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ORIGINAL ARTICLE

Synthesis and evaluation of deep cavity imidazolyl calix[*n*]arenes

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Abstract A series of deep cavity diphenyl imidazolyl calix[*n*]arenes (4, 6, 8) have been obtained from readily available starting materials through a five step synthetic methodology involving appropriate alkylation of lower rim of preformed calixarene, formylation of the upper rim and subsequent condensation with aryl diketones in the presence of ammonium acetate and glacial acetic acid. Optimized reaction conditions for obtaining the titled derivatives in their cone configuration and their characterization by spectroscopic methods (IR, UV, NMR and FAB mass) have been delineated. The synthesized imidazolyl calixarenes have preliminarily been examined for selective recognition of monovalent metal ions (Li^+, Na^+, K^+, Cs^+, Ag^+).

Keywords Imidazolyl calixarenes · Deep cavity · Cone conformation · Formylcalixarenes · Heterocyclic receptors

Introduction

Calix[*n*]arenes ($n = 4$–20) represent an important class of phenolic macrocyclic metacyclophanes [1] which possess an internal cavity carved out of distinct hydrophobic and hydrophilic binding sites. Such sites are usually referred to as the upper and the lower rim of calixarenes. They are prominently amenable to chemical modification to provide useful molecular receptors with tunable selectivity and specificity [2–7]. Though considerable efforts have been made in recent years to elaborate the lower rim of calix[n]arenes to achieve ionic and molecular recognition [2], studies related to the formation of deep and wide cavity calixarenes [3] through expansion of the upper rim of calixarenes have been limited [4]. Since the imidazole ring system can accept or donate a proton and can complex with metal ions to function as enzyme mimics on attachment to an aromatic or aliphatic template [5], we decided to synthesize calix[*n*]arenes with an imidazole skeleton appended to their upper rim for evaluation of their utility in metal ion recognition, extraction or modification of reactivity.

Recently, several calixarene receptors with imidazolyl appendages have been reported and explored as metalloenzymes. For example, Dopsil et al. [8] have reported the synthesis and characterization of imidazole substituted calix[4]arene as simple enzyme-mimics for acyltransferase activity. Likewise, Najah Cheriaa and coworkers [9] have described the synthesis of imidazolyl acetamido *p-tert*-butylcalix[4]arenes by reaction of the corresponding methyl ester derivatives with histamine. Very recently, *n*-butyl and isopropyl substituted bis(imidazolyl)calixarenes and dicationic bis(imidazolium) salts bonded to the upper rim of the calixarene structure have been published as receptors of anions [10].

Literature survey indicates that in most previously reported imidazolyl calixarenes, the imidazolyl moiety is attached to the calixarene template through a flexible spacer unit with one or more intervening carbon atoms. Such an arrangement affects the conformational mobility/rigidity of the target receptor molecule. Though

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advantageous in certain cases, the spacer unit induced change in specific calixarene conformation does not allow conformational immobilization required for realization of innovative sensor/separation devices.

In our present work direct introduction of an imidazole moiety at the para position of the calixarene framework has been used to obtain a series of cone configured *p*-imidazolyl calix[*n*]arenes ($n = 4$, 6, 8) by a five step synthetic methodology. The synthesized imidazolyl calixarenes have been identified by UV, Mass and NMR spectroscopy. The derivatives with suitable solubility characteristics were evaluated for metal ion extraction by using the widely referred picrate extraction protocol established by Cram and coworkers.

Results and discussion

The protocol adopted for the synthesis of *p*-imidazolylcalix[*n*]arenes (**7a–g**, **8a**,**b**) was similar to the one adopted for the synthesis of lophine through modified Radziszewski's reaction [11, 12]. The utilized reaction sequence involved the synthesis of *p-tert*-butylcalixarenes, their debutylation, alkylation at the lower rim of calixarenes, formylation at the upper rim and subsequent condensation of obtained formylated calixarenes with aryl diketones in the presence of ammonium acetate and glacial acetic acid as depicted in Scheme 1.

For example, compounds **7a–g** and **8a**,**b** were prepared from corresponding *p*-formylcalix[*n*]arenes (**5a–g** and **6a**,**b**). The synthesized calixarene derivatives were condensed with benzil and ammonium acetate in acetic acid (Scheme 1) as given in the experimental section. In a typical experiment, a mixture of *p*-formyl calixarene, benzil and ammonium acetate was dissolved in acetic acid and the resultant solution was refluxed for 3 h. The reaction mixture was poured into ice-cold water to obtain a thick curdy precipitate which was filtered and washed with methanol to remove unreacted benzil. The product formed was purified by crystallization from chloroform–methanol (1:1) to obtain *p*-imidazolyl calix[*n*]arenes **7a–g**, **8a**,**b** in almost quantitative yield. The resultant compounds (**7a–g**, **8a**,**b**) gave the expected IR and ^{1}H-NMR spectral patterns. For example, the IR spectrum of **7b** showed peaks at 3300 (N–H) and 1595(C = N) cm^{-1} while its ^{1}H-NMR and ^{13}C-NMR spectra were consistent with the cone conformation. The observed doublets at δ 4.46 and δ 3.36 (Fig. S1, Supplementary information) indicate the existence of **7b** in cone conformation in consonance with the previous observations [13]. The ^{13}C-NMR spectrum of **7b** showed fourteen signals (Fig. S2), in accordance with the cone conformation of **7b**. The HETCOR ^{1}H-^{13}C NMR spectrum (Fig. 1a) was also used for further assignment. The quaternary carbons at C_6, C_7, C_9, C_{10}, C_{11} and C_{12} could be easily discerned in the NOESY spectrum (Fig. 1b) of tetra(diphenylimidazolyl) tetrakisethoxyethyl calix[4]-arene. Based on the off-diagonal cross peaks between different signals, the following NOE correlations could be established:

(i) Cross peaks A and B indicated that the aromatic protons of calixarene (H_a) interact with both the methylene protons (H_{exo} and H_{endo}) through space. Since the intensity of peak cross-A was more than that of B, it could be inferred that H_{exo} is closer to the aromatic protons than H_{endo}.

(ii) Signal (C), (D), (E) and (F) showed that both the methylene bridged protons interact with the protons of the ethoxy ethyl ether group at the lower rim. Since the intensity of (C) > (D) and (E) > (F), it can be inferred that –OC$\underline{H}_2$ is closer to the methylene protons than –C$\underline{H}_2$O$^-$. No cross peak was found between –OCH$_2$CH$_3$ protons and the methylene protons. It showed that the ethoxyethyl groups are arranged in a diverging fashion, i.e., moving away from the central calixarene framework.

