ORIGINAL PAPER

An ONIOM investigation on anion recognition of alkali–metal complexes with diurea calix[4]arene receptor

Pornpan Chanapiwat · Vithaya Ruangpornvisuti

Abstract The ONIOM(B3LYP/6–31G(d):AM1) optimized structures of complexes of diurea calix[4]arene receptor (**L**) with alkali metals Li^+, Na^+ and K^+ and their complexes with halide ions F^-, Cl^-, Br^-, oxygen–containing anions HCO_3^-, HSO_4^- and CH_3COO^- ions were obtained. Binding energies and thermodynamic properties of complex receptors LiL^+, NaL^+ and KL^+ with these anions were determined. The binding stabilities according to binding energies of LiL^+, NaL^+ and KL^+ associated with anions computed either at the ZPVE-corrected ONIOM(B3LYP/6–31G(d):AM1) or BSSE-corrected B3LYP/6–31+G(d,p)//ONIOM(B3LYP/6–31G(d):AM1) are in the same order: $F^- \gg CH_3COO^- \approx HCO_3^- > Br^- \approx HSO_4^- \approx Cl^-$. All the receptors LiL^+, NaL^+ and KL^+ were found to be selective toward fluoride ion.

Keywords Diurea calix[4]arene · Alkali metal · Halide · Oxygen–containing anion · Binding energy · ONIOM approach

Introduction

Anions play an important role in several fields, including environmental [1], catalysis [2], biology [3] and potential medical [4] applications. Thus, the design of molecular sensors for anion recognition and sensing is of interest to chemists, especially in the research field of supramolecular chemistry [5]. Current major design needs are for sensors

P. Chanapiwat · V. Ruangpornvisuti (✉)
Department of Chemistry, Faculty of Science,
Chulalongkorn University,
Bangkok 10330, Thailand
e-mail: vithaya.r@chula.ac.th

for anions that are both sensitive and selective [4, 6]. Hosts containing a variety of donor (D) groups, D–H, such as urea [7–10], amines [11], amides [12, 13] and thioamides [14] have been widely investigated. Anion recognition of two binding-site receptors has led to the discovery of useful mono- and di-carboxylate sensors. Chromogenic azophenol-thiourea-based anion sensors have been developed for the selective colorimetric detection of acetate and other anions [15–17]. Furthermore, chromogenic indoaniline-thiourea-based receptors were studied as fluoride detection sensors [18]. Anthracene urea and thiourea compounds were synthesized and investigated for their effective chromogenic anion sensors [19]. A tripodal urea derivative used as an aromatic carboxylate receptor was investigated for its association constant using an NMR titration method [20]. Urea or thiourea groups incorporated as anion recognition receptors have been studied in various solvent systems [21–23]. In a previous theoretical study, the recognition of carboxylate and dicarboxylates by azophenol-thiourea derivatives was investigated by the integrated MO:MO method; oxalate was found to be the favorite ion in the formation of complexes with both receptors of azophenol-thiourea derivatives [24]. Since the binding and complexation energies of zinc(II) cation complexes with p–tert–butylsulfonylcalix[4]arene [25], p–tert–butylthiacalix[4]arene [26] and tetraamino–tert–butylthiacalix[4]arene [27] derivatives have been determined theoretically, complexes of these receptors with organic anions should now be investigated, particularly the calix[4]arene derivative functionalized by an amino group. Due to the ability of amino nitrogen atoms of tetraamino–tert–butylthiacalix[4]arene derivatives to bind to zinc (II) cations [27, 28], their amino protons must be able to bind with an anion. Since complex formation of tetraamino–tert–butylthiacalix[4]arene derivatives with
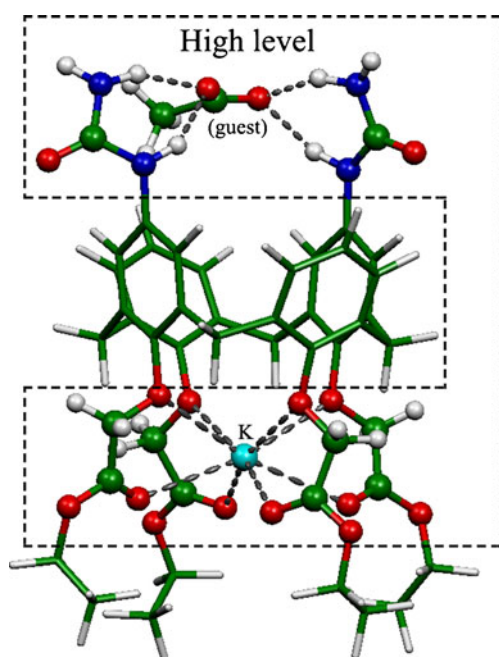
Fig. 1 Ball atoms of the receptor (KL$^+$ as representative) and molecule of guest (acetate ion as representative) treated as high level and the rest of the molecule treated as low level are modeled using in the two–layered ONIOM(MO:MO) calculation

association of pyrrolamido calix[4]arenes with anions was investigated, demonstrating its good selectivity for H$_2$PO$_4^-$ over F$^-$ and CH$_3$COO$^-$ ions [31]. A dialkoxycalix[4]arene derivative introduced as a new anion receptor was also recently investigated [32].

