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Wide-rim and outer-face functionalizations of calix[4]arene

Pierre D. Harvey *

Département de Chimie, Université de Sherbrooke, Sherbrooke, P.Q. Canada J1K 2R1

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Contents

Abstract

This review article focuses on calix[4]arene compounds in their cone conformation which exhibit organic functional groups, particularly those which are either potential soft or hard donors and halides, or organometallic-containing fragments, either at the win-rim or outer-face. This survey is presented from a structural point of view, and also includes systems involving loops and covalently bonded dimers. The attachment of various groups at these two types of sites occur mainly with carbon, nitrogen, sulfur, phosphorus, bromine, iodine, and metal atoms.

Keywords: Calix[4]arene compounds; Cone conformation; Wide-rim and outer-face functionalizations

1. Introduction

Calix[4]arene belongs to a larger family of calix[*n*]arene molecules that is relatively old, and is generated from the chemical condensation of formaldehyde and phenol [1–5]. Calix[4]arene may exist with four different known conformations called cone, partial-cone, 1,2-alternate, and 1,3-alternate. These conformations refer to the relative orientation of the phenolate fragments with each other, which in some situations, may involve dynamic interconversions in solution. When all four oxygen atoms point in the same direction the macrocycle exhibits a bowl-shape structure, and in this specific case the functionalization at various positions on the ca-

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Abbreviations: Me, methyl; Et, ethyl; Pr, propyl; Bu, butyl; Cy, cyclohexyl; calix[4]arene, pentacyclo[$19.3.1.1^{3,7}.1^{9,13}.1^{15,19}$]octacosa-1(25),3,5,7(28),9,11-13(27),15,17,19(26),21,23-dodecaene-25,26,27,28-tetraol.

* Corresponding author
E-mail address: pharvey@courrier.usherb.ca (P.D. Harvey).

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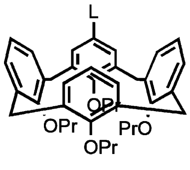
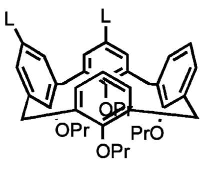
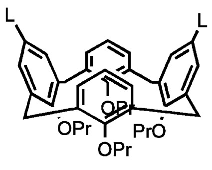
lix[4]arene is referred to as wide-rim (previously called upper-rim), narrow-rim (previously called lower-rim) and outer-face. In the unfunctionalized case, the narrow-rim is composed of four hydroxyl groups forming a very stable cyclic H-bond network, keeping the bowl-shape structure. The hydroxyl groups can be functionalized either by organic groups such as alkyls or esters, or inorganic fragments for instance. The wide-rim is located above the four aromatic rings. These aromatic rings are unsubstituted phenyl groups linked by *ortho*-methylene residues, providing a hydrophobic cavity. The outer-face region is located around the calix[4]arene four benzene rings, and their functionalization generally occurs via the formation of π-complexes with transition metals. In order to favor the cone conformation, various chemical functionalizations are employed. As mentioned above, leaving the H-bonding network provided by the four hydroxyl functions, is one way to achieve this. The narrow-rim functionalization with large alkyl groups such as *n*- and *i*-propyl and larger alkyl residues, or with the coordination of the phenolate centers with one or more metal atoms, also serves the same purpose. Finally, the molecular construction of loops, either at the lower- or wide-rims, can also favor this bowl-shape structure.



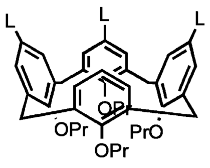
mono-



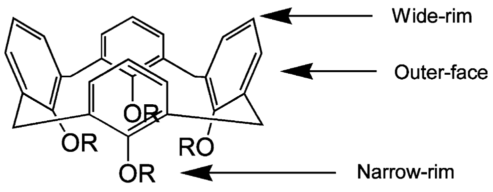
1,2-di-



1,3-di-



tri-

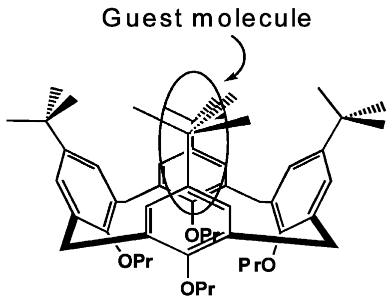


Cone conformation

In 1972 Gutsche reintroduced this molecule to modern chemistry, and this field has been received enthusiastically by research groups around the world in recent years. This great interest is primarily motivated by the ionophoric property of the narrow-rim which leads to applications in the area of cation binding and transport, as well as highly selective receptors and novel sensors for polyanionic species [3–7]. This polyfunctional property stems from the fact that the narrow-rim is relatively easy to chemically modify via well-established acid–base and nucleophilic reactions [8]. On the other hand, examples of outer-face and wide-rim modified calix[4]arenes are drastically more limited. These examples include functional groups such as –SO_3^-, –NO_2, –NH_2, –N=NR, and –PPh_2, among others [9–19], at the wide-rim, and in much rarer cases, organometallic-containing fragments on the outer-face (see sections below). Even more striking, these wide-rim modified derivatives are for the most part di-1,3- and tetrasubstituted species. In brief, the chemistry of the wide-rim has not been fully exploited until now, and this can be explained by the relatively more difficult chemistry involved in its functionalization. Numerous examples of wide-rim modified calix[4]arene compounds are already known, and represent a very rich opportunity for coordination chemistry with transition and non-transition metals via both soft and hard donors. Similarly, the rare examples of outer-face derivatized calix[4]arenes illustrate a possible exploitation of benzene ring perturbation, either via steric interactions, or via electronic back bonding effects.

A careful examination of the literature reveals an important observation of the structural properties of the calix[4]arene molecule, and concerns the molecular structure, either as an wide-rim tetra-functionalized or unsubstituted calix[4]arene. There is a significant series of examples found in the Cambridge Data Bank in which small molecules such as H_2O, CH_2Cl_2, and $CHCl_3$, as well as larger organics such as toluene, acetone, and various alkanes, are found located inside the cavity [20–29]. Many more examples are seen for unmetallated tetra-*t*-butyl calix[4]arene systems for which the cavity size is extended (see **1**). One idea that comes to mind is what novel chemistry could be achieved if these wide-rim substituents were organometallic fragments. Supramolecular associations, here called host–guest chemistry, would automatically favor strong metal–organic contacts, leading the way to new applications, or better performance in metal–substrate reactivity.

This article is timely since the latest and more general review was published by Matt et al. [8] in this journal a few years ago. However, an impressive number of new examples for wide-rim and outer-face functionalized calix[4]arene molecules has appeared in the literature since this review. These numerous and new research



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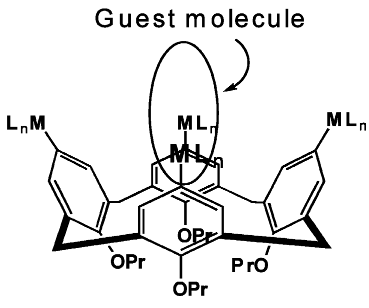

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papers establish that the field is evolving rapidly, and novel applications, notably in the field of supramolecular and organometallic chemistry, are appearing rapidly. The synthetic aspects for these molecules, although interesting, are not described in this work. Such a lengthy review would describe an important component of organic chemistry of the calix[4]arene derivatives, and would be outside the scope of this journal. One the other hand, a description of the actual library of calix[4]arene molecules, either viewed as potential ligands or precursors, or as coordination or organometallic compounds, is more appropriate at this time.

2. Review

This section is separated into four sub-sections describing the various functionalization patterns according to the resulting molecular or supramolecular architectures, including mono- and poly-substituted derivatives, loop structures, covalently bonded dimers and complex systems. However, examples of wide-rim substituted compounds using trivial saturated alkanes such as –H, –Me, –Et, –*i*-Pr, –*t*-Bu, –Cy, –CMe$_2$Et, and longer normal-alkyl groups, are not included in this review, but donor-containing functions are listed since they can act either as ligands, or precursors to ligands. One last sub-section describes examples of calix[4]arene compounds complexed with organometallic fragments on the benzenic residues (outer-face).

2.1. Mono-, di- and tetra-functionalization in the wide-rim

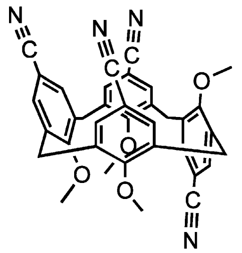
The functionalization of the calix[4]arene wide-rim may occur either at the *para*- or *meta*-positions of the phenolic residues. However, the literature reveals that the *para*-position derivatization dominates this class of molecules, as this position is readily activated by the presence of the oxygen atom in the narrow-rim. Commonly, these functionalizations occur with the connection of the benzene ring to the functional groups via a carbon, a nitrogen, a sulfur, and a phosphorus atom. Although not fully exploited in the field of coordination chemistry, many of these functional groups are also known to be soft or hard Lewis bases. These groups includes phenyls, olefins, isocyanides, phosphines, phosphine oxides, sulfides, cyanides, pyridines, carboxylates, amines, sulfates, esters, and ketones, for examples. These are now described as a function of the atom type connected to the benzene rings, excluding the organometallic-containing fragments. The latter are addressed separately.

2.1.1. Functionalization via a carbon atom

The linking carbon-containing fragments are cyanide, methylene, alkene, ketone, and phenyl residues based on the literature. The cyanide group is the simplest C-containing fragment, and it is a potential ligand for transition metals, as exemplified with the Ag(PF$_6$) salt discussed in a section below. Only the tetracyanide derivatives have been prepared so far using different narrow-rim groups which include –Me [30] (**3**, partial cone), –CH$_2$CH$_2$OMe [31] (**4**, 1,3-alternate) and –CH$_2$Ph [32] (**5**, cone). In all cases the molecules exhibit a flattened-bowl structure.

There are also some examples of CH$_2$-linked functionalized calix[4]arenes as described by Reinhoudt et al. [33]. In this series one can find the mono- [34] (**6**, 1,3-alternate), di-1,3- [35] (**7**, cone) and tetrasubstituted species [36] (**8**, cone) of 2-propene-calix[4]arenes. Compound **6** exists as a 1,3-alternate conformation because of the smaller OMe residues in the narrow-rim.

Compound **7** exhibits an auto-assembly where the 2-propene groups penetrate the cavity of a neighboring molecules in the solid state to form dimers. As a consequence the bowl structure is not flattened. Compound **8** acts as a koiland (double-acceptor) which auto-assembles in the solid state with *para*-xylene as a double-receptor to form a koilate (i.e. ...**8**-*para*-xylene-**8**-*para*-xylene–...).



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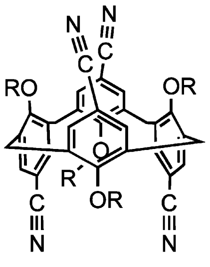

R = CH_2CH_2OMe

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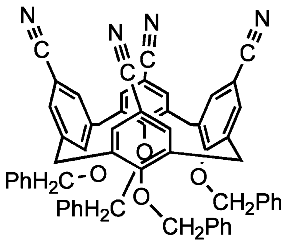

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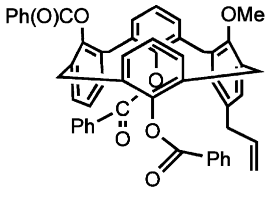

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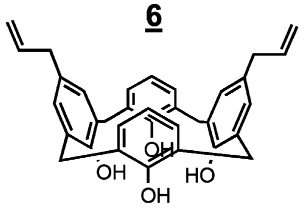

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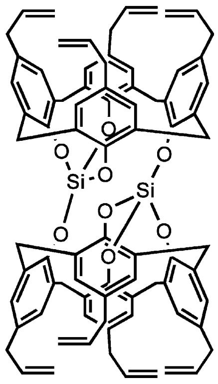
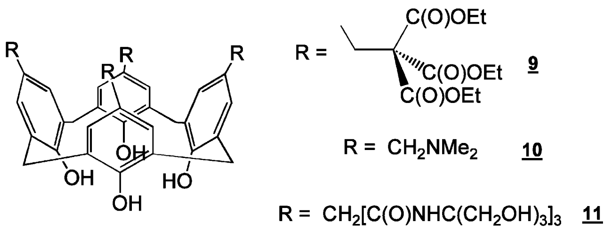
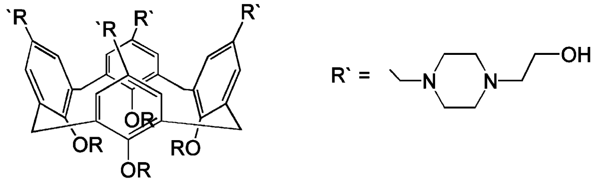


8

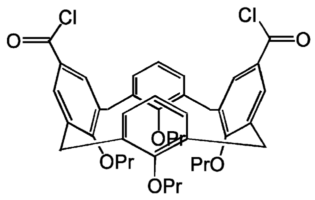
Such chemistry also gave rise to other molecular devices with exotic names such Silvanols [37] and Venus Flytrap [38]. Indeed using $-C(CO_2Et)_3$, the tetrasubstituted compound **9** groups adopts a cone conformation based upon X-ray data, despite the presence of Me residues in the narrow-rim [37]. Such a molecule possesses a water-solubilizing arborol surface on the wide-rim. In this same work, other functions were also introduced such as $-CH_2NMe_2$ (**10**) and $-CH_2[C(O)NHC(CH_2OH)_3]_3$ (**11**). In an attempt to build a deeper cavity, the incorporation of methylated 1-(2-hydroxyethyl)-piperazine substituents (compounds **12a**,**b**) was made, and subsequently the molecular devices were able to open and close in the absence or the presence of a guest molecule, respectively, similar to a Venus Flytrap. Other functional groups of this type such as $-CH_2PR_3$, $CH_2P(OR)_3$ and other $-R-PR'_2$ (R = alkyls, aryls) related groups are known, and these are discussed below with the P-containing fragments (Section 2.1.4).





