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Calix(n)arene-quinone interactions: Molecular recognition of 2,6-naphthoquinone by 5,11,17,23,29,35-hexa-tert-butyl-37,38,39,40,41,42-hexahydroxycalix(6)arene

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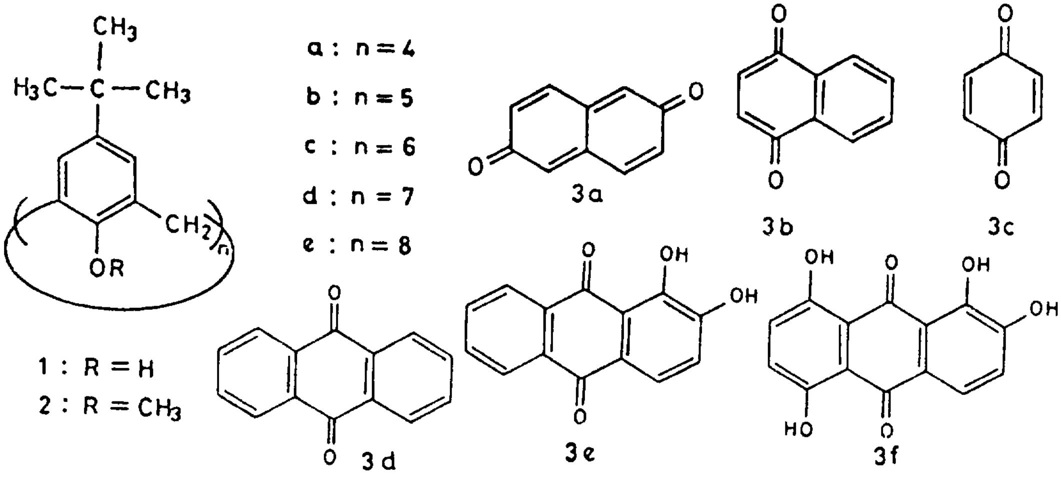
Abstract: UV, IR and NMR spectral analyses reveal that 2,6-naphthoquinone forms a 1:1 host-guest type of complex with 5,11,17,23,29,35-hexa-tert-butyl-37,38,39,40,41,42-hexahydroxycalix(6)arene while 1,4-naphthoquinone does not do so at low concentrations (1 x 10^{-4}M). 1,4-Benzoquinone forms a 2:1 molecular complex with 5,11,17,23-tetra-tert-butyl-25,26,27,28-tetrahydroxycalix(4)arene and 5,11,17,23,29,35-hexa-tert-butyl-37,38,39,40,41,42-hexahydroxycalix(6)arene but no complexation has been observed with 5,11,17,23,29,35,41,47-octa-tert-butyl-49,50,51,52,53,54,55,56-octahydroxycalix(8)arene under similar conditions. 9,10-Anthraquinone, 1,2-dihydroxy-9,10-anthraquinone and 1,2,5,8-tetrahydroxy-9,10-anthraquinone, show no interaction with p-tert-butyl-calix(n)arenes (n = 4, 6, 8). Studies carried out indicate that 2,6-naphthoquinone can be recognised by 5,11,17,23,29,35-hexa-tert-butyl-37,38,39,40,41,42-hexahydroxycalix(6)arene even when present in a mixture of quinones and other related compounds.

Calixarenes are a class of versatile molecular hosts with growing applications in the field of supramolecular chemistry[1,2]. Though lot of work has been reported on the interaction of metal ions with calix(4)arenes[3-11], very few reports are available on the recognition of organic molecules [12-19] with these synthetic receptors in organic solvents. In this paper we report our findings that 2,6-naphthoquinone can be recognised by 5,11,17,23,29,35-hexa-tert-butyl-37,38,39,40,41,42-hexahydroxycalix(6)arene (**1c**) at low concentrations ($5x10^{-4}$ M-$3.72x10^{-3}$ M) through 1:1 host-guest type of complexation in chloroform solutions



a : n = 4
b : n = 5
c : n = 6
d : n = 7
e : n = 8

1 : R = H
2 : R = CH_3

3a
3b
3c
3d
3e
3f

and 1,4-benzoquinone forms a 2:1 complex with 5,11,17,23-tetra-tert-butyl-25,26,27,28-tetrahydroxycalix(4) arene **la** and 5,11,17,23,29,35-hexa-tert-butyl-37,38,39,40,41,42-hexahydroxycalix(6)arene **1c** while 1,4-naphthoquinone **(3b)**, 9,10-anthraquinone **(3d)**, 1,2-dihydroxy-9,10-anthraquinone **(3e)** and 1,2,5,8-tetrahydroxy-9,10-anthraquinone **(3f)** do not interact with calix(n) arenes (n = 4,6,8).

