Polish J. Chem., **77**, 1079–1111 (2003) **REVIEW ARTICLE**

Resorcinarenes

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Selected examples of resorcinarenes are described, concerning their syntheses and reactivity. Formation of complexes, host-guest systems and capsules is also presented along with their possible applications. A short comment concerning pyrogalloarenes is added. In the paper references are cited of works that appeared during the years 1998–2003.

Key words: capsules, complexes, host-guest systems, monolayers, sensors

Introduction

Resorcinarenes, more shortly resorcarenes, are analogs of calixarenes; they have two hydroxyl groups in benzene rings forming a macrocycle and not one as in the case of calixarenes. Calixarenes and related compounds received a growing attention in recent years due to their properties promising for a number of applications, *e.g*. in the construction of electronic devices and solar cells, or as sensors and photosensitizers [1–6]. Calixarenes contain four [7,8], five [9], six [10], seven [11] or eight [12] phenol rings in the macrocycle, they may exist as dimers [13] or trimers [14] or form supramolecular assemblies [15–18].

Calixarenes are receptors of neutral molecules and ions; an attention is paid to calixarenes complexing metal ions [19,20], especially lanthanide [21] and actinide [22] as well as cesium [23–25] ions in the aspect of nuclear waste management.

Calixhetarenes, *i.e.* heterocalixarenes consist of heterocyclic moieties instead of phenol units [26,27], for instance calixpyrroles [28–30]. One should mention here also calixarenes bearing appended heterocyclic moieties [31–34]. Another group are heteracalixarenes, *i.e.* species containing heteroatoms (N [35,36], O [37,38] or S [39,40]) in linkages of phenol units.

Resorcinarenes are interesting for their receptor properties and as building blocks for large supramolecular assemblies of a fascinating architecture [41–44]. The bridging of hydroxyl groups of resorcinarenes leads to cavitands, bowl-shaped species serving as synthetic receptors and able to assembly into capsules [45–50].

In the present review, a continuation of our former papers concerning calixarenes and related compounds [2,18,20,33,50], selected examples of resorcinarenes are

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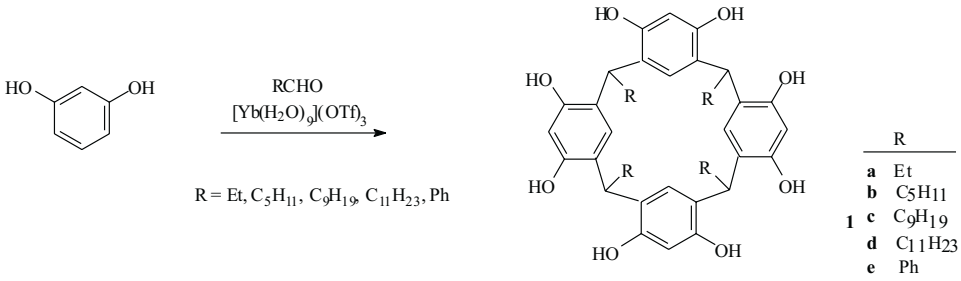
described, showing their synthetic approaches and reactivity as well as formation of complexes, host-guest systems and capsules. The preparation of mono- and multilayers of resorcinarenes, promising for their applications is also presented, and finally pyrogalloarenes, *i.e*. analogs of resorcinarenes bearing three hydroxyl groups instead of two, are described.

1. Syntheses of resorcinarenes

Resorcinarenes can be easily obtained by acid catalyzed condensation of resorcinol with aldehydes [41]; such reaction, catalyzed by ytterbium(III) triflate nonahydrate $\{[Yb(H_2O)_9](OTf)_3\}$ leads to resorcinarenes **1** [51] (Scheme 1).

Scheme 1



The condensation of resorcinol with benzaldehyde derivatives affords resorcinarenes **2–4**, which undergo acetylation to give acetylresorcinarenes **5–7** [52]. It was found that these compounds, and among them especially **7a,b** are efficient carriers of K^+ ions across liquid membranes showing enhanced K^+/ Na^+ selectivity (Scheme 2).

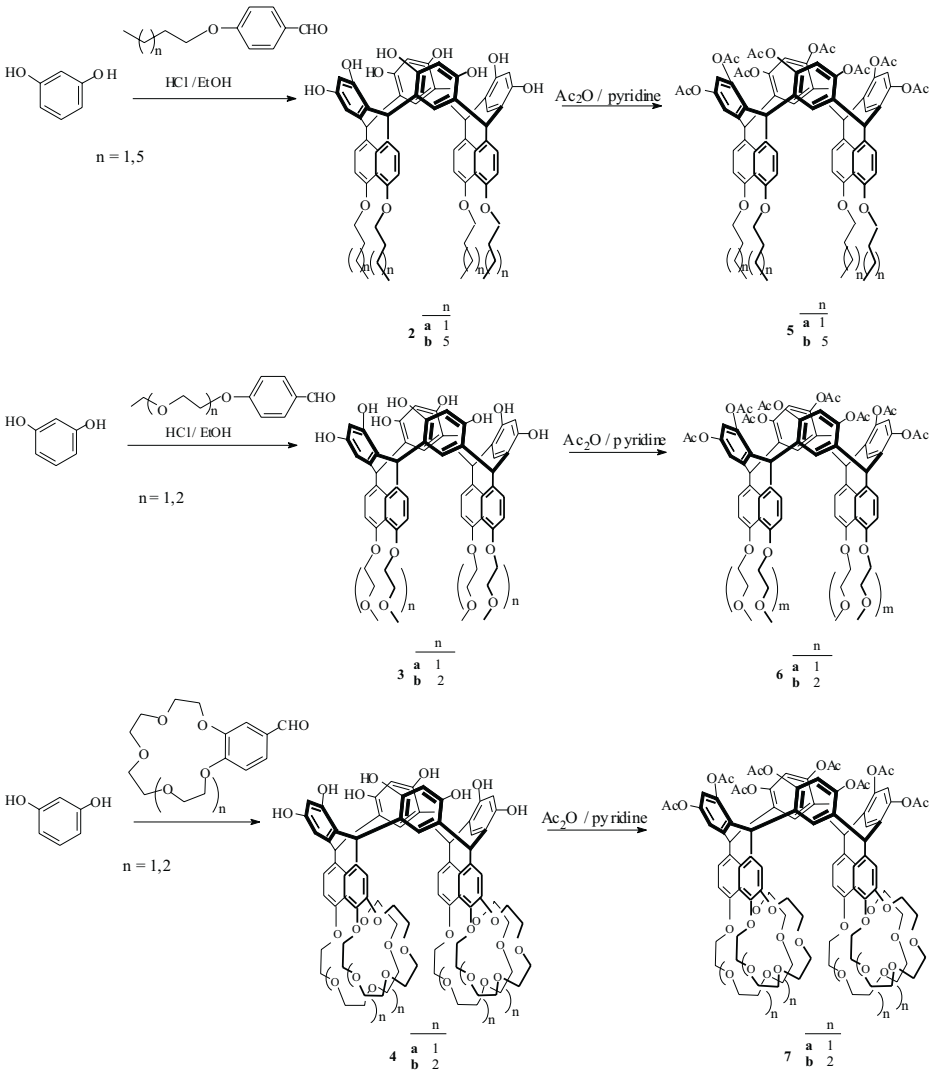
In the study of conformational properties of resorcinarenes, the relative stability of five extreme conformations of **1a** and their intramolecular hydrogen bonding was investigated by *ab initio* calculations [53]. The stabilizing influence of intramolecular hydrogen bonding has been observed.

Without intramolecular hydrogen bonds, the boat conformation was found to be the most stable. When stabilizing circular homodirectional array of intramolecular hydrogen bonds is present, the symmetrical C_4 crown conformation was identified as the most stable one. In this hydrogen bonding system each resorcinol moiety serves simultaneously as hydrogen bond donor and acceptor.

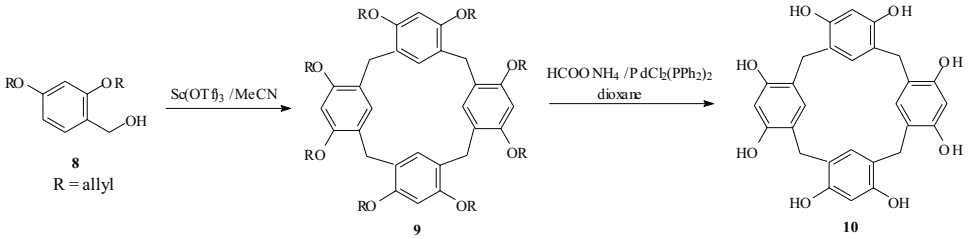
The structure of **1c,d** has been investigated by ^1H and ^{13}C NMR studies [54]. It was established that these compounds exist in CD_3CN in the crown conformation, in $CDCl_3$, however, this conformation is violated by the intramolecular associations.

Another approach involves the cyclocondensation of 2,4-bis(allyloxy)benzyl alcohol **8** catalyzed by $Sc(OTf)_3$, leading to compound **9**. The subsequent deallylation of **9** by treatment with ammonium formate and $PdCl_2(PPh_3)_2$ affords the parent resorcinarene **10** existing in 1,3-alternate conformation [55] (Scheme 3).

Scheme 2



Scheme 3



8
R = allyl

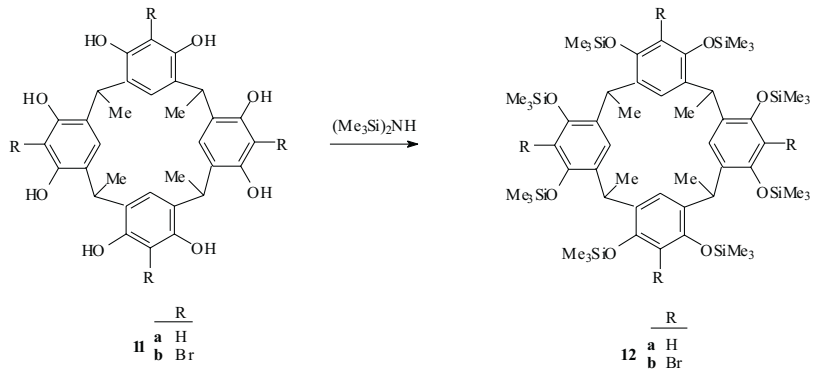
9

10

2. Reactivity of resorcinarenes

In the study of reactivity of resorcinarenes [56], **11a,b** were treated with hexamethyldisilazane to give octasubstituted resorcinarenes **12a,b** [57] (Scheme 4).

