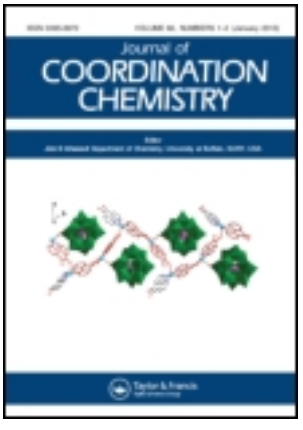

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gcoo20

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Bahram Mokhtari [a] & Kobra Pourabdollah [a]
[a] Department of Chemical Engineering , Shahreza Branch, Islamic Azad University , Shahreza , Iran
Published online: 14 Nov 2011.

To cite this article: Bahram Mokhtari & Kobra Pourabdollah (2011) Solvent extraction of alkali metals by di-ionizable nano-baskets, Journal of Coordination Chemistry, 64:23, 4029-4053, DOI: 10.1080/00958972.2011.635790

To link to this article: http://dx.doi.org/10.1080/00958972.2011.635790

Journal of Coordination Chemistry
Vol. 64, No. 23, 10 December 2011, 4029–4053

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Solvent extraction of alkali metals by di-ionizable nano-baskets

BAHRAM MOKHTARI and KOBRA POURABDOLLAH*

Department of Chemical Engineering, Shahreza Branch, Islamic Azad University, Shahreza, Iran

(*Received 4 March 2011; in final form 14 October 2011*)

The competitive solvent extractions of alkali metals by nano-baskets of di-ionizable calix[4]arenes were studied using nine scaffolds and 34 calix[4]arene derivatives. The objective of this work is to assess the effect of changing the pendant groups as well as variation of macrocycle conformation, orientation, and position of pendant moieties upon the extraction efficiency, selectivity, and $pH_{1/2}$ of calix[4]arene complexes. Alkali metal cations were extracted from aqueous solutions into chloroform by di-ionizable calix[4]arene derivatives and were measured using ion chromatography. The results revealed that alternation of aryl group in the pendant moieties, changing their orientation from *cis*- to *trans*- as well as *ortho*- to *para*-analogues revealed no changes in the selectivity, extraction efficiency and $pH_{1/2}$ of calix[4]arene complexes. Alternation of ring conformation (cone, 1,2-alternate, and partial-cone) showed a pronounced influence upon the complexation of alkali metal cations.

Keywords: Nano-basket; Solvent extraction; Calixarene; Conformation; Alkali metals

1. Introduction

Nano-baskets of calixarenes are a versatile class of macrocycles, which have been subject to extensive research in the development of many extractants [1, 2], transporters [3], stationary phases (using gas chromatograph, Teif Gostar Faraz Co.) [4], electrode ionophores, and optical and electrochemical sensors [5] over the past four decades. In the nineteenth century, Baeyer synthesized calixarenes *via* the reaction of formaldehyde with *p*-substituted phenols in basic or acidic environment [6, 7]. However, the limited analytical methods and instruments at that time were unable to interpret the structure of the newly synthesized products. In the 1940s, Zinke and Ziegler discovered that the products possessed cyclic tetrameric structures [8]. In 1975, Gutsche introduced the presently accepted name of calixarene [9, 10]. New advances in the field of metal extraction by calixarenes led to introducing ionizable moieties and crown ethers in their scaffolds. The ionizable moieties not only participate in cooperative metal ion coordination, but also eliminate the need to transfer the anions from the aqueous phase into the organic phase by operating in a cation-exchange mode with the metal cation [11]. Introducing the crown ether ring on the lower rims not only increases the

*Corresponding author. Email: pourabdollah@iaush.ac.ir

ISSN 0095-8972 print/ISSN 1029-0389 online © 2011 Taylor & Francis
http://dx.doi.org/10.1080/00958972.2011.635790

cation binding ability of the calixarenic scaffold but also enhances the selectivity through modulation of the crown ring size [12].

The small calixarenic cycles, calix[4]arene, possess a bowl-shaped conformation [13] and those with pendent proton-ionizable groups, such as carboxylic acid [14], phosphinoyl [15], *N*-(X)-sulfonyl carboxamide [16], and hydroxyamic acid [17] have been utilized for solvent extraction of metal cations. Ionizable calixarenes are more efficient in metal cation separation than non-ionizable analogs owing to charge matching within the resulted complex in the organic phase. The metal cations are transferred to the organic phase due to the production of a neutral complex. Different complexing groups at the upper-rim of calixarenes attract with predefined selectivity, while the lower rim moieties are usually responsible for physical properties of calixarenes [2].

Alkyl groups larger than ethyl introduced to the lower-rim effectively fix the calix[4]arene conformation [18]. Smirnov *et al.* [19] synthesized tetradiethylamidecalix[4]arene that exhibited excellent efficiency toward alkaline earth metals. They reported the better binding ability of tetraamide derivatives than ester and ketone analogs owing to their carbonyl groups (more basic), which significantly enhances the strength of metal ion-functional group interaction. Calix[4]arene tetrathioamides are efficient extractants for silver picrate, while they show low extraction levels for Cd^{2+}, Co^{2+}, Cu^{2+}, alkali, and alkaline earth metal picrates [20]. Calixarenes bearing carboxylic acids were found to be much more efficient interphase carriers for alkaline earth metals than related unfunctionalized calixarenes with phenolic groups on the lower-rim [21]. An example of the use of a calixarene with two proton-ionizable groups in a divalent metal ion separation is the exclusive extraction of calcium from an aqueous solution (containing four alkaline earth metal nitrate species) at pH = 5.3 into chloroform by calix[4]arene dicarboxylic acid diamide [22].

Calixarenes are used not only for cation receptors but also for binding to anions. In the design of neutral calixarene anion receptors, several different hydrogen bonding groups (such as urea and thiourea) have been incorporated in upper and lower rim frameworks. Scheerder and coworkers showed a high binding capacity for chloride and bromide in $CDCl_3$ with 1 : 1 stoichiometry [23]. Morzherin *et al.* [24] synthesized upper-rim functionalized sulphonamide receptor. Increased polarity of N–H bonds by electron-withdrawing SO_2 group resulted in stronger hydrogen bonds with anions. This receptor displayed remarkable selectivity for hydrogen sulfate over other anions in $CDCl_3$.

In solvent extraction, two immiscible liquid phases are mixed with the calixarene as extractant in the organic phase and a stripping aqueous acidic solution is used in the back extraction. The metal cation extracted by the calixarene ligands are analyzed quantitatively in the aqueous phase after back extraction [25]. Different analytical methods such as atomic absorption, inductively coupled plasma spectroscopy, UV-Vis, and ion chromatography [26–28] are routinely used to determine the metal cation concentrations after back extraction. The loading percentage is equal to the ratio of the extracted amount of metal cation over the initial macrocycle concentration in the organic phase.

In this article, the competitive solvent extractions of alkali metal cations from aqueous solutions into chloroform by di-ionizable calix[4]arene derivatives are studied. In nine scaffolds, 34 calix[4]arene derivatives were used to assess the effect of changing pendant groups as well as variation of isoconformations (conformation, orientation,

and position) upon the extraction parameters including extraction efficiency, selectivity, and $pH_{1/2}$ of complexes. The results will show the rank of the above-mentioned variables upon the extraction parameters. Such sequential ranks will be used to predict the extraction behavior of calixarene scaffolds before synthesis and extractions. Moreover, using those ranks it is possible to optimize the extraction parameters by modification of chemical structures during the synthesis steps.

2. Materials and methods

2.1. *Materials and standard solutions*

Sodium chloride and potassium chloride (99%) were purchased from Mallinckrodt. Lithium chloride, rubidium chloride, and cesium chloride (99%) were obtained from Alfa Aesar. Lithium hydroxide was purchased from Fisher Scientific, 1.0 N hydrochloric acid from J.T. Baker, chloroform from EM Science, and 2.0 N sulfuric acid from Mallinckrodt. The chloroform was shaken with deionized water to remove the stabilizing ethanol and stored in the dark. All of the experiments were carried out using four derivatives of di-ionizable *p-tert*-calix[4]arene di-[*N*-(phenyl)sulfonyl carboxamide], di-ionizable *p-tert*-calix[4]arene di-[*N*-(*para*-hydroxy phenyl)sulfonyl carboxamide], di-ionizable of *p-tert*-calix[4]arene di-[*N*-(*para*-nitro phenyl)sulfonyl carboxamide], and di-ionizable of *p-tert*-calix[4]arene di-[*N*-(*para*-methyl phenyl)sulfonyl carboxamide].

2.2. *Synthesis of di-ionizable calix[4]arenes*

Two conformers for each four of di-ionizable cone derivatives (**01**–**04** and **05**–**08**), three conformers for each four of di-ionizable 1,2-alternate derivatives (**09**–**12**, **13**–**16**, and **17**–**20**), and four conformers for each four of the partial-cone (**21**–**24**, **25**–**28**, **29**–**31**, and **32**–**34**) conformations were synthesized as discussed before. The *cis*/*trans* symbols refer to the direction of two di-ionizable moieties and the *ortho*/*para* depict the relative situation of two di-ionizable moieties. Figure 1 depicts the chemical structure of two cone conformations, three 1,2-alternate conformations, and four partial-cone conformations of calix[4]arene derivatives.

2.3. *Sample preparation*

The alkali metal cations were loaded into the aqueous solutions by adding stock solutions containing five alkali metal cations, 20.0 mmol L^{-1} lithium chloride solution, and 20.0 mmol L^{-1} lithium hydroxide solution. The solutions of alkali metal cations were made up as lithium, sodium, potassium, rubidium, and cesium chloride solutions (20.0 mmol L^{-1} in each). The pH values of the aqueous phases were adjusted using 20.0 mmol L^{-1} lithium hydroxide and 0.01–1.0 mol L^{-1} hydrochloric acid solutions.

Extraction abilities of eight distinct dangling moieties were examined on five conformation of calix[4]arene scaffold, in 13 solutions with pH range of 1.0–12.0. For each macrocyclic ligand, 13 solutions for competitive solvent extraction of alkali metal

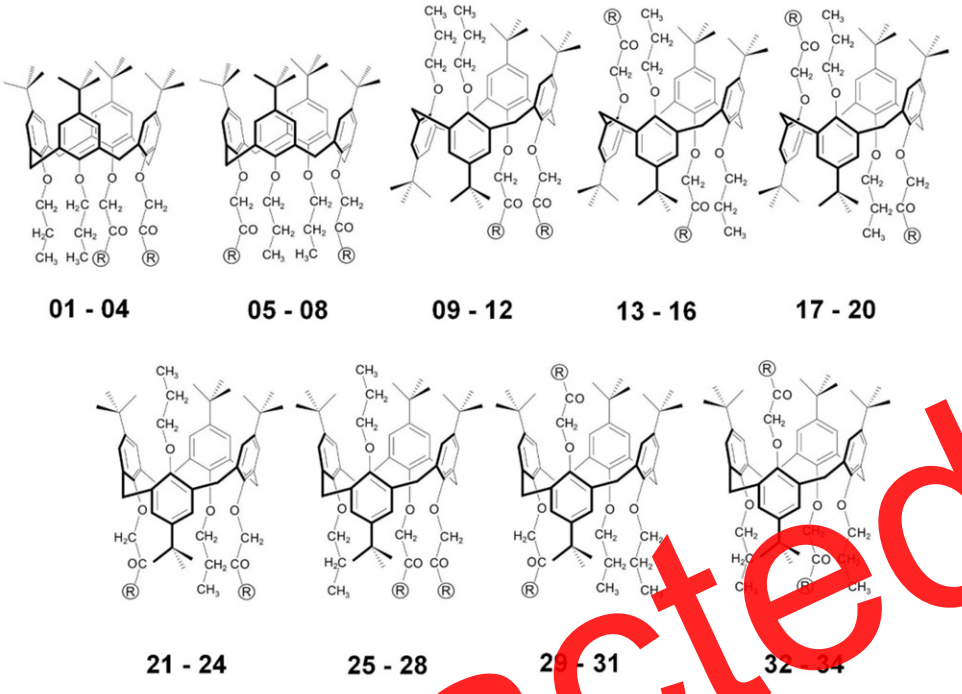

Figure 1. The structure of conformers investigated. R was defined as: –$NHSO_2$phenyl; –$NHSO_2$(*p*-CH_3phenyl); –$NHSO_2$(*p*-OCH$_3$phenyl); –$NHSO_2$(*p*-NO_2phenyl).

cations were prepared in 15 mL conical polypropylene centrifuge tubes. The samples contained 2.0 mL of the aqueous phase of 10.0 mmol L^{-1} alkali metal cations solution and 2.0 mL of 1.00 mmol L^{-1} macrocyclic ligand solution in chloroform.

2.4. *Extraction procedure*

The combined aqueous and organic phases were shaken for 5 min and centrifuged for 5 min. The pH of the aqueous phase was measured using a pH meter with a Corning 476,157 combination pH electrode. In the stripping step, 1.5 mL of the organic phase was transferred to a capped conical centrifuge tube containing 3.0 mL of 0.10 mol L^{-1} HCl. The stripping involved 5 min of mixing and 5 min centrifuging. After that, 1.0 mL of the aqueous phase was diluted to 10.0 mL for analysis by ion chromatography.

