Synthesis and evaluation of 5,11-bis-(2-thioallylphenylazo)-25,26,27,28-tetrtahydroxycalix[4]arene and 5,11,17,23-tetrakis- (2-thiohexadecylphenylazo)-25,26,27,28-tetrahydroxycalix[4]arene as chromogenic receptors of Hg(II) and Pd(II) ions

Lukesh Bajaj, H. Mohindra Chawla,* Tania Francis, and Natarajan Venkatesan

Department of Chemistry, Indian Institute of Technology, Hauz Khas, New Delhi – 110 016, India
E-mail: mohindrachawla@hotmail.com

Dedicated to Dr. A. V. Rama Rao on his 70th birthday

(received 06 Jan 05; accepted 03 Feb 05; published on the web 11 Feb 05)

Abstract

5,11-bis-(2-thioallylphenylazo)-25,26,27,28-tetrtahydroxycalix[4]arene (**1**) and 5,11,17,23-tetrakis-(2-thiohexadecylphenylazo)-25,26,27,28-tetrahydroxycalix[4]arene (**2**) have been synthesized and examined for their solution binding with soft metal ions. The electronic absorption spectra of 1 and 2 show remarkable bathochromic shifts when interacted with Hg(II) and Pd(II). IR and ^{1}H NMR spectral data reveal that the synthesized derivatives have a potential to develop into chromogenic sensors for these ions.

Keywords: Chromogenic, calixarene, electronic absorption spectra, optical sensors

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Introduction

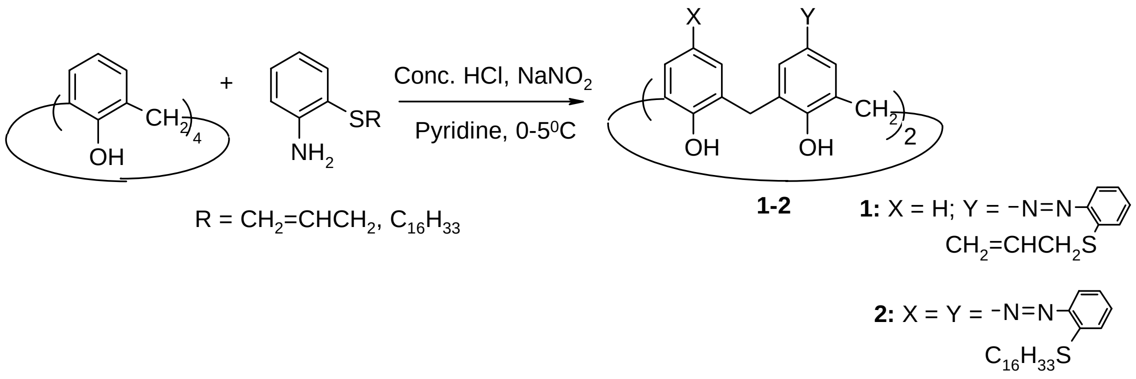
Calixarenes are a class of phenolic metacyclophanes possessing a versatile π-electron rich cavity that are comparatively easily accessible in the laboratory. Lot of research work has been reported on potential applications of calixarenes in the field of supramolecular chemistry.[1,2] The ionophoric properties of calixarene derivatives towards alkali, alkaline and certain organic substrates have been well documented.[3a,b,c] Reports on their binding with transition metal ions, however, are comparatively less. With a long term aim of developing inexpensive and real-time monitoring methods for molecular diagnostics[4], we embarked upon synthesis of chromogenic calixarenes with expected potential of changing color on specific interaction with toxic and precious metal ions. In this connection, some reports on the synthesis of azocalixarenes for related applications have appeared in the literature.[4,5] For example, Deligoz and coworkers.[6] have synthesized azocalixarene derivatives for liquid-liquid extraction of transition metal ions

(Ag^+, Hg^{2+} and Hg^+) and Lu *et al.*[7] have obtained a calixarene carboxyphenylazo derivative as a diagnostic for lead. A potassium and cesium selective azocalixarene derivatives have been reported by Kim *et al.*[8a] and Chawla *et al.*,[8b] while a nickel selective azocalixarene derivative has been reported by Ma and coworkers.[8c] Complexation of aromatic compounds with azocalixarenes have also been reported recently.[8d,8e] Reports on the synthesis and molecular recognition characteristics of lower rim derivatized calix[4]arenes towards soft metal ions such as Hg(II) and Pd(II) are available[9] but these reports either involve complex calixarenes,[10] electrochemical inputs[11] or those based upon selective transport/extraction[6] and almost all of them are less amenable to detection as a function of colour change. In the present work, it was considered important to have nitrogen, sulphur and oxygen in the calixarene framework for binding with soft metal ions like Hg(II) and Pd(II). We report herein the synthesis of two new chromogenic calixarenes containing multi-heteroatoms with a potential to develop into molecular diagnostics through the use of UV-vis spectroscopy.

