

Review Article

Optical Spectroscopy and Theoretical Studies in Calixarene Chemistry

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Abstract

This review summarizes different applications of optical spectroscopic methods in calixarene chemistry including UV/Vis spectrometry, vibrational spectroscopic techniques (FTIR and Raman spectroscopy), luminescence spectroscopy (including fluorescence and phosphorescence), ellipsometry and various optical microscopic methods. Moreover, the results of theoretical studies (AM1, PM3, DFT, *ab initio*, etc.) are summarized based on selected papers in the field of conformational studies, thermodynamics and complexation features. About 300 references are processed systematically from the results reported mainly in the recent years with emphasis on the potential of practical application of these molecules.

Abbreviations: AFM: atomic force microscopy; AM1: Austin Model 1 (quantum chemical calculations, a semi-empirical method), it is based on the Neglect of Differential Diatomic Overlap Integral approximation.; ATR-FTIR: attenuated total reflection Fourier transform IR; BSA: bovine serum albumin; C60: [60]fullerene; C70: [70]fullerene; CE: capillary electrophoresis; CD: circular dichroism; CNDO: Complete Neglect of Differential Overlap method, it is the simplest and least accurate of the "post-Hückel" Zero Differential Overlap (ZDO) methods.; COSY: two-dimensional correlated spectroscopy, an NMR technique; CT: charge transfer; CV: cyclic voltametry; DFT: density functional theory (quantum chemical calculations); DLS: dynamic light scattering; DMSO: dimethylsulfoxide; DNA: deoxyribonucleic acid; DRIFTS: diffuse reflectance Fourier transform infrared spectroscopy; EOF: electroosmotic flow; EXSY: two-dimensional exchange spectroscopy, an NMR technique; FT-IR: Fourier transform infrared spectroscopy; GC-MS: gas chromatography-mass spectrometry (a coupled or hyphenated technique); GIXD: grazing incidence X-ray diffraction; GPC: gel permeation chromatography; HF: Hartree-Fock method (quantum chemical calculations); HPLC: high performance liquid chromatography; INDO: Intermediate Neglect of Differential Overlap method; IRRAS: IR reflection-absorption spectroscopy, also known as RAIRS, reflection-absorption IR spectroscopy; LB: Langmuir-Blodgett layer; MINDO/3: Modified Intermediate Neglect of Differential Overlap method, it is a modification of the INDO method.; MNDO: Modified Neglect of Differential Overlap (quantum chemical calculations, a semi-empirical method); MOPAC: (Molecular Orbital PACKage) is a general purpose semiempirical molecular orbital package developed by J.J.P. Stewart and co-workers. The program contains the MNDO, MINDO/3, AM1 and PM3 Hamiltonians; NACE: nonaqueous capillary electrophoresis; NLO: nonlinear optics; NOESY: Nuclear Overhauser effect spectroscopy, an NMR technique; PAHs: polyaromatic hydrocarbons; PCS: photon correlation spectroscopy; PIMM: combined self-consistent field approach (i.e. SCF)/molecular mechanics program for organic molecules and complexes; PM-IRRAS: polarization modulation IR absorption spectroscopy; PM3: Parameterized Model 3 (quantum chemical calculations, a semi-empirical method), it is based on the Neglect of Differential Diatomic Overlap integral approximation, and a reparameterization of the AM1 method; PMMA: Poly(ethylmetacrylate); RAIRS: see IRRAS; RP-HPLC: reversed-phase high performance liquid chromatography; SAM: self-assembled monolayers; SEIR: surface-enhanced IR spectroscopy; SERS: surface-enhanced Raman scattering; SLN: solid lipid nanoparticles; SPR: surface plasmon resonance; STM: scanning tunneling microscopy; *t*-Boc: *tert*-butyloxycarbonyl group; TEM: transmission electron microscopy; TRIPOS: company that produces softwares (<http://www.tripos.com/>); UV/Vis: ultraviolet-visible spectroscopy; ZINDO: This model is based on the INDO model by Prof. Zerner of the University of Florida.

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Introduction

Calixarene chemistry was born in the laboratory of David Gutsche [1, 2] by evidencing the cyclic oligomer structure of these molecules about 30 years ago, in spite of the fact that the first calixarene was already reported by Zinke and Ziegler in 1941 [3, 4]. Since then extensive work has been carried out in this field with the main emphasis on synthetic chemical development. However, the increased search for potential applications of calixarenes urges the use of different physical chemical methods including optical spectroscopic techniques to evaluate the structural and material properties, i.e. the usefulness of these artificial molecules.

This work targets the highlighting of the most recent results in the field of UV/Vis spectrometry, vibrational spectroscopic techniques (FTIR and Raman spectroscopy), luminescence spectroscopy (including fluorescence and phosphorescence), ellipsometry and various optical microscopic methods. Moreover, the results of theoretical studies (e.g. AM1, PM3, DFT, *ab initio*, etc.) are analyzed. Near-IR (NIR) and far-IR techniques, sum frequency generation (SFG) and sum harmonic generation (SHG) measurements involving calixarene derivatives were not found reported during the past few years.

A classification of the literature based on the measurement techniques would seem useful for practitioners, however, the great number of the applied methods and, especially, their diverse combinations make it almost impossible. Therefore in this review, papers are classified based on the object reported. The theoretical base of these methods, certainly, cannot be discussed in a review article, therefore, here we point to some classical sources of knowledge without the intention of completeness [5–14].

Theoretical investigations

Theory in the center

Publications dealing with the properties of calixarenes concentrate to three main areas: the conformation, the complexation and the thermodynamics of calixarenes.

The used methods are either experimental, like X-ray diffraction, NMR spectroscopy and infrared spectroscopy, or theoretical, applying several methods from molecular mechanics (MM) up to DFT calculations. This section gives survey on the state of these three areas.

Difficulties of the theoretical calculations on calixarenes. Before surveying the recent results, it is important to consider the characteristics of calixarene molecules from the point of view of modeling.

During the calculation of the molecular properties of calixarenes, one has to consider the size of these molecules. The skeleton of the calix[4]arene contains 28 carbon atoms and 24 hydrogen atoms (see Figure 1). The substitution of the hydrogen atoms with hydroxy

groups or alkyl chains, the building of bridges (crowns) in the upper rim increases drastically the number of atoms, and even more increasingly the number of the necessary wavefunctions, i.e. the size of the matrices occurring during the calculations.

These problems appeared immediately during the first attempts in this field. The capacity of the memory and the velocity of the computers restricted the calculations either to relatively simple calculation methods, and/or to the calculation of the simplest derivatives. With increasing computing capacities, the size of the computable molecules increased, however for the aforementioned reasons, still only the simple methods are applicable.

Conformational properties of calixarenes. During the last 10 years, several publications dealt with the question of the conformation of calixarenes. However, not only the conformation studies were the aim of these articles. In this short review we give a report as follows, further references are listed in the referred publications.

The parent compound calix[4]arene (Figure 1) can exist in four different conformations. The four aromatic rings can rotate around the methylene groups. Three different conformational structures can be formed. If all the four ring planes build the same angle to the axis perpendicular to the center of the C2–C8–C14–C20 plane, we have a cone with C_{4v} symmetry. If one of the rings bends down, the structure becomes partially conic (paco). In the case when two neighboring rings do so, the structure is called 1,2-altering (1,2-alt), with C_{2h} symmetry. The last possibility is the conformer with two opposite downbending aromatic rings, i.e. with 1,3 alteration (1,3-alt) having D_{2d} symmetry [14]. In the case of calix[6]arene and calix[8]arene, similar, but even more conformers are possible. The positions 25, 26, 27 and 28 are called endo ones, the positions 4–6, 10–12, 16–18

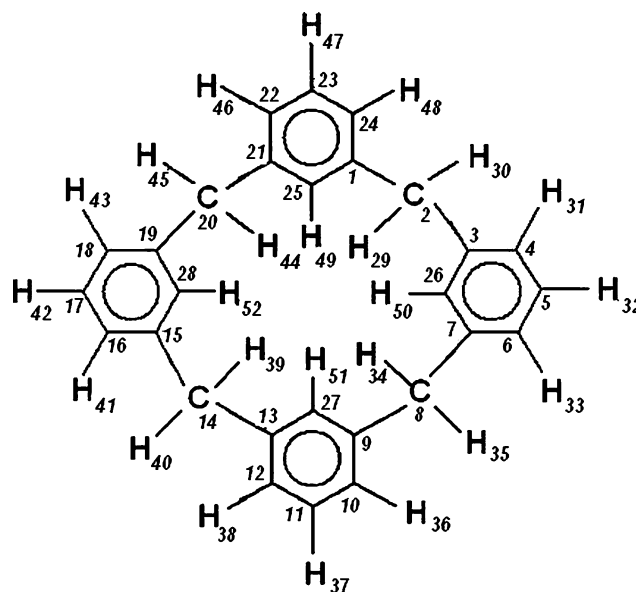


Figure 1. Calix(4)arene skeleton and its numbering.

and 22–24 ones are exo ones. The substituents in 5,11,17 and 23 positions build the upper rim, while those in 25, 26, 27 and 28 positions build the lower rim in the cone conformation.

These conformer types are strongly influenced by the substituents. The conformer studies deal with the change of the conformation under the effect of the phase (solid state or solution) and the substitution.

Soi *et al.* [14] studied the dynamic behavior of several 25,26,27,28-tetrametoxycalix[4]arene derivatives. For the determination of the substituent dependence of the conformation X-ray crystallography, 1D and 2D dynamic NMR spectroscopy and force field calculations were applied. In accordance with the molecular sizes, the molecular mechanical PIMM and the semi-empirical PM3 and MNDO calculations were carried out. These investigations revealed the preferred conformation of these compound is *paco*.

Leaving unchanged the methoxy substitution, the 5,11,17 and 23 positions were substituted with butyl groups (I) and bromines (II), respectively. The butyl groups allow the in/out change of the conformations (cone-*paco* equilibrium). This effect is hindered by the large size of the bromides. In this case only *paco*–*paco* equilibrium is possible. Solvents as guest molecules influence these equilibria. The equilibria were observed by 2D EXSY spectroscopy.

The rotational isomerism of calix[4]arene, 25,27-dihydroxy-26,28-dimethoxycalix[4]arene, and 25,26,27,28-tetrametoxycalix[4]arene in different environments were examined by Aleman and Casanovas [15] using *ab initio* and DFT calculations. Free energies in the gas phase, in chloroform, and in toluene were calculated for several minimum energy and transition state conformations. Results provide a systematic analysis of the changes induced by the partial or total OH → OCH₃ replacement in the calix[4]arene scaffold.

Liu *et al.* [16] investigated a large size lower rim substituted calixarene derivative, the 25,26-di(4-nitrobenzoate)-27,28-dihydroxy-calix[4]arene. X-ray diffraction analysis for conformation in the crystal revealed that the two nitrobenzoate substituted phenols are in almost upright positions and the two nitrophenyl groups attached to the lower rim are almost parallel to each other. The result was an 1,3-planar-2,4-upright calixarene head group.

Biali *et al.* [17] were interested in the conformation difference between endo- and exo-substituted calix[4]arenes. The studied calixarene structures were 25,26,27,28-tetrahydroxy-5,11,17,23-tetra-*tert*-butyl-calix[4]arene (I), 4,12,18,22-tetrahydroxy-5,11,17,23-tetra-*tert*-butyl-calix[4]arene (II), 4,10,27,28-tetrahydroxy-5,11,17,23-tetra-*tert*-butyl-calix[4]arene (III) and 4,10,18,22-tetrahydroxy-5,11,17,23-tetra-*tert*-butyl-calix[4]arene (IV). The I was endo-hydroxy, the II and IV were exo-hydroxy (with different substituent positions) and III was an endo/exo-hydroxy compound.

Single crystal X-ray structures were determined for alkali salts from Li⁺ to Cs⁺ of II and III. It was found

that all the salts were in 1,2-alt conformation. Besides, they calculated inversion barriers by molecular mechanical methods.

In molecules with endo-hydroxyl groups like I, the four above-listed conformations are possible. However, in the case of II, although the substituted aromatic rings were identical, two different 1,2-alt conformers existed. In one of the two hydroxyl groups were close in the ring pairs (1,2-alt[conv]), in the other they were far from each other (1,2-alt[div]). The 1,2-alt[conv] were stabilized by HO...H bonds.

Analyzing the NMR spectrum (COSY and NOESY) of III in solution, the endo endo OH groups showed minor changes in the chemical shifts but the methylene protons (connecting the rings) displayed large chemical shift differences. All the NMR data suggest the 1,2-alt form of III also in CD₂Cl₂ solution.