The choice of quinones for the present study stemmed from their structural analogy to many dyes of natural and synthetic origin, and also from the possibility of their recognition through a combination of hydrophobic and H-bond interactions[20] while choice of calixarenes **1** and **2** **(a,c,e)** was based on their ready availability in pure state and in known conformations besides their easily computable molecular dimensions available form X-ray data and CPK models. For instance, molecular dimensions of **1a-1e** could be computed to be in the range of 3x2Å ; 3x6.2Å ; 3x7.6Å, 3x8.6Å and 3x11.7Å from CPK models as against the molecular dimensions 2.44Å and 7.43Å for 2,6-naphthoquinone **(3a)**, 4.88Å and 5.29Å for 1,4-naphthoquinone **(3b)**, 2.32Å and 5.23Å for 1,4-benzoquinone **(3c)**, 5.29Å and 7.36Å for 9,10-anthraquinone **(3d)**, 5.07Å and 7.23Å for 1,2-dihydroxy-9,10-anthraquinone **(3e)** and 4.99Å and 7.15Å for 1,2,5,8-tetrahydroxy-9,10-anthraquinone **(3f)**.

Consequently **1a, 1c, 1e, 2a, 2c, 2e, 3a, 3b, 3c, 3d, 3e, 3f** were synthesized by the procedures described in the experimental section and were used in low concentrations ($1x10^{-3}$ M) as the listed calixarenes were sparingly soluble in organic solvents.

RESULTS AND DISCUSSION

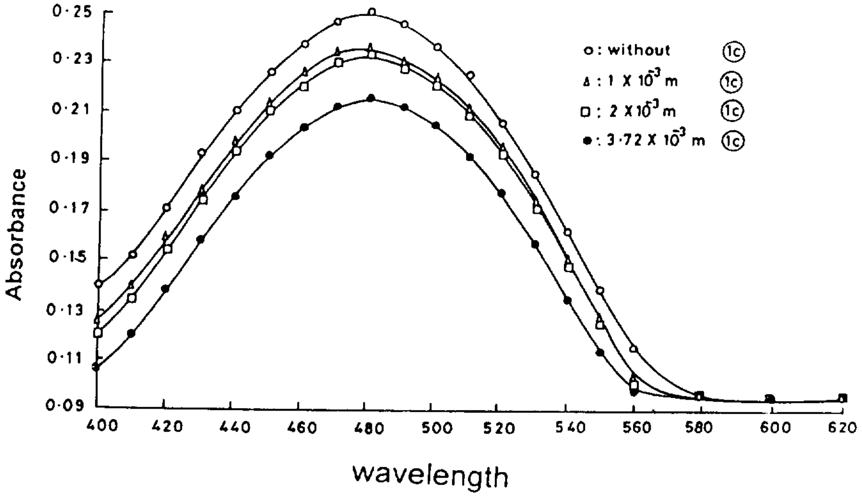


Fig.1: Optical spectra of a $3.72x10^{-3}$M chloroform solution of 2.6-naphthoquinone in the presence of different concentrations of calixarene **(1c)**

UV-visible spectroscopic analysis reveals that 2,6-naphthoquinone **(3a)**, 1,4-naphthoquinone **(3b)** and 1,4-benzoquinone **(3c)** absorb at 480nm, 335 nm and 435 nm respectively while **1** and **2** **(a,c,e)** do not absorb at these wavelengths. When $5x10^{-4}$ M solution of **1c** was added to a solution of 2,6-naphthoquinone ($3.72x10^{-3}$ M) the optical density (OD) at λ_{max} 480 was found to decrease markedly. On further addition of **1c**, the optical density further decreased till the concentration of **1c** becomes 3.72x10^{-3}M (Fig.1) after which there was no change in OD of **3a** at 480 nm. The λ_{max} of **1c** was found to gradually shift from 289 nm to 272 nm with increase in concentration of **1c** after which no change in λ_{max} could be observed. It is clear from Fig.2 that the broadness of absorption maxima also increased with increase in concentration of **1c**. When 2,6-naphthoquinone was replaced by 1,4-naphthoquinone (1x10^{-3}), no shift was observed in the λ_{max} of 1,4-naphthoquinone (335 nm) thereby revealing that there is a selective complexation of 2,6-naphthoquinone **(3a)** by **(1c)** probably through hydrogen bonding by forming a 1:1 molecular complex. As is clear from Fig. 1, UV-visible spectrum of calix(n)arene-quinone complex did not elicit any other absorption maxima other than at 480 nm. This observation ruled out the possibility of formation of charge transfer complexes between **1c**, **3a** and **3b**. This was supported by the isolation of **1c** from the molecular complex by simple dissolution with chloroform.