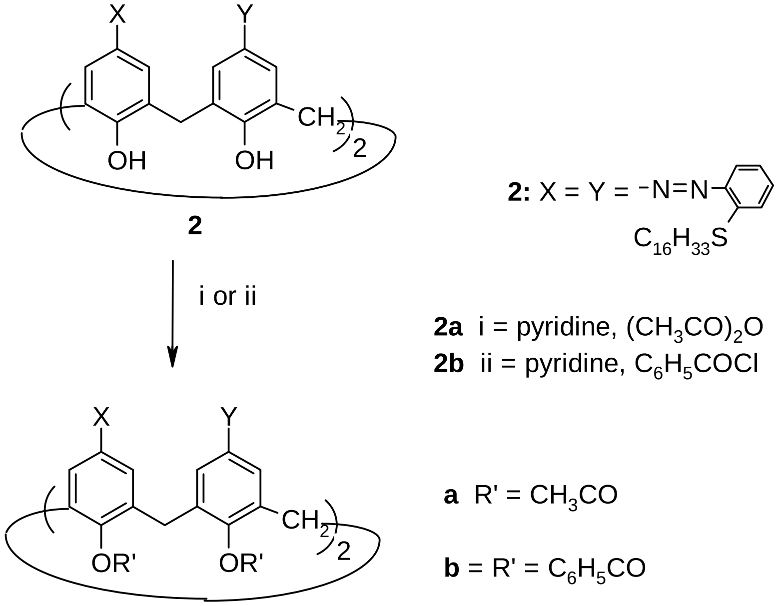
Results and Discussion

The new thiaazocalixarene dyes, **1** and **2** were synthesized by coupling a debutylated calix[4]arene and 2-alkylthiobenzenediazonium chlorides at 0-5 °C.[12,13] The products were further purified by chromatography (silica gel) to provide new chromogenic calixarenes in 40% and 35% yields respectively (Scheme 1). The structures of synthesized molecular receptors were established by analyzing their spectral and physical characteristics and chemical derivatization. For instance, characteristic IR absorptions observed at 1582 cm^{-1} and 1583 cm^{-1} in the case of **1** and **2** respectively could be attributed to $\nu_{N=N}$. The presence of azo group in the synthesized receptors was confirmed from its UV spectrum (λ_{max} at 344 nm with a shoulder at 400 nm in chloroform for **1** and λ_{max} at 338 nm with a shoulder at 394 nm in chloroform for **2**). Chemical derivatization of **2** was accomplished by its reaction with benzoyl chloride and acetyl chloride (Scheme 2) to provide as its tetrabenzoyl and tetracetyl esters respectively.

The ^1H NMR spectrum of **1** gave a deuterium exchangeable singlet at 10.22 ppm. The multiplet observed between 7.83 – 6.77 ppm (18 protons for **1**) could be assigned to the aromatic protons of thiophenylazo and calixarene aryl σ – framework. Two broad signals at 4.32 and 3.66 ppm observed in the NMR spectrum of (**1**) were assigned to the methylene protons of the calix[4]arene moiety. Integration of the NMR signals obtained indicated that I is a bisazo calixarene derivatives while **2** is a tetrazo calixarene. The ^1H NMR spectrum of **2** showed a deuterium exchangeable singlet at 10.13 ppm for -OH, multiplet for the aromatic protons of thiophenylazo and calixarene aryl σ – framework between 7.74-6.71 ppm (24 protons) and two broad singlets at 4.29 and 3.79 ppm representing the methylene bridge protons. that **1** and **2** possess a cone conformation, was evidenced by the ^{13}C NMR spectra which exhibited methylene carbons of calix[4]arene at δ 31.67 and 31.69 respectively. These observations are consonance with similar literature.[14,15]



