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Synthesis and characterization of linear molecular assembly of crystalline calix[4]arenes dithianes

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ABSTRACT

A family of six new variously substituted calix[4]arene dithianes has been prepared from respective formyl and acetyl derivatives. Shorter reaction time, mild conditions, and facile isolation of desired products are attractive features of the described method. The new 1,2-dithiane derivatives have been characterized by ^{1}H NMR, ^{13}C NMR spectroscopy, and FABMS analysis. The crystal structure of one of the acetyl calix[4]arene dithiane was determined by X-ray diffraction analysis, which revealed a dithiane capped linear molecular organization. Preliminary evaluation of bis (dithiane) calix[4]arene derivatives as molecular receptor for transition metal ions has revealed strong interaction with Hg^{2+} in 1:1 stoichiometry.

1. Introduction

Calix[*n*]arenes are useful macrocyclic substrates for obtaining a variety of cavity containing multifunctional molecular hosts to usher advances in separation science and technology.[1] Their preorganized molecular framework can provide electron rich or electron deficient cavities through appropriate functionalization as per requirements. Recent advances in calixarene chemistry have indicated their potential for self-organization to yield nanometer structures for use in molecular devices through cooperative intermolecular interactions.[2,3] Several reports have shown specific self-assembling calixarenes through[4–7] coordination bonds,[4] hydrogen bonds,[5] and ionic bonds[6] to promise calixarene based fibers,[7] micelles,[8] films,[9] and liquid crystals[7,10–14] to unravel mechanisms of molecular recognition and assembly.

Calix[4]arenes with appended or pendant heterocyclic groups can be considered as useful latent hosts for toxicant recognition and separation. In the past, calixarenes with oxygen, nitrogen, or phosphorous binding sites have been widely employed for complexation of group I and II metal ions[15] but very little work seems to have been published on the preparation of calixarene derivatives, which coordinate through other heteroatoms[16–21] or when heterocyclic ring is directly linked to the upper rim of calixarenes. Such compounds are particularly important if selectivity is desired to deal with heavy toxic metals (e.g., Hg, Pb, Cd) present in the environment. Previous work from our lab[22] as well as research work of other groups clearly evinces the fact that calix[4]arenes with sulfur based functionalities exhibit sufficiently selective binding for heavy metal ions. For instance, Hg^{2+} and Pd^{2+} selective calix[4]arene derivatives with *N* and *S* containing heterocyclic moieties and Pb^{2+} selective thiazoleazo tetrathiacalix[4]arene and nitrophenylazo tetrathiacalix[4]arene exhibiting selective binding toward Ag^{+} ion have been reported by our group. Similarly, Yordanov et al.[23] have determined that thiol (RSH), thioether (RSR′), and dithiocarbamate (R_2NCS^{2-}) groups when attached to calix[4]arene skeleton provide remarkable selectivities for heavy metal ions. Yoon and Kim[24] have reported that sulfur containing cyclic compound 5,11,17,23-bis[(2,2′-thioxydi-(*O*-phenylene)dithioxy)diphenylthio] calix[4]arene forms a 2:1 complex with Ag^{+} ions. Following this theme, we have developed a method for fusing *S*-containing five-membered heterocyclic ring onto the upper rim of calix[4]arenes. This choice was made not only because of strong affinity of sulfur for soft metal ions such as Hg^{2+}, Pb^{2+}, Au^{3+}, and Ag^{+} but also for masking the carbonyl compounds as thioacetals, which can be utilized for further structural elaboration of calixarenes through C–C bond formation.[25] The thianes could also be used as intermediates for conversion of the carbonyl function to the parent hydrocarbons by reductive desulfurisation.[26] In this paper, we report the synthesis of mono-, di-, and, tetrasubstituted dithiane derivatives of formyl and acetyl calix[4]arenes for evaluating some of the mentioned issues. The molecular architecture generated by calix[4]arene dithiane **5b** in its solid state furthers our understanding about basic concepts required for designing highly selective and functional supramolecular systems for toxicant analysis and separation.

2. Results and discussion

2.1. Thioacetalisation of formylcalix[4]arenes

The reaction pathway explored to fuse five-membered sulfur substituted heterocyclic ring on the upper rim of calix[4]arenes is

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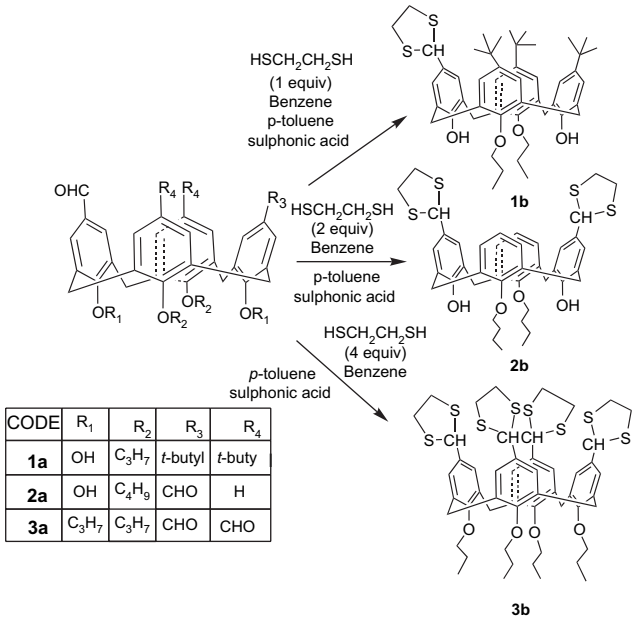