Hanna *et al.* [18] investigated the mono- and dianions of calix[2*n*]arenes (*n* = 2,3,4). The X-ray diffraction data of the alkali salts (from Li⁺ to Cs⁺) of the monoanions proved the large influence of the alkali ion on the structure of the calix[4]arenes. The Li⁺ salt was a monomer, the Na⁺ salt was a dimer, all other salts (those of K⁺, Rb⁺ and Cs⁺) were polymers. The investigated compounds were alkali salts of 25,26,27,28-tetrahydroxycalix[4]arene (I) and 25,26,27,28-tetrahydroxy-5,11,17,23-tetra-*tert*-butylcalix[4]arene (II) and their similarly substituted homologues. For the determination of the conformation of the first type compounds, temperature-dependent ¹H NMR measurements were carried out. For *n* = 2 the full alkali salt series, for *n* = 2,3, only from K⁺ to Cs⁺ were the NMR spectra measured. Coalescence temperatures were determined, and free energies of the conformational inversions were calculated. According to the measurements, I and II and the Li⁺ and Cs⁺ salts of I had cone conformation in deuterated solvents. The K⁺ and Cs⁺ salts of the homologue calix[6]arenes of I and II had 1,2,3-alternate conformations.

The cone conformation of the calix[4]arenes preferred binding of the K⁺ against Na⁺, while the *paco* conformers showed opposite binding properties.

A CEA publication [19] dealt with the effect of the bridge between the positions 25 and 27 on the conformation and on the alkali ion selectivity. With this bridge, the calixarene structure was blocked into the 1,3-alt conformation. By building a -(CHOH-CHOH-)_{*n*}-polyethylenglycol bridge, the best extraction result was found with the six oxygen crown. The selectivity can be influenced by the substituents.

Billes and Mohammed-Ziegler [20] calculated the molecular geometry of the cone conformer, and based on the *ab initio* HF/6-31G* calculation and on the IR and Raman measurements, carried out a normal coordinate analysis, then the full assignment and the characterization of the vibrational spectra.

Simultaneously, papers were reported about the conformational properties and simulated vibrational spectra of calix[4]arene and thiacalix[4]arene molecules

Table 1. Comparison of conformer energies of different calixarenes

Molecule	Energies relative to cone conformer (kcal mol ⁻¹)		
	Paco	1,2-alt	1,3-alt
25,26,27,28-tetrahydroxy-calix[4]arene [25]	10.5	18.3	17.7
25,26,27,28-tetrahydroxy-2,8,14,20-tetrathio-calix[4]arene [26]	10.1	16.5	13.8
Calix[4]pyrrol [33]	-11.2	-9.3	-16.0

and their *tert*-butyl derivatives, in good agreement with each other [21–23]. Recently, Furer *et al.* [24] measured the infrared spectrum of *p-tert*-buthyl-thiacalix[4]arene and calculated the equilibrium geometry and vibrational frequencies of the molecule using GC DFT/PBE functional. Based on this calculation, the complete vibrational assignment of the IR spectrum was published.

Bernardino and Cabral dealt with the conformations of calix[4]arenes [25] and thio-calix[4]arenes [26] in their publications. Structure optimizations was carried out in both cases by HF and DFT methods using several basis sets. The energies relative to the most stable cone conformers (applying B3LYP functional with 6–31G(d,p) basis set) are listed in Table 1. The order is the same in both cases but the differences are smaller for the thio compound.

Rozhenko *et al.* [27] discussed conformational features of calix[4]arenes (with 8 or 12 OH groups) with alkali metal cations (from Li⁺ to Cs⁺) based on calculations at the density functional (RI-BP86) and RI-MP2 level of approximation.

Williams *et al.* [28] studied the interaction between C₆₀ and a calix[8]arene. The endo positions of calix[8]arene were substituted with hydroxyl groups and *tert*-butyl groups were on all the eight *exo para* positions of the aromatic rings. They concluded from the ¹³C-NMR and IR spectra of the solid state complex that the pleated loop conformer could not exist. Besides, the NMR signals referred to two aromatic ring types, two different *tert*-butyl groups all with 2:6 ratio. Two types of the methylene bridge carbon atom signals were detected with 1:1 ratio. Based on these results, they found that two of the eight aromatic rings bow down. These rings were arranged with high probability in the opposite direction. Therefore, the calix[8]arene had two-winged (or in general an alternate) conformations in this complex.

Resorcinarenes are 4,6,10,12,16,18,22,24-octahydroxy-calix[4]arenes. Timmerman *et al.* [29] published a review on these compounds. Most of the resorcinarenes are substituted with heavy and/or long chains on the methylene bridges (at the 2,8,14, and 20 positions) and/or the hydroxy groups are esterified with acetic acid. These substitutions influence the form of the conformers: chair and boat-like alternate forms, and more crown-like cone forms are possible with different thermodynamic stabilities.

The relative stability of the five extreme conformations of tetraethylresorcarene was studied by *ab initio*

calculations by Makinen *et al.* [30]. The symmetric C₄ crown' conformation, having a circular array of hydrogen bonds, was identified as the most stable conformational form of the resorcarene molecule.

The conformations of inherently chiral resorc[4]arenes were studied by circular dichroism (CD) spectroscopy by Schiel *et al.* [31]. Whereas in aprotic solvents the crown conformation (C₄) was preferred, protic solvents favored the boat conformation (C₂). As a result of electronic coupling of the lowest L_β state of the resorcinol unit in the resorc[4]arene, the CD spectra showed a strong dependence on the conformation of the macrocycle. For the first time the solvent dependence of the CD spectra was qualitatively analyzed and simulated by using theoretical methods.

Sessler *et al.* [32] dealt with conformation of the calix[4]pyrrole (see Figure 2). The crystals were grown by slow evaporation from acetone solution. The single crystal X-ray diffraction analysis revealed the 1,3-alt conformation in solid state. Wu *et al.* [33] studied the calix[4]pyrrols more in details. The parent compound was the porphyrine skeleton, the porphyrinogen. Usually dialkyl derivatives are used, substituted at the 2,8,14 and 20 positions. Table 1. shows the relative energies of calix[4]pyrrol, calculated with BLYP/6–31 + G(d,p). The stability order was very different from both calixarenes and thio-calixarenes: 1,3-alt was the most stable conformer.

Complexation properties of calixarenes. The predominant part of the theoretical works dealt with the complexation of alkali metal ions, and with the selectivity of the complex formation. Less attention was paid to complexation with other metal ions, anions or organic molecules. The study of the electronic properties is interesting since these features influence strongly the complexation properties of calixarenes.

Morley and Naji [34] investigated the structure and dipole moments of a series of donor-acceptor complexes of calix[3 + *n*]arenes (*n* = 1–4). Cone conformations of the calixarenes were modeled using the AM1 method. The guest components were *N*-methylamino- and *N*-methoxy-4-nitroanilines. Nonlinear optical properties of these systems were evaluated in terms of their first hyperpolarizabilities using a semi-empirical sum-over-states approach. All of the calixarenes studied were predicted to have large dipole moments, but their hyperpolarizabilities were critically dependent on the number of excited states included in the evaluation and

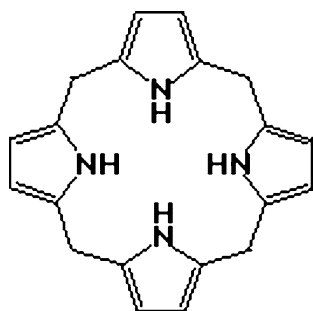


Figure 2. Calix[4]pyrrole.

on the orientation of the donor substituent. An increase in calixarene ring size had only a modest effect on the electronic properties. The limited space at the head of the calix[4]arene ring forced the substituents into unfavorable conformations in both the methoxy and methylamino derivatives; which substantially reduced the conjugation between their lone pair electrons and the pi-electron system of the respective aromatic rings to give poor hyperpolarizabilities.

Golebiewski *et al.* [35] modeled the alkali ion selectivity of benzocalixarene-21C7-crown-ethers containing on benzene substituents. DFT/B3LYP method was applied with 6-31+G* basis set. The authors focused on the Cs⁺/Rb⁺ and the Cs⁺/Na⁺ selectivities. For Rb⁺ and Cs⁺, effective core potentials (ECP) were used. The conclusion was that the determination of the parameters influence the Cs⁺ ion selectivity of these type compounds.

Golebiewski's work group [36] applied a developed method, modeling the alkali ion calixarene complex in water using quantum chemical calculation (AM1) for the main part of the complex, and the method of MM (Tip3P) for the part of less importance [36]. For modeling the water molecules, the Lennard-Jones potential was applied. Furthermore, the treated molecular size was increased to 1,3-alt-calix[4]arene-bis-crown-6. The Cs⁺ to Rb⁺ selectivity was calculated as a function of the crown size. The alkali ion – calixarene interaction energy was analyzed in terms of strain, electrostatic, polarization and van der Waals contribution. The polarization component was found about 20%. The calculated QM/MM optimized structure was in good accordance with the X-ray data.

Kane *et al.* [37] described the use of MM to model the geometry of the Na⁺ complex of a calix[4]arene tetraester, with 1,3-alt conformation.

Partial charges were assigned to the calixarene compound applying semi-empirical (AM1, PM3, MNDO, INDO, CNDO and ZINDO) calculations. The binding of the sodium ion to the calixarene was modeled using MM. The authors found very good agreement between the optimized and X-ray structures of the complex.

Bernardino and Cabral studied the complexation of alkali metal ions from Li⁺ to Cs⁺ with 25,26,27,28-tetrahydroxy-calix[4]arenes [38]. Calculations were

carried out by the HF, MP2 and DFT methods. It was found that the smaller cations, like Li⁺ and Na⁺ built complex at the lower rim of the calix[4]arene skeleton. Whereas, the larger ions (K⁺, Rb⁺ and Cs⁺) preferred higher rim of the cone conformer. In the latter case, the cations built endo-complexes with pi-electrons of the phenol rings. With potassium ion, two phenol rings participated in the complex formation.

The work of Rozhenko *et al.* [27] dealt, similarly, with the interaction of alkali cations with calixarenes, however, they focused on the effect of the number of hydroxy groups on the calix[4]arene skeleton. DFT RI-BP86 functional was applied with several large basis sets for geometry optimizations and the RI-MP2 approximation with similar basis sets for single point calculations. Three model compounds were investigated: resorc[4]arene (i.e. 4,6,10,12,16,18,22,24-octahydroxycalix[4]arene), its 2,8,14,20-teramethyl derivative and 4,5,6,10,11,12,16,17,18,22,23,24-dodecahydroxy-2,8,14,20-tetramethyl-calix[4]arene. All studied compounds preferred the crown (cone) structure with C₄ symmetry over the boat (1,3-alt) one in free (not complexed) state, as revealed from the geometry optimization. Further calculations for the optimization of alkali complex structures led partially different results. The resorc[4]arene-alkali complexes preserved the crown conformation with the exception of the Li⁺ complex. The alkali ion complexes of the tetramethyl resorcinearene derivative showed reduction of the symmetry to C₂. Further calculations led to the preference of the boat conformation or its equivalence in energy of the crown conformer. The lithium ion complexes needed a special processing since due to its small size it built complexes with the oxygen ions of the hydroxy groups.

A study on the alkali metal calixarene complexes was carried out by Casnati *et al.* [39]. In this work the crowns-6 were extended in a way that the –CH₂–CH₂– groups were changed to larger ones, e.g. 1,2-phenylene groups. The 2, 8, 14 and 20 positions were substituted by –O-isopropyl or –O-*n*-octyl groups. The aim of the work was to evidence high selectivity toward Cs⁺ in low concentration over Na⁺ present in high concentration. The structures of the alkali ion complexes were obtained in two steps: the conformation was determined by the semi-empirical PM3 method, and the equilibrium geometry of the isolated complex were positioned in the center of those four oxygen atoms of the crown that are closer to the calix. The calix[4]arene was blocked by the crown into C_{2v} symmetry. The crown moiety showed an elliptical shape, its minor axis was perpendicular to the C₂ axis (gir).

A detailed review was published by Schatz [40] about the application of *ab initio* methods for the calculation of the properties of calixarenes. One can find information about the conformations, molecular structures and complexations on calixarenes. The most important aspect of this review is that it concentrates on the

comparison of the results obtained by different computational methods. All the results suggest that the stability order is cone > paco > 1,3-alt > 1,2-alt. One can find a good summary about the stability of the different conformers of 4,6,10,12,16,18,22,24-octahydroxycalix[4]arenes. Without considering the hydrogen bonds, the boat (1,3-alt type) conformer was found the most stable, while with consideration of the secondary interactions, crown E (a cone type) conformer could be regarded as of highest stability.

The *ab initio* complexation studies on calix[4]arenes showed that the stability order of conformers was 1,3-alt > 1,2-alt > paco > cone while forming complexes with Li^+ and Na^+ ions. In the case of the K^+ complex, this order was cone > 1,3-alt > paco > 1,2-alt.

As an example how complicated systems are recently the subject of complexation studies, here is Danil de Namor's and her coworkers' publication [41]. The complexation of 5,11,17,23-tetrakis(1,1-dimethylethyl)-25,27-bis(methylthioethoxy)-26,28-bis[2-bis(diethylamine)ethoxy]calix[4]arene was investigated with silver perchlorate in solution. Using precise calorimetric measurements, Gibbs energies (ΔG) and enthalpies (ΔH) of the solvation of the aforementioned complex formation reaction were measured as a function of calixarene concentration in several polar solvents (alcohols, cyanides, tetrahydrofuran). The analysis of the standard enthalpy data was preferred in the article. The standard complex formation enthalpies of the silver complexes were $-44.39 \text{ kJ mol}^{-1}$ in methanol, $-36.34 \text{ kJ mol}^{-1}$ in ethanol, $-36.92 \text{ kJ mol}^{-1}$ in 1-propanol, and $-23.16 \text{ kJ mol}^{-1}$ in methylcyanide. These data showed a strong dependence of the complexation on the polarity of the solvent.

