J Incl Phenom Macrocycl Chem (2009) 65:129–136
DOI 10.1007/s10847-009-9631-9

ORIGINAL ARTICLE

Azacalix[3]arenes: chemistry and recent developments in functionalization for specific anion and cation recognition

Chatthai Kaewtong · Buncha Pulpoka

Received: 22 June 2009 / Accepted: 1 July 2009 / Published online: 28 July 2009

Abstract The design, synthesis and cation binding ability of azacalix[3]arene are summarized. Recent developments on its anion complexations and molecular devices are also added for better understanding.

Keywords Azacalix[3]arene · Synthesis · Complexation · Cation · Anion · Molecular device

Introduction

One ultimate goal in supramolecular chemistry is the development of reagents with a highly selective recognition for defined ligands since these can then be used in a diverse range of applications, such as selective sensors, catalysts, ion transports and nuclear waste diminishing. A wide variety of macrocyclic receptors have been designed, synthesized and evaluated for their ability to recognize or selectively interact with neutral, anionic or cationic species to form specific host–guest complexes. It is well known that the highly selective ligand recognition of any given receptor is related to the host–guest intermolecular interactions, and that these themselves depend strongly on a suitable size, shape and electronic interactions between the host and guest [1]. The most popular molecular frameworks used in supramolecular host–guest chemistry are the calixarenes and their derivatives [2–4].

It is widely known that **t**he calixarene descriptor is taken to designate only the basic macrocyclic framework. A bracketed number specifies the number of phenolic units that are incorporated into the framework. The first member of the calixarene family is *p-tert*-butylcalix[4]arene and early studies revealed that it exhibited no metal ion transport ability in a neutral solution [4]. To further understand the limited properties of calixarene, attempts to increase the interaction between calixarene and cations were made by incorporating heteroatoms between the methylene bridges of calixarene platforms, known as "heteroatom-bridged calixarenes" or "homocalixarene" [5].

Heteroatom-bridged calixarenes are currently used as specific indicators. The calixarene analogues, in which the CH_2 groups are completely inserted by heteroatoms, such as oxygen, sulfur and nitrogen, are called hexahomotrioxacalixarenes or oxacalixarenes (**1**) [6–10], hexahomotrithiacalixarenes or thiacalixarenes (**2**) [11, 12] and hexahomotriazacalixarenes or azacalixarenes (**3**) [13, 14], respectively (Fig. 1). In recent years, these calixarene analogues have been synthesized as part of a class of compounds called expanded calixarenes. From a structural point of view, hexahomooxacalix[3]arene and hexahomothiacalix[3]arene have a similar size to that of the 18-crown-6 but topologically they provide a 3-D cavity which can better envelop the substrates [5].

It is well known that increasing the number of coordinating sites generally gives a higher complex stability. Therefore, the oxygen and sulfur atoms on **1** and **2** have been replaced by nitrogen atoms, so as to attach more binding sites, leading to formation of the hexahomoazacalix[3]

Dedicated to Prof. Jack Harrowfield and Dr. Jacques Vicens on the celebration of their 65th birthday.

C. Kaewtong
Department of Chemistry, Faculty of Science, Mahasarakham University, Mahasarakham 44150, Thailand

B. Pulpoka (✉)
Supramolecular Chemistry Research Unit and Organic Synthesis Research Unit, Department of Chemistry, Faculty of Science, Chulalongkorn University, Bangkok 10330, Thailand
e-mail: buncha.p@chula.ac.th

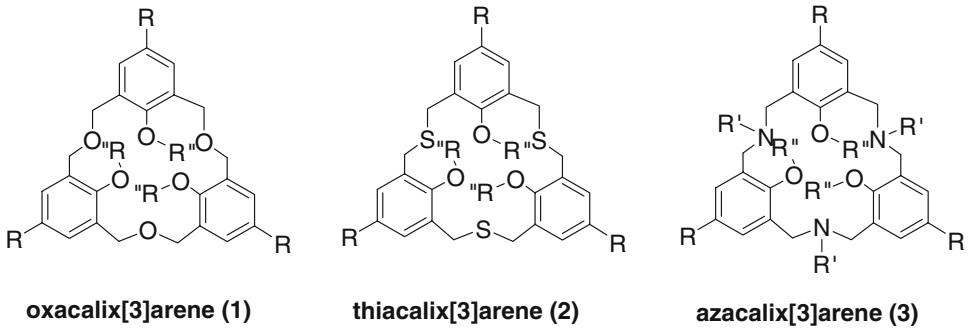

Fig. 1 Structures of heteroatom-bridged calix[3]arenes

arenes (**3**). Furthermore, the structure of azacalix[3]arenes (**3**) can be modified at not only the upper-rim (R) and lower-rim (R″), but also at the inner-rim (R′) within the macrocyclic cup [14]. As a consequence, this relatively versatile molecular platform is an interesting model for the development of selective sensors for anions, cations and/or organic molecules.

