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Chemistry of calix[4]resorcinarenes

V K Jain, P H Kanaiya

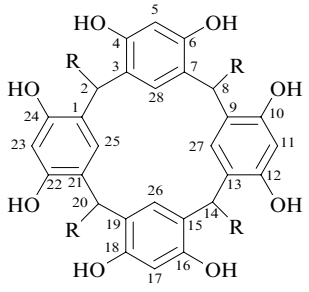
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Abstract. The review demonstrates the progress in the chemistry of calix[4]resorcinarenes over the last decade. Special attention is paid to their synthesis, conformational behaviour, functionalization and ability to serve as cavitands and capsules, to form monolayers and host – guest complexes. Practical applications of calix[4]resorcinarenes and their derivatives in various fields are surveyed. The bibliography includes 296 references.

I. Introduction

Resorcinarenes have a long history, stretching back to 1872 when Baeyer reported reactions of phenol with aldehydes.[1, 2] Several years later, Michael[3] reported that these products were formed by the combination of an equal number of benzaldehyde and resorcinol molecules with the loss of an equal number of water molecules. However, it took several decades to determine the structure of these products. In 1940, Niederl and Vogel[4] showed by molecular weight determinations that the ratio between the aldehyde and the resorcinol in these products is 4 : 4. They proposed a cyclic tetramer structure (**1**), which was finally proved in 1968 by single crystal X-ray analysis.[5, 6]



1

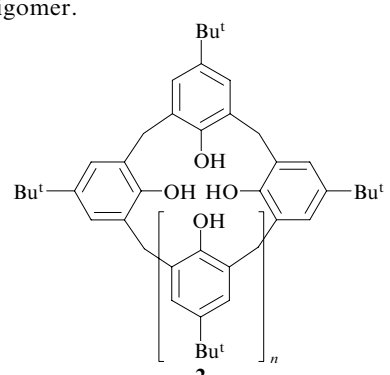
R = Alk, Ar.

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The official IUPAC name for resorcinarene (**1**) is 2,8,14,20-tetraalkylpentacyclo [19.3.1.1^{3,7}.1^{9,13}.1^{15,19}]octacosa-1-(25),3,5,7(28),9,11,13(27),15,17,19(26),21,23-dodecaene-4,6,10,12,16,18,22,24-octol. Gutsche[7] and Vicens[8] classified these molecules as calixarenes by calling them calix[4]resorcinarenes, or resorcinol-derived calix[4]arenes. Some other names, like Högberg compounds[9] and octols[10, 11] also appear in the literature. In the absence of any suitable trivial name in the literature, Schneider and Schneider[12] suggested the name resorcinarene in 1994.

The name calixarene refers to the bowl or chalice-like shape of compounds (from Latin *calix*, cup) like *p-tert*-butylcalix[4]arene (**2**), which is a phenol-derived cyclooligomer.



2

n = 1, 3, 5.

Resorcinarenes are resorcinol-derived calixarenes [*e.g.*, *C*-methylcalix[4]resocinarene (**1**) if R = Me]. The bracketed number points to the size of the oligomer; the most common are tetramers ([4]), there are very few reports on hexamers ([6]). The substituent that has been introduced from the starting aldehyde at the methylene carbon atom is indicated by a prefix of '*C*-substituent', *e.g.*, *C*-methyl. The name calix[4]resorcinarenes is often shortened to 'resorcin[4]-arenes'.[13]

Reported work on the resorcinarenes and their derivatives heralds many promises which has been reflected in various general reviews,[14 – 20] which cover their application, design, structure, synthesis, chirality,[21 – 23] characterization, functionalization,[24 – 26] complexation properties, as well as their uses as host – guest systems,[27 – 36] and cavitands and capsules.[37 – 42] Reviews on the coordinative properties of

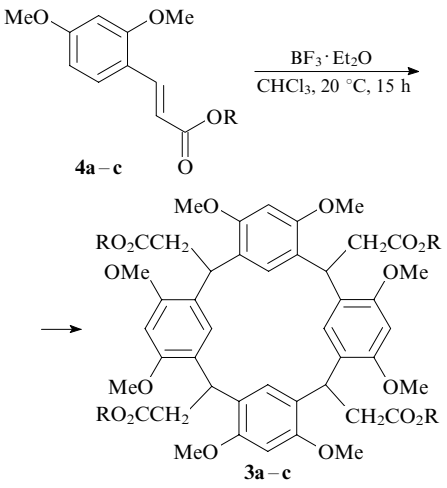
resorcinarenes toward transition metals,[43,44] resorcinarene-encapsulated nanoparticles,[45] resorcinarene-based multinuclear metal complexes[46] and self-assembled monolayers of calix[4]resorcinarenes[47] are also available in the literature. In the present review article, an effort has been made to direct the reader to the most important, recent and informative leading references, thereby providing a springboard for researchers who wish to work in a more applied area in calix[4]resorcinarene chemistry.

II. Synthesis of calix[4]resorcinarenes

Calix[4]resorcinarenes can easily be obtained by the acid-catalyzed condensation of resorcinol with various aliphatic or aromatic aldehydes, which occurs on heating the reactants to reflux in a mixture of ethanol and concentrated HCl for several hours. Usually, the cyclotetramer crystallizes out from reaction mixture in reasonable to high yields in a simple one-step untemplated reaction, although for different aldehydes different optimal reaction conditions exist.[9,11,48] Tetrameric products are not obtained when the rersorcinol involved has an electron-withdrawing substituent, such as NO_2 or Br at the 2-position.[11] Under certain conditions, reactions of formaldehyde and 2-methylresorcinol or pyrrogallol yield isolable amounts of the tetrameric product.[49] The question of which substituents are tolerated on the resorcinol and aldehyde moieties in the four-fold oligomeric cyclization reactions has been well addressed by Cram and co-workers[11] and Weinelt and Schneider.[50]

Many new synthetic routes for the various types of resorcinarenes have emerged over the years, but in this Section we will report only those routes which are somewhat different from the conventional mineral acid-catalyzed cyclooligomerization. The various derivatives of calix[4]-resorcinarene obtained by the conventional method are reported in Table 1 (Section IV).

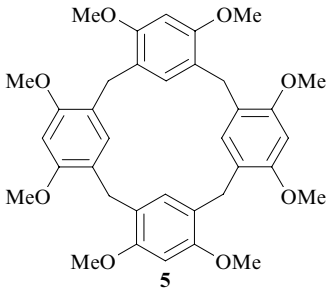
A versatile route to a series of *C*-alkoxycarbonylmethylcalix[4]resorcinarenes (**3a**–**c**) has been developed using 2,4-dimethoxycinnamates (**4a**–**c**) as starting materials under carefully controlled reaction conditions employing BF_3 as a Lewis acid catalyst.[51–53]



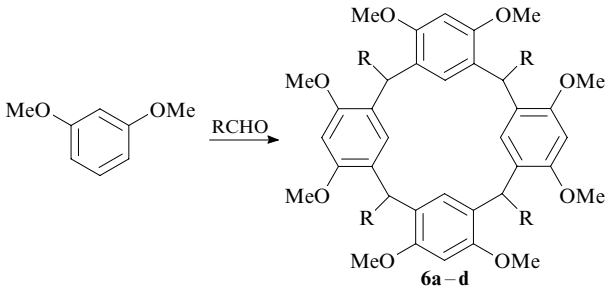
R = Me (**a**), Et (**b**), Pr^i (**c**).

The stereoselectivity of the cyclization appears to be dependent on the reaction conditions and the nature of the side chains at the bridging carbon atoms. ^1H and ^{13}C NMR spectroscopic studies[51–53] showed that compound **3a** represents two conformers, *viz*., a flattened cone (*cis*–*cis*–*cis* or *rccc*) and a 1,2-alternate (*cis*–*trans*–*cis* or *rctc*).† In the case of calix[4]resorcinarenes **3b**,**c**, the third conformer, 1,3-alternate, [(*rtct*) appears with pseudoequatorial side chains] (see Section III for resorcinarene conformers).

When 2,4-dimethoxybenzyl alcohol is treated with trifluoroacetic acid (5% in $CHCl_3$), resorcinarene (**5**) is obtained in 95% yield.[54]

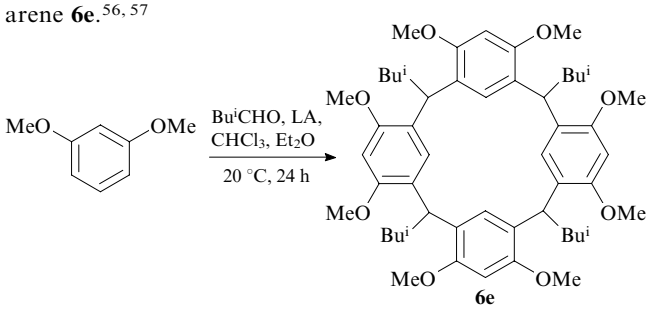


New synthetic conditions for fully selective formations of the *rctt* chair stereoisomers of octa-*O*-alkyl resorcin[4]-arenes (**6a**–**d**) in acetic acid–H_2SO_4 or acetic acid–HCl mixtures have been described, and it has been proposed[55] that this isomer is the thermodynamic product under Brønsted acid catalysis, which is an unprecedented observation in resorcinarene chemistry.



R = 4-HOC_6H_4 (**a**), 4-(n-$C_8H_{17}O$)C_6H_4 (**b**), Me (**c**), $HOCH_2CH_2$ (**d**).

The Lewis acids, $SOCl_2$, $POCl_3$, $AlCl_3$, $SiCl_2Me_2$ and $SnCl_4$ catalyze the cyclocondensation of 1,3-dimethoxybenzene with isovaleraldehyde to give high yields of resorcinarene **6e**.[56,57]

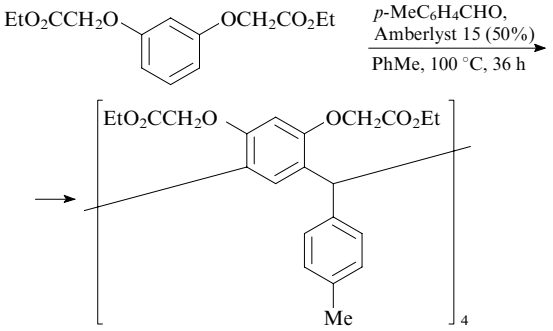


Amongst all the Lewis acids used, only $SnCl_4$ catalyzes this reaction selectively and promotes the formation of the crown conformer (*rccc*) in high yield (85%).

A cation-exchange resin-induced[58] one-step synthesis of resorcinarene **7** in a 34% yield by condensation of diethyl

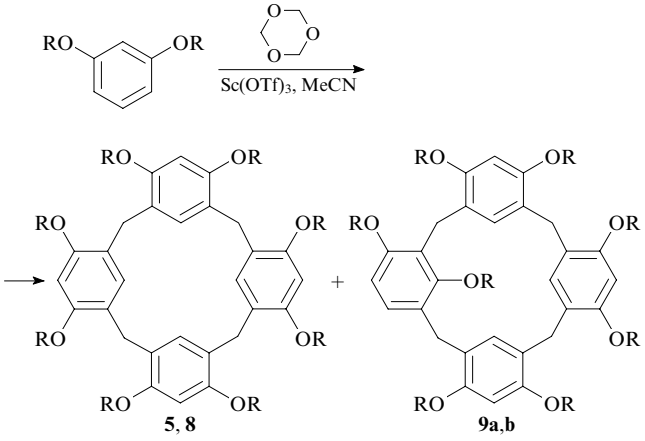
† In the short designations of calix[4]arene stereoisomers, *r* stands for the reference group relative to which the positions of the other substituents are given (*cis*, *c* or *trans*, *t*).

m-phenylenediyldioxydiacetate with *p*-tolualdehyde was reported.



7

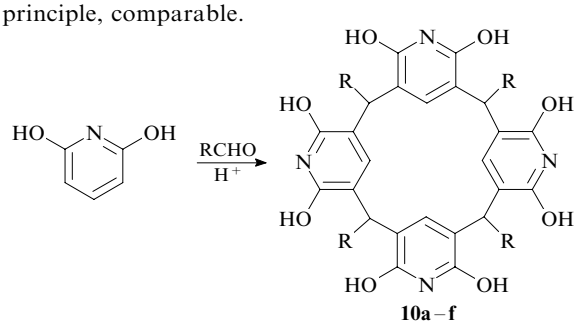
Yet another example involves the cyclocondensation of 1,3-dialkoxybenzenes with 1,3,5-trioxane catalyzed by $Sc(OTf)_3$ to produce resorcin[4]arene octaalkyl ethers (**5**, **8**) as the major products. In addition, the confused resorcin[4]arene octaalkyl ethers (**9a**,**b**) bearing one alkoxy group at the intraannular position were also obtained as minor products.[59] Their formation proceeds as a macrocyclization involving position 2 of a *m*-dialkoxybenzene.



5, **8** **9a**,**b**

R = Me (**5**, **9a**), Et (**8**, **9b**).

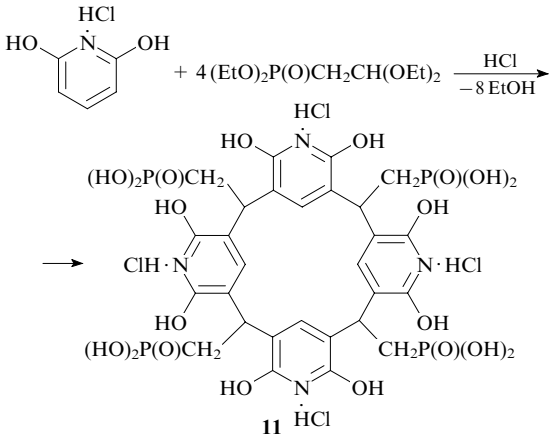
A new type of octahydroxypyridine[4]arene (**10a**–**f**) was derived from the condensation of 2,6-dihydroxypyridine with a number of aliphatic and two aromatic aldehydes in acidic media.[60] The reactivity of 2,6-dihydroxypyridine is lower than that of resorcinol or pyrogallol, so harsher conditions are required, but the cyclization reactions are, in principle, comparable.



10a–**f**

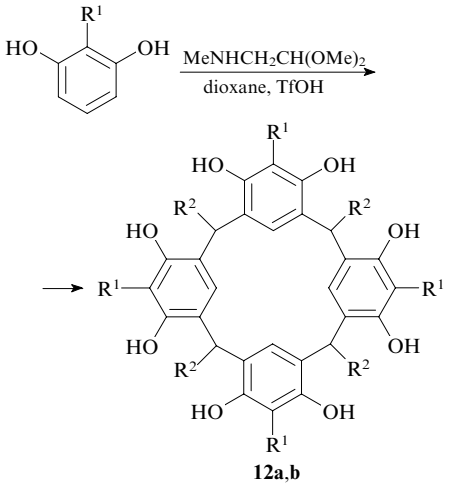
R = Me (**a**), Bu^n (**b**), Bu^i (**c**), n-$C_{11}H_{23}$ (**d**), Ph (**e**), 4-$O_2NC_6H_4$ (**f**).

The acid-catalyzed condensation of 2,6-dihydroxypyridine hydrochloride with diethyl 2,2-diethoxyethylphosphonate gives, upon prolonged heating, the water-soluble calix[4]pyridinoarene 11 with four phosphonic acid moieties (a product of full hydrolysis of the corresponding ester).[61]



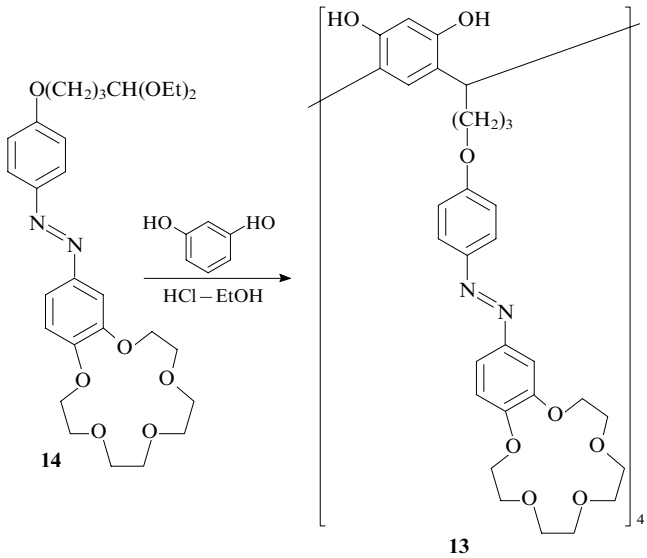
11

The new calix[4]resorcinarenes **12a**,**b** (Ref. 62) and **13** (Ref. 63) have been synthesized by the condensation of resorcinol and 2-methylresorcinol with 2-(methylamino)-acetaldehyde dimethyl acetal and acetal **14** containing a photoswitchable chromogenic azo group (which can adopt



12a,**b**

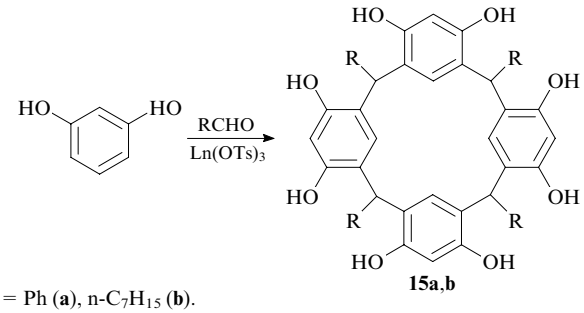
$R^2 = CH_2\overset{+}{N}H_2Me\,TfO^-$: R^1 = H (**a**), Me (**b**).



14 **13**

E and *Z* configurations) with an ionophoric moiety (*i.e.*, the benzo-15-crown-5 residue), respectively.

Ytterbium(III) and bismuth(III) trifluoromethanesulfonates (triflates)[64,65] have been described as efficient catalysts for the synthesis of calix[4]resorcinarenes. Recently, lanthanide(III) tosylates and lanthanide(III) nitrobenzenesulfonates[66–70] have also been used as efficient, inexpensive, recyclable and environmentally friendly catalysts for the synthesis of calix[4]resorcinarenes **15a**,**b**. Their catalytic efficiency was found to be comparable to that of the triflates.

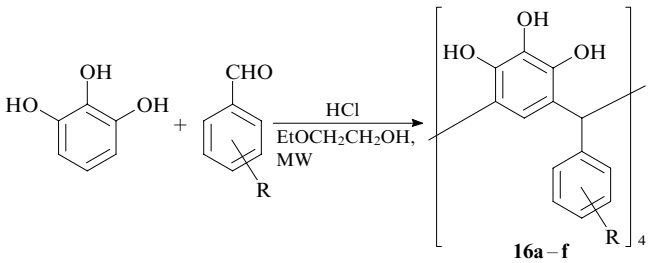


15a,**b**

R = Ph (**a**), n-C_7H_{15} (**b**).

The microwave-assisted synthesis[71] of calix[4]resorcinarenes from resorcinol and aldehydes catalyzed by the Keggin-type 12-tungstophosphoric acid ($H_3PW_{12}O_{40} \cdot 13\,H_2O$) or concentrated HCl gives excellent yields (>90%) with short reaction times (<3–5 min) and does not require harsh conditions.

Pyrogallol[4]arenes **16a**–**f** have also been synthesized[72] in excellent yields by the cyclocondensation of pyrogallol with aromatic aldehydes under conditions of microwave irradiation.



16a–**f**

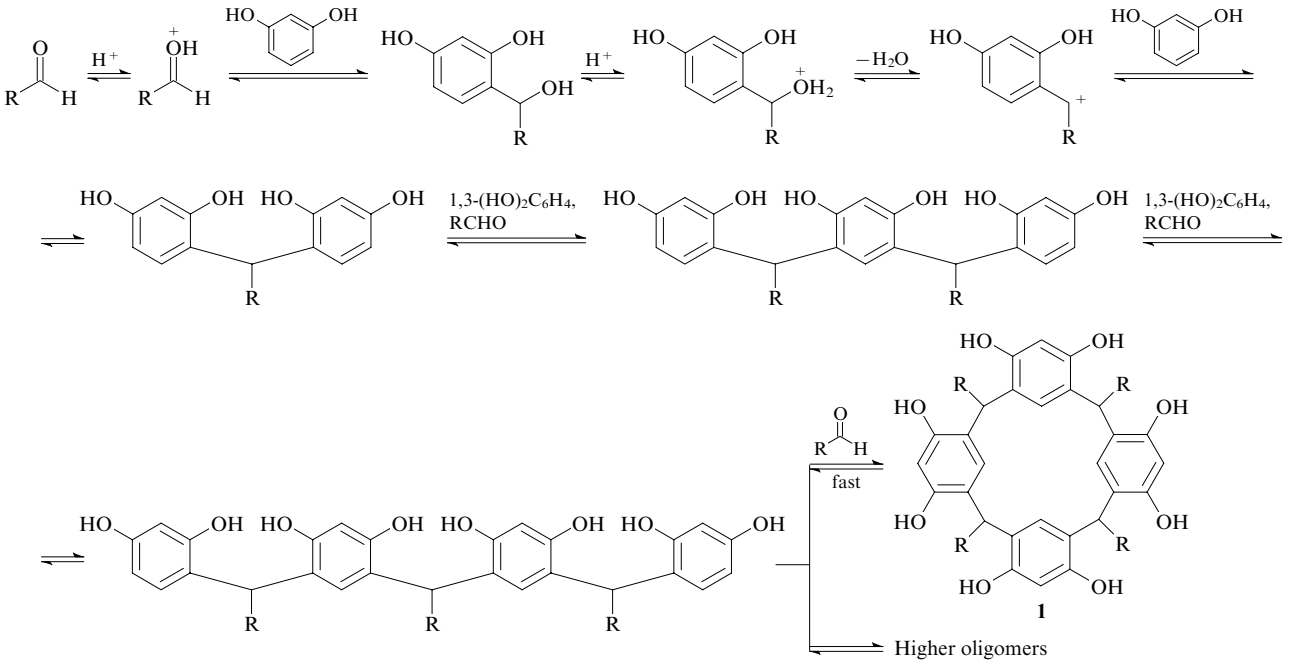
R = H (**a**), 4-Me (**b**), 4-OMe (**c**), 4-Cl (**d**), 2-Ac (**e**), 4-OAc (**f**).