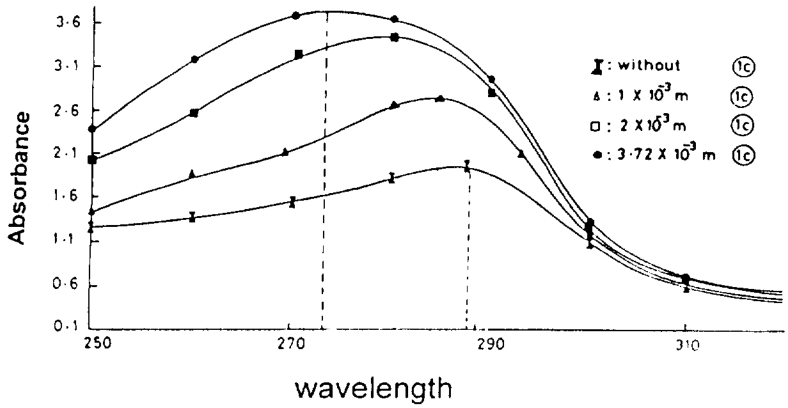


Fig.2: UV spectrum for the shift in λ_{max} of (1c) with the addtion of different concentrations of (1c) to 3.72x10-3M chloroform solution of 2.6-naphthoquinone.

Similar experiments with **1a**, **1c**, and **1e** (1x10^{-4}M) and 1,4-benzoquinone (1x10^{-4}M) were carried out and it was observed that optical density of benzoquinone at its λ_{max}(435 nm) continuously increased on addition of **1a** or **1c** (1x10^{-4}M) till concentration of calixarene reached at 0.7x10^{-4}M after which the OD sharply decreased from 0.07 to 0.04 in **1a-3c** and from 0.034 to 0.029 in **1c-3c** at 0.8x10^{-4}M (Fig. 3).

Job's plot of **[3c]/[1a or 1c] + [3c]** vs absorbance of benzoquinone (Fig. 3) showed that increase in OD of 1,4- benzoquinone is more on addition of **1a** as compared to the addition of **1c** under identical experimental conditions. On the other hand, no complexation was observed between **1e** and **3c**.The mole ratio plot of (**[1c-3c]/[3c]** vs OD of **3a**) (Fig.4) revealed a continuous decrease in the absorbance of **3a** with increase in the concentration of **1c** till they reached an equimolar ratio after which the absorbance remained constant. Detailed analysis confirmed that 1,4-benzoquinone forms a 2:1 complex with calix (n) arenes (n = 4,6) (Fig.3) while 2,6-napthoquinone forms a 1:1 molecular complex with calix(6) arene (Fig. 4).