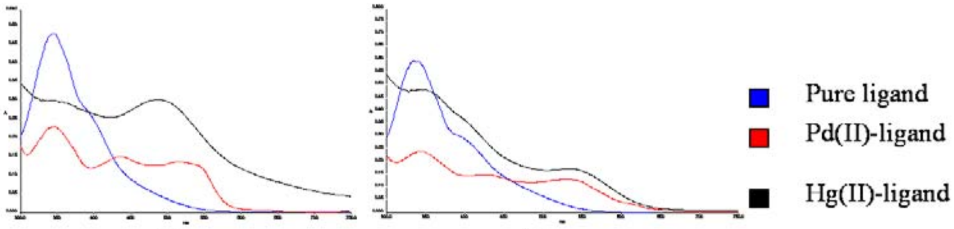
Scheme 1. Synthesis of chromoionophore **1-2**.



Scheme 2. Further chemical derivatization of chomoionophore **2**.

Evaluation of synthesized calixarenes for interaction with metal ions by absorption spectroscopy. Compounds **1** and **2** gave no change in their UV spectra ($CHCl_3$) upon addition of various transition metal ions [$Cu(OAc)_2.2H_2O$, $Ni(OAc)_2.4H_2O$, $Co(OAc)_2.4H_2O$, $Fe(OAc)_2$, $CrCl_3.6H_2O$ and $AgNO_3$] except when methanolic solution of $Hg(OAc)_2$ and K_2PdCl_4 were added to them. An immediate color change from yellow to red in the case of $Hg(OAc)_2$ and yellow to light purple in the case of K_2PdCl_4 was observed when methanolic solution of these salts were added to methanolic solution of **1** and **2**. Consequently, the study was restricted to the interaction of the ligands with Hg(II) and Pd(II). Since these metal ions do not absorb at the maximum wavelength absorbed by **1** and **2.** The shift in the λ_{max} to higher wavelength of **1** and **2** can be explained on the basis of metals interacting with their azobenzene fragment. This is evidenced by the earlier findings that λ_{max} in these compounds is due to the π–π^* and n–π^*

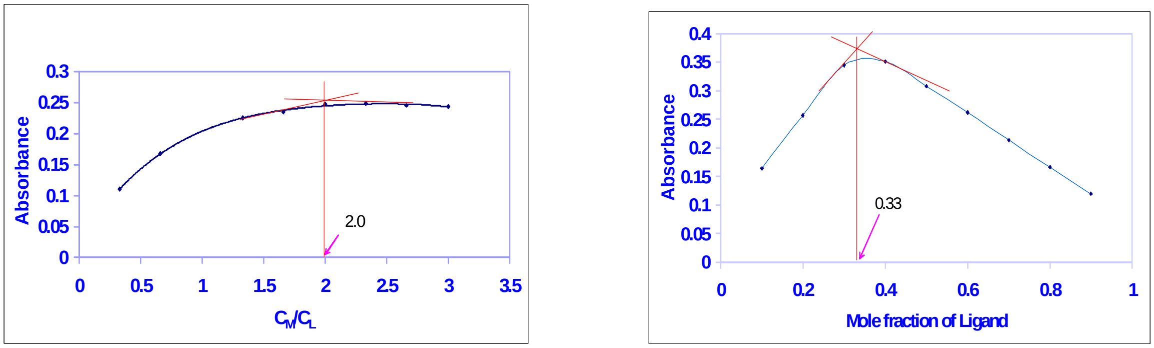
(347nm absorption[16]) transitions respectively. For instance, addition of a solution of $Hg(OAc)_2$ in $CHCl_3$: MeOH to a solution of **1** in chloroform (λ_{max} 344nm with a shoulder at 400nm) led to the disappearance of the absorptions corresponding to the ligand with concomitant appearance of bathochromically shifted peak at 500 nm in its electronic absorption spectrum. Likewise, the addition of a solution of K_2PdCl_4 in $CHCl_3$: MeOH system to the ligand **1** resulted in the reduction in peak intensities of the parent ligand with concomitant appearance of two new absorption peaks at 440 nm and 525 nm as shown in Figure 1a. The chloroform solution of **2** exhibited a λ_{max} at 338 nm with a shoulder at 394 nm which disappeared with the appearance of two new absorptions at 434 nm and 525 nm (Figure 1b) upon addition of a solution of K_2PdCl_4 in $CHCl_3$:MeOH system. Addition of a solution of $Hg(OAc)_2$ in $CHCl_3$: MeOH to **2** led to the appearance of a new absorption peak at 540 nm with decrease in the absorption of the ligand at 338 nm.



