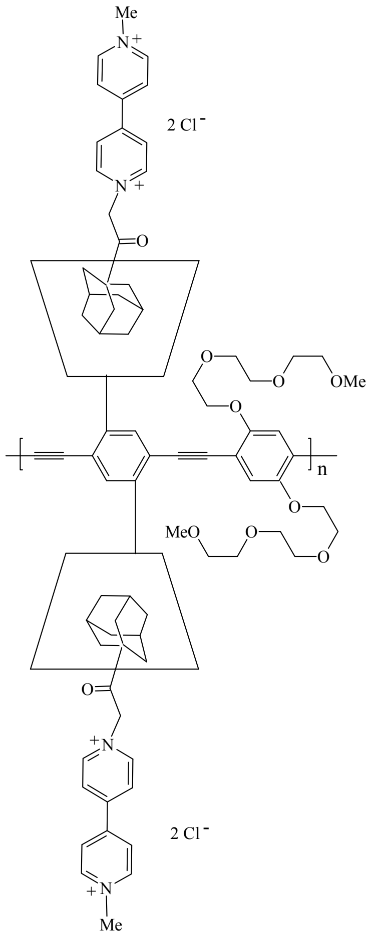

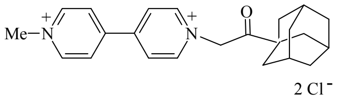

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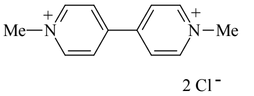
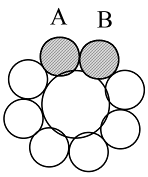


11

12

Four bispyridinio-appended γ-CD isomers (**13-16**) were synthesized to create a molecular receptor for controlling the stereoselectivity of photocyclodimerization of 2-anthracenecarboxylate (**17**).[57]



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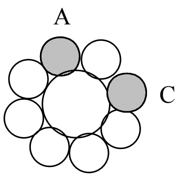

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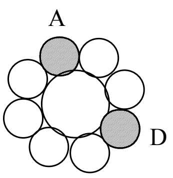

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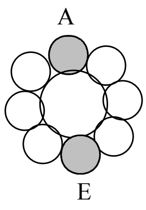

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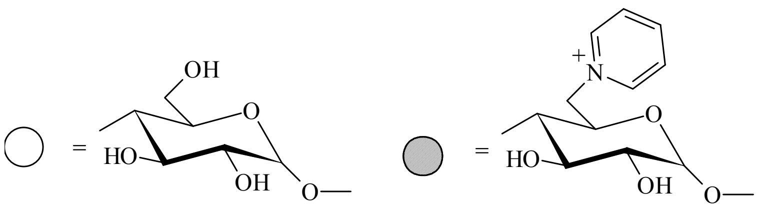
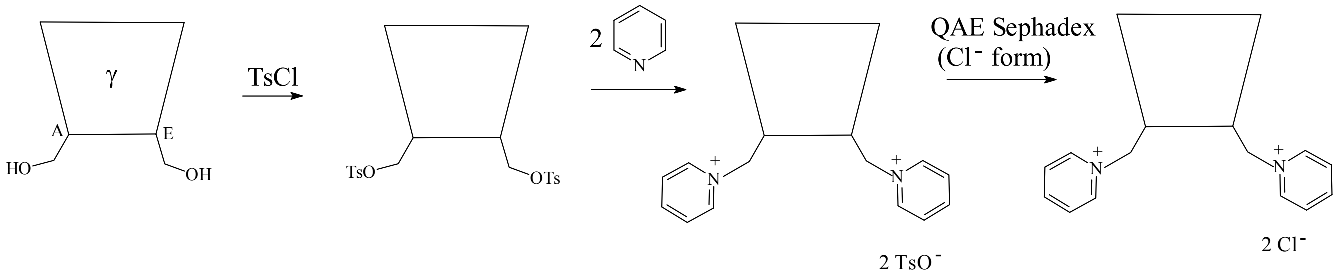
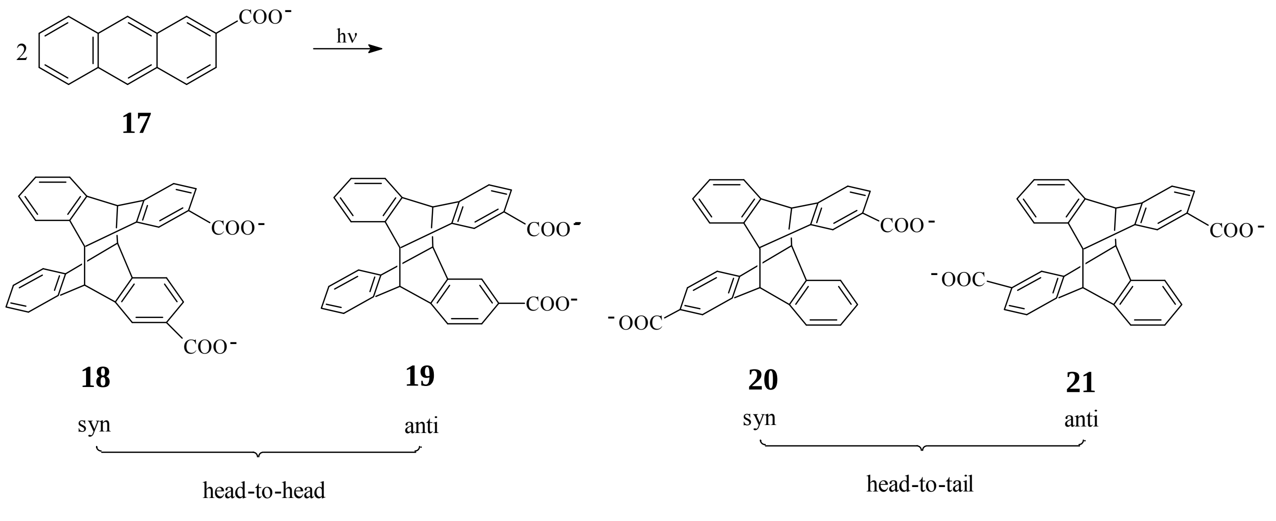




Photocyclodimerization of **17** affords four kinds of configurational isomers (**18-21**). In the molecular microreactor the interaction between two guest molecules is facilitated. The hydrophobic interaction in the CD cavity alone is insufficient for the regulation of the relative yield of configurational isomers, for this purpose the addition of another interaction, *e. g.* an ion interaction is necessary. It was found that the modification of γ-CD with two cation-charged moieties at two glucose units increases its binding affinity for **17** due to electrostatic interactions.

The major product of the photocyclodimerization of **17** in the presence of cation-charged γ-CD are head-to-head isomers (**18**) and (**19**), while in the presence of native γ-CD the main product are head-to-tail isomers (**20**) and (**21**).

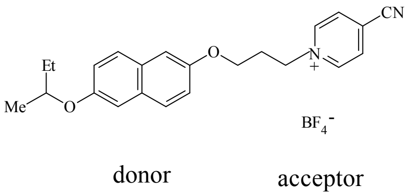


A considerable template effect of bispyridinio-modified γ-CD for the photocyclodimerization of **17** was observed. The binding constants of **17** with γ-CD and **13-16** decrease in the order **16**>**13**>**15**>**14**>γ-CD; this observation indicates that only a slight difference in the structure of bispyridinio-γ-CDs strongly influences their binding affinity. The isomer (**16**) showed to be an effective molecular vessel regulating the configurational selectivity of photocyclodimerization of **17**. This regulation results from electrostatic interactions between carboxylate anions of the guest molecules (**17**) and pyridinium cations of γ-CD.

2. INCLUSION COMPLEXES OF CUCURBITURILS

The fast development of chemistry of cucurbiturils (CB) as promising receptors results in a great number of works concerning this scientific area.[58-60] In the study of cucurbiturils the intramolecular CT dyad (**22**) was confined in γ-CD and CB8, these receptors being chosen as hosts of different nature, offering different environments.[61]

The structure of CDs is less rigid than that of CBs. It should be noted that CDs bind guests mainly *via* van der Waals interactions while the CB portals containing carbonyl groups enable ion dipole as well as hydrogen bonding interactions with guests. The inner and outer sites of CDs are almost neutral, however in the case of CBs the inner surface is negative. As a result, CDs bind neutral guests, while CBs prefer guests with a positive charge.[62,63] The proposed structures of **22**·γ-CD and **22**·CB8 are shown below.



