# NJC

# PAPER

Check for updates

Cite this: New J. Chem., 2020, 44, 20341

Received 2nd September 2020 Accepted 9th November 2020

DOI: 10.1039/d0nj04404k

rsc.li/njc

# 1 Introduction

Li is thought to be the energy metal of the 21st century, which can be used in various fields, such as lightweight metal alloys, aviation, medicine, chemical industry, and batteries.<sup>1</sup> The lithium resources mainly include lithium-rich Salt Lake brine, spodumene, lepidolite and aluminum–lithium symbiotic resources.<sup>2,3</sup> Lithium can be enriched in the solution *via* a roasting process with sulfuric acid or sulfate, evaporative crystallization, precipitation, extraction and adsorption processes. Further enrichment of lithium from the solution is a key point.<sup>4</sup>

Adsorption is the most convenient and economical method to further purify the lithium solution. Spinel-type oxide adsorbents and aluminum adsorbents are the most promising inorganic materials.<sup>5–9</sup> However, the lower adsorption capacity and the dissolution problem are the defects of these adsorbents. On the other hand, liquid–liquid extraction and resin adsorption methods are mature processes used for the enrichment of various valuable elements.<sup>10–12</sup> Crown ether is a kind of macrocyclic compound, which was synthesized by Pedersen for



Wenwen Chen, Yongpan Tian, (1)\* Chenggui Hu, Zhuo Zhao,\* Liang Xu and Bihai Tong (1)

Lithium is a critical strategic metal for world economy development and is used in various fields, such as daily life, aviation, medicine, chemical industry, *etc.* Crown ethers can adsorb Li<sup>+</sup> from a mixed ionic solution based on the size matching effect and synergistic effects of functional groups. The selective adsorption properties with Li<sup>+</sup>, Na<sup>+</sup>, Mg<sup>2+</sup> and the interaction between crown ethers and metal ions were analyzed to guide the design of crown ethers with high selectivity for Li<sup>+</sup>. The geometric structural characteristics of 1,8-dihydroxyl-4,4,5,5-tetramethylbenzo-14-crown-4 (CE) and complexes with Li<sup>+</sup>, Na<sup>+</sup>, and Mg<sup>2+</sup> metal ions were investigated using density functional theory modeling (DFT) at the M062X/def2SVP, def2TZVP level. The nature and strength of the interactions were analyzed by atoms in molecules (AIM) topological analysis and symmetry-adapted perturbation theory (SAPT) energy decomposition analysis. The results showed that the interaction strength of CE with metal ions followed the order: CE-Mg<sup>2+</sup> > CE-Li<sup>+</sup> > CE-Na<sup>+</sup>. The interaction energies can be separated into four kinds: electrostatics and induction, and dispersion. The stability of these complexes was mainly driven by electrostatics and induction. According to the analysis results of reduced density gradient (RDG), the metal ions mainly interacted with the oxygen atoms on the ring and did not interact with the hydroxyl groups directly. CE was synthesized and the extraction rates of Mg<sup>2+</sup> and Li<sup>+</sup> were better than that of Na<sup>+</sup>.

the first time in 1967. It can be grafted onto resins and form host-guest complexes with metal ions.<sup>13-15</sup> Crown ether derivatives can be designed to selectively adsorb Li<sup>+</sup> from a mixed ionic solution because of the size matching effect and synergistic effects of functional groups.

The adsorption sites of crown ether derivatives are mainly polar cavities, which are constituted by oxygen, nitrogen or sulfur atoms. According to the theory of hard and soft acids and bases (HSAB), the atoms in crown ethers with a high charge density (hard bases) can strongly interact with ions with a high charge density (hard acids).<sup>16</sup> Hence, oxygen atoms have stronger interactions with Li<sup>+</sup> compared with nitrogen or sulfur atoms. The main impurity ions in a lithium-rich solution are Na<sup>+</sup> and Mg<sup>2+</sup>. The ionic diameters of Li<sup>+</sup>, Mg<sup>2+</sup>, and Na<sup>+</sup> are 0.146 nm, 0.142 nm and 0.226 nm, respectively. Crown ethers with 12 to 16-membered rings containing four oxygen atoms were synthesized, and the experimental data showed that 14C4 derivatives had the best selectivity for Li<sup>+</sup> over Na<sup>+</sup>.<sup>17–19</sup> Thus, the ring size of 14C4 derivatives matched Li<sup>+</sup> the best. A series of derivatives incorporating bulky groups into the macrocycle of 14-crown-4 were synthesized to enhance the selectivity of the 14C4 ring for Li<sup>+</sup> over Na<sup>+</sup>. 14C4 derivatives with methyl and benzene substituent groups were synthesized easily, and the separation coefficient of lithium and sodium was higher than 2000.<sup>20-24</sup> The selective adsorption property of 14C4 derivatives



View Article Online View Journal | View Issue

School of Metallurgical Engineering, Anhui University of Technology, No. 59, Hudong Road, Ma'anshan, Anhui Province 243002, China. E-mail: tianyongpan\_ahut@163.com, nonferrous\_ahut@163.com

for Li<sup>+</sup> over Na<sup>+</sup> could also be supported by the simulation studies.<sup>25–29</sup> Previous experimental data showed that DB14C4 grafted onto a polymer preferred to interact with Li<sup>+</sup> over  $Mg^{2^+}$ .<sup>30–32</sup> However, the interaction between  $Mg^{2^+}$  and crown ethers has not been fully simulated, which may be due to similar sizes of Li<sup>+</sup> with  $Mg^{2^+}$ . Moreover, the nature of the interactions between metal ions and crown ethers has not been fully simulated.

The present work focused on the formation process of complexes constituted by 1,8-dihydroxyl-4,4,5,5-tetramethylbenzo-14-crown-4 and Li<sup>+</sup>, Na<sup>+</sup>, and Mg<sup>2+</sup>. Quantum chemical simulation analysis and adsorption experiments were conducted to analyze the interaction of complexes. The quantum chemical simulation analysis mainly included the nature of the interactions and the binding strength of interactions. M062X was used to describe the weak interactions of complexes, which is better than B3LYP. The analysis methods included AIM topological analysis, reduced density gradient (RDG) and energy decomposition analysis. The thermodynamic properties and binding energy were also calculated. 1,8-Dihydroxyl-4,4,5,5tetramethylbenzo-14-crown-4 was synthesized and adsorption experiments were done in individual and mixed ionic solutions. The main goal of this work is to provide detailed microscopic information about the host-guest interaction mechanism between crown ethers and Li<sup>+</sup>, Na<sup>+</sup>, and Mg<sup>2+</sup>, and discuss the key issues between molecular design and experimental processes.

