Polynuclear Aromatic Hydrocarbon (PAH) Inclusion in Lower Rim Substituted Calix[4]arene

Project report submitted to the Central University of Punjab

For the award of

Master of Sciences

In

CHEMISTRY

BY

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Supervisor

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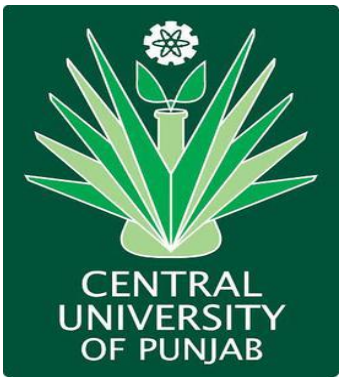

Department of Chemical Sciences

School of Basic and Applied Sciences

Central University of Punjab, Bathinda

May, 2018

CERTIFICATE

I declare that the dissertation entitled “POLYNUCLEAR AROMATIC HYDROCARBON (PAH) INCLUSION IN LOWER RIM SUBSTITUTED CALIX[4]ARENE” has been prepared by me under the guidance of Dr. J. Nagendra Babu, Assistant Professor, Department of Chemical sciences, School of Basic and Applied Sciences, Central University of Punjab. No part of this dissertation has formed the basis for the award of any degree or fellowship previously.

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CERTIFICATE

I certify that MANGE RAM has prepared her dissertation entitled “POLYNUCLEAR AROMATIC HYDROCARBON (PAH) INCLUSION IN LOWER RIM SUBSTITUTED CALIX[4]ARENE” for the award of M.Sc. degree in subject Chemistry under the faculty of Chemical Sciences of Central University of Punjab, under my supervision and guidance. She has carried out this work at the Department of chemical sciences, School of Basic and Applied Sciences, Central University of Punjab.

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Date: 30 May, 2018

Dedication

This thesis is dedicated to

My Father

who taught me that the best kind of knowledge to have is that which is learned for its own sake.

It is also dedicated to

My Mother

who taught me that even the largest task can be accomplished if it is done one step at a time.

ABSTRACT

Polynuclear Aromatic Hydrocarbon (Pah) Inclusion In Lower Rim Substituted Calix[4]Arene

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Name of school	: Basic and Applied Sciences
Keywords	: PAH, Calix[4]arene, Host-guest complex

Calix[4]arene was lower rim functionalized to furnish receptor 2-3 and 4-6, containing propyl and cynomethoxy moieties respectively. The receptors were characterized by FTIR, EI-MS, ^{1}H and ^{13}C NMR. UV-visible studies were performed with receptor 2-5 cone and 6^{th} 1-3,aternate. ($2x10^{-4}$) upon addition of Naphthalene, Anthracene and Pyrene. Upon addition of Naphthalene, Anthracene and Pyrene the UV-visible absorption showed hyperchromic shift. The one-to-one Host-Guest complexation studied by Benesi-Hildebrand equation showed stability constant in the range $2\text{-}10x10^{4}$ M^{-1}.

(Mange ram) (Dr. J. Nagendra Babu)

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At last none of this would have been possible without the love and support of my family. My parents, has been a constant source of love, concern, support and strength for all these years. Their love provided me inspiration and was my driving force. I would like to express my heart-felt gratitude to my father ***Shri Omprakash*** *and mother* ***Smt. Bimla Devi****. I want to express my deepest love and thanks to my best friend Ajay Chhimpa. He has been a true and great supporter for me during the tough and trying periods of research work.*

(Mange ram)

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LIST OF SCHEME

LIST OF ABBREVIATIONS

Sr. No	Full Form	Abbreviation
1.	Dimethylformamide	DMF
2.	Deuterated Chloroform	$CDCl_3$
3.	Chloroform	$CHCl_3$
4.	Milligram	mg
5.	Nanogram	nm
6.	Hours	H
7.	Gram	G
8.	Milli mole	mmol
9.	Quantom dots	QDs
10.	Fourier Transform-Infrared spectrophotometer	FTIR
11.	Electrospray ionization	ESI
12.	Distilled water	D.W
13.	Photosensitizer	PS
14.	Ion-Selective Electrodes	ISE
15.	Isothermal Titration Calorimetry	ITC
16.	Deuterium oxide	D_2O
17.	Sulphonated n calixarenes	SCnAs
18.	Thin layer chromatography	TLC
19.	Sodium Hydride	NaH
20.	Ultra-violet	UV
21.	Propyl Iodide	PrI

CHAPTER 1.

INTRODUCTION

INTRODUCTION:

Polynuclear aromatic hydrocarbons (PAH) are a group of >100 different chemicals explicitly containing only C and H as the constituent elements. Few of the commonly occurring PAHs are as given in Figure 1.1. PAHs are mutagenic, carcinogenic, teratogenic and toxic properties (ECSC, 2002). The higher the number of fused rings more is the carcinogenicity of the PAH. Thus, Benzo[a]pyrene is one of the PAH regulated under National Ambient Air Quality Standards is one of the most carcinogenic PAH known (Maliszewska-Kordybach, 1999). The PAH in our environment comes from various natural and anthropogenic activities. Natural activities including forest fires, volcanic eruption etc. whereas anthropogenic activities include fossil fuel burning, motor vehicles, chulha's, charboiled meat, smoking and incineration activities (Luch, 2005).

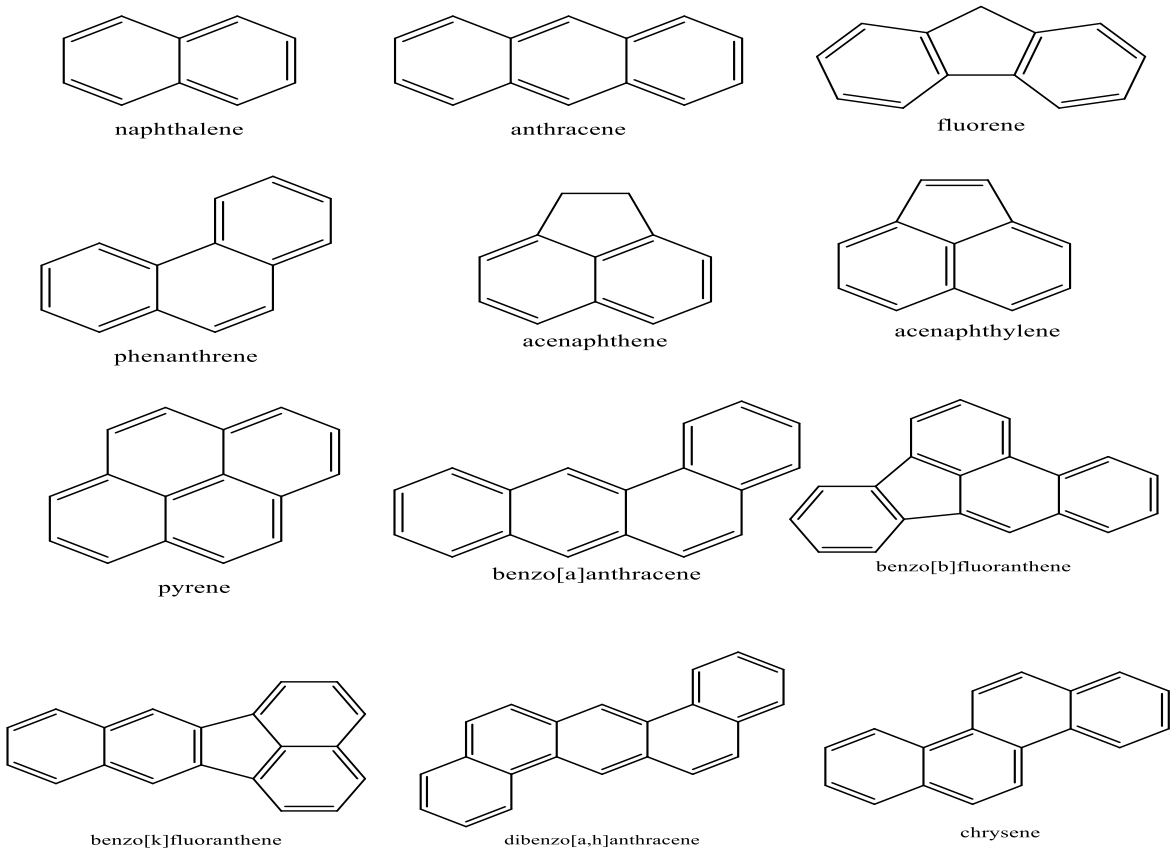


Figure 1.1: Chemical structures of some common polynuclear aromatic hydrocarbons (PAHs).

PAH are waste impurities which exist in all parts of the atmosphere, inland and sea water, sediments, soil and vegetation (Paterson & Mackay, 1989; Wania & Mackay, 1996; Wild & Jones, 1995). PAHs in their purest forms exist in solid state with low volatility at room temperature and have relatively high molecular weight. Generally all the PAHs are lipophilic and less soluble in water but some of the PAHs are soluble in water which has low molecular weight (Maliszewska-Kordybach, 1998; Masclet & Mouvier, 1988; Paterson & Mackay, 1989; Van Jaarsveld, Van Pul, & De Leeuw, 1997; Wania & Mackay, 1996; Wild & Jones, 1995). Due to their persistence in environment and health concern, it requires regular monitoring.

The present method for monitoring PAH is by extraction followed by analysis using either Gas Chromatography Flame Ionization Detector (GC-FID), Gas Chromatography – Mass Spectrometry (GC-MS), or High Performance Liquid Chromatography with Fluorescence detector (HPLC-FLD). These methods are time taking, labour intensive and instrument intensive. Further, these methods of monitoring PAH, do not serve the purpose of real-time continuous monitoring. Thus, there is a need for methods which are fast, robust and reliable for the analysis. In this endeavor, fluorogenic or chromogenic sensing of analyte would be a suitable method for analysis of PAH. However, there are limited reports on such sensors. Principally, these sensors would be based upon host-guest inclusion phenomenon. The inclusion base recognition requires host molecules with cavity for inclusion as the prima facie requirement for devising such sensors. The container molecules known to have such cavities include cylcodextrin, cucurbiturils and calixarenes. Of these molecules, calixarenes are versatile host in supramoelcular chemistry (Cram & Ho, 1986). The easiest way to produce calixarene is by condensation of p-tert-butylphenol and formaldehyde (Gutsche & CD, 1989). The flexibility of calix[4]arene as a host molecules suggest that they might serve as potential building blocks for designing more elaborate structures.

Calixarene has vastly been studied for cations and anions which have resulted in various chromogenic and fluorogenic sensors for anions (Kim & Quang, 2007) and cations (Ludwig & Dzung, 2002). The inclusion properties of small organic analytes like steroids (Millership, 2001),terpenes (Ramon et al., 2006), paraquat (Pierro et

al., 2010) and amino acids (Douteau-Guével et al., 1998), were studied in case of some parent calixarene and their water soluble derivatives. The studies on inclusion properties for aromatic analytes of calixarene are also going on as a chemosensor but they are not able to establish the binding modes of analytes with calixarene receptors.

Thus there is need of study molecular inclusion of PAH in calix[4]arene to understand the mode of binding and devising chemosensors for PAH based on Calix[4]arene.The objectives for the present study are

1. Synthesis of calix[4]arene derivatives in various conformations and with different lower rim functional moieties
2. Identification of the conformation of calix[4]arene derivatives using NMR analysis
3. UV-Visible studies on inclusion behaviour of napthalene, anthracene and pyrene as representative PAH in calix[4]arene derivatives.

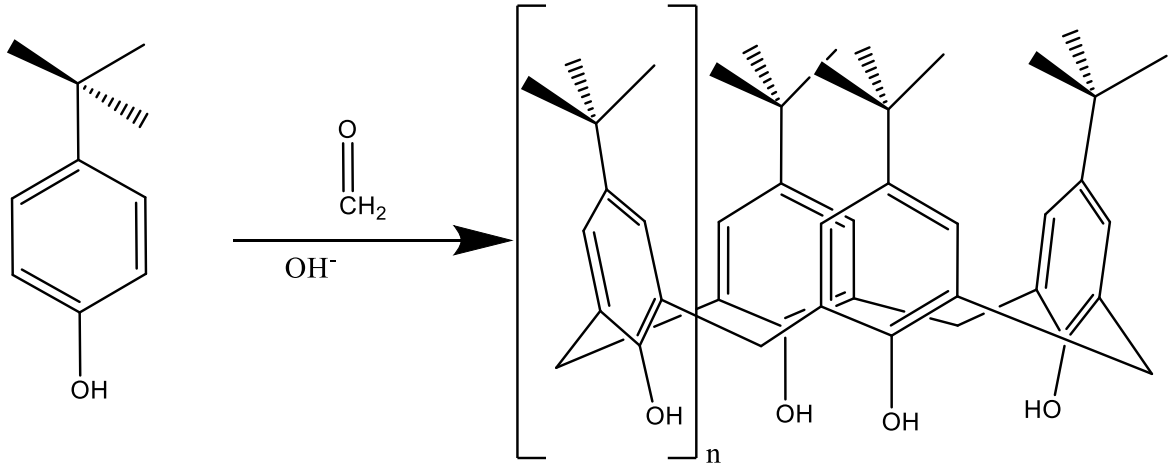
CHAPTER 2.

REVIEW OF LITERATURE

REVIEW OF LITERATURE

2.1 Calixarene

Calix is a Greek word which means ‘vase’ or ‘chalice’ and arene indicates the aryl residue present in the macrocyclic group. Generally these are represented by calix[n]arene. The number [n] enclosed in brackets, which separates ‘calix’ and ‘arene’, designates the number of aromatic ring units in the macrocycle, for example, calix[8]arene would mean eight arene moieties with alternating eight methylene bridges. Calixarenes are macrocyclic oligomers, produced by condensation of para-alkyl substituted/blocked phenol and formaldehyde. Calixarene are cyclic oligomers which can be obtained in a single step reaction of p-tert-butylphenol and formaldehyde under basic conditions **(Scheme-2.1)**. But stepwise synthesis of calixarene could also be carried out using convergent and divergent cyclization of the stepwise synthesized products. Calixarenes are sparingly soluble and high melting point solids. They are chemically and thermally stable (Vicens et al., 2012).