CODE	R_1	R_2	R_3	R_4
1a	OH	C_3H_7	*t*-butyl	*t*-buty
2a	OH	C_4H_9	CHO	H
3a	C_3H_7	C_3H_7	CHO	CHO

Scheme 1. Thioacetalisation of formyl calix[4]arene.

depicted in Scheme 1. The experimental procedure adopted for thioacetalisation is remarkably simple and involves the condensation of the formyl calix[4]arene with 1,2-ethanedithiol. The requisite starting compounds represented by mono-, di- and tetraformylated calix[4]arene were prepared according to the method published by us recently.[10c,27] Synthesis of monosubstituted calix[4]arene 1,2-dithiane has been achieved by treatment of monoformylated calix[4]arene with stoichiometric amount of 1, 2-ethanedithiol in benzene in the presence of catalytic amount of *p*-toluenesulphonic acid for 1 h with simultaneous removal of water molecule to afford dithiane appended calix[4]arene **1b** in good yield (77%). The reaction when repeated with calix[4]arenes substituted with two and four formyl groups also resulted in their complete transformation to 1,2-dithianes in excellent yields. The structure of **1b**–**3b** was established by FABMS, elemental analysis, and ^{1}H NMR spectrum, which was further supported by ^{13}C NMR and DEPT-135 analysis. For example, the ^{1}H ($CDCl_3$) spectrum of **3b** (Fig. 1) revealed a significant upfield shift of the characteristic peak of methine protons (ArCH) from δ 9.78 to 5.48 and a pair of multiplets at δ 3.23 and 3.37 that could be assigned to SCH_2 protons. The assigned structure was further confirmed by FABMS, which revealed a molecular ion peak at m/z 1009 (calcd mass 1009.58). A typical AB pattern for methylene bridge protons (δ 3.08 and 4.33) in its ^{1}H NMR and a resonance signal at δ 30.84 in the ^{13}C NMR spectrum revealed that **3b** is in a cone conformation.

2.2. Thioketalisation of acetyl calix[4]arene

The compatibility of the methodology was demonstrated by thioketalisation of calix[4]arenes ketones (**4**–**6**)**a**. The required starting materials **5a** and **6a** were obtained by applying the literature procedures.[28] The monoacetyl substituted tetrapropoxycalix[4]arene **4a** was synthesized by selective Friedel–Crafts acylation using acetyl chloride in the presence of a mild Lewis acid, $BF_3\cdot Et_2O$ as catalyst. Following the described experimental protocol for thioacetalisation, calix[4]arenes (**4**–**6**)**a** were further treated with 1,2-ethanedithiol to give mono-, di- and tetradithiane substituted calix[4]arene (**4**–**6**)**b**, respectively (Scheme 2). These compounds were easily characterized by the resonance signals obtained for the methyl protons of the thioketal ring. For instance, in compound **5b** (Fig. 2), CH_3 protons attached to thioketal ring resonate at δ 2.1 whereas in **5a** it appear at δ 2.6. Methylene bridge protons showed splitting pattern similar to that documented for the cone conformation. ^{13}C NMR and DEPT-135 further assisted in the characterization process. The presence of resonance signal at δ 40.1 for SCH_2 carbon indicated the attachment of dithiane ring to the calix[4]arene framework.

Since the ^{13}C NMR spectrum for the methylene bridge carbons showed resonances at δ 37.96 and 30.37, the conformation of tetradithiane **6b** was established as partial cone in consonance with earlier studies in calixarenes.[1]

Structure of **5b** was further proved by the analysis of its single crystal X-ray diffraction. Slow evaporation of its chloroform–methanol solution gave needle shaped crystals with space group $P21/n$ (Fig. 3).

The methylene carbon atoms (C7, C14, C21, and C28) in **5b** form an interplanar approximate plane where alternate carbon atoms lie $\pm$0.118 Å and $\pm$0.121 Å above and below the plane. The torsion angles φ and χ around $ArCH_2Ar$ bonds about C7, C14, C21, C28 are $-$103.35°, 79.03°, $-$77.36°, 99.24°, $-$105.35°, 77.20°, $-$77.14°, 100.72°, respectively. This sequence ($-+-+-+-+$) is consistent with the cone conformation as was found in the parent *p*-*tert*-butylcalix[4]arene.[1b,29] The inclination angles for the sequential aromatic groups with respect to plane through methylene carbons was found to be 47.02°, 72.47°, 40.95°, 67.40° revealed a significant deviation from coplanarity of aromatic rings. This may be due to repulsion among the substituents present both at the lower and the upper rims. An intramolecular hydrogen bond, which links phenolic protons to ether oxygen atoms stabilize the cone conformation. It has been observed that the repulsion between the alkoxy fragment tilts the rings B and D toward inside the cavity of the macrocycle. Phenolic rings (A and C) are oriented nearly orthogonal to each other and the interplanar angles between the pairs AC and BD are 87.92° and 40.13°. The orientation of the two dithiane rings seem to allow interaction of one of the heterocyclic moiety with adjacent calix[4]arene cavity as if it is capped by the second calix[4]arene (Fig. 4) molecule. The attraction leading to the