Wu *et al.* [33] also dealt with the *anion* complexes of calix[4]pyrroles. These compounds were able to bind F^- and Cl^- . The binding energies for the isolated molecules of cone conformation were calculated with BLYP/6-31+G(d,p). The binding energy values are $29.3 \text{ kcal mol}^{-1}$ for F^- , $42.1 \text{ kcal mol}^{-1}$ for Cl^- . By the simulation of the CH_2Cl_2 solvent at 0.0003 isodensity level, the results changed drastically, to -21.6 and $-6.4 \text{ kcal mol}^{-1}$, respectively.

The article of Dominik *et al.* [42] used the simple TRIPOS force field for the host/guest binding energy calculations on inclusion complexes of calixarenes with *organic* molecules. The guest molecules were e.g. carbon tetrachloride and benzene. Good agreement was found with the corresponding experimentally determined binding energies, in contrast with the results of some molecular mechanical methods.

Thermodynamics of calixarenes. Most of the thermodynamic studies of calixarenes, in general, deal with two fundamental tasks: the equilibrium of complex formation with alkali ions and the effects of the solvent.

Danil de Namor's group is very active in this field. They also studied and study recently the thermodynamics of the interactions of calixarenes with ions and

neutral molecules. During the investigations they change the applied calixarene host, the guest molecule or ion and the solvent.

More than 10 years ago [43] she summarized the problems in the thermodynamics of macrocycles. The role of the reaction media was pointed out in the binding properties of the calixarene esters toward the alkali metal ions. In this field, the properties of the lithium complexes have special importance for constructing high capacity accumulators.

The thermodynamics of the dissolution of calixarene derivatives substituted by polar groups at the lower rim was in the focus of Ref. [44]. The solutes are esters with *N*-di(isopropyl)carbamic acid and ethers with 2-hydroxypyridine moieties substituting all the four lower rim hydroxy groups. The applied polar solvents were nitriles, alcohols and *N,N*-dimethylformamide among others. The free energy, enthalpy and entropy of solution were calculated from solubility and calorimetric data. In some cases, formation of the solvate layer was observed. The presence of water seriously perturbs the nonaqueous system.

This work group summarized the advances on thermodynamics of calixarenes until 1998 in a review article [45]. Properties of about hundred compounds were discussed. Of course, this publication also contains their own results. In this work one can find several very useful data, i.e. tables of thermodynamic data of dissolution of *p-tert*-butyl-calix[*n*]arenes ($n = 4,6,8$) in solvents of different polarity were published. Another table showed a detailed list of equilibrium constants of lower rim calixarene derivatives with alkali ions in solution. The detailed list of stability constants with neutral species in various solvents was also included. Moreover, one can find a list of the thermodynamic parameters of complexation of calixcrown ligands with metal cations in nonaqueous solvents: equilibrium constants, free energies, enthalpies and entropies of the processes. The last table of this survey contains the properties of the protonation-deprotonation equilibria of upper rim calixarene derivatives in aqueous solutions.

During the first years of the present decade several articles were published by this group, dealing with the synthesis of calixarene derivatives, their complex building process and the structure of the complexes.

Lower rim calix[4]arene keto derivatives were studied in *N,N*-dimethylformamide and acetonitrile [46]. Stability constants and standard thermodynamic functions of the complexation with Na^+ were measured.

The new 5,11,17,23-tetra-*tert*-butyl-25,26,27,28-tetra(benzoyl)methoxycalix[4]arene compound was synthesized and its complex with Na^+ and acetonitrile was studied [47]. This molecular complex was isolated and its molecular structure was determined by X-ray diffraction. Thermodynamics of the aforementioned system was reported.

Similarly, the compound 5,11,17,23-tetra-*tert*-butyl[25,27-bis(ethylethanoate)oxy-26,28-bis(ethylthioethoxy)]-calix[4]arene was synthesized [48]. Its hosting

capacity was determined toward the metal cations Li^+ , Na^+ , Ag^+ , Ca^{2+} , Cu^{2+} , Hg^{2+} , and Pb^{2+} . The capacity was greater in acetonitrile than in *N,N*-dimethylformamide and ethanol. The effect of the pendant arms of the host molecule was discussed. Thermodynamics of the complexation process was discussed.

Conductometric and titration microcalorimetry measurements were applied for a study on the equilibria of calix[4]pyrroles (see Figure 2.) with phosphate and pyrophosphate anions [49]. Both in *N,N*-dimethylformamide and acetonitrile 2:1 type ligand:anion complexes were formed. Thermodynamic data of the equilibria were presented.

Recently, similar measurements were carried out for the investigation of complexation of 4-hydroxypyridine ethers of calix[4]arenes with several metal ions in solutions [50]. The article lists the equilibrium constants and the changes of the thermodynamic functions (free energy, enthalpy, entropy) during the solvation.

Liu *et al.* [51] published some articles about the thermodynamics of calixarene complexation during the last years. As model host molecules they used water soluble sulfonate derivatives. They studied the complexation process of 5,11,17,23-tetrasulfonato-25,26,27,28-tetrakis(hydroxycarbonylmethoxy)calix[4]arene and 5,11,17,23-tetrasulfonato-thiacalix[4]arene with La^{3+} , Gd^{3+} and Tb^{3+} cations [51]. The host:guest ratio was stoichiometric 1:1 in aqueous solution. The complexations were entropy driven. The large positive entropy change and the smaller positive enthalpy change contribute to the stability of the complexes.

In another work [52] they continued the elucidation of the complexation capability of calixarene sulfonates with calix[4]arene tetrasulfonate and thiocalix[4]arene tetrasulfonate. The guest molecules were diazacycloalkanes, i.e. piperazine, homopiperazine and 1,5-diazacyclooctane. The complexes were found enthalpy stabilized. The stability constants and the changes in the thermodynamic functions were presented. This work was continued using the same host molecules but their guests were in this case pyridinium ions [53]. The highest complex building ability showed the 2,6-dimethylpyridine/2,6-pyridinedicarboxylic acid pair. Similarly, the stability constants and the changes of the thermodynamic function for the complexation processes were determined.

Dynamics of molecular recognition. Some papers dealt with the molecular recognition, i.e. with the dynamics of the host-guest complexation.

Tokunaga *et al.* [54] studied an amphiphilic calix[6]arene as a model of the aggregate building in aqueous solution by hydrophobic interaction. The dynamic equilibria were investigated with variable temperature ^1H -NMR measurements. It was concluded that the amphiphilic calixarene molecules recognize each other and form oligomeric complexes in aqueous solution owing to hydrophobic interaction, and the large cavity size and deep hydrophobic cavity are important factors that allow the calixarenes to aggregate. The

results of NMR experiments indicate that the species and concentration of metal ions play important roles in regulating calixarenes' MD.

Danil de Namor *et al.* [47] found the special recognition behavior of the Hg^{2+} ion in acetonitrile solvent with 5,11,17,23-tetra-*tert*-butyl[25,27-bis(ethylethanoate)oxy-26,28-bis(ethylthioethoxy)]-calix[4]arene host in comparison with several other metal ions. The selectivity in the mentioned complexation of this ion is several times higher than the same of the other investigated ions.

Konovalov *et al.* [55] investigated the thermodynamics of the host-guest complex building of *tert*-butylcalix[4]arene, *tert*-butylthiocalix[4]arene, and 2,2'-bis(9-hydroxy-9-fluorenyl)biphenyl with several organic compounds in solution. They studied also the molecular recognition in these processes.

Theory for the benefit of experiments

In this chapter we tried to collect reports with emphasis on the practical point of view. It is obvious, classification of papers into this part or the previous one is rather subjective. However we feel the need to build bridge between theoretical and experimental considerations, thus this chapter was written to serve this intermediate function.

Kunsági-Máté and his co-workers achieved significant development in the field of simultaneous application of spectrofluorometric measurements and quantum-chemical model calculations [56–66]. By these methods, complex formation of calix[4]arene and calix[6]arene derivatives with benzotrifluorides [56, 57], 1-chloro-4-(trifluoromethyl)benzene [61] and phenol [64, 66] were studied. Moreover, calixarenes and nitrophenol derivatives also exhibit host-guest interactions as it was investigated by both optical spectroscopic methods and model calculations [65, 67]. Interaction between octacarboxyl derivative of calix[4]rezorcinarene and iron ions were also characterized [62, 64].

Less sophisticated methods are also often useful to support experimental work, e.g. MM or MD simulations. The $\text{p}K_a$ values for calixarenes were determined in acetonitrile by selective titration with bases using a spectroscopic method [68]. The trends in acidity were rationalized using structures generated by a DFT model. For mono-deprotonation, the degree and nature of hydrogen bonding in the anion was the dominant factor; for di-deprotonation, spatial separation of the anionic charges became important.

Equilibrium for the formation of complexes of C60 with a series of mono O-substituted calix[6]arenes were studied by absorption spectroscopic technique. The vertical ionization potentials of all the calix[6]arenes under study were estimated utilizing CT transition energy. The findings were completed by calculations using PM3 method [69]. Almost the same analysis was carried out for C70 mono O-substituted calix[6]arene systems [70].

A 1,3-alternate calix[4]arene with dipyrindyl pendants form stable $[\text{Cu}(\text{L})]^{2+}$ and $[\text{Cu}_2(\text{L})]^{4+}$ complexes with copper(II) in acetonitrile. ESR and UV/Vis data supported by MM calculations clearly indicate that in the $[\text{Cu}(\text{L})]^{2+}$ species the nitrogen atoms of dipyrindyl pendants are tetrahedrally arranged around copper(II) [71].

Ba^{3+} and Eu^{3+} complexes of a de-*tert*-butylated calix[6]arene were observed by IR and luminescence spectroscopy to determine the stoichiometry and its changes. Experimental data were supported by MM3 MM, and MOPAC quantum mechanical calculations [72].

Wasikiewicz *et al.* [73] synthesized calix[4]arenes in which opposite phenolic units are connected by a poly(oxyethylene) bridge at the narrow rim and a 2,6-dimethylene-4-nitrophenol bridge at the wide rim. These ligands were found to bind K^+ and Cs^+ selectively as it was studied by UV/Vis spectrometry. MM was used to model the geometry of the K^+ and Cs^+ complexes.

Molecular nanotubes were designed for entrapment and conversion of $\text{NO}_2/\text{N}_2\text{O}_4$ gases as studied by UV/Vis, FTIR, and ^1H NMR spectroscopies, and also molecular modeling [74]. Complexation of isoleucine with bis(dihydroxyphosphorylhydroxymethyl)-dipropoxycalix[4]-arene was studied by titration calorimetry, NMR and UV/Vis spectroscopies and in terms of molecular modeling [75].

Three new resorcin[4]arene-capped porphyrins were synthesized by Botta *et al.*[76]. Molecular modeling calculations explored the conformations and the cavity size of the three compounds and showed that their hydrophobic pockets can accommodate one molecule of water or methane, or benzene without any distortion.

Rhodium and iridium dimeric cyclooctadiene complexes with calix[4]arene upper rim diphosphines were prepared, characterized and tested for hydroformylation activity by Plourde *et al.* [77]. Molecular modeling provided evidence that ring stress favored the dimer over the monomer. Decrease in emission lifetimes of the iridium-dimer luminophor in the presence of 1-hexene was observed. The catalytic hydroformylation of 1-hexene, styrene and vinyl esters alkenes using $[\text{LRh}(\text{COD})]_2^{2+}$ catalyst precursors ($\text{L} = \text{a-c}, 9\text{a-c}$) was tested under various conditions.

Higher level calculations were also performed in some cases. Protonation and complex formation of calix[4]-cyclen-benzo-crown-6 with Cu^{2+} and Zn^{2+} were observed by potentiometric and UV/Vis spectrometric titration. Stabilization energies for protonations of this receptor, derived from *ab initio* Hartree-Fock method with 6-31G basis set, were calculated [78]. Incorporation of different guest molecules, like carboxylic acids and amides, in some pyridine[4]arenes were studied by electrospray mass spectrometry, NMR spectroscopy, and theoretical calculations, namely, density functional theory (DFT), B3LYP in the laboratory of Letzel *et al.* [79].

The 8-alkoxy-5-chloroquinoline fluorophore was appended at the lower rim of a calix[4]arene triamide with two different orientations by Casnati *et al.* [80]. The

binding properties of both ligands, investigated in chloroform and methanol solutions, indicated that they were efficient fluoroionophores, with selectivity for Na^+ and Sr^{2+} ions among alkali and alkaline earth metal ions. Combined NMR, photophysical, and modeling studies disclosed the peculiar conformational and coordination features of monovalent and divalent metal ion complexes. Lanthanide metal ion complexes were prepared and studied in acetonitrile solution showing good luminescence in the case of Nd^{3+} , Yb^{3+} , and Er^{3+} ions.