Where n = 1, 3, 5,

Scheme 2.1: One step synthesis of calixarene

Calixarenes are also known as synthetic molecular baskets and have found applications as drug delivery, surfactants, host-guest chemistry, chemoreceptors, catalysis, enzyme mimetic, ion-sensitive electrodes, non-linear optics; drug recognition and nanotechnology. Calixarene act as a host molecule in host-guest

chemistry, as they possess cavities. Calixarenes are like a cup or a bucket with a defined upper and lower rim along with a central annulus. Both the upper and lower rims can be modified to provide highly reorganized structures. Calixarenes can be easily functionalized at the lower rim (alkylation and acylation) and the upper rim (retro-friedel crafts followed by electrophilic substitutions). Calix[4]arenes are l_n-metacyclophanes class of molecules formed by methylene bridging of phenol precursors at their ortho position (C. Gutsche, 1998). Another feature of calix[4]arene is the rotation of aromatic rings to adopt different orientation, which leads to conformational isomers of calixarene. On the basis of orientation of phenolic groups with respect to each other calix[4]arene is capable of assuming four conformational isomers that are 'cone' (uuuu), 'partial cone' (uuud), '1-2-alternate' (uudd) and '1,3-alternate' (udud) **(FIGURE 2.1).**

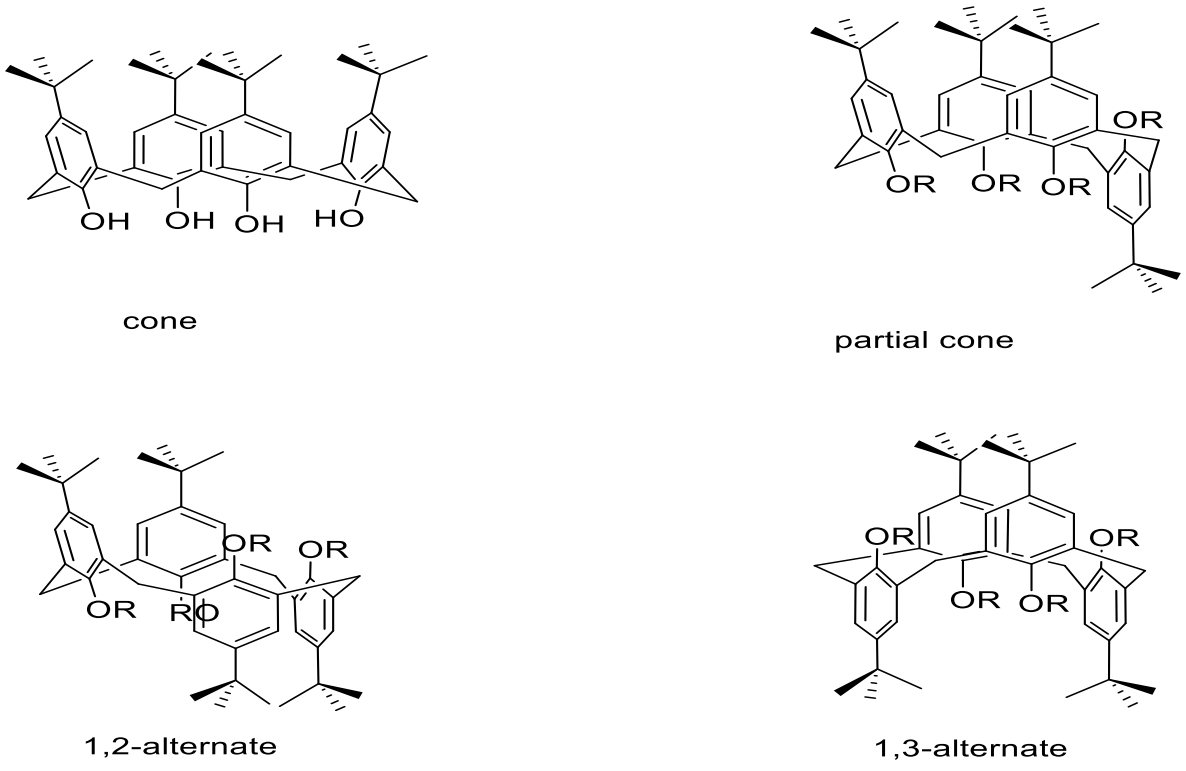
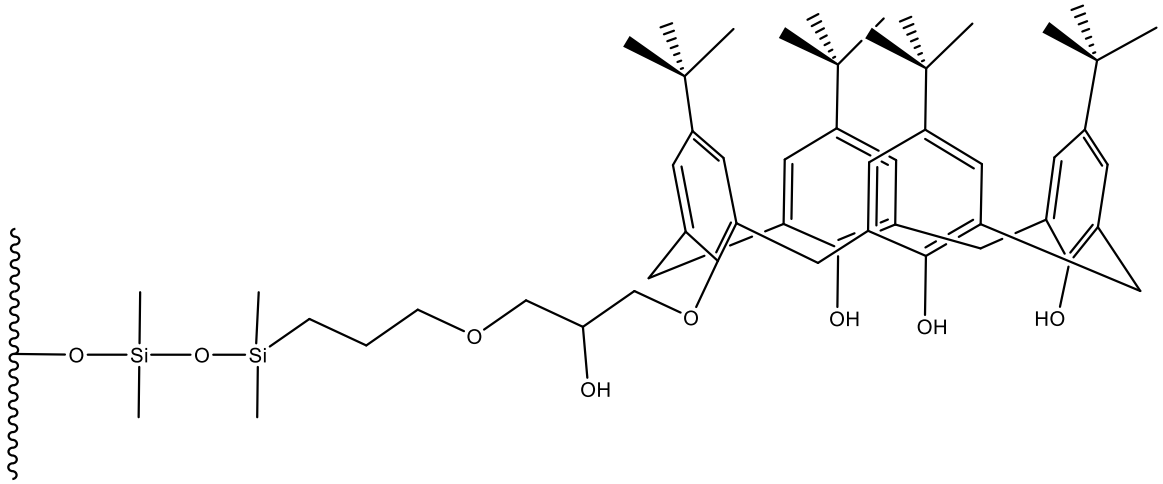
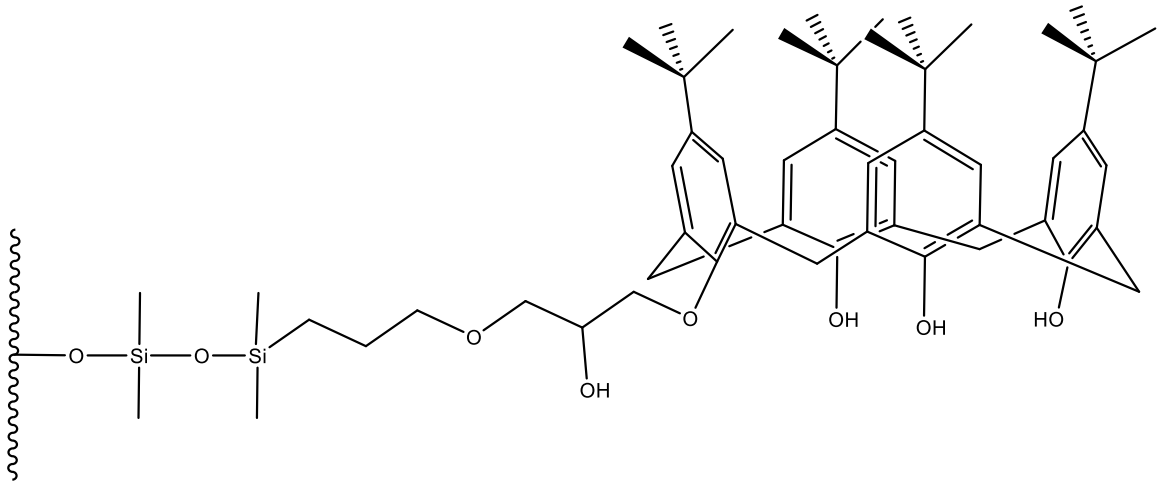


FIGURE 2.1: Various conformations of Calix[4]arene



2.1

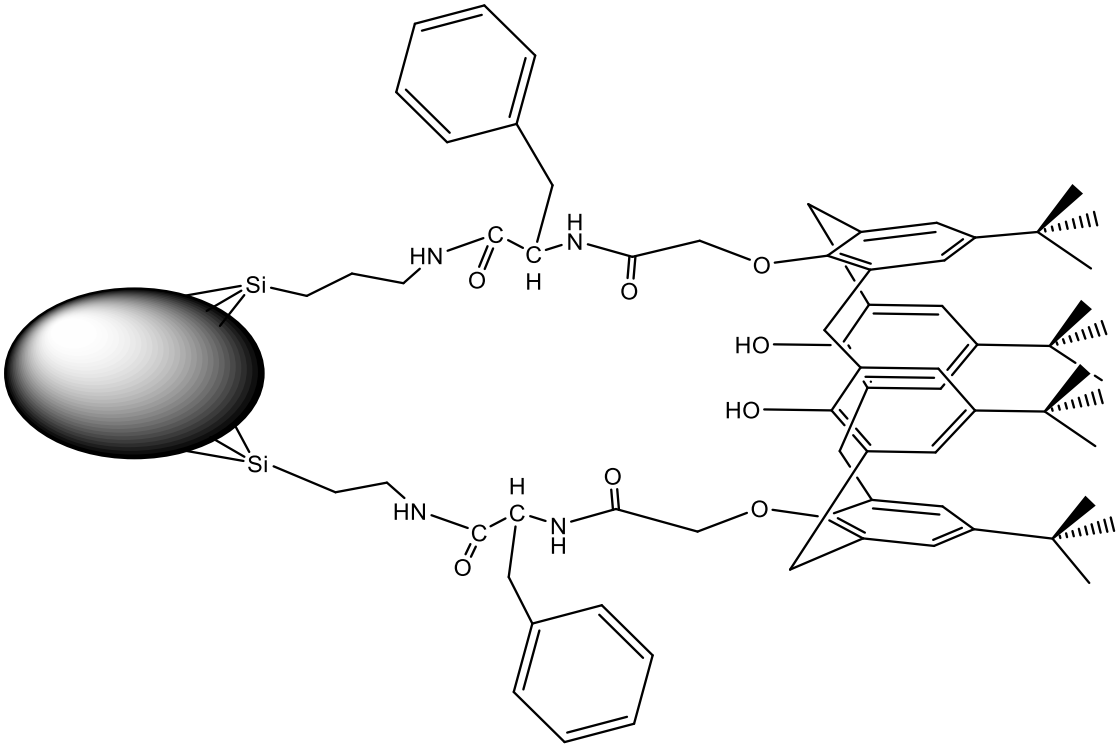
Lowering functionalized calix[4]arene**(2.1)** coupled to the silica gel surface were studied as stationary phase for napthol and benzenediols separation. β-napthol (pKα 9. 51) eluted at lower retention time in comparison to α-napthol (pKα 9. 30).



2.1

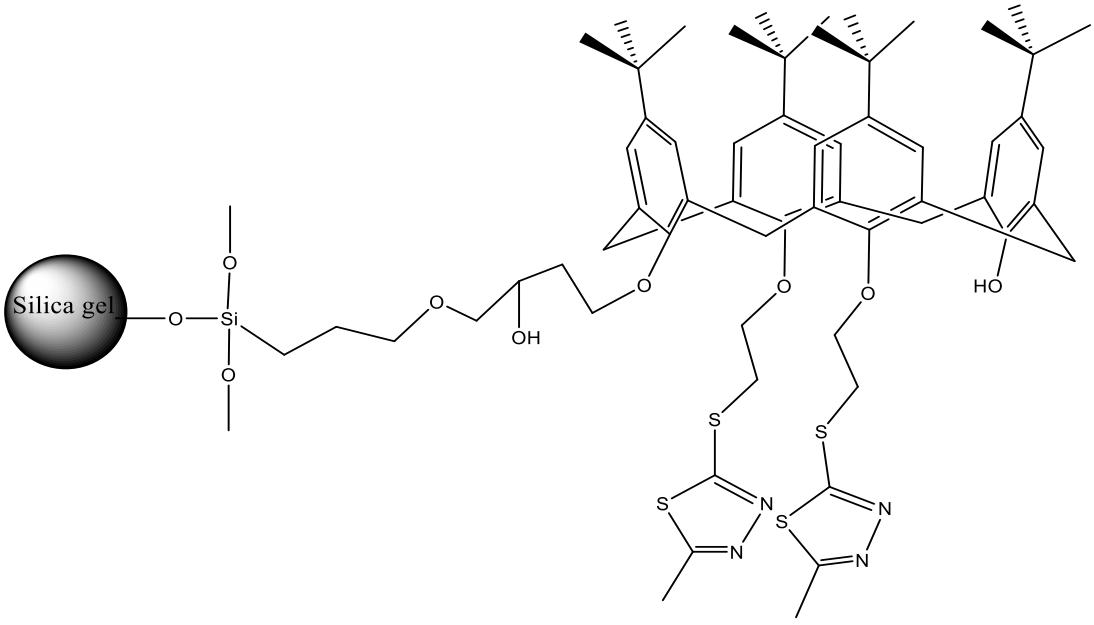
Similarly, in case of benzenediol, para substituted benzene diols eluted before meta followed by ortho substituted benzene diols. The complex formation when investigated by computational methods using DFT-B3LYP / STO-3G as basic set in solvent and in vacuum. Benzenediols were found to interact by hydrogen bonding and π–π interaction with the calix[4]arene host (Hu et al., 2008).

Bis(L-phenylaninemethyl ester-N-carbonylmethoxy)-26, 28-dihydroxy-para-tert-butylcalixt4]arene bonded to silica gel stationary phase **(2.2)** was investigated for PAH, monosubstituted benzene, aniline, tanaka test solutes, melamine, fluoroquinoloes, and flavonoids as probes (Hu et al., 2013).



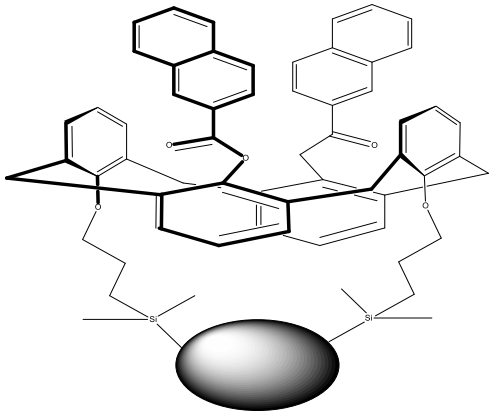
2.2

Distally lower rim substituted calix[4]arene derivative **2.3**, with Thiadiazole moiety bonded to silica gel stationary phase was studied for the separation of PAH, phenols, amine benzoic acid and its derivatives. Column packed with the stationary material bonded with **2.3** was even used for analysis of clenbuterol (Hu et al., 2012). Amine was found to be retained in the stationary phase. The method also showed better separation for benzoic acid derivatives.

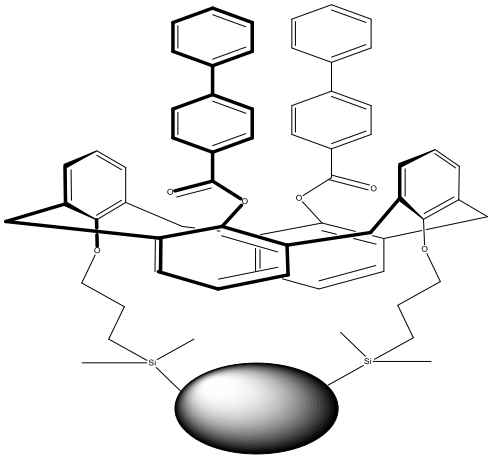


2.3

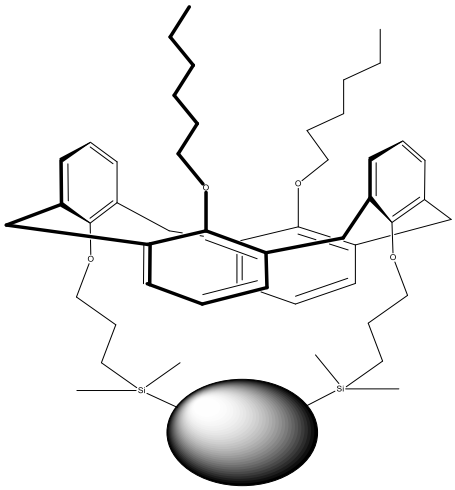
1,3-alternate calix[4]arene derivatives **(2.4a-d)** containing napthyl biphenyl, hexyl and dodecyl on distal arms were studied as a stationary phases upon silica gel bonding for inclusion based retention and resolution of guest molecules. The guests studied included alkylbenzene, fatty acid, p-bromophenacyl esters, aromatic position isomer and PAH as analytes. The napthyl and biphenyl derivative showed a lower retention factor as compared to their alkyl derivatized counterparts, which supports inclusion complexation as the mode of interaction in this retention on stationary phase (Śliwka-Kaszyńska et al., 2009).