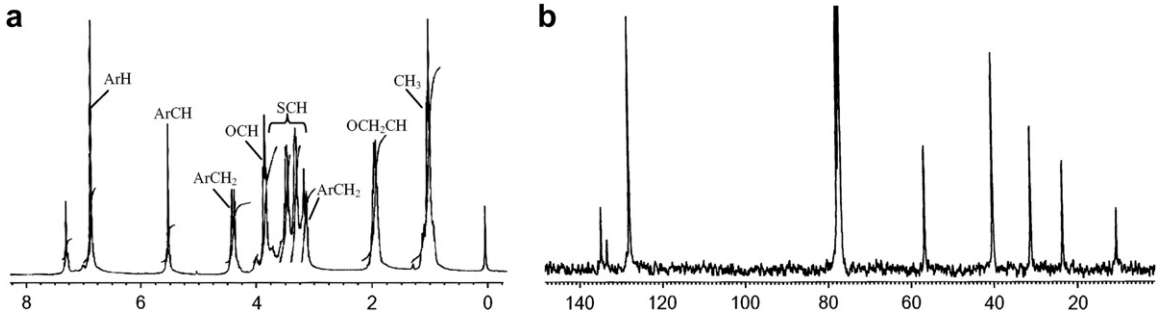
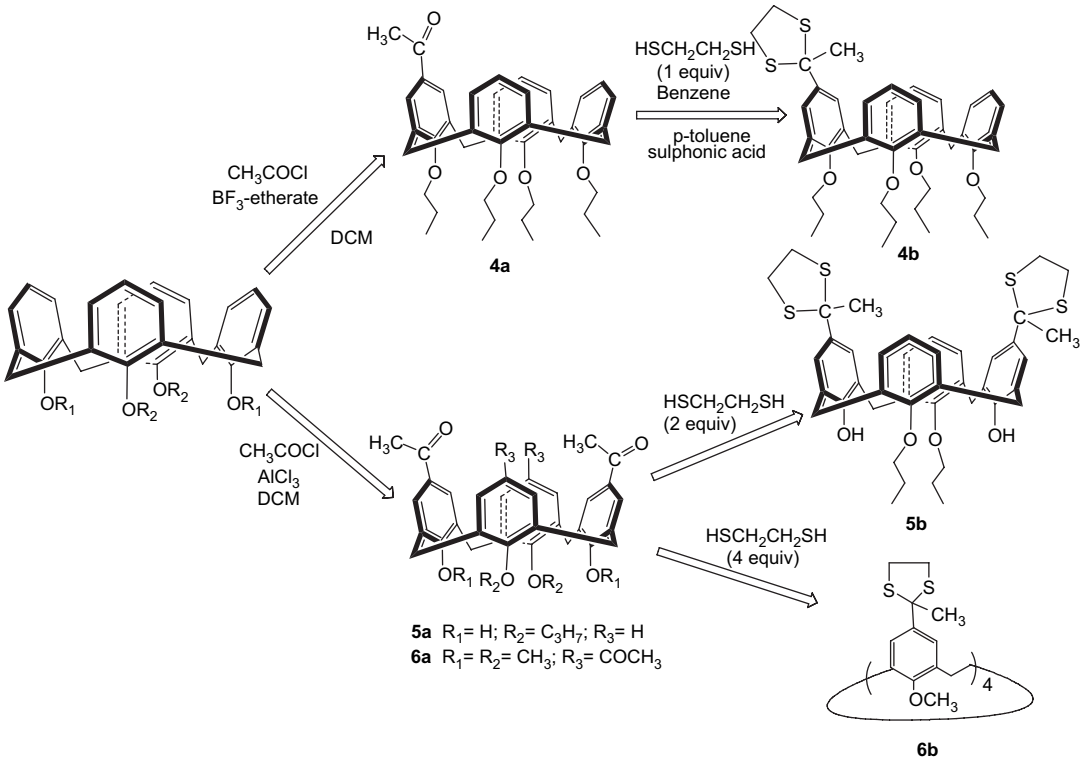


Figure 1. (a) ^{1}H NMR spectra of **3b**; (b) ^{13}C NMR spectra of **3b**.



Scheme 2. Thioacetalisation of acetyl calix[4]arene.

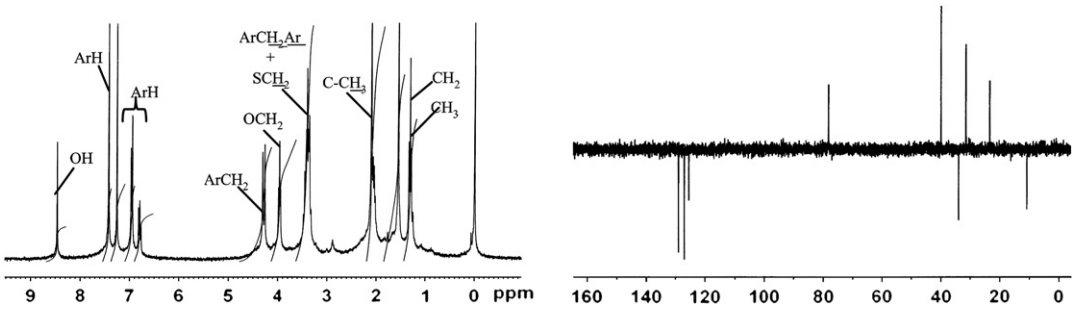


Figure 2. ^{1}H and DEPT-135 NMR spectra of **5b**.