12a,b (R = H; Me)

A large series of $-C(O)R$ substituted species has also been reported. The simplest one is the formyl functional group, which has been used to prepare the mono- (**13**), di-1,3- (**14**) and tetraformyl compounds (**15**) of tetrapropoxycalix[4]arene [39,40] (structures not shown). The ^{1}H-NMR data indicate that these adopt the cone conformation. Similarly, the corresponding di-1,3-acid chloride (**16**), -carboxylic acid (**17**), and -ethyl ester (**18**) derivatives have also been investigated [40–42]. Both the ^{1}H-NMR and X-ray data also confirm the cone conformation.



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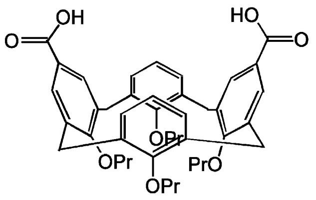

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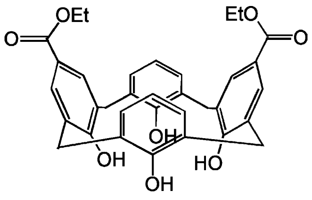

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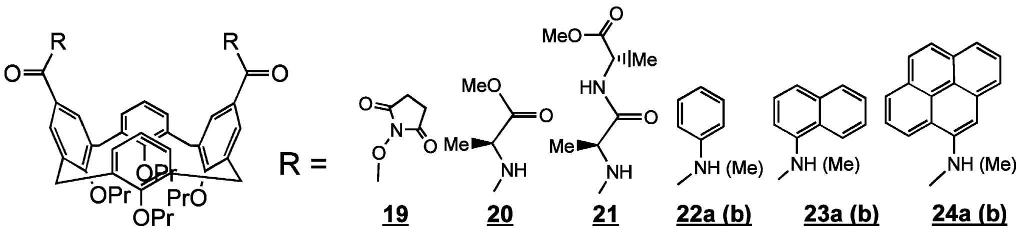
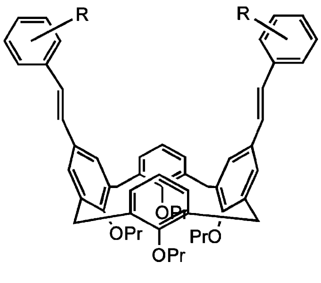
More elaborate functions are also available in this series using the amide-type linkers. In such cases chiral fragments and aromatic groups have been introduced at the 1,3-positions of the wide-rim as illustrated in compounds **19**–**24** [41,42].

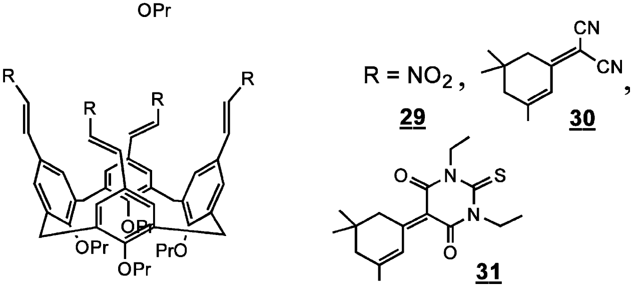
Finally the use of phenyl- or aromatic-typed linkers has also been explored in some depth. Such fragments provide a convenient way to expand the cavity in one chemical step from the corresponding bromide analogue. This precursor is common to most derivatizations.



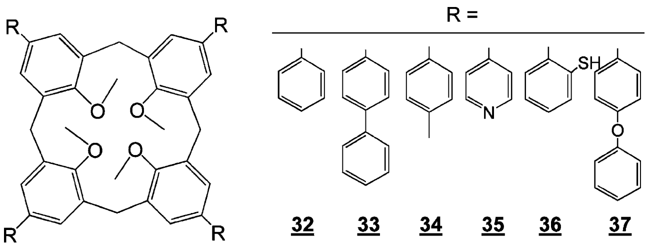
Vinyl groups have also been employed to anchor various substituted phenyl groups. The di-1,3- and tetra-functionalized unsubstituted derivatives have been reported as a di- and tetrapropoxycalix[4]arene in the cone conformation, but also in the 1,3-alternate as well in the tetrapropoxy version of the di-1,3-vinyl compounds [43]. In the cone conformation, these compounds are capable of complexing methyl-pyridinium, presumably via vinyl-π-bond interactions. A series of di-1,3-*trans*-styryl derivatives (see compounds **25**–**28** as typical examples) has also been investigated for their luminescence properties [44]. The signature of the *trans*-stilbene chromophore is easily observed in the electronic spectra. Recently, Reinhoudt et al. [45] prepared a series of wide-rim mono-, di-1,3- and tetra-functionalized tetrapropoxycalix[4]arenes (see compounds **29**–**31** as representative examples), and investigated the high hyperpolarizability properties of the charge-transfer chromophores, taking advantage of the molecular pre-organization of the donor–π-acceptor fragments.



R = H **25**
R = 4-NO_2 **26**
R = 4-$B(OH)_2$ **27**
R = 4-$B(O_2(CH_2)_3)$ **28**



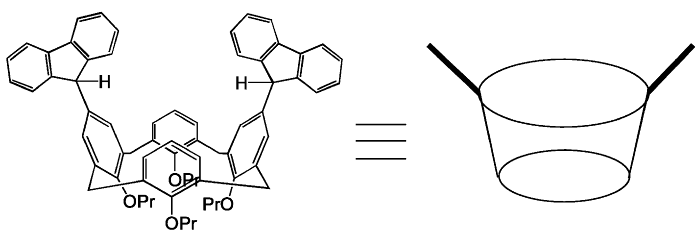
In that respect three notable works have appeared recently in the literature during the past 10 years. In one of the earlier works published by Atwood et al. [46], several tetra-functionalized tetramethoxycalix[4]arenes were prepared. This list of aromatic-linked groups includes phenyl (**32**), *p*-biphenyl (**33**), *p*-tolyl (**34**), 3-pyridyl (**35**), 2-thiophenyl (**36**), and phenoxy-*p*-phenyl (**37**). Because of the smaller methoxy fragment the cone conformation may not be the one favored, at least in the solid state. Indeed, X-ray data reveal that compounds **33**, **36** and **37** exist in the partial cone conformation, while **32** exhibits a cone geometry.



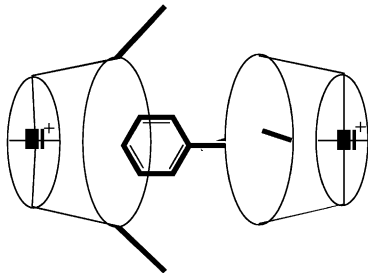
Jorgensen also explored such a chemistry for the 1,3-di-functionalized derivatives of tetrapropoxycalix[4]arene [47,48], and this list includes phenyl (**38**), 3-bromophenyl (**39**), 1-naphthyl (**40**), *N*-carbazolyl (**41**) 6-fluorenyl (**42**), which are all in their expected cone conformation. In the latest work on compound **42**, the presence of Li-ion in the lattice induces an important conformational change. This goes from a flattened bowl to a cone, for Li-uncomplexed (**42a**) to Li-interacting in the ionophoric cavity (**42b**), respectively. In the latter case an interesting egg-shape dimeric clathrate was observed in the solid state [48].

2.1.2. Functionalization via a nitrogen atom

Perhaps the most common group in this category is the nitro function since it provides precursors, notably for amino derivatives, en route toward other functiona-

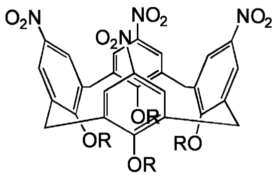


42a

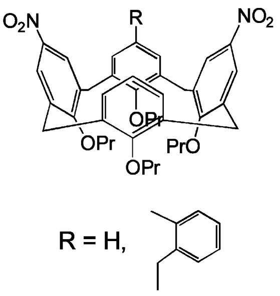


42b

lized *N*-containing derivatives. The literature is abundant in this case. Using tetraalkyl groups such as *n*-Pr and CH_2-*i*-Pr at the lower rim, several studies focused on the mono-, di-1,3-, and tetra-nitrated calix[4]arenes (compounds **43**–**47** for examples) [39,48–51]. The cone conformation is observed in most cases except that all four geometries have been crystallographically characterized for compound **43** by van Hulst and Reinhoudt et al. [51].

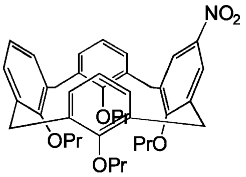


R = *n*-Pr **43**
R = CH_2-*i*-Pr **44**



R = H,

45 **46**



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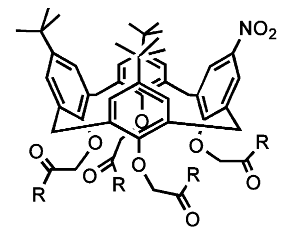
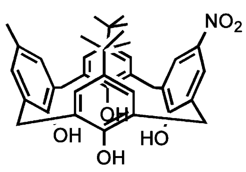
Other modified and unsubstituted narrow-rim nitrated compounds are known. This non-exhaustive list is still elaborated and includes compounds **48**–**59** as shown below [11,33,45,52–56]. Most of the compounds are found in the cone conformation, except for compound **57** which has partial cone geometry. One of the key features in this list is the introduction of the di-1,2-isomers, one of the two rarest species in the calix[4]arene with tri-functionalized compounds. The reduction of the nitro groups into the corresponding amines is trivial and some of them have indeed been prepared as exemplified by compounds **53** and **54** to form the di-amino derivatives **60** and **61** [56].

In the di-1,3-amino series, the di-(methylamido)-tetrapropoxycalix[4]arene (**62**) was prepared and characterized from crystallography [57]. Other N-containing fragments have also been anchored on the wide-rim, and may involve groups of biological relevance such as urea and melamine (compounds **63**–**67**) [53,58,59]. One of the interesting features in compounds **63**–**66** is the self-assembly to form dimers held by a complex H-bonding network [53]. These dimers form a capsule structure which are shown to encapsulate small molecules such as chloroform and dichloromethane.

More elaborate N-containing fragments have also been investigated. For instance the carbazolyl lumophore has been anchored at the 1,3-positions of the calix[4]arene molecule (compound **68**) [45]. Based upon the X-ray data, a face-to-face geometry is imposed in the flattened structure of the macrocycle. As a consequence the photophysical data show solvent dependence, suggesting the presence of charge transfer or exciplex character within the bichromophoric systems. Recently, a novel tetrafunctionalized calix[4]arene was prepared by De Cian et al. [60] using the imido connecting group, into which pyridine donors are incorporated. This new tetra-pyridine ligand (**69**) has an interesting structural property. It provides donor centers at the wide-rim, opening the door for easy cavity extension via simple coordination of transition metals. Such supramolecular applications prove to be particularly interesting. The photo-sensitive phenylazo substituent has also been anchored at the calix[4]arene wide-rim as exemplified by compounds **70**–**72** [61–63]. This functional group can be luminescent at 77 K, and can act as a probe for host–guest interactions [64]. These species are found to be fluorescent (S_2–S_0); a luminescence arising from a π–π^* state.



