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Synthesis of calix[4]arene(amido)monocrowns and their photoresponsive derivatives

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Abstract—A series of new calix[4]arene(amido)mono-crown compounds have been synthesized through aminolysis of calix[4]arene esters and intramolecular cyclization of the intermediates. The title compounds were converted into their nitro and azo substituted derivatives to provide novel photoresponsive molecular receptors for transition metal ions. Single crystal X-ray analysis of calix[4]arene(ethyleneamido)-mono-crown (**2a**) revealed that the compound is present in a cone conformation with an amido loop that caps the lower rim of calix[4]arene cavity to result in stacking along axis *a* and axis *c* to provide supramolecular aggregates in the solid state. Evaluation of synthesized macrocycles in the solution phase for recognition of transition metal cations (Cr^{3+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Ag^{+}, Cd^{2+}, Pb^{2+}, Hg^{+}, Hg^{2+}, Pd^{2+}, and Pt^{2+}) by UV–visible spectroscopy revealed that *p-tert*-butyl-calix[4]arene mono-(amidocrown) **1c** selectively shows a blue shift at 38 nm on interaction with Hg^{+} ions.

1. Introduction

Calix[*n*]arenes (*n*=4–20) are phenolic [1$_n$]-*meta*cyclophanes that are known to provide useful building blocks for hollow molecular architectures with functionalizable hydrophilic and hydrophobic sites.[1] Calixarenes containing –CONH– groups at their hydrophilic end possess inherent hydrogen bond possibilities akin to those present in neutral peptides and proteins[2] and possibly can resolve some complex issues in molecular recognition. Literature search on calixarene based molecular receptors revealed that *p-tert*-butyl-calix[4]arene tetraethyl acetate, on treatment with mono-amines, provides amido calix[4]arenes in good yield. However, when the mono-amines are replaced by diamines and triamines, the same reaction provides double amido bridged calix[4]arenes[3] (Fig. 1). Recently, it has been suggested that the latter series of compounds results from a regioselective but sequential reaction of one of the amino functions of the diamine with the ester function followed by an intramolecular nucleophilic reaction of the remaining amino group with ester functions as depicted in Figure 1.[3] The reaction of calix[4]arene tetraethyl acetate should, therefore, lead to possible proximal or distal calix[4]arene mono-(amido)crowns, bis(amido)crowns, and alkyl amino amido methoxy calix[4]arenes. Since no other product could be isolated in the published experiments, the proposed pathway based upon precedents in esterification reactions of calix[4]arenes remains a conjecture. In this paper, we report

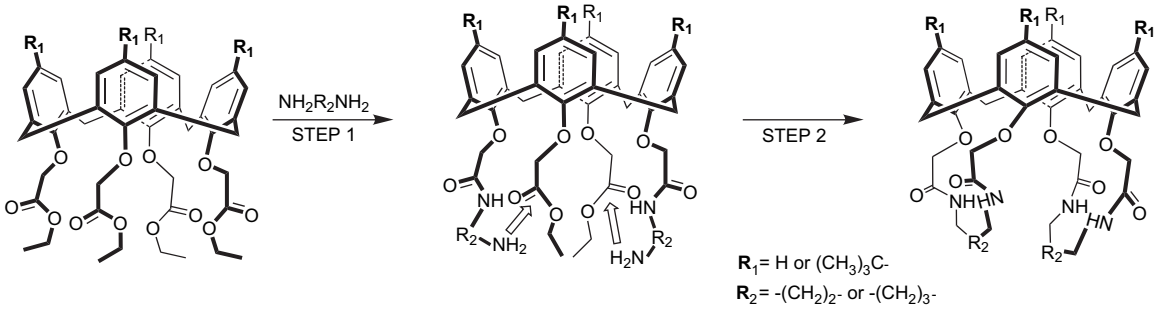

Figure 1. Proposed mechanism for the synthesis of 1,2,3,4-bis-amide-bridge calix[4]arenes.

Keywords: Calix[*n*]arenes; Diazotization; Nitration; Aminolysis.
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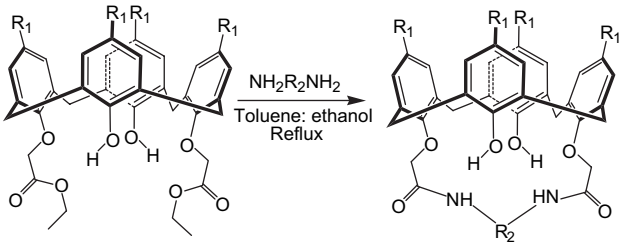
the synthesis of *p-tert*-butyl-calix[4]arene mono-(amido-crown) derivatives and their debutylated analogs to suggest a plausible mechanism for the reaction and to obtain photoresponsive derivatives of calix[4]amidocrowns for recognition of transition metal ions. The structures of the calix[4]arene(amido) crowns were established by spectroscopic and single crystal X-ray diffraction analyses.

2. Results and discussion

2.1. Characterization of the products

5,11,17,23-Tetra(*p-tert*-butyl)-25,27-di(ethoxycarbonylmethoxy)-26,28-dihydroxy-calix[4]arene (**1**) and 25,27-di-(ethoxycarbonylmethoxy)-26,28-dihydroxy-calix[4]arene (**2**) were synthesized by refluxing the corresponding calix[4]arene with ethyl bromoacetate in the presence of K_2CO_3 in acetone for 15 h.[4] When **1** and **2** were refluxed with different diamines in a mixture of toluene and methanol (Scheme 1) for a period of 24 h, they were converted into **1a**–**2e**, which could be isolated by recrystallization from the solvents mentioned in Section 4.



S.N.	R_1
1	*p-tert* butyl-
2	H

S.N.	R_1	R_2	Yield (%)
1a	*p-tert* butyl-	$-(CH_2)_2-$	92
1b	*p-tert* butyl-	$-(CH_2)_4-$	88
1c	*p-tert* butyl-	$-CH_2CH_2NHCH_2CH_2-$	72
1d	*p-tert* butyl-	$-CH_2(CH_2NHCH_2)_2CH_2-$	56
1e	*p-tert* butyl-	$-(CH_2)_6-$	48
2a	H	$-(CH_2)_2-$	83
2b	H	$-(CH_2)_4-$	82
2c	H	$-CH_2CH_2NHCH_2CH_2-$	76
2d	H	$-CH_2(CH_2NHCH_2)_2CH_2-$	51
2e	H	$-(CH_2)_6-$	26

Scheme 1. Synthesis of calix[4]arene(amido)mono-crown derivatives. Reagents: 20 equiv, diamine (H_2N-R_2-NH_2), toluene/MeOH (1:1), refluxing, 24 h.

The structures of **1a**–**1e** and **2a**–**2e** were established by the analysis of their ^1H and ^{13}C NMR spectra as well as other NMR experiments. For instance, the molecular structure of **2b** could be confirmed by the analysis of its two dimensional HSQC spectrum (Fig. 2). It was determined that the pair of doublets at δ 4.18 and 3.51 for ArCH_2Ar protons in the ^1H NMR spectrum could be correlated with the signal at δ 31.17 in its ^{13}C NMR spectrum. A multiplet at δ 6.74–6.81 region in the ^1H NMR spectrum for ArH_{para} protons correlated well with two signals at δ 120.4 and 126.3 in the ^{13}C NMR spectrum of **2b**. Similarly, two doublets at δ 6.88 and 7.14 for ArH_{meta} protons observed in the ^1H NMR spectrum correlated well with the two signals at 129.0 and 129.5 ppm in the ^{13}C NMR spectrum of **2b**. This specific correlation pattern indicated that **2b** is a symmetrical compound

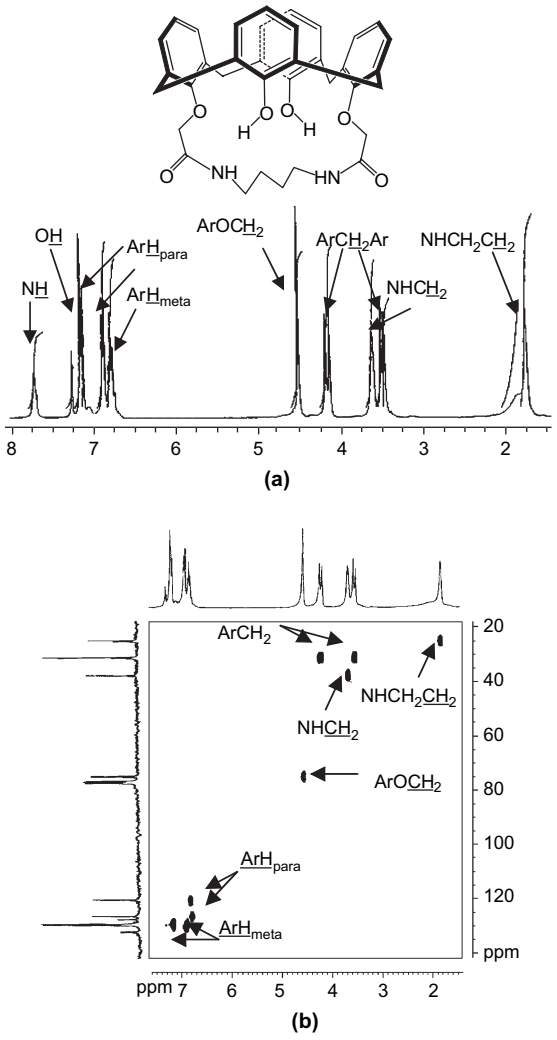
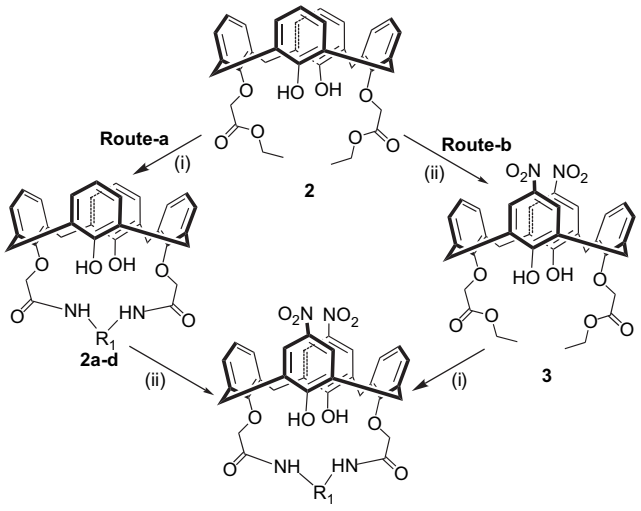