# 2 Experimental and computational methods

### 2.1 Reagents and synthesis of 14C4 derivatives

Anhydrous acetonitrile, DCM and *t*-BuOH were used as the reaction solvents. Catechol, allyl bromide, *m*-CPBA and 2,3-dimethyl-2,3-butanediol were used to obtain the intermediate and final products. High purity metal salts ( $K_2CO_3$ , NaOH, Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>, NaHCO<sub>3</sub>, KOH) were used during the production. All intermediates and CEs were purified *via* silica gel column chromatography (0.035–0.070 mm, 60 Å). Petroleum ether/EtOAc, DCM/diethyl ether and CHCl<sub>3</sub>/MeOH were used as the eluent to isolate the intermediate and final products. The reaction steps for 1,8-dihydroxyl-4,4,5,5-tetramethylbenzo-14C4 are shown in Fig. 1.

#### 2.2 Lithium separation experiments

The lithium ion extraction efficiency of the crown ether was analyzed by the liquid–liquid extraction method. The organic phase was dichloromethane, and the ratio of the organic phase with aqueous phase was 1:1. The organic phase was prepared by dissolving appropriate amounts of 1,8-dihydroxyl-4,4,5,5tetramethylbenzo-14C4 in dichloroethane. Aqueous phases were prepared by dissolving lithium chloride in demineralized water. The molar ratio of metal ion to crown ether is 1:1. LiCl, NaCl and MgCl<sub>2</sub> were used to prepare the solutions. The extraction experiments were performed at room temperature and vibrated for 30 min. The concentration of lithium ions was



Fig. 1 Synthetic route for 1,8-dihydroxyl-4,4,5,5-tetramethylbenzo-14crown-4.

measured using ICP-AES. The extraction efficiency E was calculated by eqn (2.1).

$$E = \frac{C_t - C_0}{C_0} \times 100\%$$
 (2.1)

where  $C_0$  and  $C_t$  (mg L<sup>-1</sup>) are the initial and equilibrated concentrations of lithium ion in the aqueous phase, respectively.

### 2.3 Computational methods

Density functional theory (DFT) can be applied to capture a considerable amount of quantitative information about the complexes of 14C4 derivatives with Li<sup>+</sup>, Na<sup>+</sup>, and Mg<sup>2+</sup> metal ions.<sup>33–35</sup> The simulation and visualization of molecules were carried out using Gauss16, Multiwfn3.6 and Visual Molecular Dynamics.<sup>36,37</sup> Geometry optimization was performed with M062X/ def2-SVP and carefully characterized through harmonic frequency analysis with no imaginary frequencies at stationary points. The energy calculations were conducted with M062X/def2-TZVP.

Quantum theory of atoms in molecules (QTAIM) analysis was used to study the bond paths and the corresponding bond critical points to reveal the strength and nature of interactions between the crown ether and metal ions.<sup>38,39</sup> The nature of the interaction was also studied by the reduced density gradient.<sup>40</sup> It is a kind of real space function and can be used to distinguish areas with different characteristics in the system. As shown by eqn (2.2),  $\nabla$  represents the gradient operator and  $|\nabla \rho(r)|$  is the modulus of the electron density gradient.

$$RDG(r) = \frac{1}{2(3\pi^2)^{1/3}} \frac{|\nabla\rho(r)|}{\rho(r)^{4/3}}$$
(2.2)

The nature of the interaction was analyzed using symmetryadapted perturbation theory (SAPT) which has the highest acceptability in weak interaction research.<sup>41,42</sup> The zeroth-order SAPT analysis was performed using the Psi4 code. Geometry optimization was performed with M062X/def2SVP. The aug-cc-pVDZ-RI DF basis was used for the evaluation of the SAPT0 electrostatics, induction and dispersion components. The frozen core was also invoked during the evaluation. Eqn (2.3) represents the SAPT0 interaction energy, E(SAPT0), which is the sum of the component energies arising from electrostatics ( $E_{ele}$ ), exchange ( $E_{exch}$ ), induction ( $E_{ind}$ ), and dispersion ( $E_{disp}$ ).

$$E_{\text{tot}} = E_{\text{ele}} + E_{\text{exch}} + E_{\text{ind}} + E_{\text{disp}}$$
(2.3)

The effects of the aqueous solvent on the energies were considered using the implicit solvation model (SMD, solvation model based on density). The molecular simulation provides molecular insight and microscopic understanding of the interactions between 1,8-dihydroxyl-4,4,5,5-tetramethylbenzo-14C4 and Li<sup>+</sup>, Na<sup>+</sup>, Mg<sup>2+</sup>. The formation Gibbs free energy of the complex in the aqueous phase was calculated by the solvation free energy and the Gibbs free energy in the gas phase.<sup>43</sup> The Gibbs correction energy ( $G_{corr}(T)$ ) was calculated by the SMD model, which consists of zero-point correction and thermal correction to the Gibbs free energy. The standard state conversion difference between gas and liquid was added and the unit is kcal mol<sup>-1</sup>. The formulae used for these calculations are shown as (2.4)-(2.7).

$$G_{\text{metalion}} = G_{\text{corr-ion-solv}}(T) + \varepsilon_{\text{ion-gas}} + \Delta G_{\text{ion-solv}} + 1.89$$
(2.4)

$$G_{ce} = G_{corr-ce-solv}(T) + \varepsilon_{ce-gas} + \Delta G_{ce-solv} + 1.89 \quad (2.5)$$

$$G_{\rm cm} = G_{\rm corr-cm-solv}(T) + \varepsilon_{\rm cm-gas} + \Delta G_{\rm cm-solv} + 1.89$$
(2.6)

$$G = G_{\rm cm} - G_{\rm metalion} - G_{\rm ce}$$
(2.7)

where  $G_{\text{metalion}}$ ,  $G_{\text{ce}}$  and  $G_{\text{cm}}$  represent the Gibbs free energy of the metal ion, crown ether, and complex, respectively;  $G_{\text{corr-ion-solv}}(T)$ ,  $G_{\text{corr-ce-solv}}(T)$  and  $G_{\text{corr-cm-solv}}(T)$  represent the thermal correction to the Gibbs free energy of the metal ion, crown ether, and complex in solution, respectively;  $\Delta G_{\text{ion-solv}}$ ,  $\Delta G_{\text{ce-solv}}$  and  $\Delta G_{\text{cm-solv}}$  represent the solvation free energy of the metal ion, crown ether, and complex, respectively;  $\varepsilon_{\text{ion-gas}}$ ,  $\varepsilon_{\text{ce-gas}}$ and  $\varepsilon_{\text{cm-gas}}$  are the single energies of metal ion, crown ether and complex in the gas phase, respectively;  $\Delta G$  represents the formation Gibbs free energy of complexes.

