HETEROCYCLES,Vol. 57, No. 11, 2002, pp. 2179 - 2206, Received, 22nd July, 2002

CAVITANDS AND RELATED CONTAINER MOLECULES

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Abstract- The chemistry of cavitands and container molecules, so covalently as noncovalently linked, is reviewed. Synthetic approaches and complexing properties of some of the above species are described.

1. INTRODUCTION

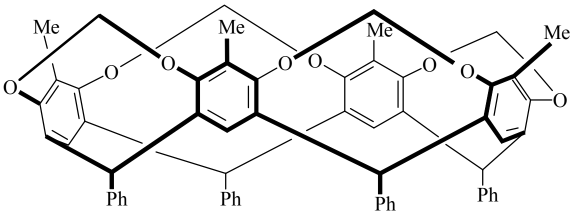
Cavitands are rigid, bowl-shaped molecules, the name being derived from their interior forming a cavity. The classification of these species into simple and deep ones depends on dimensions of their building walls. They are prepared from resorcinarenes by bridging hydroxyl groups – in the case of simple cavitands by small units, often methylenes, and in the case of deep cavitands by larger moieties, often those of a heterocyclic character.[1]

Cavitands of a simple [2-4] or deep structure, [5-7] as well as related containers [8-11] are a topic of a growing interest due to their binding abilities as host molecules; this domain of supramolecular chemistry is developing rapidly. [12-17]

In a continuation of our studies concerning cavitands [18] and calixarenes, [19-23] including calixpyrroles [24] and heteracalixarenes (i.e. calixarenes having in their bridges N, O or S atoms), [25-27] in this paper we describe selected examples of simple and deep cavitands as well as related container molecules, among these latter so covalently as noncovalently linked ones.

2. SIMPLE CAVITANDS

An example of a simple cavitand is **1**, able to include two C_{60} molecules.[28] In the case when single crystal structure determination of host-guest system is impossible, the vibrational spectroscopic study may be of use. The FTIR spectra of cavitands (**2a,b**) and their clathrates with ethanol and toluene have been investigated.[29] The obtained results are in accordance with their crystal structure analysis.



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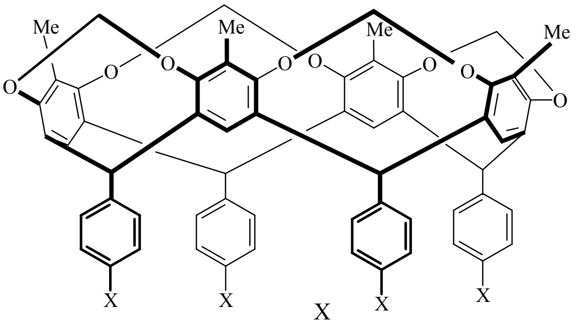
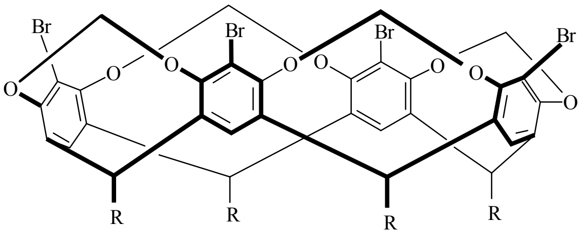


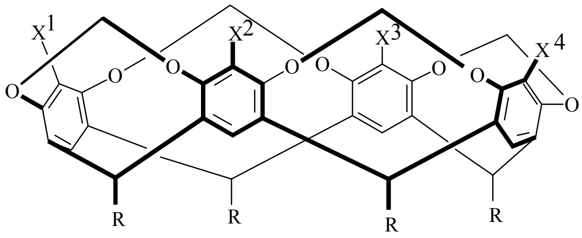
		X
2	**a**	Br
	b	CN

One-pot reactions of tetrabromocavitand (**3**) with *n*-butyllithium followed by trimethyl borate and the subsequent oxidative cleavage with basic H_2O_2 afford , depending on conditions, mono-, di- (two isomers vicinal and distal ones), tri- and tetrahydroxycavitands (**4a-e**).[30,31]



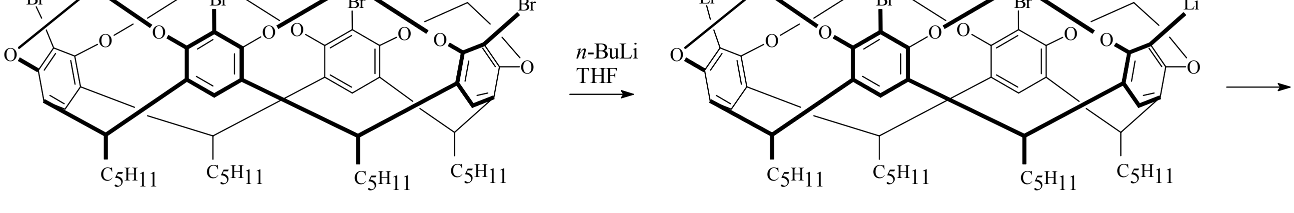
$R = C_{11}H_{23}$

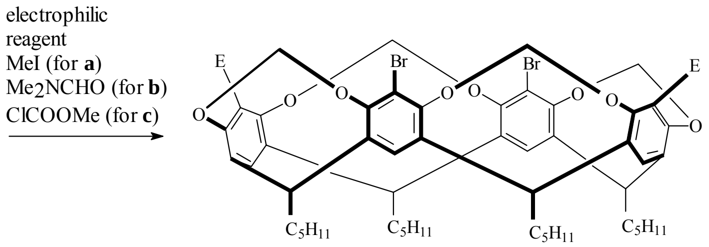
3



		X^1	X^2	X^3	X^4
4	**a**	OH	Br	Br	Br
	b	OH	OH	Br	Br
	c	OH	Br	OH	Br
	d	OH	OH	OH	Br
	e	OH	OH	OH	OH

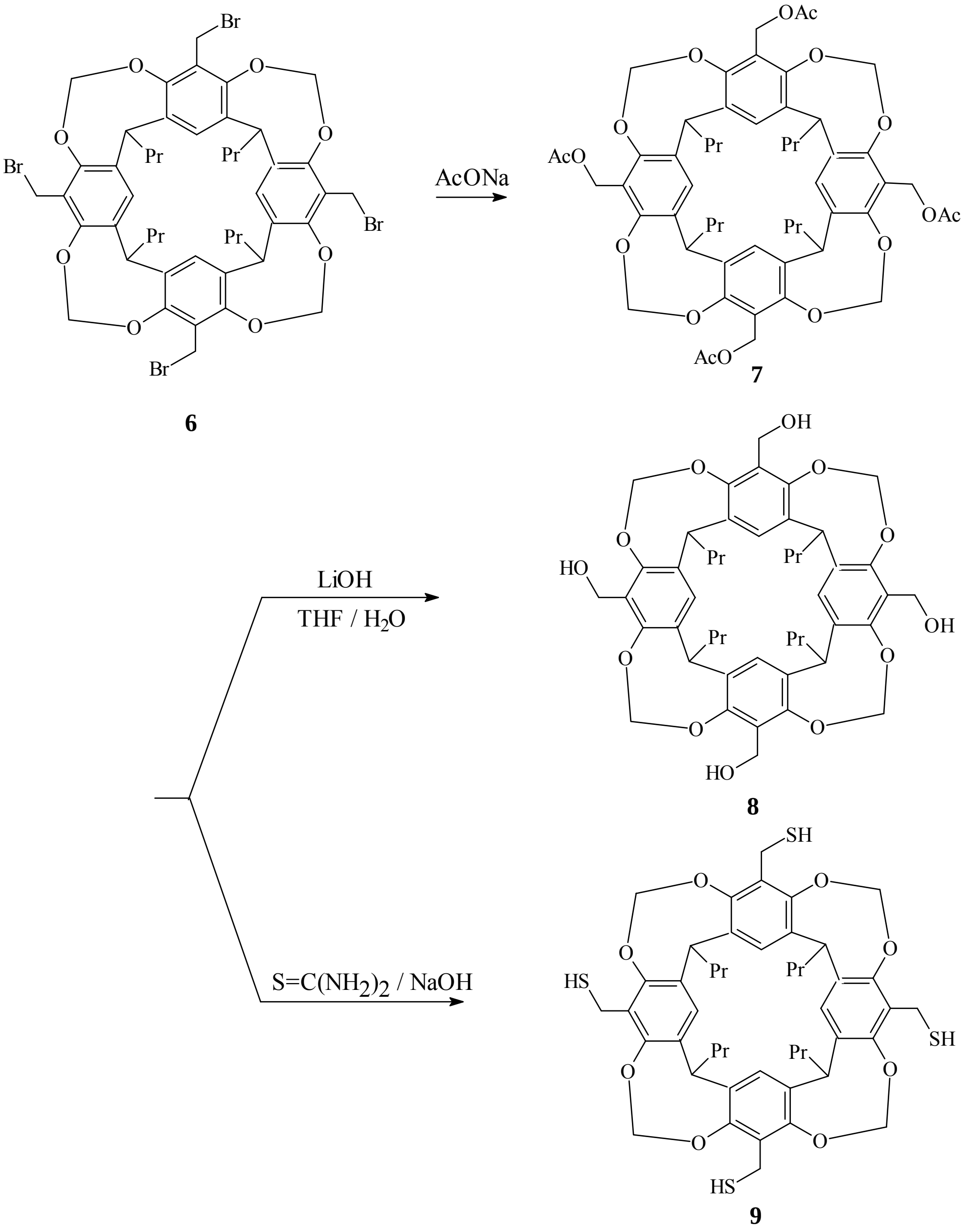
In the study of substituted cavitands, distally difunctionalized species (**5a-c**) have been obtained by the following procedure.[3]





		E
	a	Me
5	**b**	CHO
	c	COOMe

Cavitand (**6**) undergoes substitutions, for example its reaction with AcONa gives five different $(CH_2OAc)_{4-n}$ $(CH_2Br)_n$ cavitands (**7**) (n=0 – 3). The hydrolysis of **7** with LiOH leads to $(CH_2OH)_{4-n}$ $(CH_3Br)_n$ cavitands (**8**), and treatment with thiourea and NaOH yields $(CH_2SH)_{4-n}$ $(CH_2OH)_n$ cavitands (**9**) (n= 0 – 3). [4] These reactions, affording **7** – **9** (n=0) are shown below.



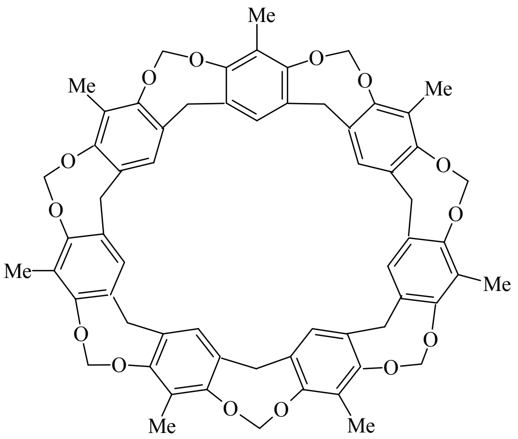
6

7

8

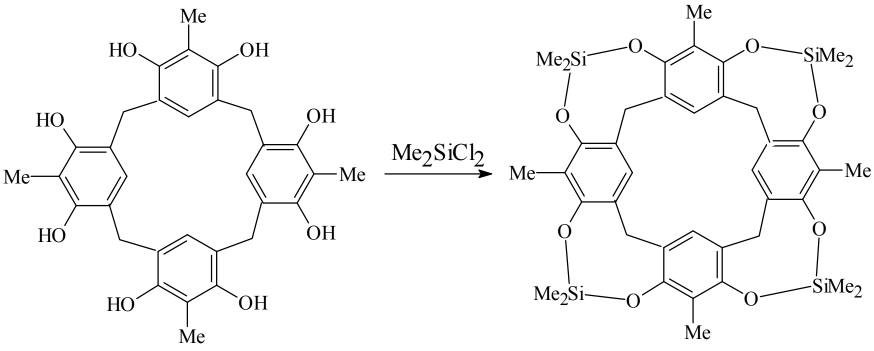
9

An example of an expanded cavitand is **10**. Cavitands containing 4 and 5 aromatic moieties exist in cone conformations, while in the case of larger molecules (n= 6 and 7) the deviation of cone conformation is observed, due to steric crowding of $ArOCH_2OAr$ bridges. [32]



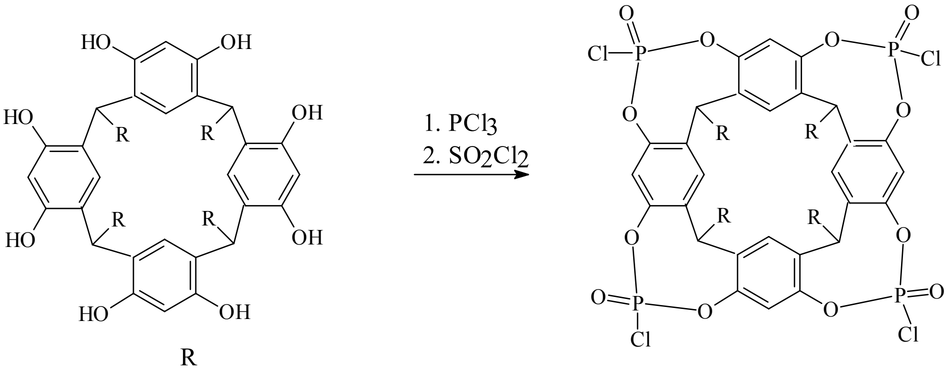
10

The reaction of calix[4]resorcinarene (**11**) with Me_2SiCl_2 affords dimethylsilyl-bridged cavitand (**12**), which encapsulates H_2O molecule. [33]