R = OH **48**, OEt **49**, Cl **50**



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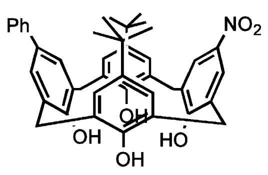

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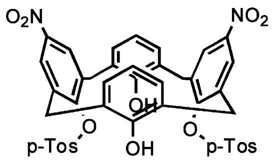

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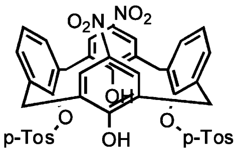

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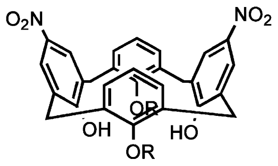
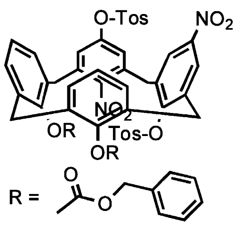


R = Me **55**, Pr **56**



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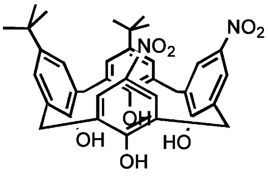

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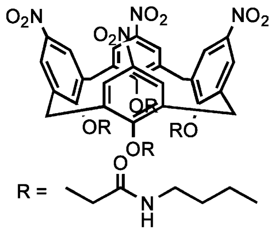

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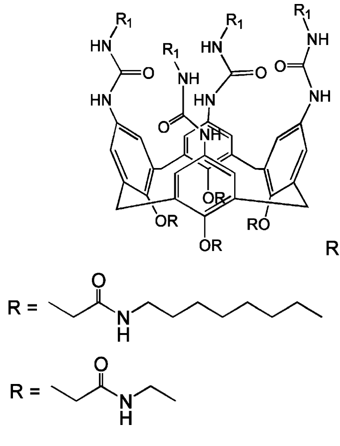
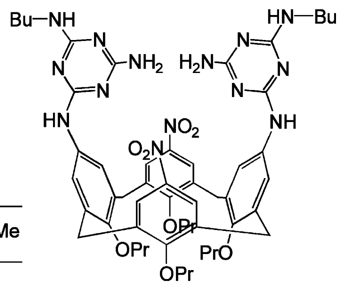


R_1 = p-C_6H_4Me,	$(CH_2)_7Me$
63	**64**
65	**66**



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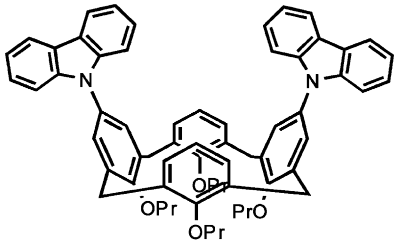
2.1.3. Functionalization via a sulfur atom

This category of species is impressive and interestingly dominated by the tetraanionic and water soluble p-sulfonatocalix[4]arene (**73**) [65,66]. The four hydroxyl groups in the narrow-rim secure the bowl-shape of the macrocycle, but also may exist in the mono-deprotonated form (3 OH/1 O^-) [67–73]. In addition this molecule may also exist in its multi-protonated form, with the possibility of up to four sulfonated residues [74,75]. Literature on its supramolecular chemistry is abundant. It strongly relies on the interactions between the sulfonato groups and either metallic centers, or protons of water molecules. Many examples for inclusion phenomena with cationic species (metallic [76] and



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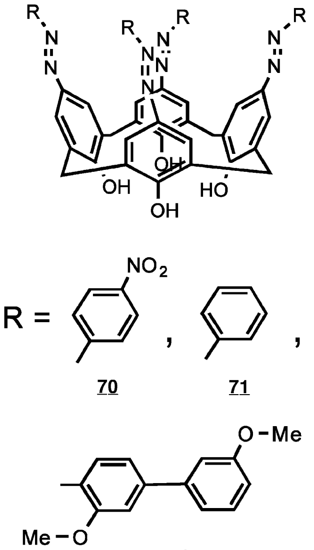
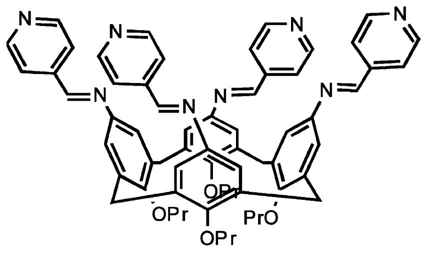


70 **71** **72**



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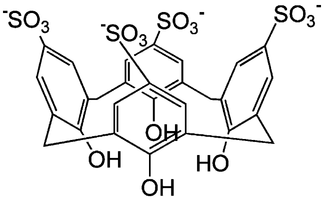
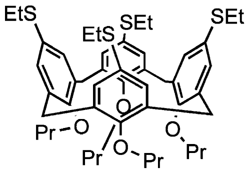
non-metallic listed below) have been observed as well. As such, this topic merits a review of its own. Although not clearly demonstrated, the structural nature of these species (*p*-sulfonatocalix[4]arene.... metallic fragments) is rarely if not ever addressed for solutions. This chemistry is essentially focused on the solid state, where polymeric H-bond or coordination-bond structures are often observed. Because of the weak and strongly labile binding ability of the sulfonato ligand, it is strongly suspected that these species dissociate in solution.



73

In recent years, **73** has been thoroughly investigated. Its complexation of various transition metals such as Y, Mn, Ni, Cu, Pb, La, Yb and Eu, for example, has been performed, and X-ray structures of the complexes have been determined [68–70,77–86]. Host–guest interactions (i.e. inclusions) have been noted for numerous species. Negatively charged guests such as methyl sulfate [67], neutral molecules such as acetone [71,82] and *N*-pyridine oxide [83], cationic organics such as tetramethyl ammonium [73], pyridinium [69,70], and trimethyl anilinium [76], crown ether complexes [75,81,85], and the pyridine ligand of a coordination compounds [77,78], have been localized in the cavity according to X-ray crystallography. More spectacular, the inclusion of a dication (here diammonium) has recently been reported [68]. The common point for all these supramolecular systems is the extensive H-bonding network at the lower- and wide-rims, forming various bilayers, and polymeric solids.

The thio compounds have been the topic of significantly fewer studies in the literature. These compounds are of interest in the sense they may serve as potential polydentate ligands for Au(I) species. Two alkyl thio calix[4]arenes are known (tetraethylthio-tetrapropoxycalix[4]arene (**74**, cone) [87] and tetramethylthiotetramethoxycalix[4]arene (**75**) [88]). The latter exhibits a conformation that lies between the 1,3-alternate and partial cone. Although much less developed, the chemistry of calix[4]resorcinarenes has also been focused on thio compounds, and IR-spectra suggested the presence of H-bonding between the OH residues and S atoms [89], which contribute to keep the cone conformation. In **75** such interactions do not exist and the solid state packing seems to be the sole reason for this unusual geometry.



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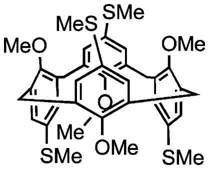

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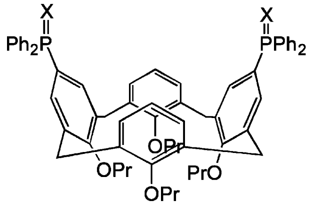
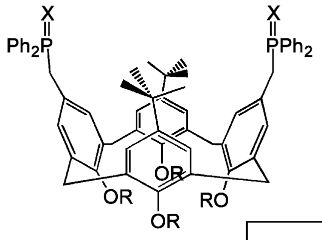
2.1.4. Functionalization via the P atom

This class of calix[4]arene compounds includes phosphines, phosphine oxides, and phosphates. Among the better characterized examples of phosphine and phosphine oxide, diphenylphosphine (and corresponding



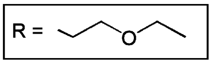
X = - , O

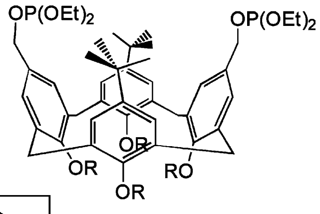
76, **77**



X = - , O

78, **79**





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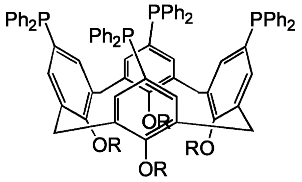
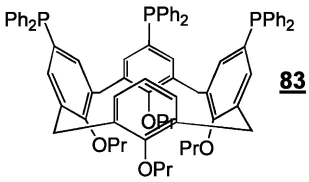


R = Me **81a**

R = *i*-Pr **81b**



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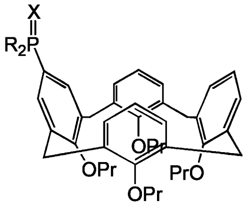
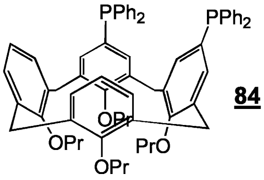


X = ---; R = Ph **85**
X = O ; R = Ph **86**
X = ---; R = i-Pr **87**
X = O ; R = i-Pr **88**

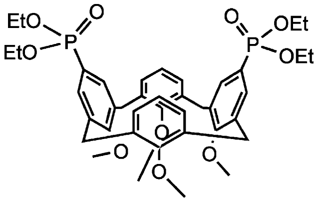


84

oxide) residues have been anchored at the 1,3-positions of the tetrapropoxycalix[4]arene macrocycle (see compounds **76**–**80**) [13,18].

Earlier work from Atwood et al. [90] focused on the tetra(diphenylphosphine)-tetramethylcalix[4]arene ligand (**81a**) in relation to the binding ability with metals. However, Tsuji et al. [91] reported its crystal structure and it turned out to adopt the partial cone conformation in the solid state. In solution, ^{1}H and ^{31}P NMR data indicated the presence of a mirror plane in this same conformation, but also the presence of fluxional behavior. This research group proposed the presence of the 1,3-alternate conformer to explain their results.

The 1,3-($(EtO)_2P(O))_2$-tetramethoxycalix[4]arene (**82**) was recently prepared and characterized crystallographically [92]. In this case the cone conformation is observed despite the small methoxy groups in the narrow-rim, and a flattened structure is obtained with the P-containing groups placed away from each other.



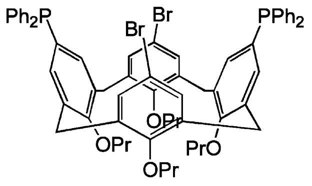
82

Perhaps the most complete work on this particular series has been reported by Gagnon et al. [93] and Vézina et al. [94]. They prepared the complete series of mono-, di-1,3-, di-1,2-, tri- and tetra-diphenylphosphined tetra-*n*- and tetra-*i*-propoxy-calix[4]arene. They also extended this to the mono(di-*i*-propylphosphino)tetra-propoxycalix[4]arene and its corresponding oxide [95].

Gloede et al. [96,97] performed the selective introduction of phosphoryl groups ($-P(O)-(O\text{-}i\text{-}Pr)_2$) in the wide-rim of calix[4]arene containing various narrow-rim chains such as Me, $-n\text{-}C_{12}H_{25}$, and $-CH_2OCH_2CH_2OMe$. These new ligands were characterized by ^{1}H-NMR only. Among these interesting compounds one finds the di-1,3-derivatives, as well as the di-1,3-$(P(O)(O\text{-}i\text{-}Pr)_2)$-di-2,4-$(CH_2P(O)(O\text{-}i\text{-}Pr)_2$, di-1,3-$(P(O)(O\text{-}i\text{-}Pr)_2)$-di-2,4-$(CH_2P(O)Ph_2)$ and di-1,3-$(P(O)Ph_2)$-di-2,4-$(CH_2P(O)(O\text{-}i\text{-}Pr)_2$ congeners. Finally Shimizu et al. [98] prepared an elegant series of water-soluble polysulfonated di-1,3-(diphenyl-phosphino)-long arm-calix[4]arene where long arm = $-C_6H_4(CH_2)_n-$ (with $n = 1, 2$). In the presence of Rh species, the catalysis of biphasic hydroformylation of water-insoluble oct-1-ene was performed in good conversion yields.