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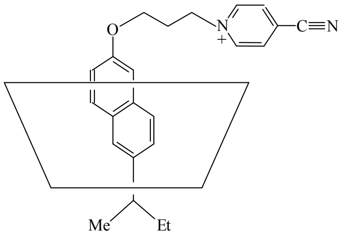
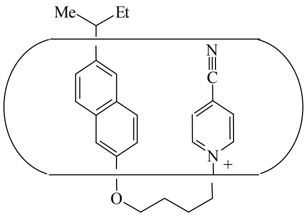
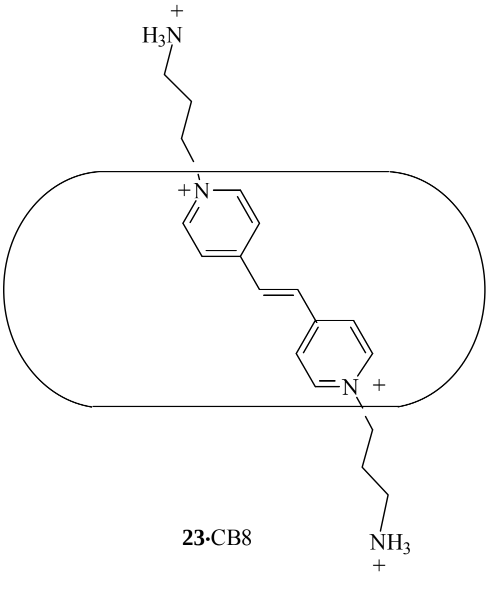


22·γ-CD



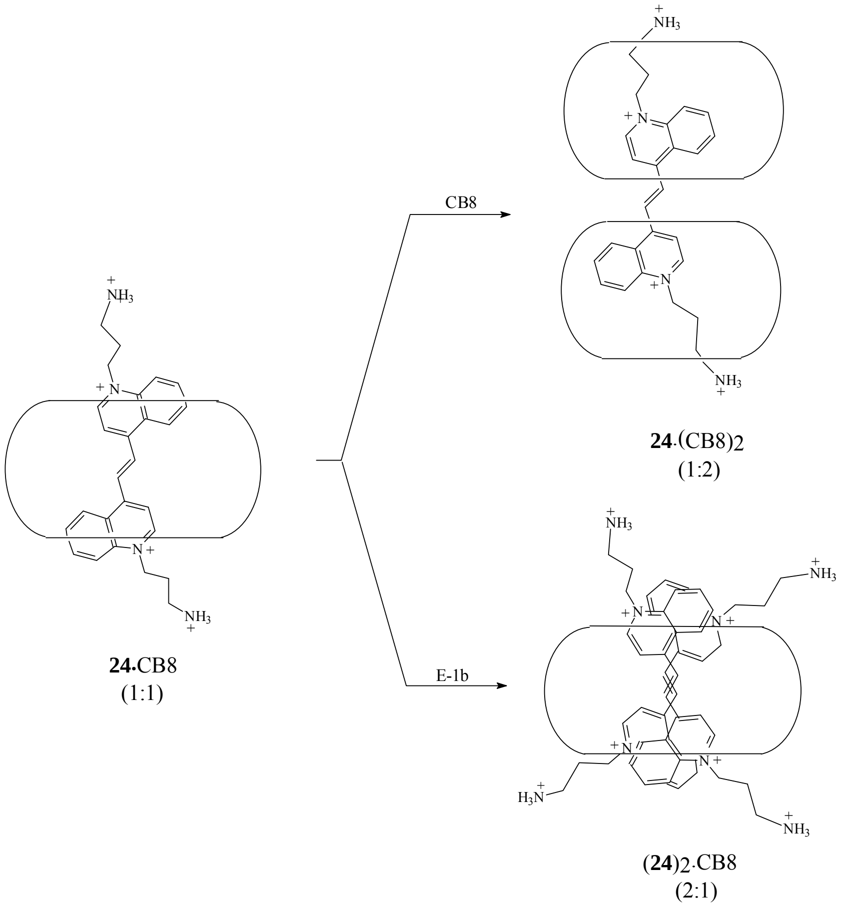
22·CB8

It was found that stilbene (**23**) forms with CB8 the 1:1 inclusion complex (**23**·CB8); its high stability results from hydrogen bonding between carbonyl fragments of both portals of CB8 and two ammonium groups of **23**.[64,65]



23·CB8

However, **24** forms with CB8 three types of inclusion complexes: **24**·CB8, **24**·$(CB8)_2$ and $(\mathbf{24})_2$·(CB8), *i.e.* 1:1, 1:2 and 2:1 complexes, respectively. The stability of **24**·CB8 is lower than that of **23**·CB8, due to more bulky shape of **24** as compared to **23**.[64]

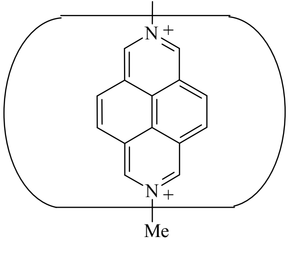


24·CB8
(1:1)

24·(CB8)2
(1:2)

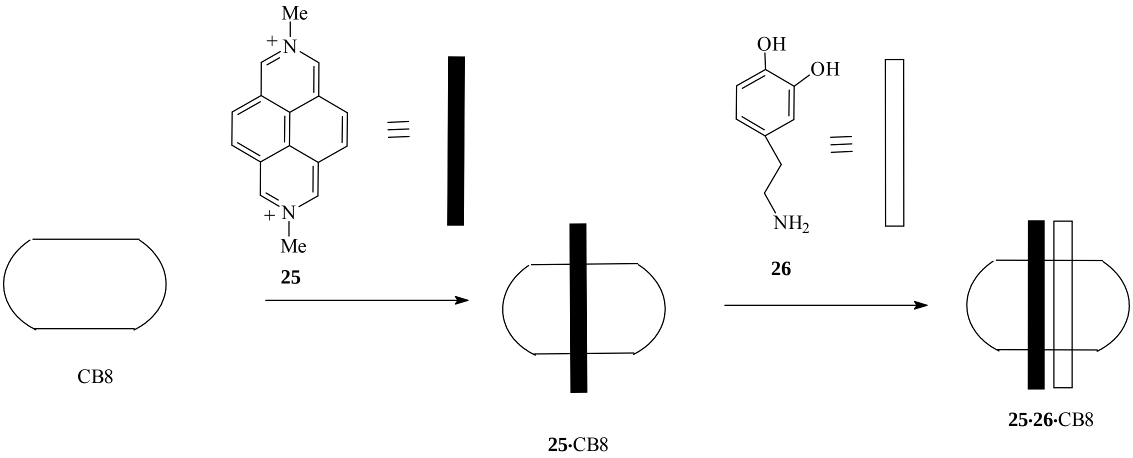
(**24**)2·CB8
(2:1)

The dicationic diazapyrenium (**25**) forms a very stable inclusion complex with CB7. One should note that **25** is the largest molecule hitherto confined in the CB7 cavity. The encapsulation of a such bulky guest requires a distortion of the host; the cross section of the cavity is no more circular, but adopts an elliptical form.[66] The fluorescence intensity of **25** increases upon inclusion into CB7.



25·CB7

In investigation of cucurbiturils it was established that **25** forms with CB8 a highly stable inclusion complex which may encapsulate compounds containing aromatic π-donor units, such as catechol or dopamine (**26**).[67] Dopamine was used as a second guest due to its biological properties; catechol served as a model guest. The CB8 cavity is large enough to include two identical or different aromatic guests. Diazapyrenium compounds have luminescent properties, therefore they are often used as fluorescent probes for the detection of neurotransmitters.[68] The treatment of CB8 with **25** affords binary complex **25**·CB8, which upon addition of **26** gives ternary complex **15**·**26**·CB8.

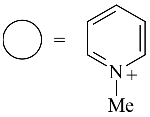


The fluorescence intensity of **25** increases after addition of CB8. It was observed that the fluorescence quenching of **25** by electron-rich guests is stronger when CB8 is present in the solution, *i. e.* the presence of CB8 highly increases the sensitivity of **25** for these aromatic π-donors. The investigation was made also on the surface of silica nanoparticles to which units of **25** have been covalently attached. Similarly as in the solution, the fluorescence quenching was stronger in the presence of CB8.

The above results show the possibility of design of sensors for detection of catechol and dopamine involving their inclusion into **25**·CB8 fluorescent complex. The highly stable inclusion complex (**25**·CB8) may be used for sensitive fluorescent detection of catecholamine neurotransmitters in solution or on the surface of silica nanoparticles.

3. INCLUSION COMPLEXES OF CALIXARENES

Chemistry of calixarenes is developing rapidly since they can form a variety of inclusion complexes with ions and neutral molecules.[69-71] In the study of these compounds it was found that calixarenes (**27**) and (**28a**,**b**,**d**) form 1:1 inclusion complexes with N-methylpyridinium cation (**29**), whereas no complexation of **28c** with **29** occurs; the values of association constants decrease in the order **28b** > **27** > **28a** ≅ **28d**.[72] The inclusion complex (**29·28b**) is shown below.



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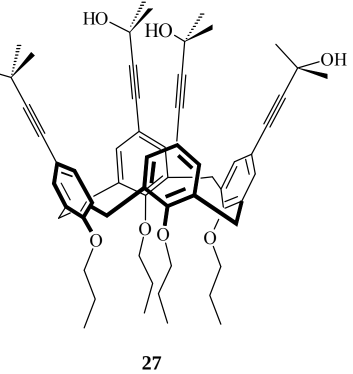

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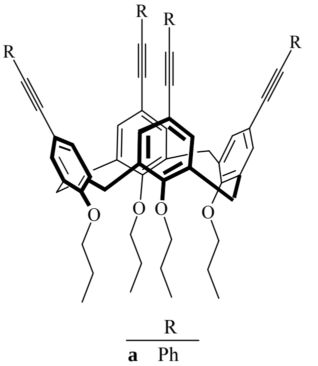
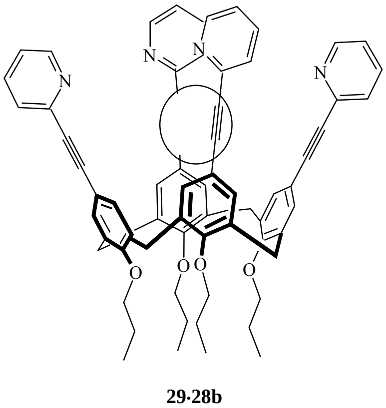


