Abstract:
This chapter deals with the synthesis of a series of novel calix[4]arene and calix[4]resorcinarene compounds and their characterization. The synthesis of calixarenes and calixresorcinarene compounds were carried out by the following procedure.


(3) Synthesis of lower rim substituted calix[4]arene were carried out by substituting phenyl urea to calix[4]arene.

The compounds were purified and characterized by elemental analysis, FT-IR, UV-VIS, $^1$H NMR, $^{13}$C NMR, ESI- MS and FAB-MASS.
**Introduction:**

Calixarenes are a well known class of macrocyclic compounds [1], obtained in very high yield through a one-step condensation of formaldehyde with p-tert butyl phenol in basic conditions. In 1872 Adolf von Baeyer heated aqueous formaldehyde with phenol, to give a hard resinous product. However, these compounds did not become popular until Gutsche elaborated simple conditions for the preparation of larger quantities of these oligomers. He also coined the name “calixarenes” which is now generally accepted [2]. The calixarene family can be subdivided into two major branches, the phenol derived cyclooligomers i.e. calixarenes and the resorcinol-derived cyclooligomers i.e. calixresorcinarene.

Calixarene have wide range applications in supramolecular chemistry. Calixarenes are versatile classes of macrocyclic compounds which have attracted extensive interest due to their ability to form host-guest complexes and can also act as an enzyme mimic [3-4]. These macrocyclic phenol-formaldehyde tetramers are easily synthesized and functionalized not only at their narrow rim (by derivatization of the phenolic -OH groups), but also at their wide rim (by substitution of the para positions of the phenolic rings). Calix[4]arenes are one of the most extensively developed platforms for the design of synthetic receptors [5]. This interest stems from the synthetic availability of large quantities, the ability to produce rigid well-defined binding sites, and the versatility of these compounds for further functionalization. The utility of calixarenes in materials applications has also been recognized, and these materials have been employed for the formation of porous monolayer’s [6], nonlinear optical chromophores [7], liquid crystals [8], cation receptors [9-12], anion receptors[13-14], organic neutral and charged molecular recognition devices [15] ion selective electrodes [16] and fluorescent devices [17]. The cavity of conventional calixarene...
has been most studied for encapsulation abilities toward alkali and alkaline earth [18-19]. In short, calixarene derivatives have been mainly utilized for their active role in host–guest chemistry.

Chemical sensing, which is accompanied by combining a recognition element with an optical or electronic transduction element, has received much attention as an efficient analytical technique for the detection of particular species. Among these sensing systems, chromogenic receptors give rise to a specific color change upon selective complexation with guest species, which are not only used as spectrophotometric analytical reagents but also as the tools for the detailed understanding of receptor–substrate interaction because that molecular recognition process could be efficiently amplified as an optical signal. For constructing a chemically based sensor, the task is first to design a system that is sensitive specifically to the species being monitored and then to devise a way for transducing the chemical response, which is at the molecular level, to an electrical level or as an optical signal at the macroscopically observable and measurable level. Therefore, the design of new and highly efficient chromogenic receptors is always a challenge for supramolecular chemistry and analytical techniques. Calixarenes have been employed in such devices in a variety of interesting ways.

Calixarenes can be ideal frameworks or building blocks for the development of chromogenic receptors in molecular recognition since the incorporation of an appropriate sensory group into the calixarene having a preorganized substrate binding site results in a tailored chromogenic receptor.

The azo functionalized calixarenes have been widely studied for their chromogenic effect. Apart from metal binding abilities, azo calixarenes could be promising
molecules in the field of dyes and pigments. With these in view, a series of calix[4]arene and calix[4]resorcinarene dyes were synthesized in the present investigation to explore the possibilities of their application in the field of dyes and also in the field of chemical sensing.


All the compounds synthesized were purified and characterized systematically by elemental analysis, FT-IR, UV-VIS, $^1$H NMR, $^{13}$C NMR, FAB-MASS, ESI-MASS.
Experimental:

Chemicals and Reagents

All the chemicals used were of analytical grade of BDH, Qualigens, Aldrich and Merck unless otherwise specified.