In this work, the molecular structures of complexes of diurea calix[4]arene receptor (**L**) with alkali metals Li$^+$, Na$^+$ and K$^+$ were obtained using the ONIOM approach. Binding interactions between **L** complexes with Li$^+$, Na$^+$ and K$^+$ ions and halide ions (F$^-$, Cl$^-$, Br$^-$) and oxygen–containing anions (HCO$_3^-$, HSO$_4^-$ and CH$_3$COO$^-$ ions) have been investigated. Binding energies, thermodynamic properties and association constants of complexes between **L** receptor and Li$^+$, Na$^+$ and K$^+$ ions, between Li$^+$, Na$^+$ and K$^+$ complexes, and between the alkali–metal receptors LiL$^+$, NaL$^+$ and KL$^+$ and F$^-$, Cl$^-$, Br$^-$, HCO$_3^-$, HSO$_4^-$ and CH$_3$COO$^-$ anions were obtained using ONIOM(B3LYP/ 6–31G(d):AM1) calculations.

Computational methods

Geometries of the tested host–guest complexes, as well as the host and guest components were optimized using the hybrid density functional B3LYP [33, 34] method and the two–layered ONIOM(MO:MO) approach (ONIOM) [35, 36] using B3LYP/6–31G(d) as a high model and semiempirical AM1 [37] as a low model. The reliability of the ONIOM(B3LYP/6–31G(d):AM1) [38] level of theory was examined previously by its use in the geometrical optimization of the tetraamino-*tert*-butylthiacalix[4]arene receptor and its complex with oxalate. The geometrical data were compared to the data of the target geometry optimized at B3LYP/6–31G(d) level of theory [39]. The ONIOM(B3LYP/ 6–31G(d):AM1) calculation of the examined system pro-

anions is expected, and their anion recognition could lead to the development of anion sensors, investigating the binding interactions between detected anions and their receptors is therefore crucial to the discovery of novel colorimetric and other detecting sensors. The calix[4]arene derivative of 1,3-alternate association with anions was investigated by ^{1}H NMR and UV–VIS spectroscopy; it was found that this calix recognizes chloride ions very well [29]. Anion complexation by amido derivatives of p–*tert*–butyl calix[4]arene with anions was studied by ^{1}H NMR spectroscopy [30]. The
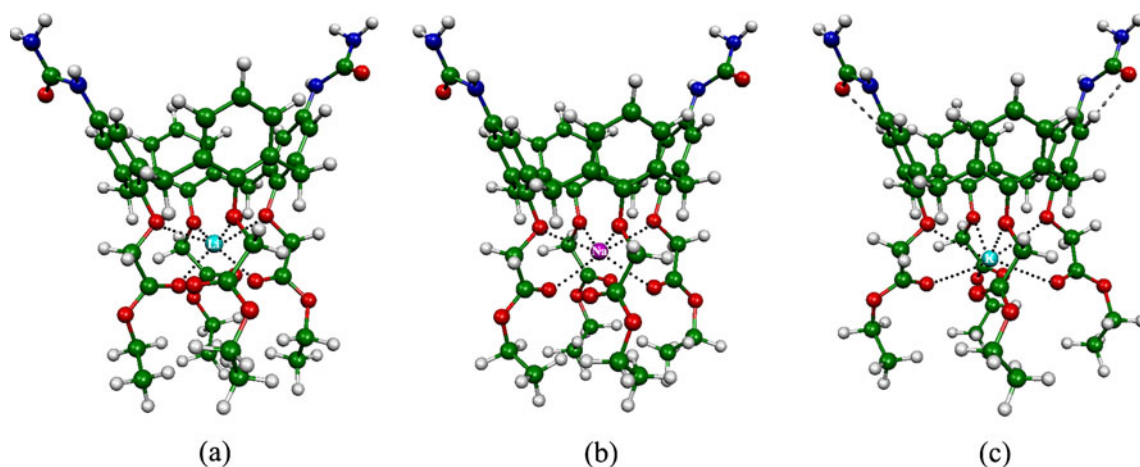

Fig. 2 ONIOM(B3LYP/6–31G(d):AM1)-optimized structures of receptors **a** LiL$^+$, **b** NaL$^+$ and **c** KL$^+$