28

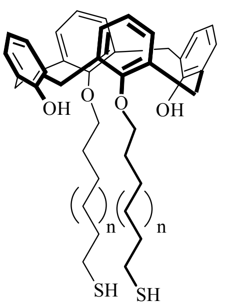
	R
a	Ph
b	2-Py
c	3-Py
d	4-Py



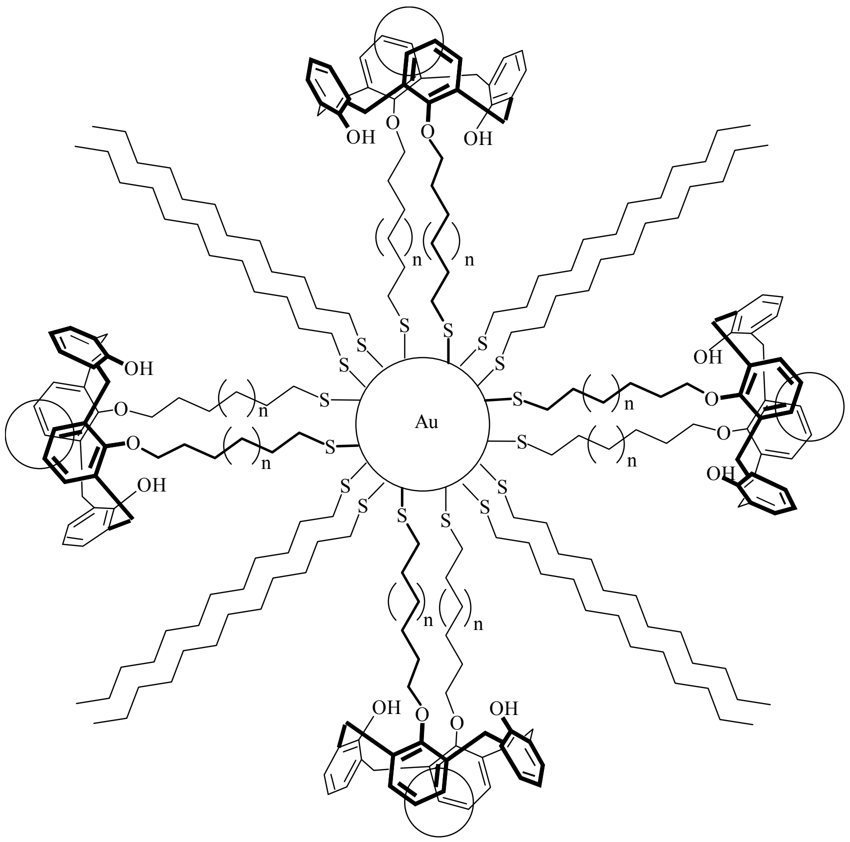
29·28b

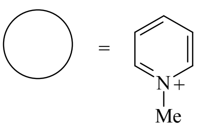
The high complexation energies of **28b** and **27** result from the synergetic influence of additional electron lone pairs of 2-pyridyl and hydroxyl groups, respectively, directing in a synergetic manner to the cavity. The similar association constants in the case of **28a** and **28d** indicate that the presence of nitrogen atom in 4-position has neither an additive binding effect as in the case of **28b** nor a blocking effect as in the case of **28c**.

In the study of monolayer protected clusters containing recognition elements on their surfaces, calixarenes (**30a,b**) have been supported on gold nanoparticles covered with dodecanethiol chains; in the presence of **29** complexes (**31a,b**) are formed.[73] The efficiency of binding increases with the percentage of calixarenes versus dodecanethiol chains, and with the length of the two alkyl chains of calixarenes; it should be noted that in apolar media it is higher than that of corresponding unsupported **30a,b**.



		n
30	**a**	1
	b	6

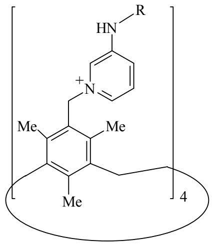




29

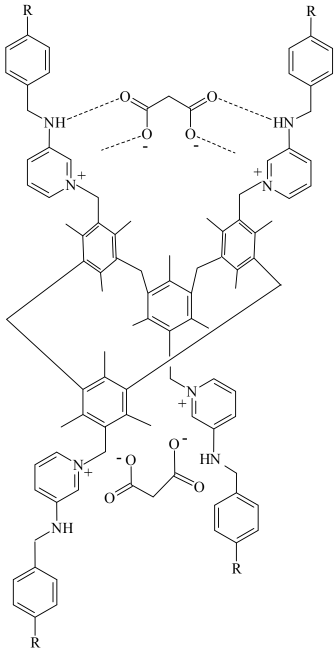
		n
31	**a**	1
	b	6

It was established that calixarene (**32**) in the 1,3 alternate conformation binds dicarboxylate anions such as malonate and succinate; an example is (malonate)$_2$·**32**.[74]



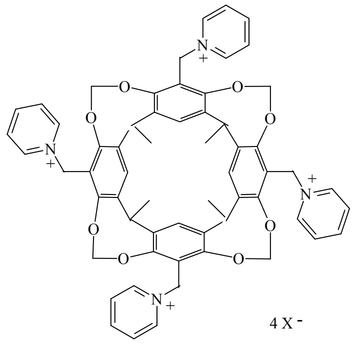
R = $CH_2C_6H_4(CH_2)_4CH_3$

32



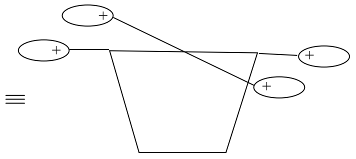
(malonate)$_2$·**32**

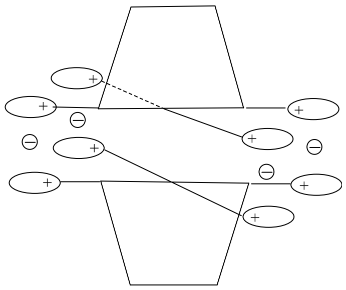
Calixarene- and cavitand-based capsules are a topic of an intense research.[75-77] The triple-ion interactions[78,79] between two cavitand molecules (**33**) have been used for construction of capsules **34**$^{4+}$ linked by four walls. The linking occurs by monovalent ions (bromide, nitrate, acetate and tosylate) leading to pyridinium - anion - pyridinium interactions. The capsule structures have been confirmed by ESI - MS results.[80]



X = Br, NO3, OAc, TsO

33

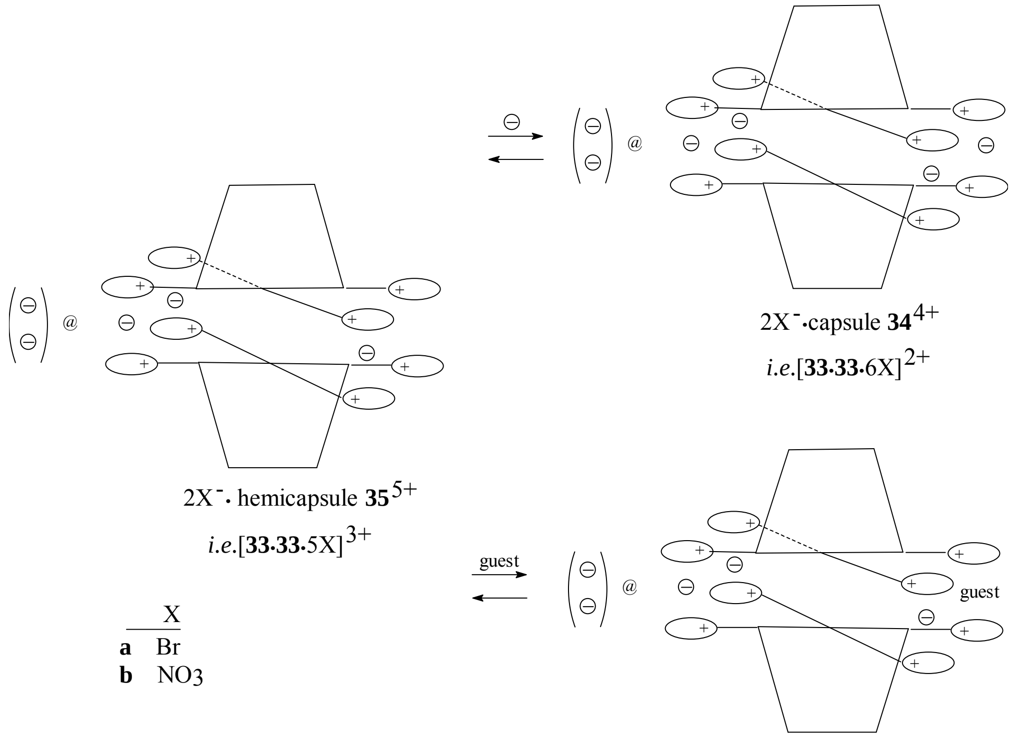




capsule **34**$^{4+}$

i.e.[**33**·**33**·4X]$^{4+}$

Hemicapsules are linked by only three walls, they are a new type of self-assembled receptors.[81-83] Capsules and hemicapsules depending on their size include one or two anions. It was established that 2X$^-$•hemicapsule **35**$^{5+}$, *i.e.* [**33**•**33**•5X]$^{3+}$ upon addition of an anion affords 2X$^-$•capsule **34**$^{4+}$, *i.e.* [**33**•**33**•6X]$^{2+}$ and upon addition of a guest gives rise to the capsule (**36**) incorporating a guest molecule between two proximal pyridinium units; **36** contains three pyridinium-anion-pyridinium walls and one pyridinium-guest-pyridinium wall.[84] The decreasing order of the guest affinity toward [**33**·**33**·5Br]$^{3+}$ is shown below.