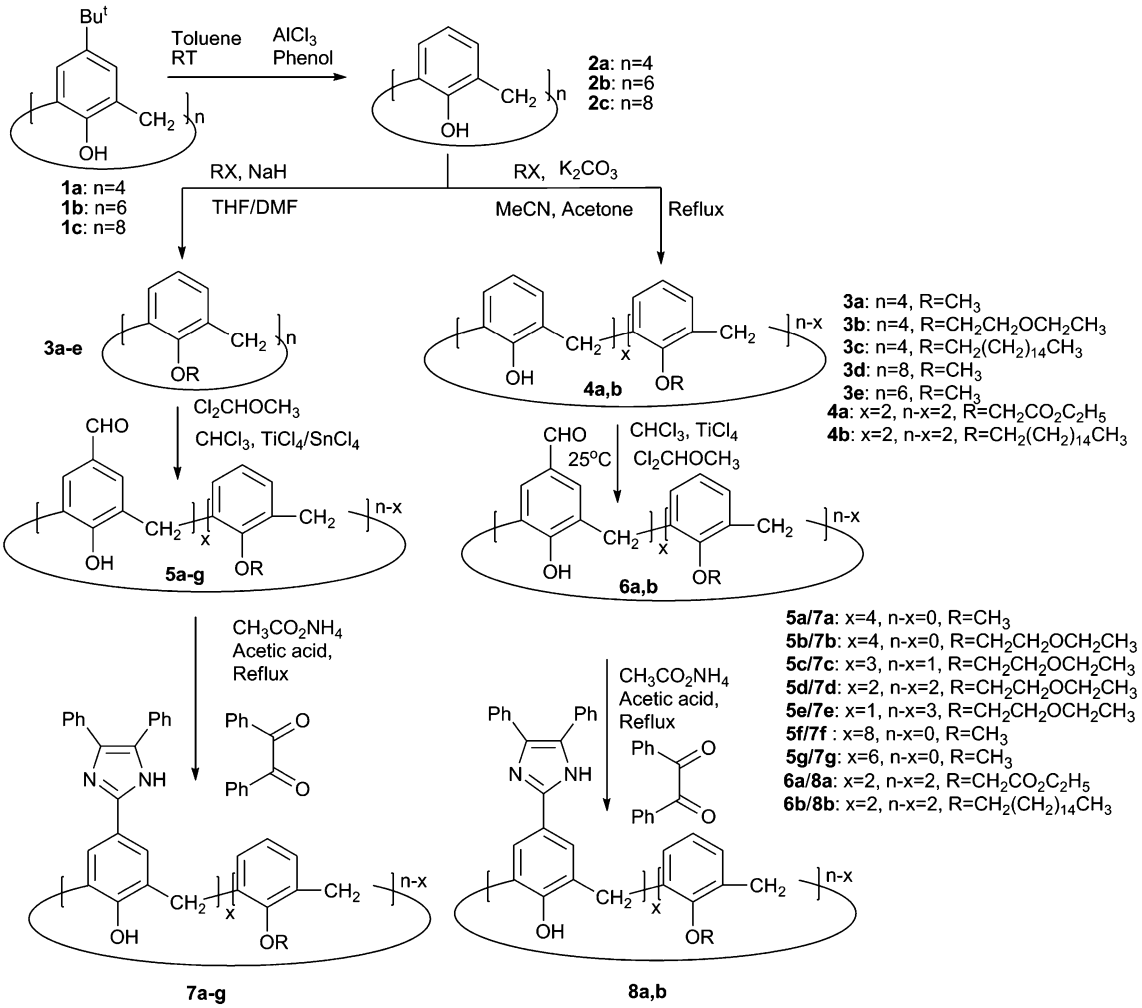
(iii) Since the intensity of signals (C) and (D) was greater than that for signals (E) and (F), it can be stipulated that the H_{endo} was more proximal to the –CH$_2$CH$_2$OCH$_2$CH$_3$ group as compared to H_{exo}.

While **7b–e** and **8a–b** existed in a cone conformation, **7a** (R = –CH$_3$) was found to have a partial cone conformation. The singlet observed at δ 4.08 for the ArCH$_2$Ar protons in the ^{1}H-NMR spectrum of *p*-imidazolyl calix[8]arene **7f** (Fig. 2) showed that it is still a very flexible molecule and conformational interconversion in this case is so fast, that it gave averaged out signals for the protons in the molecule. Effect of solvent on the NMR spectra of **7f** could be readily observed when addition of a few drops of CD$_3$OD to the CDCl$_3$ solution of the compound made the signals much sharper (Fig. 2).

All the imidazolyl calixarenes synthesized were determined to have high melting points (>250 °C). They were found to be less soluble in chloroform than DMSO. The solubility in chloroform was found to increase on addition of methanol, but when used in excess, it led to precipitation of imidazolyl calixarenes from solution. The synthesized imidazolyl calixarenes were soluble in pyridine as well as acetic acid.

Preliminary evaluation of binding characteristics of synthesized imidazolyl calixarenes (7a, 7g) with those of corresponding debutylated calixarenes (3a, 3e)

For example, *p*-(4,5-diphenyllimidazol-2-yl)calix[*n*]arenes (**7a**, **7g**) and debutylated methoxy calixarenes (**3a**, **3e**) were



Scheme 1 Synthetic pathways of *p*-imidazolyl calix[*n*]arenes **7a–f** and **8a**,**b**

examined through extraction of metal ion picrates. It was determined that imidazolyl calix[*n*]arenes are better extractants of metal ion picrates compared with those of methoxy calixarenes **3a**, and **3e** by using the procedure described by Cram et al. [14], and **7a** showed pronounced extraction capability (94%) for silver picrate while **7g** showed a moderate (53%) silver extractability in comparison to other metal cation (Li^+, K^+, Cs^+, Ca^{2+} and Ba^{2+}) picrates which showed weak extractability (<15%). Though studies on the interaction of **7a** with other metal ion picrates commonly associated with silver ion in the photographic and other silver containing wastes is in progress, it is important to report that **7a** is an excellent extractant for silver. Semi quantification of metal ion extraction was carried out by calculation of association constants as presented in Table 1.

Detailed analysis of complexation properties of other *p*-imidazolyl calixarenes and other metal ions and their conformational analysis are in progress and will be reported in due course.

Table 1 Association constants for the extraction of metal picrates Li^+, Na^+, K^+, Cs^+, Ag^+ by **3a**, **3e**, **7a** and **7g**

	Association constants Ka (10^{-3}) mol^{-1} L				
	Li^+	Na^+	K^+	Cs^+	Ag+
3a	15	13.2	3.5	1.65	5.23
3e	12	19	5.98	3.38	5.12
7a	9.36	14.13	13.28	11.95	54.8
7g	15	18	23	6.59	43.6

Experimental

All the starting materials were purchased from Merck and Sigma–Aldrich and were used without further purifications. The solvents used were purified and dried before use by recommended procedures ["Purifications of Laboratory Chemicals" by W.L.F. Armarego and D. D. Perrin, Bath Press, Bath, Britain].

