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Synthesis and cation binding properties of new arylazo- and heteroarylazotetrathiacalix[4]arenes

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Abstract—New macrocyclic tetrathiacalix[4]arenes have been synthesized by incorporating arylazo-, thiazoleazo- and β-naphthylazo- units in the tetrathiacalix[4]arene molecular architecture through diazotization and coupling reactions. The new compounds have been characterized by ^{1}H NMR, ^{13}C NMR and FAB-MS spectroscopic analysis. X-ray crystallography for one of the new dyes (**4a**) reveals that the compound is present in the cone conformation. The synthesized macrocycles have been examined for their binding with alkali (Li^+, Na^+, K^+, Cs^+ and Rb^+), alkaline earth (Ca^{2+}, Mg^{2+} and Ba^{2+}) and transition metal cations (Cr^{3+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Hg^+, Hg^{2+}, Pd^{2+} and Pt^{2+}) by UV–visible spectroscopy to reveal selective bathochromic shifts for heavier alkali metal ions (cesium and rubidium) and palladium in a 1:1 and 2:1 stoichiometry respectively. The study has a significant bearing on the development of useful ionic filters and sensor materials.

1. Introduction

Calix[*n*]arenes are now well recognized molecular receptors for chemical and biochemical analysis through principles of molecular recognition. The replacement of the four methylene bridges of *p*-*tert*-butylcalix[4]arene by sulfide linkages provides tetrathiacalix[4]arenes which are expected to have different chemical behaviour from that of the classical calixarenes first described by Gutsche et al.[1] and a large number of subsequent workers.[2] The difference in chemical and spectral behaviour of calixarenes and tetrathiacalixarenes is primarily due to the possibility of varying oxidation states of the bridging sulfur atoms. The parent tetrathiacalix[4]arene architecture was first achieved by Sone et al. in 1997 via stepwise replacement of methylene linkages of *p*-*tert*-butylcalix[4]arene by sulfur bridges.[3] In the same year, Kumagai et al. reported a facile synthesis of *p*-*tert*-butyltetrathiacalix[4]arene in satisfactory yields by the reaction of *p*-*tert*-butylphenol with elemental sulfur.[4] Considerable efforts have been made thereafter to derivatize *p*-*tert*-butyltetrathiacalix[4]arenes to achieve molecular scaffolds and novel molecular receptors. Though a small number of tetrathiacalix[4]arenes with substituents at the lower rim are known, information on upper rim derivatization of tetrathiacalix[4]arenes is limited. This is probably due to the ease with which the bridging sulfur atoms can be oxidized to sulphoxide[5] or sulphone[6] derivatives by many of the oxidation catalysts used for derivatization which complicates the outcome of reactions. A few interesting reports on upper rim substitution of tetrathiacalix[*n*]arenes have appeared in the literature recently. For instance, sulphonation,[7] bromination,[8] nitration,[9,10] chloromethylation[11] and organophosphorylation[11] of tetrathiacalix[4]arenes have been reported. Lhotak et al. have reported the synthesis of aminotetrathiacalix[4]arenes via diazocoupling and reduction[12] of the tetrathiacalix[4]arene analogue. Tetrathiacalix[4]arenes bearing ethynylic groups on the lower rim have also been reported by Parola et al.[13] To the best of our knowledge, very little work seems to have been reported on tetrathiacalix[4]arenes with chromogens at the upper rim, despite the fact that these derivatives are attractive targets for supramolecular assemblages for molecular recognition through visual colour change.[14–18] We describe herein the synthesis and evaluation of new chromogenic tetrathiacalix[4]arenes bearing phenylazo-, thiazoleazo-, pyridylazo- and β-naphthylazo- groups (Table 1) for ionic recognition in the hope to obtain new molecular filters and devices for specific use. While all compounds have been identified by physical and spectroscopic measurements (UV, IR, NMR and FAB MS), structure of one of these chromogenic compounds has been elucidated by X-ray crystallography. The ionic recognition by the synthesized molecular receptors reported in this paper has been investigated by UV–visible spectroscopic methods.

Keywords: Tetrathiacalix[4]arenes; Chromogenic; Diazotization; Ionic recognition.

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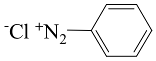
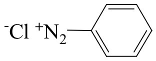
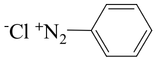
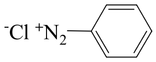
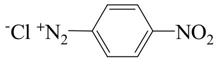
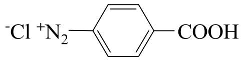
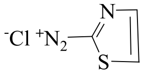
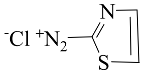
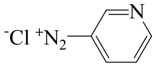
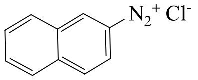
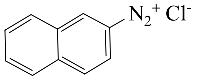
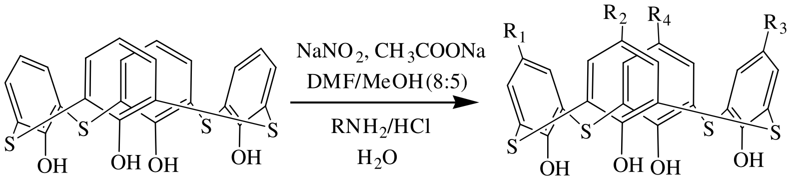
Table 1. Different products of reactions under optimized reaction conditions and their yields