A new chiral rigid bisetherketone macrocycle containing binaphthyl and thioether moieties was synthesized by Cao *et al.* [81]. The compound was characterized by means of IR absorption and vibrational circular dichroism (VCD). The experimental IR and VCD spectra were compared with those computed based on DFT calculations at B3LYP/6-31G (d) level. Good agreement was observed between the experimental and calculated spectra, and, thus, the absolute configuration was determined.

NLO polarizations were investigated by Datta and Pati [82] for various geometric arrangements of the dipolar chromophores in a calix[*n*]arene geometry. The interactions were studied by using $(\text{HF})_3$ as model compounds both in parallel and frustrated orientations. Quantum chemical calculations at both *ab initio* and semiempirical levels, showed that the all-parallel arrangement of the dipoles exhibit the maximum magnitude for the nonlinear optical coefficients at small interdipolar angles for all interdipolar distances. Crystallographic database analysis for calix[3]arenes showed that optical properties in real molecular systems could be modeled based on their simple interaction theory.

Searching for potential applications

Potential analytical applications

A detailed survey was presented by Ludwig [83] about the role of calixarenes in analytical and separation chemistry in 2000. McMahan *et al.* [84] also published a review on the synthesis and applications of the most important calixarenes in 2003, therefore we highlight only the most recent results reported after the presentation of these reviews.

Sensing neutral molecules. In the papers of Leyton *et al.* [85, 86], polycyclic aromatic hydrocarbons (PAHs) were successfully detected at trace concentrations utilizing adsorbed self-assembled calix[4]arene molecules on silver nanoparticles studied by surface-enhanced Raman scattering (SERS) spectroscopy.

In the same laboratory [87], Surface-enhanced IR (SEIR) and SERS were employed to study the adsorption of ester functionalized *tert*-butyl calix[4]arenes on Ag and Au nanostructured surfaces as well as their complexes with pyrene. The influence of adsorption and complexation with pyrene on the host calixarene

structure was tested for two different calixarene molecules bearing carboethoxy groups ($\text{CH}_3\text{CH}_2\text{COOCH}_2$) in the low rim at positions 1,3- and 1,2,3,4-.

A selective receptor for ephedrine and a simple sensitive spot optical test for the rapid one-shot detection of ephedrine using lipid films were developed with an incorporated receptor. The lipid films provided fluorescence under a UV lamp, but the receptor quenched it. A drop of aqueous solution of ephedrine “switched on” the fluorescence, which allows the rapid detection of this stimulant in human urine at the levels of 10^{-8} M concentration [88]. Similarly, simple, sensitive spot test was evolved for the rapid detection of dopamine in human urine using lipid films with incorporated resorcin[4]arene receptor based on fluorescence quenching [89]. The technique is not based on a calibration graph but is a semi-quantitative method for the detection of dopamine in real samples of urine that can be complementary to HPLC methods. It was also found that the colors remain stable in the samples containing dopamine for periods of more than 2 months.

A comparative study of benzophenone inclusion within *p*-*tert*-butylcalixarenes, silicalite and microcrystalline cellulose was reported by Ferreira *et al.* [90]. Diffuse reflectance and laser-induced techniques were used to access photochemical and photophysical processes in solid phase. Moreover, analogous experiments were carried out with benzil(bibenzoyl), bonded by *p*-*tert*-butylcalixarenes and silicalite (a hydrophobic zeolite) [91].

The interactions between Nile Blue base and tetraundecylcalix [4] resorcinarene in two apolar solvents, dichloromethane and toluene were studied by steady state absorption and fluorescence spectroscopy supplemented by fluorescence lifetime measurements in order to determine the equilibrium constants [92]. A similar cationic dye, Oxazine 1 and the polyvalent anionic host calix[8]arenesulfonate formed two complexes in simultaneous reactions as it was shown by combined absorption and fluorescence measurements [93]. The effects of pressure were examined for the inclusion complexation of water-soluble *p*-sulfonated calix[*n*]arenes ($n = 4, 6, 8$) with Methylene Blue dye [94].

The other way round, Dimethylmethylene Blue (DMMB) could be used as probe for the spectrometric assay for the determination of concentration of *para*-sulfonato-calix[*n*]arenes and their derivatives as it was described by Rousseau *et al.* [95]. Interaction with *para*-sulfonato-calix[*n*]arenes led to a metachromatic shift in the spectrum of DMMB with appearance of a peak at 536 nm and diminution of the spectral intensity of the bands at 594 and 649 nm.

The synthesis of water soluble sulfonated calixarenes derived from *p*-benzylcalix[5,6,7,8]arenes and *p*-cumylcalix[4,6]arene along with their chlorosulfonyl derivatives were reported by Makha *et al.* [96]. Inclusion phenomena of the sulfonated *p*-benzyl- and *p*-phenylcalix[5,6]arenes towards carotenoids were also reported; ^1H NMR, UV/Vis and light scattering experiments were consistent with a model in which the carotenoid was

surrounded by two calixarenes and these supermolecules formed large aggregates, 100–150 nm in diameter.

Molecular tweezers, i.e. (thia)calix[4]arene-porphyrin conjugates, were constructed by Dudic *et al.* [97] from a (thia)calix[4]arene unit serving as a scaffold and from two and/or four porphyrin units. These molecules formed stable complexes with fullerenes in a toluene solution and exhibited selectivity towards C70. Measurements showed efficient quenching of porphyrin fluorescence emission.

Saha *et al.* [98] reported about a resorcin[4]arene host compound (with eight –OH groups) that formed charge-transfer complexes with electron acceptors including C60 and C70. By UV/Vis spectrophotometric method, CT energies and stoichiometry of the complexes were established besides enthalpies and entropies of complexation. Furthermore, Haino *et al.* [99] described a new class of fullerene sensors based on calix[5]arenes produced the highly sensitive detection of C60 and C70.

Some calix[4]pyrroles also exhibited receptor abilities toward neutral electron-deficient guests, such as 1,3,5-trinitrobenzene, tetrafluoro-*p*-benzoquinone, and tetrachloro-*p*-benzoquinone as it was studied by UV/Vis and ^1H NMR spectroscopies in solution as well as by X-ray crystallography in the solid-state [100].

Optical absorption and fluorescence emission spectroscopic techniques were employed to study the solvent effects on 2-Me-1,4-naphthoquinone (2-mNQ) and the molecular recognition of 2-mNQ in calix[8]arene by Umadevi *et al.* [101]. The orientation of 2-mNQ on Ag surface was analyzed by SERS. The evidence for the formation of inclusion complexes of calix[8]arene with 2-mNQ in CH_2Cl_2 was obtained by optical absorption and fluorescence emission experiments.

A functionalized calix[4]arene exhibited typical naphthalimide fluorescence bands in nonpolar solvents. Its ability to interact with guest species was verified with absorption and fluorescence measurements using *N*-ethanol-1,8-naphthalimide as guest species [102].

Zhou *et al.* [103] reported that the characteristics of host–guest complexation between *p*-sulfonated calix[4]arene and lomefloxacin were investigated by fluorescence spectrometry. 1:1 stoichiometry was established for the complexation. A novel sensitive spectrofluorimetric method for the determination of lomefloxacin was developed with a linear range of $0.01\text{--}3.0 \mu\text{g ml}^{-1}$ and a detection limit of $0.008 \mu\text{g ml}^{-1}$. The proposed method was applied satisfactorily to determine lomefloxacin in pharmaceutical preparations.

Some cyclopenta[2,1-*b*; 3,4-*b'*]bithiophenes differently substituted at the four position with a calix[4]arene group were synthesized and electrochemically polymerized by anodic coupling by Rizzo *et al.* [104]. The polymers were characterized by cyclic voltammetry (CV), UV/Vis and FTIR spectroscopy. Quartz crystal microbalance analysis showed strong affinity and selectivity of the polymers for toluene and acetone from the gas phase.

Zyryanov *et al.* [105] presented an approach toward visual detection of $\text{NO}_2/\text{N}_2\text{O}_4$, employing simple calix[4]arenes. It was based on that exposure of tetra-*O*-alkylated calix[4]arenes possessing either a cone or a 1,3-alternate conformation, to $\text{NO}_2/\text{N}_2\text{O}_4$, both in chloroform solution and in the solid state, resulted in deeply colored calixarene-nitrosonium (NO^+) complexes. Some isolated complexes were characterized by UV/Vis, FTIR, high-resolution ^1H NMR spectroscopy and elemental analysis. Preliminary, it was evidenced that reaction of NO_2 with simple calix[4]arenes in chloroform in the presence of a Lewis acid rapidly results in intense coloration caused by the encapsulation of nitrosonium cation [106].

Similarly, Rosokha *et al.* [107] developed bridged diarenes (including calixarenes) that formed very strong [1:1] complexes with nitrosonium/nitric oxide in which the NO moiety was optimally sandwiched in the cleft between a pair of cofacial aromatic rings which acted as a molecular “Venus flytrap”. The spectral features of these associates were generally similar to those for [1:1] and [2:1] nitrosonium complexes with mononuclear alkyl-substituted benzenes.

Spectrofluorometric titrations were performed by Zhou *et al.* [108] to investigate the inclusion behavior of *p*-sulfonatocalix[4]arene (SC4A) and 9-amino-acridine (AA) in citrate buffer solution (pH 5.92). It was found that the fluorescence intensity of AA quenched regularly upon the addition of SC4A. The inclusion ratio was 1:1 and the inclusion constant was $1.84 \times 10^5 \text{ L mol}^{-1}$ at 25.0 °C.

Amines, ammonium ions, amino acids. Abraham [109] reviewed results obtained with the complexation of various calix[*n*]arenes and five structural types of organic cations, namely ammonium ions, quaternary ammonium ions, phosphonium ions, iminium ions and tropylium ions in 2002. General considerations on complex forming properties of calixarenes as carriers in transport through liquid membranes of different biological amine compounds (e.g. ammonium ion, amines, amino acids, and peptides) were presented recently in detail by Mutihac *et al.* [110].

Spun films of nitrophenylazo-derivatives of calix[4]arene were studied as gas phase optical sensors for organic amines. A bathochromic shift of the visible absorption band was observed as the chromogenic calix[4]arene film was exposed to amine vapors. The effect was the largest for the primary amine, less for the secondary, and the least for the tertiary amine [111]. A mechanism based on deprotonation of the azophenol group is proposed. This mechanism is consistent with experimental observations as well as results from molecular simulations [112].

Novel calixarenes were designed to behave as fluorescent molecular sensors capable of distinguishing between chiral amines [113] or amino acid anions [114] on the basis of their size and/or chirality. Complex formation of calixarenes with amines are often studied by UV/

Vis spectroscopy [115–118]. The interactions of calix[6]arene and *p*-*tert*-butylcalix[6]arene with aliphatic amines was studied in acetonitrile solution by spectrophotometric titrations in the UV region and by ^1H NMR spectrometry. It is based on that calix[6]arenes can undergo two deprotonations by aliphatic amines and the extent of the second proton transfer is mainly governed by the size of the α -substituent of the amine [115]. This mechanism was also evidenced by FTIR measurements [119]. These findings are analogous with that reported earlier by Brouwer *et al.* [120]. A novel structure involving a 2(*p*-*tert*-butylcalix[4]arene)·3.5(1,4-butanediamine) inclusion compound showed amine sites both exo and endo to the cavity, with the amine hydrogen-bonding to itself as well as to the host hydroxyl groups; for bulky amines with large $\text{pK}(\text{a})$ values, steric factors were more important than basicity, and the formation of a 1:1, high-symmetry host–guest structure was preferred over a low-symmetry hydrogen-bonded structure [120].

Some scientists also reported enantiomer selectivity of calixarenes based on UV/Vis detection [121]. Absorption, fluorescence, and CD spectroscopic studies were performed on the chiral recognition of the enantiomers of α -methylbenzylamine and phenylglycinol by a binaphthyl-derived chromogenic calixcrown host [122].

A new method for the fluorometric detection of the neurotransmitter acetylcholine in water was presented by Jin [123]. Use of the fluorescence of dansylcholine bound to *p*-sulfonated calix[8]arene afforded a new fluorometric method for the detection of acetylcholine.

A fluorescent poly(phenylene ethynylene) containing calix[4]arene-based receptor has a sensitivity to quenching by *N*-methylquinolinium ion [124].

Metal ions. Alkali/alikaline earth ions. The complex formation of calixarenes with metal ion is also a widely studied area. A fundamental study was carried out, for instance, in which the complexation of tri-*o*-propyl-*p*-*tert*-butyl-calix[4]arene with Li^+ , Na^+ , K^+ , Rb^+ , and Cs^+ were studied in carbon tetrachloride, using UV/Vis spectrophotometric techniques [125].

