Thiacalix[4]arene Derivatives Bearing Imidazole Units: A Ditopic Hard/Soft Receptor for Na^+ and K^+/Ag^+ with an Allosteric Effect and a Reusable Extractant for Dichromate Anions

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Abstract: Two novel receptors 5,11,17,23-tetra-tert-butyl-25,27-bis[(ethoxycarbonyl)methoxy]-26,28-bis-[1-methyl-(imidazole)-methoxy]-2,8,14,20-tetra-thiacalix[4]arene (**L1**) and 5,11,17,23-tetra-tert-butyl-25,27-bis-[(benzyl)methoxy]-26,28-bis-[1-methyl-(imidazole)-methoxy]-2,8,14,20-tetrathiacalix[4]arene (**L2**) possessing imidazole moieties based on thiacalix[4]arene in the 1,3-*alternate* conformation have been synthesized and characterized. The crystal structures of **L1** and **L2** have been determined. The binding behaviour towards Li^+, Na^+, K^+ and Ag^+ ions has been examined by ^1H NMR titration experiments in ($CDCl_3/CD_3CN$; 10:1, v/v) solution. The exclusive formation of mononuclear complexes of **L1** with metal cations is of particular interest revealing a negative allosteric effect in the thiacalix[4]arene family. Liquid-liquid extraction experiments indicate that synthesized **L2** can be utilized as an efficient reusable extractant for dichromate anion by controlling the pH of the aqueous solution.

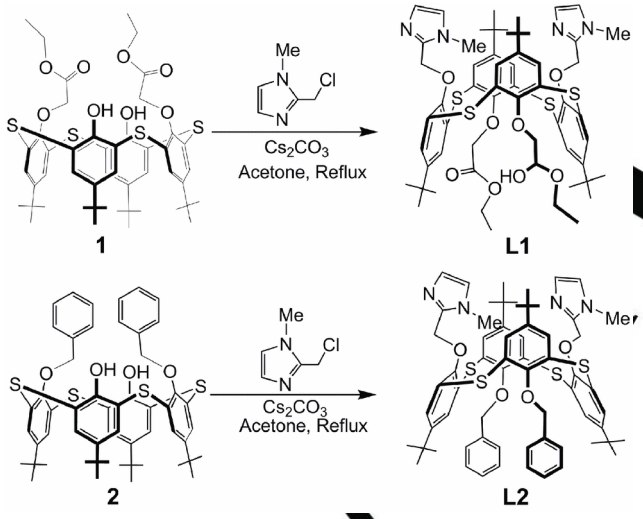
Introduction

Allosteric regulation between subunits within a receptor system is one of nature's elegant strategies for precisely regulating and controlling the diverse functions in biological systems.[1] The use of allosteric regulation has also been utilized by chemists to control molecular function by external stimuli to transduce chemical signals, and to achieve chemical feedback regulation.[2] Inspired by this, much effort has been devoted in supramolecular chemistry to construct artificial systems to achieve analogous functions such as molecular recognition and signal amplification.

Di- or poly-topic receptors have been constructed with two or more binding subunits within the same macrocyclic structure.[3] It is well known that such systems are suitable candidates for the allosteric regulation of host-guest interactions with metal cations.[1d,4] Thiacalix[4]arenes are macrocyclic molecules which can be relatively easily functionalized and have pre-organized binding sites. In particular, the 1,3-*alternate* conformation is capable of possessing binding subunits in the two opposite domains of the molecule, and is thus a potentially ideal structure for allosteric regulation.[5] Consequently, we have been interested in being able to incorporate two subunits having different binding properties onto a thiacalix[4]arene and to control or maintain a 1,3-*alternate* conformation. This would therefore permit the construction of a di-topic receptor system which should possess allosteric features.

The development of systems for the fast estimation, removal and separation of silver (soft metal), together with the use of Ag^+ complexes in photographic materials and their potential use in cancer radioimmunotherapy has attracted the attention of supramolecular chemists towards designing effective Ag^+-selective receptors.[6] Recently, we undertook the synthesis and evaluation of thiacalix[4]arene and homotrioxacalix[3]arene ligands as Ag^+ ionophores and found that the introduction of imidazole groups at the lower rim of the calixarene skeleton resulted in a high affinity for Ag^+.[7] On the other hand, it has been reported that by introducing an ester group at its lower or upper rim, the thiacalix[4]arene derivative can selectively complex alkali metal cations (hard metals), such as Na^+ and K^+.[8] Thus, the introduction of imidazole groups onto the thiacalix[4]arene framework as one binding subunit and the introduction of ester groups on the opposite side as the other binding subunit, was envisioned. Such a system could be used as a ditopic receptor with two binding subunits pre-organised for both hard (Na^+ and K^+) and soft (Ag^+) cations, and with possible switching of complexation preferences.