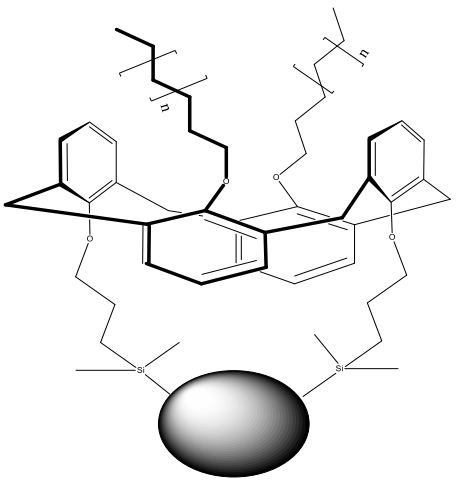
2.4(a)



2.4(b)

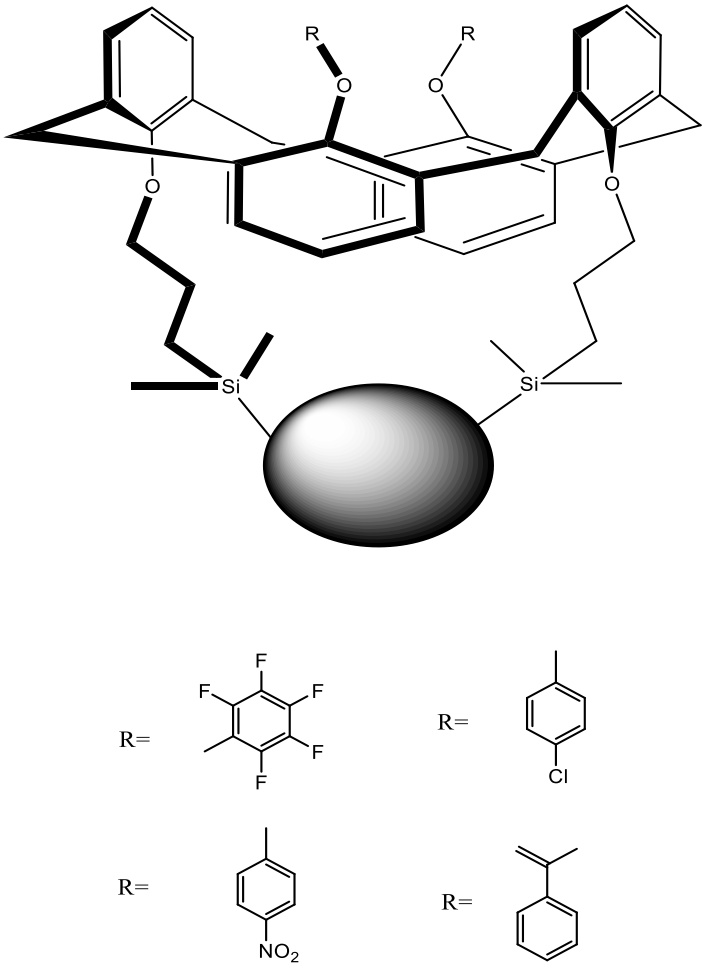


2.4(c)



2.4(d)

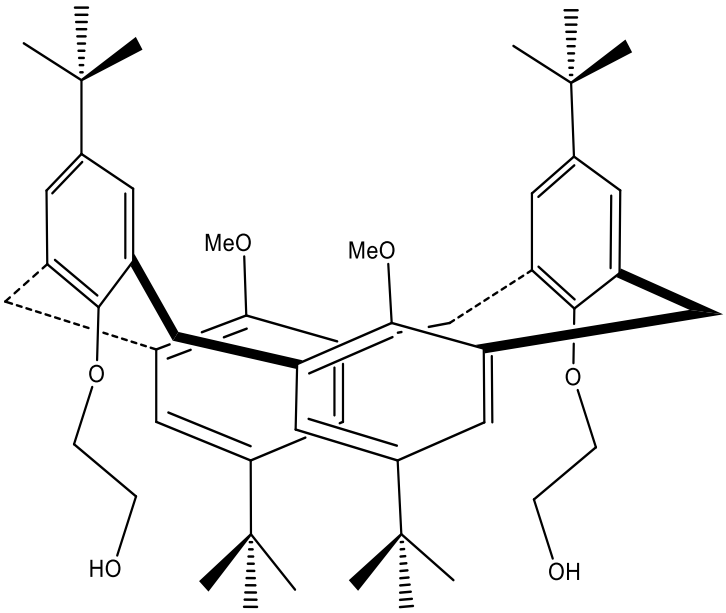
Calix[4]arene derivative **(2.5)** containing pentafluorobenzyl-, p-nitrobenzyl-, p-chlorobenzyl- and napthoyl- moiety were bonded to silica gel stationary phase and were investigated for retention and resolution of twelve PAHs. The PAHs used for the study included benzene, napthelene, 1, 2-dihydro acenaphylene, anthracene, pyrene, tetraphene, chrysene, tetraleve, benzo(e)pyrenes, pyrelwene, benzo(e)acephenanthrylene and benzo(a)pyrene. The electron withdrawing groups on the lower rim derivatized arene moieties showed enhanced resolution/retention towards PAH solues. This characteristic observed is due to the pie-pie and pie-electrons transfer interactions between aromatic ring functionalized at upper rim (M. Śliwka-Kaszyńska & Ślebioda, 2014).



2.5

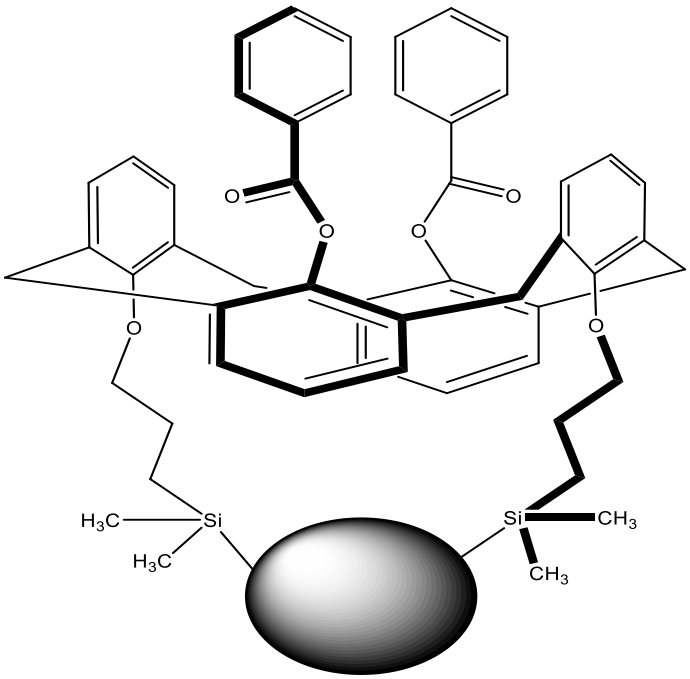
1,3-alternate conformational derivative with lower rim functionalization calix[4]arene **(2.6)** impregnated in amberlite XAD-4 was used for the adsorption of

industrial dyes (Memon & Memon, 2015). Methyl violet (MV), methyl green (MG) and methylene blue (MB) were used for the adsorption study. An adsorption up to 800 mg/g for these aromatic dyes was observed for 2.6 impregnated materials, thus were further reinvestigated by batch and column adsorption studies.



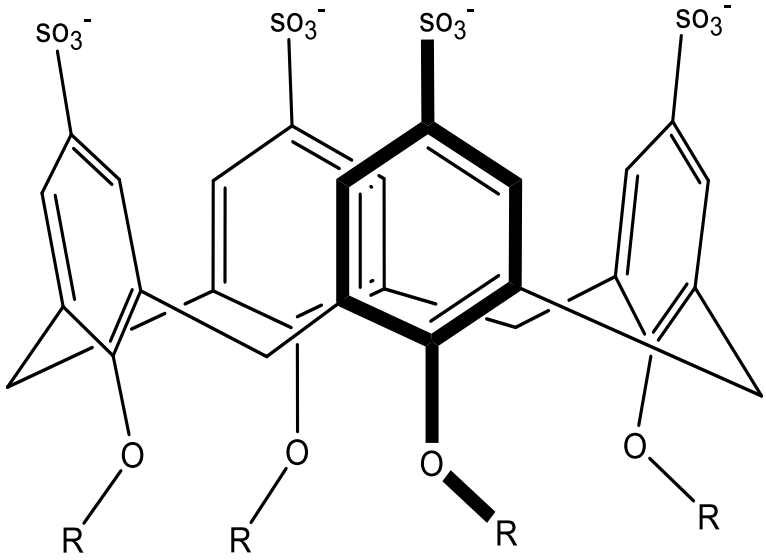
2.6

Lower rim substituted calix[4]arene in 1, 3-alternate conformation 25, 27-bis-[p-chlorobenzyloxi]-26,28-bis-[3-propyloxy]-calix[4]arene **(2.7)** bonded to silica gel was studied for retention and resolution of PAHs (Śliwka-Kaszyńska et al., 2006). The study revealed a selective resolution for six PAHs namely naphthalene, fluorene, phenanthrene, cyclopenta[d,e,f]phenanthrene, pyrene and chrysene. The stationary phase with **2.7** was also useful for separation of sulfonamide antibacterial agents like sulfanilic acid, sulfanilamide, sulfadiazine, sulfamerazene, sulphathiazole and sulfamethazine.



2.7

Fluorogenic CdSe/ZnS quantum dot capped with TOPO and upper rim calixarene derivative **2.8**, were studied by Jin et al., (2006) for sensing of acetylcholine. There was a red shift in the optical spectra of quantum dots at calixarene carboxylic acid derivatives with increasing oligomer size of the calix[n]arene used. The mechanism of sensing involved the water-QD interfacial interaction of capped calix[4]arene, with Acetylcholine (Jin et al., 2006) leading to further diffusion into the organic layer of the coating, heading to interact ion with the semiconductor surface to reduce the core electron-hole recombination (Jin et al., 2005a).



2.8

From the above review of literature, it is delineated that

a. Calix[4]arene has the tendency to host a PAH in its π-cavity inscribed by its benzene ring.
b. Calix[4]arene in some conformations have been studied very widely. However only few reports where other conformations of calix[4]arene have been investigated.
c. Characterization of calix[4]arene and PAH association behavior not being studied.

Thus, it is proposed that the lower rim functional moieties and conformation of calix[4]arene have a vital role to play in binding of PAH and requires further investigation.

CHAPTER 3.

MATERIALS AND METHODS

Materials and Methods:

All chemicals were purchased from commercial sources and used as received. Solvents were well purified by using a standard protocol, p-tert-butylcalix[4]arene, n-propanol, Chloroform, n-Hexane, Ethyl acetate, Petroleum ether, Dichloromethane was obtained from LobaChem, Methanol from Fisher Chemicals, Tetrahydrofuran from Spectrochem.

3.1 Instruments used:

All chemicals and reagents were weighted on a weighing balance (Metler Toledo, Swiss made, 1 mg-120 mg+0.1 mg). Characterization of substituted products -1H NMR, was carried out on a Bruker Avance II 400 Nuclear Magnetic Resonance (FT-NMR) using $CDCl_3$ as solvent and TMS as internal standard. Resonances are reported in ppm downfield from TMS. IR Spectra was carried out on Fourier Transform-Infrared Spectrophotometer (FTIR) Bruker Model: Tensor 27, using KBr pellet method for the solid sample.

3.2 Synthesis of M-2:

In a 250 mL round bottom flask (RBF), calix[4]arene (5 g) and K_2CO_3 (10.64 g) suspended in acetone (150 mL) were stirred at room temperature for 30 minutes. To this stirred solution was added PrI (3.68 mL) and kept for reflux for 24 hours. Upon monitoring TLC, the reaction mixture was filtered under suction. The filtrate collected was transferred to a 250 mL RBF and evaporated under vacuum. The residue obtained was the partitioned between water and chloroform to remove the inorganic impurities using a separating funnel. Water layer was extracted thrice with CH_3Cl 50 mL each. The collected solution was dried using Na_2SO_4 anhydrous. The solvent was evaporated under vacuum to furnish colourless residue, which was recrystallized in $CHCl_3$/methanol to furnish **M-2**.

M-2 Characterization: Colourless crystalline compound; yield=3.58 g; ^{1}H NMR ($CDCl_3$ 400 MHz) δ (ppm): 1.00 (s, 18H, $C(CH_3)_3$), 1.25 (t, J=6.08 Hz, 6H, CH_3),J=1.26 (s, 18H, $C(CH_3)_3$, 2.01 (m, 4H, CH_2), 3.43 (d, J=13.4 Hz, 4H, $ArCH_2Ar$),3.95 (t, J=6.12 Hz, 4H, OCH_2),4.20 (d, J=13.4 Hz, 4H, $ArCH_2Ar$), 6.83

(s, 4H,ArH), 7.02 (s, 4H, ArH); FTIR ν_{max}(KBR,cm^{-1}), 1596cm^{-1} C-O str.; FAB-MS m/z 810 (M^+).

3.3 Synthesis of M-3:

In a 100 mL RBF, NaH in mineral oil suspension equivalent to 1.59 g NaH and calix[4]arene (4 g) was added to 25 mL of DMF and kept for stirring under for 30 minutes. Upon 30 minutes, PrI (2.9 mL) was added and stirred further for 32 hrs. Upon completion of reaction as monitored by TLC, the reaction mixture was poured into ice cold water. The residue filtered and solubilized in $CHCl_3$. The product was partially soluble in chloroform, to this was added 50 mL water in a separating funnel, vigorously shaken to separate organic and inorganic layer. The washing with water was repeated thrice with 50 mL water each. The collected water layer was partitioned with fresh chloroform. Chloroform layer containing product were collected and filtered through anhydrous sodium sulphate. The chloroform solution was then evaporated under reduced pressure. The residue was recrystallized using chloroform and methanol to furnish the product **M-3**.

M-3 Characterization: White crystalline compound; yield=3.06 g;^{1}H NMR ($CDCl_3$ 400 MHz) δ (ppm):), 0.9 (t, J=7.32 Hz,12H, CH_3), 1.06 (s, 36H, $C(CH_3)$, 2.01 (m, 8H, CH_2), 3.05 (d, J=12.8 Hz, 4H, $ArCH_2Ar$), 3.80 (t, J=4.28 Hz,8H, OCH_2), 4.35 (d, J=12.2 Hz, 4H, $ArCH_2Ar$), 6.83 (s, 8H, ArH), FAB-MS m/z 810 (M^+).

3.4 Synthesis of M-4:

In a 500 mL RBF, calix[4]arene(10 g) and K_2CO_3 (6.53 g) were added with acetone (250 mL) and stirred at room temperature. Upon 30 minute of stirring, NaI (9.8 g) and chloroacetonitrile (4.5 mL) were added and reaction mixture was refluxed for 4 h. Upon completion of the reaction as monitored by TLC, the hot reaction mixture was filtered through celite bed under suction. The filtrate was collected in an RBF and evaporated under reduce pressure. The resulting residue was washed and filtered using methanol as solvent till colorless residues obtained. The obtained colorless residue was then recrystallized from methanol to furnish the residue 5,11,17,23-tert-butyl-syn-25,27-bis(cyanomethoxy)-26,28-dihydroxycalix[4]arene **M-4**.