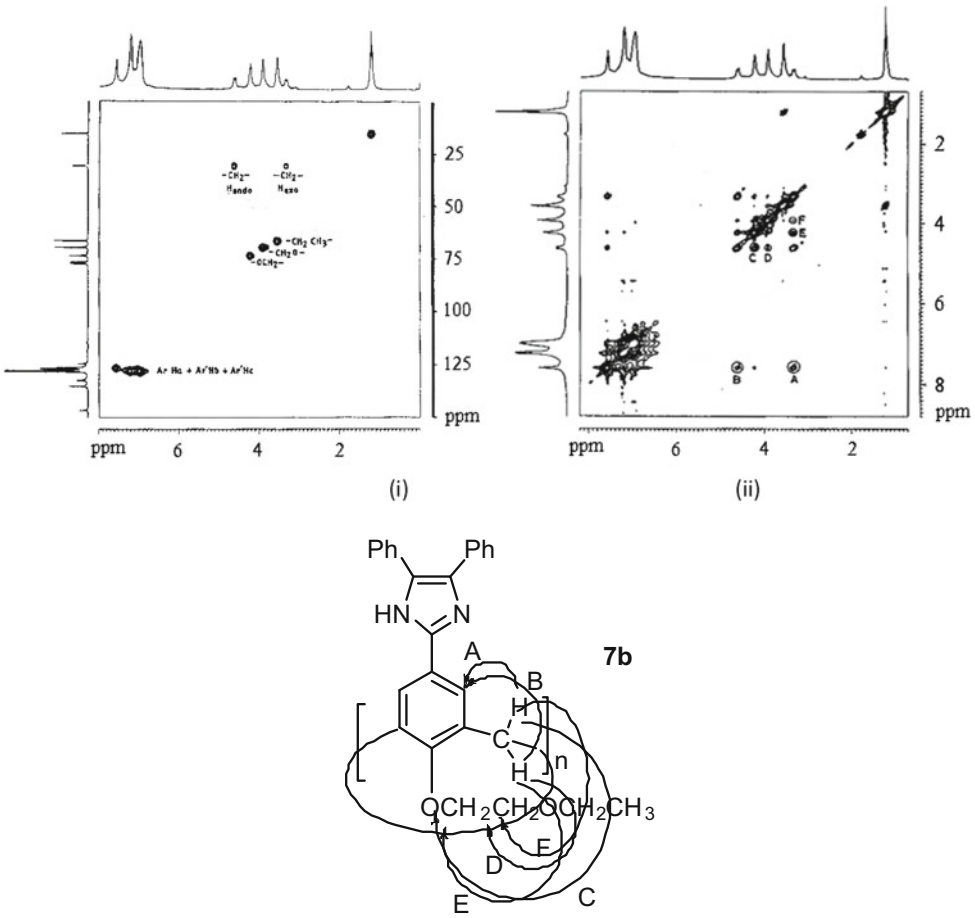


Fig. 1 (**a**) ^{13}C–^{1}H HETCOR Spectrum of 5,11,17, 23-tetrakis(4′,5′-diphenyl imidazolyl) 25,26,27, 28-tetrakis(2-ethoxyethoxy) calix[4]arene, **7b** in $CDCl_3$ at 25 °C. (**b**) ^{1}H–^{1}H NOESY spectrum of 5,11,17, 23-tetrakis(4′,5′-diphenyl imidazolyl) 25,26,27,28-tetrakis (2-ethoxyethoxy) calix[4]arene,**7b** in $CDCl_3$ at 25 °C

The melting points reported in this paper are uncorrected and were taken on an electric melting point apparatus (Toshniwal, India). UV spectra were recorded on Hitachi 330 and Perkin Elmer's (Lambda-3B) spectrophotometers. IR spectra were recorded in KBr discs on a [5-DX] Nicolet FT-IR and Nicolet protégé 460 ESP spectrophotometers using TMS as internal standard and values reported are on δ scale. FAB-Mass spectra of some of the synthesized compounds were recorded on a Jeol SX 103/DA-6000 mass spectrophotometer at CSRI Lucknow. Elemental analysis has been carried out on a Perkin Elmer's 240C-CHN Analyzer.

Synthesis of p-tert-butylcalix[*n*]arene **1a**,**b** and their corresponding debutylated calixarenes **2a**,**b**

p-tert-Butylcalix[4]arene **1a** and *p-tert*-butylcalix[8]arene **1c** were synthesized by the condensation of *p-tert*-butylphenol with formaldehyde or paraformaldehyde in the presence of sodium hydroxide according to the procedure reported by Gutsche et al. [15]. *p-tert*-Butylcalix[6]arene was synthesized by condensation of *p-tert*-butylphenol with formaldehyde or paraformaldehyde in presence of potassium hydroxide according to the procedure reported by Gutsche [16]. The *p-tert*-butylcalix[*n*]arenes were debutylated by reaction with anhydrous aluminum chloride and phenol in toluene to give calixarenes **1a**–**c** [17].

General procedure for the synthesis of alkylated calix[*n*]arenes **3a**–**e**, **4a**–**b**

The next step in the reaction sequence involved the lower rim alkylation of the phenolic –OH groups as per the reported literature [18, 19]. When a strong base like sodium hydride was used in conjunction with a highly polar aprotic solvent like THF/DMF, exhaustive alkylation occurred while use of a weak base like potassium carbonate in conjunction with a solvent like acetonitrile and acetone resulted in partial alkylation of calix[*n*]arenes. Thus tetra-alkylated calix[4]arenes (**3a**–**c**) were obtained from **2a** by using sodium hydride as the base in conjunction with corresponding alkyl halides. Octamethoxycalix[8]arene **3d** was synthesized by refluxing calix[8]arene **2c** with methyl iodide and sodium hydride in THF/DMF while hexamethoxycalix[6]arene **3e** was synthesized using calix[6]arene **2b** and methyl iodide in presence of sodium hydride in THF/DMF. The selective alkylation of calix[4]arene, i.e., the 1,3-dialkylated calix[4]arene **4a** and **4b** were

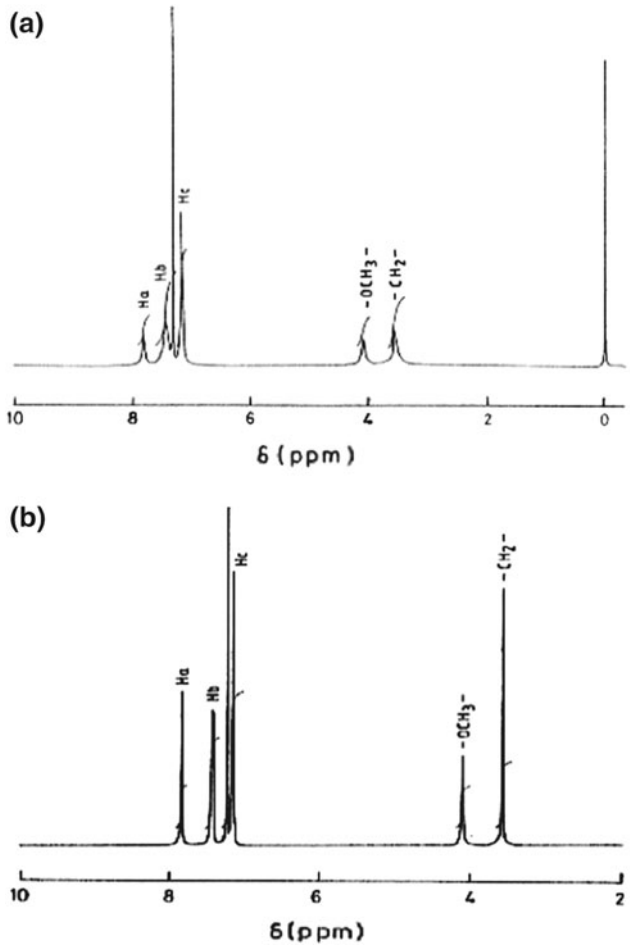


Fig. 2 ^{1}H-NMR spectrum of **7f** in (**a**) $CDCl_3$ (**b**) 2% CD_3OD-$CDCl_3$ at 25 °C

synthesized by refluxing the tetrahydroxycalix[4]arene **2a** with athe corresponding alkyl halide with potassium carbonate in 1:2:1 ratio.