11 **12**

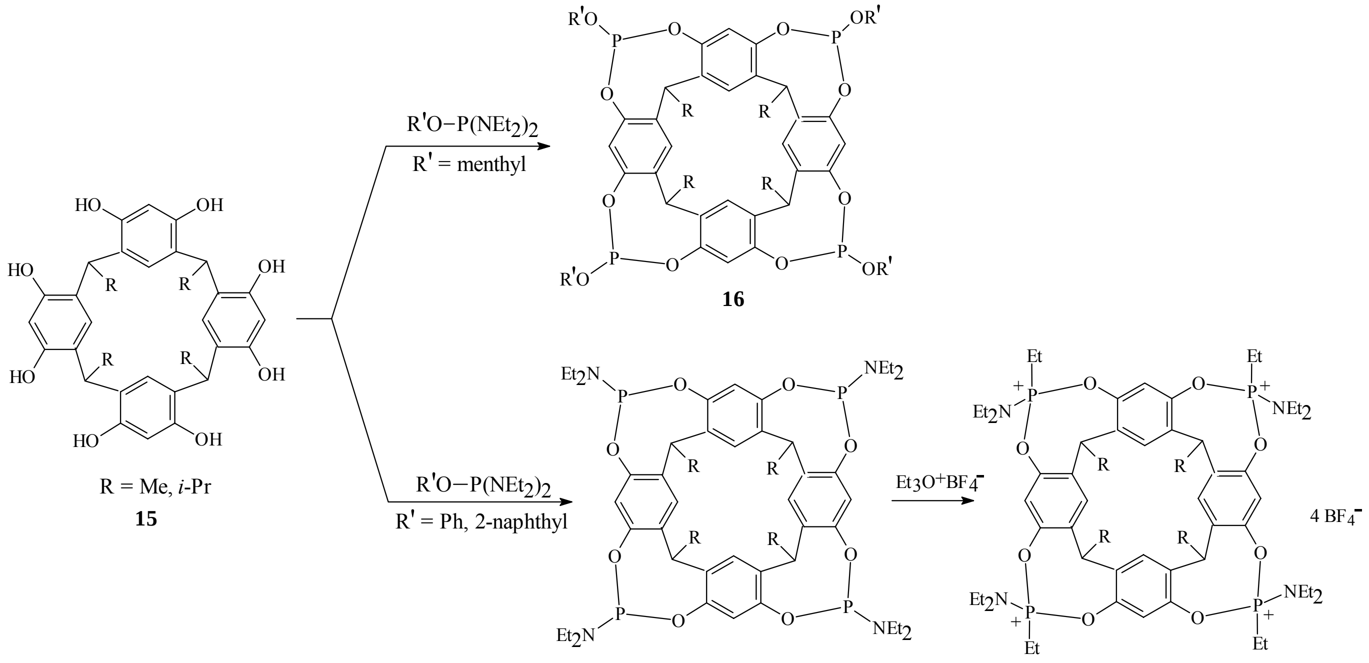
In the study of cavitands bridged by phosphorous groups, [34-38] cavitands (**13**) have been obtained from corresponding resorcinarenes (**14**) by treatment with PCl_3, followed by SO_2Cl_2 oxidation. [39]



		R
	a	C_5H_{11}
14	**b**	C_6H_{13}
	c	$C_{11}H_{23}$

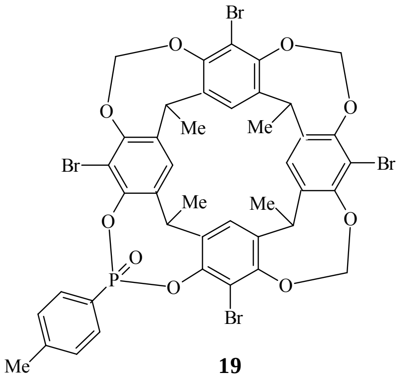
13

Examples of reactions of **15** leading to differently bridged cavitands (**16**) [40] and (**17**) [41-43] and the reaction of the latter with $Et_3O^+BF_4^-$ affording **18** are shown below. [44]



15 **16** **17** **18**

The formation of host-guest complexes between cavitands (**19-21**) and alkyl- or arylammonium ions was investigated by liquid secondary-ion mass spectrometry (LSIMS). As guests served methylammonium > dimethylammonium > benzylammonium > trimethylammonium ions (shown in the decreasing order of their binding constants). [45,46]



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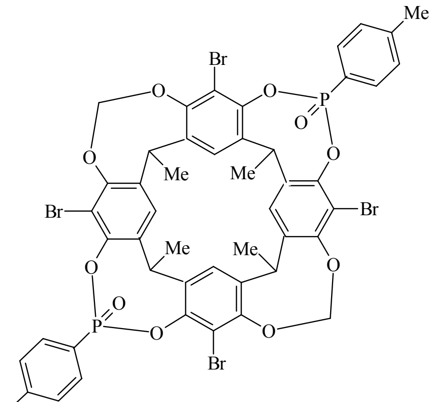

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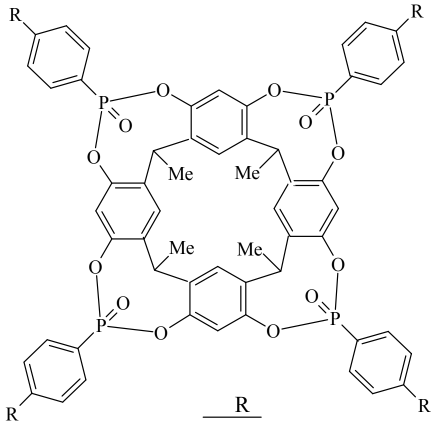
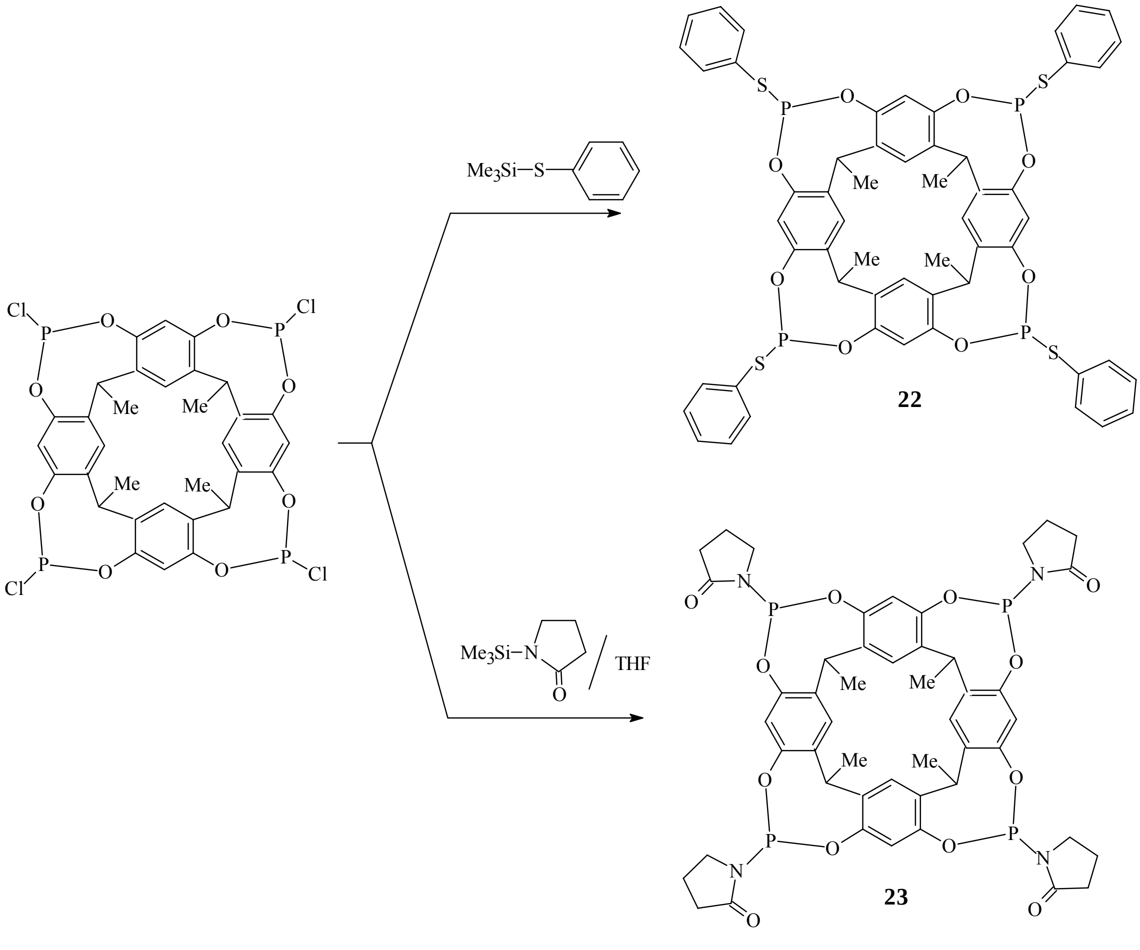
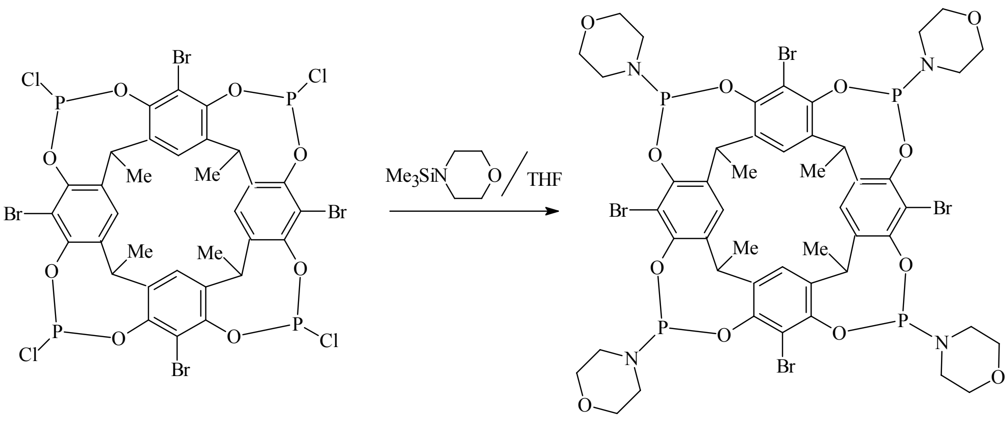


	R
a	H
21 b	Me
c	*t*-Bu

It was established that only cavitands bearing three P=O groups oriented inwards form strong host-guest complexes; those bearing two converging P=O groups (either vicinal or distal) form weaker complexes, and those with no converging P=O group do not act as hosts. Such cavitands have high proton affinities and are rigid; they are able to form strong hydrogen bonds. It was found that the binding properties of cavitands (**21**) increase in the order **21a**<**21b**<**21c**.

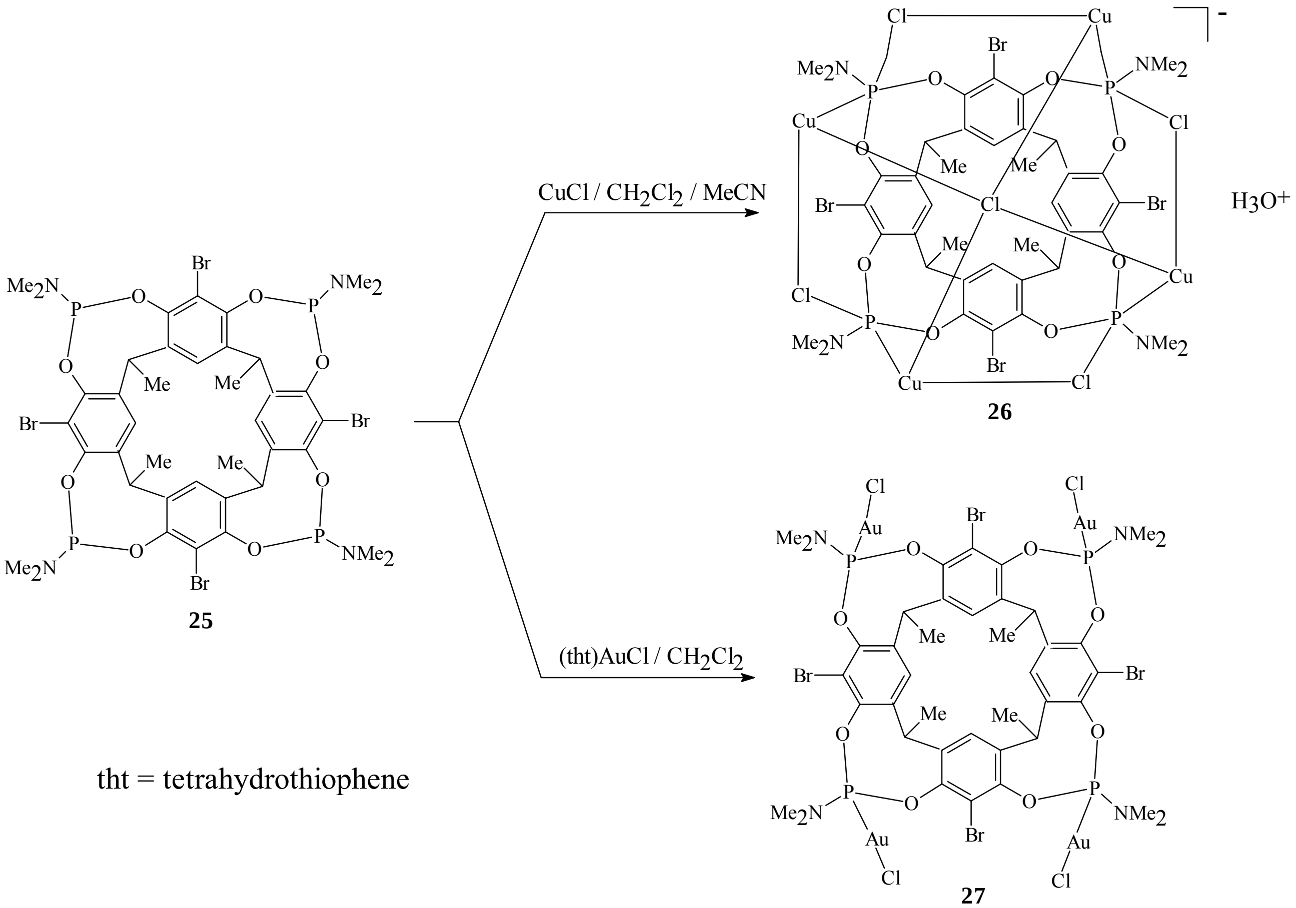
The binding of guests results from the fact that the convergence of three P=O (inwards) groups forms a multipoint hydrogen-bonding pattern. The methylammonium ion has the highest affinity resulting from its possibility to form three hydrogen bonds, while trimethylammonium ion, having only one hydrogen atom shows the lowest affinity. LSIMS experiments allow to predict the behavior of phosphate-bridged cavitands as receptors in analytical applications, for example the detection of ammonium ions in water. [45] Cavitands (**22** – **24**) have been obtained as follows. [47]





24

Complexation reactions of **25** with CuCl and (tht)AuCl lead to cavitands (**26**) and (**27**), respectively. [47]