A one-pot condensation reaction of resorcinol with 1,4-butanedial [$(CH_2)_2(CHO)_2$] in the presence of concentrated HCl in ethanol at 80 °C for 48 h afforded a soluble ladder polymer[73] in quantitative yield.

III. The mechanism of cyclocondensation and stereochemistry of resorcinarenes

The mechanism of the acid-catalyzed condensation reaction that forms calix[4]resorcinarenes has been thoroughly studied[50] (Scheme 1). First, the aldehyde is protonated to serve as the initial electrophile, which adds to resorcinol. The alcoholic hydroxyl of the subsequent adduct is protonated again to eliminate a mole of water. The loss of the water molecule affords a carbocation intermediate, which undergoes a second electrophilic addition to another resorcinol to form a dimer. Sequential couplings of the dimer with other resorcinol units results in trimers, tetramers, or higher oligomers containing more than four monomers. Since the condensation reaction is reversible under acidic conditions, most of the higher oligomers are consumed toward the end of the reaction, although they are present during the intermediate stages of the reaction. The linear tetramers cyclize rapidly to form calix[4]resorcinarenes once they are formed in the reaction mixture. This cyclization is

Scheme 1



R = Alk or Ar.

too fast to allow the linear tetramers to be isolated. The cyclization is favoured due to the lack of conformational strain, and by the formation of hydrogen bonds between the proximal phenolic hydroxyl groups of adjacent resorcinol units in the folded structures.[20]

A kinetic and molecular modelling study [50] of the acid-catalyzed reaction of acetaldehyde with resorcinol concluded that:

1. Ring closure to the calix[4]resorcinarenes is at least as fast as chain propagation.

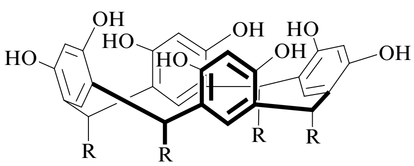
2. The macrocyclic products are thermodynamic sinks for the reaction

3. Linear oligomers having more than four aryl units depolymerize fast in comparison with ring opening, thus promoting the formation of the cyclic tetramers, pentamers and hexamers.

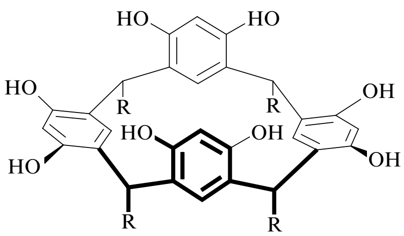
Although reactions with RCHO appear to yield only calix[4]resorcinarenes, the cyclocondensation of 2-alkylresocinarenols with 1,3,5-trioxane in ethanol – conc. HCl (4 : 1 by volume) yields mixtures containing both calix[4]resorcinarene and calix[6]resorcinarene, but the later is isomerized to the former upon prolonged heating in the reaction media.[74]

Calix[4]resorcinarenes are non-planar molecules because they exist in different isomeric forms [11, 75, 76] The stereochemistry is generally defined by a combination of the following three stereochemical criteria (strictly speaking, these criteria are not independent):

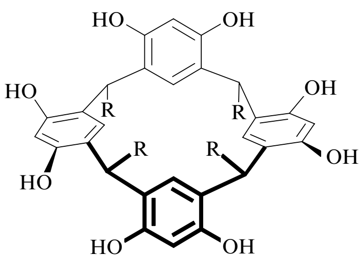
The first criterion is the conformation of the macrocyclic ring. The macrocycle can adopt one of five highly symmetrical conformations, *viz*., crown (C_{4v}), boat (C_{2v}), chair (C_{2h}), diamond (C_s) and saddle (D_{2d}).



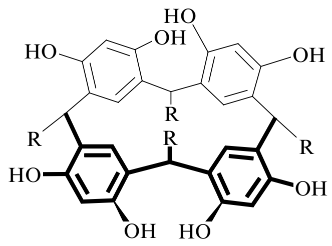
Crown (cone) (C_{4v})



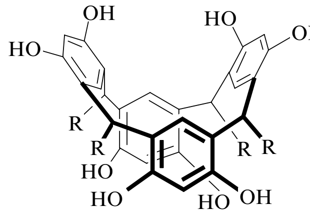
Boat (C_{2v})



Chair (C_{2h})

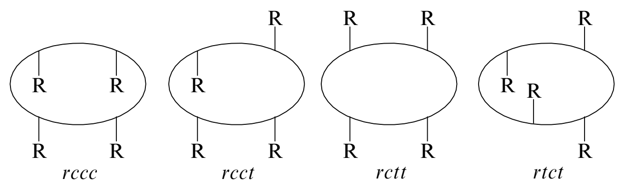


Diamond (C_s)



Saddle (D_{2d})

The second criterion is the relative configuration of the substituents at the methylene bridges, which can be all-*cis* (*rccc*), *cis – cis – trans* (*rcct*), *cis – trans – trans* (*rctt*) or *trans – cis – trans* (*rtct*).



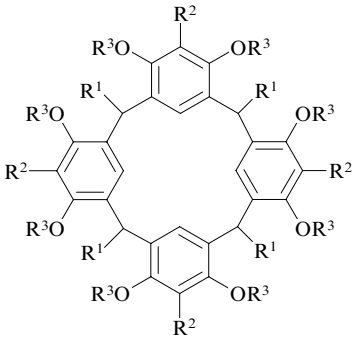
The last criterion is the individual configuration of methylene bridge substituents, which may be either axial or equatorial in macrocycles with *C* symmetry.

The combination of these three criteria results in a great number of possible stereoisomers. However, only several of them have ever been reported experimentally. The 'boat' conformation is usually reported as a 'crown' conformation, partially due to the presence of two boat isomers, which interconvert rapidly to give a time-averaged crown conformation. However, the interconversion between boat, chair and diamond isomers does not occur, since it would require the breaking of at least two covalent bonds. They are diastereomeric isomers, and all of them can be produced in a reaction. Under homogeneous acidic conditions, the product ratio is mainly determined by the thermodynamic stability of the different isomers, because the condensation reaction is reversible under such conditions.[50] The relative solubility of the different isomers in the reaction solvent plays a key role in determining the product ratio if the reaction is performed under heterogeneous conditions.[75] The ratios of different diastereoisomers depend greatly on the reaction conditions used, although there are many factors that may affect the presence or absence of a specific isomer.

The conformational properties of calix[4]resorcinarenes that have free hydroxyl groups are affected by the solvent, which influences the formation of intra- and intermolecular hydrogen bonds.

IV. Derivatization of calix[4]resorcinarenes

Calix[4]resorcinarenes are a very versatile molecular platform and can be functionalized at two, four, six, eight, twelve, sixteen or more sites depending on the reagent, aldehyde, resorcinol and conditions used to carry out the reaction. Any functional group can occupy all or any combination of the three available positions (R^1, R^2, R^3) in the structure **17**. The number of functional groups introduced can be controlled to give various calix[4]resorcinarene derivatives.



17

One can expect these derivatives to exhibit somewhat different or additional properties relative to those exhibited by the corresponding monofunctionalized molecules. In this Section, we will review the various possible functionalizations of calix[4]resorcinarenes. These have been divided into two categories. In one of them, the similar positions are all substituted or non-substituted. In the second group molecules, the substitution of the similar positions is selective.

Since there are many reports on routine full functionalization, they have been summarized in Table 1 without any special comments.

1. Dendrimers

Dendrimers are well-defined, highly branched, three-dimensional compounds with a large number of reactive end groups. Recently, they have received considerable attention as new synthetic functional materials,[119] and their use in nanotechnology geared toward biochemical and medical applications is within sight.[120, 121]

Calix[4]resorcinarenes are suitable as core molecules because of their easy synthesis and adequate space between functional groups. A number of synthetic approaches toward dendrimers have been described in the literature. All of the methods involve stepwise processes, such as several protection and deprotection steps and multiple purification steps.

Table 1. Calix[4]resorcinarenes with full functionalization of similar positions.

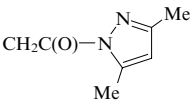
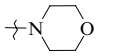
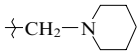
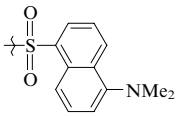
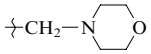
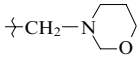
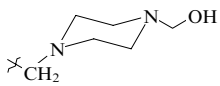
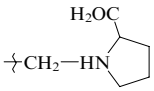
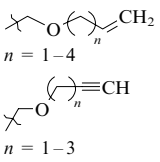
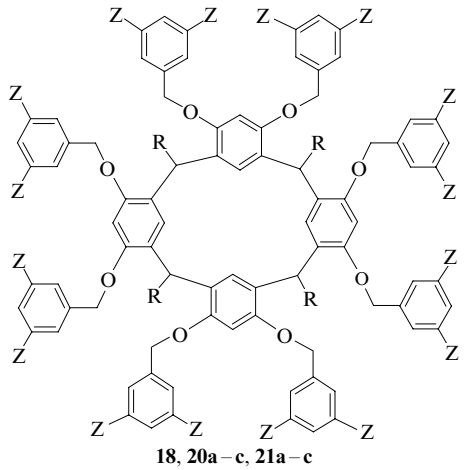
Substituents in the general formula **17**			Ref.	Substituents in the general formula **17**			Ref.
R^1	R^2	R^3		R^1	R^2	R^3	
C_6H_4Br-4	H	$C(O)Pr^n$	6				
$CH_2CO_2Pr^i$	H	Me	51 – 53	Ph, Fc	H		91
Bu^i	H	Me	57				
Et	OAc	Ac	77				
n-$C_{11}H_{23}$	CO_2H	Me	78	Me		H	92
Me	H	Ts	79				
C_6H_4Br-4	H	Ac	80	Et		H	93
Pr^n	OAc	Ac	81				
Pr^n	OTs	Ts	81	Me, Et, n-C_5H_{11}	$CH_2N^+H_2Z$ ($Z = Bu^n$, n-C_6H_{11})	H	94
Bu^i	H	$CH_2C{\equiv}CH$	82				
Me	$CH_2N^+HMe_2$	H	83				
Pr^n	H		84	Ph		H	95
				n-C_5H_{11}		H	96
n-$C_{11}H_{23}$	H	CH_2CO_2H	85	Me	CH_2NMe_2, CH_2NEt_2	H	97
n-C_5H_{11}, n-C_6H_{13}	CH_2NZAc (Z = n-C_6H_{11}, Bu^n)	H	86	Ph	$CH_2NPr^n_2$	H	98
				Me	$CH_2NH(CH_2)_2NMe_2$	H	99
Me	$CH_2N^+H_2CHMePh$	H	87	Me, n-C_9H_{19}, $C_6H_4OC_{12}H_{25}$-n	CH_2SO_3Na	H	100
CH_2Bn	H	$CH_2C{\equiv}CH$, $CH_2C{\equiv}CMe$, $CH_2C{\equiv}CH\{Co_2(CO)_6\}$, $CH_2C{\equiv}CMe\{Co_2(CO)_6\}$	88	Bu^i	CH_2OMe, CH_2OEt, CH_2OPr^n, CH_2OBu^n, $CH_2OC_5H_{11}$-n, $CH_2OC_6H_{13}$-n	H	101
C_6H_4Me-4	H, Me	Ac	89				
n-C_9H_{19}		H	90	Me	CH_2SR (R = 2-naphthyl, Ph, 4-ClC_6H_4, 4-MeC_6H_4, Bu^t)	H	102
Ph, C_6H_4OH, Fc (see [a])	H	CH_2CO_2Et, $CH_2C(O)NHNH_2$, $CH_2C(O)NHN{=}CH(Fc)$	91	Me	NO_2	H	103
				Me	$N_2C_6H_4SO_3Na$	H	104

Table 1 (continued).

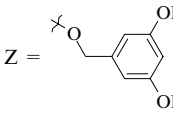
Substituents in the general formula **17**			Ref.	Substituents in the general formula **17**			Ref.
R^1	R^2	R^3		R^1	R^2	R^3	
Me	H	CH_2CO_2Et, $CH_2C(O)NHCHR^4$. .CHR^5OH (R^4 = Et, Me; R^5 = H, Ph), $CH_2C(O)NHCHRMe$ (R = Ph, cyclo-C_6H_{11})	105	Me	H	$C(O)CH_2CH_2Br$, $C(O)(CH_2)_2$. .$(NAcCH_2CH_2)_nH$ (n = 3, 5)	111
				Me	H	CH_2CO_2Et, CH_2CH_2OH, $CH_2CH_2OC(O)$. .CHMeBr, $CH_2CH_2OC(O)$. .CMe_2Br	112
CH_2Bn	H	PPh_2	106				
Me	N_2Ph, $N_2C_6H_4CO_2H$-4, $N_2C_6H_4NO_2$-4, $N_2C_6H_4Cl$-4, $N_2C_6H_4Me$-4, $N_2C_6H_4OMe$-4, $N_2C_6H_4OH$-2, $N_2C_6H_4SO_3H$-4, $N_2C_6H_4CO_2H$-2	H	107, 108	Et	H	$C(O)CH(Me)Br$, $C(O)CMe_2Br$	112
				Me	H	see [b]	113
				n-$C_{11}H_{23}$	$N_2C_6H_4NO_2$	H	114
				CH_2CH_2. .SO_3Na		H	115
Me	N=CHZ (Z = Ph, C_6H_4OH-4, C_6H_4OH-2, $C_6H_4NO_2$-3, C_6H_3OH-2-OMe-3, C_6H_3OH-2-OMe-4, CH=CHPh, 1-naphthyl, 2-hydroxy-1-naphthyl)	H	109				
				Bu^i		H	116
Ph	H	$CH_2C(O)NEt_2$, $CH_2C(O)NPr^n_2$, $CH_2C(O)NMePh$, $CH_2C(O)NNH$. .CH(Me)Ph	110				
				CH_2CH_2Br, $CH_2CH_2N_3$, $CH_2CH_2NH_2$, CH_2CH_2. .NHBn, CH_2CH_2. .$NHCH_2C_5H_4N$-4	H	Me	117
Fc	H	$CH_2C(O)NEt_2$, $CH_2C(O)NHMe$, $CH_2C(O)NHBu^n$	110				
				CH_2CH_2CH. .$(CH_2C_{10}F_{21}$-n)$_2$	H	H	118

[a] Fc is ferrocenyl, [b] R^3-R^3 is 4,5-dicyanophenylene-1,2.

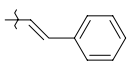
Martínez-Garcia and co-workers [122] have done a great amount of work in the area and have reported poly(aryl ether) dendritic branches with peripheral n-propyl (**18**) and allyl chains,[123] dendrimers with π-conjugated oligo(phenylenevinylene) (OPV) systems [124] and their supramolecular complexes with fullerene C_{60} (**19a**,**b**).



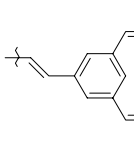
18, **20a**–**c**, **21a**–**c**



Z = , R = CH_2Bn (**18**);

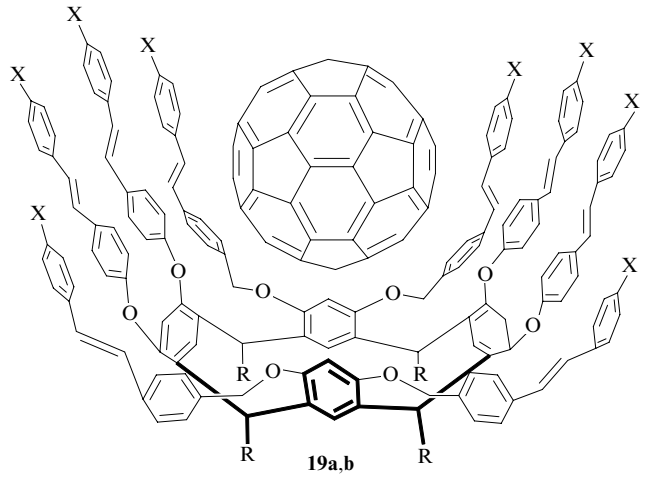


Z = : R = CH_2Bn (**20a**), n-C_5H_{11} (**20b**), n-$C_{11}H_{23}$ (**20c**);



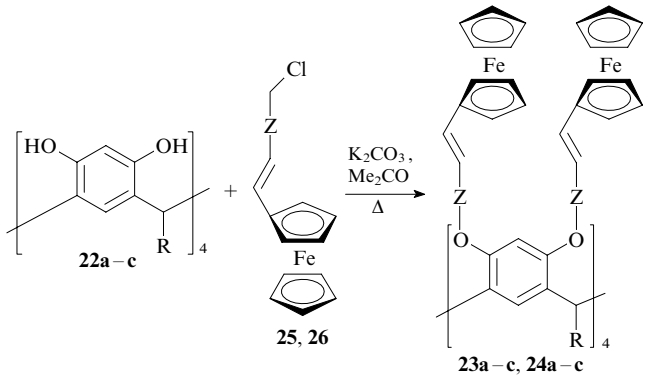
Z = : R = CH_2Bn (**21a**), n-C_5H_{11} (**21b**), n-$C_{11}H_{23}$ (**21c**).

Dendrimers comprising a resorcinarene core with stilbene and 4-styrylstilbene units have been synthesized.[125] Thus dendrimers **20a**–**c** and **21a**–**c** contain 16 or 32 π-conjugated stilbene groups, respectively.[126] They have also demonstrated the possibility of using these materials



19a,**b**

R = CH_2Bn: X = H (**a**), CH═CHPh (**b**).



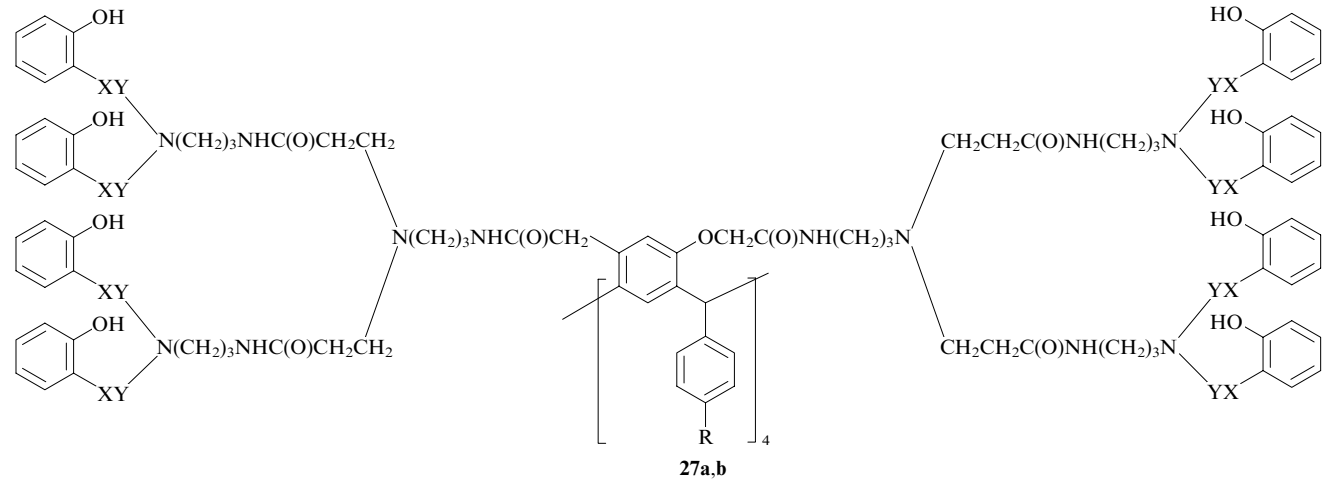
22a–**c**

25, **26**

23a–**c**, **24a**–**c**

R = CH_2Bn (**a**), n-C_5H_{11} (**b**), n-$C_{11}H_{23}$ (**c**);

Z = (**23**, **25**), (**24**, **26**).



27a,**b**

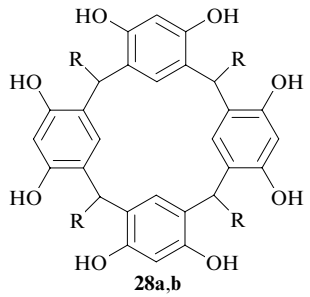
R = H (**a**), $OCH_2C(O)NH(CH_2)_3N\{CH_2CH_2C(O)NH(CH_2)_3N[CH_2CH_2C(O)NH(CH_2)_3N{=}CHC_6H_4OH\text{-}2]_2\}_2$ (**b**);
XY = $CH{=}N(CH_2)_3NHC(O)CH_2CH_2$.

for the development of electrochromic devices, such as smart windows.

Martínez-Garcia and co-workers [127] reported a series of ferrocenyl-capped dendrons with π-conjugated systems, which used resorcinarenes as the core molecule, and also studied cubic nonlinear optical behaviour [128] of these first generation resorcinarene dendrimers. The dendrons were attached to an eightfold-functionalized resorcinarene using the Williamson reaction to obtain high-molecular dendrimers. Compounds **22a**–**c** were prepared by reacting resorcinol with aldehydes. The dendrimers **23a**–**c** and **24a**–**c** were obtained by heating the dendron (**25** and **26**) with resorcinarenes **22a**–**c** in acetone with K_2CO_3 under reflux for 3 days.

A simple and efficient synthesis of polyamidoamine-type dendrimers [129] with up to three generations based on calix[4]resorcinarene with terminal salicylideneimine groups has been reported. Compounds **27a**,**b** were prepared using a divergent method in seven steps from the corresponding tetraphenyl and tetrakis(hydroxyphenyl) calix[4]resorcinarenes.