Instrumentation

Melting points were taken on Veego (VMP-DS) using a Mel-Temp apparatus. The FT-IR spectra were recorded as KBr pellet on Bruker TENSOR-27 in the range of 4000-400 cm$^{-1}$. Discover BenchMate system-240 V (CEM Corporation) microwave synthesizer was used for synthesis. $^1$H NMR spectra was scanned on 400 MHz FT-NMR Bruker Avance-400 in the range of 0.5 ppm -15 ppm and $^{13}$C NMR spectra was recorded on a Bruker DPX-300 spectrometer using internal standard tetramethylsilane (TMS) and deuterated DMSO as a solvent in the range of 0.5 ppm to 250 ppm. ESI Mass spectra were taken on a Shimadzu GCMS-QP 2000A. the FAB-MS were recorded on a Jeol/SX/102/Da-600 mass spectrometer data system using Argon/Xenon as the accelerating gas. M-Nitro benzyl alcohol (NBA) was used as a matrix with the peak at m/z 136, 137,154,289,307.


The synthesis of p-tert butylcalix[4]arene were carried out for the first time by our group [26] using base-catalysed condensation of p-substituted phenol and formaldehyde using microwave irradiation with an improvement of yield to 90-95% (Scheme 1).

For the microwave synthesis of p-tert butyl calix[4]arene, 10 g of p-tert-butylphenol was mixed with NaOH (0.05 g, 1.2 mmol) dissolved 0.5 ml of water and 6.2 ml 37% formaldehyde solution and was heated in a Discover BenchMate system-240 V(CEM Corporation) microwave at 300 watt output power for 5 min to give a yellow solid. To this was added 7 ml of diphenyl ether and 1 ml toluene and the mixture was heated at 300 watt output power for 15 min to obtain corresponding calix[4]arene. The purity was checked by TLC and the results of mp, FT-IR, $^1$H NMR, $^{13}$C NMR and MS were compared with standard sample.

Scheme 1: Microwave synthesis tert-butyl calix[4]arene


To a solution of p- tert-butyl calix[4]arene (5.0 g, 0.1 mol), phenol crystal (0.9 g, 0.01 mol), added anhy. AlCl$_3$ (5.0 g, 0.1 mol) in 100 ml of toluene and stirred the solution for 4 h. After the completion of the reaction, the reaction mixture was poured in to the ice containing water. Taken the mixture in a separatory funnel containing 250 ml of dichloromethane (DCM). Collected the organic layer and washed with 100 ml (2 N) HCl. Evaporated the solvent under reduced pressure by flash evaporator, dissolved the residue in 25 ml of diethyl ether and kept the solution at 0-5$^\circ$C overnight. Filtered and dried.
Chapter 2 Synthesis & Characterization


To a solution of resorcinol (11.01 g, 0.1 mol) and acetaldehyde (4.41 g, 0.1 mol) in 40 ml of water, was carefully added in 10 ml of conc. HCl. The precipitate obtained were stirred at 75 °C for 4 h, cooled in ice bath and filtered. The phenolic precipitate was washed and dried [25].

Synthesis of azo calix[4]resorcinarene dyes (Scheme 4)

The novel azo calix[4]resorcinarene dyes (d₁-d₅ & d₁₀) were prepared from the parent calix[4]resorcinarene by coupling with diazonium salt of the following amines like p-anisidine m-sulphonic acid, p-amino sulphonic acid, p-amino benzoic acid, p-anisidine, p-amino phenol and o-amino benzoic acid. The selected amines are

