



## Design of lithium selective crown ethers: Synthesis, extraction and theoretical binding studies



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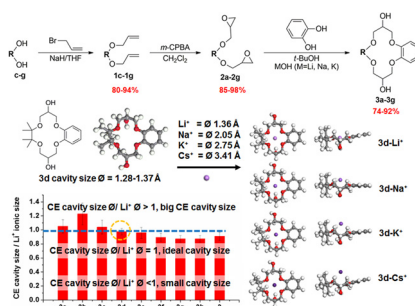
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### HIGHLIGHTS

- Li<sup>+</sup> selective crown ethers (CEs) with bulky and rigid subunits were efficiently synthesized.
- Suitable solvents, catalysts, and reaction conditions for CE synthesis were determined.
- Rigid subunits prevented preorganization effect while bulky groups acted as blocking moiety for bigger metals.
- Liquid-liquid extraction and DFT calculations provided insights on CE-M<sup>+</sup> complexes.

### GRAPHICAL ABSTRACT



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### ABSTRACT

Lithium-selective (Li<sup>+</sup>) di-hydroxy crown ethers (CEs 3a–3h) were efficiently synthesized via intermolecular cyclization of bulky bis-epoxide with 1,2-dihydroxybenzene. Bis-epoxides were produced by etherifying allyl bromides with bulky diols to afford diene intermediates, which were subsequently epoxidized. Optimized cyclization reactions were established by changing the solvent, catalyst, and reaction temperature. Complexation abilities of CEs 3a–3h with Li<sup>+</sup> and other alkali metals (Na<sup>+</sup>, K<sup>+</sup>, Cs<sup>+</sup>) were assessed by liquid-liquid extraction in dichloromethane-water system. Among the CEs, the highest Li<sup>+</sup>/Na<sup>+</sup> selectivities were obtained from 3d ( $\alpha_{\text{Li}/\text{Na}} = 2519$ ) and 3e ( $\alpha_{\text{Li}/\text{Na}} = 1768$ ). DFT calculations reveal that 3d (1.28–1.37 Å) and 3e (1.23–1.38 Å) had the closest cavity sizes with Li<sup>+</sup> diameter (1.36 Å). This result affirms that the size-match selectivity of CEs with Li<sup>+</sup> was due to the presence of bulky tetramethyl (3d) or bicyclopentyl (3e) subunits with the rigid benzo groups. Complexation with larger cations like Na<sup>+</sup>, K<sup>+</sup> and Cs<sup>+</sup> greatly distorted the 3d and 3e rings as indicated by the larger O–M<sup>+</sup> distances on their bulky sides than on their benzo sides. Thus, their (3d, 3e) superior selectivities were due to their Li<sup>+</sup> preference and unstable complexation with larger M<sup>+</sup>. Enthalpy exchange reaction mechanisms reveal the tendency of all CEs to form 2:1 CE–M<sup>+</sup> complexes with larger cations except for 3d, which mainly forms 1:1 CE–M<sup>+</sup> hence it is considered most suitable for Li<sup>+</sup>. The efficient synthesis of di-hydroxy CEs widens their application not only as extractants but also as solid-supported Li<sup>+</sup> adsorbents given the amenability of their OH<sup>–</sup> groups to further functionalization.

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## 1. Introduction

The demand to recover lithium ( $\text{Li}^+$ ) from alternative aqueous resources that contain diluted  $\text{Li}^+$  with abundant competing alkali metal ions ( $\text{M}^+ = \text{Na}^+, \text{K}^+$  and  $\text{Cs}^+$ ) has renewed research interests to develop highly selective  $\text{Li}^+$  sequestrants [1–6]. Established  $\text{Li}^+$  recovery technologies include precipitation, electrochemical process, membrane-based separation, liquid-liquid extraction (LLE), adsorption and ion exchange [1–6]. These systems have used inorganic lithium ion sieves (e.g.  $\text{Li}_x\text{H}_y\text{MnO}_4$ ,  $\text{H}_2\text{TiO}_3$ ) and organic  $\text{Li}^+$  chelates like crown ethers (CEs) [7–12]. The latter are either employed as extractants in LLE or as adsorbents immobilized in nano-structured supports [4,11,12]. Inorganic adsorbents have rigid lattice structures which impart  $\text{Li}^+$  sieving effects through size exclusion mechanism [13]. Meanwhile, CEs have flexible structures but their cavity sizes or metal ion affinities can be tailored to impart selectivity towards  $\text{Li}^+$  [14–16].

Among the CEs, 12–14 membered CE rings are known to form stable  $\text{Li}^+$  complexes in the presence of other alkali metal ions (Fig. 1) [15,17,18]. Specifically, dibenzo-14-crown-4 ether (DB14C4) **3** and its derivatives are known  $\text{Li}^+$  complexants due to their ideal cavity dimensions ( $d = 1.2\text{--}1.52 \text{ \AA}$  for 4–6 coordination number with  $\text{Li}^+$ ) [19,20]. Furthermore, the dibenzo groups impart rigidity to the CE ring in contrast to the flexible unsubstituted 14-crown-4 ether (**2**) (1.2–1.8  $\text{ \AA}$ ), which permits perching complexation with bigger  $\text{M}^+$  [15,19,21,22]. Despite this ideal cavity size-match relationship, complexation of DB14C4 and its derivatives with larger  $\text{M}^+$  remains a challenge. The sandwich type 2:1 crown ether-metal ion ( $\text{CE-M}^+$ ) complex is still remarkable in currently known 14-membered CE derivatives. This problem limits their application as  $\text{Li}^+$  selective chelates in separation process [4,22,23,24].

To alleviate non-selective 2:1 sandwich type  $\text{CE-M}^+$  complexes, 14-membered CEs containing bulky subunits **4** and **5** have been designed [23]. The bulky subunits act as blocking moieties, which deterred the formation of other types of complexation but promoted 1:1  $\text{CE-M}^+$  complex. Thus, a 14-membered CE with bulky subunits exhibited higher  $\text{Li}^+$  selectivity than its rigid counterpart **3** [24,25]. But due to the strong complex formation and steric hindrance of two bulky subunits, de-complexation of  $\text{Li}^+$  became more difficult. Since de-complexation is an important step for the reusability of CEs, another group of 14-membered CEs with only one bulky subunit **5** have been developed (Fig. 1). However, these types of CEs exhibited lower selectivity than **4** and their synthesis routes are difficult; they require numerous reaction steps but afford low overall yields of 1–5% associated with the low nucleophilicity of bulky tertiary diols as starting substrates [23,24].

Another strategy to obtain 14-membered CEs with better  $\text{Li}^+$  selectivity and more convenient  $\text{Li}^+$  de-complexation is to incorporate both rigid and bulky groups in one CE ring. Earlier studies have shown that this type of 14-membered CEs exhibited very high  $\text{Li}^+$  selectivities [26,27]. The aromatic group enhanced the rigidity of the 14-membered CE backbone while the bulky subunits provided

a blocking mechanism to prevent bigger  $\text{M}^+$  from forming higher order of complexes. But to this date, the overall reaction yields for these 14-membered CEs are still very poor ( $\sim 1\%$ ). Their application is currently limited to the biological field as selective  $\text{Li}^+$  ion sensing [26,27].

Thus herein, the efficient synthesis of 14-membered CEs with both rigid and bulky subunits is presented. Ring closure reactions of the CEs were performed through intermolecular cyclization of reactive bulky bis-epoxides with catechol (Fig. 2). The resulting 14-membered CEs are terminated with hydroxyl groups, which were generated from the ring opening of the bis-epoxides. These hydroxyl groups could widen the application of the 14-membered CEs in extraction, recovery and sensing as they could serve as reactive sites for CE immobilization on solid supports or conversion to lariat ethers, cryptands and other derivatives [12,28–31].

Through this approach, current work reports the convenient synthesis of 14-membered di-hydroxy CEs having bulky and rigid subunits, with overall yields (63–80%) remarkably higher than those neutral counterparts ( $<1\%$ ) reported in the literature [26,27]. Optimized reaction conditions were established by changing the solvent-catalyst systems. Different types of 14-membered di-hydroxy CEs were prepared by incorporating different bulky structures. The influence of the bulky subunits in the CEs on their  $\text{Li}^+$  selectivity in the presence of different  $\text{M}^+$  was observed through LLE studies, which were further elucidated through density functional theory (DFT) calculations. Parameters such as cavity size,  $\text{O-M}^+$  distance and binding energies ( $\Delta E_M^*$ ) of the  $\text{CE-M}^+$  complexes were determined from the DFT and were correlated with the results from the LLE experiments.

## 2. Material and methods

### 2.1. Reagents and analytical tools

Reaction solvents (tetrahydrofuran, THF; dichloromethane, DCM; tertiary butanol, *t*-BuOH; dimethyl sulfoxide, DMSO; and dimethylformamide, DMF), reagents allyl bromide, 1,2-dihydroxybenzene (catechol), 15-crown-5, 1-bromohexane, bulky diols (2,2-diethyl-1,3-propanediol, 2,3-dimethyl-2,3-butanediol, [1,1'-bicyclopentyl]-1,1'-diol, *cis*-1,2-cyclohexanediol, *cis*-1,2-cyclopentanediol), commercially available bis-epoxides (neopentyl glycol diglycidyl ether, **2a** and 1,4-bis(2,3-epoxypropyloxy)butane, **2b**, metal hydroxides ( $\text{LiOH}$ ,  $\text{NaOH}$  and  $\text{KOH}$ ) and catalysts ( $\text{LiH}$ ,  $\text{NaH}$  and *m*-chloroperoxybenzoic acid, *m*-CPBA) used in the reactions (Fig. 2) were of highest grade available from either Sigma-Aldrich (Mo, USA) or Fischer Scientific (Korea). High purity grades of alkali metal perchlorates ( $\text{LiClO}_4$ ,  $\text{NaClO}_4$ ,  $\text{KClO}_4$ , and  $\text{CsClO}_4$ ) used in the extraction experiments were also from Sigma-Aldrich (Mo, USA) or Fischer Scientific (Korea). The perchlorates were dissolved in milli-Q deionized water (18.2  $\text{M}\Omega\text{-cm}$ ). Eluents (*n*-hexane; ethyl acetate, EtOAc; diethyl ether,  $\text{Et}_2\text{O}$ ;

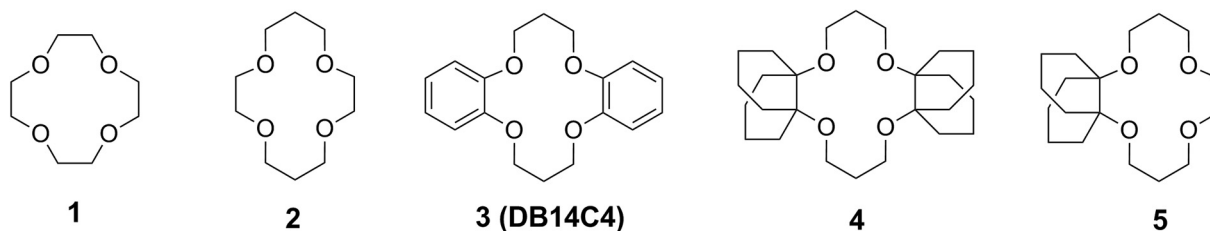


Fig. 1.  $\text{Li}^+$  selective 14-crown-4 ether derivatives developed. 12-crown-4 (**1**), 14-crown-4 (**2**), Dibenzo-14-crown-4 (**3**, DB14C4), Didecalino-14-crown-4 (**4**), Decalino-14-crown-4 ether (**5**).

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