The highly functionalized core molecules **28a**,**b** can be transformed very rapidly into second-generation dendrimers in just three steps.[130]



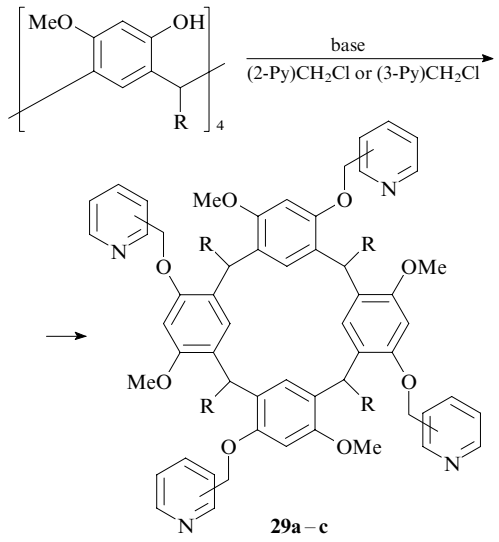
28a,**b**

R = 4-HOC_6H_4 (**a**), 3,5-$(HO)_2C_6H_3$ (**b**).

2. Selective functionalization

A simple and effective method has been developed for the introduction of monofunctionality (*e.g.*, alcohol, carboxylic acid, thiol, amine, carbamate, alkyl halide) on the lower rim of resorcinarenes.[131] These functional groups provide a site on the lower rim for additional functionalization.

Picolyl-functionalized resorcinarenes **29a**–**c** serve as multidentate ligands for the coordination of transition metals, such as palladium, zinc, nickel and copper.[132]

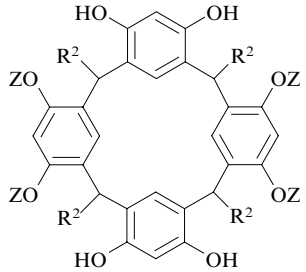


29a–c

Isomers: 2-picolyl: R = n-C_7H_{15} (**a**), Pr^n (**b**); 3-pycolyl, R = n-C_7H_{15} (**c**); Py is pyridyl.

Arnott and Hunter[133,134] have synthesized bridged resorcinarenes and have used them as templates for asymmetric catalysis.

Resorcinarene tetrasulfonates **30a–f** and tetraphosphates **31a–c** have C_{2v} symmetry and are useful as molecular platforms for the design of cation receptors that contain different binding units in each molecule.[135]

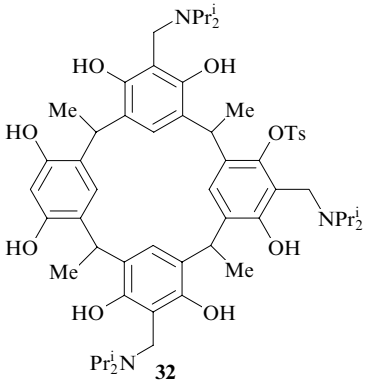


30a–f, 31a–c

Compound **30**[a]	R^1	R^2	Compound **31**[b]	R^1	R^2
a	4-MeC_6H_4	Me	**a**	Pr^i	Me
b	4-ClC_6H_4	Me	**b**	Bu^n	Me
c	2,4,6-$Me_3C_6H_2$	Me	**c**	Et	n-C_5H_{11}
d	4-MeC_6H_4	Pr^n			
e	4-MeC_6H_4	n-C_5H_{11}			
f	Bz	Me			

[a] Z = SO_2R^1; [b] Z = $P(O)(OR^1)_2$.

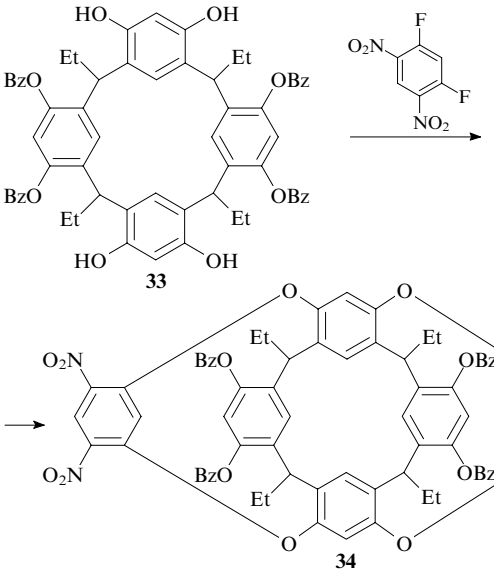
Aminomethylation of resorcinarenes on their upper rim with diisopropylamine and formalin leads to trisubstituted derivatives (*e.g.*, **32**), whereas the analogous reaction with a C_{2v}-symmetric resorcinarene tetratosylate gives the monoaminomethylated compound. The remaining unsubstituted positions on the resorcinol can be substituted to give novel resorcinarene derivatives.[136] This group has also reported the regioselective acylation of aminoresorcinarenes.[137]



32

Resorcinarene tetramesitylsulfonates **30c** in both the solid state and in chloroform solutions adopt conformations governed by intramolecular S=O···H–O hydrogen bonds, and dimerize due to intermolecular O–H···O–H hydrogen bonding.[138]

Resorcinarene tetraesters **33** react with 1,3-difluoro-4,6-dinitrobenzene to give rigid tetranitroresorcinarene **34**, a potential scaffold for the design of supramolecular structures.[139]



33

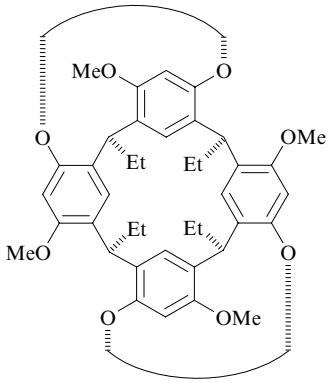
34

3. Resorcinarene crowns

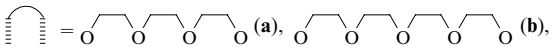
The number of oxygen atoms in a crown ether moiety determines its selectivity toward binding various cations (*i.e.*, crown-4 is selective for sodium, crown-5 is selective for potassium and crown-6 is selective for caesium cations). Studies have been carried out to explore the cation–π-interaction, which occurs when a crown ether moiety is attached to a resorcinarene skeleton. The hydroxyl groups, which are situated on the upper rim of resorcinarene, enable the crown to have an open end, and make the resorcinarene (bowl shape) available for cation binding.

Tetramethoxyresorcinarene was used as the platform for the synthesis of resorcinarene bis-crowns,[140] BC4 (**35a**) and BC5 (**35b**). The later was found to accommodate two cations simultaneously inside the crown pockets formed by the crown ether linkages and the resorcinarene skeleton.

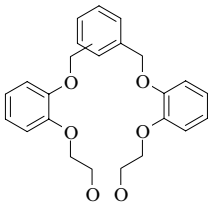
BC5 was further improved by introducing tribenzo-bis-crown ethers,[141] *m*-TBBC6 (**35c**) and *p*-TBBC6 (**35d**) with the expectation that the added aromatic functionality would improve its cation binding ability. The flexibility of the resorcinarene bis-crowns in boat conformations was also compared with the resorcinarene core and the tetramethoxy-resorcinarene derivative.[142] Although *m*-TBBC6 and BC5 were found to be capable of binding several cations (*e.g.*, K^+, Rb^+ and Cs^+), the highest affinity was observed for Cs^+, while no binding was observed with *p*-TBBC6, which exemplifies the significance of complementarity and preorganization for complexation in supramolecular chemistry.



35a–d

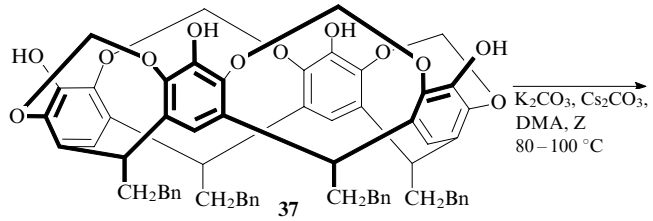


(**a**), (**b**),



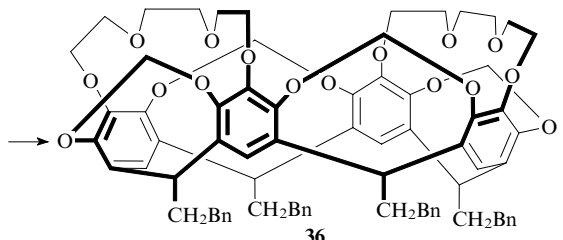
[*meta* (**c**), *para* (**d**)].

The combination of 1,2-crown[6]cavitands with resorcin[4]arenes provides potential receptor molecules[143] with large hydrophobic surfaces. A new cavitand **36** bearing two rigid crown-ether groups was synthesized from tetrahydroxycavitand **37**.



K_2CO_3, Cs_2CO_3, DMA, Z, 80–100 °C

37

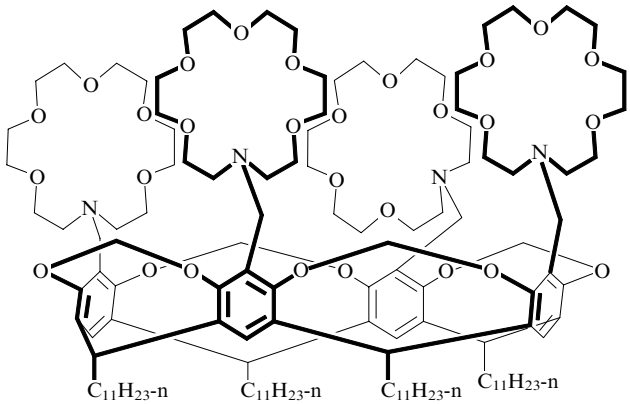


36

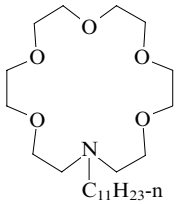
Z = TsO OTs, DMA is *N*,*N*-dimethylacetamide.

The binding properties of the cavitand **36** towards alkali metal ions, as well as the ammonium ion, were examined.[144]

New macrocyclic carriers based on aza-18-crown-6, aza-crown resorcinarene (**38**, ACR) and aza-18-crown-6 bound to an undecyl chain (aza-crown undecyl, ACU, **39**) scaffolds have been used in dichloromethane as bulk liquid membranes to study the effect of cations on competitive transport among anions (*e.g.*, ReO_4^-, NO_3^-, ClO_4^-).



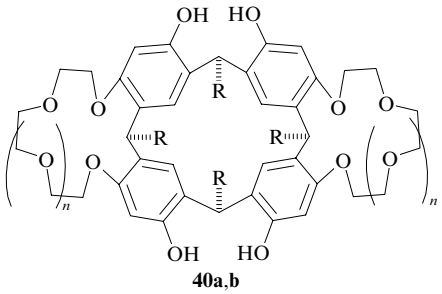
38 (ACR)



39 (ACU)

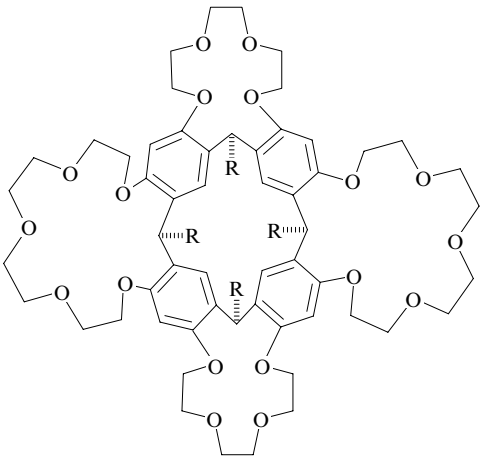
In most cases, ACR was found to transport anions better than ACU. The carriers also showed selectivity for ReO_4^- and ClO_4^- over NO_3^- with K^+ and Na^+ acting as the co-transported cations using neutral and basic aqueous phases. It was established[145] that if the individual cations in a mixture promote anion transport, a mixture containing those cations will also transport anions. Additionally, if one of the cations in a mixture does not promote anion transfer, it may inhibit anion transport even though a promoting cation is present.

To further extend this family of crown ether calix[4]resorcinarenes, novel cloverleaf crown ether calix[4]resorcinarenes **40a**,**b** and **41** have been synthesized.[146]



40a,**b**

n = 1 (**a**), 2 (**b**).



41

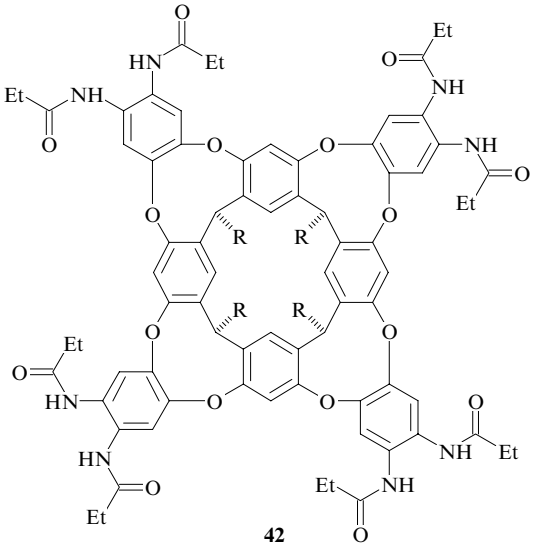
R = n-C_6H_{11}.

They have one or two distal pairs of crown ethers annulated directly to the macrocycle through the peripheral resorcyl oxygen atoms.

4. Cavitands and capsules

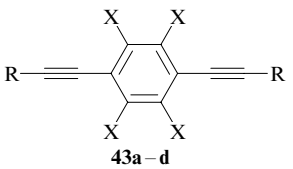
A class of receptors that is widely exploited in investigations of the forces involved in recognition is the resorcin[4]arene-based cavitands and capsules. We can define [147] self-assembling capsules as receptors with enclosed cavities that are formed by the reversible non-covalent interaction of two or more, not necessarily identical, subunits. The aggregate so formed should have a well-defined structure in solution and be capable of binding behaviour that none of its individual components display alone. The efficient synthesis of cavitands and capsules, which are large enough to entrap various guests, is a great challenge.

Weak forces of interaction, like the dispersion force and CH – π-interactions, stabilize a new multicomponent assembly between the cavitand host **42** and ditopic guests **43a** – **d**.[148]



42

R = n-$C_{11}H_{23}$.



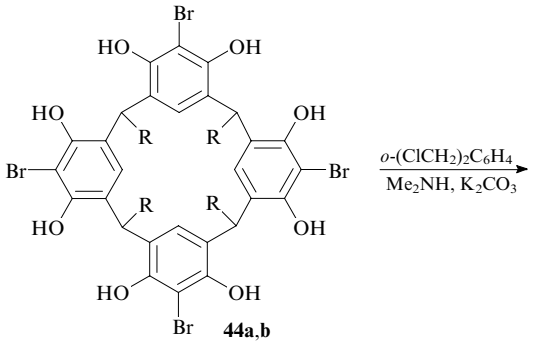
43a – **d**

Compound **43**	R	X
a	1-Ad	H
b	1-Ad	F
c	cyclo-C_6H_{11}	F
d	n-C_6H_{13}	H

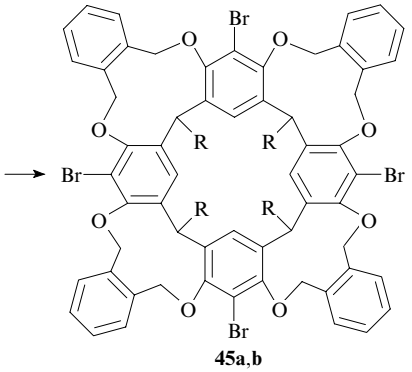
Ad is adamantyl.

Deep cavitands with three fixed walls and one mobile wall have been synthesized and shown to exhibit tighter binding and slower exchange of a few guests.[149]

The reaction of resorcinarenes **44a**,**b** leads to bromo-*o*-xylyl cavitands **45a**,**b**.[150]



44a,**b**

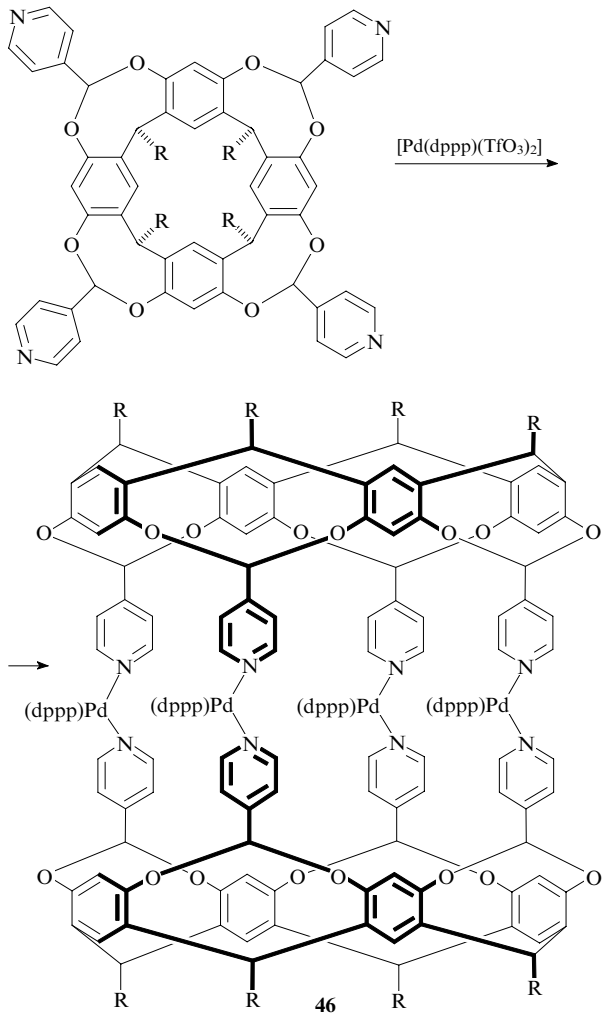


45a,**b**

R = Me (**a**), CH_2Bn (**b**).

Resorcin[4]arene cavitands, in which the adjacent phenyl rings are connected covalently through an ethenylenedioxy bridge by tandem ring closing metathesis reactions, have been prepared.[151] This type of cavitand presents interesting opportunities for various applications, for example, the encapsulation of much larger molecules may now be possible in the enlarged cavity, while the modification of the alkenylene bridge could lead to functionalization/deepening of the upper rim/cavity. This work has been extended by synthesizing a highly crystalline spatially directional multi-arm poly(ε-caprolactone) based on a resorcin[4]arene cavitand core.[152]

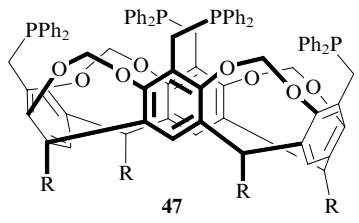
In contrast to metallation strategies that lead to either *endo* or *exo* functionalization, the functionalization of deep-cavity cavitands by electrophilic substitution has been investigated.[153] Aminopyridine-substituted resorcinarene-based cavitands,[154] dipyridyl-based cavitands [155] and self-assembled coordination cages [156] have also been synthesized. Self-assembled coordination cage **46** is comprised of two tetrapyridyl-substituted resorcin[4]arene cavitands coupled through four square-planar palladium complexes. This coordination cage has the correct size to allow the inclusion of large molecules, such as fullerenes, and forms 1 : 1 complexes with methano[60]fullerene derivatives bearing dimethyl and diethyl malonate moieties, respectively.



46

R = CH_2Bn, dppp is 1,3-bis(diphenylphosphino)propane.

Two novel tetrathiolated cavitands, a tetra(arenethiol) cavitand and a tetra(arenemethanethiol) cavitand, were used to encapsulate gold nanoparticles and to subsequently transform them into non-desorptive cross-linked shells.[157] The synthesis and coordination properties of the first tetraphosphine built upon a resorcinarene cavitand **47** have been described.[158] In the presence of $Pd(OAc)_2$ and a base, ligand **47** is an active catalyst for the Heck couplings.

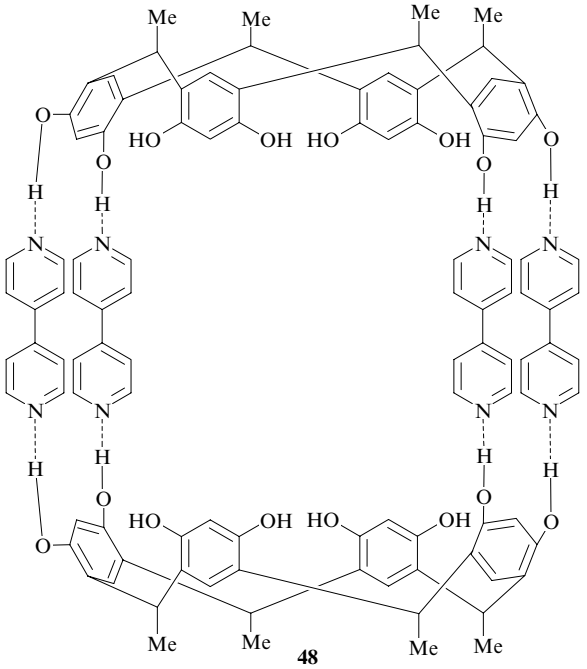


47

R = n-C_5H_{11}.