General procedure for the synthesis of formylated calix[*n*]arenes **5a–g**, **6a**,**b**

*Synthesis of 5,11,17,23-tetraformyl-25,26,27,28-tetramethoxycalix[4]arene **5a***

A solution of tetramethoxy calix[4]arene (0.24 g, 0.5 mmol) **3a** in chloroform (10.0 mL) was taken in a 100 mL round bottom flask. A solution of 1,1-dichloromethyl methyl ether (2.03 g, 17.7 mmol) in chloroform (10.0 mL) was added to the reaction mixture with stirring at room temperature followed by addition of a solution of titanium tetrachloride (4.5 g, 23.7 mmol) in $CHCl_3$ (10.0 mL) in one lot and as quickly as possible. The reaction mixture was stirred for a further period of 1 h and then treated with water (~50 mL). The organic layer was separated, washed twice with water and dried (Na_2SO_4) and the solvent evaporated under reduced pressure. The residue was purified by passing through a column of silica gel and eluted with hexane–ethyl acetate (75:25) to yield tetraformyl calix[4]arene **5a** as pale yellow crystals (0.18 g, yield 61%), m.p. 218–220 °C. Anal. calcd. for $C_{36}H_{32}O_8$: C, 72.97; H, 5.40; found: C, 72.86; H, 5.59. MS (m/z) 593 ($M + H^+$). UV ($CHCl_3$) λ_{max}: 269 nm. IR (ν_{max}, KBr): 1692, 1597, 1471, 1428.3, 1385, 1283, 1128 cm^{-1}. ^{1}H-NMR ($CDCl_3$, δ): 9.99, 9.50, 9.63 (2s and 1d, $J = 9.8$ Hz, 4H, C<u>H</u>O) 7.84, 7.71, 7.46, 6.82 (4s, 8H, Ar<u>H</u>), 4.44-2.96 (m, 20H, ArC<u>H</u>$_2$Ar and OC<u>H</u>$_3$),

*Synthesis of 5,11,17,23-tetraformyl-25,26,27,28-tetrakis (2-ethoxyethoxy)calix[4]arene **5b***

A solution of **3b** (0.50 g, 0.7 mmol) in chloroform (12 mL) and a solution of titanium tetrachloride (3.32 g, 17.5 mmol) in chloroform (12 mL) were simultaneously added through dropping funnels to a stirred solution of 1,1-dichloromethyl ether (4.0 g, 35.0 mmol) in chloroform (12 mL) at 40 °C over a period of 10 min. The reaction an mixture was stirred for an additional 20 min and then treated with water (150 mL). The organic layer was separated, washed twice with water and dried (Na_2SO_4) and the solvent evaporated under reduced pressure. The residue was purified by column chromatography (hexane/ethyl acetate 3:7) to give **5b** as a viscous oil (0.26 g, yield 45%); Anal. calcd. for $C_{48}H_{56}O_{12}$: C, 69.90, H, 6.79; found C, 69.48; H, 6.53. MS (*m/e*) 825 ($M + H^+$). IR (ν_{max} KBr): 1691, 1591, 1470, 1384, 1268, 1152, 840 cm^{-1}. ^{1}H-NMR ($CDCl_3$, δ): 9.59 (s, 4H, C<u>H</u>O), 7.16 (s, 8H, Ar<u>H</u>), 4.62 (d, $J = 13.9$ Hz, 4H, ArC<u>H</u>$_2$Ar), 4.20 (t, $J = 4.7$ Hz, 8H, OC<u>H</u>$_2$CH$_2$O), 3.78 (t, $J = 4.7$ Hz, 8H, OCH$_2$C<u>H</u>$_2$O), 3.50 (q, $J = 7.0$ Hz, 8H, OC<u>H</u>$_2$CH$_3$), 3.33 (d, $J = 13.9$ Hz, 4H, ArC<u>H</u>$_2$Ar), 1.17 (t, $J = 7.0$ Hz, 12H, OCH$_2$C<u>H</u>$_3$); ^{13}C-NMR ($CDCl_3$, δ): 191.2, 161.9, 135.7, 131.5, 130.2, 73.9, 69.6, 66.4, 30.8, 15.2.

*Synthesis of 5,11,17-triformyl-25,26,27,28-tetrakis (2-ethoxyethoxy)calix[4]arene **5c***

To a solution of **3b** (0.20 g, 0.28 mmol) and 1,1-dichlorodimethyl ether (1.61 g, 14.0 mmol) in $CHCl_3$ (20 mL) was added titanium tetrachloride (2.12 g, 11.2 mmol) at room temperature. The mixture was stirred for 1.5 h and then water (100 mL) was added to it. The organic layer was separated, washed twice with water and dried (Na_2SO_4) and the solvent was evaporated under reduced pressure. Purification by column chromatography (hexane/ethyl acetate 4:6) gave 0.09 g of **13c** (yield 40%): m.p. 58–60 °C; Anal. calcd. for $C_{47}H_{56}O_{11}$: C, 70.85; H, 7.03; found; C, 71.22; H, 7.09. MS (*m/e*) 797 ($M + H^+$). IR (ν_{max}, KBr): 1693 cm^{-1}; ^{1}H-NMR ($CDCl_3$, δ): 9.56 (s, 2H,

CHO), 9.54 (s, 1H, CHO), 7.16 (s, 4H, ArH), 7.01 (s, 2H, ArH), 6.45 (s, 3H, ArH), 4.56 (d, $J = 13.4$ Hz, 2H, $ArCH_2Ar$), 4.47 (d, $J = 13.4$ Hz, 2H, $ArCH_2Ar$), 4.10–4.23 (m, 6H, OCH_2CH_2O), 4.01 (t, $J = 5.3$ Hz, 2H, OCH_2CH_2O), 3.67–3.79 (m, 8H, OCH_2CH_2O), 3.39–3.49 (m, 8H, OCH_2CH_3), 3.18 and 3.25 (2d, $J = 13.4$ Hz, 4H, $ArCH_2Ar$), 1.07–1.18 (m, 12H, OCH_2CH_3). ^{13}C NMR ($CDCl_3$, δ): 191.4, 191.2, 162.2, 156.0, 136.0, 135.5, 134.0, 131.4, 130.4, 130.1, 130.0, 128.4, 122.7, 74.0, 73.8, 73.4, 69.7, 69.5, 69.3, 66.3, 30.7, 15.1.