Herein, the synthesis, X-ray structure, and complexation studies of a novel ditopic receptor **L1** which possesses two binding subunits (imidazole and ester moieties) based on a thiacalix[4]arene in the 1,3-*alternate* conformation is reported. In order to further investigate the allosteric effects, the monotopic receptor **L2**, with a similar structure, was also produced. Additionally, due to the amphoteric nature of the imidazole group can function not only as an effective cation but also as an anion receptor under appropriate conditions. Also, as a continuation of our search for



Scheme 1. The synthetic routes to receptors **L1** and **L2**.

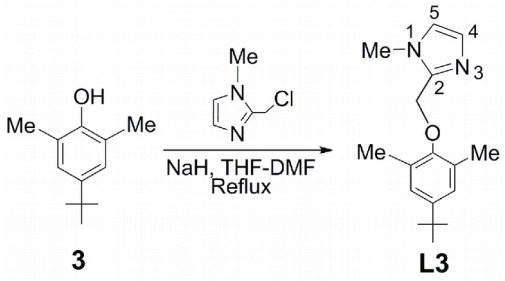
dichromate anion extractants based on thiacalixarene derivatives,[7,13] the extraction efficiency of the systems described herein towards dichromate anion was conducted by liquid-liquid extraction experiments.

Results and Discussion

Synthesis

The preferential formation of the 1,3-*alternate* conformer of thiacalix[4]arene occurs in the presence of a cesium cation whose size is compatable with that of the thiacalix[4]arene cavity and thus contributes significantly to the cation-π interaction.[5] Receptor **L1** could therefore be obtained in 55% yield by the stereoselective *O*-alkylation of **1**[10] with 2-chloromethyl-1-methyl-1*H*-imidazole[9] in the presence of Cs_2CO_3 in dry acetone (Scheme 1). Similarly, receptor **L2** was obtained in 44% yield by the stereoselective *O*-alkylation of **2**[11] with 2-chloromethyl-1-methyl-1*H*-imidazole in the presence of Cs_2CO_3 in dry acetone (Scheme 1).

The ^{1}H NMR spectrum of **L1** exhibits two singlets for the *tert*-butyl protons at up-field positions, *viz*□□□□1.10 and 1.26 ppm; two singlets for the aromatic protons at □□7.24 ppm and 7.46 ppm (Figure S1), all of which is indicative of a C_2-symmmetric structure for the 1,3-*alternate* conformation. Obviously, receptor **L2** is also in the 1,3-*alternate* conformation revealing two singlets for the *tert*-butyl protons (□□0.82 and 1.15 ppm) and two singlets for the aromatic protons (□□7.12 and 7.27 ppm, Figure S4). Surprisingly, remarkable shielding effects are experienced by the N-CH_3 protons of **L1** and **L2** (Table 1), compared with the



Scheme 2. The synthetic route of reference compound **L3**.

Table 1. Partial **c**hemical shifts of **L1**, **L2** and reference compound **L3**.[a]

Compound	Chemical shifts, □ (ppm)		
	-N-CH_3	H_4	H_5
L1	2.78	6.65	6.96
L3	3.70	6.82	6.94
L2	2.57	6.68	6.99
□□$_{L1}$[b]	–0.92	–0.17	+0.02
□□$_{L2}$[b]	–1.13	–0.14	+0.05

[a]□□□ value is the difference of the chemical shift between **L1**, **L2** and reference compound **L3** in $CDCl_3$ at 27 °C. [b] A plus sign (+) denotes a shift to lower magnetic field, whereas, a negative sign (–) denotes a shift to higher magnetic field.

reference compound **L3**,[7] which is prepared by *O*-alkylation of 4-*tert*-butyl-2,6-dimethylphenol **3**[12] with 2-chloromethyl-1-methyl-1*H*-imidazole in the presence of NaH (Scheme 2). It strongly suggests that the heteroaromatic protons of the imidazole groups for both of **L1** and **L2** are exposed to the ring current shielding effect area operating between two of the thiacalixarene benzene rings.[7,13]