2.5. *Ion chromatographic analysis*

Determination of alkali metal cation was accomplished by Dionex DX-120 ion chromatographs with a CS12A column, a conductivity detection and membrane suppression. The eluent was 0.011 mol L^{-1} sulfuric acid after filtration through a millipore 0.22 μm filtration membrane, while the pump flow rate at 1700 psi was about 1 mL min^{-1}. To obtain a stable baseline, the eluent was flowed through the column for 60 min and then, 2.0 mL of standard solutions were injected; they were repeated twice.

3. Results and discussion

The results of complexation ability for the cone, the 1,2-alternate, and the partial-cone conformations of calix[4]arene derivatives are discussed. The cone conformers in two categories of *trans*-cone and *cis*-cone isomers are discussed first, followed by presenting the results of three isomers of 1,2-alternate conformer including *cis*-1,2-alternate, *ortho-trans*-1,2-alternate, *para-trans*-1,2-alternate. In the last section, four isoconformers of *ortho-cis* partial-cone, *para-cis* partial-cone, *ortho-trans* partial-cone, and *para-trans* partial-cone are considered. The identities of the dangling proton-ionizable moieties affect the acidity of macrocycle derivatives and their ability to extract alkali metal cations. Hence, the pH for half loading, which is defined as $pH_{1/2}$, is used to measure qualitatively the ligand acidity.

3.1. *Two cone conformations*

The total loadings of metal : macrocycle complexes were determined by the sum of individual complexes toward each cation and were calculated to be about 200% which depict a 2 : 1 ratio of metal:macrocycle and was expected for the complexation of di-ionizable calixarenes toward monovalent cations. The extraction characteristics of cone isoconformers (*ortho*-cone and *para*-cone) are discussed in this section.

3.1.1. *ortho*-Cone isoconformers. For all four of the *ortho*-cone di-ionizable *p-tert*-butylcalix[4]arenes **01**–**04**, the maximum loadings were in the range of 179–197%. In derivatives **01**–**04**, the $pH_{1/2}$ values were computed as 7.2, 7.8, 7.7, and 7.2, respectively. The results of competitive solvent extractions by ligand derivatives **01**–**04** in chloroform are presented in the upper row of figure 3. Because of the selective 1 : 1 binding of Na^+ with the ionizable moieties and unselective binding of other alkali cations with those moieties, the selectivity order for calix[4]arene derivatives **01**–**04** at $pH \geq 8.0$ was determined to be Rb^+, Cs^+, $K^+ < Li^+ \ll Na^+$; all maximum Na^+ loadings exceed 100%. This macrocycle presented a Na^+/Li^+ selectivity of 4 under conditions of high loading. This reveals that the binding of different alkali metal cation species by this derivative was influenced by the pH and the identity of the dangling proton-ionizable moieties. According to figure 2, for derivative **01**, the amount of Li^+ extracted increased to its maximum loading at pH of 7.5, and then diminished as the pH increased.

3.1.2. *para*-Cone isoconformers. For all four of the *para*-cone di-ionizable *p-tert*-butylcalix[4]arenes **05**–**08**, the maximum loadings were in the range of 197–224%. In derivatives **05**–**08**, the $pH_{1/2}$ values were determined as 7.5, 8.0, 7.7, and 7.2, respectively. The results of competitive solvent extractions by ligand derivatives **05**–**08** in chloroform are depicted in the lower row of figure 2. Owing to selective 1 : 1 binding of Na^+ with the ionizable moieties and unselective binding of other alkali cations with those moieties, the selectivity order for calix[4]arene derivatives **05**–**08** at $pH \geq 7.5$ was determined to be K^+, Rb^+, $Cs^+ < Li^+ \ll Na^+$ and all maximum Na^+ loadings exceed 100%. This macrocycle presented a Na^+/Li^+ selectivity of 4 under conditions of high

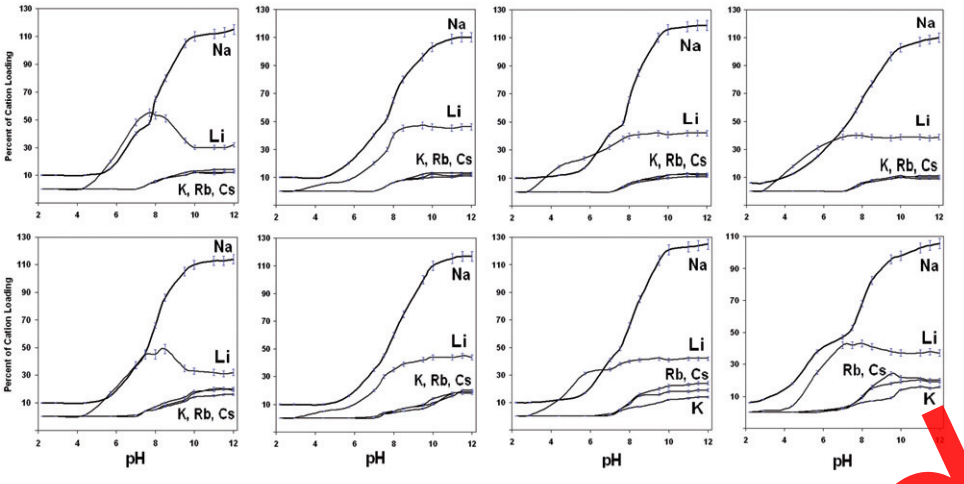

Figure 2. Competitive solvent extractions of alkali metal cations by *ortho*-cone isoconformers **01**–**04** (upper row) and *para*-cone isoconformers **05**–**08** (lower row).

loading. According to figure 2, for derivatives **05** and **08**, the amount of Li^+ extracted increased to its maximum loading at pH of 8.5 and 8.0.

3.2. *Three 1,2-alternate conformations*

The total loading of metal : macrocycle complexes were determined to be about 230%, which depict 2 : 1 and 3 : 1 ratios for *cis*- and *trans*-1,2-alternate conformers, respectively. In the following, the extraction characteristics of *cis*-, *ortho-trans*, and *para-trans*-1,2-alternate isoconformers are discussed.

3.2.1. *cis*-1,2-alternate isoconformers. The results of competitive solvent extractions by ligand derivatives **09**–**12** in chloroform are presented in the upper row of figure 3. For all four di-ionizable *cis*-1,2-alternate *p-tert*-butylcalix[4]arenes **09**–**12**, the maximum loadings were in the range of 150–183%. In derivatives **09**–**12**, the $pH_{1/2}$ values were computed as 6.8, 6.8, 7.0, and 6.7, respectively. Because of the selective 1 : 1 binding of Na^+ with the ionizable moieties and unselective binding of other alkali cations with those moieties, the selectivity order for calix[4]arene derivatives **09**–**12** at pH $\geq$ 7.0 was determined to be Li^+, Na^+, $Cs^+ < Rb^+ \ll K^+$ and all maximum K^+ loadings exceed 60%. This macrocycle presented a Na^+/Li^+ selectivity of 2 under conditions of high loading.

3.2.2. *ortho-trans*-1,2-Alternate isoconformers. For all four of the *ortho-trans*-1,2-alternate di-ionizable *p-tert*-butylcalix[4]arenes **13**–**16**, the maximum loadings were in the range of 241–284%. In derivatives **13**–**16**, the $pH_{1/2}$ values were computed as 6.7, 6.7, 6.7, and 6.6, respectively. The results of competitive solvent extractions by ligand derivatives **13**–**16** in chloroform are presented in the middle row of figure 3. Owing to the unselective binding of all alkali metal cations with the moieties, the low selectivity

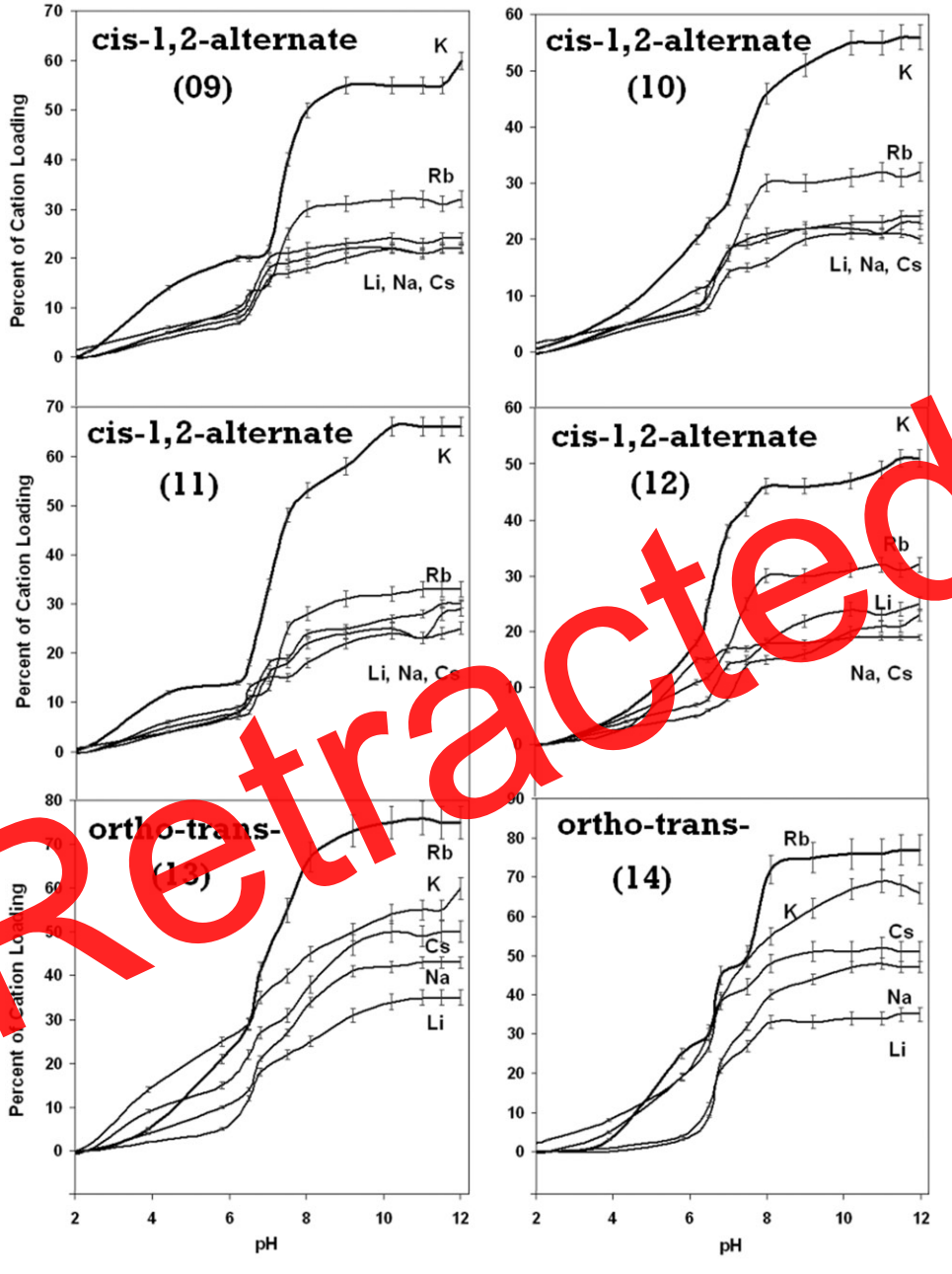

Figure 3. Competitive traces for solvent extractions of alkali metal cations by 1,2-alternate isoconformers.

order for calix[4]arene derivatives **13**–**16** at pH ≥ 7.5 was determined to be $Li^+ < Na^+$, $Cs^+ < K^+ < Rb^+$ and all maximum Rb^+ loadings exceed 80%. This macrocycle presented a Rb^+/K^+ selectivity of 1.5 in derivative **13** under conditions of high loading. According to figure 3, for derivatives **15** and **16**, the amount of K^+ extract increased to its maximum loading at pH of 9.0 and then diminished as the pH increased.