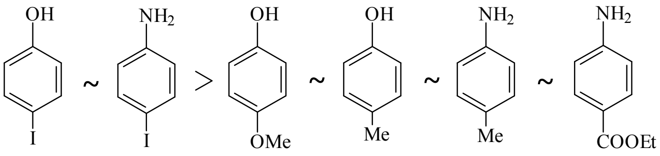


2X$^-$• hemicapsule **35**$^{5+}$
i.e.[**33**•**33**•5X]$^{3+}$

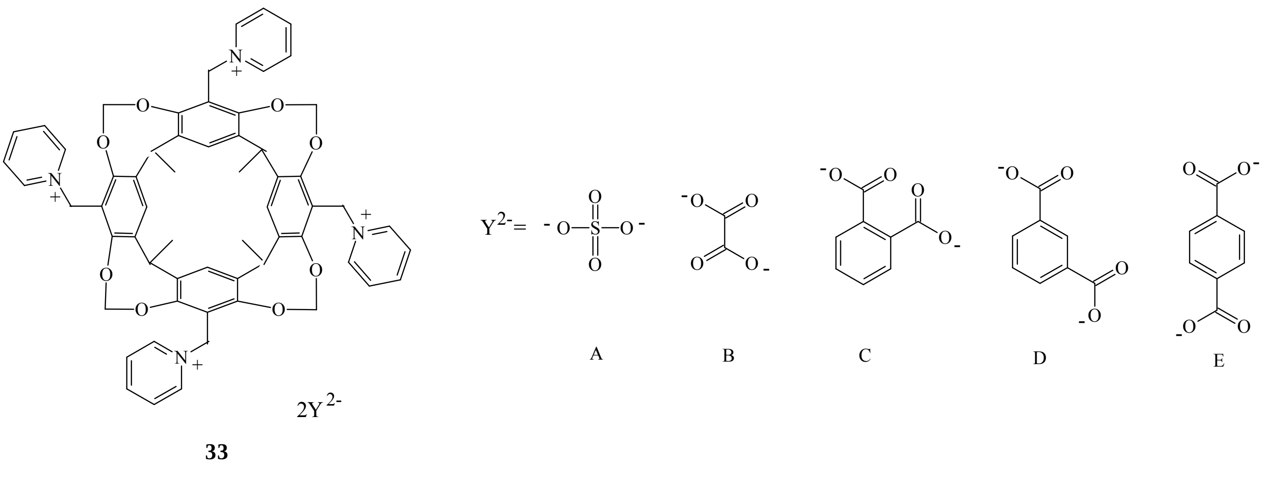
2X$^-$•capsule **34**$^{4+}$
i.e.[**33**•**33**•6X]$^{2+}$

	X
a	Br
b	NO3

36

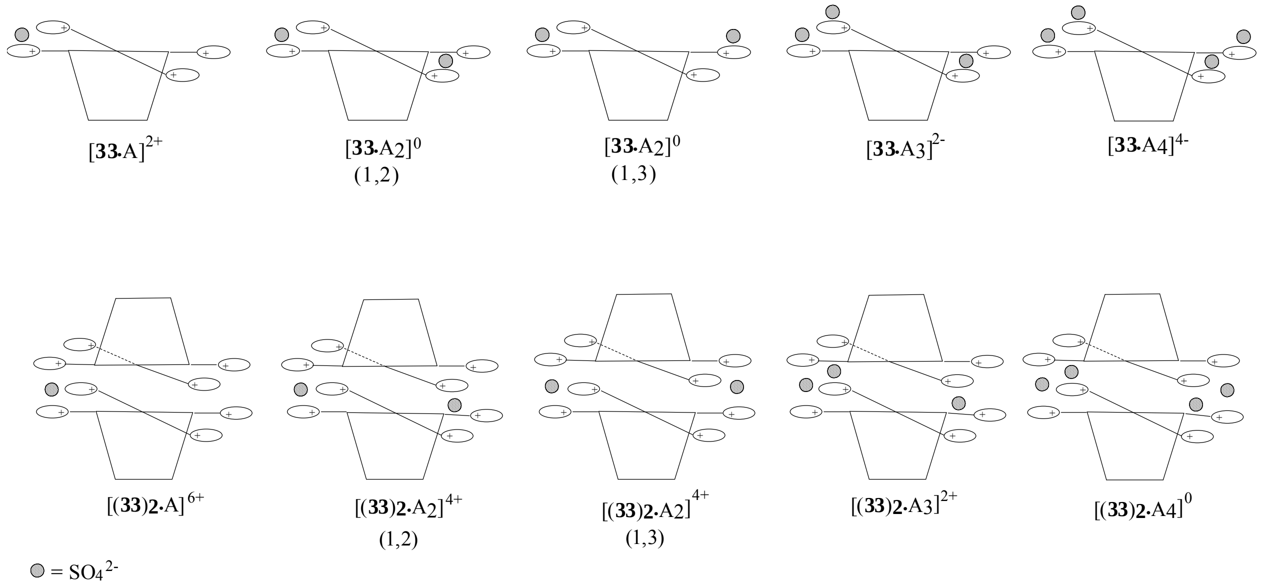


Numerous reports are dealing with self-assembled receptors.[85,86] In the study of self-assemblies[87,88] consisting of multivalent and low-valent components, the salts of cavitand (**33**) with divalent anions A-E have been obtained.[89] In these compounds the multivalent component is **33** having four valencies, and low valent components A – E are doubly charged anions: sulfate, oxalate, phthalate, isophthalate and terephthalate, respectively.



33

The interactions of pyridinium moieties with anions are relatively weak, therefore they lead to formation of numerous intermediates consisting of one or two molecules of **33**, *i.e.* cavitands and capsules, respectively, and one or more anions. The modeling results of assembly of **33** with sulfate (A) connected with ^{1}H NMR dilution experiments show the composition of the mixture at different concentrations. Complexes containing one molecule of **33** are: $[\mathbf{33}\cdot A]^{2+}$, $[\mathbf{33}\cdot A_2]^{0}$, $[\mathbf{33}\cdot A_3]^{2-}$, $[\mathbf{33}\cdot A_4]^{4-}$, and complexes containing two molecules of **33** are: $[(\mathbf{33})_2\cdot A]^{6+}$, $[(\mathbf{33})_2\cdot A_2]^{4+}$, $[(\mathbf{33})_2\cdot A_3]^{2+}$, $[(\mathbf{33})_2\cdot A_4]^{0}$.

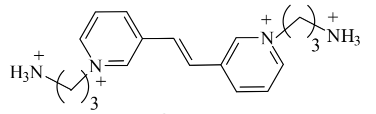


The $[(\mathbf{33})_2\cdot A_3]^{2+}$ hemicapsules, *i. e.* species linked by only three walls form complexes with guest molecules due to the presence of two closely situated pyridinium units which are not connected by an anion. The ESI - MS results show that electrostatic self-assembly of **33** with A in methanol leads to an equilibrium mixture consisting mainly of $[(\mathbf{33})_2\cdot A_3]^{2+}$ hemicapsules and $[(\mathbf{33})_2\cdot A_4]^{0}$ capsules. Their ratio depends on concentration, $[(\mathbf{33})_2\cdot A_3]^{2+}$ prevailing at lower concentrations.

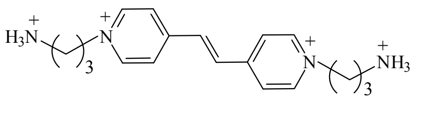
As guests methyl and ethyl 4-aminobenzoates, 4-iodophenol and 4-iodoaniline were used. It was observed that $[(\mathbf{33})_2\cdot(SO_4)_3]^{2+}$, containing small sulfate linkers A incorporates the guest molecule between two closely situated pyridinium units. It should be noted that in the case of large anions, e. g. iso- and terephthalate (D and E, respectively), the guest complexation does not occur, since the distance between two pyridinium moieties is too long.

4. COMPLEXES OF CROWN ETHERS

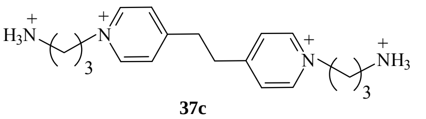
In the study of crown ethers, being efficient ligands for metal and ammonium ions, it was found that viologen analogs (**37a-c**), (*i.e.* electron acceptors A) form with bis (18-crown-6) stilbene (**38**), (*i.e.* electron donor D) very stable1:1 (A·D) and 1:2 (D·A·D) inclusion complexes.[90] Compound (**39**) served as a model species.