Hexahomotriazacalix[3]arenes or azacalix[3]arenes

Although the published literature on azacalix[3]arenes is more scarce than that on oxacalix[3]arenes, their chemistry is, in principle, more rich. Both the reactivity of the amino groups and the interaction of the substituents on the side arms with those on the upper and on the lower rims need to be be considered. Azacalix[3]arene can be synthesized by both one-pot and stepwise methods [13–16].

One-pot synthesis of azacalix[3]arenes: a divergent synthesis

The typical one-pot synthesis of azacalix[3]arenes involves the condensing of bis(hydroxymethyl)phenol derivatives with benzylamine by refluxing in toluene or xylene for 3 days [13, 14]. The template effect occurs in the reaction by forming OH· ·OH and OH· ·N hydrogen bonds, due to the choice of non-polar solvents used, and plays an important role in the cyclization and, thus, a high dilution technique is not required [13]. The desired cyclic trimers are obtained selectively in moderate to high yields and can usually be easily purified by simple column chromatography. The C–N bond formation in the condensation reaction between the hydroxymethylphenols and amine groups occurs under relatively mild conditions compared to that of the condensation reaction between alcohols and amines. This might be due to the fact that the reaction is not a simple dehydration reaction but rather seems to be a kind of Mannich reaction proceeding via quinonemethides [14].

The first reported azacalix[3]arene synthesized using a one-pot synthesis method was *p*-methyl-*N*-benzylhexahomotriazacalix[3]arene (**4**) [17] (Fig. 2). The azeotropic refluxing of 2,6-bis(hydroxyl-methyl)phenol in the presence of benzylamine in toluene provided azacalix[3]arene **4** at a yield of 38% after precipitation from a 4:1 (v/v) methanol:acetone mixture followed by recrystallization from a 5:1 (v/v) benzene:methanol mixture. The ease of this divergent synthesis methodology was confirmed by the subsequent successful synthesis of azacalix[3]arenes **5** [13] (Fig. 2). Note that the *p*-substituent of phenol plays important role in choosing the solvent. The alkyl substituents require a lower cyclization temperature that those of halogen substituent. Toluene is usually used for synthesis of *p*-alkylazacalix[3]arenes, while xylene is employed for preparation of *p*-haloazacalix[3]arenes [14].

Subsequentially, Hampton and co-workers [18] developed an alternative approach for the synthesis of azacalix[3]arenes (**6**) which is compatible with volatile amines

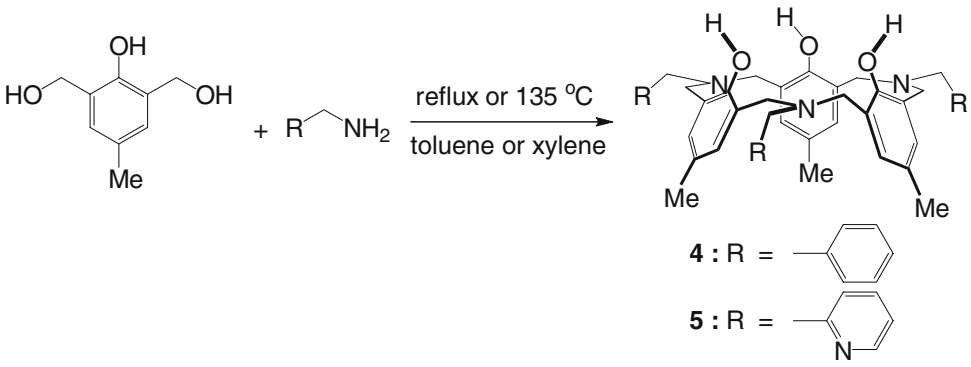

Fig. 2 First azacalix[3]arenes (**4** and **5**) synthesized by divergent synthesis

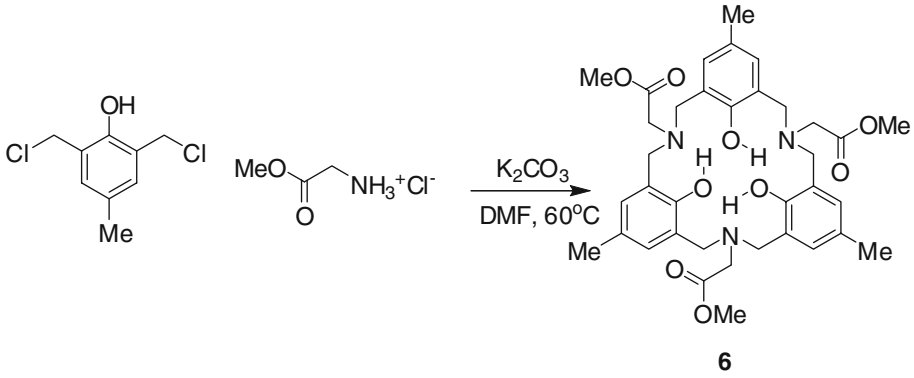

Fig. 3 Synthesis of azacalix[3]arene by using K_2CO_3 as base

and involves the cyclooligomerization reaction between 2,6-bis(chloromethyl)-4-methylphenol and glycine methyl ester hydrochloride in dimethylformamide (DMF) under high-dilution condition in the presence of potassium carbonate (Fig. 3).