Figure 2. (a) Molecular structure and ^1H NMR spectrum of **2b**; (b) HSQC spectrum of **2b** in $CDCl_3$ at 25 °C and 300 MHz.

in its cone conformation. Similarly, the presence of a pair of doublets for ArCH_2Ar protons in the ^1H NMR spectra of synthesized derivatives and only one signal for methylene carbon in the range of 29–32 ppm in their ^{13}C NMR spectra suggested that the synthesized calix[4]arene(amido)-mono-crowns were in a symmetrical cone conformation in solution.[5]

When **2a**–**2d** were reacted with HNO_3/CH_3COOH, they gave products, which were identified as their nitro derivatives **3a**–**3d** (Scheme 2, route a).[6]

Compound **3a** exhibited prominent signals at δ 9.41 and 8.14 for hydroxyl and amide protons, while signals for aromatic protons appeared at δ 8.27, 7.28, and 6.95. The ArOCH_2–protons appeared at δ 4.57 while ArCH_2Ar and –NHCH_2 protons appeared at δ 4.26 and 3.82, and δ 3.51, respectively (Fig. 3). These data suggested that **3a** possessed a symmetric cone structure. A prominent downfield shift in the position of hydroxyl signal suggested that nitro groups were present at positions *para* to the hydroxyl groups. Similarly, other compounds of the series (**3b**–**3d**) could be characterized by their ^1H NMR spectra.



	R_1	Yield (%)
3a	$-(CH_2)_2-$	78
3b	$-(CH_2)_4-$	80
3c	$-CH_2CH_2NHCH_2CH_2-$	77
3d	$-CH_2CH_2NHCH_2CH_2NHCH_2CH_2-$	58

Scheme 2. Synthesis of *p*-nitro calix[4]arene(amido)mono-crown derivatives Reagents: (i) 20 equiv, diamine, toluene/MeOH (1:1), refluxing, 24 h; (ii) 100% nitric acid, glacial acetic acid/dichloromethane (1:1), 0 °C, 10 min.

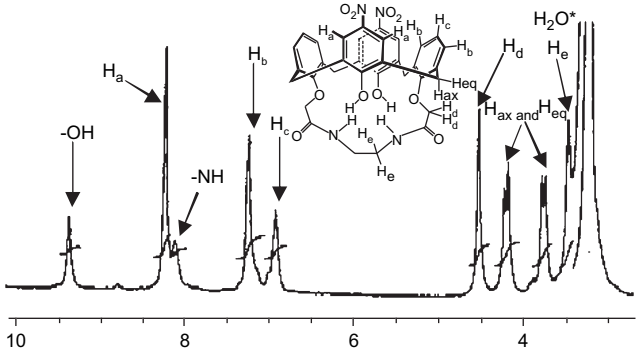
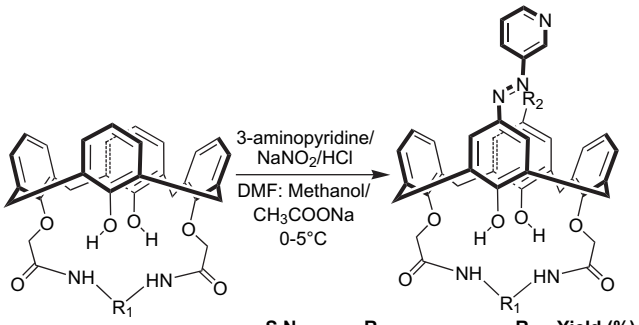


Figure 3. Molecular structure and ^{1}H NMR spectrum of **3a**.

The same nitro substituted derivatives could also be obtained by nitration of 25,27-di(ethoxycarbonylmethoxy)-26,28-dihydroxy-calix[4]arene (**2**) followed by aminolysis with diamines as depicted in Scheme 2, but it was determined that nitration of amidocrowns (route a) resulted in better yields of **3a** and **3b**. When the compounds were less soluble in dichloromethane (e.g., **2c** and **2d**), the reaction gave lower yields of the products (**3c** and **3d**). In such cases, route b was determined to be a better pathway for obtaining products in good yields.

To confer chromogenicity of calix[4]arene(amido)mono-crown derivatives for ionic and molecular recognitions, compounds **2a**–**2d** were also reacted with diazotized 3-aminopyridine under basic conditions to provide mixtures of compounds, which could be separated by column chromatography to give **4a**, **4b**, **5a**, **5b**, **6a**, and **6b** in moderate yields[7] as described in Section 4 (Scheme 3).

The ^{1}H NMR spectra of **4a**–**6b** suggested them to be (pyridylazo)calix[4]arene(amido)mono-crown derivatives. For instance, **4b** exhibited broad signals at δ 8.94 and 8.38 for



S.N	R_1	R_2	Yield (%)
4a	$-(CH_2)_2-$	H	28
4b	$-(CH_2)_2-$	3-AP	58
5a	$-(CH_2)_4-$	H	7
5b	$-(CH_2)_4-$	3-AP	28
6a	$-CH_2CH_2NHCH_2CH_2-$	H	27
6b	$-CH_2CH_2NHCH_2CH_2-$	3-AP	51

Scheme 3. Synthesis of (pyridylazo)calix[4]arene(amido)mono-crown derivatives. Reagents: (i) diazonium salt obtained from 3-aminopyridine, DMF/MeOH (8:5), CH_3COONa, 0–5 °C, 3 h.

hydroxyl and amide group protons in its ^{1}H NMR spectrum, while 3-azopyridyl protons appeared at δ 9.15, 8.65, 8.10, and 7.44, calix[4]arene core aromatic protons appeared at δ 7.81, 7.19, and 6.99. The ArOCH_2–, ArCH_2Ar, and –NHCH_2 protons could be observed at δ 4.65, 4.25, and 3.73, respectively, in its ^{1}H NMR spectrum (Fig. 4). The pattern of a pair of doublets for methylene protons suggested that **4b** was present in its cone conformation. Assignment of different NMR signals has been indicated in Figure 4. Similarly, other (pyridylazo)calix[4]arene(amido)mono-crown derivatives could be characterized.

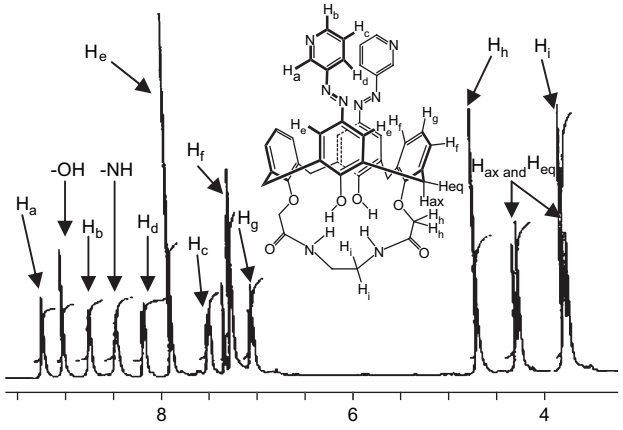


Figure 4. Molecular structure and ^{1}H NMR spectrum of **4b**.