Starting compound	Diazotizing unit	Product no.	Optimized conditions (base/solvent)	% Yields
2		**3a**	DMF:MeOH (8:5)/CH_3COONa	37
2		**3b**	DMF/CH_3COONa	68
2		**3c**	DMF:MeOH (8:5)/CH_3COONa	25
2		**3d**	DMF: MeOH (8:5)/NaOH	74
2		**3e**	DMF/CH_3COONa	71
2		**3f**	DMF/CH_3COONa	77
2		**4a**	DMF:MeOH (8:5)/CH_3COONa	41
2		**4b**	DMF:MeOH (8:5)/CH_3COONa	32
2		**5**	DMF:MeOH (8:5)/CH_3COONa	46
2		**6a**	DMF:MeOH (8:5)/CH_3COONa	47
2		**6b**	DMF:MeOH (8:5)/CH_3COONa	79

2. Results and discussion

2.1. Synthesis and characterization of chromogenic tetrathiacalix[4]arenes

In this work, seven new diazo-coupled tetrathiacalix[4]arenes were synthesized by a weak base catalyzed coupling reaction of 25,26,27,28-tetrahydroxy-2,8,14,20-tetrathiacalix[4]arene **2** with diazotized solutions of aniline, 2-aminothiazole, 3-aminopyridine and β-naphthylamine (Scheme 1). The parent *p-tert*-butyltetrathiacalix[4]arene and tetrathiacalix[4]arene **2** were obtained by employing literature procedures.[4,19] The coupling reaction was performed at 0–5 °C in a mixed DMF/MeOH (8:5) solvent and sodium acetate as the base[11] followed by separation of the products by column chromatography to yield pure products in reasonable to good yields (Table 1). Detailed ^1H NMR spectral analysis of the synthesized compounds revealed that the phenylazo tetrathiacalix[4]arenes **3a–c** exhibited a singlet for the aromatic protons of the substituted tetrathiacalix[4]arene ring in the range δ 8.15–8.24 while protons on the unsubstituted aromatic tetrathiacalix[4]arene rings gave signals between δ 6.77–7.80. **3d** exhibited a singlet for the aromatic protons of the tetrathiacalix[4]arene ring at δ 8.24. Since sulfur bridges in the present compounds have replaced the methylene bridge



Scheme 1.

3a	$R_1=C_6H_5–N{=}N–$	$R_2, R_3, R_4=H$
3b	$R_1, R_3=C_6H_5–N{=}N–$	$R_2, R_4=H$
3c	$R_1, R_2, R_3=C_6H_5–N{=}N–$	$R_4=H$
3d	$R_1, R_2, R_3, R_4=C_6H_5–N{=}N–$	—
3e	$R_1, R_2, R_3, R_4=O_2N–C_6H_4–N{=}N–$	—
3f	$R_1, R_2, R_3, R_4=HOOC–C_6H_4–N{=}N–$	—
4a	$R_1=NSH_2C_3–N{=}N–$	$R_2, R_3, R_4=H$
4b	$R_1, R_2=NSH_2C_3–N{=}N–$	$R_3, R_4=H$
5	$R_1=C_5H_4N–N{=}N–$	$R_2, R_3, R_4=H$
6a	$R_1=C_{10}H_7–N{=}N–$	$R_2, R_3, R_4=H$
6b	$R_1, R_3=C_{10}H_7–N{=}N–$	$R_2, R_4=H$

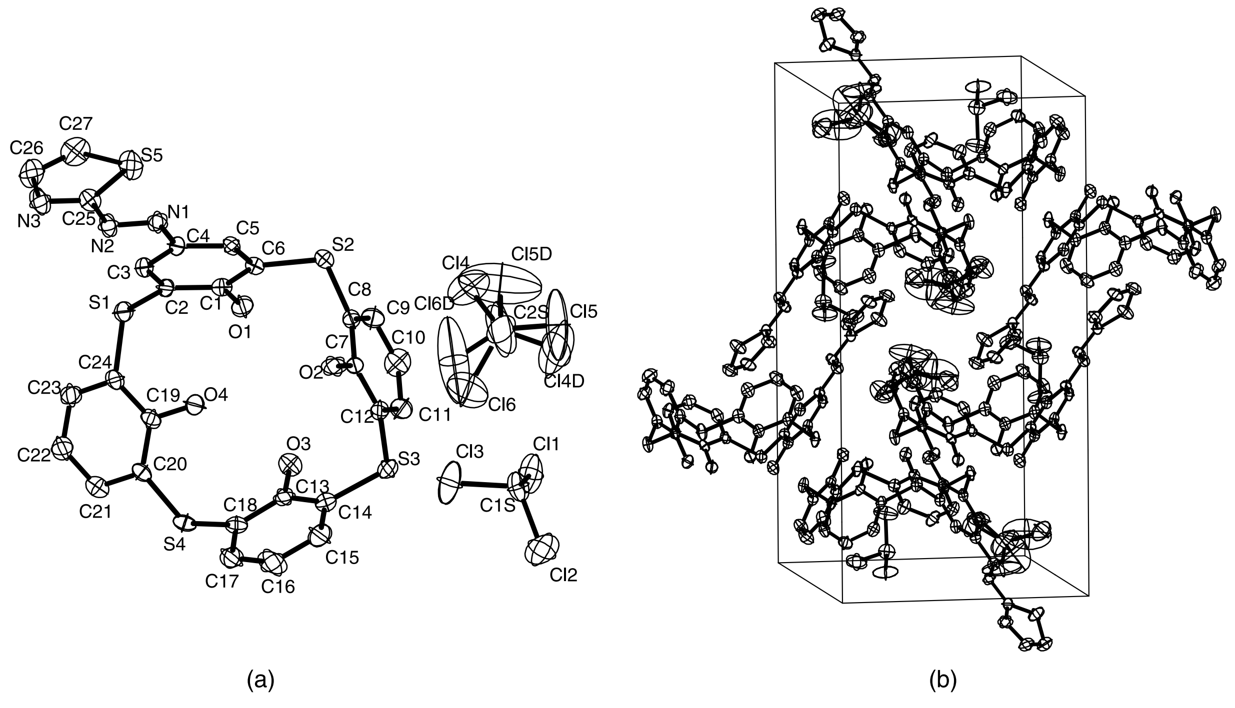
present in classical calixarenes, exact information regarding the conformation of these chromoionophores could not be obtained from ^{1}H NMR and ^{13}C NMR spectroscopic techniques. A single crystal X-ray of one of the derivatives (**4a**) revealed that the synthesized compound was present in the cone conformation. By analogy and comparison of the NMR spectral data, it appears that the other synthesized tetrathiacalix[4]arenes probably also have the cone conformation but X-ray structure determinations of compounds other than **4a** are yet to be achieved.