(a) (b)

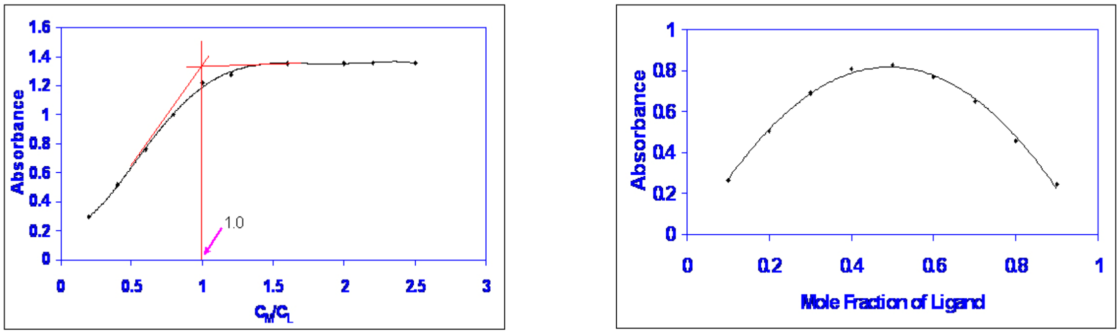
Figure 1. Molecular interaction of **1** (a) and **2** (b) towards Hg(II) and Pd(II) as monitored by electronic absorption spectroscopy.

Further studies on the interaction of **1** and **2** with Pd(II) and Hg(II) have been carried out for determining the stoichiometry of plausible complexation in these cases by using mole-ratio method as well as by Job's method of continuous variation.[17] The optical response on addition of incremental quantities of known concentrations of solution of K_2PdCl_4 in $CHCl_3$: MeOH to a fixed concentration of ligand solution ($1x10^{-4}$M) has been recorded. From the plot of metals to ligand ratio (C_M/C_L) versus OD at 525 nm, the metal to ligand ratio was found to be 2 : 1 in the case of Pd(II) towards **1** (Figure 2a). The above value of metal to ligand ratio was further confirmed by Job's continuous variation method (Figure 2b). The optical response on addition of incremental quantities of known concentrations of solution of $Hg(OAc)_2$ in $CHCl_3$:MeOH to a fixed concentration of ligand solution ($1x10^{-4}$ M) recorded at 500 nm (Figure 3a), the metal to ligand ratio (mole ratio method) has been determined to be 1 : 1. This stoichiometry has been further confirmed by Job's continuous variation method in which the plot of OD versus (L/L+M) gave a value of 0.5 for ligand to metal ratio (Figure 3b). Similar studies with **2** towards Pd(II) at 525 nm gave the metal to ligand ratio of binding in solution as being equal to 3 : 1 as depicted in Figure 4a and 4b). However, in the case of Hg(II) it has been observed that two molecules of the ligand interacts with one Hg(II) atom in solution (Figure 5a & 5b).



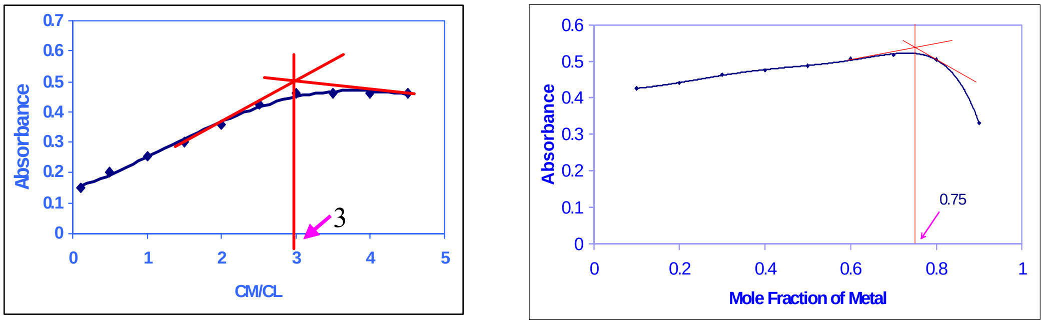
(a) (b)

Figure 2. (a) Mole-ratio plot for interaction of **1** with Pd(II); (b) Job's Plot for interaction of **1** with Pd(II).