Instead of using a two components synthesis, a single reagent synthesis methodology was developed (Fig. 4), where the condensation of chloromethylmethanaminium monomer **7** gave an inseparable mixture of azacalix[3]arene and azacalix[4]arene [19], but the cyclization of the aminomethylhydroxymethyl monomer **8** afforded azacalix[3]arene **9** in a reasonable yield (37%) [14]. However, the cyclization of aminomethylsalicylaldehyde derivative **10** led to a separation problem since the imine-linked macrocycles can not be easily separated by column chromatography due to their similar chromatographic properties [19].

Stepwise synthesis of azacalix[3]arenes

Due to the relatively low yield attained and the difficulty in separating azacalix[3]arene from azacalix[4]arene, Chirakul et al. [20] developed a new selective convergent synthesis of azacalix[3]arenes (**13a-d**), where the key transformation involves the coupling of the triamines with 2,6-bis-(chloromethyl)-4-methylphenol (Fig. 5). This condensation proceeds with an exceptionally high yield (~95%) and without the formation of other macrocyclic products, i.e. without azacalix[4]arene. The desired compounds (**13a-d**) were obtained with an overall yield of

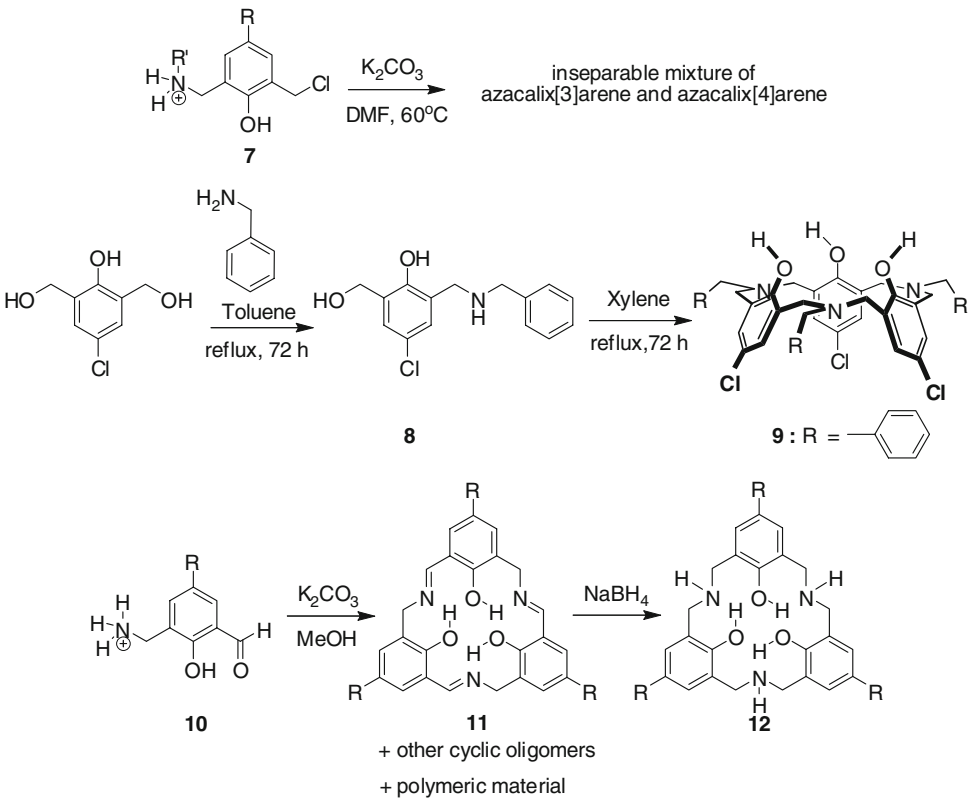

Fig. 4 Synthesis of azacalix[3]arene by passing through aminophenolic intermediates

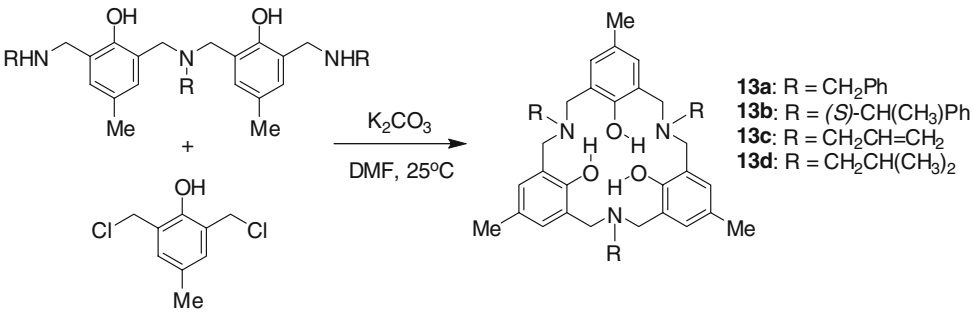

Fig. 5 Synthesis of azacalix[3]arene **13** by a coupling of triamines with 2,6-bis-(chloromethyl)-4-methylphenol

~57% starting from,6-bis-(chloromethyl)-4-methylphenol. Deprotection of azacalix[3]arene **13c** to form the *N*-unsubstituted azacalix[3]arene was accomplished by using 2-mercaptobenzoic acid with palladium complex as the catalyst [20].