Complexation of alkali metal cations with 5,11,17,23-tetra-*tert*-butyl-26, 28,25,27-tetrakis (*O*-methyl-*D*- α -phenylglycylcarbonylmethoxy) calix[4]arene (L) was studied by means of spectrophotometric, conductometric and potentiometric titrations as it was reported by Tomišić *et al.* [126]. Despite the presence of intramolecular $\text{NH}\cdots\text{O}=\text{C}$ hydrogen bonds in L, which need to be disrupted to allow metal ion binding, this calix[4]arene amino acid derivative was shown to be an efficient binder for smaller Li^+ and Na^+ cations in acetonitrile, moderately efficient for K^+ , whereas larger Rb^+ and Cs^+ did not fit in its hydrophilic cavity.

As shown, ditopic calix[4]biscrown containing 1 or 2 dioxocoumarin fluorophores could form 1:1 and 2:1 (metal:ligand) complexes with Cs^+ [127]. Kim and his co-workers [128] prepared 1,3-alternate chromogenic

azo-coupled calix[4]biscrowns, which exhibited UV/Vis band shift upon metal ion complexation and it revealed K^+ or Cs^+ ion selectivity. In the same laboratory [129], calixcrown-6 compounds carrying a pair of phenylazo moieties on the upper rim and two OH groups, one OH group, and two OR (R = C1-8-alkyl) groups on the lower rim were prepared in both the cone and partial cone conformations. UV/Vis spectral measurements showed a red shift upon the addition of Ca^{2+} to the calixcrown carrying two OH groups and a blue shift for the calixcrown carrying two OR groups.

New water-soluble calix[4]arene-bis(benzocrown-6) derivatives were synthesized by Pellet-Rostaing *et al.* [130], and applied for Cs^+ - Na^+ separation by nanofiltration-complexation. Stability constants were determined by UV/Vis spectroscopy. A novel azo-pyridyl calix[4]arene was synthesized in the 1,3-alternate conformation. The synthesized chromoionophore gave a large bathochromic shift (119 nm) on addition of a methanolic solution of Cs_2CO_3 [131].

Four novel calix[4]crowns-4 and calix[4]crowns-5 with two pendant groups were synthesized, their exhibited selectivity for Na^+ and K^+ . The measurement of UV and fluorescent spectra of the hosts and their complexes revealed that calix[4]crowns-4 with the 6-methoxy-2-naphthoylmethyl pendant groups could be utilized as a selective photophysical sensor for Ca^{2+} [132].

Liu *et al.* [133] reported on the complex formation of novel double-armed calix[4]arene derivatives (R = 4- O_2N , 2- O_2N , 4-Cl) containing alternated *O*-phenylazo-salicylideneaminoethyl arms. The UV/Vis spectra showed that the complexation of these ligands exhibited remarkable bathochromic shifts with Na^+ accompanied by a unique color change in the solution from yellow to red upon complexation and they show selectivity for Na^+ with respect to K^+ , Rb^+ and Cs^+ in acetonitrile-water (99:1/V:V) solution.

The synthesis of a ditopic fluorescent sensor for cations associating a 1,3-alternate calix[4]bisazacrown-5 as an ionophore and substituted boron-dipyrromethene dyes as fluorophores was reported [134]. Photophysical studies revealed that in medium and high polarity solvents an efficient charge transfer reaction occurred in the excited state leading to a dual emission and a strong quenching of fluorescence. The stability constants of complexes with Na^+ , K^+ , Cs^+ , Ca^{2+} and Ba^{2+} cations were measured in acetonitrile and ethanol. A test under physiological conditions was successfully achieved.

From the UV and fluorescent spectra of some novel calix[4]crowns with two pendant groups, it was showed that the cation was encapsulated inside the preorganized ionophoric cavity defined by carbonyl oxygens, the crown ether and the phenoxy oxygens [135]. Remarkable cation-induced photophysical effects ensured the opportunity for these molecules to be utilized as a selective fluorescent sensor for Ca^{2+} .

A series of mixed [2+2'] *p*-*tert*-butylcalix[4]arene were also synthesized. The extraction and complexation

properties of these calixarenes were observed towards alkali and alkaline earth metal cations in acetonitrile by means of UV spectrophotometry and 1H NMR spectroscopy [136].

Cha *et al.* [137] prepared a new fluorogenic ionophore by conjugating calix[4]-crown-5 ether with boron-dipyrromethene fluorophore. The ionophore exhibited a pronounced selective ON-OFF type response toward Ca^{2+} ions over other physiologically important metal ions like Na^+ , K^+ , and Mg^{2+} .

Baklouti *et al.* [138] reported about the complex formation of four dimalonate and one diester calix[4]-arene derivatives toward alkali and alkaline earth cations as it was investigated in acetonitrile by means of UV spectrophotometry and supported by 1H -NMR and FAB^+ MS measurements.

Thermal conversion of a new spiropyran-calixcrown derivative from merocyanine to the spiropyran form was studied in ethanol and in acetonitrile by UV/Vis spectroscopy [139]. Moreover, chromogenic 1,3-calix[4] (crown-5 and -6) ethers containing azophenol and indophenol or indolo-spiropyran signaling groups were synthesized and their optical recognition was investigated toward alkali and alkaline earth metal cations by UV/Vis spectrophotometry. A calcium ion preference was found to be characteristic of most ligands [140]. The synthesis of benzothiazolium derivative of calix[4]arene (merocyanine-type chromoionophore) were described by Kim *et al.* [141] and its calcium-selective chromogenic ion binding properties were observed using UV/Vis spectroscopy.

A photochromic 1,3-calix[4]arene compound with spirobenzopyran groups was obtained and the photochromism was studied under alternating irradiation with UV and visible light in acetonitrile. The compound may be applied as a photochromic material for the high thermal stability of its colored forms since the addition of metal ions (Mg^{2+} , Ca^{2+} , Eu^{3+}) decreased the thermal decoloration rate constants to different extents [142].

Metal-chelating properties – in the ground and excited states – of fullerencalix[4]arenes containing four alkyl ester chains at the lower rim were studied by means of steady-state absorption, fluorescence spectroscopy, and time-resolved transient absorption spectra. Direct interactions between Ag^+ and the surface of C60, and the indirect effect of Na^+ , Mg^{2+} , and Ba^{2+} stemming from the coordination in the calix[4]arene cavity were evidenced [143].

FTIR techniques were found suitable for the differentiation between alkali/alkaline earth cations and thallium ions based on the complex formation of these ions with ester-type calix[4]arene derivatives [144, 145]. Complex formation of the same ligands were studied in detail by 1H and 7Li NMR spectroscopy complemented by UV/Vis measurements [146].

Yaftian *et al.* [147] reported stability constants of alkali metal complexes of *O*-substituted calix[4]arenes determined by UV/Vis spectroscopy in methanol. The

amide-containing calixarenes were found to be more efficient for alkali metal complexation than those bearing ester substituents. With all four ligands, the lowest stability constants were found for the Li^+ and Cs^+ ions.

Casnati *et al.* [148] studied naphthyl, binaphthyl, and dansyl calix[4]arene-crown-6 derivatives bearing a fluorophoric unit on the ether bridge. All these compounds coordinated alkali metal picrates in chloroform, and the naphthocrown also showed high efficiency for Cs^+ ion binding. For naphthyl and binaphthyl containing ligands a luminescence intensity decrease was observed upon cation binding, which allowed an easy detection of Cs^+ even at very low concentrations (10^{-7} M).

A novel multi-responsive host, in which two ester and two polyether moieties, two urea sites, and two bipyridine units as ion binding sites were arranged on the calix[4]arene skeleton, was found to recognize Na^+ and Ag^+ simultaneously and to capture an anionic guest as studied by UV/Vis spectroscopy [149].

The excimer fluorescence of a new chemosensor with two different types of cation binding sites was quenched by Pb^{2+} , but revived by addition of K^+ to the Pb^{2+} ligand complex [150]. Furthermore, *p-tert*-butylcalix[4]arene-crown-6 derivatives were able to complex alkali, alkaline earth and some “softer” cations as it was shown by using these compounds as ionophores in ion-selective membrane electrodes. The complexing properties of the two cone and partial cone conformers of some compounds in the PVC membrane were compared with those in acetonitrile solution studied by UV absorption spectrophotometry [151].

The ion-transport behavior of methacrylic-acrylic-based polymers for ion-selective electrode (ISE) membranes was investigated by a spectrophotometric method to determine the apparent diffusion coefficient by Heng *et al.* [152]. By observing the degree of deprotonation of the chromoionophore or chromogenic ionophore, the extent of penetration of cations into the polymer films was determined. The transport of the cations into the optode films depended on the stoichiometry of complexation by the ionophores. The apparent diffusion coefficients, estimated from the deprotonation data, were of the order of 10^{-12} to 10^{-11} $\text{cm}^2 \text{s}^{-1}$.

Heavy metal ions. A review on transition metal complexes of calixarenes were published at the beginning of 2005 [153]. Therefore we lay stress mainly on the latest results in this section.

A new calix[4]arene-based fluorescent compound with two thio-ether groups as ionophore and one 3-alkoxy-2-naphthoic acid moiety as fluorophore were designed by Liu *et al.* [154]. The macrocycle exhibited highly selective binding of Cu^{2+} over alkali, alkaline earth and some transition metal ions, including Co^{2+} , Ni^{2+} , Zn^{2+} , Mn^{2+} , Cd^{2+} , Pb^{2+} , Hg^{2+} , Ag^+ , Cu^+ , in methanol:water = 2:1 mixture within wide pH region. Similar work was presented by Yang *et al.* [155], who synthesized a fluorescent compound based on calix[4]arene skeleton. The complexation ability of that calix-

arene with transition metal ions, such as Fe^{3+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} and Ag^+ , was investigated by UV/Vis and fluorescent spectra.

Wang *et al.* [156] reported results on ion-binding properties of several new nitrogen-containing calixarene derivatives investigated by UV/Vis spectroscopy and solvent extraction. Some of these molecules bound Pb^{2+} in tetrahydrofuran.

With the aim of optical sensing of Hg^{2+} in water, a calixarene bearing two dansyl fluorophores was grafted on a large pore mesoporous silica material (SBA-15) and the study of its complexing and fluorescence properties are reported by Metivier *et al.* [157]. This system offers a high selectivity over several interfering cations (Na^+ , K^+ , Ca^{2+} , Cu^{2+} , Cd^{2+} , Pb^{2+}). The same research group [158] reported on Pb^{2+} and Hg^{2+} selective calixarene-based fluoroionophores.

Dessingou *et al.* [159] reported that the bis- $\{N$ -(2-hydroxynaphthyl-1-methylimine) $\}$ anchored 1,3-*di*-derivative of lower rim *p-tert*-butyl-calix[4]arene possessing a N_2O_2 , N_2O_4 or N_2O_6 binding core was found to be selective for Zn^{2+} ions by eliciting fluorescence-on behavior while the other ions, e.g. Ti^{4+} , VO^{2+} , Cr^{3+} , Mn^{2+} , Fe^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Mg^{2+} , Cd^{2+} and Hg^{2+} caused no change in the fluorescence. The reaction between one of the ligands and Zn^{2+} was found to be stoichiometric with the formation of a 1:1 complex; while H^+ quenched the fluorescence of the complex, OH^- restored it. The studies of the 1:1 isolated complexes of Zn^{2+} , Ni^{2+} and Cu^{2+} augmented the results.

A porphyrin derivative of calix[4]arene formed Zn_2L -type zinc complex, which exhibited characteristic photophysical properties dependent on the conformation of the ligand [160]. Oueslati *et al.* [161] reported the synthesis of six calix[4]arenes functionalized with 2,2'-bipyridyl and azophenyl groups at the lower rim and the upper rim. Their complex forming properties towards Zn^{2+} were determined by UV/Vis titrations in organic media.

Among other analytical methods, diffuse reflectance Fourier transform IR (DRIFTS) spectra and Raman scattering spectra were applied to study the ion binding ability of calixarene modified polysiloxane resins towards Cu^{2+} , Pb^{2+} and Hg^{2+} ions [162].

Chromogenic properties of calix[4]arenes were studied by UV/Vis spectra and some of them showed substantial bathochromic shifts upon the addition of soft metal ions, such as Hg^{2+} , Cr^{3+} , and Cu^{2+} [163]. A new water-soluble Cr-selective chromogenic azocalix[4]arene formed the base for a simple and selective spectrophotometric method to determine the concentration of Cr^{3+} [164].

Complexes of M(II) -perchlorate (for $\text{M} = \text{Co}$, Ni , Cu , Zn) and chloride (for $\text{M} = \text{Cu}$, Zn) transition metal salts with a calix[4]arene derivatives were studied by Videva *et al.* [165]. The coordination mode and structure of the complexes were studied by several spectroscopic and magnetochemical methods, both in the solid state and in solution.

Two dipyriddy pendant groups were attached to the 1,3 positions of a calix[4]arene, with the purpose of having a ligand able to complex Cu^{2+} and Co^{2+} [166]. Indeed, the new ligand, fixed in its 1,3-alternate conformation, formed stable complexes with both Cu^{2+} and Co^{2+} , as shown by UV/Vis titrations in acetonitrile.