2.2. X-ray crystal structural analysis of the calix[4]arene (ethyleneamido)crown (2a)

The ORTEP diagram of **2a** is shown in Figure 5a. The torsion angles φ and χ around ArCH_2Ar bonds about C7, C14, C21, and C28 are 77.5°(12), −100.6°(°(12), 98.3°(12), −78.0°(13), 74.4°(12), −103.9°(12), 100.7°(11), and −78.5°(13), respectively. This alternate ± sequence is characteristic for the cone conformation.[8] All the four aromatic rings are planar with a maximum deviation of 0.022 Å from a least square plane. The connecting methylene carbon

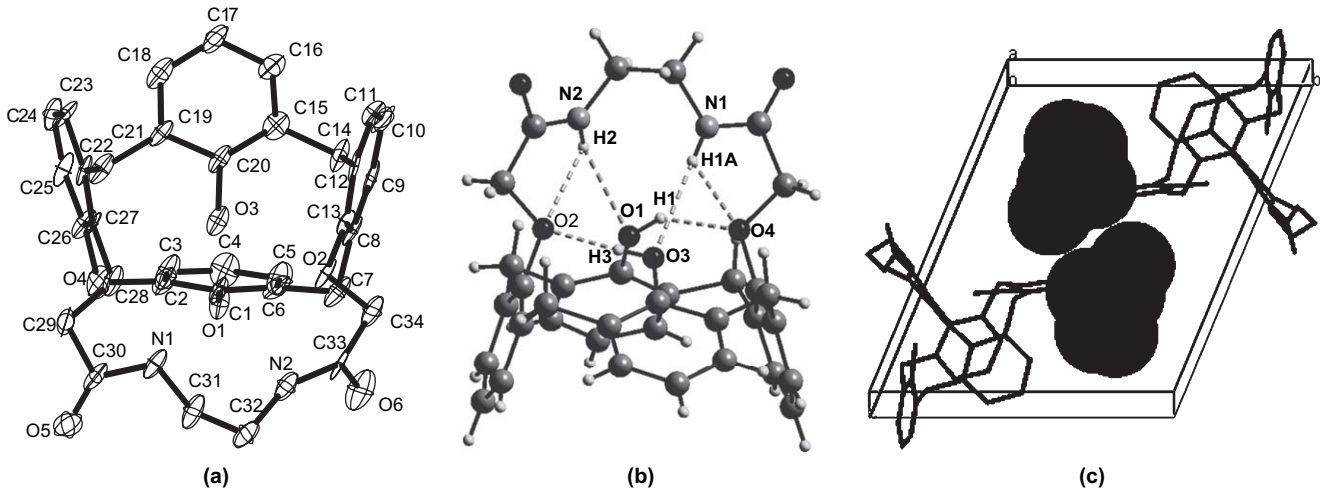


Figure 5. (a) ORTEP diagram showing labeling of atoms in **2a** (hydrogens and solvent molecule have been omitted for clarity); (b) intramolecular hydrogen bonding in **2a**; (c) the content of a single unit cell.

atoms C7, C14, C21, and C28 form an approximate plane where alternate carbon atoms lie ±0.136 and ±0.137 Å above and below the plane. The interplanar angles found between this plane (hypothetical plane along methylene carbons C7, C14, C21, and C28) and the rings A(C1–C6), B(C8–C13), C(C15–C20), D(C22–C27) are 40.39°(1), 73.62°(1), 35.19°(2), 71.95°(1), respectively. The interplanar angle between the pairs A and C is determined to be 75.57(2)° while it is 34.45(2)° between ring B and D. Thus, two opposite rings B and D are almost parallel while rings A and C are almost perpendicular to each other. The O···O separation between O(1) and O(3), and O(2) and O(4) is 3.151 and 4.542 Å, respectively. Likewise, the O···O distance between adjacent phenolic oxygens O(1)–O(2), O(2)–O(3), O(3)–O(4), O(4)–O(1) is 2.879, 2.735, 2.851, and 2.705 Å, respectively. Both the O2–C34–C33–O6 and O4–C29–C30–O5 are *trans* thereby making both the carbonyl groups *exo* with respect to the calixarene cavity.

The main deciding factor for determining the conformation of this molecule is the presence of four intramolecular H-bond (H···O) interactions (Fig. 5b) given in Table 1. The protons of the nitrogen atoms N1 and N2 point inward to the calixarene cavity and are bound to the phenolic oxygens of the calixarene through hydrogen bonds. The contents of the unit cell are shown in Figure 5c.

Table 1. Intramolecular H-bonding interactions of **2a**

S.no.	D–H···A	D–H(Å)	H···A(Å)	D···A(Å)	∠D–H···A(°)
1	O1–H1···O4	0.820	2.121	2.706	128.12
2	O3–H3···O2	0.820	1.937	2.734	163.77
3	N1–H1A···O3	0.860	2.500	3.356	173.23
4	N2–H2···O1	0.860	2.519	3.338	159.56

D = Donor, A = Acceptor.

Dimer formation via tail to tail (Fig. 6a) and head to head (Fig. 6b) has been observed in the X-ray diffraction pattern of **2b**. Two sets of intermolecular hydrogen bonds among C31–H31A···O3′ [C–H···O=2.705 Å] and a prominent C–H–π interaction between C31–H31B and ring C′ (3.147 Å) bring the ethyleneamido crown ring much closer to the plane of ring C, which results in a tail to tail dimer (Fig. 6a). A set of a strong intermolecular C–H–π interaction between *para*-hydrogen of ring D′ (C24′–H24′) with ring B (3.080 Å) and *ortho*-hydrogens of ring D′, i.e., C23′–H23′ with ring A (3.432 Å) and C25′–H25′ with ring C (3.008 Å), seems to be responsible for the formation of head to head dimer (Fig. 6b). A weak intermolecular hydrogen bond between C34–H34B···O5′ (2.669 Å) was associated with the formation of a long supramolecular chain in the solid state (Fig. 6c, Fig. 7).

2.3. Discussion

It has earlier been proposed that aminolysis of the cone conformation of 25,26,27,28-tetra(ethoxycarbonylmethoxy)-calix[4]arene with diamine to yield bisamido-calix[4]arenes (Fig. 1)[3] proceeds through a distally substituted intermediate to yield 25,27-bis(amino alkyl amido methoxy)-26,28-bis(ethoxycarbonylmethoxy)-calix[4]arene (Fig. 8a). Consequently, the reaction of diamine with diester derivatives of calix[4]arenes should result in a 25,27-bis(amino alkyl amido methoxy)-26,28-bishydroxycalix[4]arenes (Fig. 8b). However, it has been observed that the reaction gives only the mono-(amido)crown derivatives. This suggests that the reaction of diamines with 25,26,27,28-tetra-(ethoxycarbonylmethoxy)calix[4]arene would have also proceeded in a manner different from the previously proposed reaction of amine with calix[4]arene ethyl acetates.

The formation of proximally substituted calix[4]arene(bisamido)crowns can be considered to proceed stepwise via aminolysis to yield the alkyl amino amido methoxy calix[4]-arenes followed by intramolecular cyclization as depicted in Figure 9. The possibility of intermolecular reaction of intermediate aminoamides could be discounted as biscalix[4]arenes could not be isolated or detected in the reaction mixture (FABMS analysis). This conclusion was confirmed by repeating the reaction with excess of diamine (40 equiv) when the reaction resulted in the synthesis of calix[4]arene mono-(amidocrown) derivatives in very good yield. The aminolysis reaction of calix[4]arene ester with diamines

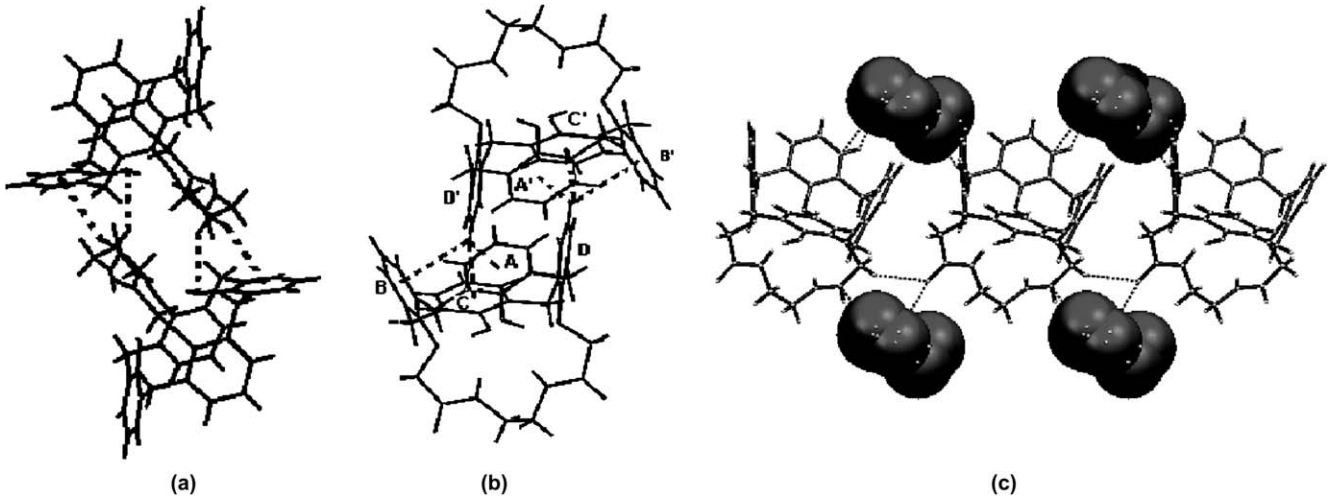


Figure 6. (a) A tail to tail dimer; (b) a head to head dimer; (c) supramolecular aggregates along *c* axis (intermolecular interactions are shown as dotted lines).