Functionalization of azacalix[3]arene

Unlike calixarenes which conventional procedures of functionalization to give desired conformations were well described, a few *O*-substitutions of azacalix[3]arenes were reported up to now. Most *O*-functionalization is still over control to obtain partial cone/cone conformational selectivity [13, 14, 21, 22]. Nearly 1:1 of partial cone/cone ratio was usually obtained even a hard metal base, NaH, was used [21, 22]. Moreover, a substituent having a chain length more than 3 atoms, methoxyacetyl group, cannot prevent cone to partial cone conversion upon further modification [21]. This may be due to more flexibility of azacalix[3]arene framework than that of calix[4]arene or a different mode of aromatic flipping is used. To the best of our knowledge, the only report of a cone selective functionalization was *O*-silylation of azacalix[3]arene with 1-(trimethylsilyl)imidazol or 1,1,1,3,3,3-hexamethyidisilazane provided exclusively cone conformation while its *O*-silylation with bis(trimethylsilyl)trifluoroacetamide gave a mixture [23].

Complexation properties of azacalix[3]arenes

Although azacalix[3]arene was believed to be a promising receptor, its complexation studies have mainly been focused on cations, especially lanthanide ions, with very little information on the binding of anions or neutral compounds. Thus, the versatility of azacalix[3]arene has not been evaluated let alone substantiated, despite the fact that it provides not only cation binding sites (inner nitrogen and phenolic oxygen atoms), but also anion binding sites (phenolic groups).

Anion complexes of the azacalix[3]arenes

Normally, when azacalix[3]arene combines with cations the phenolic protons are transferred to nitrogen atoms to form intramolecular zwitter-ionic structures [24]. This is an interesting character of this molecular platform and implies that the phenolic protons can bind with anions through hydrogen bonding, which led us to investigate its ability to can bind anions.

In these anion binding studies, it was found that, after addition of 30 equivalents of anions, the color of *p*-chloro-*N*-benzylhexahomotriazacalix[3]arene (**9**) solution changed from colorless to yellow and pale yellow for fluoride and dihydrogen phosphate ions, respectively (Fig. 6). That the color changes occurred by deprotonation was supported by ^{1}H NMR spectroscopy analysis (K. Chatthai, B. Pulpoka, unpublished), and so this finding suggests that azacalix[3]arene (**9**) is a potential colorimetric sensor for anion.

Metal ion complexation of the azacalix[3]arenes

In the solid state, the receptor **6** exhibits a cone-shape with all three of its ester functional groups surrounding the cavity of the macrocycle. Although the macrocycle possesses a well defined pocket for inclusion chemistry, it does not extract alkali metal picrates because of the intramolecular hydrogen bonding which prevents both the phenolic oxygens and amines from participation in the molecular recognition processes [18].

The azacalix[3]arene macrocycles have the potential to bind trivalent metal ions to form a neutral (LM) or tricationic (LM^{3+}) complex, depending on the reaction conditions. The reaction of macrocycle **6** with a stoichiometric amount of MX_3 ($M = Sc^{3+}$, Y^{3+} or La^{3+}; $X = Cl^-$ or ^-OTf) resulted in the likely formation of $M(H_3L)X_3$ complexes. The phenolic protons are predicted to be transferred to the three nitrogen atoms and the resulting phenolate ions then bind the metal ion. This notion was supported by the analysis of the ^{1}H-NMR spectrum of the complex, which indicated an N–H signal coupling with the adjacent methylene protons [19].

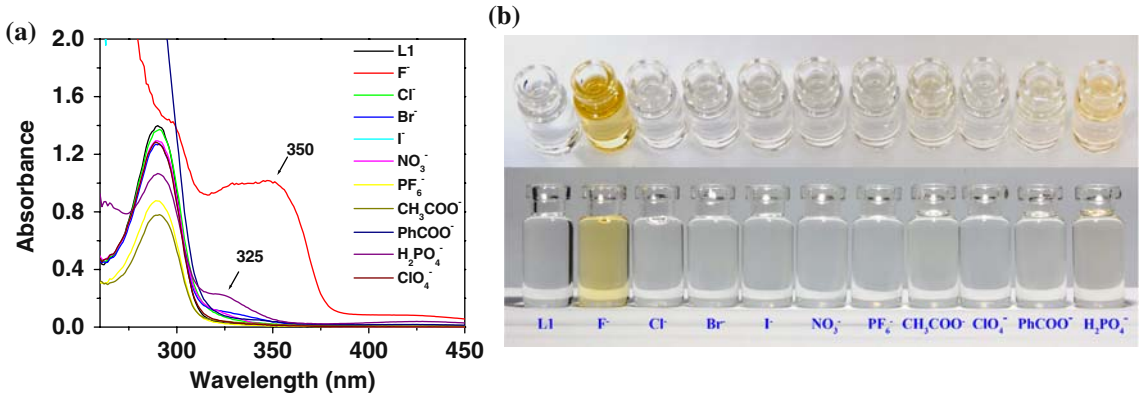

Fig. 6 (**a**) Absorption spectra of *p*-chloro-*N*-benzylhexahomotriazacalix[3]arene (**9**) solution (1×10^{-4} M in DMSO) upon addition excess of anions (30 equivalents), (**b**) its corresponding color changes