**The synthesis of p-(4-methoxy phenylazo) calix[4]resorcinarene (d4)**

A solution of 4- methoxyphenyl diazonium chloride, which was prepared from 4-methoxy aniline (2.3 g, 20 mmol) sodium nitrite (1.30 g, 11 mmol) and conc. HCl (7 ml) in water (25 ml), was added slowly to a cold (0-5°C) solution of calix[4]resorcinarene (2.0 g, 5 mmol) and sodium acetate trihydrate (2.10 g, 15 mmol) in NaOH solution (1.12 g, 8 mmol) to get an orange-red suspension. It was stirred for another 1 h at the same temperature. After 1 h the solution was removed from ice bath and stirred for further 1 h at room temperature. After the completion of the reaction, the reaction mixture was acidified with aqueous HCl (150 ml, 0.25%) and the mixture was then warmed to 60°C for 30-35 min to give (Yield, 1.72 g, 78 %) dark orange solids. This was filtered and washed with water and MeOH. A sample for analysis was obtained as follows: compound (d4) was dissolved in 50 ml of hot solution of NaHCO3 (3.0 g) solution; to this solution was added activated charcoal (1.0 g). Stirred this solution for 15 min after the charcoal was filtered the filtrate was cooled (room temperature, 30°C) and acidified with concentrated HCl (1-2 ml). The solution was heated to 60°C for 30-35 min. and then cooled. The resulting solid was filtered and wash with water and dried. Recrystallization from DMF-MeOH gave the orange-red product. (Yield, 1.60 g, 67 %) m.p.dec.>240°C.
Scheme 4: synthesis of azocalix[4]resorcinarene (d₁-d₅ & d₁₀)
Synthesis of azo calix[4]arene dyes (Scheme 5)

The novel azo calix[4]arene dyes (d_6-d_9) were prepared from the parent calix[4]arene by coupling with diazonium salt of the following amines like p- anisidine, o-anisidine, p-amino phenol and o-amino phenol. The selected amines are diazotized and coupled with calix[4]arene to get the azo calix[4]arene (d_6-d_9). The procedure followed for the synthesis is essentially the same for all the azo calix[4]arene (d_6-d_9) dyes. A typical procedure for the synthesis of p-(4- methoxy phenylazo) calix[4]arene (d_6) is described below.

The synthesis of p-(4-methoxy phenylazo) calix[4]arene (d_6)

A solution of 4- methoxyphenyl diazonium chloride, which was prepared from 4-methoxy aniline (2.4 g, 24 mmol) sodium nitrite (1.18 g, 11 mmol) and conc. HCl (7 ml) in water (25 ml), was added slowly to a cold (0-5°C) solution of calix[4]arene (2.0 g, 6.5 mmol) and sodium acetate trihydrate (2.10 g, 15 mmol) in DMF-Methanol (25 ml 8:5,v/v) get a dark orange suspension. After standing for 2 hrs at room temperature, the suspension was acidified with aqueous HCl (150 ml, 0.25%) and the mixture was then warmed to 60°C for 30 min get (yield, 1.7 g, 74%) as a dark orange solid, which was filtered and washed with water and MeOH.

A sample for analysis was obtained as follows: compound d_6 was dissolved in 100 ml of hot aqueous NaHCO_3 (4.0 g) solution; to this solution was added activated charcoal (1 g). After the charcoal was filtered, the filtrate was cooled (room temperature) and acidified with conc. HCl (1 or 2 ml). The solution was heated to 60°C for 30 min and then cooled. The resulting solid was filtered washed with water and dried. Recrystallization from DMF/Methanol gave a dark orange product (yield, 1.55 g (66%),m.p.dec.>230°C).
Scheme 5: synthesis of azocalix[4]arene (d6-d9)

R : d6) o- amino phenol
d7) p-amino phenol
d8) o-amino anisol
d9) p-amino anisol
Synthesis of sulphonated calix[4]resorcinarene (C₁, C₂)

Sulphonation of calix[4]resorcinarene (Scheme 6)

A mixture of calix[4]resorcinarene (5.44 g, 0.01 mol), a solution of 37% formaldehyde (4.1 g, 0.05 mol) and sodium sulfite (6.3 g, 0.05 mol) in distilled water (50 ml) was stirred and heated at 90-95°C for 4 h, dilute hydrochloric acid (2 N) was added after cooling to adjust the pH to 7, followed by acetone (150 ml) to precipitate the product. The solid was filtered, washed with acetone (25 ml) and dried to get (C₁). Same procedure was followed for (C₂).