M-4 Characterization: Yield=7.87 g; colorless solid;^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 0.86(18H, s, $C(CH_3)_3$), 1.31 (18H, s, $C(CH_3)_3$, 3.43 (4H, d, J=13.4 Hz, $ArCH_2Ar$), 4.20 (4H, d, J=13.4Hz, $ArCH_2Ar$), 5.00 (4H, s, OCH_2CN), 5.54 (2H, S, ArOH), 6.40 (4H, s, ArH) and 7.15 (4H, s, ArH); FTIR ν_{max} (KBR, cm^{-1}), 2269(C≡N), FAB-MS m/z 726(M^+).

3.5 Synthesis of M-5:

In a 100 mL RBF, NaH (175 mg) was added **M-4** (2.178 g) and DMF (25 mL) were added and kept under stirring for 30 minutes followed by the addition of n-Propyl Iodide (2.5 mL). The reaction mixture was then stirred for 7 days under anhydrous conditions. The completion of reaction was monitored by TLC. The reaction workup was carried out by pouring the reaction mixture into ice cold water. The suspension was filtered on a Buchner funnel and residue collected. The residue was dissolved in chloroform and portioned with water in a separating funnel. The organic layer was washed with 50 mL of water each, thrice. Organic layer was separated and passed through anhydrous sodium sulphate to remove traces of water. Filtrate was collected in a conical flask(100 mL), it was distilled followed by recrystallization in 2-3 mL of methanol to furnish.5,11,17,23,- tetra-tert-butyl-25,27-dicyanomethoxy-26,28-dipropoxycalix[4]arene (**M-5**).

Characterization of M-5: Yield=0.31 g, white solid; ^{1}H NMR($CDCl_3$, 400 MH_Z) δ(ppm): 0.80 (s, 18H, $C(CH_3)_3$),1.03 (t, J=7.36 Hz, 6H, CH_3) 1.35 (s, 18H, $C(CH_3)_3$), 1.9 (m, 4H, CH_2), 3.23 (d, J=13.4 Hz, 4H, $ArCH_2Ar$), 3.73 (t, 4H, OCH_2), 4.38 (d, J=13.4 Hz, 4H, $ArCH_2Ar$), 5.00 (s, 4H, OCH_2CN), 6.40 (s, 4H, ArH), 7.15 (s, 4H, ArH); FTIR (ν_{max}KBr, cm^{-1}): 2269 (C≡N); FAB-MS m/z 810 (M^+).

3.6 Synthesis of M-6:

To a 100 mL RBF, **M-4** (2.17 g), Cs_2CO_3 (2.93 g) and DMF(20-25 mL) were added and stirred. After 30 minutes of stirring, PrI (0.87 mL) was added and kept under stirring in anhydrous condition for seven days. TLC was monitored for completion of reaction. Upon completion of reaction, the reaction mixture was poured into ice cold water and residue filter collected on a Buchner funnel. The residue was

collected dissolved in chloroform and partitioned with water in a separating funnel. The organic layer was collected after washing with water (3 x 50 mL) and filtered through anhydrous sodium sulphate to remove traces of water. The solvent was evaporated under reduced pressure and the residue collected recrystallized using chloroform/methanol to furnish **M-6**.

M-6 Characterization: Yield=1.3 g, white solid; ^{1}H NMR($CDCl_3$, 400 MH_Z) δ(ppm): 0.06 (t, J=7.36 Hz, 6H, CH_3),1.12 (m, 4H, CH_2),1.25(s, 18H, $C(CH_3)_3$), 1.33(s, 18H, $C(CH_3)_3$), 3.2 (s,4H, OCH_2CN), 3.39 (t, J=7.92 Hz, 4H, OCH_2), 3.85 (d, J=16.48Hz, 4H, $ArCH_2Ar$), 3.91 (d, J=15.88Hz, 4H, $ArCH_2Ar$), 7.01 (s, 4H, ArH), 7.17 (s, 4H, ArH); FTIR (ν_{max}KBr, cm^{-1}): 2269 (C≡N); FAB-MS m/z 810 (M^+).

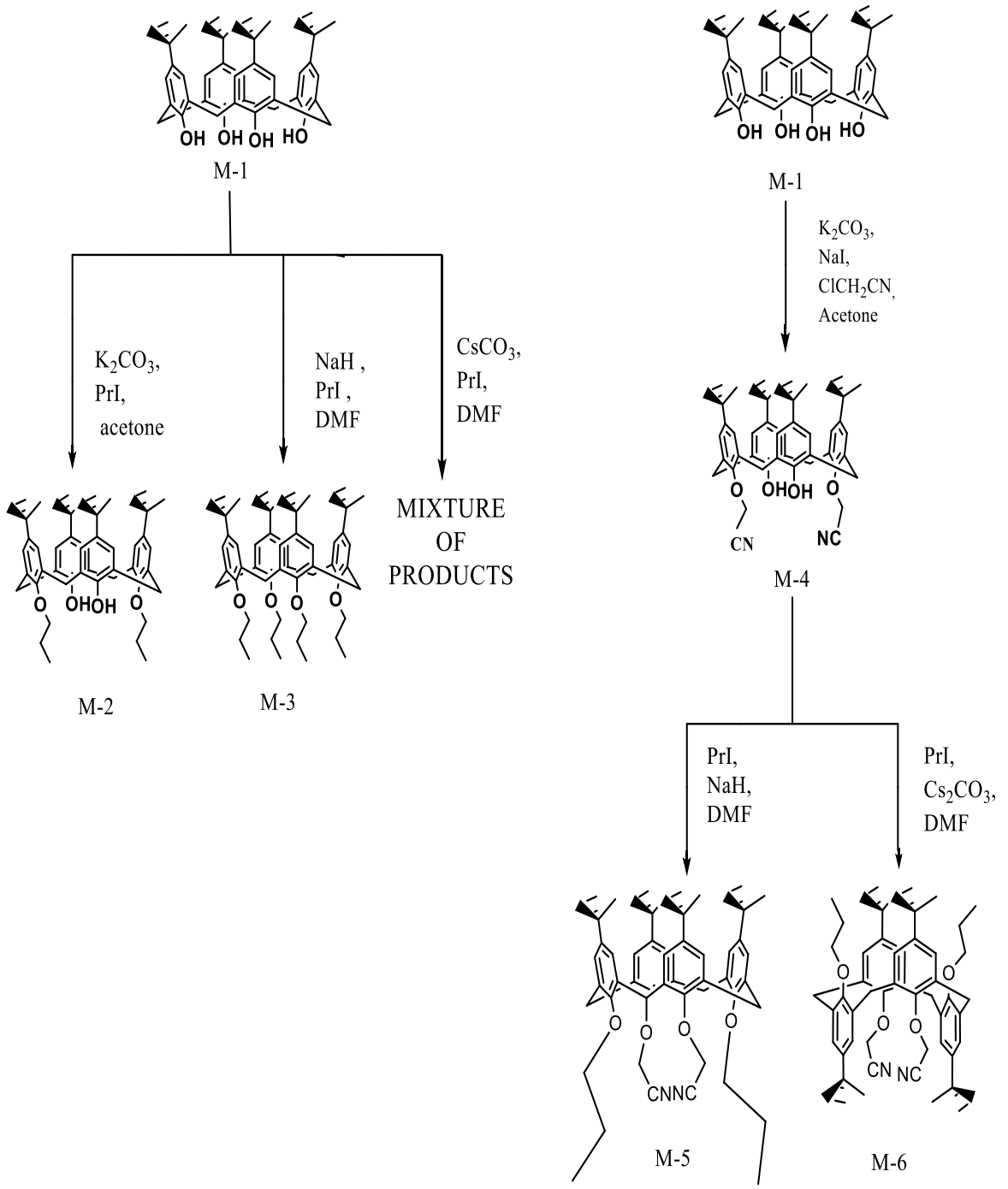
CHAPTER 4.

RESULTS AND DISCUSSION

RESULTS AND DISCUSSION:

4.1 Synthesis and Characterization of calix[4]arene derivative in cone and 1,3-alternate conformation:

Calix[4]arene 1 synthesized according to reported method which is condensation of p-tert-butylphenol with formaldehyde in presence of base NaOH as per the reported method (Gutsche & David, 1983). Alkylation of calix[4]arene (**M-1)** with alkylating agent propyl iodide, in presence of excess base K_2CO_3 in solvent acetone under reflux conditions for 24 h furnished 25,27-dipropoxy-26,28-dihydroxycalix[4]arene, the product **M-2** upon recrystallization in CH_2Cl_2: MeOH. (**Scheme 1**) The crystallized product was confirmed by FTIR, ^{1}H NMR and Mass spectral analysis. The IR spectra showed strong absorption peak around at 3200-3600, 2900 and 1596 cm^{-1} which are characteristics of hydroxyl moiety and phenolic C-O str. ^{1}H NMR spectra of **M-2** in $CDCl_2$ showed a triplet at d 1.25 ppm, multiplet at δ 2.01 ppm and a triplet at δ3.95ppm for 6,4,4 protons, respectively corresponds to CH_3, CH_2, and OCH_2 of propyl moiety. Further the meta-protons of the phenolic moieties were observed at δ 6.83 and 7.02 ppm for 4H is characteristic of meta-aromatic hydrogen. Further showed two singlets at δ 1.00 ppm and 1.26 ppm for 18H each corresponding to the methyl groups of t-Bu moiety of calix[4]arene. Two doublets at δ 3.29 (J=16 Hz) and 4.29 (J=16 Hz) ppm, for four proton are separated by 1>0.7 ppm, respectively corresponds to bridging axial and equatorial protons of methylene moiety in syn orientation. Further the structure of **M-2** was elucidated by EI-MS spectra, whereby a molecular ion peak at 732 (M^+). The findings of FTIR, EI-MS and ^{1}H NMR corroborate with the structure **M-2**.



Scheme: 4.1: Synthesis of calix[4]arene **M-2-6** in various conformation

4.1.1 ANALYSIS OF CALIX[4]ARENE DERIVATIVE M-2:

Calix[4]arene 1 synthesized according to reported method which is condensation of p-tert-butylphenol with formaldehyde in presence of base NaOH as per the reported method (Gutsche & David, 1983). Alkylation of calix[4]arene (**M-1)** with alkylating agent propyl iodide, in presence of excess base K_2CO_3 in solvent acetone under reflux conditions for 24 h furnished 25,27-dipropoxy-26,28-dihydroxycalix[4]arene, the product **M-2** upon recrystallization in CH_2Cl_2:MeOH (**Scheme1**). The crystallized product was confirmed by FTIR, ^{1}H NMR and Mass spectral analysis. The IR spectra showed strong absorption peak around at 3200-3600, 2900 and 1596 cm-^{1} which are characteristics of hydroxyl moiety and phenolic C-O str. ^{1}H NMR spectra of **M-2** in $CDCl_2$ showed a triplet at d 1.25 ppm, multiplet at δ 2.01 ppm and a triplet at δ3.95ppm for 6,4,4 protons, respectively correspons to CH_3, CH_2, and OCH_2 of propyl moiety. Further the meta-protons of the phenolic moieties were observed at δ 6.83 and 7.02 ppm for 4H is characteristic of meta-aromatic hydrogen. Further showed two singlets at δ 1.00 ppm and 1.26 ppm for 18H each corresponding to the methyl groups of t-Bu moiety of calix[4]arene. Two doublets at δ 3.29 (J=16 Hz) and 4.29 (J=16 Hz) ppm, for four proton are separated by 1>0.7 ppm, respectively corresponds to bridging axial and equatorial protons of methylene moiety in syn orientation. Further the structure of **M-2** was elucidated by EI-MS spectra, whereby a molecular ion peak at 732 (M^+). The findingS of FTIR, EI-MS and ^{1}H NMR corroborates with the structure **M-2**.