2.1.5. Functionalization with halides

Although these are not considered to be functional groups, they represent leaving groups providing access to other functionality. For kinetic and synthesis reasons, the most convenient halide in this respect is the bromide. Some of these starting materials were characterized by crystallographic methods as for di-1,3- or tetrabromo tetraalkyl-calix[4]arene (see, for examples Refs. [32,87,92]). In the tetrabromotetramethyl-calix[4]arene, the cone conformation is observed [87], which can be considered unusual due to the presence of the smaller –OMe groups in the narrow-rim. The conformational conversion dynamic properties of such species have recently been investigated by X-ray and NMR, in the presence and absence of guest molecules [99]. The preparation of some chloro derivatives is also known (see, e.g. Ref. [55]), but again these are not often used as starting materials. Finally, the X-ray structure of a tetraiodo analogue was recently reported where the narrow-rim is derivatized with four benzyl groups [100]. The macrocycle adopts the expected cone conformation, but in a flattened form.



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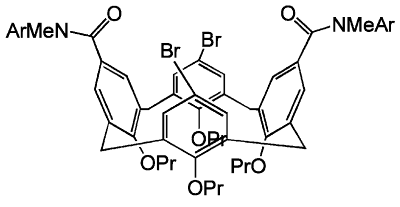
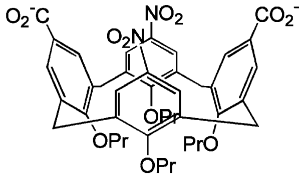


Ar = Ph **90**, 1-Naphth **91**



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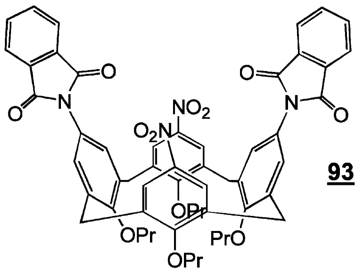

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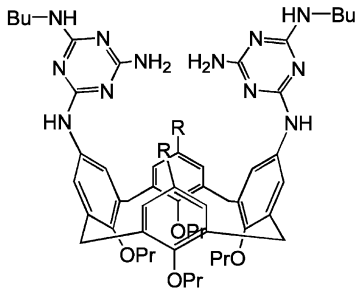


R = CN **94**
R = I **95**
R = NH_2 **96**
R = NHC(O)Me **97**
R = $CCSiMe_3$ **98**
R = CCH **99**

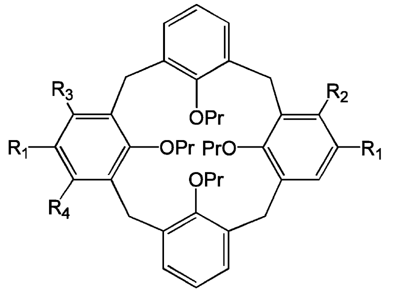
2.1.6. Mixed functions

The wide-rim modification using different functional groups offers an opportunity to build a very large number of new molecular architectures, putting emphasis on cavity extension, anchoring metallic and non-metallic fragments with various properties, and supramolecular chemistry. By considering the nitro and phthalimido groups as precursor for amines, and bromo derivatives as starting materials, numerous functional groups can be anchored. In addition, the literature exhibits an impressive number of examples of mixed-functionalized calix[4]arenes in the wide-rim including groups such as carboxylate and carboxylate acid, amides, aldehyde, and phosphines (see for instance Refs. [42,49,50,59,92,101,102]). Some typical examples are illustrated above (compounds **89**–**99**). This list clearly shows that this chemistry is dominated by the 'di-1,3-di-2,4-' derivatives.

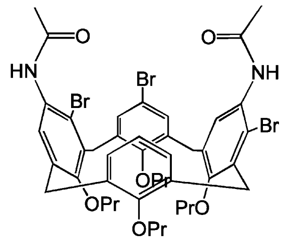
One interesting class of derivatives the *meta*-substituted compounds. Such compounds open the door to new structures, but face the obvious problem of steric hindrance, when the functional groups are somewhat too large. To our knowledge the functionality at the *meta*-position is limited to H, Br, and Me [55,101]. Some known derivatives are shown below (compounds **100**–**103**). This versatile chemistry will, in the future, be explored more and more.

2.1.7. Functionalization with organometallic fragments

One of the smallest metallic fragments involving a single transition metal is the Ag(I) cation. A direct interaction of a simple silver salt with a calix[4]arene molecule would suggest that, at a first glance, a reactivity that is similar to other typical bare M(I) cations. One may anticipate an encapsulation of the cation in the ionophoric cavity in the narrow-rim, or a typical host–guest interaction of the metal atom inside the hydrophobic cavity [103]. However, neither one is the case with Ag(I). The Ag(I) ion exhibits a great affinity for olefins and benzene rings via π-bonding. This being mentioned, one may suggest that both inner- and outer-faces of the benzene rings are candidates for coordination. Experimentally, Ag(I) binds inside the cavity because it takes advantage of a chelating effect with the neighboring rings. This complexation is not a host–guest interaction but rather a wide-rim coordination with a metal atom, as the *para*-C are strongly involved in the bonding. Some examples have been reported and X-ray data are available [104–107]. Two conformers were found in the solid state as partial cone (**104**, **105**) and cone (**106**).



R_1 = NHC(O)Me, $R_2 = R_3$ = Br, R_4 = H **100**
R_1 = NHC(O)Me, $R_2 = R_3 = NO_2$, R_4 = H **101**
R_1 = NHC(O)Me, $R_2 = R_4 = NO_2$, R_3 = H **102**



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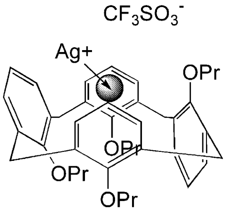

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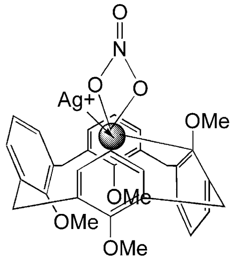

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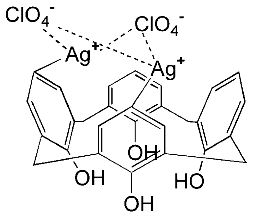


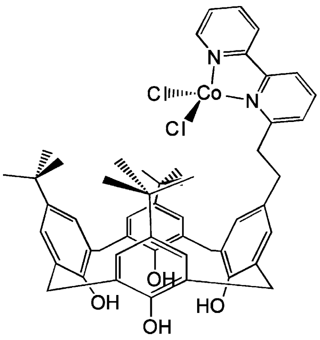
106

These molecules turns out to be fluxional where interconversion occurs in solution and these conformers are obtained from pre-organized forms prior to complexation [106,107]. The partial cone conformation found for a calix[4]arene containing a propyl group at the narrow-rim is somewhat unusual.

The most common way to coordinate a metal atom at the wide-rim is certainly via the use of a ligand. Literature shows that a very large number of strategies have been employed to connect organometallic fragments at the wide-rim. Such ligand groups include cyanide, isocyanide, phosphines, bipyridines, cyclopentadienyls, and sulfur-containing frameworks. This section briefly describes these calix[4]arene species as a function of the number of connections made to the wide-rim, i.e. mono-, di-1,3- and tetra-substituted species. A few mono-functionalized calix[4]arenes are known as shown below (compounds **107**–**112**) [94–96,108,109]. The cone conformation is confirmed from ^{1}H-NMR and crystallography. The flexible arm induces many possible conformations in solutions, and V–T NMR data [96] show that such molecules do indeed exhibit fluxionality. This is obviously not the case for **112**, which was prepared for luminescence probing purposes [109].

The di-1,3-substituted species represent the largest group in this category, and can be divided into two subclasses. The first one is the double-armed bimetallic system, and the second is the chelating device. The first series of bimetallic complexes is composed of a large series of different flexible arms. For instance these arms can be amide linkers such as shown in compounds **113**–**119** [56,110,111], or ethane and ethene [108], or phosphines (compounds **120**–**122**) [18]. The first series is interesting because the bipyridine complexes are known to luminesce in solution, while the ferrocene-type compounds are known to be redox-active. In this manner, these molecular devices can be used as sensors for host–guest interactions.

The second class are the chelating ligands which forms very large metal-containing macrocycles. The 1,3-bisphosphine ligand **76** can coordinate numerous metal centers such as Ag(I), Pd(II), Pt(II) and Ru(II) [13] as shown below (compounds **123**–**126**).



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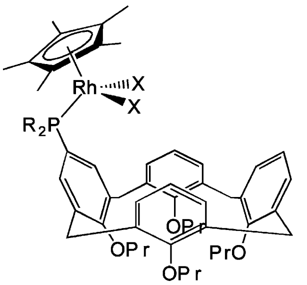
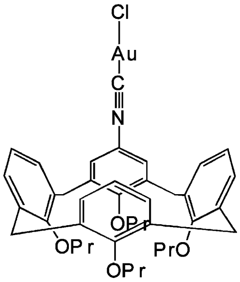


R = Ph, X= Cl (**108**); X = H (**109**)
R = i-Pr, X = Cl (**110**), X= H (**111**)

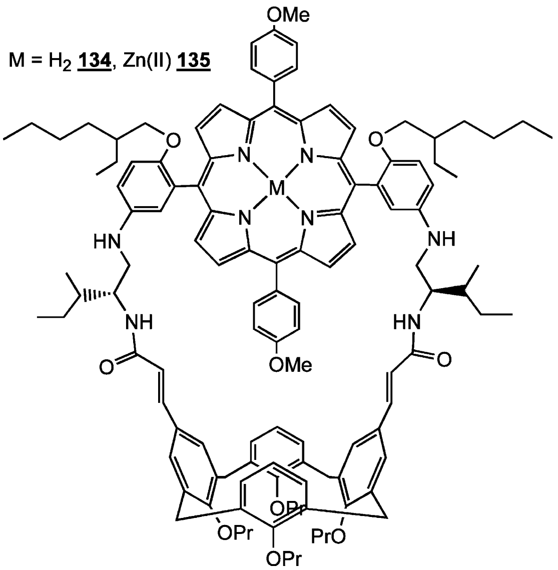


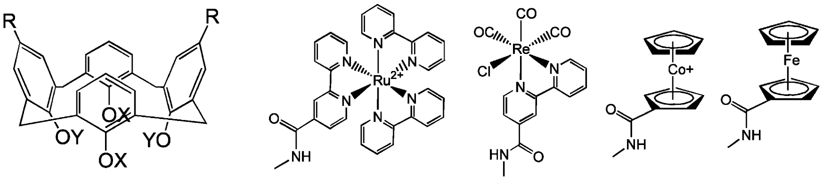
112

The encapsulation of methyl and carbonyl group is interesting and unique. In this respect Reinhoudt et al. [112] reported the characterization of Re(V) compounds such as **127** and **128**, the Re=O bond points toward the cavity but the NMR data indicate that the complexes lack symmetry, presumably placing this group with an angle relative to calix[4]arene symmetry axis. On the other hand, the Re=O group in **129** was assumed to be outward, perhaps for steric reasons. Compound **130** is interesting because of the incorporation of a redox-active center very close to the cavity [113]. This proximity increases the chance of a better sensor property of the device towards guest cations, but the wide-rim is practically completely blocked, and larger substrates cannot penetrate the cavity.

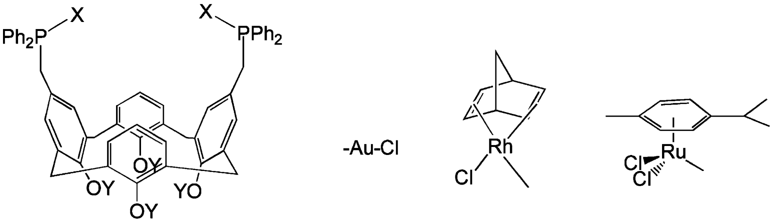
For such a purpose larger loops are necessary, and some examples were prepared (**131**, **132**), and even tested successfully [17,114]. Compound **133** was prepared as a shape-selective catalyst [18], but requires further investigation.

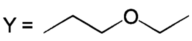
Perhaps the largest macrocycle is the porphyrin-capped tetrapropoxycalix[4]arene (**134**, **135**) recently reported by Shinkai et al. [115].