It was interesting to note that the solvent used for the coupling reaction has a profound effect on the outcome of the reaction, i.e., the extent of substitution as well as the yield of the final product obtained. For example, when DMF was employed instead of DMF-methanol in the coupling reaction, orange crystals of pure **3b** in far better yields (68%) were obtained in contrast to the yields obtained from the use of DMF-MeOH mixture (43%). In addition, the latter solvent afforded a mixture of **3a**, **3b** and **3c**.

The thiazoleazo coupled tetrathiacalix[4]arenes **4a** and **4b** exhibited a pair of doublets for the protons of the thiazole moiety in the range of δ 7.41 and 8.01 respectively. **4a** and **4b** were identified as cone conformers by a comparative study of their NMR patterns with those of known tetrathiacalix[4]arenes.[20] The pyridylazo substituted tetrathiacalix[4]arene exhibited a singlet at δ 9.06, a pair of doublets at δ 8.00 and 8.60, and a triplet at δ 7.34 for the protons of the 3-pyridylazo moiety and a singlet at δ 8.18 for the protons of the tetrathiacalixaryl aromatic ring bearing the 3-pyridylazo group and two multiplets for the tetrathiacalixaryl protons of the unsubstituted rings at δ 6.75 and 7.64. The characterization of the tetrathiacalix[4]arenes bearing β-naphthylazo substituents on the upper rim by NMR spectroscopic techniques proved difficult due to the complexity of the spectral data. However, elemental analysis and FAB MS spectroscopic measurements proved useful for identification of compounds **6a** and **6b**.

2.2. Results obtained from X-ray crystallography of 5-[(1-thiazole)azo]-25,26,27,28-tetrahydroxy-2,8,14,20-tetrathiacalix[4]arene, 4a

Recrystallization of **4a** from chloroform afforded crystals suitable for X-ray diffraction. It was found that **4a** crystallized with chloroform located outside the tetrathiacalixarene cavity with torsion angles ϕ and χ around Ar–S–Ar bonds about S1, S2, S3 and S4 as −89.3(3), 94.7(3), −94.5(3), 91.6(3), −86.6(3), 97.9(3), −97.4(3) and 87.4(3) respectively. The alternate ± sequence observed was consistent with the cone conformation found in parent *p-tert*-butyltetrathiacalix[4]arene[21] and tetrathiacalix[4]arene.[22] The unit cell of **4a** (Fig. 1) consisted of four molecules, each molecule having one chloroform molecule near the outer periphery of the tetrathiacalix[4]arene cavity. All four aromatic rings A (C1–C6), B (C7–C12), C (C13–C18) and D (C19–C24) were found to be almost planar with angles C2–S1–C24 = 101.62(14), C6–S2–C8 = 103.28(14), C12–S3–C14 = 101.31(15) and C18–S4–C20 = 101.94(15). The connecting sulfur atoms S1, S2, S3 and S4 formed an approximate plane where alternate sulfur atoms lay ±0.053 and ±0.053 Å above and below the plane. The interplanar angles found between this plane and the rings A (C1–C6), B (C7–C12), C (C13–C18) and D (C19–C24) were 57.66, 49.22, 61.91, and 50.97° respectively. The interplanar angles between the rings AC and BD were 60.43 and 79.81° respectively. The dihedral angle between the substituted azothiazole group plane was found to be 8.26°, which corroborated the alignment of the heterocyclic ring with the cone conformation of the tetrathiacalix[4]arene skeleton. The corresponding hydroxyl substituents O1, O2,



(a) (b)

Figure 1. (a) ORTEP diagram of **4a** showing labeling scheme used and (b) contents of a single unit cell.

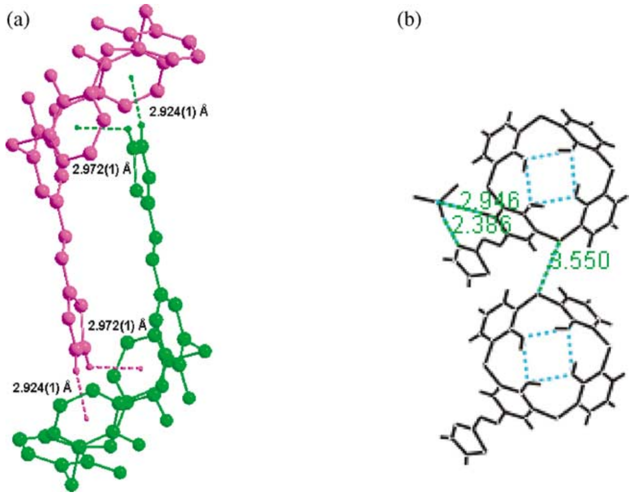


Figure 2. (a) CH–π interaction between two adjacent molecules and (b) H-bonding and S…S interactions in two molecules along *b* axis.