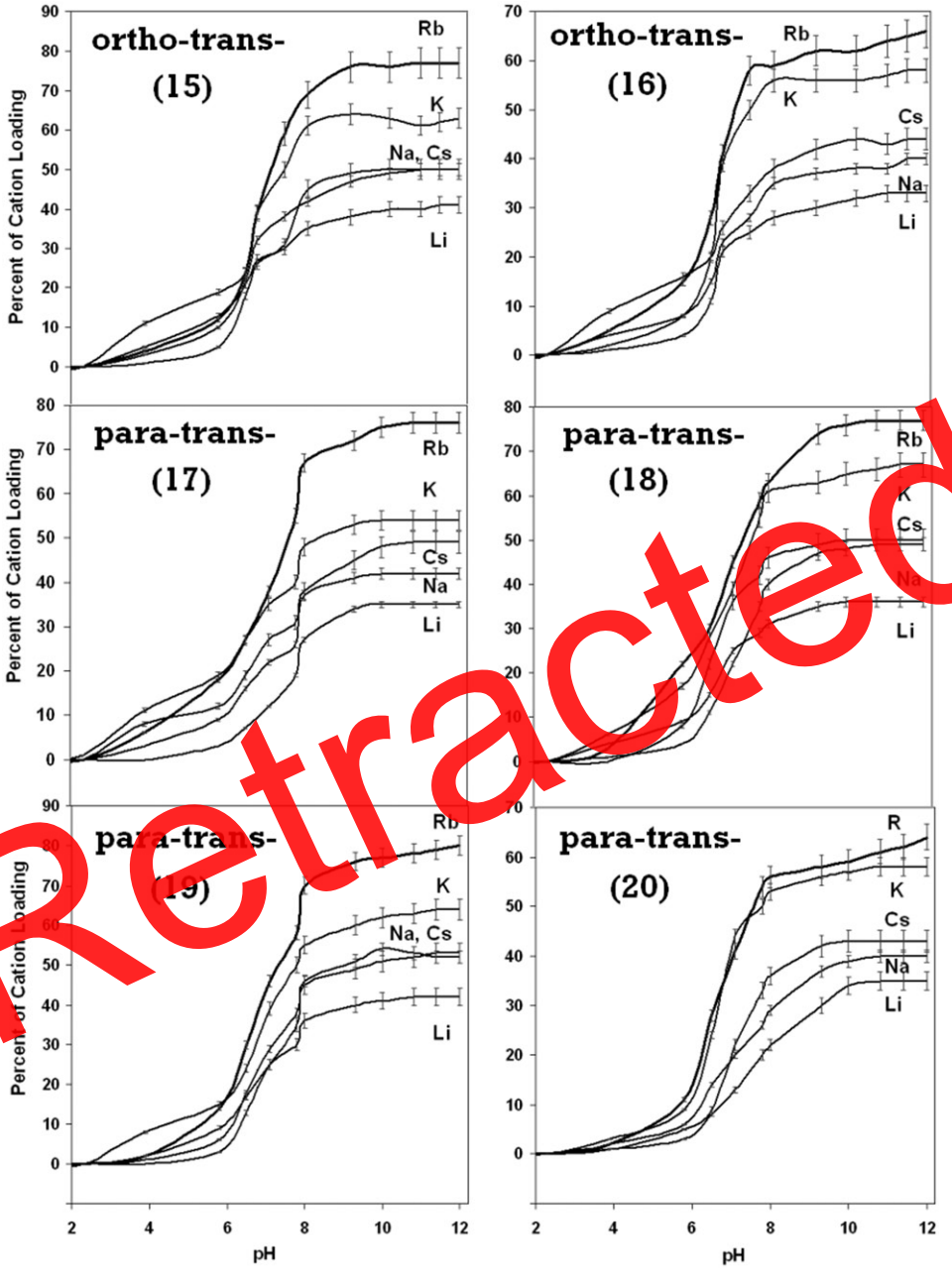

Figure 3. Continued.

3.2.3. *para-trans*-1,2-Alternate isoconformers. For all four of the *para-trans*-1,2-alternate di-ionizable *p-tert*-butylcalix[4]arenes **17**–**20**, the maximum loadings were in the range of 240–294%. In derivatives **17**–**20**, the $pH_{1/2}$ values were computed as 7.0, 6.9, 7.0, and 6.9, respectively. The results of competitive solvent extractions by ligand

derivatives **17**–**20** in chloroform are presented in the lower row of figure 3. Due to the unselective binding of all alkali metal cations with the di-ionizable moieties, the poor selectivity order for calix[4]arene derivatives **17**–**20** at pH $\geq$ 8.0 was determined to be as $Li^+ < Na^+$, $Cs^+ < K^+ < Rb^+$ and all maximum Rb^+ loadings exceed 80%. This macrocycle showed a Rb^+/K^+ selectivity of 1.5 for **17** under conditions of high loading.

3.3. *Four partial-cone conformations*

The total loading of metal : macrocycle complexes were determined to be about 90% and 20% for *cis*- and *trans*-isomers of partial-cone conformers, respectively. This depict a 1 : 1 ratio of metal:macrocycle and was expected for the complexation of di-ionizable calixarenes toward monovalent cations. The extraction characteristics of partial-cone isoconformers (*cis*- and *trans*-) are discussed in the following.

3.3.1. *ortho-cis* Partial-cone isoconformers. For all four of the *ortho-cis* partial-cone di-ionizable *p-tert*-butylcalix[4]arenes **21**–**24**, the maximum loadings were 57–115%. In derivatives **21**–**24**, the $pH_{1/2}$ values were computed as 8.1, 7.8, 7.9, and 7.8, respectively. The results of competitive solvent extractions by ligand derivatives **21**–**24** in chloroform are presented in the first row of figure 4. The unselective binding of alkali metal cations with the ligand shows no selectivity for calix[4]arene derivatives **21**–**24.** All maximum Na^+ loadings exceed 25%.

3.3.2. *para-cis* Partial-cone isoconformers. For all four of the *para-cis* partial-cone di-ionizable *p-tert*-butylcalix[4]arenes **25**–**28**, the maximum loadings were in the range of 59–112%. In derivatives **25**–**28**, the $pH_{1/2}$ values were computed as 7.8, 7.5, 7.6, and 7.8, respectively. The results of competitive solvent extractions by ligand derivatives **25**–**28** in chloroform are presented in the second row of figure 4. Using this macrocycle, all maximum Na^+ loadings exceed 25% and there is poor selectivity toward the cations.

3.3.3. *ortho-trans* Partial-cone isoconformers. The di-ionizable *ortho-trans* partial-cone *p-tert*-butylcalix[4]-arenes with di-[*N*-(*para*-nitro phenyl)sulfonyl carboxamide] moieties could not be synthesized. For all three of the *ortho-trans* partial-cone **29**–**31**, the maximum loadings were in the range of 17–24%. In derivatives **29**–**31**, the $pH_{1/2}$ values were computed as 8.3, 8.6, and 8.1, respectively. The results of competitive solvent extractions by ligand derivatives **29**–**31** in chloroform are presented in the third row of figure 4. These derivatives did not show any binding tendency toward Cs^+ and Rb^+. Due to the selective 1 : 1 binding of K^+ with the ionizable moieties and unselective binding of other alkali cations, the selectivity order for calix[4]arene derivatives **29**–**31** at pH $\geq$ 8.0 was determined to be $Li^+ < Na^+ < K^+$ and all maximum K^+ loadings exceed 12%. This macrocycle presented a K^+/Li^+ selectivity of 3, K^+/Na^+ selectivity of 2, and Na^+/Li^+ selectivity of 1.5 under conditions of high loading. This reveals that the binding of different alkali metal cations by this derivative was influenced by the pH and the identity of the dangling proton-ionizable moieties.

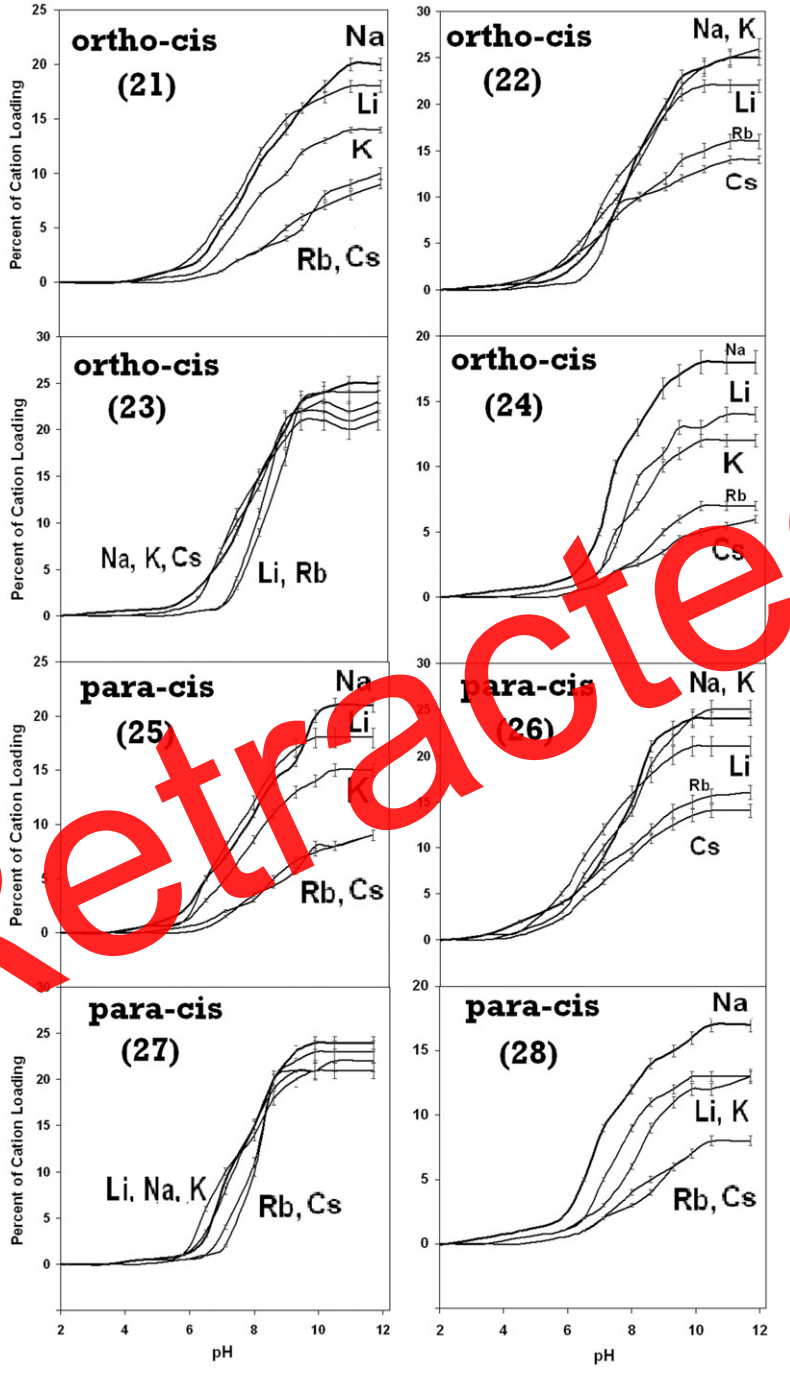

Figure 4. Solvent extractions of alkali metal cations by partial-cone isoconformers.

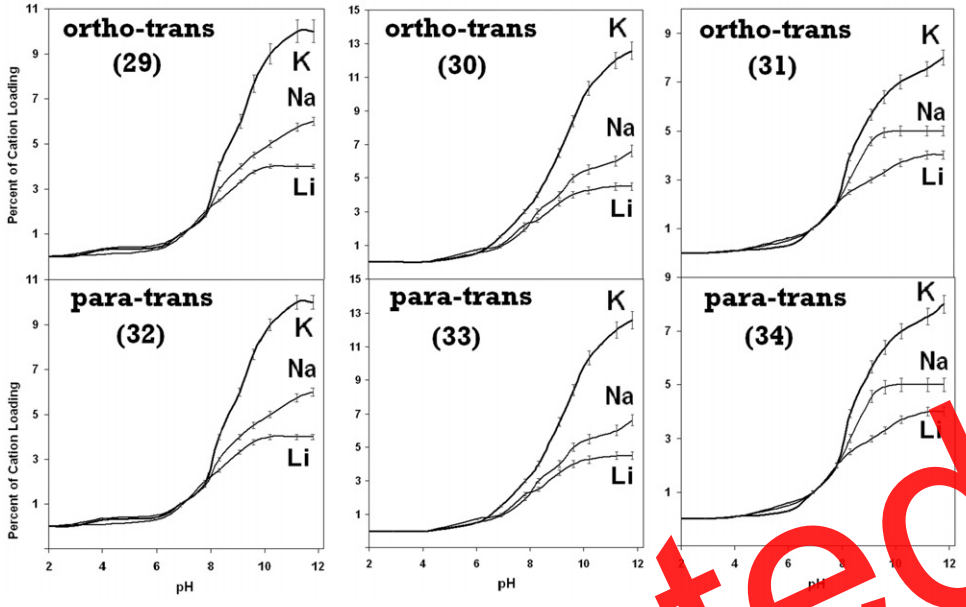

Figure 4. Continued.

3.3.4. ***para-trans*** **Partial-cone isoconformers.** The third derivative with di-[*N*-(*para*-nitro phenyl)sulfonyl carboxamide] moiety could not be synthesized. For all three of the *para-trans* partial-cone di-ionizable *p-tert*-butylcalix[4]arenes **32**–**34**, the maximum loadings were 17–22%. In derivatives **32**–**34**, the $pH_{1/2}$ values were 8.6, 8.6, and 8.1, respectively. The results of competitive solvent extractions by ligand derivatives **32**–**34** in chloroform are presented in the fourth row of figure 4. These derivatives did not show any binding tendency toward Rb^+ and Cs^+. Owing to the selective 1 : 1 binding of K^+ with the ionizable moieties and unselective binding of other alkali cations, the selectivity order for calix[4]arene derivatives **32**–**34** at $pH \geq 8.0$ was determined to be $Li^+ < Na^+ < K^+$; all maximum K^+ loadings exceed 12%. This macrocycle presented the K^+/Li^+, K^+/Na^+, and Na^+/Li^+ selectivities of 3, 2, and 1.5 under high loading conditions, respectively.