Scheme 4

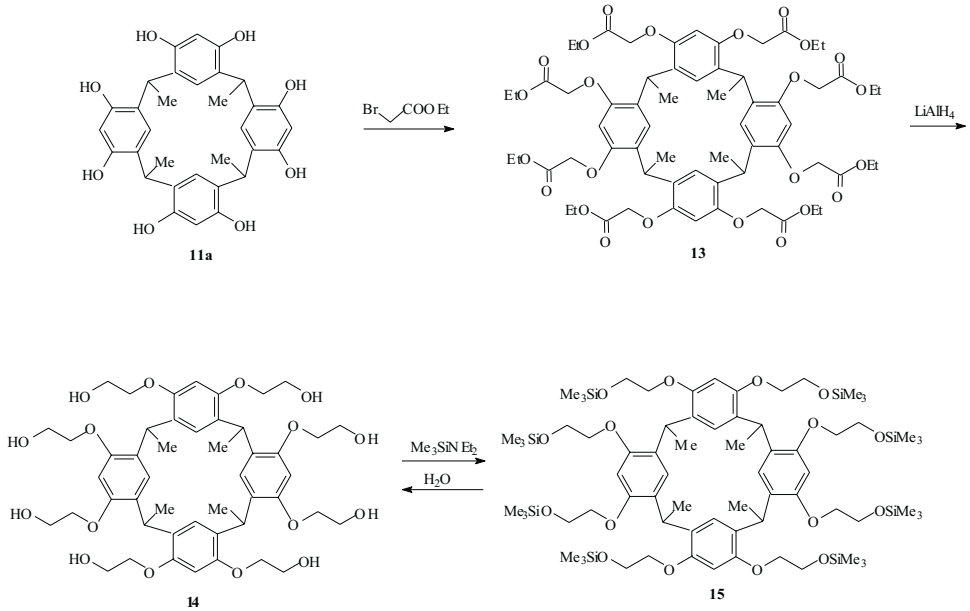


11 a R = H; b R = Br

12 a R = H; b R = Br

The reaction of **11a** with ethyl bromoacetate leads to the ester **13**, which was reduced with $LiAlH_4$ to yield hydroxyethyl derivative **14**. Since **14** could not be obtained in the pure state, this compound as the crude substance was treated with diethylaminotrimethylsilane affording **15**, which by hydrolysis yielded pure **14** [57] (Scheme 5).

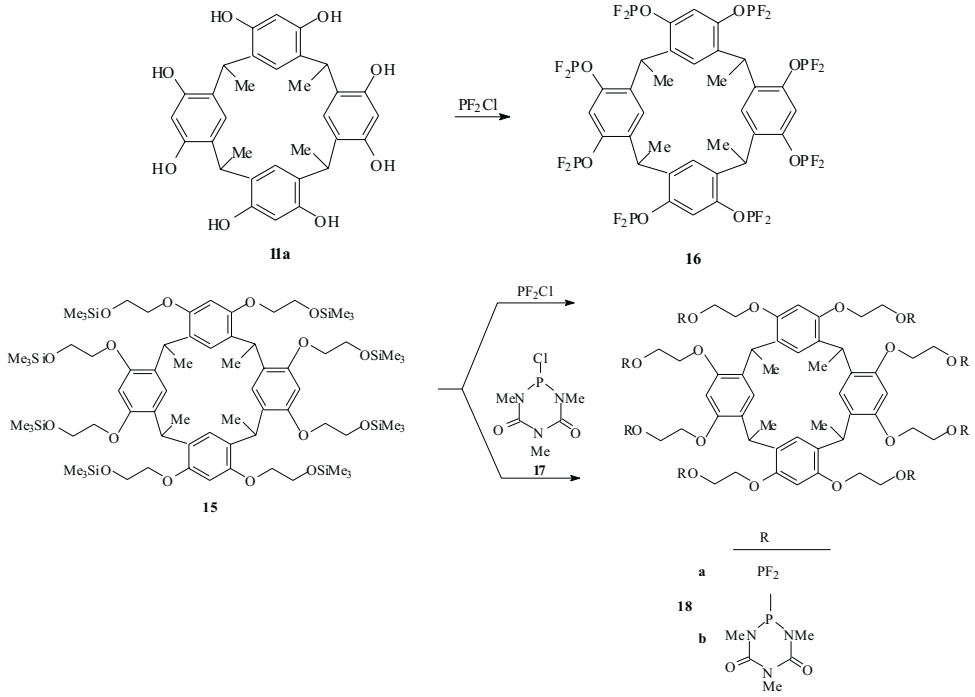
Scheme 5



11a **13** **14** **15**

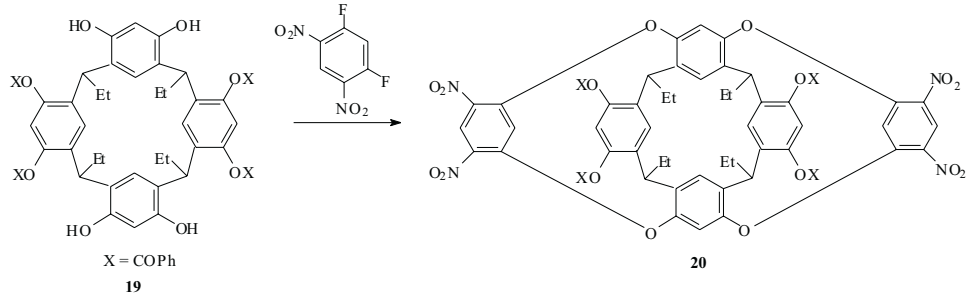
The reaction of **11a** with chlorodifluorophosphine leads to the unstable derivative **16**, while reactions of **15** with this reagent and with chlorotriazaphosphorindione **17** afford stable compounds **18a,b** [58] (Scheme 6).

Scheme 6



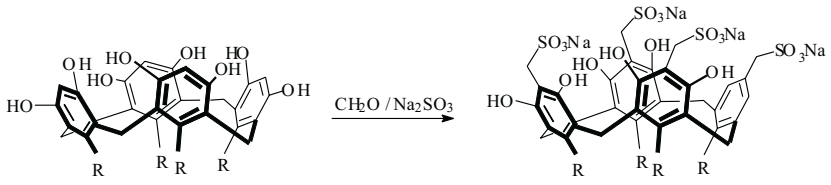
Resorcinarene derivative **19** reacts with 1,3-difluoro-4,6-dinitrobenzene to give the rigid tetranitroresorcinarene **20** [59] (Scheme 7).

Scheme 7



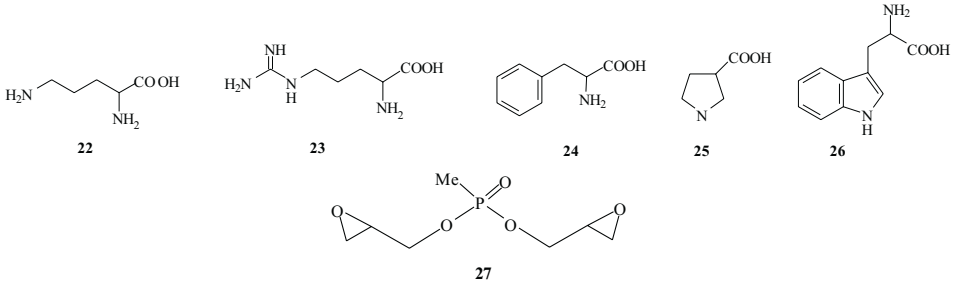
The reaction of resorcinarenes **1a** and **1c** with formaldehyde and sodium sulfite affords water soluble compounds **21a,b** [60]. It was observed that **21a** forms host-guest complexes with α-amino acids **22–26** and a stable 1:1 complex with diglycidylmethyl phosphonate **27** [61] (Scheme 8).

Scheme 8



	R
11a	Me
1c	C_9H_{19}

		R
21	**a**	Me
	b	C_9H_{19}

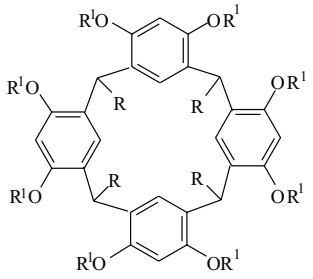


22 **23** **24** **25** **26**

27

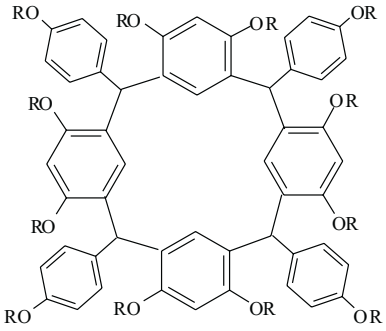
Investigating functionalization of hydroxyl groups of resorcinarenes it was shown that resorcinarene **28a** may be converted into **28b,c** [62] and resorcinarene **29a** into **29b–e** derivatives [63] (Scheme 9).

Scheme 9



R = Me, Et

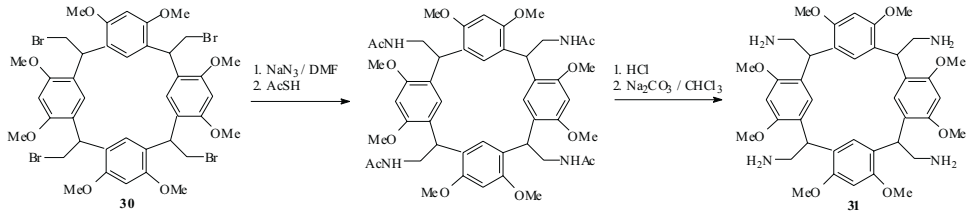
	R^1
a	H
28 **b**	Me
c	Ac



	R
a	H
b	Me
29 **c**	Ac
d	COPr
e	CH_2Ph

In the study of aminomethylation of resorcinarenes [64,65] following reactions of tetra(bromomethyl)resorcinarene **30** leading to tetra(aminomethyl)resorcinarene **31** have been made. It was observed that **31** forms the 2:1 complex with Cu^{2+} ion [66] (Scheme 10).

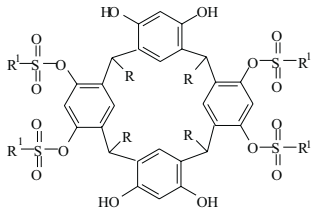
Scheme 10



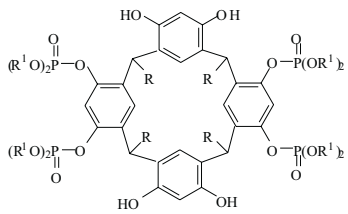
30 **31**

Resorcinarene of C_{2v} symmetry tetrasulfonates, **32a–e** and tetraphosphates, **33a–c** are useful as molecular platforms for the design of cation receptors, containing different binding units in the molecule [67]. In order to obtain **32a–c** the resorcinarene **11a** was treated with arylsulfonylchlorides. The intramolecular hydrogen bonds S=O...H–O enable asymmetric arrangement of four arylsulfonyl groups and molecular chirality of **32a–c**. It was observed that **32c** forms in the solid state and in $CDCl_3$ the cross-shaped dimer linked by four intermolecular O–H. . . OH hydrogen bonds [68] (Scheme 11).