Synthesis of 5,17-diformyl-25,26,27,28-tetrakis (2-ethoxyethoxy) calix[4]arene ***5d***

To a solution of **3b** (0.5 g, 0.7 mmol) in chloroform (35 mL) cooled at −10 °C were added 1,1-dichlorodimethylether (1.45 g, 12.6 mmol) and stannic chloride (3.28 g, 12.6 mmol). The reaction mixture was stirred at −10 °C for 30 min and then treated with water (100 ml). The organic layer was washed twice with water and dried over sodium sulphate and the solvent evaporated under reduced pressure. Purification by column chromatography using hexane/ethyl acetate as the eluent 1:1 afforded 0.35 g of **13d** (yield 65%): m.p. 64–66 °C; Anal. calcd. for $C_{46}H_{56}O_{10}$: C, 71.87; H, 7.29; found: C, 71.53; H, 7.54. MS (*m/e*) 769 ($M + H^+$). IR (KBr): 2780, 1695 cm^{-1}. ^{1}H-NMR ($CDCl_3$, δ): 9.48 (s, 2H, CHO), 7.05 (s, 4H, ArH), 6.68–6.76 (m, 6H, ArH), 4.58 (d, $J = 13.7$ Hz, 4H, $ArCH_2Ar$), 4.14 and 4.18 (2t, $J = 5.3$ Hz, 8H, OCH_2CH_2O), 3.81–3.84 (m, 8H, OCH_2CH_2O), 3.51 and 3.54 (2q, $J = 6.9$ Hz, 8H, OCH_2CH_3), 3.26 (d, $J = 13.7$ Hz, 4H, $ArCH_2Ar$), 1.17 and 1.20 (2t, $J = 6.9$ Hz, 12H, OCH_2CH_3). ^{13}C NMR ($CDCl_3$, δ): 191.6, 162.3, 156.0, 136.4, 134.2, 131.2, 130.0, 128.5, 122.8, 73.6, 73.4, 69.7, 69.6, 66.3, 30.7, 15.3.

Synthesis of 5,17-diformyl-25,26,27, 28-tetrakis(hexadecyloxy)calix[4]arene ***5e***

A solution of **3c** (0.72 g, 0.55 mmol) in chloroform (15 ml) and a solution of titanium tetrachloride (3.12 g, 16.4 mmol) in chloroform (15 mL) were simultaneously added through dropping funnels to a stirred solution of 1,1-dichlorodimethylether (3.8, 33.0 mmol) in chloroform (15 mL) at 40 °C over a period of 20 min. The reaction mixture was stirred for an additional 130 min. and then treated with water (150 ml). The organic layer was separated, washed twice with water and dried (Na_2SO_4) and the solvent evaporated under reduced pressure. The residue was purified by column chromatography by using hexane-chloroform 60:30 as the eluent to obtain **13e** as pale yellow solid (0.18 g, 23%); m.p. 52 °C; Anal. calcd. for $C_{94}H_{152}O_6$: C, 81.97; H, 11.04; found: 81.63; H, 11.42. Molecular mass (vapour pressure osmometry): 1352 (Calcd. 1376). IR (ν_{max}, KBr): 2880, 1690, 1595, 1452, 1268, 1132 cm^{-1}. ^{1}H-NMR ($CDCl_3$, δ): 9.41 (s, 2H, CHO), 7.04 (m, 4H, ArH), 6.62–6.58 (m, 6H, ArH), 4.53 (d, $J = 13.1$ Hz, 4H, $ArCH_2Ar$), 4.12–4.08 (m,8H,–CH_2–), 3.48 (d, $J = 13.1$ Hz, 4H, $ArCH_2Ar$), 2.08–1.29 (m, 112H, CH_2–), 0.92(t, $J = 6.8$ Hz, 12H,–CS_3).

Synthesis of 5,11,17,23,29,35,41,47-octaformyl-49,50, 51,52,53,54,55,56-octamethoxy calix[8]arene **5f**

To a solution of **3d** (0.82 g, 0.86 mmol) in dichloromethane (20 mL), a solution of 1,1-dichlorodimethylether (2.54 g, 22.1 mmol) in dichloromethane (15 ml) was added with stirring. Immediately after, a solution of freshly distilled titanium tetrachloride (4.3 g, 22.8 mmol) in dichloromethane (15 mL) was added to the reaction mixture very quickly with vigorous stirring. Reaction temperature was maintained between 38–42 °C by using an oil bath. Stirring was continued for an hour and ice cold water (50 mL) was slowly added to the solution. The reaction mixture was further stirred for fifteen minutes and extracted with dichloromethane. The organic layer was washed twice with water (50 mL × 2) and dried over anhydrous sodium sulphate. The solvent was evaporated under reduced pressure and the residue was purified by passing through a column of silica gel to give a pale yellow solid (0.69 g, 68%), m.p. >250 °C. Anal. calcd. for $C_{72}H_{64}O_{16}$. C, 72.97; H, 5.40; found: C, 72.83; H, 5.33. Molecular Mass (vapour pressure osmometry) 1160 (Calcd. 1184); UV ($CHCl_3$, λ_{max}) 265 nm; IR (ν_{max}, KBr): 1694, 1598, 1472, 1428, 1385, 1283 cm^{-1}; ^{1}H-NMR ($CDCl_3$, δ): 9.67 (s, 8H, CHO), 6.95 (s, 16H, ArH), 4.12 (s, 16H, $ArCH_2Ar$), 3.63 (s, 24H, –OCH_3).

Synthesis of 5,11,17,23,29,35-hexaformyl-37,38, 39,40,41,42-hexamethoxycalix[6]arene ***5g***

To a mixture of 1,1-dichloromethylmethyl ether (2.9 g, 25 mmol) and titanium tetrachloride (6.62 g, 35 mmol) in chloroform (50 mL), a solution of 37,38,39,40,41,42-hexamethoxycalix[6]arene (0.72 g, 11 mmol) **3e** was added at room temperature and the mixture stirred for 8 h. The reaction was quenched by addition of ice cold water (100 mL), the organic phase was separated and evaporated under reduced pressure to give a solid which on recrystallization from chloroform:methanol (3:7) gave compound **5g** (0.64 g, 72%) as pale yellow crystals, m.p. 263 °C. Anal. calcd. for $C_{54}H_{48}O_{12}$: C, 72.97; H, 5.40; found: C, 72.93; H, 5.42. Molecular mass (vapour pressure osmometry) 896 (calcd. 888); IR (ν_{max}, KBr): 2482, 1705, 1496, 1246, 1121, 1060, 785 cm^{-1}. ^{1}H-NMR ($CDCl_3$, δ): 9.81 (s, 6H, CHO), 7.42 (s, 12 H, ArH), 4.11 (s, 12H, $ArCH_2Ar$),

3.64 (s, 18H, $ArCH_2Ar$). ^{13}C-NMR ($CDCl_3$, δ): 190.9, 161.6, 135.2, 134.4, 132.6, 130.7, 129.3, 60.8, 30.3.