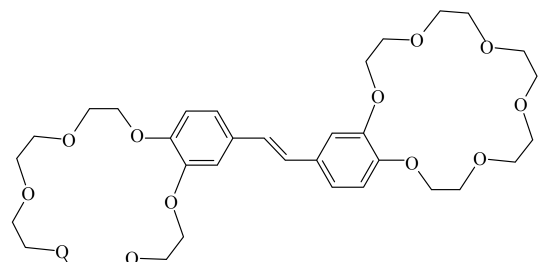
37a



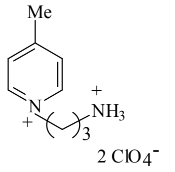
37b



37c

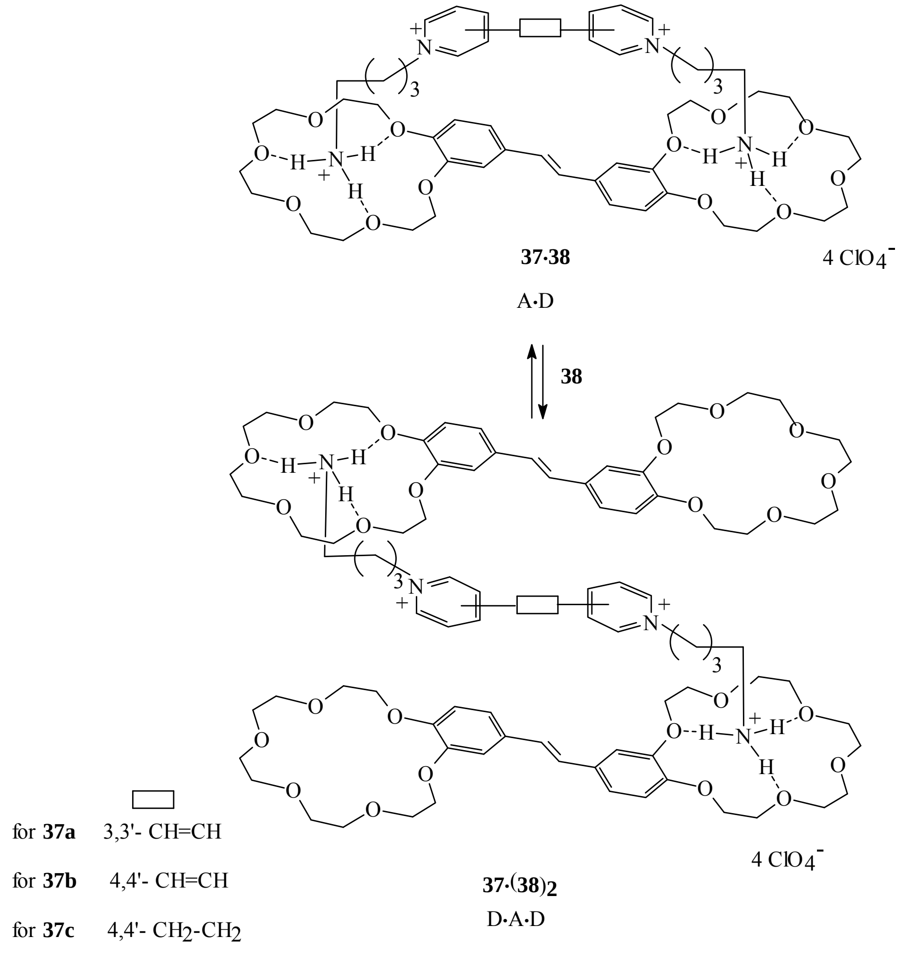


38



39

The stability of A•D and D•A•D complexes is ensured by two types of interactions: relatively strong two-centre host-guest interactions and weaker through-space interactions between the electron acceptor and donor systems, resulting in charge-transfer. The ^{1}H NMR analysis indicates that D•A•D complexes have a sandwich-like layered structure and their acceptor-donor distances are shorter than those in corresponding A•D dyads. These shorter distances result from lower steric hindrances in D•A•D complexes. It was observed that A·D complexes (**37·38**) upon addition of **38** afford D·A·D complexes, *i.e.* **37•**(**38**)$_2$.



37·38 4 ClO_4^-

A·D

38

for **37a** 3,3'- CH=CH

for **37b** 4,4'- CH=CH

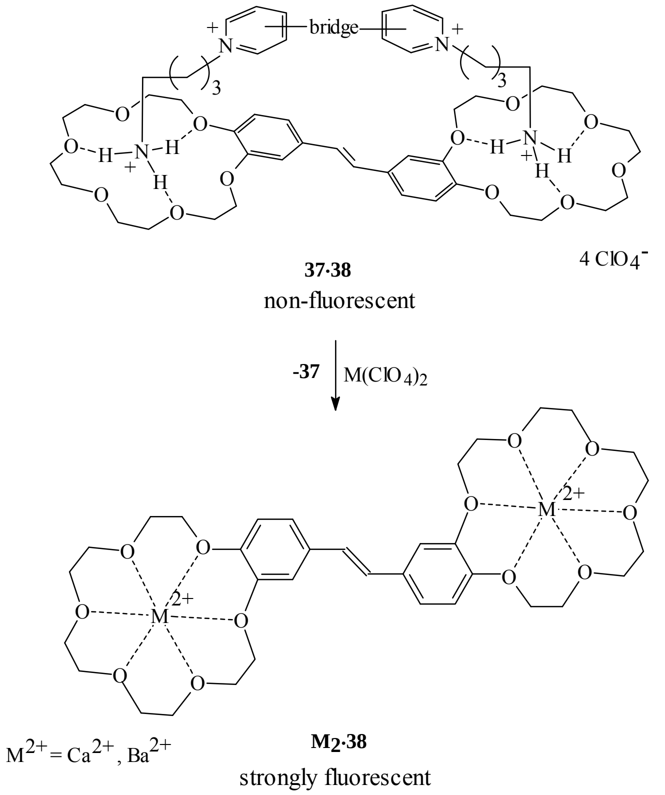
for **37c** 4,4'- CH_2-CH_2

4 ClO_4^-

37·(38)2

D·A·D

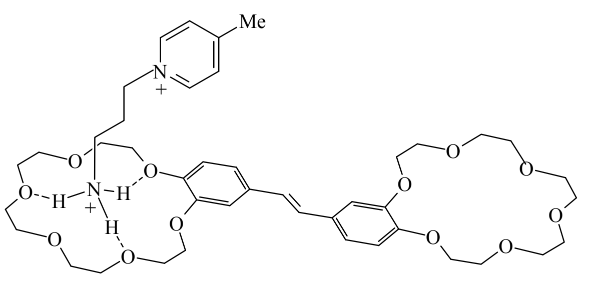
Highly stable A·D complexes (**37·38**) may serve as selective fluorescence sensors for metal ions in non-aqueous media. A dilute solution of the complex (**37·38**) in MeCN is non-fluorescent, however the addition of $Ca(ClO_4)_2$ or $Ba(ClO_4)_2$ induces a strong fluorescence enhancement. This behavior results from the displacement of the diammonium groups from the crown ether molecules by metal ions to give M_2**·38**, the ability of **38** to bind Ca^{2+} and Ba^{2+} ions being higher than the ability to bind diammonium groups of **37**.



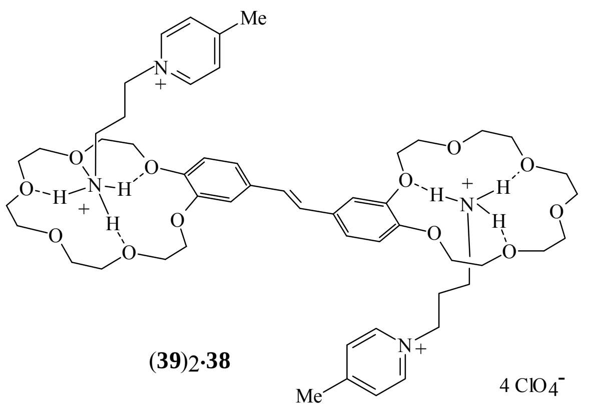
37·38
non-fluorescent

M_2·38
strongly fluorescent

It was found that the model compound (**39**) forms with **38** the 1:1 and 2:1 complexes, *i.e.* **39·38** and (**39**)$_2$·**38**, respectively.

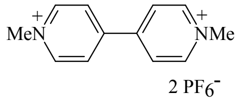


39·38

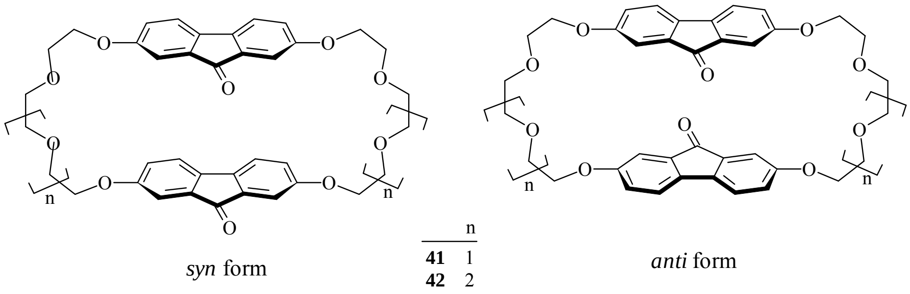


(39)$_2$·38

In investigation of viologens it was established that **40** forms inclusion complexes in gas phase with cyclophanes (**41**) and (**42**) containing crown ether moieties; in complexes viologen is sandwiched between two molecules of **41** or **42** in *anti* conformations.[91]



40

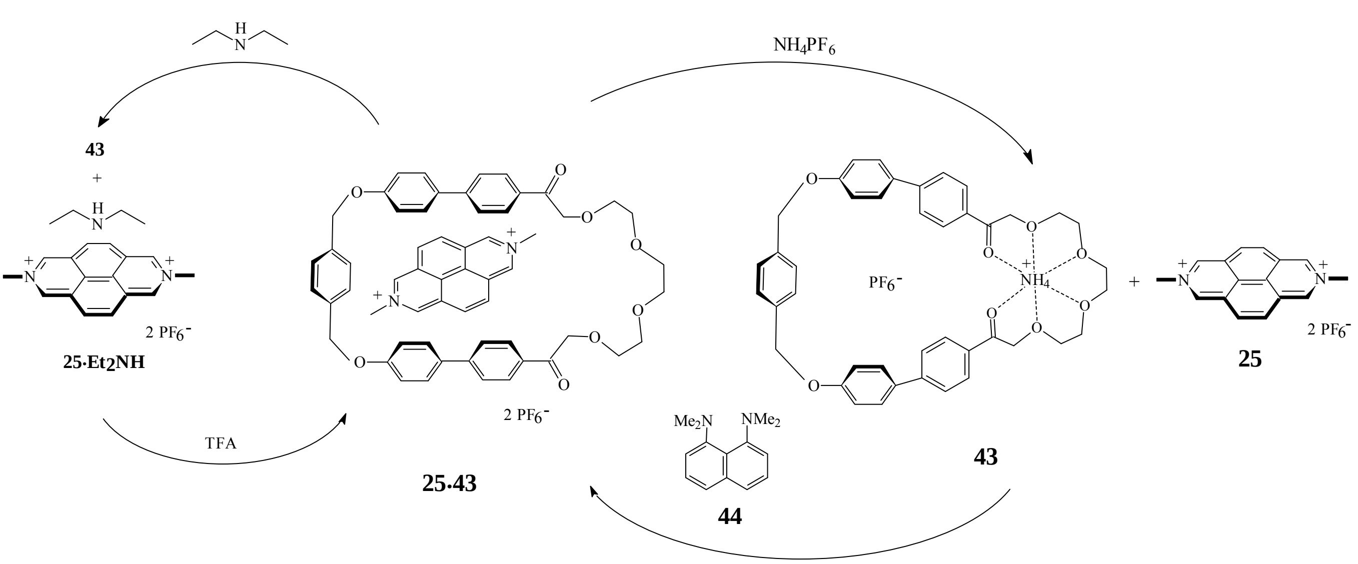


Complexes (**40·41**) and (**40·42**) are held by π-π stacking as well as by dipole-charge interactions between viologen and carbonyl groups of fluorenone units; the additional stabilization results from hydrogen bonds CH…O formed between acidic hydrogen atoms of viologen methyl groups with oxygen atoms of polyether loops of **41** and **42**. The calculated stabilization energy of the complex (**40·41**) is lower than that of **40·42** , in agreement with FAB-MS (fast atom bombardment mass spectrometry) analysis.