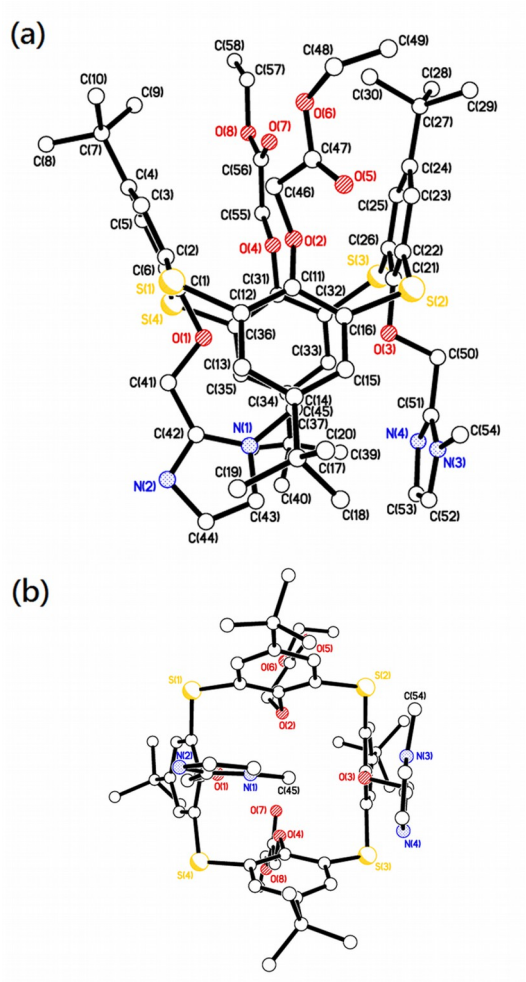


Figure 1. Single-crystal structure of **L1** showing (a) the side view (b) the top view. Hydrogen atoms, ethanol and water molecules as solvent of crystallization, and minor disorder components have been omitted for clarity.

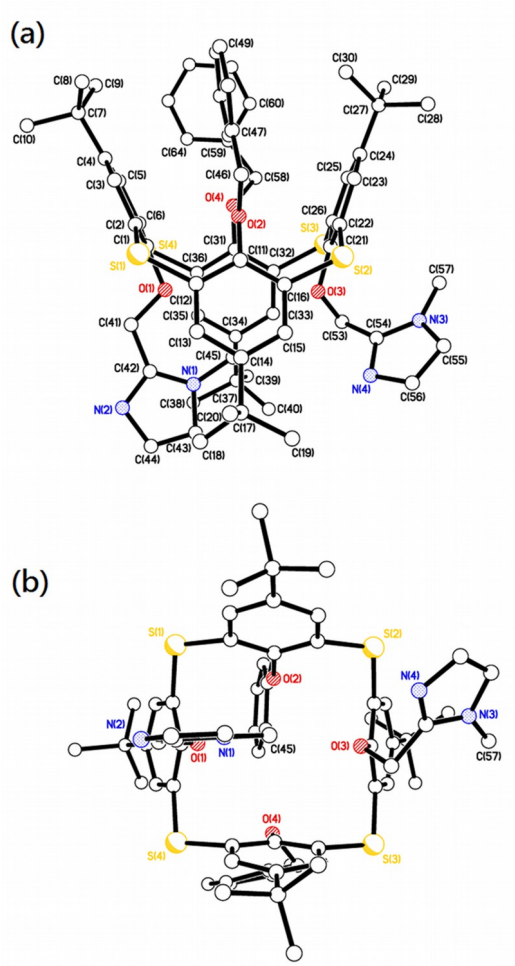


Figure 2. Single-crystal structure of **L2** showing (a) the side view (b) the top view. Hydrogen atoms, ethanol and water molecules as solvent of crystallization, and minor disorder components have been omitted for clarity.