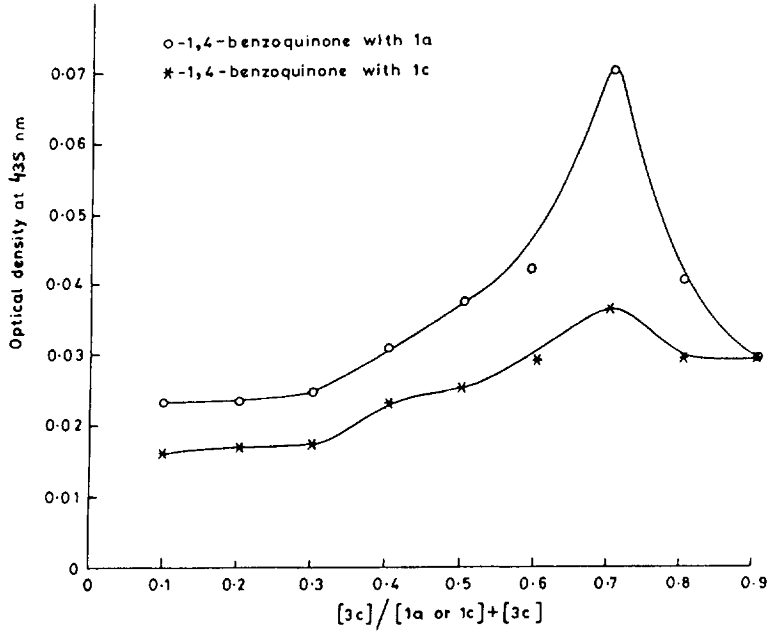


Fig.3: Job's Plot of [3c] / [1a or 1c] + [3c] Vs absorbance of benzoquinone at λ_{max} 435 nm.

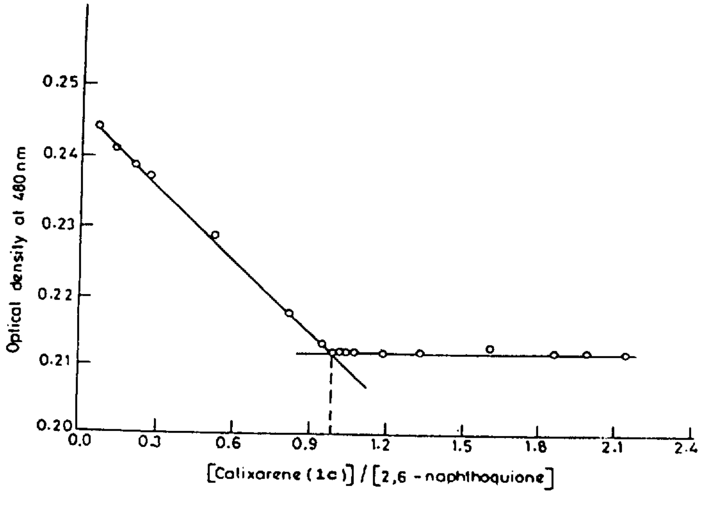


Fig.4: The mole ratio plot of optical density of 2,6-naphthoquinone at λ_{max}: 480 nm Vs [calixarene 1c] / [2,6-naphthoquinone]

Spectrophotometric titrations of 9,10-anthraquinone, 1,2-dihydroxy-9,10-anthraquinone and 1,2,5,8-tetrahydroxy-9,10-anthraquinone revealed that these quinones do not form complexes with calix(n) arenes **(1a-1e)** at low concentrations (0.25 x 10^{-4}M) as no change in their λ_{max} (325, 435 and 490 nm respectively) or their OD at λ_{max} was noticed on addition of calix(n) arenes **(1a-1e)**.

The calixarene-quinone interaction was further investigated by determination of association constant (K_a) between calixarenes and quinones as per the following equation.

$$\text{Calix(n)arene} + \text{quinone} \leftrightarrows \text{Calixarene-quinone complex}$$

$$\text{H} \quad \text{G} \leftrightarrows \text{HG}$$

$$K_a = \frac{[\text{HG}]}{[\text{H}][\text{G}]} \qquad (1)$$

The obtain association constants absorptivities were measured at various ratios of calixarenes to quinones and the data were analyzed by the Hildebrand-Benesi expression (Equation 2)

$$\frac{[\text{H}]}{\text{A}} = \frac{1}{k_a \epsilon_c [\text{G}]} + \frac{1}{\epsilon_c} \qquad (2)$$

Where [H] is the concentration of calixarene, [G] is the concentration of quinone, [HG] is the concentration of calixarene-quinone complex, A is absorptivity at 480 and 435 mm for 2,6-naphthoquinone and 1,4-benzoquinone respectively. ϵ_c is the molar absorptivity of calixarene-quinone complex and K_a is the association constant for the reaction. A plot of [H]/A *vs.* 1/[G] gave the values for association constant, K_a (Table 1)

The absorption data was also analyzed by the computer program using equation 3.

$$\frac{1}{K_a} = K_a^{-1} = \frac{A - A^\circ}{\epsilon_c - \epsilon_1} - C_1 - C_2 + \frac{C_1 C_2 (\epsilon_c - \epsilon_1)}{A - A^\circ} \qquad (3)$$

where A^0 and A is the absorbance of quinone at its initial concentration and when involved in complexation, C_1 and C_2 are concentration of quinone and calixarene respectively. ϵ_C is molar absorptivity of complex and ϵ_1 is the molar absorptivity of that of quinone at its initial concentration while K_a is the association constant.