Scheme 6: sulphonation of calix[4]resorcinarene (C₁, C₂)
Synthesis of phenyl urea substituted calix[4]arene (C₃)

Scheme 7 illustrates the successive steps of the inophore synthesis used. To get the 5,11,17,23-tetra-tert-butyl-25,27-bis(chlorocarbonyl-methoxy)-26,28 dihydroxy calix[4]arene from 5, 11, 17, 23-tetra-tert-butyl-25, 26, 27, 28-tetrahydroxy calix[4]arene were synthesized according to the literature methods [42-43].

The synthesis of the novel compound C₃ is carried out as follows:


The compound 5, 11, 17, 23-tetra-tert-butyl-25, 27-bis (phenyl urea)-26, 28-dihydroxy calix[4]arene (C₃) was synthesized by treating 5, 11, 17, 23-tetra-tert-butyl-25, 27-bis (chlorocarbonyl-methoxy)-26, 28 dihydroxy calix[4]arene) (1.66 g; 1.89 mmol), obtained in the previous step was dissolved in dry THF (75 mL). The addition of pyridine (2 mL; 12.4 mmol) and the solution of phenyl urea (1.3 g; 9.5 mmol) in THF (15 mL) was made sequentially and added drop wise in a period 30 min. with continuous stirring at room temperature. The reaction mixture was then stirred and refluxed for 4 h, after which most of the solvent was distilled off under vacuum. The residue was diluted with water (100 mL) and neutralized by 0.1 M HCl. The solid material was then filtered and washed with 1 N HCl, NaHCO₃ and distilled water sequentially. Recrystallization of residue from ethanol-THF furnished (C₃). Yield 1.5 g (81%), m.p. 203–205°C.
Scheme 7: Synthesis of phenyl urea substituted calix[4]arene (C₃)

Synthesis involves successive steps i) AlCl₃, Toluene; ii) Dry acetone, Ethyl bromoacetate, K₂CO₃; iii) KOH: EtOH; iv) SOCl₂, THF; v) Phenyl urea, THF
Results and discussion:

Characterization of p-(4-methoxy-m-sulfophenylazo) calix[4]resorcinarene (d₁)

**Elemental analysis** calculated for C₈₄H₇₆N₈O₂₈S₄  %C 56.88, %H 4.28 %N 6.22

found %C 56.75 %H 4.12 %N 6.28. **¹H NMR** (400 MHz, CDCl₃, Me₄Si): δ 10.42 (s, 8H, Ar-OH), 7.4-8.2 (m, 32H, Ar-H), 4.17 (s, 4H, bridge –CH), 2.12 (s, 24H, -OCH₃), **¹³C NMR** (125 MHz , CDCl₃, Me₄Si) :160,152,150, 145.3, 140.1, 134.2, 132.2, 130.4, 129.3, 127.6, 125.4, 115.0, 112.6 (Ar-C), 106.7, 73.3, 70.5, 26.8, 13.5 (-CH₂)

**FT-IR** (KBr) υ: 3250 (-OH), 2830 (Ar-CH), 1457 (-N=N-) cm⁻¹ **ESI-MS** observed m/z 1773 (M+).

Characterization of p-(4-sulfo phenylazo) calix[4]resorcinarene (d₂)

**Elemental analysis** calculated for C₈₀H₆₈N₈O₂₄S₄  %C 58.11, %H 4.11 %N 6.77

found %C 58.27 %H 4.0 %N 6.52. **¹H NMR** (400 MHz, CDCl₃, Me₄Si): δ 10.41 (s, 8H, Ar-OH), 7.12-7.89 (m, 36H, Ar-H), 4.18 (s, 4H, bridge –CH), 2.12 (s, 12H, –OCH₃), **¹³C NMR** (125 MHz , CDCl₃, Me₄Si) : 168,145.5, 142, 136.2, 132.2, 130.4, 128.7, 125, 115 (Ar-C), 106.7, 73.8, 72.5, 26, 22, 15, 14.7 (-CH₃), 13 (-CH₂). **FT-IR** (KBr) υ: 3336 (-OH), 2855 (Ar-CH), 1457 (-N=N-) cm⁻¹ **FAB-MS** observed m/z 1653 (M+).