Furthermore, X–ray crystallographic analysis further confirmed the molecular structure of **L1** and **L2** as shown in Figure 1. Both **L1** (Fig. 1a) and **L2** (Fig. 2a) are in the 1,3-*alternate* conformation. As expected, the imidazole ring containing N(1) and C(45) of **L1** and **L2** are pointing into the thiacalix[4]arene cavity which is consistent with the significant up-field shift for the N-CH_3 group in the ^{1}H NMR spectra. A slightly distorted square is observed for receptor **L1** (Fig. 1b, S1···S2 = 5.636 Å, S2···S3 = 5.562 Å, S3···S4 = 5.546 Å and S4···S1 = 5.579 Å); however, an approximate square is observed for receptor **L2** (Fig. 2b, S1···S2 = 5.559 Å, S2···S3 = 5.552 Å, S3···S4 = 5.535 Å and S4···S1 = 5.558 Å). In other words, the cavity size of receptor **L1** is a little larger than receptor **L2** based on the sum of the S···S distances.

Complexation studies

At the onset of the study, it was anticipated that multi-recognition of both hard metals (Na^+, K^+) and soft metals (Ag^+) by the ditopic receptor **L1** could be detected. This of course, being due to the presence of the two ester moieties[8] at one face of the thiacalix[4]arene cavity and the two imidazole moieties[7] at the opposite face. The binding affinities of **L1** and **L2** toward metal cations were therefore evaluated by ^{1}H NMR titration experiments ($CDCl_3$:CD_3CN = 10:1, v/v).

^{1}H NMR titration studies

Both **L1** and **L2** possess imidazole moieties which would preferentially exhibit higher affinity towards Ag^+ ion. Hence, we conducted ^{1}H NMR titration experiments with CF_3SO_3Ag. Titration of a solution of **L1** with Ag^+ ions resulted in dramatically downfield shifts (□□□= +0.86 ppm) for the imidazole-N-CH_3 protons at □□3.68 ppm after complexation with 1.0 equiv. Ag^+ (Figure 3). It was noteworthy that □□3.68 ppm was almost the same chemical shift for the imidazole-N-CH_3 protons (□□3.70 ppm, Table 1) of the reference compound **L3**. It strongly suggested that the imidazole-N-CH_3 group of **L1** escaped from the shielding area to the deshielding area upon Ag^+ capture by receptor **L1**. Subsequently, the adjacent imidazolyl- proton H_4 was also affected by the change in the position of the N-CH_3 group, and exhibited a downfield shift (□□□= +0.46 ppm) at □□7.14 ppm. In contrast, another significantly up-field shift (□□□= –0.15 ppm) for the methylene protons of OCH_2Imid at □□5.04 ppm was also observed. Thus chemical shift change may be attributed to the OCH_2Imid methylene protons being folded into the shielding area of the thiacalix[4]arene-cavity in order to form an efficient complex with Ag^+. All of the evidence strongly suggested that Ag^+ was complexed by the nitrogen atoms of the imidazole moieties via N···Ag^+ interactions.

Similar phenomena were observed for the titration experiment of **L2** with Ag^+ (Figure S7). The proton resonances of N-CH_3 and H_4 in the imidazole rings were gradually shifted to downfield upon addition of Ag^+ ions which could be attributed to the conformational change of receptor **L2** with a concomitant deshielding effect. The methylene protons of OCH_2Imid were slightly shifted up-field after being complexed with one equiv. Ag^+, which may also be attributed to the OCH_2Imid methylene protons being folded into the shielding field of the thiacalix[4]arene-cavity. Both **L1** and **L2** exhibited slight chemical shift changes of the aromatic protons which are also attributed to the conformational changes upon complexation. On increasing the titration amount of Ag^+ to 2.0 equiv., no further significant changes were observed for **L1** and **L2**. According to the corresponding titration curve, the association constants were calculated to be 44 M^{-1} and 83 M^{-1}, respectively (Figure S16 and S19). All of the observed phenomenon suggested that receptor **L1** and **L2** possess higher affinity towards Ag^+ ion via N···Ag^+ interactions.

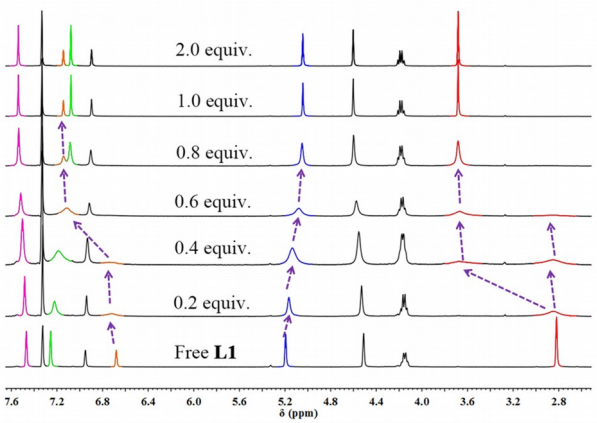


Figure 3. Partial ^{1}HNMR spectra of **L1** (5.0mM) and increasing concentrations of Ag^+ in $CDCl_3/CD_3CN$(10:1, v/v) at 298K.