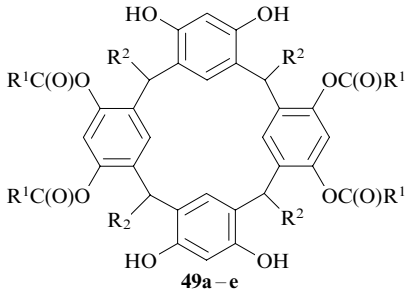
Covalent attachment to antimony(V) bromide has been found to induce capsule formation (like alkylammonium salts) and leaves enough room inside to reversibly co-encapsulate various aromatic guests. Hexameric capsules of resorcinarene **22c**, which encapsulate tetraphenylantimony bromide, are also able to include benzene, toluene and *p*-xylene.[159]

The co-crystallization of calix[4]resorcinarenes with 4,4′-bipyridine in the presence of nitrobenzene gives a crystalline assembly consisting of the large capsule **48**, which is held together by hydrogen bonds, and accommodates two nitrobenzene molecules.[160]



48

The C_{2v}-symmetric resorcinarene tetraesters **49** form dimeric hydrogen-bonded capsules that encapsulate one Me_4N^+ cation in the presence of tropylium cations. The homodimeric capsules of tetrakis(3,4,5-trimethoxybenzoate) **49d** and tetrabenzoate **49b** (or tetrafuroate **49c**) disproportionate quantitatively in solution to give the heterodimers.[161]



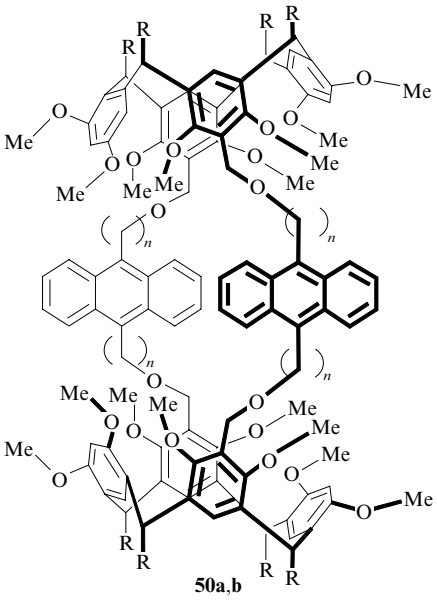
49a – e

Compound **49**	R^1	R^2
a	2-thienyl	n-C_5H_{11}
b	Ph	Pr^n
c	2-furyl	$BnCH_2$
d	3,4,5-$(MeO)_3C_6H_2$	$BnCH_2$
e	BnO	Me

Russian-doll-type multicomponent assemblies derived from hexameric resorcinarene nanocapsules, which form inclusion complexes of calix[4]arenes that contain tetramethylammonium and trimethylsulfoxonium cations, have been prepared.[162] Studies of the macrocyclic tetrakis{2-[*N*′-(2-hydroxyethyl)piperazino]}calix[4]resorcinarene (as a solvate with three molecules of ethanol and one molecule of

water) revealed a self-assembled dimeric capsule-like complex held together by an array of intermolecular hydrogen bonds.[90] A teflon-footed resorcinarene [R = $CH_2CH_2CH.(CH_2C_{10}F_{21}\text{-n})_2$] was synthesized by cyclooligomerization of resorcinol with a highly fluorinated aldehyde. This material further assembles into hexameric capsules in fluorous solvents, a process in which water molecules play a crucial role.[118] Chain-link hydrogen-bonded capsules have been formed by the self-assembly of a series of bipyrimidines, namely, 5,5′-bipyrimidine, 1,2-bis(5-pyrimidyl)ethyne and 1,2-bis(5-pyrimidyl)ethane, with *C*-methylcalix[4]resorcinarenes.[163–165] The synthesis of self-assembled supramolecular capsules based on DNA-like complementary purine–pyrimidine base pairing has been demonstrated.[166] 2,5-Diazahexamethylene-bridged resorcin[4]arene dimers, which exist in a closed capsular conformation that includes its bridging chain, have been reported.[167] When resorcin[4]-arenes are dissolved in polar solvents containing alcohols, they exist in three types of self-assembled aggregates (monomeric, dimeric and hexameric species).[168]

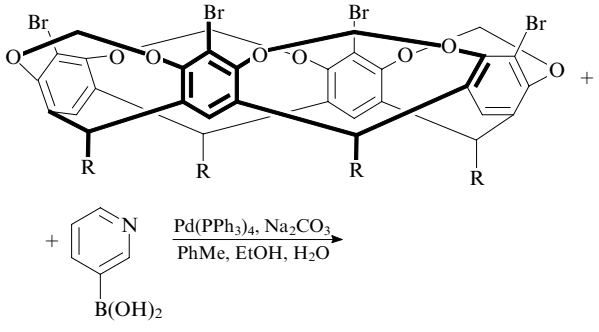
Photocyclizable systems of covalently linked dimers **50a**,**b**, which contain two resorcin[4]arene moieties connected by two 9,10-functionalized anthracene units, have been reported.[169]

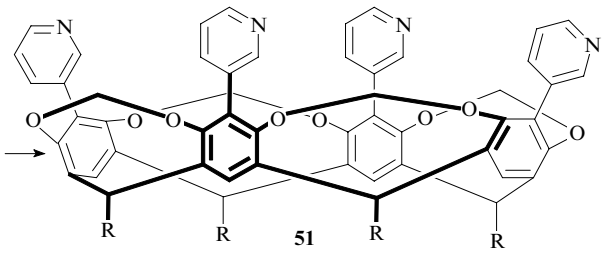


50a,**b**

R = n-$C_{11}H_{23}$, *n* = 2 (**a**), 1 (**b**).

Paek and Park[170] have reported versatile molecular capsules formed from resorcin[4]arene-based benzoylhydrazide cavitands. The synthesis of pyridyl-functionalized cavitand **51**, which contains suitable hydrogen-bond acceptor moieties for the construction of asymmetric cavitand-based capsules, has been described.[171]



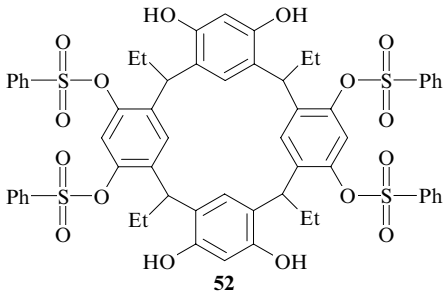


51

R = n-C_5H_{11}.

Surfactants derived from *C*-undecylcalix[4]resorcinarene, namely, tetra(arenemethanethiol)resorcinarene and a poly(dithiocarbamate) derived from tetra-N-methyl(aminomethyl)resorcinarene were used for the encapsulation of gold nanorods (GNRs) and for their extraction into organic solvents.[172] The resorcinarene-encapsulated GNRs can be used as intermediates to form magnetic nanoshells and to prepare core–shell nanostructures. *C*-Methylpyrogallolarene forms dimeric capsules with small quaternary and tertiary alkyl ammonium cations.[173] *C*-Alkylresorcin[4]arenes form hexameric capsules with two molecules of tetraethylammonium acting as guest molecules, regardless of the anionic counter ion.[174]

An unprecedented dimeric capsular assembly of a tetramethylated *C*-hexylresorcinarene has been reported.[175] Despite having no apparent possibility for intra-capsular hydrogen bonds, it forms a capsule that is held together solely by cation–π-interactions and the complementary geometries of the spherical guest cation and the concave resorcinarene host. The size and the nature of the cation, and how those parameters relate to its cation–π-interaction properties, seem to play the most important role in driving solid-state capsule formation. The design of resorcinarene-based host–guest systems to a degree of precision that would enable the prediction or inducement of a specific crystal packing or structural arrangement of the host and guest is very difficult due to the chameleon-like nature of resorcinarenes in their ability to form weak interactions. The boat conformers of calix[4]resorcinarene **52** form hydrogen-bonded, solid-state capsules that incorporate two triethylammonium cations simultaneously.[176]

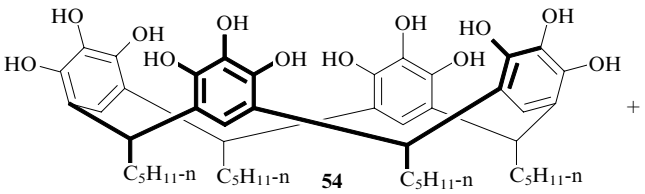


52

Two molecules of calix[4]resorcinarene in the boat conformation are linked through four hydrogen bonded chloride anions of $Et_3NH^+Cl^-$ to form dimers. The resulting large, negatively charged chambers may encapsulate two triethylammonium cations due to strong electrostatic and hydrogen-bonding interactions.

Atwood and co-workers[177] have made a rich contribution with respect to self-assembled capsule-derived *C*-alkylpyrogallol[4]arenes under various conditions. Six *C*-methylresorcin[4]arenes have been shown to self-assemble with eight structural water molecules through hydrogen

bonding into hexameric nanocapsules.[177] The related *C*-alkylpyrrogallol[4]arenes self-assemble without structural water molecules to form similar hydrogen-bonded nanocapsules.[178] Large multicomponent nanospheroid assemblies **53** have been prepared that consist of six *C*-pentylpyrogallol[4]arene **54** molecules and 12 Ga^{3+} metal ions and are held together by a combination of metal ion coordination and hydrogen bonding interactions.[179]

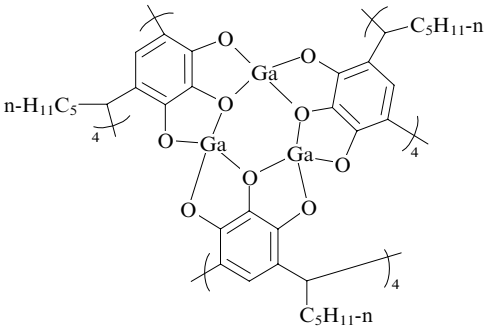


54

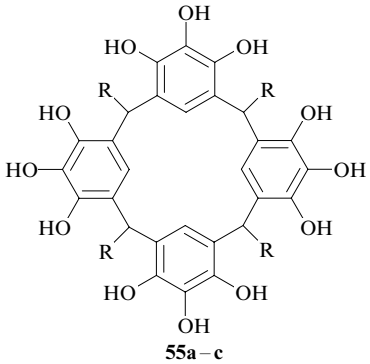
$+ 12\,Ga^{3+} \longrightarrow [Ga_{12}(\mathbf{54})_6] + 36\,H^+$

53

One of the four $[Ga_3(\mu_3\text{-}O)_3(O)_6]$ fragments of the assembly **53** is presented below (the water molecules are omitted for simplicity).



This research group has also prepared *C*-chlorobutylpyrogallol[4]arene (**55a**) and *C*-bromooctylpyrogallol[4]arene (**55b**) using the acid-catalyzed condensation of the corresponding aldehyde and pyrogallol in ethanol, and found that compound **55a** favours the formation of bilayer arrays, while compound **55b** preferentially forms nanocapsules.[180]



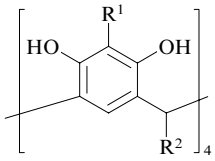
55a–c

R = $(CH_2)_4Cl$ (**a**), $(CH_2)_8Br$ (**b**), n-C_6H_{13} (**c**).

The first metal-coordinated pyrrogallol[4]arene encapsulating dimer, having high nuclearity with respect to Zn^{2+} ions, which are arranged in a polar coordination belt, has been synthesized. This high-nuclearity zinc-pyrogallol[4]arene dimer capsule is a successful realization of a model concept. This structure offers a spectrum of new and unusual opportunities for further investigations into metal chelation with molecular encapsulation.[181] Structural studies on two complexes formed in either water or acetonitrile and comprised of caesium chloride and pyrogallol[4]arenes with very different lower rim characteristics (*i.e.*, compounds **55a** and **55c**) have been carried out. These studies afforded two related dimeric capsules, a head-to-head structure and an offset structure (**55a**)·CsCl and (**55c**)·CsCl, respectively, that are stabilized by varied coordination modes of caesium to the upper rim oxygen atoms and in one case to the host aromatic ring.[182]

It was shown that fluorescence resonance energy transfer occurs from a fluorescent guest to labelled resorcinarene and pyrogallolarene capsules with an acceptor fragment (perylene) that are used as hosts.[183–185] In these studies, information was also gleaned regarding the degree of assembly and the stability of the hexameric capsules under a variety of conditions.

Reversible encapsulation has changed the way scientists view molecular interactions. It is now becoming clearer that the behaviour of molecules in dilute solution is quite different from their behaviour in capsules. These capsules self-assemble through a variety of forces, including hydrogen bonding, metal–ligand interactions and hydrophobic effects. Their lifetimes range from milliseconds to hours, which is often long enough for NMR spectroscopy to reveal what is happening inside the capsules. A brief account of physical properties of these systems and how the mechanical boundaries of the capsules dictate the behaviour of the molecules inside has been given.[186] Additionally, the various regions of the capsule interior with guests of different shapes has been probed. The spontaneous self-assembly of molecules **10d**, **22c**, **56a**,**b** and **57a**,**b** into hexameric capsules in organic solvents has been demonstrated with the aid of diffusion NMR systems.[187]



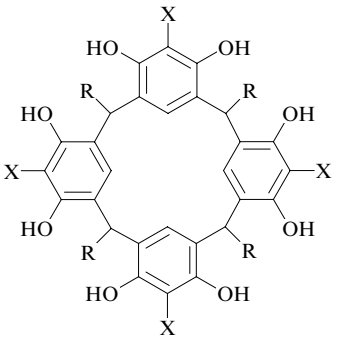
R^1 = H: R^2 = Bu^i (**56a**), Me (**56b**);
R^1 = OH: R^2 = Bu^i (**57a**), n-$C_{11}H_{23}$ (**57b**).

56a,**b**; **57a**,**b**

5. Self-assembled monolayers

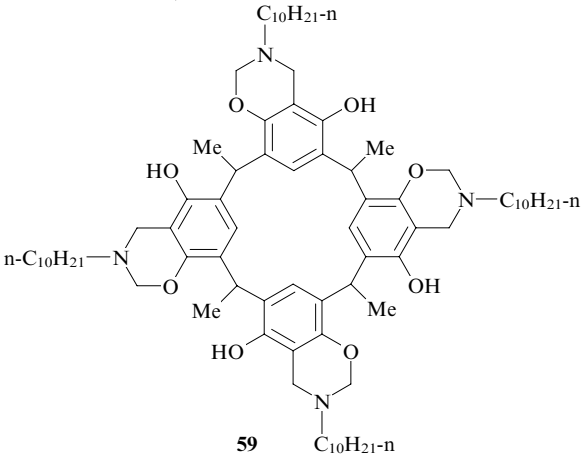
The incorporation of calix[4]resorcinarenes into the molecular assemblies of the Langmuir–Blodgett films, monolayers and lipid bilayers allows selective molecular association. The organic molecules used to form monolayers are amphiphilic and spontaneously spread at the air/water interface. The aqueous phase provides an ideal smooth surface and a reservoir for water-soluble material. Self-assembled monolayers are formed as the result of van der Waals interactions between the long-chain alkyl groups, which contain molecular cavities for targeted recognition of guest molecules. In order to be able to translate intrinsic molecular properties into material properties, it is essential to control the molecular interactions and orientation of the material. Researchers motivated by different goals working in this area have accepted the challenge of manipulating molecular organization, structure and forces, and thereby, selectively controlling binding. The works mentioned in this Section are either recent, or if covered in an earlier review on monolayers,[47] are very important.

Calix[4]resorcinarenes **58a**,**b**, **59** form stable monolayers at the air/water interface. The interaction with Cu^{2+} ions (using a $CuCl_2$ laden aqueous phase) is weak in the case of calix[4]resorcinarene **58a** and strong in the cases of **58b** and **59**.[188]



58a,**b**

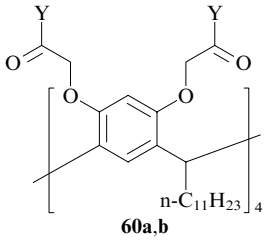
R = n-C_9H_{19}:
X = H (**a**), CH_2NMe_2 (**b**).



59

The self-assembled monolayers formed from hosts, such as calix[4]resorcinarenes with lower-rim long alkyl chains (*e.g.*, n-$C_{12}H_{25}$) provide a unique environment to study the relationships between the molecular structure and organization, on the one hand, and the forces that drive intermolecular association at the solid–liquid interface, on the other hand. By using structural isomers of guest molecules, such as bipyridine and nitrophenol, which are also multidentate hydrogen bond acceptors,[189] it has been established that the steric match between the guest and host molecules is an integral aspect of the recognition phenomena.

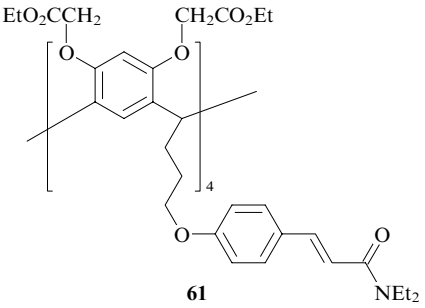
Calix[4]resorcinarenes, which have been octafunctionalized with methyl acetoacetate or *N*,*N*-diethyl acetoacetamide **60a**,**b**, have been used to prepare liquid monolayers on subphases containing terbium solutions in Milli-Q water.[190]



60a,**b**

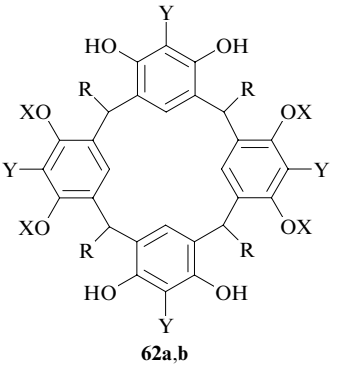
Y = CH_2CO_2Me (**a**), $CH_2C(O)NEt_2$ (**b**).

The crown conformer of a calix[4]resorcinarene **61** that possesses eight carboxymethylated units at the lower rim and four cinnamamide residues at the upper rim was prepared to fabricate photofunctional monolayers. Monolayers of calix[4]resorcinarene containing cinnamamide residues are applied to silica plates in order to provide photocontrol of liquid crystal alignment, and to display the photofunctionality of this monolayer.[191]



61

The Langmuir–Blodgett films of two novel amphiphilic calix[4]resorcinarene derivatives, which are phosphorylated (**62a**) and azobenzene substituted (**62b**) compounds, respectively, show good adsorption of several organic vapours, including benzene, toluene, *p*-xylene, aniline, hexane and chloroform. These films consist of a nanoporous matrix formed from the intrinsic calix[4]resorcinarene cavities and the empty spaces between the molecules and alkyl chains, which allow the penetration of organic vapours through these pores into the film's matrix and to condense there.[192]

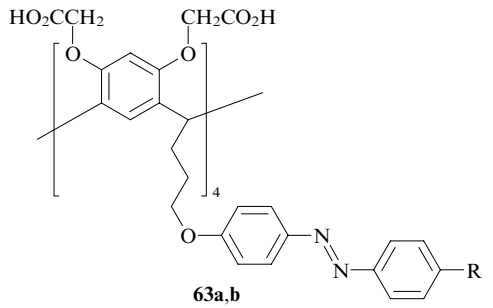


62a,**b**

R = n-C_5H_{11}, X = $P(OPr^i)_2$, Y = H (**a**);
R = n-$C_{11}H_{23}$, X = H, Y = N═NPh (**b**).

Amphiphilic water-insoluble tetrakis(sulfonatomethyl)-calix[4]resorcinarene was synthesized and studied tensiometrically. Due to the presence of four sulfonatomethyl groups at the upper rim, it is able to form stable non-collapsing films at the water/air interface. Compression isotherms were used to investigate the interactions inside the films of the macrocycle when two polymers were fed into the aqueous subphase: synthetic, polyethyleneimine, and a natural polymer, the enzyme ceruloplasmin (oxidase).[193]

The co-adsorption of *O*-octacarboxymethylated calix[4]-resorcinarenes with either perfluorooctyl- (**63a**) or octylazobenzene (**63b**) units, respectively, provides a method for generating photoresponsive surfaces that exhibit varied surface compositions and levels of photoisomerization, which would in turn influence both the photoinduced liquid crystalline alignments and the wetting properties of monolayers.[194]

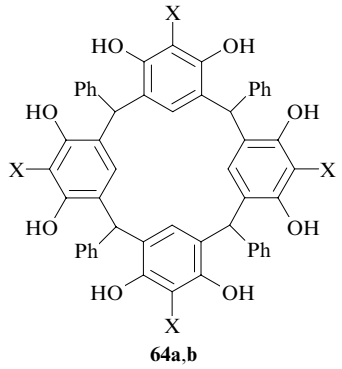


63a,**b**

R = n-C_8F_{17} (**a**), n-C_8H_{17} (**b**).

The interactions of dopamine with calix[4]resorcinarene **57b**, which depend on the orientation of the calixarene molecules in the monolayer formed at the air/water interface, were studied by analyzing their mechanical, thermodynamic and electrical properties as evaluated by measurements of pressure-area isotherms and the Maxwell displacement currents.[195]

The sensing behaviour of two calix[4]resorcinarenes (**64a**,**b**) has been characterized in terms of modifications to their surface pressure – one molecule area isotherms and their UV-Vis solution and the Langmuir-Blodgett film spectra over a wide range of analytes, including three amino acids (*viz*., lysine, alanine and glutamic acid). In particular, the Langmuir – Blodgett films of resorcinarene **64a** have been shown to bind selectively to lysine, an important amino acid.[196]



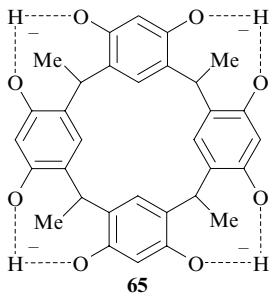
64a,**b**

X = $CH_2\overset{+}{N}Et_2CH_2CH_2OH\ Br^-$ (**a**), CH_2NEt_2 (**b**).