Characterization of p-(4-carboxy phenylazo) calix[4]resorcinarene (d₃)

**Elemental analysis** calculated for C₈₄H₆₈N₈O₂₀  %C 66.84, %H 4.50 %N 7.42

found %C 66.68 %H 4.25 %N 7.58. **¹H NMR** (400 MHz, CDCl₃, Me₄Si): δ 10.42 (s, 8H, Ar-OH), 11.57 (s, 4H, -COOH), 7.3-7.95 (s, 36H, Ar-H), 4.18 (s, 4H, bridge –CH), 2.12 (s, 12H, –OCH₃), **¹³C NMR** (125 MHz , CDCl₃, Me₄Si) : 13.2 (-CH₂), 14.1 (-CH₃), 38.96, 39.51, 40.07, 40.35, 54.35,78, 123.66, 126.0, 140, 151, 152.2, 170 (Ar-
C). **FT-IR** (KBr) 3278 cm\(^{-1}\) (-OH), 2989 cm\(^{-1}\) (Ar-CH), 1545 cm\(^{-1}\) (-N=N-), 1710 cm\(^{-1}\) (-C=O-). **FAB-MS** observed m/z 1510 (M+2).

**Characterization of p-(4-methoxy phenylazo) calix[4]resorcinarene (d\(_4\))**

**Elemental analysis** calculated for C\(_{84}\)H\(_{76}\)N\(_8\)O\(_{16}\) %C 69.42, %H 5.23 %N 7.71 found %C 69.61 %H 5.15 %N 7.83. 1\(^H\) **NMR** (400 MHz, CDCl\(_3\), Me\(_4\)Si): \(\delta\) 2.17 (s, 24H, –OCH\(_3\)), 4.11 (s,4H, bridge –CH), 7.42 (s, 16H, Ar-H), 7.8 (s, 20H, Ar-H), 10.51 (s, 8H, Ar-OH), 13\(^C\) **NMR** (125 MHz , CDCl\(_3\), Me\(_4\)Si) : 13 (-CH\(_2\)), 14.5 (-CH\(_3\)), 37.66, 39.31, 40.07, 40.3, 56.85, 121.46, 124, 142, 151, 154, 160 (Ar-C). **FT-IR** (KBr) \(\nu\): 3378 cm\(^{-1}\) (-OH), 2999 cm\(^{-1}\) (Ar-CH), 1547 cm\(^{-1}\) (-N=N-), **ESI-MS** observed m/z 1453 (M+1).

**Characterization of p-(4-hydroxy phenylazo) calix[4]resorcinarene (d\(_5\))**

**Elemental analysis** calculated for C\(_{80}\)H\(_{68}\)N\(_8\)O\(_{16}\) %C 66.84, %H 4.50 %N 7.42 found %C 66.68 %H 4.25 %N 7.58. 1\(^H\) **NMR** (400 MHz, CDCl\(_3\), Me\(_4\)Si): \(\delta\) 2.15 (s, 12H, –OCH\(_3\)), 4.1 (s,4H, bridge –CH), 7.22 (s, 16H, Ar-H), 7.65 (s, 20H, Ar-H), 10.45 (s, 12H, Ar-OH), 13\(^C\) **NMR** (125 MHz , CDCl\(_3\), Me\(_4\)Si) : 163.8, 162.6,150, 145.2, 142.2, 134.9, 130.0, 128.8, 121.3, 116.1, 115.1 (Ar-C), 106.9, 72.8, 70.4, 26.7, 14.3 (-CH\(_3\)), 13.5(-CH\(_2\)). **FT-IR** (KBr) \(\nu\): 3299 cm\(^{-1}\) (-OH), 2849 cm\(^{-1}\) (Ar-CH), 1545 cm\(^{-1}\) (-N=N-), **ESI-MS** observed m/z 1397 (M+).