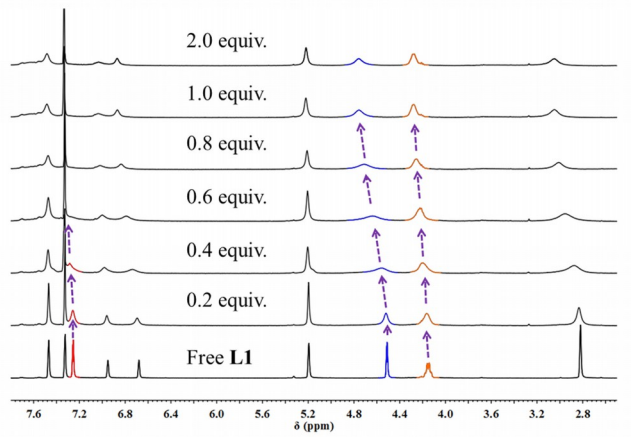


Figure 4. Partial ^{1}HNMR spectra of **L1** (5.0mM) and increasing concentrations of K^+ in $CDCl_3/CD_3CN$(10:1, v/v) at 298K.

The affinity towards alkali metal cations was also investigated, given that K^+ and Na^+ ions are known to interact with the ester moiety.[8] ^{1}H NMR titration experiments with CF_3SO_3K, CF_3SO_3Na and CF_3SO_3Li were carried out. The addition of an equiv. of CF_3SO_3K to **L1** caused immediate complexation as demonstrated by the downfield shifts of the ester ethyl group resonances (OCH_2CO, □□□= +0.25; COOCH_2, □□□= +0.12 ppm, Figure 4) for the 1:1 complex of **L1** with an association constant of 253 M^{-1} (Figure S17). The slightly downfield shifts of the thiacalixarene benzene protons may be attributed to the decreased shielding effect operating in two of the thiacalixarene benzene rings upon complexation of the ester moieties with K^+. The signals of the imidazole group's protons were broadened, showing slow ligand exchange on the NMR time scale. A similar phenomenon was observed in the presence of an equiv. of CF_3SO_3Na (OCH_2CO, □□□= +0.15; COOCH_2, □□□= +0.07 ppm, Figure S8) which formed a 1:1 complex of **L1** with an association constant of 92 M^{-1} (Figure S18). CF_3SO_3Li did not cause detectable spectral changes for **L1** due to the small atom radius which could not form an efficient complex (Figure S9). According to the corresponding association constants for these processes, it is clear that the association constants for alkali metal cations directly follow the radius of the alkali metal cations: $K^+ > Na^+ > Li^+$ which reflects the size recognition ability of receptor **L1**.

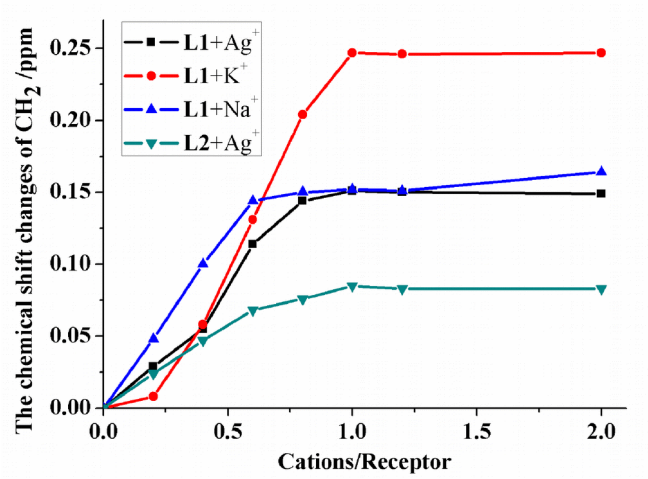


Figure 5. ^{1}H NMR shift of CH_2 (blue peak) in **L1** with Ag^+, K^+, Na^+ and **L2** with Ag^+. [In the presence of 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 2.0 equiv. of cations in $CDCl_3/CD_3CN$(10:1, v/v), respectively.]