3.4. *Analysis of variables*

The effect of different substitutions in the pendant groups as well as different isoconformations (conformation, orientation, and position) of di-ionizable calix[4]arene derivatives on the sensitivity (extraction efficiency), selectivity, and $pH_{1/2}$ values of five alkali metal cations were determined and compared. Based upon the results, alternation of aryl group in the pendant moieties, changing their orientation from *cis*- to *trans*- as well as *ortho*- to *para*-analogs revealed no changes in the selectivity of macrocyclic ligands. Besides, the cone conformers were selective to sodium cations and the 1,2-alternate conformers showed a relative selectivity to potassium and rubidium cations. The partial-cone conformers were selective to potassium and to one of the lithium or sodium cations.

Alternation of aryl group in the pendant moieties showed no changes in the extraction efficiency of macrocyclic ligands. The lower extraction efficiency of partial-cone conformers than their 1,2-alternate and cone analogues demonstrated that conformation variation had a pronounced influence upon complexation of alkali metal cations. The 1,2-alternate conformers showed the widest range of extraction efficiency, which was 4 and 2 times of partial-cone and cone analogues. The extraction efficiency of *cis*-isomers than their *trans*-analogues revealed that orient variation of pendant moieties had a pronounced influence upon the complexation of alkali metal cations. The *cis*-isomers presented a middle range of extraction efficiency, while the extraction efficiency for *trans*-analogs was too much high or too much low. The percent of loading, which is related to the sensitivity of extraction method, was compared in *ortho*-isomers and their *para*-analogues. The results depicted that the variation in position of pendant moieties can have a pronounced influence on the extraction efficiency of alkali metal cations. The percent of loading in *ortho*-isomers was equal and lower than that of *para*-analogues.

Replacement of aryl group in the pendant moieties as well as changing from *ortho*- to *para*-analogues showed no changes in the $pH_{1/2}$ of the resulting complex. The lower $pH_{1/2}$ of 1,2-alternate conformers than their cone and partial-cone analogues demonstrated that conformation variation had a pronounced influence upon the complexation of alkali metal cations. The partial-cone conformers showed the widest range of $pH_{1/2}$ from 7.5 to 8.7, while this range in cone and 1,2-alternate conformers were determined to be 7.7–8.0 and 6.6–7.0, respectively. The $pH_{1/2}$ in *cis*-isomers than their *trans*-analogs revealed that orient variation of pendant moieties had an influence upon the complexation of alkali metal cations. The *cis*-isomers presented a middle range of $7.0 < pH_{1/2} < 8.0$, while in the *trans*-analogs it was in $pH_{1/2} < 7.0$ or $pH_{1/2} > 8.0$.

The selectivity of macrocycles **01**–**34** toward alkali metals was systematically investigated with respect to the orientation and position of pendant moieties as well as the functional groups on the pendant chains. Based upon the results, the cone conformations were selective toward Na^+, while the 1,2-atlernate conformers showed two distinct selectivities for *cis*- (toward K^+) and *trans*- (toward Rb^+) isomers. Likewise, the partial-cone conformers showed two selectivities for *cis*- (toward Na^+) and *trans*- (toward K^+) isomers.

4. Experimental

4.1. *Characteristics of the reaction products*

4.1.1. Synthesis of *ortho*-cone conformers (01–04). 5,11,17,23-Tetrakis(1,1-dimethylethyl)-25,26-dihydroxy-27,28-di(1-propoxy)calix[4]arene has been synthesized by the procedure reported here. 7.00 g (10.80 mmol) *p*-*tert*-butylcalix[4]arene was added to a solution of DMSO (50 mL) and 40% aqueous NaOH (7.06 mL, 100.00 mmol). After that, the mixture was warmed to 50°C and 9.20 g (43.00 mmol) PrOTs was added. The mixture was stirred for 24 h at 70°C. After cooling to room temperature, the reaction mixture was poured into a 5% aqueous HCl solution (100 mL). The crude product was extracted with dichloromethane and the solution was dried over $MgSO_4$. The

dichloromethane was evaporated *in vacuo* and the residue was washed with MeOH to give 5,11,17,23-tetrakis(1,1-dimethylethyl)-25,26-dihydroxy-27,28-di(1-propoxy)calix[4]arene (6.31 g, 88%) with m.p. 168–170°C.

A mixture of THF (32 mL) and NaH (0.56 g, 22.19 mmol) was stirred and a solution of THF (25 mL) and 5,11,17,23-tetrakis(1,1-dimethylethyl)-25,26-dihydroxy-27,28-di(1-propoxy)calix[4]arene (2.75 g, 3.70 mmol) was added dropwise. The solution was stirred at room temperature under nitrogen for 3 h, and then ethyl bromoacetate (2.4 mL, 22.19 mmol) was added. The reaction mixture was refluxed for 24 h and was quenched with 25 mL of 5% aqueous HCl. After evaporating the THF *in vacuo*, the residue was allowed to cool to room temperature. The residue was washed with 5% HCl (150 mL) and dichloromethane was used to extract 5,11,17,23-tetrakis(1,1-dimethylethyl)-25,26-bis[(ethoxycarbonyl)methoxy]-27,28-di(1-propoxy)calix[4]arene. The organic layer was washed with water, dried over $MgSO_4$, and evaporated *in vacuo*. The crude product was recrystallized from MeOH to obtain 5,11,17,23-tetrakis(1,1-dimethylethyl)-25,26-bis[(ethoxycarbonyl)methoxy]-27,28-di(1-propoxy)calix[4]arene (2.72 g, 78%) as a white solid with m.p. 78–80°C.

A solution of 5,11,17,23-tetrakis(1,1-dimethylethyl)-25,26-bis[(ethoxycarbonyl)-methoxy]-27,28-di(1-propoxy)calix[4]arene (3.54 mmol), 10% aqueous Me_4NOH (75 mL), and THF (75 mL) was refluxed for 24 h. The reaction mixture was cooled to room temperature and was stirred with 6 N HCl (30 mL) for 2 h. After evaporating the THF *in vacuo*, a white precipitate was filtered and dissolved in CH_2Cl_2 (75 mL). The aqueous filtrate was extracted with CH_2Cl_2 (2 × 75 mL). The combined organic layers were washed with 6 N aqueous HCl until pH = 1 and dried over $MgSO_4$. The dichloromethane was evaporated *in vacuo* to give 5,11,17,23-tetrakis(1,1-dimethylethyl)-25,26-bis(carboxymethoxy)-27,28-di(1-propoxy)calix[4]arene (3.40 g, 96% yield) as a white solid with m.p. 169–171°C.

4.1.1.1. *Synthesis of 5,11,17,23-tetrakis(1,1-dimethylethyl)-25,26-bis(N-phenylsulfonyl carbamoylmethoxy)-27,28-di(1-propoxy)calix[4]arene (01).* A solution of 5,11,17,23-tetrakis(1,1-dimethylethyl)-25,26-bis(chlorocarboxymethoxy)-27,28-di(1-propoxy) calix[4]arene in THF (10 mL) was added to a mixture containing NaH (0.58 g, 24.0 mmol) and 9.50 mmol of phenyl sulfonamide in 100 mL THF, and the mixture was stirred under nitrogen for 6 h at room temperature. Then 2 mL H_2O was added to decompose the excess NaH and the THF was evaporated *in vacuo* and 200 mL CH_2Cl_2 was added to the residue. The organic layer was washed with 200 mL 1N HCl and water, and was dried over $MgSO_4$ and was evaporated *in vacuo* to give the crude di-ionizable calix[4]arene. After purification, the product was dissolved in CH_2Cl_2, washed with 10% aqueous HCl and water, and dried over $MgSO_4$. The solution was evaporated *in vacuo* to give the derivative **01**. Product **01** was obtained in 90% yield after chromatography on silica gel with CH_2Cl_2–MeOH (80 : 1) as eluent. White solid; m.p. 130–142°C; ν_{max} (film) (cm^{-1}): 3240 (NH), 1724 (C=O), 1360 and 1188 (S=O); ^1H NMR ($CDCl_3$): δ 0.96 (br s, 18H), 1.24 (br s, 18H), 2.00–4.28 (br m, 26H), 6.22–7.32 (br m, 8H), 7.68 (t, $J = 7.52$, 4H), 7.82 (t, $J = 7.42$, 2H), 7.98 (d, $J = 7.52$, 4H), 9.32 (br s, 2H); ^{13}C NMR ($CDCl_3$): δ_C 171.20, 171.00, 155.68, 153.70, 144.50, 138.12, 133.90, 132.60, 129.02, 128.20, 125.80, 72.88, 60.22, 33.88, 33.12, 33.14, 31.82, 31.04, 25.30; Anal. Calcd $C_{66}H_{82}N_2O_{10}S_2$: C, 70.30; H, 7.36; N, 2.42. Found: C, 70.20; H, 7.28; N, 2.52.

4.1.1.2. *Synthesis of 5,11,17,23-tetrakis(1,1-dimethylethyl)-25,26-bis[N-(4-methylphenyl)sulfonyl carbamoylmethoxy]-27,28-di(1-propoxy)calix[4]arene (02).* 2.40 mmol of 5,11,17,23-tetrakis(1,1-dimethylethyl)-25,26-bis(chlorocarboxymethoxy)-27,28-di(1-propoxy)calix[4]arene was dried by benzene-azeotropic distillation. 24.0 mmol (3.04 g) oxalyl chloride was added and the reaction mixture was refluxed for 4 h under nitrogen atmosphere. The solvent was removed *in vacuo* to provide the corresponding acid chloride. A solution of the acid chloride in 10 mL THF was added to a mixture of 9.60 mmol (*p*-methyl)phenyl sulfonamide and 0.58 g NaH (24.0 mmol) in 100 mL THF, and the mixture was stirred under nitrogen for 4 h at room temperature. H_2O (2 mL) was added to decompose the excess NaH. The THF was evaporated *in vacuo* and 200 mL CH_2Cl_2 was added to the residue. The organic layer was washed with 200 mL HCl (1N) and water, dried over $MgSO_4$, and evaporated *in vacuo* to give the di-ionizable calix[4]arene. After purification, the product was dissolved in CH_2Cl_2, washed with 10% aqueous HCl and water, and dried over $MgSO_4$. The solution was evaporated *in vacuo* to give product **02**, which was obtained in 88% yield after chromatography on silica gel with CH_2Cl_2:MeOH (80 : 1) as eluent. White solid; m.p. 148–154°C; ν_{max} (film) (cm^{-1}): 3254 (NH), 1720 (C=O), 1342 and 1188 (S=O); ^1H NMR ($CDCl_3$): δ 0.98 (br s, 18H), 1.24 (br s, 18H), 2.08–4.16 (br m, 32H), 6.50–7.10 (br m, 8H), 8.22 (d, $J = 4.76$, 4H), 8.32 (d, $J = 4.68$, 4H), 9.38 (br s, 2H); ^{13}C NMR ($CDCl_3$): δ_C 174.42, 170.62, 152.62, 150.82, 144.42, 143.68, 134.26, 132.48, 129.32, 125.84, 124.66, 34.24, 33.42, 33.12, 31.28, 31.04, 25.26, 21.28; Anal. Calcd $C_{68}H_{86}N_2O_{10}S_2 \cdot 0.1CH_2Cl_2$: C, 65.12; H, 7.38; N, 4.52. Found: C, 65.24; H, 7.28; N, 4.62.