Self-assembly of calix[4]resorcinarene octaaminoamido derivatives in aqueous solutions have been found to form monolayer, bilayer and multilayer structures. Dynamic light scattering study and scanning electron microscope images have demostrated the formation of nanodimensional aggregates and submicron-scale 'cell-like' aggregates, respectively.[197]

6. Complexation

Calix[4]resorcinarenes are highly soluble in basic aqueous media because the phenolic hydroxyl groups can be deprotonated. Potentiometric titration studies reveal that of the eight phenolic protons, the first four protons have pK_a values that are two units lower than the pK_a of resorcinol, while the last four protons cannot be removed even with strong bases. The stability of tetraphenolate **65** is due to the ability of the negative charges to be delocalized and the ideal geometric disposition of the O – H – O arrangement.[198]

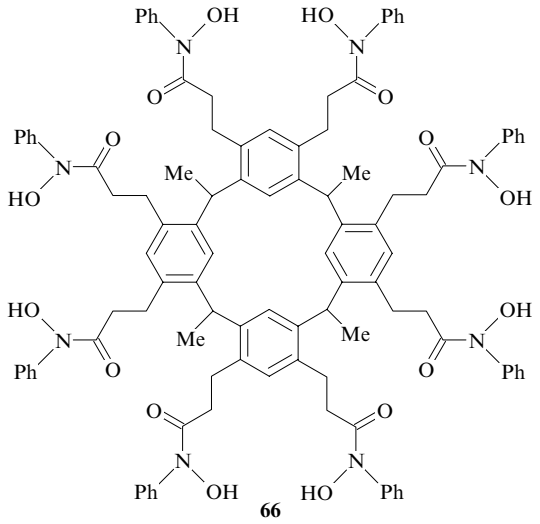


65

The binding strength of various alkyl ammonium ions to tetraphenolate ions **65** is moderately affected by changing the ionic strength[199] and solvent polarity,[200] but decreases strongly when the length of the alkyl groups on the ammonium ion increases.

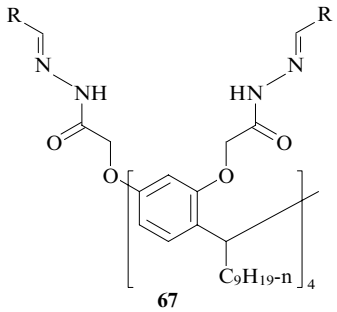
a. Complexation with metal ions

Calix[4]resorcinarene **66**, which bears eight hydroxamic acid groups, has been used for liquid – liquid extractions, separations and preconcentrations of vanadium, uranium, thorium, lanthanum and cerium.[201 – 205]



66

Tetranonylcalix[4]resorcinarenes **67**, which bear acetylhydrazone groups, were found to be effective reagents for the liquid – liquid extraction of various metal ions (*e.g*., Li^+, Na^+, K^+, Cs^+, Ca^{2+}, Pb^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, La^{3+}, Gd^{3+} and Lu^{3+}).[206, 207]

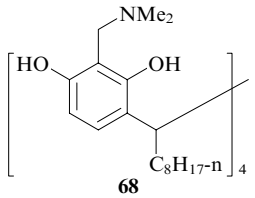


67

R = Ph, 4-BrC_6H_4, 4-$O_2NC_6H_4$, 2-Py, 4-Py.

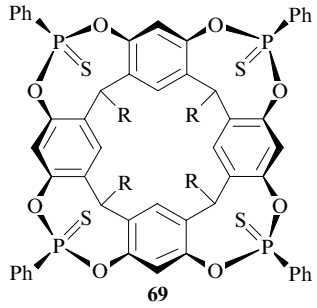
When dissolved in dichloroethane and heptan-1-ol, dimethylaminomethylated resorcinarene **68** was found to extract the Am^{III} and Eu^{III} ions from neutral aqueous

solutions. The separation factor increases as the concentrations of the extractant and supporting electrolyte are increased.[208]



68

Tetrathiophosphonate-calix[4]resorcinarene host **69** exhibited excellent extraction properties toward soft metal ions. Specifically, it showed a better affinity for Ag^+ (91%), than for Tl^+ (38%) and Hg^{2+} (16%).[209]

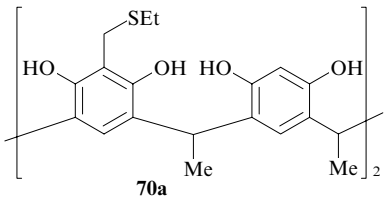


69

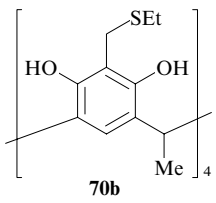
R = n-$C_{11}H_{23}$.

New phosphorylated calix[4]resorcinarenes and cavitands have also been synthesized. Their ability to extract La^{III}, Gd^{III} and Yb^{III} ions were studied, and it was determined that the cavitands are more efficient extracting agents than the octasubstituted calix[4]resorcinarenes. The literature and spectral data (^{31}P NMR) suggest that the ligand in the extracted complex most probably has a 'kite' conformation.[210] Resorcinarene octamethyl ethers bearing alkyloxycarbonyl groups as the side chains have been shown to interact with Fe^{III} in organic media,[211] while cyano- and aminoresorcinarenes have been found to interact with copper(II).[212] Octacarboxy-*C*-methyl-calix[4]resorcinarene[213] forms complexes with both Fe^{II} and Fe^{III}, but Fe^{II} ions seem to form complexes through favourable cation–π-interactions, while Fe^{III} complexation is mainly based on the formation of a chelate with the carboxylate moieties of the resorcinarene molecule. Tetranuclear copper(II) calix[4]-resorcinarene complexes, which possess four structurally different copper centres, have also been reported.[214]

Calix[4]pyrogallarenes have been shown to be alkali metal receptors, and in the resulting hydrogen-bonded molecular cages, alkali metal cations are η^6-coordinated to aromatic rings due to strong cation–π-interactions.[215] Picolyl-functionalized resorcinarenes serve as multidentate ligands for the coordination of some transition metals, such as palladium, zinc, nickel and copper.[132] Partially functionalized 5,17-ethylthiomethylated calix[4]resorcarene **70a** interacts only with Ag^+ in methanol, but reacts with Hg^{2+} in propylene carbonate, acetonitrile, methanol and *N*,*N*-dimethylformamide. The above-mentioned results can be compared with the fully functionalized resorcinarene **70b**, which forms complexes with Ag^+ and Pb^{2+} in acetonitrile, and with Cu^{2+} and Ag^+ in methanol.[216,217]

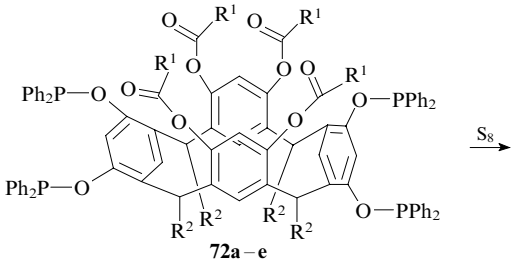


70a

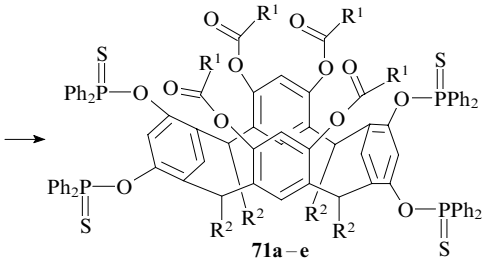


70b

The selectivity and thermodynamic characteristics of the exchange of protons for Na^+, Cu^{2+} and In^{3+} cations in the SO_3H groups of a sulfonated network polymer based on *cis*-tetraphenylcalix[4]resorcinarene in aqueous solutions has been studied.[218] The coordination chemistry of the versatile tetrakis(tetrathiophosphinate) calix[4]resorcinarene ligands **71a**–**e**, which differ significantly from that of the tetraphosphinite ligands **72a**–**e** from which they were derived by oxidation with sulfur has been described.[219]



72a–**e**

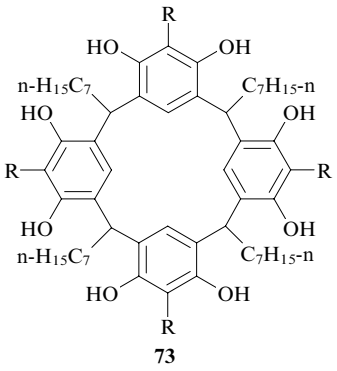


71a–**e**

$R^2 = CH_2Bn$: R^1 = OBn (**a**), 4-MeC_6H_4 (**b**), 2-thienyl (**c**), $CH_2C{\equiv}CH$ (**d**), n-C_6H_{11} (**e**).

The coordination chemistry of these new sulfur-donor ligands (L) has been investigated with silver(I), gold(I) and palladium(II). Both silver(I) and gold(I) form cationic complexes of the type $[LM_2]^{2+}$ in which the ligand acts as a bis(chelate). Gold(I) also forms the unusual complex $[L(AuCl)_2][LAu_2]^{2+}$, which further forms a supramolecular polymer through intermolecular aurophilic attractions. Palladium(II) forms the complex $[LPd_2Cl_2(\mu\text{-}Cl)_2]$. In that complex, the dipalladium(II) unit extends the natural bowl structure of the resorcinarene. In addition to these results, this work establishes the value of the resorcinarene skeleton for forming polydentate ligands with very unusual and interesting coordination chemistry.[219]

The acid-base and complexing properties of copper(II) and lanthanum(III) with aminoacetal-containing calix[4]resorcinarene **73** were studied in 80% isopropyl alcohol. The effects of surfactants on various characteristics of the protolytic process and complexation have also been considered.[220]

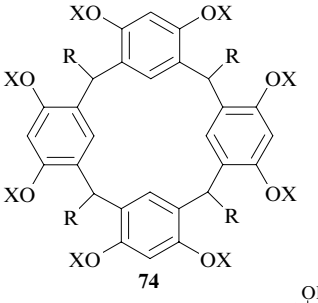


73

R = $CH_2N(Me)CH_2CH_2CH(OMe)_2$.

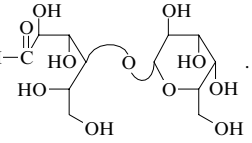
b. Host – guest complexation

Resorcinol – dodecanal cyclotetramer **22c** extracts monosaccharides into CCl_4 selectively from aqueous solutions in the form of 1 : 1 complexes.[221,222] Calix[4]resorcinarene binds hydroxylic guest compounds including sugars in apolar organic media. The driving force of this complexation is a combination of hydrogen bonding and CH – π-interaction. The latter interaction gives rise to not only a 1 : 1 host : guest stoichiometry but also a sizable selectivity arizing from the apolar alkyl moiety of the guests. Sugars and related guests can also be bound in water to tetrasulfonate derivatives of resorcinarenes. The CH – π-interaction again provides the major driving force. It is sensitive to the π-electron density of the aromatic cavity of the host. Thus the guest (sugar) binding ability of the host is enhanced either by introduction of additional electron-donating OH groups on the benzene rings or upon deprotonation of the OH groups giving rise to anionic host. The CH – π-interactions may be regarded as a kind of hydrogen bonding between a π-base and a σ-acid.[223–225] Octa(galactose) derivative of calix[4]-resorcarene **74** have been reported as a versatile host in water,[226] can be absorbed, together with included guest molecules, on the silica surface due to multiple hydrogen bonding,[227] mediates a novel ternary complexation [228] with concanavalin A providing guest delivery to the lectin. Anions, especially the phosphates, are readily incorporated into clustering oligosaccharide pools through hydrogen bonding, thereby inducing chain-length dependent agglutination of the clusters.[229]



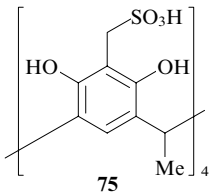
74

R = n-$C_{11}H_{23}$, X = CH_2CH_2–NH–C(=O)–



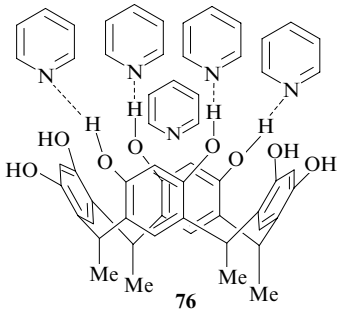
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Water-soluble tetrasulfonatomethylcalix[4]resorcinarene **75** forms a host – guest complex with some α-amino acids (L-Lys, L-Arg, D- and L-Phe, L-Pro and L-Trp).[100]



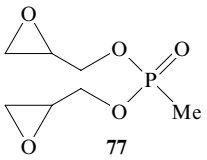
75

The crystallization of calix[4]resorcinarene **56b** from pyridine leads to the complex **76**,[230] which has four pyridine molecules situated over the calix[4]resorcinarenes molecule through hydrogen bonds with the four hydroxyl groups of the resorcinol moieties on opposite sides of the calix[4]resorcinarene and a fifth pyridine molecule situated loosely over the calix[4]resorcinarene cavity.



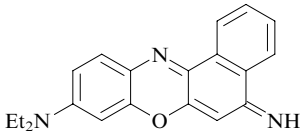
76

Calix[4]resorcinarene **56b** also forms complexes with amines [Me_2NH, Et^2NH, Pr^i_2NH, morpholine, piperidine, (cyclo-C_6H_{11})NH_2, $PhMeCHNH_2$, (cyclo-C_6H_{11})MeCH.NH_2], amino alcohols [$EtCH(CH_2OH)NH_2$, BnCH.$(CH_2OH)NH_2$, (*R*)-$PhCH(OH)CHMeNH_2$] (Ref. 231) and diglycidyl methylphosphonate (**77**) (Ref. 232).



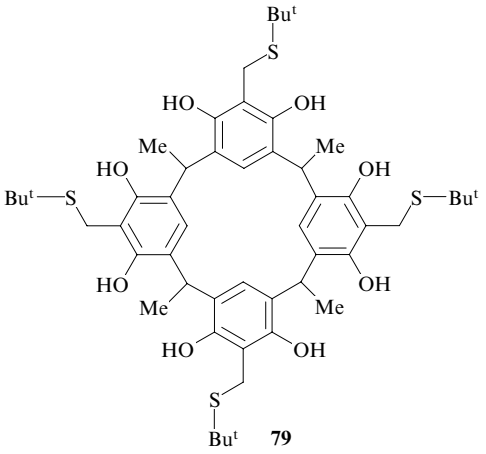
77

Tetrakis(*C*-undecyl)calix[4]resorcinarene **22c** forms a 1 : 4 host – guest complexes with dioxane [233] and Nile Blue (**78**),[234] but forms solid complexes with secondary and tertiary amines [morpholine, piperidine, 2,6-dimethylmorpholine, Pr^i_2NH, Et_3N, (cyclo-C_6H_{11})$_2NH$] from dioxane solutions by crystallization.[235]



78 (Nile Blue)

Host – guest interactions of *C*-methylresorcin[4]arene **56b** and its derivative **79**, which have been appended with four *tert*-butylsulfanylmethyl groups at the extra-annular positions, have been studied and it has been determined that bulky substituents create a deep cavity with a narrow entrance that improves size and shape selectivity.[236]

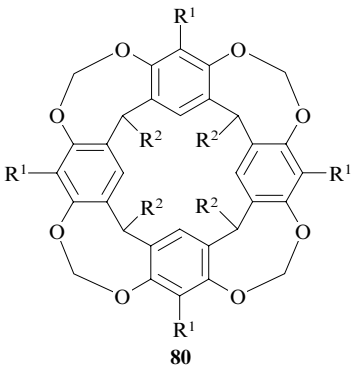


79

Host–guest complexes that have been obtained by co-crystallizing *C*-methylresorcin[4]arene with 1,10-phenanthroline, coumarin or thiocoumarin from polar solvents were studied using single crystal X-ray diffraction techniques.[237, 238]

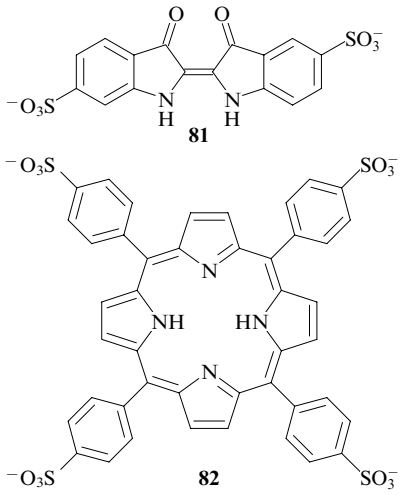
The preparation of water-soluble tetrakis(methylviologen)calix[4]resorcinarenes has been described. They were found to form stable charge-transfer complexes with electron-rich aromatic compounds in aqueous media.[239] Detailed investigations of eight water-insoluble complexes of tetrakis(sulfonatomethyl)calix[4]resorcinarenes with phenothiazine derivatives under substoichiometric conditions were carried out by mixing aqueous solutions of the reactants.[240] The complexation properties of the Langmuir–Blodgett films containing an amphiphilic calix[4]resorcinarene appended with four arylazo groups and some heavy metal ions using UV-Vis spectral measurements have been investigated.[241] The mechanism of interaction for thin films of tetrakis(undecyl)tetrakis(*p*-nitrophenyl)azocalix[4]-resorcinarene with benzene, toluene, n-hexane, *m*-xylene, and butan-1-ol vapours in a range of concentrations has further been investigated. The film interactions with the above vapours were monitored using surface plasmon resonance methods.[114, 242] A single report is available on selective enclathration of picoline isomers by a resorcinarene host.[243] A wide range of transition metal-dependent polymetallic dithiocarbamate nanosized host structures were prepared, which were found to bind strongly nanosized fullerene guest species.[244]

The electrospray ionization Fourier-transform ion-cyclotron resonance mass spectrometric experiments have been performed [245] to assess the anion-binding behaviour of hosts **22b**, **80** and anions [SO_4^{2-}, PF_6^-, BPh_4^-, $B(3,5\text{-}Me_2C_6H_3)_4^-$, **81**, **82**]. These experiments provide evidence of a cavitand–anion interaction mediated by C–H···anion hydrogen bonds that involve the acetal protons that point into the cavitand bowl.



80

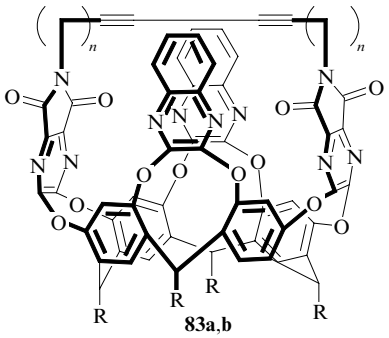
R^2 = n-C_5H_{11}: R^1 = H, OMe, CO_2Me, Br, I, CN, 4-NCC_6H_4;
R^2 = CH_2Bn: R^1 = H, CN.



81

82

The switchable baskets have been synthesized from a resorcin[4]arene bowl that was appended with two quinoxaline flaps in an *anti*-orientation. The two diazaphthalimide walls were connected to each other by a rigid hexa-2,4-diyne-1,6-diyl bridge (compound **83a**) or an octa-3,5-diyne-1,8-diyl unit (**83b**).[246]



83a,**b**

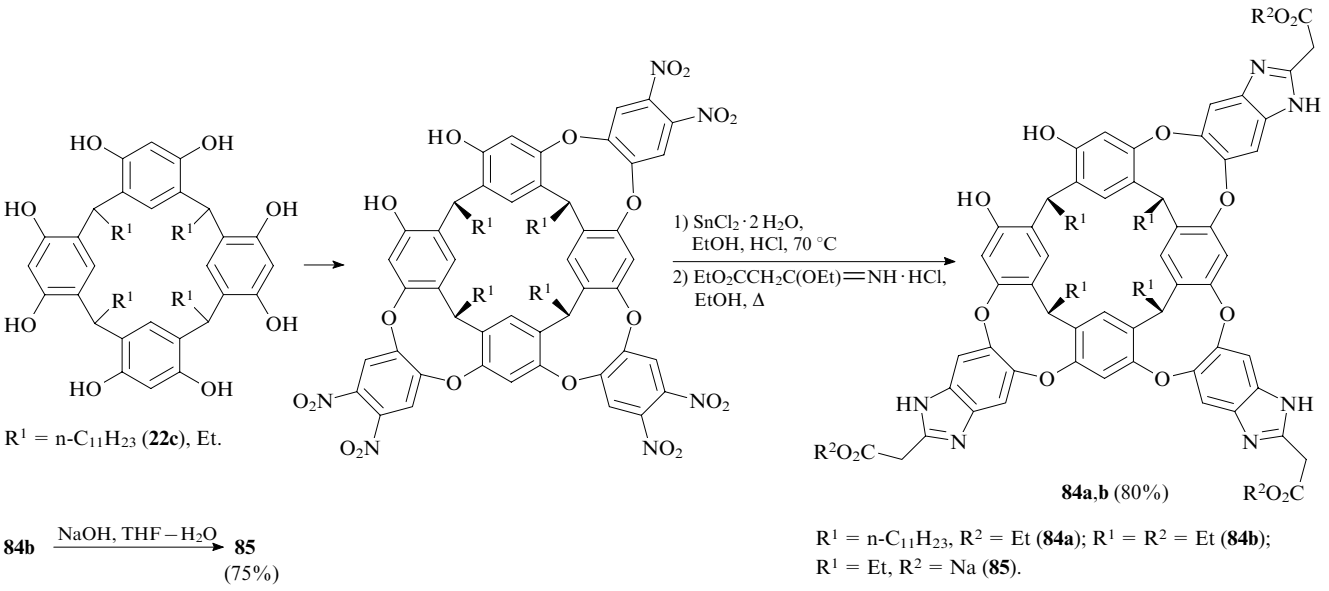
R = n-C_6H_{13}, *n* = 1 (**a**), 2 (**b**).

These molecules completely surround suitable guests, such as cyclo- or oxacycloalkanes, and bind them with high strength. However, the hosting ability of both molecules can be suspended by an external stimulus. Portals delimiting the cavity are open upon the addition of acid, and instantly release the guest. This process is fully reversible because the addition of a base completely and immediately restores the hosting properties of the switchable molecular baskets.

New water-stable deep cavitands **84a**,**b** and **85** with three walls and an open side have been synthesized;[247] they were shown to be receptors for amines and ammonium cations bearing bulky aliphatic groups (Scheme 2).