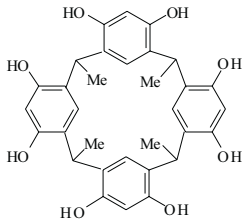
Scheme 11



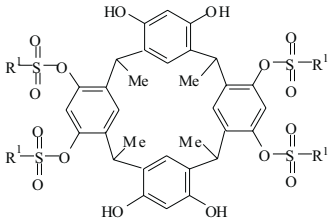
	R	R^1
a	Me	*p*-Tol
b	Me	*p*-ClC_6H_4
32 c	Me	Mes
d	Pr	*p*-Tol
e	C_5H_{11}	*p*-Tol



	R	R^1
a	Me	*i*-Pr
33 b	Me	Bu
c	C_5H_{11}	Et



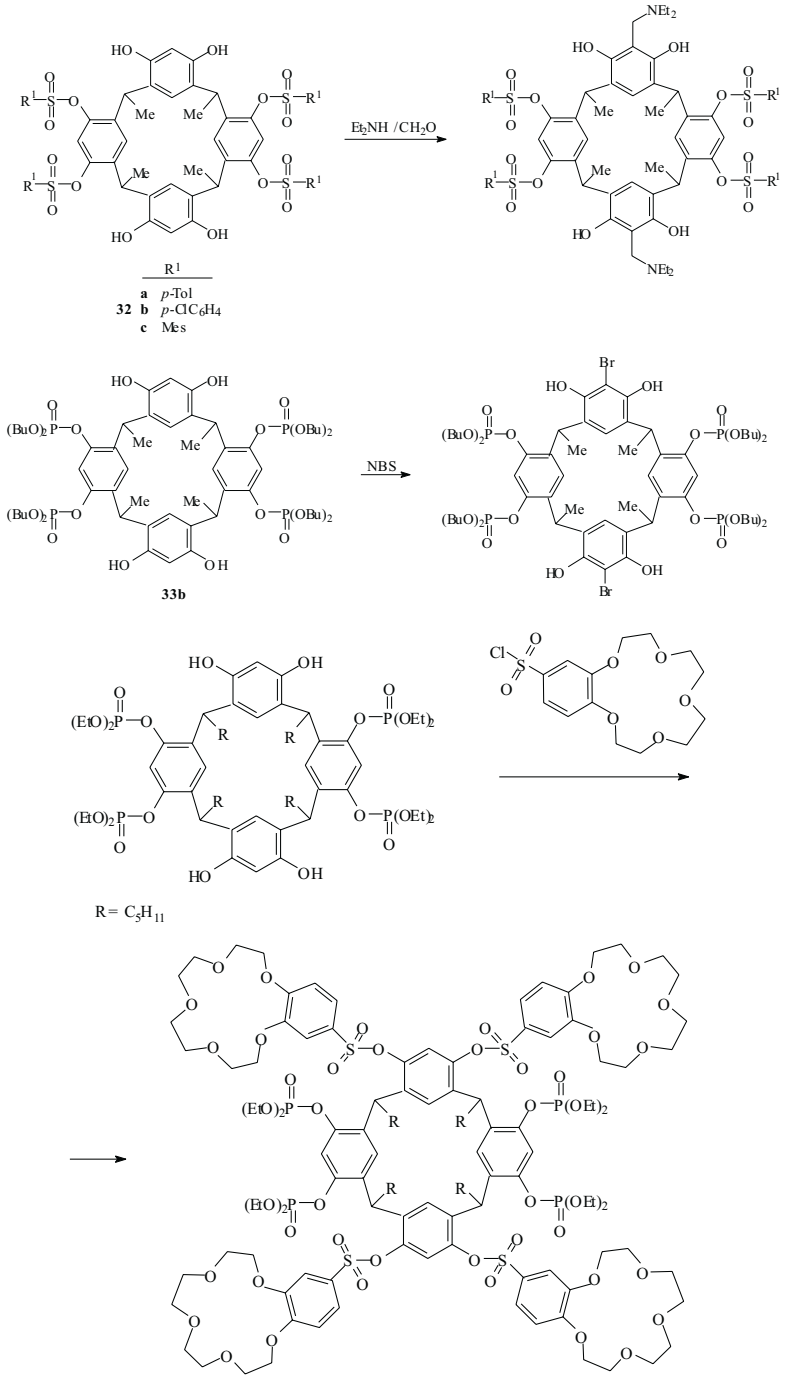
11a



a	*p*-Tol
32 b	*p*-ClC_6H_4
c	Mes

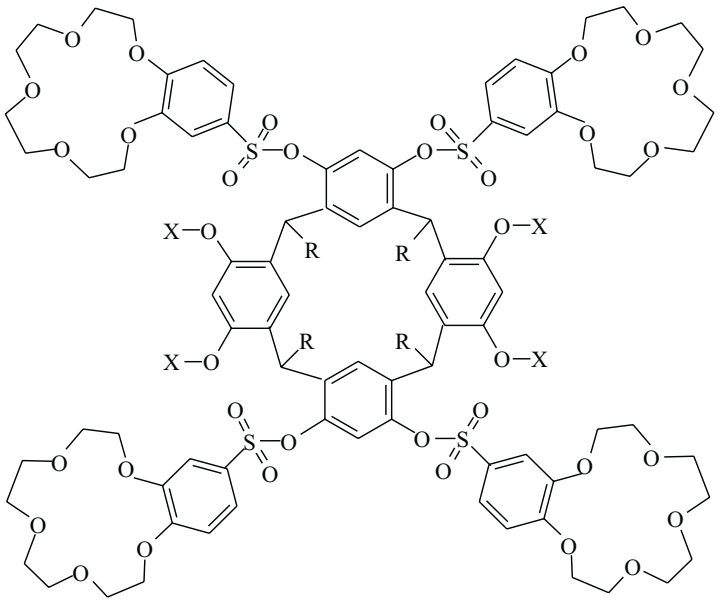
Following reactions of tetrasulfonates and tetraphosphates have been made [67] (Scheme 12).

Scheme 12



Compounds **34a–c** may complex alkali metal and NH_4^+ ions [67] (Scheme 13).

Scheme 13



		R	X
34	**a**	Me	SO_2Mes
	b	Me	$P(O)((OPr)_2$
	c	C_5H_{11}	$P(O)(OEt)_2$

Inherently chiral, enantiomerically pure resorcinarenes (+)-**35** and (–)-**35** have been synthesized. For this purpose resorcinarene **11a** was mono *O*-functionalized with (S)-(+)-10-camphorsulfonyl chloride serving as a chiral auxiliary to give diastereomers (+)-**36a** and (–)-**36b**, which were separated by HPLC [69].

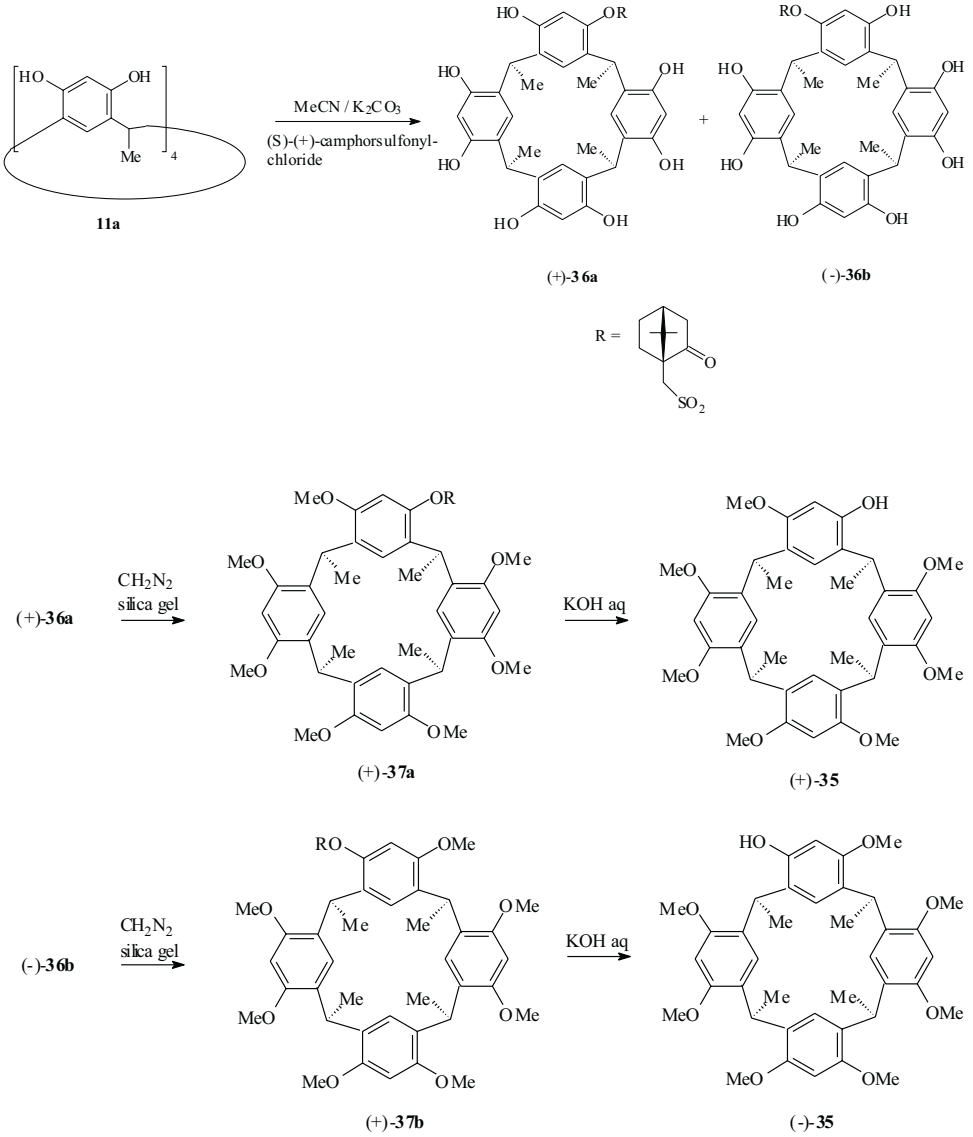
The treatment of (+)-**36a** and (–)-**36b** with ethereal diazomethane solution in the presence of silica gel as a Lewis acid gave permethylated resorcinarenes (+)-**37a** and (+)-**37b** without epimerization. The chiral auxiliary was removed by treatment of (+)-**37a** and (+)-**37b** with potassium hydroxide solution to give enantiomeric (+)-**35** and (–)-**35**, stable towards moderate acid and basic conditions [69] (Scheme 14).

For the inherently chiral tetrabenzoxazine resorcinarene **38** the enantiomerization barrier has been determined by computer simulation of the dynamic HPLC experiments [70] (Scheme 15).

The reaction of **39a,b** leads to bromo-*o*-xylyl cavitands **40a,b** [71] (Scheme 16).