4.1.1.3. *Synthesis of 5,11,17,23-tetrakis(1,1-dimethylethyl)-25,26-bis[N-(4-hydroxyphenyl)sulfonyl carbamoylmethoxy]-27,28-di(1-propoxy)calix[4]arene (03).* 2.40 mmol of 5,11,17,23-tetrakis(1,1-dimethylethyl)-25,26-bis(chlorocarboxymethoxy)-27,28-di(1-propoxy)calix[4]arene was dried by benzene-azeotropic distillation. 24.0 mmol (3.04 g) oxalyl chloride was added and the reaction mixture was refluxed for 5 h under nitrogen atmosphere. The solvent was removed *in vacuo* to provide the corresponding acid chloride. A solution of the acid chloride in 10 mL THF was added to a mixture of 9.60 mmol (4-hydroxy)phenyl sulfonamide and 0.58 g NaH (24.0 mmol) in 100 mL THF, and the mixture was stirred under nitrogen at room temperature for 4 h. Then, 2 mL H_2O was added to decompose the excess NaH. The THF was evaporated *in vacuo* and 200 mL CH_2Cl_2 was added to the residue. The organic layer was washed with 200 mL HCl (1N) and water, dried over $MgSO_4$, and evaporated *in vacuo* to give the crude di-ionizable calix[4]arene. After purification, the product was dissolved in CH_2Cl_2, washed with 10% aqueous HCl and water, and dried over $MgSO_4$. The solution was evaporated *in vacuo* to give product **03**. Derivative **03** was obtained in 84% yield after chromatography on silica gel with CH_2Cl_2:MeOH (80 : 1) as eluent. White solid; m.p. 170–176°C; ν_{max} (film) (cm^{-1}): 3238 (NH), 1724 (C=O), 1362 and 1168 (S=O); ^1H NMR ($CDCl_3$): δ 0.96 (br s, 18H), 1.24 (br s, 18H), 2.08–4.04 (br m, 26H), 6.38–7.46 (br m, 8H), 7.62 (t, $J = 7.76$, 4H), 8.02 (d, $J = 7.42$, 4H), 8.54 (t, $J = 7.30$, 2H), 9.44 (br s, 2H); ^{13}C NMR ($CDCl_3$): δ_C 171.38, 171.02, 155.06, 153.72, 144.18, 138.96, 133.32, 132.44, 129.20, 128.34, 125.28, 73.06, 60.08, 34.28, 33.96, 33.42, 31.14, 31.06, 22.27; Anal. Calcd $C_{66}H_{82}N_2O_{12}S_2$: C, 70.66; H, 7.42; N, 2.44. Found: C, 70.28; H, 7.32; N, 2.40.

4.1.1.4. *Synthesis of 5,11,17,23-tetrakis(1,1-dimethylethyl)-25,26-bis[N-(4-nitrophenyl)sulfonyl carbamoylmethoxy]-27,28-di(1-propoxy)calix[4]arene (04).* 2.40 mmol of 5,11,17,23-tetrakis(1,1-dimethylethyl)-25,26-bis(chlorocarboxymethoxy)-27,28-di(1-propoxy)calix[4]arene was dried by benzene-azeotropic distillation. 3.04 g (24.0 mmol) oxalyl chloride was added and the reaction mixture was refluxed for 7 h under nitrogen atmosphere. The solvent was removed *in vacuo* to provide the corresponding acid chloride. A solution of the acid chloride in 10 mL THF was added to a mixture of 12.20 mmol (4-nitro)phenyl sulfonamide and 28.8 mmol NaH (0.70 g) in 100 mL THF, and the mixture was stirred under nitrogen at room temperature for 6 h. Then, 2 mL H_2O was added to decompose the excess NaH. The THF was evaporated *in vacuo* and 200 mL CH_2Cl_2 was added to the residue. The organic layer was washed with 1N HCl (200 mL) and water, dried over $MgSO_4$, and evaporated *in vacuo* to give the crude di-ionizable calix[4]arene. After purification, the product was dissolved in CH_2Cl_2, washed with 10% aqueous HCl and water, and dried over $MgSO_4$. The solution was evaporated *in vacuo* to give product **04**, which was obtained in 68% yield after chromatography on silica gel with CH_2Cl_2:MeOH (80 : 1) as eluent. Yellow solid, m.p. 174–176°C; ν_{max} (film) (cm^{-1}): 3232 (NH), 1704 (C=O), 1358 and 1196 (S=O); ^1H NMR ($CDCl_3$): δ 0.96 (br s, 18H), 1.24 (br s, 18H), 2.10–4.02 (br m, 26H), 6.32–7.48 (br m, 8H), 7.44 (t, $J = 7.08$, 4H), 8.26 (d, $J = 7.38$, 4H), 9.42 (br s, 2H); ^{13}C NMR ($CDCl_3$): δ_C 171.02, 171.24, 155.62, 153.24, 144.28, 138.82, 133.38, 132.66, 129.04, 128.48, 125.24, 73.20, 60.15, 34.40, 33.28, 33.00, 31.38, 31.10, 20.14; Anal. Calcd $C_{66}H_{80}N_4O_{14}S_2$: C, 70.16; H, 7.18; N, 4.48. Found: C, 70.26; H, 7.24; N, 4.52.

4.1.2. Synthesis of *para*-cone conformers (05–08). K_2CO_3 (82.93 g, 600 mmol) and *n*-propyl *p*-toluensulfonate (12.85 g, 60.0 mmol) were added to the suspension of the *p-tert*-butylcalix[4]arene (19.46 g, 30.0 mmol) in 200 mL of dry *n*-C_3H_7CN. The reaction mixture was refluxed for 20 h and then another portion of *n*-propyl *p*-toluenesulfonate (6.43 g, 30.0 mmol) was added. The mixture was heated for another 20 h. After cooling, the reaction mixture was filtered and the solvent was evaporated *in vacuo*. The residue was partitioned between 200 mL of CH_2Cl_2 and 200 mL of HCl (1N). The organic layer was separated, washed with water, and evaporated *in vacuo*. The crude product was purified by chromatography on silica gel column with CH_2Cl_2:hexanes (20 : 1) as eluent to give 5,11,17,23-tetrakis(1,1-dimethylethyl)-25,27-dihydroxy-26,28-di(1-propoxy)calix[4]arene (88%) as a white solid. The product was recrystallized from *n*-C_3H_7OH–CH_2Cl_2 in 71% yield; m.p. 240–242°C.

10 mmol of 5,11,17,23-tetrakis(1,1-dimethylethyl)-25,27-dihydroxy-26,28-di(1-propoxy)calix[4]arene was added to the suspension of sodium NaH (0.96 g, 40 mmol) in DMF (100 mL), and the mixture was stirred at room temperature. Once the evolution of hydrogen ceased, a solution of ethyl bromoacetate (22 mmol) in DMF (10 mL) was added over a period of 30 min. The mixture was stirred for 3 h, and another portion of ethyl bromoacetate (10 mmol) in DMF (5 mL) was added. The reaction mixture was stirred for another 2 h and the excess of NaH was carefully decomposed by dropwise addition of water. The mixture was diluted with 200 mL HCl (1N) and was extracted with CH_2Cl_2 (2×200 mL). The combined organic extracts were washed with water, dried over $MgSO_4$, and evaporated *in vacuo*. The DMF and the unreacted ethyl bromoacetate were removed by distillation under vacuum (60°C, 1 mm Hg). The residual pale-yellow oil was purified by chromatography on silica gel with

hexanes:EtOAc (40 : 1) as eluent to give the final product 5,11,17,23-tetrakis(1,1-dimethylethyl)-25,27-bis[(ethoxycarbonyl)methoxy]-26,28-di(1-propoxy)calix[4]arene in 80% yield as a white solid; m.p. 108–110°C.

A solution of 5,11,17,23-tetrakis(1,1-dimethylethyl)-25,27-bis[(ethoxycarbonyl)-methoxy]-26,28-di(1-propoxy)calix[4]arene (5.0 mmol), THF (150 mL), and 10% aqueous Me_4NOH (150 mL) was refluxed overnight. The reaction mixture was acidified with HCl (10%) to pH ~ 1. The solvent was removed *in vacuo* and 200 mL CH_2Cl_2 was added. The organic layer was washed with water, dried over $MgSO_4$, and evaporated *in vacuo* to give the final product 5,11,17,23-tetrakis(1,1-dimethylethyl)-25,27-bis(carboxymethoxy)-26,28-di(1-propoxy)calix[4]arene in 96% yield as a white solid; m.p. 252–254°C.

2.40 mmol of 5,11,17,23-tetrakis(1,1-dimethylethyl)-25,27-bis(carboxymethoxy)-26,28-di(1-propoxy)calix[4]arene was dried by benzene-azeotropic distillation. Oxalyl chloride (3.04 g, 24.0 mmol) was added to the solution and the reaction mixture was refluxed for 5 h under nitrogen atmosphere. The solvent was removed *in vacuo* to provide the corresponding acid chloride 5,11,17,23-tetrakis(1,1-dimethylethyl)-25,27-bis(chlorocarboxymethoxy)-26,28-di(1-propoxy)calix[4]arene.

4.1.2.1. *Synthesis of 5,11,17,23-tetrakis(1,1-dimethylethyl)-25,27-bis(N-phenylsulfonyl carbamoylmethoxy)-26,28-di(1-propoxy)calix[4]arene (05).* A solution of 5,11,17,23-tetrakis(1,1-dimethylethyl)-25,27-bis(chlorocarboxymethoxy)-26,28-di(1-propoxy)calix[4]arene in THF (10 mL) was added to a mixture of the appropriate sulfonamide (9.50 mmol) and NaH (0.58 g, 24.0 mmol) in THF (100 mL), and the mixture was stirred under nitrogen at room temperature for 6 h. Then 2 mL H_2O was carefully added to decompose the excess NaH. The THF was evaporated *in vacuo* and CH_2Cl_2 (200 mL) was added to the residue. The organic layer was washed with 200 mL HCl (1N) and water, was dried over $MgSO_4$, and was evaporated *in vacuo* to give the crude di-ionizable calix[4]arene. After purification, the product was dissolved in CH_2Cl_2, washed with 10% aqueous HCl and water, and dried over $MgSO_4$. The solution was evaporated *in vacuo* to give product **05**. Derivative **05** was obtained in 86% yield after chromatography on silica gel with CH_2Cl_2:MeOH (80 : 1) as eluent. White solid; m.p. 136–140°C; ν_{max} (film) (cm^{-1}): 3248 (NH), 1722 (C=O), 1362 and 1186 (S=O); ^1H NMR ($CDCl_3$): δ 0.96 (br s, 18H), 1.24 (br s, 18H), 2.04–4.22 (br m, 26H), 6.20–7.22 (br m, 8H), 7.50 (t, $J = 7.72$, 4H), 7.59 (t, $J = 7.32$, 2H), 8.07 (d, $J = 7.50$, 4H), 9.48 (br s, 2H); ^{13}C NMR ($CDCl_3$): δ_C 171.22, 171.02, 155.81, 153.72, 144.53, 138.15, 133.09, 132.60, 129.20, 128.02, 125.09, 72.98, 60.04, 33.96, 33.06, 33.44, 31.94, 31.02, 25.31; Anal. Calcd $C_{66}H_{82}N_2O_{10}S_2$: C, 70.31; H, 7.33; N, 2.48. Found: C, 70.13; H, 7.23; N, 2.59.

4.1.2.2. *Synthesis of 5,11,17,23-tetrakis(1,1-dimethylethyl)-25,27-bis[N-(4-methylphenyl)sulfonyl carbamoylmethoxy]-26,28-di(1-propoxy)calix[4]arene (06).* 2.40 mmol of 5,11,17,23-tetrakis(1,1-dimethylethyl)-25,27-bis(chlorocarboxymethoxy)-26,28-di(1-propoxy)calix[4]arene was dried by benzene-azeotropic distillation. 3.04 g (24.0 mmol) oxalyl chloride was added and the reaction mixture was refluxed for 5 h under nitrogen atmosphere. The solvent was removed *in vacuo* to provide the corresponding acid chloride. A solution of the acid chloride in THF (10 mL) was added to a mixture of the appropriate sulfonamide (9.60 mmol) and NaH (0.58 g, 24.0 mmol) in THF (100 mL), and the mixture was stirred under nitrogen at room temperature for 5 h. Then, 2 mL

H_2O was added to decompose the excess NaH. The THF was evaporated *in vacuo* and CH_2Cl_2 (200 mL) was added to the residue. The organic layer was washed with 1N HCl (200 mL) and water, dried over $MgSO_4$, and evaporated *in vacuo* to give the crude di-ionizable calix[4]arene. After purification, the product was dissolved in CH_2Cl_2, washed with 10% aqueous HCl and water, and dried over $MgSO_4$. The solution was evaporated *in vacuo* to give product **06**. Derivative **06** was obtained in 84% yield after chromatography on silica gel with CH_2Cl_2:MeOH (80 : 1) as eluent. Yellow solid; m.p. 144–148°C; ν_{max} (film) (cm^{-1}): 3255 (NH), 1726 (C=O), 1346 and 1180 (S=O); ^1H NMR ($CDCl_3$): δ 0.98 (br s, 18H), 1.24 (br s, 18H), 2.06–4.20 (br m, 32H), 6.52–7.12 (br m, 8H), 8.27 (d, $J = 4.80$, 4H), 8.30 (d, $J = 4.82$, 4H), 9.35 (br s, 2H); ^{13}C NMR ($CDCl_3$): δ_C 174.32, 170.82, 152.66, 150.28, 144.96,143.08, 134.52, 132.80, 129.08, 125.68, 124.02, 34.20, 33.76, 33.48, 31.46, 31.22, 25,62, 21.50; Anal. Calcd $C_{68}H_{86}N_2O_{10}S_2 \cdot 0.1\ CH_2Cl_2$: C, 65.16; H, 7.33; N, 4.50. Found: C, 65.22; H, 7.24; N, 4.42.