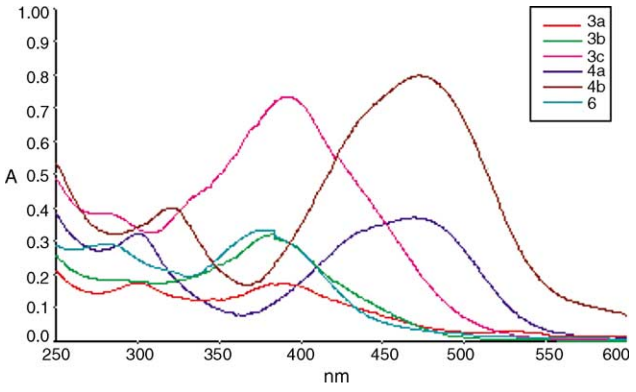


Figure 3. UV–visible spectra showing λ_{max} of chromoionophores **3a–c** and **4a**,**b**.

O3 and O4 were directed inwards the cavity of the calixarene architecture. The average distance between two oxygen atoms was 2.82 Å. Although one cannot exclude the stabilizing role of the solvent, the rather short distance between adjacent oxygen atoms might indicate the existence of an intramolecular H-bond array stabilizing the cone conformation. The average distance between two adjacent sulfur atoms was 5.51 Å which demonstrated that the size of the cavity in tetrathiacalix[4]arene was approximately 0.5 Å bigger than that in classical calix[4]arene. The exocyclic chloroform molecule showed three prominent non bonding interactions between the H of the chloroform molecule and the thiazole moiety attached to the ring A with average CH–π distances of 2.399, 2.473 and 2.944 Å respectively. The CH–π interaction between two adjacent tetrathiacalix[4]arene molecules is given in Fig. 2(a). There was significant S–S interaction between adjacent tetrathiacalix[4]arene molecules with a distance of 3.550 Å (Fig. 2(b)).

2.3. UV–visible spectroscopic studies of synthesized chromoionophores 3a–c and 4a,b.

In order to obtain insight into the metal affinity of the chromogenic tetrathiacalix[4]arenes, the changes in their λ_{max} upon interaction with a variety of hard and soft metal cations was investigated as follows:

2.3.1. Interaction with alkali and alkaline earth metal ions. The affinity of tetrathiacalix[4]arenes **3a–c** and **4a**,**b** for group I (Li^+, Na^+, K^+, Cs^+ and Rb^+) and group II (Ca^{2+}, Mg^{2+} and Ba^{2+}) cations was examined in solution using chloroform/methanol (1:1) as the solvent. Fig. 3 depicts the wavelengths of absorption of the different chromoionophores. The changes in λ_{max} of these chromoionophores upon addition of various cations are listed in Table 2. It has been observed that **3a–c** and **4a**,**b** exhibited

Table 2. $\Delta\lambda_{max}$/nm of the synthesized chromoionophores **3a–c** and **4a**,**b** on addition of 100 equiv. of metal salts using methanol–chloroform (v/v = 1/1) as the cosolvent

Metal salts	Blank solutions of ligands[a]							
	3a		**3b**	**3c**	**4a**		**4b**	
	298	389	378	392	301	469	320	473
λ_{max}/nm of chromoionophores after adding metal salts								
Li^+	*nc*	*nc*	*nc*	*nc*	+9	+10	−22	*nc*
Na^+	+21	+14	+19	*s*(329)	+18	+20	*nc*	+13
K^+	+6	+10	+21	*s*(332)	+13	+34	*nc*	+16
Cs^+	+21	+60	+91 (*np* at 320)	+61	+18	+55	+12	+54
Rb^+	+10	+73	+77 (*np* at 318)	+46	+18	+57	+12	+46
Mg^{2+}	+5	*nc*	*ns*	−19	*nc*	*nc*	−22	−43
Ca^{2+}	*nc*	*nc*	*ns*	*nc*	*nc*	−36	−20	*nc*
Ba^{2+}	+33	+12	+20 (*np* at 335)	*nc*	+25	+19	*nc*	*nc*
Sr^{2+}	*nc*	*nc*	*nc*	*nc*	*nc*	*nc*	*nc*	*nc*
Cr^{2+}	+51	+66	−39	−43	+90	−22	—	−67
Fe^{2+}	*ns*	*nc*	−41 (*np* at 293)	−14	*nc*	*nc*	−22	*nc*
Co^{2+}	+19	−17	−9	−24	+11	−44	*nc*	−51
Ni^{2+}	+24	*nc*	*s*(327)	−17	+16	−54	*nc*	−57
Cu^{2+}	*nc*	−26	−15	*nc*	*nc*	−46	*nc*	−50
Cd^{2+}	+7	*nc*	*nc*	−20	*nc*	*nc*	−20	−46
Hg^{2+}	+24	*nc*	*nc*	*nc*	+18	*nc*	*nc*	*nc*
Hg^+	+26	*ns*	*nc*	*nc*	+20	−20	*nc*	+17 *s*(554)
Ag^+	*nc*	*nc*	*nc*	*nc*	*nc*	*nc*	*nc*	*nc*
Pd^{2+}	*nc*	*nc*	*nc*	−45	+20	+148	*nc*	*s*(603)
Pt^{2+}	*nc*	*nc*	*nc*	*nc*	*ns*	*nc*	*nc*	*nc*

[a] Concentration for **3a–c** and **4a**,**b** was 10^{-4} M. + and − indicate bathochromic and hypsochromic shifts respectively. $\lambda_{max} = \lambda_{complex} - \lambda_{max}$ (free host). *nc* denotes no detectable change in λ_{max} upon metal ion complexation. *ns* indicates negligible shifts in λ_{max}. *np* indicates new peak position. *s* indicates shoulder in addition to the main peak.