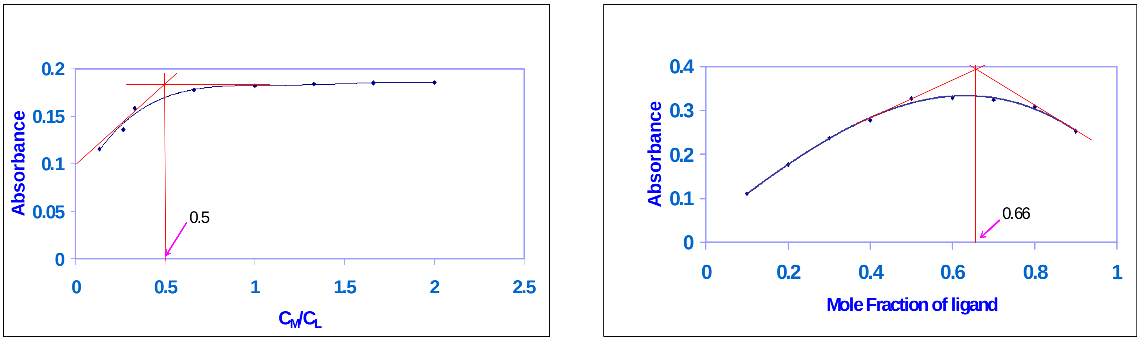
(a) **(b)**

Figure 3. (a) Mole-ratio plot for interaction of **1** with Hg(II); (b) Job's Plot for interaction of **1** with Hg(II).



(a) (b)

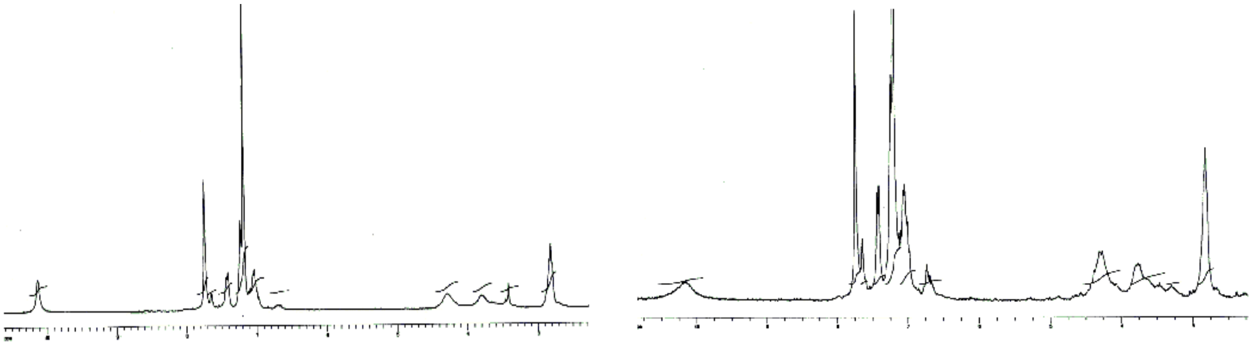
Figure 4. (a) Mole-ratio plot for interaction of **2** with Pd(II); (b) Job's Plot for interaction of **2** with Pd(II).



(a) (b)

Figure 5. (a) Mole-ratio plot for interaction of **2** with Hg(II); (b) Job's Plot for interaction of **2** with Hg(II).

To determine possible complexation or reasons for change of colour on interaction with Hg(II) and Pd(II) an equimolar solution of the metal ion ($CHCl_3$:CH_3OH (1:4) and the synthesized molecular receptor **1** ($CHCl_3$) was equilibrated at room temperature for 3 h. The IR spectrum of the residue obtained on slow evaporation of these solutions in a desiccator showed considerable reduction in the $\nu_{N=N}$ stretching frequency absorption frequencies to 1539 cm-1 and 1558 cm-1 as compared to that of the parent calixarene (1583 cm-1). This shift could be attributed to the metal-azo back bonding. The peaks at 758 cm-1 in the case of **2-Pd(II)** and 753 cm-1 in the case of **2-Hg(II)** respectively in comparison to 749 cm-1 in the free calixarenes could be due to $\nu_{S\text{-}C}$ of sulfur of the thioalkyl group that may be coordinated to the metal ion. The 1H NMR spectra of the **2-Pd(II)** showed a small downfield shift in the δ values and broadening of the peaks occurred in the aromatic region as well as in the methylene bridge region of the calixarene protons [Figure 6(a)-(b)]. These observations indicated that Pd(II) interacted with the chromogenic calixarene but characterization of the final product and exact mode of binding could not be completely ascertained as suitable crystals for single crystal X-ray diffraction were not achieved.