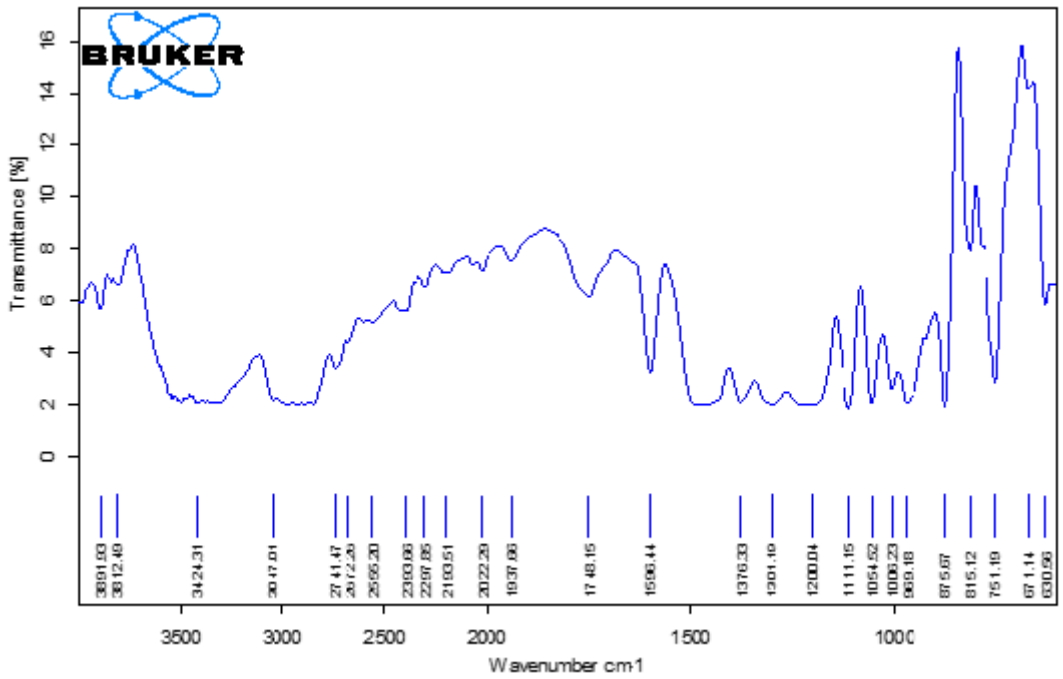


Figure: 4.1FTIR of calix[4]arene derivative **M-2**

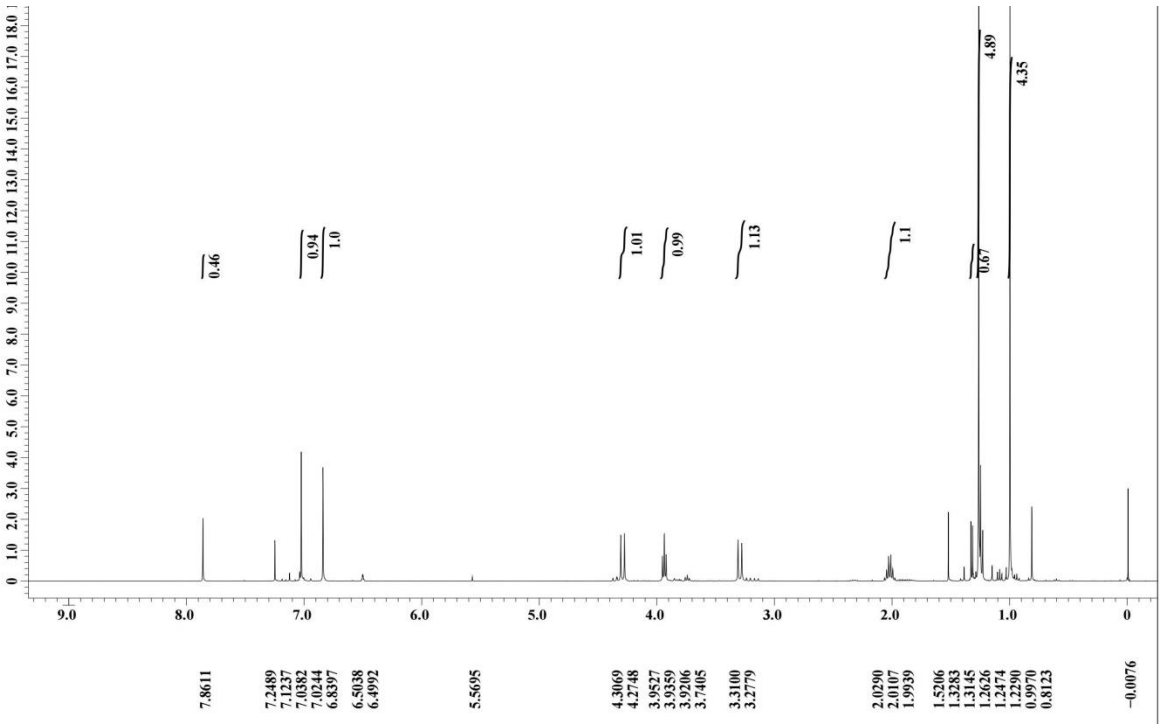


Figure: 4.2^{1}H NMR of **M-2**

Alkylation of **M-1** with alkylating agent propyl iodide using base as NaOH in sovent DMF kept for stirring at room temperature (48 h) furnished **M-3** upon recrystallization in CH_2Cl_2: MeOH. The crystallized product was confirmed by FTIR, ^{1}H NMR and Mass spectral analysis. The IR spectra showed strong absorption peak around at 3200-3600 cm-^{1}. ^{1}H NMR spectra of **M-3** in $CDCl_2$ showed a triplet at δ 0.9 ppm, multiplet at δ 2.01 ppm and a triplet at δ3.80 ppm for 12,8,8 protons, respectively corresponds to CH_3, CH_2, and OCH_2 of propyl moiety. Further showed one singlets at δ 1.06 ppm for 36 protons corresponding to the methyl groups of t-Bu moiety of calix[4]arene. Two doublets at δ 3.05 (J=12.84 Hz) and 4.35 (J=12.2 Hz) ppm, for four proton are separated by 1>0.7 ppm, respectively corresponds to bridging axial and equatorial protons of methylene moiety in syn orientation. Further the structure of **M-3** was elucidated by EI-MS spectra, whereby a molecular ion peak at 816 (M^+). The findings of FTIR, EI-MS and ^{1}H NMR corroborates with the structure **M-3**.

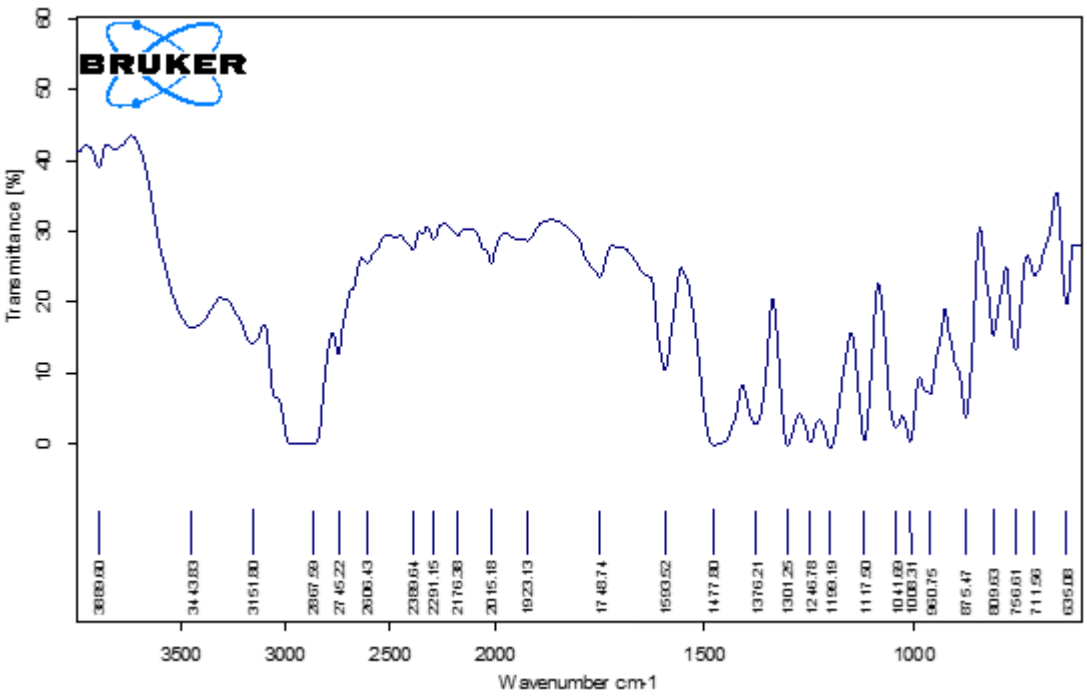


Figure: 4.3FTIR of calix[4]arene derivative **M-3**

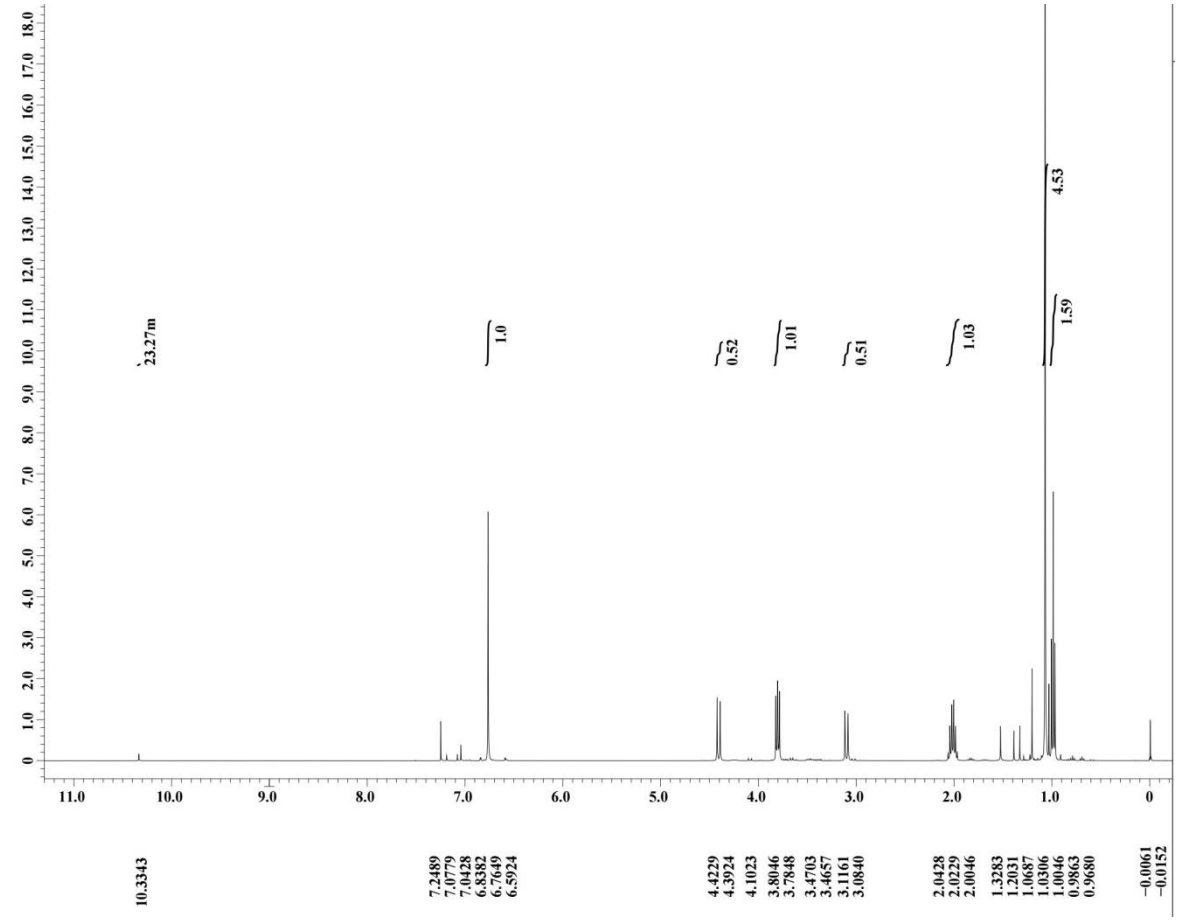


Figure: 4.4^{1}H NMR of **M-3**

M-4 in cone conformation was synthesized via alkylation with chloroacetonitrile/NaI/K_2CO_3. The product was confirmed by FTIR, ^{1}H NMR and Mass spectral analysis. The IR spectra showed strong absorption band at 2269 cm-^{1}. ^{1}H NMR spectra of **M-4** in $CDCl_2$ showed a singlet at δ 4.79 ppm and at δ 5.54 ppm for 4 and 2 protons respectively which corresponds to nitrile methylene and phenolic moieties in **M-4**. Further showed two singlets at δ 1.31 ppm and at δ 0.86 ppm for 18 protons corresponding to the methyl groups of t-Bu moiety of calix[4]arene. . Further the presence of two singlet at δ 6.71 and 7.10 ppm for 4H is characteristic of meta-aromatic hydrogen. Another showed a singlet at d 5.54 corresponds to aromatic OH. Two doublets at δ 3.43 (J=13.4 Hz) and 4.20 (J=13.4 Hz) ppm, for four proton are separated by 1>0.7 ppm, respectively corresponds to bridging axial and equatorial protons of methylene moiety in syn orientation. Further the structure of **M-4** was elucidated by EI-MS spectra, whereby

a molecular ion peak at 726 (M^+). The findings of FTIR, EI-MS and ^1H NMR corroborates with the structure **M-4**.

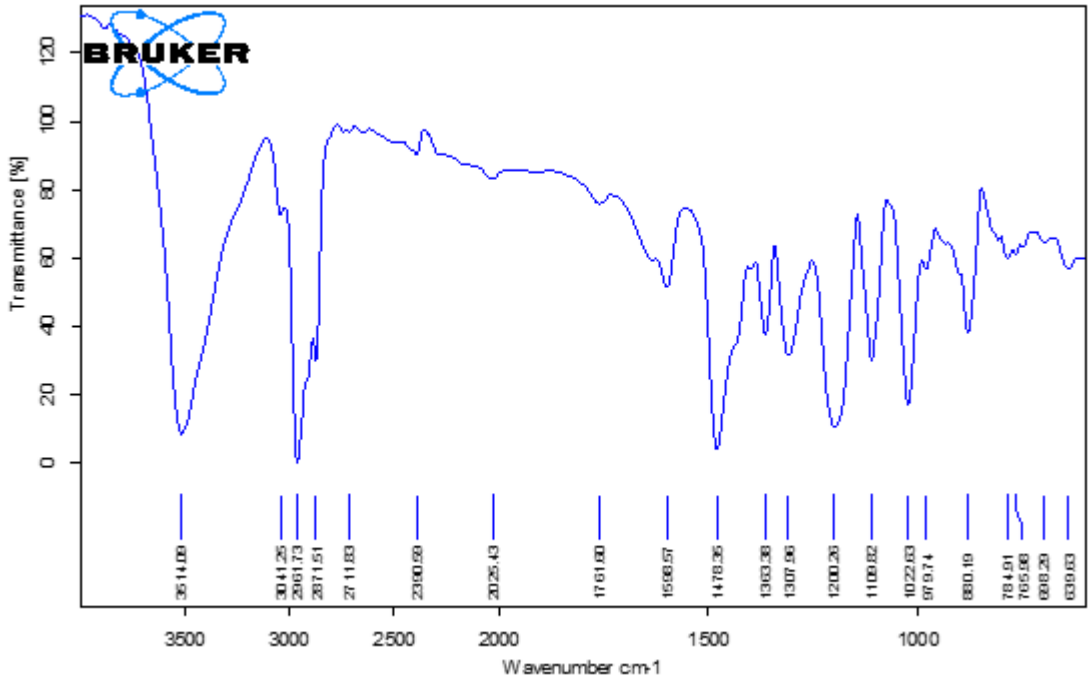


Figure: 4.5FTIR of calix[4]arene derivative **M-4**

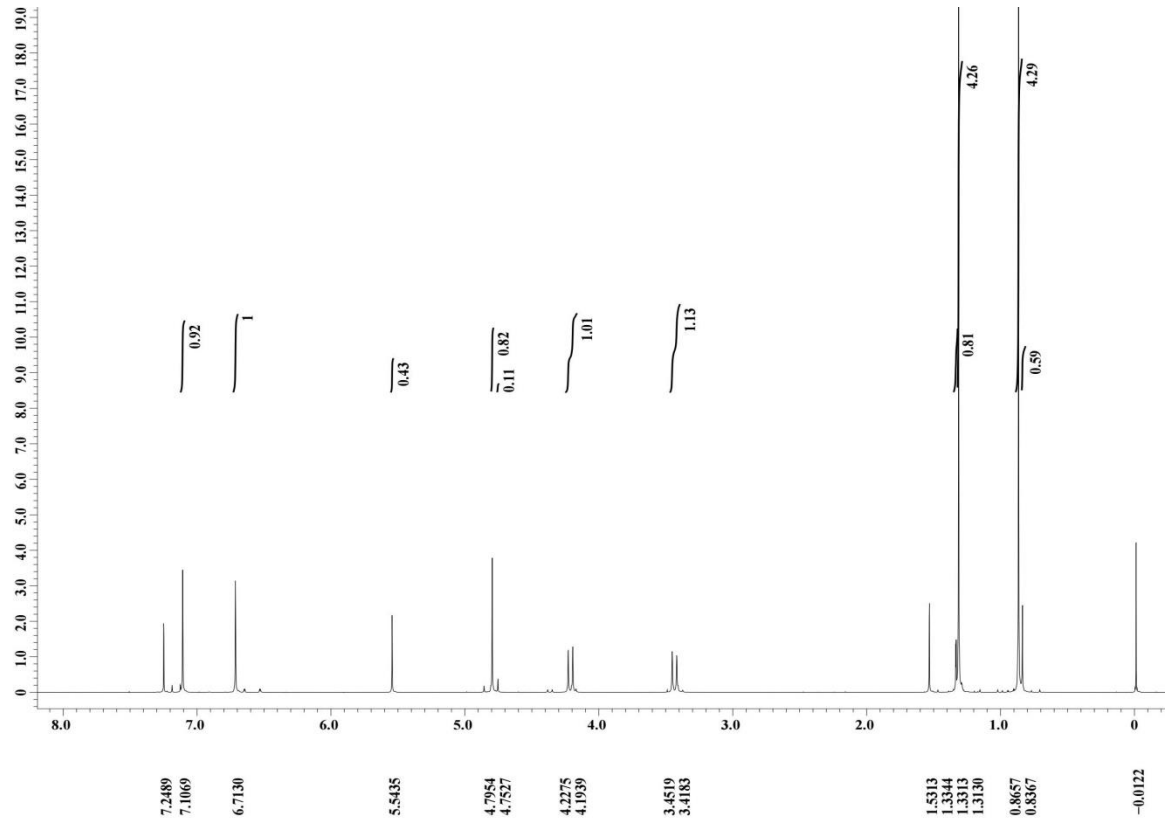


Figure: 4.6 ^{1}H NMR of **M-4.**

M-5 in cone conformation was synthesized via alkylation with alkylating agent propyl iodide in solvent DMF at room temperature for 7 days. The product was confirmed by FTIR, ^{1}H NMR and Mass spectral analysis. The IR spectra showed strong absorption band at 2269 cm-^{1} corresponds to CΞN. ^{1}H NMR spectra of **M-5** in $CDCl_2$ showed a singlet at δ 5.00 ppm for 2 protons which corresponds to methoxyacetonitrile. Further showed a triplet at δ 1.03 ppm, multiplet at δ 1.99 ppm and a triplet at δ3.73 ppm for 6,4,4 protons, respectively corresponds to CH_3, CH_2, and OCH_2 of propyl moiety. Further showed two singlets at δ 1.35 ppm and at δ 0.80 ppm for 18 protons corresponding to the methyl groups of t-Bu moiety of calix[4]arene. . Further the presence of two singlet at δ 6.40 and 7.15 ppm for 4H is characteristic of meta-aromatic hydrogen. Another showed a singlet at δ 1.53 ppm corresponds to H_2O protons. Two doublets at δ 3.23 (J=13.4 Hz) and 4.38 (J=13.4 Hz) ppm, for four proton are separated by >0.7 ppm, respectively corresponds to bridging axial and equatorial protons of methylene moiety in syn-orientation. Further the structure of **M-5** was elucidated by EI-MS spectra, whereby a molecular ion peak at 810 (M^{+}). The findings of FTIR, EI-MS and ^{1}H NMR corroborates with the structure **M-5**.