The binding energy can be calculated by eqn (2.8) and has been corrected with basis set superposition errors (BSSE) at the M062X/def2TZVP level according to the counterpoise method of Boys and Bernardi.<sup>44</sup> BSSE was calculated according to the following eqn (2.9).

$$\Delta E_{\rm b} = E_{\rm ele}(\rm complex) - E_{\rm ele}(M^{+}) - E_{\rm ele}(\rm crown \ ether)$$

$$(2.8)$$

$$BSSE = E_{\rm AB}^{\rm A}(A) + E_{\rm AB}^{\rm B}(B) - E_{\rm AB}^{\rm A+B}(A) - E_{\rm AB}^{\rm A+B}(B) \quad (2.9)$$

# 3. Theoretical insights of the M(I, II) - O interaction

### 3.1 Geometry of the crown ether and complexes

The geometric structural characteristics of complexes composed of alkali metal ions ( $Li^+$ ,  $Na^+$ ,  $Mg^{2+}$ ) and 1,8-dihydroxyl-4,4,5,5tetramethylbenzo-14-crown-4 (CE) were studied. The atoms are numbered in Fig. 2. The optimized structures of the crown ether and complexes in the top and side views are shown in Fig. 3 and 4. The atoms are shown by different colors: O (red), C (cyan), H (white),  $Li^+$  (pink),  $Mg^{2+}$  (purple), and  $Na^+$  (blue).

The ionic diameters of Li<sup>+</sup>, Mg<sup>2+</sup>, and Na<sup>+</sup> are 0.146 nm, 0.142 nm and 0.226 nm, respectively, for the quadridentate groups. As shown in Fig. 4, Li<sup>+</sup> and Mg<sup>2+</sup> lie slightly higher than the plane of oxygen atoms, while Na<sup>+</sup> lies the highest above the plane because of its largest ionic diameter. As shown in Table 1, the angle of O–M–O bond in complexes containing Na<sup>+</sup> is the minimum, which supports the regularity quantitatively.

The distances between non-adjacent oxygen atoms are shown in Table 2. The distances show that the oxygen ring is narrow before the formation of a complex. The difference between O19-O22 and O20-O21 is 1.294 Å for the crown ether, while the differences of the complexes were reduced to 0.114 Å (CE-Li<sup>+</sup>), 0.260 Å (CE-Na<sup>+</sup>) and 0.078 Å (CE-Mg<sup>2+</sup>), respectively. The difference of CE-Mg<sup>2+</sup> is the minimum. The M–O distances shown in Table 3 suggest that the bond length of O-Na<sup>+</sup> is the highest, which is because of the largest ionic diameter of Na<sup>+</sup>. The ionic diameters of  $\mathrm{Li}^{\scriptscriptstyle +}$  and  $\mathrm{Mg}^{2^{\scriptscriptstyle +}}$  are similar with each other, thus the bond lengths of them are almost the same with each other. The bond length in Table 4 shows the same regularity for all the C–O bonds:  $CE-Mg^{2+} > CE-Li^+ > CE-Na^+ > CE$ . The increase in C-O bond length is due to the interactions between ions and oxygen atoms. Therefore, the results may suggest that the strength of interactions follow the order:  $CE-Mg^{2+} > CE-Li^+ > CE-Na^+$ .

#### 3.2 AIM topological analysis

To characterize the interaction between metal ions and 1,8dihydroxyl-4,4,5,5-tetramethylbenzo-14-crown-4, topological analysis



**Fig. 2** Numbering of the oxygen and carbon atoms of 1,8-dihydroxyl-4,4,5,5-tetramethylbenzo-14-crown-4.



Fig. 3 Optimized structures of 1,8-dihydroxyl-4,4,5,5-tetramethylbenzo-14-crown-4.



Fig. 4 Optimized structures of complexes composed of 1,8-dihydroxyl-4,4,5,5-tetramethylbenzo-14-crown-4 and Li<sup>+</sup>, Na<sup>+</sup>, Mg<sup>2+</sup>.

Table 1 Calculated angles of O–M–O bond for the crown ethers and their complexes with Li<sup>+</sup>, Na<sup>+</sup>, and Mg<sup>2+</sup> (°, 298.15 K, SMD)

О-М-О	$CE-Li^+$	CE-Mg <sup>2+</sup>	CE-Na <sup>+</sup>
O20-M-O21	147.811	136.222	114.916
O19-M-O22	158.358	140.020	126.175

Table 3 Calculated values of M–O bond length for the complexes with Li<sup>+</sup>, Na<sup>+</sup>, and Mg<sup>2+</sup> (Å, 298.15 K, SMD)

М-О	$CE-Li^+$	CE-Mg <sup>2+</sup>	CE-Na <sup>+</sup>
M-O19	2.031	2.094	2.336
M-O21	1.989	2.069	2.278
M-O22	1.896	2.001	2.235
M-O20	1.907	1.994	2.250

Table 2 Distances between oxygen atoms for the crown ether and complexes with Li^+, Na^+, and Mg^{2+} (Å, 298.15 K, SMD)

Non-adjacent oxygen atoms	CE	$CE-Li^+$	CE-Na <sup>+</sup>	CE-Mg <sup>2+</sup>
019-022	3.406	3.858	4.077	3.848
O20-O21	4.700	3.744	3.817	3.770

of the electron density was conducted with the atoms in molecules (AIM) theory. The molecular structure of CE-Li<sup>+</sup> with the bond critical points between lithium and oxygen atoms is shown in Fig. 5. The properties shown in Table 4 are the density of electrons ( $\rho(r)$ ), Lagrangian kinetic energy G(r), potential

Table 4 Calculated values of C–O bonds for the crown ethers and complexes with Li^+, Na^+, and Mg^{2+} (Å, 298.15 K, SMD)

Crown ether or complex	C2-	C4-	C3-	C11-	C10-	C9-	C6-	C5-
	O22	O22	O21	O21	O19	O19	O20	O20
CE	1.408	1.435	1.422	1.369	1.360	1.418	1.412	1.435
CE-Na <sup>+</sup>	1.416	1.442	1.433	1.378	1.379	1.433	1.414	1.437
CE-Li <sup>+</sup>	1.419	1.447	1.436	1.378	1.380	1.437	1.418	1.442
CE-Mg <sup>2+</sup>	1.432	1.464	1.450	1.389	1.390	1.452	1.431	1.458

energy density V(r), total energy E(r) (E(r) = G(r) + V(r)), and Laplacian of electron density  $\nabla^2 \rho(r)((1/4)\nabla^2 \rho(r) = 2G(r) + V(r))$ .