a) (b)

Figure 6. (a) 1H-NMR spectrum of **2** (b) **2-Pd(II)** adduct in $CDCl_3$.

Since both **1** and **2** gave similar spectral response on interaction with Hg(II) and Pd(II), the alkyl chain (hexadecyl or allyl) does not seem to play a major role in the recognition process despite the presence of S-allyl chain that contained a double bond in the proximity. Since both K_2PdCl_4 and $Hg(OAc)_2$can act as oxidizing agents, the possibility of oxidation of the ligands **1** and **2** by $Hg(OAc)_2$ or K_2PdCl_4 was ruled out on the basis of their IR and 1H NMR spectra which remained unchanged after interacting with the metal salts to reveal that calixarene structure remained unaffected (no S=O absorptions) during the recognition process. Small shifts in the $\nu_{N=N}$ and $\nu_{S\text{-}C}$ bands in the IR spectra of free calixarene derivative confirmed that the binding centers are the softer azo as well as the –S in the calixarene σ-framework. Though exact pattern of binding of these metal ions to the chromogenic calixarenes and further refinement and optimization of processes for development of colourimetric sensors is in progress, can be concluded that **1** and **2** have the potential of detecting ppm quantities of target ions through a visual change being investigated.

Experimental Section

General procedure for the synthesis of chromogenic calixarenes. A solution of 2-alkylthioaniline (14 mmol) (prepared from 2.0 g of 2-aminothiophenol and alkylhalide), sodium nitrite (14 mmol) and concentrated HCl (7 mL) in water (5 mL) and methanol (5 mL) was slowly added (over a period of about 30 min.) into an ice cold (0-5 ^oC) solution of tetrahydroxycalix[4]arene (2.35 mmol) and sodium acetate trihydrate (30 mmol) in MeOH-DMF (26 mL, 5:8, v/v) to give a red suspension. After being allowed to stand for 3h at room temperature, the suspension was acidified with aqueous HCl (150 mL, 0.25 %). The mixture was warmed to 60 ^oC for 30 min to give azocalix[4]arenes and the crude products (red semisolid in the case of reaction with diazotized S-allyl thioaniline and a solid in the case of reaction with diazotized hexadecyl thioaniline. Pure **1** and **2** were obtained through column chromatography using hexane: chloroform as the eluent (8 : 2).

5,11-Bis-(2-thioallylphenylazo)-25,26,27,28-tetrahydroxycalix[4]arene (1). (Yield 0.727g; 40%). m.p.181-184^{o}C (Anal. Calcd. for $C_{46}H_{40}N_4O_4S_2$: C, 71.11; H, 5.19; N, 7.21). Found: C, 71.20; H, 5.11; N, 7.25. Mol. Mass (vapor pressure osmometry): 775. (Calcd.) 776.25. UV (λ_{max}, $CHCl_3$): 346 and 392(s) nm. IR (KBr; ν_{max}, cm^{-1}): 1582. ^{1}H NMR ($CDCl_3$; δ, ppm): 10.22 (4H, bs, exchangeable with D_2O, OH); 7.83-6.77 (18H, m, ArH); 5.94-5.92 (4H, m, $SCH_2CH=CH_2$); 5.27-5.10 (2H, m, $SCH_2CH=CH_2$); 4.32 (4H, bs, $ArCH_2Ar$), 3.66 (4H, bs, $ArCH_2Ar$), 3.64 (4H, d, SCH_2). ^{13}C{H}NMR : 151.73, 150.05, 148.51, 147.84, 137.66, 133.23, 130.48, 129.4, 128.78, 127.6, 125.60, 125.14, 124.37, 123.77, 122.56, 120.17, 118.05, 117.01, 48.26, 35.60, 31.67, 29.68, 20.07, 11.48.