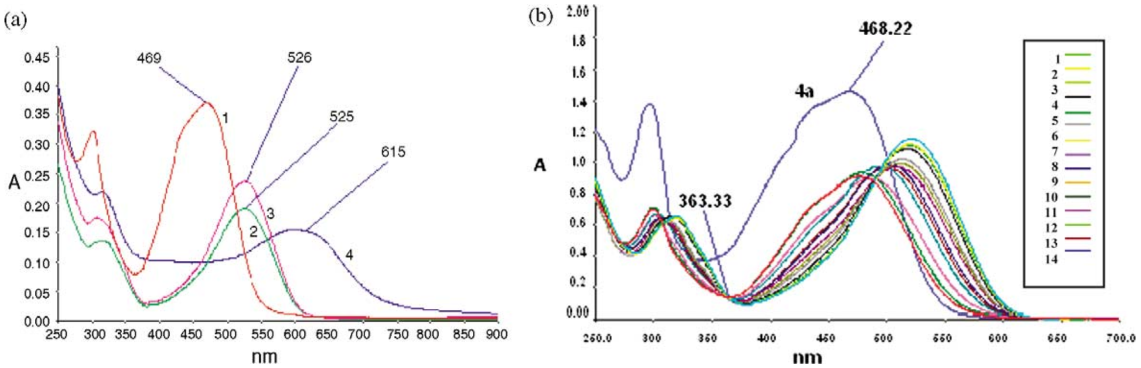


Figure 4. (a) UV–visible spectra of (1)10^{-4} M solution of **4a** and shifts in its λ_{max} upon the addition of 10^{-4} M solutions of (2) Cs_2CO_3, (3) Rb_2CO_3 and (4) K_2PdCl_4 in a Methanol–chloroform (v/v = 1/1) cosolvent; (b) changes in the UV–visible spectra of **4a** upon titration by Cs_2CO_3 in a methanol–chloroform (v/v = 1/1) cosolvent where the concentration of Cs_2CO_3 (1) 1×10^{-4} (2) 2×10^{-4} (3) 3×10^{-4} (4) 4×10^{-4} (5) 5×10^{-4} (6) 6×10^{-4} (7) 7×10^{-4} (8) 8×10^{-4} (9) 9×10^{-4} (10) 1×10^{-3} (11) 2×10^{-3} (12) 3×10^{-3} (13) 4×10^{-3} (14) 5×10^{-3}.

little or no shifts for the smaller alkali metal ions (Li^+ and Na^+) but significant bathochromic shifts were observed in the case of larger alkali metal ions (Cs^+ and Rb^+) indicating that the availability of the required number of donor oxygen atoms is not the major factor for the interaction of alkali metal cations and the synthesized tetrathiacalix[4]arenes. The cavity size of these azo coupled tetrathiacalix[4]arenes seems to have been affected by somewhat restricted conformational isomerization which fails to provide appropriate binding sites for relatively smaller alkali metal ions. For example, **3b** showed bathochromic shifts of 91 and 77 nm with concomittant appearance of new peaks at 320 and 318 nm respectively in their UV spectra on addition of solutions of Cs_2CO_3 and Rb_2CO_3 in methanol/chloroform. Significant bathochromic shifts in the absorption maximum were accompanied by significant colour changes in the visible region. For instance when UV–visible spectral measurements were carried out for interaction of **4a** with Cs^+ and Rb^+ by addition of Cs_2CO_3 and Rb_2CO_3 in chloroform/methanol to the chloroform–methanol solution of **4a** (Fig. 4(a)), it revealed that absorption of **4a** shifted from 468 to 524 nm with an isobestic point at 365 nm. Quantitative analysis through Job's continuous variation plots indicated that the metal:tetrathiacalix[4]arene interaction was in a 1:1 stoichiometric ratio of **4a** with Cs(I) and Rb(I).

Since significant shifts were not observed in the case of the smaller alkali metal ions and alkaline earth metal cations with the synthesized tetrathiacalix[4]arenes, they seemed to have good potential to be developed into molecular filters for ionic separations.

2.3.2. Interaction with transition metal ions.

An investigation into the ionic recognition properties (Table 2) of synthesized chromoionophores with transition metal ions (Cr^{3+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Hg^+, Hg^{2+}, Pd^{2+} and Pt^{2+}) was also investigated but surprisingly significant interaction was not observed despite the fact that sulfur containing molecular receptors should be expected to exhibit pronounced changes on interaction with transition metal ions. A marked bathochromic shift was however observed when a chloroform/methanol (1:4) solution of K_2PdCl_4 was added to **4a** (Fig. 4(a)), which was accompanied by a visual change from yellow to bluish green. This observation revealed a change in the coordination sphere of palladium in the presence of tetrathiacalix[4]arene, **4a**. The absorption intensity of the free tetrathiacalix[4]arene at 468 nm was found to gradually decrease in intensity with the formation of a new absorption band at 617 nm ($\Delta\delta = 148$ nm). This observation is consistent with the earlier observation that complexes of palladium with thioethers exhibit a typical blue or green colour due to a d–d transition around 610 nm.[23] Two isobestic points at 363 and 414 nm could be easily discerned from the UV–visible titration spectra of **4a** with K_2PdCl_4 (Fig. 5(a)). The spectral features in the figure are consistent with a 1:2 binding of 4a