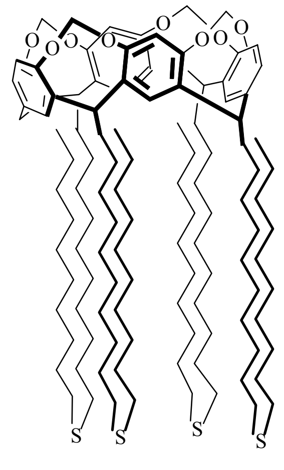
25

26

27

tht = tetrahydrothiophene

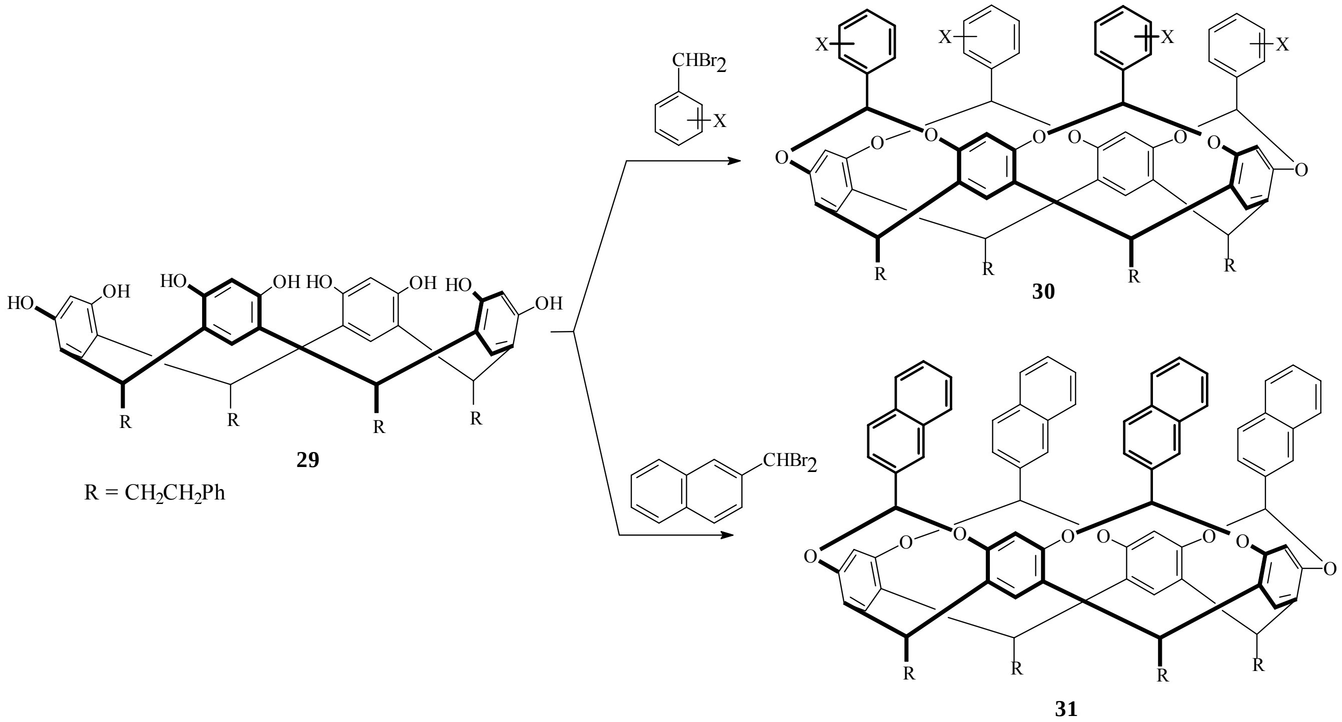
Cavitand (**28)** may be used as an ink in microcontact printing on gold; it has high molecular weight and forms well-ordered self-assembled monolayers (SAMs) protective to ferro/ferricyanide etchants.[48]



28

3. DEEP CAVITANDS

Numerous works concern chemistry and applications of deep cavitands.[49-52] An example of the synthesis of deep cavitands is the reaction of the resorcinarene (**29**) with substituted benzal bromides and with 2-naphthal bromide leading to compounds (**30**) and (**31**).[53]



29

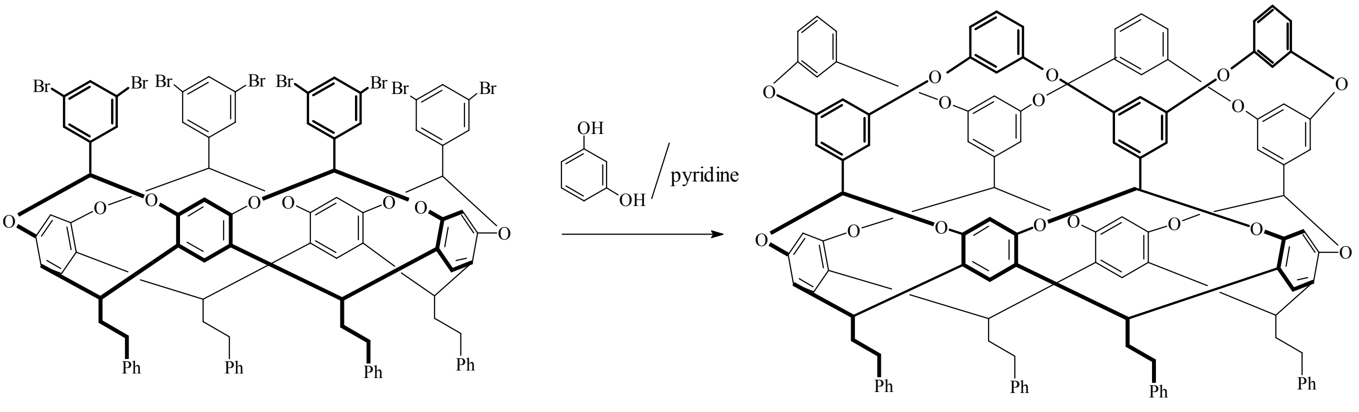
R = CH_2CH_2Ph

30

31

X =2-Br, 3-Br, 4-Br, 4-I, 3-Me, 4-Me

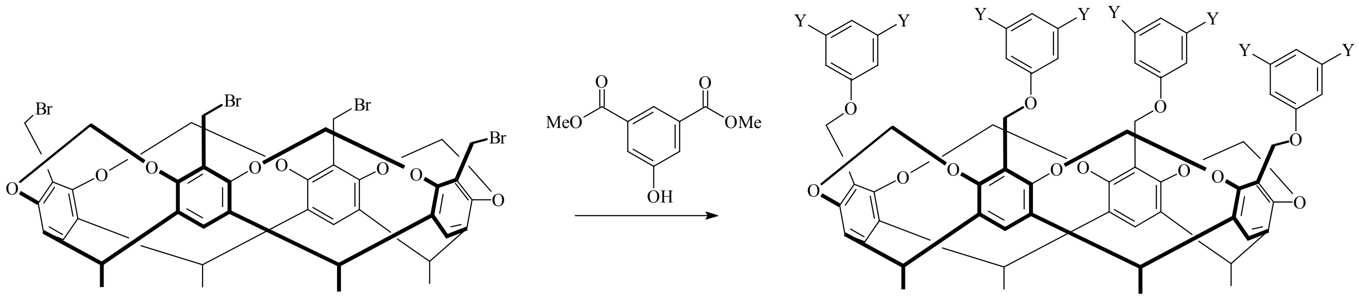
Deep cavitand (**32**) has been obtained as follows. [54]



32

The binding constants of **32** with 1-haloadamantanes have been determined by titration in $CDCl_3$ and d_8-toluene· It was established that binding constants of **32·guest** complexes decrease in the order of guests:1-iodoadamantane > 1-bromoadamantane > 1-chloroadamantane > 1-fluoroadamantane. The guest molecule is not deep immersed in the cavity but it hovers over it, this fact suggesting that the stability of these complexes is strongly dependent of C-H · · X-Ad hydrogen bonds (X = halogeno). With the decrease of the halogen atom size, decreases also the number of simultaneous hydrogen bonds with the host, being 4, 3, 2 and 1 for I, Br, Cl and F, respectively. [54]

The reaction of the cavitand (**33**) with 5-hydroxydimethyl isophthalate leads to the compound (**34a**), converted by treatment with NaOH into water-soluble anionic **34b**. [55]

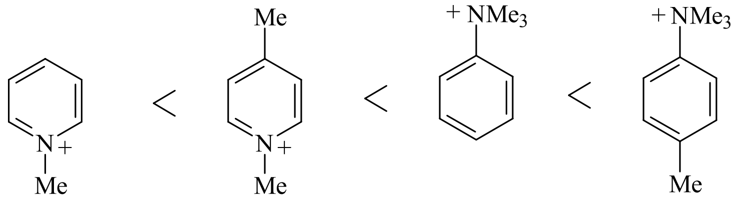


33

		Y
34	**a**	COOMe
	b	$COO^{-}Na^{+}$

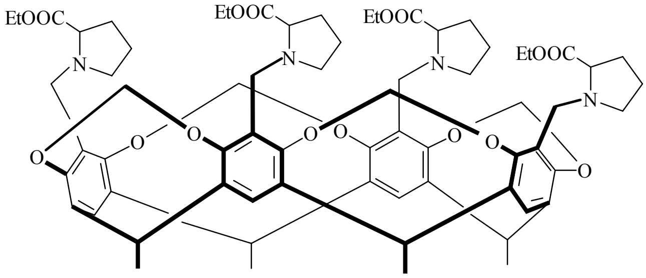
NaOH

Cavitand (**34b**) binds quaternary ammonium and pyridinium cations, forming 1 : 1 complexes; [55] these compounds, shown in the order of their increasing binding constants are given below.



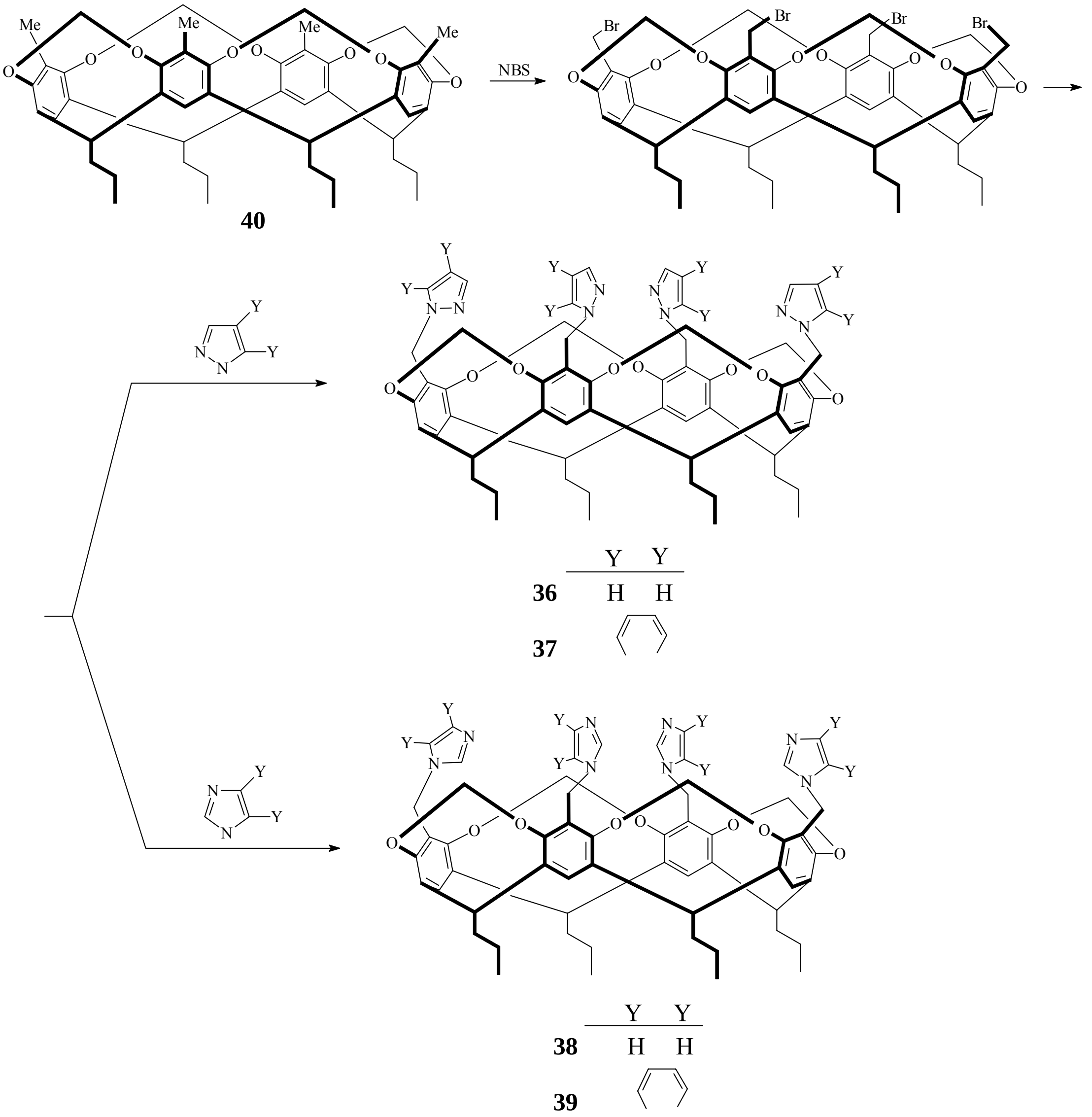
The binding constants for the guests bearing substituents at the phenyl ring are larger than those for guests without the side chain. This observation indicates the importance of the hydrophobic interaction in the complex formation in aqueous media.

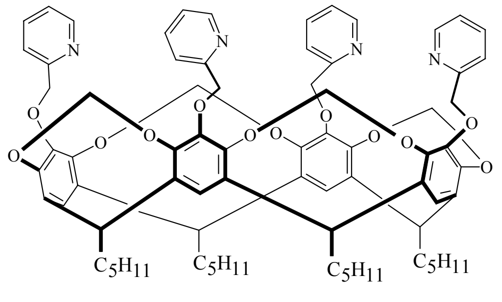
It was established that cavitand (**35**), containing chiral L-proline ethyl ester moieties has helical chirality in the solid state. [56]



35

Cavitands (**36** - **39**), bearing azaaromatic units, with sp^2 nitrogen atoms as cation binding ligands have been synthesized from tetramethylcavitand (**40**) by bromination with NBS (*N*-bromosuccinimide) and subsequent reactions with pyrazole and indazole, affording **36** and **37**, or with imidazole and benzimidazole affording **38** and **39**. Cavitand (**41**) has been obtained in a similar way. [57]

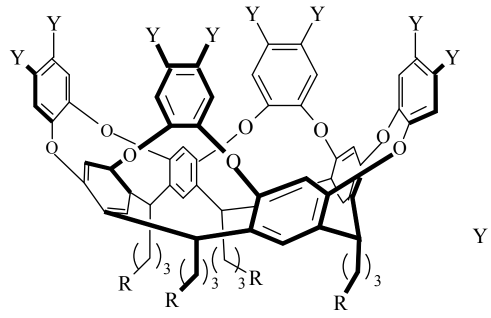




41

These rigid species have much higher affinities towards metal cations than corresponding flexible calix[4]arenes; [57] four sp^2 nitrogen atoms can face inward to form a cation binding site. Cavitand (**38**) shows high affinity for IIA and transition metal cations, the highest in the case of Ag^+. The high selectivity for Ag^+ over Mg^{2+}, Ca^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+} and Cd^{2+} ions has been observed in the case of **36** and **41**.