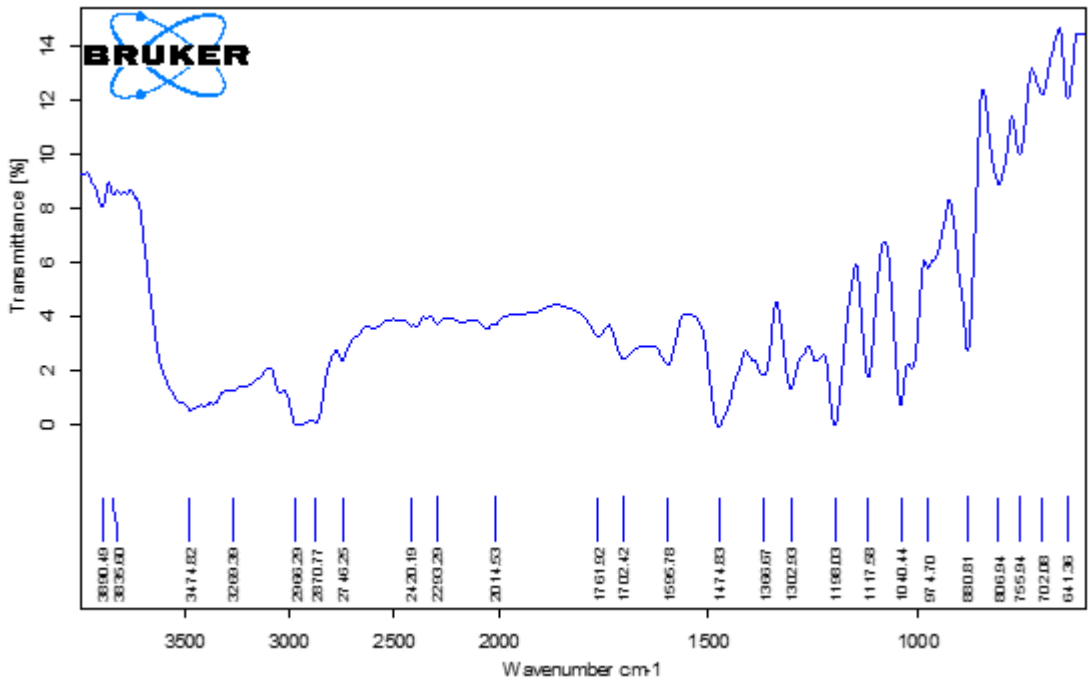


Figure: 4.7FTIR of calix[4]arene derivative **M-5**

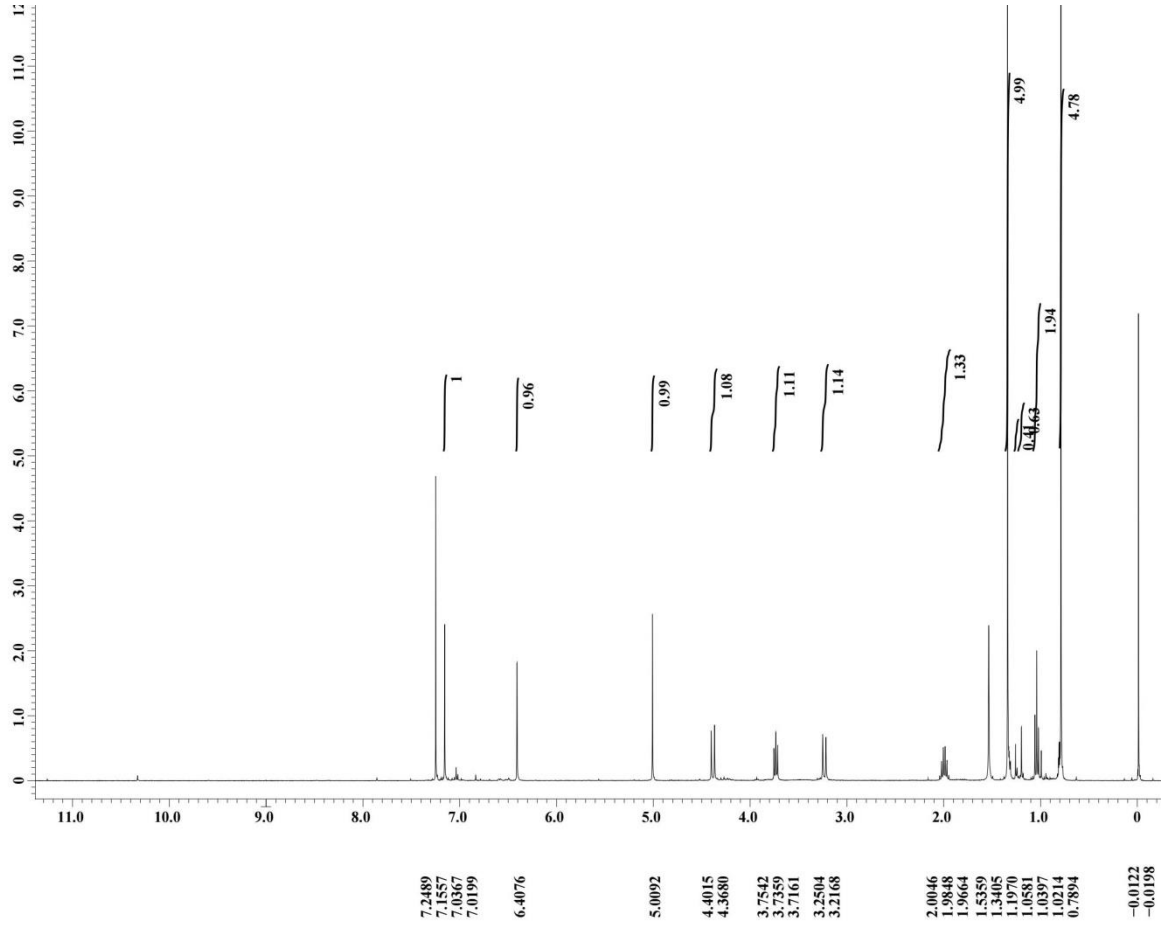


Figure: 4.8^{1}H NMR of **M-5**

For investigating other conformational isomers, the bis(cyanomethoxy) derivative of calix[4]arene was synthesized in 1,3-alternate (Babu et al., 2009). Alkylation of dicyanomethoxy derivatives **M-4** with alkylating agent propyl iodide in solvent dry N,N-dimethylformamide (DMF) and base cesium carbonate(Cs_2CO_3) was carried out for 7 days resulted in the formation of product **M-6**. The product was confirmed by FTIR, ^{1}H NMR and Mass spectral analysis. The IR spectra showed strong absorption band at 2269 cm-^{1} corresponds to CΞN. ^{1}H NMR spectra of **M-6 in** $CDCl_2$ showed a singlet at δ 3.2 ppm for 4 protons which corresponds to methoxyacetonitrile. Further showed a triplet at δ 0.66 ppm, multiplet at δ 1.12 ppm and a triplet at δ 3.39 ppm for 6,4,4 protons, respectively corresponds to CH_3, CH_2, and OCH_2 of propyl moiety. Further showed two singlets at δ 1.25 ppm and at δ 1.33 ppm for 18 protons corresponding to the methyl groups of t-Bu moiety of

calix[4]arene. Two doublets at δ 3.85 (J=16.48 Hz) and 4.38 (J=3.91 Hz) ppm, for four proton are separated by <0.6 ppm, respectively corresponds to bridging axial and equatorial protons of methylene moiety in anti-orientation. Further the structure of **M-6** was elucidated by EI-MS spectra, whereby a molecular ion peak at 810 (M^+). The findings of FTIR, EI-MS and ^{1}H NMR corroborates with the structure **M-6**.

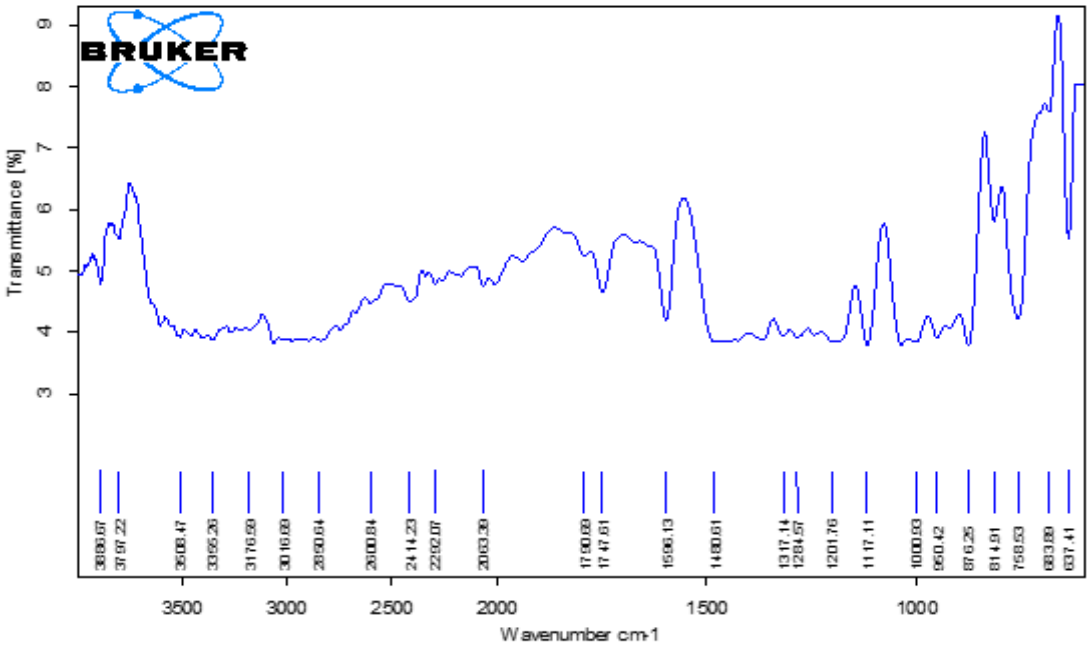


Figure: 4.9FTIR of calix[4]arene derivative **M-6**

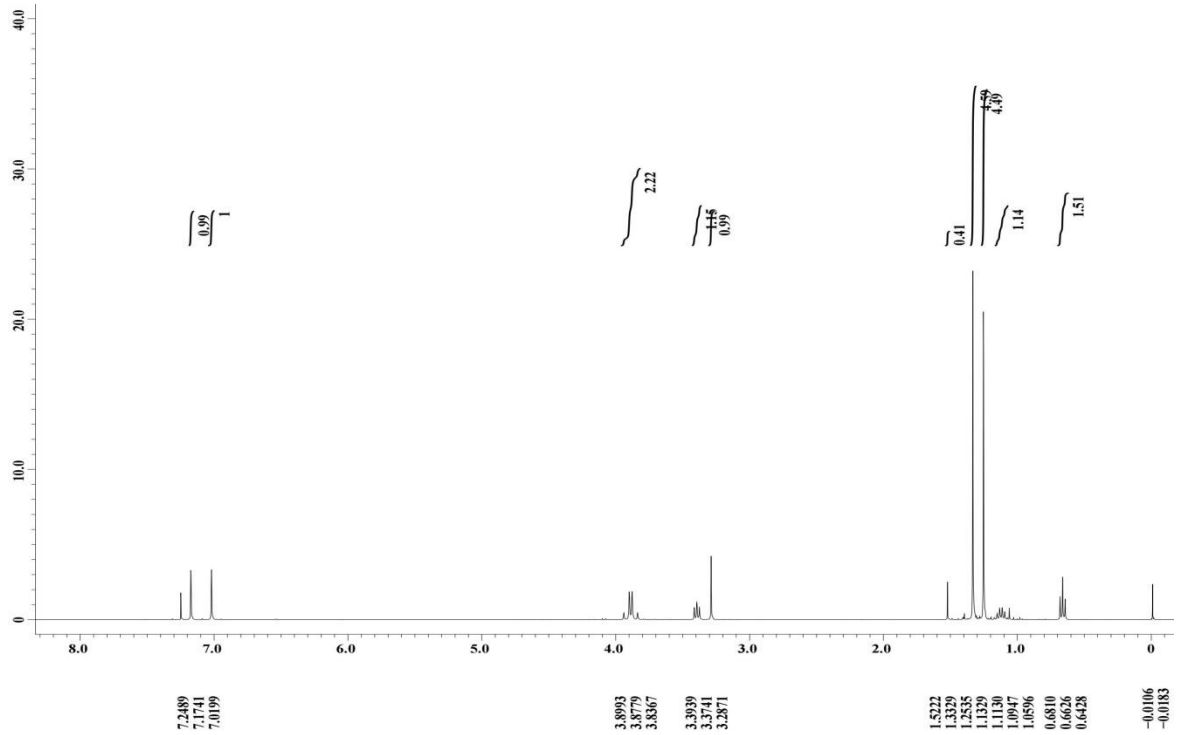


Figure: 4.10^{1}H NMR of **M-6**

4.2UV-Visible Studies and stability constant:

4.2.1 Naphthalene Absorption study with M-2 to M-6 molecules:

The studies of UV-Visible of **M-2** ,**M-3, M-4** and **M-6** were reported in presence of Naphthalene (0-100 eq.) in $CHCl_3$.

The UV-Visible spectra shown by an absorption band of **M-2** were at 263, 267.5 and 276 nm. The analysis was done at λ_{max}**= 276.5** absorption band followed by evaluation purpose. A hyperchromic shift was reported at the absorption band at 276.5 nm on addition of **M-2** (0-100 equiv.) in naphthalene **(Figure-4.11)**.