The sign of  $\nabla^2 \rho(r)$  shows the contributions of G(r) and V(r). When  $\nabla^2 \rho(r)$  is negative, the interactions belong to shared interactions suggesting that there are shared electrons in the interacting region. When  $\nabla^2 \rho(r)$  is positive, the situation is characteristic of closed-shell interactions suggesting that there are no shared electrons in the interacting region.

As shown in Table 5,  $\nabla^2 \rho(r)$  is positive, so the interactions between Li<sup>+</sup>, Na<sup>+</sup>, Mg<sup>2+</sup> (Lewis acid) and oxygen atom (Lewis base) present a typical closed-shell interaction. Moreover, the eta index is less than 1 indicating that the interaction belongs to a kind of noncovalent interaction. Hence, the interaction may mainly be constituted by electrostatic interaction.

The benzene ring is an electron-withdrawing group, so the electron densities of O21 and O19 are lower than that of O20 and O22. Thus,  $\rho(r)$  is lower at points 54 and 56 compared with points 55 and 57. Moreover, the electron density of CE-Mg<sup>2+</sup> is the highest, so the interaction between CE and Mg<sup>2+</sup> is the strongest.

#### 3.3 RDG analysis of complexes

The regions in these complexes could be divided into four kinds: regions around the nucleus, regions around the covalent bond, regions at the edge of the complexes and regions with weak interactions. The values of RDG are much smaller in regions around the covalent bond and regions with weak interactions compared with other regions, while the value of  $\rho(r)$  in regions with weak interactions is smaller compared with regions around the covalent bond. Moreover, the value of  $\rho(r)$  is an indicator of the bonding strength. Therefore, the regions with weak interactions of RDG and  $\rho(r)$ .

The Laplacian of the density  $(\nabla^2 \rho(r))$  is a widely used tool to distinguish the different types of strong interactions. It is often decomposed into three eigenvalues  $\lambda_i$  of the electron-density Hessian (second derivative) matrix, such that  $\nabla^2 \rho(r) = \lambda_1 + \lambda_2 + \lambda_3$ . The second eigenvalue  $(\lambda_2)$  of the electron-density Hessian matrix can be used to distinguish a strong attractive effect ( $\lambda_2 < 0$ ) from a strong repulsive effect ( $\lambda_2 > 0$ ). Hence, the strength and nature of the interactions can be shown by mapping  $\rho(r)$ sign( $\lambda_2$ ) against RDG. The interactions are expressed by the

Fig. 5 Bond paths linking lithium and oxygen atoms: small golden dots indicate the BCP critical points.

Table 5 Topological properties of the M(I, II)-O bond at the bond critical points of complexes calculated at the M062X/def2-TZVP level (a.u.)

Complex	Number	$\rho(r)$	E(r)	$\nabla^2 \rho(r)$	G(r)	V(r)	Eta index
CE-Li <sup>+</sup>	54	0.0231	0.0065	0.150	0.0308	-0.0243	0.171594
	55	0.0320	0.0107	0.228	0.0463	-0.0356	0.166054
	56	0.0256	0.0078	0.172	0.0351	-0.0273	0.171834
	57	0.0324	0.0113	0.235	0.0476	-0.0363	0.165451
$CE-Na^+$	54	0.0201	0.0042	0.122	0.0263	-0.2219	0.152909
	55	0.0254	0.0058	0.162	0.0346	-0.2888	0.150875
	56	0.0231	0.0053	0.146	0.0312	-0.2592	0.153370
	57	0.0127	0.0063	0.167	0.0354	-0.2914	0.150214
CE-Mg <sup>2+</sup>	54	0.0343	0.0079	0.238	0.0516	-0.0437	0.152227
	55	0.0437	0.0125	0.342	0.0729	-0.0604	0.147275
	56	0.0363	0.0090	0.260	0.0560	-0.0470	0.151431
	57	0.0425	0.0122	0.331	0.0706	-0.0584	0.147068

colors of regions with the "blue-green-red" color scheme ranging from -0.035 to 0.02 a.u. (the color bar) according to the values of  $\rho(r) \operatorname{sign}(\lambda_2)$ . The interactions are mainly divided into three kinds: strong attractive interactions (blue), van der Waals interactions (green) and strong repulsion interactions (red).

As shown in Fig. 6, RDG-1 is the color-scatter plot of RDG *versus*  $\rho(r) \operatorname{sign}(\lambda_2)$  for CE-Li<sup>+</sup>, and the corresponding colormapped isosurfaces when RDG is 0.5 a.u. is shown by RDG-2. As shown by RDG-1, the negative value of  $\rho(r) \operatorname{sign}(\lambda_2)$  is about -0.03 a.u. suggesting stronger attractive interactions. The  $\rho(r)$  $\operatorname{sign}(\lambda_2)$  calculated by AIM at the bond critical points of CE-Li is also around -0.03 a.u., which is shown in Table 6. Hence, the interactions between Li<sup>+</sup> and oxygen atoms are mainly strong electrostatic interactions, which is also proved by the blue color between them.

The regions around zero correspond to van der Waals interactions in the complexes. The larger values of  $\rho(r)$  sign( $\lambda_2$ ) at approximately 0.01 and 0.02 a.u. correspond to a strong repulsion steric effect in the complex molecule, which mainly exists in the center of benzene and regions between oxygen atoms.

According to the AIM theory, the value of  $sign(\lambda_2)$  is -1 at the bond critical points. The absolute value of  $\rho(r) sign(\lambda_2)$ shown in Table 4 follows the order: CE-Mg<sup>2+</sup> > CE-Li<sup>+</sup> > CE-Na<sup>+</sup>. Hence, the strength of interaction follows the same order. Moreover, the analyzed results of RDG show that the two hydroxyl oxygen atoms do not interact with lithium ion directly.

### 3.4 Energy decomposition analysis

The analysis results of RDG could only show the strong attractive interaction between the metal ions and the oxygen atoms on the crown ether ring. The nature of the strong attractive interaction could be studied by SAPT. The SAPT theory is a rigorous way to evaluate the interaction energy and can be decomposed into four physical terms: electrostatics ( $E_{ele}$ ), induction ( $E_{ind}$ ), exchange ( $E_{exch}$ ) and dispersion ( $E_{disp}$ ).  $E_{ele}$ represents the classical Coulomb interaction,  $E_{exch}$  represents the exchange repulsion interaction,  $E_{ind}$  represents the interaction of charge polarization and electron transfer and  $E_{disp}$ represents long-range Coulomb interactions.

Paper



**Table 6** Results of  $\rho(r)$ sign( $\lambda_2$ ) at the bond critical points of complexes

(a.u.)		
Complex	Position	$\rho(r) \operatorname{sign}(\lambda_2)$
CE-Li <sup>+</sup>	54	-0.023
	55	-0.032
	56	-0.026
	57	-0.032
CE-Na <sup>+</sup>	54	-0.020
	55	-0.025
	56	-0.023
	57	-0.025
CE-Mg <sup>2+</sup>	54	-0.034
	55	-0.044
	56	-0.036
	57	-0.043

The interaction energies calculated by SAPT are shown in Table 7. The distances between the center of oxygen atoms and ions are from 0.151 Å to 1.501 Å. Within that range,  $E_{tot}$  of CE-Li<sup>+</sup>, CE-Na<sup>+</sup>, and CE-Mg<sup>2+</sup> are all below zero suggesting that the complexes are stable in aqueous solution.  $E_{ele}$ ,  $E_{disp}$  and  $E_{\rm ind}$  are favorable factors for the stability of complexes, while  $E_{\text{exch}}$  is an unfavorable factor. Comparing the absolute values, the formation of these complexes is mainly affected by electrostatics ( $E_{ele}$ ), induction ( $E_{ind}$ ), and exchange ( $E_{exch}$ ). Dispersion  $(E_{\text{disp}})$  plays a small role in the formation of complexes. Moreover, the formation of these complexes is mainly driven by electrostatics and induction. In contrast, the induction interaction plays a more important role in the stabilization of complexes composed of Mg<sup>2+</sup>. The ionic diameters of Mg<sup>2+</sup> and  $Li^+$  are similar with each other while  $Mg^{2+}$  is a positive divalent metal ion and Li<sup>+</sup> is a monovalent metal ion. Thus, the charge

Complex	Distance	$E_{ele}$	Eexch	$E_{\rm disp}$	Eind	$E_{\rm tot}$
CE-Li <sup>+</sup>	0.151	-85.430	27.735	-1.250	-48.552	-107.497
	0.301	-86.218	26.018	-1.180	-47.302	-108.682
	0.451	-85.482	23.421	-1.087	-45.725	-108.874
	0.601	-83.376	20.248	-0.979	-43.840	-107.946
	0.751	-80.124	16.837	-0.864	-41.696	-105.846
	0.901	-75.997	13.494	-0.748	-39.369	-102.620
	1.051	-71.275	10.453	-0.638	-36.945	-98.404
	1.201	-66.219	7.863	-0.538	-34.509	-93.403
	1.351	-61.053	5.784	-0.452	-32.130	-87.851
	1.501	-55.947	4.204	-0.378	-29.860	-81.981
CE-Mg <sup>2+</sup>	0.151	-177.606	82.325	-1.063	-172.641	-268.985
U	0.301	-178.375	76.874	-1.012	-169.010	-271.522
	0.451	-175.796	68.769	-0.957	-164.829	-272.813
	0.601	-170.299	58.951	-0.898	-160.042	-272.288
	0.751	-162.509	48.483	-0.832	-154.607	-269.465
	0.901	-153.155	38.353	-0.759	-148.535	-264.095
	1.051	-142.930	29.313	-0.680	-141.909	-256.206
	1.201	-132.385	21.784	-0.598	-134.876	-246.076
	1.351	-121.899	15.878	-0.520	-127.617	-234.158
	1.501	-111.713	11.481	-0.447	-120.312	-220.991
CE-Na <sup>+</sup>	0.151	-108.857	101.203	-1.534	-34.676	-43.864
	0.301	-108.013	94.483	-1.477	-34.063	-49.069
	0.451	-104.844	84.570	-1.423	-33.498	-55.195
	0.601	-99.826	72.640	-1.362	-32.893	-61.441
	0.751	-93.526	59.990	-1.284	-32.164	-66.985
	0.901	-86.505	47.773	-1.186	-31.261	-71.179
	1.051	-79.234	36.826	-1.072	-30.171	-73.650
	1.201	-72.064	27.619	-0.949	-28.917	-74.310
	1.351	-65.231	20.293	-0.827	-27.539	-73.304
	1.501	-58.876	14.749	-0.713	-26.086	-70.926

polarization and electron transfer phenomenon of CE-Mg<sup>2+</sup> is more obvious than that of CE-Li<sup>+</sup>. The induction interaction reflects the charge polarization and electron transfer

 Table 7
 Energy decomposition of the complexes by SAPT (kcal mol<sup>-1</sup>)

(2.1.)

phenomenon, so induction plays a greater role in the stability of CE-Mg<sup>2+</sup>.

As shown in Fig. 7, 8 and 9, the results of  $E_{\text{tot}}$  are fitted and the values of  $R^2$  are 0.99975, 0.99801 and 0.9993 for CE-Li<sup>+</sup>, CE-Na<sup>+</sup> and CE-Mg<sup>2+</sup>, respectively. The data are very close to 1, so the fitted results are believable. The lowest  $E_{\text{tot}}$  of CE-Li<sup>+</sup>, CE-Na<sup>+</sup>, and CE-Mg<sup>2+</sup> are -109.09 kcal mol<sup>-1</sup>, -74.72 kcal mol<sup>-1</sup> and -273.21 kcal mol<sup>-1</sup> at the distances of 0.39 Å, 1.21 Å and 0.46 Å, respectively. Hence, the order of stability is CE-Mg<sup>2+</sup> > CE-Li<sup>+</sup> > CE-Na<sup>+</sup>.

# 4. Selective adsorption for metal ions in solution

### 4.1 Extraction of metal ions in solution

LiCl, NaCl and MgCl<sub>2</sub> solutions were prepared for the adsorption experiments. The initial concentration of ions were 280 mg L<sup>-1</sup>, 344 mg L<sup>-1</sup> and 502 mg L<sup>-1</sup> for Li<sup>+</sup>, Mg<sup>2+</sup> and Na<sup>+</sup>, respectively. As shown in Table 8, the extraction efficiencies of Mg<sup>2+</sup>, Li<sup>+</sup> and Na<sup>+</sup> are 8.72%, 3.93% and 0.60%, respectively. The extraction efficiencies are all under 10%, which is not very ideal. However, the difference in the extraction efficiency of Mg<sup>2+</sup> is the best. 1,8-Dihydroxyl-4,4,5,5-tetramethylbenzo-14-crown-4 almost has no ability to extract sodium ions from aqueous solution.

The concentrations of  $Li^+$  and  $Na^+$  in the mixed ionic solution were detected by ICP, which are 282 and 267 mg  $L^{-1}$ , respectively. As shown in Table 9, the extraction efficiencies of  $Li^+$  and  $Na^+$  in the mixed ionic solution are 4.61% and 0.37%, respectively. Thus, the crown ether preferred to adsorb  $Li^+$  in the mixed ionic solution. The adsorption rates of  $Li^+$  and  $Mg^{2+}$  in the mixed ionic solution are 3.52% and 9.36%, respectively. Thus, the crown ether preferred to adsorb  $Mg^{2+}$  in the mixed ionic solution.

In conclusion, the stability sequence of complexes is  $\rm CE-Mg^{2+}> \rm CE-Li^+> \rm CE-Na^+,$  which is consistent with the



Fig. 7 Total energy analysis results of the CE-Li<sup>+</sup> complex.



Fig. 8 Total energy analysis results of the CE-Na<sup>+</sup> complex.



Fig. 9 Total energy analysis results of the CE-Mg<sup>2+</sup> complex.

Table 8 Analysis results of extraction rates for metal ions in ionic solution

Metal ion	Initial concentration $(mg L^{-1})$	Equilibrated concentration $(mg L^{-1})$	Extraction rate/%
$Li^+$	280	269	3.93
$Mg^{2+}$	344	314	8.72
Na <sup>+</sup>	502	499	0.60

theoretical analysis results. 1,8-Dihydroxyl-4,4,5,5-tetramethylbenzo-14-crown-4 could only selectively adsorb  $Li^+$  from the mixed ionic solution containing  $Li^+$  and  $Na^+$  and could not adsorb  $Li^+$  from the mixed solution containing  $Mg^{2+}$ .

### 4.2 Formation Gibbs free energies of complexes

The thermodynamic properties and binding energies were calculated to study the stability and selectivity trends of CE for Li<sup>+</sup>, Na<sup>+</sup> and Mg<sup>2+</sup>. The formation Gibbs free energies and binding energies were calculated under vacuum ( $\Delta G_1$ ,  $\Delta E_{b1}$ ) or

Mixed ionic solution		Initial concentration $(mg L^{-1})$	Equilibrated concentration (mg L <sup>-1</sup> )	Extraction rate/%
Li <sup>+</sup> –Na <sup>+</sup>	$Li^+$	282	269	4.61
	$Na^+$	267	266	0.37
Li <sup>+</sup> -Mg <sup>2+</sup>	$\mathrm{Li}^+$	284	274	3.52
U	$Mg^{2+}$	299	271	9.36

solvent ( $\Delta G_2$ ,  $\Delta E_{b2}$ ) environment. The complex with a lower value is more stable. The analysis results are shown in Table 10. The BSSE values are all below 1.00, which indicates that the BSSE error can be ignored at this calculation level for the system. The  $\Delta G_1$  and  $\Delta G_2$  of the complexes follow the order: CE-Na<sup>+</sup> > CE-Li<sup>+</sup> > CE-Mg<sup>2+</sup>. The binding energy of the complexes follows the same order. Therefore, the stability sequence of the complexes is CE-Mg<sup>2+</sup> > CE-Li<sup>+</sup> > CE-Na<sup>+</sup>. And the extraction efficiencies of Mg<sup>2+</sup>, Li<sup>+</sup> and Na<sup>+</sup> follow the same order. Thus, the analysis results are consistent with each other. Noticeably,  $\Delta G_2$  and  $\Delta E_{b2}$  are higher compared with  $\Delta G_1$  and  $\Delta E_{b1}$ . Thus, the complexes in aqueous solution are less stable. The aqueous solution environment greatly reduces the stabilities of the complexes.

The  $\Delta G_1$  difference between CE-Na<sup>+</sup> and CE-Li<sup>+</sup> is 29.23 kcal mol<sup>-1</sup>, while the  $\Delta G_2$  difference is 11 kcal mol<sup>-1</sup>. The  $\Delta G_1$  difference between CE-Mg<sup>2+</sup> and CE-Li<sup>+</sup> is 174.10 kcal mol<sup>-1</sup>, while the  $\Delta G_2$  difference is 21.2 kcal mol<sup>-1</sup>. Therefore, the difference of formation Gibbs free energies between different complexes is narrowed dramatically because of the solvent effect. The  $\Delta E_{b1}$  difference between CE-Na<sup>+</sup> and CE-Li<sup>+</sup> is 32.29 kcal mol<sup>-1</sup>, while the  $\Delta E_{b2}$  difference is 13.27 kcal mol<sup>-1</sup>. The  $\Delta E_{b1}$  difference between CE-Mg<sup>2+</sup> and CE-Li<sup>+</sup> is about 180.47 kcal mol<sup>-1</sup>, while the  $\Delta E_{b2}$  difference is 26.76 kcal mol<sup>-1</sup>. Therefore, the difference is narrowed dramatically, especially for CE-Mg<sup>2+</sup> and CE-Li<sup>+</sup>.

The interaction energies  $E_{\rm tot}$  calculated by SAPT do not include the solvent effect. However, the influence of the polar portion of the solvent (*R*) on the interaction could be investigated by the difference of the binding energy under vacuum and solvent environment ( $R = \Delta E_{\rm b2} - \Delta E_{\rm b1}$ ). Therefore, the sum of *R* and  $E_{\rm tot}$  represents the overall interaction between metal ions and the crown ether in aqueous solution. The smaller the value of *T*, the stronger the bond strength. As shown in Table 11, the interactions are shielded by the solvent environment.  $E_{\rm tot}$  and *T* have the same trend: CE-Mg<sup>2+</sup> < CE-Li<sup>+</sup> < CE-Na<sup>+</sup>, which suggests that Mg<sup>2+</sup> has the strongest connection with the crown ether.

 
 Table 10
 The standard formation Gibbs free energy and binding energy of complexes under vacuum or solvent environment (298.15 K, kcal mol<sup>-1</sup>)

Complex	$\Delta G_1$	$\Delta G_2$	$\Delta E_{\mathrm{b1}}$	$\Delta E_{\mathrm{b2}}$	BSSE
CE-Li <sup>+</sup> CE-Na <sup>+</sup> CE-Mg <sup>2+</sup>	$-85.99 \\ -56.76 \\ -260.09$	$-30.49 \\ -19.49 \\ -51.69$	-107.68 -75.39 -288.15	$-45.09 \\ -31.82 \\ -71.85$	0.28 0.54 0.61

 Table 11
 Interaction energy calculated by energy decomposition analysis considering the solvent effect (kcal mol<sup>-1</sup>)

Complex	$E_{ m tot}$	R	Т
CE-Li <sup>+</sup>	-109.09	62.60	-46.49
CE-Mg <sup>2+</sup>	-273.21	216.30	-56.91
CE-Na <sup>+</sup>	-74.72	43.57	-31.15

It can be concluded that 1,8-dihydroxyl-4,4,5,5-tetramethylbenzo-14-crown-4 needs to be grafted onto resins to improve the extraction effect of Li<sup>+</sup> by avoiding the adverse effect of the water-solubility of the crown ether. 1,8-Dihydroxyl-4,4,5,5tetramethylbenzo-14-crown-4 could not separate Li<sup>+</sup> from the mixed solution containing  $Mg^{2+}$  due to similar ionic diameters, while it can selectively adsorb Li<sup>+</sup> over Na<sup>+</sup>. The size matching effect is the main reason for the selectivity of 1,8-dihydroxyl-4,4,5,5-tetramethyl-benzo-14-crown-4. The solvent effect narrows the difference of the interaction strength remarkably, which is closely connected with the substituent groups. As shown in the previous studies of authors, the selective adsorption property may be changed by different substituent groups.<sup>45</sup> Therefore, more molecular design research needs to be done to separate Li<sup>+</sup> from a mixed ionic solution containing  $Mg^{2+}$ .