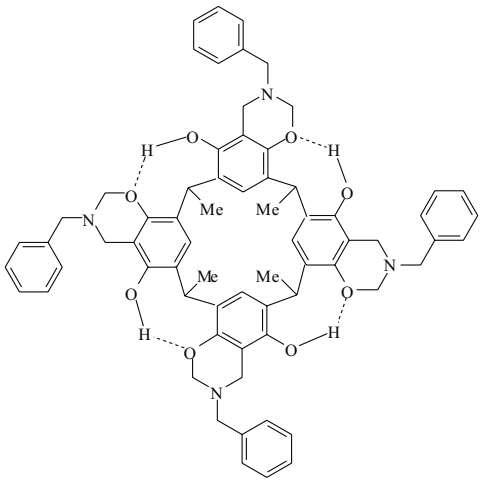
A rapid, three-step synthesis of dendrimers by divergent method, using resorcinarenes as core molecules, was made; highly functionalized resorcinarenes **41** and **42** having 12 and 16 hydroxyl groups, respectively, served for this purpose [72].

Scheme 14



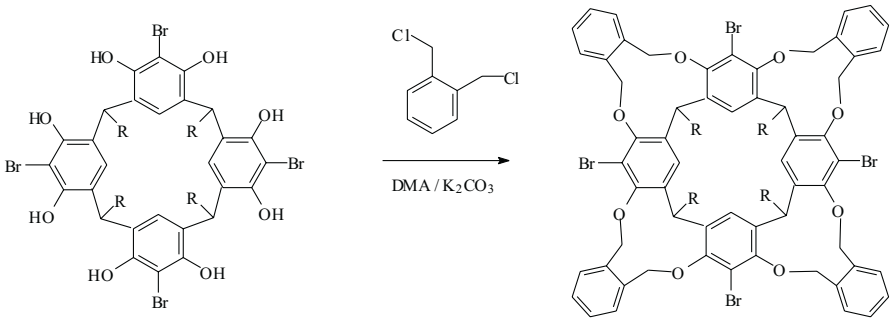
Compounds **41** and **42** have been prepared by a reaction of resorcinol with 4-hydroxybenzaldehyde and 3,5-dihydroxybenzaldehyde, respectively. They were treated with dendron **43** used as the building block; the deprotection of the formed first-generation dendrimers **44** and **45** leading to **46** and **47** has been made by reduction with bis(triphenylphosphine)palladium dichloride and ammonium formate. The subsequent reaction with **43** afforded second generation dendrimers **48** and **49**, containing 48 and 64 terminal groups, respectively [72] (Scheme 17).

Scheme 15



38

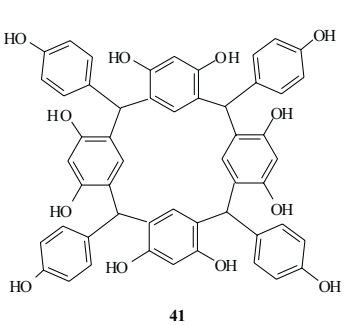
Scheme 16



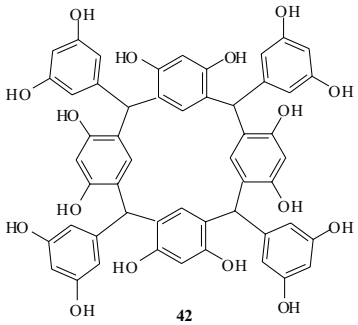
	R
39a	Me
39b	CH_2CH_2Ph

	R
40a	Me
40b	CH_2CH_2Ph

Scheme 17

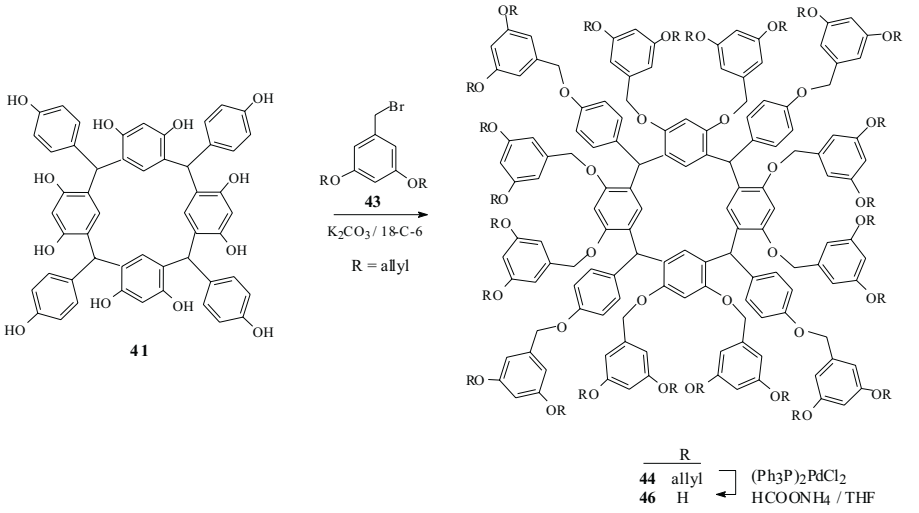


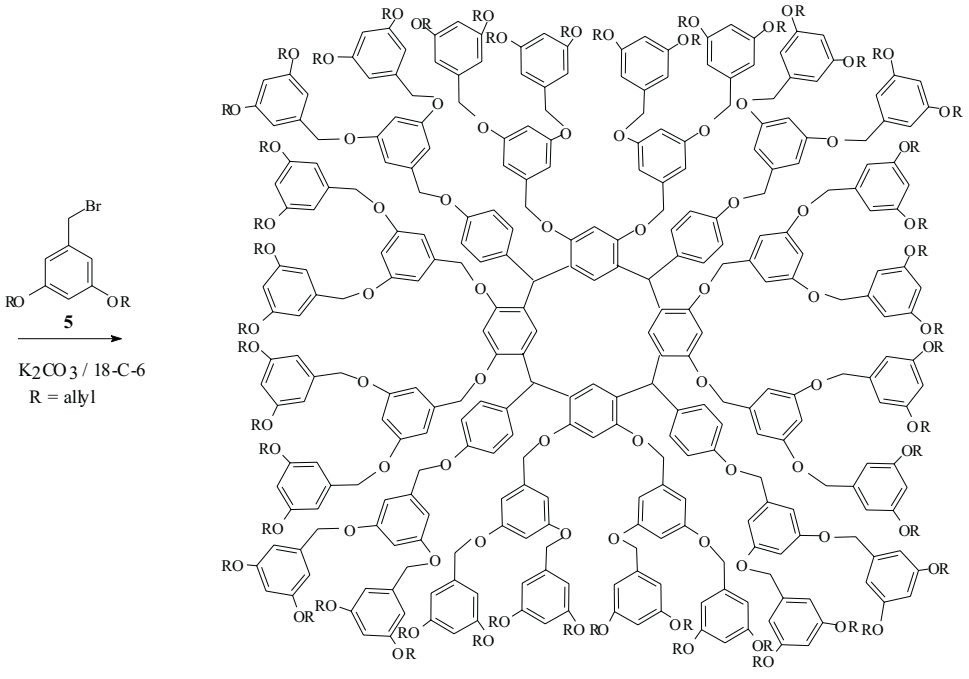
41



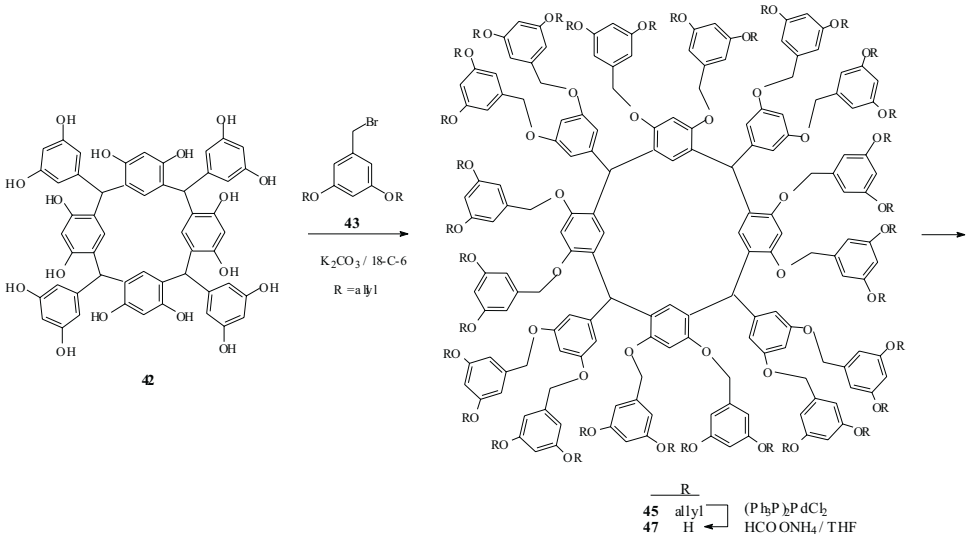
42

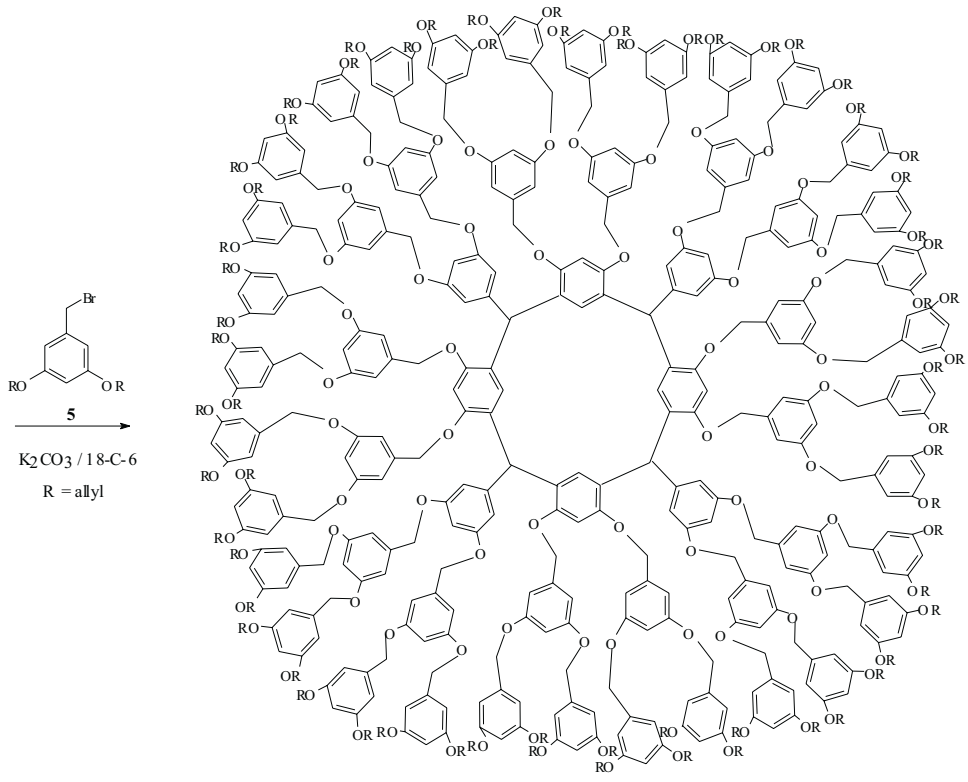
Scheme 17 (continuation)





Scheme 17 (continuation)

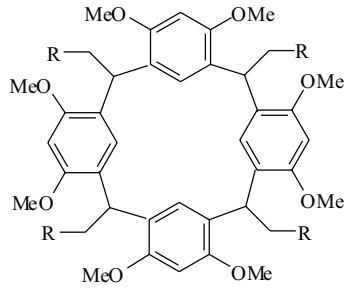




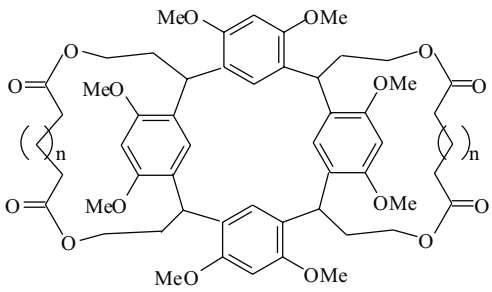
3. Complexes of resorcinarenes

Resorcinarenes **50a,b** interact with $FeCl_3$ and $GaCl_3$ in chloroform [73]. More rigid resorcinarene derivatives **51a–c** give 2:1 complexes with $GaCl_3$ [73] (Scheme 18).