X = p-Tos, Y = H **113** **114** **115** **116**
X = H, Y = p-Tos **117** **118** **119** -----



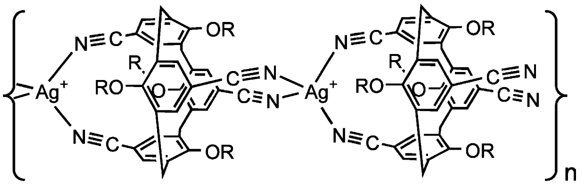


120 **121** **122**

The large porphyrin ring is doubly linked via two distal *meso*-phenyl groups to the two distal *p*-positions of the tetrapropoxy-calix[4]arene. Compound **135** shows a high affinity toward the guest molecule C-(1-methylpyridium-4-methylamino)-L-isoleucine. Although the porphyrin compounds show a strong Soret band in the UV–vis spectra allowing one to monitor the host–guest binding, many metalloporphyrins also exhibit a very strong luminescence, hence providing new sensoring applications.

Surprisingly much less investigated, the tetrametallo-functionalized calix[4]arenes represent a smaller group of compounds in the literature. Perhaps this may be attributed to steric hindrance, as this series is indeed limited to cyanide [31,32] and isocyanide [109] complexes of Ag(I) and Au(I), respectively. Interestingly one exception is seen in compound **136** where four porphyrin macrocycles are attached to calix[4]arene [116]. In the solid state **136** auto-assembles to form an egg-shaped dimer similar to that mentioned for compound **65** above, where the porphyrin rings stack face-to-face promoting π···π interactions. Luminescence and photophysical studies should prove extremely valuable with respect to intra- and intermolecular energy transfer. Compound **137** is luminescent in solutions, a phosphorescence that originates from the π–π* state of the phenyl isocyanide fragment, with little perturbation from the Au(I) center (i.e. heavy metal atom effect on the photophysical parameters).

Tetracyanide ligands **4** and **5** were complexed with Ag(I) cations, and both formed polymers in the solid state. However the polymers turned out to be very different as **4** adopts the 1,3-alternate conformation and forms a 1D structure of the type $\{(MeOCH_2CH_2)_4calix(CN)_4(Ag^+)\}_n$ (**138**) [31]. The 1,3-alternate conformation places all benzene rings fairly parallel to each other, and the flexibility of the calix[4]arene allows two cyanide groups to chelate the same Ag atom. In this way all Ag atoms are tetracoordinated with a distorted tetrahedral geometry.



R = CH_2CH_2OMe

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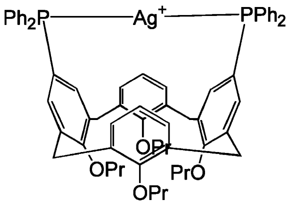
On the other hand **5** adopts a flattened cone conformation and the polymer $\{(PhCH_2)_4calix(CN)_4(Ag^+)\}_n$ (**139**) forms a zig–zag structure. This structure is rendered viable again because the cyanide



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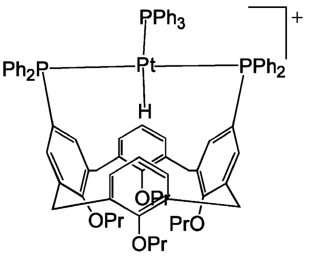

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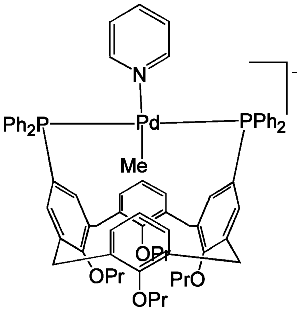

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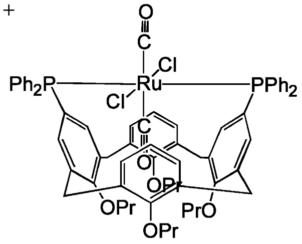

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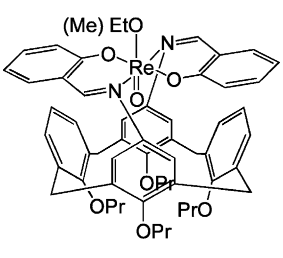

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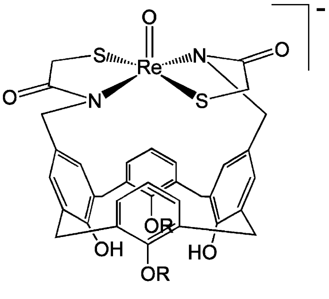

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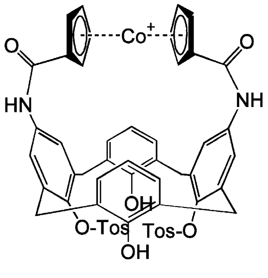

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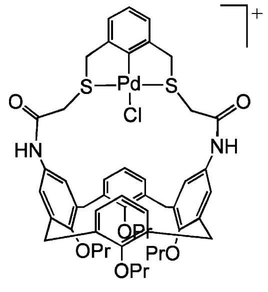

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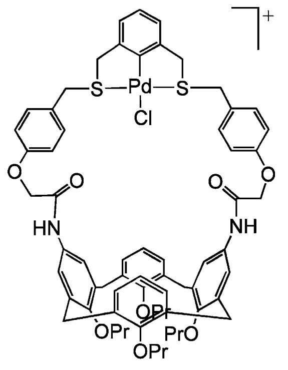

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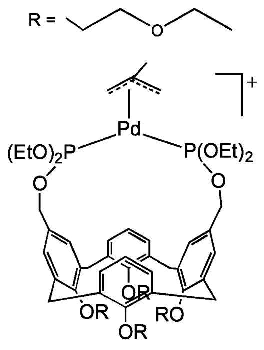

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groups chelate an Ag atom in the flattened geometry, leaving the two others to bridge other tetracyanocalix[4]arene-silver(I) fragments [32].

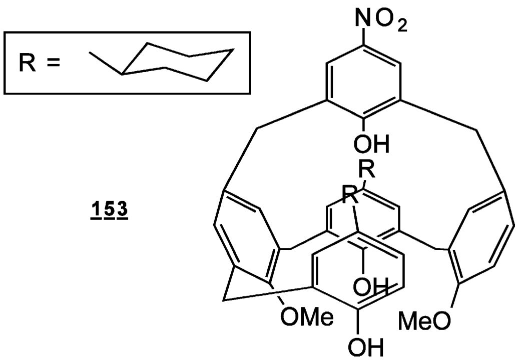
2.2. Loop structure in the wide-rim

One of the strategies to secure the cone conformation is the use of loop structures in the narrow-rim. This includes loops formed of covalently bonded atoms and of both covalent and coordination links. Such a concept was recently and briefly presented by Pochini et al. [117]. The strategy analogous to this one is the construction of loops in the wide-rim at the 1,3-positions. In this respect Böhmer et al. [118–122] synthesized just about every calix[4]arene which contains different saturated chains $(CH_2)_n$ with $n = 4–10$, 12 and 14, as well as some ketone-containing chain species (compounds **140–149**).

However, Pochini et al. [123] pointed out that a loop structure generates a cone structure but is not the criterion for the design of an efficient host device such as in compounds **150** and **151** [124,125]. However by incorporating a functionality such as a pyridine, additional interactions promote binding with a substrate as was well demonstrated in compound **152** and its related derivatives [123].

Böhmer et al. [121] reported a loop compound belonging to this same family, where the linking chain is a CH_2-(p-$NO_2C_6H_4OH$)-CH_2– group anchored on a dimethylcalix[4]arene derivative (see compound **153**).

The presence of a phenolate offers similar possibilities for binding via intermolecular H-bonds. The key feature is that the pinched structure of the calix[4]arene macrocycle precludes the use of the cavity, but the use of extending groups such as cyclohexyl in **153** generates a new cavity that resembles a pincer shape molecule. In this respect the calix[4]arene molecule becomes more of a platform for the construction of architectures. One may also functionalize the remaining 2,4-positions with bases or acids, which extends the cavity size.



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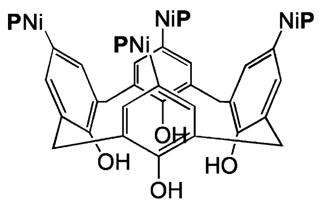

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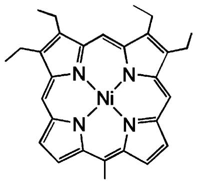
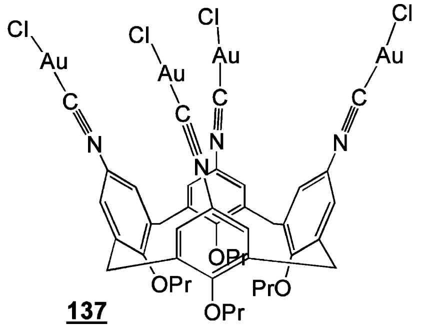


NiP



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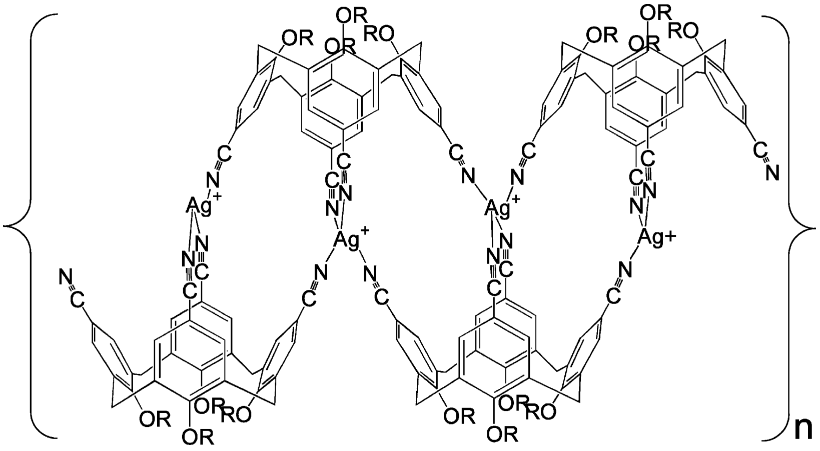


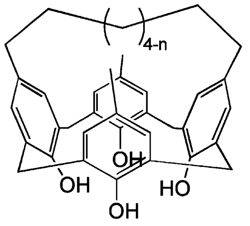
139 R = CH_2Ph

2.3. Covalently bonded dimers

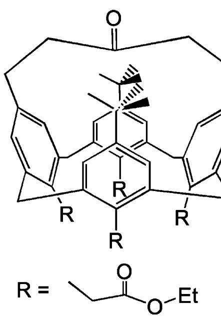
This is a very interesting class of molecules since it offers, at least on paper, the possibility of generating large capsules with an opening mimicking a ‘mouth’. The question is how can two calix[4]arene fragments can be attached to accomplish such a structure and, hopefully, act as an efficient supramolecular binder. Numerous bis-calix[4]arene dimers linked via a single bond or a single chain have already been prepared (compounds **154**–**159**) [11,61,126,127], two of which have been characterized from X-ray crystallography (**154**, **159**).

The X-ray data indicate that in both cases the dimers adopt an *anti* conformation, although solution NMR results suggest the presence of a *syn*–*anti* equilibrium. These molecules (**154**, **159**) are flexible in solutions, and the egg-shape structure is difficult to obtain with this strategy. A head-to-head double anchorage seems more beneficial in this respect, as is well illustrated by representative examples (**160** and **161**) [128]. Reinhoudt et al. have indeed demonstrated that these molecules were good receptors for silver ions, and could be used for ionic transport [129]. Compound **162** also forms a head-to-head structure [127], but this dimer exhibits the 1,3-conformation for the two calix[4]arene macrocycles. The egg-shape structure is not obtained in this case, and the small cavity located between the two linkers is obscured by the flexible ether chains. The reasons for this unexpected conformation are unknown at this time.

Another dimer is the methylene-linked bis-calix[4]arene **163**, which is a special case since it is, in fact, a fused triple calix[4]arene [130]. Indeed, two of the phenyl groups for each of the two methylene-linked calix[4]arenes also describe a central macrocycle. The X-ray structure for **163** reveals the presence of two monoprotonated *endo*-calix[4]arene structures in the cone conformation, with an *exo*-calix[4]arene for the middle unit in the 1,2-alternate conformation. As a consequence the egg-shape structure is not obtained in this case. This compound is particularly interesting because it offers the possibility of functionalization at the narrow-rim (–OH), as well as the wide-rim (–NO_2). Such systems should prove particularly interesting if investigated. Finally, belonging to this same family is the head-to-tail dimer **164**, one of two examples reported by Böhmer et al. [131]. This compound does not appear to be crystallographically characterized.