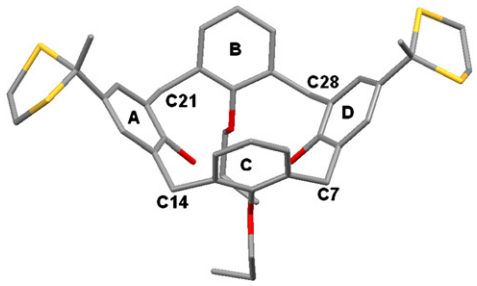


Figure 3. X-ray crystal structure of **5b**. Chloroform molecule and hydrogens are omitted for clarity.

supramolecular structure seems to be stabilized by weak intermolecular interactions between S and S···H–CH_2 groups shown in green (S···H distance is 2.851(9) Å) and two CH/π interactions among S–CH_2 hydrogens and the aromatic rings shown in blue [*r*(H···C) being 2.737(6) Å and 2.819(3) Å] (Fig. 4). Subsequent zigzag channel is adopted by calix[4]arene dithiane. The molecule seems to accommodate chloroform in the continuous channels in the crystal lattice. The Cl in the chloroform molecule is disordered at two cystallographically independent positions and the solvent molecule seemed to reside outside the concave cavity of calix[4]-arene molecule to be responsible for holding two independent chains of dithiane capped linear molecular assembly representing the supramolecular architecture (Fig. 5). The four independent molecules of **5b** can form a spherical cage, which can include two $CHCl_3$ molecules (Fig. 4c).

2.3. Interaction with toxic metal ions

In order to ascertain the utility of some of the synthesized calixarene dithiane derivatives for toxic metal ion analysis, preliminary study of the ionophoric response of **2b** was investigated by examining its UV–vis absorption behavior in the presence of transition metal ions (Pb^{2+}, Cr^{3+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cd^{2+}, Hg^{2+}, and Hg_2^{2+}). Stock solution of **2b** (1×10^{-4}) and transition metal ions (1×10^{-4}) were prepared in $CHCl_3$–MeOH (1:1). Ionophore **2b** was determined to show a strong absorption band at 296 nm apparently corresponding to π–π* transition and a weak band at 450 nm. Upon addition of Hg^{2+} in $CHCl_3$–MeOH, the absorption intensity at 450 nm observed for **2b** increased significantly and the band at

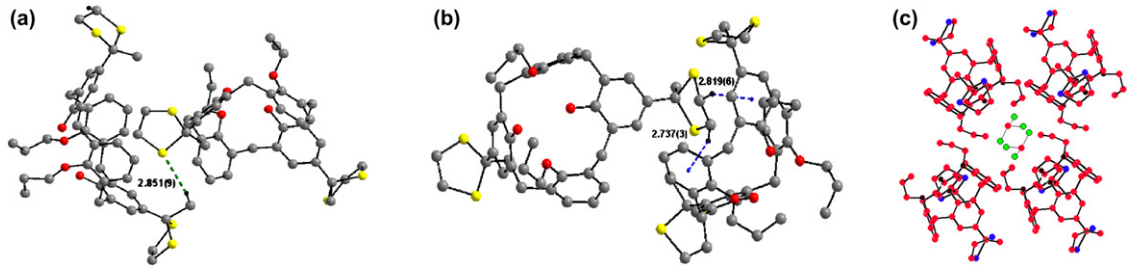


Figure 4. View of calix[4]arene (**5b**) dimer illustrating the inter-cavity interactions: (a) CH–π interactions; (b) interactions between S and C–H hydrogen; (c) self assembling of **5b** tetramer with two chloroform guest molecules in between.

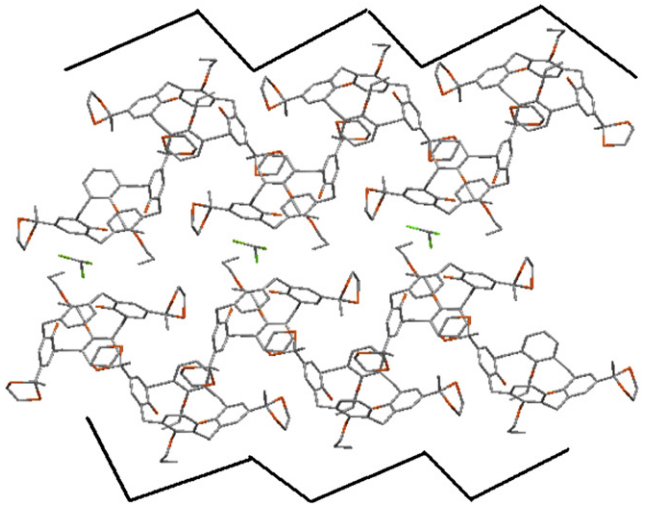


Figure 5. View of crystal packing and the zigzag architecture of interconnected layers where dithiane moiety in calix[4]arene **5b** capped by another calix[4]arene molecule.

296 nm underwent blue shift from λ_{max} 296 nm to 284 nm. No change in absorption spectra was observed on addition of other metal ions in our analysis. However, the change in absorption intensity on addition of mercuric ions was accompanied by color change from light yellow to brown.