**Characterization of p-(4-methoxy phenylazo) calix[4]arene (d\(_6\))**

**Elemental analysis** calculated for C\(_{56}\)H\(_{40}\)N\(_8\)O\(_{12}\) %C 66.14, %H 3.93 %N 11.02 found %C 66.28 %H 4.12 %N 11.15. 1\(^H\) **NMR** (400 MHz, CDCl\(_3\), Me\(_4\)Si): \(\delta\) 10.12 (s, 4H, Ar-OH), 7.8 (s, 8H, Ar-H), 7.52 (s, 16H, Ar-H), 2.72 (s, 12H, –OCH\(_3\)), 2.12 (s, 8H, bridge –CH\(_2\)), 13\(^C\) **NMR** (125 MHz , CDCl\(_3\), Me\(_4\)Si) : 12.7 (-CH\(_2\)), 13, 13.9, 14(-
CH₃), 26, 38.96, 39.1, 40.25, 54.35, 123, 126.3, 140.2, 151, 152.2, 168(Ar-C). FT-IR (KBr) υ: 3412 cm⁻¹ (-OH), 2985 cm⁻¹ (Ar-CH), 1542 cm⁻¹ (-N=N-), ESI-MS observed m/z 1017 (M+).

Characterization of p-(2-methoxy phenylazo) calix[4]arene (d₇)

Elemental analysis calculated for C₅₆H₄₀N₈O₁₂ %C 66.14, %H 3.93 %N 11.02 found %C 66.28 %H 4.12 %N 11.15. ¹H NMR (400 MHz, CDCl₃, Me₄Si): δ 10.14 (s, 4H, Ar-OH), 7.6 (s, 8H, Ar-H), 7.45 (s, 16H, Ar-H), 2.78 (s, 12H, –OCH₃), 2.42 (s, 8H, bridge –CH₂), ¹³C NMR (125 MHz , CDCl₃, Me₄Si) : 12.7 (-CH₂), 13, 13.9, 14(-CH₃), 24, 38.26, 39.1, 40.15, 54.38, 127, 129.3, 142.2, 151, 153.2, 165 (Ar-C). FT-IR (KBr) υ: 3412 cm⁻¹ (-OH), 2985 cm⁻¹ (Ar-CH), 1542 cm⁻¹ (-N=N-), FAB-MS observed m/z 1018 (M+).

Characterization of p-(4-hydroxy phenylazo) calix[4]arene (d₈)

Elemental analysis calculated for C₅₂H₄₀N₈O₈ %C 68.95, %H 4.42 %N 12.37 found %C 68.65 %H 4.28 %N 12.46. ¹H NMR (400 MHz, CDCl₃, Me₄Si): δ 9.95 (s, 8H, Ar-OH), 7.85 (s, 16H, Ar-H), 7.3 (s, 8H, Ar-H), 2.8 (s, 8H, bridge –CH₂), ¹³C NMR (125 MHz , CDCl₃, Me₄Si) : 13.96 (-CH₂), 29.1, 40.07, 70 , 121.66, 124.20, 139, 151.3, 155.2, 163 (Ar-C). FT-IR (KBr) υ: 3265 cm⁻¹ (-OH), 2950 cm⁻¹ (Ar-CH), 1495 cm⁻¹ (-N=N-), 1710 cm⁻¹ (-C=O-). FAB-MS observed m/z 905 (M+).