Counterion effects have been studied in sodium dodecyl sulfate–calix[4]resorcinarene micellar solutions in combination with tetrabutyl-, tetraethyl- and tetramethylammonium bromide, as well as choline chloride.[248] The self-aggregation behaviour of two amphiphilic sulfonatomethylated calix[4]resorcinarene derivatives have been evaluated by various NMR techniques in aqueous solution and has been shown that it depends on the size, structure and concentration of calix[4]resorcinarene derivatives and also

Scheme 2



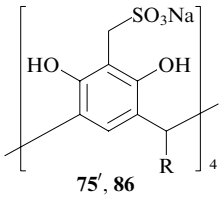
on the guest cations (tetramethylammonium and *N*-methylpyridinium).[249] The binding properties of functionalized resorcin[4]arenes toward a range of aliphatic alcohols (from methanol to pentanol) have been reported. The detection limit achieved in these experiments was about 1000 ppm for methanol and less than 50 ppm for pentanol.[250] Supported liquid membranes containing a resorcinarene carrier have been used for the selective transport of methyl glucopyranoside.[251]

In addition to the synthesis and characterization of tribenzobis(crown)tetramethoxyresorcinarene [*m*- (**35c**) and *p*-TBBC6 (**35d**)], the effect of the crown-ether bridge added aromatic functionality on alkali metal complexation (K^+, Rb^+ and Cs^+) was described.[141] A comprehensive investigation into the molecular recognition properties of a silicon surface decorated with phosphonate cavitands with respect to methylpyridinium and methylammonium guests has been reported.[252] The entire process, which consists of methylpyridinium complexation, guest exchange with a methylammonium salt, base-driven decomplexation of the latter and restoration of the initial complex, is fully reversible. Each step of the process was monitored using two independent techniques, X-ray photoelectron spectroscopy and fluorescence spectroscopy.

c. Solid phase extraction

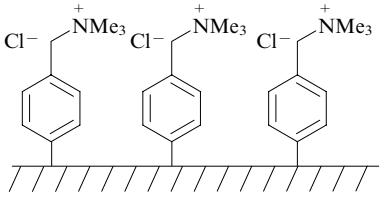
Once octakis(carboxymethyl)-*C*-methylcalix[4]resorcinarene has been impregnated into the polymeric matrix, Amberlite XAD-4, it exhibits high chemical stability and reusability. It has been used for the separation of Th^{IV} and U^{VI} from other metal cations in synthetic solutions.[253] The resin Amberlite XAD-16 impregnated with octakis(carboxymethyl)-*C*-methylcalix[4]resorcinarene has been used for the separation of La^{3+}, Ce^{3+} and Y^{3+} from each other, and also from UO_2^{2+} and Th^{4+} using a sequential elution system. The sorption capacity of the impregnated XAD-16 resin was found to be higher than XAD-4 impregnated with the same reagent because the larger pore diameter of the former allowed higher adsorption.[254] Calix[4]resorcinarenes have been used to develop a molecular imprinting by using them as host sites targeted for α-tocopherol, a natural antioxidant.[255]

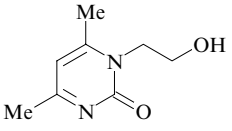
A polymer inclusion membrane system using cellulose triacetate polymer as the support, calix[4]resorcinarenes as the carrier and the new synthetic plasticizer 2-nitrophenyl octanoate has been developed; it was used to investigate the facilitated transport of Zn^{II}, Cd^{II} and Pb^{II} ions from aqueous nitrate source phase.[256] The ion-exchange resin Amberlite IRA-900-Cl has been transformed into a sorbent of organic molecules from aqueous solutions by immobilizing tetrakis(sulfonatomethyl)calixresorcin[4]arenes **75′** (**75′** is sodium salt of acid **75**) and **86** with methyl and pentyl substituents, respectively, at their lower rim.[257] The binding properties of macrocycles **75′** and **86** that determine their complexation with neutral organic molecules are characterized by a great potential for many-point hydrogen binding with the groups of the upper rim of the macrocycle {active principles of drugs Xymedon [*N*-(2-hydroxyethyl)-4,6-dimethyl-2-oxo-1,2-dihydro-pyrimidine, **87**] and Dimephosphon (dimethyl 1,1-dimethyl-3-oxobutylphosphonate, **88**) served as the guests}.



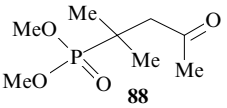
75′, **86**

R = Me (**75′**), n-C_5H_{11} (**86**).





87



88

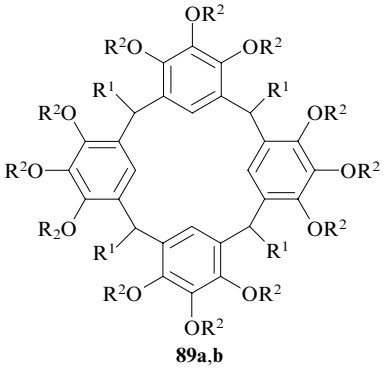
7. Applications

a. Liquid crystalline behaviour

Liquid crystals are materials with potential uses as active media in optical applications. Their quick response to changes in electric fields enables them to be used in the production of liquid crystalline displays. Resorcinarenes in the boat conformation are able to self-organize in ferroelectric (head-to-tail) or antiferroelectric (head-to-head) columnar arrangements.[258] Their liquid crystalline properties have been studied in detail.[259, 260] The interest in such columnar mesophases originates from the potential ferroelectricity that could result when all of the columns of molecules are oriented in the same direction.

Resorcinarenes become liquid crystalline when all of the following requirements are met.[261]

— The groups R^1 are small (*e.g.*, in compounds **89a**,**b**, maximum $R^1 = CH_3$), which allows an optimal core stacking.



89a,**b**

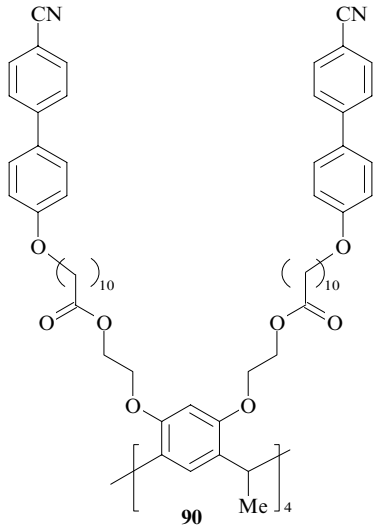
R^1 = Me, R^2 = C(O)Pr^n (**a**); R^1 = H, R^2 = C(O)C$_n$H$_{2n+1}$-n.

— At least twelve linear R^2 side chains containing from 12 to 17 carbon atoms to cover the periphery of the core in a homogeneous manner.

— The ester groups, which are used to connect the side chains to the core, should not have any bulky substituents close to the macrocyclic core.

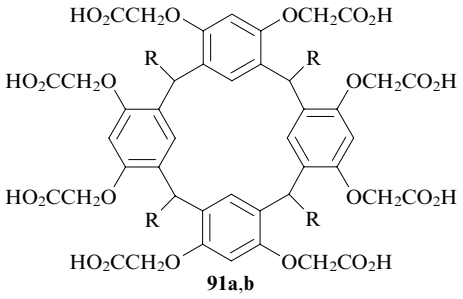
Single crystal X-ray study of dodecabutyrate **89a** reveals that the molecules are oriented in an antiferroelectric arrangement. This is most probably a result of the large dipole moment, which is calculated at 10.3 D (based on X-ray data) for the monomer, but has an almost zero value for the antiferroelectric pair.[258] Dodecaesters of type **89b**, which have a conformationally mobile macrocyclic core, exhibit liquid crystalline behaviour with only 9 to 12 carbon atoms in the R^2 side chains.[262] In this case, the presence of a fast ring-inversion process overcomes the constraint of antiferroelectric coupling of the molecules within the columns. In this way, the mesogens should be able to align their dipoles freely under the influence of an electric field.

C-Methyloctakis(2-hydroxyethyl)calix[4]resorcinarenes **90**, which were found to adopt a specific molecular structure due to the rigid-bowl calix[4]resorcinarene core (*i.e.*, a cone-like structure with mesogenic units aligned within the molecule), were found to possess a smectic A phase that can transform to a nematic phase.[263, 264] The supercooling of compound **90** required to cause the phase transition was very small due to its molecular structure, and thus the nematic texture rapidly appears upon cooling. As a result, molecules like **90** are expected to act as high-response liquid crystals in their nematic phase.



90

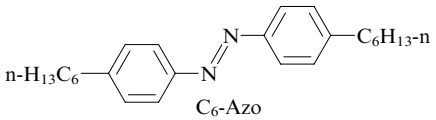
The crown conformers of *O*-octakis(carboxymethoxy)-calix[4]resorcinarenes (CRA-CM, **91a**,**b**) have a cylindrical framework with eight polar substituents at the upper rim, while the hydrophobic alkyl groups are tethered to the lower rim.



91a,**b**

R = n-C$_{11}$H$_{21}$ (**a**, C$_{11}$-CRA-CM), n-C$_{20}$H$_{41}$ (**b**, C$_{20}$-CRA-CM).

As a result, this molecule acts as a macrocyclic amphiphile that forms stable monolayers of nematic liquid crystals and provides a novel model system to mimic the interface between a liquid crystalline layer and a substrate surface. Because C$_{11}$-CRA-CM has a hydrophobic free space, it acts as a host with respect to 4,4′-di-n-hexylazobenzene (C$_6$-Azo guest) molecules to form a host–guest monolayer film at the air/water interface with C$_6$-Azo molecules perpendicular to the water surface.[265]



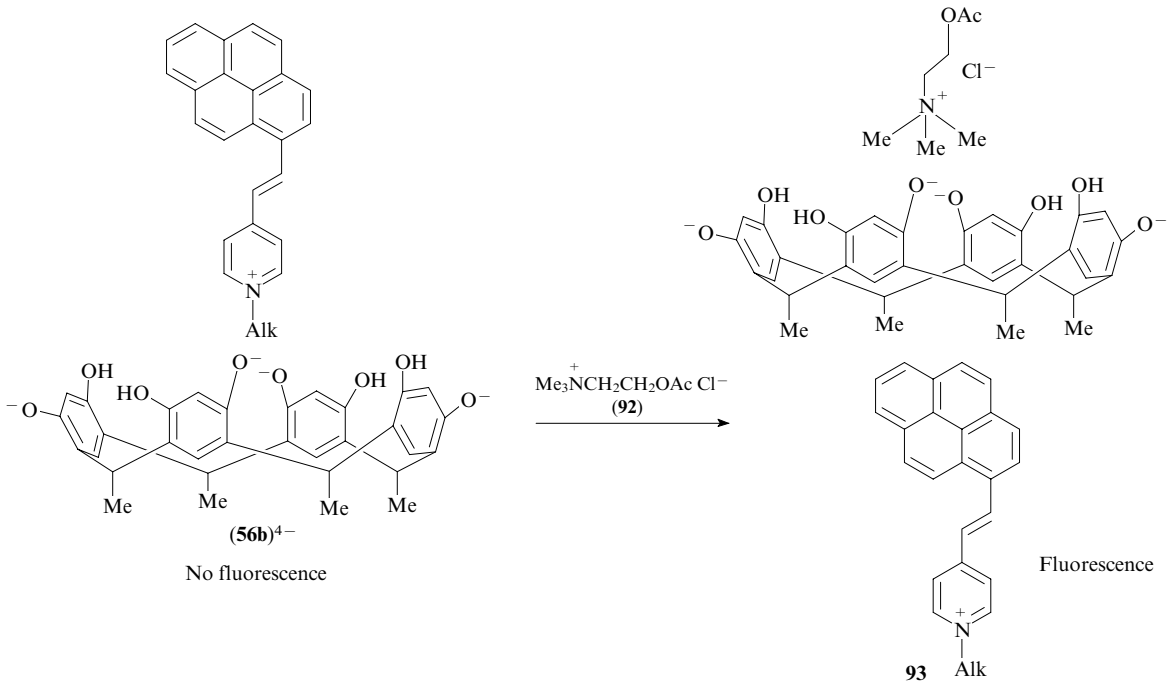
C$_6$-Azo

b. Fluorescence

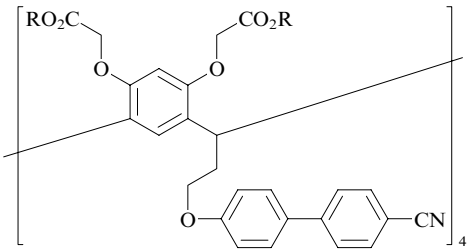
The fluorophore displacement[266] method has been used for the detection of acetylcholine chloride (**92**). When pyrene-modified *N*-alkylpyridinium cation **93**, which serves as a fluorophore, is bound in the cavity of **56b**, its fluorescence is quenched. However, the addition of compound **92** results in the release of fluorophore **93** from the cavity and allows its fluorescence to be observed again (Scheme 3).

Calix[4]resorcinarenes (CRA) **94a**,**b** with four cyanobiphenyl units (CB) at the lower rim were synthesized[267] and adsorbed on silica surface (size of the silica plates was 9 mm × 30 mm × 1 mm) to reveal the effect that surface

Scheme 3



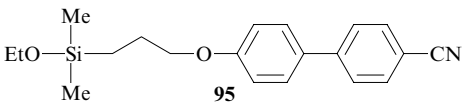
binding would have on the fluorescent behaviour of the cyanobiphenyl moieties.



94a,**b**

R = H (**a**), Et (**b**).

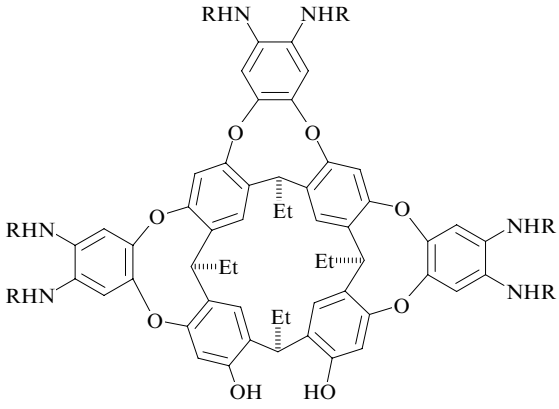
A plate modified with CB−CRA exhibited a markedly lower fluorescence intensity and a blue shift in air when compared to a plate that was CB-modified using silylation with compound **95**. It is clear that the restricted orientation of the fluorescent probe attached through the CRA unit (the CB fragments are oriented normal to the surface) contributes to the intermolecular interactions between the surface CB and the fluid.[267]



95

Two different hybrid cavitand resorcin[4]arenes **96a**,**b** were shown to be effective and selective for the molecular inclusion of positively charged organometallic sandwich complexes of the appropriate size. The binding constants for the 1 : 1 complexes formed with a series of neutral and positively charged metallocenes have been calculated using different titration techniques.[268] Additionally, compound **96a** is a good supramolecular fluorescent sensor system for choline and displays a pH-modulated binding affinity toward trimethylalkylammonium ions.[269]

Novel tetraaza[6.1.6.1]-*p*-cyclophane-based resorcinarene tetramers and dodecamers, as well as dansyl-appended



96a,**b**

R = H (**a**), C(O)Et (**b**).

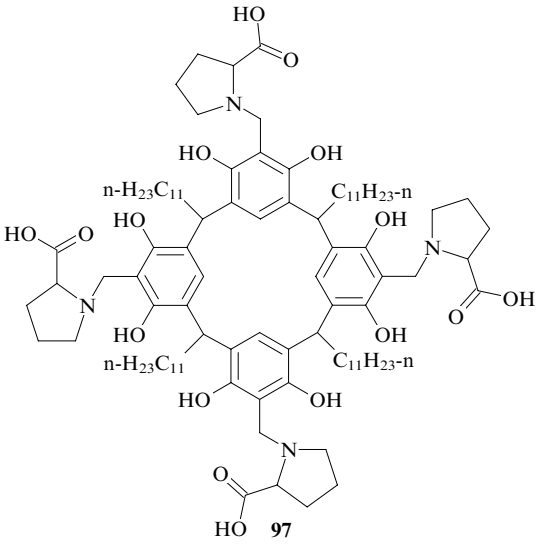
cyclophane-based resorcinarene trimers as fluorophores and rotaxane-type resorcinarene tetramer receptors[270−272] show unique properties as multivalent hosts of histone and other hydrophobic molecular guests. These properties were demonstrated by surface plasmon resonance measurements and fluorescence spectroscopy. These systems were reported to manifest high selectivity with respect to histones as compared with acetylated histone and other proteins, *e.g.*, albumin, cytochtome *c*, lysozyme, myoglobin, concanavalin A.

The fluorescence behaviour of pyrene in the presence of different derivatives of calix[4]resorcinarene in basic media has been studied.[273]

c. Nanoparticles

Atwood and co-workers[274] have demonstrated the formation of *C*-n-hexylpyrogallol[4]arene-based organic nanotubes in the solid state that show some potential to maintain their structure in solution. *C*-Undecylcalix[4]resorcinarene-capped anatase (TiO_2) nanoparticles have been synthesized; they could be isolated and then redispersed in

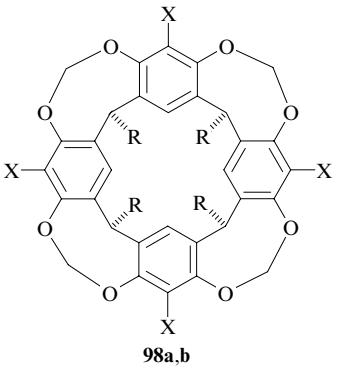
different nonaqueous solvents.[275] Self-assembled solid lipid nanoparticles based on prolyl-appended resorcinarene **97** have been chemically modified with bovine serum albumin and have been studied with regard to interactions with surface bound anti-albumin antibodies.[276]



97

This new approach to the modification of resorcinarene-based nanoparticles may open new lines of study, such as the use of these systems in drug targeting.

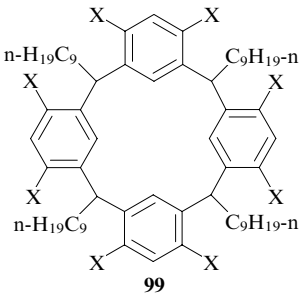
Two resorcinarene-derived tetrathiolated tetraene cavitands **98a**,**b** can extract colloidal gold nanoparticles from aqueous solutions and stabilize the dispersion of gold nanoparticles in organic solvents.[157]



98a,**b**

R = $(CH_2)_8CH{=}CH_2$: X = SH (**a**), CH_2SH (**b**).

The effect of gold nanoparticles on the self-assembly of thioether-footed resorcin[4]arenes was studied.[277] A novel amphiphilic polyaminoresorcinarene surfactant **99** has been

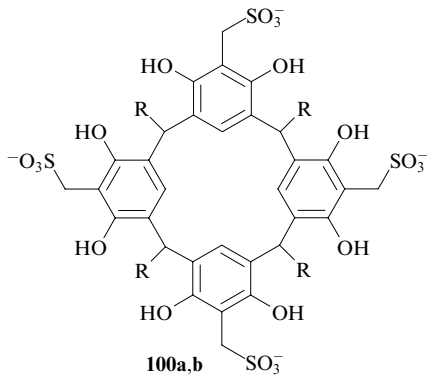


99

X = $OCH_2C(O)NH(CH_2)_2NH_2$.

synthesized,[278] which has a large hydrophilic head group comprised of eight amino groups and four hydrophobic chains. This surfactant not only can be used as a good ligand for gold nanoparticles, but also has a strong deaggregating effect on gold nanoaggregates under microwave irradiation.

Highly organized calix[4]resorcinarene-based nanostructured materials have been synthesized by an ionic self-assembly route. A series of complexes formed from anionic calix[4]resorcinarenes **100a**,**b** and cationic surfactants, $(n\text{-}C_{12}H_{25})_2N^+Me_2$ and $(n\text{-}C_{16}H_{33})_2N^+Me_2$, have been studied to determine their structures and binding capacities for selected guests. These complexes have been shown to be composites consisting of four surfactant molecules for each (tetraanionic) calix[4]resorcinarene. Cast films of these materials were exposed to a variety of species, and the adsorption of these species into the films was studied.[279]



100a,**b**

R = Ph (**a**), n-$C_{11}H_{23}$ (**b**).

Macrocyclic glycocluster compounds with four alkyl (undecyl) chains and eight oligosaccharide fragments on the opposite sides of the calix[4]resorcarene macrocycle are prepared from the reactions of the corresponding octaamine derivative with maltooligosaccharide-derived lactones comprising from 2 to 7 monosaccharide residues. These compounds form small micelle-like nanoparticles (d = 3 nm) in water, which are highly adhesive in the presence of the phosphate ions to form larger particles (d from 60 to 100 nm).[280] These nanoparticles are assembled on plasmid DNA in a number-, size-, and shape-controlled manner to give artificial glycoviral particles capable of transfection.[281] The hierarchical growth of glycocluster amphiphiles from nano particles to glycoviruses was described and a remarkably manipulated adhesion performance of saccharides was noted.