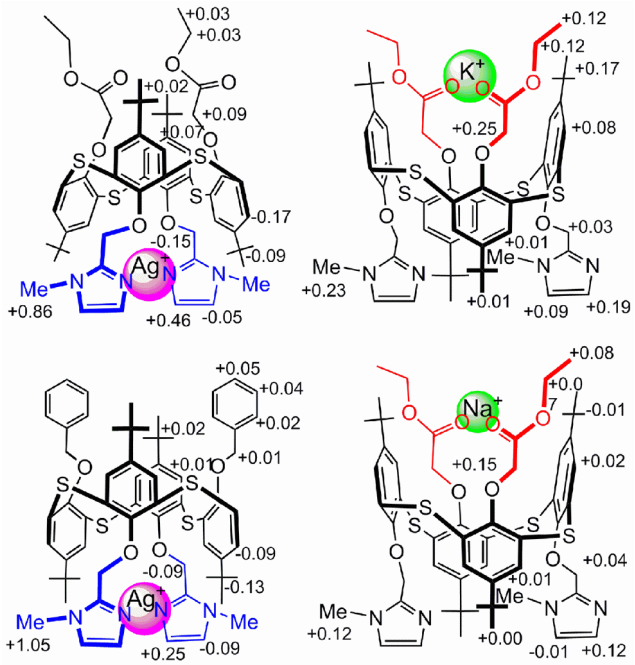


Figure 6. Chemical shift changes of **L1** and **L2** in the presence of different metal ions; (+) denotes the downfield shift and (–) denotes the up field shift.

Given the fact that receptor **L2** is unable to bind alkali metal cations due to one side having phenyl moieties present, which are inactive for recognition of alkali metal cations, as expected, no significant changes were observed during the ^{1}H NMR titration experiments with alkali metal cations. The change of the chemical shift of the *CH_2* groups of receptor **L1** and **L2** plotted against the amount of cations (Ag^+, K^+ and Na^+) is shown in Figure 5. The □□□value increased in proportion to the amount of cations and became almost constant after the addition of 1.0 equiv. of cations, which indicated the 1:1 stoichiometry of the receptors–cations complex that was formed.

MALDI-TOF-MS data also supported the formation of a stable 1:1 host–guest complex. As shown in Figure S10 ~ S12, the mass spectrum of **L1** with cations exhibited peaks at 1187.123, 1119.301 and 1103.285 corresponding to masses of [**L1** + Ag]$^+$, [**L1** + K]$^+$ and [**L1** + Na]$^+$, respectively. And the mass spectrum of **L2** with cation exhibited peaks at 1195.107 corresponding to masses of [**L2** + Ag]$^+$ (Figure S13). In other words, the 1:1 stoichiometry complex between receptors and guest cations were unambiguously confirmed by Mass. Consequently, the proposed binding model and chemical shift changes (□□) of **L1** and **L2** with metal ions are summarized in Figure 6.

Allosteric studies

The presence of an allosteric effect with **L1** was studied by ^{1}H NMR titration. Upon titration with one equiv. of Ag^+ to the 1:1 M^+ □□**L1** (M^+ = Li^+, Na^+ or K^+) complex solution, the corresponding peaks were dramatically shifted to the same chemical shift positions as

were noted for the 1:1 Ag^+ □□**L1** complex. This therefore implied that Ag^+ was bound to the imidazole site and induced the decomplexation of hard metal cations (Li^+, Na^+ or K^+) from the ester site (Figure 7). Furthermore, the□1:1 Ag^+ □ **L1** complex was also titrated with an equiv. of M^+ ions (M^+ = Li^+, Na^+

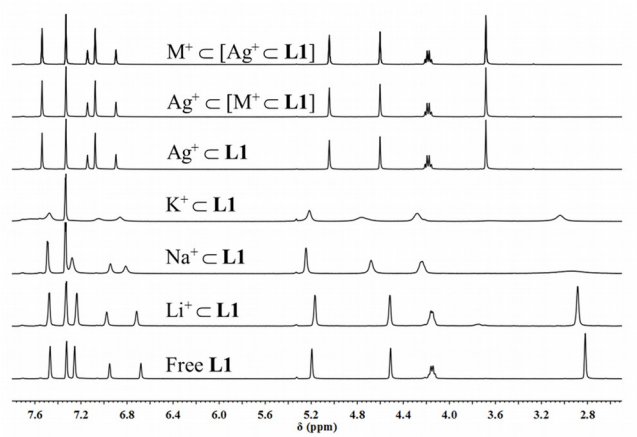


Figure 7. Partial ^{1}H NMR spectra of receptor **L1** (5.0 mM) in $CDCl_3/CD_3CN$ (10:1, v/v) complex with an equiv. of various metal ions; M^+ denoted the alkali metal cations (M^+ = Li^+, Na^+ or K^+).

or K^+). None of the spectral patterns of Li^+□□ [Ag^+□□ **L1**], Na^+ □ [Ag^+□□ **L1**] and K^+ □ [Ag^+□□□**L1**] complexes showed any detectable signal changes. These results indicated that the complexation of Ag^+ completely suppressed the recognition of Li^+, Na^+ or K^+ by the ester moiety. The concept of a negative allosteric effect by receptor **L1** is shown in Figure 8.

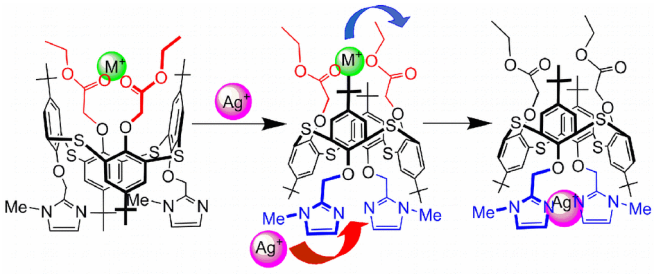


Figure 8. Proposed negative allosteric effect of ditopic recptor **L1**. M^+ denotes the alkali metal cations (M^+ = Li^+, Na^+ or K^+).

Two-phase solvent extraction

Chromium and its compounds are widely used in our daily life, such as., tanning, plating, leather dyes, and in the photographic industry, all of which produce large quantities of toxic pollutants.[14] However, high concentrations of hexavalent chromium (VI) ion is toxic to the human body, as it can diffuse as $Cr_2O_7^{2-}$ or $HCr_2O_7^-$ through cell membranes and oxidize biological molecules.[15] Thus, selective treatment of pollutional water containing Cr (VI) prior to discharge is essential. The dichromate ($Cr_2O_4^{2-}$ and $HCr_2O_7^-$) ions are anions with oxide functionalities at their periphery. These oxide moieties are potential sites for hydrogen bonding to the complexant or host molecule(s). Imidazole group, among such heterocyclic units, the imidazole ring behaves as an excellent hydrogen bond donor moiety in synthetic anion receptor systems, and the acidity of the NH proton of the imidazole can be tuned by changing the electronic properties of the imidazole substituents.[16] Thus, the introduction of a imidazole moiety to thiacalix[4]arene would potentially lead to an effective extractant for dichromate anions.

To investigate further the applicability of the receptors **L1** and **L2** which possess imidazole groups, liquid-liquid extraction experiments were performed to examine the extraction ability of **L1** and **L2** toward dichromate anion from the aqueous phase

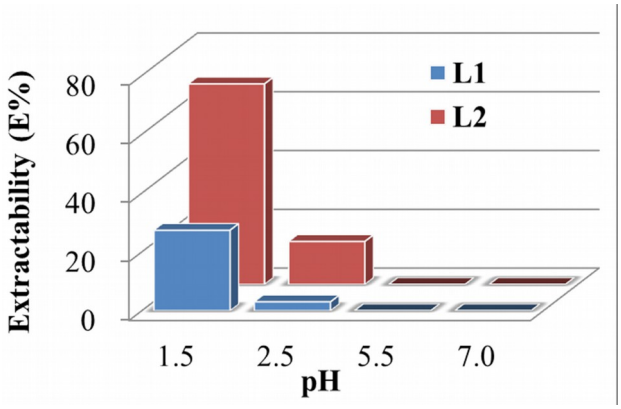


Figure 9. E% values of dichromate anion with ionophores **L1** and **L2** (2.0 × 10^{-4} M, 2 h at 25 °C) at pH 1.5–7.0 (H_2O/CH_2Cl_2:10/10 (v/v); $K_2Cr_2O_7$ = 1 × 10^{-4} M).