Characterization of p-(2-hydroxy phenylazo) calix[4]arene (d₀)

Elemental analysis calculated for C₅₂H₄₀N₈O₈ %C 68.95, %H 4.42 %N 12.37 found %C 68.69 %H 4.2 %N 12.42. ¹H NMR (400 MHz, CDCl₃, Me₄Si): δ 10.1 (s, 8H, Ar-OH), 7.65 (s, 16H, Ar-H), 7.87 (s, 8H, Ar-H), 2.35 (s, 8H, bridge –CH₂), ¹³C NMR (125 MHz , CDCl₃, Me₄Si) : 13.6(-CH₂), 27.1, 41.7, 54.34, 120.46, 122.70, 138.7,
150.3, 153.2, 160, 171 (Ar-C). **FT-IR** (KBr) \( \nu: 3265 \text{ cm}^{-1} \) (-OH), 2950 cm\(^{-1}\) (Ar-CH), 1495 cm\(^{-1}\) (-N=N-), 1710 cm\(^{-1}\) (-C=O-). **FAB-MS** observed m/z 905 (M+).

**Characterization of p-(2-carboxy phenylazo) calix[4]resorcinarene (d\(_{10}\))**

**Elemental analysis** calculated for C\(_{84}H_{68}N_{8}O_{20}\) %C 66.84, %H 4.50 %N 7.42 found %C 66.68 %H 4.25 %N 7.58. **\(^1\)H NMR** (400 MHz, CDCl\(_3\), Me\(_4\)Si): \( \delta \) 10.42 (s, 8H, Ar-OH), 11.57 (s, 4H, -COOH), 7.3-7.95 (s, 36H, Ar-H), 4.18 (s, 4H, bridge –CH), 2.12 (s, 12H, –OCH\(_3\)), **\( ^{13} \)C NMR** (125 MHz, CDCl\(_3\), Me\(_4\)Si) : 13.2 (-CH\(_2\)), 14.1 (-CH\(_3\)), 123.66, 126.0, 140, 151, 152.2, 163,166 (Ar-C). **FT-IR** (KBr) \( \nu: 3278 \text{ cm}^{-1} \) (-OH), 2989 cm\(^{-1}\) (Ar-CH), 1545 cm\(^{-1}\) (-N=N-), 1710 cm\(^{-1}\) (-C=O-). **ESI-MS** observed m/z 1509 (M+).

**Characterization of sulphonated calix[4]resorcinarene (C\(_1\))**

**Elemental analysis** calculated for C\(_{56}H_{44}O_{24}S_{4}Na_{4}\) %C 50.83, %H 3.32 found %C 50.72 %H .3.24. **\(^1\)H NMR** (400 MHz, CDCl\(_3\), Me\(_4\)Si): \( \delta \) 10.42 (s, 8H, Ar-OH), 7.5 (s, 20H, Ar-H), 4.18 (s, 4H, bridge –CH), 2.12 (s, 12H, –OCH\(_3\)), **\( ^{13} \)C NMR** (125 MHz, CDCl\(_3\), Me\(_4\)Si) : 13, 13.6, 14, 15.3, 23, 28, 30, 32, 39.51, 123.66, 126.0, 140, 160,162,164 (Ar-C). **FT-IR** (KBr) \( \nu: 3278 \text{ cm}^{-1} \) (-OH), 2989 cm\(^{-1}\) (Ar-CH), 1545 cm\(^{-1}\) (-N=N-), 1710 cm\(^{-1}\) (-C=O-). **ESI-MS** observed m/z 1322 (M+).

**Characterization of sulphonated calix[4]resorcinarene (C\(_2\))**

**Elemental analysis** calculated for C\(_{32}H_{27}O_{20}S_{4}Na_{4}\) %C 40.29, %H 2.83 found %C 40.32 %H 2.71. **\(^1\)H NMR** (400 MHz, CDCl\(_3\), Me\(_4\)Si): \( \delta \) 10.61 (s, 8H, Ar-OH), 7.42 (s, 4H, Ar-H), 4.18 (s, 4H, bridge –CH), 1.45 (s, 12H, –CH\(_3\)), **\( ^{13} \)C NMR** (125 MHz, CDCl\(_3\), Me\(_4\)Si) : 13, 13.5, 22, 23, 29, 31, 54.35, 111, 114, 118, 123.6, 126.0,130, 144,
155, 156.2, 160 (Ar-C). **FT-IR** (KBr) $\nu$: 3278 cm$^{-1}$ (-OH), 2989 cm$^{-1}$ (Ar-CH), 1545 cm$^{-1}$ (-N=N-), 1710 cm$^{-1}$ (-C=O-). **FAB-MS** observed m/z 955 (M+2).