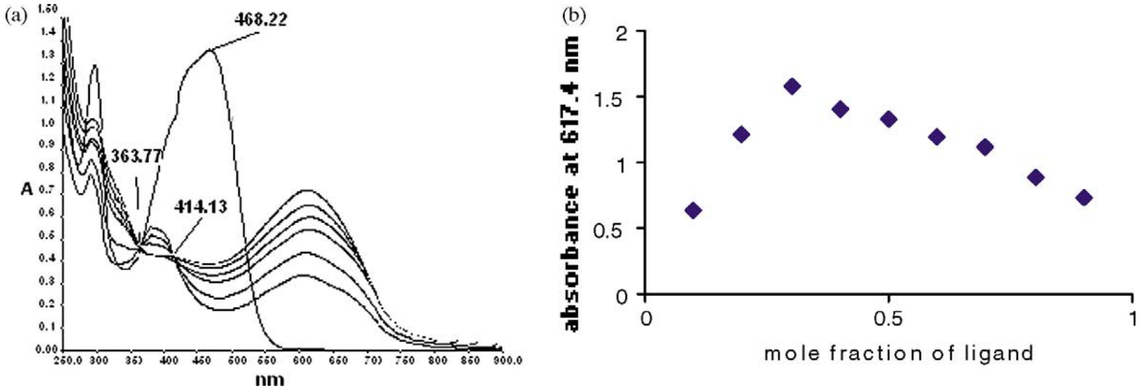


Figure 5. (a) Changes in the UV–visible spectra of 10^{-4} M solution of **4a** upon titration by K_2PdCl_4 in a methanol–chloroform (v/v = 1/1) cosolvent where the concentration of K_2PdCl_4 varies from 2 to 8×10^{-4} M and (b) Job plot of 2:1 complex of **4a** and Pd^{2+}.

and Pd^{2+}. Analysis of the molar ratio as well as data from Job's plot experiment (Fig. 5(b)) confirmed a 1:2 binding ratio of **4a** with Pd^{2+}. The coordination of palladium may be visualized through metal–oxygen or through metal–sulfur interactions besides the cavity of the tetrathiacalix[4]arene core although a possible coordination mode through the N=N bonds is not ruled out. Knowledge of the exact coordination mode of palladium would require further investigations. Since negligible or small hypsochromic shifts were observed in the case of other transition metal ions, no quantitative experiments were carried out for these chromoionophores.

3. Experimental

All the reagents used in the study were purchased from Sigma-Aldrich or Merck and were chemically pure. The solvents used were distilled or dried according to the requirement. Column chromatography was performed on silica gel (60–120 mesh) obtained from Merck. Melting points were recorded on an electric melting point apparatus (Toshniwal, India) and are uncorrected. ^{1}H NMR spectra were recorded on a 300 MHz Bruker DPX 300 instrument at room temperature using tetramethylsilane (TMS) as an internal standard. X-ray data was 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.

3.1. Preparation of the starting materials

p-tert-Butyltetrathiacalix[4]arene[4] and tetrathia calix[4]arene[19] **2** were synthesized by methods reported earlier.

3.1.1. Synthesis of 5-[(1-phenyl)azo]-25,26,27,28-tetrahydroxy-2,8,14,20-tetrathiacalix[4]arene (3a) and 5,11,17-*tris*[(1-phenyl)azo]-25,26,27,28-tetrahydroxy-2,8,14,20-tetrathia calix[4]arene (3c). *General procedure*. A solution of phenyl diazonium chloride prepared from aniline (1.396 g, 15.0 mmol), sodium nitrite (0.69 g, 10.0 mmol) and conc. HCl (7 mL) in water (25 mL), was added slowly into a cold (5 °C) solution of tetrathiacalix[4]arene (0.5 g, 1.0 mmol) and sodium acetate trihydrate (2.72 g, 20 mmol) in MeOH-DMF (15 mL, 5:8, v/v) to give an orange suspension. After allowing it to stand for 3 h at room temperature, the suspension was acidified with aqueous HCl (50 mL, 2 M). The resulting red precipitate was filtered and washed with water and methanol to yield a crude product which was purified by column chromatography on silica gel using chloroform to give **3a** (0.22 g, 37%, $R_f=0.60$) as a bright yellow solid and **3c** (0.20 g, 25%, $R_f=0.34$) as a red powder.

*Compound **3a***: mp 208 °C. Anal. Calcd for $C_{30}H_{20}N_2O_4S_4$: C, 59.98; H, 3.36; N, 4.66. Found: C, 60.02; H, 3.51; N, 4.58.]. ^{1}H NMR (300 MHz, $CDCl_3$) δ_H 9.42 (s, 4H, –OH); 8.22 (s, 2H, tetrathiacalixarene ArH); 7.82 and 7.46 (m, 5H, phenylazo ArH); 7.70 (d, 2H, $J=6$ Hz, tetrathiacalixarene ArH); 7.63 (d, 4H, $J=6$ Hz, tetrathiacalixarene ArH); 6.72–6.80 (m, 3H, tetrathiacalixarene ArH). MS-FAB: calcd for $C_{30}H_{20}N_2O_4S_4$: $m/z=600.75$ [M^+]; found: $m/z=601$ [M^+, 90%].

*Compound **3c***: Anal. Calcd for $C_{42}H_{28}N_6O_4S_4$: C, 62.36; H, 3.49; N, 10.39. Found: C, 62.52; H, 3.67; N 10.30. ^{1}H NMR (300 MHz, $CDCl_3$) δ_H 9.43 (s, 4H, –OH); 8.24 (s, 4H, tetrathiacalixarene ArH); 8.16 (s, 2H, tetrathiacalixarene ArH); 7.77 (m, 6H, phenylazo ArH); 7.65 (d, 2H, $J=7.6$ Hz, tetrathiacalixarene ArH); 7.39 (m, 9H, phenylazo ArH); 6.76 (t, 1H, $J=15.4$ Hz, tetrathiacalixarene ArH). MS-FAB: calcd for $C_{42}H_{28}N_6O_4S_4$: $m/z=808.97$ [M^+]; found: $m/z=809$[M^+, 42%].