A unique dual-action supramolecular system that can be switched between its complexed and decomplexed states using not only an acid/base reagent pair but also a base/acid pair was reported.[92] The complex (**25·43**) contains diazapyrenium ion (**25**) and the macrocycle (**43**). The macrocycle (**43**) consists of a [18]crown-6 moiety which can bind ammonium ion, and π–electron aromatic system, which can bind an electron poor unit, e. g. diazapyrenium ion (**25**).

The addition of an acid, e.g. NH_4^+ ion which binds to [18]crown-6 of the macrocycle (**43**) results in the dissociation of the complex (**25·43**); the subsequent addition of Proton Sponge (**44**) which deprotonates NH_4^+ ions regenerates the complex (**25·43**).[93] The treatment of the complex (**25·43**) with Et_2NH which binds to **25** results in its dissociation; the subsequent addition of TFA protonating Et_2NH affords again the complex (**25·43**).

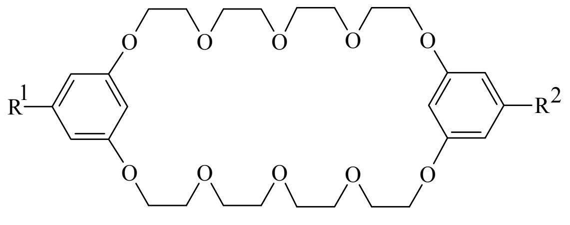
The above system not only can be switched by the sequential addition of acid and base (NH_4^+ ions and Proton Sponge, respectively) but also by a sequential addition of a base and an acid (Et_2NH and TFA), *i.e.* it works as a dual action acid/base and base/acid controllable switch.



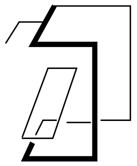
5. TACO AND CRYPTAND COMPLEXES

In the study of taco complexes it was found that folding of the host is an addressable step for complexation; it can be promoted by introduction of substituents that provide additional attractive host-guest interactions. Taco complexes of methyl viologen (**40**) and bis (*m*-phenylene)-32-crown-10 derivatives (**45**) have been investigated.[94] The association constant values of taco complexes decrease in the order **40·45c** > **40·45b** > **40·45a**; this result shows that the presence of CH_2OH groups has a stabilizing effect.

Mixing of **40** with **45b** affords the complex (**40·45b**), stabilized by C-H...O hydrogen bonding and face-to-face π-stacking interactions between pyridinium rings of the guest and phenylene rings of the host. In this complex two β-pyridinium hydrogen atoms form hydrogen bond with oxygen atom of the CH_2OH group. A schematic representation of complex (**40·45b**) is shown below.



		R^1	R^2
	a	H	H
45	**b**	H	CH_2OH
	c	CH_2OH	CH_2OH

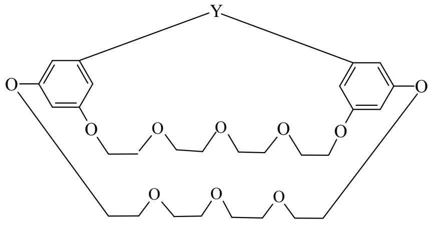


40·45b

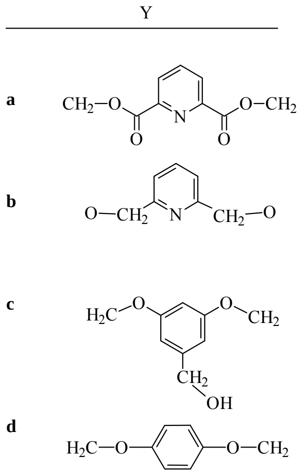
Methyl viologen (**40**) forms strong inclusion complexes with cryptands (**46a-d**).[95] It was observed that cryptands are more powerful receptors for **40** than simple crown ether host (**45a**).[96] The number of atoms in the third bridge of cryptands (**45a-d**) is 9, 7, 7 and 8, respectively. The cryptands (**46a**) and (**46b**) bear pyridyl moiety as a H-bond acceptor site; **46a** contains electron withdrawing carbonyl groups, while **46b** is more electron rich due to the presence of CH_2O moieties. Comparing the length of third bridge, for **46b** and **46c** it is the same (7 atoms), but **46c** has not an additional binding site, *i.e.* pyridyl unit on the third bridge, as it is the case in **46b**.

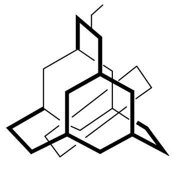
In acetone solutions of **40** with **46a-d** the charge transfer from electron rich aromatic rings of the host to electron poor pyridinium rings of **40** leads to formation of 1:1 complexes.[95] The association constant of **40·46a** is high, equal to 5.0 x 10^6 M^{-1}; it is one of the highest K_a values of viologen complexes. The K_a values of complexes of **40** with **46a-d** decrease in the order **46a** > **46d** > **46b** > **46c**; as compared with K_a values of **40·45a** they are about 9000, 40, 17 and 11 times higher.

Complexes (**40·46c**) and (**40·46d**) are stronger than **40·45a** due to the preorganization of hosts **46c** and **46d**; the complex (**40·46b**) is stronger than **40·46c** since **46b** contains an additional binding site, *i.e.* the pyridyl unit. It was observed that in the solid state **40** forms with **46b** the 1:2 complex, *i.e.* **40**·(**46b**)$_2$. The structures of **40·46c** and **40·**(**46b**)$_2$ are schematically shown below.

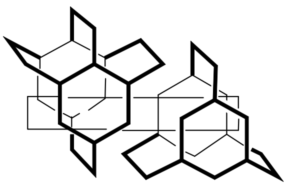


46





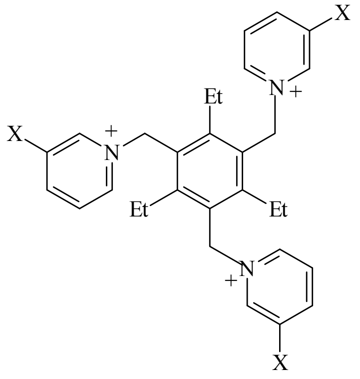
40· 46c



40· (**46b**)2

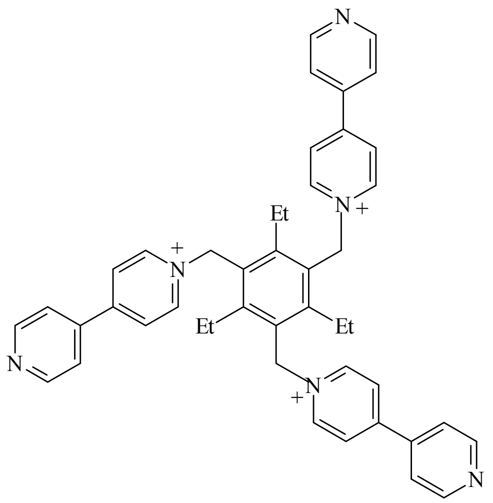
6. COMPLEXES OF TRIPODAL RECEPTORS AND RELATED SPECIES

Many works deal with anion binding systems;[97-100] among flexible tripodal receptors for anions[101-105] the compounds (**47** – **50**) have been investigated.[106] The conformational sensing mechanism of **49** and **50** for halide ion is shown below.

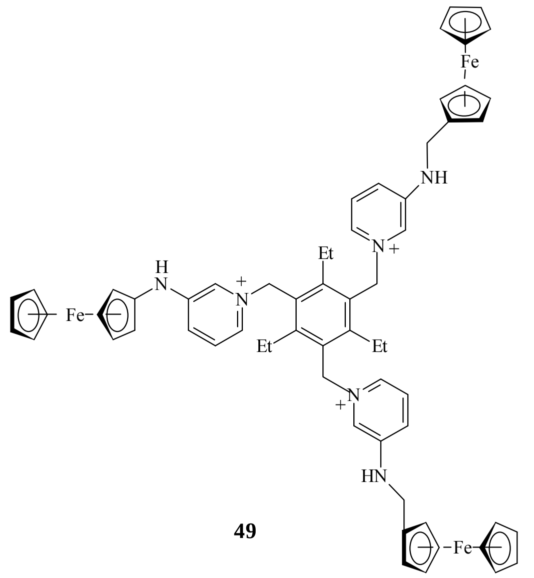


	X
a	H
b	NH_2
c	COOH
d	COOEt
e	$NHCH_2Ph$
f	NHCONHR (R = *p*- tolyl)
g	NHCONHR (R = *n*- octyl