# 5 Conclusion

The shape of the crown ether ring changed from a rectangle to a square during the formation of complexes. The elongation of C–O bonds suggested that the interaction strength of the complexes followed the order: CE-Mg<sup>2+</sup> > CE-Li<sup>+</sup> > CE-Na<sup>+</sup> in aqueous solution.

The results of AIM topological analysis, energy decomposition analysis and formation Gibbs free energies calculation all showed that the stability of the complexes in the gas phase followed the order:  $CE-Mg^{2+} > CE-Li^+ > CE-Na^+$ . The solvent effect narrowed the difference of the interaction strength prominently without changing the order.

According to the analysis results of RDG, the hydroxyl substituents did not interact directly with metal ions. The interactions can be divided into four kinds: electrostatic, induction, exchange and dispersion. Electrostatic and induction were the main factors maintaining the stability of the complexes.

The experimental data also showed that 1,8-dihydroxyl-4,4,5,5-tetramethylbenzo-14-crown-4 preferred to adsorb  $Li^+$ over Na<sup>+</sup> and preferred to adsorb Mg<sup>2+</sup> over Li<sup>+</sup> in a mixed ionic solution. The size matching effect is the main reason for the selectivity of 1,8-dihydroxyl-4,4,5,5-tetramethylbenzo-14crown-4 compared with the synergistic effects of functional groups.

### Appendix A

### A.1. Synthesis of 1,2-bis(allyloxy)-benzene

A mixture of catechol (2.0 g, 18.16 mmol), allyl bromide (5.5 g, 45.46 mmol),  $K_2CO_3$  (6.3 g, 45.58 mmol), and anhydrous acetonitrile (40 mL) was stirred under a  $N_2$  atmosphere for

12 h at 65 °C. Then, water was added after the reaction was completed and the solution was extracted with EtOAc. The separated organic phase was evaporated to dryness and the residue was purified by column chromatography on silica gel using petroleum ether/EtOAc ( $V_p: V_E = 5:1$ ) as the eluent to give the pure 1,2-bis(allyloxy)-benzene product.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  6.91 (s, 4H), 6.08 (ddd, *J* = 17.3, 10.5, 5.2 Hz, 2H), 5.44 (dd, *J* = 17.3, 1.7 Hz, 2H), 5.27 (dd, *J* = 10.5, 1.5 Hz, 2H), 4.58 (dt, *J* = 5.3, 1.6 Hz, 4H).

### A.2. Synthesis of 1,2-bis(oxiran-2-ylmethoxy)-benzene

To a stirred solution of chilled (0 °C in ice bath) *m*-CPBA (2.3 g, 13.33 mmol) in 50 mL of DCM, 1,2-di(allyl)-benzene (1 g, 5.26 mmol) in DCM was slowly added within 30 min. Then, the mixture was stirred for 24 h at room temperature. After the reaction, 50 mL of DCM was added and the mixed solution was washed several times with saturated Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> and 10% NaHCO<sub>3</sub>. The separated organic phase was evaporated to dryness and the residue was purified by column chromatography on silica gel using DCM/diethyl ether ( $V_{\text{DCM}}$ :  $V_{\text{diethyl ether}} = 5:1$ ) as the eluent to give the pure 1,2-bis(oxiran-2-ylmethoxy)-benzene product.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  6.89 (s, 4H), 4.23 (ddd, *J* = 11.3, 3.1, 1.4 Hz, 2H), 3.93 (ddd, *J* = 11.3, 5.8, 4.5 Hz, 2H), 3.34 (d, *J* = 1.5 Hz, 2H), 2.84 (t, *J* = 4.6 Hz, 2H), 2.76–2.67 (m, 2H).

### A.3. Synthesis of 1,8-dihydroxyl-4,4,5,5-tetramethylbenzo-14crown-4

1,2-Bis(oxiran-2-ylmethoxy)-benzene (2.1 g, 9.45 mmol) was added to the mixture of 2,3-dimethyl-2,3-butanediol (2.38 g, 20.14 mmol), LiOH and *t*-BuOH (50 mL) under a N<sub>2</sub> atmosphere within 5 h at 60 °C. Then, the reaction was continued for 24 hours under the same conditions. After the reaction, the solvent was evaporated *in vacuo*. The residue was dissolved in CHCl<sub>3</sub> and washed with 10% NaOH aqueous solution. The separated organic phase was evaporated to dryness and the residue was purified by column chromatography on silica gel using CHCl<sub>3</sub>/MeOH ( $V_{\text{CHCl}_3}$ :  $V_{\text{MeOH}} = 10:1$ ) as the eluent to give the pure 1,8-dihydroxyl-4,4,5,5-tetramethylbenzo-14-crown-4 product.

<sup>1</sup>H NMR (399 MHz, DMSO-d<sub>6</sub>)  $\delta$  1.04–1.08 (m, 5H), 1.10 (s, 1H) 1.12 (s, 1H) 1.11–1.13 (m, 1H) 1.13–1.17 (m, 5H) 1.13–1.17 (m, 5H) 1.97–2.00 (m, 1H) 3.33–3.39 (m, 2H) 3.42–3.49 (m, 1H) 3.43–3.48 (m, 1H) 3.65–3.72 (m, 1H) 3.72–3.84 (m, 4H) 3.84–3.96 (m, 3H) 3.84–3.99 (m, 3H) 3.99–4.06 (m, 1H) 4.82–4.86 (m, 1H) 4.82–4.86 (m, 1H) 4.87–4.94 (m, 2H) 6.87–6.97 (m, 2H) 6.97–7.07 (m, 2H).

# Conflicts of interest

There are no conflicts to declare.

### Acknowledgements

The authors acknowledge funding from the National Natural Science Foundation of China (contract/grant number: 51704011, U1703130, and 51904003).