into the organic phase (dichloromethane) over the range of pH 1.5–7.0. It has been clearly demonstrated that the lower the pH, the higher the extractability is found for both of **L1** and **L2** (Figure 9). This could be attributed to an ion-pair (hydrogen bonded) complex formed in the two-phase extraction system following proton transfer to the nitrogen atoms of the imidazole units in **L1** and **L2** and then complexation of $Cr_2O_7^{2-}$/$HCr_2O_7^-$.[7]

Interestingly, according to the reference reports,[7] the reference compound **L3** showed almost no significant selective binding of dichromate anions even at low pH. It strongly suggests that the thiacalix[4]arene platform plays an important role in confirming cooperative participation of the peripheral imidazole groups. Furthermore, the extraction results also indicated that extractant **L2** was more effective for the extraction of dichromate anions at low pH (pH 1.5) than extractant **L1**. This could be ascribed to the cavity size of extractant **L2** is smaller and more symmetrical than extractant **L1** (Figure 1, X-ray results). In other words, extractant **L2** maybe provided a more ideal mutual distance needed for hydrogen bonding between two imidazole groups to extract dichromate anions.

Additionally, the extractants **L1** and **L2** possess 'proton-switchable' binding sites, namely the imidazole moieties, which can be protonated at low pH.[17] The protonated forms of **L1** and **L2** are more effective at complexing with dichromate anion through hydrogen bonds. In other words, the extraction of dichromate anion by extractants **L1** and **L2** only occurs when the aqueous phase is acidic, especially at lower pH, in order to form efficient hydrogen bonds. Thus, a reusable extractant concept is possible for extractants **L1** and **L2** by controlling the pH of the aqueous solution (Figure 10).

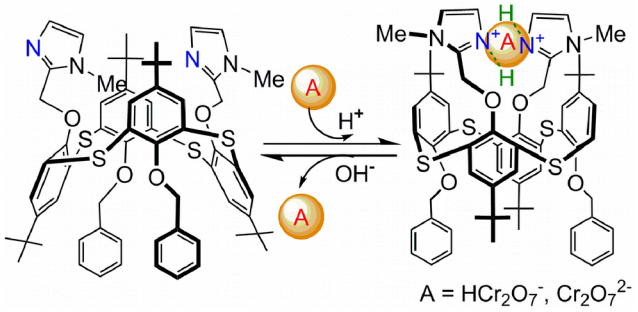


Figure 10. A proposed reusable extractant concept of **L2** with $Cr_2O_7^{2-}$.

Conclusions

Two new thiacalix[4]arene receptors **L1** and **L2** which each possess imidazole moieties in the 1,3-*alternate* conformation have been synthesized and characterized. The X-ray crystal structures of both **L1** and **L2** have been determined, confirming their 1,3-*alternate* conformations. The binding behaviour towards Na^+, K^+ and Ag^+ ions have been examined by ^1H NMR titration experiments in ($CDCl_3/CD_3CN$; 10:1, v/v) solutions. The ditopic receptor **L1** showed affinity not only toward hard alkali metal cations but also toward soft metal Ag^+ cations, owing to the presence of the two ester moieties at one face of the thiacalix[4]arene cavity and two imidazole moieties at the opposite face. However, the monotopic receptor **L2** only exhibited affinity toward Ag^+ and was unable to bind alkali metal cations due to its lack of the ester groups. The exclusive formation of mononuclear complexes of **L1** with metal cations is of particular interest with respect to negative allosteric effects in the thiacalix[4]arene family. These findings further demonstrate that preorganization, suitable conformational changes and affinity have a pronounced effect on the complexation process between the two different arms placed at the two edges of the thiacalix[4]arene platform. Due to its amphoteric nature, the imidazole ring can function as an effective cation and/or anion receptor system. Furthermore, the extraction abilities of **L1** and **L2** toward dichromate anion were

evaluated by a liquid-liquid extraction method. The extraction results indicate that the synthesized **L2** can be utilized as a reusable extractant by control of the pH of the aqueous solution.

Electronic Supplementary Information (ESI) available: Details of single-crystal X-ray crystallographic data. ^{1}H, ^{13}C NMR and MS spectra of **L1** and **L2**.

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Keywords: Thiacalix[4]arene • Imidazole • Allosteric effect• Dichromate

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