Table 1 Energetics, thermodynamic properties and association constants of associations between calix[4]arene (**L**) and alkali metals, computed at the ONIOM(B3LYP/6–31G(d):AM1) level

Host/guest formation					$\Delta E_{binding}^{ZPE}$ [a]	ΔH_{298}^{o} [a]	ΔG_{298}^{o} [a]	K	Log K	$K_B^{KL^+}$ [b]
L	+	Li$^+$	→	Li**L**$^+$	−119.03	−119.72	−110.61	1.28×10^8	8.11	3.98×10^2
L	+	Na$^+$	→	Na**L**$^+$	−114.68	−115.17	−104.81	4.82×10^7	7.68	1.49×10^2
L	+	K$^+$	→	K**L**$^+$	−81.48	−81.37	−75.15	3.23×10^5	5.51	1.00×10^0

[a] In kcal mol^{-1}

[b] Selectivity coefficient of guests with respect to **KL**$^+$ complex

vides reasonable results at relatively lower cost for the present host–guest interaction. Two-layered ONIOM (B3LYP/6–31G(d):AM1) was therefore employed throughout this work for geometry optimization of the present host–guest investigation. The reliability of the ONIOM(B3LYP/6–31G(d):AM1) method used in a similar system has been discussed in the literature [40, 41]. The real and model systems used in the two-layered ONIOM(MO:MO) calculations for the hosts and host–guest interaction models are

shown in Fig. 1. Due to the system being partitioned into the two–layered ONIOM, the extrapolated energy (E_{ONIOM2}) is therefore defined as $E_{ONIOM2} = E_{Low}^{Real} - E_{Low}^{Model} + E_{High}^{Model}$ [38], where the Real and Model (superscripts) denote the whole system and the active site region, respectively. The Low and High (subscripts) represent the low–level and high–level of theory in the ONIOM calculations. The geometrical structures of anionic guests and their total energies were optimized and computed at the B3LYP/

Table 2 Energetics, thermodynamic properties and association constants complexes of calix[4]arene (**L**) alkali metals associated with anions, computed at the ONIOM(B3LYP/6–31G(d):AM1) level

Associations	$\Delta E_{binding}^{BSSE}$ [a,b]	$\Delta E_{binding}^{ZPE}$ [a,c]	ΔH_{298}^{o} [a]	ΔG_{298}^{o} [a]	K	Log K	$K_B^{ML^+/HSO_4^-}$ [d]
Receptor Li**L**$^+$:							
Li**L**$^+$/F$^-$	−101.46	−152.81	−154.52	−141.69	2.44×10^{10}	10.39	1.53×10^5
Li**L**$^+$/Cl$^-$	−75.89	−82.95	−84.07	−72.66	2.12×10^5	5.33	1.33×10^0
Li**L**$^+$/Br$^-$	−70.16	−86.40	−87.43	−76.56	4.10×10^5	5.61	2.57×10^0
Li**L**$^+$/HCO$_3^-$	−87.52	−96.75	−97.30	−82.84	1.18×10^6	6.07	7.41×10^0
Li**L**$^+$/HSO$_4^-$	−77.22	−84.68	−84.50	−70.98	1.60×10^5	5.20	1.00×10^0
Li**L**$^+$/CH$_3$COO$^-$	−87.01	−99.15	−99.96	−84.99	1.70×10^6	6.23	1.07×10^1
Receptor Na**L**$^+$:							
Na**L**$^+$/F$^-$	−100.61	−153.03	−154.40	−142.89	2.98×10^{10}	10.47	1.20×10^6
Na**L**$^+$/Cl$^-$	−74.69	−82.86	−83.65	−73.07	2.27×10^5	5.36	9.13×10^0
Na**L**$^+$/Br$^-$	−68.93	−86.29	−87.03	−76.65	4.16×10^5	5.62	1.67×10^1
Na**L**$^+$/HCO$_3^-$	−79.26	−89.63	−90.13	−75.17	3.24×10^5	5.51	1.30×10^1
Na**L**$^+$/HSO$_4^-$	−65.44	−74.38	−74.51	−59.97	2.49×10^4	4.40	1.00×10^0
Na**L**$^+$/CH$_3$COO$^-$	−78.53	−91.00	−91.44	−76.82	4.28×10^5	5.63	1.72×10^1
Receptor K**L**$^+$:							
K**L**$^+$/F$^-$	−99.44	−153.02	−154.71	−140.01	1.84×10^{10}	10.26	5.33×10^5
K**L**$^+$/Cl$^-$	−73.85	−82.78	−83.78	−71.27	1.68×10^5	5.22	4.86×10^0
K**L**$^+$/Br$^-$	−76.10	−86.22	−87.73	−72.64	2.12×10^5	5.33	6.14×10^0
K**L**$^+$/HCO$_3^-$	−77.91	−89.74	−90.49	−73.17	2.31×10^5	5.36	6.71×10^0
K**L**$^+$/HSO$_4^-$	−67.41	−76.00	−75.76	−61.90	3.45×10^4	4.54	1.00×10^0
K**L**$^+$/CH$_3$COO$^-$	−77.69	−91.03	−91.65	−75.25	3.28×10^5	5.52	9.52×10^0