4-n	#
5	**140**
6	**141**
7	**142**
8	**143**
9	**144**
10	**145**
12	**146**
14	**147**



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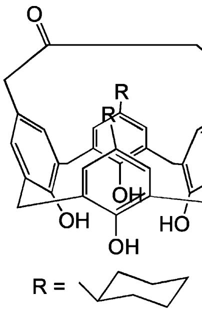

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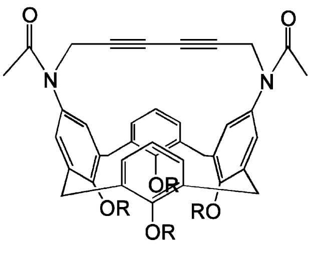

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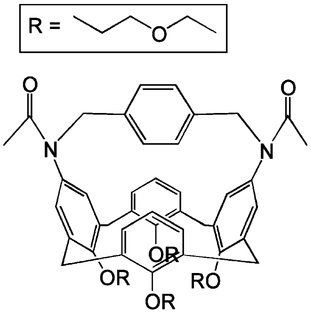

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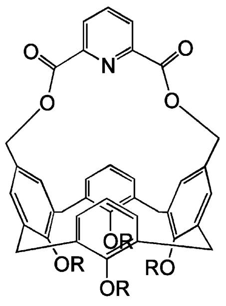

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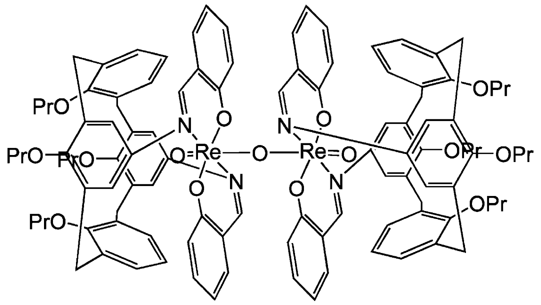
2.4. Complex systems

Other interesting molecules related to calix[4]arenes in a structural sense, are the more complex systems such as trimers, fused calix[4]arenes, polynuclear complexes of calix[4]arene, and calix[4]naphthalenes. Compounds **165** and **166** are examples of trimers that were recently reported, and they were characterized by NMR [11]. Flexible chains link the various units in the upper rim for **165**, but in **166** the calix[4]arene bridging unit connects the other two via an amide chain placed in the narrow-rim.

Other special molecules have recently been synthesized such as fused calix[4]arenes [132] and calix[4]naphthalenes [133] (see compounds **167** and **168**). The chiral compound **167** forms an S-shape molecule where the two cavities are placed in opposite directions. The cavities are well open, but binding with small substrates does not seem to have been explored, as yet. On the other hand although one may assume that **168** exhibits an extended cavity, the flattened structure renders the cavity unavailable, at least according to solid state data [133].

Another interesting compound is the dimeric species connected in the wide-rim via coordination of O=Re–O–Re=O linear units as shown below (**169**) [112]. This inorganic unit is placed parallel to the calix[4]arene molecular axes in a way that the oxo groups are well encapsulated. This molecule was intended for drug delivery purposes.



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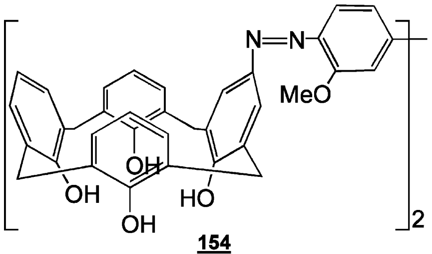

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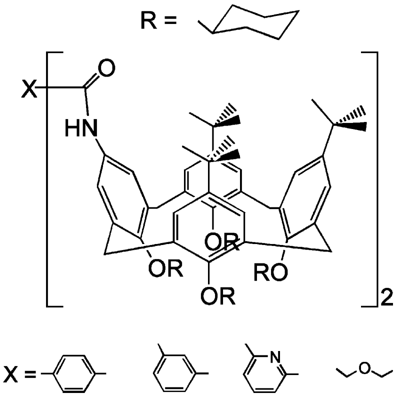
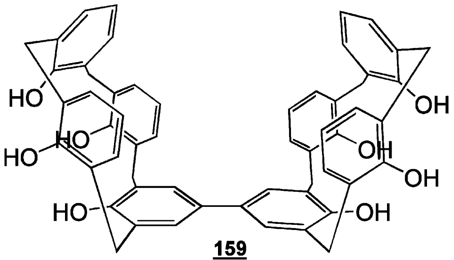


155 **156** **157** **158**



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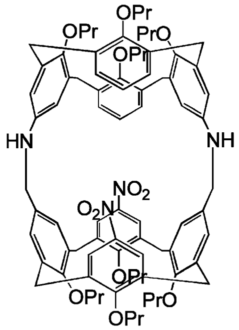

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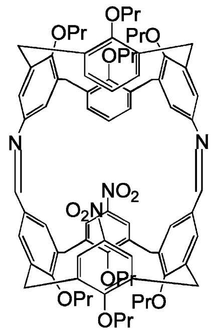

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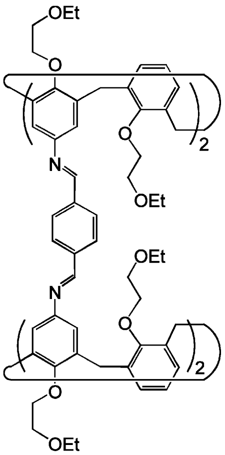

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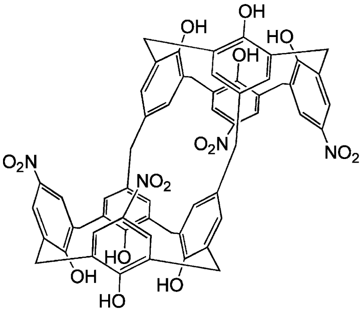

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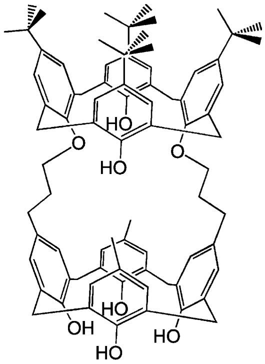

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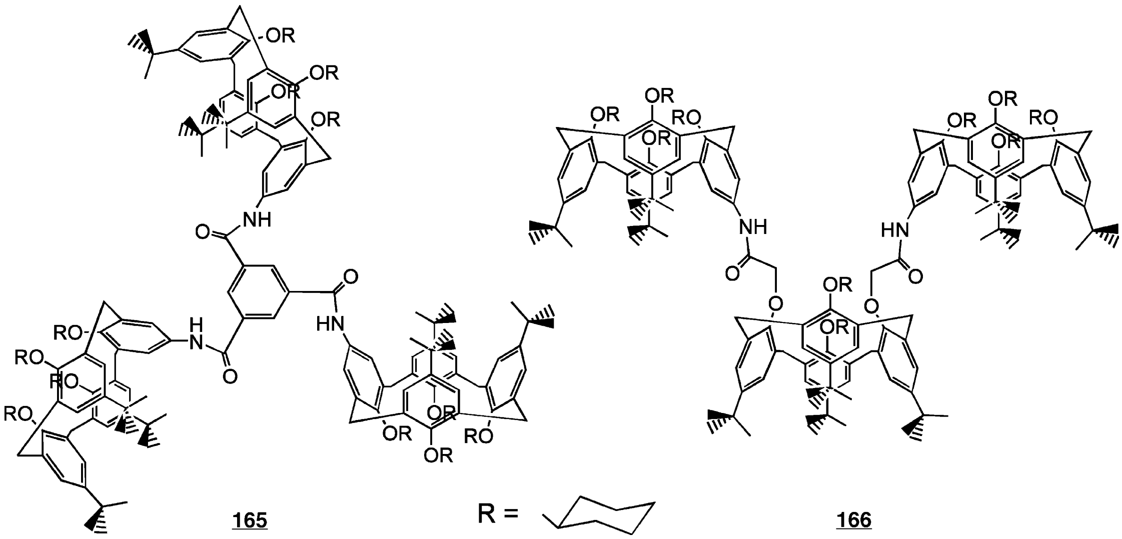
2.5. Outer-face functionalization

This class of calix[4]arene molecules is entirely related to the coordination chemistry of the benzene rings, and low-valent metals are prime candidates for functionalization. Steric hindrance favored the connection of the metallic fragments on the outside of the macrocycle. The literature includes the mono-, di-1,3- and tetra-metallated calix[4]arenes and -alkyl calix[4]arenes, but the number of differently anchored metallic residues is somewhat limited, so far. These fragments include –$Cr(CO)_3$ (**170** and **171**), –Ru(arene) (arene = C_6H_6, C_6Me_6, p-MeC_6H_4-i-Pr), –RhCp* and –IrCp* [133–138].

This coordination does not drastically change the cavity size of the macrocycle, but electronically the benzene rings are poorer, as seen experimentally by the high acidity of the hydroxyl groups. Some of the di- and tri-cationic species of compounds **172**–**175** have also been isolated and characterized. As a consequence alterations in the binding properties of the cavity are anticipated, because of the presence of the metallic π-acceptor and the various deprotonation forms that are



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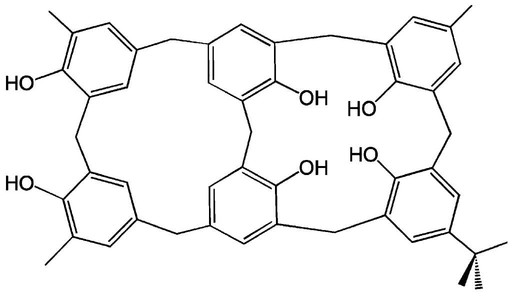

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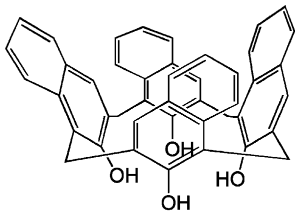

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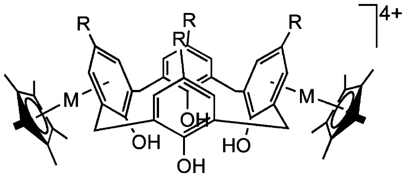
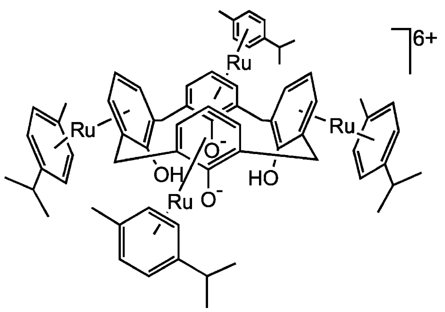
available in a given experimental condition. In all cases the cone conformation is observed from X-ray and ^{1}H-NMR. For the unsubstituted narrow-rims, the H-bonding network secures not only the cone geometry but also keeps the cavity open.



M = Rh(III), R = H **172**
M = Ir(III), R = H **173**
M = Rh(III), R = *t*-Bu **174**
M = Ir(III), R = *t*-Bu **175**

On the other hand, the propylated species do not have these interactions and a pinched structure is observed. Surprisingly the metallic fragments are localized on the quasi face-to-face rings of the pinched macrocycle in the solid state. This result suggests that interconversion between 'flattened-away' and 'flattened-close' may be facile in these Cr(CO)$_3$ systems (compounds **170**, **171**) [138].

The tetrametallated systems are very crowded molecules but the cavity remains available. The most complete work in this area is certainly the one reported by Atwood and coworkers [135] which accounts for the preparation and characterization of a series of di- and tetra-functionalized calix[4]arenes by the Rh, Ir, and Ru groups listed above. In all cases the bis-deprotonated systems were isolated and characterized. In particular compound **176** showed a popensity to bind halides selectively (not other larger common anions such as acetate and sulfate), and the binding constant obtained by ^{1}H-NMR varies as $Cl^- > Br^- > I^-$. The corresponding MCp* derivatives (M = Rh, Ir) were also investigated but their binding ability for halides was not established.