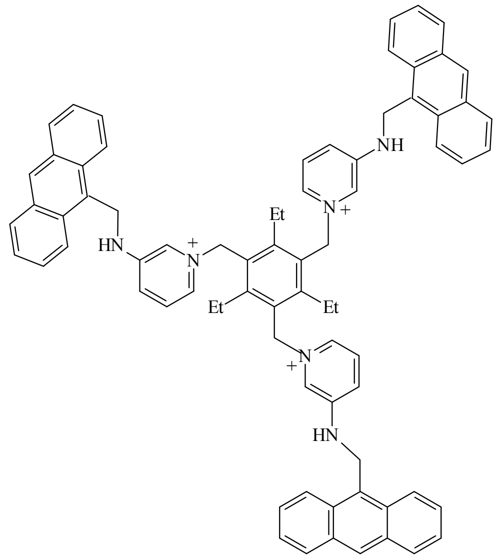
47



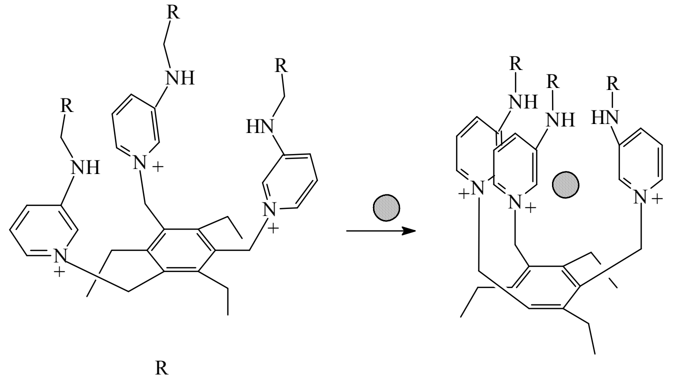
48



49

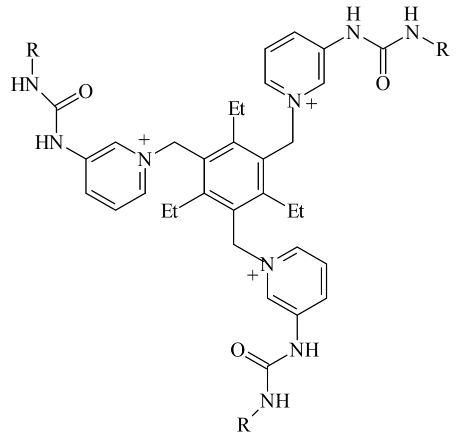


50



R	
49	ferrocenyl
50	anthryl

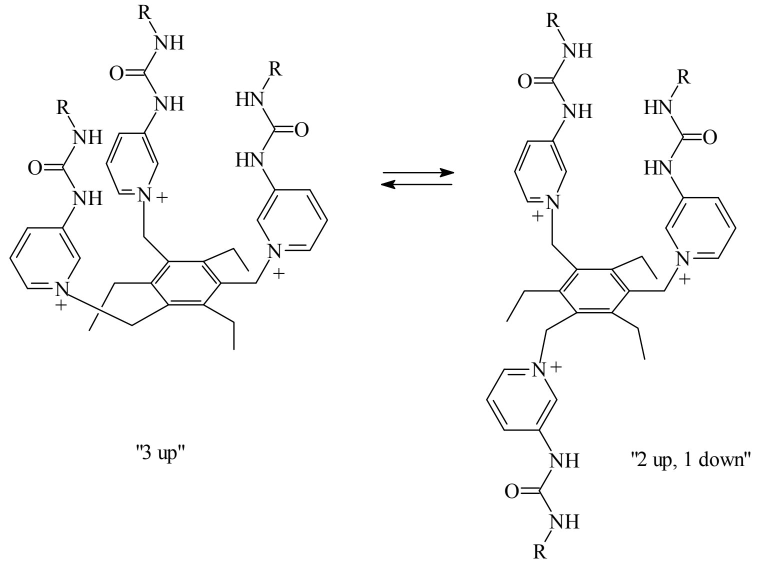
● = halide ion

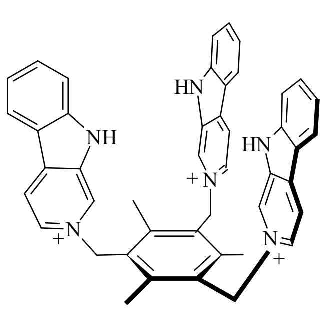


	R
47 **f**	*p*-tolyl
g	*n*-octyl

Tripodal tris(urea) cationic receptors (**47f,g**) form 1:1 complexes with anionic guests. In these complexes anions are situated within the central cavity of hosts, complexes being held by hydrogen bonds from both NH and CH donors. The results of X-ray crystallography of host-anion complexes (**47f** $\cdot Br_3$, **47f** $\cdot$PF6 $\cdot$ $2Me_2CO$ and **47f** $\cdot (NO_3)_{1.5}(PF_6)_{1.5}$) have shown that each structure contains the receptor in a different geometry; this fact confirms the flexibility of the receptor (**47f**) and the dependence of its geometry of the kind of anion.[107]

In solution the flexible nature of receptors enables complexation of a variety of simple inorganic anions. The results of ^{1}H NMR spectroscopic titrations have revealed that **47f** and **47g** show a high affinity for halides and hydrogen sulfate. The computational study using density functional theory has been employed for investigation of binding of **47f** and **47g** with chloride ion. The obtained results have shown that for **47f** ·Cl the "3 up" is the lowest energy conformation enabling the existence of an unimolecular capsule sealed by CH.... π interactions, while in the case of **47g**·Cl the less symmetrical "2 up, 1 down" conformation is the most stable.





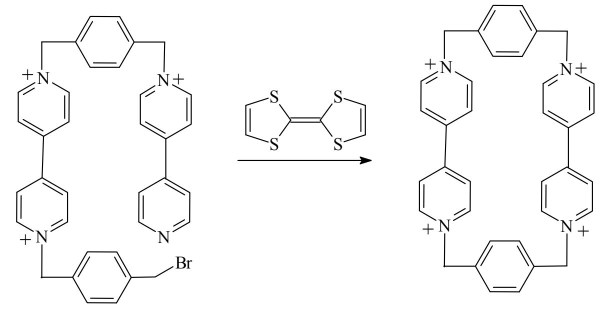
51

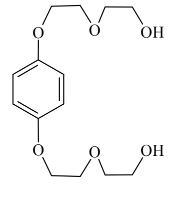
The trifurcate trication (**51**) forms hydrogen-bonded complexes with anions; their stability decreases in the order Cl$^-$ > Br$^-$ > OH$^-$ >≅ NO$_3^-$ > F$^-$ > I$^-$ ≅ AcO$^-$. (As a source of all anions tetrabutylammonium salts were used, except for Cl$^-$ for which benzyltributylammonium chloride was more convenient).[108] The receptor donates to the included anion up to six hydrogen bonds, formed from three pyrrole N-H groups and from three C-H groups adjacent to quaternary nitrogen atoms.

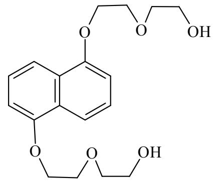
It was observed that **51** forms very stable 1:1 complexes with halides; it selectively recognizes Cl$^-$ in the presence of fluoride and bromide ions. The high stability of complexes with Cl$^-$ and Br$^-$ is due to the presence of positively charged pyridinium moieties enhancing the hydrogen-bond donor abilities of three CH groups adjacent to nitrogen atoms. The F$^-$ ion is too small to attain the full coordination shown by the larger Cl$^-$ ion, and interacts with only a single arm of **51**.

One should also mention here the observation of a high template effect of tetrathiafulvalene (TTF) in the ring closure of **52** leading to cyclophane (**53**). The results of UV-Vis spectroscopy have shown that the reaction affording **53** is ca 80 times faster in the presence of TTF.[109,110]

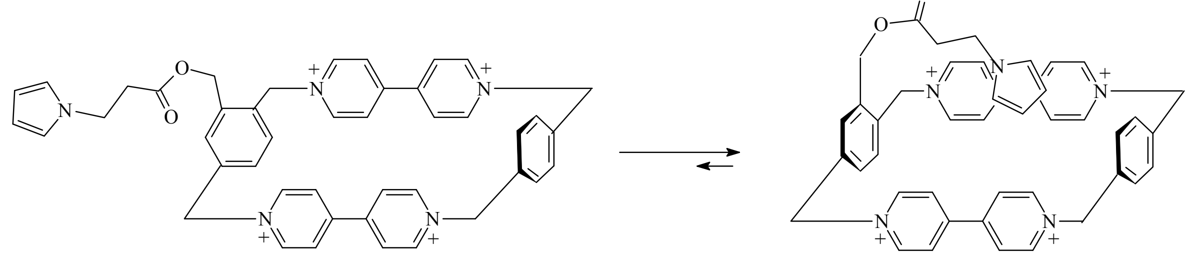
The above study indicates that the electron-rich molecule TTF, which does not possess polyethereal side chains has a higher template ability than that of such electron-rich aromatic molecules containing polyethereal side chains as **54** or **55**.


52 53

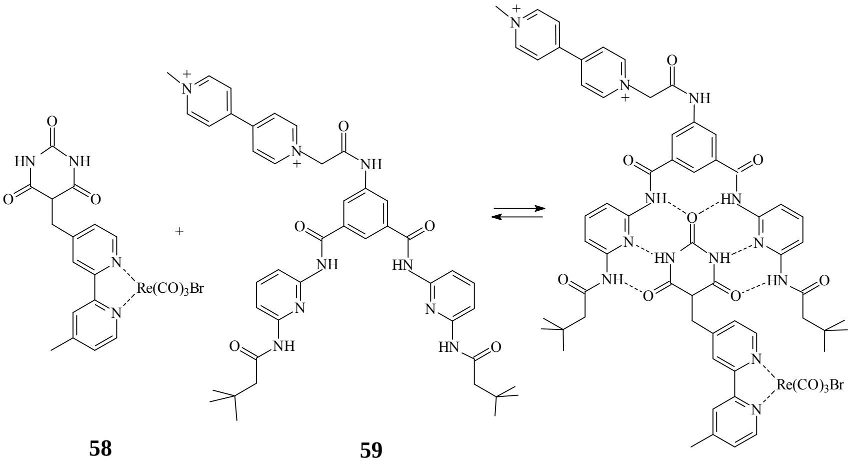

54

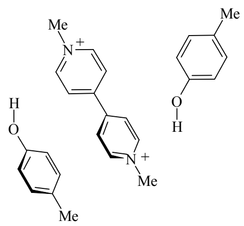

55

It was found that the donor-acceptor system (**56**) undergoes a self-complexation affording **57**.[111] In **56** the cyclophane is an electron poor moiety, and the arm containing pyrrole group serves as an electron rich unit. It was observed that **57** may be decomplexed by using external stimuli such as heat, electrochemical reduction or addition of the competitive guest, for example TTF.