When A^0 and $\epsilon_1 = 0$

$$K_a^{-1} = \frac{A}{\epsilon_C} - C_1 - C_2 + \frac{C_2 C_1}{A} \cdot \epsilon_C \qquad (4)$$

Since this equation contains two unknowns K_a^{-1} and ϵ_C, a graphical procedure was adopted for obtaining various values of ϵ_C (0-15000) at random for a given set of experimental data and calculation of the corresponding values of K_a^{-1}, The values of K_a^{-1} and ϵ_c (for one set of experimental values) were plotted as ordinate and abscissa, respectively and a curve was drawn. Similarly, second set of experimental values was employed and a curve of K_a^{-1} vs ϵ_c was drawn again. When several sets of experimental data were obtained, all the curves were plotted in one figure and point of intersection was taken as the value of K_a^{-1} and ϵ_c as recommended by Drago and Rose[21].

The values of association constants (K_a) using equation(4) appear to be more accurate as it does not depend on the Hildebrand-Benesi assumptions.

Fourier transform infrared spectroscopic analysis of **3a-1c** complex revealed a marked shift of 32 cm^{-1} (From 3232 to 3200 cm^{-1}) and 22 cm^{-1} (from 1650-1628 cm^{-1}) in the stretching frequency of -OH of calixarene and $>C = 0$ of quinone respectively as compared to their uncomplexed state. On the other hand, **1a-3c** and **1c-3c** molecular complexes showed a shift in the carbonyl $> C = 0$ frequency of 1,4-benzoquinone

Table 1: Association constants of calix(n)arene-quinone complexes in $CHCl_3$

Calix(n)arene (Conc.)	Quinone	Calix(n)arene -quinone complex	λ_{max} of Complex (nm)	O.D. of the Complex	Association constant (K_a, M^{-1}) From eqn.2	Association constant (K_a, M^{-1}) From eqn.4
1c ($5x10^{-3}$ M)	**3a**($5x10^{-3}$ M)	**1c-3a** (1:1)	480	0.22	$7.78x10^2$	$7.15x10^2$
1c ($3x10^{-4}$ M)	**3c**($7x10^{-4}$ M)	**1c-3c** (1:2)	435	0.034	$1.36x10^4$	3.5×10^2
1a ($3x10^{-4}$ M)	**3c**($7x10^{-4}$ M)	**1a-3c** (1:2)	435	0.070	$3.85x10^4$	3.3×10^2

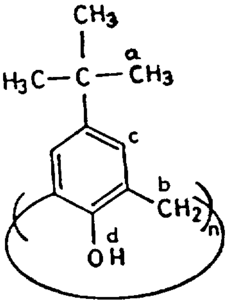
from 1644 to 1660 cm^{-1} and change in the —OH frequency of **1a** or **1c** from 3232 to 3264 cm^{-1} indicating thereby the presence of hydrogen bonding between the —OH of calixarenes and $> C = 0$ of quinones.

Low temperature H NMR analysis of the isolated **3a-1c** solid complex revealed that the —CH_2 protons of **1c** which usually appear at δ3.499 and δ4.365 were shifted to δ3.534 and δ4.319 where as —OH of **1c** which usually appears at δ9.624 was shifted to δ9.830 at —50°C (Table 2).

In the case of **1c-3a** and **1c-3c** complexes, the benzoquinone protons which usually appear at δ6.792 shifted to δ6.859 at —50°C. The —CH_2 protons of **1a** which appear at δ3.497 and δ4.365 were shifted to δ3.533 and δ4.310 while —OH of **1a** was observed to shift to δ9.832 from δ9.596 at -50°C (Table 2). In the **1c-3c** complex, the position of —CH_2 protons was observed to be shifted from δ3.499 and δ 4.365 to δ 3.536 and δ4.313 respectively while —OH protons were observed at δ9.835 instead of δ9.624. Detailed ^1H NMR analysis (Table 2) revealed that the interaction between the —OH of calix(n)arene and $> C = O$ of benzoquinone is stronger at low temperatures than at room temperature which is in conformity with known facts about molecular complexes and freezing of conformtaions of calix(n)arenes at low temperatures.