Synthesis of 5,17-diformyl-25,27-dihydroxy-26, 28-bis(ethoxycarbonylmethoxy)calix[4]arene ***6a***

A solution of 1,1-dichlorodimethylether (0.63 g, 5.5 mmol) in chloroform (10 mL) was added to a solution of **4a** (0.10 g, 0.17 mmol) in chloroform (4 mL) with stirring at room temperature followed by addition of a solution of titanium tetrachloride (0.87 g, 4.6 mmol) in chloroform (4 mL). The reaction mixture was stirred for a further period of 1 h and then treated with water (50 mL) and dried (Na_2SO_4). The solvent was evaporated under reduced pressure. Purification of the residue (0.2 g) by column chromatography by using hexane/ethyl acetate (7:3) as the eluent gave **6a** as a pale yellow crystalline solid. Yield (0.043 g, 40%); m.p. 203 °C; Anal. calcd. for $C_{38}H_{36}O_{10}$: C, 69.93; H, 5.52; found: C, 69.82; H, 5.61; Molecular mass (vapour pressure osmometry): 638 (calcd. 652). IR (ν_{max}, KBr): 3373, 3013, 1919, 1750, 1675, 1586, 1481, 1310, 1211, 1159, 1085, 773 cm^{-1}. ^{1}H-NMR ($CDCl_3$, δ): 9.78 (s, 2H, C<u>H</u>O), 8.68 (s, 2H, O<u>H</u>), 7.62 (s, 4H, Ar<u>H</u>), 6.97 (d, $J = 7.5$ Hz, 4H, Ar<u>H</u>), 6.82 (t, $J = 7.5$ Hz, 2H, Ar<u>H</u>), 4.72 (s, 4H, $OC\underline{H}_2COO$), 4.46 (d, $J = 13.2$ Hz, 4H, $ArC\underline{H}_2Ar$), 4.36 (q, $J = 7.1$ Hz, 4H, $OC\underline{H}_2CH_3$), 3.51 (d, $J = 13.2$ Hz, 4H, $ArC\underline{H}_2Ar$), 1.36 (t, $J = 7.2$ Hz, 6H, $OCH_2C\underline{H}_3$). ^{13}C NMR ($CDCl_3$, δ): 190.6, 168.5, 159.0, 152.0, 132.1, 130.8, 129.4, 128.5, 128.3, 125.9, 72.3, 61.5, 31.1, 14.0.

Synthesis of 5,17-diformyl-25,27-dihydroxy-26, 28-bis(hexadecyloxy)calix[4]arene ***6b***

A solution of 1,1-dichlorodimethylether (0.63 g, 5.5 mmol) in chloroform (10 mL) was added to a solution of **4b** (0.15 g, 0.17 mmol) in chloroform (4 ml) with stirring at room temperature followed by addition of a solution of titanium tetrachloride (0.88 g, 4.6 mmol) in chloroform (4 mL). The reaction mixture was stirred for a further period of 1 h and then treated with water (50 ml) and dried (Na_2SO_4). The solvent was evaporated under reduced pressure to yield a crude product which was purified by column chromatography using hexane/ethyl acetate (9:1) as the eluent to afford **6b** as a pale yellow powder. Yield (0.11 g, 71%); Anal. calcd. for $C_{62}H_{88}O_6$: C, 80.17; H, 9.48; Found: C, 80.21; H, 9.40; Molecular mass (vapour pressure osmometry): 910 (calcd. 928); IR(ν_{max}, KBr): 2920, 2849, 1684, 1599, 1458, 1312, 1262, 1132, 1077, 1018, 955, 802 cm^{-1}; ^{1}H-NMR ($CDCl_3$, δ): 9.78 (s, 2H, C<u>H</u>O), 9.20 (s, 2H, O<u>H</u>), 7.63 (s, 4H, Ar<u>H</u>), 6.96 (d, $J = 7.5$ Hz, 4H, Ar<u>H</u>), 6.79 (t, $J = 7.5$ Hz, 2H, Ar<u>H</u>), 4.29 (d, $J = 13.1$ Hz, 4H, $ArC\underline{H}_2Ar$), 4.03 (t, $J = 6.4$ Hz, 4H, $OC\underline{H}_2$), 3.49 (d, $J = 13.1$ Hz, 4H, $ArC\underline{H}_2Ar$), 2.07 (quintet, $J = 7.3$ Hz, 4H, $OCH_2C\underline{H}_2CH_2C_{12}H_{24}$–), 1.69 (quintet, $J = 7.5$ Hz, 4H, $OCH_2CH_2C\underline{H}_2C_{12}H_{24}$–), 1.25 (bs, 48H, $OCH_2CH_2CH_2C_{12}\underline{H}_{24}CH_3$), 0.87 (t, $J = 6.8$ Hz, 6H, –$C\underline{H}_3$).

Synthesis of *p*-imidazolyl calixarenes 7a–g, 8a,b

Synthesis of 5,11,17,23-tetrakis (4′,5′-diphenylimidazolyl)-25, 26,27,28-tetramethoxy calix[4]arene **7a**

To a solution of 5,11,17,23-tetraformyl-25,26,27,28-tetrakis methoxy calix[4]arene **5a** (0.4 g, 0.84 mmol) in acetic acid (60 mL), benzil (1.5 g, 7.1 mmol) and ammonium acetate (3.0 g, 37.5 mmol) were added and the resultant mixture was refluxed for 3 h after which it was poured into ice cold water (150 mL). The precipitate obtained was dissolved in chloroform (15 mL) and methanol (75 mL) was added. The off-white precipitate thus obtained which was filtered, washed with methanol (15 mL × 2) and dried and crystallized from chloroform–methanol (1:1) to provide a cream colored compound which was identified as 5,11,17,23-tetra(3,5-diphenyl imidazolyl)-25,26,27,28-tetramethoxy calix[4]arene **7a** (0.8 g, 76%); m.p. > 250 °C, UV (λ_{max}, $CHCl_3$): 298 nm; Anal. calcd. for $C_{92}H_{72}O_4N_8$: C, 81.65; H, 5.32; N, 8.28; found: C, 81.88, H, 5.45; N, 8.78. Molecular mass (vapour pressure osmometry): 1340 (Calcd. 1352); IR (ν_{max}, KBr): 3220, 3042, 1590, 1472, 1373, 1261, 1201, 1115, 989, 757 cm^{-1}; ^{1}H-NMR ($CDCl_3$, δ): 7.13–6.8 (m, 40H, ArH), 7.93–7.27 (m, 8H, ArH), 4.45–3.22 (m, 10H, $ArCH_2Ar$, -OCH_3).

Synthesis of 5,11,17,23-tetra(4′,5′-diphenylimidazolyl)-25, 26,27,28-tetrakis(2-ethoxyethoxy)calix[4]arene **7b**

To a solution of 5,11,17,23-tetraformyl-25,26,27,28-tetrakis(2-ethoxyethoxy) calix[4]arene **5b** (0.13 g, 0.15 mmol) in acetic acid (20 mL), benzil (0.43 g, 0.15 mmol) and ammonium acetate (1.2 g, 15.0 mmol) were added and the resultant solution refluxed for 3 h after which it was poured into ice cold water (100 mL). The precipitate obtained was dissolved in chloroform (15 mL) and methanol (75 mL) was added. The light cream colored precipitate formed was filtered, washed well with methanol (15 mL × 2) and dried and crystallized from water: acetic acid (1:2) to yield white needles of tetrakis(4′,5′-diphenylimidazolyl)-25,26,27,28-tetrakis(2-ethoxyethoxy)calix[4]arene **7b** (0.23 g, 91%); m.p. >250 °C; UV(λ_{max}, $CHCl_3$): 303 nm; Anal. calcd. for $C_{104}H_{96}O_8N_8$: C, 78.78; H, 6.06; N, 7.07; found: C, 78.70; H, 6.11; N, 7.38. MS (*m/e*) 1586 ($M + 2H^+$). IR (ν_{max}, KBr) cm^{-1}: 3300, 3053, 1646, 1603, 1595, 1502, 1479, 1456, 1406, 1247, 1008, 764, 696 cm^{-1}; ^{1}H-NMR ($CDCl_3$, δ): 7.32-7.30 (m, 16H, ArH), 7.15-6.90 (m, 24H, ArH), 7.62 (s, 8H, ArH), 4.46 (d, $J = 13.8$ Hz, 4H, $ArCH_2Ar$),

4.26 (t, $J = 4.9$ Hz, 8H, OCH_2), 3.94 (t, $J = 4.9$ Hz, 8H, CH_8O), 3.60 (q, $J = 4.8$ Hz, 8H, $-CH_2CH_3$), 3.36 (d, $J = 13.8$ Hz, 4H, $ArCH_2Ar$), 1.26 (t, $J = 4.8$ Hz, 12H, $-CH_2CH_3$); ^{13}C NMR ($CDCl_3$, δ): 156.44, 146.57, 135.18, 132.40, 128.16, 127.84, 126.86, 126.47, 124.61, 73.47, 69.52, 66.40, 30.77, 15.30.