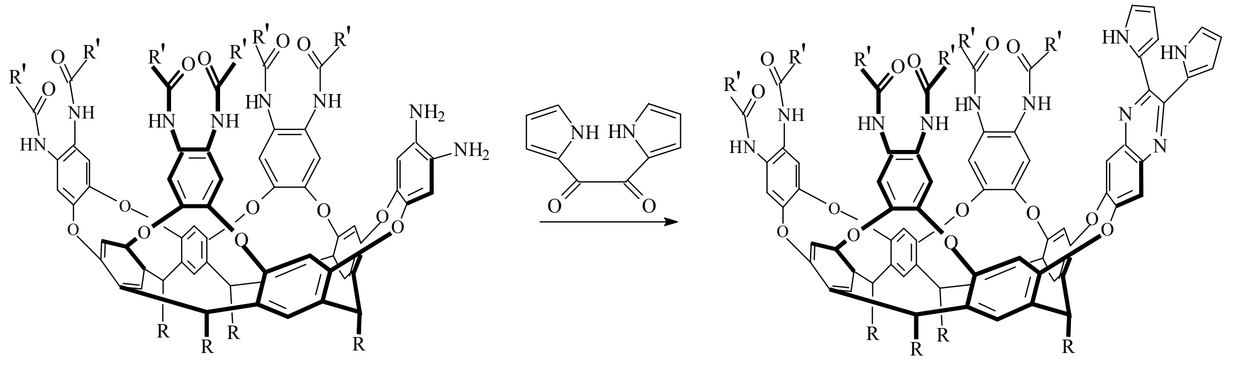
In the study of deep cavitands it was found that **42a,b** are soluble in water due to the presence of four primary ammonium groups at the lower rim and eight secondary amide groups at the upper rim. [58]



Y = NHC(O)Et

		R
42	**a**	$NH_3^+CF_3C(O)O^-$
	b	$CH_2OC(O)NHCH_2C(O)OCH_2C(CH_2OH)NH_3^+Cl^-$

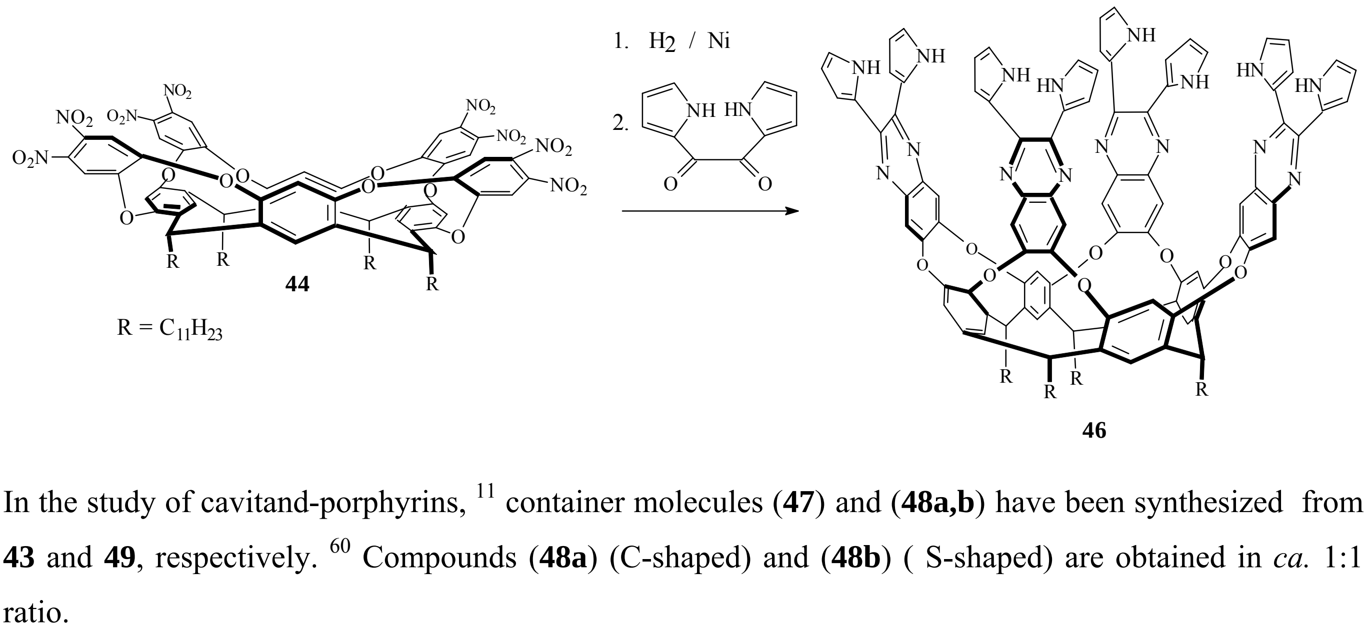
Compounds (**43**) and (**44**) have been used as starting materials in the synthesis of deep cavitands (**45**) and (**46**).[59] It was established that **45** and **46** form complexes with fluoride and acetate anions (as tetrabutylammonium salts), but not with chloride ions. These cavitands may be used as visual detectors of F^- and AcO^- ions, since the binding is accompanied by a distinct color change from yellow to dark red.



43

R = $C_{11}H_{23}$; R' = C_7H_{15}

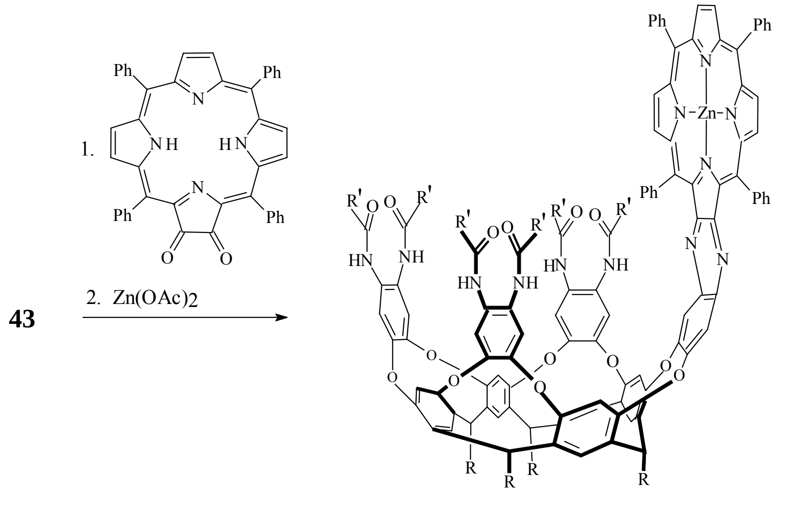
45



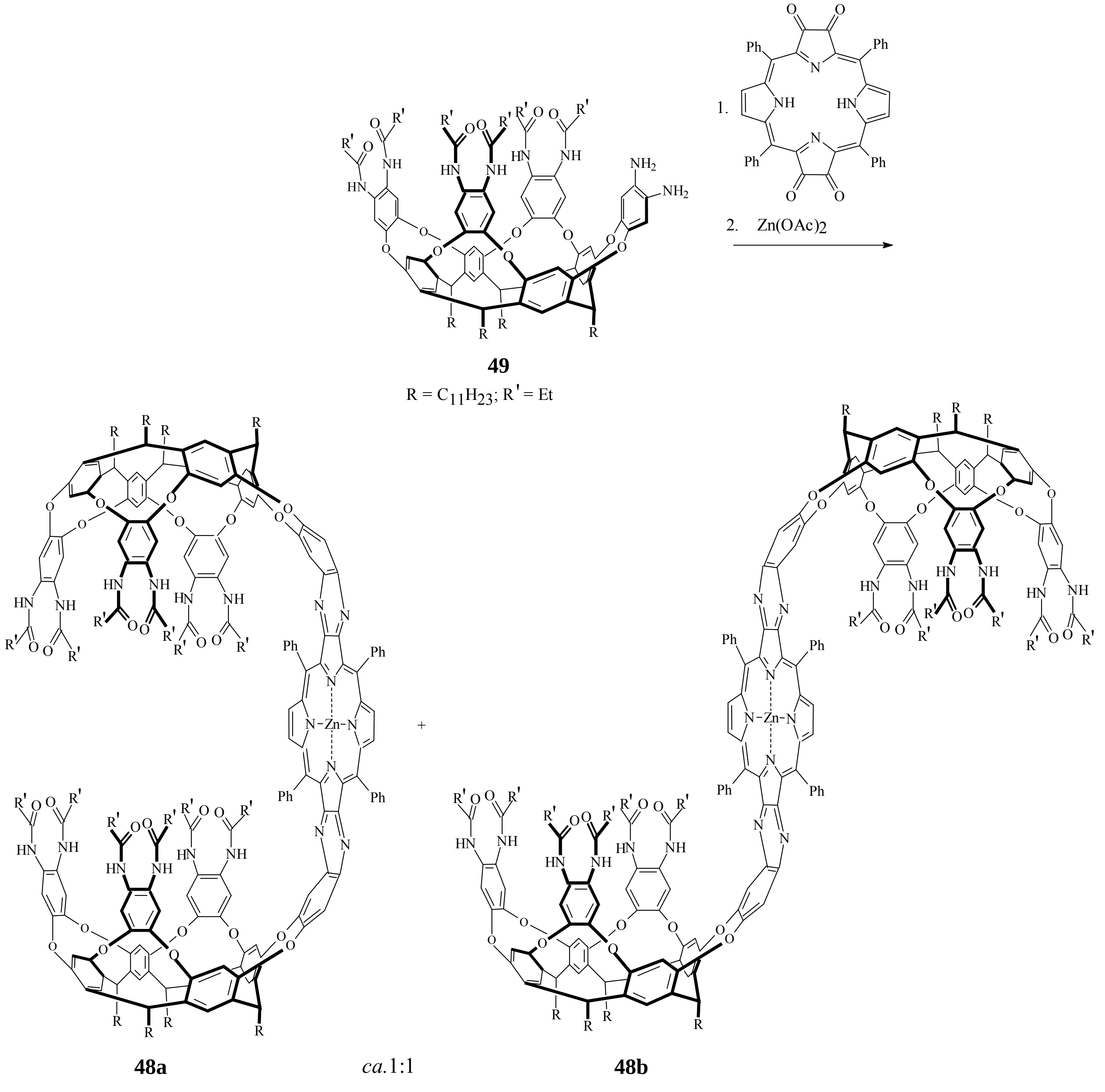
R = $C_{11}H_{23}$

46

In the study of cavitand-porphyrins, [11] container molecules (**47**) and (**48a,b**) have been synthesized from **43** and **49**, respectively. [60] Compounds (**48a**) (C-shaped) and (**48b**) (S-shaped) are obtained in *ca.* 1:1 ratio.



47

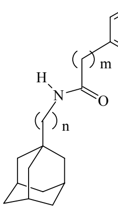


49

R = $C_{11}H_{23}$; R' = Et

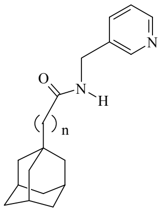
48a *ca.*1:1 **48b**

Binding properties of **47** and **48a** have been investigated using as guests compounds (**50** – **52**), containing adamantane and pyridine moieties. It was observed that zinc porphyrin may bind pyridine bases interacting with both sides.



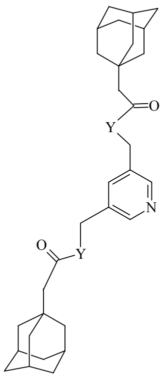
50

	m	n
a	1	0
b	2	0
c	1	1



51

	n
a	0
b	1



52

	Y
a	O
b	NH

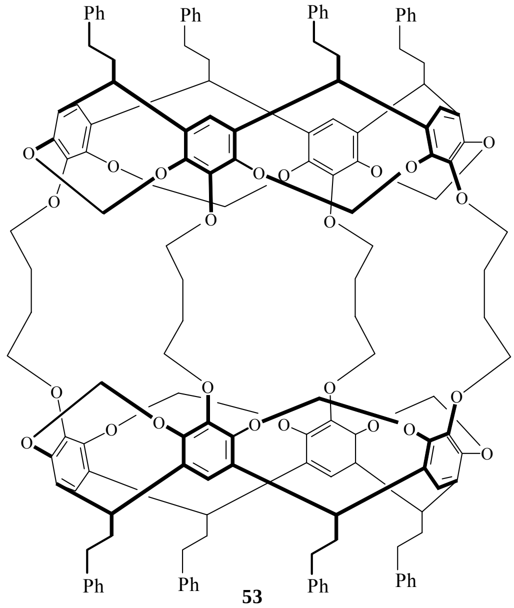
Cavitand-porphyrin (**47**) forms the 1:1 complex with the guest (**51b**), the adamantane moiety being held within the cavity of **47**, and pyridine bound to Zn ion of porphyrin; the complexation of **47** with guests (**50b,c**) proceeds in a similar way. In the case of cavitand-porphyrin (**48a**) the formation of complexes with long guests (**52a,b**) was observed; the diamide (**52b**) has a stronger affinity than diester (**52a**) due to the involvement of the C(O)-NH proton of **52b** in the hydrogen bonding with the cavity amide walls. [60]

4. COVALENTLY LINKED CONTAINER MOLECULES

Among covalently linked species the hemicarcerands, i.e. molecules composed of the same hemispheres will be described first, and then capped containers composed of two different moieties will follow.