The foregoing observations can be explained by assuming the exo or endo complexation of the studied quinones (2,6-naphthoquinone and 1,4-benzoquinone) with calix(n)arenes. The change in λ_{max} and OD after reaching the 1:1 or 2:1 stoichiometry in their complexes would have reflected the exo nature of the calixarene-quinone complexes but this was not revealed from the spectral (UV and NMR) analysis. The endo nature of **1c-3a** complex was also established by analysis through CPK models and low temperature NMR analysis of **1c-3a** (1:1) molecular complex which revealed a shift in -OH from δ9.624 to δ9.830 and shift in $ArCH_2Ar$ protons from δ3.499 and δ 4.365 to 3.534 and δ4.319 (Table 2) respectively. The ^{13}C NMR spectral analyses of **3c** and **1c-3c** complex revealed that the carbonyl carbons of **3c** were shifted from δ146.6 and 144.7 to δ147.1 ($\Delta\delta = +0.5$) and 133.64 ppm ($\Delta\delta = -11$) thereby establishing the weakening of one of the carbonyl double bonds due to hydrogen bonding of **1c**. Analysis with CPK models confirmed that 2,6-naphthoquinone could be easily incorporated in the cavity of **1c** with its carbonyl group at a hydrogen bond distance from the calixarene hydroxyls.

Table 2 : Chemical shift values for protons in p-tert-butyl-calix(n)arene in the presence of 1,4-benzoquinone (0.7×10^{-4}M) and 2,6-naphthoquinone (3.72×10^{-3}M) in $CDCl_3$ at —50°C



P-tert-butyl-calix(n)arene	Proton observed	Position of proton observed in the presence of an added guest [δ (ppm)]		
		None	1,4- benzoquinone	2,6-naphthoquinone
n=4	a	1.250	1.244	-
	b	3.500	3.533	-
		4.360	4.310	-
	c	7.165	7.210	-
	d	9.596	9.832	-
n=6	a	1.251	1.246	1.245
	b	3.499	3.536	3.534
		4.365	4.313	4.319
	c	7.176	7.213	7.211
	d	9.624	9.835	9.830

EXPERIMENTAL

Melting points were taken in open capillaries on an electric melting point apparatus (Toshniwal) and are uncorrected. IR spectra were recorded on Perkin-Elmer FT-IR spectrophotometer in KBr pellets while PMR spectra were acquired on Nicolet-99.55 MHz Jeol-FT NMR spectrometer and Brucker 300 MHz NMR spectrometer available at RSIC, Bombay, in CDCl using tetramethylsilane as an internal standard. UV spectra were recorded on Perkin-Elmer (Lambda) spectrophotometer using analytical grade chloroform as the reference solvent. Column chromatography was performed on silica gel (60-120 mesh) and organic solvents were usually dried over anhydrous sodium sulphate. Petroleum ether refers to the fraction with the boiling range of 60-80°C. Molecular mass of calixarenes was determined by osmometry using vapour pressure osmometer (Knaur, Germany). The synthesized calix(n)arenes were compared with authentic samples (T.L.C, IR).

Synthesis of 5,11,17,23-tetra-tert-butyl-25,26,27,28-tetrahydroxycalix(4)arene (1a), 5,11,17,23,29,35-hexa-tert-butyl-37,38,39,40,41,42-hexahydroxycalix(6)arene (1c) and 5,11,17,23,29,35,41,47-octa-tert-butyl-49,50,51,52,53,54,55,56-octahydroxycalix(8)arene (1e)

Synthesisof5,11,17,23-tetra-tert-butyl-25,26,27,28-tetrahydroxycalix(4)arene(**1a**),5,11,17,23,29,35-hexa-tert-butyl-37,38,39,40,41,42-hexahydroxycalix(6)arene(**1c**), and5,11,17,23,29,35,41,47-octa-tert-butyl-49,50,51,52,53,54,55,56-octahydroxycalix(8)arene (**1e**) were prepared by the reported procedure[22].

Synthesis of 5,11,17,23,29,35-hexa-tert-butyl-37,38,39,40,41,42-hexamethoxycalix(6)arene (2c)

A solution of **1c** (1.10 , 0.7 mmol), NaH (1.10 g, 42 mmol) and methyliodide (10.25, 72 mmol) in THF (50 mL) and DMF (5 mL) was refluxed for 20 h. The solvent was removed by evaporation, cold water was added to the residue and the spearated solid was recrystallized from MeOH-$CHCl_3$ to give **2c** (1.20 g, 96%) as colourless needles; m.p. 326°C, ^1H NMR ($CDCl_3$, δ) 6.9 (s,12H, ArH), 3.9(s,12H,$ArCH_2Ar$) 3.2(s,18H, -OCH_3), 1.3(s,54H,-$C(CH_3)_3$).