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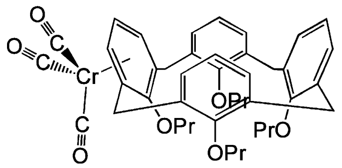
3. Conclusions

This review provides clear evidence that the chemistry of the calix[4]arene macrocycle at its wide-rim and outer-face is well understood and relatively well developed. Just about all common organic functions have been exploited, and most in detail. Some functional groups may still be used extensively such as the rigid alkynyl and isocyanide groups, which are known to coordinate transition metals, providing an opportunity to enlarge the cavity, but also to build new supramolecular structures.

The possibility of chemically modifying the narrow- and wide-rim and outer-face, make the calix[4]arene molecule a very versatile compound. This unique building block may also act as a bowl shape or a platform molecule, or simply as a bridging fragment for the construction of the desired device. In comparison with



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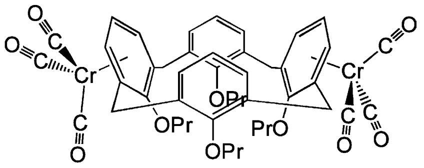

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molecular devices where modifications were made at the narrow-rim, applications involving wide-rim and outer-face metalla-functionalized calix[4]arenes are still in their infancy. The chemical control for securing the bowl shape structure is also well established, and wide-rim modifications for the design of molecular recognition devices are well known. Many successful examples are just beginning to emerge in the literature. This leaves no doubt that research in this area will continue to flourish over the years.

Acknowledgements

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References

[1] C.D. Gutsche, Calixarenes, Royal Society of Chemistry, Cambridge, UK, 1989.

[2] C.D. Gutsche, Calixarenes Revisited, Royal Society of Chemistry, Cambridge, UK, 1998.

[3] J. Vicens, V. Böhmer (Eds.), Calixarenes: Versatile Class of Macrocyclic Compounds, Kluwer Academic Publishers, Dordrecht, 1991.

[4] (a) J. Vicens, Z. Asfari, J.M. Harrowfield (Eds.), Calixarenes 50th Anniversary: Commemorative Issue, Kluwer Academic Publishers, Dordrecht, 1994;
(b) Z. Asfari, V. Böhmer, J.M. Harrowfield, J. Vincens (Eds.), Calix[4]arenes 2001, Kluwer Academic Publishers, Dordrecht, 2001.

[5] D. Diamond, M.A. McKervey, Chem. Soc. Rev. 25 (1996) 15.

[6] V. Böhmer, Angew. Chem. Int. Ed. Engl. 34 (1995) 713.

[7] J. Scheerder, M. Fochi, J.F.J. Engbersen, D.N. Reinhoudt, J. Org. Chem. 59 (1994) 7815.

[8] C. Wieser, C.B. Dieleman, D. Matt, Coord. Chem. Rev. 165 (1997) 93.

[9] S. Shinkai, S. Mori, H. Koreishi, T. Tsubaki, O. Manabe, J. Am. Chem. Soc. 108 (1986) 2409.

[10] K. No, Y. Noh, Bull. Korean Chem. Soc. 7 (1986) 314 (CA 107: 115347p).

[11] O. Mogck, P. Parzuchowski, M. Nissinen, V. Böhmer, G. Rokicki, K. Rissanen, Tetrahedron 54 (1998) 10053.

[12] S. Shinkai, K. Araki, J. Shibata, D. Tsugawa, O. Manabe, J. Chem. Soc. Perkin Trans. 1 (1990) 3333.

[13] C. Wieser-Jeunesse, D. Matt, A. De Cian, Angew. Chem. Int. Ed. Engl. 37 (1998) 2861.

[14] A. Arduini, S. Fanni, G. Manfredi, A. Pochini, R. Ungaro, A.R. Sicuri, F. Ugozzoli, J. Org. Chem. 60 (1995) 1448.

[15] B. Xu, T.M. Swager, J. Am. Chem. Soc. 115 (1993) 1159.

[16] P.D. Beer, D. Hesek, K.C. Nam, M.G.B. Drew, Organometallics 18 (1999) 3933.

[17] B.R. Cameron, S.J. Loeb, Chem. Commun. (1996) 2003.

[18] I.A. Bagatin, D. Matt, H. Thönnessen, P.G. Jones, Inorg. Chem. 38 (1999) 1585.

[19] M. Almi, A. Arduini, A. Casnati, A. Pochini, R.U.

[20] L. Giannini, A. Caselli, E. Solari, C. Floriani, A. Chiesi-Villa, C. Rizzoli, N. Re, A. Sgamellotti, J. Am. Chem. Soc. 119 (1997) 9198.

[21] L. Giannini, A. Caselli, E. Solari, C. Floriani, A. Chiesi-Villa, C. Rizzoli, N. Re, A. Sgamellotti, J. Am. Chem. Soc. 119 (1997) 9709.

[22] M.G. Gardiner, G.A. Koutsantonis, S.M. Lawrence, P.J. Nichols, C.L. Raston, Chem. Commun. (1996) 2035.

[23] S.E. Biali, V. Böhmer, S. Cohen, G. Ferguson, C. Grüttner, F. Grynszzpan, E.F. Paulus, I. Thondorf, W. Vogt, J. Am. Chem. Soc. 118 (1996) 12938.

[24] E.B. Brouwer, K.A. Udachin, G.D. Enright, C.I. Ratcliffe, J.A. Ripmeester, Chem. Commun. (1998) 587.

[25] E.B. Brouwer, G.B. Enright, J.A. Ripmeester, J. Am. Chem. Soc. 119 (1997) 5404.

[26] G.D. Andreetti, O. Ori, F. Ugozzoli, C. Alfieri, A. Pochini, R. Ungaro, J. Inclusion Phenom. 6 (1988) 523.

[27] M.H. Chisholm, K. Folting, W.E. Streib, W. De-Dong, Chem. Commun. (1998) 379.

[28] B. Castelleno, A. Zanotti-Gerosa, E. Solari, C. Floriani, A. Chiesi-Villa, C. Rizzoli, Organometallics 15 (1996) 4894.

[29] F. Hajek, E. Graf, M.W. Hosseini, X. Delaigue, A. De Cian, J. Fischer, Tetrahedron Lett. 37 (1996) 1401.

[30] F. Hamada, G.W. Orr, H. Zhang, J.L. Atwood, J. Crystallogr. Spectrosc. Res. 23 (1993) 681 (CA 119: 282669z).

[31] G. Mislin, E. Graf, M.W. Hosseini, A. De Cian, N. Kyritsakas, J. Fischer, Chem. Commun. (1998) 2545.

[32] E. Elisabeth, L.J. Barbour, G.W. Orr, K.T. Holman, J.L. Atwood, Supramol. Chem. 12 (2000) 317.

[33] J.-D. van Loon, A. Arduini, W. Verboom, R. Ungaro, G.J. van Hummel, S. Harkena, D.N. Reinhoudt, Tetrahedron Lett. 30 (1989) 2681.

[34] A. Vrielink, P.W. Codding, C.D. Gutsche, L.G. Lin, J. Inclusion Phenom. Macrocyclic Chem. 4 (1986) 199.

[35] S. Harkema, J.-D. van Loon, W. Verboom, D.N. Reinhoudt, Acta Crystallogr. Sect. C 54 (1998) 269.

[36] F. Hajek, M.W. Hosseini, E. Graf, A. De Cian, J. Fischer, Angew. Chem. Int. Ed. Engl. 36 (1997) 1760.

[37] G.R. Newkome, Y. Hu, M.J. Saunders, Tetrahedron Lett. 32 (1991) 1133.

[38] J.L. Atwood, G.W. Orr, S.G. Bott, K.D. Robinson, Angew. Chem. Int. Ed. Engl. 32 (1993) 1093.

[39] E. Kelderman, L. Derheag, W. Verboom, J.F.J. Engbersen, S. Harkema, A. Persoons, D.N. Reinhoudt, Supramol. Chem. 2 (1993) 183.

[40] F. Sansone, S. Barboso, A. Casnati, M. Fabbi, A. Pochini, F. Ugozzoli, R. Ungaro, Eur. J. Org. Chem. (1998) 897.

[41] V. Böhmer, G. Ferguson, O. Mogk, Acta Crystallogr. Sect. C 52 (1996) 2000.

[42] F.C. Krebs, M. Larsen, M. Jorgensen, P.R. Jensen, M. Bielecki, K. Schaumburg, J. Org. Chem 63 (1998) 9872.

[43] P. Lhotak, R. Nakamura, S. Shinkai, Supramol. Chem. 8 (1997) 333.

[44] R.K. Juneja, K.D. Robinson, C.P. Johnson, J.L. Atwood, J. Am. Chem. Soc. 115 (1993) 3818.

[45] P.J.A. Kenis, E.G. Kerver, B.H.M. Snellink-Ruel, G.J. van Hummel, S. Harkema, M.C. Flipse, R.H. Woudenberg, J.F.J. Engbersen, D.N. Reinhoudt, Eur. J. Org. Chem. (1998) 1089.

[46] R.K. Juneja, K.D. Robinson, C.P. Johnson, J.L. Atwood, J. Am. Chem. Soc. 115 (1993) 3818.

[47] M. Larsen, F.C. Krebs, N. Harrit, M. Jorgensen, Chem. Soc. Perkin Trans. 2 (1999) 1749.

[48] A. Faldt, F.C. Krebs, M. Jorgensen, Tetrahedron Lett. 41 (2000) 1241.

[49] O. Struck, J.P.M. van Duynhoven, W. Verboom, S. Harkema, D.N. Reinhoudt, Chem. Commun. (1996) 1517.

[50] O. Struck, W. Verboom, W.J.J. Smeets, A.L. Spek, J. Chem. Soc. Perkin Trans. Chem. Commun. 2 (1997) 223.

[51] P.J.A. Kenis, O.F.J. Noordman, S. Houbrechts, G.J. van Hummel, S. Harkena, F.C.J.M. van Veggel, K. Clays, J.F.J.