Hemicarcerands

In the study of excitation transfer reactions, the triplet excitation transfer through the walls of hemicarcerands (**53** – **55**) was investigated, using biacetyl as a triplet donor guest. [61]



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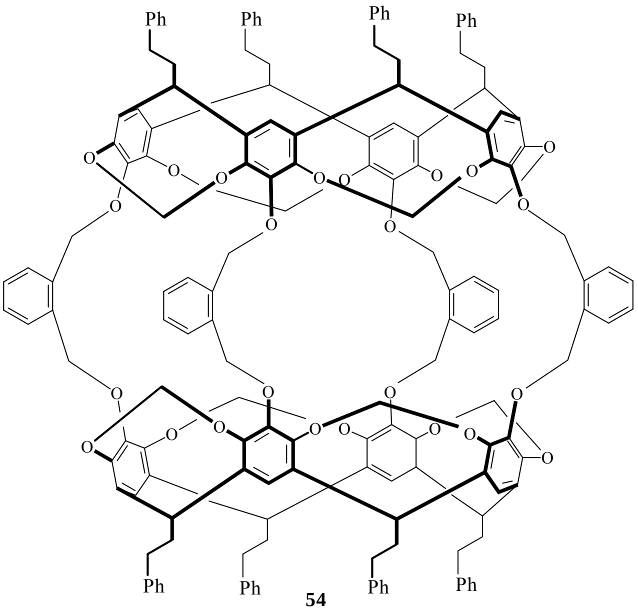

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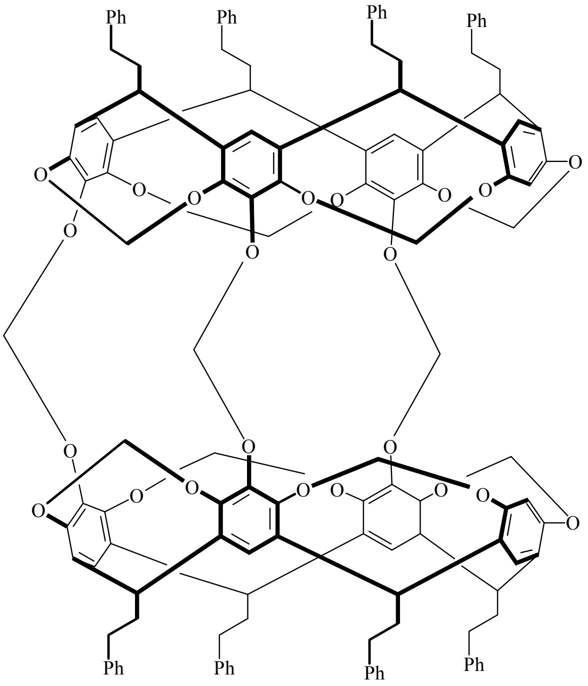
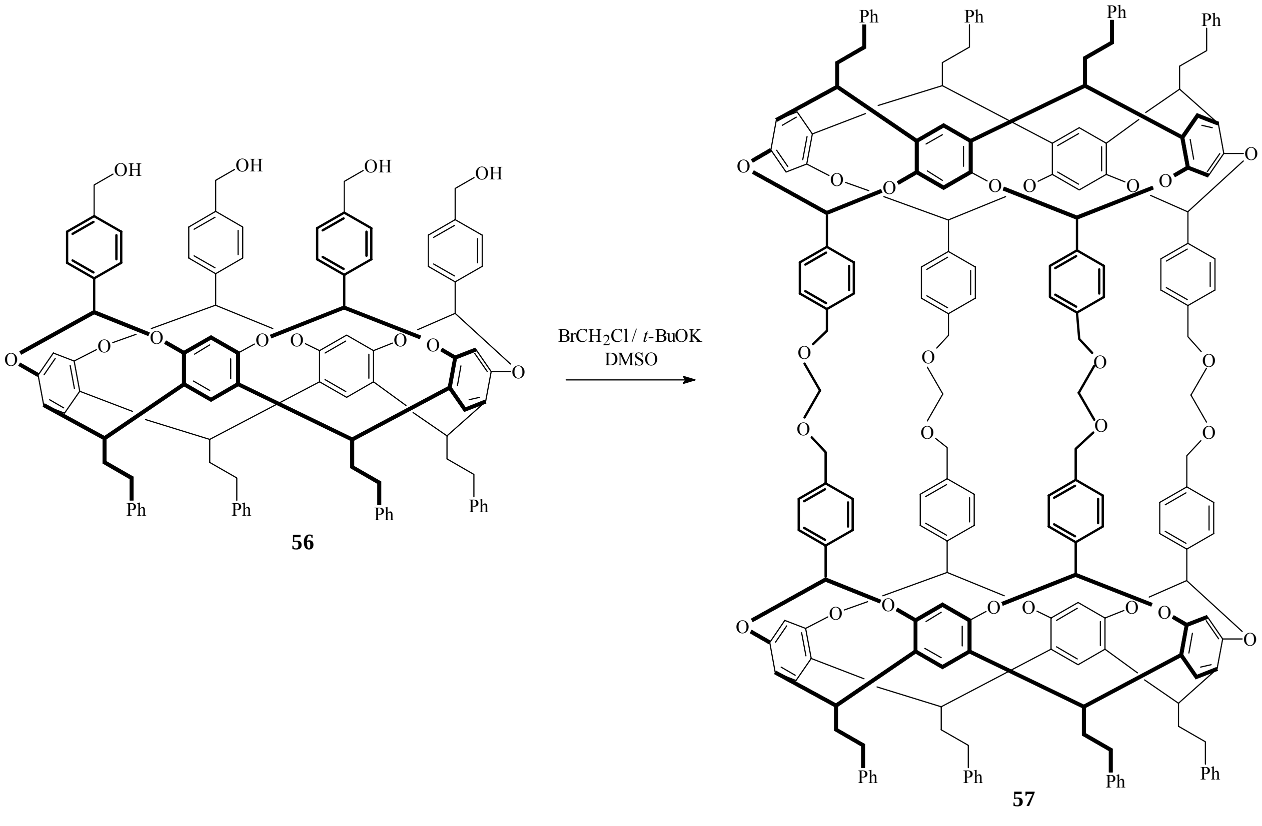


55

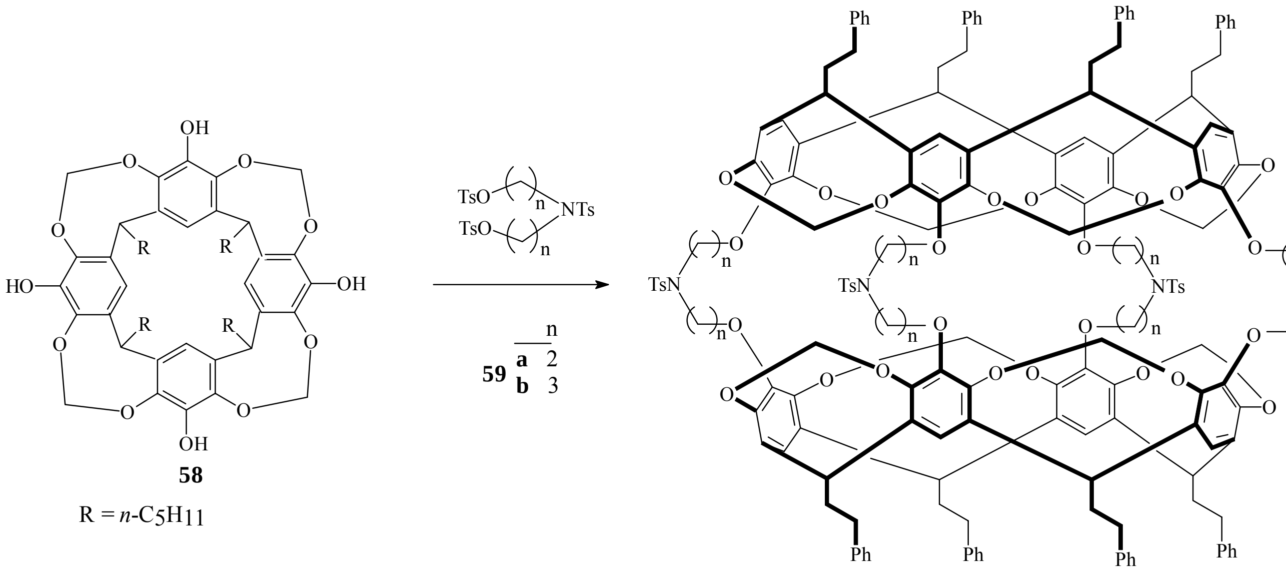
It was found, that the cavitand (**56**) reacts with $BrCH_2Cl$ to give hemicarcerand (**57**) (80% yield) under dilute conditions, in the absence of a template.[62]



56

57

The reaction of cavitand (**58**) with tosylamides (**59a,b**) affords hemicarcerands (**60a,b**), respectively. It was observed that **60a** forms unstable 1 : 1 complexes with guests (**61**) and (**62**), and hemicarcerand (**60b**) forms a stable 1 : 1 complex with the guest (**63**).[63]



58

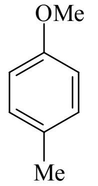
R = n-C_5H_{11}

	n
59 **a**	2
b	3

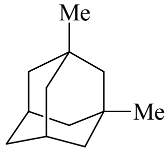
	n
60 **a**	2
b	3

$Br_2CH{-}CHBr_2$

61

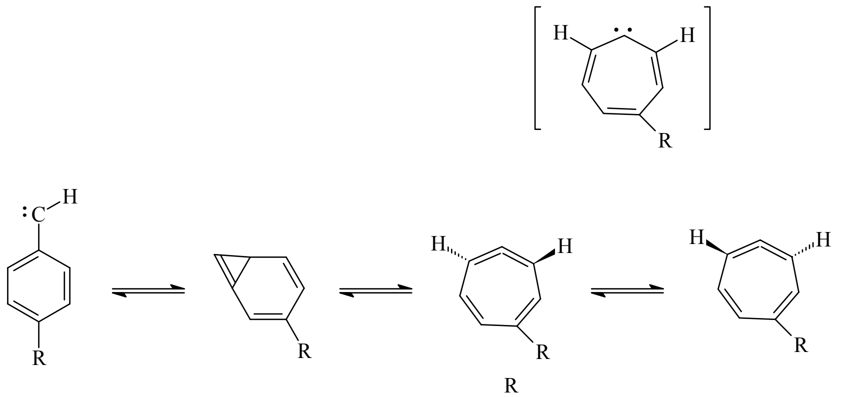


62

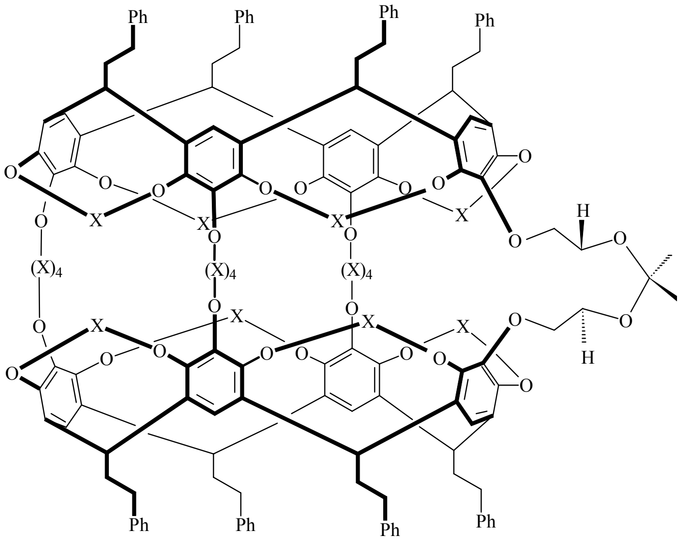


63

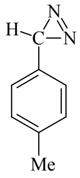
In the study of arylcarbenes [64] it was shown that cyclohepta-1,2,4,6-tetraene (**64a**) is stable at room temperature if protected from bulk phase reactants by incorporation inside a hemicarcerand. [65-67] The inner-phase stabilization of 5-methylcyclohepta-1,2,4,6-tetraene (**64b**) inside chiral hemicarcerands (*S,S)*-**65** and (*S,S*)-d_{40}-**65** have been reported along with experimental determination of its enantiomerization barrier. As *p*-tolylcarbene precursor complexes served (*SS*)-**65·66** and (*SS*)-d_{40}-**65·66**, which were subjected to photolysis. [68]



	R
64 **a**	H
b	Me



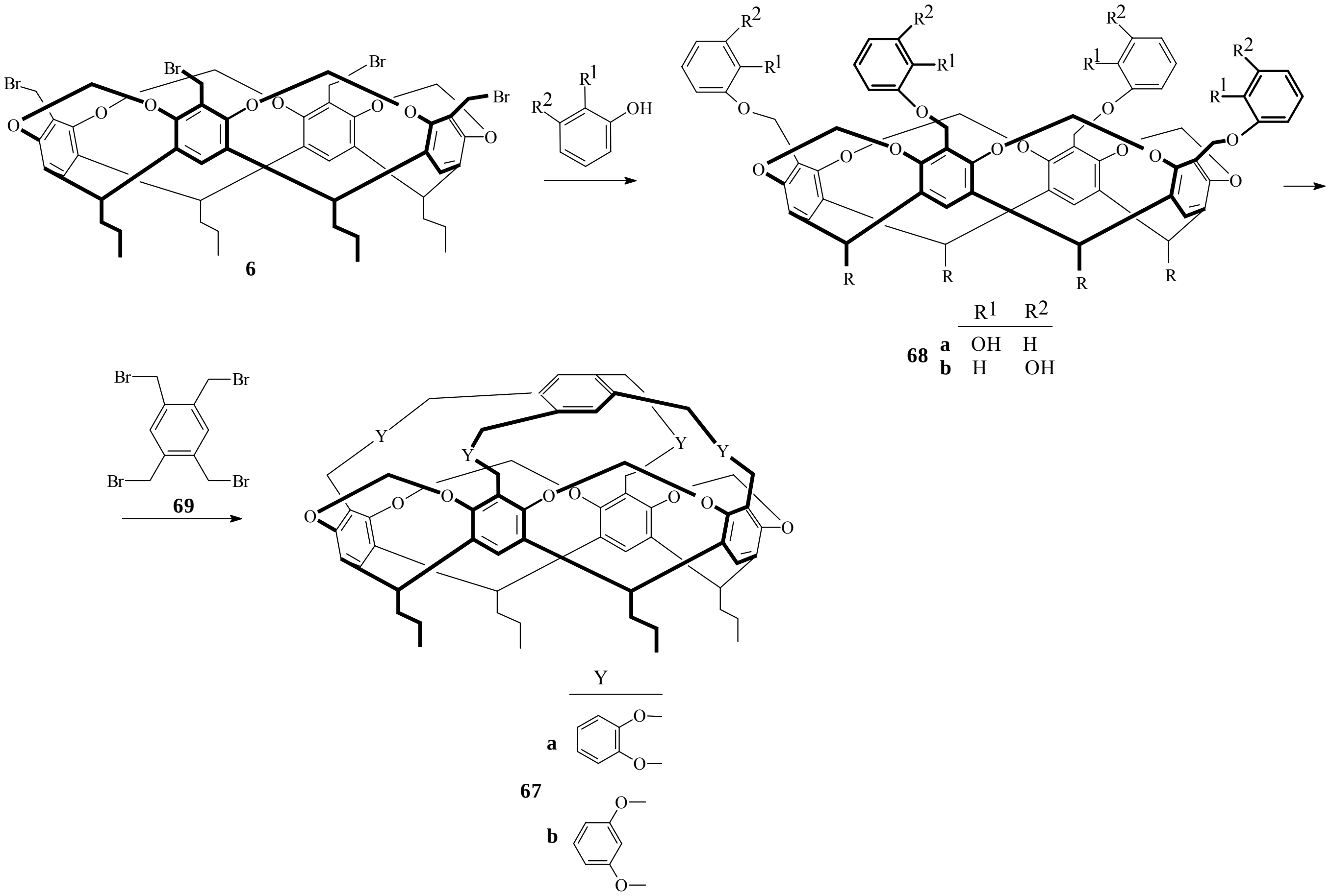
	X
(*S,S*) - **65**	CH_2
(*S,S*) - d40 - **65**	CD_2