Synthesis of 5,11,17-tris(4′,5′-diphenylimidazolyl)-25,26,27,28-tetrakis(2-ethoxyethoxy) calix[4]arene **7c**

To a solution of 5,11,17-triformyl-5,26,27,28-tetrakis(2-ethoxyethoxy)calix[4]arene **5c** (0.2 g, 0.25 mmol) in acetic acid (30 mL), benzil (0.32 g, 1.5 mmol) and ammonium acetate (0.6 g, 7.5 mmol) were added and the resultant solution was refluxed for 3 h. After the work-up as described in the above procedure, a light cream colored solid was obtained and was identified as 5,11,17-tris(4′,5′-diphenylimidazolyl)-25,26,27,28-tetrakis(2-ethoxyethoxy)calix[4]arene **7c** (0.29 g, 85%); m.p. >250 °C; Anal. calcd. for $C_{89}H_{86}O_8N_6$: C, 78.18; H, 6.29; N, 8.19; found: C, 77.98; H, 6.02; N, 8.68. Molecular mass (vapour pressure osmometry): 1360 (calcd. 1366). IR (ν_{max}, KBr); 3302, 3055, 2428, 1645, 1594, 1481, 1453, 1411, 1408, 1104, 765 cm^{-1}; UV(λ_{max}, $CHCl_3$): 301 nm; ^{1}H-NMR ($CDCl_3$, δ): 7.41–6.98 (m, 30H, ArH), 7.72 (s, 6H, ArH), 7.15–6.92 (m, 3H, ArH), 4.68 (d, $J = 13.6$ Hz, 2H, $ArCH_2Ar$), 4.52 (d, $J = 13.6$ Hz, 2H, $ArCH_2Ar$), 4.4–4.21 (m, 6H, $-OCH_2$), 4.16 (t, $J = 5.3$ Hz, 2H, $-CH_2$), 4.02–3.9 (m, 8H, $-CH_2$), 3.28 (d, $J = 13.6$ Hz, 2H, $ArCH_2Ar$) and 3.12(d, $J = 13.6$ Hz, 2H, $ArCH_2Ar$), 1.29–1.17 (m, 12H, $-CH_3$).

Synthesis of 5,17-bis(4′,5′-diphenylimidazolyl)-25,26,27,28-tetrakis(2-ethoxyethoxy) calix[4]arene **7d**

To a solution of 5,11,17-triformyl-5,26,27,28-tetrakis(2-ethoxyethoxy)calix[4]arene **5c** (0.2 g, 0.25 mmol) in acetic acid (30 mL), benzil (0.32 g, 1.5 mmol) and ammonium acetate (0.6 g, 7.5 mmol) were added and the resultant solution was refluxed for 3 h. After the usual work-up as described in the above procedure, a light cream colored solid was obtained and was identified as 5,17-bis(4′,5′-diphenylimidazolyl)-25,26,27,28-tetrakis(2-ethoxyethoxy)-calix[4]arene **7d**. Yield (0.26 g, 87%); m.p. >250 °C. UV (λ_{max}, $CHCl_3$): 298 nm. Anal. calcd. for $C_{74}H_{76}O_8N_4$: C, 77.35; H, 6.62; N, 4.88; found: C, 77.04; H, 6.53; N, 3.99. Molecular mass (vapour pressure osmometry): 1160 (calcd. 1148). IR (ν_{max}, KBr): 3310, 3058, 1650, 1595, 1505, 1481, 1415, 1316, 1242, 1181, 1104, 1009, 868, 764 cm^{-1}; ^{1}H-NMR ($CDCl_3$, δ): 7.25–7.22 (m, 8H, ArH), 7.06–7.04 (m, 12H, ArH), 7.28 (s, 4H, ArH), 6.81–6.77 (m, 6H, ArH), 4.51 (d, $J = 13.6$ Hz, 4H, $ArCH_2Ar$), 4.27 (t, $J = 4.9$ Hz, 4H, $-CH_2$), 4.20 (t, $J = 4.9$ Hz, 4H, $-CH_2-$), 3.63 (q, $J = 4.9$ Hz, 4H, CH_2CH_3), 3.60 (q, 4H, $J = 4.9$ Hz, CH_2CH_3), 3.32 (d, $J = 13.6$ Hz, 4H, $ArCH_2Ar$), 3.98–3.94 (m, 8H, $-CH_2-$), 1.24 (t, $J = 4.9$ Hz, 6H, $-CH_3$), 1.21 (t, $J = 4.9$ Hz, 12H, $-CH_3$).

Synthesis of 5,17-bis(4′,5′-diphenylimidazolyl)-25,26, 27,28-tetrakis(hexadecyloxy)calix[4]arene **7e**

To a solution of **5e** (0.25 g, 0.17 mmol) in acetic acid (30 mL), benzil (0.45 g, 2.1 mmol) and ammonium acetate (1.4 g, 17.5 mmol) were added and the resultant solution was refluxed for 3 h. After the work-up as described earlier, a light cream colored solid was obtained and was identified as 5,17-bis(4′,5′-diphenylimidazolyl)-25,26,27,28-tetrakis (hexadecyloxy) calix[4]arene **7e**. Yield (0.31 g, 83%): UV (λ_{max}, $CHCl_3$): 300 nm. Anal. calcd. for $C_{122}H_{172}O_4N_4$: C, 83.37; H, 9.79; N, 3.19; found: C, 83.20; H, 9.85; N, 2.79. Molecular mass (vapour pressure osmometry): 2206 (calcd. 2192). IR (ν_{max}, KBr): 3305, 3092, 2917, 2850, 1588, 1385, 1261, 1163, 1079, 804, 762 cm^{-1}; ^{1}H-NMR ($CDCl_3$, δ): 7.48–7.45 (m, 8H, ArH), 7.37–7.34 (m, 12H, ArH), 7.78 (s, 4H, ArH), 7.18–7.06 (m, 6H, ArH), 4.30 (d, $J = 13.8$ Hz, 4H, $ArCH_2Ar$), 4.23–4.12 (m, 8H, $-CH_2$), 3.51 (d, $J = 13.8$ Hz, 4H, $ArCH_2Ar$), 2.21–1.31 (m, 128H, $-CH_2$), 1.16 (t, $J = 7.3$ Hz, 12H, $-CH_3$).