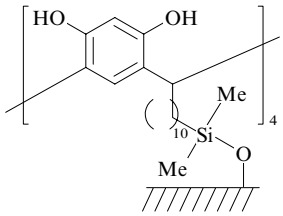
d. Catalysis

Self-assembled supramolecular systems based on amphiphilic sulfonatomethylated calix[4]resorcinarenes,[282, 283] aminomethylated calix[4]resorcinarenes[284, 285] and poly(ethyleneimines) possess good catalytic activity in the hydrolysis of phosphates. Additionally, bridged resorcinarenes have been used as templates for asymmetric catalysis[133, 134] and water-soluble calix[4]resorcinarene with sulfonic acid groups in substituents act as catalysts for the dehydrative amination of alcohols in water.[286]

d. Miscellaneous applications

In addition to the aforementioned uses and applications of calix[4]resorcinarenes and their functionalized derivatives such as cavitands, capsules, dendrimers, crowns, mono-

layers, extractors of metals, non-metals and neutral guests, host–guest complexation templates, liquid crystals, fluorophores and nanoparticles, they have been used as HPLC stationary phases. It was found [287] that silica gel covalently modified with calix[4]resorcinarene **101** has a different selectivity in the separation of the *cis*- and *trans*-isomers of thioxanthene and dibenzo[*b*,*e*]oxepin derivatives then unmodified silica gel. In comparison with a typical RP-C_{18} phase, the resorcinarene phase was found to be good for the separation of the isomers of Flupentixol and Clopenthixol.[287] The resorcinarene-based phase is able to interact specifically with the isomers of Flupentixol and Clopenthixol that possess a hydroxyl group in their polar side chains. Mobile phases containing MeOH were found to be advantageous for separations on the resorcinarene column.



101

Light-gated artificial ion channels [288] based on calix[4]-resorcinarene have been developed. They represent a necessary component for the construction of biosensors based on natural ion channels. The opening and closing of the artificial ion channel is achieved by azo groups, which work like a lid. The azo groups change conformation upon irradiation with light, but are chemically quite stable. The addition of a gate function may enhance the potential of synthetic channels to be used in sensors or as molecular switches. The synthesis of new chiral boron derivatives of resorcinarenes by the Mannich reaction of boron chelates obtained from chiral amino alcohols and triethylborane has been described.[289] Furthermore, calix[4]resorcinarene-based compounds and materials have found applications as molecular glass resists,[290–292] imaging materials for organic electronics,[293] chiral NMR solvating agents,[115] PVC supported liquid membrane electrodes,[294] multifunctional antiradical and antioxidant agents [295] and photoresist materials.[296]

V. Conclusion

In the last two decades, the chemistry of calix[4]resorcinarenes has been established to the extent that the field is now ready to extend an open invitation to all researchers who are already working on any monofunctional group, chelating moiety or non-conventional molecular attractive force, and who wish to explore the effects of those moieties when present collectively. By using calix[4]resorcinarenes, they can functionalize at 2 to 16 available sites with the moiety or functionality of their choice by manipulating the reagent and reaction conditions. It is of great interest to study the effects of putting a large number of the same or different functional groups into a single molecule or macrocycle (*e.g.*, calix[4]resorcinarene). Certainly it will exhibit some additional binding properties, which have yet to be discovered, when compared to a monofunctionalized molecule or macrocycle. There are several reasons for these effects: (i) the functional groups may be circularly arranged, or preorganized; (ii) the molecule may acquire a different conformation (*e.g.*, cone or partial cone); (iii) enhanced/reduced binding due to cooperative hydrogen bonding; (iv) the hydrophobic nature of the macrocycle may influence binding; (v) the intrinsic cavity and hydrogen bonding possibilities of calix[4]resorcinarene may allow it to behave as a ditopic or tritopic receptor; (vi) after functionalization, calix[4]resorcinarenes may form supramolecular structures by self-assembling. Overall, this molecular framework provides a springboard for researchers who wish to work in a more applied area in calix[4]resorcinarene chemistry.

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References

1. A Bayer *Ber. Dtsch. Chem. Ges.* **5** 25 (1872)
2. A Bayer *Ber. Dtsch. Chem. Ges.* **5** 280 (1872)
3. A Michael *Am. Chem. J.* **5** 338 (1883)
4. J B Niederl, H J Vogel *J. Am. Chem. Soc.* **62** 2512 (1940)
5. H Erdtman, S Högberg, S Abrahamsson, B Nilsson *Tetrahedron Lett.* **9** 1679 (1968)
6. B Nilson *Acta Chem. Scand.* **22** 732 (1968)
7. C D Gutsche *Calixarenes; Monographs in Supramolecular Chemistry* Vol. 1 (Ed. J F Stoddart) (Cambridge: Royal Society of Chemistry, 1989)
8. J Vicens *Calixarenes: a Versatile Class of Macrocyclic Compounds* (Ed. V Böhmer) (Dordrecht: Kluwer Academic, 1991)
9. R J M Egberink, P L H M Cobben, W Verboom, S Harkema, D N Reinhoudt *J. Inclusion Phenom. Macrocycl. Chem.* **12** 151 (1992)
10. D J Cram, S Karbach, H-E Kim, C B Kobler, E F Maverck, J L Ericson, R C Helgeson *J. Am. Chem. Soc.* **110** 2229 (1988)
11. L M Tunstad, J A Tucker, E Dalcanale, J Weiser, J A Bryant, J C Sherman, R C Helgeson, C B Knobler, D J Cram *J. Org. Chem.* **54** 1305 (1989)
12. U Scinder, H J Scinder *Chem. Ber.* **127** 2455 (1994)
13. E U Thoden van Velzen, J F J Engbersen, P J Delange, J W G Mahy, D N Reinhoudt *J. Am. Chem. Soc.* **117** 6853 (1995)
14. O M Shivanyuk *Zh. Org. Farm. Khim.* **4** (4) 3 (2006)
15. Y K Agrawal, R N Patadia *Rev. Anal. Chem.* **25** 155 (2006)
16. B Botta, M Cassani, I D'Acquarica, D Subissati, G Zappia, G Delle Monache *Curr. Org. Chem.* **9** 337 (2005)
17. M Guowei, X Yuesheng *Huaxue Tongbao* **66** w116/1-w116/7 (2003)
18. W Sliwa, T Zujewska, B Bachowska *Pol. J. Chem.* **77** 1079 (2003)
19. Y Shizhu, D Xuzhong, L Zhong *Huaxue Shiji* **21** 214 (1999)
20. P Timmerman, W Verboom, D N Reinhoudt *Tetrahedron* **52** 2663 (1996)
21. A Xiaohong, C Yixin, Y Shizhu *Guangzhou Daxue Xuebao, Ziran Kexueban* **4** 122 (2005)
22. H Konishi, in *New Trends in Structural Organic Chemistry* (Kerala, India: Research Signpost, 2005) P. 145
23. W Iwanek, A Wzorek *Mini-Rev. Org. Chem.* **6** 398 (2009)
24. P Wu, J Han, Y Ge, C Yan *Youji Huaxue* **26** 431 (2006)
25. I Neda, T Kaukorat, R Schmutzler *Main Group Chem. News* **6** (2–3) 4 (1998)
26. D Moore, S E Matthews *J. Inclusion Phenom. Macrocycl. Chem.* **65** 137 (2009)
27. L C Palmer, J Rebek Jr *Org. Biomol. Chem.* **2** 3051 (2004)
28. M Vincenti, A Irico *Int. J. Mass Spectrom.* **214** 23 (2002)

29. K Shibata, Y Ono, K Kikukawa *Kurume Kogyo Daigaku Kenkyu Hokoku* **24** 59 (2000); *Chem. Abstr*. **134** 131082m (2001)
30. L R MacGillivray, J L Atwood *J. Solid State Chem*. **152** 199 (2000)
31. L R MacGillivray, J L Atwood, in *Crystal Engineering: from Molecules and Crystals to Materials (NATO Sci. Ser. C)* Vol. 538 (Dordrecht: Kluwer Academic, 1999) p. 407
32. B Botta, M Cassani, I D'Acquarica, D Subissati, G Zappia, G D Monache *Curr. Org. Chem*. **9** 1167 (2005)
33. A Arduini, A Casnati, E Dalcanale, A Pochini, F Ugozzoli, R Ungaro, in *Calixarenes and Resorcinarenes in Molecular Recognition and Supramolecular Devices (NATO ASI Ser. C)* Vol. 527 (Dordrecht: Kluwer Academic, 1999) p. 67
34. I Higler, P Timmerman, W Verboom, D N Reinhoudt *Eur. J. Org. Chem*. **12** 2689 (1998)
35. H-J Schneider, U Schneider *J. Inclusion Phenom. Mol. Recognit. Chem*. **19** 67 (1994)
36. Y Aoyama, R Yanagihara, T Fujimoto *Yuki Gosei Kagaku Kyokaishi* **52** 572 (1994)
37. W Sliwa, B Dondela *ARKIVOC* (ii) 201 (2007)
38. S M Biros, J Rebek Jr *Chem. Soc. Rev*. **36** 93 (2007)
39. B W Purse, S M Butterfield, P Ballester, A Shivanyuk, J Rebek Jr *J. Org. Chem*. **73** 6480 (2008)
40. B W Purse, J Rebek Jr *Proc. Natl. Acad. Sci. USA* **102** 10777 (2005)
41. D M Rudkevich, J Rebek Jr *Eur. J. Org. Chem*. **9** 1991 (1999)
42. E E Nifantyev, V I Maslennikova, R V Merkulov *Acc. Chem. Res*. **38** 108 (2005)
43. C Wieser, C B Dieleman, D Matt *Coord. Chem. Rev*. **165** 93 (1997)
44. R J Puddephatt *Can. J. Chem*. **84** 1505 (2006)
45. W Alexander, K Beomseok, S V Pusztay, S L Tripp, R Balasubramanian *J. Inclusion Phenom. Macrocycl. Chem*. **41** 83 (2001)
46. R G Harrison *Commun. Inorg. Chem*. **22** 187 (2000)
47. K Ichimura, M Fujimaki, Y Matsuzawa, Y Hayashi, M Nakagawa *Mater. Sci. Eng., C* **8**–**9** 353 (1999)
48. B A Roberts, G W V Cave, C L Raston, J L Scott *Green Chem*. **3** 280 (2001)
49. H Konishi, Y Iwasaki, O Morikawa, T Okano, J Kiji *Chem. Express* **5** 869 (1990)
50. F Weinelt, H J Schneider *J. Org. Chem*. **56** 5527 (1991)
51. B Botta, M C Di Giovanni, G Delle Monache, M C De Rosa, E Gacs-Baitz, M Botta, F Corelli, A Tafi, A Santini, E Benedetti, C Pedone, D Misiti *J. Org. Chem*. **59** 1532 (1994)
52. E Benedetti, C Pedone, R Iacovino, B Botta, G Delle Monache, M C De Rosa, M Botta, F Corelli, A Tafi, A Santini *J. Chem. Res. (S)* 476 (1994)
53. B Botta, P Iacomacci, M C Di Giovanni, G Delle Monache, E Gacs-Baitz, M Botta, A Tafi, F Corelli, D Misiti *J. Org. Chem*. **57** 3259 (1992)
54. O M Falana, E Al-Farhan, P M Keehn, R Stevenson *Tetrahedron Lett*. **35** 65 (1994)
55. D Moore, G W Watson, T Gunnlaugsson, S E Matthews *New J. Chem*. **32** 994 (2008)
56. W Iwanek, B Syzdol *Synth. Commun*. **29** 1209 (1999)
57. W Iwanek *Tetrahedron* **54** 14089 (1998)
58. B Vuano, O I Pieroni *Synthesis* 72 (1999)
59. O Morikawa, Y Nagamatsu, A Nishimura, K Kobayashi, H Konishi *Tetrahedron Lett*. **47** 3991 (2006)
60. T Gerkensmeier, J Mattay, C Näther *Chem.–Eur. J*. **7** 465 (2001)
61. A R Burilov, I R Knyazeva, M A Pudovik, V V Syakaev, Sh K Latypov, I Baier, V D Khabikher, A I Konovalov *Russ. Chem. Bull., Int. Ed*. **56** 364 (2007)
62. A R Burilov, N S Gazizov, N I Kharitonova, M A Pudovik, V D Khabikher, I Baier, A N Konovalov *Russ. Chem. Bull., Int. Ed*. **56** 330 (2007)
63. Z Muchlado-Poleska, E Luboch, J F Biernat *Synth. Commun*. **38** 3062 (2008)
64. A G M Barrett, D C Braddock, J P Henschke, E R Walker *J. Chem. Soc., Perkin Trans. 1* 873 (1999)
65. K E Peterson, R C Smith, R S Mohan *Tetrahedron Lett*. **44** 7723 (2003)
66. K Deleersnyder, H Mehdi, I T Horvath, K Binnemans, T N Parac-Vogt *Tetrahedron* **63** 9063 (2007)
67. T N Parac-Vogt, K Binnemans *Tetrahedron Lett*. **45** 3137 (2004)
68. T N Parac-Vogt, K Deleersnyder, K Binnemans *J. Alloys Compd*. **374** 46 (2004)
69. T N Parac-Vogt, S Pachini, P Nockemann, K Van Hecke, L Van Meervelt, K Binnemans *Eur. J. Org. Chem*. 4560 (2004)
70. T N Parac-Vogt, K Deleersnyder, K Binnemans *Eur. J. Org. Chem*. 1810 (2005)
71. M Hedidi, S M Hamidi, T Mazari, B Boutemeur, C Rabia, F Chemat, M Hamidi *Tetrahedron* **62** 5652 (2006)
72. C Yan, W Chen, J Chen, T Jiang, Y Yao *Tetrahedron* **63** 9614 (2007)
73. H Kudo, K Shigematsu, K Mitani, T Nishikubo, N C Kasuga, H Uekusa, Y Ohashi *Macromolecules* **41** 2030 (2008)
74. H Konishi, K Ohata, O Morikawa, K Kobayashi *J. Chem. Soc., Chem. Commun*. 309 (1995)
75. A G S Högberg *J. Am. Chem. Soc*. **102** 6046 (1980)
76. A G S Högberg *J. Org. Chem*. **45** 4498 (1980)
77. S Nummelin, D Falabu, A Shivanyuk, K Rissanen *Org. Lett*. **6** 2869 (2004)
78. D Volkmer, M Fricke, C Agena, J Mattay *CrystEngComm*. **4** 288 (2002)
79. V I Kalchenko, A V Solov'ov, N R Gladun, A N Shivanyuk, L I Atamas, V V Pirozhenko, L N Markovsky, J Lipkowski, Y A Simonov *Supramol. Chem*. **8** 269 (1997)
80. K J Palmer, R Y Wong, L Jurd, K Stevens *Acta Crystallogr., Sect. B* **32** 847 (1976)
81. A Ahman, M Luostarinen, C A Schalley, M Nissinen, K Rissanen *Eur. J. Org. Chem*. 2793 (2005)
82. X Liu, Y-J Liu, Q-F Zhang *Chin. J. Struct. Chem*. **24** 952 (2005)
83. T Gubaidullin, Y E Morozova, A R Mustafina, E Kh Kazakova, I A Litvinov, A I Konovalov *Mendeleev Commun*. 9 (1999)
84. N K Beyeh, J Aumanen, A Ahman, M Luostarinen, H Mansikkamaki, M Nissinen, J Korppi-Tommola, K Rissanen *New J. Chem*. **31** 370 (2007)
85. D Volkmer, M Fricke, C Agena, J Mattay *J. Mater. Chem*. **14** 2249 (2004)
86. C Schmidt, E F Paulus, V Bohmer, W Vogt *New J. Chem*. **24** 123 (2000)
87. W Iwanek *Pol. J. Chem*. **73** 1777 (1999)
88. D Eisler, W Hong, M C Jennings, R J Puddephatt *Organometallics* **21** 3955 (2002)
89. S Miao, R D Adams, D-S Guo, Q-F Zhang *J. Mol. Struct*. **659** 119 (2003)
90. R Becker, G Reck, R Radeglia, A Springer, B Schulz *J. Mol. Struct*. **784** 157 (2006)
91. J Han, Y H Cai, L Liu, C G Yan, Q Li *Tetrahedron* **63** 2275 (2007)
92. Yu E Morozova, A T Gubaidullin, E Kh Kazakova, A R Mustafina, V V Zotkina, I A Litvinov, A I Konovalov *Russ. J. Gen. Chem*. **71** 119 (2001)
93. D Falabu, A Shivanyuk, M Nissinen, K Rissanen *Org. Lett*. **4** 3019 (2002)
94. A Shivanyuk, T P Spaniol, K Rissanen, E Kolehmainen, V Bohmer *Angew. Chem., Int. Ed*. **39** 3497 (2000)
95. O D Fox, K Dalley, R G Harrison *J. Inclusion Phenom. Macrocycl. Chem*. **34** 403 (1999)
96. C Schmidt, T Straub, D Falabu, E F Paulus, E Wegelius, E Kolehmainen, V Bohmer, K Rissanen, W Vogt *Eur. J. Org. Chem*. 3937 (2000)

97. A T Gubaidullin, I L Nikolaeva, D N Kharitonov, I ALitvinov, N I Bashmakova, A R Burilov, M A Pudovik, A I Konovalov *Russ. J. Gen. Chem.* **72** 259 (2002)
98. D A Leigh, P Linnane, R G Pritchard, G Jackson *J. Chem. Soc., Chem. Commun.* 389 (1994)
99. A R Burilov, N I Bashmakova, I L Nikolaeva, M A Pudovik, V A Al'fonsov, A I Konovalov *Russ. J. Gen. Chem.* **71** 480 (2001)
100. E K Kazakova, N A Makarova, A U Ziganshina, L A Muslinkina, A A Muslinkina, W D Habicher *Tetrahedron Lett.* **41** 10111 (2000)
101. M Urbaniak, W Iwanek *Tetrahedron* **62** 1508 (2006)
102. H Konishi, H Yamaguchi, M Miyashiro, K Kobayashi, O Morikawa *Tetrahedron Lett.* **37** 8547 (1996)
103. Y K Agrawal, R N Patadia *Synth. Commun.* **36** 1083 (2006)
104. O Manabe, K Asakura, T Nishi, S Shinkai *Chem. Lett.* **19** 1219 (1990)
105. W Iwanek *Tetrahedron: Asymmetry* **9** 3171 (1998)
106. W Xu, J P Rourke, J J Vittal, R J Puddephatt *Inorg. Chem.* **34** 323 (1995)
107. V K Jain, P H Kanaiya, N Bhojak *Fib. Polym.* **9** 720 (2008)
108. V K Jain, S G Pallia, P H Kanaiya *E.-J. Chem.* **5** 1037 (2008)
109. V K Jain, P H Kanaiya *J. Inclusion Phenom. Macrocycl. Chem.* **62** 111 (2008)
110. J Han, C Yan *J. Inclusion Phenom. Macrocycl. Chem.* **61** 119 (2008)
111. J Jeerupan, T Ogoshi, S Hiramitsu, K Umeda, T Nemoto, G-i Konishi, T-a Yamagishi, Y Nakamoto *Polym. Bull.* **59** 731 (2008)
112. S Strandman, H Tenhu *Polymer* **48** 3938 (2007)
113. C Kantar, E Agar, S Sasmaz *Dyes Pigm.* **77** 487 (2008)
114. A K Hassan, C Goy, A V Nabok *Thin Solid Films* **516** 9006 (2008)
115. M Courtney, J O'Farrell, C Matthew, J M Collins, C F Dignam, T J Wenzel *J. Org. Chem.* **73** 2843 (2008)
116. M Urbaniak, J Mattay, W Iwanek *Synth. Commun.* **38** 4345 (2008)
117. B Botta, M Pierini, G Delle Monache, D Subissati, F Subrizi, G Zappia *Synthesis* **13** 2110 (2008)
118. S Shimizu, T Kiuchi, N A Pan *Angew. Chem., Int. Ed.* **46** 6442 (2007)
119. S M Grayson, J M J Fréchet *Chem. Rev.* **101** 3819 (2001)
120. A M Caminade, J-P Majoral *Acc. Chem. Res.* **37** 341 (2004)
121. E R Gillies, J M J Fréchet *Drug Discov. Today* **10** 35 (2005)
122. A Gareía Márquez, M Gutiérrez Nava, J G Domínguez Chavez, E Klimova, T Klimova, M Martínez-Garcia *Fullerenes, Nanotubes, Carbon Nanostruct.* **14** 357 (2006)
123. J G Domínguez Chavez, M Gutiérrez Nava, J Flores Maturano, T Klimova, E Klimova, M Martínez-Garcia *J. Nanosci. Nanotechnol.* **7** 1377 (2007)
124. I V Lijanova, T K Berestneva, M M García *Supramol. Chem.* **19** 655 (2007)
125. I V Lijanova, I Moggio, E Arias, R Vazquez-Garcia, M Martínez-Garcia *J. Nanosci. Nanotechnol.* **7** 3607 (2007)
126. I V Lijanova, I Moggio, E Arias, T Klimova, M Martínez-Garcia *Tetrahedron* **64** 10258 (2008)
127. M I Reyes-Valderrama, R A Vázquez Garcia, T Klimova, E Klimova, L Ortiz-Frade, M Martínez-Garcia *Inorg. Chim. Acta* **361** 1597 (2008)
128. I V Lijanova, M I Reyes-Valderrama, J-L Maldonado, G Ramos-Ortiz, K Tatiana, T Klimova, M Martínez-Garcia *Tetrahedron* **64** 4460 (2008)
129. H Jun, G Yun, C Yan *Chem. Res. Chin. Univ.* **22** 537 (2006)
130. Y Yamakawa, M Ueda, R Nagahata, K Takeuchi, M Asai *J. Chem. Soc., Perkin Trans. 1* 4135 (1998)
131. K Fairfull-Simth, P M J Redon, J W Haycock, N H Williams *Tetrahedron Lett.* **48** 1317 (2007)
132. M J McIldowie, M Mocerino, M I Ogden, B W Skelton *Tetrahedron* **63** 10817 (2007)
133. G Arnott, R Hunter, H Su *Tetrahedron* **62** 977 (2006)
134. G Arnott, R Hunter *Tetrahedron* **62** 992 (2006)
135. O Lukin, A Shivanyuk, V V Pirozhenko, I F Tsymbal, V I Kalchenko *J. Org. Chem.* **63** 9510 (1998)
136. M Luostarinen, A Shivanyuk, K Rissanen *Org. Lett.* **3** 4141 (2001)
137. M Loustarinen, M Nissinen, M Nieger, A Shivanyuk, K Rissanen *Tetrahedron* **63** 1254 (2007)
138. A Shivanyuk *Chem. Commun.* 1472 (2001)
139. A Shivanyuk, A R Far, J Rebek Jr *Org. Lett.* **4** 1555 (2002)
140. K Salorinne, M Nissinen *Org. Lett.* **8** 5473 (2006)
141. K Salorinne, M Nissinen *Tetrahedron* **64** 1798 (2008)
142. K Salorinne, M Nissinen *CrystEngComm.* **11** 1572 (2009)
143. I Higler, H Boerrigter, W Verboom, H Kooijman, A L Spek, D N Reinhoudt *Eur. J. Org. Chem.* 1597 (1998)
144. A Kang, S K Kim, K Nakamura, J H Park, Y J Yoon, K D Lee, J Yoon *Tetrahedron Lett.* **46** 245 (2005)
145. J D Lamb, C A Morris, J N West, K T Morris, R G Harrison *J. Membr. Sci.* **321** 15 (2008)
146. Y Cai, P P Castro, L M G Tunstad *Tetrahedron Lett.* **49** 2146 (2008)
147. M M Conn, J Rebek Jr *Chem. Rev.* **97** 1647 (1997)
148. A Lledo, P Restorp, J Rebek Jr *J. Am. Chem. Soc.* **131** 2440 (2009)
149. S Xiao, D Ajami, J Rebek Jr *Org. Lett.* **11** 3163 (2009)
150. C Naumann, B O Patrick, J C Sherman *Tetrahedron* **58** 787 (2002)
151. S N Parulekar, K Muppalla, F R Fronczek, K S Bisht *Chem. Commun.* 4901 (2007)
152. R Wu, T F Al-Azemiz, K S Bisht *Chem. Commun.* 1822 (2009)
153. K Srinivasan, B C Gibb *Org. Lett.* **9** 745 (2007)
154. C Aakeröy, N Schultheiss, J Desper *CrystEngComm.* **9** 211 (2007)
155. E Menozzi, M Busi, C Massera, F Ugozzoli, D Zuccaccia, A Macchioni, E Dalcanale *J. Org. Chem.* **71** 2617 (2006)
156. L Pirondini, D Bonifazi, B Cantadori, P Braiuca, M Campagnolo, R D Zorzi, S Geremia, F Diederichd, E Dalcanale *Tetrahedron* **62** 2008 (2006)
157. R Balasubramanian, Y G Kwon, A Wei *J. Mater. Chem.* **17** 105 (2007)
158. H E Moll, D Sémeril, D Matt, M T Youinou, L Toupet *Org. Biomol. Chem.* **7** 495 (2009)
159. A Shivanyuk, J Rebek Jr *Chem. Commun.* 2424 (2001)
160. L R MacGillivray, P R Diamente, J L Reid, J A Ripmeester *Chem. Commun.* 359 (2000)
161. A Shivanyuk *Tetrahedron* **61** 349 (2005)
162. A Shivanyuk *J. Am. Chem. Soc.* **129** 14196 (2007)
163. E Bosch *CrystEngComm.* **9** 191 (2007)
164. C L Barnes, E Bosch *J. Chem. Crystallogr.* **37** 783 (2007)
165. J M Matheny, E Bosch, C L Barnes *Cryst. Growth Des.* **7** 984 (2007)
166. S J Park, K Yamaguchi, J I Hong *Bull. Korean Chem. Soc.* **29** 205 (2008)
167. O Morikawa, S Matsubara, S Fukuda, K Kawakami, K Kobayashi, H Konishi *Tetrahedron Lett.* **48** 7489 (2007)
168. B Schnatwinkel, I Stoll, A Mix, M V Rekharsky, V V Borovkov, Y Inoue, J Mattay *Chem. Commun.* 3873 (2008)
169. C Schafer, F Strube, S Bringmann, J Mattay *Photochem. Photobiol. Sci.* **7** 1457 (2008)
170. Y S Park, K Paek *Org. Lett.* **10** 4867 (2008)
171. C B Aakero1y, N Schultheiss, J Desper *Org. Lett.* **8** 2607 (2006)
172. M N Hansen, L-S Chang, A Wei *Supramol. Chem.* **20** 35 (2008)
173. A Ahman, M Luostarinen, K Rissanen, M Nissinen *New J. Chem.* **31** 169 (2007)
174. L Avram, Y Cohen *Org. Lett.* **10** 1505 (2008)