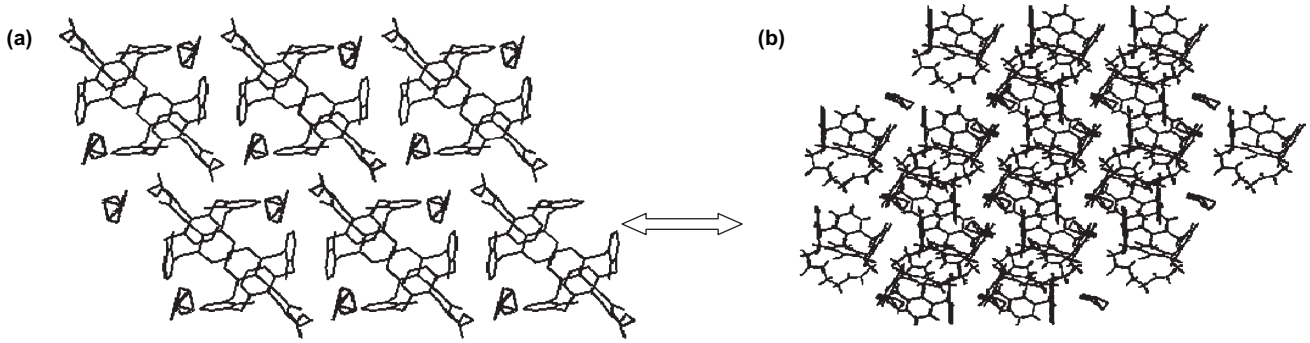


Figure 7. (a) Stacking of molecules along *a* axis; (b) stacking of molecules along *c* axis to yield supramolecular aggregates with disordered chloroform.

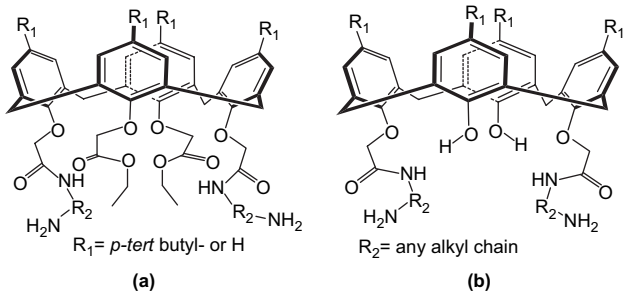


Figure 8. Ester derivatives with pendant amine groups.

can, therefore, lead to monoamido crown compounds or proximally substituted bisamido crown compounds as depicted in Figure 9. Thus, one of the ester groups in the tetraester (**A**) can be envisaged to get aminolyzed to yield mono-amide (**B**) when reacted with diamines in first step. This intermediate can be considered to react with the neighboring ester group to form a calix[4]arene (monoamido)crown (**C**) in second step, which can further react in a similar fashion to provide proximally bridged calix[4]arene(bisamido)crowns (**E**). Alternatively, the mono-amide (**B**) formed in the first step can further react with the diamine to provide a di-amide (**F**), which in turn can give calix[4]arene monoamido crown (**D**) or proximally bridged calix[4]arene-(bisamido)crowns (**E**).

It was interesting to note that the nitration of calix[4]arene mono-(amido)crown derivatives (**2a**–**2d**) with 5 equiv of HNO_3 (100%) in CH_3COOH/dichloromethane was determined to be complete within 5 min at room temperature to yield **3a**–**3d** (monitored by TLC). When the reaction was continued for more than 10 min, it gave a complex mixture while prolonged reaction almost always resulted in the degradation of calixarene framework. Again when the reaction was not conducted under dry conditions, it resulted in the hydrolysis of the ester function in **2a**–**2d**.

3. Preliminary investigation of synthesized calix[4]-amidocrowns for ionic recognition

In order to obtain insight into the affinity of the synthesized calix[4]amidocrowns for metal ions, the changes in their λ_{max} upon interaction with a variety of hard and soft metal cations were investigated. The affinity of calix[4]amidocrowns (**1c**, **2b**) and chromogenic calix[4]amidocrowns (**4a**, **4b** and **6a**, **6b**) for group I (Li^+, Na^+, K^+, Cs^+, and Rb^+), group II (Ca^{2+}, Mg^{2+}, and Ba^{2+}), and transition metal cations (Cr^{3+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Ag^+, Cd^{++}, Pb^{++}, Hg^+, Hg^{2+}, Pd^{2+}, and Pt^{2+}) was examined in solution using methanol as the solvent. The changes in λ_{max} of these chromoionophores upon addition of various cations are listed in Table 2. Fig. 10 depicts the change in wavelength of absorption

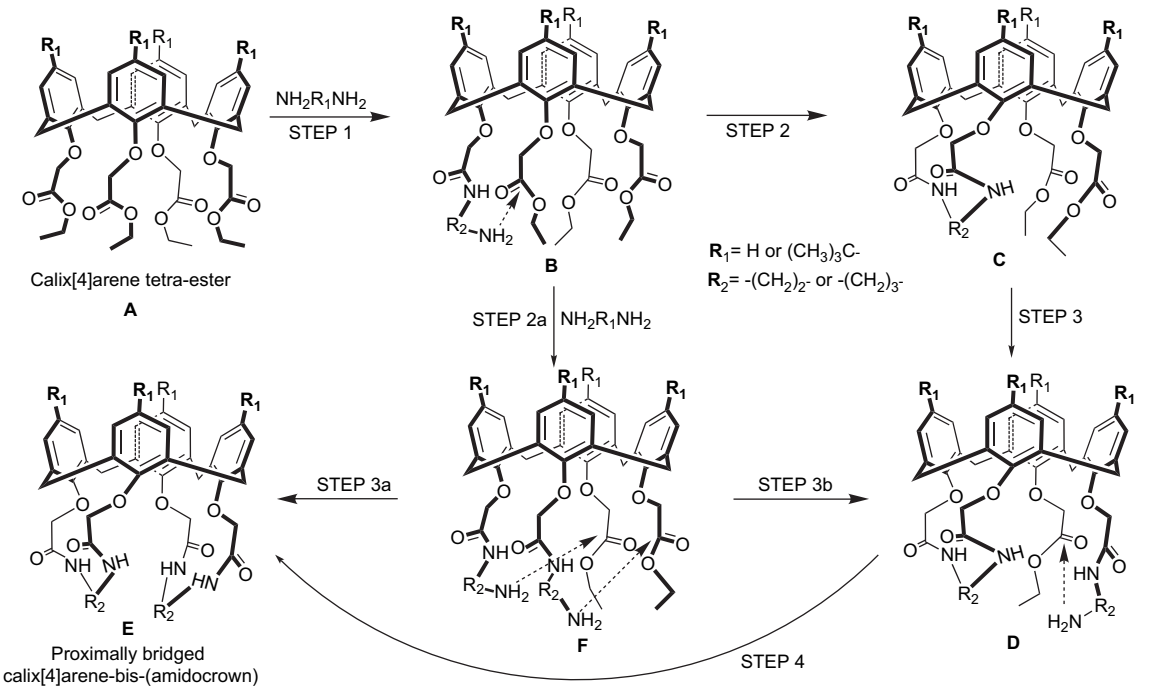


Figure 9. Mechanistic possibilities for the synthesis of proximally bridged calix[4]arene-bis-(amidocrown) derivatives from calix[4]arene tetraester.

of the synthesized compounds on addition of different alkali metal salts. Calix[4]arene (amido)crowns (**4a**, **4b** and **6a**, **6b**) were found to exhibit a red shift at about 130 nm accompanied by a profound color change on addition of excess of alkali metal ions with the appearance of a new absorption band near 500 nm. These changes could be ascribed to the basicity of the alkali metal carbonates, which tends to ionize the phenolic hydroxyls.

Table 2. Observed $\Delta\lambda_{max}$ (nm) of synthesized compounds on addition of 100 equiv. of metal ions

No.	**1c**	**2b**	**4a**	**4b**	**6a**	**6b**
λ_{max} (nm)	214, 281[a]	215, 276[a]	257, 360[a]	273, 361[a]	273, 361[a]	269, 365[a]
Salts	Metal-induced wavelength changes ($\Delta\lambda_{max}$, nm)					
Li^+	nc[b]	nc	+137	+138	+138	nc
Na^+	nc	nc	+133	+137	+138	+114
K^+	nc	nc	+134	+137	+138	+113
Rb^+	nc	nc	+134	+137	+138	+117
Cs^+	nc	nc	+130	+133	+133	+131
Mg^{2+}	nc	nc	nc	nc	nc	nc
Ca^{2+}	nc	nc	nc	nc	nc	nc
Ba^{2+}	nc	nc	nc	nc	nc	nc
Cr^{3+}	nc	nc	nc	nc	nc	nc
Fe^{3+}	nc	nc	nc	nc	nc	nc
Co^{2+}	nc	nc	nc	nc	nc	nc
Ni^{2+}	nc	nc	nc	nc	nc	nc
Cu^{2+}	nc	nc	nc	nc	nc	nc
Hg^+	−38	−4	+16	+16	+17	+15
Cd^{2+}	nc	nc	nc	nc	nc	nc
Ag^+	nc	nc	nc	+14	nc	nc
Pb^{2+}	nc	nc	nc	nc	nc	nc
Pd^{2+}	nc	nc	+10	+6	nc	nc
Pt^{2+}	nc	−12	nc	nc	nc	nc

[a] Metal-induced wavelength changes have been shown with regard to this absorption peak.
[b] nc = no change.

A selective but significant interaction was observed when Hg^+ metal ion interacted with a dilute solution of calix[4]-arene(amido)crown **1c**. A blue shift at 38 nm could be observed when excess of Hg^+ (Fig. 11a) was added to a solution of **1c** in methanol. The observed change ($\Delta\lambda_{max}$, nm) in the absorption maxima of synthesized derivatives (**1c**, **2b**, **4a**, **4b**, **6a**, and **6b**) on addition of 100 equiv of various transition metal ions has been tabulated in Table 2. It is clear from Table 2 that **1c** and **2b** have the capability to interact with Hg^+. These ionophores did not give any shift in the λ_{max} when interacted with other transition metal ions examined (Fig. 11b) (a marginal shift with platinum was observed in the case of **2b**). No interference from other ions could be observed in the present study. The inference that the interaction is due to the mercurous ions and not due to nitrate ions was confirmed by examining the effect of addition of tetrabutyl ammonium nitrate to a methanolic solution of **1c** when no shift in its λ_{max} or its intensity was observed.