**Characterization of phenyl urea substituted calix[4]arene (C$_3$)**

**Elemental analysis** calculated for C$_{46}$H$_{40}$N$_4$O$_8$: %C 71.13, %H 5.15, %N 16.49 found: %C 71 %H 5.03 %N 16.26. **$^1$H NMR** (400 MHz, CDCl$_3$, Me$_4$Si): $\delta$ 9.80 (s, 2H, Ar-OH), 8.50 (s, 4H, -NH), 4.25 (s, 12H, Ar-CH$_2$-Ar (bridge) and CH$_2$-O-), 6.70-7.30 (s, 22H, Ar-H). **$^{13}$C NMR** (125 MHz, CDCl$_3$, Me$_4$Si): $\delta$ 165,162, 150,151,145, 141, 128, 123, 121, 115 and 113 (Ar-C), 23, 17.18, 12.0 (-CH$_2$-). **FT-IR** (KBr) $\nu$: 3390cm$^{-1}$ (-NH), 1670-1650 cm$^{-1}$ (-NH-CO), 1145cm$^{-1}$ (-C-O-C). **FAB-MS** observed (m/z) 778 (M+2).
Conclusion:

The newly synthesized calix[4]arene and calix[4]resorcinarene azo dyes \( (d_1-d_8) \) were well characterized and had intense as well as bright hues. The synthesized calix[4]arene and calix[4]resorcinarene dyes \( (d_3-d_8) \) have been used as colorants for flexographic and gravure inks which is discussed in Chapter III, and water soluble calix[4]resorcinarene dyes \( (d_1-d_2) \) have been used for dyeing leather, wool, silk, nylon and cotton. The performance as well as various studies like wet fastness, light fastness has been thoroughly studied which is discussed in Chapter III.

The newly synthesized para sulphonato calix[4]resorcinarene \( (C_2) \) have been used for the formation of inclusion complex of a poorly soluble drug mycophenolate mofetil (MMF). The interaction between para sulphonatocalix[4]resorcinarene (PSC[4]R) and MMF in solid state inclusion complexes was accomplished by aqueous phase solubility studies, Thermal Analysis, HPLC, PXRD, FT-IR, and UV-VIS.spectroscopy which is discussed in Chapter IV.

The synthesized azo calix[4]arene dye \( (d_9) \) have been used in the preparation of ion selective electrode for the detection of \( \text{Nd}^{3+} \) ions at low concentration. The electrode characteristics such as pH range, lower detection limit, response time and selectivity especially were comparable to the previously reported neodymium ion- selective electrodes, as discussed in Chapter V.

The newly synthesized phenylurea substituted calix[4]arene \( (C_3) \) have been used in the preparation of ion selective electrode for the detection of monohydrogenphosphate (MHP) ions at low concentration. The proposed sensor was successfully applied for the direct determination of monohydrogen phosphate in real life samples, which is discussed in Chapter VI.
The synthesized para sulphonato calix[4]resorcinarene (C₁) attached with silver nanoparticles have been used as readily detectable markers of specific recognition events demonstrating a high potential for simple, color-based diagnostic tests, for dimethoate (organophosphorus insecticide) which is required for many routine environmental applications. Prepared supra-nano assembly have been characterized by dynamic light scattering (DLS), UV-VIS spectroscopy, FT-IR and transmission electron microscopy (TEM), as discussed in Chapter VII (A).

The newly synthesized and characterized, calix[4]resorcinarene azo dye (d₁₀) has application in the field of microbiology. The newly designed molecule showed excellent binding ability to stain the gram +ve cocci, which is discussed in Chapter VII (B).
References: