

**DESIGN AND SYNTHESIS OF CALIX[4]ARENE BASED
MOLECULAR PROBES**

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**DEPARTMENT OF CHEMISTRY
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**DESIGN AND SYNTHESIS OF CALIX[4]ARENE BASED
MOLECULAR PROBES**

by

PREETI GOEL

Department of Chemistry

Submitted

in fulfilment of the requirements of the degree of

Doctor of Philosophy

to the



Indian Institute of Technology Delhi

APRIL, 2015

*DEDICATED
TO
MY PARENTS*

CERTIFICATE

This is to certify that the thesis titled “**Design and synthesis of calix[4]arene based molecular probes**” being submitted by **Ms. Preeti Goel** to the Indian Institute of Technology, Delhi, for the award of degree of **Doctor of Philosophy** is a record of bonafide research work carried out by her. **Ms. Preeti Goel** has worked under my guidance and supervision and has fulfilled the requirements for the submission of this thesis, which to my knowledge has reached the requisite standard.

The results contained in this thesis are original and have not been submitted, in part or full, to any other University or Institute for the award of any other degree or diploma.

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ABSTRACT

The thesis entitled, “*Design and Synthesis of Calix[4]arene based Molecular Probes*” presents the research work carried out on the synthesis, characterization and applications of some novel calix[4]arene derivatives achieved through modification, optimization and innovation of procedures available in the literature. Synthesized new chemical entities have been characterized by utilizing spectroscopic techniques (FT-IR, UV-Visible, ^1H , ^{13}C and high resolution mass spectral analysis) while their ion recognition potential has been examined by using UV-Visible, NMR, fluorescence and colorimetric methods of analysis. The accomplished research work has been divided into five chapters.

Chapter I of the thesis highlights some of the general aspects of molecular recognition. An effort has been made to present an overview of various calixarene based receptors for sensing cations and anions published in the scientific literature during the last ten years.

Chapter II of the thesis primarily focuses on the synthesis and characterization of some new macrocyclic calix[4]arenes derivatives by incorporation of Schiff base unit as binding site and oxalylamido and coumarinyl groups as signaling unit both at the upper and lower rims of the calix[4]arene molecular architecture.

Chapter III describes the experiments done to examine the synthesized molecular receptors for their interaction with various cations in the form of their perchlorate salts through the use of colorimetric change, UV-visible, fluorescence, IR and mass spectroscopy. The synthesized calix[4]arene derivatives exhibit selective binding with Cu^{2+} in preference to related transition metal ions and elicit distinct color change through a 1:1 binding stoichiometry.

Chapter IV describes the research work done on the synthesis and characterization of novel calixarene derivatives for multi-ion recognition. The synthesis involves

modification of calixarene scaffold at the lower rim through bis(2-aminophenyl)isophthalamidoyl group as well naphthalene units

Chapter V describes the experiments done to evaluate the molecular receptors whose synthesis have been given in chapter IV for their interaction with various cations (as perchlorate salts) and anions (as tetrabutylammonium salts) through the use of colorimetric change, UV-visible, fluorescence, IR and mass spectroscopy. The synthesized receptor exhibits selective recognition and high binding affinity for copper ions. The resulting Cu^{2+} -calixarene complexes have been determined to further utilize for the detection of anions, *i.e.*, HSO_4^- and S^{2-} . Both molecular receptors have been found to display a high selectivity and sensitivity for Cu^{2+} , HSO_4^- and S^{2-} .

TABLE OF CONTENTS

Title	Page No.
Certificate	i
Acknowledgement	ii
Abstract	iv
List of Figures, Schemes and Tables	vi
Notes	xiv
<i>CHAPTER I</i>	
Calix[4]arene based molecular probes for ionic and molecular recognition	1
<i>CHAPTER II</i>	
Synthesis of new calix[4]arene based molecular receptors	96
<i>CHAPTER III</i>	
Evaluation of synthesized calix[4]arene based molecular receptors	133
<i>CHAPTER IV</i>	
Synthesis of molecular receptors for multi-ion analysis	181
<i>CHAPTER V</i>	
Evaluation of new calix[4]arene based supramolecular adduct for sensing S^{2-} and HSO_4^-	212
Brief Bio-Data of the Author	258

LISTS OF FIGURES, SCHEMES AND TABLES

	Page No.
Figure 1.1. (a) Pederson's crown ether- K^+ complex; (b) Lehn's cryptand- K^+ complex and (c) Cram's host-guest complex with Li^+ .	1
Figure 1.2. Some common molecular scaffolds examined as receptors for molecular recognition.	2
Figure 1.3. Molecular structure and the 3-D architecture of <i>p</i> - <i>tert</i> -butylcalix[4]arene.	3
Figure 1.4. Two different modes for inversion of phenolic units.	4
Figure 1.5. Possible conformations of calix[4]arenes: (a) cone; (b) partial cone; (c) 1,2-alternate and (d) 1,3-alternate (R= H or <i>tert</i> -butyl).	4
Figure 1.6. Different conformations of calix[6]arene.	5
Figure 1.7. Pleated loop conformation of <i>p</i> - <i>tert</i> -butylcalix[8]arene.	5
Figure 1.8. Transition metal complex as chemoreceptor.	49
Figure 1.9. Macrocyclic receptors for anions.	50
Figure 1.10. Some functional groups used for anions sensing.	50
Figure 2.1. Chromatogram of an HPLC analysis of a crude product obtained from acid-catalysed reaction of <i>p</i> - <i>tert</i> -butylphenol and <i>s</i> -trioxane.	100
Figure 2.2. ^1H NMR spectra of diethyl- <i>N,N'</i> -(1,2-phenylene)dioxalamate recorded in $CDCl_3$.	110
Figure 2.3. ^1H NMR spectra of <i>N,N'</i> -1,2-bis[(2-hydrazino)oxalyl]phenylenediamine recorded in $DMSO-d_6$.	111
Figure 2.4. ^1H NMR of Compound 7 recorded in $CDCl_3$.	113
Figure 2.5. ^{13}C NMR spectra of receptor 7 recorded in $DMSO-d_6$.	113
Figure 2.6. HRMS of compound 7 .	114
Figure 2.7. ^1H NMR of Compound 8 recorded in $DMSO-d_6$.	115
Figure 2.8. ^{13}C NMR spectra of receptor 8 recorded in $DMSO-d_6$.	115
Figure 2.9. HRMS of compound 8 .	116
Figure 2.10. ^1H NMR spectrum of coumarinyl hydrazide.	117
Figure 2.11. ^1H NMR spectrum of coumarin based calix[4]arene derivative (13).	119

Figure 2.12.	^{13}C NMR spectrum of compound 13 .	119
Figure 2.13.	Mass spectrum of coumarin based calix[4]arene derivative 13	120
Figure 2.14.	Mass spectrum of reference compound 14 .	120
Figure 3.1.	UV-Vis titration of 5a with 0-8 equiv of F^- ions.	135
Figure 3.2.	UV-Vis titration of compound 6 with F^- and Ag^+ .	136
Figure 3.3.	(a) Partial ^1H NMR spectra of 6 upon addition of 1 equiv. of silver ion and (b) Partial ^1H NMR spectra of sensor 6 in the presence of 1 equiv. of fluoride ion.	137
Figure 3.4.	Mechanism causing quenching in the fluorescence intensity due to paramagnetic effect.	138
Figure 3.5.	Mechanism operating in photoinduced electron transfer process.	138
Figure 3.6.	Mechanism operating in photoinduced charge transfer process.	139
Figure 3.7.	Mechanism functioning in resonance energy transfer (FRET) process.	140
Figure 3.8.	Mechanism functioning during formation of excimer or exciplex complexes.	140
Figure 3.9.	Mechanism functioning in the irreversible chemical reaction promoted by metal ions.	141
Figure 3.10.	(a) Proposed binding model of compound 7 towards Zn^{2+} ; (b) Change in the IR spectra of compound 7 upon addition of Zn^{2+} .	142
Figure 3.11.	Molecular structures of synthesized calixarene based derivatives 23 , 24 , 25 and 26	149
Figure 3.12.	Color change of 24 ($20\ \mu\text{M}$) in THF.	150
Figure 3.13.	Absorbance change in the UV-Vis spectra of 24 ($20\ \mu\text{M}$) on addition of various metal ions in THF.	151
Figure 3.14.	Absorbance change in the UV-Vis spectra of 23 ($20\ \mu\text{M}$) on addition of various metal ions in THF.	152
Figure 3.15.	Absorbance change in the UV-Vis spectra of 24 ($20\ \mu\text{M}$) upon addition of 7.5 equivalents of Cu^{2+} in THF.	153
Figure 3.16.	Absorbance change in the UV-Vis spectra of 23 ($20\ \mu\text{M}$) upon addition of 7.5 equivalents of Cu^{2+} .	153
Figure 3.17.	Job's plot of Cu^{2+} complex formation. $\{[\text{L}]/[\text{L}]+[\text{Cu}^{2+}]$ is the mole fraction of ligand.	154

Figure 3.18.	Quenching in the fluorescence intensity of 24 (20 μ M) in THF in presence of Cu^{2+} ($\lambda_{\text{excitation}} = 327$ nm); Inset shows change in the fluorescence intensity of the ligand with varying concentration of Cu^{2+} .	155
Figure 3.19.	Quenching in the fluorescence intensity of 23 (20 μ M) in THF in presence of Cu^{2+} ($\lambda_{\text{excitation}} = 313$ nm).	156
Figure 3.20.	Change in the fluorescence intensity of the ligand upon addition of 7.5 equivalents of various metal ions to ligand 24 in THF ($\lambda_{\text{excitation}} = 327$ nm).	157
Figure 3.21.	Selectivity coefficients, $K_M^{n+}/\text{Cu}^{2+} = \Delta F_M^{n+} / \Delta F_{\text{Cu}^{2+}}$.	158
Figure 3.22.	A plot of $F_0 - F/F_0$ versus $\log [\text{Cu}^{2+}]$ to calculate LOD from fluorescence data of 24 .	159
Figure 3.23.	(a) A plot of F_0/F versus $[\text{Cu}^{2+}]$ to calculate quenching constant K_{sv} and (b) Plot of $\log(F_0 - F/F)$ versus $\log[\text{Cu}^{2+}]$ to calculate association constant of 24 .	160
Figure 3.24.	(a) A plot of F_0/F versus $[\text{Cu}^{2+}]$ to calculate K_{sv} and (b) Plot of $\log(F_0 - F/F)$ versus $\log[\text{Cu}^{2+}]$ to calculate association constant of 23 .	160
Figure 3.25.	ESI-MS spectrum of supramolecular complex between receptor 24 and Cu^{2+} [24 + Cu + ClO_4] $^+$.	161
Figure 3.26.	Comparative study of molecular receptor 24 in THF of peak at 443 nm in presence of 7.5 equivalents of various metal ions + 7.5 equivalents of Cu^{2+} by exciting at 327 nm.	162
Figure 3.27.	Color change before and after addition of Cu^{2+} to the solution of receptor 25 (15 μ M) in CH_3CN .	163
Figure 3.28.	Change in UV-Vis absorption spectra of ligand 25 (15 μ M) upon addition of various metal ions.	164
Figure 3.29	Change in the UV-Vis spectra of 25 (15 μ M) upon addition of 5.5 equivalents of Cu^{2+} in CH_3CN .	165
Figure 3.30.	Job's plot of Cu^{2+} complex formation with 25 revealing 1:1 stoichiometry.	166
Figure 3.31.	Enhancement of fluorescence intensity of 25 in the presence of Cu^{2+} in CH_3CN ($[\text{25}] = 15 \mu\text{M}$, $\lambda_{\text{excitation}} = 340$ nm).	167
Figure 3.32.	Relative enhancement in the fluorescence intensity of 25 , 27 and reference compound 26 upon addition of Cu^{2+} in CH_3CN ($\lambda_{\text{excitation}} = 340$ nm).	168
Figure 3.33.	Benesi- Hildebrand plot between $1/(F - F_0)$ vs $1/[\text{Cu}^{2+}]$ to calculate binding constant.	169

Figure 3.34.	(a) Percentage enhancement in the fluorescence intensity of the receptor 25 (15 μM) upon addition of various metal ions in CH_3CN ($\lambda_{\text{excitation}} = 340 \text{ nm}$); (b) Fluorescence emission spectra obtained by addition of various metal ions (130 μM) to ligand solution (15 μM) in CH_3CN .	170
Figure 3.35.	Proposed model for rationalizing the enhancement in fluorescence intensity upon addition of Cu^{2+} to the solution of receptor 25 (15 μM) in CH_3CN .	171
Figure 3.36.	Selectivity coefficients, $K_M^{n+}/_{\text{Cu}^{2+}} = \Delta F_M^{n+} / \Delta F_{\text{Cu}^{2+}}$.	172
Figure 3.37.	Selectivity of 25 in CH_3CN in presence of 10 equivalents of various metal ions + 10 equivalents of Cu^{2+} ($\lambda_{\text{excitation}} = 340 \text{ nm}$).	173
Figure 4.1.	The three main strategies for anion sensing: (a) chemodosimeter; (b) Chemosensor bearing a signaling unit as well as binding site; (c) Displacement approach.	182
Figure 4.2.	Proposed binding mechanism of 6 and 7 towards CN^- .	184
Figure 4.3.	Proposed binding mechanism of 11 towards PO_4^{2-} .	186
Figure 4.4.	Proposed binding mechanism for 14 and S^{2-} ions.	187
Figure 4.5.	Proposed binding mechanism of 15 towards Cu^{2+} and S^{2-} .	187
Figure 4.6.	Proposed binding mechanism of 16 towards S^{2-} .	188
Figure 4.7.	Proposed binding mechanism of 18 towards F^- .	189
Figure 4.8.	Proposed binding mechanism of 20 towards I^- .	190
Figure 4.9.	Proposed binding mechanism of 21 towards CN^- .	191
Figure 4.10.	^1H NMR spectra of bis(2-aminophenyl) isophthalamide.	197
Figure 4.11.	^1H NMR spectra of the synthesized compound 27 .	199
Figure 4.12.	^{13}C NMR spectra of the synthesized compound 27 .	200
Figure 4.13.	Mass spectrum of lower rim looped calix[4]arene derivative 27 .	200
Figure 4.14.	^1H NMR spectra of 2-hydroxy-1-naphthaldehyde hydrazone.	201
Figure 4.15.	^1H NMR spectra of the synthesized compound 29 .	203
Figure 4.16.	^{13}C NMR spectra of the synthesized compound 29 .	203
Figure 4.17	HRMS of compound 29	204

Figure 5.1.	Two different approaches used for the detection of second analyte using host guest complex formation.	214
Figure 5.2.	Proposed binding model of 1 for the detection of S^{2-} ions.	216
Figure 5.3.	Proposed binding model of 4 for the detection of S^{2-} ions.	217
Figure 5.4.	Proposed binding model of 5.Cu for the detection of CN^- ions.	217
Figure 5.5.	Proposed binding model of 6.Zn for the detection of $HP_2O_6^{3-}$ ions.	218
Figure 5.6.	Proposed binding model of 7.Zn for the detection of $H_2PO_4^-$ ions.	219
Figure 5.7.	Molecular structures of synthesized calixarene based derivatives 9 and 10 .	220
Figure 5.8.	Color change from colorless to yellow on addition of Cu^{2+} ion to the sensor solution.	221
Figure 5.9.	UV-Vis absorption spectra of sensor (20 μM) upon addition of different metal cations in $CHCl_3$ - CH_3CN (4:1v/v). Inset: Relative responses of absorbance of receptor 9 (20 μM) versus tested metal ions.	222
Figure 5.10.	UV-Vis absorption changes of sensor 9 (20 μM) upon addition of 2 equivalents of Cu^{2+} in $CHCl_3$: CH_3CN (4:1 v/v).	223
Figure 5.11.	Change in the absorption of sensor at 365 nm as a function of Cu^{2+} added.	223
Figure 5.12.	A plot of A_{365}/A_{289} for 9 in the presence of Cu^{2+} .	224
Figure 5.13.	Job's plot of Cu^{2+} complex formation. $\{[L]/[L]+[Cu^{2+}]$ is the mole fraction of ligand 9 .	225
Figure 5.14.	Comparative absorbance of ligand 9 (20 μM) at 368 nm in presence of Cu^{2+} ion and Cu^{2+} plus other metal ions ($CHCl_3$: CH_3CN (4:1 v/v)) (black bar represents absorbance in presence of Cu^{2+} ion and grey bar represents absorbance of sensor in the presence of Cu^{2+} in conjunction with other metal ions).	226
Figure 5.15.	UV-Vis reversibility studies of receptor 9 (a) in presence of Cu^{2+} ion (b) receptor + Cu^{2+} +1 equivalent EDTA (c) receptor + Cu^{2+} + 3 equivalent EDTA.	227
Figure 5.16.	Benesi–Hildebrand plot (absorbance at 289 nm) of 9 assuming 1:1 binding stoichiometry with Cu^{2+} .	227
Figure 5.17.	A plot of A_0-A/A_0 Versus $\text{Log}Cu^{2+}$ to calculate limit of detection.	228
Figure 5.18.	Proposed binding model of supramolecular complex of receptor 9 and copper (II).	229

Figure 5.19.	Change in the UV-Vis spectrum of 9 .Cu ²⁺ complex upon gradual addition of HSO ₄ ⁻ .	230
Figure 5.20.	Relative change in the absorbance intensity of 9 .Cu ²⁺ in presence of various anions.	231
Figure 5.21.	Selectivity of 9 .Cu ²⁺ for HSO ₄ ⁻ over all other anions.	231
Figure 5.22.	Change in the color of solution of receptor 10 upon addition of F ⁻ ions.	232
Figure 5.23.	Change in the UV-Vis spectra of 10 (20 μM) on addition of various metal ions in acetonitrile.	233
Figure 5.24.	Change in the UV-Vis spectra of ligand 10 (20 μM) upon addition of F ⁻ (0-47 μM) in CH ₃ CN.	234
Figure 5.25.	Quenching in the fluorescence intensity of 10 (20 μM) in CH ₃ CN in presence of F ⁻ (0-65 μM).	235
Figure 5.26.	Relative change in fluorescence intensity upon addition of various anions to the solution of receptor 10 in CH ₃ CN.	236
Figure 5.27.	Comparative study of molecular receptor 10 in CH ₃ CN in presence of 3.5 equivalents of various metal ions + 3.5 equivalents of F ⁻ by exciting at 337 nm.	237
Figure 5.28.	Job's plot of F ⁻ complex formation. {[10]/[10]+[F ⁻]} is the mole fraction of ligand 10 .	238
Figure 5.29.	Partial ¹ H NMR spectra of 10 in CDCl ₃ at 25 ^o C and the corresponding changes after the addition of 0.2 equivalents of tetrabutylammonium fluoride.	239
Figure 5.30.	Binding model for the interaction of 10 with F ⁻ .	239
Figure 5.31.	Color change upon addition of Cu ²⁺ to the solution of molecular receptor 10	240
Figure 5.32.	Change in the UV-Vis spectra of 10 (20 μM) upon addition of Cu ²⁺ (0 - 28 μM) in CH ₃ CN.	241
Figure 5.33.	Quenching in the fluorescence intensity of 10 (20 μM) in CH ₃ CN in presence of Cu ²⁺ (0 - 29 μM).	242
Figure 5.34.	Relative change in fluorescence intensity upon addition of various cations to the solution of receptor 10 in CH ₃ CN.	243
Figure 5.35.	A comparative study of molecular receptor 10 in CH ₃ CN in the presence of 1.5 equivalents of various metal ions + 1.5 equivalents of Cu ²⁺ on excitation at 337 nm.	244
Figure 5.36.	Job's Plot of Cu ²⁺ complex formation. {[10]/[10]+[Cu ²⁺]} is the mole fraction of receptor 10 .	245

Figure 5.37.	Relative change in the fluorescence intensity upon addition of various anions to the solution of 10 -Cu ²⁺ (48 μM) in CH ₃ CN.	246
Figure 5.38.	Changes in fluorescence spectrum of 10 -Cu ²⁺ solution (48 μM) upon addition of S ²⁻ (0-145 μM).	247
Figure 5.39.	Selectivity of 10 .Cu ²⁺ for S ²⁻ over all other anions.	248
Figure 5.40.	ESI-MS spectra showing a peak corresponding to 10 + Cu ²⁺ complex formation.	248
Scheme 2.1.	Synthesis of <i>p</i> - <i>tert</i> -butylcalix[n]arene from <i>p</i> - <i>tert</i> -butylphenol.	97
Scheme 2.2.	First step of the mechanism involved during the synthesis of <i>p</i> - <i>tert</i> -butylcalix[n]arenes.	98
Scheme 2.3.	Mechanism of the formation of <i>p</i> - <i>tert</i> -butylcalix[n]arenes.	99
Scheme 2.4.	Synthesis of <i>p</i> - <i>tert</i> -butylcalix[n]arenes.	100
Scheme 2.5.	Synthesis of novel calixarene derivatives 7 and 8 .	102
Scheme 2.6.	Synthesis of lower appended coumarinyl calix[4]arene derivative	103
Scheme 2.7.	Synthesis of Diethyl- <i>N,N'</i> -(1,2-phenylene)dioxalamate .	104
Scheme 2.8.	Synthesis of <i>N,N'</i> -1,2-bis[(2-hydrazino)oxalyl]phenylenediamine .	104
Scheme 2.9.	Synthesis of precursors. <i>Reagents and conditions:</i> (ii) 1,3 dibromopropane, K ₂ CO ₃ , reflux; (iii) <i>p</i> -hydroxybenzaldehyde, K ₂ CO ₃ , reflux.	105
Scheme 2.10.	Synthesis of precursor molecules. <i>Reagents and conditions:</i> (v) ethyl bromoacetate, K ₂ CO ₃ , reflux; (vi) HMTA, TFA, reflux	106
Scheme 2.11.	Synthesis of novel calixarene derivatives. <i>Reagents and conditions:</i> (iv) acetic acid, ethanol reflux.	107
Scheme 2.12.	Synthesis of coumarin hydrazone.	108
Scheme 2.13.	Synthesis of lower appended coumarinyl calix[4]arene derivative .	109
Scheme 2.14.	Synthesis of novel upper derivatized coumarin appended calix[4]arene derivative.	109
Scheme 2.15.	Synthesis of reference compound.	110
Scheme 4.1.	Synthesis of novel lower looped calix[4]arene derivative 27 .	192
Scheme 4.2.	Synthesis of novel naphthalene appended calix[4]arene derivative 29 .	193
Scheme 4.3.	Synthesis of precursor molecules.	194

Scheme 4.4	Synthesis of bis(2-aminophenyl)isophthalamide.	195
Scheme 4.5.	Synthesis of lower rim looped calix[4]arene derivative 27 .	195
Scheme 4.6.	Synthesis of 2-hydroxy-1-naphthaldehyde hydrazone.	196
Scheme 4.7.	Synthesis of novel hydroxyl naphthalene appended calix[4]arene derivative 29 .	196
Table 1.1.	Calix[4]arene receptors for alkali and alkaline earth metal ions.	8
Table 1.2.	Calix[4]arene receptors for the detection of transition metal ions.	19
Table 1.3.	Calix[4]arene receptors for lanthanide ions.	44
Table 1.4.	Calix[4]arene receptors for the detection of anions.	51
Table 1.5.	Calix[4]arene receptors for amino acids and amines	69
Table 3.1.	Comparison between molecular receptors 23 and 24	162
Table 3.2.	Optical density of solutions of different compositions of 24 and Cu ²⁺ solutions at λ_{max} 327 nm	175
Table 3.3.	Optical density of solutions of different compositions of 25 and Cu ²⁺ solutions at λ_{max} 339 nm.	175
Table 5.1.	Vibrations parameters for compound 9 and its complex with Cu ²⁺	229
Table 5.2.	Optical density of solutions of different compositions of 9 on addition of different Cu ²⁺ ions at λ_{max} 380 nm.	251
Table 5.2.	Optical density of solutions of different compositions of 10 on addition of Cu ²⁺ ions at λ_{max} 400 nm.	251

NOTES

1. All melting points reported in this thesis are uncorrected and have been recorded on an electric melting point apparatus (Toshniwal, India).
2. UV-visible spectra have been recorded on Perkin Elmer's (Lambda 35) spectrophotometer.
3. FT-IR spectra have been recorded on KBr discs on a [5-DX] Nicolet FT-IR spectrophotometer.
4. Fluorescence spectra have been recorded on FL 3-11, Fluorolog-3 modular spectrofluorometer with single Czerny-Turner grating excitation and emission monochromators having 450 W Xe arc lamp as the excitation source and PMT as the detector.
5. ^1H and ^{13}C NMR spectra have been recorded on a 300 MHz Bruker 300 DPX 300 instrument at room temperature in deuterated solvents (CDCl_3 , D_2O , CD_3OD , CD_3SOCD_3) using tetramethylsilane (TMS) as an internal standard with the values of chemical shifts reported on δ scale. The abbreviations s, brs, d, dd, t, q and m indicate singlet, broad singlet, doublet, double doublet, triplet, quartet and multiplet respectively.
6. FAB-mass spectra of the synthesized compounds have been recorded on a JEOL SX 102/DA- 6000 Mass Spectrometer at Central Drug Research Institute, Lucknow using m-Nitrobenzylalcohol as the matrix and Argon/Xenon (6kV, 100mA) as the FAB gas.
7. The high resolution mass spectra of the synthesized compounds have been recorded on a micrOTOF-Q II 10262 mass spectrophotometer in positive mode by ESI technique.
8. Elemental analysis has been carried on a Perkin Elemer's 240C-CHN Analyzer.

9. The completion of the reactions have been monitored by *Thin Layer Chromatography* performed on silica gel (Silica gel-G; Merck) coated glass plates using iodine for visualizing the spots.
10. Purification of the synthesized compounds has been carried out by column chromatography over silica gel (60-120 mesh; Merck).
11. For the sake of convenience, the names of calixarene derivatives used in this thesis have been shortened.
12. Abbreviations used in this thesis are:
- DMF- N,N'-Dimethylformamide;
- CDCl₃- Deuterated Chloroform
- D₂O- Deuterated water;
- DMSO-*d*₆- Deuterated dimethyl sulfoxide;
- TBA- Tetra butyl ammonium.
- THF- Tetrahydrofuran