Synthesis of 2,6-naphthoquinone (3a)

2-aminonaphthalene (0.1 g, 70 mmol) was dissolved in a mixture of chloroform and methanol (100 ml, 1:1, v/v) and a dye sensitizer (methylene blue, 5 mg) was added to it. The reaction mixture was irradiated with tungsten filament lamp (2x200 watt) through a potassium chromate screen while oxygen was bubbled through the solution for 18 h. The reaction mixture was worked up as described earlier[23] to give 2,6-naphthoquinone, m.p. 132-134°C.

Synthesis of 1,4-naphthoquinone (3b)

1,4-naphthoquinone was obtained by the oxidation of naphthalene with chromium trioxide as reported in literature[24] and was recrystallized from pet-ether (60-80°C) as yellow needles, m.p.120-124°C (lit[24]. m.p. 123-124°C), IR (KBr) >C = O 1644 cm^{-1} in 50% yield.

Synthesis of 1,4-benzoquinone (3c)

1,4-benzoquinone was synthesised as yellow needles by oxidation of 1,4-dihydroxybenzene with chromium trioxide as reported in literature[24] in 70% yield ; m.p. 110-112°C (lit[24]m.p. 114-115°C). IR (KBr) C=O 1644 cm^{-1}

Isolation of Molecular Complexes:

Calix(n)arene-quinone complexes were prepared by stirring a mixture of equimolar amounts of calix(n)arene and 2,6-naphthoquinone in $CHCl_3$ for 8 h and slowly evaporating the solution in a vacuum desicator. The solid thus obtained was analysed by UV, IR and NMR spectrscopy.

1c-3a: UV ($CHCl_3$), 480,272 nm;IR (KBr), 3200, 1628 cm^{-1}; ^1H NMR ($CDCl_3$,δ), 1.245 (s,54H,$C(CH_3)_3$), 3.534 (d, 6H, $ArCH_2Ar$), 4.319 (d,6H, $ArCH_2Ar$), 7.211 (s,12H, ArH), 7.04 (d,1H), 6.86 (s,1H), 6.68 (d,1H),9.830 (s,6H, D_2O exchangeable,–OH).

1c-3c: UV ($CHCl_3$), 435 nm;IR (KBr), 1660, 3264 cm^{-1}; ^1H NMR ($CDCl_3$,δ), 1.246 (s,54H, C $(CH_3)_3$), 3.536 (d, 6H, $ArCH_2Ar$), 4.313 (d,6H, $ArCH_2Ar$), 6.859 (s,8H), 7.213 (s, 12H, ArH), 9.835 (s,6H, D_2O

exchangeable, —OH).

1c-3c:UV ($CHCl_3$), 435 nm;IR (KBr), 1660, 3264 cm^{-1}; ^1H NMR ($CDCl_3$,δ), 1.244 (s,36H,C $(CH_3)_3$), 3.533 (d, 4H, $ArCH_2Ar$), 4.310 (d,4H,$ArCH_2Ar$), 6.859 (s,8H), 7.210 (s, 8H, ArH), 9.832 (s, 4H, D_2O exchangeable, —OH).

General procedure for examination of interaction between 5,11,17,23,29,35-hexa-tert-butyl-37,38,39,40,41,42-hexahydroxycalix(6)arene with 2,6-naphthoquinone

2,6-naphthoquinone (3.72×10^{-3} M) was added to a dilute solution of **1c** at different concentrations (viz. 0.25×10^{-3}M, 0.5×10^{-3}M, 0.75×10^{-3}M, 1.0×10^{-3}M, 2.0×10^{-3}M, 3.0×10^{-3}M, 3.72×10^{-3}M, 4×10^{-3}M, 5×10^{-3}M, 6×10^{-3}M, 7×10^{-3}M, 8×10^{-3}M). The mixtures were examined for complete solution homogeneity under a microscope, transferred to a clean and a dry quartz cuvette (5 mL) and allowed to equilibrate (5 min, 25°C) before recording the absorption spectrum. All measurements were accompanied by experiments with blank solutions and maintenance of uniform conditions of experiments conducted through out to eliminate mixed solvent effects. For NMR measurements analytical grade chloroform was replaced by $CDCl_3$

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