Moreover, Thuéry and coworkers [24, 25] prepared Nd^{3+}, UO_2^{2+} and Yb^{3+} complexes of azacalix[3]arene (**9**) without using any bases and succeeded in obtaining single crystals of complexes suitable for crystallographic analyses (Fig. 7). The crystalline structures strongly confirmed the phenolic proton transfer phenomena, revealing that they were deprotonated from phenolic groups and transferred to nitrogen atoms to form intramolecular zwitter-ionic structures. Due to the $NH^+ \cdot \cdot M^+$ repulsion, the metal ions are placed out of the $O \cdot \cdot NH^+ \cdot \cdot O$ plane. Evaluation of the ability of these macrocycles to extract alkali and alkyl ammonium ions revealed that *p*-chloro-*N*-benzyl-hexahomotriazacalix[3]arene (**9**) could not extract the alkaline metal ions, NH_4^+ or $PrNH_3^+$ picrates while, under identical conditions, the ligand **14**, prepared by *O*-methylation of **9** (Fig. 8), exhibited a greater extraction ability than **9**. This is likely due to the fact that the *O*-methylation of **9** eliminates the protonation of inner nitrogen atoms by phenolic protons and so results in no $NH^+ \cdot \cdot M^+$ repulsion [19].

Azacalix[3]arene (**9**) extracted UO_2^+ efficiently even in the presence of a high concentration of NaCl [25]. This ligand proved to be a weak complexant with a remarkable K^+ selectivity. In order to improve its binding efficiency, the side arm of the inner rim nitrogen of azacalix[3]arene was modified by Takemura and coworkers [13]. Its analogue, containing a 2-picolyl substituent (**7**) at the side arm, was much more effective in alkali metal ion complexation but its selectivity was very poor because of the flexibility of the picolyl side arms.

Ditopic receptor based on azacalix[3]arene

The synthesis and anion complexation of a cone conformation of N_7-hexahomotriazacalix[3]-cryptand (**15**) has been reported, and found to be able to serve as a highly selective receptor for chloride ions. After complexation with zinc ions, its selectivity can be tuned to bind bromide ions over other halide ions. This was because of the positive allosteric and ion-pair effects, as shown in Fig. 9 [22].

Recently, the partial-cone conformation of *p*-chloro-*N*-benzylhexahomotriazacalix[3]-trinaphthylamide (**16**) was selectively synthesized from both cone and partial-cone triester intermediates coupled with 1-aminomethyl-naphthalene. The crystal structures of **16** and its ester intermediate were confirmed by X-ray crystallography. Cation and anion complexation studies, using fluorescent and ^{1}H-NMR

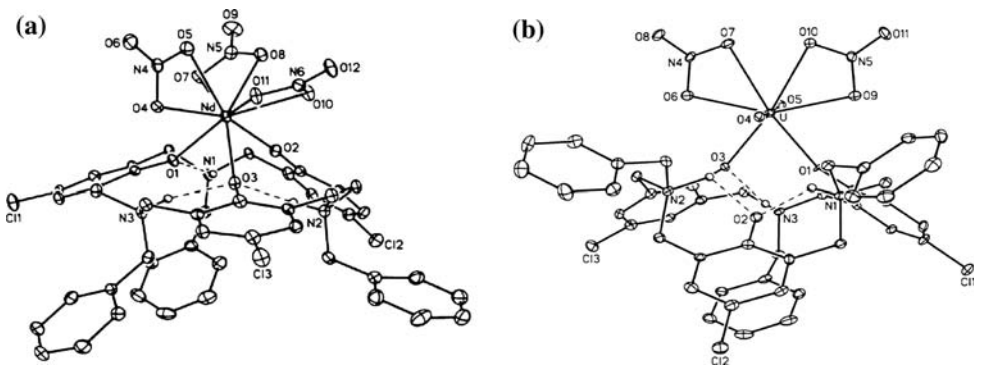

Fig. 7 View of the complex of *p*-chloro-*N*-benzylhexahomotriazacalix[3]arene (**9**) with (a) Nd^{3+} [24] and (**b**) UO_2^{2+} [25], where the hydrogen bonds are shown as dashed lines, and the ammonium group (protons are represented as small spheres of arbitrary radii)