4.1.2.3. *Synthesis of 5,11,17,23-tetrakis(1,1-dimethylethyl)-25,27-bis[N-(4-hydroxyphenyl)sulfonyl carbamoylmethoxy]-26,28-di(1-propoxy)calix[4]arene (07).* 2.40 mmol of 5,11,17,23-tetrakis(1,1-dimethylethyl)-25,27-bis(chlorocarboxymethoxy)-26,28-di(1-propoxy)calix[4]arene was dried by benzene-azeotropic distillation. 3.04 g (24.0 mmol) oxalyl chloride was added and the reaction mixture was refluxed for 5 h under nitrogen atmosphere. The solvent was removed *in vacuo* to provide the corresponding acid chloride. A solution of the acid chloride in THF (10 mL) was added to a mixture of the appropriate sulfonamide (9.60 mmol) and NaH (0.58 g, 24.0 mmol mmol) in THF (100 mL), and the mixture was stirred under nitrogen at room temperature for 5 h. Then, 2 mL H_2O was added to decompose the excess NaH. The THF was evaporated *in vacuo* and CH_2Cl_2 (200 mL) was added to the residue. The organic layer was washed with 1N HCl (200 mL) and water, dried over $MgSO_4$, and evaporated *in vacuo* to give the crude di-ionizable calix[4]arene. After purification, the product was dissolved in CH_2Cl_2, washed with 10% aqueous HCl and water, and dried over $MgSO_4$. The solution was evaporated *in vacuo* to give product **07**. Derivative **07** was obtained in 84% yield after chromatography on silica gel with CH_2Cl_2:MeOH (80 : 1) as eluent. White solid; m.p. 166–170°C; ν_{max} (film) (cm^{-1}): 3244 (NH), 1720 (C=O), 1360 and 1180 (S=O); ^1H NMR ($CDCl_3$): δ 0.96 (br s, 18H), 1.24 (br s, 18H), 2.04–4.24 (br m, 26H), 6.39–7.42 (br m, 8H), 7.60 (t, $J = 7.66$, 4H), 8.26 (d, $J = 7.40$, 4H), 8.28 (t, $J = 7.30$, 2H), 9.96 (br s, 2H); ^{13}C NMR ($CDCl_3$): δ_C 171.20, 171.04, 155.14, 153.74, 144.48, 138.12, 133.10, 132.44, 129.22, 128.32, 125.22, 73.04, 60.04, 34.00, 33.02, 33.42, 31.96, 31.04, 22.18; Anal. Calcd $C_{66}H_{82}N_2O_{12}S_2$: C, 70.22; H, 7.24; N, 2.40 Found: C, 70.12; H, 7.18; N, 2.55.

4.1.2.4. *Synthesis of 5,11,17,23-tetrakis(1,1-dimethylethyl)-25,27-bis[N-(4-nitrophenyl)sulfonyl carbamoylmethoxy]-26,28-di(1-propoxy)calix[4]arene (08).* 2.40 mmol of 5,11,17,23-tetrakis(1,1-dimethylethyl)-25,27-bis(chlorocarboxymethoxy)-26,28-di(1-propoxy)calix[4]arene was dried by benzene-azeotropic distillation. 3.04 g (24.0 mmol) oxalyl chloride was added and the reaction mixture was refluxed for 7 h under nitrogen atmosphere. The solvent was removed *in vacuo* to provide the corresponding acid chloride. A solution of the acid chloride in THF (10 mL) was added to a mixture of the appropriate sulfonamide (12.20 mmol) and NaH (0.70 g, 28.8 mmol) in THF (100 mL), and the mixture was stirred under nitrogen at room temperature for 7 h. Then, 2 mL H_2O was added to decompose the excess NaH. The THF was evaporated *in vacuo* and

CH_2Cl_2 (200 mL) was added to the residue. The organic layer was washed with 1N HCl (200 mL) and water, dried over $MgSO_4$, and evaporated *in vacuo* to give the crude di-ionizable calix[4]arene. After purification, the product was dissolved in CH_2Cl_2, washed with 10% aqueous HCl and water, and dried over $MgSO_4$. The solution was evaporated *in vacuo* to give product **08**. Derivative **08** was obtained in 80% yield after chromatography on silica gel with CH_2Cl_2 : MeOH (80 : 1) as eluent. Green solid; m.p. 184–188°C; ν_{max} (film) (cm^{-1}): 3244 (NH), 1720 (C=O), 1360 and 1182 (S=O); ^1H NMR ($CDCl_3$): δ 0.96 (br s, 18H), 1.24 (br s, 18H), 2.04–4.22 (br m, 26H), 6.24–7.24 (br m, 8H), 7.52 (t, $J = 7.33$, 4H), 8.02 (d, $J = 7.45$, 4H), 9.24 (br s, 2H); ^{13}C NMR ($CDCl_3$): δ_C 171.08, 171.44, 155.88, 153.42, 144.34, 138.16, 133.12, 132.56, 129.22, 128.00, 125.10, 73.02, 60.08, 34.04, 33.12, 33.68, 31.88, 31.12, 20.32; Anal. Calcd $C_{66}H_{80}N_4O_{14}S_2$: C, 70.12; H, 7.14; N, 4.42. Found: C, 70.04; H, 7.20; N, 4.54.

4.1.3. Synthesis of 1,2-alternate Conformers (09–20). 5,11,17,23-Tetrakis(1,1-dimethylethyl)-25,26-bis(N-X-sulfonyl carbamoylmethoxy)-27,28-di(1-propoxy)calix[4]arene was dissolved in 1,1,2,2-tetrachloroethane and heated to temperatures above 100°C. It was isomerized to the *cis*-1,2-alternate conformations until equilibrium was reached. The X represented phenyl, *p*-CH_3phenyl, *p*-OHphenyl, and *p*-NO_2phenyl moieties. The organic layer was washed with 200 mL 1N HCl and water, dried over $MgSO_4$, and was evaporated *in vacuo* to give the crude di-ionizable calix[4]arene. After purification, the product was dissolved in CH_2Cl_2, washed with 10% aqueous HCl and water, and dried over $MgSO_4$. The solution was evaporated *in vacuo* to give the derivatives **09–20**. Products **9–12** were obtained in 15%, products **13–16** were obtained in 35%, and products **17–20** were obtained in 50% yield after chromatography on silica gel with CH_3Cl:MeOH (60 : 1) as eluent.

4.1.3.1. *Characteristics of product 09.* White solid; m.p. 118–122°C; ν_{max} (film) (cm^{-1}): 3254 (NH), 1720 (C=O), 1366 and 1178 (S=O); ^1H NMR ($CDCl_3$): δ 0.96 (br s, 18H), 1.24 (br s, 18H), 2.08–4.26 (br m, 26H), 6.12–7.40 (br m, 8H), 7.62 (t, $J = 7.42$, 4H), 7.80 (t, $J = 7.16$, 2H), 8.04 (d, $J = 7.36$, 4H), 9.30 (br s, 2H); ^{13}C NMR ($CDCl_3$): δ_C 171.58, 171.24, 155.34, 153.08, 144.06, 138.56 133.76, 132.08, 129.24, 128.74, 125.48, 72.42, 60.12, 33.54, 33.08, 32.96, 31.48, 31.12, 25.42; Anal. Calcd $C_{66}H_{82}N_2O_{10}S_2$: C, 70.32; H, 7.32; N, 2.16. Found: C, 70.38; H, 7.42; N, 2.28.

4.1.3.2. *Characteristics of product 10.* White solid; m.p. 142–146°C; ν_{max} (film) (cm^{-1}): 3226 (NH), 1722 (C=O), 1332 and 1182 (S=O); ^1H NMR ($CDCl_3$): δ 0.98 (br s, 18H), 1.24 (br s, 18H), 2.12–4.12 (br m, 32H), 6.46–7.08 (br m, 8H), 8.24 (d, $J = 4.74$, 4H), 8.34 (d, $J = 4.78$, 4H), 9.36 (br s, 2H); ^{13}C NMR ($CDCl_3$): δ_C 174.24, 170.26, 152.42, 150.28, 144.36,143.34, 135.02, 132.36, 129.28, 125.72, 124.86, 34.26, 33.04, 32.92, 31.24, 31.32, 25,54, 21.86; Anal. Calcd $C_{68}H_{86}N_2O_{10}S_2 \cdot 0.1\ CH_2Cl_2$: C, 65.34; H, 7.34; N, 4.48. Found: C, 65.30; H, 7.26; N, 4.58.

4.1.3.3. *Characteristics of product 11.* Yellow solid; m.p. 174–178°C; ν_{max} (film) (cm^{-1}): 3230 (NH), 1728 (C=O), 1326 and 1144 (S=O); ^1H NMR ($CDCl_3$): δ 0.96 (br s, 18H), 1.26 (br s, 18H), 2.26–4.68 (br m, 26H), 6.52–7.18 (br m, 8H), 7.82 (t, $J = 7.26$, 4H), 8.12 (d, $J = 7.52$, 4H), 8.64 (t, $J = 7.02$, 2H), 9.52 (br s, 2H); ^{13}C NMR ($CDCl_3$): δ_C 171.54, 170.98, 155.02, 153.56, 144.30, 138.78, 133.24, 132.42, 129.08,

128.28, 125.26, 73.18, 60.16, 34.34, 33.88, 33.02, 31.18, 31.00, 22.58; Anal. Calcd $C_{66}H_{82}N_2O_{12}S_2$: C, 70.04; H, 7.28; N, 2.52. Found: C, 70.26; H, 7.16; N, 2.42.

4.1.3.4. *Characteristics of product 12.* White solid; m.p. 168–170°C; ν_{max} (film) (cm^{-1}): 3216 (NH), 1724 (C=O), 1396 and 1168 (S=O); ^1H NMR ($CDCl_3$): δ 0.96 (br s, 18H), 1.22 (br s, 18H), 2.18–4.32 (br m, 26H), 6.18–7.40 (br m, 8H), 7.44 (t, $J = 7.02$, 4H), 8.26 (d, $J = 7.14$, 4H), 9.28 (br s, 2H); ^{13}C NMR ($CDCl_3$): δ_C 171.28, 171.14, 155.26, 153.48, 144.52, 138.68, 133.58, 132.26, 129.52, 128.84, 125.50, 73.32, 60.18, 34.46, 33.02, 32.68, 31.58, 31.42, 20.50; Anal. Calcd $C_{66}H_{80}N_4O_{14}S_2$: C, 70.10; H, 7.22; N, 4.54. Found: C, 70.18; H, 7.26; N, 4.40.

4.1.3.5. *Characteristics of product 13.* White solid; m.p. 138–142°C; ν_{max} (film) (cm^{-1}): 3256 (NH), 1718 (C=O), 1350 and 1166 (S=O); ^1H NMR ($CDCl_3$): δ 0.96 (br s, 18H), 1.22 (br s, 18H), 2.24–4.22 (br m, 26H), 6.18–7.48 (br m, 8H), 7.56 (t, $J = 7.48$, 4H), 7.78 (t, $J = 7.38$, 2H), 8.02 (d, $J = 7.48$, 4H), 9.28 (br s, 2H); ^{13}C NMR ($CDCl_3$): δ_C 171.32, 171.18, 155.54, 153.86, 144.52, 138.06, 133.58, 132.78, 129.12, 128.32, 125.54, 72.34, 60.58, 33.52, 33.08, 32.98, 31.86, 31.12, 25.58; Anal. Calcd $C_{66}H_{82}N_2O_{10}S_2$: C, 70.28; H, 7.42; N, 2.34. Found: C, 70.16; H, 7.52; N, 2.40.

4.1.3.6. *Characteristics of product 14.* White solid; m.p. 144–146°C; ν_{max} (film) (cm^{-1}): 3240 (NH), 1724 (C=O), 1328 and 1158 (S=O); ^1H NMR ($CDCl_3$): δ 0.98 (br s, 18H), 1.26 (br s, 18H), 2.24–4.56 (br m, 32H), 6.08–7.52 (br m, 8H), 8.00 (d, $J = 4.54$, 4H), 8.88 (d, $J = 4.02$, 4H), 9.32 (br s, 2H); ^{13}C NMR ($CDCl_3$): δ_C 174.58, 170.52, 152.38, 150.04, 144.42, 143.52, 134.82, 132.66, 129.72, 125.98, 124.46, 34.92, 33.88, 33.02, 31.12, 30.98, 25.38, 21.52; Anal. Calcd $C_{68}H_{86}N_2O_{10}S_2 \cdot 0.1\ CH_2Cl_2$: C, 65.96; H, 7.20; N, 4.38. Found: C, 65.88; H, 7.32; N, 4.54.

4.1.3.7. *Characteristics of product 15.* White solid; m.p. 176–178°C; ν_{max} (film) (cm^{-1}): 3228 (NH), 1724 (C=O), 1364 and 1158 (S=O); ^1H NMR ($CDCl_3$): δ 0.96 (br s, 18H), 1.24 (br s, 18H), 2.28–4.32 (br m, 26H), 6.78–7.86 (br m, 8H), 7.64 (t, $J = 7.46$, 4H), 8.12 (d, $J = 7.42$, 4H), 8.44 (t, $J = 7.32$, 2H), 9.64 (br s, 2H); ^{13}C NMR ($CDCl_3$): δ_C 171.48, 171.02, 155.66, 153.72, 144.12, 138.46, 133.82, 132.54, 129.22, 128.36, 125.88, 73.26, 60.12, 34.58, 33.76, 33.32, 31.04, 31.08, 22.37; Anal. Calcd $C_{66}H_{82}N_2O_{12}S_2$: C, 70.68; H, 7.32; N, 2.20. Found: C, 70.58; H, 7.22; N, 2.16.