[a] In kcal mol^{-1}

[b] Binding energy corrected by basis set super position error (BSSE) correction computed at the B3LYP/6–31+G(d,p)//ONIOM(B3LYP/6–31G(d):AM1) level

[c] Binding energy corrected by zero point vibrational energy (ZPVE) correction

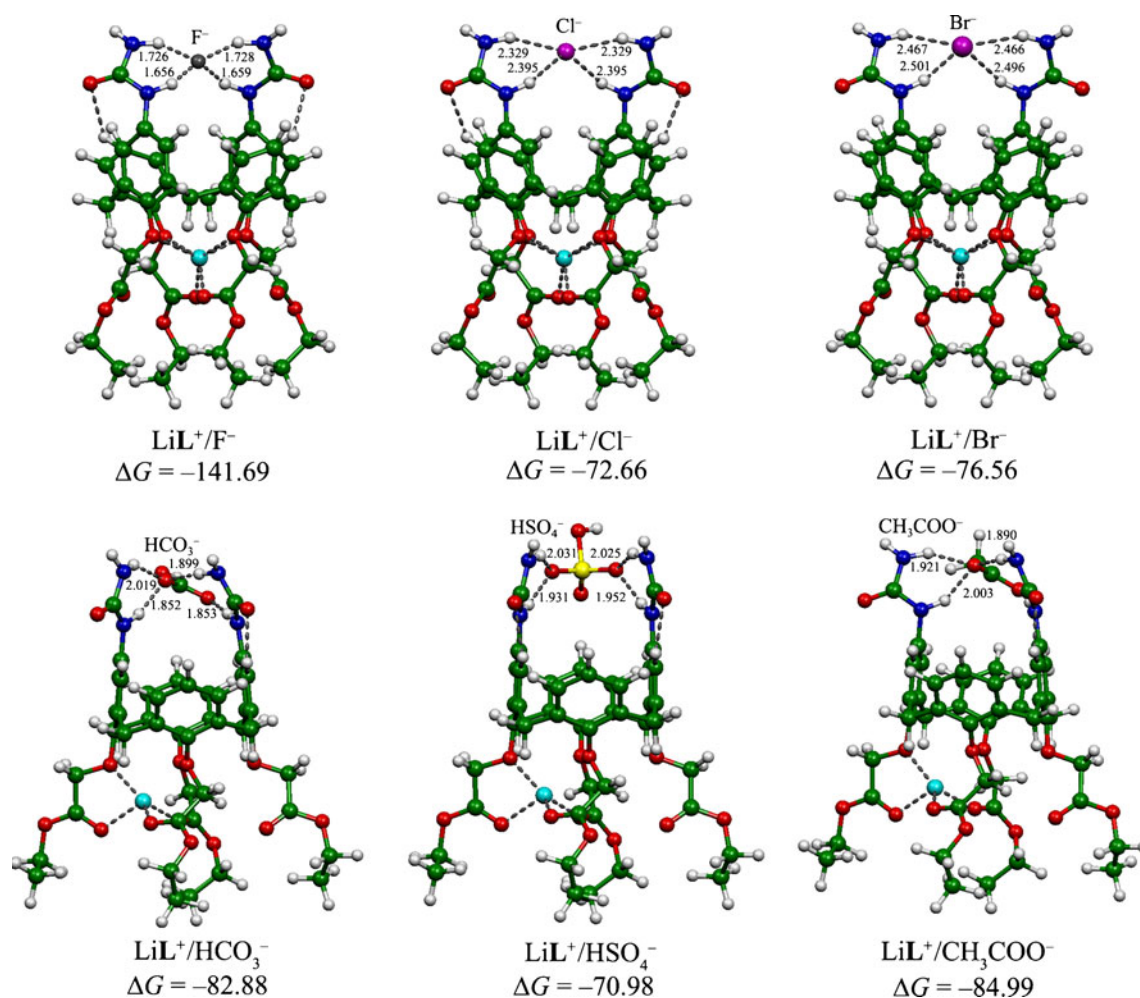[d] Selectivity coefficient of guests with respect to ML$^+$/HSO$_4^-$ complex

Fig. 3 ONIOM(B3LYP/6–31G(d):AM1)-optimized structures of complexes of LiL$^+$ with anionic guests. The hydrogen-bond distances and binding free energies (ΔG_{298}^o) are in Ångstroms and kcal mol^{-1}, respectively

6–31 G(d) level of theory. All calculations were performed using the GAUSSIAN 03 program [42], and the structures were visualized using the MOLEKEL 4.3 program [43].