5,11,17,23-Tetrakis-(2-thiohexadecylphenylazo)-25,26,27,28-tetrahydroxycalix[4]arene (2). (Yield 1.546 g; 35%). m.p. 103-104 ^{o}C. (Anal. Calcd. for $C_{116}H_{168}N_8O_4S_4$: C, 74.63; H, 9.07; N, 6.00). Found: C, 74.5; H, 9.01; N, 6.01. Mol. Mass (vapor pressure osmometry): 1867. (Calcd.) 1866.89. UV (λ_{max}, $CHCl_3$): 338 and 398(s) nm. IR (KBr; ν_{max}, cm^{-1}): 1583. ^{1}H NMR ($CDCl_3$; δ, ppm): 10.13(4H, bs, exchangeable with D_2O, OH); 7.74-6.71 (24H, m, ArH); 4.29 (4H, bs, $ArCH_2Ar$); 3.79 (4H, bs, $ArCH_2Ar$); 2.81 (8H, t, SCH_2); 1.57 (16H, m, $SCH_2CH_2CH_2$); 1.17 (96H, m, $SCH_2CH_2CH_2(CH_2)_{12}CH_3$); 0.80 (12H, t, $SCH_2CH_2(CH_2)_{13}CH_3$).^{13}C{H}NMR : 149, 130.52,129.18, 128.99, 127.42, 126.5, 125.04, 124.34, 122.41, 116.71, 32.07, 31.69, 30.67, 29.15, 28.77, 22.62, 14.06.

Reaction of diazocalix[4]arene 2 with acetic anhydride. A solution of diazocalix[4]arene **2** (0.75 mmol) was treated with acetic anhydride (5 mL) on boiling water bath for 20 h. The reaction mixture was cooled and poured into ice-cold dilute HCl (5%, 300 mL) yielded a yellow precipitate which was charcoalized with active charcoal (2 g) in $CHCl_3$ (30 mL). Recrystallisation of the product from $CHCl_3$-methanol (1:1) gave a yellow crystalline solid **(2a)**. (0.31 g, 20%) m.p. > 236 ˚C (decomp.), Calcd. for $C_{124}H_{176}N_8O_8S_4$: C, 73.18; H, 8.72; N, 5.51. Found: C, 74.04; H, 8.22; N, 5.96. UV (λ_{max}, $CHCl_3$): 420 nm. IR (KBr; ν_{max}, cm^{-1}): 2850(m), 1754(s), 1576(s), 1560(m), 1492(m), 1436(w), 1372(w), 1256(w), 1210(w), 765(m), 635(w). ^{1}H-NMR ($CDCl_3$; δ, ppm): 7.92-6.72 (24H, bm, ArH), 4.12 (8H, bs, $ArCH_2Ar$), 2.42 (8H, s, SCH_2), 2.04 (12H, s, $OCCH_3$), 1.74-1.67 (124H, bs, $SCH_2.C_{15}H_{31}$). The compound was identified as 25,26,27,28-tetraacetyloxy - 5,11,17,23 - tetra(2-thiohexadecylphenylazo) calix[4]arene 2a.

Reaction of diazocalix[4]arene 2 with benzoyl chloride and pyridine. A solution of diazocalix[4]arene **2** (0.75 mmol) was taken in pyridine (15 mL) and benzoyl chloride (0.60 g, 4.25 mmol) was added to it. After heating on boiling water bath for 15 h, the reaction mixture was cooled and poured into crushed ice (200 g) when a yellow precipitate obtained after filtration under vacuum. It was dissolved in $CHCl_3$ (30 mL) and successively washed with very dilute HCl, saturated $NaHCO_3$ solution and water. The residue obtained on evaporation of organic layer was recrystallized from $CHCl_3$-methanol (1:1) to provide **2b** as a pale yellow crystalline solid, **2b** (0.23 g, 13%), m.p.>226°C(decomp.), Calcd. for $C_{144}H_{184}N_8O_8S_4$: C, 75.75; H, 8.12; N, 7.38. Found: C, 75.64; H, 8.22; N, 7.36**.** UV (λ_{max}, $CHCl_3$): 420 nm. IR (KBr; ν_{max}, cm^{-1}): 2850(m), 1764(s), 1632(m), 1584(s), 1560(m), 1492(m), 1436(w), 1372(w), 1256(w), 1210(w), 765(m), 635(w). ^{1}H-NMR ($CDCl_3$; δ, ppm): 7.92-7.73 (20H, m, ArH), 7.72-6.72 (24H, bm, ArH), 3.97 (8H, bm, $ArCH_2Ar$), 2.42 (8H, s, SCH_2), 1.53-0.51 (124H, bs, $SC.C_{15}H_{31}$). The compound was identified as 25, 26, 27, 28-tetrabenzoyloxy-5, 11, 17, 23-tetra(2-thiohexadecylphenylazo) calix[4]arene.