The complexation mode of **2b** with Hg^{2+} was determined by observing Job's continuous variation plot, which revealed that **2b**–Hg^{2+} complex concentration approached a maximum when the molar fraction of ligand was about 0.5 (Fig. 6). This suggested a 1:1 stoichiometry for mercury–**2b** interaction. To determine

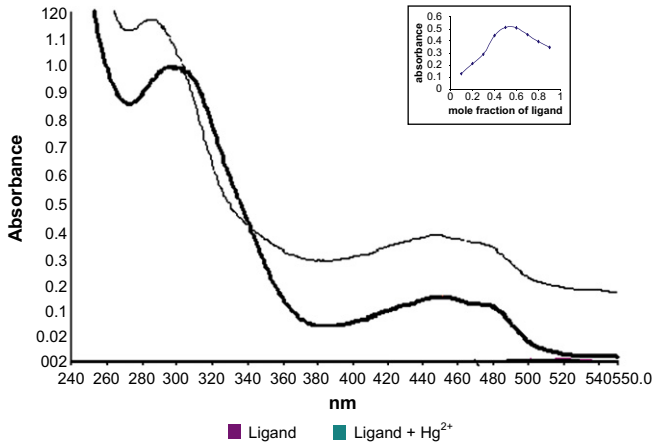


Figure 6. UV–vis spectral change in ligand **2b** upon addition of Hg^{2+} ions and Job's continuous variation plot of **2b**–Hg^{2+} complex.

the presumable role of cavity of calix[4]arene, the interaction was also studied with the 1,2-dithiane of 4-hydroxybenzaldehyde, which indicated a blue shift of 13 nm in the presence of mercuric chloride with a 2:1 stoichiometric ratio (Job's continuous variation plot). Further work to determine exact mode of interaction and its utility for development of sensor materials for mercury is in progress.

3. Conclusion

We have described an experimental protocol for obtaining dithiane appended calix[4]arenes through thio acylation and acetalization to obtain attractive precursors for umpolung reactions to explore elaboration of calixarene scaffolds. X-ray diffraction analysis of **5b** has revealed that dithiane moiety is capped by the cavity of second calix[4]arene molecule to result in the formation of linear molecular assembly similar to the one obtained in biological molecular organization. Preliminary interaction of **2b** with toxicants indicates that Hg^{2+} ion can selectively interact with it through 1:1 stoichiometry with a color change detectable through a naked eye to provide utility of these derivatives for separation and estimation of environmental toxicants.

4. Experimental

4.1. General

All the reagents used in the study were purchased from Sigma–Aldrich or Merck and were considered chemically pure to be used without further purification. The solvents used were distilled. 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. 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. IR spectra were recorded on a Nicolet Protègè 460 spectrometer in KBr discs while CHN analysis were obtained by using a Perkin–Elmer 240C elemental analyzer.

4.2. General procedure for the synthesis of 5-monoacetyl-25,26,27,28-tetrapropoxycalix[4]arene 4a

To a solution of tetrapropoxycalix[4]arene (150 mg, 0.25 mmol) in dichloromethane (35 mL) were added borontrifluoride etherate (0.64 mL, 5 mmol) in dichloromethane (5 mL) and acetyl chloride (1.79 mL, 2.5 mmol) in dichloromethane (5 mL) simultaneously. The reaction mixture was stirred at room temperature for 3 days. The reaction mixture was quenched with ice-cold water and stirred for another half an hour. Organic layer was separated and washed with a saturated mixture of $NaHCO_3$ and KF thrice followed by washing with water. Evaporation of the organic layer gave a crude

mixture, which was purified by coloumn chromatography using hexane–ethylacetate 9:1 (R_f 0.23) as eluent to afford a white solid **4a** (55% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.87 (m, 12H, J=7.41, CH_3), 1.79 (m, 8H, J=7.3, $-OCH_2CH_2CH_3$), 2.23 (s, 3H, $COCH_3$), 3.05 (t, 4H, J=14.2, $ArCH_2Ar$), 3.70 and 3.78 (t, 8H, J=7.1, OCH_2), 4.34 (dd, 4H, J=$ArCH_2Ar$), 6.26 (s, H, J=8.6, ArH), 6.32 (d, 2H, J=6.3, ArH), 6.55 (t, 2H, J=8.4, ArH), 6.60 (d, 4H, J=6.5, ArH), 7.02 (s, 2H, ArH). ^{13}C NMR: (300 MHz, $CDCl_3$): δ 10.13, 22.45, 30.96, 31.33, 31.58, 78.77, 125.55, 126.01, 126.98, 127.83, 128.5, 131.56, 142.67, 144.35, 153.78. FABMS m/z calcd 634.84; found 635. Found: C 79.41, H 7.90. $C_{42}H_{50}O_5$ requires C 79.46, H 7.94. Mp 240–242 °C. IR (KBr): ν_{max} 2920, 1675, 1125, 1078.

4.3. General procedure for prepration of cyclic thioacetals and thioketals

To a solution of calix[4]aryl methyl ketone or aldehyde in benzene (35 mL) and stoichiometric amount of 1,2-ethanedithiol was added a catalytic amount of *p*-toluenesulphonic acid. The homogeneous reaction mixture was refluxed for 1 h. After completion of the reaction, the reaction mixture was poured into water and stirred for 18 h. The product was then extracted with chloroform and washed twice with water. The organic layer was separated, dried over anhydrous sodium sulfate, and concentrated. Pure 1,2-dithiane calix[4]arene was obtained by crystallization from $CHCl_3$–MeOH solution.