Scheme 18



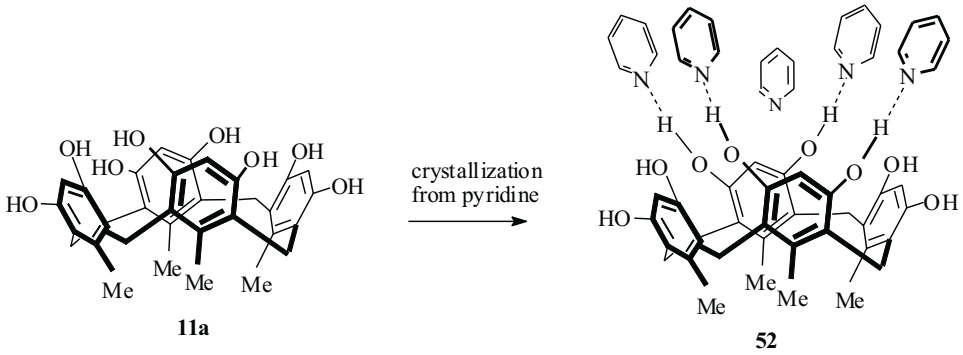
	R
50 a	Me
b	COO-*i*Pr



	n
a	1
51 b	2
c	3

The crystallization of resorcinarene **11a** from pyridine leads to the formation of the complex **52** [74]. In **52** four pyridine molecules are situated over resorcinarene molecule; they form hydrogen bonds with four hydroxyl groups of two opposite resorcinol rings; the fifth pyridine molecule is situated loosely over the resorcinarene cavity (Scheme 19).

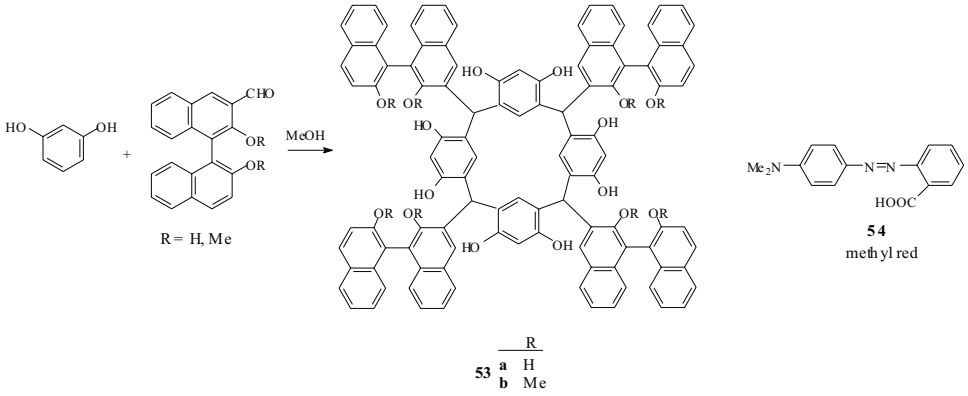
Scheme 19



11a **52**

The analysis of saccharides is of importance, due to their therapeutic properties [75,76], as well as in diabetes treatment and in industrial fermentation processes [77]. In this study [78], binaphthyl resorcinarenes **53a,b** have been used [79]; they are obtained as follows (Scheme 20).

Scheme 20



Resorcinarenes **53a,b** form water soluble complexes with methyl red **54**, which bind saccharides. Methyl red, serving as a chromophore is weakly, non covalently bound to the resorcinarene molecule. Complexes **53a**/**54** and **53b**/**54** show intensive absorption at visible spectral range. Resorcinarenes **53a,b** form 1:1 complexes with saccharides by a competition with color label **54**; this process can be monitored visually, in this way allowing the chemical sensing for saccharides.

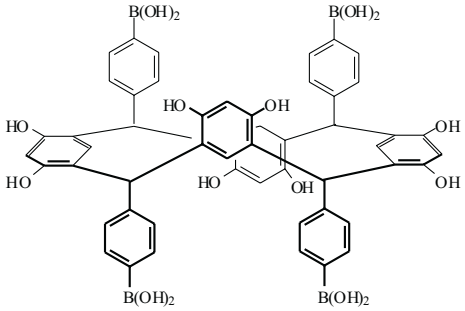
It was shown that **53a,b** are selective receptors, they bind oligosaccharides (D(+) maltose, maltotriose, maltotetraose, α-D-lactose and β-D-lactose) more strongly than monosaccharides (α-D-glucose, D(+)galactose, D(–)fructose) and two saccharide-like species – L-sorbitol and L-gulonic acid γ-lactone [79].

Another analysis of saccharides is based on observation that colorless DMSO solutions of **55**, **11a** and **56** upon heating undergo significant color appearance [77,80]. This behavior results from the formation of xanthenes **57**, which are strongly absorbing species. The complexation of xanthenes, serving as chromophores with mono- or oligosaccharides, enables their visual detection [77].

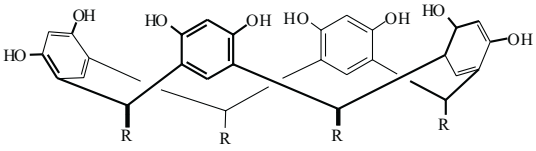
The formation of xanthenes begins with the ring opening of the macrocycle leading to acyclic resorcinol oligomers, an example is the conversion of **11a** into the compound **58**. This process is catalyzed by strong acids, which form *in situ* by O_2-induced radical decomposition of DMSO. The subsequent oxidation of **58** gives xanthene **57**. The heating of solutions of maltodextrins **59** in DMSO/H_2O (9:1) in the presence of resorcinarene **56** enables their visual detection due to color changes [77] (Scheme 21).

Slow evaporation of the solution of resorcinarene **11a** in acetone, no precautions taken to exclude adventitious water leads to formation of an ice-like, cyclic $(H_2O)_8$ cluster in the solid-state structure of an organic supramolecular complex [81]. The crystal structure consists of two-dimensional bilayers of **11a** incorporating water and acetone molecules. The water octamer is stabilized by its environment in the supramolecular lattice; the network is hydrogen bonded.

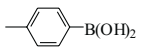
Scheme 21

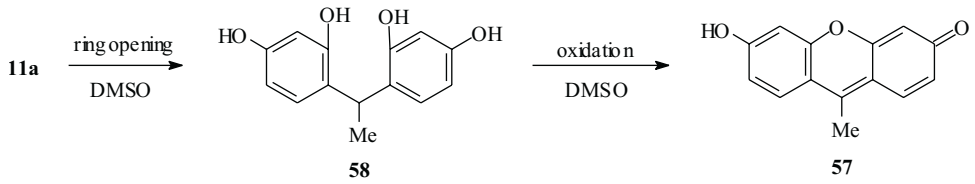


55

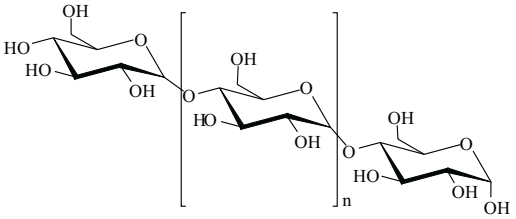


	R
11a	Me

56 



58 **57**



59 n = 0-5

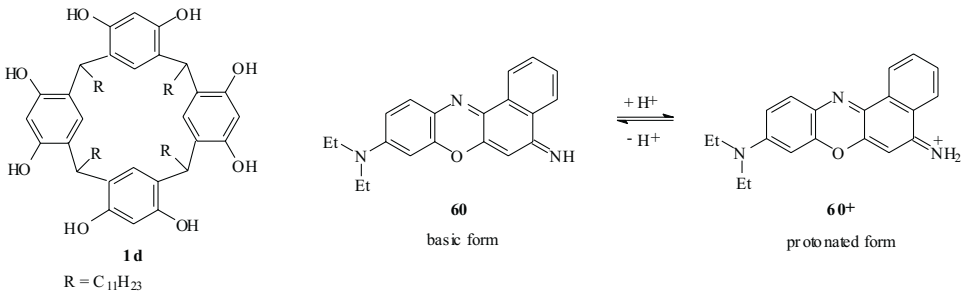
Co-crystallization of **11a** with 2,2′-bipyridine from methanol gives a doubly solvated 1:1 adduct **11a**-2,2′bpy-MeOH-H_2O (1:1:1:1.16); in the case of 4,4′-trimethylenebipyridine the solvated 1:2 adduct **11a**-4,4′-trimethylenebipyridine-MeOH (1:2:0.5) is formed. Both adducts are held by hydrogen bonds [82].

4. Host-guest systems of resorcinarenes

In the study of host-guest systems of resorcinarenes [83], it was observed that resorcinarene **1d** forms a host-guest complex with Nile Blue $\mathbf{60}^+$ [84]. The Nile Blue exists in a basic and in a protonated form, **60** and $\mathbf{60}^+$, respectively. The Nile Blue salts serve as indicator dyes in optical sensors [85] and are used as photosensitizers in photodynamic therapy [86].

This host-guest interaction has been investigated by dissolving resorcinarene **1d** and Nile Blue base **60** in two apolar solvents, dichloromethane and toluene. In the first step the weakly bound complex **1d·60** is formed, and simultaneously the formation of the tightly bound ionic species $\mathbf{1d}^-\cdot\mathbf{60}$ takes place ($\mathbf{1d}^-$ is the monophenolate form of **11d**). The subsequent step affords supramolecular complex $\mathbf{1d}\cdot\mathbf{60}^+$. It was observed that the fluorescence lifetime of $\mathbf{60}^+$ significantly decreases upon complexation [84] (Scheme 22).

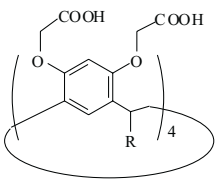
Scheme 22



Resorcinarene **61** is a macrocyclic amphiphile able to form interfacial ultrathin liquid crystalline layers. By spreading a mixture of **61** (a host) with the nematic liquid crystalline azobenzene **62** (a guest), the homogeneous host-guest mixed monolayers are formed on a water surface; they display bilayered structure by further compression [87].

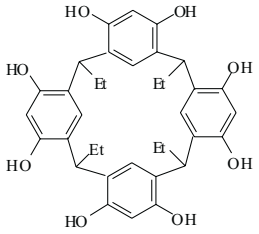
The X-ray analysis of the complex of resorcinarene **1a** with 3-phenylpropionic acid choline ester (as a chloride) **63** with composition of $2(\mathbf{1a}\cdot\mathbf{63}^+)\cdot 2Cl^-\cdot 9H_2O$ formed through multiple cation-π interactions between aromatic rings of **1a** and quaternary ammonium groups of **63** has been reported [88] (Scheme 23).

Scheme 23

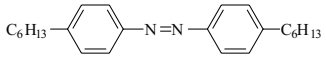


61

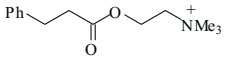
R = $C_{11}H_{23}$



1a



62



Cl^-

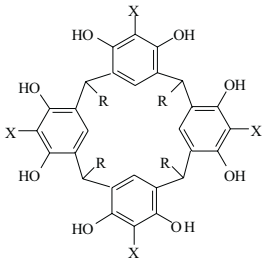
63

Lipophilic compounds **1d** and **64** have been investigated in view of their molecular recognition of pyrimidine and xanthine bases [89]. Extraction experiments have shown following sequence of extraction abilities in chloroform for **1d**: cytosine > uracil > thymine, and for **64**: thymine > uracil > cytosine. One should mention here also that resorcinarene **1d** forms 1:4 host-guest complex with dioxane [90].

The complex **65** consisting of resorcinarene **11a** and 4,4′-bipyridine may serve as a host for ferrocene, acetyl ferrocene and diacetyl ferrocene **66** [91]. It was observed that **66**, when serving as a guest adopts 1,1′ conformation **66a**, although it usually exists as 1,3′ conformer **66b**.

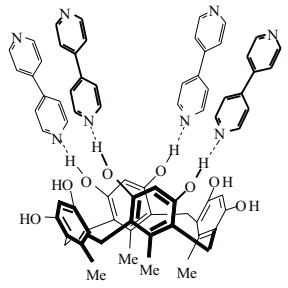
Resorcinarenes **67a,b** may self-assemble selectively to form vesicles, stabilized by hydrogen bonds [92]. Vesicles from **67a** and **67b** consist of unimolecular membranes, in which the hydroxyl groups face the aqueous phase. It was shown that resorcinarene **67a** plays a role of an artificial potassium ion channel when embedded in planar bilayers of soyabean lecithin [92] (Scheme 24).

Scheme 24



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

	X
1d	H
64	OH



65

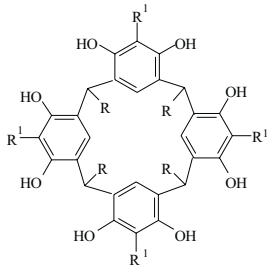
1,1'-conformer

a

1,3'-conformer

b

66

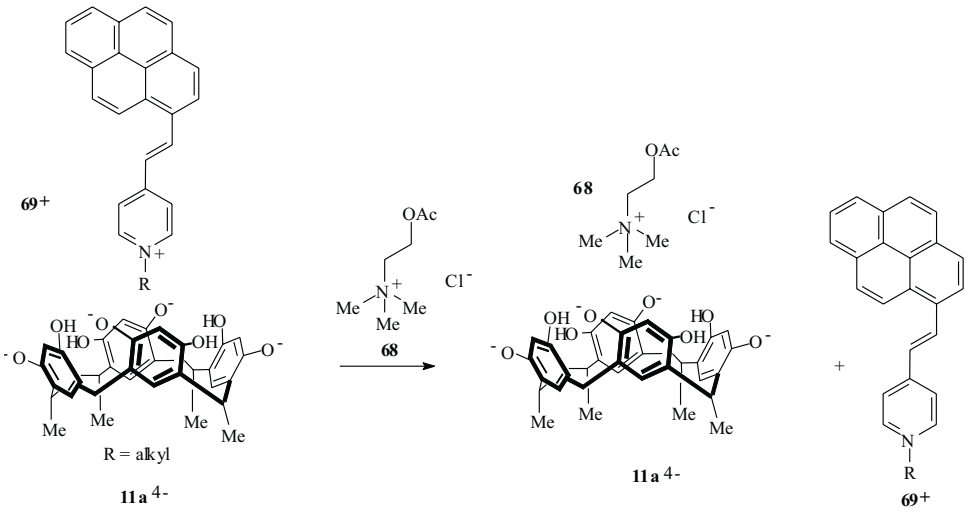


R = $C_{17}H_{35}$

	R^1
67 a	H
b	OH

In the study of synthetic sensors [93], for the detection of acetylcholine chloride **68** the fluorophore displacement, shown below, may be used (Scheme 25).

Scheme 25



When pyrene-modified N-alkylpyridinium cation $\mathbf{69}^+$, serving as fluorophore is bound in the cavity of $\mathbf{11a}^{4-}$, its fluorescence is quenched. The addition of **68** results in the release of $\mathbf{69}^+$ and the regeneration of its fluorescence [93]. One should take into account that strongly basic conditions necessary to deprotonate four hydroxyl groups of **11a** may cause degradation of **68**. In order to overcome this inconvenience, resorcinarene **11a** may be replaced by calix[n]arene *p*-sulfonates (n = 4 or 6) [93].

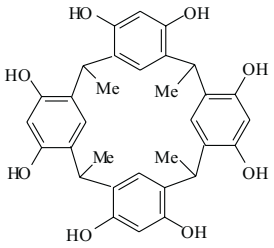
5. Capsules of resorcinarenes

Formation of large capsules from resorcinarenes is discussed in numerous works [94,95]. The dimer of resorcinarene **1a** linked by ten hydrogen-bonding water molecules encapsulates in the crystalline state the hydrogen-bonded complex Et_3N^+–H....OH_2; bromide anions are situated outside the cavity [96].

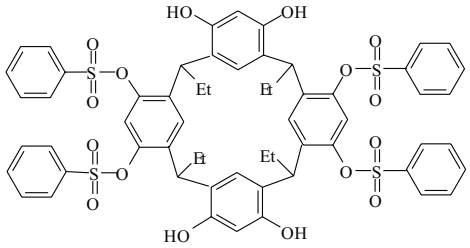
The boat conformers of resorcinarenes **11a** and **70** form hydrogen-bonded, solid-state capsules including two triethylammonium cations $\mathbf{71}^+$ simultaneously [97]. Two molecules of **11a** or **70** in the boat conformation are linked *via* four hydrogen bonded chloride anions from $Et_3N^+HCl^-$ to form dimers. The resulting large, negatively charged chambers may encapsulate two $\mathbf{71}^+$ cations by strong electrostatic and hydrogen-bonding interactions (Scheme 26).

Co-crystallization of resorcinarene **11a** with 4,4′-bipyridine in the presence of nitrobenzene (**72**) gives crystalline **73**·2(**72**) assembly consisting of the large capsule **73** held together by hydrogen bonds, which accomodates two nitrobenzene molecules [98] (Scheme 27).

Scheme 26



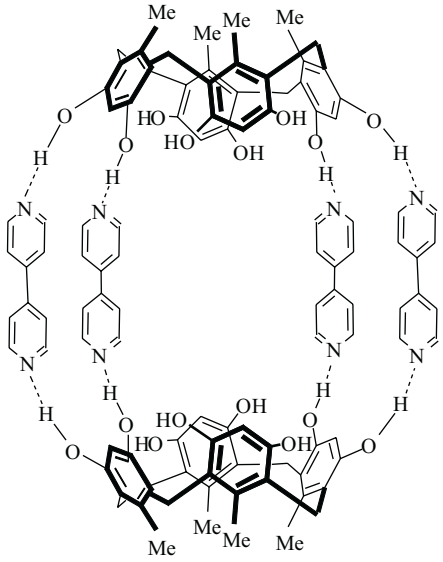
11a



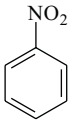
70

71$^+$

Scheme 27



73

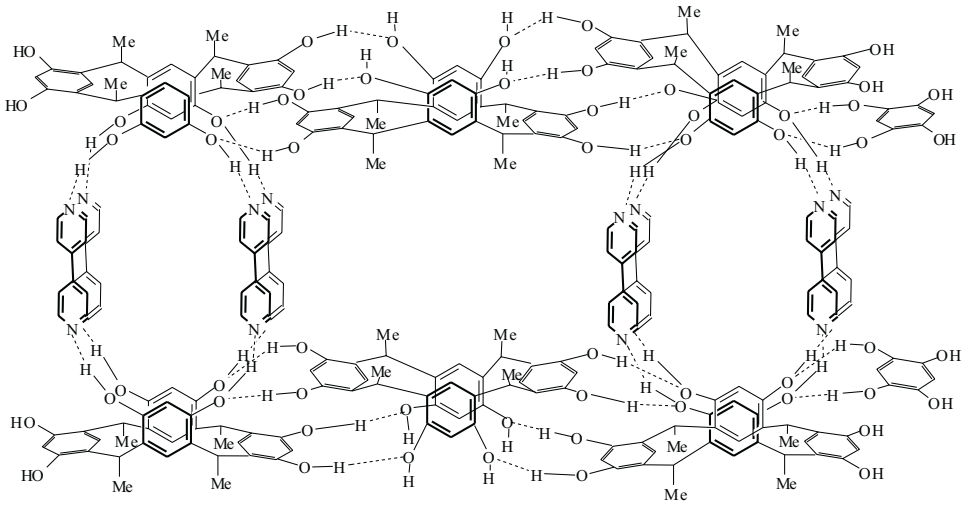


72

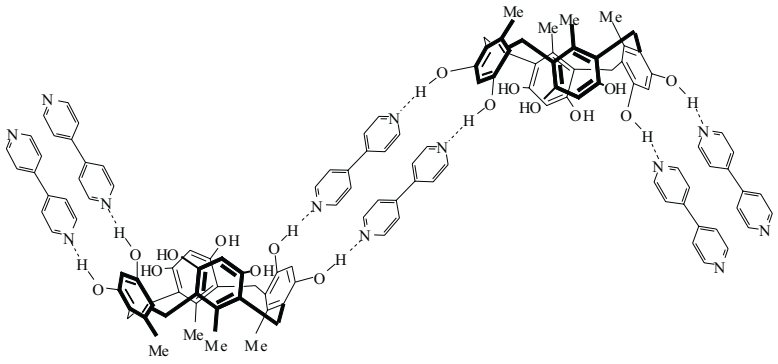
Co-crystallization of resorcinarene **11a** with 4,4′-bipyridine from ethanol in the presence of *m*-xylene yields a two-dimensional extended framework **74** [99]. This process involves the structural reorganization of the wave-like, hydrogen bonded network **75** [91] and capsule **73** [98] affording in the presence of a suitable aromatic guest, *e.g. m*-xylene, the two-dimensional **74**. Resorcinarene **11a** adopts in **74** a "T-shaped" conformation [100]. The above process is an example of the conformational isomerism, leading to supramolecular isomerism [99,101] (Scheme 28).