Synthesis of 5,11,17,23,29,35,41,47-octakis (4′,5′-diphenylimidazolyl)-49,50,51,52, 53,54,55, 56-octamethoxycalix[8]arene **7f**

To a solution of **5f** (0.2 g, 0.24 mmol) in acetic acid (30 mL), benzil (0.66 g, 3.1 mmol) and ammonium acetate (1.5 g, 19.5 mmol) were added and the resultant solution was refluxed for 3 h. After the work-up as described earlier, a light cream colored solid was obtained and was identified as 5,11,17,23,29,35,41,47-octa(4′,5′-diphenylimidazolyl)-49,50,51,52,53,54,55,56-octamethoxycalix[8]arene **7f**. Yield (0.485 g, 75%). UV (λ_{max}, $CHCl_3$): 299 nm. Anal. calcd. for $C_{184}H_{144}N_{16}O_8$: C, 81.65; H, 5.32; N, 8.28; found: C, 81.55; H, 5.53; N, 7.03; MS-FAB Mass(*m/e*): 1353 ($M/2 + H^+$). IR (ν_{max}, KBr): 3308, 3056, 2929, 1604, 1598, 1503, 1479, 1246, 1116, 1008, 765, 696 cm^{-1}; ^{1}H-NMR ($CDCl_3$, δ): 7.42–7.39 (m, 32H, ArH), 7.14–7.12 (m, 48H, ArH), 7.83 (s, 16H, ArH), 4.08 (s, 16H, $ArCH_2Ar$), 3.55 (s, 24H, OCH_3); ^{13}C NMR ($CDCl_3$, δ): 156.6, 145.5, 136.8, 135.1, 134.1, 131.3, 128.4, 128.37, 127.9, 127.5, 126.9, 126.4, 125.9, 60.3, 30.1.

Synthesis of 5,11,17,23,29,35-hexakis (4′,5′-diphenylimidazolyl)-37,38,39,40, 41,42-hexamethoxycalix[6]arene **7g**

To a solution of **5g** (0.45 g, 0.50 mmol) in acetic acid (50 mL), benzil (1.50 g, 7.15 mmol) and ammonium

acetate (1.2 g, 33 mmol) were added and the resultant solution was refluxed for 4 h. After the work-up as described earlier, a light cream colored solid was obtained and was identified as 5,11,17,23,29,35-hexakis(4′,5′-diphenylimidazolyl)-37,38,39,40,41,42-hexamethoxycalix[6]arene **7g**. Yield (0.690 g, 68%); m.p. >300 °C (decomp.); Anal. calcd. for $C_{138}H_{108}N_{12}O_6$; C, 81.66; H, 5.32; N, 8.28; found C, 81.56; H, 5.38; N, 8.20. Molecular mass (vapour pressure osmometry) 1992 (calcd. 2028). IR (ν_{max}, KBr): 3250, 1638, 1580, 1564, 1496, 1458, 1328, 1272, 1222, 1190, 1027, 884, 765, 723, 702, 646 cm^{-1}; ^{1}H-NMR ($CDCl_3$, δ): 14.25 (brs, 6H, NH), 7.92–7.23 (m, 60H, ArH), 7.14 (s, 12H, ArH), 3.86 (brs, 12H, $ArCH_2Ar$), 3.50 (s, 18H, CH_3).

Synthesis of 5,17-bis(4′,5′-diphenylimidazolyl)-25,27-dihydroxy-26,28-bis(2-ethoxy-carbonylmethoxy)calix[4]arene **8a**

cTo a solution of **6a** (0.12 g, 0.18 mmol) in acetic acid (20 mL), benzil (0.40 g, 1.8 mmol) and ammonium acetate (1.2 g, 15.0 mmol) were added and the resultant solution was refluxed for 3 h. After the work-up as described earlier, a light cream colored solid was obtained and was identified as 5,17-bis(4′,5′-diphenylimidazolyl)-25,27-dihyddroxy-26,28-bis(ethoxy carbonylmethoxy)calix[4]arene **8a**. Yield (0.043 g, 40%); m.p. >250 °C. Anal. calcd. for $C_{66}H_{56}O_8N_4$: C, 76.74; H, 5,42; N, 5.42; found: C, 76.32; H, 5.39; N, 5.84. Molecular mass (vapour pressure osmometry) 1013 (Calcd. 1032). IR (ν_{max}, KBr): 3373, 3310, 3013, 2919, 1750, 1601, 1586, 1481, 1310, 1211, 1159, 1085, 773 cm^{-1}; ^{1}H-NMR ($CDCl_3$, δ): 8.68 (s, 2H, D_2O exch., OH), 7.40 (m, 10H, Ar′H), 7.20–7.18 (m, 10H, ArH), 6.97 (d, $J = 7.5$ Hz, 4H, ArH), 6.82 (t, $J = 7.5$ Hz, 2H, ArH), 4.75 (s, 4H, $-OCH_2$), 4.51 (d, $J = 13.2$ Hz, 4H, $ArCH_2Ar$), 4.38 (q, $J = 7.0$ Hz, 4H, $-OCH_2$), 3.55 (d, $J = 13.2$ Hz, 4H, $ArCH_2Ar$), 1.36 (t, $J = 7.0$ Hz, 6H, OCH_2CH_3).

Synthesis of 5,17-bis(4′,5′-diphenylimidazolyl)-25,27-dihydroxy-26,28-bis(hexadecyloxy)-calix[4]arene **8b**

To a solution of **6b** (0.3 g, 0.34 mmol) in acetic acid (40 mL), benzil (1.0 g, 4.5 mmol) and ammonium acetate (3.5 g, 44.0 mmol) were added and the resultant solution was refluxed for 3 h. After the work-up as described in the earlier procedure, a light cream colored solid was obtained and was identified as 5,17-bis(4′,5′-diphenylimidazolyl)-25,27-dihydroxy-26,28-bis(hexadecyloxy)calix[4]arene, **8b**. Yield (0.35 g, 81%). UV (λ_{max}, $CHCl_3$): 299 nm. Anal. calcd. for $C_{90}H_{108}O_4N_4$: C, 82.56; H, 8.25; N, 4.28; found: C, 82.26; H, 8.51; N, 4.69. Molecular mass (vapour pressure osmometry): 1336 (calcd. 1308); IR (ν_{max}, KBr): 3312, 3018, 2917, 2850, 1586, 1463, 1268, 1079, 805, 764 cm^{-1}; ^{1}H-NMR ($CDCl_3$, δ): 9.2 (s, 2H, D_2O exch., OH), 7.42–7.39 (m, 16H, ArH), 7.23–7.20 (m, 24H, ArH), 7.60 (s, 4H, ArH), 7.08 (d, $J = 7.5$ Hz, 8H, ArH), 6.84 (t, 4H, $J = 7.5$ Hz, ArH), 4.27 (d, $J = 13.3$ Hz, 4H, $ArCH_2Ar$), 3.52 (d, $J = 13.3$ Hz, 4H, $ArCH_2Ar$), 4.12 (t, $J = 6.2$ Hz, 12H, $-OCH_2$), 2.16-1.28 (m, 62H, $-CH_2$), 0.91 (t, $J = 7.2$ Hz, 6H, $-CH_3$).

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