Engbersen, A. Persoons, N.F. van Hulst, D.N. Reinhoudt, J. Am. Chem. Soc. 120 (1998) 7875.
[52] S. Rantsordas, M. Perrin, F. Gharnati, S. Lecocq, W. Vogt, T. Fey, V. Böhmer, J. Inclusion Phenom. Mol. Recognit. Chem. 9 (1990) 145.
[53] D. Hesek, Y. Inoue, M.G.B. Drew, P.D. Beer, G.A. Hembury, H. Ishida, F. Aoki, Org. Lett. (2000) 2237.
[54] Y.L. Chao, D.M. Rudkevich, A. Shivanyuk, K. Rissanen, J. Rebek, Jr, Chem. Eur. J. 6 (2000) 3788.
[55] M. Backes, V. Böhmer, G. Ferguson, C. Grüttner, C. Schmidt, W. Vogt, K. Ziat, J. Chem. Soc. Perkin Trans. 2 (1997) 1193.
[56] P.D. Beer, M.G.B. Drew, D. Hesek, M. Shade, F. Szemes, Chem. Commun. (1996) 2161.
[57] W. Verboom, R.H. Vreekamp, P.J. Bobewes, S. Harkema, D.N. Reinhoudt, Rec. Trav. Chim. Pays-Bas 115 (1996) 402 (CA 125: 312865).
[58] O.Mogck. E.F. Paulus, V. Böhmer, I. Thondorf, W. Vogt, Chem. Commun. (1996) 2533.
[59] P. Timmerman, R.H. Vreekamp, R. Hulst, W. Verboom, D.N. Reinhoudt, K. Rissanen, K.A. Udachin, J. Ripmeester, Chem. Eur. J. 3 (1997) 1823.
[60] W. Jaunky, M.W. Hosseini, J.M. Planix, A. De Cian, N. Kyrisakas, J. Fischer, Chem. Commun. (1999) 2313.
[61] S. Bouoit-Montésinos, J. Bassus, M. Perrin, R. Lamartine, Tetrahedron Lett. 41 (2000) 2563.
[62] N. Ehlinger, S. Lecocq, R. Perrin, M. Perrin, Supramol. Chem. 2 (1993) 77.
[63] N. Ehlinger, M. Perrin, J. Inclusion Phenom. Macrocyclic Chem. 22 (1995) 33.
[64] P.D. Harvey, J. Gagnon, R. Provencher, B. Xu, T.M. Swager, Can. J. Chem. 74 (1996) 2279.
[65] M. Selkti, A.W. Coleman, I. Nicolis, N. Douteua-Guevel, F. Villain, A. Tomas, C. de Rango, Chem. Commun. (2000) 161.
[66] J.L. Atwood, L.J. Barbour, E.S. Dawson, P.C. Junk, J. Kienzle, Supramol. Chem. 7 (1996) 271.
[67] S.G. Bott, A.W. Coleman, J.L. Atwood, J. Am. Chem. Soc. 110 (1988) 610.
[68] P.C. Leverd, P. Berthault, M. Lance, M. Nierlich, Eur. J. Org. Chem (2000) 133.
[69] J.L. Atwood, G.W. Orr, F. Hamada, S.G. Bott, K.D. Robinson, Supramol. Chem. 1 (1992) 15.
[70] L.J. Barbour, A.K. Damon, G.W. Orr, J.L. Atwood, Supramol. Chem. 7 (1996) 209.
[71] A.W. Coleman, S.G. Bott, S.D. Morley, C.M. Means, K.D. Robinson, H. Zhang, J.L. Atwood, Angew. Chem. Int. Ed. Engl. 27 (1988) 1361.
[72] J.L. Atwood, A.W. Coleman, H. Zhang, S.G. Bott, J. Inclusion Phenom. Macrocyclic Chem. 7 (1989) 203.
[73] J.L. Atwood, L.J. Barbour, P.C. Junk, G.W. Orr, Supramol. Chem. 5 (1995) 105.
[74] A. Drljaca, M.J. Hardie, C.L. Raston, L. Spiccia, Chem. Eur. J. 5 (1999) 2295.
[75] A. Drljaca, M.J. Hardie, C.L. Raston, J. Chem. Soc. Dalton Trans. (1999) 3639.
[76] S. Shinkai, K. Araki, T. Matsuda, N. Nishiyama, H. Ikeda, I. Takasu, M. Iwanoto, J. Am. Chem. Soc. 112 (1990) 9053.
[77] J.L. Atwood, G.W. Orr, F. Hamada, R.L. Vincent, S.G. Bott, K.D. Robinson, J. Am. Chem. Soc 113 (1991) 2760.
[78] J.L. Atwood, G.W. Orr, F. Hamada, R.L. Vincent, S.G. Bott, K.D. Robinson, J. Inclusion Phenom. Macrocyclic Chem. 14 (1992) 37.
[79] S. Alrey, A. Drljaca, M.J. Hardie, C.L. Raston, Chem. Commun. (1999) 1137.
[80] G.W. Orr, L.J. Barbour, J.L. Atwood, Science 285 (1999) 1049.
[81] A. Drljaca, M.J. Hardie, J.A. Johnson, C.L. Raston, H.R. Webb, Chem. Commun. (1999) 1135.
[82] J.L. Atwood, G.W. Orr, N.C. Means, F. Hamada, H. Zhang, S.G. Bott, K.D. Robinson, Inorg. Chem. 31 (1992) 603.
[83] J.L. Atwood, G.W. Orr, K.D. Robinson, Supramol. Chem. 3 (1994) 89.
[84] A.T. Yordanov, O.A. Gansow, M.W. Brechbiel, L.M. Rogers, Polyhedron 18 (1999) 1055.
[85] M.J. Hardie, J.A. Johnson, C.L. Raston, H.R. Webb, Chem. Commun. (2000) 849.
[86] H. Iki, H. Tsuzuki, H. Kijima, I. Hamachi, S. Shinkai, Supramol. Chem. 4 (1995) 223.
[87] F. Hamada, S.G. Bott, G.W. Orr, A.W. Coleman, H. Zhang, J.L. Atwood, J. Incluison Phenom. Mol. Recognit. Chem. 9 (1990) 195.
[88] T.M. Schultz, R.G. Hazell, M. Larsen, Acta Crystallogr. Sect. C 53 (1997) 1495.
[89] O. Morikawa, M. Miyashiro, H. Yamaguchi, K. Kobayashi, H. Konishi, Supramol. Chem. 11 (1999) 67.
[90] F. Hamada, T. Fukugaki, K. Murai, G.W. Orr, J.L. Atwood, J. Inclusion Phenom. Mol. Recognition. Chem. 10 (1991) 57.
[91] K. Takenaka, Y. Obora, L.H. Jiang, Y. Tsuji, Bull. Chem. Soc. Jpn. 74 (2001) 1709.
[92] G. Reck, M. Schneider, J. Gloede, D. Vollhardt, Z. Kristallogr.-New Cryst. Struct. 214 (1999) 501 (CA 131: 279522).
[93] J. Gagnon, M. Vézina, M. Drouin, P.D. Harvey, Can. J. Chem. 79 (2001) 1439.
[94] M. Vézina, J. Gagnon, K. Villeneuve, M. Drouin, P.D. Harvey, Chem. Commun. (2000) 1073.
[95] M. Vézina, J. Gagnon, K. Villeneuve, M. Drouin, P.D. Harvey, Organometallics 20 (2001) 273.
[96] S. Ozegowski, B. Costisella, J. Glöde, Phosphorus Sulfur Silicon Rel. Elem. 119 (1996) 209 (CA 127: 234354).
[97] J. Glöde, S. Ozegowski, A. Köckritz, I. Keitel, Phosphorus Sulfur Silicon Rel. Elem. 131 (1997) 141 (CA 130: 3891).
[98] S. Shimizu, S. Shirakawa, Y. Sasaki, C. Hirai, Angew. Chem. Int. Ed. Engl. 39 (2000) 1256.
[99] A. Soi, W. Bauer, H. Mauser, C. Moll, F. Hampel, A. Hirsch, J. Chem. Soc. Perkin Trans. 2 (1998) 1471.
[100] L.J. Barbour, G.W. Orr, J.L. Atwood, Chem. Commun. (1997) 1439.
[101] W. Verboom, P.J. Bodewes, G. van Essen, P. Timmerman, G.J. van Hummel, S. Harkema, D.N. Reinhoudt, Tetrahedron Lett. 51 (1995) 499.
[102] A.L. Spek, H. Börrigter, W. Verboom, D.N. Reinhoudt, Acta Crystallogr. Sect. C 54 (1998) 1023.
[103] J.M. Harrowfield, M.I. Ogden, W.R. Richmond, A.H. White, J. Chem. Soc. Chem. Commun. (1991) 1159.
[104] M. Munakata, L.P. Wu, T. Kudora-Sowa. M. Maekawa, Y. Suenaga, K. Sugimoto, I. Ino, J. Chem. Dalton Trans. (1999) 373.
[105] W. Xu, R.J. Puddephatt, K.W. Muir, A.A. Torabi, Organometallics 13 (1994) 3054.
[106] A. Ikeda, S. Shinkai, J. Am. Chem. Soc. 116 (1994) 3102.
[107] A. Ikeda, H. Tsuzuki, S. Shinkai, J. Chem. Soc. Perkin Trans. 2 (1994) 2073.
[108] J.-O. Dalbavie, J.-B. Regnouf-de-Vains, R. Lamartine, S. Lecocq, M. Perrin, Eur. J. Inorg. Chem. (2000) 683.
[109] J. Gagnon, M. Drouin, P.D. Harvey, Inorg. Chem. 40 (2001) 652.
[110] P.D. Beer, M.G.B. Drew, C. Hazlewood, D. Hesek, J. Hodacova, S.E. Stokes, J. Chem. Soc. Chem. Commun. (1993) 229.
[111] P.D. Beer, D. Hesek, J.E. Kingston, D.K. Smith, S.E. Stokes, M.G.B. Drew, Organometallics 14 (1995) 3288.
[112] K.J.C. van Bommel, W. Verboom, R. Huslt, H. Kooijman, A.L. Spek, D.N. Reinhoudt, Inorg. Chem. 39 (2000) 4099.
[113] P.D. Beer, M.G.B. Drew, D. Hasek, K.C. Nam, Chem. Commun. (1997) 107.

[114] B.R. Cameron, S.J. Loeb, G.P.A. Yap, Inorg. Chem. 36 (1997) 5498.

[115] R. Nakamura, A. Ikeda, L.D. Sarson, S. Shinkai, Supramol. Chem. 9 (1998) 25.

[116] R.G. Khoury, L. Jaquinod, K. Aoyagi, M.M. Olmstead, A.J. Fischer, K.M. Smith, Angew. Chem. Int. Ed. Engl. 36 (1997) 2497.

[117] A. Arduini, F.F. Nachtigall, A. Pochini, A. Secchi, F. Ugozzoli, Supramol. Chem. 12 (2000) 273.

[118] V. Böhmer, H. Goldmann, W. Vogt, E.F. Paulus, F.L. Tobiason, M.J. Thielman, J. Chem. Soc. Perkin Trans. 2 (1990) 1769.

[119] H. Goldmann, W. Vogt, E. Paulus, V. Böhmer, J. Am. Chem. Soc. 110 (1988) 6811.

[120] E. Paulus, V. Böhmer, H. Goldmann, W. Vogt, J. Chem. Soc. Perkin Trans. 2 (1987) 1609.

[121] B. Berger, V. Böhmer, E. Paulus, A. Rodriguez, W. Vogt, Angew. Chem. Int. Ed. Engl. 31 (1992) 96.

[122] F. Amaud-Nue, V. Böhmer, L. Guerre, M.A. McKervey, E.F. Paulus, A. Rodriguez, M.-J. Schwing-Weill, M. Tabatabai, W. Vogt, Private communication, 1994, Cambridge Data Bank.

[123] A. Arduini, W.M. McGregor, A. Pochini, A. Secchi, F. Ugozzolo, R. Ungaro, J. Org. Chem. 61 (1996) 6881.

[124] A. Arduini, M. Cantoni, E. Graviani, A. Pochini, A. Secchi, A.R. Sicuri, R. Ungaro, M. Vincenti, Tetrahedron 51 (1995) 599.

[125] A. Arduini, W.M. McGregor, D. Paganuzzi, A. Pochini, A. Secchi, F. Ugozzoli, R. Ungaro, J. Chem. Soc. Perkin Trans. 2 (1996) 839.

[126] P. Neri, A. Bottino, F. Cunsolo, M. Piattelli, E. Gavuzzo, Angew. Chem. Int. Ed. Engl. 37 (1998) 166.

[127] J.-A. Perz-Ademar, H. Abraham, C. Sànchez, K. Rissanen, P. Prados, J. de Mendoza, Angew. Chem. Int. Ed. Engl. 36 (1996) 1009.

[128] W. Wasikiewicz, G. Rokiki, J. Kielkiewicz, V. Böhmer, Angew. Chem. Int. Ed. Engl. 33 (1994) 214.

[129] O. Struck, L.A.J. Chrisstoffels, R.J.W. Lugtenberg, W. Verboom, G.J. van Hummmel, S. Harkema, D.N. Reinhoudt, J. Org. Chem. 62 (1997) 2487.

[130] E.F. Paulus, M. Frings, A. Shivanyuk, C. Schmidt, V. Böhmer, W. Vogt, J. Chem. Soc. Perkin Trans. 2 (1998) 2777.

[131] V. Böhmer, R. Dörrenbächer, M. Frings, M. Heydenreich, D. de Paoli, W. Vogt, G. Ferguson, I. Thondorf, J. Org. Chem. 61 (1996) 549.

[132] P.E. Georgiou, M. Ashram, H.J. Clase, J.N. Bridson, J. Org. Chem. 63 (1998) 1819.

[133] J.W. Steed, R.K. Juneja, R.S. Burthalter, J.L. Atwood, J. Chem. Soc. Chem. Commun. (1994) 2205.

[134] J.W. Steed, R.K. Juneja, J.L. Atwood, Angew. Chem. Int. Ed. Engl. 33 (1994) 2456.

[135] M. Staffilani, K.S.B. Hancock, J.W. Steed, K.T. Holman, J.L. Atwood, R.K. Juneja, R.S. Burkhalter, J. Am. Chem. Soc. 119 (1997) 6324.

[136] T. Kikuchi, H. Iki, H. Tsuzuki, S. Shinkai, Supramol. Chem. 2 (1993) 103.

[137] H. Iki, T. Kikuchi, H. Tsuzuki, S. Shinkai, J. Inclusion Phenom. Macrocyclic Chem. 19 (1994) 227.

[138] H. Iki, T. Kikuchi, H. Tsuzuki, S. Shinkai, Chem. Lett. (1993) 1735.