The binding energy ($\Delta E_{binding}$) of guest on host of the ONIOM calculations of the present system were evaluated using the following equation:

$$
\begin{aligned}
\Delta E_{binding}(host/guest) = {} & E[ONIOM(B3LYP/6\text{–}31G(d):AM1)](host/guest) \\
& - E[ONIOM(B3LYP/6\text{–}31G(d):AM1)](host) \\
& - E[B3LYP/6\text{–}31G(d)](guest)
\end{aligned}
\tag{1}
$$

Binding energies were corrected by zero point vibrational energy (ZPVE) correction ($\Delta E_{binding}^{ZPE}$) and basis set super position error (BSSE) correction ($\Delta E_{binding}^{BSSE}$) [44]. The enthalpy $\Delta H°$ and Gibbs free energy changes $\Delta G°$ of all complexation reactions were derived from the frequency computations at ONIOM(B3LYP/6–31G(d):AM1) level of theory. The equilibrium constant, K of binding process at 298.15 and 1 atmosphere was computed using thermodynamic relation of $\Delta G°=-RT \ln K$.

The binding selectivity of calix[4]arene receptor to guest B with respect to guest A were derived from the selectivity coefficient (K_B^A) [45], which is defined as the equilibrium constant of the ion exchange between ions A and B. Since this exchange is a chemical reaction, i.e., AX+B ↔ BX+ A, it can be treated like any other mass action expression. Therefore, the selectivity coefficient can be defined as $K_B^A = \frac{[BX][A]}{[AX][B]}$. If complexations of BX and AX are observed,
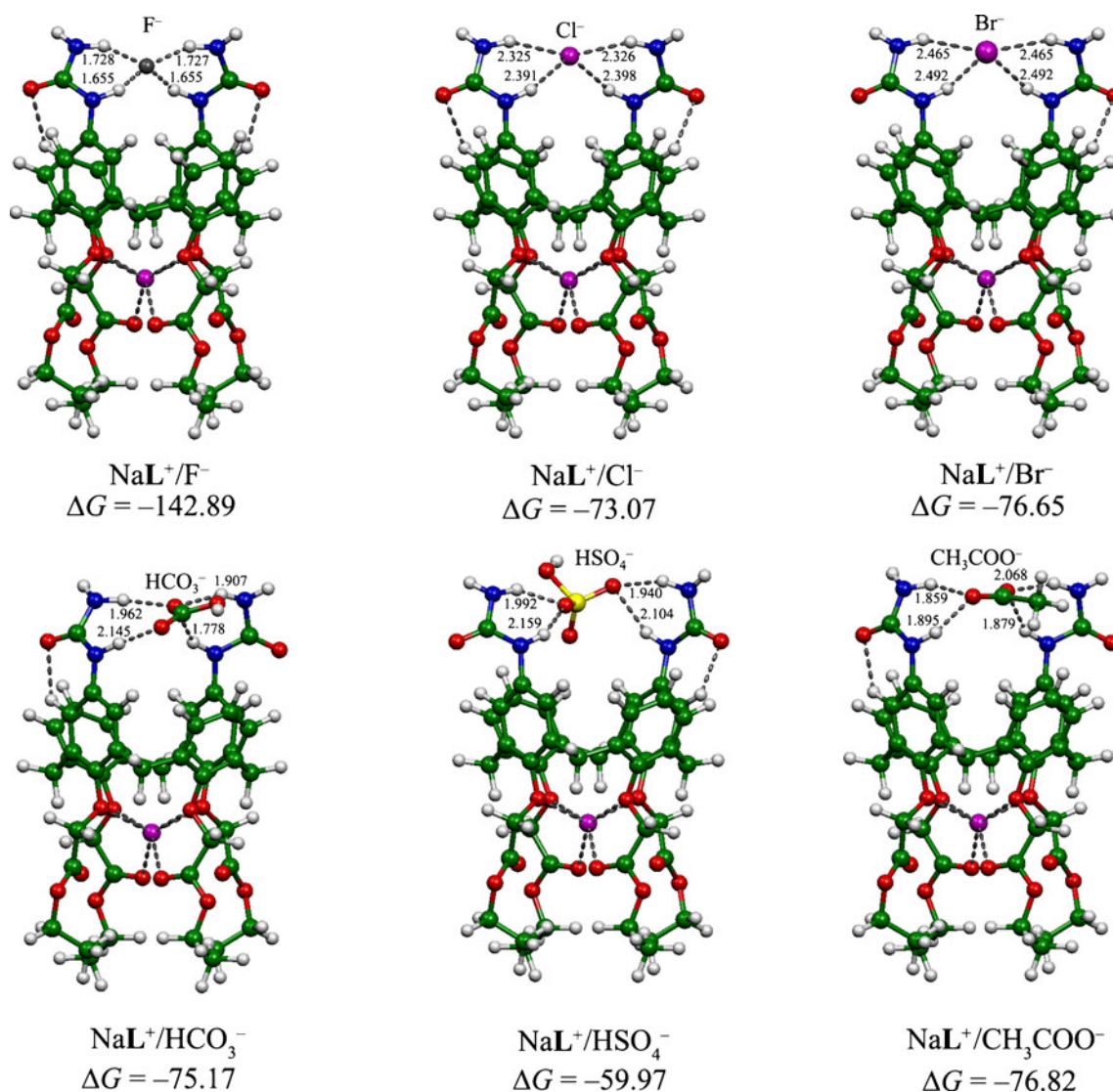
Fig. 4 ONIOM(B3LYP/6–31G(d):AM1)-optimized structures of complexes of NaL$^+$ with anionic guests. The hydrogen-bond distances and binding free energies (ΔG^o_{298}) are in Ångstroms and kcal mol^{-1}, respectively