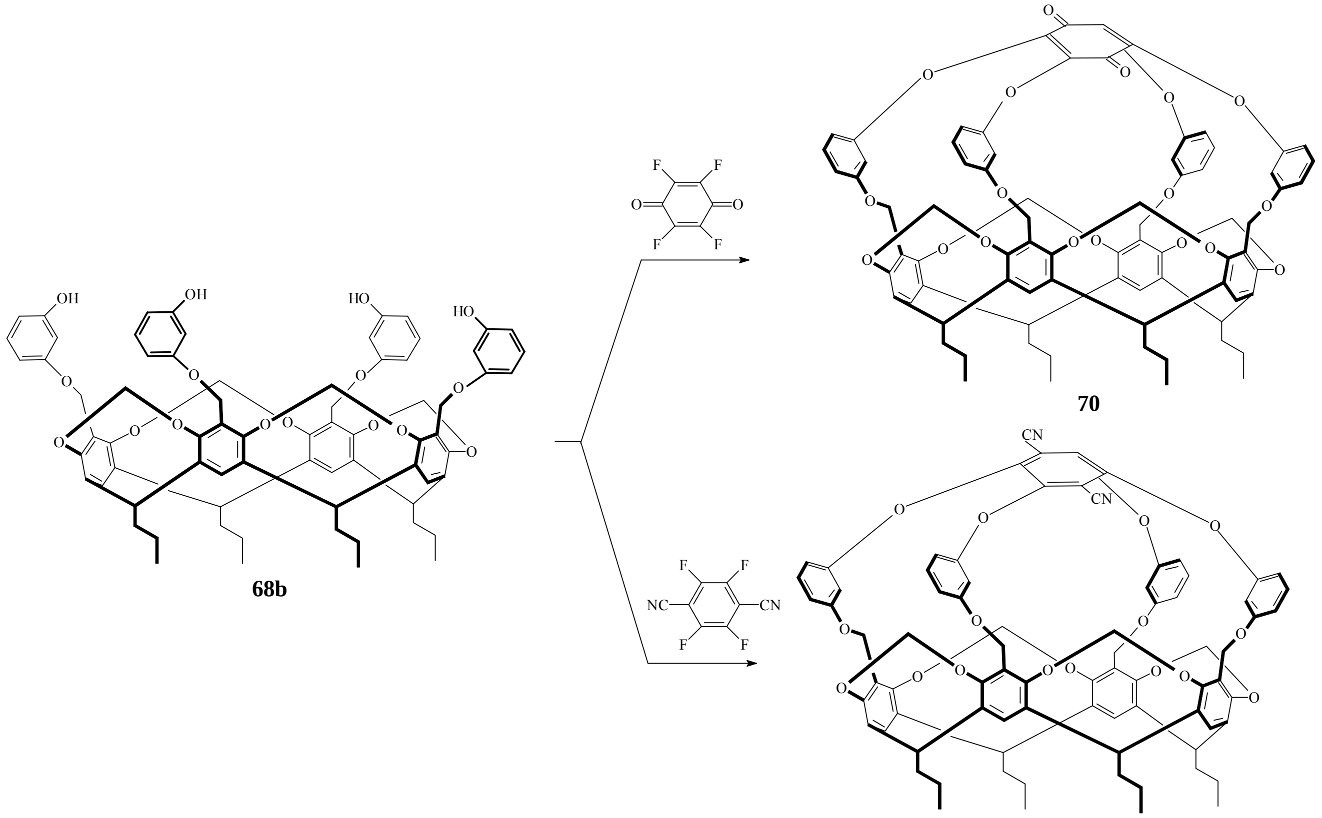
66

Capped containers

The synthesis of containers (**67a,b**) involves the reaction of the cavitand (**6**) with catechol or resorcinol affording aryl fenced cavitands (**68a,b**) which were capped with 1,2,4,5-tetrakis(bromomethyl)benzene (**69**). Compound (**67a**) shows binding properties for alcohols, methylene chloride and THF. [69]



Following reactions of cavitand (**68b**) lead to containers (**70**) and (**71**) able to encapsulate ethanol, 1-propanol, ethylene glycol and acetaldehyde. [70]

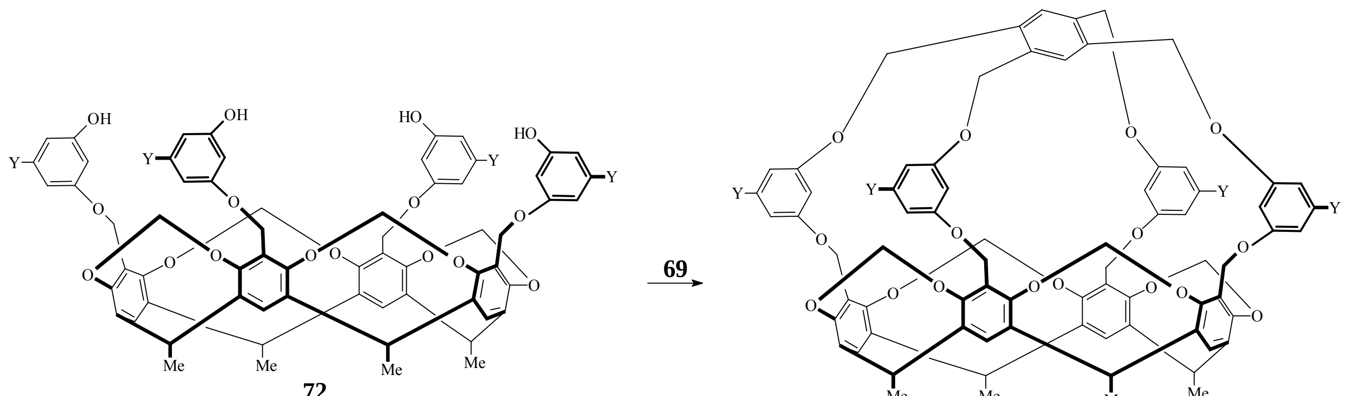


68b

70

71

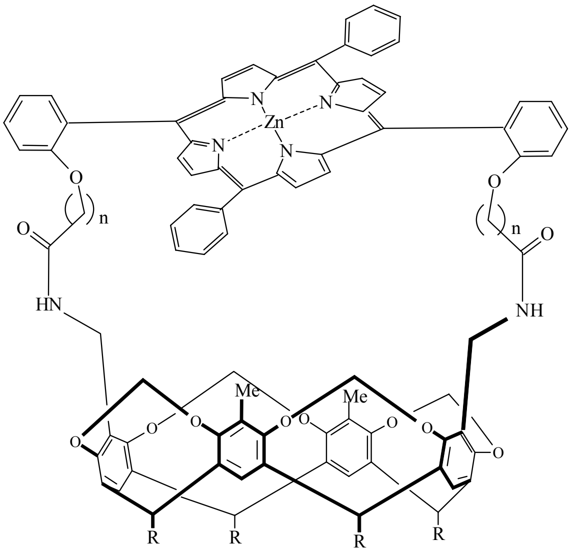
The capping of cavitand (**72**) with **69** gives the container (**73a**) which after hydrolysis yields **73b**. It was observed that **73b** binds 2-propanol but not 1-propanol; butanols are too large as guests. [71]

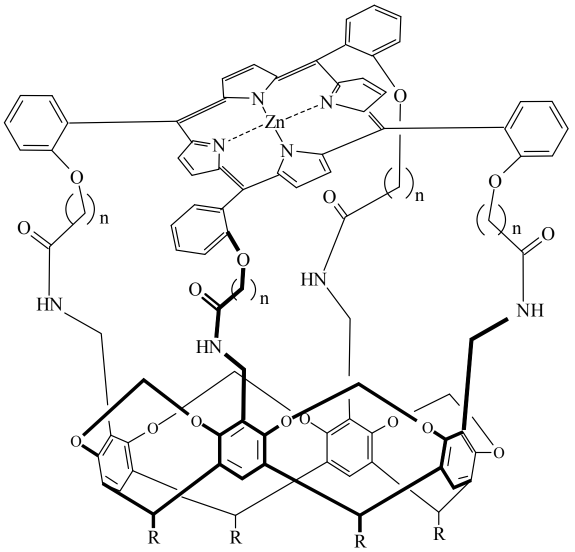


Y = COOEt **72**

		Y	
73	**a**	COOEt	hydrolysis
	b	COOH	

Containers (**74**) and (**75**), in which cavitands are linked with zinc porphyrin by two spacers and by four spacers, respectively, have been synthesized. [72]





R = C_5H_{11}

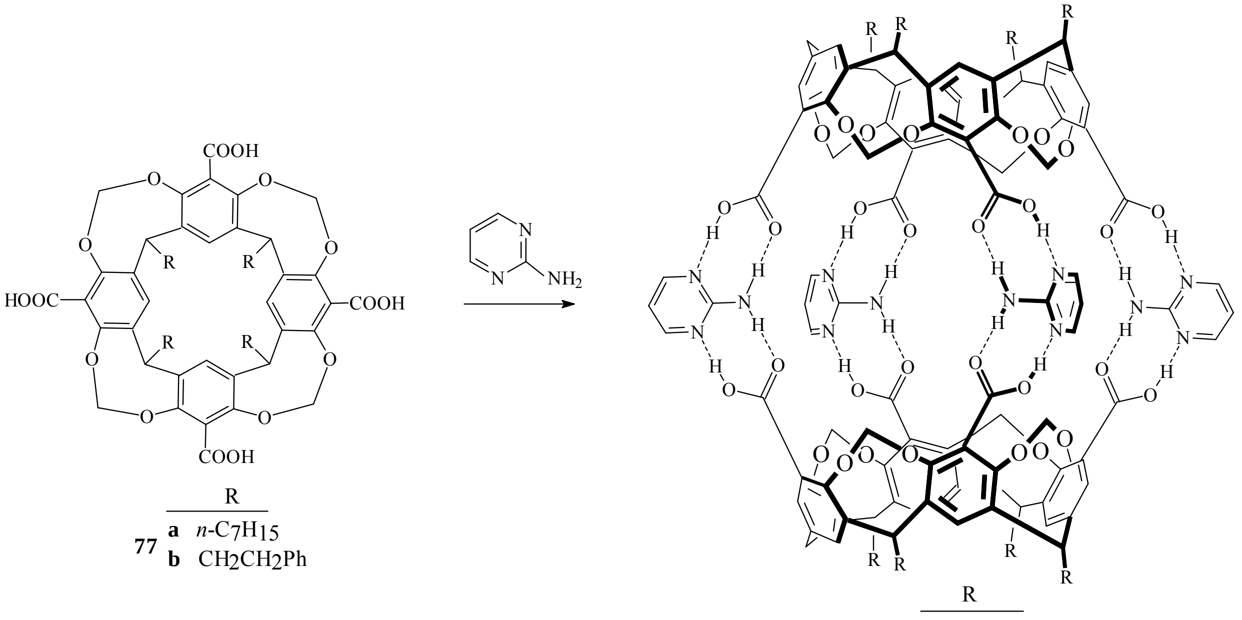
74	n
a	1
b	5

75	n
a	1
b	5

Containers (**74a**) and (**75a**) are very good receptors for heterocycles, e.g. for *N*-methylimidazole and 2-picoline. Complexing properties of **75a** are stronger than those of **74a**, because two additional spacers in **75a** rigidify its structure. [72]

5. NONCOVALENTLY LINKED CONTAINER MOLECULES

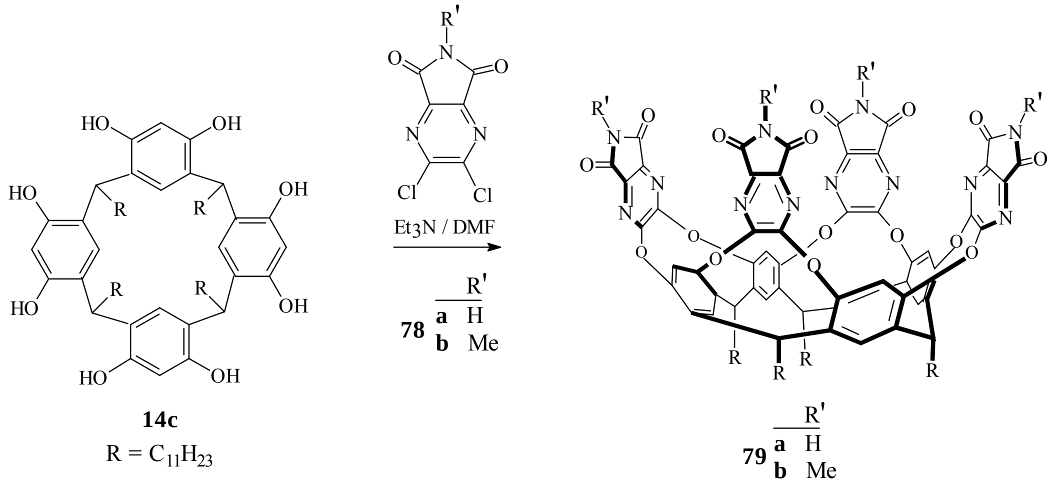
Capsule (**76a,b**) held together in a rim-to-rim fashion by hydrogen bonds has been constructed by self-assembly of cavitands (**77a,b**) with 2-aminopyrimidine. Capsule (**76b**) may accomodate two molecules of nitrobenzene. [73]