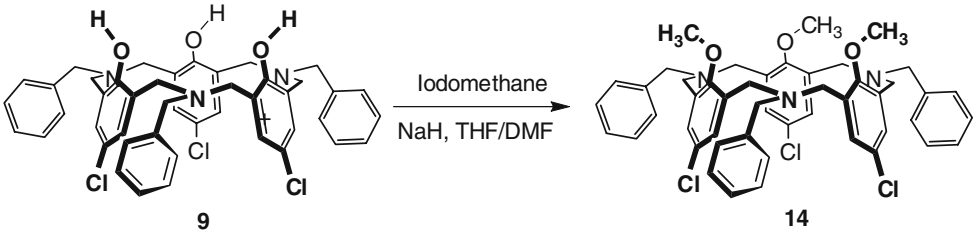

Fig. 8 Alkylation of the hydroxyl groups of azacalix[3]arene (**9**) to provide tri-*O*-methylated **14**

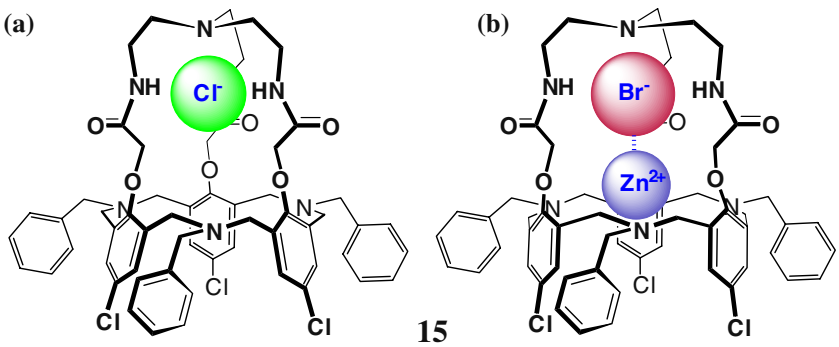

Fig. 9 Proposed structures of chloride complex and zinc bromide complex of **15** (**a**) proposed chloride ion location in **15** and (**b**) proposed bromide ion position in **15** ⊂ Zn^{2+}

spectroscopies, revealed that ligand **16** strongly bound Cd^{2+} by using the inner rim nitrogen of azacalix[3]arene, resulting in enhanced fluorescence, while Pb^{2+} was complexed by the amide groups causing a quenching of the fluorescence (Fig. 10). With respect to anion binding, receptor **16** preferred to bind F^- ions over the other anions studied, using hydrogen bonds between the NH group of the amide and the F^- anion (Fig. 10). According to UV–vis spectroscopic titrations, the high stability constants of cation binding of **16** are 4.68 and 4.53 M^{-1} for Pb^{2+} and Cd^{2+}, respectively, while the highest stability constant for anion complexation was with the F^- ion (4.21 M^{-1}) [21].

Molecular device based on azacalix[3]arene

As it is well-known that azacalix[3]arenes are good receptors for uranyl ion, the $(UO_2)^{2+}$-ion selective electrode was realized by Khan and co-workers [26]. This membrane sensor demonstrated better potentiometric response to $(UO_2)^{2+}$-ion over alkali (Na^+, K^+), alkaline earth (Mg^{2+}, Ca^{2+}, Ba^{2+}), transition and heavy metal (Co^{2+}, Ni^{2+}, Cu^{2+}, Ag^+, Zn^{2+}, Cd^{2+}, Pb^{2+}, Fe^{3+}) ions. The use of hybrid materials has attracted considerable interest as a basis for new methodologies for ion recognition and sensing. Receptor-immobilized conducting (π-conjugated) polymer materials, such as polythiophenes, polypyrroles, polyanilines, etc., have been used successfully for sensor and device applications [27–30]. A new class of chemosensor recognition elements based on *conjugated polymer network ultra-thin films* and derived from the electrochemical crosslinking of hexahomotriazacalix[3]arene-carbazole have been successfully developed (Fig. 11), while their selectivity and sensitivity towards Zn^{2+} was demonstrated using potentiometry, QCM and SPR combined with electrochemistry [31]. The results showed that *cation interactions to the film* might increase the charge carrier transport properties on *a conjugated polymer* through azacalix[3]arene bound cations. It also reduces the doping states by interfering ions through ion-ion interaction and disturbs the electron cloud on the π-extended conjugated polymer through cation–π interactions (Fig. 11). Specifically, these observed changes in the electrical and spectroelectrochemical properties of the films are related to the cation-dipole interactions between Zn^{2+} and azacalix[3]arene that result in a higher binding constant and subsequent specificity for chemical sensing [31].

Concluding remarks

Azacalix[3]arene derivatives certainly have their merits in the presence of nitrogen atoms and side arms, which can increase the potential supramolecular interactions with guest molecules. Making the appropriate ligand structures for stable and highly selective receptor molecules has, at least in some cases, been achieved. This examination provides an insight how synthetizing and modifying azacalix[3]arene can be utilized for cation and anion, as well as allosteric-species, sensing within the UV–vis, NMR, fluorescent and color changes. In addition, polycarbazole-based azacalix[3]arene immobilization was demonstrated for molecular devices. However, it is also believed that the excellent properties of azacalix[3]arene derivatives will

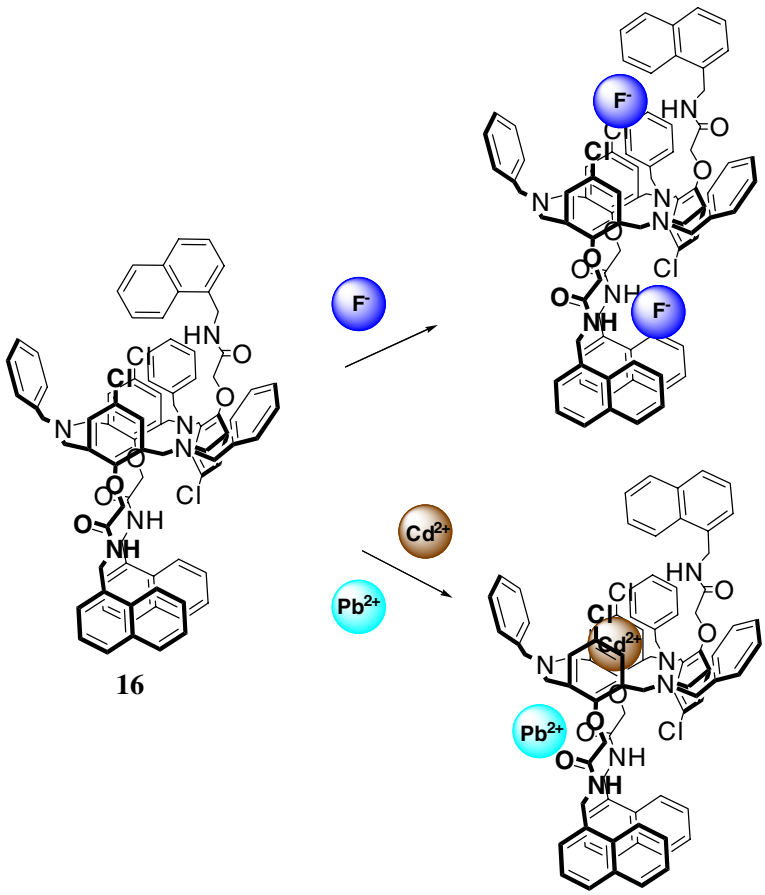

Fig. 10 Proposed binding modes of **16** with two cations (Cd^{2+}, Pb^{2+}) and the F^- anion

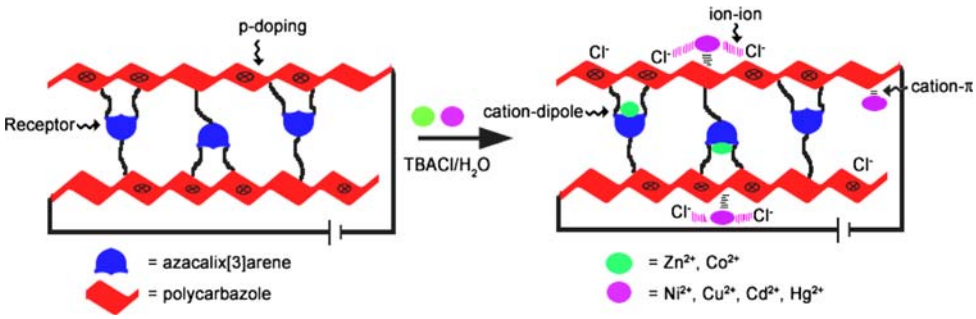

Fig. 11 Molecular device based on hexahomotriazacalix[3]arene [31]

interest many organic chemists, analytical chemists and biochemists in the future.

References

1. Lehn, J.-M.: Supramolecular Chemistry: Concepts and Perspectives. Wiley-VCH, Weinheim (1995)
2. Gutsche, C.D., Stoddart, J.F. (eds.): Calixarenes, monographs. In: *Supramolecular Chemistry*. vol. 1. The Royal Society of Chemistry, Cambridge (1989)
3. Vicens, J., Bohmer, V. (eds.): Calixarenes: A Versatile Class of Compounds. Kluwer Academic Publishers, Dordrecht (1991)
4. Vicens, J., Harrowfield, J. (eds.): Calixarenes in the Nanoworld. Springer, Dordrecht (2007)
5. Asfari, Z., Böhmer, V., Harrowfield, J., Vicens J. (eds.): Calixarenes 2001. Kluwer Academic Publishers, Dordrecht (2001)
6. Dhawan, B., Gutsche, C.D.: Calixarenes. 10 oxacalixarenes. J. Org. Chem. **48**, 1536–1539 (1983)
7. Hampton, P.D., Bencze, Z., Tong, W., Daitch, C.E.: A new synthesis of oxacalix[3larene macrocycles and alkali-metal-binding studies. J. Org. Chem. **59**, 4838–4843 (1994)
8. Ashram, M., Mizyed, S., Georghiou, P.E.: Synthesis of hexahomotrioxacalix[3]naphthalenes and a study of their alkali-metal cation binding properties. J. Org. Chem. **66**, 1473–1479 (2001)
9. Tsubaki, K., Morimoto, T., Otsubo, T., Kinoshita, T., Fuji, K.: Synthesis, structure, and ion-binding properties of new tetraoxacalix[3]arenes. J. Org. Chem. **66**, 4083–4086 (2001)