their stability constants from equations, X+B $\leftrightarrow$ BX and X+A $\leftrightarrow$ AX, can be expressed as $K_A = \frac{[AX]}{[X][A]}$ and $K_B = \frac{[BX]}{[X][B]}$, respectively. The selectivity coefficient can be therefore written as $K^A_B = \frac{K_B}{K_A}$.

Results and discussion

The L receptor associated with alkali metals

The ONIOM(B3LYP/6–31G(d):AM1) optimized structures of complexes between calix[4]arene receptor (**L**) with alkali metals Li$^+$, Na$^+$ and K$^+$ are shown in Fig. 2. The binding energies, thermodynamic properties and association constants of associations between receptor **L** and alkali metals computed at the ONIOM(B3LYP/6–31G(d):AM1) level are listed in Table 1. Associations between anions and receptor **L** and metal ions Li$^+$, Na$^+$ and K$^+$ to form LiL$^+$, NaL$^+$ and KL$^+$ are exothermic and spontaneous reactions. The association constants for complexations of LiL$^+$, NaL$^+$ and KL$^+$ are, in order: LiL$^+(K = 1.28 \times 10^8)$ > NaL$^+(K = 4.82 \times 10^7)$ > KL$^+(K = 3.23 \times 10^5)$.

Binding energies of anions with alkali–metal/L receptors

The binding energies to receptors LiL$^+$, NaL$^+$ and KL$^+$ of halide ions F$^-$, Cl$^-$, Br$^-$, and oxygen-containing anions HCO$_3^-$, HSO$_4^-$ and CH$_3$COO$^-$ ions are shown in Table 2. Evaluation of the binding stabilities according to binding energies for LiL$^+$, NaL$^+$ and KL$^+$ associated with anions corrected by ZPVE correction ($\Delta E^{ZPE}_{binding}$) and BSSE
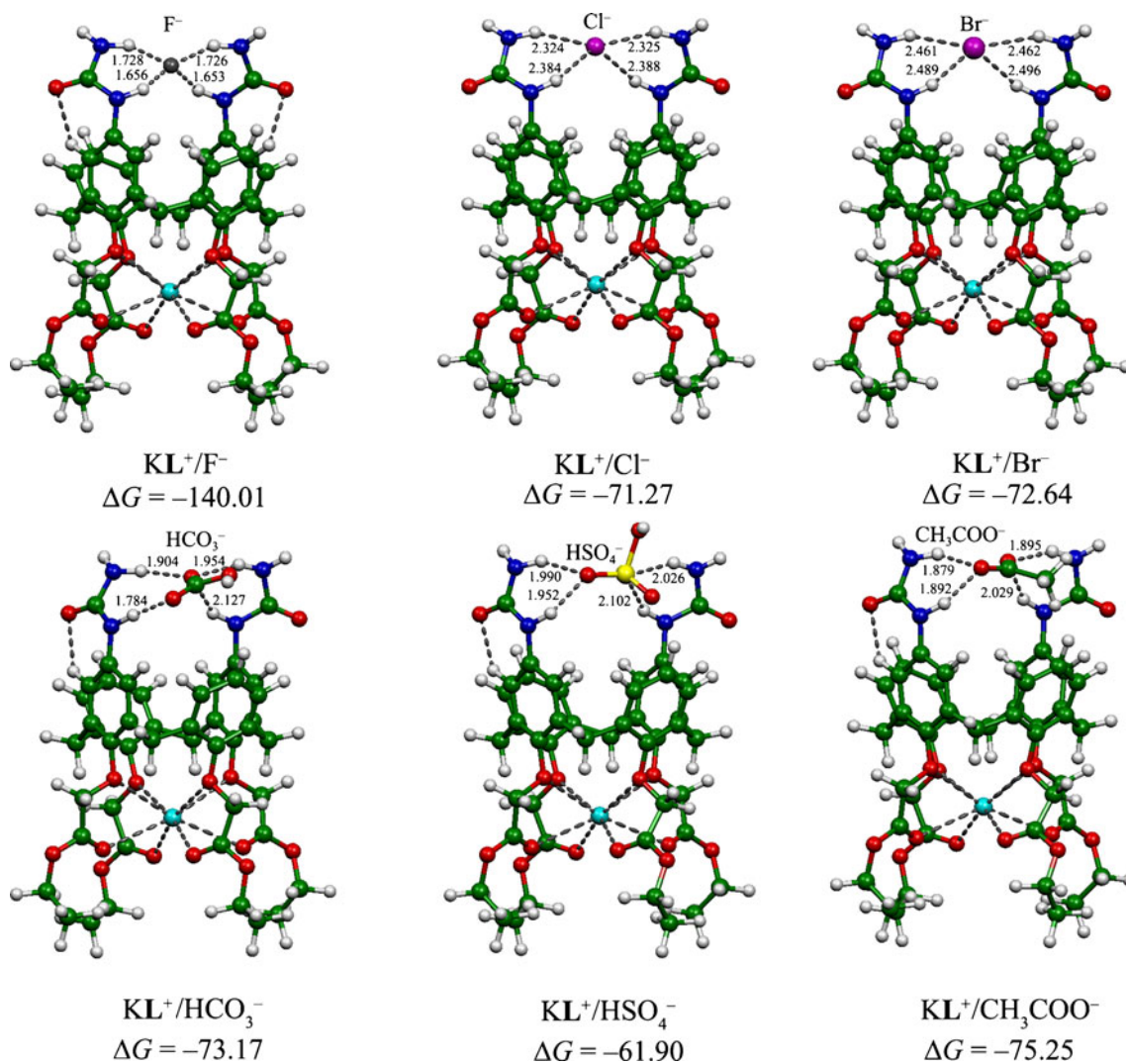