77	R
a	n-C_7H_{15}
b	CH_2CH_2Ph

76	R
a	n-C_7H_{15}
b	CH_2CH_2Ph

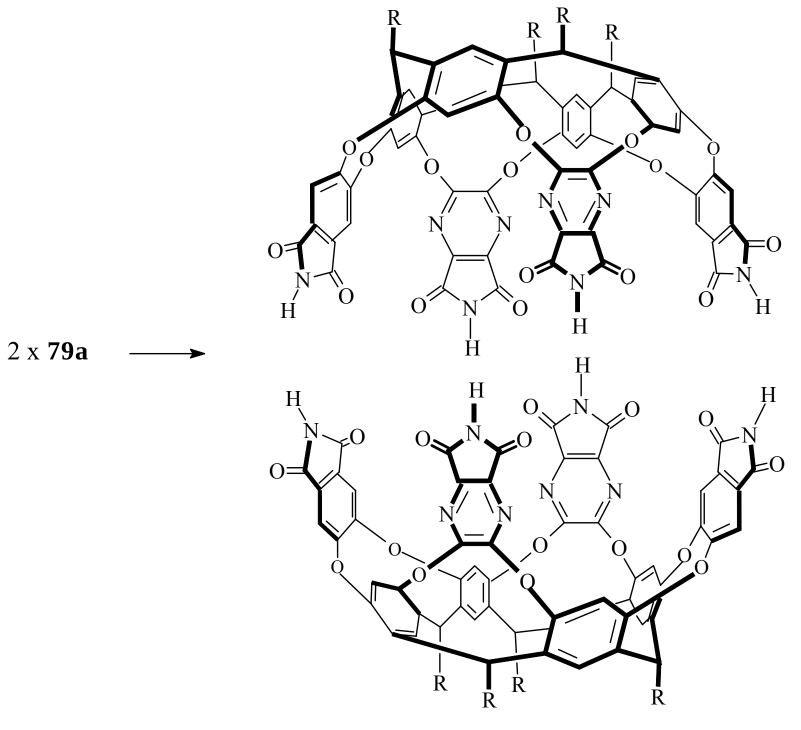
Reaction of resorcinarene (**14c**) with imide (**78a,b**) affords cavitands (**79a,b**).[74] It was observed that **79a** can dimerize to give the capsule (**79a·79a**) held together by a seam of eight hydrogen bonds.[74] This capsule of a volume of ca 460 A^3 may incorporate two $CDCl_3$, two benzene or two toluene molecules.



14c
$R = C_{11}H_{23}$

78

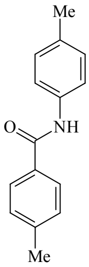
79



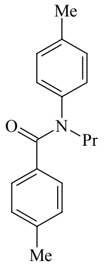
79a · 79a

It is known that a solvent poorly accomodated in a cavity can be easily replaced by a fitting well guest. Using this procedure, it was observed that bibenzyl, *p*-terphenyl, dicyclohexylcarbodimide, and (*E*)-4,4'-dimethylstilbene within seconds replace solvents in the d_{12}- mesitylene solution of **79a·79a** with the formation of 1: 1 complexes.

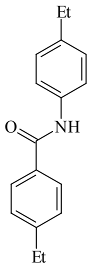
Among amides (**80** - **82**) used as potential guests, only **80** has proven to be a good guest for capsule (**79a·79a**), compounds (**81**) and (**82**) being too large for inclusion. A supramolecular cage effect could be observed in these experiments using benzoyl peroxide (**83**) as a guest. Namely, it was found that the incorporation protects **83** not only from external reagents, but also from thermal decomposition; it can be stored inside **79a·79a** for a long time, and released, when necessary to the bulk solution. The encapsulated **83** can be released by DMF, which competes for the inner hydrogen bond donors. In this way the capsule exists no more, only two monomeric cavitands (**79a**) could be detected. Benzoyl peroxide (**83**) readily oxidizes Ph_3P present in d_{12}-mesitylene to give $Ph_3P{=}O$, while when encapsulated in **79a·79a**, no reactions occurs. [74]



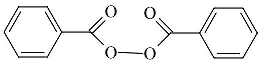
80



81

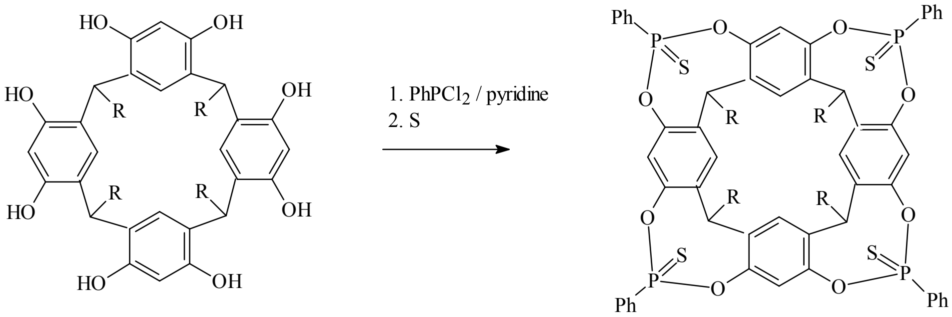


82



83

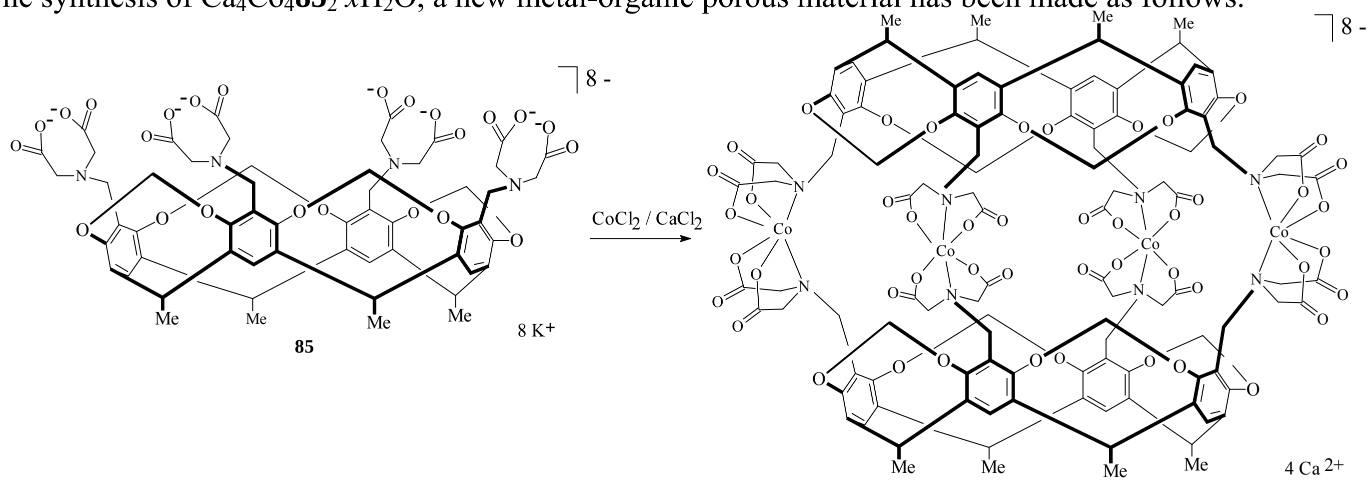
In the study of phosphorylated cavitands as ligands for cationic species, it was found that P(O) derivatives bind hard cations, while P(S) derivatives bind soft cations, Ag^+ serving here as an example. [75] Cavitand (**84**) with four P=S bonds oriented inwards has been obtained from resorcinarene (**14c**) by treatment with $PhPCl_2$ and the subsequent sulfur oxidation. With the use of picrate extraction method it was established that **84** binds Ag^+ forming a capsule $[\mathbf{84}_2{\cdot}Ag_4{\cdot}Pic_4]$ held *via* Ag^+ coordination.



14c
$R = C_{11}H_{23}$

84

The synthesis of $Ca_4Co_4\mathbf{85}_2{\cdot}xH_2O$, a new metal-organic porous material has been made as follows. [76]

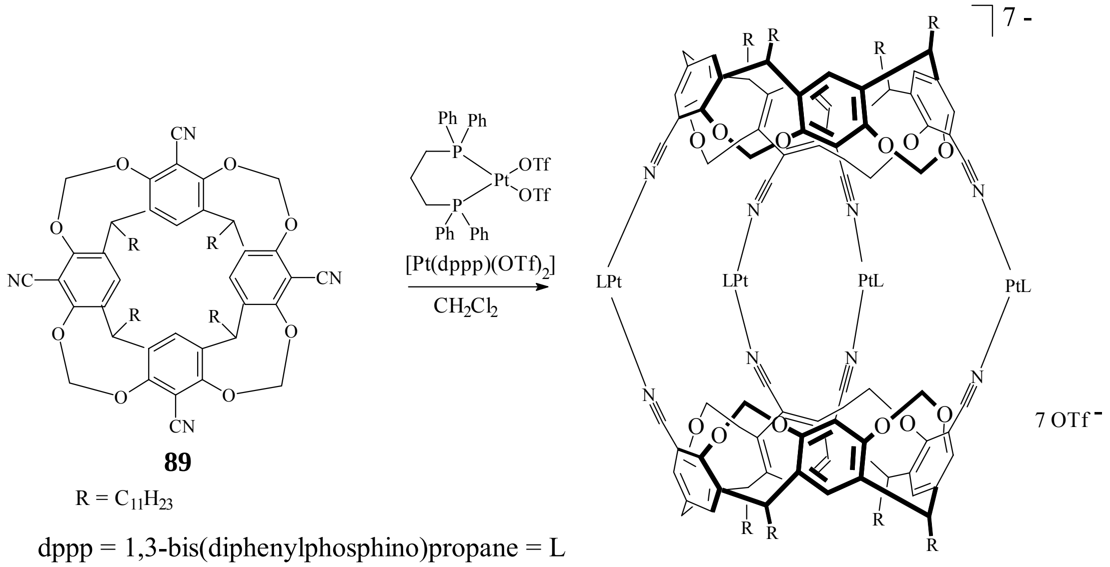


$Ca_4Co_4\mathbf{85}_2$

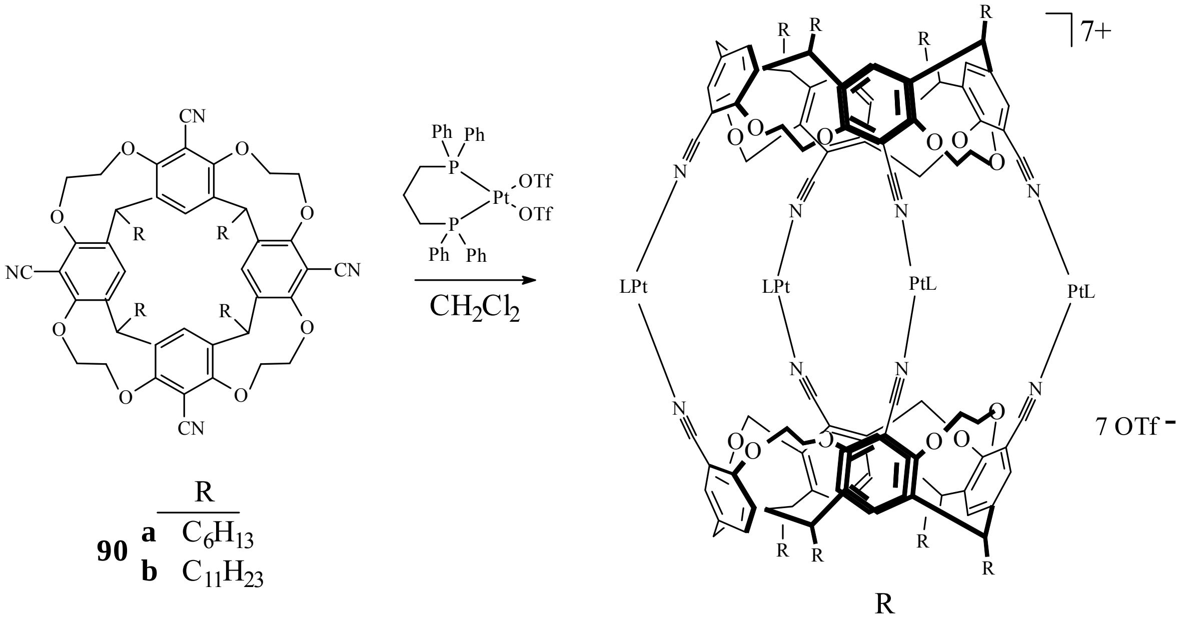
Such new materials are promising due to their different properties than those of zeolites; they may be used as selective trapping agents or catalysts. The binding of metal ions by carboxylate anions results in the formation of porous structure. The Ca^{2+} ions may coordinate to carboxylate groups from two cages; in this way pores and channels are formed by creating of bridges between two cages.