We conclude that the reaction of di(ethoxycarbonylmethoxy)calix[4]arenes with diamines results in the formation of calix[4]arene(amido)mono-crown compounds through aminolysis followed by an intramolecular cyclization reaction. The calix[4]arene(amido)mono-crown compounds could be nitrated with HNO_3 (100%, obtained from the distillation of a mixture of HNO_3 and H_2SO_4)/glacial acetic acid to provide nitro substituted calix[4]arene(amido)-mono-crown compounds. They can also be converted to their azo calix[4]arene(amido)mono-crown compounds to provide additional hydrophilic and hydrophobic cavities at the lower rim and upper rim of calix[4]arenes, which can be tailored for sensing toxic and precious metal ions. Further work to modify calix[4]arene(amido) crown compounds for end use applications is in progress.

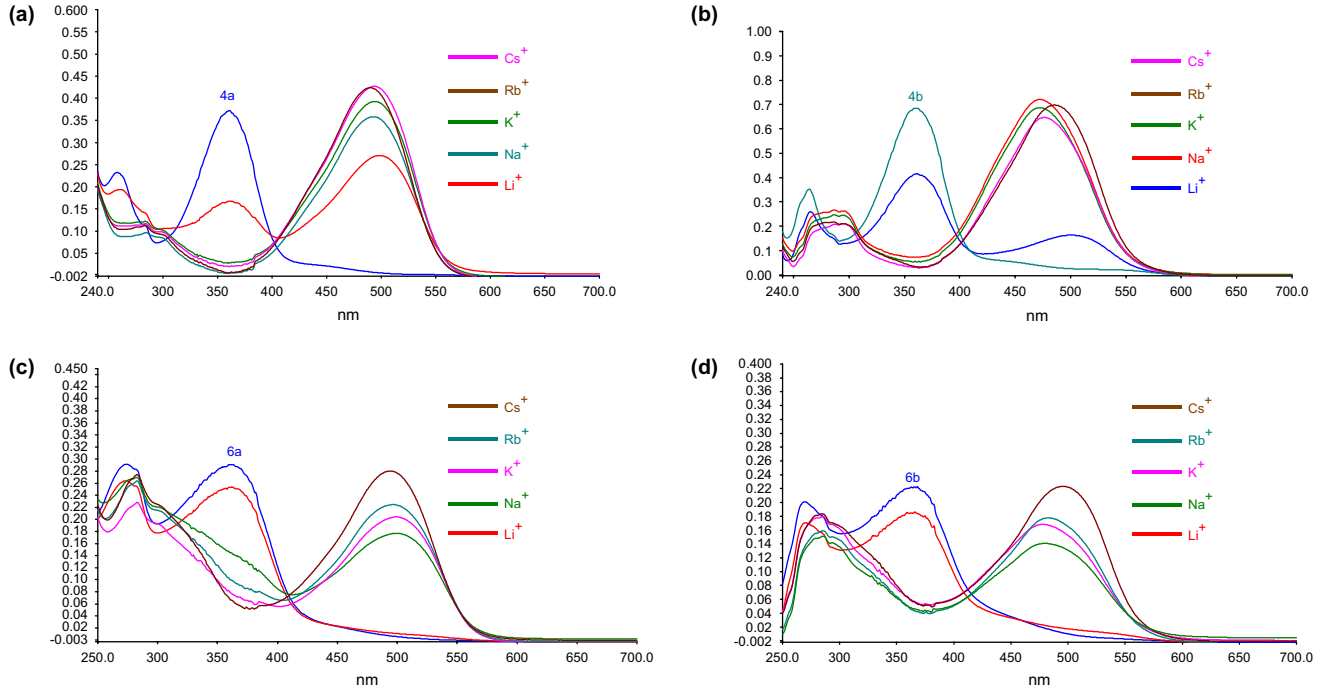


Figure 10. (a) UV–visible spectra of **4a** and shifts in its λ_{max} upon the addition of 100 equiv of alkali metal salts; (b) UV–visible spectra of **4b** and shifts in its λ_{max} upon the addition of 100 equiv of alkali metal salts; (c) UV–visible spectra of **6a** and shifts in its λ_{max} upon the addition of 100 equiv of alkali metal salts; (d) UV–visible spectra of **6b** and shifts in its λ_{max} upon the addition of 100 equiv of alkali metal salts.

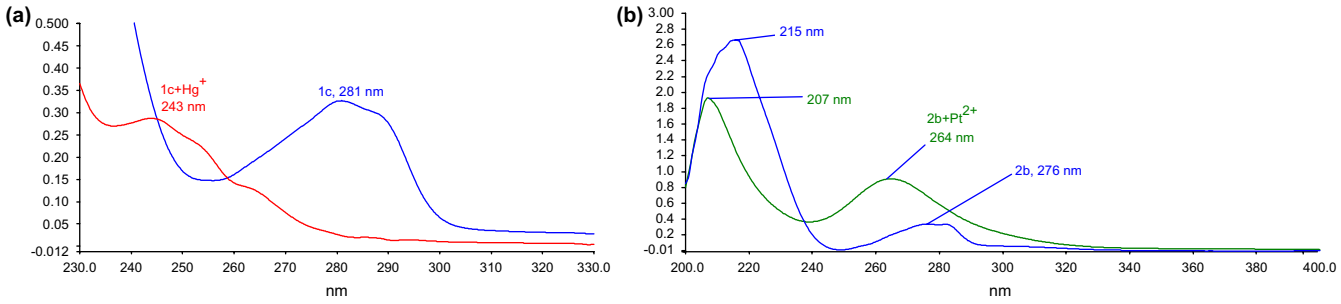


Figure 11. (a) UV–visible spectra of **1c** and shifts in its λ_{max} upon the addition of 100 equiv of Hg^{+} metal salts; (b) UV–visible spectra of **2b** and shifts in its λ_{max} upon the addition of 100 equiv of Pt^{2+} metal salts.

4. Experimental

4.1. General

All the reagents used in the study were purchased from Sigma–Aldrich or Merck and were chemically pure. The solvents used were distilled. Column chromatography was performed on silica gel (60–120 mesh) obtained from Merck. ^{1}H NMR, ^{13}C NMR, DEPT-135, and HSQC spectra were recorded on a 300 MHz Bruker DPX 300 instrument at room temperature using tetramethylsilane (TMS) at 0.00 as an internal standard. IR spectra were recorded on a Nicolet Protégé 460 spectrometer in KBr disks while X-ray data were recorded using a Bruker SMART CCD single crystal diffractometer. UV–visible spectra were obtained on a Perkin–Elmer (Lambda-3B) recording spectrophotometer. The FAB mass spectra were recorded on a JEOL SX 102/DA-6000 Mass spectrometer/Data System using Argon/Xenon (6 kV, 10 mA) as the FAB gas. Melting points were determined on an electrothermal melting point apparatus obtained from M/S Toshniwal and were uncorrected.

4.2. Preparation of starting materials

p-tert-Butylcalix[4]arene, calix[4]arene, 5,11,17,23-tetra (*p-tert*-butyl)-25,27-di(ethoxycarbonylmethoxy)-26,28-dihydroxy-calix[4]arene (**1**), 25,27-di(ethoxycarbonylmethoxy)-26,28-dihydroxy-calix[4]arene (**2**), and 5,17-dinitro-25,27-di(ethoxycarbonylmethoxy)-26,28-dihydroxy-calix[4]arene (**3**) were synthesized as described previously.[4] The analytical data for compounds **1a**, **1c**, and **2c** were found to be same as reported earlier.[9]

4.3. General procedure for the synthesis of calix[4]-arene(amido)mono-crown derivatives

Diesters (**1**, **2**) and diamines (20-30 equiv) were taken in toluene:methanol (1:1 ratio) and refluxed for 24 h. The solvent was removed under reduced pressure to yield yellowish semisolid (or solid), which was dissolved in chloroform or ethyl acetate and washed with 1 N H_2SO_4 followed by washing with water. The organic layer was collected and evaporated to dryness under reduced pressure to yield

calix[4]arene(amido)mono-crown derivatives as white solids, which were further purified by recrystallization from $CHCl_3/CH_3OH$ or CH_3OH/H_2O. Pure compounds could be isolated by leaving the recrystallizing mixture overnight at 0 °C.

4.3.1. Compound 1a. White solid, yield: 92%, mp>232 °C (decomp.). IR (KBr, ν_{max}/cm^{-1}): 3366, 2958, 1689. ^1H NMR (300 MHz, $CDCl_3$, δ in ppm): 8.58 (br t, 2H, CONH), 8.29 (s, 2H, OH), 7.06 (s, 4H, ArH), 7.04 (s, 4H, ArH), 4.53 (s, 4H, OCH_2), 4.16 (d, 4H, J=13.2 Hz, $ArCH_2Ar$), 3.67 (br d, 4H, $NHCH_2$), 3.49 (d, 4H, J=13.2 Hz, $ArCH_2Ar$), 1.24 (s, 18H, $C(CH_3)_3$), 1.15 (s, 18H, $C(CH_3)_3$). FABMS m/z: 789 (M^+). Anal. Calcd for $C_{50}H_{64}N_2O_6$: C, 76.11; H, 8.18; N, 3.55. Found: C, 76.25; H, 8.20; N, 3.61. UV (λ_{max}, MeOH): 223, 280, 288 nm.