10. Masci, B., Nierlich, M., Thuéry, P.: Supramolecular assemblies from uranyl ion complexes of hexahomotrioxacalix[3]arenes and protonated [2.2.2]cryptand. New. J. Chem. **26**, 766–774 (2002)
11. Ashram, M.: Syntheses of novel hexahomotrithiacalix[3]arenes. J. Incl. Phenom. Macro. Chem. **54**, 253–259 (2006)
12. Kohno, K., Takeshita, M., Yamato, T.: Preparation of a novel C_3 symmetrical hexahomotrithiacalix[3]arene that binds Ag^+ with high selectivity. J. Chem. Res. **25**, 1–253 (2006)
13. Takemura, H., Shinmyozu, T., Miyura, H., Khan, I.U., Inazu, T.: Synthesis and properties of *N*-substituted azacalix[*n*]arenes. J. Incl. Phenom. Macro. Chem. **19**, 193–206 (1994)
14. Takemura, H.: Azacalixarenes: synthesis, complexation, and structures. J. Incl. Phenom. Macro. Chem. **42**, 169–186 (2002)
15. Khan, I.U., Takemura, H., Suenaga, M., Shinmyozu, T., Inazu, T.: Azacalixarenes: new macrocycles with dimethyleneaza-bridged calix[4]arene systems. J. Org. Chem. **58**, 3158–3161 (1993)
16. Takemura, H., Shinmyozu, T., Inazu, T.: Nitrogen-bridged macrocycles: synthesis, structures and inclusion phenomena. Coord. Chem. Rev. **156**, 183–200 (1996)
17. Takemura, H., Yoshimura, K., Khan, I.U., Shinmyozu, T., Inazu, T.: The first synthesis and properties of hexahomotriaza[3]arene. Tetrahedron Lett. **33**, 5775–5778 (1992)
18. Hampton, P.D., Tong, W.D., Wu, S., Duesler, E.N.: Synthesis, X-ray structure and alkali-metal binding properties of a new hexahomotriazacalix[3]arene. J. Chem. Soc. Perkin Trans. **2**, 1127–1130 (1996)
19. Lumetta, G.J., Rogers, R.D., Gopalan, A.S.: Calixarenes for Separations, p. 195. American Chemical Society, Washington, DC (2000)
20. Chirakul, P., Hampton, P.D., Bencze, Z.: A convergent synthesis of hexahomotriazacalix[3]arene macrocycles. J. Org. Chem. **65**, 8297–8300 (2000)
21. Kaewtong, C., Muangsin, N., Chaichit, N., Pulpoka, B.: Conformation-selective synthesis and binding properties of *N*-benzylhexahomotriaza-*p*-chlorocalix[3]trinaphthylamide. J. Org. Chem. **73**, 5574–5577 (2008)
22. Kaewtong, C., Fuangswasdi, S., Muangsin, N., Chaichit, N., Vicens, J., Pulpoka, B.: Novel C_{3v}-symmetrical N_7-hexahomotriazacalix[3]cryptand: a highly efficient receptor for halide anions. Org. Lett. **8**, 1561–1564 (2006)
23. Chirakul, P., Hampton, P.D., Duesler, E.N.: Synthesis and crystal structure of an O-silylated hexahomotriazacalix[3]arene. Tetrahedron Lett. **39**, 5473–5476 (1998)
24. Thuéry, P., Nierlich, M., Vicens, J., Takemura, H.: Crystal structure of *p*-chloro-*N*-benzylhexahomotriazacalix[3]arene and of the complex of its zwitterionic form with neodymium(III)nitrate. J. Chem. Soc. Dalton Trans. **42**, 279–283 (2000)
25. Thuéry, P., Nierlich, M., Vicens, J., Masci, B., Takemura, H.: Oxa- and azacalixarenes as ligands for uranyl ions-evidence for two different complexation modes. Eur. J. Inorg. Chem. 637–643 (2001)
26. Khan, S., Maheshwari, M., Singh, J.D.: Organochalcogen-supported azacalix[3]arenes as membrane sensor for potentiometric determination of uranyl ions. Phosphorus, Sulfur Silicon Relat. Elem. **183**, 961–965 (2008)
27. Richard, D.M.: The chemistry of conducting polythiophenes. Adv. Mater. **10**, 93–116 (1998)
28. Roncali, J.: Electrogenerated functional conjugated polymers as advanced electrode materials. J. Mater. Chem. **9** 1875–1893 (1999)
29. Janata, J., Mira Josowicz, M.: Conducting polymers in electronic chemical sensors. Nat. Mater. **2**, 19–24 (2003)
30. Bobacka, J., Ivaska, A., Lewenstam, A.: Potentiometric ion sensors based on conducting polymers. Electroanalysis **15**, 366–374 (2003)
31. Kaewtong, C., Jiang, G., Park, Y., Baba, A., Fulghum, T., Pulpoka, B., Advincula, R.: Azacalix[3]arene-carbazole conjugated polymer network ultrathin films for specific cation sensing. Chem. Mater **20**, 4915–4924 (2008)