56 57

The rhenium complex (**58**) acting as an efficient electron donor serves as a guest, and viologen derivative (**59**) acting as an electron acceptor serves as a host in the formation of the photoactive supramolecular hydrogen bonded dyad (**58·59**).[112] Investigating **58·59** it was observed that upon excitation of **58**, an ultrafast electron-transfer process occurs from the metal-based **58** to **59**.


58 59 58·59


60

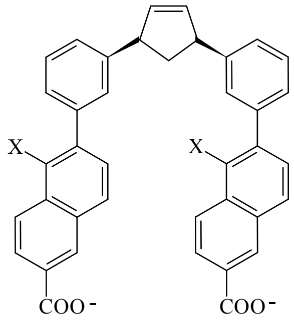
In the study of inclusion complexes containing an inorganic host, polycyano-polycadmate host clathrates including a guest (**60**) which is a CT complex of methylviologen dication with an aromatic donor have been synthesized.[113] The host built with Cd^{2+} ions as coordination centers and cyanide ions as ligands has a negative charge and includes a cationic species together with the neutral electron donor.

The polycyano-polycadmate host clathrates embedding a CT complex of methyl viologen dication with an aromatic donor were prepared by treating an aqueous solution of $K_2[Cd(CN)_4]$, $CdCl_2 \cdot 2.5H_2O$ and viologen dichloride with a donor; as such *o*-cresol, *m*-cresol, *p*-cresol, aniline or pyrrole have been used. A schematic representation of the CT complex serving as a guest which consists of methyl viologen and *p*-cresol is shown.

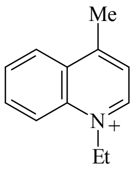
Investigation of crystal structures of obtained polycyano-polycadmate host clathrates including a CT complex of methylviologen dication and aromatic donor has shown the large red shift of their CT transition bands as compared to those observed in acetonitrile solution.

7. COMPLEXES OF TWEEZERS AND CLIPS

Tweezers and clips binding aromatic guest molecules are a topic of numerous works.[114] Tweezers (**61a,b**) have been designed with the use of the computer program CAVEAT.[115-118] The complex formation of **61a** and **61b** with 1-ethyl-4-methylquinolinium cation (**62**) was studied by ^1H NMR titration. It was observed that **61a** binds the guest stronger than **61b** does. The weaker binding of **61b** with the guest is due to the inductive effect of chlorine atom, and resulting diminished binding of the electron-poor guest.

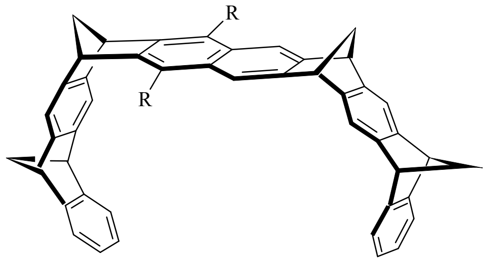


61	X
a	H
b	Cl



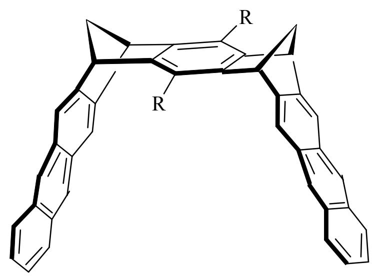
62

It was established that water soluble naphthalene tweezer (**63**) and anthracene clip (**64**) form highly stable inclusion complexes with N-methylnicotinamide (**65**) in methanol; **65** is the enzyme cofactor model. Compounds (**63**) and (**64**) are water soluble. The true binding constants of formation of **65·63** and **65·64** in water are significantly higher than those observed in methanol.[119] The thermodynamic parameters determined by ^1H NMR titration experiments show that the strong binding of **63** and **64** with **65** observed in aqueous solution is enthalpy driven.



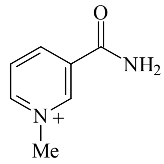
63

R = OP(CH$_3$)O$_2^-$ Li$^+$



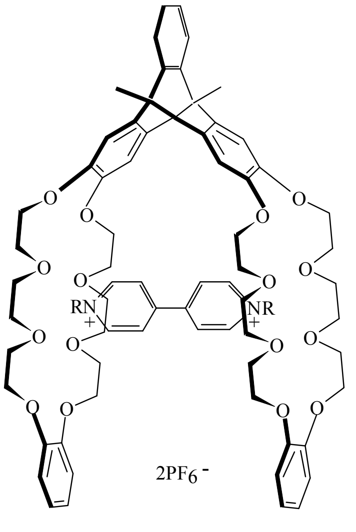
64

R = OP(CH$_3$)O$_2^-$ Li$^+$

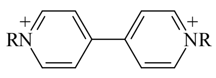


65

Triptycenes have a rigid structure enabling their use as building blocks of supramolecular species.[120-122] It was found that triptycene (**66**) forms with viologens (**67a,b**) the 1:1 clip-shaped complexes in acetonitrile solution and in solid state.[123] The apparent association constant for **67a·66** is higher than that for **67b·66**, this fact presumably being due to shorter distance contacts for **67a·66** as compared with **67b·66**. It should be pointed out that complexation processes between **66** and **67a,b** may be controlled by changing pH, this fact being promising in the design of chemically controlled molecular machines.[124]



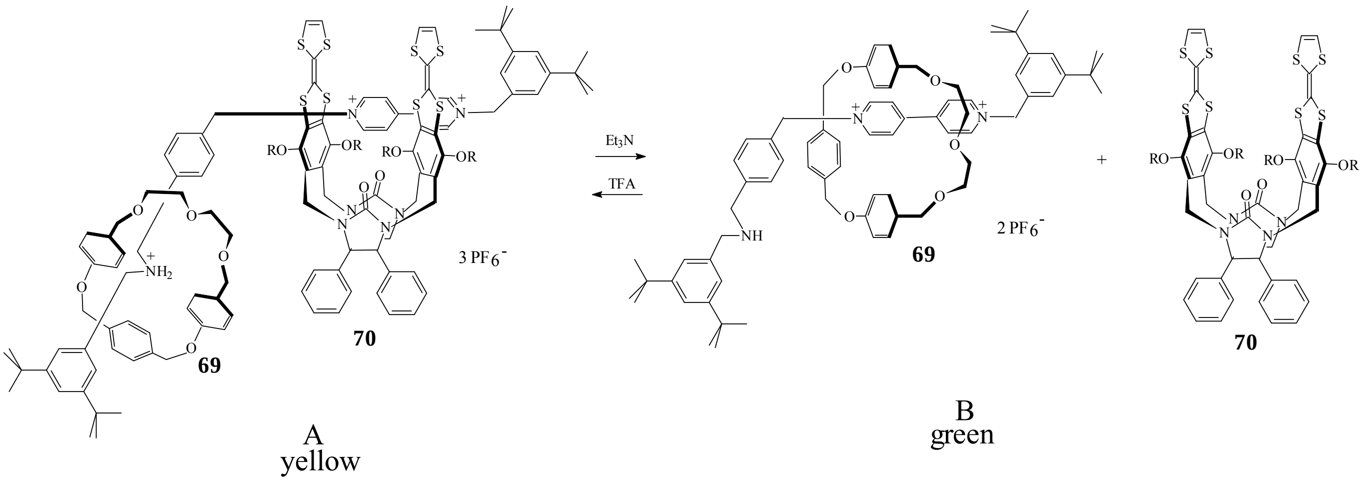
67·66



2PF$_6^-$

		R
67	**a**	Me
	b	*n*-Pr

A monitored by a naked eye, pH-controllable molecular switch (**68**) has been reported.[125] The system consists of [2]rotaxane (built from the ring (**69**) and the thread with dibenzylammonium and 4,4'-bipyridinium stations) and of the TTF-side-walled molecular clip (**70**).[43,126] Molecular clip (**70**) can attach only to bipyridinium site. The treatment of **68** (state A, yellow) with a base results in the shift of the ring (**69**) to bipyridinium station resulting in the formation of [2]rotaxane and the release of the clip (**70**) (state B, green). The subsequent addition of TFA results in the return of the ring (**69**) to the original position around the ammonium ion and the attachment of clip (**70**) leading back to the state A.



R = $(CH_2CH_2O)_3CH_3$

An advantage of this visually monitored switch is the fact that it can be operated as a molecular logic gate; it is promising for design of supramolecular nanovalves[127] allowing to control the flow of molecules within porous materials.

CONCLUSION

The study of inclusion complexes containing quaternary azaaromatic moieties deserves an attention; it is a part of supramolecular chemistry developing rapidly and promising the design of new interesting materials useful for switches and for molecular machines.[13,14]

An intense research concerning chemistry of inclusion complexes has its reflection in a great number of appearing reports. Many works deal with receptors such as cyclodextrins,[128] calixarenes[129] and cucurbiturils[130] due to their interesting properties and application possibilities; an increasing attention is paid now also to complexes of cryptands,[131,132] tweezers[133] and clips.[134]

Cyclodextrins, among other applications, are promising in polymer design[135] and in biosensing.[128,136] Calixarenes are of interest for example in the construction of nanomaterials[129] and may serve as receptors for anions [137,138] and metal ions.[139,140] It should be pointed out that relatively easy syntheses of cyclodextrins, calixarenes and cucurbiturils are an additional advantage in their use as receptors in inclusion complexes.

Although in the above review only chosen examples of inclusion complexes have been shown, one may hope that some insight into this promising research area was achieved.

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