It was observed that **11a** and **1d** form hexameric hydrogen bonded capsules. The hexamer of **11a** has a shape of a cube with six resorcinarenes as its sides and eight water molecules at corners. It was found that hexamer of **1d** may encapsulate tetraalkylammonium and phosphonium salts [102].

Scheme 28



74

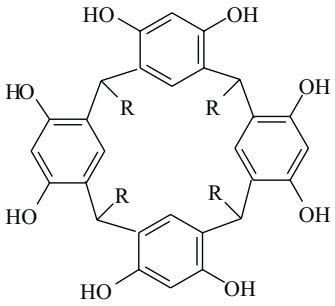


75

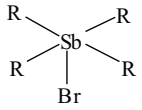
Covalent antimony(V) bromides may induce capsule formation; inside the capsule there is enough space to co-encapsulate aromatic guests, such as benzene, toluene or *p*-xylene [103]. Capsule consisting of six **1d** molecules, which incorporates Bu_4SbBr **76a,** may encapsulate benzene, toluene, *p*-xylene and *p*-phenyltoluene. In the absence of **76a** no encapsulation of these aromatics takes place, since **76a** playing the role of a principal guest determines the inner space of the capsule.

Capsule consisting of six **1d** molecules, which incorporates Ph_4SbBr **76b**, may accomodate benzene, toluene and *p*-xylene, however, no encapsulation of *p*-phenyltoluene takes place. This fact results from larger volume of **76b** than that of **76a**, therefore, there is not enough space for encapsulation of *p*-phenyltoluene [103] (Scheme 29).

Scheme 29



	R
11a	Me
1d	$C_{11}H_{23}$



		R
76	**a**	Bu
	b	Ph

6. Mono- and multilayers of resorcinarenes

Multi-point adsorptivity of **1b,d**, **77a–c** and **78** crown conformers on polar surfaces of amorphous polar substrates, such as silica and poly(vinyl alcohol) from solutions of less polar solvent (*e.g.* toluene), may serve for an easy formation of monomolecular layers [104]. The surface adsorption is achieved by simple immersing of substrate plates in a solution of less polar solvents and the desorption by immersion in polar solvents.

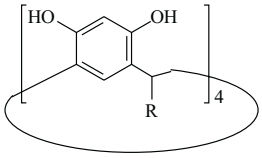
Langmuir monolayers and multibilayered Langmuir-Blodgett (LB) films of resorcinarenes **79a,b** deposited on hydrophobic substrates have been characterized using UV-vis and emission spectroscopies [105]. Luminescence spectra of multilayered LB films of **79a**/Tb^{3+} and **79b**/Tb^{3+} have been also discussed [105] (Scheme 30).

Studying adsorption of resorcinarenes on polar substrate plates [106], it was observed that resorcinarenes and their *O*-carboxylated derivatives adsorb readily on silica surface to form self-assembled monolayers (SAMs) with relatively dense packing. The crown conformer of **80** may be used for preparation of photofunctional monomolecular layers [107]. In order to enhance the desorption resistance, its photodimerization leading to **81** or **82** may be of use (Scheme 31).

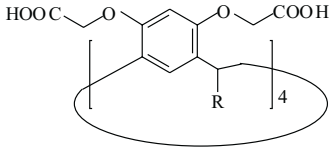
It was found that resorcinarene **83** shows liquid crystalline behavior. It possesses smectic A phase, which is transformed into nematic phase, in which a corn-like structure is formed [108]. Resorcinarene **83** is promising to act as a high response liquid crystal in its nematic phase.

Resorcinarenes **84a,b** were adsorbed on silica surface in order to investigate the fluorescence of cyanobiphenyl moieties and to compare it with fluorescence of **85**, *i.e.* cyanobiphenyl modified by silylation [109]. It was found that in the case of **84a,b** the fluorescence intensity is significantly lower, this fact resulting from the high rigidity of resorcinarene structure [109] (Scheme 32).

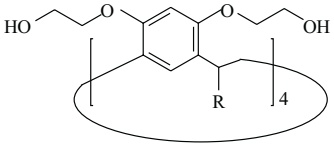
Scheme 30



	R
1b	C_5H_{11}
1d	$C_{11}H_{23}$

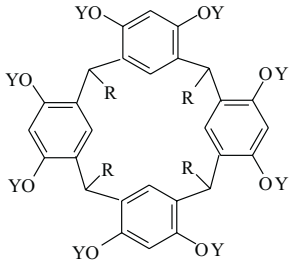


	R
a	C_5H_{11}
77 b	C_7H_{15}
c	$C_{11}H_{23}$



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

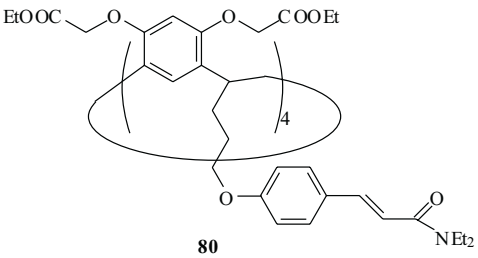
78



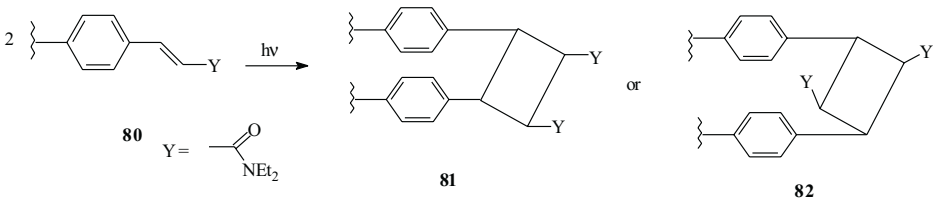
$R = C_{11}H_{23}$

	Y
a	CH_2COOMe
79 b	CH_2CONEt_2

Scheme 31



80

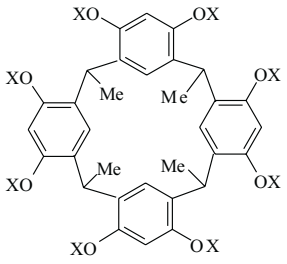


80 Y =

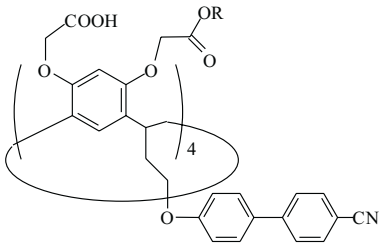
81

82

Scheme 32



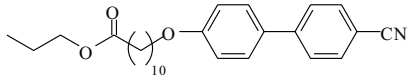
83

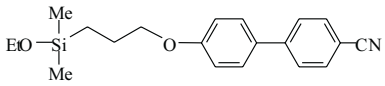


84

	R
a	H
b	Et

X =

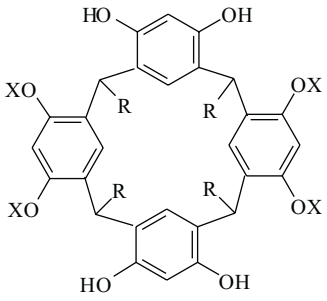




85

In the study of condensation of organic vapors within nanoporous thin films, resorcinarenes **86** and **87** have been used for LB films [110]. Adsorption of vapors of hexane, chloroform, benzene, toluene, *p*-xylene and aniline was investigated *in situ* using quartz-crystal microbalance (QCM), ellipsometry and surface plasmon resonance (SPR) techniques.The adsorption mechanism was proposed (Scheme 33).

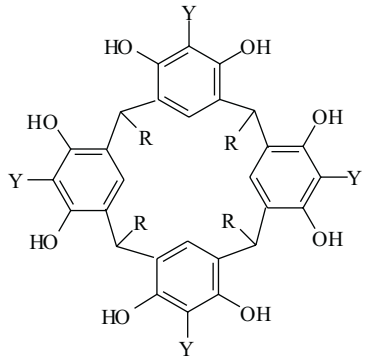
Scheme 33



86

$R = C_5H_{11}$

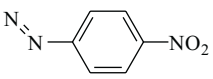
X = P(O)(O *i*-Pr)$_2$



87

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

Y =



Azobenzene units, incorporated into resorcinarenes **88a** and **88b** existing in a crown conformation show efficient E/Z photoisomerization in densely packed monolayers on a water surface, in LB films and in surface-adsorbed monolayers [111].

Resorcinarenes **88c** and **88d** may adsorb on a silica surface *via* hydrogen bonding affording densely packed SAMs; they may be used in the preparation of photofunctional monolayers containing azobenzene moieties [112]. However, due to the presence of hydrogen bonds between the polar heads and silica surface, in the case of exposure to polar solvents, *e.g.* water, the partial desorption of macrocyclic amphiphiles, deteriorating the structure of SAMs occurs. In order to overcome this difficulty, self-assembled monolayers were constructed by the multi-point adsorption of **88c** and **88d** as crown conformers on aminated silica substrates [112]. Resorcinarenes **88c** and **88d** form densely packed monolayers on the aminated plates; these monolayers show very good desorption resistance due to the $COOH/NH_2$ interactions. The monolayers show a high level of E/Z photoisomerization of incorporated azobenzene moieties. The level of E/Z conversion of **88d** is lower than in the case of **88c**, due to steric hindrances in **88d** [112].

A correlation was reported between the ability to control nematic liquid crystal alignment and wetting properties of mixed monolayers formed by coadsorption of **88c** and **88d** [113]. Mixed monolayers of **88c** and **88d** have been prepared by the chemisorption *via* electrostatic interactions between aminated silica substrates and mixtures of **88c** and **88d** (Scheme 34).

Enantiomeric recognition of amino acids by resorcinarenes **89a–c** in Langmuir monolayers has been investigated [114]. It was established that **89a–c** in the contrary to nonderivatized **1d** show differences in parameters of their Langmuir monolayers, depending on the pH of the subphase. The protonation of the amine groups determines the properties of the monolayer [114].

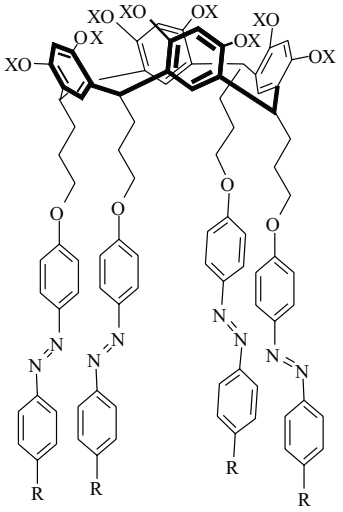
The transport of inorganic and organic cations across liquid membranes containing resorcinarenes **1d** and **89c,d** has been studied [115]. Alkali metal picrates **90** and primary ammonium picrates such as ethanoloamine picrate **91** and *n*-butylamine picrate **92** have been used as inorganic and organic salts, respectively. It was observed that **89d** showed a high ionoselectivity for lithium ion (Scheme 35).