Fig. 5 ONIOM(B3LYP/6–31G(d):AM1)-optimized structures of complexes of KL^+ with anionic guests. The hydrogen-bond distances and binding free energies (ΔG_{298}^o) are in Ångstroms and kcal mol^{-1}, respectively

correction ($\Delta E_{binding}^{BSSE}$) revealed that they are in the same order: $F^- \gg CH_3COO^- \approx HCO_3^- > Br^- \approx HSO_4^- \approx Cl^-$. The strongest binding ability of F^- is with the receptors LiL^+, NaL^+ and KL^+, and the binding energies of F^- with receptors LiL^+, NaL^+ and KL^+ corrected by BSSE and ZPVE (in parentheses) corrections are −101.46 (−152.81), −100.61 (−153.03) and −99.44 (−153.02) kcal/mol, respectively.

Thermodynamics for associations of alkali–metal/L receptors with anions

The ONIOM(B3LYP/6–31G(d):AM1) optimized structures of alkali–metal receptors LiL^+, NaL^+ and KL^+ associated with halide ions F^-, Cl^-, Br^-, and oxygen-containing anions HCO_3^-, HSO_4^- and CH_3COO^- ions are shown in Figs. 3, 4 and 5. The thermodynamic properties and association

constants of complexes of receptor **L** and alkali metals associated with anions, computed at the ONIOM(B3LYP/6–31G(d):AM1) level, are shown in Table 2. Associations between anions and alkali–metal receptors LiL^+, NaL^+ and KL^+ are exothermic and spontaneous reactions. The bindings of all anions to the receptor NaL^+ are more stable thermodynamically than the receptors LiL^+ and KL^+, except for the HSO_4^- ion. The selectivity coefficients of studied anions for the receptors LiL^+, NaL^+ and KL^+ have the same order of binding abilities.