General procedures involved in electronic absorption spectroscopic studies

Preparation of the stock solutions of potential molecular receptors (1 and 2) and ions to be sense. The chromogenic calixarenes **1** (0.077 g) and **2** (0.093 g) were accurately weighed and made up in a 100 mL standard flask using $CHCl_3$: MeOH (1:4) and $CHCl_3$: MeOH (2:3) respectively to give 1x10^{-3} M solutions. Potassium tetrachloropalladate(II) (K_2PdCl_4) was accurately weighed (0.0326 g) and dissolved in $CHCl_3$:MeOH (2:3) in a 100 mL standard flask. Complete dissolution of the salt was achieved by adding a small amount of water (~1 mL). The concentration of the solution was determined to be 1.0029 x 10^{-3} M. Mercury acetate $Hg(OAc)_2$ solution was prepared by dissolving an accurately weighed amount (0.0159 g) in $CHCl_3$:MeOH (1:4) in a 50 mL standard flask (1.1049 x 10^{-3} M).

Spectrophotometric analysis of interaction of synthesized chromogenic calixarenes and metal ions. The stock solutions of the ligands were diluted 2.5 times to get the optical density within the aptitude range of the spectrophotometer. This solution was divided into several 3 mL portions and 0.5 mL of the following metals (in methanol): K^+, Pd^{2+}, Ni^{2+}, Fe^{2+}, Cr^{3+}, Co^{2+} and Hg^{2+} prepared from KCl, K_2PdCl_4; $Ni(OAc)_2.4H_2O$; $Fe(OAc)_2$; $CrCl_3.6H_2O$; $Co(OAc)_2.4H_2O$ and $Hg(OAc)_2$ were added to them followed by a record of UV-vis spectrum of each solution. Among the various metal ions studied, only $Hg(OAc)_2$ and K_2PdCl_4 showed interaction with the chromogenic ligands.

General procedure for quantitative examination of the interaction between chromogenic calixarenes with metal ions

The metal to ligand ratio of the ligand-metal interaction was ascertained by mole-ratio plots and further confirmed by the Jobs' continuous variation method.

(a) Mole-ratio method. A series of solutions was prepared by maintaining the concentration of potential molecular receptors **1** and **2** as gradually varying the concentration of metal ions. The mixed solutions were shaken well and left for about 5 to 10 minutes for attainment of equilibrium between the **1** (or **2**) and the metal ions. The optical spectrum of each solution was then recorded. The optical density (OD) at 525 nm in the case of Pd(II) ion and at 500 nm in the case of Hg(II) ion was plotted against the metal to calixarene mole ratio, *i.e.*, C_M/C_L where C_M and C_L are the concentrations of the metal ion and the ligand respectively. The metal to ligand ratio (M/L) was then calculated for each metal ion.

(b) Job's method of continuous variation. A series of solutions with varying metal ion and calixarene concentrations were prepared by maintaining the total calixarene and metal ion concentration constant (*i.e.,* $C = C_M+C_L$ where C, C_M and C_L are the total concentration of metal ion and ligand, the concentration of the metal ion and the concentration of the ligand respectively). The optical densities (OD) were measured at 525 nm and 500 nm for K_2PdCl_4 and $Hg(OAc)_2$ respectively and were plotted against the mole fraction of the ligand, X_L (C_L/C). Assuming that only one complex was formed with a composition ML_n, the value of 'n' was calculated from the X_{max} (mole-fraction of the ligand (X_L) at maximum absorption) from the relation:

$$n = \{X_{max}/ 1- X_{max}\}$$

Acknowledgements

Authors LB and NV wish to thank Indian Institute of Technology, Delhi for providing the necessary facilities and financial assistance for the research work and TF is thankful to Council of Scientific and Industrial Research, India, for providing Junior Research Fellowship.

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