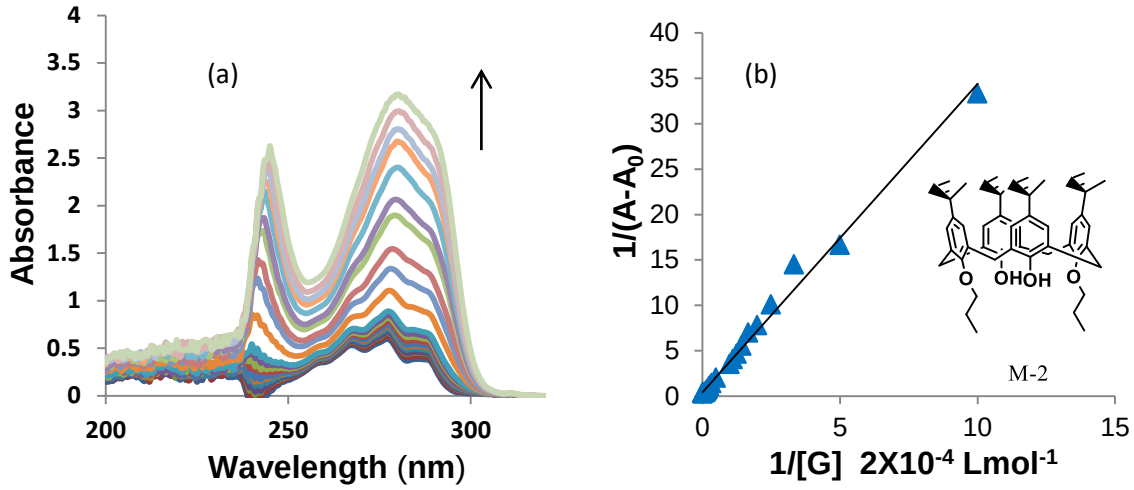


Figure 4.11: (a) Changes in UV-visible spectra of naphthalene (2 x 10^{-4}M) upon addition of 0-100 equivalent of **M-2** in chloroform and **(b)** Benesi-Hildebrand plot for host-guest complexation between **M-2** and naphthalene

C/M = 0.126756; K = $2.53X10^{3}$

The UV-Visible spectra shown by an absorption band of **M-3** were at 269, 277 and 285 nm. The analysis was done at λ_{max}**= 269 nm** absorption band followed by evaluation purpose. A hyperchromic shift was reported at the absorption band at 269 nm on addition of **M-3** (0-100 equiv.) in naphthalene **(Figure- 4.12)**.

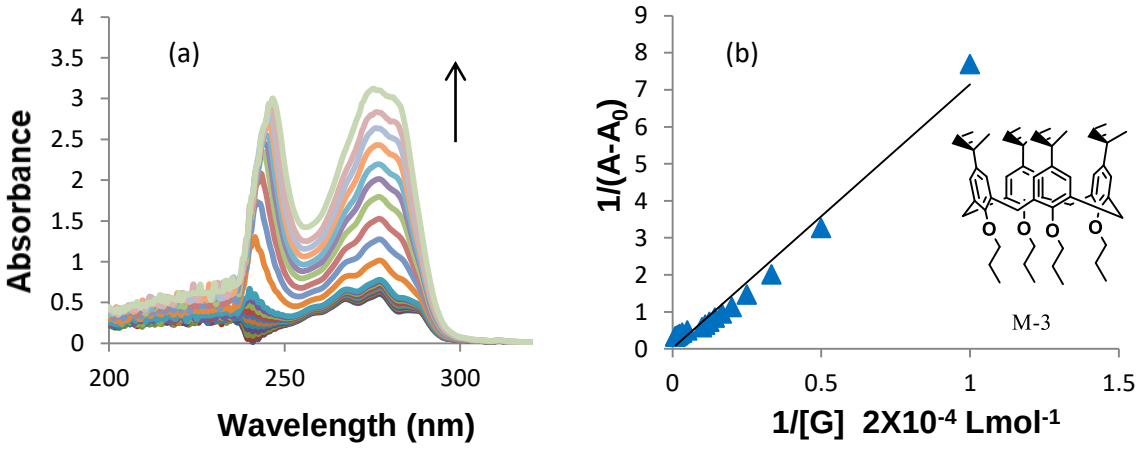


Figure 4.12: (a) Changes in UV-visible spectra of naphthalene (2 x 10^{-4}M) upon addition of 0-100 equivalent of **M-3** in chloroform and **(b)** Benesi-Hildebrand plot for host-guest complexation between **M-3** and naphthalene

C/M = 0.01812; K = $3.62X10^{2}$

The UV-Visible spectra shown by an absorption band of **M-4** were at 267.5, 277 and 285.5 nm. The analysis was done at λ_{max}**= 285.5 nm** absorption band followed by evaluation purpose. A hyperchromic shift was reported at the absorption band at 285.5 nm on addition of **M-4** (0-100 equiv.) in naphthalene **(Figure-4.13)**.

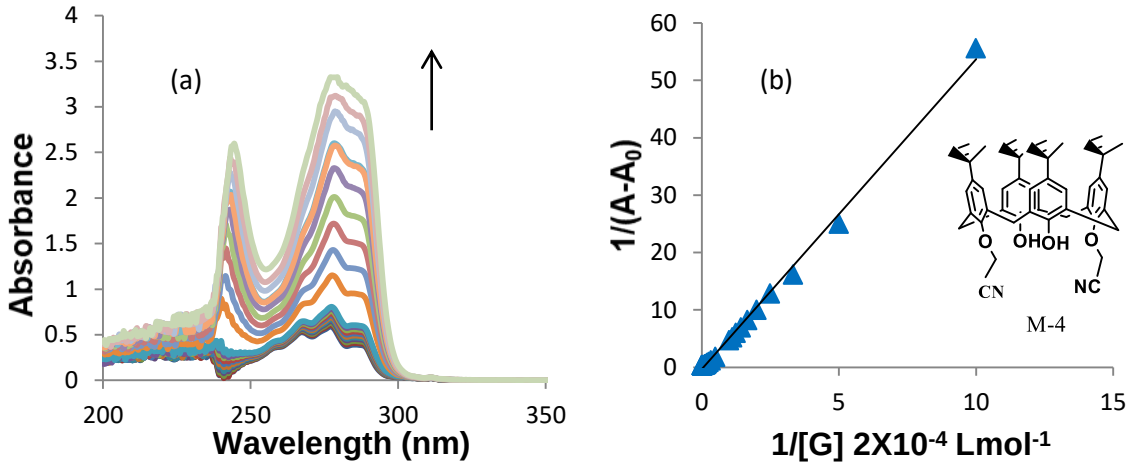


Figure 4.13: (a) Changes in UV-visible spectra of naphthalene (2 x 10^{-4}M) upon addition of 0-100 equivalent of **M-4** in chloroform and **(b)** Benesi-Hildebrand plot for host-guest complexation between **M-4** and naphthalene

$$C/M = 0.059747;\ K = 1.19X10^{3}$$

The UV-Visible spectra shown by an absorption band of **M-6** were at 285, 267.5 and 277 nm. The analysis was done at λ_{max}**= 276.5 nm** absorption band followed by evaluation purpose. A hyperchromic shift was reported at the absorption band at 276.5 nm on addition of **M-6** (0-100 equiv.) in naphthalene **(Figure-4.14)**.

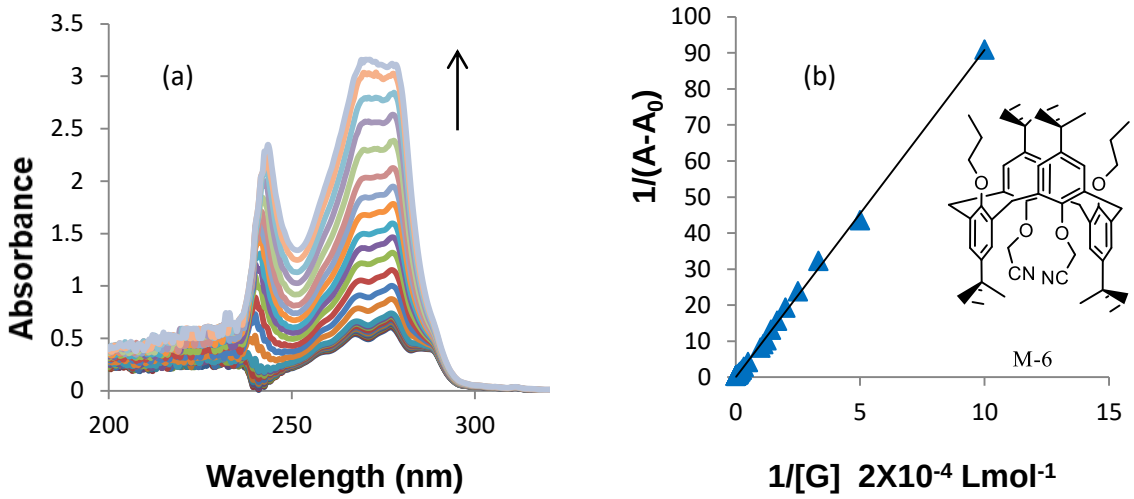


Figure 4.14: (a) Changes in UV-visible spectra of naphthalene (2 x 10^{-4}M) upon addition of 0-100 equivalent of **M-6** in chloroform and **(b)** Benesi-Hildebrand plot for host-guest complexation between **M-6** and naphthalene

C/M = 0.000198; K = 3.96

These studies of UV-visible spectra shows that **M-2, M-3, M-4** and **M-6** have the properties to form host-guest complexes with naphthalene respectively. Further Benesi-Hildebrand Equation was used to calculate the stability constants for each. The linear plot form of Benesi-Hildebrand Equation is shown in **Figure 4.11, 4.12, 4.13 and 4.14** for **M-2, M-3, M-4** and **M-6** respectively. Accordingly **M-2** and **M-4** have maximum values of stability constant which implies **M-2** and **M-4** show strongest inclusion towards naphthalene.

4.2.2 Anthracene Absorption study with M-2 to M-6 molecules:

The UV-Visible spectra shown by an absorption band of **M-3** were at 341.5, 359 and 378 nm. The analysis was done at λ_{max}**= 359 nm** absorption band followed by evaluation purpose. A hyperchromic shift was reported at the absorption band at 359 nm on addition of **M-2** (0-100 equiv.) in anthracene **(Figure-4.15)**.

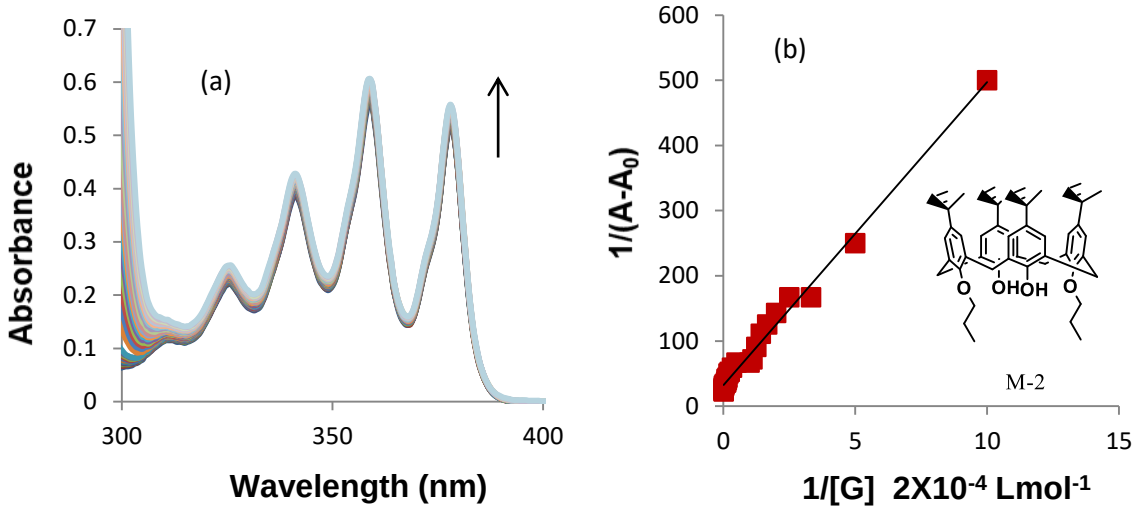


Figure 4.15: (a) Changes in UV-visible spectra of anthracene (2 x 10^{-4}M) upon addition of 0-100 equivalent of **M-2** in chloroform and **(b)** Benesi-Hildebrand plot for host-guest complexation between **M-2** and anthracene

C/M = 0.692384; K = $1.38X10^{4}$

The UV-Visible spectra shown by an absorption band of **M-3** were at 341, 359 and 378 nm. The analysis was done at λ_{max}**= 359 nm** absorption band followed by evaluation purpose. A hyperchromic shift was reported at the absorption band at 359 nm on addition of **M-3** (0-100 equiv.) in anthracene **(Figure-4.16)**.

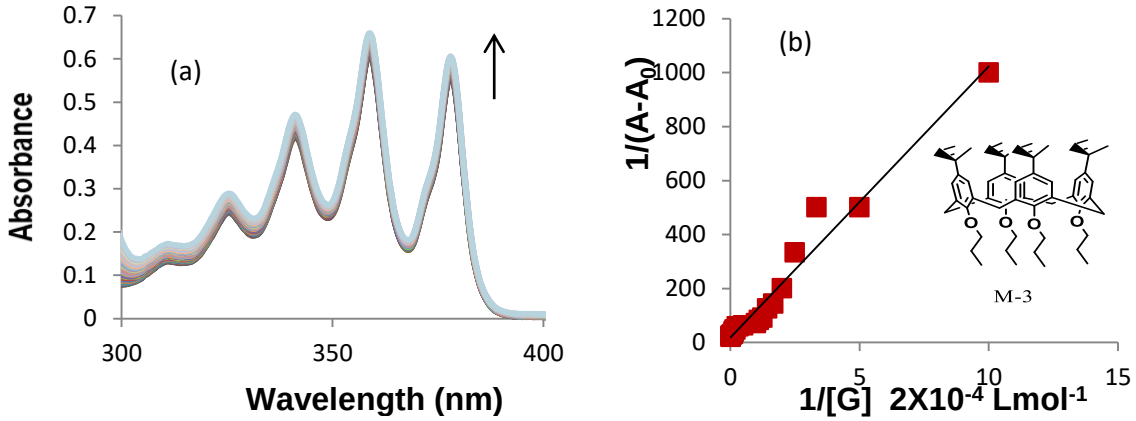


Figure 4.16: (a) Changes in UV-visible spectra of anthracene (2 x 10^{-4}M) upon addition of 0-100 equivalent of **M-3** in chloroform and **(b)** Benesi-Hildebrand plot for host-guest complexation between **M-3** and anthracene

C/M = 0.182539; K = $3.65X10^{3}$

The UV-Visible spectra shown by an absorption band of **M-4** were at 341, 359 and 378 nm. The analysis was done at λ_{max}**= 359 nm** absorption band followed by evaluation purpose. A hyperchromic shift was reported at the absorption band at 359 nm on addition of **M-4** (0-100 equiv.) in anthracene **(Figure-4.17)**.