4.1.3.8. *Characteristics of product 16.* White solid; m.p. 172–176°C; ν_{max} (film) (cm^{-1}): 3198 (NH), 1786 (C=O), 1334 and 1156 (S=O); ^1H NMR ($CDCl_3$): δ 0.96 (br s, 18H), 1.24 (br s, 18H), 2.12–4.12 (br m, 26H), 6.36–7.42 (br m, 8H), 7.46 (t, $J = 7.18$, 4H), 8.16 (d, $J = 7.38$, 4H), 9.52 (br s, 2H); ^{13}C NMR ($CDCl_3$): δ_C 171.52, 171.14, 155.52, 153.84, 144.68, 138.32, 133.08, 132.60, 129.84, 128.08, 125.28, 73.22, 60.15, 34.00, 33.26, 32.96, 31.58, 31.06, 20.76; Anal. Calcd $C_{66}H_{80}N_4O_{14}S_2$: C, 70.76; H, 7.38; N, 4.28. Found: C, 70.50; H, 7.32; N, 4.42.

4.1.3.9. *Characteristics of product 17.* Yellow solid; m.p. 132–136°C; ν_{max} (film) (cm^{-1}): 3238 (NH), 1722 (C=O), 1348 and 1176 (S=O); ^1H NMR ($CDCl_3$): δ 0.96 (br s, 18H), 1.24 (br s, 18H), 2.14–4.32 (br m, 26H), 6.22–7.24(br m, 8H), 7.54 (t, $J = 7.62$, 4H), 7.56 (t, $J = 7.22$, 2H), 8.18 (d, $J = 7.48$, 4H), 9.58 (br s, 2H); ^{13}C NMR ($CDCl_3$): δ_C 171.42, 171.12, 155.71, 153.62, 144.63, 138.25, 133.12, 132.64, 129.32,

128.42, 125.98, 72.48, 60.04, 33.68, 33.22, 33.00, 31.88, 31.12, 25.48; Anal. Calcd $C_{66}H_{82}N_2O_{10}S_2$: C, 70.32; H, 7.34; N, 2.46. Found: C, 70.14; H, 7.26; N, 2.58.

4.1.3.10. *Characteristics of product 18*. White solid; m.p. 144–148°C; ν_{max} (film) (cm^{-1}): 3245 (NH), 1736 (C=O), 1336 and 1186 (S=O); ^{1}H NMR ($CDCl_3$): δ 0.98 (br s, 18H), 1.24 (br s, 18H), 2.16–4.28 (br m, 32H), 6.58–7.16 (br m, 8H), 8.26 (d, $J = 4.72$, 4H), 8.32 (d, $J = 4.72$, 4H), 9.25 (br s, 2H); ^{13}C NMR ($CDCl_3$): δ_C 174.02, 170.02, 152.46, 150.48, 144.90,143.48, 134.42, 132.84, 129.00, 125.48, 124.62, 34.26, 33.96, 33.28, 31.26, 31.00, 25,02, 21.40; Anal. Calcd $C_{68}H_{86}N_2O_{10}S_2 \cdot 0.1\ CH_2Cl_2$: C, 65.26; H, 7.35; N, 4.70. Found: C, 65.32; H, 7.34; N, 4.62.

4.1.3.11. *Characteristics of product 19*. Yellow solid; m.p. 168–174°C; ν_{max} (film) (cm^{-1}): 3234 (NH), 1722 (C=O), 1364 and 1182 (S=O); ^{1}H NMR ($CDCl_3$): δ 0.96 (br s, 18H), 1.24 (br s, 18H), 2.04–4.24 (br m, 26H), 6.30–7.32 (br m, 8H), 7.50 (t, $J = 7.46$, 4H), 8.22 (d, $J = 7.42$, 4H), 8.08 (t, $J = 7.30$, 2H), 9.86 (br s, 2H); ^{13}C NMR ($CDCl_3$): δ_C 171.30, 171.24, 155.24, 153.14, 144.42, 138.52, 133.24, 132.14, 129.26, 128.22, 125.42, 73.54, 60.64, 34.02, 33.03, 33.32, 31.98, 31.14, 22.12; Anal. Calcd $C_{66}H_{82}N_2O_{12}S_2$: C, 70.20; H, 7.22; N, 2.44. Found: C, 70.22; H, 7.16; N, 2.52.

4.1.3.12. *Characteristics of product 20*. Green solid; m.p. 180–186°C; ν_{max} (film) (cm^{-1}): 3226 (NH), 1728 (C=O), 1350 and 1186 (S=O); ^{1}H NMR ($CDCl_3$): δ 0.96 (br s, 18H), 1.26 (br s, 18H), 2.08–4.12 (br m, 26H), 6.34–7.26 (br m, 8H), 7.58 (t, $J = 7.43$, 4H), 8.12 (d, $J = 7.47$, 4H), 9.14 (br s, 2H); ^{13}C NMR ($CDCl_3$): δ_C 171.18, 171.44, 155.28, 153.32, 144.54, 138.12, 133.52, 132.46, 129.28, 128.50, 125.12, 73.22, 60.48, 34.14, 33.10, 33.08, 31.86, 31.32, 20.82; Anal. Calcd $C_{66}H_{80}N_4O_{14}S_2$: C, 70.18; H, 7.18; N, 4.22. Found: C, 70.14; H, 7.22; N, 4.34.

4.1.4. Synthesis of partial-cone conformers (21–34). To determine appropriate reaction conditions for the preparation of conformationally pH restricted calix[4]arene carboxylic acid of 25,27-dipropoxy-26,28-bis(carboxymethoxy)calix[4]arene in the partial-cone conformation, 0.10 g of 25,27-dipropoxy-26,28-dihydroxycalix[4]arene (0.19 mmol) was treated with methyl bromoacetate (0.70 mmol, 4,0 equivalents) together with different bases and solvents. 4.0 equivalents of NaH and K_2CO_3, 5.0 equivalents of KH, and 15.0 equivalents of CS_2CO_3 were used. In general, sodium, potassium, and cesium cations favor the cone, partial-cone, and 1,3-alternate conformations, respectively, irrespective of the solvent system. Interestingly, CS_2CO_3 produced mostly the partial-cone isomer instead of the 1,3-alternate isomer in both acetone and DMF solvents. This contradicts the literature prediction that CS_2CO_3 should favor the formation of 1,3-alternate conformational isomer. This result indicates the effect of *para* substituents in controlling the conformational outcome.

On silica gel TLC, the cone and partial-cone isomers have almost the same R_f value of 0.7, but the 1,3-alternate isomer has a very low R_f value of 0.2 with EtOAc : hexane (1 : 8) as the eluent. As a result, the partial-cone (75%) and the 1,3-alternate (25%) isomers, formed using KH in THF, were easily separated by column chromatography, even on a large scale. The resulted esters were hydrolyzed with 10% Me_4NOH/H_2O and THF to produce 25,27-dipropoxy-26,28-bis(carboxymethoxy)calix[4]arenes in cone and partial-cone conformers.

4.1.4.1. *Synthesis of products 21–28 (propoxy-up).* To a solution of 25,27-dipropoxy-26,28-bis(carboxymethoxy)calix[4]arene and 25,26-dipropoxy-27,28-bis(carboxymethoxy)calix[4]arene (1,50 g, 2.30 mmol) in benzene (50 mL), 5.0 mL of oxalyl chloride (7.30 g, 57,5 mmol) was added. The reaction mixture was refluxed for 5 h. The benzene and excess oxalyl chloride was evaporated *in vacuo,* and the crude product was dried under high vacuum. The residue was dissolved in 30 mL THF and added into a mixture of NaH (0.57 g, 95% dry, 23.0 mmol) and appropriate sulfonamide (6.90 mmol, 3,0 equiv) in THF (50 mL) under nitrogen at room temperature. The reaction mixture was stirred for 15 h (except for *p*-nitrobenzenesulfonamide, 2 h) under nitrogen at room temperature. The reaction was quenched with a small amount of H_2O and the THF was evaporated *in vacuo*. The THF layer was separated and dried under high vacuum to give a pale yellow solid. The solid was purified by column chromatography on silica gel with CH_2Cl_2, MeOH : CH_2Cl_2 (1 : 99), and MeOH : CH_2Cl_2 (2 : 99) as eluents to produce a white solid. The solid was dissolved in CH_2Cl_2 (100 mL) and washed with 1 N HCl (100 mL). The organic layer was separated, washed with de-ionized H_2O (100 mL), and evaporated *in vacuo* to give a white solid. The solid was dissolved in small amount of CH_2Cl_2 (10 mL) and hexane was added little by little (50 mL). The flask was put in the freezer for at least 6 h. The organic solution was decanted and the oil, which was stuck to the surface of the glassware, was washed gently with hexane. The oil was again dissolved in CH_2Cl_2, which was evaporated *in vacuo* to produce a pale-yellow oil. The oil became a white solid under high vacuum.

4.1.4.2. *Characteristics of product 21.* White solid; m.p. 112–114°C; ν_{max} (film) (cm^{-1}): 3200 (NH), 1710 (C=O), 1360 and 1108 (S=O); ^{1}H NMR ($CDCl_3$): δ 0.96 (br s, 18H), 1.22 (br s, 18H), 2.04–4.16 (br m, 36H), 6.10–7.46 (br m, 8H), 7.48 (t, $J = 7.32$, 4H), 7.82 (t, $J = 7.14$, 2H), 8.24 (d, $J = 7.26$, 4H), 9.32 (br s, 2H); ^{13}C NMR ($CDCl_3$): δ_C 171.28, 171.54, 155.54, 153.42, 144.02, 138.92 133.48, 132.28, 129.22, 128.24, 125.38, 72.46, 60.14, 34.12, 33.48, 33.02, 31.44, 31.06, 25.52; Anal. Calcd $C_{66}H_{82}N_2O_{10}S_2$: C, 70.12; H, 7.42; N, 2.06. Found: C, 70.18; H, 7.22; N, 2.08.

4.1.4.3. *Characteristics of product 22.* White solid; m.p. 112–116°C; ν_{max} (film) (cm^{-1}): 3206 (NH), 1712 (C=O), 1312 and 1154 (S=O); ^{1}H NMR ($CDCl_3$): δ 0.98 (br s, 18H), 1.22 (br s, 18H), 2.14–4.22 (br m, 32H), 6.36–7.18 (br m, 8H), 8.32 (d, $J = 4.14$, 4H), 8.94 (d, $J = 4.58$, 4H), 9.32 (br s, 2H); ^{13}C NMR ($CDCl_3$): δ_C 174.04, 170.28, 152.22, 150.18, 144.16,143.04, 135.82, 132.34, 129.26, 125.54, 124.80, 34.00, 33.34, 32.98, 31.94, 31.42, 25,04, 21.00; Anal. Calcd $C_{68}H_{86}N_2O_{10}S_2 \cdot 0.1\ CH_2Cl_2$: C, 65.36; H, 7.30; N, 4.40. Found: C, 65.40; H, 7.28; N, 4.56

4.1.4.4. *Characteristics of product 23.* White solid; m.p. 114–118°C; ν_{max} (film) (cm^{-1}): 3252 (NH), 1758 (C=O), 1324 and 1104 (S=O); ^{1}H NMR ($CDCl_3$): δ 0.96 (br s, 18H), 1.24 (br s, 18H), 2.16–4.64 (br m, 26H), 6.32–7.98 (br m, 8H), 7.84 (t, $J = 7.16$, 4H), 8.12 (d, $J = 7.32$, 4H), 8.94 (t, $J = 7.08$, 2H), 9.32 (br s, 2H); ^{13}C NMR ($CDCl_3$): δ_C 171.54, 170.88, 155.14, 153.52, 144.50, 138.58, 133.26, 132.52, 129.18, 128.26, 125.66, 73.58, 60.12, 34.36, 33.58, 33.00, 31.98, 31.08, 22.38; Anal. Calcd $C_{66}H_{82}N_2O_{12}S_2$: C, 70.44; H, 7.16; N, 2.50. Found: C, 70.36; H, 7.12; N, 2.40.

4.1.4.5. *Characteristics of product 24.* Yellow solid; m.p. 112–116°C; ν_{max} (film) (cm^{-1}): 3210 (NH), 1734 (C=O), 1376 and 1188 (S=O); ^{1}H NMR ($CDCl_3$): δ 0.96

(br s, 18H), 1.22 (br s, 18H), 2.08–4.52 (br m, 26H), 6.38–7.44 (br m, 8H), 7.40 (t, $J = 7.82$, 4H), 8.28 (d, $J = 7.04$, 4H), 9.58 (br s, 2H); ^{13}C NMR ($CDCl_3$): δ_C 171.38, 171.12, 155.56, 153.42, 144.72, 138.58, 133.98, 132.06, 129.02, 128.78, 125.54, 73.92, 60.78, 34.48, 33.82, 32.78, 31.48, 31.54, 20.38; Anal. Calcd $C_{66}H_{80}N_4O_{14}S_2$: C, 70.16; H, 7.38; N, 4.42. Found: C, 70.08; H, 7.36; N, 4.30.

4.1.4.6. *Characteristics of product 25.* White solid; m.p. 112–114°C; ν_{max} (film) (cm^{-1}): 3208 (NH), 1716 (C=O), 1362 and 1138 (S=O); ^{1}H NMR ($CDCl_3$): δ 0.96 (br s, 18H), 1.22 (br s, 18H), 2.24–4.36 (br m, 26H), 6.18–7.58 (br m, 8H), 7.38 (t, $J = 7.02$, 4H), 7.42 (t, $J = 7.24$, 2H), 8.20 (d, $J = 7.06$, 4H), 9.38 (br s, 2H); ^{13}C NMR ($CDCl_3$): δ_C 171.28, 171.54, 155.54, 153.42, 144.02, 138.92 133.48, 132.28, 129.20, 128.34, 125.34, 72.44, 60.24, 34.32, 33.44, 33.08, 31.84, 31.16, 25.12; Anal. Calcd $C_{66}H_{82}N_2O_{10}S_2$: C, 70.10; H, 7.32; N, 2.22. Found: C, 70.16; H, 7.26; N, 2.18.

4.1.4.7. *Characteristics of product 26.* White solid; m.p. 112–116°C; ν_{max} (film) (cm^{-1}): 3216 (NH), 1726 (C=O), 1312 and 1172 (S=O); ^{1}H NMR ($CDCl_3$): δ 0.98 (br s, 18H), 1.24 (br s, 18H), 2.02–4.42 (br m, 32H), 6.56–7.28 (br m, 8H), 8.34 (d, $J = 4.46$, 4H), 8.44 (d, $J = 4.58$, 4H), 9.32 (br s, 2H); ^{13}C NMR ($CDCl_3$): δ_C 174.22, 170.36, 152.82, 150.78, 144.56,143.54, 135.72, 132.16, 129.78, 125.62, 124.06, 34.18, 33.84, 32.52, 31.34, 31.36, 25,54, 21.66; Anal. Calcd $C_{68}H_{86}N_2O_{10}S_2 \cdot 0.1\ CH_2Cl_2$: C, 65.38; H, 7.26; N, 4.58. Found: C, 65.32; H, 7.36; N, 4.48.

4.1.4.8. *Characteristics of product 27.* White solid; m.p. 114–116°C; ν_{max} (film) (cm^{-1}): 3216 (NH), 1720 (C=O), 1358 and 1164 (S=O); ^{1}H NMR ($CDCl_3$): δ 0.96 (br s, 18H), 1.22 (br s, 18H), 2.06–4.50 (br m, 26H), 6.54–7.02 (br m, 8H), 7.98 (t, $J = 7.06$, 4H), 8.18 (d, $J = 7.42$, 4H), 8.98 (t, $J = 7.32$, 2H), 9.02 (br s, 2H); ^{13}C NMR ($CDCl_3$): δ_C 171.52, 170.78, 155.12, 153.54, 144.34, 138.58, 133.54, 132.72, 129.14, 128.18, 125.22, 73.12, 60.56, 34.54, 33.98, 33.10, 31.94, 31.10, 22.50; Anal. Calcd $C_{66}H_{82}N_2O_{12}S_2$: C, 70.14; H, 7.38; N, 2.42. Found: C, 70.16; H, 7.36; N, 2.36.

4.1.4.9. *Characteristics of product 28.* Yellow solid; m.p. 114–118°C; ν_{max} (film) (cm^{-1}): 3218 (NH), 1734 (C=O), 1356 and 1158 (S=O); ^{1}H NMR ($CDCl_3$): δ 0.96 (br s, 18H), 1.24 (br s, 18H), 2.08–4.42 (br m, 26H), 6.14–7.42 (br m, 8H), 7.42 (t, $J = 7.22$, 4H), 8.22 (d, $J = 7.04$, 4H), 9.20 (br s, 2H); ^{13}C NMR ($CDCl_3$): δ_C 171.20, 171.18, 155.86, 153.44, 144.54, 138.48, 133.78, 132.24, 129.72, 128.04, 125.80, 73.30, 60.08, 34.06, 33.92, 32.18, 31.56, 31.02, 20.58; Anal. Calcd $C_{66}H_{80}N_4O_{14}S_2$: C, 70.12; H, 7.24; N, 4.50 Found: C, 70.16; H, 7.36; N, 4.48.

4.1.5. Synthesis of products 29–34 (Carbonyl-up). To a solution of 1.00 g of 25,27-dipropoxy-26,28-bis(carboxymethoxy)calix[4]arene and 25,26-dipropoxy-27,28-bis(carboxymethoxy)calix[4]arene (1.53 mmol) in 30 mL benzene, 10.0 mL oxalyl chloride (14.6 g, 122 mmol) was added. The reaction mixture was refluxed for 24 h. The benzene and excess oxalyl chloride was evaporated *in vacuo,* the crude product was dried under high vacuum. The residue was dissolved in THF (30 mL) and added to a mixture of 0.38 g NaH (95% dry, 15.3 mmol) and 0.74 g proper sulfonamide (4.59 mmol) in 50 mL THF under nitrogen at room temperature. The reaction mixture was stirred for 15 h at room temperature under nitrogen. The reaction was quenched with a small amount of

H_2O and the THF was evaporated *in vacuo* to give a white solid. The solid was purified by column chromatography on silica gel witii CH_2Cl_2, EtOAc : CH_2Cl_2 (2 : 98), and EtOAc : CH_2Cl_2 (5 : 95) as eluents to produce a white solid. The solid was dissolved in CH_2Cl_2 (100 mL) and washed with 1 N HCl (100 mL). The organic layer was separated, washed with deionized H_2O (100 mL), and evaporated *in vacuo* to give a white solids.

4.1.5.1. *Characteristics of product 29*. White solid; m.p. 124–126°C; ν_{max} (film)/cm^{-1}: 3200 (NH), 1716 (C=O), 1350 and 1158 (S=O); ^{1}H NMR ($CDCl_3$): δ 0.96 (br s, 18H), 1.22 (br s, 18H), 2.04–4.16 (br m, 26H), 6.10–7.42 (br m, 8H), 7.38 (t, J = 7.22, 4H), 7.52 (t, J = 7.22, 2H), 8.26 (d, J = 7.16, 4H), 9.22 (br s, 2H); ^{13}C NMR ($CDCl_3$): δ_C 171.28, 171.54, 155.54, 153.42, 144.02, 138.92 133.48, 132.28, 129.42, 128.64, 125.48, 72.56, 60.54, 34.52, 33.38, 33.08, 31.54, 31.00, 25.58; Anal. Calcd $C_{66}H_{82}N_2O_{10}S_2$: C, 70.32; H, 7.46; N, 2.16. Found: C, 70.48; H, 7.62; N, 2.18.

4.1.5.2. *Characteristics of product 30*. White solid; m.p. 122–126°C; ν_{max} (film) (cm^{-1}): 3220 (NH), 1702 (C=O), 1302 and 1152 (S=O); ^{1}H NMR ($CDCl_3$): δ 0.98 (br s, 18H), 1.22 (br s, 18H), 2.02–4.32 (br m, 32H), 6.36–7.48 (br m, 8H), 8.22 (d, J = 4.46, 4H), 8.24 (d, J = 4.76, 4H), 9.24 (br s, 2H); ^{13}C NMR ($CDCl_3$): δ_C 174.24, 170.26, 152.42, 150.28, 144.36,143.34, 135.02, 132.36, 129.28, 125.72, 124.84, 34.46, 33.48, 32.98, 31.84, 31.02, 25,04, 21.76; Anal. Calcd $C_{68}H_{86}N_2O_{10}S_2 \cdot 0.1$ CH_2Cl_2: C, 65.38; H, 7.36; N, 4.48. Found: C, 65.32; H, 7.46; N, 4.38.

4.1.5.3. *Characteristics of product 31*. White solid; m.p. 124–128°C; ν_{max} (film) (cm^{-1}): 3210 (NH), 1708 (C=O), 1320 and 1104 (S=O); ^{1}H NMR ($CDCl_3$): δ 0.96 (br s, 18H), 1.22 (br s, 18H), 2.06–4.60 (br m, 36H), 6.12–7.58 (br m, 8H), 7.98 (t, J = 7.06, 4H), 8.22 (d, J = 7.02, 4H), 8.68 (t, J = 7.12, 2H), 9.72 (br s, 2H); ^{13}C NMR ($CDCl_3$): δ_C 171.24, 170.96, 155.52, 153.26, 144.50, 138.58, 133.54, 132.02, 129.18, 128.84, 125.96, 73.10, 60.26, 34.48, 33.58, 33.00, 31.10, 30.96, 22.48; Anal. Calcd $C_{66}H_{82}N_2O_{12}S_2$: C, 70.14; H, 7.22; N, 2.32. Found: C, 70.16; H, 7.26; N, 2.22.

4.1.5.4. *Characteristics of product 32*. White solid; m.p. 122–124°C; ν_{max} (film) (cm^{-1}): 3216 (NH), 1752 (C=O), 1368 and 1122 (S=O); ^{1}H NMR ($CDCl_3$): δ 0.96 (br s, 18H), 1.22 (br s, 18H), 2.24–4.56 (br m, 26H), 6.18–7.56 (br m, 8H), 7.28 (t, J = 7.02, 4H), 7.92 (t, J = 7.04, 2H), 8.34 (d, J = 7.16, 4H), 9.34 (br s, 2H); ^{13}C NMR ($CDCl_3$): δ_C 171.18, 171.48, 155.84, 153.08, 144.36, 138.62 133.08, 132.22, 129.12, 128.32, 125.08, 72.24, 60.04, 34.10, 33.40, 33.00, 31.04, 31.00, 25.32; Anal. Calcd $C_{66}H_{82}N_2O_{10}S_2$: C, 70.42; H, 7.32; N, 2.16. Found: C, 70.38; H, 7.20; N, 2.18.

4.1.5.5. *Characteristics of product 33*. White solid; m.p. 122–126°C; ν_{max} (film) (cm^{-1}): 3228 (NH), 1782 (C=O), 1302 and 1142 (S=O); ^{1}H NMR ($CDCl_3$): δ 0.98 (br s, 18H), 1.22 (br s, 18H), 2.02–4.08 (br m, 32H), 6.56–7.18 (br m, 8H), 8.14 (d, J = 4.14, 4H), 8.54 (d, J = 4.58, 4H), 9.12 (br s, 2H); ^{13}C NMR ($CDCl_3$): δ_C 174.14, 170.56, 152.52, 150.48, 144.34,143.38, 135.08, 132.86, 129.98, 125.92, 124.96, 34.56, 33.54, 32.98, 31.98, 31.04, 25,38, 21.46; Anal. Calcd $C_{68}H_{86}N_2O_{10}S_2 \cdot 0.1$ CH_2Cl_2: C, 65.24; H, 7.30; N, 4.40. Found: C, 65.32; H, 7.24; N, 4.28.

4.1.5.6. *Characteristics of product 34*. White solid; m.p. 124–126°C; ν_{max} (film) (cm^{-1}): 3220 (NH), 1722 (C=O), 1322 and 1124 (S=O); ^{1}H NMR ($CDCl_3$): δ 0.96

(br s, 18H), 1.24 (br s, 18H), 2.16–4.88 (br m, 26H), 6.58–7.08 (br m, 8H), 7.42 (t, $J = 7.26$, 4H), 8.02 (d, $J = 7.82$, 4H), 8.64 (t, $J = 7.32$, 2H), 9.82 (br s, 2H); ^{13}C NMR ($CDCl_3$): δ_C 171.54, 170.98, 155.02, 153.56, 144.32, 138.38, 133.54, 132.52, 129.58, 128.24, 125.56, 73.58, 60.18, 34.84, 34.28, 33.92, 31.98, 31.50, 22.58; Anal. Calcd $C_{66}H_{82}N_2O_{12}S_2$: C, 70.14; H, 7.08; N, 2.50. Found: C, 70.28; H, 7.06; N, 2.40.

5. Conclusions

Alternation of aryl group in the pendant moieties was ineffective, while changing their orientation (*cis*- and *trans*-) and position (*ortho*- and *para*-) as well as the scaffold conformation (cone, 1,2-alternate, partial-cone) analogs presented a pronounced effect on the efficiency of extractions. Changing the scaffold conformation affected the selectivity of extractions, while alternation of aryl groups, changing their orientation and position showed no effect. Replacement of aryl groups and changing the moiety's position showed no changes in the $pH_{1/2}$ of extractions, while variations of conformations and the orientation of pendant moieties have pronounced effect on the $pH_{1/2}$ of extractions.

Acknowledgments

This work was supported by Islamic Azad University (Shahreza Branch) and Iran Nanotechnology Initiative Council.

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