4.3.1. Compound **1b**

The condensation procedure described above was followed by using **1a** (100 mg, 0.14 mmol) and 1,2-ethanedithiol (0.011 mL, 0.14 mmol) affording a yellow solid (85.4 mg, 77% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.03 (s, 18H, $-C(CH_3)_3$), 1.24 (m, 15H, $-C(CH_3)_3$+CH_3), 2.01 (m, 4H, $-OCH_2CH_2CH_3$), 3.28 (m, 6H, $ArCH_2Ar$+SCH_2), 3.47 (m, 2H, $-SCH_2$), 3.92 (m, 4H, OCH_2), 4.24 (dd, 4H, $ArCH_2Ar$), 5.58 (s, 1H, $-CH$), 6.86, 6.90, 7.03, 7.22 (4s, 8H, Ar*H*), 7.96 and 8.35 (2s, 2H, D_2O exch. O*H*). ^{13}C NMR: (300 MHz, $CDCl_3$): δ 10.85, 23.43, 26.92, 31.16, 31.66, 31.84, 33.8, 34.08, 39.93, 78.26, 125.02, 125.28, 126.21, 127.68, 128.29, 133.4, 141.65, 147.38, 149.86. FABMS m/z calcd 781.16; found 782. Calcd for $C_{49}H_{64}O_4S_2$: C 75.34, H 8.26. Found: C 75.40, H 8.30. Mp >250 °C. IR (KBr): ν_{max} 2929, 2900, 1109, 1056.

4.3.2. Compound **2b**

The condensation procedure described above was followed by using **2a** (100 mg, 0.16 mmol) and 1,2-ethanedithiol (0.028 mL, 0.33 mmol) to afford a yellow solid (79.38 mg, 63% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.08 (t, 6H, J=7.3, $-CH_3$), 1.66 (m, 4H, $-OCH_2CH_2CH_2$), 20.9 (m, 4H, $-OCH_2CH_2CH_2$), 3.28 (m, 4H, $-SCH_2$), 3.42 (m, 4H, $-SCH_2$), 4.10 (t, 4H, J=6.7, $-OCH_2$), 4.17 (d, 4H, J=13.8, $ArCH_2Ar$), 4.17 (d, 4H, J=13.0, $ArCH_2Ar$), 5.57 (s, 2H, $-CH$), 6.91 (t, 4H, J=7.2, Ar*H*), 7.08 (d, 2H, J=7.53, Ar*H*), 7.17 (s, 4H, Ar*H*), 5.51 (s, 1H, D_2O exch. O*H*). ^{13}C NMR: (300 MHz, $CDCl_3$): δ 14.0, 19.23, 19.38, 31.47, 31.92, 32.0, 39.89, 39.99, 56.12, 56.32, 76.60, 126.32, 127.82, 128.09, 128.41, 128.48, 128.58, 129.47, 131.40, 132.65, 133.91, 132.65, 133.91, 149.15, 150.75. FABMS m/z calcd 745.09; found 746. Calcd for $C_{42}H_{48}O_4S_4$: requires C 67.70, H 6.49. Found: C 67.74, H 6.44. Mp >250 °C. IR (KBr): ν_{max} 2912, 2963, 1178, 1073, 762.

4.3.3. Compound **3b**

The condensation procedure described above was followed by using **3a** (100 mg, 0.14 mmol) and 1,2-ethanedithiol (0.035 mL, 0.43 mmol) to give a yellow solid (116.09 mg, 81% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.94 (m, 12H, $-CH_3$), 1.87 (m, 8H, $-OCH_2CH_2$), 3.08 (d, 4H, $ArCH_2Ar$), 3.32 (m, 4H, J=13.0, $ArCH_2Ar$), 3.2 (m, 8H, $-SCH_2$), 3.37 (m, 8H, $-SCH_2$), 3.77 (m, 8H, $-OCH_2$), 4.33 (d, 4H, J=12.9, $ArCH_2Ar$), 5.48 (s, 4H, –CH), 6.8 (s, 8H, Ar*H*). ^{13}C NMR: (300 MHz, $CDCl_3$): δ 10.28, 23.22, 30.84, 39.96, 56.49, 77.42,127.66, 133.14, 134.53, 156.16. FABMS m/z calcd 1009.58; found 1009. Calcd for $C_{52}H_{64}O_4S_8$ requires C 61.86, H 6.39. Found: C 61.80, H 6.44. Mp >250 °C. IR (KBr): ν_{max} 2988, 1116, 892, 756.

4.3.4. Compound **4b**

The condensation procedure described above was followed by using **4a** (100 mg, 0.15 mmol) and 1,2-ethanedithiol (0.013 mL, 0.15 mmol) as substrates to give a yellow solid (66.25 mg, 59% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.85, 1.14, 1.03 (m, 12H, $-CH_3$), 1.47 (s, 3H, $-C-CH_3$), 1.82, 1.99, 2.13 (m, 8H, $-OCH_2CH_2$), 3.11 (dd, 4H, J=14.1, $ArCH_2Ar$), 3.41 (s, 4H, $-SCH_2$), 3.66, 3.90, 4.05 (m, 8H, $-OCH_2$), 4.22 (t, 4H, J=14.6, $ArCH_2Ar$), 6.32 (s, 2H, Ar*H*), 6.56–6.69 (m, 3H, J=7.53, Ar*H*), 6.83 (d, 4H, J=7.5, ArH), 6.94 (t, 2H, J=8.3, Ar*H*). ^{13}C NMR: (300 MHz, $CDCl_3$): δ 10.28, 17.65, 22.41, 31.1, 31.35, 31.84, 34.30, 38.91, 78.13, 125.11, 125.36, 125.41, 126.63, 127.86, 127.99, 131.3, 142.6, 147.44, 154.6. FABMS m/z calcd 711.03; found 712. Calcd for $C_{44}H_{54}O_4S_2$: C 74.32, H 7.65. Found: C 74.38, H 7.61. Mp >250 °C. IR (KBr): ν_{max} 2965, 1215, 1079, 826.