### References

- 1 W. Xiang, S. Liang, Z. Zhou, W. Qin and W. Fei, *Hydro-metallurgy*, 2016, **166**, 9–15.
- 2 W. Yu, Y. Cui, J. Yang, H. Wen, Y. Li, S. Du, K. Ling, H. Gu and C. Luo, *Sci. Bull.*, 2020, **65**, 53–59.
- 3 P. Meshram, B. D. Pandey and T. R. Mankhand, *Hydro-metallurgy*, 2014, **150**, 192–208.
- 4 B. Swain, Sep. Purif. Technol., 2017, 172, 388-403.
- 5 R. Chitrakar, H. Kanoh, Y. Miyai and K. Ooi, *Chem. Mater.*, 2010, **12**, 3151–3157.
- 6 H. J. Hong, I. S. Park, J. Ryu, T. Ryu, B. G. Kim and K. S. Chung, *Chem. Eng. J.*, 2015, **271**, 71–78.
- 7 M. J. Park, G. M. Nisola, A. B. Beltran, R. E. C. Torrejos,
   J. G. Seo, S. P. Lee, H. Kim and W. J. Chung, *Chem. Eng. J.*,
   2014, 254, 73–81.
- 8 K. Yoshizuka, K. Fukui and K. Inoue, Apcche, 2005, 2004, 995.
- 9 J. Chen, S. Lin and J. Yu, J. Hazard. Mater., 2020, 388, 122101.
- 10 K. Onishi, T. Nakamura, S. Nishihama and K. Yoshizuka, Ind. Eng. Chem. Res., 2010, 49, 6554–6558.
- 11 Y. Pranolo, Z. Zhu and C. Y. Cheng, *Hydrometallurgy*, 2015, 154, 33–39.
- 12 S. Tsuchiya, Y. Nakatani, R. Ibrahim and S. Ogawa, J. Am. Chem. Soc., 2002, 124, 4936–4937.
- 13 C. J. Pedersen, J. Am. Chem. Soc., 1967, 89, 7017-7036.
- 14 W. Qin, S. Xu, G. Xu, Q. Xie, C. Wang and Z. Xu, *Chem. Eng.* J., 2013, 225, 528–534.
- 15 T. Hayashita, J. H. Lee, M. G. Hankins, J. C. Lee, J. S. Kim, J. M. Knobeloch and R. A. Bartsch, *Anal. Chem.*, 1992, 64, 815–819.
- 16 G. Pearson, Surv. Prog. Chem., 1969, 5, 1-52.
- 17 R. A. Bartsch, B. P. Czech, S. I. Kang, L. E. Stewart and B. Son, *Chem. Informationsdienst*, 1985, **16**, 4997–4998.
- 18 Y. Inoue, T. Hakushi, Y. Liu and L. H. Tong, J. Org. Chem., 1993, 58, 5411–5413.
- 19 B. P. Czech, D. A. Babb, B. Son and R. A. Bartsch, J. Org. Chem., 1984, 49, 4805–4810.
- 20 S. Faulkner, R. Kataky, D. Parker and A. Teasdale, J. Chem. Soc., Perkin Trans. 1, 1995, 1761–1769.
- 21 K. Kimura, H. Yano, S. Kitazawa and T. Shono, *J. Chem. Soc.*, *Perkin Trans.* 2, 1986, 1945.
- 22 R. E. C. Torrejos, G. M. Nisola, H. S. Song, L. A. Limjuco, C. P. Lawagon, K. J. Parohinog, S. Koo, J. W. Han and W.-J. Chung, *Chem. Eng. J.*, 2017, **326**, 921–933.
- 23 D. Citterio, J. Takeda, M. Kosugi, H. Hisamoto, S. Sasaki, H. Komatsu and K. Suzuki, *Anal. Chem.*, 2007, **79**, 1237–1242.
- 24 Y. Ando, Y. Hiruta, D. Citterio and K. Suzuki, *Analyst*, 2009, 134, 2314–2319.
- 25 H. Hou, X. Zeng and X. Liu, J. Mol. Model., 2009, 15, 105–115.
- 26 J. C. López, C. Pérez, S. Blanco, V. A. Shubert, B. Temelso, G. C. Shields and M. Schnell, *Phys. Chem. Chem. Phys.*, 2019, 21, 2875–2881.
- 27 J. D. Rodriguez, T. D. Vaden and J. M. Lisy, J. Am. Chem. Soc., 2009, 131, 17277–17285.
- 28 J. D. Rodriguez and J. M. Lisy, J. Am. Chem. Soc., 2011, 133, 11136–11146.

- 29 Y. Inokuchi, O. V. Boyarkin, R. Kusaka, T. Haino, T. Ebata and T. R. Rizzo, J. Am. Chem. Soc., 2011, 133, 12256-12263.
- 30 L. A. Limjuco, G. M. Nisola, R. E. C. Torrejos, J. W. Han, H. S. Song, K. J. Parohinog, S. Koo, S. P. Lee and W. J. Chung, ACS Appl. Mater. Interfaces, 2017, 9, 42862-42874.
- 31 J. Cai, Q. Liang, X. L. Zhao, S. S. Pang and K. Liu, Chem. Reagents, 2017, 39, 1029-1034.
- 32 X. L. Zhao, Q. Liang and J. Cai, Chem. Res. Appl., 2016, 28, 1098-1102.
- 33 J. D. Patterson, Ann. Nucl. Energy, 1989, 16, 611.
- 34 E. S. Kryachko and E. V. Lude, Energy Density Functional Theory of Many-Electron Systems, 1990.
- 35 N. H. March, J. Phys. Chem., 1982, 86, 2262-2267.
- 36 T. Lu and F. Chen, J. Comput. Chem., 2012, 33, 580-592.
- 37 L. M. Surhone, M. T. Timpledon and S. F. Marseken, Visual Molecular Dynamics, 2010.

- 38 R. F. W. Bader and C. F. Matta, Found. Chem., 2013, 15, 253-276.
- 39 N. J. M. Amezaga, S. C. Pamies, N. L. M. Peruchena and G. L. Sosa, J. Phys. Chem. A, 2010, 114, 552-562.
- 40 E. R. Johnson, S. Keinan, P. Mori-Sánchez, J. Contreras-García, A. J. Cohen and W. Yang, J. Am. Chem. Soc., 2010, 132, 6498-6506.
- 41 K. Patkowski, Wiley Interdiscip. Rev.: Comput. Mol. Sci., 2020, 10, e1452.
- 42 K. Szalewicz, Wiley Interdiscip. Rev.: Comput. Mol. Sci., 2012, 2, 254-272.
- 43 J. Ho, A. Klamt and M. L. Coote, J. Phys. Chem. A, 2010, 114, 13442-13444.
- 44 S. F. Boys and F. Bernardi, Mol. Phys., 1970, 19, 553-566.
- 45 Y. Tian, W. Chen, Z. Zhao, L. Xu and B. Tong, J. Mol. Model., 2020, 26, 67.

Paper