Crown ether-bridged calixarenes behaved as fluorescent complexing agents for transition metal cations as it was evidenced by their UV/Vis and fluorescence spectra as well as their fluorescence decay [167]. Moreover, Bagatin *et al.* [168] described the luminescence behavior of bis(8-quinolinylxypropyl)calix[4]arene. In the presence of Zn^{2+} ions, coordination of the quinoline groups was observed leading to characteristic changes in the absorption, fluorescence and NMR spectra. In the resulting complex, a significant decrease in the emission quantum yields took place. However, by incorporating an additional bathophenanthroline ligand, a great emission enhancement was detected, revealing the occurrence of synergistic effects in the formed zinc(II)-complex.

The synthesis of a new series of β -ketoimine calix[4]arene derivatives were described by Halouani *et al.* [169]. The complexation properties of the keto imines were investigated toward different metal ions by UV/Vis titrations in organic media. These novel receptors selectively complexed Cu^{2+} , Hg^{2+} , and Ag^+ . Moreover, the extraction properties of this ligand toward cations was studied by liquid-liquid extraction and atom absorption spectrometry. It had good affinity and selectivity toward Pb^{2+} .

A new calix[4]crown chemosensor based on dual sensing probes revealed Pb^{2+} ion selectivity over other metal ions, which arises from a hypsochromic shift of azo units in UV spectrum as well as a fluorescence enhancement of pyrenyl parts in fluorescence spectrum [170].

Kumar *et al.* [171] reported about the synthesis of bis-calix[4]arenes containing different aromatic and heteroaromatic moieties. The studies of complex forming behavior of these macrocycles evidenced that these bis-calix[4]arenes bind Ag^+ selectively over other metal ions as it was observed by liquid-liquid extraction, NMR and IR spectroscopy.

As a novel sensing system, *N*-(1-pyrenylmethyl) amide-appended calix[4]crown-5(2) and crown-6(3) were newly synthesized. Judging from the fluorescence changes upon the addition of cations, one of the studied ligands having crown-6 ring showed Pb^{2+} ion selectivity over other cations tested regarding fluorescence quenching [172].

Lanthanide and actinide ions. A calix[4]arene derivative bearing two spirobenzopyran moieties could recognize lanthanide ions, and alternating irradiation with UV and visible light controlled the ligand-to-metal charge transfer and energy transfer of the host- Eu^{3+} complexes, thus, the system had potential to be applied as molecular logic switch [173]. A four phosphonic acid bearing calix[4]arene based ligand was used as an

extractant for certain lanthanide ions (La^{3+} , Eu^{3+} , Yb^{3+}) [174].

Liu *et al.* [175] reported a new fluorescent probe based on calix[6]arene that was functionalized with three naphthoic acid groups and showed selective fluorescence enhancement in the presence of La^{3+} and Y^{3+} . Similarly, complexation and spectroscopic behavior of three *p-tert*-butylcalix[4]arene Schiff bases were studied with lanthanoid nitrates (Tb^{3+} and Eu^{3+}) in anhydrous acetonitrile by using UV/Vis and FTIR as well as fluorescence spectra [176].

Synthesis and photophysical properties of novel luminescent Ru^{2+} bipyridyl complexes containing one, two, or six lower rim acid-amide-modified calix[4]arene moieties covalently linked to the bipyridine groups were reported which are designed to coordinate and sense luminescent lanthanide ions [177].

Two calix[4]arene isomers with benzaldehyde moieties were synthesized and their crystal structures were determined by X-ray crystallographic study by Wang *et al.* [178]. The photophysical behavior on complexation of calix[4]arene derivatives was investigated with terbium(III) nitrate in anhydrous acetonitrile at 25 °C by UV/Vis and fluorescence spectroscopies.

Zhang *et al.* [179] reported on the complexation and luminescence behavior of a water soluble calix[4]arene derivative with lanthanoid ion (Tb^{3+}) observed in gelatin solution at 25 °C by using UV/Vis and fluorescence spectra. Absorption and fluorescence spectral analysis showed that the -COO- groups of gelatin had a definite binding ability to Tb^{3+} , and thus, gelatin could compete in binding with the calix[4]arene derivative upon complexation with Tb^{3+} .

Hexakis(dimethylphosphinomethoxy)calix[6]arene was synthesized and studied by temperature dependent ^1H and ^{31}P NMR spectroscopy in DMSO- d_6 [180]. Stability constants with La^{3+} was determined by UV/Vis spectrophotometric titration in acetonitrile. The corresponding complexes with La^{3+} , Eu^{3+} , Gd^{3+} and Tb^{3+} were isolated and characterized.

Horiuchi *et al.* [181] studied the energy-transfer luminescence of complexes formed between Tb^{3+} and calix-, thiacalix-, and sulfonylcalix[4]arene-*p*-tetrasulfonates, and applied them to an ultratrace determination of Tb^{3+} .

Klimchuk *et al.* [182] reported on a new series of cone-shaped tetraalkoxycalix[4]arenes substituted at the wide rim with four phosphomethyl groups. Their binding properties towards Eu^{3+} and Am^{3+} cations were investigated by the liquid-liquid extraction method.

In the report of Hidayat *et al.* [183], incorporation of lanthanide ions in polymerizable macrocyclic molecules, such as calixarene and calix-resorcinarene monomers, were studied by ^1H NMR and fluorescence spectroscopies. The complexation resulted in broadening of fluorescence peak and elongation of the fluorescence decay, which are attributed to increasing anisotropy of ligand field due to this complexation.

Complexing properties of some chromogenic calix[4]arenes towards metallic cations and lanthanides, and the photophysical properties of the formed complexes in acetonitrile solution were studied by UV/Vis spectroscopy in the laboratory of Rouis *et al.* The molar ratio method revealed that the stoichiometry of calix[4]arenes to Eu^{3+} in the complex is 1:1. The stability constants of the complexes were determined [184].

Anions. Two fluorogenic cone calix[4]triazacrown-5 ligands bearing two pyrene amide groups were able to sense anions and cations [185].

New calixarene derivatives were designed, synthesized, and successfully applied by Blazejczyk *et al.* [186] as neutral anion-binding receptors in electrolytes with potential sensorial application, tested by FTIR spectroscopy and other physical chemical techniques.

Moreover, the binding properties of tetraamide calix[4]arenes with some anions ($p\text{-O}_2\text{NPhOPO}_3^{2-}$, $p\text{-O}_2\text{NPhO}^-$, H_2PO_4^- , Ac^- , Cl^- , Br^- and I^-) were studied by UV/Vis spectra [187]. Two-armed neutral anion receptors were prepared and examined for their anion-binding (e.g. dicarboxylate anions) ability using UV/Vis, fluorescence and ^1H NMR spectra in DMSO [188]. A new neutral fluorescent chemosensor based on a calix[4]arene tetraamide derivative was synthesized by Chen and Chen [189]. It exhibited high selectivity for H_2PO_4^- over a wide range of anions in acetonitrile.

A calix[6]arene wheel, whose cavity was extended and rigidified by *N*-phenylureido groups on the upper rim, formed pseudorotaxane species with molecules containing the viologen (4,4'-bipyridinium) unit in CH_2Cl_2 solution and could be used for ion-pair recognition [190].

Calix(4)arenes bearing two *p*-nitrophenyl-ureido functions at the upper rim were also effective anion binders. The stoichiometry of complexation depended on the substitution pattern (distal versus proximal) and anion concentration [191].

Dudič *et al.* [192] showed that appending tetraphenylporphyrin units to the calix[4]arene skeleton via ureido function led to novel anion receptors designed for anion and/or cation detection by UV/Vis spectroscopy. Calixarenes in the cone or 1,3-alternate conformations bearing two ureido moieties on the upper rim represented well-preorganized cavities where the anion could be held by synchronous H bonding interaction with the NH groups.

He *et al.* [193] reported that two new types of chiral calix[4](aza)crowns containing L-valine were synthesized. Preliminary application of one ligand in chiral recognition was studied by ^1H and ^{13}C NMR, and UV/Vis spectroscopy. It was found that this calix[4](aza)crown exhibited different recognition properties toward (\pm)-2,3-bis(benzoyloxy)butanedioic acid and towards the D- and L-forms of tartaric acid, i.e., (+)-2,3-dibenzoyl-D-tartaric acid and (-)-2,3-di-*O*-benzoyl-L-tartaric acid.

Song *et al.* [194] evidenced that if furans, thiazoles, fluorene or thiophene were incorporated in the macrocycle as calix[4]pyrrole analogs, the calculated binding constants with anions were far less than those observed for normal calix[4]pyrroles as it was studied by incremental fluorescence quenching.

An example of substitution reaction in the free α -position of N-confused calix[4]pyrroles was reported in which the obtained azocompounds were used for studies of their anion-binding properties by UV/Vis spectroscopy [195]. Linking a calix[4]pyrrole anion recognition subunit to chromophores or fluorophores via an alkynyl spacer produced a new class of anion sensor that permitted the detection of halide and phosphate anions in organic media via fluorescence quenching-based spectroscopic means [196].

Shao *et al.* [197] published about a noncovalent calix[4]pyrrole-chloranyl complex, that can be considered as a new class of supramolecular assembly. As potential colorimetric anion sensors, the charge-transfer aggregation may be used for effective and selective detection of F^- and H_2PO_4^- by dramatic visual color changes.

Calix(4)arene-based two-armed chiral anion receptors were synthesized by Qing *et al.* [198] and examined for their chiral anion-binding abilities by UV/Vis absorption and ^1H NMR spectroscopy. The results of nonlinear curve fitting indicated that the ligands formed 1:1 stoichiometric complexes with the L- or D- α -phenylglycine anion by multiple hydrogen-bonding interactions and exhibited good enantioselective recognition for the enantiomers of the α -phenylglycine anions.

Chromatography. A new *p*-*tert*-butyl-calix[4]arene-bonded silica gel stationary phase was developed for high performance liquid chromatography (HPLC). The structure of the new stationary phase was characterized by FTIR spectroscopy, elemental and thermal analysis. As it was evaluated by chromatographic tests, this material was found an excellent reversed-phase packing suitable for fast analysis of hydrocarbons and high selectivity for sulfonamides [199].

Another stationary phase, based on *p*-*tert*-butyl-calix[8]arene bonded silica gel was prepared and characterized by elemental and thermal analysis completed with FTIR observations. Steroid hormones were baseline separated with a half time on the stationary phase with respect to traditional octadecyl silylated support [200].

A *p*-*tert*-butyl-calix[6]-1,4-benzocrown-4-bonded silica gel stationary phase was also prepared for HPLC and characterized by DRIFTS, elemental and thermal analysis. It exhibited high selectivity in the separation of alkylated aromatic hydrocarbons [201].

3-Glycidoxypropyltrimethoxysilane as a coupling reagent was also suitable for the preparation of a new *p*-*tert*-butyl-calix[8]arene-bonded silica gel stationary phase for HPLC. Its structure was characterized by diffuse reflectance DRIFTS, elemental analysis and

thermal analysis. Chromatographic performance studies revealed that the new stationary phase had an excellent reversed-phase property and high selectivities for substituted aromatics [202].

β -Cyclodextrin, *p*-*tert*-butyl-calix[8]arene and chloropropyl bonded silica stationary phases were prepared and applied at the same time to develop a chromatographic procedure to separate steroids [203].

The preparation and characterization of *p*-*tert*-butylcalix[4]arene-1,3-bis(allyloxyethoxy)ether chemically coated capillaries were reported by IR spectroscopy and decreased electroosmotic flow (EOF) measurements. This coated capillary showed improved separations of toluidine isomers, naphthol isomers and PAHs compared with an uncoated capillary [204].

Kalchenko *et al.* [205] reported that reversed-phase high performance liquid chromatography (RP-HPLC, Separon SGX CN, UV detection at 254 nm and water as mobile phase) was applied to study the host-guest complexation of *p*-H-37-(2-carboxy-methyloxy)-calix[6]arene and *p*-sulfonato-37-(2-carboxy-methyloxy)-calix[6]arene with 15 amino acids in the mobile phase.

Baudry *et al.* [206] found that under RP-HP liquid chromatographic conditions [Spherisorb ODS 1 stationary phase, UV detection at 254 nm, and acetonitrile-dichloromethane-acetic acid-methyl-*tert*-butylether (84.6/4.5/0.9/10, vol./vol./vol./vol.) as the mobile phase], adding *p*-*tert*-butylcalix[8] (10-5-3.10-5)-[12]arenes (10-5-4.10-5 mol/l) to the mobile phase led to decreased sorption of aromatic solutes on the surface of the sorbent because of the formation of host-guest inclusion complexes between the calixarenes and the aromatic molecules.

Potentiometric detection of *N,N'*-diethylaminoethanol and a series of related physiologically relevant lysosomotropic amino alcohols was carried out by cation-exchange HPLC in the laboratory of Bazylak and Nagels [207]. Poly(vinylchloride) (PVC)-based liquid membrane electrode coatings were used which contained the lipophilic cation exchanger tetrakis(*p*-chlorophenyl)borate either alone or in combination with one of the macrocyclic ionophores hexakis-(2,3,6-tri-*O*-octyl)- α -cyclodextrin, dibenzo-18-crown-6 or calix[6]arene hexaethylacetate ester. With all the PVC membrane electrodes used, improved sensitivity of the UV detection at 210 nm was obtained for the aliphatic amino alcohols under study.

The same authors [208] used potentiometric detection with PVC based liquid membrane electrode coatings for eighteen beta-adrenoceptor binding drugs (five agonists and 13 antagonists) in cation exchange-HPLC and RP-HPLC systems. The quantitative structure – potentiometric response relationships were developed for a set of beta-adrenenergic drugs and a set of PVC based electrodes using TCPB alone or in admixture with trioctylated α -cyclodextrin, dibenzo-18-crown-6 or calix[6]arene hexaethylacetate ester.

Five acidic calix[4]arenes with carboxylic or sulfonic groups at either the upper or lower rim of the cavity and

one resorc[4]arene were studied by Sokolies *et al.* [209] to separate three thioxanthenes (flupentixol, clopenithiol, chlorprothixene) and a dibenz[*b,e*]oxepin derivatives (doxepin) based on *cis*-/*trans*-isomerism by nonaqueous capillary electrophoresis (NACE). Partial filling of the capillary with the UV-absorbing selectors led to a low detection limit and an advantageous signal-to-noise ratio (S/N).

Xing *et al.* [210] reported a dimethylsulfoxide (DMSO) phase offered by a coordination polymer gel that consisted of metal ions and a calixarene having multiple binding sites. This metallogel, virtually 98% of which was DMSO, had high stability in aqueous solution over a wide range of pH (1–13), even at 100 °C. It rejected ions (almost) completely, and allowed nonionic organic molecules enriching spontaneously into the gel with high efficiency, up to ~60 times enrichment from aqueous solution and ~2000 times enrichment from the gas phase.

Polymers, catalysis

Nishikubo *et al.* [211] reviewed the synthesis, thermal stability and photochemical reactivity of calixarene derivatives containing polymerizable groups in 2003. As high performance UV-curing oligomers, certain calixarene derivatives containing (meth)acrylate, vinyl ether, propargyl ether, oxetane, oxirane, or spiroorthoester groups were synthesized.

A very stable calixarene-based polymeric chelating resin was synthesized by covalently linking calix[4]arene-*o*-vanillinthiosemicarbazone through its lower rim to Merrifield resin [212, 213]. It was characterized by FTIR, ¹H NMR and elemental analysis. The resin was efficiently used to separate and preconcentrate toxic metals such as Cu²⁺, Cd²⁺ and Pb²⁺ in a column prior to their detection by UV/Vis spectrophotometry and atomic absorption spectrophotometry (GFAAS) with a relative standard deviation of 1.0–1.4% [212, 213].

The work of Jansen *et al.* [214] described the development of a textile filter material for the separation of heavy metals from aqueous solution using calixarenes. These ligands were permanently fixed on a textile substrate such as polyester fabric by a process comparable to a disperse dyeing procedure. These calixarene modified textiles were used for the elimination of Cu²⁺, Co²⁺ and Ni²⁺ from aqueous solution, as it was studied using UV/Vis spectroscopy.

Calix[4]crown-6-containing polyamide and polyimide were synthesized and the chemical structures were characterized by IR, ¹H NMR spectroscopy and elemental analysis [215]. It was observed that polyamide had a high binding ability towards various metal cations as compared to polyimide, which showed Cs⁺ selectivity.

Li *et al.* [216] reported that seven kinds of poly(methylmethacrylate) (PMMA) films doped with C60 or its inclusion complex of *p*-*tert*-butylcalix[8]arene were prepared and characterized using FTIR and UV/Vis spectra, thermogravimetric analysis and differential

scanning calorimetry. The thermal stability of PMMA was much improved by doping with the inclusion complex in comparison with C60 itself, i.e., the inclusion complex retarded the thermal depolymerization of PMMA very effectively.

The paper of Engrand and Regnouf-de-Vains [217] described the multi-step synthesis of a new bifunctional calix[4]arene designed for grafting on natural polymeric materials, such as water-soluble dextrans, and for metal complexation. The podand was then anchored to the polymer by means of a cyanuric linker.

Przygorzewska *et al.* [218] developed a method for studying the preliminary properties of calixarene macromonomer, which exhibited the ability of dihydrophosphate anions selective complexation associated with changes in UV/Vis spectra. The calixarene macromonomer contained polymerizable group and urea groups that allowed anion complexation at the wide rim of the molecule.

Electrochemical properties of oligophenylenevinylene and oligophenyleneethynylene functionalized calix[4]arenes were investigated. These studies were complemented with absorption, emission and fluorescence spectroscopic measurements [219].

A fluorescence-labeled calix[4]arene library substituted with peptides at the upper rim was synthesized by Hioki *et al.* [220]. Screening of the library for binding a dye-labeled oligopeptide indicated that some peptidocalix[4]arenes selectively bound the oligopeptide.

The preparation of some hybrid materials from anion hosting calixarenes with polyoxometalates ions was carried out. The interactions of the components dissolved simultaneously in the same solvent were analyzed by UV/Vis spectroscopy, whereas the isolated crystalline materials, at the interface between two dispersion media were studied by FTIR spectroscopy [221].

The mechanism and kinetics of the solvolysis of complexes of the type $[(L-L)Pd(C(O)CH_3)(S)] + [CF_3SO_3]^-$ ($L-L$ = diphosphine ligand, S = solvent, CO , or donor atom in the ligand backbone) was studied by NMR and UV/Vis spectroscopy with the use of nine different ligands [222]. Acetyl palladium complexes containing trans-coordinating ligands that resisted cis coordination showed no methanolysis.

Acid induced polymerization of pyrrole proceeded in aqueous solution that contained calix[6]arene-hexasulfonic acid in the absence of either an oxidant or electrochemical oxidation resulting in an unstable colloidal suspension of spherical polypyrrole [223]. IR spectroscopy and microanalysis confirmed that the obtained polypyrrole included the calixarene derivative as counterion.

Two novel regioisomeric calix[4]arene derivatives bearing two aza [18] crown-6 units were synthesized and the catalytic activities of their dinuclear Ba^{2+} complexes were investigated in the ethanolysis of four different esters, endowed with a carboxylate anchoring group [224].

Other physical or physico-chemical studies supported by optical methods

Optical and photophysical properties

Optical properties of a series of calixarenes, obviously, were determined by optical spectroscopic techniques. For instance, the refractive index of calixarene films were determined by m-lines spectroscopy [225].

Rigid, highly conjugated tetraalkynyl-calix[4]arenes gave rise to improved second-order hyperpolarizability values as determined by hyper-Rayleigh scattering – a technique that in addition to X-ray crystallography also allowed for the conformational analysis of the calixarene structures in solution [226]. Similar results were published by Regayeg *et al.* [227], who synthesized functionalized *p*-nitrocalix[4]arenes that can be used as intermediates or for second-order nonlinear optics (NLO). These calixarenes adopted a cone or partial cone conformation both in solution and in the solid state.

The results of supramolecular organic light emitting diodes using a calix[4]arene complex thin film as emitter and electron transporting layer were also presented [228]. The devices were grown onto glass substrates coated with In–Sn-oxide layer and Al thick (150 nm) cathode. The electroluminescent emission peak could be tuned between 470 and 510 nm changing the applied voltage bias from 4.3 to 5.4 V.

Organic diodes formed by sandwiching azo-calix[4]arene layers between indium-thin oxide (ITO) and (Al) contacts were elaborated by Rouis *et al.* [229]. Studies of devices by current–voltage characteristics $I(V)$ and electrical impedance spectroscopy measurements in a wide frequency range were reported. The optical excitation of the organic structure revealed enhancement in electrical properties.

Gidwani *et al.* [230] reported optical measurements on fluorescence and lasing characteristics of fluorescein calix[4]aryl hydroxamic acid. Moreover, the photophysical properties of calixarenes bearing two and four dansyl moieties were investigated by potentiometric titration, absorption spectra, emission spectra, quantum yield and fluorescence decay measurements [231].

Laser-induced room temperature luminescence of air-equilibrated benzophenone/*O*-propylated *p*-*tert*-butylcalix[4]arene solid powder samples revealed the existence of a novel emission, in contrast with benzophenone/*p*-*tert*-butylcalix[4]arene complexes, where only benzophenone emitted. This novel emission was identified as phosphorescence of 1-phenyl-1,2-propanedione, as diffuse reflectance laser flash photolysis and gas chromatography-mass spectrometry (GC-MS) techniques provided complementary information about its mechanism [232].

Selective removal of *t*-Boc (*tert*-butyloxycarbonyl) protecting groups in a polymer film imbedded, pyrene-containing calixarene derivative resulted in the generation of a patterned fluorescence image without employing wet developing processes as it was reported by Kim *et al.* [233].

A simple method for the preparation of highly fluorescent and stable, water-soluble CdSe–ZnS quantum dots was reported using calix[4]arene carboxylic acids as surface coating agents. The coating of the surface with the calixarene and the conjugation of antibodies to the quantum dots were confirmed by fluorescence correlation spectroscopy [234].

Hayashida *et al.* [235] prepared macrocyclic glyco-cluster compounds with four alkyl (undecyl) chains and eight oligosaccharide moieties on the opposite sides of the calix[4]resorcinarene macrocycle. Combined evidence from dynamic light scattering (DLS), gel permeation chromatography (GPC), and transmission electron microscopy (TEM) indicated that they formed small micelle-like nanoparticles (d equivalent 3 nm) in water.

Host–guest complexes of calix[4]resorcinarene with chiral molecules were efficiently formed by solid-solid grinding and exhibited CD Cotton effects reflecting the absolute configuration of the guest [236].

Colloid and surface chemical developments

Some special features of calixarenes are connected to their colloid and surface chemical characteristics. Certain calixarenes, for instance, are able to form surface complexes on solid salts as it was evidenced by different FTIR and FT-Raman spectroscopic techniques [145, 237]. Film formation of a calix[8]arene derivative was studied at the air/H₂O interface by BAM and IR spectroscopy accompanying other classical surface chemical methods [238]. Hybrid molecular floating films consisting of nematic liquid crystals and calix[4]resorcinarene derivatives having amphiphilic nature were obtained on the H₂O surface and their aggregation mechanism was studied by UV/Vis spectroscopy [239].

Monolayers of some amphiphilic calixarene derivatives bearing chiral bicyclic guanidinium on the surface of pure water and of aqueous subphases containing L-phenylalanine or D-phenylalanine (L/D-Phe) were studied by film balance measurements [240]. Langmuir–Blodgett films deposited from the monolayers on the three kinds of subphases were investigated by CD spectra. It was concluded that their enantioselectivities for L-Phe depended on the molecular structures.

Oliviere *et al.* [241] carefully examined the attenuated total reflection Fourier transform IR (ATR-FTIR) spectra of LB alternate multilayers of two different calixarene carboxylic acid/amine systems as a function of temperature. Neither the molecular arrangements nor the degree of proton transfer appeared to change (within the detection limits) over the 20–80 °C temperature range. The results were confirmed by a detailed analysis of the IR spectra for different acid/amine LB films (including ones published previously).

Brook *et al.* [242] described the effect of a host matrix on the LB deposition, UV/Vis spectra and gas-sensing properties of 5,10,15,20-tetrakis[3,4-bis(2-ethylhexyloxy)phenyl]-21H,23H-porphine (EHO) in the presence of a carboxylic acid substituted calix[8]arene as host material. The studied phenomena were based on that

functional properties of LB films of many organic dyes, such as porphyrins and phthalocyanines, could be enhanced using a host material that formed a deposition vehicle for the preparation.

Kazakova *et al.* [243] reported the preparation of four octaaminoamide resorcin[4]arenes having hydrocarbon chains of different lengths and different terminal groups. Surface tension and self-assembly of their aqueous solutions were studied, the latter one by DLS measurements.

A photosensitive ultra-thin film was fabricated by Yang and Cao [244] from diphenylamine-4-diazonium sulfate-paraformaldehyde diazo resin and various calixarenes by a self-assembly technique. Upon crosslinking under UV irradiation, covalent bonds were formed. As a result, the stability of the multilayer toward polar solvents increased dramatically.

The ionization of a self-assembled monolayer (SAM) of tetrathiol calix[4]resorcinarene and the metal ion binding properties (e.g. Cu²⁺) of these ionized surfaces were studied using surface plasmon resonance (SPR) measurements. The structure of the molecular assemblies was characterized using polarization modulation-IRRAS [245].

Stable monolayers of novel amphiphilic calix[4]resorcinarene derivatives at the air/H₂O interface were prepared and their interactions with Cu²⁺ ions from the aqueous subphase were studied by measuring surface pressure-area and surface potential-area isotherms, as well as by BAM [246].