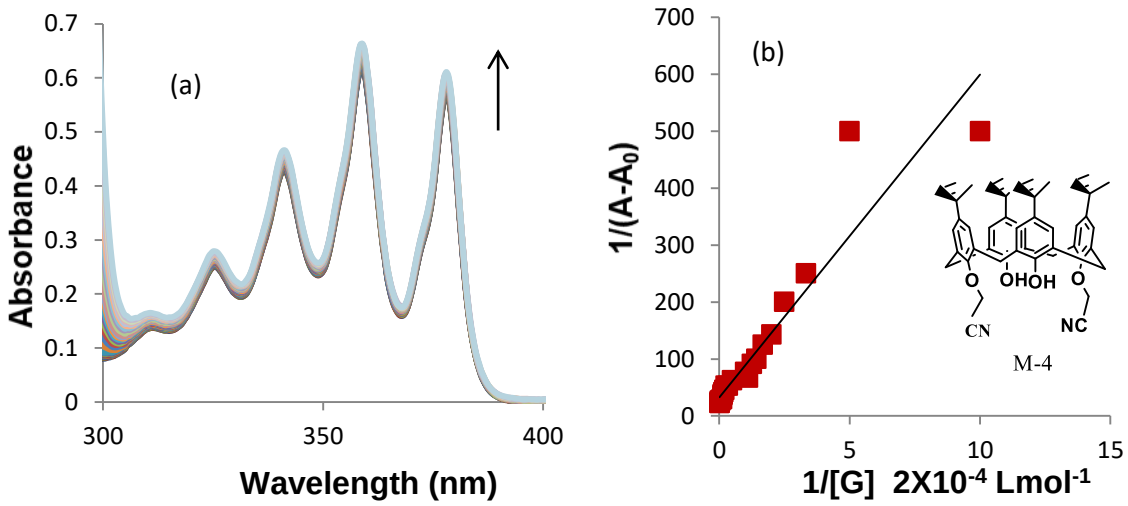


Figure 4.17: (a) Changes in UV-visible spectra of anthracene (2 x 10^{-4}M) upon addition of 0-100 equivalent of **M-4** in chloroform and **(b)** Benesi-Hildebrand plot for host-guest complexation between **M-4** and anthracene

$$C/M = 0.570159;\ K = 1.14X10^{4}$$

The UV-Visible spectra shown by an absorption band of **M-6** were at 341, 359 and 378 nm. The analysis was done at λ_{max}**= 359 nm** absorption band followed by evaluation purpose. A hyperchromic shift was reported at the absorption band at 359 nm on addition of **M-6** (0-100 equiv.) in anthracene **(Figure-4.18)**.

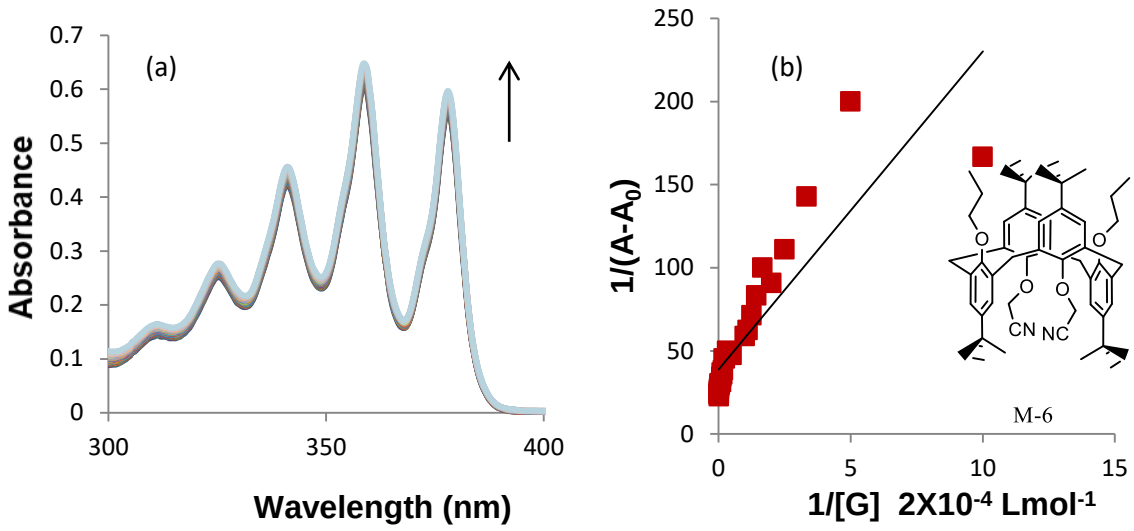


Figure 4.18: (a) Changes in UV-visible spectra of anthracene (2 x 10^{-4}M) upon addition of 0-100 equivalent of **M-6** in chloroform and **(b)** Benesi-Hildebrand plot for host-guest complexation between **M-6** and anthracene

$$C/M = 2.024707;\ K = 4.04X10^{4}$$

These studies of UV-visible spectra shows that **M-2, M-3, M-4** and **M-6** have the properties to form host-guest complexes with anthracene respectively. Further Benesi-Hildebrand Equation was used to calculate the stability constants for each. The linear plot form of Benesi-Hildebrand Equation is shown in **Figure 4.11, 4.12, 4.13 and 4.14** for **M-2, M-3, M-4** and **M-6** respectively. Accordingly **M-6** has maximum values of stability constant which implies **M-6** shows strongest inclusion towards anthracene.

4.2.3 Pyrene Absorption study with M-2 to M-6 molecules:

The UV-Visible spectra shown by an absorption band of **M-2** were at 274, 321 and 336 nm. The analysis was done at λ_{max}**= 274 nm** absorption band followed by evaluation purpose. A hyperchromic shift was reported at the absorption band at 274 nm on addition of **M-2** (0-100 equiv.) in pyrene **(Figure-4.19)**.

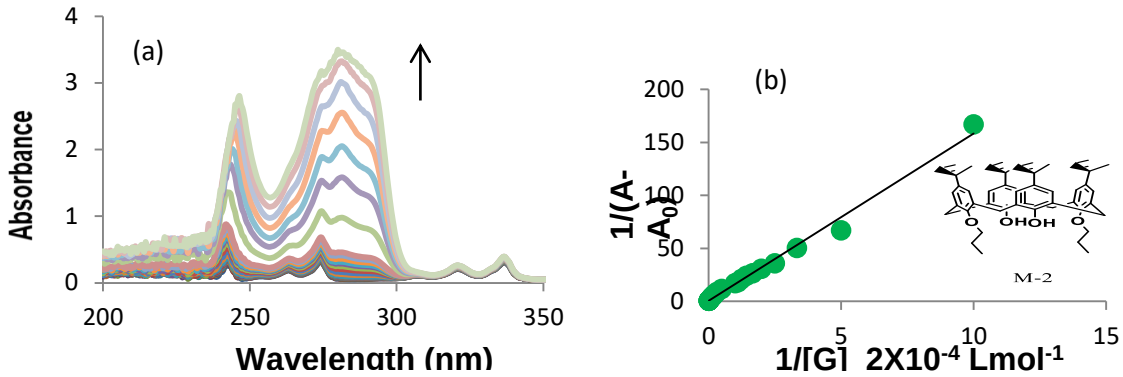


Figure 4.19: (a) Changes in UV-visible spectra of pyrene (2 x 10^{-4}M) upon addition of 0-100 equivalent of **M-4** in chloroform and **(b)** Benesi-Hildebrand plot for host-guest complexation between **M-4** and pyrene

C/M = 0.0366068; K = $7.32X10^{2}$

The UV-Visible spectra shown by an absorption band of **M-3** were at 307.5, 321.5 and 337 nm. The analysis was done at λ_{max}**= 307.5 nm** absorption band followed by evaluation purpose. A hyperchromic shift was reported at the absorption band at 307.5 nm on addition of **M-3** (0-100 equiv.) in pyrene **(Figure-4.20)**.

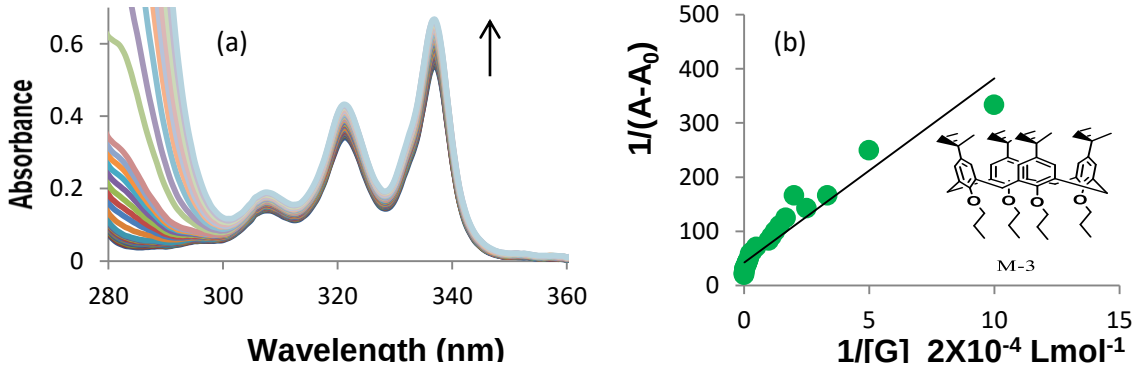


Figure 4.20: (a) Changes in UV-visible spectra of pyrene (2 x 10^{-4}M) upon addition of 0-100 equivalent of **M-3** in chloroform and **(b)** Benesi-Hildebrand plot for host-guest complexation between **M-3** and pyrene

C/M = 1.249154; K = $2.49X10^{4}$

The UV-Visible spectra shown by an absorption band of **M-4** were at 274.5, 321.5 and 337 nm. The analysis was done at λ_{max}**= 337 nm** absorption band followed by

evaluation purpose. A hyperchromic shift was reported at the absorption band at 337 nm on addition of **M-4** (0-100 equiv.) in pyrene **(Figure-4.21)**.

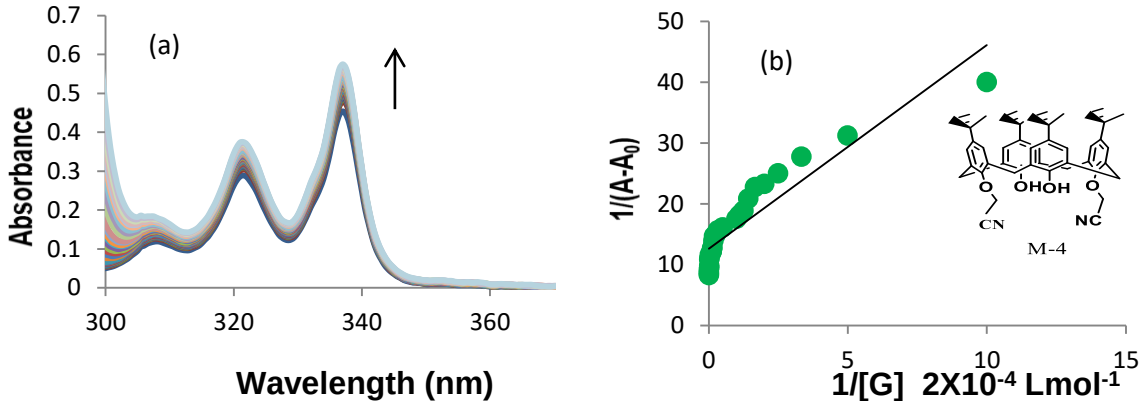


Figure 4.21: (a) Changes in UV-visible spectra of pyrene (2 x 10^{-4}M) upon addition of 0-100 equivalent of **M-4** in chloroform and **(b)** Benesi-Hildebrand plot for host-guest complexation between **M-4** and pyrene

C/M = 3.758988; K = 7.51X10^{4}

The UV-Visible spectra shown by an absorption band of **M-6** were at 274.5, 321.5 and 337 nm. The analysis was done at λ_{max}**= 337 nm** absorption band followed by evaluation purpose. A hyperchromic shift was reported at the absorption band at 337 nm on addition of **M-6** (0-100 equiv.) in pyrene **(Figure-4.22)**.

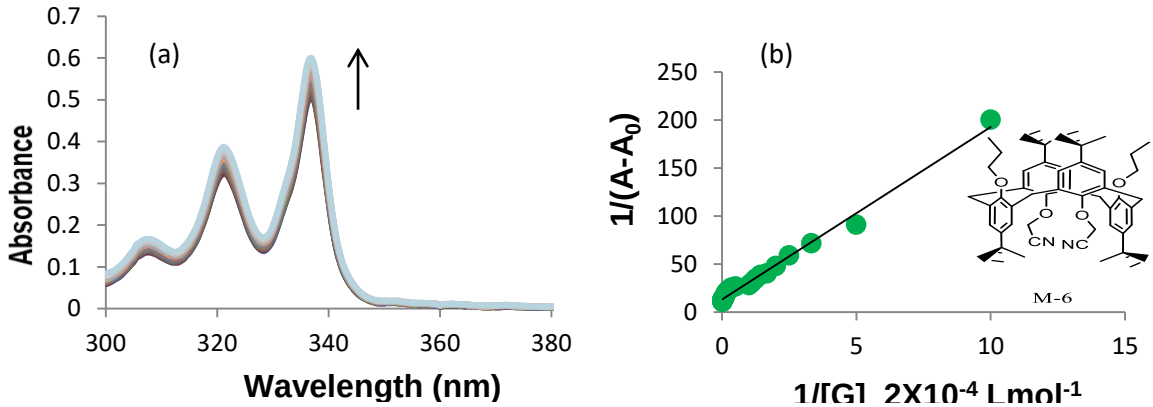


Figure 4.22: (a) Changes in UV-visible spectra of pyrene (2 x 10^{-4}M) upon addition of 0-100 equivalent of **M-6** in chloroform and **(b)** Benesi-Hildebrand plot for host-guest complexation between **M-6** and pyrene

C/M = 0.736628; K = 1.47X10^{4}

These studies of UV-visible spectra shows that **M-2, M-3, M-4** and **M-6** have the properties to form host-guest complexes with pyrene respectively. Further Benesi-Hildebrand Equation was used to calculate the stability constants for each. The linear plot form of Benesi-Hildebrand Equation is shown in **Figure 4.11, 4.12, 4.13 and 4.14** for **M-2, M-3, M-4** and **M-6** respectively. Accordingly **M-4** has maximum values of stability constant which implies **M-4** shows strongest inclusion towards pyrene.

4.2 Discussion

The results of the stability constant K, for the association behavior of naphthalene, anthracene and pyrene with **M-2-6**, is tabulated in **Table 4.1**. The results show that **M-2** and **M-4** forms a stronger inclusion complex with naphthalene which indicates that cone conformation of dipropylcalix[4]arene and dinitrilecalix[4]arene with the common phenol moiety has a role to play in naphthalene inclusion. **M-6** is better as compare to the cone for inclusion of anthracene which indicates 1,3alternate dinitrilecalix[4]arene of 1,3 alternate conformation bind anthracene strongly. **M-2** and **M-4** comprising of phenolic hydroxyl moiety also showed inclusion for anthracene. **M-4** has shown better inclusion for pyrene, which is attributed to the anti-orientation of the nitrile group.

Table 4.1: Stability constant for Host-Guest complexation of calix[4]arene derivatives M-2 to M-6 with Naphthalene, Anthracene and Pyrene

Calix[4]arene	Naphthalene	Anthracene	Pyrene
M-2	$2.53X10^3$	$1.38\ X10^4$	$7.32\ X10^2$
M-3	$3.62\ X10^2$	$3.65X10^3$	$2.49X10^4$
M-4	$1.19X10^3$	$1.14X10^4$	$7.51\ X10^4$
M-6	3.96	$4.04X10^4$	$1.47\ X10^4$

CHAPTER 5.

CONCLUSION

Conclusion

The study on PAH (naphthalene, anthracene, pyrene) inclusion using UV-visible study showed a significant effect of phenolic hydroxyl moiety, conformation of calix[4]arene and lower rim derivatives. Further studies are required to analyze the association behavior of **M-2-6** with PAH by 1H NMR titration and Isothermal Calorimetry (ITC) studies.

Chapter 6.

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