3.1.2. Synthesis of 5,17-bis[(1-phenyl)azo]-25,26,27,28-tetrahydroxy-2,8,14,20-tetrathiacalix[4] arene (3b). A solution of aniline diazonium chloride, which was prepared from aniline (1.396 g, 15.0 mmol), sodium nitrite (0.69 g, 10.0 mmol) and conc. HCl (7 mL) in water (25 mL) was added slowly into a cold (5 °C) solution of tetrathiacalix[4]arene (0.5 g, 1.0 mmol) and sodium acetate trihydrate (2.72 g, 20 mmol) in DMF (15 mL) to give an orange suspension. After being allowed to stand for 3 h at room temperature, the suspension was acidified with aqueous HCl (50 mL, 2 M). The resulting red precipitate was filtered, washed with water and methanol and dried to yield (0.36 g, 68%) of **3b** as a bright yellow solid. Anal. Calcd for $C_{36}H_{24}N_4O_4S_4$: C, 61.34; H, 3.43; N, 7.95. Found: C, 61.28; H, 3.54; N, 8.01. ^{1}H NMR (300 MHz, $CDCl_3$) δ_H 9.37 (s, 4H, –OH); 8.15 (s, 4H, tetrathiacalixarene ArH); 7.75 (m, 4H, phenylazo ArH); 7.66 (d, 4H, $J=7.4$ Hz, tetrathiacalixarene ArH); 7.38 (m, 6H, phenylazo ArH); 6.77 (t, 2H, $J=15.3$ Hz, tetrathiacalixarene ArH). MS-FAB calcd for $C_{36}H_{24}N_4O_4S_4$: $m/z=704.86$ [M^+]; found: $m/z=705$ [M^+, 47%].

3.1.3. Synthesis of 5,11,17,23-tetrakis[(1-phenyl)azo]-25,26,27,28-tetrahydroxy-2,8,14,20-tetrathiacalix[4]-arene (3d). A solution of aniline diazonium chloride, which was prepared from aniline (1.396 g, 15.0 mmol), sodium nitrite (0.69 g, 10.0 mmol) and conc. HCl (7 mL) in water (25 mL) was added slowly into a cold (5 °C) solution of tetrathiacalix[4]arene (0.5 g, 1.0 mmol) and sodium hydroxide (0.8 g, 20 mmol) in MeOH-DMF (15 mL, 5:8, v/v) to give a dark red suspension. After being allowed to stand for 3 h at room temperature, the suspension was acidified with aqueous HCl (50 mL, 2 M). The resulting brownish precipitate was filtered and washed with water and methanol to give (0.68 g, 74%) of **3d** as a light brown solid. Anal. Calcd for $C_{48}H_{32}N_8O_4S_4$: C, 63.14; H, 3.53; N, 12.27. Found: C, 63.21; H, 3.67; N, 12.12. ^{1}H NMR (300 MHz, $CDCl_3$) δ_H 9.41 (s, 4H, –OH); 8.24 (s, 8H, tetrathiacalixarene ArH); 7.37–7.77 (m, 20H, phenylazo ArH). MS-FAB calcd for $C_{48}H_{32}N_8O_4S_4$: (m/z)=913.08 [M^+]; found: $m/z=913$ [M^+, 34%].

3e and **3f** were synthesized according to the literature procedures.[12]

3.1.4. Synthesis of 5-[(1-thiazole)azo]-25,26,27,28-tetrahydroxy-2,8,14,20-tetrathia calix[4]arene (4a) and 5,11-bis[(1-thiazole)azo]-25,26,27,28-tetrahydroxy-2,8,14,20-tetrathiacalix[4]arene (4b). Compounds **4a** and **4b** were prepared as described above for **3a** using 2-aminothiazole. Column purification using chloroform/ethyl acetate (9:1) gave **4a** (0.25 g, 41%, $R_f = 0.68$) as dark red crystals and **4b** (0.23 g, 32%, $R_f = 0.31$) as a dark red powder. It should be noted that products formed under these condition do not contain complexed chloroform.

*Compound **4a***: mp > 250 °C. Anal. Calcd for $C_{27}H_{17}N_3O_4S_5$: C, 53.36; H, 2.82; N, 6.91. Found: C, 53.25; H, 2.67; N, 7.01. ^1H NMR (300 MHz, $CDCl_3$) δ_H 9.37 (s, 4H, –OH); 8.34 (s, 2H, tetrathiacalixarene ArH); 8.02 (bs, 1H, thiazole ArH); 7.70 and 6.82 (m, 6H and 3H, tetrathiacalixarene ArH); 7.41 (bs, 1H, thiazole ArH).

*Compound **4b***: mp 170 °C. Anal. Calcd for $C_{30}H_{18}N_6O_4S_6$: C, 50.12; H, 2.52; N, 11.69. Found: C, 50.28; H, 2.34; N, 11.57. ^1H NMR (300 MHz, $CDCl_3$) δ_H 8.41 (s, 2H, tetrathiacalixarene ArH); 8.36 (s, 2H, tetrathiacalixarene ArH); 8.01 (bs, 2H, thiazole ArH); 7.70 (d, 2H, $J = 7.8$ Hz, tetrathiacalixarene ArH); 7.64 (d, 2H, $J = 7.5$ Hz, tetrathiacalixarene ArH); 7.41 (bs, 2H, thiazole ArH); 6.89 (t, 2H, $J = 14.8$ Hz, tetrathiacalixarene ArH).

3.1.5. Synthesis of 5-[(3-pyridyl)azo]-25,26,27,28-tetrahydroxy-2,8,14,20-tetrathia calix[4]arene (5). It was prepared as described above for **3a** using 3-aminopyridine. Column purification using chloroform/ethyl acetate (8:2) gave **5** (0.36 g, 59%, $R_f = 0.66$) as an orange solid. Anal. Calcd for $C_{29}H_{19}N_3O_4S_4$: C, 57.88; H, 3.18; N, 6.98. Found: C, 57.65; H, 3.20; N, 6.93. ^1H NMR (300 MHz, $CDCl_3$) δ_H 9.40 (s, 4H, –OH); 8.18 (s, 2H, tetrathiacalixarene ArH); 9.06 (s, 1H, pyridylazo ArH); 7.34 (t, 1H, $J = 15$ Hz, pyridylazo ArH); 8.60 (d, 1H, $J = 7.7$ Hz, pyridylazo ArH); 8.00 (d, 1H, $J = 7.7$ Hz, pyridylazo ArH); 6.75 and 7.64 (m, 9H, tetrathiacalixarene ArH), MS-FAB calcd for $C_{29}H_{19}N_3O_4S_4$: $m/z = 601.74$ [M^+]; found: $m/z = 602$ [M^+, 88%].