175. S Busi, H Saxell, R Fröhlichd, K Rissanen *CrystEngComm*. **10** 1803 (2008)
176. A Shivanyuk, E F Paulus, K Rissanen, E Kolehmainen, V Bohmer *Chem. – Eur. J.* **7** 1944 (2001)
177. L R MacGillivrayand, J L Atwood *Nature (London)* **389** 469 (1997)
178. G W V Cave, J Antesberger, L J Barbour, R M McKinly, J L Atwood *Angew. Chem., Int. Ed.* **43** 5263 (2004)
179. R M McKinlay, P K Thallapally, J L Atwood *Chem. Commun*. 2956 (2006)
180. S J Dalgarno, N P Power, J Antesberger, R M McKinlay, J L Atwood *Chem. Commun*. 3803 (2006)
181. N P Power, S J Dalgarno, J L Atwood *New J. Chem*. **31** 17 (2007)
182. S J Dalgarno, N P Power, J L Atwood *Chem. Commun*. 3447 (2007)
183. E S Barrett, T J Dale, J Rebek Jr *J. Am. Chem. Soc*. **129** 3818 (2007)
184. E S Barrett, T J Dale, J Rebek Jr *Chem. Commun*. 4224 (2007)
185. E S Barrett, T J Dale, J Rebek Jr *J. Am. Chem. Soc*. **130** 2344 (2008)
186. J Rebek Jr *Acc. Chem. Res*. **42** 1660 (2009)
187. Y Cohen, T Evan-Salem, L Avram *Supramol. Chem*. **20** 71 (2008)
188. A A Turshatov, N B Melnikova, Yu D Semchikov, I S Ryzhkina, T N Pashirova, D Mobius, S Yu Zaitsev *Colloids Surf., A* **240** 101 (2004)
189. J D Faull, V K Gupta *Thin Solid Films* **440** 129 (2003)
190. J P Santos, M E D Zaniquelli, P J Dutton *Colloids Surf., A* **198** 605 (2002)
191. Y Hayashi, S Suzuki, K Ichimura *J. Mater. Chem*. **11** 1805 (2001)
192. A V Nabok, A K Hassan, A K Ray *J. Mater. Chem*. **10** 189 (2000)
193. N B Mel'nikova, E Kh Kazakova, I V Guljaev, A A Volkov, M S Gusikhina, L Ya Zakharova, M A Voronin, N A Makarova, L A Muslinkina, A I Konovalov *Supramol. Chem*. **21** 532 (2009)
194. S-K Oh, M Nakagawa, K Ichimura *J. Mater. Chem*. **11** 1563 (2001)
195. M Weis, R Janicek, J Cirak, T Kianik *J. Phys. Chem. B* **111** 10626 (2007)
196. M W Sugden, T H Richardson, F Davis, S P J Higson, C F J Faul *Colloids Surf., A* **321** 43 (2008)
197. E K Kazakova, J E Morozova, A V Prosvirkin, A Z Pich, E P Gubanov, A A Muslinkin, W D Habicher, A I Konovalov *Eur. J. Org. Chem*. **15** 3323 (2004)
198. W Saenger, C Betzel, B Hingerty, G M Brown *Angew. Chem., Int. Ed. Engl*. **22** 883 (1983)
199. H-J Schneider, D Güttes, U Schneider *Angew. Chem., Int. Ed. Engl*. **25** 647 (1986)
200. H-J Schneider, R Kramer, S Simova, U Schneider *J. Am. Chem. Soc*. **110** 6442 (1988)
201. V K Jain, S G Pillai, H S Gupte *J. Iran. Chem. Soc*. **5** 646 (2008)
202. V K Jain, S G Pillai, R A Pandya, Y K Agrawal, P S Shrivastav *Anal. Sci*. **21** 129 (2005)
203. V K Jain, S G Pillai, R A Pandya, Y K Agrawal, P S Shrivastav *Talanta* **2** 466 (2005)
204. V K Jain, S G Pillai, H C Mandalia *J. Chil. Chem. Soc*. **52** 1177 (2007)
205. V K Jain, S G Pillai, P H Kanaiya *J. Braz. Chem. Soc*. **17** 1316 (2006)
206. S N Podyachev, N E Burmakina, V V Syakaev, S N Sudakova, R R Shagidullin, A I Konovalov *Tetrahedron* **65** 408 (2009)
207. S N Podyachev, V V Syakaev, S N Sudakova, R R Shagidullin, D V Osyanina, L V Awakumova, B I Buzykin, S K Latypov, I Bauer, W D Habicher, A I Konovalov *J. Inclusion Phenom. Macrocycl. Chem*. **58** 55 (2007)
208. L S Kuznetsova, G A Pribylova, A R Mustafina, I G Tansnaev, B F Myasoedov, A I Konovalov *Radiochemistry* **46** 277 (2004)
209. B Bibal, J P Declercq, J P Dutasta, B Tinantb, A G Valadea *Tetrahedron* **59** 5849 (2003)
210. A R Mustafina, I Ya Zagidullina, V I Maslennikova, O S Serkova, T V Guzeeva, A I Konovalov *Russ. Chem. Bull., Int. Ed*. **56** 313 (2007)
211. B Botta, G Delle Monache, P Ricciardi, G Zappia, C Seri, E Gacs-Baitz, P Csokasi, D Misiti *Eur. J. Org. Chem*. 841 (2000)
212. B Botta, G Delle Monache, G Zappia, D Misiti, M C Baratto, R Pogni, E Gacs-Baitz, M Botta, F Corelli, F Manetti, A Tafi *J. Org. Chem*. **67** 1178 (2002)
213. S Kunsagi, L Nagy, G Nagy, I Bitter, L Kollar *J. Phys. Chem. B* **107** 4727 (2003)
214. O D Fox, N K Dalley, R G Harrison *Inorg. Chem*. **39** 620 (2000)
215. A Ahman, M Nissinen *Chem. Commun*. 1209 (2006)
216. A F Danil de Namor, J K Chaaban, O E Piro, E E Castellano *J. Phys. Chem. B* **110** 2442 (2006)
217. A F Danil de Namor, J K Chaaban *J. Phys. Chem. B* **112** 2070 (2008)
218. G N Al'tshuler, L A Sapozhnikova, E V Ostapova, O G Al'tshuler *Russ. J. Phys. Chem., Ser. A* **81** 1011 (2007)
219. D J Eisler, R J Puddephatt *Inorg. Chem*. **45** 7295 (2006)
220. Yu I Sal'nikov, G A Boos, I S Ryzhkina, L I Vaganov, M I Vishnev *Russ. J. Gen. Chem*. **78** 1553 (2008)
221. Y Aoyama, Y Tanaka, H Toi, H Ogoshi *J. Am. Chem. Soc*. **111** 634 (1988)
222. Y Aoyama, Y Tanaka, S Sugahara *J. Am. Chem. Soc*. **111** 5397 (1989)
223. K Kobayashi, Y Asakawa, Y Kikuchi, H Toi, Y Aoyama *J. Am. Chem. Soc*. **115** 2648 (1993)
224. Y Aoyama, R Yanagihara, T Fujimoto *Yuki Gosei Kagaku Kyokaishi (J. Synt. Org. Chem.)* **52** 572 (1994)
225. R Yanagihara, Y Aoyama *Tetrahedron Lett*. **35** 9725 (1994)
226. T Fujimoto, C Shimizu, O Hayashida, Y Aoyama *Gazz. Chim. Ital*. **127** 749 (1997)
227. T Fujimoto, C Shimizu, O Hayashida, Y Aoyama *J. Am. Chem. Soc*. **119** 6676 (1997)
228. T Fujimoto, C Shimizu, O Hayashida, Y Aoyama *J. Am. Chem. Soc*. **120** 601 (1998)
229. O Hayashida, M Kato, K Akagi, Y Aoyama *J. Am. Chem. Soc*. **121** 11597 (1999)
230. W Iwanek, R Frohlich *Pol. J. Chem*. **72** 2342 (1998)
231. W Iwanek, R Frohlich, M Urbaniak, C Näther, J Mattay *Tetrahedron* **54** 14031 (1998)
232. E K Kazakova, N A Makarova, A I Rakhmatullin, L A Muslinkina, A A Muslinkina *J. Inclusion Phenom. Macrocycl. Chem*. **36** 153 (2000)
233. T Borowiak, M Maczynski, M Pietraszkiewicz, O Pietraszkiewicz *J. Inclusion Phenom. Macrocycl. Chem*. **35** 131 (1999)
234. M Kubinyi, J Brátán, A Grofcsik, L Biczók, B Poór, I Bitter, A Grün, B Bogáti, K Tóth *J. Chem. Soc., Perkin Trans. 2* 1784 (2002)
235. E Utzig, O Pietraszkiewicz, M Pietraszkiewicz *J. Therm. Anal. Calorim*. **78** 973 (2004)
236. O Morikawa, H Yamaguchi, Y Katsube, K Abe, K Kobayashi, H Konishi *Phosphorus, Sulfur, Silicon Relat. Elem*. **181** 2877 (2006)
237. M Lepakshaiah, T N G Row *J. Mol. Struct*. **918** 10 (2009)
238. M Lepakshaiah, P P Das, T N G Row *J. Chem. Sci*. **120** 39 (2008)
239. A Y Ziganshina, S V Kharlamov, E Kh Kazakova, S K Latypov, A I Konovalov *Mendeleev Commun*. **17** 145 (2007)

240. E Kh Kazakova, V V Syakaev, J E Morozova, N A Makarova, L A Muslinkina, G A Evtugyn, A I Konovalov *J. Inclusion Phenom. Macrocycl. Chem.* **59** 143 (2007)
241. A K Hassan, A V Nabok, A K Ray, F Davis, C J M Stirling *Thin Solid Films* **327**–**329** 686(1998)
242. A K Hassan, A K Ray, A V Nabok, F Davis *Sens. Actuators, B* **77** (3) 638 (2001)
243. M R Caira, T Le Roex, L R Nassimbeni *CrystEngComm.* **8** 275 (2006)
244. O D Fox, J Cookson, E J S Wilkinson, M G B Drew, E J MacLean, S J Teat, P D Beer *J. Am. Chem. Soc.* **128** 6990 (2006)
245. S S Zhu, H Staats, K Brandhorst, J Grunenberg, F Gruppi, E Dalcanale, A Luetzen, K Rissanen, C A Schalley *Angew. Chem., Int. Ed.* **47** 788 (2008)
246. T Gottschalk, P D Jarowski, F Diederich *Tetrahedron* **64** 8307 (2008)
247. A Lledo, R J Hooley, J Rebek Jr *Org. Lett.* **10** 3669 (2008)
248. A R Mustafina, L Ya Zakharova, J G Elistratova, M A Voronin, V V Syakaev, A I Konovalov *J. Colloid Interface Sci.* **333** 613 (2009)
249. V V Syakaev, A R Mustafina, J G Elistratova, S K Latypov, A I Konovalov *Supramol. Chem.* **20** 453 (2008)
250. I A Koshets, Z I Kazantseva, A E Belyaev, V I Kalchenko *Sens. Actuators, B* **140** 104 (2009)
251. K Touaj, N Tbeur, M Hor, J-F Verchère, M Hlaïbi *J. Membr. Sci.* **337** 28 (2009)
252. E Biavardi, M Favazza, A Motta, I L Fragalà, C Massera, L Prodi, M Montalti, M Melegari, G G Condorelli, E Dalcanale *J. Am. Chem. Soc.* **131** 7447 (2009)
253. N Demirel, M Merdivan, N Piringcioglu, C Hamamci *Anal. Chim. Acta* **485** 213 (2003)
254. C Gok, S Seyhan, M Merdivan, M Yurdakoc *Microchim. Acta* **157** 13 (2007)
255. K M C Faizal, Y Kikuchic, T Kobayashi *J. Membr. Sci.* **334** 110 (2009)
256. N Benosmane, S M Hamdi, M Hamdi, B Boutemeura *Sep. Purif. Technol.* **65** 211(2009)
257. Yu E Morozova, Ya V Shalaeva, N A Makarova, V V Syakaev, E Kh Kazakova, A I Konovalov *Colloid J.* **71** 380 (2009)
258. E Dalcanale, A Du Vosel, A-M Levelut, J Malthere *Liq. Cryst.* **10** 185 (1991)
259. G Cometti, E Dalcanale, A Du Vosel, A-M Levelut *J. Chem. Soc., Chem. Commun.* 163 (1990)
260. L Abis, V Arrighi, G Cometti, E Dalcanale, A Du Vosel *Liq. Cryst.* **9** 277 (1991)
261. S Bonsignore, G Cometti, E Dalcanale, A Du Vosel *Liq. Cryst.* **8** 639 (1990)
262. G Cometti, E Dalcanale, A Du Vosel, A-M Levelut *Liq. Cryst.* **11** 93 (1992)
263. K Yonetake, T Takahashi *Sci. Technol. Adv. Mater.* **7** 332 (2006)
264. K Yonetake, T Nakayamaa, M Ueda *J. Mater. Chem.* **11** 761 (2001)
265. Y Matsuzawa, T Seki, K Ichimura *J. Inclusion Phenom. Macrocycl. Chem.* **35** 199 (1999)
266. M Inouye, K Hashimoto, K Isagawa *J. Am. Chem. Soc.* **116** 5517 (1994)
267. Y Hayashi, K Ichimura *J. Photochem. Photobiol. A* **149** 199 (2002)
268. M A Sarmentero, P Ballester *Org. Biomol. Chem.* **5** 3046 (2007)
269. M A Sarmentero, P Ballester *Org. Lett.* **8** 3477 (2006)
270. O Hayashida, M Uchiyama *J. Org. Chem.* **72** 610 (2007)
271. O Hayashida, N Ogawa, M Uchiyama *J. Am. Chem. Soc.* **129** 13698 (2007)
272. O Hayashida, M Uchiyama *Org. Biomol. Chem.* **6** 3166 (2008)
273. Sh Pandey, M Ali, A Bishnoi, A Azam, S Pandey, H M Chawla *J. Fluorescence* **18** 533 (2008)
274. S J Dalgarno, G W V Cave, J L Atwood *Angew. Chem., Int. Ed.* **45** 570 (2006)
275. T K Misra, C-Y Liu *J. Colloid Interface Sci.* **310** 178 (2007)
276. S Ehrler, U Pieles, A Wirth-Heler, P Shahgaldian *Chem. Commun.* 2605 (2007)
277. E Wirtheim, L Avram, Y Cohen *Tetrahedron* **65** 7268 (2009)
278. M Shen, Y Sun, Y Han, R Yao, C Yan *Langmuir* **24** 13164 (2008)
279. F Davis, C F J Faulb, S P J Higsona *Soft Matter* **5** 2746 (2009)
280. O Hayashida, K Mizuki, K Akagi, A Matsuo, T Kanamori, T Nakai, S Sando, Y Aoyama *J. Am. Chem. Soc.* **125** 594 (2003)
281. Y Aoyama *Chem.–Eur. J.* **10** 588 (2004)
282. L Ya Zakharova, F G Valeeva, A R Ibragimova, M A Voronin, L A Kudryavtseva, V V Syakaev, E Kh Kazakova, Yu E Morozova, N A Makarova, N B Mel'nikova, O B Zemnyakova, A I Konovalov *Russ. Chem. Bull., Int. Ed.* **57** 374 (2008)
283. L Ya Zakharova, V V Syakaev, M A Voronin, F G Valeeva, A R Ibragimova, Y R Ablakova, E Kh Kazakova, S K Latypov, A I Konovalov *J. Phys. Chem. C* **113** 6182 (2009)
284. T N Pasharova, S S Lukashenko, E M Kosacheva, L Z Rizvanova, G A Gainanova, I R Knyazeva, A R Burilov, L A Kudryavtseva, A I Konovalov *Russ. Chem. Bull., Int. Ed.* **56** 959 (2007)
285. T N Pashirova, S S Lukashenko, E M Kosacheva, M V Leonova, L I Vaganova, A R Burilov, M A Pudovik, L A Kudryavtseva, A I Konovalov *Russ. J. Gen. Chem.* **78** 402 (2008)
286. S Shirakawa, S Shimizu *Synlett* **10** 1539 (2008)
287. T Sokolieβ, U Menyes, U Roth, T Jira *J. Chromatogr., A* **948** 309 (2002)
288. L Husaru, R Schulze, G Steiner, T Wolff, W D Habicher, R Salzer *Anal. Bioanal. Chem.* **382** 1882 (2005)
289. A Wzorek, J Mattay, W Iwanek *Tetrahedron: Asymmetry* **18** 815 (2007)
290. D Bratton, R Ayothi, H Deng, H B Cao, C K Ober *Chem. Mater.* **19** 3780 (2007)
291. H Ito, T Nakayama, M Sherwood, D Miller, M Ueda *Chem. Mater.* **20** 341 (2008)
292. A De Silva, L K Sundberg, H Ito, R Sooriyakumaran, R D Allen, C K Ober *Chem. Mater.* **20** 7292 (2008)
293. J K Lee, M Chatzichristidi, A A Zakhidov, P G Taylor, J A DeFranco, H S Hwang, H H Fong, A B Holmes, G G Malliaras, C K Ober *J. Am. Chem. Soc.* **130** 11564 (2008)
294. K Kurzatkowska, H Radecka, W Dehaen, M Wasowicz, I Grzybowska, J Radecki *Combin. Chem. High Throughput Screen.* **10** 604 (2007)
295. A I Vovk, A M Shivanyuk, R V Bugas, O V Muzychka, A K Melnyk *Bioorg. Med. Chem. Lett.* **19** 1314 (2009)
296. O Haba, K Haga, M Ueda, O Morikawa, H Konishi *Chem. Mater.* **11** 427 (1999)