4.3.2. Compound 1b. White solid, yield: 88% mp>285 °C (decomp.). IR (KBr, ν_{max}/cm^{-1}): 3369, 2958, 1684. ^1H NMR (300 MHz, $CDCl_3$, δ in ppm): 8.02 (br t, 2H, NH), 7.13 (s, 4H, ArH), 6.77 (s, 4H, ArH), 6.75 (s, 2H, OH), 4.50 (s, 4H, OCH_2), 4.14 (d, 4H, J=13.5 Hz, $ArCH_2Ar$), 3.57 (br s, 4H, NCH_2), 3.44 (d, 4H, J=13.5 Hz, $ArCH_2Ar$), 1.75 (br s, 4H, NCH_2CH_2), 1.31 (s, 18H, $C(CH_3)_3$), 0.90 (s, 18H, $C(CH_3)_3$). FABMS m/z: 817 (M^+). Anal. Calcd for $C_{52}H_{68}N_2O_6$: C, 76.44; H, 8.39; N, 3.43. Found: C, 76.61; H, 8.37; N, 3.49. UV (λ_{max}, MeOH): 208, 282, 287 nm.

4.3.3. Compound 1c. White solid, yield: 72%, mp 185 °C. IR (KBr, ν_{max}/cm^{-1}): 3430, 2958, 1673. ^1H NMR (300 MHz, $CDCl_3$, δ in ppm): 8.89 (br s, 1H, NH), 8.35 (br t, 2H, NH), 8.03 (br s, 2H, NH), 7.13 (s, 4H, ArH), 7.11 (s, 4H, ArH), 4.54 (s, 4H, OCH_2), 4.19 (d, 4H, J=12.3 Hz, $ArCH_2Ar$), 3.57 (br s, 4H, $CONHCH_2CH_2$), 3.46 (d, 4H, J=12.3 Hz, $ArCH_2Ar$), 3.30 (br s, 4H, $CONHCH_2CH_2$), 1.15 (s, 18H, $C(CH_3)_3$), 1.09 (s, 18H, $C(CH_3)_3$). FABMS m/z: 832 (M^+). Anal. Calcd for $C_{52}H_{69}N_3O_6$: C, 75.06; H, 8.36; N, 5.05. Found: C, 75.29; H, 8.38; N, 5.15. UV (λ_{max}, MeOH): 221, 281, 287 nm.

4.3.4. Compound 1d. White solid, yield: 56%. ^1H NMR (300 MHz, $CDCl_3$, δ in ppm): 8.88 (br s, 2H, OH), 8.33 (br t, 2H, NH), 8.03 (br s, 2H, NH), 7.13 (d, 4H, ArH), 7.11 (s, 4H, ArH), 4.54 (s, 4H, OCH_2), 4.22 (d, 4H, J=12.9 Hz, $ArCH_2Ar$), 3.67 (br s, 4H, $CONHCH_2$), 3.50 (d, 4H, J=12.9 Hz, $ArCH_2Ar$), 3.24 (br m, 8H, $CONHCH_2CH_2NHCH_2$), 1.17 (s, 18H, $C(CH_3)_3$), 1.02 (s, 18H, $C(CH_3)_3$). FABMS m/z: 875 (M^+). Anal. Calcd for $C_{54}H_{74}N_4O_6$: C, 74.11; H, 8.52; N, 6.40. Found: C, 74.34; H, 8.54; N, 6.47. UV (λ_{max}, MeOH): 220, 282, 288 nm.

4.3.5. Compound 1e. White solid, yield: 48%, mp 180 °C. ^1H NMR (300 MHz, $CDCl_3$, δ in ppm): 8.03 (br t, 2H, NH), 7.79 (s, 2H, OH), 7.13 (s, 4H, ArH), 6.67 (s, 4H, ArH), 4.48 (s, 4H, OCH_2), 4.16 (d, 4H, J=13.2 Hz, $ArCH_2Ar$), 3.45 (br s, 4H, NCH_2), 3.39 (d, 4H, J=13.2 Hz, $ArCH_2Ar$), 1.78 (br s, 4H, $NHCH_2CH_2CH_2$), 1.25 (s, 18H, $C(CH_3)_3$), 1.03 (br s, 4H, $NHCH_2CH_2CH_2$), 0.87 (s, 18H, $C(CH_3)_3$). FABMS m/z: 845 (M^+). Anal. Calcd for $C_{54}H_{72}N_2O_6$: C, 76.74; H, 8.59; N, 3.31. Found: C, 76.95; H, 8.57; N, 3.23. UV (λ_{max}, MeOH): 220, 281, 288 nm.

4.3.6. Compound 2a. White solid, yield: 83%, mp 352 °C. ^1H NMR (300 MHz, $CDCl_3$, δ in ppm): 8.43 (br s, 2H, NH), 8.26 (s, 2H, OH), 7.03 (d, 4H, J=7.5 Hz, ArH), 6.96 (d, 4H, J=7.5 Hz, ArH), 6.82 (t, 2H, J=7.5 Hz, ArH), 6.68 (t, 2H, J=7.5 Hz, ArH), 4.49 (s, 4H, OCH_2), 4.10 (d, 4H, J=13.2 Hz, $ArCH_2Ar$), 3.63 (br s, 4H, NCH_2), 3.46 (d, 4H, J=13.2 Hz, $ArCH_2Ar$). FABMS m/z: 565 (M^+). Anal. Calcd for $C_{34}H_{32}N_2O_6$: C, 72.32; H, 5.71; N, 4.96. Found: C, 72.48; H, 5.71; N, 4.86. UV (λ_{max}, MeOH): 218, 276, 283 nm.

4.3.7. Compound 2b. White solid, yield: 82%, mp 260 °C (decomp.). IR (KBr, ν_{max}/cm^{-1}): 3410, 3355, 1683. ^1H NMR (300 MHz, $CDCl_3$, δ in ppm): 7.71 (br t, 2H, NH), 7.15 (s, 2H, OH), 7.14 (d, 4H, J=7.2 Hz, ArH), 6.88 (d, 4H, J=7.2 Hz, ArH), 6.81–6.74 (m, 4H, ArH), 4.51 (s, 4H, OCH_2), 4.18 (d, 4H, J=13.2 Hz, $ArCH_2Ar$), 3.63 (br s, 4H, NCH_2), 3.51 (d, 4H, J=13.2 Hz, $ArCH_2Ar$), 1.77 (br s, 4H, NCH_2CH_2). ^{13}C NMR (75 MHz, $CDCl_3$, δ in ppm): 168.0, 152.2, 150.3, 132.1, 129.5, 129.0, 127.6, 126.3, 120.4 (ArCH, ArC, CONH), 74.9 (OCH_2), 37.6 ($CONHCH_2$), 31.1 ($ArCH_2Ar$), 25.0 ($CONHCH_2CH_2$). FABMS m/z: 593 (M^+). Anal. Calcd for $C_{36}H_{36}N_2O_6$: C, 72.95; H, 6.12; N, 4.73. Found: C, 72.69; H, 6.13; N, 4.78. UV (λ_{max}, MeOH): 218, 276, 282 nm.

4.3.8. Compound 2c. White solid, yield: 76%, mp 265 °C. IR (KBr, ν_{max}/cm^{-1}): 3405, 3350, 1680. ^1H NMR (300 MHz, DMSO-d_6, δ in ppm): 9.02 (br s, 1H, NH), 8.73 (br t, 2H, CONH), 8.03 (s, 2H, OH), 7.19 (d, 4H, J=7.5 Hz, ArH), 7.06 (d, 4H, J=7.5 Hz, ArH), 6.85 (t, 2H, J=7.5 Hz, ArH), 6.66 (t, 2H, J=7.5 Hz, ArH), 4.53 (s, 4H, OCH_2), 4.22 (d, 4H, J=12.9 Hz, $ArCH_2Ar$), 3.67 (br s, 4H, $CONHCH_2$), 3.50 (d, 4H, J=12.9 Hz, $ArCH_2Ar$), 3.30 (br s, 4H, $CONHCH_2CH_2$). ^{13}C NMR (75 MHz, DMSO-d_6, δ in ppm): 170.6, 152.3, 134.0, 129.7, 129.3, 127.9, 126.4, 120.3 (ArCH, ArC, CONH), 74.4 (OCH_2), 47.3, 36.2, 30.9 ($CONHCH_2CH_2$, $ArCH_2Ar$). FABMS m/z: 608 (M^+). Anal. Calcd for $C_{36}H_{37}N_3O_6$: C, 75.15; H, 6.14; N, 6.91. Found: C, 75.32; H, 6.12; N, 6.97. UV (λ_{max}, MeOH): 210, 276, 282 nm.

4.3.9. Compound 2d. White solid, yield: 51%, mp 210 °C. ^1H NMR (300 MHz, $CDCl_3$, δ in ppm): 9.05 (br s, 2H, NH), 8.54 (br t, 2H, CONH), 8.10 (s, 2H, OH), 7.15 (d, 4H, J=7.5 Hz, ArH), 6.86 (t, 2H, J=7.5 Hz, ArH), 6.76 (d, 4H, J=7.5 Hz, ArH), 6.62 (t, 2H, J=7.5 Hz, ArH), 4.58 (s, 4H, OCH_2), 4.32 (d, 4H, J=12.9 Hz, $ArCH_2Ar$), 3.69 (br s, 4H, $CONHCH_2$), 3.51 (d, 4H, J=12.9 Hz, $ArCH_2Ar$), 3.24 (br s, 8H, $CONHCH_2CH_2NHCH_2$). FABMS m/z: 651(M^+). Anal. Calcd for $C_{38}H_{42}N_4O_6$: C, 70.13; H, 6.51; N, 8.61. Found: C, 70.30; H, 6.53; N, 8.65. UV (λ_{max}, MeOH): 216, 276, 283 nm.

4.3.10. Compound 2e. White solid, yield: 26%, mp 290 °C. ^1H NMR (300 MHz, $CDCl_3$, δ in ppm): 8.73 (br s, 2H, NH), 8.01 (s, 2H, OH), 7.01 (d, 4H, J=7.2 Hz, ArH), 6.88 (d, 4H, J=7.2 Hz, ArH), 6.76 (t, 2H, J=7.2 Hz, ArH), 6.66 (t, 2H, J=7.2 Hz, ArH), 4.51 (s, 4H, OCH_2), 4.07 (d, 4H, J=13.2 Hz, $ArCH_2Ar$), 3.44 (br s, 4H, NCH_2), 3.40 (d, 4H, J=13.2 Hz, $ArCH_2Ar$), 1.70 (br s, 8H, $NHCH_2CH_2CH_2$). FABMS m/z: 621 (M^+). Anal. Calcd for $C_{38}H_{40}N_2O_6$: C, 73.53; H, 6.50; N, 4.51. Found: C, 73.79; H, 6.51; N, 4.57. UV (λ_{max}, MeOH): 218, 277, 284 nm.

4.4. General procedure for the synthesis of nitro substituted calix[4]arene(amide)mono-crown analogs

4.4.1. Route-A. To a solution of corresponding calix[4]-arene(amide)mono-crown (**2a**, **2b**, **2d**, and **2e**) in a mixture of dichloromethane and glacial acetic acid was added 100% HNO_3 at 0 °C. The reaction mixture was stirred at room temperature for 5–10 min after which it was poured into water. The water layer was extracted with dichloromethane, the organic layer was washed with water, and then evaporated. Recrystallization of the residue from chloroform/methanol produced sufficiently pure compounds for characterization through spectroscopy.

4.4.2. Route-B. Dinitro diester derivative (**3**) and diamine (20–30 equiv) in toluene:ethanol (1:1 ratio) were refluxed for 24 h. The solvent was removed under reduced pressure to yield a yellowish solid, which was dissolved in chloroform or ethyl acetate and washed with 1 N H_2SO_4 followed by washing with water. The organic layer was collected and evaporated to dryness under reduced pressure to yield nitro substituted calix[4]arene(amido)mono-crown derivatives as yellowish solids.

4.4.2.1. Compound 3a. Yellow solid, yield: 78%, mp>220 °C (decomp.). IR (KBr, ν_{max}/cm^{-1}): 3376, 1687, 1520, 1442, 1338. ^1H NMR (300 MHz, $CDCl_3$, δ in ppm): 9.41 (s, 2H, O*H*), 8.27 (s, 4H, Ar*H*), 8.14 (br s, 2H, N*H*), 7.28 (d, 4H, *J*=5.7 Hz, Ar*H*), 6.97 (t, 2H, *J*=5.7 Hz, Ar*H*), 4.57 (s, 4H, OCH_2), 4.26 (d, 4H, *J*=12.9 Hz, ArCH_2Ar), 3.82 (d, 4H, *J*=12.9 Hz, ArCH_2Ar), 3.51 (br s, 4H, NCH_2). FABMS *m/z*: 655 (M^+). Anal. Calcd for $C_{34}H_{30}N_4O_{10}$: C, 62.38; H, 4.62; N, 8.56. Found: C, 62.54; H, 4.60; N, 8.59.

4.4.2.2. Compound 3b. Yellow solid, yield: 80%, mp>220 °C (decomp.). IR (KBr, ν_{max}/cm^{-1}): 3410, 3355, 1683. ^1H NMR (300 MHz, $CDCl_3$, δ in ppm): 8.17 (s, 2H, O*H*), 8.11 (s, 4H, Ar*H*), 7.31 (br s, 2H, N*H*), 6.99 (d, 2H, *J*=7.2 Hz, Ar*H*), 6.92 (t, 2H, *J*=7.2 Hz, Ar*H*), 4.65 (s, 4H, OCH_2), 4.22 (d, 4H, *J*=13.2 Hz, ArCH_2Ar), 3.66 (br s, 4H, NCH_2), 3.62 (d, 4H, *J*=13.2 Hz, ArCH_2Ar), 1.77 (br s, 4H, NCH$_2$CH_2). FABMS *m/z*: 683 (M^+). Anal. Calcd for $C_{36}H_{34}N_4O_{10}$: C, 63.34; H, 5.02; N, 8.21. Found: C, 63.61; H, 5.00; N, 8.25.

4.4.2.3. Compound 3c. Yellow solid, yield: 77%, mp>220 °C (decomp.). IR (KBr, ν_{max}/cm^{-1}): 3394, 1655, 1592, 1464, 1263. ^1H NMR (300 MHz, DMSO-d_6, δ in ppm): 8.31 (D_2O exchangeable, br s, 2H, O*H*), 8.24 (br s, 4H, ArH_{nitro}), 7.80 (D_2O exchangeable, br t, 2H, N*H*), 7.17 (br d, 4H, Ar*H*), 6.90 (br t, 2H, Ar*H*), 4.47–2.91 (br m, 21H, CH_2, N*H*). FABMS *m/z*: 698 (M^+). Anal. Calcd for $C_{36}H_{35}N_5O_{10}$: C, 61.97; H, 5.06; N, 10.04. Found: C, 62.02; H, 5.05; N, 10.08.

4.4.2.4. Compound 3d. Yellow solid, yield: 58%, mp>220 °C (decomp.). IR (KBr, ν_{max}/cm^{-1}): 3390, 1659, 1547, 1464, 1259. ^1H NMR (300 MHz, DMSO-d_6, δ in ppm): 8.38 (D_2O exchangeable, br s, 2H, O*H*), 8.26 (br s, 4H, ArH_{nitro}), 7.82 (D_2O exchangeable, br t, 2H, N*H*), 7.17 (br d, 4H, Ar*H*), 6.95 (br t, 2H, Ar*H*), 4.50–2.82 (br m, 26H, CH_2, N*H*). DEPT-135 NMR (75 MHz, DMSO-d_6, δ in ppm): 129.5, 125.4, 124.4 (Ar*C*H), 73.1 (O*C*H_2), 46.4, 42.3, 35.3, 30.9 (NH*C*H_2, Ar*C*H_2Ar). FABMS *m/z*: 741 (M^+). Anal. Calcd for $C_{38}H_{40}N_6O_{10}$: C, 61.61; H, 5.44; N, 11.35. Found: C, 61.81; H, 5.46; N, 11.40.

4.5. General procedure for the synthesis of (pyridylazo)calix[4]arene(amido)mono-crown derivatives

The pyridyl diazonium chloride solutions were prepared by the addition of an aqueous solution of sodium nitrite (1.5 equiv of amine) into a solution of 3-aminopyridine (3 equiv of calix[4]arene(amido)mono-crown) in concd HCl (10–20 equiv) and distilled water (5–10 ml) at 0–5 °C. The diazotized 3-aminopyridine solution was slowly added into an ice-cold (0–5 °C) solution of calix[4]arene(amido)-mono-crown in dimethylformamide/methanol (8:5) and sodium acetate (pH 7–9) with constant stirring to give a dark red suspension. The reaction mixture was stirred for 3 h at 0–5 °C and then for 30 min at room temperature. The suspension was poured into water, acidified with concd HCl to give a yellow to dark red precipitate, which was filtered to give a mixture of products. The mixture was then separated by column chromatography (silica gel) to give substituted (pyridylazo)calix[4]arene(amido)mono-crown derivatives.

4.5.1. Compound 4a. This was separated by column chromatography of the crude mixture by using chloroform/methanol (9.9:0.1) as the eluant as a yellowish solid, yield: 28%, mp>240 °C (decomp.). ^1H NMR (300 MHz, $CDCl_3$, δ in ppm): 9.08 (s, 1H, Py*H*), 8.88 (s, 1H, O*H*), 8.58 (d, 1H, *J*=7.5 Hz, Py*H*), 8.37 (br s, 2H, N*H*), 8.25 (s, 1H, O*H*), 8.02 (d, 1H, *J*=8.1 Hz, Py*H*), 7.72 (s, 2H, Ar*H*), 7.35 (dd, 1H, *J*=4.8 Hz, Py*H*), 7.10–6.63 (m, 9H, Ar*H*), 4.57 (t, 4H, OCH_2), 4.17 (d, 4H, *J*=13.5 Hz, ArCH_2Ar), 4.11 (d, 2H, *J*=13.5 Hz, ArCH_2Ar), 3.63 (br s, 4H, NCH_2), 3.62 (d, 2H, *J*=13.2 Hz, ArCH_2Ar), 3.50 (d, 2H, *J*=13.2 Hz, ArCH_2Ar). FABMS *m/z*: 670 (M^+). Anal. Calcd for $C_{39}H_{35}N_5O_6$: C, 69.94; H, 5.27; N, 10.46. Found: C, 69.78; H, 5.29; N, 10.49. UV (λ_{max}, MeOH): 257, 360 nm.

4.5.2. Compound 4b. This was separated by column chromatography using chloroform/methanol (9.9:0.1) as the eluant as a yellowish solid, yield: 58%, mp>240 °C (decomp.). ^1H NMR (300 MHz, $CDCl_3$, δ in ppm): 9.15 (s, 2H, Py*H*), 8.94 (s, 2H, O*H*), 8.65 (br s, 2H, Py*H*), 8.43 (broad s, 2H, N*H*), 8.10 (d, 2H, *J*=8.1 Hz, Py*H*), 7.81 (s, 2H, Ar*H*), 7.44 (dd, 2H, *J*=4.8 Hz, Py*H*), 7.19 (d, 4H, *J*=7.8 Hz, Ar*H*), 6.99 (t, 2H, *J*=7.5 Hz, Ar*H*), 4.65 (s, 4H, OCH_2), 4.25 (d, 4H, *J*=13.5 Hz, ArCH_2Ar), 3.74 (s, 4H, NCH_2), 3.73 (d, 4H, *J*=13.5 Hz, ArCH_2Ar). FABMS *m/z*: 775 (M^+). Anal. Calcd for $C_{44}H_{38}N_8O_6$: C, 68.21; H, 4.94; N, 14.46. Found: C, 68.01; H, 4.96; N, 14.51. UV (λ_{max}, MeOH): 263, 360 nm.

4.5.3. Compound 5a. This was obtained by column chromatography using chloroform/methanol (9.9:0.1) as the eluant in the form of a yellowish solid, yield: 7%, mp>240 °C (decomp.). ^1H NMR (300 MHz, $CDCl_3$, δ in ppm): 9.14 (s, 1H, Py*H*), 8.88 (s, 1H, OH), 8.58 (d, 1H, *J*=7.5 Hz, Py*H*), 8.37 (br s, 2H, N*H*), 8.25 (s, 1H, O*H*), 8.02 (d, 1H, *J*=8.1 Hz, Py*H*), 7.72 (s, 2H, Ar*H*), 7.35 (dd, 1H, *J*=4.8 Hz, Py*H*), 7.10–6.63 (m, 9H, Ar*H*), 4.51 (s, 4H, OCH_2), 4.18 (d, 4H, *J*=13.2 Hz, ArCH_2Ar), 3.63 (br s, 4H, NCH_2), 3.51 (d,

4H, J=13.2 Hz, ArCH_2Ar), 1.77 (br s, 4H, NCH$_2$CH_2). FABMS m/z: 698 (M^+). Anal. Calcd for $C_{41}H_{39}N_5O_6$: C, 69.94; H, 5.27; N, 10.04. Found: C, 69.78; H, 5.28; N, 9.98.

4.5.4. Compound 5b. This was obtained by column chromatography using chloroform/methanol (9.9:0.1) as the eluant as a yellowish solid, yield: 28%, mp>240 °C (decomp.). ^{1}H NMR (300 MHz, $CDCl_3$, δ in ppm): 9.15 (s, 2H, PyH), 8.94 (s, 2H, OH), 8.65 (br s, 2H, PyH), 8.43 (br s, 2H, NH), 8.10 (d, 2H, J=8.1 Hz, PyH), 7.81 (s, 2H, ArH), 7.44 (dd, 2H, J=4.8 Hz, PyH), 7.19 (d, 4H, J=7.8 Hz, ArH), 6.99 (t, 2H, J=7.5 Hz, ArH), 4.51 (s, 4H, OCH_2), 4.18 (d, 4H, J=13.2 Hz, ArCH_2Ar), 3.63 (br s, 4H, NCH_2), 3.51 (d, 4H, J=13.2 Hz, ArCH_2Ar), 1.77 (br s, 4H, NCH$_2$CH_2). FABMS m/z: 803 (M^+). Anal. Calcd for $C_{46}H_{42}N_8O_6$: C, 68.81; H, 5.27; N, 13.96. Found: 68.72; H, 5.29; N, 13.76.

4.5.5. Compound 6a. This was purified by column chromatography using chloroform/methanol (9.9:0.1) as the eluant as a red solid, yield: 27%, mp>240 °C (decomp.). ^{1}H NMR (300 MHz, DMSO-d_6, δ in ppm): 9.10 (s, 1H, PyH), 8.64 (s, 1H, OH), 8.61 (d, 1H, J=2.7 Hz, PyH), 8.24–8.16 (br m, 4H, OH and NH), 8.05 (d, 1H, J=8.1 Hz, PyH), 7.70 (s, 2H, ArH), 7.38 (dd, 1H, J=4.5 Hz, PyH), 7.07–6.71 (m, 9H, ArH), 4.48 (dd, 4H, J=5.1 Hz, OCH_2), 4.11 (d, 4H, J=13.2 Hz, ArCH_2Ar), 3.91–3.31 (br m, 8H, CONHCH_2CH_2), 3.54 (d, 2H, J=13.5 Hz, ArCH_2Ar), 3.43 (d, 2H, J=13.5 Hz, ArCH_2Ar). FABMS m/z: 713 (M^+). Anal. Calcd for $C_{41}H_{40}N_6O_6$: C, 69.09; H, 5.66; N, 11.79. Found C, 68.90; H, 5.64; N, 11.76. UV (λ_{max}, MeOH): 273, 361 nm.

4.5.6. Compound 6b. This was separated by column chromatography using chloroform/methanol (9.8:0.2) as the eluant as a red solid, yield: 51%, mp>240 °C (decomp.). ^{1}H NMR (300 MHz, DMSO-d_6, δ in ppm): 9.17 (s, 2H, PyH), 8.73 (s, 2H, OH), 8.68 (d, 2H, J=3.3 Hz, PyH), 8.28–8.16 (br m, 3H, NH), 8.13 (d, 2H, J=8.4 Hz, PyH), 7.77 (s, 4H, ArH), 7.46 (dd, 2H, J=5.1 Hz, PyH), 6.97 (d, 4H, J=8.4 Hz, PyH), 6.83 (t, 2H, J=8.4 Hz, PyH), 4.57 (s, 4H, OCH_2), 4.18–3.82 (br m, 12H, ArCH_2Ar and CONHCH_2CH_2), 3.56 (d, 4H, J=13.8 Hz, ArCH_2Ar). FABMS m/z: 818 (M^+). Anal. Calcd for $C_{46}H_{43}N_9O_6$: C, 67.55; H, 5.30; N, 15.41. Found C, 67.42; H, 5.28; N, 15.37. UV (λ_{max}, MeOH): 269, 365 nm.

4.6. X-ray structure determination of 2a

The crystals of **2a** were obtained when the compound was crystallized from $CHCl_3$/CH_3OH (9:1). X-ray crystal data for **2a**—$C_{34}H_{32}N_2O_6\cdot CCl_3$, M=682.98, triclinic, a=10.170(11) Å, b=12.208(13) Å, c=14.442(16) Å, α=112.667(19)°, β=95.41(2)°, γ=90.08(2)°, V=1646(3) Å^3, Z=2, Dc=1.378 gcm^{-3}, μ (Mo Kα)=0.327 mm^{-1}, GOF = 1.065, space group = P-1. Intensity data were collected up to θ=40° by using 2θ scanning mode with graphite filtered Mo Kα radiation (λ=0.71073) on a 0.219×0.168×0.098 mm^3 crystal at 298 K. A total of 8897 reflections were measured, 3075 were independent and of which 1463 [I>2(I)] were observed. The structure was solved by direct methods and refined by full matrix least-square techniques on F^2 using SHELXTL. All the nonhydrogen atoms were refined anisotropically. The solvent molecule present in exocyclic fashion was highly disordered. C–H hydrogen atoms were placed in geometrically calculated positions by using a riding model. SADABS was applied for absorption correction. Final R indices [I>2σ(I)]R1=0.0987, wR2=0.2044, and R indices (all data) R1=0.1600, wR2=0.2435 was found for 3075 observed reflections, 0 restraints, and 444 parameters. The apparently high value for R factor probably originates from the disorder due to the solvent. Torsion angles and H-bonding were calculated by using PARST. Crystal data have been deposited at the Cambridge Crystallographic Data Center, under reference CCDC 281639.

4.7. General procedures for UV–visible experiments

All the UV–visible experiments were carried out in methanol unless otherwise specified. Any shifts in the UV–visible spectra of the synthesized compound were recorded on addition of metal salt (100 equiv) solutions. Carbonates-(Li^+, Na^+, K^+, Rb^+, Cs^+, Ag^+), Chlorides-(Mg^{2+}, Ca^{2+}, Ba^{2+}, Cr^{3+}, Fe^{2+}, Cd^{2+}, Pb^{2+}, Hg^{2+}, Pd^{2+}, and Pt^{2+}), acetate (Co^{2+}, Ni^{2+}, Cu^{2+}), and nitrate (Hg^+) salts were used for the UV–visible experiments.

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Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2006.07.047.

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