Plots of the binding free energy of these receptors with halide anions and oxygen-containing anions against the radius of alkali metals of the receptors are shown in Fig. 6. As shown in Fig. 6b, the alkali metals Li^+, Na^+ and K^+ hardly ever affect the stability of the halide complexes of the receptor **L** with alkali metals but affect the stability of CH_3COO^-, HCO_3^- and HSO_4^-.
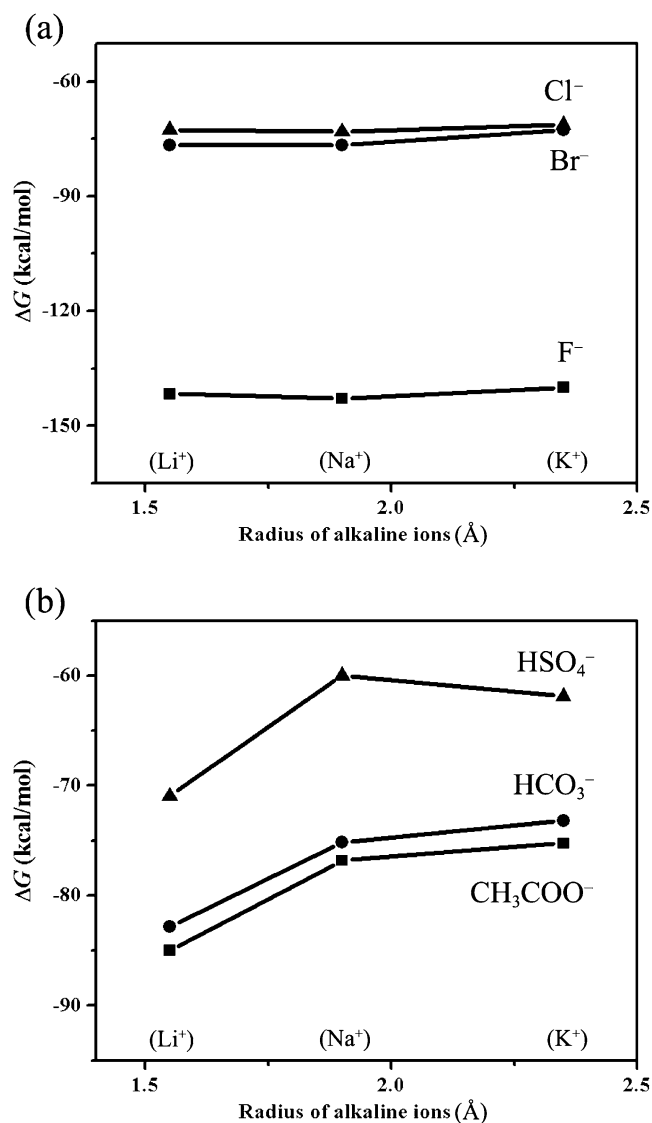
Fig. 6 Plots of the binding free energy of the receptors with **a** halide anions and **b** oxygen-containing anions against the radius of alkaline metals of the receptors

It can be concluded that all the alkali–metal receptors LiL^+, NaL^+ and KL^+ exhibit the ability to selectively bind fluoride ion. However, the association constants for the alkali–metal receptors LiL^+, NaL^+ and KL^+ bound to fluoride ion are very similar, namely $K(LiL^+) = 2.44 \times 10^{10}$, $K(NaL^+) = 2.98 \times 10^{10}$ and $K(KL^+) = 1.84 \times 10^{10}$. Thus, the alkali metals Li^+, Na^+ and K^+ have practically no differential influence on the fluoride recognition of the alkali–metal receptors LiL^+, NaL^+ and KL^+.

Conclusions

The structures of calix[4]arene receptor (**L**), alkali–metal receptors LiL^+, NaL^+ and KL^+ and their complexes with

anions F^-, Cl^-, Br^-, HCO_3^-, HSO_4^- and CH_3COO^- were optimized using the ONIOM(B3LYP/6–31G(d):AM1) method. Binding energies computed using both ZPVE-corrected ONIOM(B3LYP/6–31G(d):AM1) and BSSE-corrected B3LYP/6–31+G(d,p)//ONIOM(B3LYP/6–31G(d):AM1) methods were in good agreement. Determinations of thermodynamic properties and association constants of complexes between LiL^+, NaL^+ and KL^+ receptors and the studied anions were carried out at the ONIOM(B3LYP/6–31G(d):AM1) level with ZPVE correction. The association constants for all complexes are in order: $LiL^+ > NaL^+ > KL^+$. The binding stabilities based on binding energies of LiL^+, NaL^+ and KL^+ toward anions are in the same order: $F^- \gg CH_3COO^- \approx HCO_3^- > Br^- \approx HSO_4^- \approx Cl^-$. The selectivity coefficients of the receptors LiL^+, NaL^+ and KL^+ to all anions are in the same order as the binding abilities. It can be concluded that the receptors LiL^+, NaL^+ and KL^+ are all selective for the fluoride ion.

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