The Ca^{2+} ions also bind to water molecules, which complete their coordination sphere. It was observed that the material retains its structure after water release up to 300°C. When the dehydrated material is cooled in a stream of water vapor, the amount of water which was lost is regained. [76]

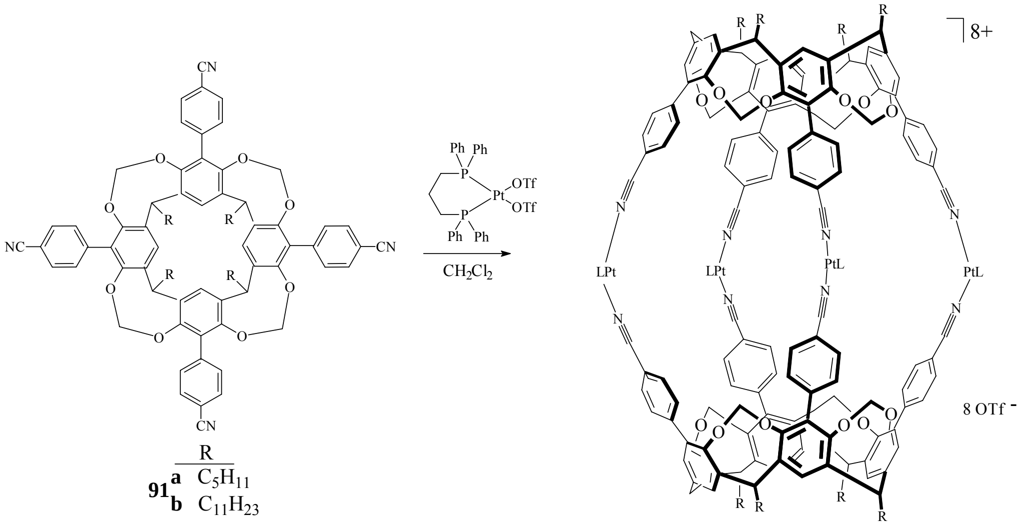
Coordination cages (**86** - **88**) have been formed by metal-directed self-assembly of cavitands (**89** - **91**) with [Pt(dppp)(OTf)$_2$]; it was observed that they can encapsulate counterions. [77] In the case of **88** the entrapped counterions undergo a fast exchange with solvent molecules due to the large portals of cages. [78]



86



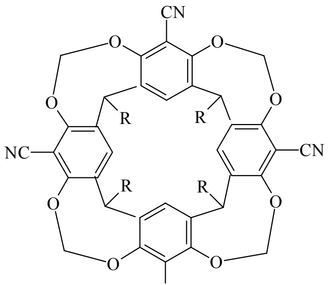
	R
87 **a**	C_6H_{13}
b	$C_{11}H_{23}$



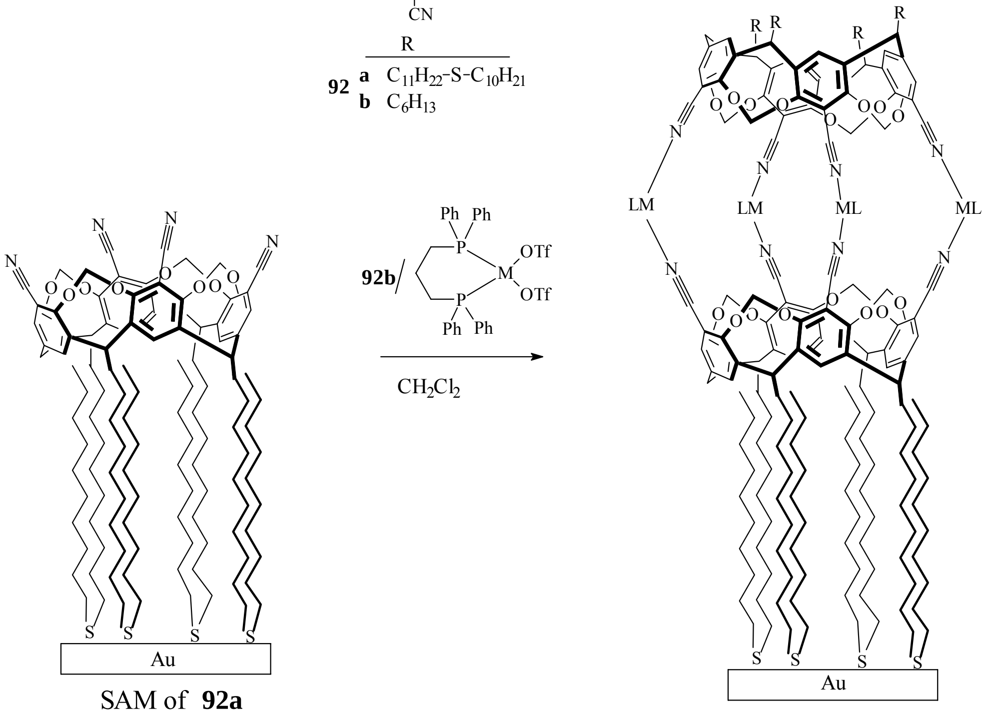
	R
91 a	C_5H_{11}
b	$C_{11}H_{23}$

	R
88 a	C_5H_{11}
b	$C_{11}H_{23}$

It is possible to generate coordination cages directly on gold surfaces by using self-assembled monolayers (SAMs) as molecular platforms. The soaking of SAM of **92a** in a CH_2Cl_2 solution of **92b** and [M(dppp)$(OTf)_2$] (M=Pd, Pt) leads to formation of monolayers of cages (**93a,b**), on gold surfaces; this process may be monitored directly by atomic force microscopy (AFM). [79]



	R
92 a	$C_{11}H_{22}$-S-$C_{10}H_{21}$
b	C_6H_{13}

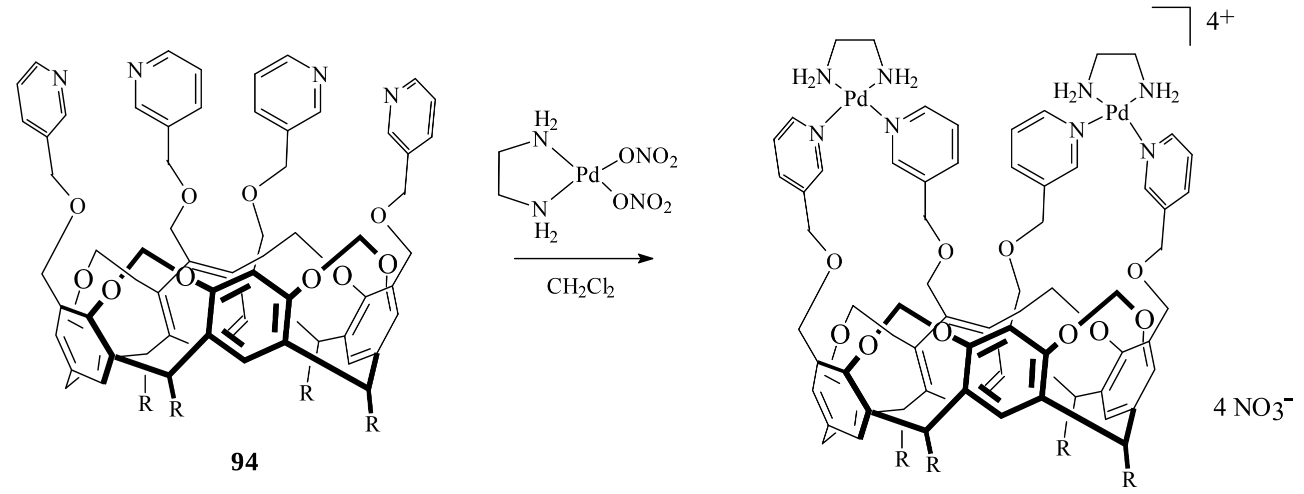


SAM of **92a**

	M
SAM of **93** a	Pd
b	Pt

R = C_6H_{13}

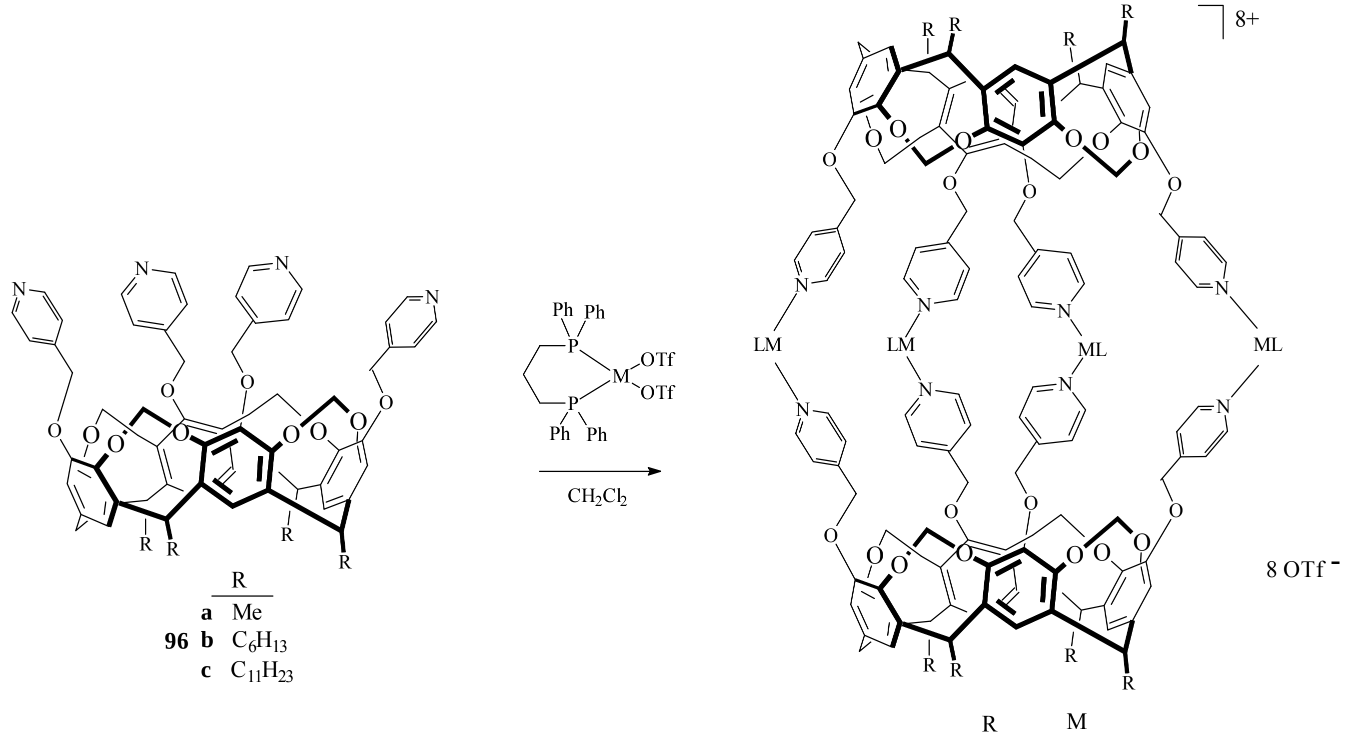
Cavitand (**94**) reacts with [Pd(en)(NO_3)$_2$] to give intramolecularly assembled structure (**95**). [80] However, the treatment of cavitands (**96a-c**) with [M(dppp)(OTf)$_2$] (M= Pd, Pt) affords nanoscale self-assembled molecular capsules (**97a-c**). [81] Capsule (**97c**) forms 1:1 complexes with *N*-alkylpyridinium derivatives, such as 1-methyl-4-phenylpyridinium triflate and methylviologen, these positively charged species being entrapped inside cavity due to strong cation - π interactions.



94

R = Me

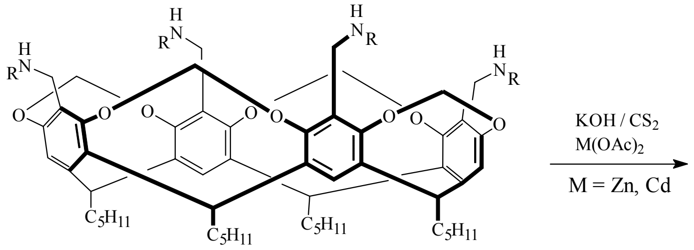
95



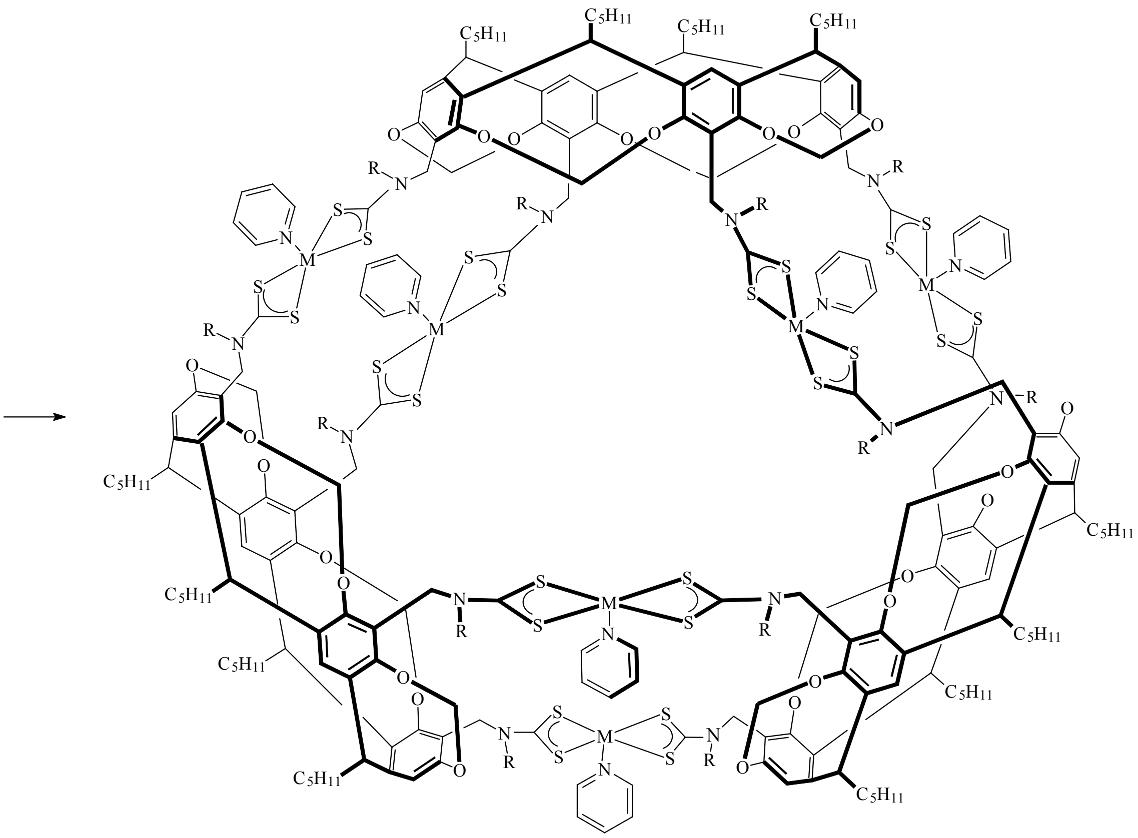
		R
	a	Me
96	b	C_6H_{13}
	c	$C_{11}H_{23}$

		R	M
	a	Me	Pt
97	b	C_6H_{13}	Pt
	c	$C_{11}H_{23}$	Pd

One should describe here also trimers (**98a-d**) obtained from cavitands (**99a,b**). [82]



		R
99	**a**	*n*-Pr
	b	*n*-Bu



		R	M
98	**a**	*n*-Pr	Zn
	b	*n*-Bu	Zn
	c	*n*-Pr	Cd
	d	*n*-Bu	Cd

It was observed that **98a-d** strongly bind C_{60} molecule in benzene or toluene solutions, [82,83] the binding constants of cadmium complexes (**98c,d**) being higher than those of zinc complexes (**98a,b**).

CONCLUSION

The number of works concerning cavitands increases rapidly; [84-90] these compounds are promising for various applications due to their unique properties in molecular recognition. In the paper only selected examples of cavitands and related container molecules have been presented, pointing out their receptor properties.

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