Similarly, combined application of surface pressure-area isotherms, BAM, and grazing incidence X-ray diffraction (GIXD) offered a powerful possibility to characterize amphiphilic P-functionalized calix[4]arene monolayers at the air/H₂O interface as it was studied by Vollhardt *et al.* [247]. Moreover, the monolayer features of 5,11,17,23-tetra-*tert*-butyl-25,27-di(benzoylamidoethoxy)-26,28-dihydroxyl calix[4]arene at the air/H₂O interface were studied using combined studies of surface pressure-area isotherms, surface pressure relaxation, and monolayer morphology by BAM [248]. It was demonstrated that this calix[4]arene type, having no long alkyl chain, nevertheless, could form stable Langmuir monolayers.

Kazakova *et al.* [249] reported about the surface activity and self-organization of aminoamide calix[4]resorcinarenes with hydrophobic groups of various lengths and various peripheral groups. IR spectroscopy data, along with the data on viscometry and tensiometry, allowed one to suggest the qualitative model of gel structure formation [249].

Zhang *et al.* [250] reported on the synthesis and SAM formation of three conformational isomers of *p-tert*-butylcalix[4]crown-6 derivatives and one *p-tert*-butylcalix[4]arene derivative as studied by electrochemical methods, IRRAS and contact angle measurements. The monolayers exhibit selective binding and sensing abilities with alkali earth metal cations such as Ca²⁺ and Ba²⁺ over alkali metal ions.

Cavalleri *et al.* [251] investigated the self-assembly of thioether modified calix[4]arene on gold surfaces. The calix[4]arene/gold interface was investigated by means of spectroscopic ellipsometry (SE), scanning tunneling microscopy (STM) and CV. It was found that calix[4]arene-covered electrodes were able to complex K^+ and Ba^{2+} , while no complexation was observed in the case of Li^+ , Na^+ , Cs^+ , Mg^{2+} and Ca^{2+} .

Faull *et al.* [252] observed selective molecular interactions at an interface formed by self-assembly of calix[4]resorcinarene having four thiol groups. The recognition of guest adsorbates from aqueous solution was monitored using SPR and the orientation of the guest-molecule was probed by PM-IRRAS.

Calix(4)arenes equipped with two and four zinc porphyrins were prepared, and their self-assembly properties were observed by a combination of UV/Vis and 1H NMR spectroscopy [253]. Moreover, using alternating electrostatic layer-by-layer assembly of *p*-octasulfonato-calix[8]arene and polyvinylamine, multilayer assemblies were built up on porous polymer supports [254].

The self-assembly of hydrogen-bonded aggregates (rosettes) in solvent mixtures of different polarity was studied by calorimetry [255]. The assembly of calixarene derivatives under study was proven in pure methanol by 1H NMR and CD spectroscopy.

Reinhoudt and his co-workers [256] reported the formation of a hydrogen-bonded receptor in niosomal membranes provided in a stable self-assembly system that was investigated by CD, TEM and Confocal Microscopy.

Facile preparation of a C60-porphyrin bilayer on an ITO glass was achieved using electrostatic alternate adsorption. Unmodified C60 encapsulated in cationic homooxacalix[3]arenes and porphyrins sustained by an anionic polymer were used for the C60 layer and the porphyrin layer, respectively, and studied by spectroscopic methods [257].

A new calix[4]pyrrole-based macrocycle was synthesized and transferred onto solid surface by using Langmuir-Schafer method. The layer was studied by scanning force microscopy and induced CD experiments, and was found that in the presence of chiral alcohol vapors, such as R(-)-2-butanol, R(-)-2-pentanol and R(-)-2-hexanol, the studied molecules exhibit chirality within the film induced by the binding with the chiral guests [258, 259].

Oil coated silicone fiber was prepared with 5,11,17,23-tetra-*tert*-butyl-25,27-diethoxy-26,28-dihydroxycalix[4]arene/hydroxy-termination and applied for solid-phase microextraction. The possible sol-gel mechanism was discussed and confirmed by IR spectra [260].

A homopolymer of 2-(2'-methoxyethoxy)ethyl methacrylate (DM) dissolved in pure water demonstrated an abrupt increase in its turbidity at a critical temperature (LCST). The addition of macrocycles such as hexasodium calix[6]arenehexasulfonic acid, α -cyclo-

dextrin and 2,6-di-*O*-methyl- β -cyclodextrin changed the LCST. ROESY, fluorescence and UV/Vis absorption spectroscopic, and viscosity measurements were also carried out [261].

Reverse micelles of (2-hydroxyethyl)dimethylpentadecylammonium bromide catalyzed the reaction in which aminomethyl fragment in the calix[4]resorcinolarene molecules favored its phosphorylation in chloroform [262].

By UV/Vis absorption and fluorescence spectroscopy, it was established that 25,27-dihydroxy-26,28-dimethoxycalix[4]arene formed reverse micelles in CCl_4 and *n*-hexane media [263]. This compound could incorporate water molecules even before micelle formation. The inclusion complex of this calixarene with C70 had a CT absorption band. The inclusion complex of C60 was studied by 1H NMR spectroscopy.

Intermolecular interaction between pyrenyl units linked on the silica surface and *N,N*-dimethylaniline units of polymer segments coated on the silica was investigated by Hayashi and Ichimura [264] based on exciplex emission.

The electrochemical features of the ferri/ferrocyanide redox couple was studied at Au electrodes modified with calix[4]resorcinarenetetrathiol based on CV measurements supported by the FTIR spectroscopic study of the calix[4]resorcinarene-coated Au electrodes [265].

A detailed study of the luminescence decay curves of pyrene included within *p-tert*-butylcalix[4]arene cavities and benzophenone into silicalite channels was reported and a new methodology for a lifetime distribution analysis of the decay curve of probes onto heterogeneous surfaces was presented [266].

The paper of Wang *et al.* [267] is an odd-one-out in this chapter, because it is about the acid-base properties of calix[4]arene derivatives studied with chemometric methods based on their UV absorbances under different pHs.

Biological interactions

Biological interactions are, in general, very closely related to surface characteristics of the studied molecules. However, the practical importance of these studies account for collecting these results in a separate paragraph, as follows.

A cationic L-lysine-modified polyazo-benzene dendrimer (Lys-G2) was examined by Nagasaki *et al.* [268] as a nonviral vector to mammalian cells. UV irradiation (365 nm) after the incorporation of Lys-G2/DNA polyplex into the nucleus caused a 50% enhancement in the transfection efficiency as compared with the case without UV irradiation.

Formation of SAMs with calix[4]arene ethylester and carboxylic acid derivatives on Au surface was carefully characterized by atomic force microscopy (AFM), IRRAS and SPR. Immobilization process of protein using bovine serum albumin (BSA) on the artificial linker layer was measured by SPR [269].

The monolayers of the amphiphilic calix[4]arene derivatives at the lower rim with two adenino units on the surface of pure water, the aqueous subphases containing complementary nucleosides were studied by film balance measurement and relaxation expts. LB films deposited from all subphases were investigated by UV spectra and FTIR spectra [270]. Similar studies were carried out by Wang *et al.* [271] on the Langmuir–Blodgett layers of some amphiphilic calix[4]arene-nucleobase derivatives investigated by UV spectra and FTIR spectroscopy.

The miscibility of three amphiphilic calix[4]arenes were studied in mixed monolayers, with cholesterol by Langmuir film method and BAM. [272]. Gualbert *et al.* [273] also studied the interaction of solid lipid nanoparticles (SLN) based on amphiphilic calix[4]arene with serum albumin by photon correlation spectroscopy (PCS) and AFM. This work was a continuation of a preliminary study in which the preparation and stability parameters of *para*-acyl-calix[4]arene based SLNs were investigated [274]. AFM and PCS showed a mean particle size of 130 nm. Ultrasonic, UV or microwave treatments of the SLN suspensions had no effect on the size of the SLNs. ^1H NMR, X-ray powder diffraction (XPD) and AFM were also carried out on the calix-arene based SLNs and demonstrated the presence of a semi-organized matrix structure for the SLNs.

Kim *et al.* [275] synthesized three types of calix[4]arene-nucleoside hybrids and designed the calix[4]arene-oligonucleotide hybrids. Thermal denaturation experiments, monitored by UV spectroscopy at 260 and 284 nm, and CD spectra of the calix[4]arene-oligonucleotide hybrids suggested that the modified oligonucleotides adopted V-shaped conformations.

Optical spectroscopy in structural elucidation – the point of view of the organic chemist

The molecular structure of novel calixarene derivatives are evidenced by different spectroscopic methods including optical spectroscopic measurements [276–286]. Numerous azocalix[6]arene derivatives were synthesized and, in some cases, fully characterized using UV/Vis, FTIR, and ^1H -NMR spectroscopic techniques as well as elemental analysis. The colour changes as a function of pH, solvent and concentration was discussed in detail [287–290]. Arimura *et al.* [291] reported on the spectroscopic behavior of arenediazonium ions in the absence and the presence of a novel calix[4]arene 1,3-alternate conformer possessing two (ethoxycarbonyl)methoxy groups.

A new tetraferrocenylurea calix[4]arene was prepared and its dimerization equilibrium was studied in dependence of oxidation state of the ferrocene units by PGSE NMR and IR spectroscopic techniques [292]. C60-linked calix[5]arenes were synthesized and the self-inclusion ratio of the C60 moiety was determined by using UV/Vis spectroscopy [293]. Based on similar

inclusion phenomenon, the interaction of triplet excited C60 with *p*-*tert*-butyl-calix[*n*]arenes (BCX_{*n*}, *n* = 4, 6 or 8) and with their 2,4,6-trimethylpyridine and pyridine complexes were studied with laser flash photolysis experiments [294].

Klimova *et al.* [295] reported on two cavitands that formed complexes hosting one and two C60 molecules, respectively. The cavitands were studied by solution NMR and solid-state ^{13}C and ^{29}Si CP-MAS NMR. The complexes obtained were characterized by elemental analysis, ^{13}C and ^{29}Si CP-MAS NMR, UV and FTIR.

The strong Lewis acid tungsten oxo complex of calix[4]arene was obtained in both hydrated and nonhydrated forms. The water host was characterized – among other methods like TGA, DSC and ^1H NMR – by FTIR spectroscopy [296].

Resolved (Sa)-2'-methoxy-1,1'-binaphthalene-2-carboxylic ester derivative of calixarene was observed by CD spectroscopy and X-ray crystallography [297].

The synthesis and photoinduced deprotection reaction of calix[4]resorcinarene derivatives with pendant acetal moieties were also examined upon UV irradiation [298]. Another deprotection reaction of calix[4]resorcinarene bearing *tert*-Bu ester moieties were also examined [299].

Bunzli and Besancon [300] evidenced a reaction intermediate in the formation of the Eu^{3+} bimetallic complex with *p*-*tert*-butylcalix[8]arene by different spectroscopic techniques. (ES-MS, visible, luminescence, FT-IR) and conductometric techniques.

The mechanism of electrochemical reduction of calix[4]quinones to calix[4]hydroquinones was studied using transient electrochemistry, electrochemical quartz crystal microbalance and spectroelectrochemical measurements [301].

Electrochemical oxidation of 5,11,17,23-Tetra-*tert*-butyl-25,27-bis(*p*-toluenesulfonyl)-26,28-bis(hydroxy)-calix[4]arene was studied by Vataj *et al.* [302] in dichloromethane solution at a platinum electrode. The mechanism of formation of the corresponding phenoxylum cation was clarified by detailed voltammetric, coulometric and spectroelectrochemical experiments. Nucleophilic attack of residual water on one of the calixarenes ultimately led to the corresponding calix[4]diquinone.

Yam *et al.* [303] described the synthesis and structural characterization of a series of luminescent dinuclear Au^+ alkynylcalix[4]crown-5 complexes. The dinuclear Au^+ alkynylcalix[4]crown-5 complexes were shown to exhibit preferential binding toward K^+ over Na^+ ions by UV/Vis spectrophotometry.

Cyclization of resorcinol monoalkyl ethers with aliphatic aldehydes led to the corresponding racemic mixtures of C4-symmetric rccc-resorc[4]arenes [304]. They were separated and the resulting diastereomeric resorc[4]arenes were examined by CD spectroscopy, showing a perfect mirror image in all solvents used. This result indicated that the resorcarene cavities were essentially enantiomers of each other.

Azov *et al.* [305] reported the synthesis of modified Cram-type cavitands bearing one or two fluorescent labels for single-molecular spectroscopic studies of vase-kite conformational switching from resorcin[4]arene bowls. ^1H NMR investigations showed that the new partially and differentially bridged cavitands feature temperature- and pH-triggered vase-kite conformational isomerism similar to symmetrical cavitands with four identical quinoxaline bridges and the vase-kite switching of cavitands were strongly solvent-dependent.

A calix[4]arene including two alternately arranged phloroglucinols and *p*-*tert*-butylphenols was synthesized by Sato *et al.* [306], and its $\text{p}K_{\text{a}}$ values were estimated to be 3–4 and 7.5, while those of the other six phenolic hydroxyls were approximately 11. Its UV/Vis spectrum at $\text{pH} = 11$ and ^1H and ^{13}C NMR spectra in $\text{NaOD-D}_2\text{O}$ solution ($\text{pH} = 12.8$) showed a dramatic change like those of the phloroglucinol when compared to those in acidic or neutral solution, which suggested a change in the phloroglucinol moiety to the keto-form.

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