3.1.6. Synthesis of 5-[(β-naphthyl)azo]-25,26,27,28-tetrahydroxy-2,8,14,20-tetrathia calix[4]arene (6a) and 5,17-bis[(1-phenyl)azo]-25,26,27,28-tetrahydroxy-2,8,14,20-tetrathia calix[4]arene (6b). **6a** and **6b** were prepared as described above for **3a** using β-naphthylamine. Column purification using chloroform/hexane (1:1) gave **6a** (0.31 g, 47%, $R_f = 0.68$) as a dark red solid and **6b** (0.64 g, 79%, $R_f = 0.39$) as a maroon coloured powder.

*Compound **6a***: mp 192 °C. Anal. Calcd for $C_{34}H_{22}N_2O_4S_4$: C, 62.75; H, 3.41; N, 4.30. Found: C, 62.66; H, 3.39; N, 4.49. ^1H NMR (300 MHz, $CDCl_3$) δ_H 9.37 (s, 4H, OH); 8.20 (s, 2H, tetrathiacalixarene ArH); 6.74 and 7.83 (m, 9H, tetrathiacalixarene ArH); 7.45–7.57 and 7.88–8.13 (m, 7H, β-naphthylazo ArH) MS-FAB calcd for $C_{34}H_{22}N_2O_4S_4$: $m/z = 650.81$ [M^+]; found: $m/z = 651$ [M^+, 50%].

*Compound **6b***: mp 161 °C. Anal. Calcd for $C_{44}H_{28}N_4O_4S_4$: C, 65.65; H, 3.51; N, 6.96. Found: C, 65.81; H, 3.66; N, 6.84. ^1H NMR (300 MHz, $CDCl_3$) δ_H 9.37 (s, 4H, OH); 8.65 (s, 4H, tetrathiacalixarene ArH); 7.74 (d, 4H, $J = 7.7$ Hz, tetrathiacalixarene ArH); 7.38–7.60 and 7.92–8.06 (m, 14H, β-naphthylazo ArH); 6.80 (t, 2H, $J = 15.1$ Hz, tetrathiacalixarene ArH). MS-FAB calcd for $C_{44}H_{28}N_4O_4S_4$: $m/z =$ 804.98 [M^+]; found: $m/z = 804$ [M^+, 49%].

3.2. Crystallography

The crystals suitable for single crystal X-ray diffraction were obtained by slow cooling of a warm solution of **4a** in chloroform. Dark red crystals of a 1:1 **4a**. chloroform complex were obtained with molecular formula $C_{29}H_{18}Cl_6$-$N_3O_4S_5$, $M = 845.46$, monoclinic, space group P2(1)/n with $a = 10.9745(7)$, $b = 22.1150(14)$, $c = 14.8313(9)$, $\alpha = 90.0$, $\beta = 90.96(10)$, $\gamma = 90.0°$ and $D_c = 1.560$ g/cm^3 for $Z = 4$. Intensity diffraction data were calculated up to $\theta = 26.86°$ by using 2ω step scanning mode with Mo Ka radiation $\lambda = 0.71073$ Å) at 273 K. A total of 6693 reflections were calculated and used in structure analysis and refinement. All the non-hydrogen atoms were refined anisotropically using restraints on the bond lengths and thermal parameters. All hydrogen atoms were placed in their geometrical positions and were not refined. The labeling scheme followed is in agreement with that followed in calix[4]arene–solvent host guest complexes.[24,25] The final R index using observed data, refining 455 parameters with no restraints was $R_{all} = 0.0769$, $R_{gt} = 0.0569$, $wR_{ref} = 0.1808$ and $wR_{gt} = 0.1677$. Low e.s.d.'s for other atoms suggest that the overall geometry and accuracy of the structure has not been compromised to any significant extent. All the calculations involving structure solution, using SHELXTL-PC performed refinement and graphics. Crystallographic data for the structure have been deposited with Cambridge Crystallographic Database as supplementary publication number CCDC 280307.

3.3. General procedure for UV–visible experiments

Because of the poor solubility of metal salts in chloroform, all of the UV–visible experiments reported in this work were carried out in chloroform–methanol (1:1) unless otherwise specified.

3.3.1. Job's plot experiments. Stock solutions of compound **4a** (10^{-4} M) in chloroform–methanol (1:1) and metal salt solutions Cs_2CO_3 (10^{-4} M), Rb_2CO_3 (10^{-4} M) in chloroform–methanol (1:1) and K_2PdCl_4 (10^{-4} M) in chloroform–methanol (1:4) were prepared. The concentrations of each chloroform–methanol solutions were varied, but their volumes were fixed at 5.0 mL. After the mixture was shaken for 2 min, the UV–visible absorbances at 524 nm for Cs_2CO_3, 526 nm for Rb_2CO_3 and at 617 nm for K_2PdCl_4 were recorded. Assuming that only one complex (ML_n) was formed at equilibrium; the value of 'n' could be calculated from the plot of χ_{max} [mole fraction of the ligand (χ_L) at maximum absorption] by the following relationship, $n = \chi_{max}/1 - \chi_{max}$. The value of χ_{max} was noted from the plot of absorbance vs χ_L.

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