4.3.5. Compound **5b**

Compound **5a** (100 mg, 0.16 mmol) and 1,2-ethanedithiol (0.028 mL, 0.33 mmol) when reacted by the described method afford a yellow solid (85.7 mg, 68% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.25 (t, 4H, J=7.5, CH_3), 2.02 (m, 4H, OCH_2CH_2) 2.1 (s, 6H, $-C-CH_3$), 3.32–3.45 (m, 12H, $ArCH_2Ar$+SCH_2), 3.94 (t, 4H, J=6.3, OCH_2), 4.26 (d, 4H, J=12.9, $ArCH_2Ar$), 6.61 (d, 4H, J=7.5, ArH), 6.79 (t, 2H, J=7.5, ArH), 7.42 (s, 4H, ArH), 8.55 (s, 2H, OH). ^{13}C NMR: (300 MHz, $CDCl_3$): δ 10.95, 23.5, 31.64, 34.08, 40.09, 68.67, 78.35, 125.45, 127.05, 127.02, 129.02, 133.44, 135.46, 151.88 and 152.48. DEPT-135: δ CH, CH_3 10.95, 34.08, 125.43, 127.03, 129 and CH 23.48, 31.64, 40.1, 78.35. FABMS m/z calcd 745.09; found 746. Calcd for $C_{42}H_{48}O_4S_4$: C 67.7, H 6.49. Found: C 67.51, H 6.55. Mp >250 °C. IR (KBr): ν_{max} 2913, 1197, 1067, 799.

4.3.6. Compound **6b**

Compound **6a** (100 mg, 0.15 mmol) and 1,2-ethanedithiol (0.038 mL, 0.46 mmol) when reacted by similar protocol gave a yellow solid (76.5 mg, 52% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.92, 2.09, 2.23 (s, 12H, $-C-CH_3$), 2.89–4.06 (m, 36H, $ArCH_2Ar$+SCH_2+OCH_2), 4.06 (m, 4H, $ArCH_2Ar$), 7.05, 7.30, 7.40, 7.42, 7.60 (s, 8H, Ar*H*). ^{13}C NMR: (300 MHz, $CDCl_3$): δ 30.37, 31.60, 34.27, 37.96, 60.67, 78.35, 124.45, 126.52, 127.39, 129.41, 130.91, 131.7, 133.0, 134.5, 136.3, 137.4, 152.48 and 156.9. FABMS m/z calcd 953.48; found 954. Calcd for $C_{48}H_{56}O_4S_8$: C 60.46, H 5.92; Found: C 60.51, H 5.95. Mp >250 °C. IR (KBr): ν_{max} 2990, 1185, 963, 719.

4.4. Crystallographic data for 5b

Single crystal **5b** was obtained from $CHCl_3$–MeOH solution. Crystal data and refinement details: molecular formula $C_{42}H_{48}O_4S_4$, M=745.08, monoclinic, space group $P2\ 1/n$ with a=10.9794(19) Å, b=34.998(6) Å, c=11.755(2) Å, β=108.65(0)°, V=4279.78(130) Å^3, Z=48, D_c=1.798 g cm^{-3}, R=0.0912. All the calculations involving structure solution, refinement, and graphics were performed by using SHELXTL-PC; CCDC 63203.

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References and notes

1. Gutsche, C. D. In *Calixarenes: Monographs in Supramolecular Chemistry*; Stoddart, J. F., Ed.; The Royal Society of Chemistry: Cambridge, UK, 1989; (b) Bohmer, V. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 713–745; (c) *Calixarenes 50th Anniversary: Commemorative Issue*; Vicens, J., Asfari, Z., Harrowfield, J. M., Eds.; Kluwer Academic: Dordrecht, The Netherlands, 1994; (d) Scheerder, J.; Fochi, M.; Engbersen, J. F. J.; Reinhoudt, D. N. *J. Org. Chem.* **1994**, *59*, 7815–7820.
2. Orr, G. W.; Barbour, L. J.; Atwood, J. L. *Science* **1999**, *285*, 1049–1052.
3. Ikeda, A.; Tsudera, T.; Shinkai, S. *J. Org. Chem.* **1997**, *62*, 3568–3574.
4. Ikeda, A.; Udzu, H.; Yoshimura, M.; Shinkai, S. *Tetrahedron* **2000**, *56*, 1825–1832.
5. Vysotsky, M. O.; Thondorf, I.; Böhmer, V. *Chem. Commun.* **2001**, 1890–1891; (b) Shivanyuk, A.; Friese, J. C.; Döring, S.; Rebek, J., Jr. *J. Org. Chem.* **2003**, *68*, 6489–6496.
6. Corbellini, F.; Fiammengo, R.; Timmerman, P.; Crego-Calama, M.; Versluis, K.; Heck, A. J. R.; Luyten, I.; Reinhoudt, D. N. *J. Am. Chem. Soc.* **2002**, *124*, 6569–6575; (b) Corbellini, F.; Costanzo, L. D.; Crego-Calama, M.; Geremia, S.; Reinhoudt, D. N. *J. Am. Chem. Soc.* **2003**, *125*, 9946–9947.
7. Castellano, R. K.; Nuckolls, C.; Eichhorn, S. H.; Wood, M. R.; Lovinger, A. J.; Rebek, J., Jr. *Angew. Chem., Int. Ed.* **1999**, *38*, 2603–2606.
8. Lee, M.; Lee, S.; Jiang, L. *J. Am. Chem. Soc.* **2004**, *126*, 12724–12725.
9. Yan, X.; Janout, V.; Hsu, J. T.; Regen, S. L. *J. Am. Chem. Soc.* **2003**, *125*, 8094–8095; (b) Uragami, T.; Meotoiwa, T.; Miyata, T. *Macromolecules* **2003**, *36*, 2041–2048; (c) Ikeda, A.; Hatano, T.; Shinkai, S.; Akiyama, T.; Yamada, S. *J. Am. Chem. Soc.* **2001**, *123*, 4855–4856.
10. Xu, B.; Swager, T. M. *J. Am. Chem. Soc.* **1993**, *115*, 1159–1160; (b) Komori, T.; Shinkai, S. *Chem. Lett.* **1993**, 1455–1458; (c) Komori, T.; Shinkai, S. *Chem. Lett.* **1992**, 901–904; (d) Lippmann, T.; Dalcanale, E. *Gazz. Chim. Ital.* **1995**, *125*, 595–599.
11. Koh, K. N.; Araki, K.; Komori, T.; Shinkai, S. *Tetrahedron Lett.* **1995**, *36*, 5191–5194.
12. Xu, B.; Swager, T. M. *J. Am. Chem. Soc.* **1995**, *117*, 5011–5012.
13. Yonetake, K.; Nakayama, T.; Ueda, M. *J. Mater. Chem.* **2001**, *11*, 761–767.
14. Oh, S.-K.; Nakagawa, M.; Ichimura, K. *J. Mater. Chem.* **2001**, *11*, 1563–1569.
15. Tumcharem, G.; Tuntulani, T.; Coles, J. S.; Hursthose, M. B.; Kilburn, J. D. *Org. Lett.* **2003**, *5*, 4971–4974; (b) Stephan, H.; Gloe, K.; Paulus, E. F.; Saadioui, M.; Böhmer, V. *Org. Lett.* **2000**, *2*, 839–841.
16. Yordanov, A. T.; Falana, O. M.; Koch, H. F.; Roundhill, D. M. *Inorg. Chem.* **1997**, *36*, 6468–6471; (b) Floriani, C.; Jacoby, D.; Chiesi-Villa, A.; Guastini, C. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1376–1377.
17. Arimura, T.; Matsumoto, S.; Teshima, O.; Nagasaki, T.; Shinkai, S. *Tetrahedron Lett.* **1992**, *32*, 5111–5114.
18. Moran, J. K.; Roundhill, D. M. *Inorg. Chem.* **1992**, *31*, 4213–4215.
19. Gibbs, C. G.; Gutsche, C. D. *J. Am. Chem. Soc.* **1993**, *115*, 5338–5339.
20. Cobben, P. L. M.; Egberink, R. J. M.; Bomer, J. G.; Bergveld, P.; Verboom, W.; Reinhoudt, D. N. *J. Am. Chem. Soc.* **1992**, *214*, 10573–10582.
21. Koh, K. N.; Imada, T.; Nagasaki, T.; Shinkai, S. *Tetrahedron Lett.* **1994**, *35*, 4157–4160.
22. Bajaj, L.; Chawla, H. M.; Francis, T.; Venkateshan, N. *ARKIVOC* **2005**, 200–210; (b) Chakrabarti, A.; Chawla, H. M.; Francis, T.; Pant, N.; Upreti, S. *Tetrahedron* **2006**, *62*, 1150–1157.
23. Yordanov, A. T.; Whittlesey, B. R.; Roundhill, D. M. *Inorg. Chem.* **1998**, *37*, 3526–3531.
24. Yoon, K.; Kim, K. *J. Org. Chem.* **2005**, *70*, 427–432.
25. (a) Utimoto, K.; Nakamura, A.; Motsubara, S. *J. Am. Chem. Soc.* **1990**, *112*, 8189–8190; (b) Page, P. C. B.; Van Niel, M. B.; Prodger, J. C. *Tetrahedron* **1989**, *45*, 7643–7677; (c) Lynch, J. E.; Eliel, E. L.; Morris-Natsche, S. S. *J. Am. Chem. Soc.* **1984**, *106*, 2943–2948.
26. Karaulova, E. N. *Russ. Chem. Rev.* **1988**, *57*, 648–667.
27. (a) Chawla, H. M.; Pant, N.; Srivastava, B. *Tetrahedron Lett.* **2005**, *46*, 7259–7262; (b) Arora, V.; Chawla, H. M.; Santra, A. *Tetrahedron* **2002**, *58*, 5591–5597.
28. Kumar, S.; Chawla, H. M.; Varadarajan, R. *Tetrahedron Lett.* **2002**, *43*, 2495–2498.
29. Ugozzoli, F.; Andretti, G. D. *J. Inclusion Phenom. Macrocycl. Chem.* **1992**, *13*, 337–348.