The chromatographic behavior of the resorcinarene HPLC stationary phase **93** has been characterized for the separation of *cis*- and *trans*- isomers of thioxanthene derivatives such as flupentixol, clopenthixol, chlorprothixene **94–96**, respectively, and of benz[*b,e*]oxepin **97** [116] (Scheme 36).

The lipophilic resorcinarene **1d** and its octamethyl ether **98** may serve as dynamic coatings for modified stationary RP-18 phase for HPLC [117]. Resorcinarenes **1d** and **98** are strongly adsorbed on the modified silica gel RP-18 during HPLC of cresols, chlorophenols and nitrophenols. It was found that **1d** coated RP-18 phases are useful beds for HPLC separation of pyrimidine bases, such as thymine, cytosine and uracil [118] (Scheme 37).

Other examples of resorcinarenes are given in [119–129].

Scheme 34

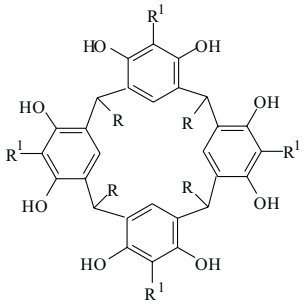


X = CH_2COOH

88

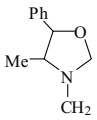
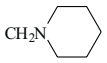
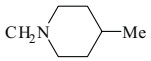
	R
a	H
b	cyclohexyl
c	C_8H_{17}
d	C_8F_{17}

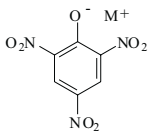
Scheme 35



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

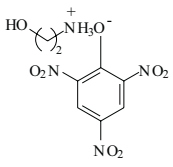
89

	R^1
a	CH_2NMe_2
b	
c	
d	

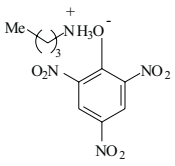


90

M = alkali metal

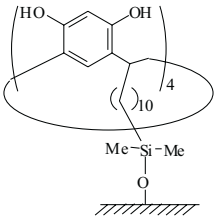


91

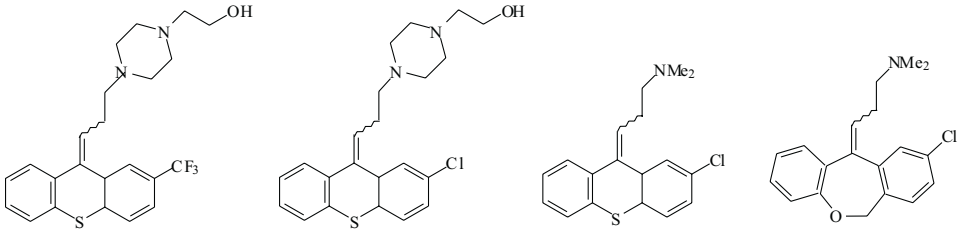


92

Scheme 36

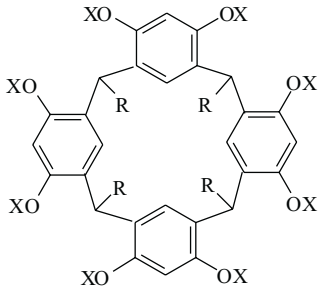


93



94 **95** **96** **97**

Scheme 37



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

	X
1d	H
98	Me

7. Pyrogalloarenes

Pyrogalloarenes **99**, *i.e*. hydroxyresorcinarenes are obtained by condensation of pyrogallol with aldehydes [130].

Pyrogalloarenes usually are bowl-shaped, all-*cis*, *i.e. rccc* isomers (cone conformation). A most common alternative are *cis-trans-trans*, *i.e. rctt* isomers, (chair conformation), in which two opposite rings occupy axial, and two remaining rings – two equatorial positions. It was observed that aliphatic aldehydes usually lead to *rccc*, and aromatic aldehydes to *rctt* isomers.

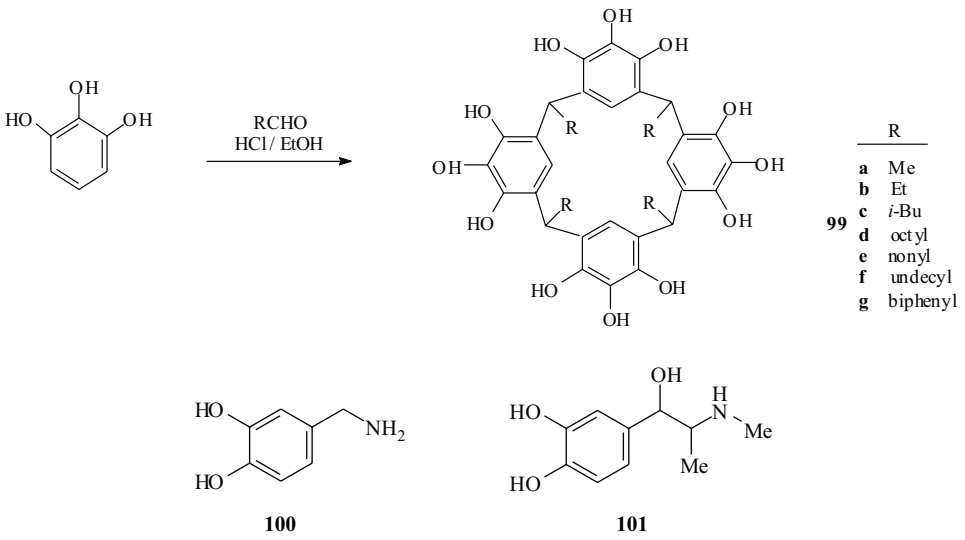
For **99a** the *rccc* and *rctt* isomers have been isolated, **99g** however is a *rctt* isomer. The *rccc* pyrogalloarenes are generally well crystallizing compounds. The polar heads bearing hydroxyl groups and apolar residues of pyrogalloarenes enable their assembling. They usually form double layer-aggregates except for *rccc* **99a**, which forms molecular piles. However, *rctt* pyrogalloarenes because of their shape cannot arrange in double layers; *rctt* **99a** forms monolayers separated by solvent molecules, and *rctt* **99g** forms molecular chains [130].

It was found that the interaction of pyrogalloarene receptor **99f** with bilayer lipid membranes may serve for the electrochemical biosensing of stimulants dopamine and ephedrine **100** and **101**, respectively [131]. Pyrogalloarenes may also be used as receptors in biosensors for the detection of metals [131] (Scheme 38).

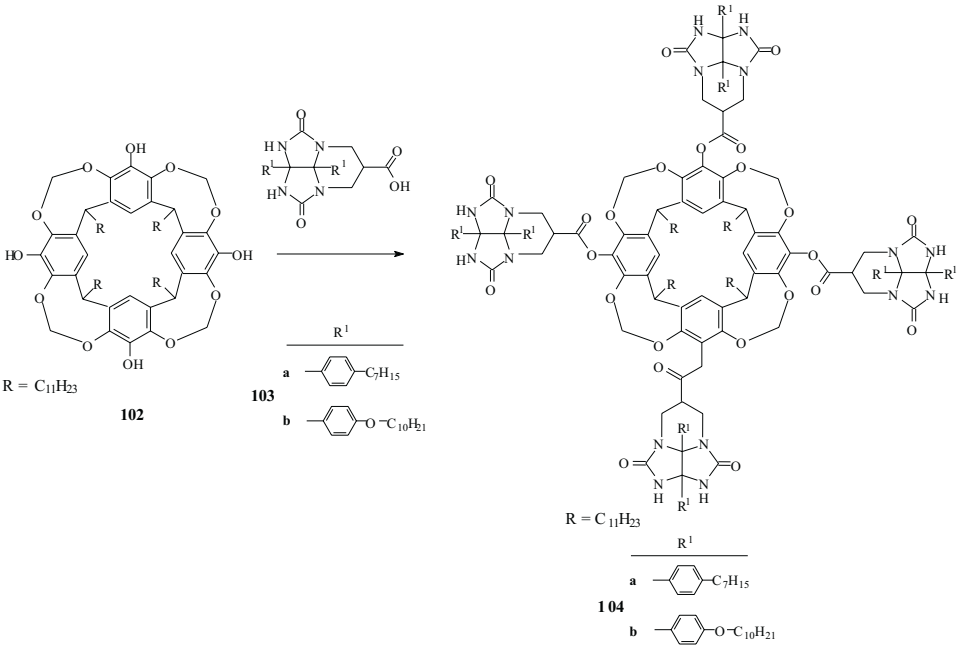
The dissolving of pyrogalloarenes containing R = C_1–C_3 in ether or their thermal treatment leads to the formation of hexameric, spheric capsules held together by hydrogen bonds [132]. The appropriate choice of R enables the formation of hexameric capsules stable in polar or apolar solvents. In the case of R = *n*-C_3H_7, *n*-C_4H_9, *i*-C_4H_9 and *n*-C_5H_{11}, they are stable in highly polar media and exist also in the solid state; due to large free volume (1.510 nm^3) the accomodation of *ca* 20 methanol molecules is possible [132].

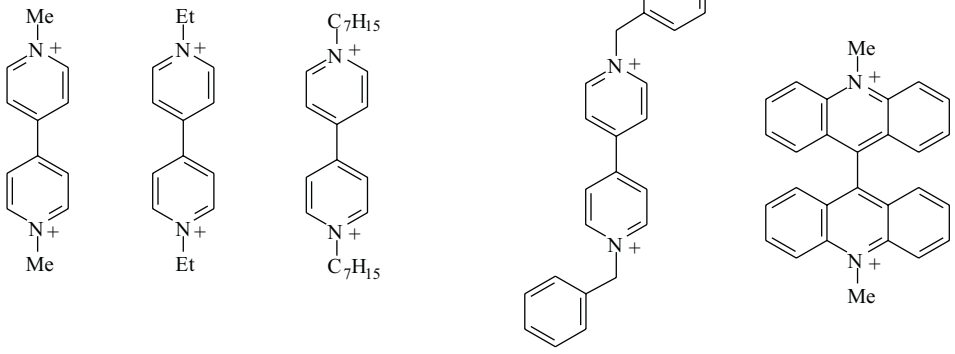
Cavitand **102** derived from pyrogalloarene reacts with carboxyglycolurils **103a,b** to give cavitands **104a,b** substituted by four ester groups [133]. Cavitands **104a,b** form hydrogen-bonded dimeric D_{4d} capsules of a large cavity of *ca* 0.95 nm^3. It was found that quaternary species $\mathbf{105}^{2+}$–$\mathbf{109}^{2+}$ (in the form of their BF_4^- salts) may serve as guests of capsule **104a·104a**. The formed host-guest complexes have been examined using ESI-MS (electrospray ionization mass spectrometry) methods [133,134] (Scheme 39).

Scheme 38



Scheme 39





105^{2+} **106**$^{2+}$ **107**$^{2+}$ **108**$^{2+}$ **109**$^{2+}$

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